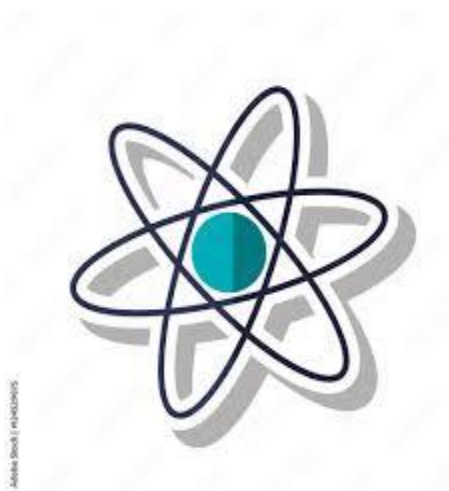




INORGANIC CHEMISTRY2

Dr. Sarab Mahdi Alazawi

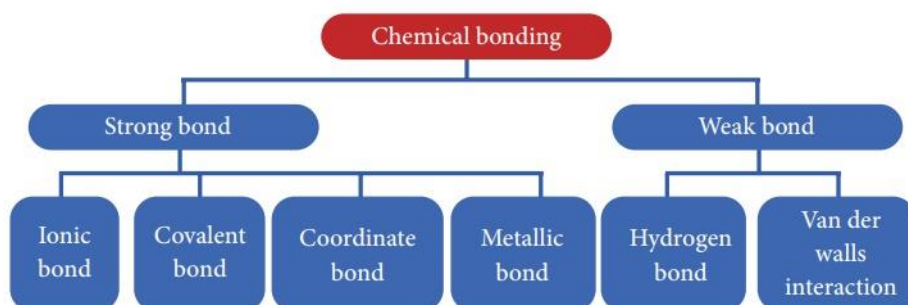


2024-2025

FIRST GRADE OF CHEMISTRY

Chemical compound

The **Chemical bonds** are the forces that hold the atoms together in a compound.



Ionic Bond

Requirements For the formation of Ionic Compounds

- 1- The two elements must be different (Metal & Nonmetal), and have an opposite charges (cation & anion).
- 2- One of the two atoms (Metal) should have low ionization potential and low electron affinity.
- 3- Another atom (Nonmetal) should have high ionization potential and high electron affinity.
- 4- Difference of electronegativity between two Elements (Metal & Nonmetal) must be greater than or equal to 1.7
- 5- The formed ionic compound must be having high lattice energy.

Note

- Ionic compounds are composed of ions, charged particles that form when an atom or small group of atoms gains or loses one or more electrons. The simplest type of ionic compound is a binary ionic compound, one composed of two elements.
- It typically forms when a metal reacts with a nonmetal: Each metal atom loses one or more electrons and becomes a **cation**, a positively charged ion. Each nonmetal atom gains one or more of the electrons lost by the metal atom and becomes an **anion**, a negatively charged ion.

Which is the type of element can formation ionic compound?

- **Metals lose electrons**
 - 1- Elements in Group 1A(1) lose one electron
 - 2- Elements in Group 2A(2) lose two
 - 3- Elements in Group 3A (13) loses three such as aluminum.
- **Nonmetals gain electrons:**

elements in Group 7A(17) gain one electron, oxygen and sulfur in Group 6A(16) gain two, and nitrogen in Group 5A(15) gains three.

Q- What monatomic ions do the following elements form? (a) Iodine ($Z = 53$) (b) Calcium ($Z = 20$) (c) Aluminum ($Z = 13$)

Solution (a) I_2 Iodine (${}_{53}I$) is in Group 7A(17). this group, it gains 1 electron to attain the same number as the nearest Group 8A(18) member, in this case, ${}_{54}Xe$.

(b) Calcium (${}^{20}Ca$) is in Group 2A(2), the alkaline earth metals. Like any Group 2A member, it loses 2 electrons to attain the same number as the nearest noble gas, 18Ar. (c) Al_{31} Aluminum (${}^{13}Al$) is a metal in the boron family (Group 3)

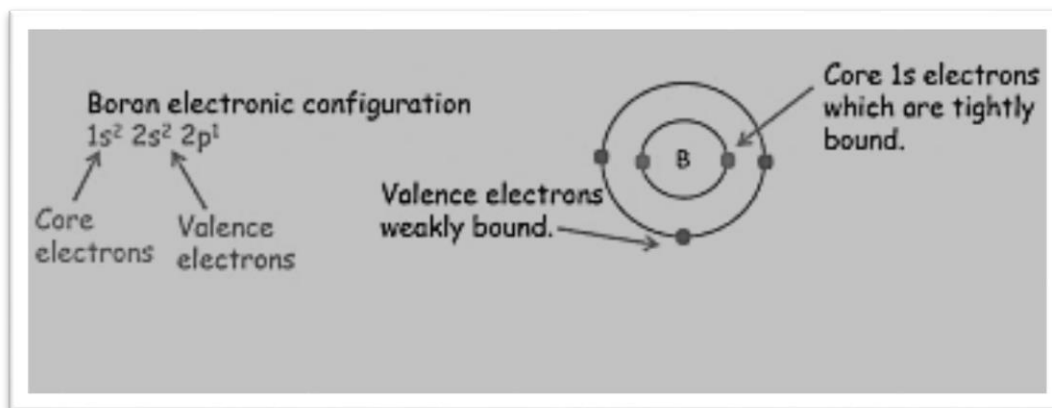
For example

- Lithium fluoride: Li^+ and F^- combine to form LiF .
- Calcium chloride: Ca^{2+} and Cl^- combine to form $CaCl_2$.
- Iron (II) oxide: Fe^{2+} and O^{2-} combine to form FeO .

Note

In order to know which electron gain or loss to form ionic compound or shared electron to form covalent compound we need to know about the type of electrons in atom. There are two types of electrons

- 1- Inner shell or core electron
- 2- Outermost shell or valence electron

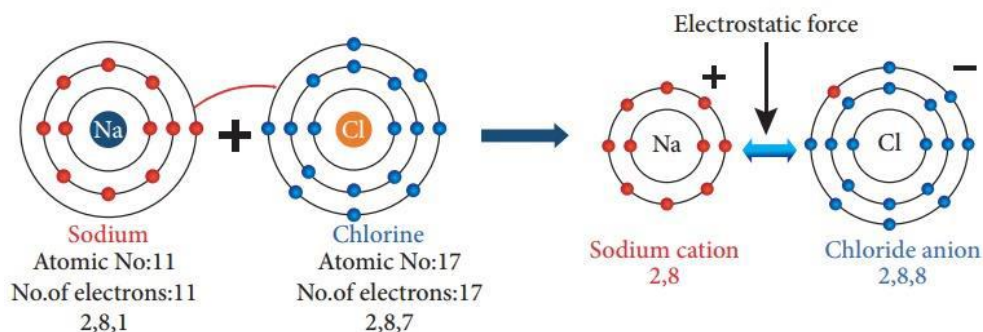


The differences between core electron and valence electron

Core electron	Valence electron
1-Occupy the filled and lowest energy levels	1- Electrons of the outermost shell occupy the partly filled and highest energy levels.
2- Increase in the group	2-Increase in the period.
3- Does not represent the group number in main group elements	3- Represent the group number in main group elements.
4- Effect strongly in atomic size, because it screening the outer electron from nuclear charge.	4-Not effect strongly in atomic size
5- Never involved in hybridization and chemical bonding.	5- Involved in hybridization and chemical bonding.

Ionic bond: Is a chemical bond results from the electrostatic force of attraction between two oppositely charged ions.

The binding arises from the electrostatic attraction between two oppositely charged ions (positive metal and negative non-metal), If the difference in electronegativity between two atoms is equal or greater than (1.7). The electron of metallic atom completely transferred to nonmetallic one. The electrons are not shared at all between two atoms. For example, consider the bond between Na (Electronegativity= 0.93) and Cl (Electronegativity=3.16) in sodium chloride (NaCl).

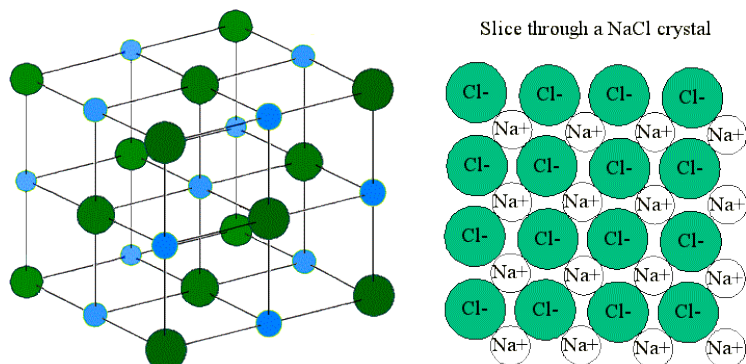


There are three steps to form ionic compound

- 1- First step: formation of ions
- 2- Second step: attraction between opposite charges
- 3- Third step: formation of ionic compound

Note: Ionic Lattices Sodium Chloride is a typical ionic compound. Each sodium ion is surrounded by six chloride ions and each chloride ion is surrounded by six sodium ions. In this arrangement,

each ion is strongly attracted to each of its neighbors. The large attractive forces result in a strong ionic bond.

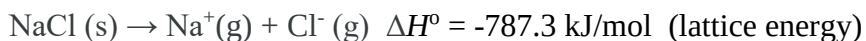


Characteristic properties of ionic compounds

- 1- Ionic compounds are solid (rigid) but (brittle) due to strong forces of attraction between the oppositely charged ions.
- 2- Ionic compounds have high melting and boiling points, due to strong forces of attraction between the ions.
- 3- Ionic compounds dissolve easily in water.
- 4- Solid Ionic compounds do not conduct electricity because their constituent ions are fixed in their positions. But, when melted or dissolved in water, they conduct electricity because the ions become free in a solution.
- 5- Ionic compounds are crystalline due to the orderly distribution of ions in them. This gives characteristic geometrical shapes to the ionic compounds.

Definition of Lattice Energy

Lattice energy is an estimate of the bond strength in ionic compounds. It is defined as the heat of formation for ions of opposite charge in the gas phase to combine into an ionic solid. As an example, the lattice energy of sodium chloride (NaCl), is the energy released when gaseous Na^+ and Cl^- ions come together to form a lattice of alternating ions in the NaCl crystal. Or can define the **lattice energy as the energy required to separate a mole of an ionic solid into the gaseous form of its ions** (that is, the reverse of the reaction shown above).



Note

Lattice energy cannot be determined experimentally due to the difficulty in isolating gaseous ions. The energy value can be estimated using the Born-Haber cycle, or it can be calculated theoretically with an electrostatic examination of the crystal structure.

Factors Affecting Lattice Energy

Two main factors that contribute to the lattice energy of an ionic solid:

- 1- **The charge on the ions**, as the charge of the ions increases, the lattice energy increases
- 2- **The radius, or size**, as the size of the ions increases, the lattice energy decreases.

Note

Lattice energies are also important in predicting the solubility of ionic solids in H₂O. Ionic compounds with smaller lattice energies tend to be more soluble in H₂O.

- Lattice energy decreases as you go down a group (as atomic radii goes up, lattice energy goes down).
- Going across the periodic table, atomic radii decreases, therefore lattice energy increases

1- Born-Landé equation

The Born-Landé equation is a concept originally formulated in 1918 by the scientists Born and Lande and is used to calculate the lattice energy (measure of the strength of bonds) of a compound. This equation proposed by Max Born and Alfred Landé states that lattice energy can be derived from ionic lattice based on electrostatic potential and the potential energy due to repulsion. To solve for the Born-Landé equation, you must have a basic understanding of lattice energy. The Born-Landé equation was derived from these two following equations. The first is the electrostatic potential energy:

$$\Delta U = \frac{N_A M |Z^+| |Z^-| e^2}{4\pi\epsilon^0 r} \text{ --- 1}$$

- NA is Avogadro's constant (6.022×10²³)
- M is the Modeling constant (a constant that varies for different structures)
- e is the charge of an electron (1.6022×10⁻¹⁹ C)
- Z⁺ is the cation charge
- Z⁻ is the anion charge
- ε^o is the permittivity of free space
- 4πε^o = 1.112×10⁻¹⁰ C²/(J·m)

The second equation is the repulsive interaction:

$$\Delta U = \frac{N_A B}{r^n} \text{ ----- 2}$$

- B is the repulsion coefficient
- n is the Born Exponent (typically ranges between (5-12) that is used to measure how much a solid compresses

These equations combine to form:

$$\Delta U(OK) = \frac{N_A M |Z^+| |Z^-| e^2}{4\pi\epsilon_0 r^0} \left(1 - \frac{1}{n}\right) \dots \dots \dots -3$$

n value	5	7	9	10	12
Symbol	He	Ne	Ar	Kr	Xe

- r^0 is the distance to closest ion
- n = the

number of ions in the formula unit

Problems

1- Which compound has the greatest lattice energy?

- AlF_3
- NaCl
- LiF
- CaCl_2

2- What is the lattice energy of NaCl ?

- AlF_3
-

$$\Delta U = \frac{(1.747)(6.022 \times 10^{23})2(1.6022 \times 10^{-19})}{4(3.14)8.85 \times 10^{-12} \times 282 \times 10^{-12}} \left(1 - \frac{1}{9}\right) = -756 \text{ KJ/mol}$$

Born Haber cycle

Born Haber process or more commonly referred to as Born Haber cycle is a method that allows us to observe and analyze energies in a reaction. It mainly helps in describing the formation of ionic compounds from different elements.

Born Haber cycle is a cycle of enthalpy change of process that leads to the formation of a solid crystalline ionic compound from the elemental atoms in their standard state and of the enthalpy of formation of the solid compound such that the net enthalpy becomes zero.

Note

Hess's Law: The total change in enthalpy of the complete course of a chemical reaction is the same, whether the reaction is made in one step or in several steps

Standard Molar Enthalpy of Formation (ΔH_f^0):- The change in enthalpy when one mole of a substance formed from its pure elements in standard state (pressure= 1 atm, Temp= 298K).

Example 1: Born Haber cycle of sodium chloride NaCl, (or any AB-type Mono-valent ionic solid).

The heat of formation of sodium chloride (ΔH_f^0) from the sodium metal and chlorine gas can be experimentally measured.



The formation of ionic solid sodium chloride from solid sodium metal and gaseous chlorine is not a single step process but goes through several processes. Heat changes of all the processes except the lattice energy can be experimentally measured. The processes or steps in the formation of sodium chloride are:

- 1- Solid sodium atom sublimates to gaseous atom by absorbing heat energy (ΔH_{sub}).

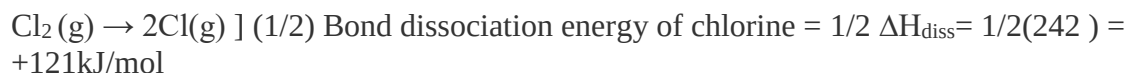


Note: Heat of atomization (ΔH_{Am} or ΔH_{Sub}): The energy change when the metal atom turn directly to a gas.

- 2- Gaseous sodium atom absorbs the ionization energy to release one electron and forms gaseous sodium ion.



Note: Ionization energy is the energy required to remove an electron from a gaseous atom or ion. Diatomic gaseous chlorine breaks into two individual atoms by absorbing bond energy, such that each chlorine atom absorbs half of the bond energy of chlorine molecule.



Note: Heat of dissociation (ΔH_{D}): The energy required for breaking one mole of a bond to give separate atoms

- 3- Chlorine atom accepts an electron to form chloride ion and releases energy equivalent to electron affinity.

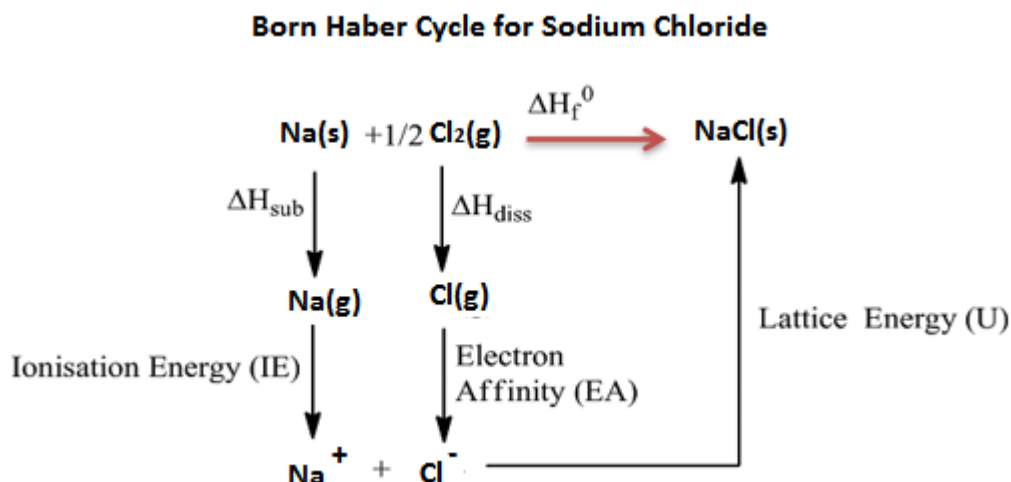


Note: electron affinity of an atom or molecule is defined as the amount of energy released when an electron is added to a neutral atom or molecule to form a negative ion

- 4- Gaseous sodium ion and gaseous chloride ion combine to form solid sodium chloride molecule and releases energy equivalent to lattice energy.



Summation of enthalpy of all the processes from step 1 to step 5 give the net enthalpy of formation of solid crystalline sodium chloride from sodium and chlorine in their standard conditions of solid and gas respectively. This should be equal to the experimentally measured enthalpy of formation of solid sodium chloride. The enthalpies are represented as a cycle in the figure.



So, $\Delta H_f^0 = \Delta H_{\text{sub}} + \Delta H_{\text{IE}} + \Delta H_{\text{dis}} + \Delta H_{\text{EA}} + U$ or $\Delta H_f^0 - (\Delta H_{\text{sub}} + \Delta H_{\text{IE}} + 1/2 \Delta H_{\text{dis}} + \Delta H_{\text{EA}} + U) = 0$

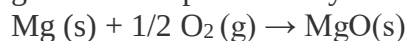
$$411 + 107 + 502 + 121 - 355 + U = 0$$

Here, except lattice energy, all other enthalpies can be experimentally measured.

$$\begin{aligned} \text{Lattice energy of the sodium chloride solid} &= U = \Delta H_f^0 - (\Delta H_{\text{sub}} + \Delta H_{\text{IE}} + 1/2 \Delta H_{\text{dis}} + \Delta H_{\text{EA}}) \\ &= -411 - 107 - 502 - 121 + 355 \\ &= -786 \text{ kJ/mol} \end{aligned}$$

Example 2: Lattice energy of magnesium oxide (or any AB-type Divalent ionic solid).

The heat of formation of magnesium oxide (ΔH_f^0) from the magnesium metal and oxygen gas can be experimentally measured.



$$\Delta H_f^0 = -602 \text{ kJ/mol}$$

The processes or steps in the formation of magnesium oxide are:

1. Solid magnesium atom sublimates to gaseous atom by absorbing heat energy (ΔH_{sub}).



2. Gaseous magnesium atom releases two electrons in two steps with corresponding ionization energies.



$$\text{So energy of ionization} = \Delta H_{\text{IE}} = 738 + 1450 = 2188 \text{ kJ/mol}$$

3. Diatomic oxygen breaks into two individual atoms by absorbing bond energy, such that

each chlorine atom absorbs half of the bond energy of the chlorine molecule.

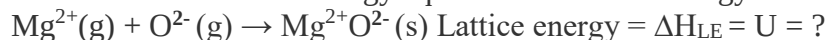


4. Oxygen atom accepts two electrons to form oxide ion and releases energy equivalent to two-electron affinities.

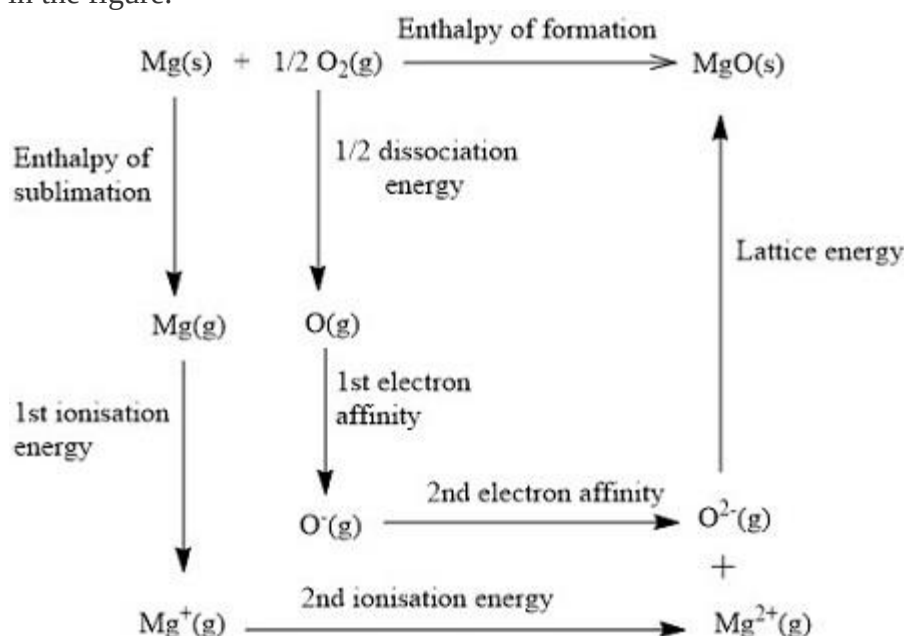


Total energy released as electron affinity by the oxygen atom is $= \Delta H_{\text{EA}} = +656 \text{ kJ/mol}$

5. Gaseous magnesium ion and gaseous oxide ion combine to form solid magnesium oxide molecule and releases energy equivalent to lattice energy.



Summation of enthalpy of all the processes from the starting step to the final step gives the net enthalpy of formation of solid crystalline magnesium oxide from magnesium and oxygen in their standard conditions of solid and gas respectively. This should be equal to the experimentally measured enthalpy of formation of solid magnesium oxide. The enthalpies are represented as a cycle in the figure.



So, $\Delta H_{\text{f}}^0 = \Delta H_{\text{sub}} + \Delta H_{\text{IE}} + 1/2 \Delta H_{\text{dis}} + \Delta H_{\text{EA}} + U$ or $\Delta H_{\text{f}}^0 - (\Delta H_{\text{sub}} + \Delta H_{\text{IE}} + 1/2 \Delta H_{\text{dis}} + \Delta H_{\text{EA}} + U) = 0$

$$602 + 136 + 2188 + 249 + 656 + U = 0$$

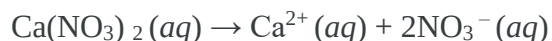
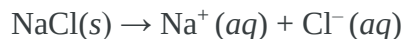
Here, except lattice energy, all other enthalpies can be experimentally measured.

Lattice energy of the magnesium oxide solid = $U = \Delta H_{\text{f}}^0 - (\Delta H_{\text{sub}} + \Delta H_{\text{IE}} + 1/2 \Delta H_{\text{dis}} + \Delta H_{\text{EA}})$.

$$= -602 - 136 - 2188 - 249 - 656 = -3831 \text{ kJ/mol}$$

Solubility of ionic compounds

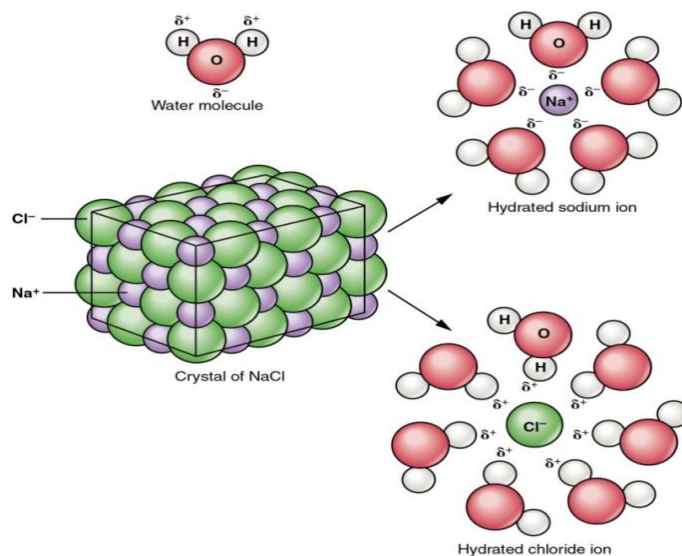
Solubility: An ionic crystal lattice breaks apart when it is dissolved in water. **Dissociation** is the separation of ions that occurs when a solid ionic compound dissolves. Shown below are dissociation equations for NaCl, $\text{Ca}(\text{NO}_3)_2$, and $(\text{NH}_4)_3\text{PO}_4$.



The tendency for a compound to dissolve in water depends on the strength of the bonds holding the compound together compared to the strength exerted on the individual ions by the water molecules. **Highly soluble compounds**, such as NaCl, break apart completely, while compounds with **low solubility**, such as lead sulfate (**PbSO₄**) do so only partially. Compounds with nonpolar molecules do not dissolve. The concept of solubility versus insolubility in ionic compounds is a matter of degree. Some ionic compounds are very soluble, some are only moderately soluble, and some are soluble so little that they are considered insoluble. For most ionic compounds, there is also a limit to the amount of compound that can be dissolved in a sample of water. For example, you can dissolve a maximum of 36.0 g of NaCl in 100 g of water at room temperature, but you can dissolve only 0.00019 g of AgCl in 100 g of water. **Water typically dissolves many ionic compounds and polar molecules.**

The process that occurs when an ionic compound such as (sodium chloride) dissolves in water,

Water molecules move about continuously due to their kinetic energy. When a crystal of sodium chloride is placed into water, the water's molecules collide with the crystal lattice. Recall that the crystal lattice is composed of alternating positive and negative ions. **Water** is attracted to the sodium chloride crystal because water is polar and has both a positive and a negative end. **The positively charged sodium ions** in the crystal attract the **oxygen** end of the water molecules because they are partially negative. **The negatively charged chloride ions** in the crystal attract the **hydrogen** end of the water molecules because they are partially positive. The action of the polar water molecules takes the crystal lattice apart (see image below).



After coming apart from the crystal, the individual ions are then surrounded by solvent particles in a process called **solvation**.

Note: that the individual Na^+ ions are surrounded by water molecules with the oxygen atom oriented near the positive ion. Likewise, the chloride ions are surrounded by water molecules with the opposite orientation. **Hydration is the process of solute particles being surrounded by water molecules arranged in a specific manner.** Hydration helps to stabilize aqueous solutions by preventing the positive and negative ions from coming back together and forming a precipitate. Enthalpy of hydration, (ΔH_{hyd}) of an ion is the amount of heat released when a mole of the ion dissolves in a large amount of water forming an infinite dilute solution in the process.

Relating Hydration Energy to Lattice Enthalpy

In the discussion of lattice energy, we consider the ions separated into a gas form whereas in the dissolution process, the ions are also separated, but this time into ions dispersed in a medium with solvent molecules between ions. The medium or solvent has a dielectric constant. **The molar enthalpy of solution, ΔH_{sol} , is the energy released when one mole solid is dissolved in a solvent.** This quantity, the enthalpy of crystallization, and energy of hydration forms a cycle. Taking the salt NaCl as an example,

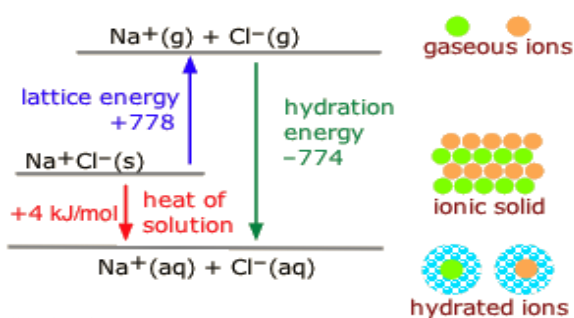


Figure 2: cycle for dissolving NaCl in water

Note

Enthalpy of hydration is a thermodynamic concept that measures the energy change when one mole of a substance is dissolved in a large amount of water. It is typically expressed in kilojoules per mole (kJ/mol). When an ionic compound dissolves in water, the ions in the compound are separated and surrounded by water molecules. This process is known as hydration. The energy released or absorbed during hydration is the enthalpy of hydration. The enthalpy of hydration can be positive or negative. If the enthalpy of hydration is positive, then the process is endothermic, meaning that heat is absorbed from the surroundings. If the enthalpy of hydration is negative, then the process is exothermic, meaning that heat is released to the surroundings. The enthalpy of hydration is an important factor in determining the solubility of a substance in water. In general, substances with a negative enthalpy of hydration are more soluble in water than substances with a positive enthalpy of hydration. This is because the exothermic process of hydration releases heat, which helps to overcome the energy required to break the bonds between the ions in the compound.

$$\Delta H_{\text{hydration}} = \Delta H_{\text{lattice}} (\Delta U) + \Delta H_{\text{sol}}$$

$$\Delta H_{\text{hyd}} = \Delta H_{\text{hdy}} [\text{cation}] + \Delta H_{\text{hdy}} [\text{anion}]$$

Example: Calculate the enthalpy of hydration of the chloride ion using the Following $\Delta H_{\text{Lat}} \text{ KCl} = -711 \text{ KJ/mol}$, $\Delta H_{\text{Sol}} \text{ KCl} = +26 \text{ KJ/mol}$, $\Delta H_{\text{hdy}} \text{ K}^+ = -322 \text{ KJ/mol}$

$$\Delta H_{\text{hydr}} = \Delta H_{\text{latt}} (\Delta U) + \Delta H_{\text{sol}}$$

$$= (-711) + (+26) = -685 \text{ KJ/mol}$$

$$\Delta H_{\text{hyd}} = \Delta H_{\text{hdy}} [\text{cation}] + \Delta H_{\text{hdy}} [\text{anion}]$$

$$(-685) = (-322) + \Delta H_{\text{hdy}} [\text{anion}]$$

$$\Delta H_{\text{hdy}} [\text{anion}] = (-685) + 322 = -363 \text{ KJ/mol}$$

Example: The enthalpy of crystallization for KCl is -715 kJ/mol . The enthalpies of hydration for potassium and chloride are -322 and -363 kJ/mol respectively. From these values, estimate the enthalpy of solution for KCl.

$$\Delta H_{\text{hyd}} = -322 + (-363) = -685 \text{ kJ/mol}$$

$$\Delta H_{\text{sol}} = (-685) - (-715) = 30 \text{ kJ/mol}$$

Factors that affect ion solubility Solutions Solubility

- 1- **Ion charge** - Ions with small charges tend to be soluble - Increasing the charge increases the force that holds the ions together - (i.e. phosphates, PO_4^{3-} , tend to be insoluble).
- 2- **Ion size** - Small ions tend to be less soluble than large ions - Small ions bond more closely together than large ions - Thus the bond between small ions is stronger than the bond between large ions with the same charge.

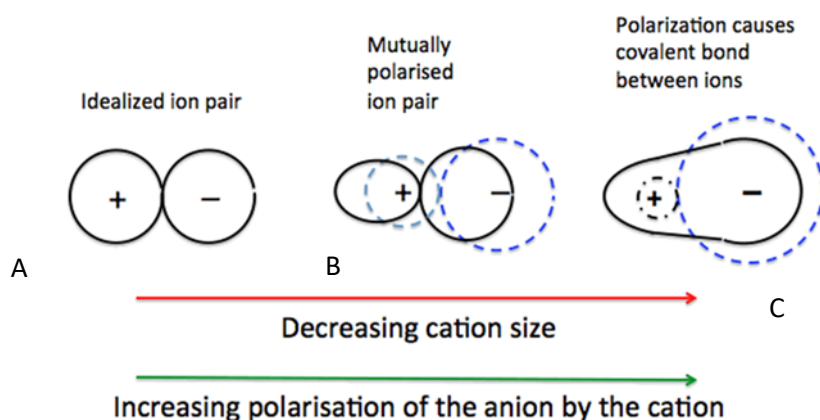
Polarization

The **polarising power**: The ability of cation to polarize an anion. A polarizing power of positive ion (cation) depends on its size and charge and the larger the charge and the smaller the radius. The **polarisability** represents the ability of an anion to become polarized. Polarisability of the negative ion (anion) also depends on its size and charge. The larger the anion radius and the lower its charge the more polarisable it is.

NOTE

The breakdown of the ionic model occurs because one ion is much smaller than the other. More specifically, the breakdown in the ionic model for some compounds occurs when the positive ion is much smaller than the negative ion. The suggestion is that the small positive ion **polarises** the

larger negative ion. Also the suggestion is that this **process of polarisation** is more effect at distortion of the ionic model if the positive ion is small and highly charged and the negative ion is large with a low charge. We see in the graphic below a stylised picture of how the polarization of an anion by a cation can happen. This figure show that A is idealized ion pair and no polarizing B is exchange polarized of ion pair and C refer to enough polarizing to form covalent bond.



Fajans' rules

Fajans' rules was formulated by Kazimierz Fajans in 1923. It is used to predict whether a chemical bond will be covalent or ionic.

Postulates of Fajans' Rule

- 1- **Size of the ion:** Smaller the size of cation, the larger the size of the anion, greater is the covalent character of the ionic bond.
- 2- **The charge of Cation:** Greater the charge of cation, greater is the covalent character of the ionic bond.
- 3- **Electronic configuration:** For cations with same charge and size, the one, with $(n-1)d^n ns^0$ which is found in transition elements have greater covalent character than the cation with $ns^2 np^6$ **electronic configuration**, which is commonly found in alkali or alkaline earth metals.

Explanation of Fajans' Rule

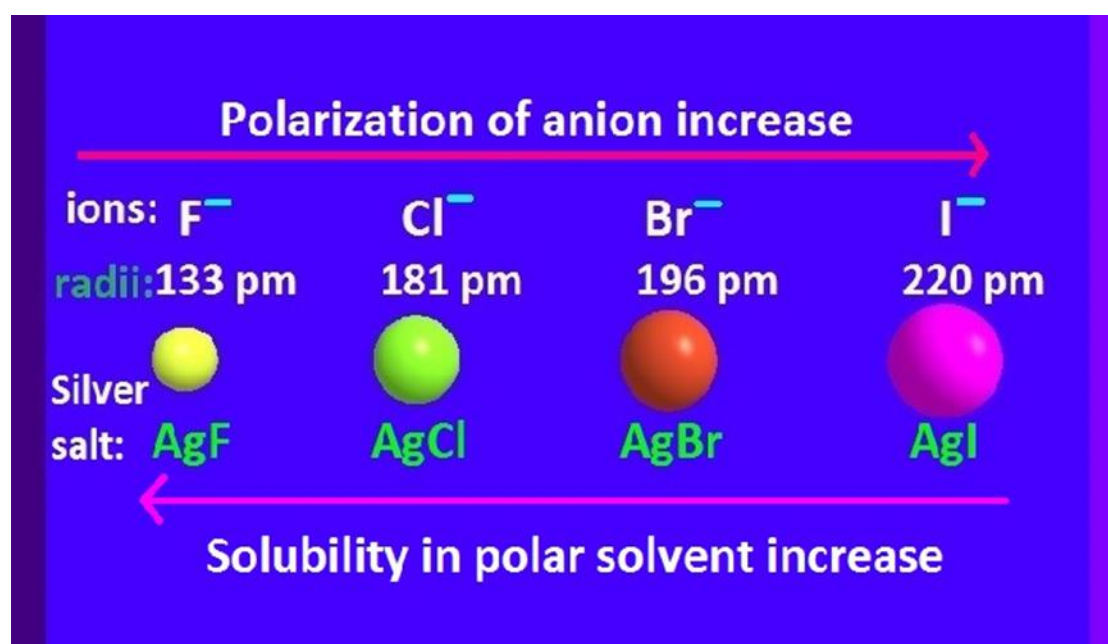
Rule 1:

The **first rule** speaks about the polarising power of the cation. If the cation is smaller, then we can say that the volume of the ion is less. If the volume is less, we can conclude that the charge density of the ion would be high. Since the charge density is high, the polarising power of the ion would be

high. This makes the compound to be more covalent. This explains why LiBr is more covalent than KBr (Li^+ 90 pm cf. K^+ 152 pm).

Rule 2:

The **second rule** speaks about the polarizability of the anion. Larger the anion, less is the effective nuclear charge that holds the valence electron of the ion in place. Since the last electron is loosely bound in large anions, it can easily be polarised by a cation, thereby making the compound more covalent. Polarizability of an anion increase with increase in anionic size or anionic charge. For example, the polarizability of I^- ion is higher than F^- ion, due to large size of iodide ion. If the polarizability of an anion increases, then covalent character of the resulting compound increases. Such as, AgI is more covalent than AgF



Rule 3:

The **third rule** is a special case. Let us use an example to explain this point. **Example:** If we want to find the more covalent compound among HgCl_2 and calcium chloride. We cannot use size as a factor to conclude. This is because both Hg^{2+} and Ca^{2+} are of almost equal size. To explain this, we employ the **third rule**. The electronic configuration of Hg^{2+} is $6s^0 5d^{10}$. This configuration is called pseudo-octet because d-orbital is fully filled, but the element does not have 8 electrons or an octet. We know that d orbitals are not good at shielding, so we can say that the anion (Cl^-) would be more polarised because the d orbital is poor at shielding making HgCl_2 more covalent than CaCl_2 because Ca^{2+} ion has a noble gas configuration. Now to answer the question that we asked first, amongst the alkali chlorides, which one is the most covalent? Since the anion is the same, we have to compare the cations. According to **Fajans' rules**, smaller the cation, more is the covalence. Therefore, LiCl is the most covalent.

Examples on Fajans' rule

Illustration 1: Which compound should theoretically be the most ionic and the most covalent amongst the metal halide?

Solution:

The smallest metal ion and the largest anion should technically be the most covalent. Therefore, LiI is the most covalent. The largest cation and the smallest anion should be the most ionic. Therefore, CsF should be the most ionic.

Illustration 2: Arrange the following according to the increasing order of covalency:

- NaF, NaCl, NaBr, NaI
- LiF, NaF, KF, RbF, CsF

Solution:

Since the cation is the same, compare the anions. Amongst the anions, larger the size more would be the covalency. Therefore the order is: NaF < NaCl < NaBr < NaI Here the anion is the same, so we compare with cations. Smaller the cation more is the covalency.

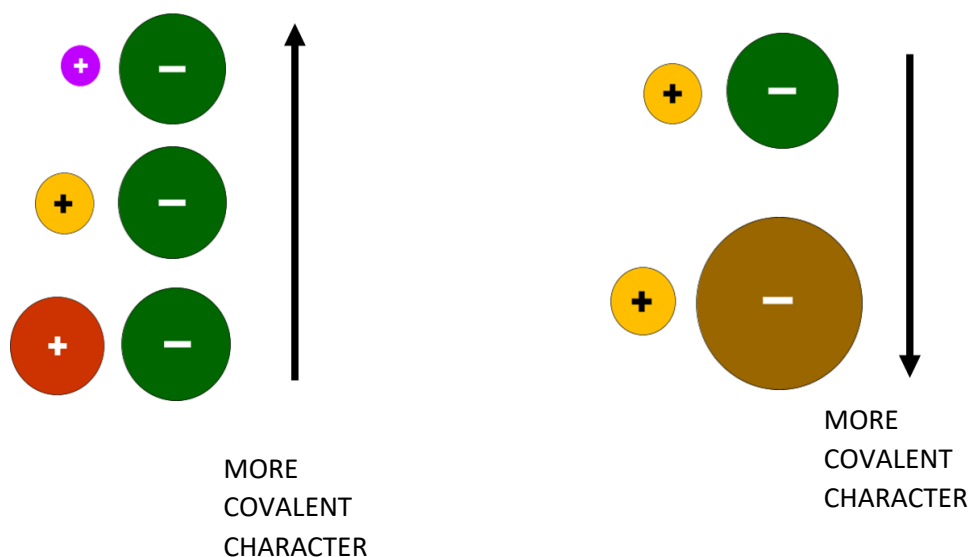
Therefore, the order is $\text{CsF} < \text{RbF} < \text{KF} < \text{NaF} < \text{LiF}$

Fajans' Rule can be summarized as

Ionic Characteristic	Covalent Characteristic
Large Cation	Small Cation
Small Anion	Large Anion
Small-charge	Large Charge

Note

- 1- THE CATION IS SMALL AND/OR HAS A HIGH CHARGE - HIGHLY POLARISING.
- 2- THE ANION IS LARGE AND/OR HAS A HIGH CHARGE - HIGHLY POLARISABLE.



Q1: Tell whether each of the following bonds will be ionic.

- H-H
- O-Cl
- Na-F**
- C-N
- Cs-F**
- Zn-Cl**

Q2: For each pair, indicate which bond will be stronger.

- C-H, Li-F
- Li-F, Mg-O
- Li-F, Cs-I

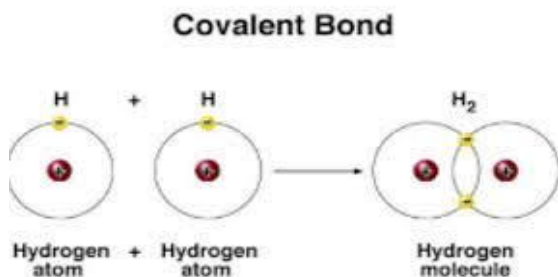
Q3. Which one of the two elements could form an ionic compound?

- 6 carbon and 8 oxygen
- 1 hydrogen and 7 nitrogen
- 3 lithium and 9 fluorine

Covalent bond

Covalent bond: Is a chemical link between two atoms or ions in which the electron pairs are shared equally between them. The binding arises from the electrostatic attraction of their nuclei for the same electrons.

- A covalent bond forms when the bonded atoms have lower total energy than that of widely separated atoms.
- A covalent bond forms between two nonmetals or (metalloid with nonmetal) atoms with identical or relatively close electronegativity values.

Note

Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons. It is measured using a scale known as the **Pauling scale** and ranges from 0.5 to 4. The following table explains the different type's chemical bond due to the electronegativity differences.

Type of Chemical Bond	Electronegativity Difference
<u>Nonpolar covalent</u>	<u>0</u>
<u>Slightly polar covalent</u>	<u>0.1 to 0.4</u>
<u>Polar covalent</u>	<u>0.5 to 1.6</u>
<u>Ionic</u>	<u>>1.7</u>

Condition require to formation covalent bond

- 1- Number of valence electrons of both the participating atoms should have four or more valence electrons in their valence shell.
- 2- Equal electronegativities: the combining atoms should have equal electronegativities. So that no transfer of electrons takes place
- 3- Equal electron affinities: the combining atoms should also have equal electron affinities
- 4- Ionization energy: it should be high for both the atoms so that there is no chance of removal of electrons.

Properties of Covalent Molecular Compounds

- 1- Low melting points and boiling points.
- 2- Low enthalpies of fusion and vaporization. These properties are usually one or two orders of magnitude smaller than they are for ionic compounds.
- 3- Soft or brittle solid forms.
- 4- Poor electrical and thermal conductivity.

Covalent bond types

- 1- Polar covalent bond: The covalent bond is likely to be polar when the electrons are unequally shared.

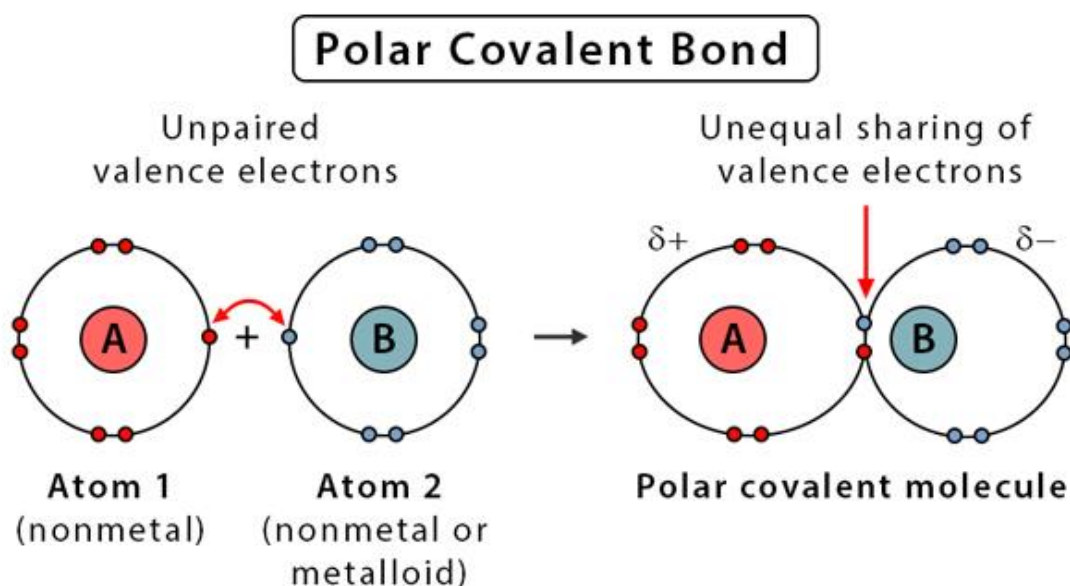
Properties of Polar Covalent Bonds

Here are some facts about polar covalent bond

- 1- Takes place between two nonmetals or between a nonmetal and a metalloid (O-H)
- 2- Unequal sharing of electrons in a compound.
- 3- Electronegativity difference between atoms is between 0.5 and 1.7.
- 4- One end of the bond is positively charged, and the other end is negatively charged
- 5- Polar compounds dissolve in a polar solvent (Example H_2O , HF , SO_2)

Note

In a polar covalent bond, one atom will have a partial negative charge and other a partial positive charge, e.g. $\text{H}\delta^+ + \text{Cl}\delta^-$. For example, consider a (C-O) bond. Oxygen is more electronegative (3.44) than carbon (2.55), and therefore oxygen will more strongly attract the electrons of the bond. The withdrawal of electrons toward oxygen is called induction, which is often indicated with an arrow. Induction causes the formation of partial positive and partial negative charges, symbolized by the Greek symbol delta (δ).

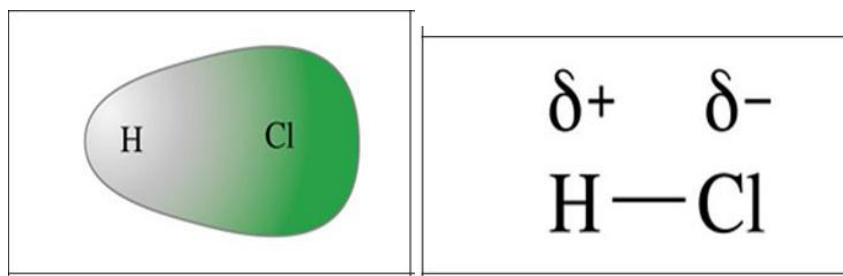
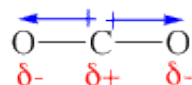
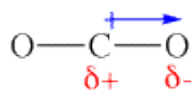


The C-O bonds in carbon dioxide are polar and yet the dipole moment is zero because the 2 bond dipoles cancel each other.

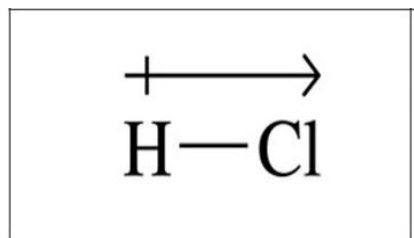
electronegativity: O = 3.5
C = 2.5

Bond polarity = $3.5 - 2.5 = 1.0$

Dipole moment = $1.0 - 1.0 = 0.0$



HCl polar bond showing the partial (+ δ) change on hydrogen and the partial (- δ) change on chlorine. HCl polar bond showing the unequal sharing of a cloud of electron. HCl polar bond showing the direction of the dipole with an arrow pointing toward the more negative atom. The + on the opposite end also reminds us which atom is more positive.

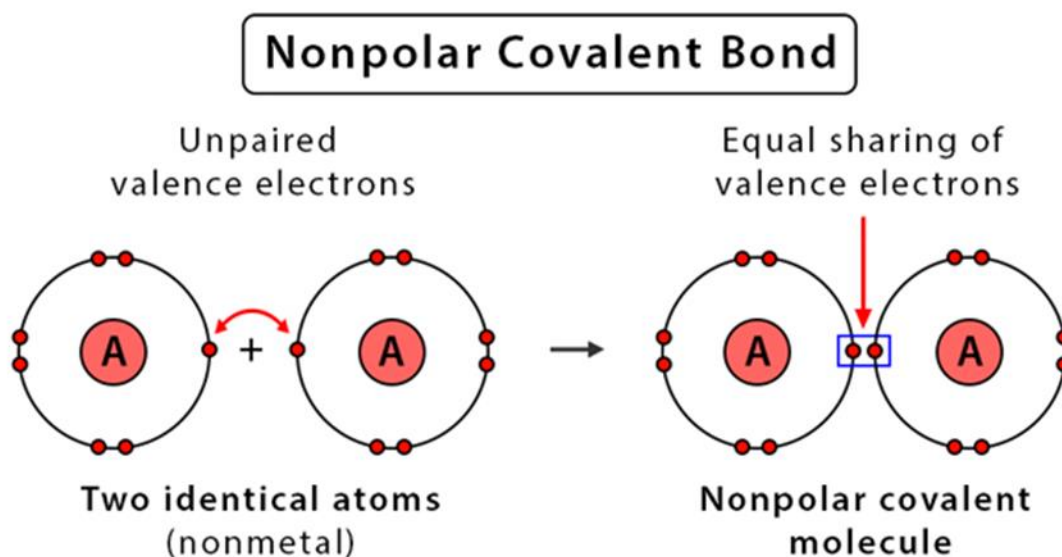


Electronegativity values of the elements (Pauling scale)																			He
H 2.1												B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne		
Li 1.0	Be 1.5												Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar	
Na 0.9	Mg 1.2												Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr	
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe		
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	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn			
Cs 0.7	Ba 0.9	La 1.1	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	Rn		
Fr 0.7	Ra 0.7	Ac 1.1																	
Ce 1.1	Pr 1.1	Nd 1.1	Pm 1.1	Sm 1.1	Eu 1.1	Gd 1.1	Tb 1.1	Dy 1.1	Ho 1.1	Er 1.1	Tm 1.1	Yb 1.1	Lu 1.2						
Th 1.3	Pa 1.5	U 1.7	Np 1.3	Pu 1.3	Am 1.3	Cm 1.3	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr						

2- Non polar covalent bond: the electron paired is shared equally by both atoms

Properties of Nonpolar Covalent Bond

- 1- Takes place between two identical nonmetals
- 2- Equal sharing of electrons between the two atoms
- 3- Electronegativity difference between the atoms is 0
- 4- Nonpolar compounds dissolve in a nonpolar solvent
- 5- Physical properties: The compounds are generally liquid or gas at room temperature.
Example H_2, Cl_2, Br_2 --- etc



Q: Use the electronegativity difference to determine the type of bond that would form between each pair of atoms listed.

Cobalt and bromine, $\Delta EN = 0.9$

Nickel and oxygen, $\Delta EN = 1.6$

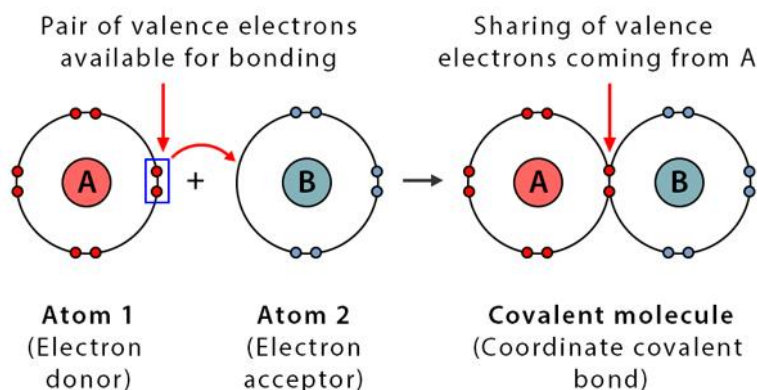
Sodium and fluoride, $\Delta EN = 3.1$

Hydrogen and oxygen, $\Delta EN = 1.4$

Carbon and hydrogen, $\Delta EN = 0.4$

Coordinate covalent bond

is a type of covalent bond in which the shared pair of electrons comes from one of the atoms. The atoms are held together because both of the nuclei attract the electron pair.



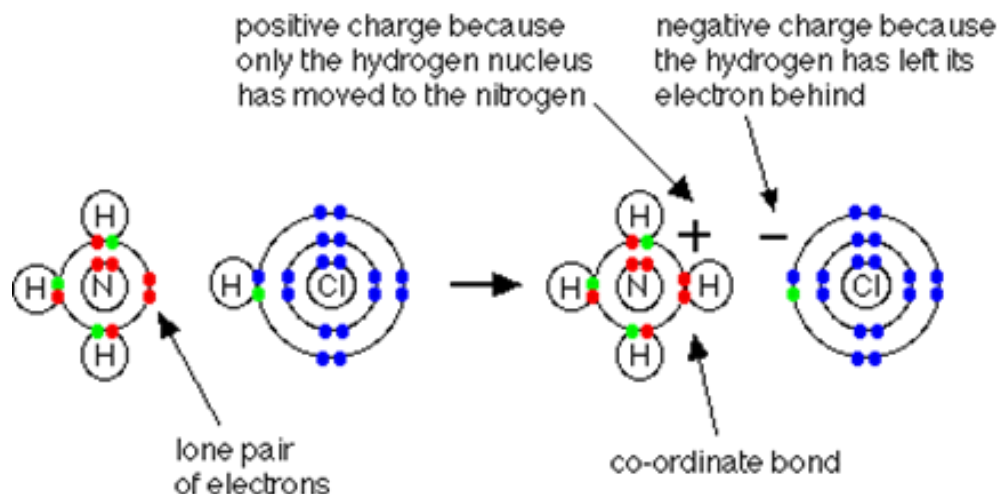
Properties of Coordinate Covalent Bond

Takes place between an electron donor and an electron acceptor, typically between a metal and a ligand. Takes place between dissimilar atoms Formed by the sharing of electrons donated by one of the atoms

- 1- Rigid and directional
- 2- Polar
- 3- Atoms follow the octet rule
- 4- The atom donating the electrons is called a donor, and the atom accepting them (electrons) is called an acceptor.
- 5- Compounds are moderately soluble in water

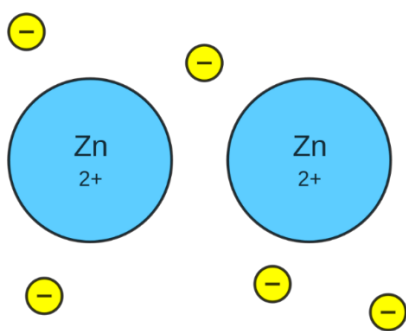
Example of coordinate covalent bond

Ammonium ions, NH_4^+ , are formed by the transfer of a hydrogen ion from the hydrogen chloride to the lone pair of electrons on the ammonia molecule. When the ammonium ion, NH_4^+ , is formed, the fourth hydrogen is attached by a dative covalent bond, because only the hydrogen's nucleus is transferred from the chlorine to the nitrogen. The hydrogen's electron is left behind on the chlorine to form a negative chloride ion. the ammonium ion has been formed it is impossible to tell any difference between the dative covalent and the ordinary covalent bonds. Although the electrons are shown differently in the diagram, there is no difference between them in reality.



Metallic bond

Is a type of chemical bond formed between positively charged atoms in which the free electrons are shared among a lattice of cations. A metallic bond is the sharing of many detached electrons between many positive ions. Metallic bonds are seen in pure metals and alloys and some metalloids. Metals have low ionization energy. Therefore, the valence electrons can be delocalized throughout the metals. Valence electrons (Delocalized electrons) are free to move from one atom to another, so they are move throughout the whole crystalline structure forming an "electron sea". As shown below:



Ionic bond	Covalent bond	Metallic bond
1-Crystalline solid	1-Gas, liquid, or a soft solid.	1-Malleable solid
2- Very high melting point and boiling Point	2-Low melting point and low boiling point	2-High melting point and boiling point

3- Soluble in H₂O Insoluble in nonpolar solvents	3- Insoluble in H ₂ O Soluble in polar solvents	3-Insoluble in H ₂ O Insoluble in Nonpolar solvents
4-conductor of heat and electricity Conducts electricity in aqueous solutions.	4- Nonconductor of heat and electricity	4-Conducts heat and electricity.
5-Nonlustrous	5-Nonlustrous	5- lustrous
6- Examples: NaCl CaCO₃.	6-Examples: H ₂ , O ₂ , N ₂ , benzene.	6-Example gold, copper

Properties of metallic compound

Properties of metals can be explained by metallic bonding.

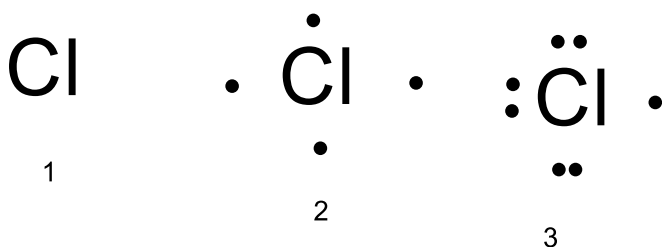
- High Melting Point High Boiling Point
- Malleable (can be hammered into the thin sheet)
- Ductile (they can be drawn into wires)
- Durable (hard)
- Conductors of heat and electricity
- Shiny

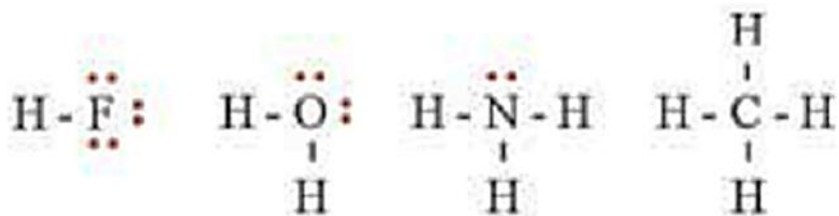
Lewis Dot structures

Lewis dot structures: A representation of covalent bonding in a molecule that is drawn using Lewis symbols. Shared electron pairs are shown as lines, and unshared electron pairs are shown as pairs of dots. Only the valence-shell electrons are shown.

How to write them

- 1- Write the symbol.
- 2- Put one dot for each valence electron. Don't pair up until they are forced to pair up.

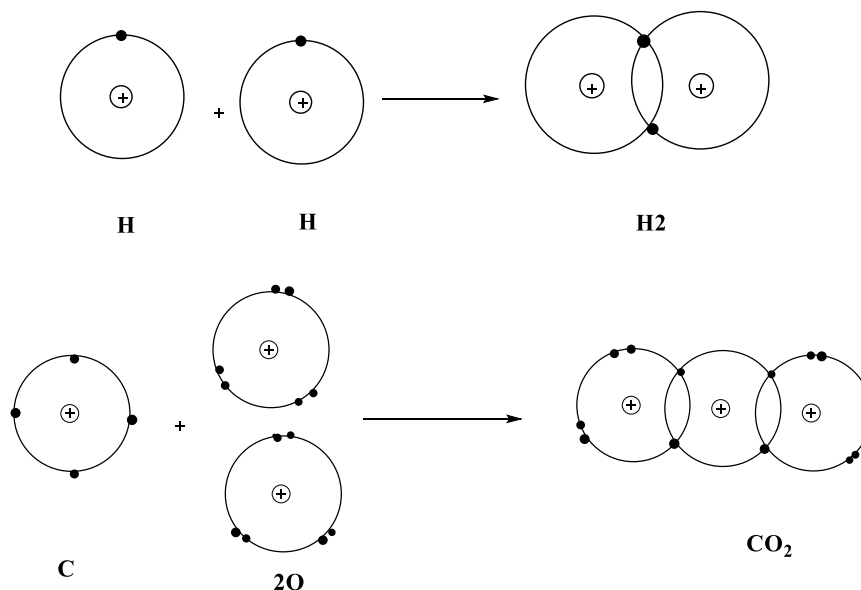




Q: Write the Lewis dot diagram for following below: Na, Mg, C, O, F, Ne, He

Lewis Octet rule

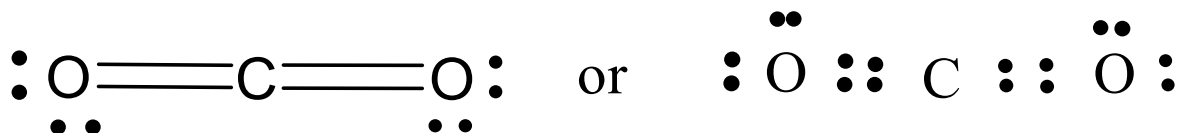
When we write the electronic configurations of the noble gases we find that except helium all of them have 8 electrons in their outermost shell. When two atoms combine, their electrons in each of outer shell will rearrange them, and the electron configuration of atoms (number of electrons outer shell) become similar of the nearest noble gas electron configuration in the other word the outer shell of each atom has 8 electrons. In case of the elements atoms of the nearest of the helium element in the Periodic Table, their outer shell will contain two electron.



$$\text{C} = 4e \quad (\text{in valence shell})$$

$$2\text{O} = 2 \times 2 = 4 \quad (\text{unpaired electron})$$

$$8 \rightarrow 8/2 = 4 \quad (\text{paired electrons})$$



How to draw the Lewis dot structure

1. Find the number of valence electrons for each of the atoms in the molecule.

Note

The number of valence electrons is usually the same as the group number where the element is located.

- The number of valence electrons for alkaline metals is 1 (group 1).
- the number of valence electrons for alkaline earth metals is 2 (group 2)
- The number of valence electrons for group 3 elements is 3
- The number of valence electrons for group 4 elements is 4
- The number of valence electrons for group 5 elements is 5
- The number of valence electrons for group 6 elements is 6
- The number of valence electrons for group 7 elements is 7

Example: Methane: CH₄

- C is located in group 4, thus possess 4 valence electrons
- H is located in group 1, thus possess 1 valence electron

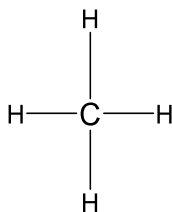
2. Count the total number of valence electrons in the molecule: Sum the valence electrons from each atom in the molecule for methane CH₄

Total valence e. from C: 4, 4 e. x 1 C = 4

Total valence e. from H: 4, 1 e. x 4H = 4

Total valence e. in the molecule: 4 + 4 = 8

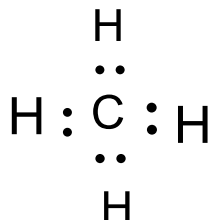
3. Determine the central atoms (the element there is only one for methane: the atom with low electronegativity be the central atom.



- 1- Each bond in a molecule is made up from two electrons. Each atom in the molecule needs to be bonded together to its nearest atom.
- 2- At the end, each atom should be surrounded by eight electrons (following the octet rule)
Remember that H only needs 2 electrons

6- Turn lone pairs into double or triple bond to give atom an octet

$$\begin{array}{r}
 \text{total valence electron of H} = 1e \times 4H \\
 \text{C} = 4e \times 1C \\
 \hline
 \text{Total} = 8 \\
 \text{used in bond} = 2 \times 4 = 8 \\
 \hline
 \text{remain} = 0
 \end{array}$$



Note: Remember these simple rules when drawing Lewis structures:

- Hydrogen and the halogens form single bonds
- The oxygen family forms single or double bonds. They need at least 2 bonds.
- The nitrogen family forms single, double or triple bonds. They need at least 3 bonds.
- The carbon family needs 4 bonds

Note

1 line bond = 2 electron

2 line bond = 4electrons

3 line bond =6 electrons

Q: Draw the Lewis dot structure for H₂O

- 1- Count all v.e for each atom
- 2- Determine the central atom (oxygen is central atom)
- 3- Draw the single bonds to the central atom



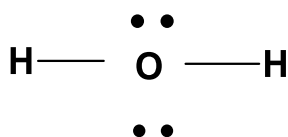
$$H_2 = 2 \times 1e = 2$$

$$O = 1 \times 6e = 6$$

$$\text{total} = 8 \text{ v.e}$$

$$\text{electron bond} = 4$$

$$\text{remaining v.e} = 4 \text{ lone pair}$$



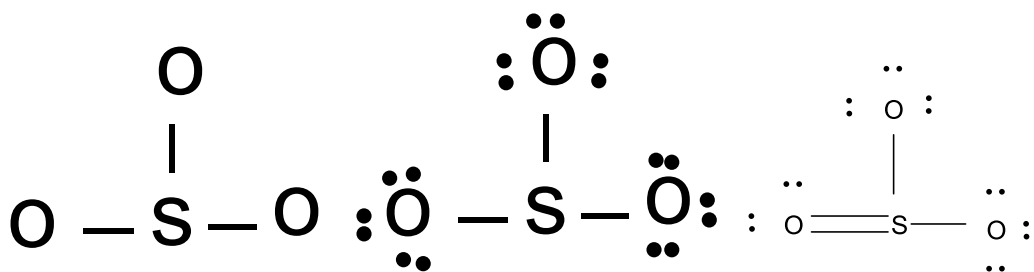
Q: Draw the Lewis Dot structure for SO₃

Here the sulphur atom is unhappy because it doesn't have an octet structure. So it needs to turn on lone pairs into double bond and become as shown below:

$$S = 6e \times 1S = 6$$

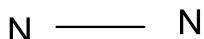
$$O = 6 \times 3O = 18,$$

$$\text{total} = 18 + 6 = 24 - 6e (\text{used in bond}) = 18e \text{ ion pairs}$$



Q: Draw the Lewis Dot structure for the following molecules, N₂, F₂, CO₂

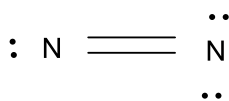
$$N = 5 \times 2 = 10 \text{ v.e}$$



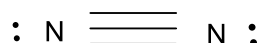
$$10 - 2 (\text{used in bond}) = 8 \text{ are lone pairs}$$



Need to turn one lone pairs to double bond

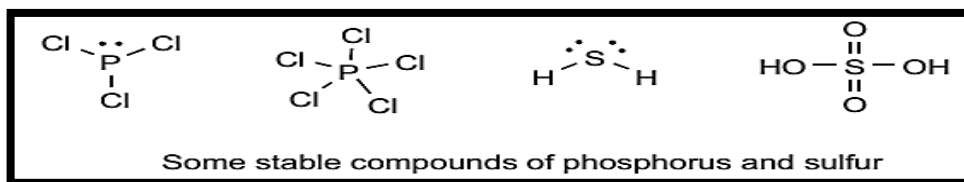


Another lone pairs need to turn to be triplet bond



EXCEPTIONS TO THE OCTET RULE

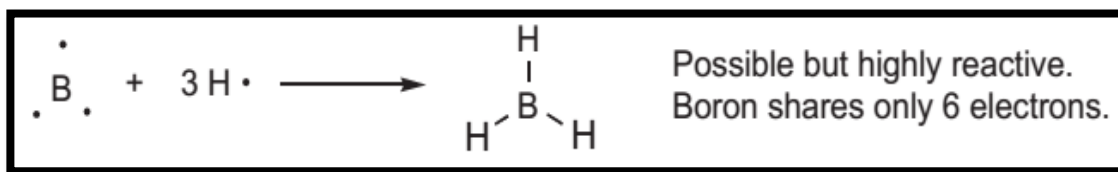
The maximum number of electrons possible in the valence shell of the second row elements is eight. However, the elements of the third row, such as phosphorus and sulfur, can form stable systems by sharing eight or more electrons. The presence of d-orbitals, which can accommodate up to ten electrons, makes this possible.



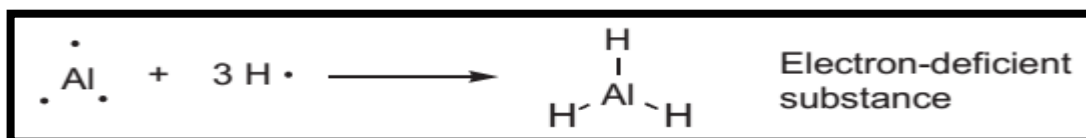
Now, back to the second row, what happens when the first nonmetal, Boron ($Z=3$), combines with hydrogen. By repeating the process outlined before for Carbon, Nitrogen, Oxygen, and Fluorine, we conclude that Boron needs to bond to 5 hydrogen atoms to fulfill the octet rule. The problem is that with only three electrons in the valence shell this is impossible.



The only possibility for Boron is to bond to three hydrogen atoms, in which case it forms a compound (borane, BH_3) that does not fulfill the octet rule. The compound actually exists, but it is highly reactive, that is to say, unstable. Substances such as BH_3 are referred to as electron-deficient molecules, and are very reactive towards electron-rich substances. Borine molecule called Lewis acid.



Aluminum, which is also in group III, exhibits similar behavior.



Free Radicals

Some elements, most notably nitrogen, can form compounds that do not obey the octet rule. One class of such compounds is those that have an odd number of electrons. As the octet rule requires eight electrons around each atom, a molecule with an odd number of electrons must disobey the octet rule. Molecules with unpaired electrons are termed 'free radicals.' While typically highly unstable, and therefore highly reactive, some free radicals exhibit stability of days, months, or even years. These latter compounds are said to be 'metastable,' meaning they will decompose or react if given enough time, but are stable enough for a considerable amount of time, from days to even years, when subjected to only minor disturbances.



Nitric oxide

How to find the formal charge for Lewis structure

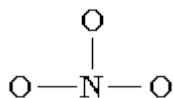
An outline of how to determine the "best" Lewis structure for an example, NO_3^- is given below:

- 1- Determine the total number of valence electrons in a molecule

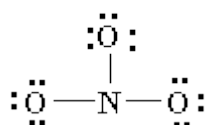
$$\begin{array}{r} \text{N} \quad 5 \\ 3 \text{ O} \quad 18 \\ \hline -\text{ve} \quad 1 \\ \hline 24 \end{array}$$

2. Draw a skeleton for the molecule which connects all atoms using only single bonds. In simple molecules, the atom with the most available sites for bonding is usually placed central. The

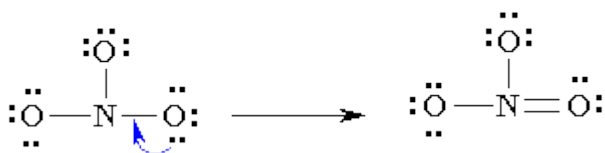
number of bonding sites is determined by considering the number of valence electrons and the ability of an atom to expand its octet. As you become better, you will be able to recognize that certain groups of atoms prefer to bond together in a certain way.



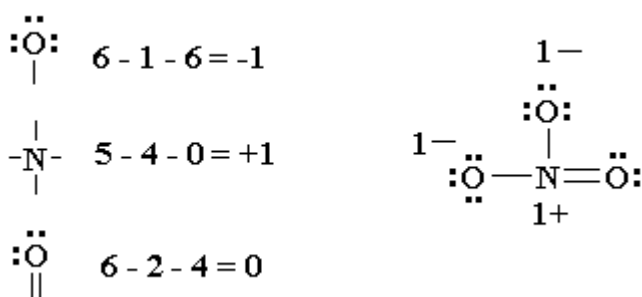
3. Of the 24 valence electrons in NO_3^- , 6 were required to make the skeleton. Consider the remaining 18 electrons and place them so as to fill the octets of as many atoms as possible (start with the most electronegative atoms first then proceed to the more electropositive atoms).



- 4- Are the octets of all the atoms filled? If not then fill the remaining octets by making multiple bonds (make a lone pair of electrons, located on a more electronegative atom, into a bonding pair of electrons that is shared with the atom that is electron deficient).

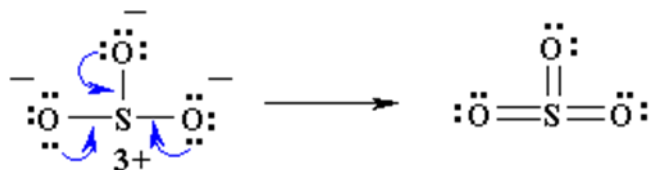


- 4- Check that you have the lowest **FORMAL CHARGES** possible for all the atoms, without violating the octet rule; (valence e-) - (bonding e-) - (lone electrons).

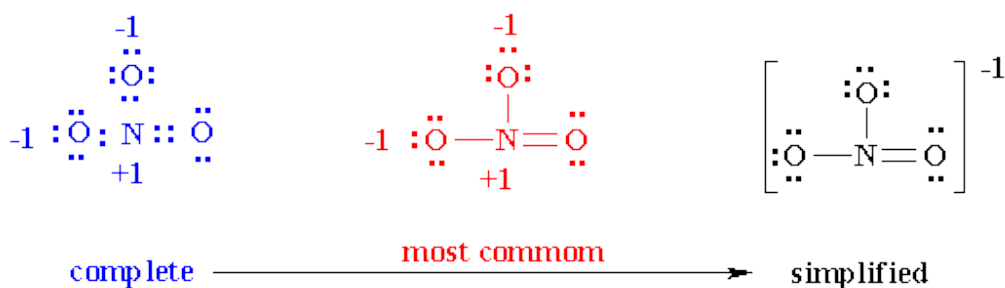


IMPORTANT: is best to have a formal charge of 0 for as many of the atoms in a structure as possible. If a formal charge of 1- is located next to a formal charge of 1+, the formal charges can usually be minimized by having a lone pair of electrons, located on the atom with the (-1) charge become a bonding pair of electrons that is shared with the atom that has the 1+ formal charge.

CAUTION : octets can be expanded to minimise formal charges *but only* for atoms in the second row of the periodic table (where $n=3$ or greater), N cannot expand its octet so keeps a formal charge of 1+ and both singly bonded oxygens a formal charge of 1-. If our molecule were SO_3 , however, it would be possible to minimize all formal charges by having the sulfur expand its octet.



- 5- You may find that the best Lewis diagram (the one with the lowest formal charges and all octets satisfied) is given in a number of different ways. For NO_3^- , three different diagrams are given below. From left to right they start with the most complete Lewis diagram to the most simplified.



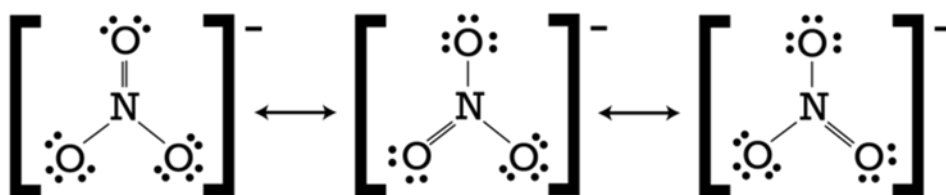
Formal charge equation formally compares the number of valence electrons in an isolated neutral atom (which can be determined from the older style group number of the periodic table with the number of valence electrons around the atom in the molecule:

$$\text{formal charge} = VE - NE - BE$$

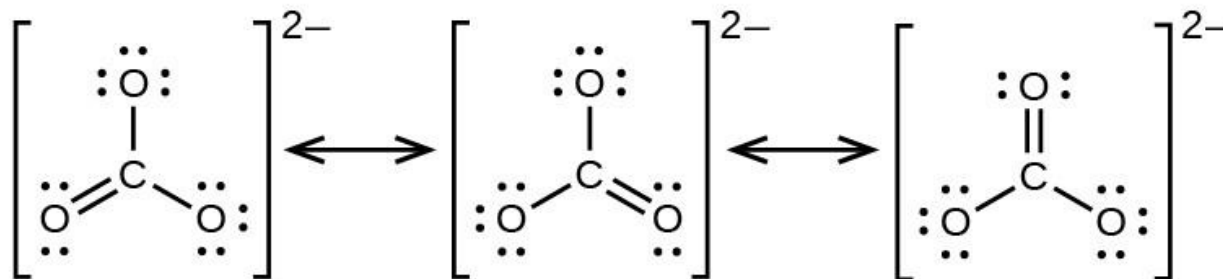
- Draw a circle around the atom of interest
- Count the number of electrons in the atoms circle (electrons in covalent bonds are shared)

Resonance

Resonance structures describe possible electronic configurations; the actual configuration is a combination of the possible variations. In chemistry terms, resonance describes the fact that electrons are delocalized, or flow freely through the molecule, which allows multiple structures to be possible for a given molecule. For example, the nitrate ion, NO_3^- , has more than one valid Lewis structure. The structure contains two N-O single bonds and one N=O double bond. Therefore, three valid resonance structures can be drawn. Double-ended arrows are used to indicate that the structures are chemically equivalent. The electronic configuration does not change between the three structures.



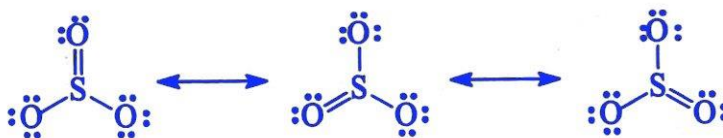
The carbonate anion, CO_3^{2-} , provides a second example of resonance:



One oxygen atom must have a double bond to carbon to complete the octet on the central atom. All oxygen atoms, however, are equivalent, and the double bond could form from any one of the three atoms. This gives rise to three resonance forms of the carbonate ion. Another example is ozone molecule (O_3)

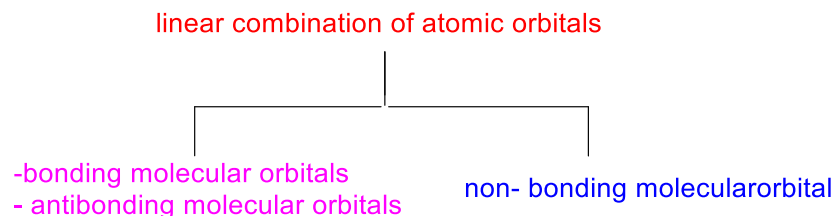


Resonance structure of SO_3



The molecular orbital theory (MOT)

Is a method for describing the electronic structure of molecules using quantum mechanics. This method depends directly to linear combination of the atomic orbitals to form molecular orbitals. According to MOT, two atomic orbitals overlap resulting in the formation of molecular orbital. Number of atomic orbitals overlapping together is equal to the molecular orbital formed. The two atomic orbital formed by LCAO (linear combination of atomic orbital) in the same phase or in the different phase are known as bonding and antibonding molecular orbitals respectively. The energy of bonding molecular orbital is less than that of the pure atomic orbital by an amount Delta.



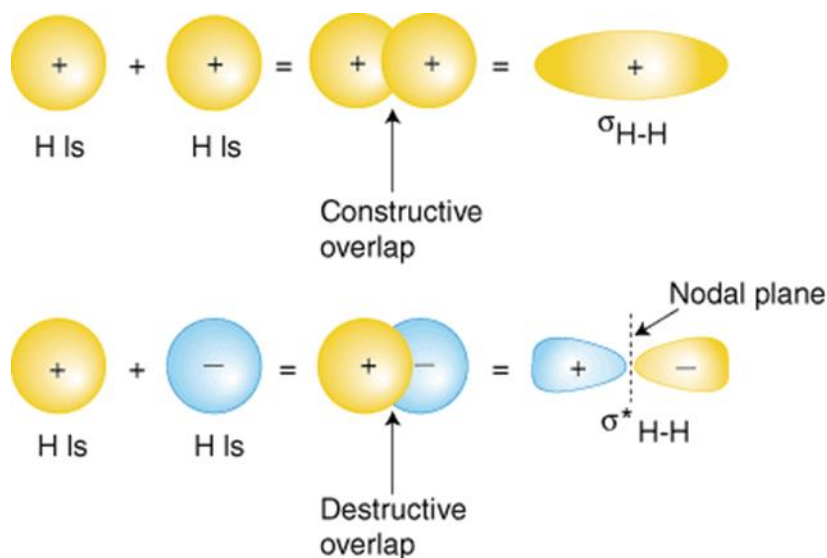
Bonding molecular orbitals: molecular orbitals with overlap integral $S > 0$ these orbital can be either σ or π

Antibonding molecular orbitals: molecular orbitals with overlap integral $S < 0$ these orbitals can be either σ^* or π^*

Nonbonding molecular orbitals: molecular orbital with overlap $S = 0$.

Overlap integral(s): is a quantitative the measure for overlap atomic orbitals.

1- Linear combination (overlap) of s-orbital (molecular orbital from s-orbitals)



Bonding order:

Bond order is the amount of bonds formed between two atoms. For example, two bonds are formed between oxygen atoms, so the bond order is 2. The following is the equation to find bond order. In molecular orbital theory, bond order is also defined as the difference, divided by two, between the number of bonding and antibonding electrons.

$$\text{bond order} = \frac{e' \text{ s in bonding orbitals} - e' \text{ s in antibonding}}{2}$$

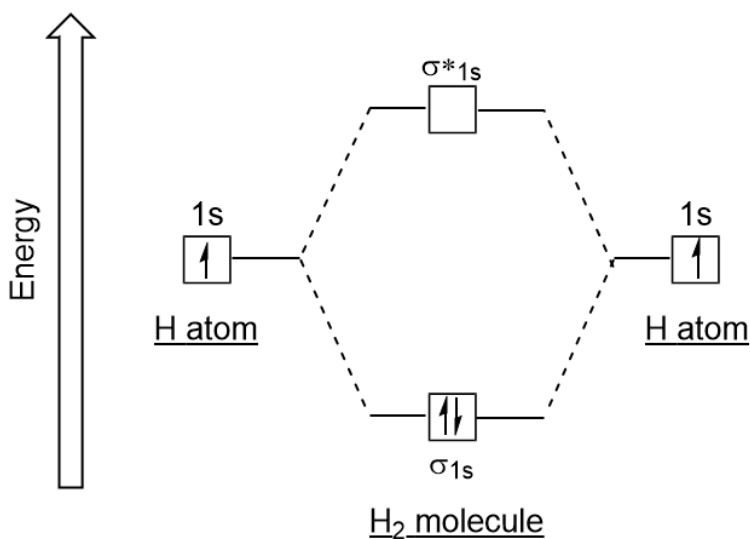
Bond order gives information about bond length and strength. Generally, higher bond order correlates to a shorter bond length. This is due to the greater number of bonds between the atoms. In addition, because of the greater number of bonds between the atoms, the strength should also be greater as bond order increases.

Filling Electrons in MO Diagrams

The next step in constructing an MO diagram is filling the newly formed molecular orbitals with electrons. Three general rules apply:

- The Aufbau principle states that orbitals are filled starting with the lowest energy
- The Pauli Exclusion Principle states that (the maximum number of electrons occupying an orbital is two, with opposite spins) .
- Hund's rule states that when there are several MOs with equal energy, and the electrons occupy the MOs one at a time before two occupy the same MO. The filled MO that is highest in energy is called the Highest Occupied Molecular Orbital, or HOMO; the empty MO just above it is the Lowest Unoccupied Molecular Orbital, or LUMO. The electrons in the bonding MOs are called bonding electrons, and any electrons in the antibonding orbital are called antibonding electrons. The reduction these electrons' energy is the driving force for chemical bond formation.

The molecular orbital energy level diagram for H₂ molecule is shown in Fig number 1



$$\text{Bond order} = \frac{1}{2} (\text{e}^- \text{ in bonding MO} - \text{e}^- \text{ in antibonding MO})$$

For H₂, bond order = $\frac{1}{2} (2-0) = 1$, which means H₂ has only one bond. The antibonding orbital is empty. Thus, H₂ is a stable molecule. There is no unpaired electron, so H₂ is diamagnetic. The molecular orbital electronic configuration of Homo nuclear Diatomic Molecule H₂ is: $(\sigma 1s)^2$

Hydrogen molecule ion (H_2^+)

Combination of hydrogen atom containing one electron and hydrogen ion having no electron results in the formation of H_2^+ . Therefore, this ion consists of only one electron. The molecular orbital diagram is given in figure below.

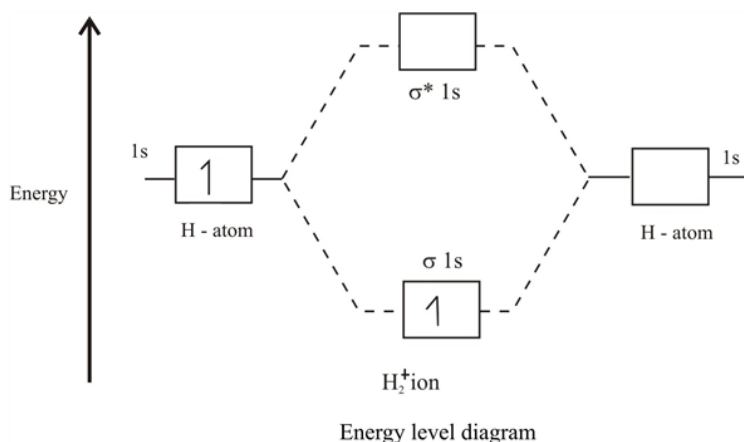


Fig. No. 2 Molecular Orbital Energy Level Diagram for H_2^+ ion

The electronic configuration of the molecule is

$$H_2^+: (\sigma 1s)^1$$

$$\text{Bond order} = \frac{1-0}{2} = \frac{1}{2}$$

The molecule is considered stable the bond order has positive value. As H_2^+ consists of unpaired electrons therefore it is considered as a **paramagnetic** molecule. Experimental data confirms the stability of the ion as well as its paramagnetic character. The bond length of H_2^+ ion is larger when compared with H_2 molecule (bond length $H_2^+ = 104$ pm; $H_2 = 74$ pm) but H_2^+ has less bond.

Hypothetical Helium Molecule (He_2)

Helium atom consists of two electrons in 1s-orbital, which means four electrons in He_2 molecule. These electrons will fit in $\sigma 1s$ and $\sigma^* 1s$ MOs as shown in figure number. The electronic configuration for helium molecule may be written as:

$$\text{Electron configuration: } (\sigma 1s)^2(\sigma^* 1s)^2$$

$$\text{bond order} = \frac{e b - e a}{2} = \frac{2 - 0}{2} = 0$$

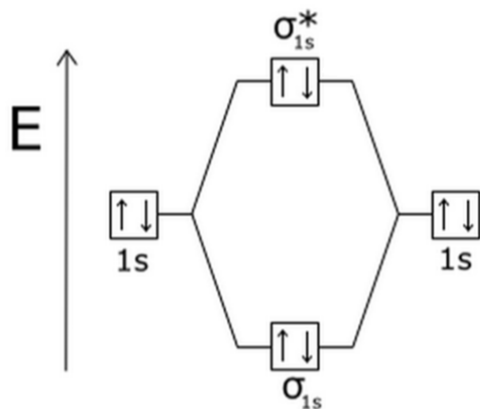
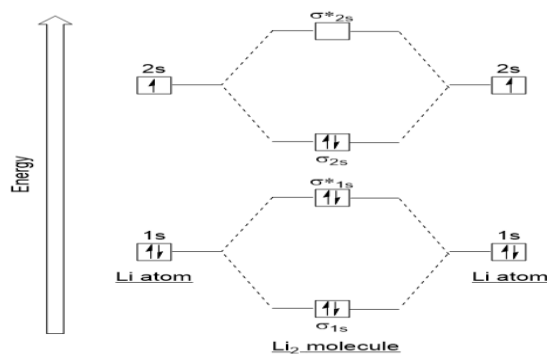
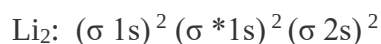


Fig. No. 3 Molecular Orbital Energy Diagram for He₂ molecule (hypothetical)

There is no net bonding as it has zero bond order and therefore He₂ molecule cannot exist. There is no experimental evidence for the existence of this molecule.

Lithium Molecule (Li₂)

The electronic configuration of lithium is 1s²2s¹ that is, lithium molecule has six electrons. The electronic configuration of Li₂ molecule may be written as:



From the above electronic configuration of Li₂ molecule we conclude that there are 4 electrons in bonding MOs and 2 electrons in antibonding MOs. Therefore, its bond order is:

$$\text{Bond Order} = 4 - 2 / 2 = 1$$

Thus, there is one Li-Li sigma bond. The bond energy of the molecule is about 110 kJ mol⁻¹ which is quite low. The bond length of the molecule is 265 pm. It is **diamagnetic** as it has **no unpaired** electrons and diamagnetic Li₂ molecules are known to **Exist**.

Note

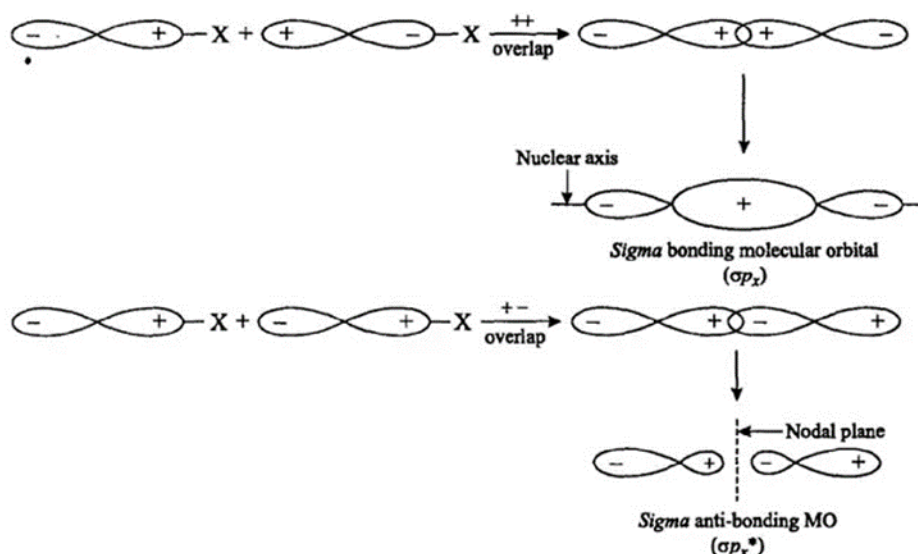
To write the electron configuration of the molecule, we just give the number of electrons in each orbital:



2- Linear combination (overlap) of p-orbital (Molecular orbitals from p-orbital)

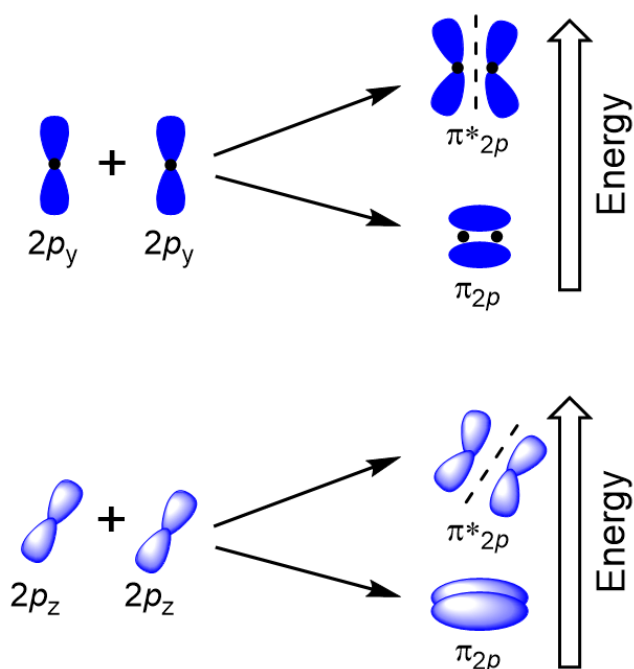
The p orbitals can overlap in two ways: head-to-head or sideways. Head-to-head overlap of p atomic orbitals results in a bonding and antibonding molecular orbital, where the electron density is centred along the internuclear axis, making them σ orbitals

1- Combination of p-orbitals



2- Combination of two pz-atomic orbitals

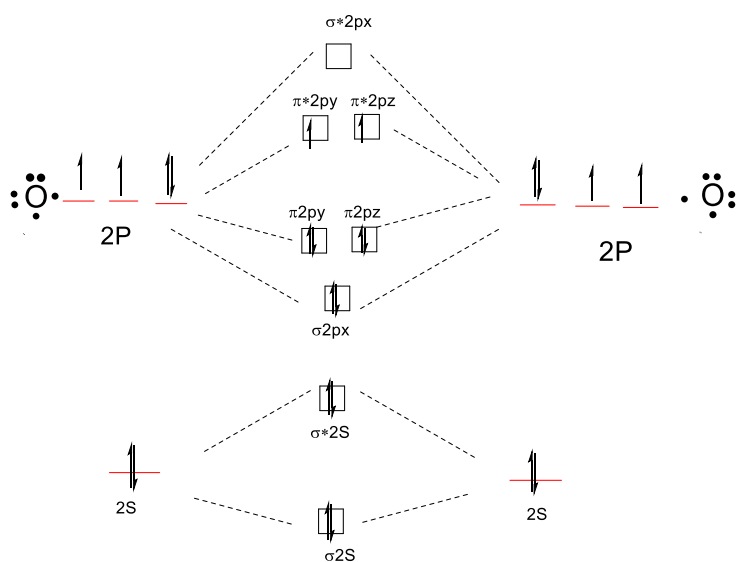
Sideways overlap of the remaining four p atomic orbitals can occur along the two other axis, generating four π molecular orbitals having electron density on opposite sides of the internuclear axis.



- The head-to-head overlap giving σ molecular orbitals results in greater overlap, making its bonding molecular orbital the most stable and lowest energy,
- The σ^* antibonding is least stable and has the highest energy (figure below). Sideways overlap gives four π molecular orbitals, two lower-energy degenerate-bonding molecular orbitals, and two higher-energy antibonding orbitals.

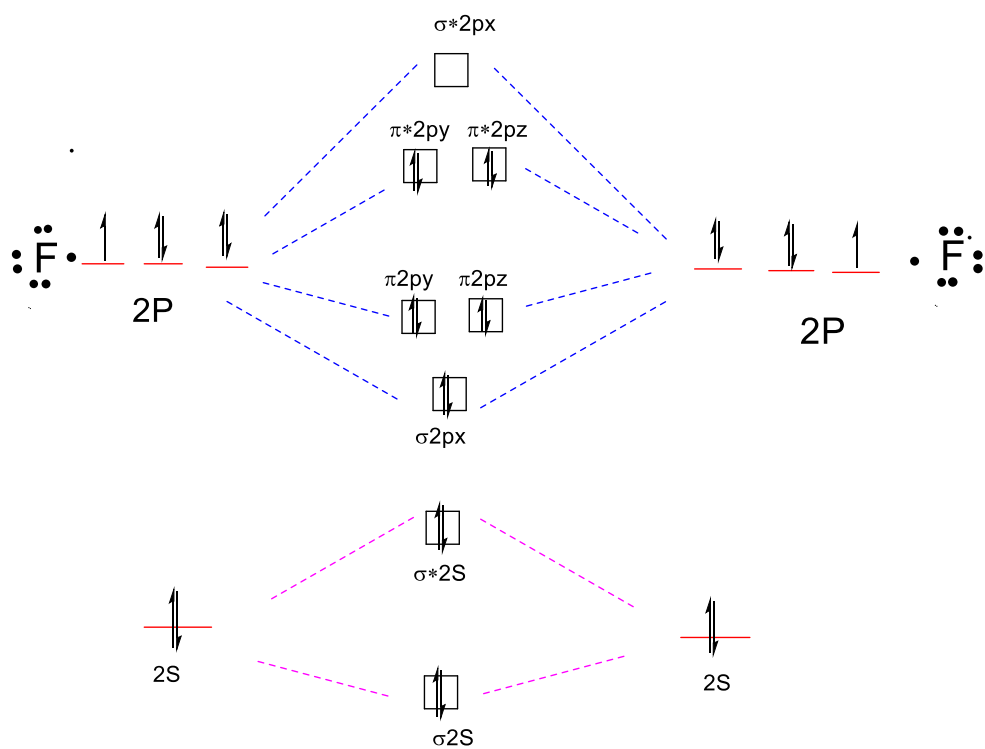
Example: N_2 , C_2 , F_2 , O_2 , O_2^+ , O_2^{-2} , C_2^{-2}

Since O_2 is a molecule, we must write its electron configuration using molecular orbitals.

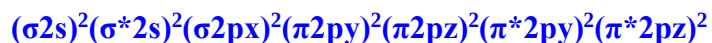


Electron configuration = $(\sigma2s)^2(\sigma^*2s)^2(\pi2p)^4(\pi^*2p)^2$

$$\text{bond order} = \frac{e \text{ in bonding orbital} - e \text{ in antibonding orbital}}{2} = \frac{6-2}{2} = \frac{4}{2} = 2$$



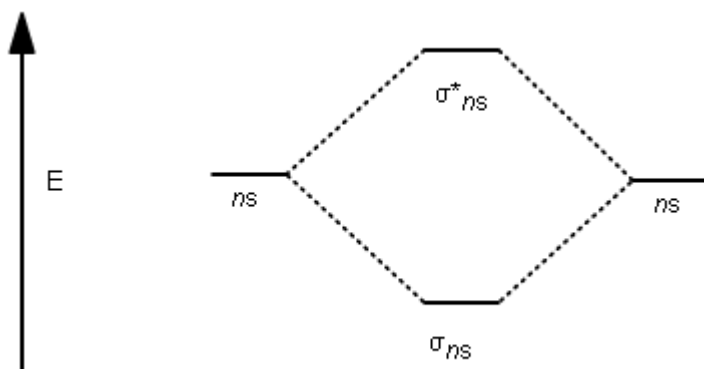
Thus, **electron configuration** is:



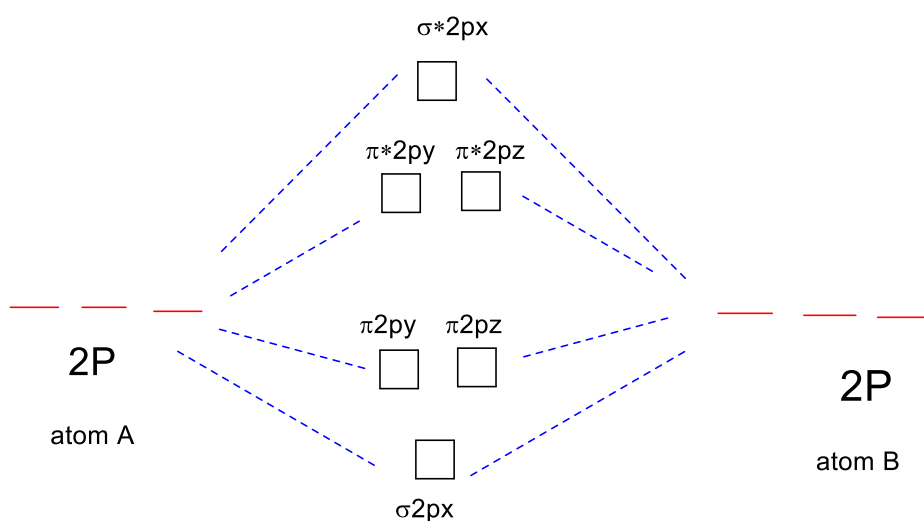
$$\text{Bond order} = 6 - 4 / 2 = 1$$

NOTE

- 1- ns/ns overlap for a homonuclear diatomic molecule gives rise to a partial MO diagram like this:

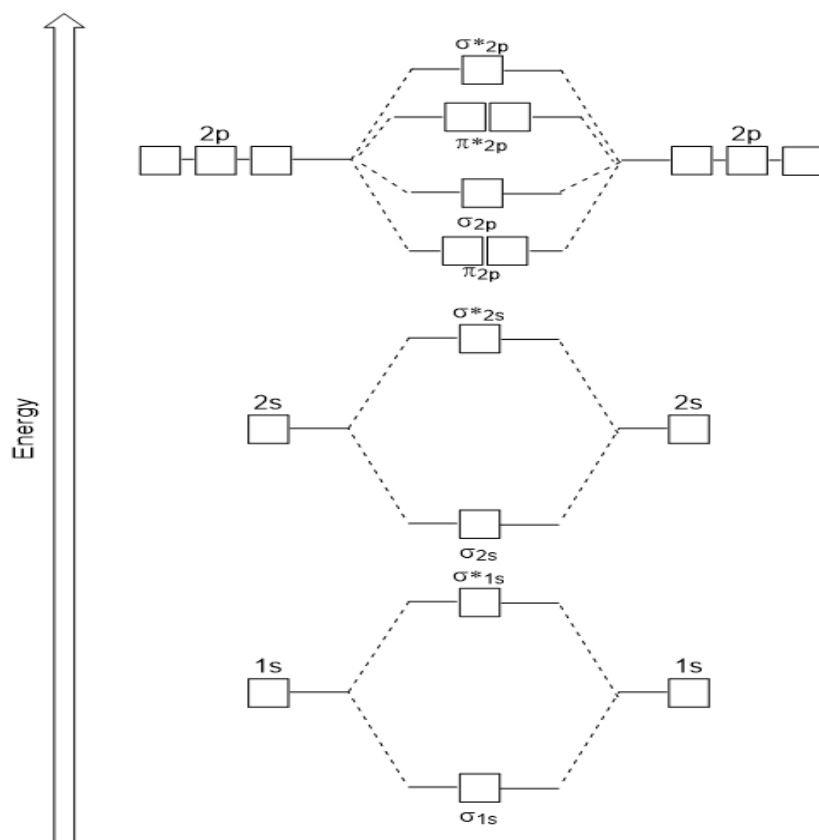


- 2- np/np overlap for O₂ and F₂ gives:

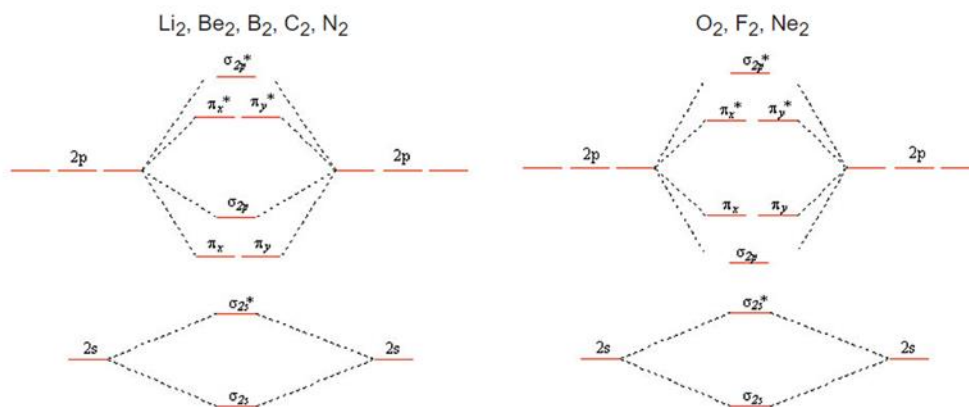


The energy diagram we have just generated fits experimentally with O₂, F₂, and Ne₂, but does not fit for B₂, C₂, and N₂. In the latter, homonuclear diatomic molecules (B₂, C₂, and N₂),

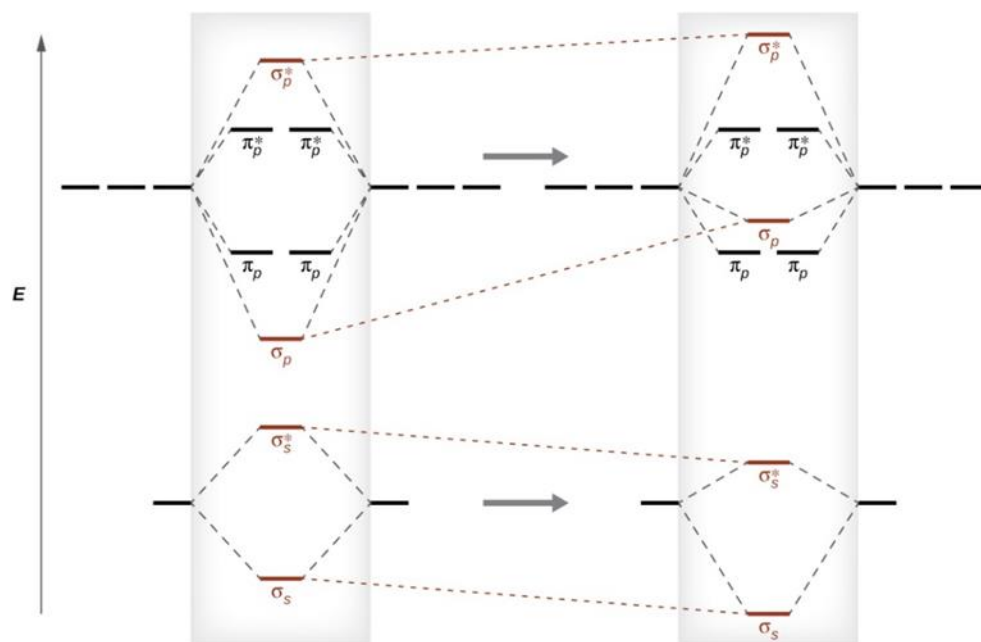
interactions take place between the 2s and 2p atomic orbitals that are strong enough to swap the ordering of the σ_{2p} and π_{2p} molecular orbitals as shown in Figure below.



This switch in orbital ordering occurs because of a phenomenon called **s-p mixing**. s-p mixing does not create new orbitals; it merely influences the energies of the existing molecular orbitals. The σ_s wave function mathematically combines with the σ_p wave function, with the result that the σ_s orbital becomes more stable, and the σ_p orbital becomes less stable. Similarly, the antibonding orbitals also undergo **s-p mixing**, with the σ_s^* becoming more stable and the σ_p^* becoming less stable.

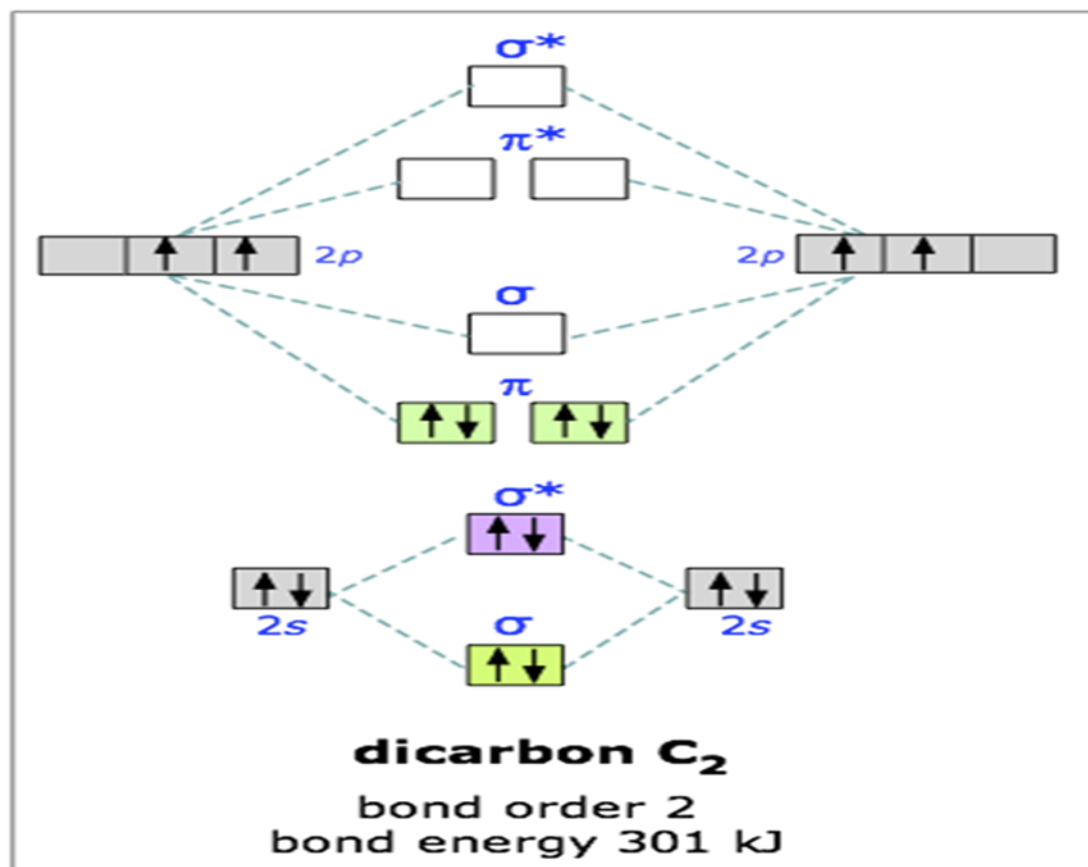


s-p mixing occurs when the *s* and *p* orbitals have similar energies. When a single *p* orbital contains a pair of electrons, the act of pairing the electrons raises the energy of the orbital. Thus the 2*p* orbitals for O, F, and Ne are higher in energy than the 2*p* orbitals for Li, Be, B, C, and N. Because of this, O₂, F₂, and N₂ only have negligible s-p mixing (not sufficient to change the energy ordering), and their MO diagrams follow the normal pattern, as shown before. All of the other period 2 diatomic molecules do have s-p mixing, which leads to the pattern where the σ_p orbital is raised above the π_p set.



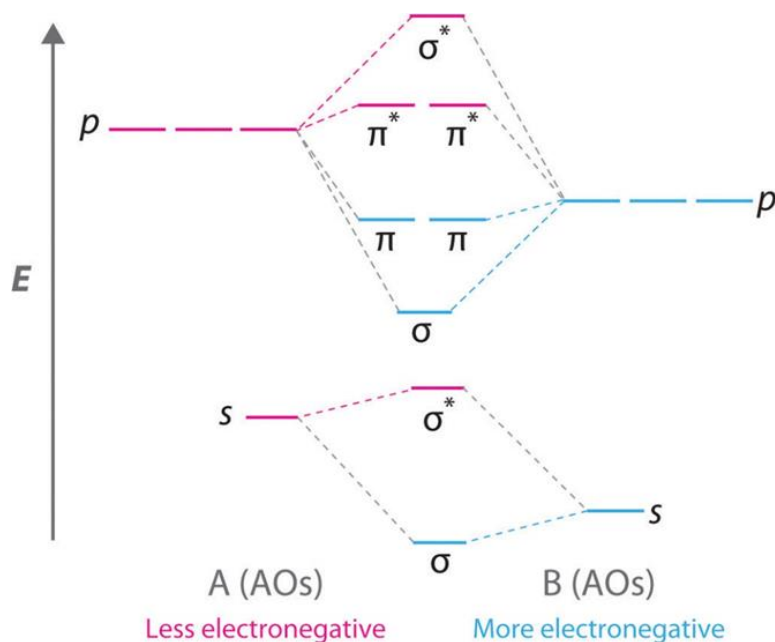
Q- Draw MOT diagram for C₂?

Bond order= $4-0/2 = 2$ double bond



Molecular Orbitals for Heteronuclear Diatomic Molecules

Diatomic molecules with two different atoms are called heteronuclear diatomic molecules. When two nonidentical atoms interact to form a chemical bond, the interacting atomic orbitals do not have the same energy. If, for example, element B is more electronegative than element A ($\chi_B > \chi_A$), the net result is a “skewed” molecular orbital energy-level diagram, such as the one shown for a hypothetical A–B molecule in the Figure below. The atomic orbitals of element B are uniformly lower in energy than the corresponding atomic orbitals of element A because of the enhanced stability of the electrons in element B. The molecular orbitals are no longer symmetrical, and the energies of the bonding molecular orbitals are more similar to those of the atomic orbitals of B. Hence the electron density of bonding electrons is likely to be closer to the more electronegative atom. In this way, molecular orbital theory can describe a polar covalent bond.

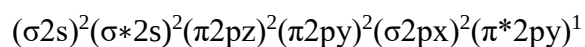


The bonding molecular orbitals are closer in energy to the atomic orbitals of the more electronegative B atom. Consequently, the electrons in the bonding orbitals are not shared equally between the two atoms. On average, they are closer to the B atom, resulting in a polar covalent bond.

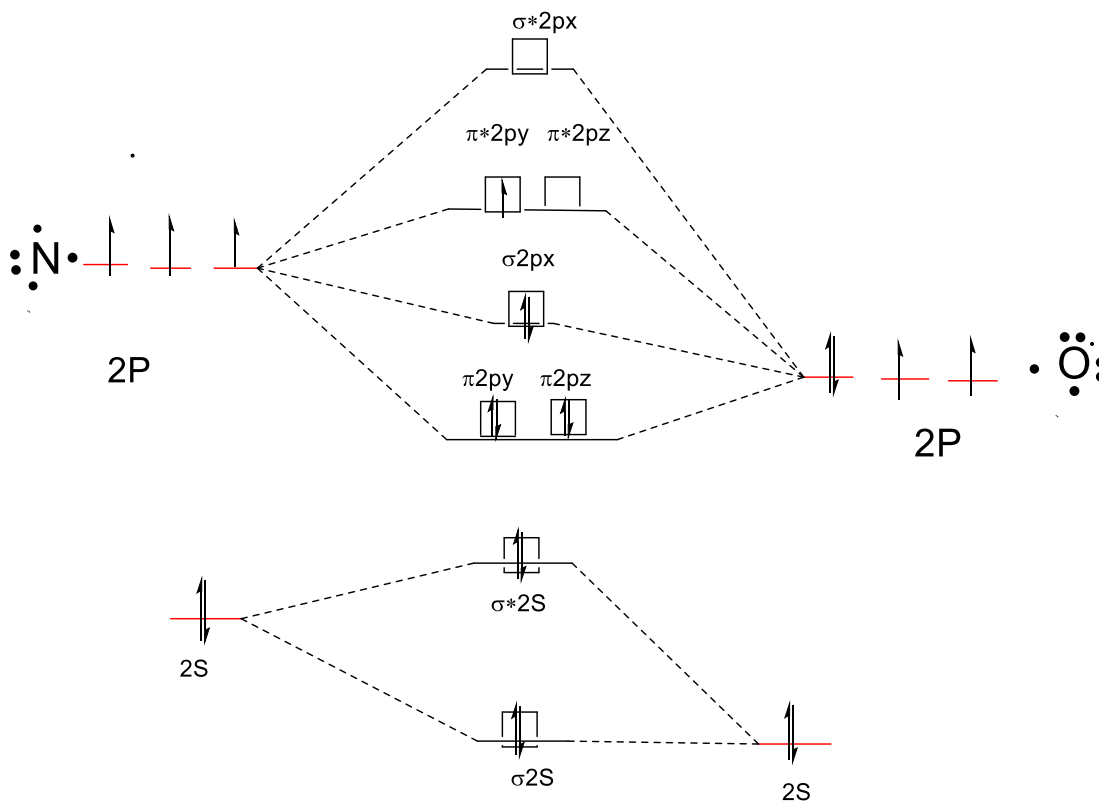
Note A molecular orbital energy-level diagram is always skewed toward the more electronegative atom.

Draw the MO diagram of NO.

The total number of electrons in NO is 15 as nitrogen has 7 electrons and oxygen has 8 electrons. The molecular orbital configuration of NO is shown below:



The molecular orbital diagram of NO is shown below: The bond order of NO is calculated using the formula shown below: $B.O. = (N_b - N_a)/2$



Since the above diagram has one lone pair of electrons, it is **paramagnetic**.

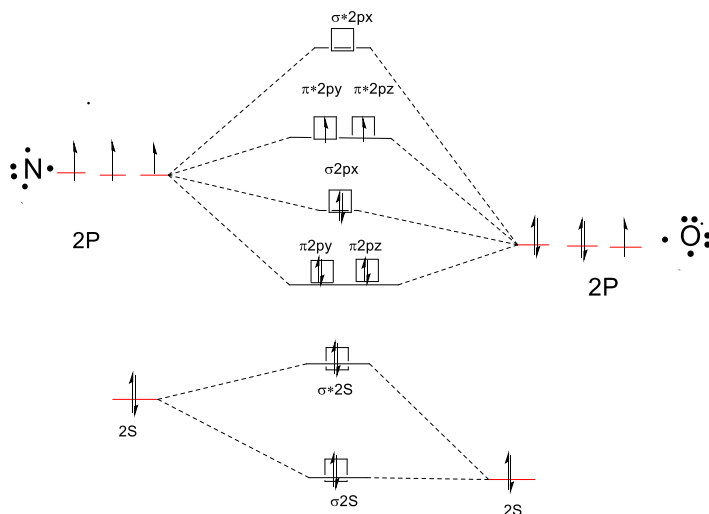
$$\text{Bond order} = \frac{6 - 1}{2} = \frac{5}{2} = 2.5$$

Electron configuration: $(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_z)^2 (\pi 2p_y)^2 (\sigma 2p_x)^2 (\pi^* 2p_y)^1$

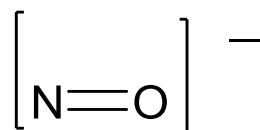
Draw the MOT diagram for NO^{-1}

${}^7\text{N}: 1s^2 2s^2 2p^3$

${}^8\text{O}^{-1}: 1s^2 2s^2 2p^5$



Bond order: $(6 - 2) / 2 = 4 / 2 = 2$



- 1- Electron configuration: $(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2pz)^2 (\pi 2py)^2 (\sigma 2px)^2 (\pi^* 2py)^2$
- 2- **Paramagnetic**

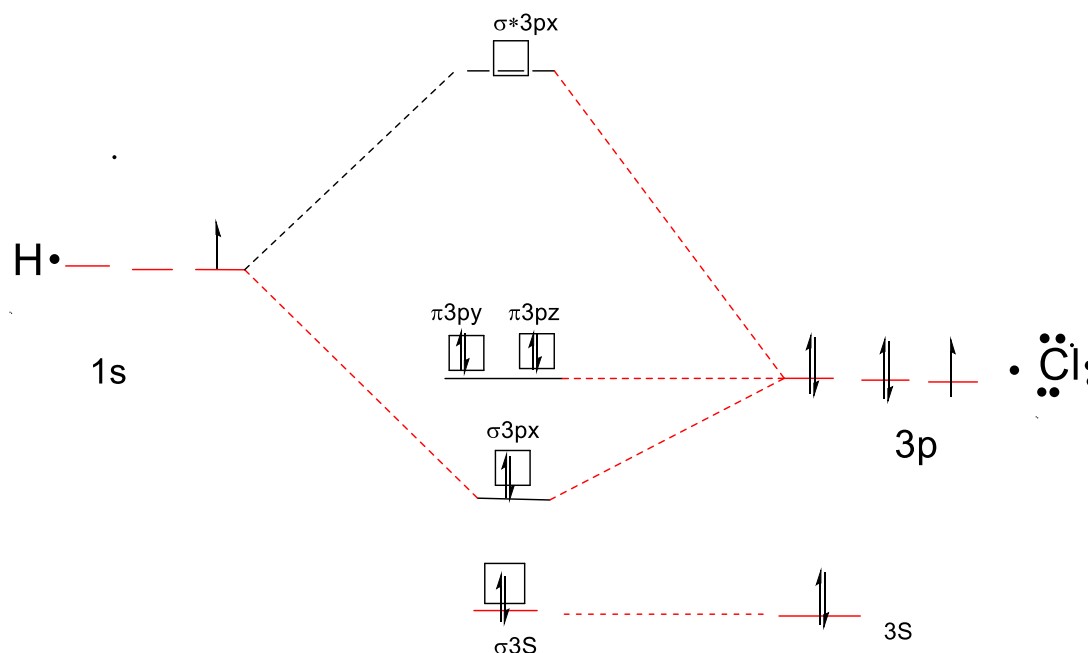
Draw the MOT diagram for HCl molecule

H: 1s¹

17Cl: 1s² 2s² 2p⁶ **3s² 3p⁵**

Bond order = $2 - 0 / 2 = 1$ H-Cl

In this molecule the one orbital from H (1s) overlap with one orbital from Cl (3p) to form two molecular orbitals ($\sigma 3px$), ($\sigma^* 3px$) as shown below



Valence Bond Theory (V.B.T)

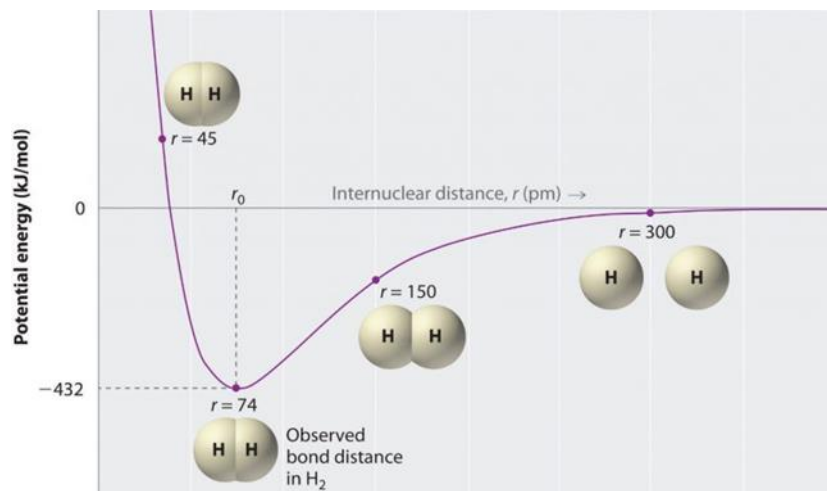
In the year 1927, Heitler and London came up with the concept of Valence Bond Theory. It was then modified and developed by L Pauling and J.C Slater in 1931. The valence bond theory is based on certain things like electronic configurations of elements, overlap criteria of atomic orbitals, atomic orbital and stability of the molecule. Many approaches have been put forth to explain the nature of bonding in coordination compounds. One of them is the Valence Bond (VB) Theory. The Valence Bond Theory was developed in order to explain chemical bonding using the method of quantum mechanics. This theory primarily focuses on the formation of individual bonds from the atomic orbitals of the participating atoms during the formation of a molecule. **Chemical bonds are formed from the overlapping of atomic orbitals wherein the electrons are localized in the corresponding bond region.** It also emphasizes that the nucleus of one atom in a molecule is attracted to the electrons of the other atoms.

Postulates of Valence Bond Theory

The important postulates of the valence bond theory are listed below.

- 1- Covalent bonds are formed when two valence orbitals (half-filled) belonging to two different atoms overlap on each other.
- 2- The presence of many unpaired electrons in the valence shell of an atom enables it to form multiple bonds with other atoms. The paired electrons present in the valence shell do not take part in the formation of chemical bonds as per the valence bond theory.
- 3- Covalent chemical bonds are directional and are also parallel to the region corresponding to the atomic orbitals that are overlapping.

- 4- Sigma bonds and pi bonds differ in the pattern that the atomic orbitals overlap in, i.e. pi bonds are formed from sidewise overlapping whereas the overlapping along the axis containing the nuclei of the two atoms leads to the formation of sigma bonds.



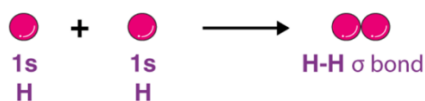
Attractive forces bring two atoms closer to each other while repulsive forces create more and more distance between the atoms. As the two atoms come closer and closer, the system becomes more and more stable due to decrease of energy. So there comes a stage where the force of attraction becomes equal to the repulsive forces and the system has minimum energy, the bonded Hydrogen atoms forms a stable molecule and the distance (r_0) between the atoms is known as bond length. For hydrogen molecule the distance between two hydrogen atoms having minimum energy is 74 pm. Potential energy is assumed to be zero when the two atoms are far apart as there is no attractive or repulsive interactions between them.

Thus bond formation results in release of energy making the hydrogen molecule more stable than the individual hydrogen atoms. That is,

$\text{H} + \text{H} \rightarrow \text{H}_2 + 435.8 \text{ kJ mol}^{-1}$. The energy corresponding to a minimum in the curve is called **Bond Energy**. Conversely, when one mole of H_2 molecules is dissociated into two hydrogen atoms, 435.8 kJ of energy is needed.



It must be kept in mind that the two hydrogen atoms cannot be brought closer than 74 pm because then the repulsive forces will become larger and the potential energy would rise.



Orbital Overlapping of Covalent Bond

When two atoms comes closer to each other, and when two bonding orbital merges, it is known as overlapping of the orbitals. The overlapping orbitals results in the pairing of electrons. The strength of a covalent bond depends upon the amount of overlapping taking place. Greater overlapping results in stronger bond formation between the atoms.

Types of Covalent Bond

Depending upon the type of overlapping, the covalent bonds may be divided into following types
(a) Sigma bond (σ) (b) Pi bond (π)

- **Sigma bond (σ bond)**

The bond formed because of overlapping of two half-filled atomic orbitals along their axis is called as sigma (σ) bond. σ bond is a strong bond because overlapping is large as compared to pi bond. The hybrid orbitals always form σ -bond.

- **S-S Overlapping:** Overlapping of two half-filled s-orbitals taking place along the inter-nuclear axis results in S-S overlapping.
- **S-P overlapping:** Overlapping of half-filled s orbital of one atom with half-filled p orbital of another atom along the inter-nuclear axis to form bonds results in S-P overlapping.
- **P-P overlapping:** In this type, overlapping of one half-filled p orbital from each bonding atom undergoes head-on overlapping along the inter-nuclear axis.

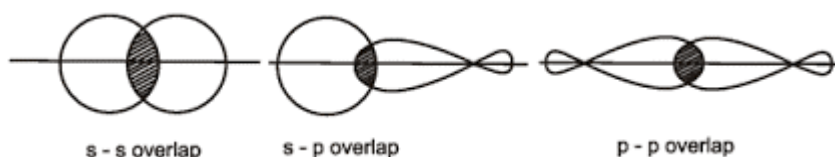


Fig. No. 5 Types of Sigma Bond Formation

- **Pi bond (π bond)**

- Lateral overlapping of half-filled atomic orbitals results in the formation of pi bond.
- The sidewise overlapping is quite less as compared to sigma bond. Therefore, a pi bond formed is a weak bond. π bond overlapping takes place only at the sides of two lobes.
- A π bond is formed only when a **bond** already exists between combining atom.

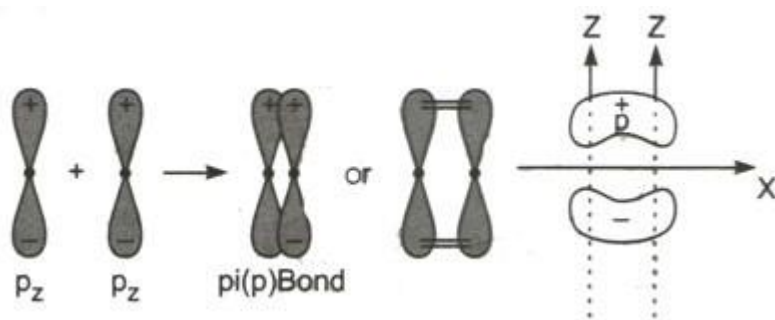


Fig. No.6 Pi Bond Formation

Strength of sigma and pi- bonds

The strength of a covalent bond depends upon the amount of overlapping taking place in atomic orbitals at the time of bond formation. During the formation of a sigma bond the overlapping of orbitals takes place to a larger extent, but quite less at the time of formation of a pi-bond. Therefore **the sigma bond is stronger than a pi-bond**. It is interesting to note that pi- bond between two atoms is formed in addition to a sigma bond. It is always present in the molecules having multiple bonds.

Difference between sigma and pi

Sigma Bond	Pi Bond
1-Formed by end to end filled atomic orbitals along the intermolecular axis. The overlapping takes place between two s-orbitals, one s and p orbitals.	1- Formed by sidewise overlap of two half-filled p-orbitals.
2- Overlapping takes place to a greater extent, thereby forming a stronger bond.	2- Overlapping takes place to lesser extent, thereby forming a weaker bond.
3-The molecular orbital is symmetrical about inter nuclear axis.	3- Molecular orbital are discontinuous.
4- Atoms can freely rotate around sigma bond.	4- Because of overlapping of electron cloud above and below the plane of atoms, they cannot rotate freely.
5- Bond may be present between two atoms either alone or along with sigma bond.	5- The bond is always present only when there is a sigma bond. They cannot exist alone.
6- S orbital participates in the formation of sigma bond.	6- S orbitals cannot participate in the formation of pi bond.

Limitations of Valence Bond Theory

- 1- Failure to explain the tetravalency exhibited by carbon.
- 2- No insight offered on the energies of the electrons.
- 3- The theory assumes that electrons are localized in specific areas.
- 4- It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.
- 5- No distinction between weak and strong ligands.
- 6- No explanation for the colour exhibited by coordination compounds.

Hybridization

The phenomenon of mixing up of atomic orbitals of similar energies and formation of equivalent number of entirely new orbitals of identical shape and energy and the new orbitals so formed is called as "hybrid orbitals".

Important points for understanding the hybridization:

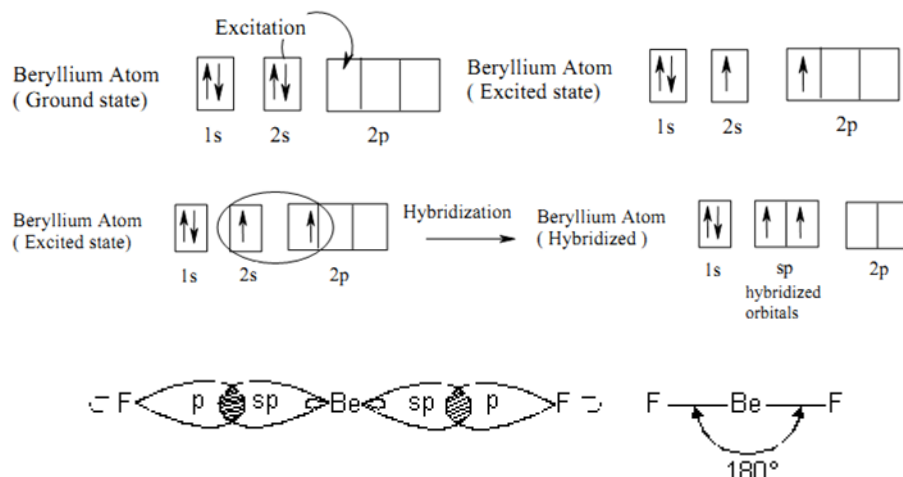
- 1- The number of hybrid orbitals generated is equal to the number of pure atomic orbitals
- 2- Hybridization concept is not applicable to isolated atoms. It is used to explain the bonding scheme in a molecule
- 3- Covalent bonds in polyatomic molecules are formed by the overlap of hybrid orbitals or of hybrid orbitals with unhybridized ones. Participate in hybridization process.

Types of Hybridization

sp Hybridisation	linear	180 °
sp ² Hybridisation	trigonal planar	120°
sp ³ Hybridisation	tetrahedral	109.5°
sp ³ d Hybridisation	trigonal bipyramidal	
dsp ² hybridisation	square planar	
sp ³ d ² Hybridisation	octahedral	

- 1- **sp-hybridization**: The combination of one s and one p-orbitals to form two hybrid orbitals of equal energy is known as sp-hybridization.

Example: In BeF₂ Molecule the sp-hybridized orbitals of Be overlap with the half-filled orbitals of two fluorine atoms to give a linear shape.

Figure. Orbital diagram of BeF_2 .

Ethyne (C_2H_2) is a linear molecule with a triple bond between the two carbon atoms. Since each carbon atom is bonded to two other atoms and has no lone pairs, the hybridization of each carbon is sp .

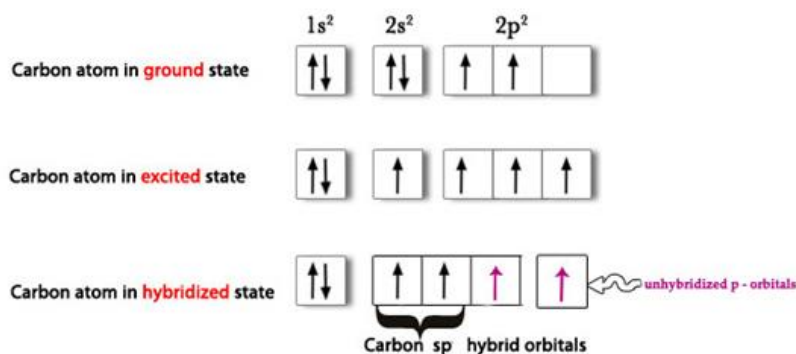


Again, the promotion of an electron in the carbon atom occurs in the same way. However, the hybridization now involves only the $2s$ orbital and the $2p_x$ orbital, leaving the $2p_y$ and the $2p_z$ orbitals unhybridized. In acetylene molecule, the central carbon atom is sp hybridized.

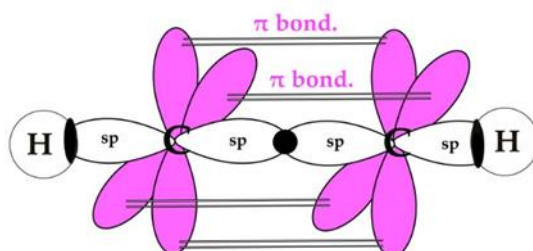
Carbon (6) $1s^2 2s^2 2p^2 \rightarrow$ Ground state.

$\text{C}(6) 1s^2 2s^1 2p^3 \rightarrow$ One $2s$ electron is promoted to $2p$ orbital.

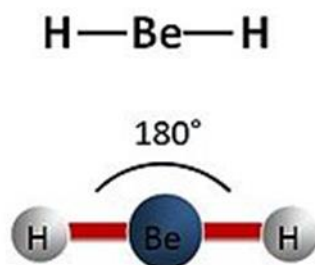
Then, $2s$ and one $2p$ orbital hybridise to form two sp hybrid orbitals



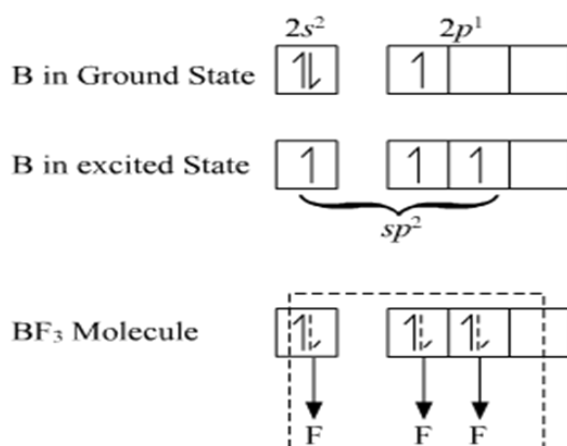
The sigma bond between the two carbon atoms is formed from sp hybrid orbitals, and the remaining hybrid orbitals form sigma bonds to the two hydrogen atoms. Both the p_y and the p_z orbitals on each carbon atom form pi bonds with each other. As with ethene, these side-to-side overlaps are not directly on the line between the two bonded atoms. Additionally, these two pi bonds are perpendicular to one another (Figure below); one pi bond is above and below the line of the molecule, while the other is in front of and behind the page.



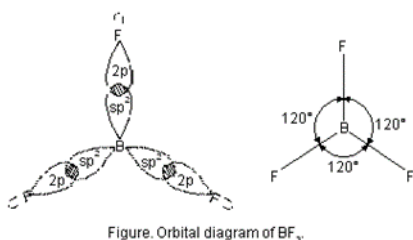
The bond angle is 180° and the molecule has linear geometry. Other molecules with sp hybridized central atom are BeCl_2 , XeF_2 , BeH_2 . The geometry of the sp hybrid orbitals is linear.



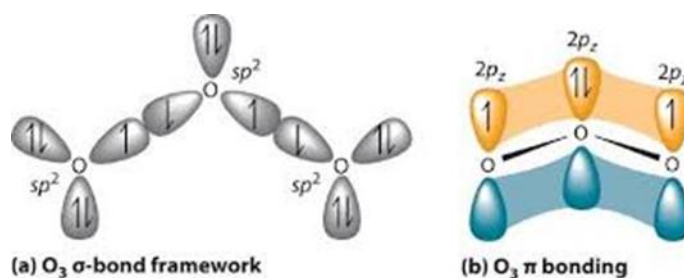
- 2- **sp^2 -hybridization:** The combination of one s and two p -orbitals to form three hybrid orbitals of equal energy is known as sp^2 -hybridization. **Example:** BF_3 Molecule.



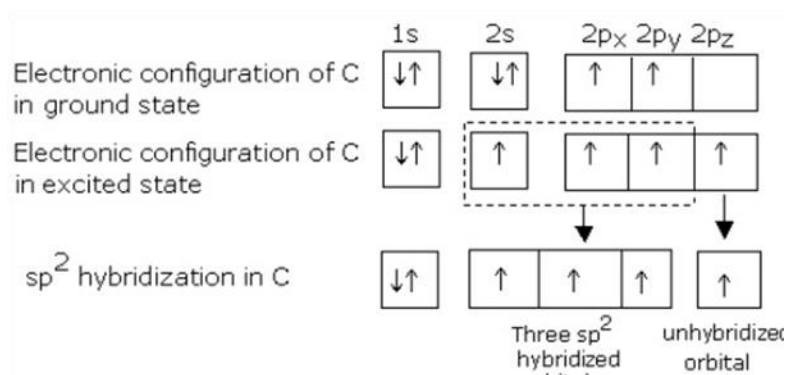
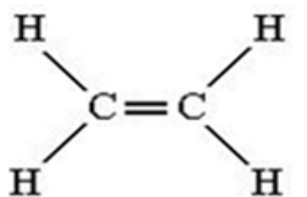
Fluorine, three σ -bonds are formed with bond angle 120° . The shape of BF_3 molecule is triangular planar shape.



Other molecules with a trigonal planar electron domain geometry form sp^2 hybrid orbitals. Ozone (O_3) is an example of a molecule whose electron domain geometry is trigonal planar, though the presence of a lone pair on the central oxygen makes the molecular geometry bent. The hybridization of the central O atom of ozone is sp^2 . These sp^2 hybridized orbitals are oriented at an angle of 120° .

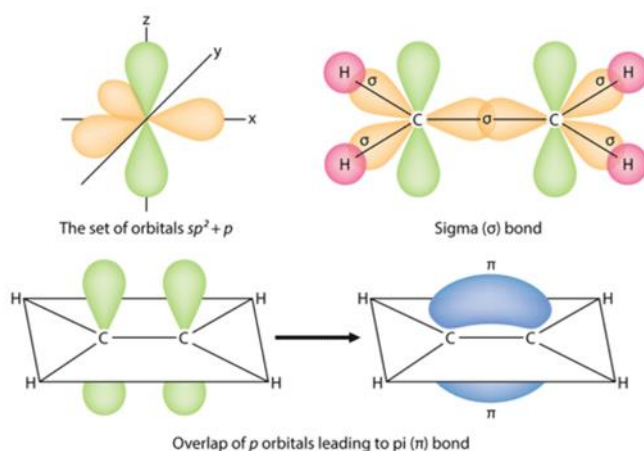


Ethylene molecule



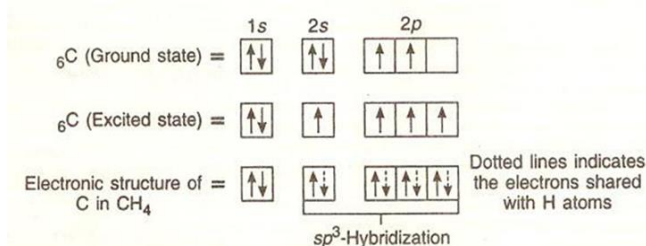
As can be seen above (Figure above), the electron domain geometry around each carbon atom is trigonal planar, which corresponds to sp^2 hybridization. Previously, we saw carbon undergo sp^3 hybridization in a CH_4 molecule, so how does it work in this case? As seen below, the electron promotion is the same, but the hybridization occurs only between the single s orbital and two of the three p orbitals. Thus generates a set of three sp^2 hybrids along with an unhybridized $2p_z$ orbital. Each orbital contains one electron and is capable of forming a covalent bond. The three sp^2 hybrid orbitals lie in one plane, while the unhybridized $2p_z$ orbital is oriented perpendicular to that plane.

The bonding in C_2H_4 is explained as follows. One of the three sp^2 hybrids forms a bond by overlapping with the identical hybrid orbital on the other carbon atom. The remaining two hybrid orbitals form bonds by overlapping with the $1s$ orbital of a hydrogen atom. Finally, the $2p_z$ orbitals on each carbon atom form another bond by overlapping with one another sideways.

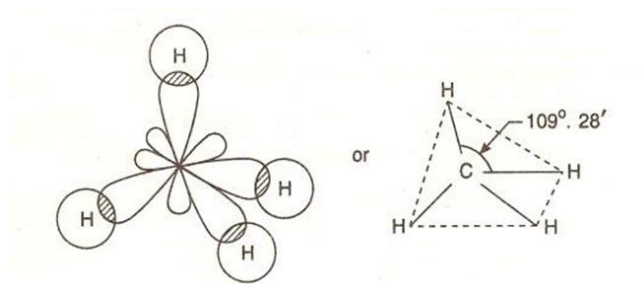


In a conventional Lewis electron-dot structure, a double bond is shown as two lines between the atoms, as in $C=C$. It is important to realize, however, that the two bonds are different; one is a sigma bond, while the other is a pi bond. In the ethene molecule, C_2H_4 , there are five σ bonds. One $C-C$ σ bond results from overlap of sp^2 hybrid orbitals on the carbon atom with one sp^2 hybrid orbital on the other carbon atom. Four $C-H$ bonds result from the overlap between the sp^2 orbitals with s orbitals on the hydrogen atoms. The π bond is formed by the side-by-side overlap of the two unhybridized p orbitals in the two carbon atoms, the two lobes of the π bond are above and below the plane of the σ system. In an ethene molecule, the four hydrogen atoms and the two carbon atoms are all in the same plane.

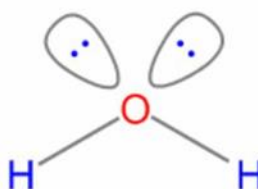
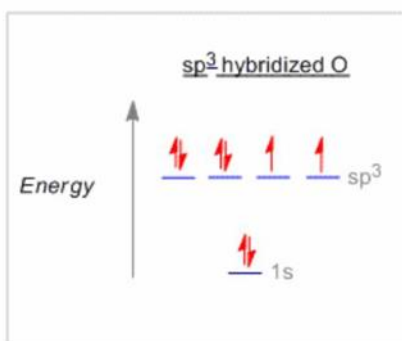
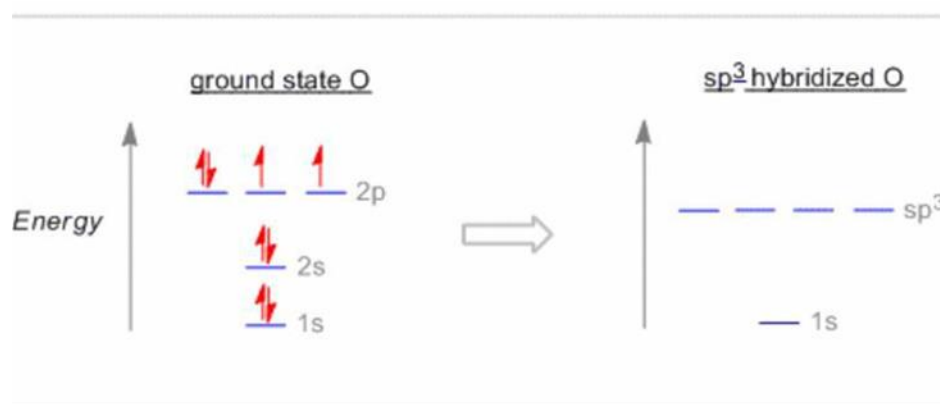
- 3- **sp^3 -hybridization:** The combination of one s and three p -orbitals to form four hybrid orbitals of equal energy is known as sp^3 -hybridization. For example CH_4 .



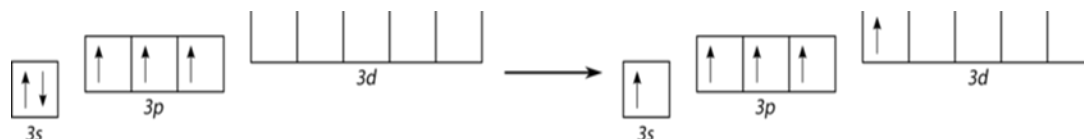
These sp^3 -hybridized orbitals are oriented at an angle of $109^\circ 28'$. When these four sp^3 hybrid orbitals overlaps with four $1s$ orbitals of hydrogen, a symmetrical tetrahedral shaped CH_4 molecule form.



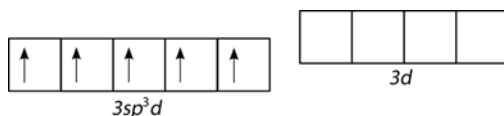
The **atomic orbitals** on O and that they must overlap with $1s$ orbitals from H to give H_2O



4- sp^3d -hybridization: The combination of one s , three p and one d -orbitals to form five hybrid orbitals of equal energy is known as sp^3d -hybridization. For phosphorus pentachloride (PCl_5), the electron domain and molecular geometries are trigonal bipyramidal. The electron promotion is from the $3s$ orbital **to an empty $3d$ orbital**.

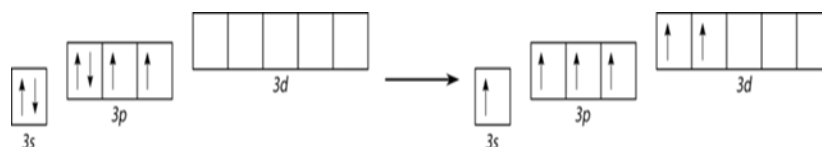


The hybridization then occurs with a single s orbital, three p orbitals, and a single d orbital. The set of five hybrid orbitals are called sp^3d hybrids.

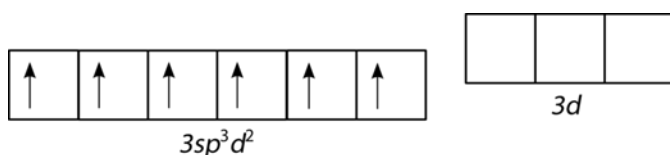


The overlap of the five hybrid sp^3d orbitals with the $3p$ orbital of each chlorine atom results in the five covalent bonds of PCl_5 . Other molecular geometries derived from trigonal bipyramidal electron domain geometry (seesaw, T-shaped, linear) also display the same hybridization.

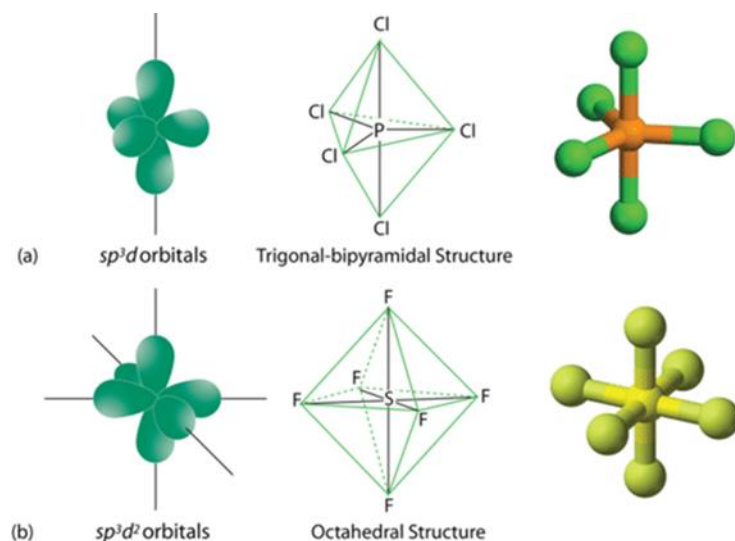
5- sp^3d^2 -hybridization: The combination of one s , three p and two d -orbitals to form six hybrid orbitals of equal energy is known as sp^3d^2 -hybridization. Examples: SF_6 Molecule. Sulfur hexafluoride (SF_6) has an octahedral electron domain and molecular geometry. In this case, a $3s$ and a $3p$ electron are each promoted to two empty $3d$ orbitals.



The hybridization now occurs with one s orbital, three p orbitals, and two d orbitals. The resulting set of six equivalent orbitals is called sp^3d^2 hybrids.



The overlap of the six hybrid sp^3d^2 orbitals with the $2p$ orbital of each fluorine atom results in the six covalent bonds of SF_6 . Other molecular geometries derived from octahedral electron domain geometry (square pyramidal, square planar) also exhibit this type of hybridization. The figure below (Figure below) shows the shape and orientation of the sp^3d and sp^3d^2 hybrid orbital sets.



VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

Definition: this theory proposes that the stereochemistry of an atom in a molecule is determined primarily by the repulsive interactions among all the electron pairs.

The postulates of the VSEPR theory are listed below

- 1- In polyatomic molecules (i.e. molecules made up of three or more atoms), one of the constituent atoms is identified as the central atom to which all other atoms belonging to the molecule are linked.
- 2- The total number of valence shell electron pairs decides the shape of the molecule.
- 3- The electron pairs have a tendency to orient themselves in a way that minimizes the electron-electron repulsion between them and maximizes the distance between them.
- 4- The valence shell can be thought of as a sphere wherein the electron pairs are localized on the surface in such a way that the distance between them is maximized.
- 5- Should the central atom of the molecule be surrounded by bond pairs of electrons, then, the asymmetrically shaped molecule can be expected.
- 6- Should the central atom be surrounded by both lone pairs and bond pairs of electrons, the molecule would tend to have a distorted shape.
- 7- The strength of the repulsion is strongest in two lone pairs and weakest in two bond pairs.

Lone Pair- lone pair > Lone Pair- bond- pair > Bond Pair- bond pair.

- 8- If electron pairs around the central atom are closer to each other, they will repel each other. This results in an increase in the energy of the molecules.

Limitations of VSEPR Theory

Some significant limitations of the VSEPR theory include:

- 1- This theory fails to explain isoelectronic species (i.e. elements having the same number of electrons). The species may vary in shapes despite having the same number of electrons.
- 2- The VSEPR theory does not shed any light on the compounds of transition metals.
- 3- Another limitation of VSEPR theory is that it predicts that halides of group 2 elements will have a linear structure, whereas their actual structure is a bent one.

Steric number (SN)

The VSEPR model counts both bonding and nonbonding (lone) electron pairs, and calls the total number of pairs the steric number (SN). If the element A has m atoms bonded to it and n nonbonding pairs, then

$$SN = m + n$$

SN is useful for predicting shapes of molecules. If X is any atom bonded to A (in single, double, or triple bond), a molecule may be represented by AX_mE_n where E denotes a lone electron pair. This formula enables us to predict its geometry. The common SN, descriptor, and examples are given in the table below. Note that the SN is also called the number of VSEPR pairs or number of electron pairs

Predicting the Shapes of Molecules:

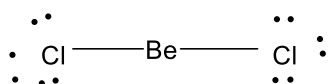
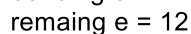
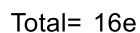
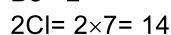
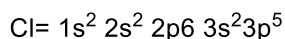
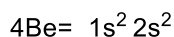
There are three basic steps to determining the molecular shape of a molecule:

- 1- Write the Lewis dot structure of the molecule. That gives you the steric number (SN) -the number of bond pairs and lone pairs around the central atom.
3. Use the SN and VSEPR theory to determine the electron pair geometry of the molecule.
4. Use the VSEPR shape to determine the angles between the bonding pairs.

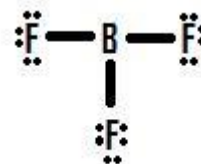
Molecules shapes

- 1- The central atom has two electron pair SN = 2

The Lewis dot structure for BeCl_2 is.



The central Be atom has two bond pairs in its outer shell ($SN = 2$). Repulsion between these two pairs causes the atoms to be as far apart as possible. The shape of the molecule is linear, and the Cl-Be-Cl bond angle is 180° .

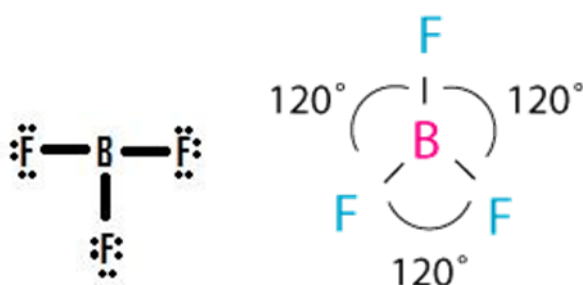


2- The central atom has three electron pair $SN = 3$

There are two possibilities.

i. AX_3 — Three bonding pairs

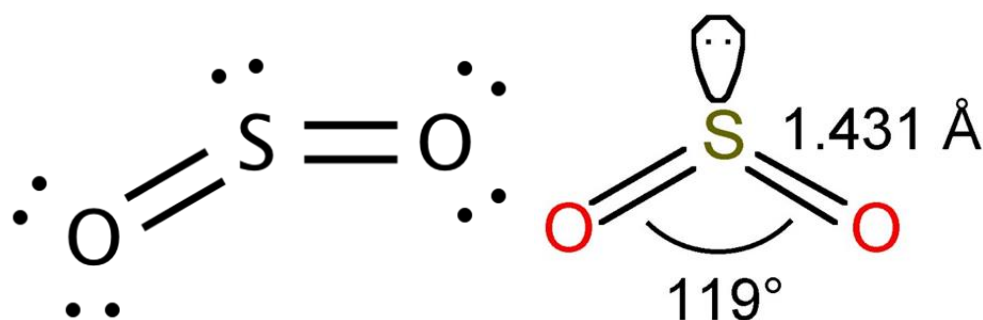
What is the shape of BF_3 ? The B atom has three bond pairs in its outer shell. Minimizing the repulsion causes the F atoms to form an equilateral triangle about the B atom, as shown below.



The shape of the molecule is trigonal planar. All the atoms are in the same plane, and the F-B-F bond angles are all 120° .

ii. AX_2E — two bond pairs and one lone pair

What is the shape of SO_2 ? The Lewis dot structure SO_2 is



The central atom, S, has three groups bonded to it, two oxygen atoms and a lone pair. The electron pair geometry of SO_2 is trigonal planar. In determining the molecular shape, we consider only the positions of the atoms, not the lone pairs. Hence, the molecular shape of SO_2 is bent (v-shape). The lone pair of electrons occupies a relatively large volume, since they are held by only one atom. They compress the bond angle between the oxygens and sulfur to about 119.5° .

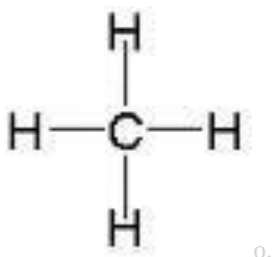
3-The central atom has four electron pair $SN = 4$

There are three possibilities.

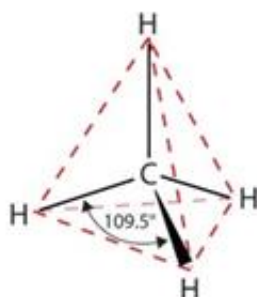
i. AX_4 — four bond pairs

What is the shape of CH_4 ?

The Lewis dot structure CH_4 is



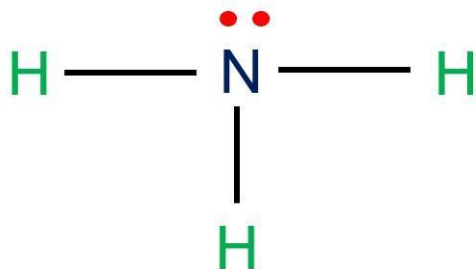
The shape of this molecule, however, is not planar, as you might think from the way we draw this dot structure. The four bond pairs are arranged about the C atom, pointing toward the corners of a regular tetrahedron. This shape minimizes the repulsion between the bond pairs.



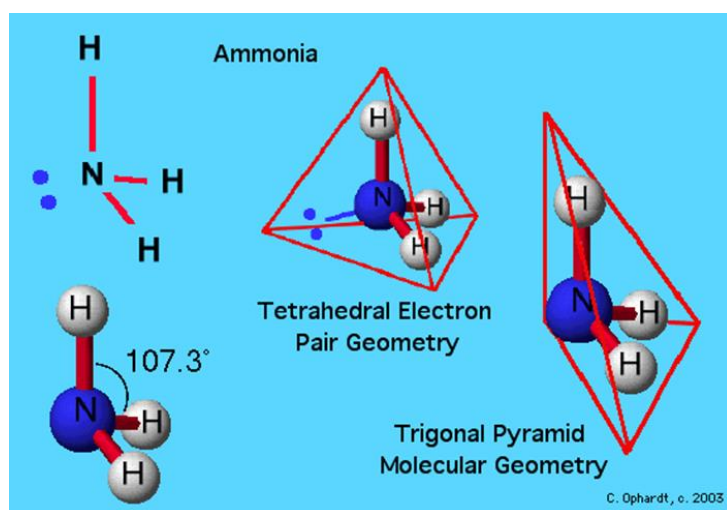
The 109.5° angle is the same for all H-C-H bond angles and is called the tetrahedral bond angle. The shape of the CH_4 molecule is tetrahedral.

ii. AX_3E — three bond pairs and one lone pair.

What is the molecular geometry of NH_3 ? The Lewis dot structure of NH_3 is



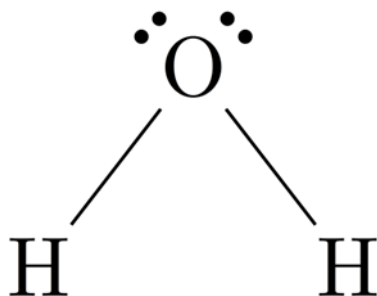
The central atom, N, has four groups bonded to it: three hydrogen atoms and a lone pair. The electron pair geometry of NH_3 is tetrahedral. It is drawn as shown below:



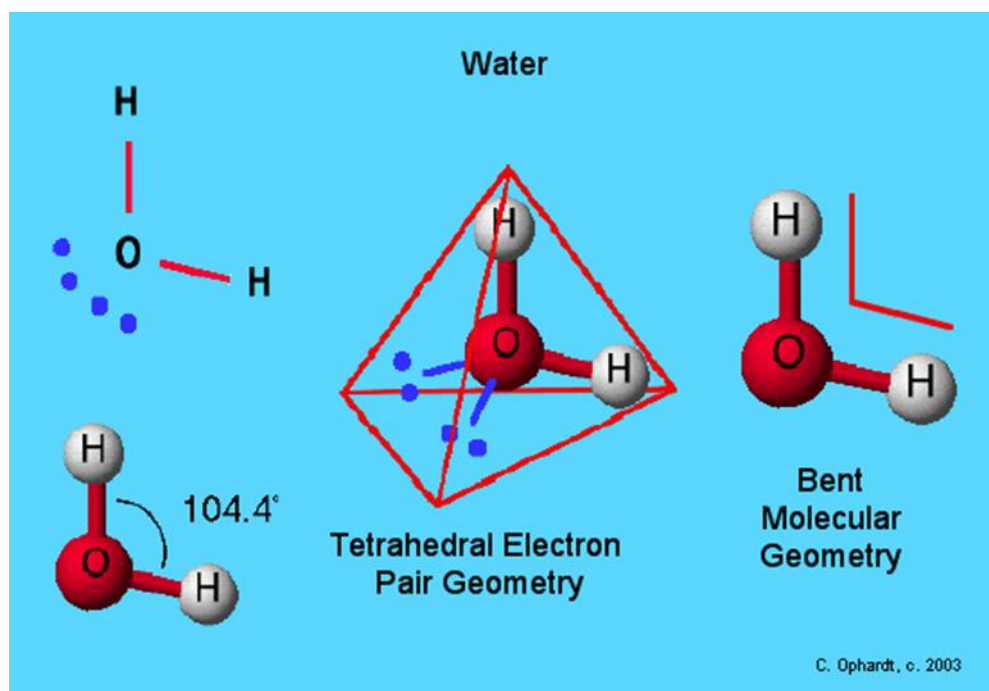
Remember that, in determining the molecular shape, we consider only the positions of the atoms, not the lone pairs. If we look only at the atoms, we see a short, rather distorted tetrahedron. This is called a pyramid. The NH_3 pyramid has a triangular base. Hence the shape is **trigonal pyramidal**. The greater repulsion of the lone pair causes the H atoms in NH_3 to be bent closer together than the normal tetrahedral angle of 109.5° . In NH_3 the observed H-N-H bond angle is 107.3° .

iii. AX₂E₂ — two bond pairs and two lone pairs

What is the molecular geometry of H_2O ? The Lewis dot structure of H_2O is



The central atom, O, has four groups bonded to it, two hydrogen atoms and two lone pairs. The electron pair geometry of H_2O is tetrahedral. It is drawn as shown below:

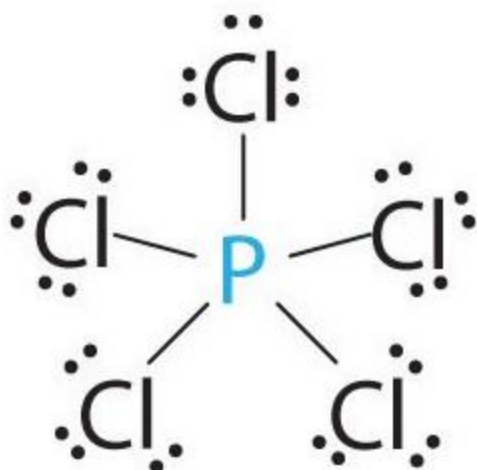


The shape is called bent. The H-O-H bond angle is less than that in NH_3 , partly because of the greater repulsions caused by two lone pairs. In water, the observed H-O-H bond angle is 104.5° . All bond angles in AX_2E_2 molecules are significantly less than 109.5° .

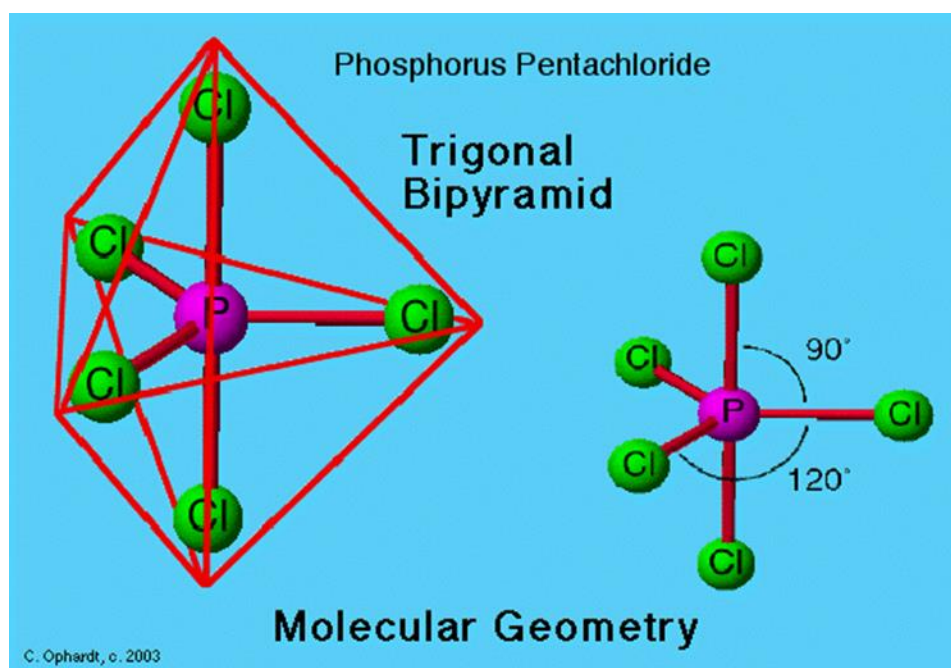
4- The central atom has five electron pair SN = 5 There are four possibilities.

i. AX₅ — five bond pairs

What is the molecular shape of PCl_5 ? The Lewis dot structure of PCl_5 is



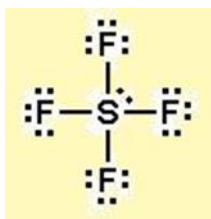
Atoms past Si in the periodic table can “expand their octet” and have more than eight valence electrons. Here, the P atom has ten valence electrons. If you view the P atom at the center of a sphere like the earth, you have one Cl atom at the North Pole, one Cl atom at the South Pole, and three Cl atoms spread evenly around the equator.



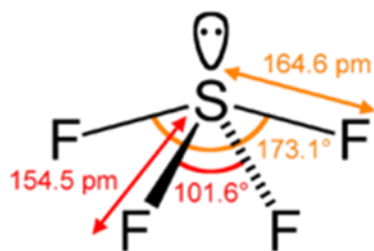
Note that the Cl atoms occupy two types of positions. The two Cl atoms that are on a straight line that passes through the P nucleus are said to occupy axial positions. The other three Cl atoms are in equatorial positions. If you join the Cl atoms by straight lines, the diagram looks like two trigonal pyramids joined together at the base. The PCl₅ molecule has a trigonal bipyramidal shape. There are two different bond angles in the molecule. The axial Cl atoms are at angles of 90° to the equatorial Cl atoms, while the equatorial Cl atoms are at angles of 120° to each other.

ii. AX₄E — Four bond pairs and one lone pair. What is the molecular shape of SF₄?

The Lewis dot structure of SF₄ is



The five electron pairs assume a trigonal bipyramidal geometry. The lone pair occupies an equatorial position, because that gets it furthest away from the other electron pairs. If you turn the molecule on its side, it looks like a see-saw, with the axial F atoms at the ends, and the equatorial F atoms acting as the pivot. The shape is called a see-saw.

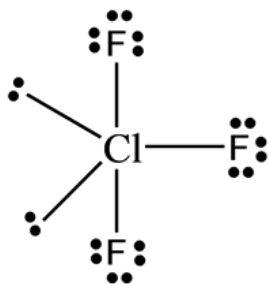


The axial F-S-F bond angle is 173.1° rather than 180°, because of the lone pair of electrons in the equatorial plane. The shape of molecule is seesaw. The equatorial F-S-F bond angle is compressed to 101.6° from its normal value of 120°.

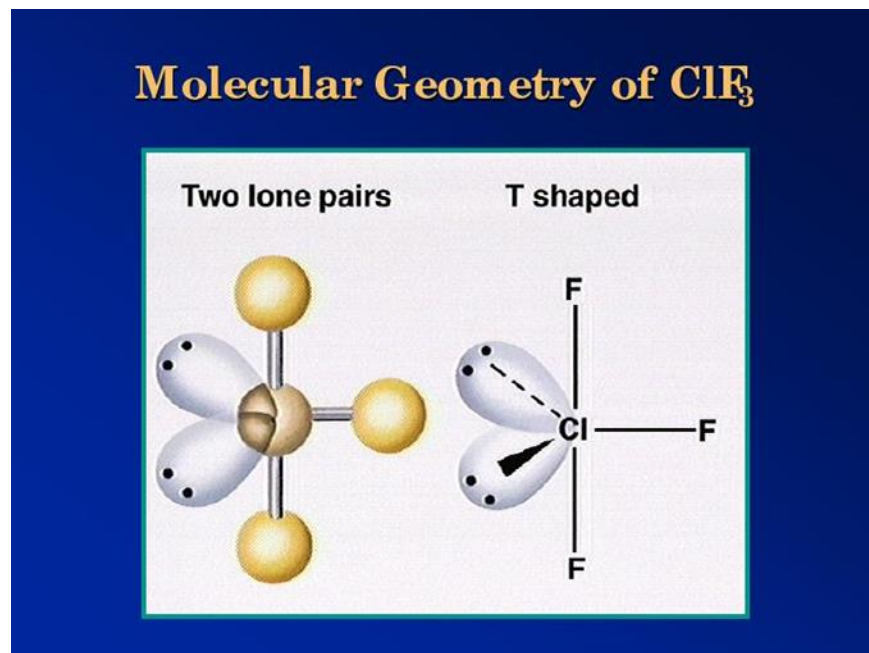
iii. AX₃E₂ — three bonding pairs and two lone pairs

What is the molecular shape of ClF₃?

The Lewis dot structure of ClF₃ is



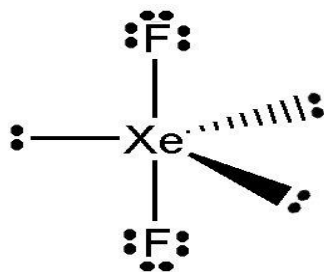
The five electron pairs assume a trigonal bipyramidal geometry.



The two lone pairs occupy the equatorial positions in order to minimize repulsions. The bonding pairs form a T-shape, and that is the shape of the molecule. Actually, the molecule has a “distorted-T” shape because the two lone pairs reduce the F-S-F bond angle from 90° to 86.98° , and the F-S-F bond angle across the top of the T is reduced from 180° to 173.96° .

iv. AX_2E_3 — two bonding pairs and three lone pairs

The Lewis dot structure of XeF_2 , the five electron pairs assume a trigonal bipyramidal geometry. But according to VSEPR theory the shape is a linear shape for the XeF_2 molecule, and the F-Xe-F bond angle is 180° .

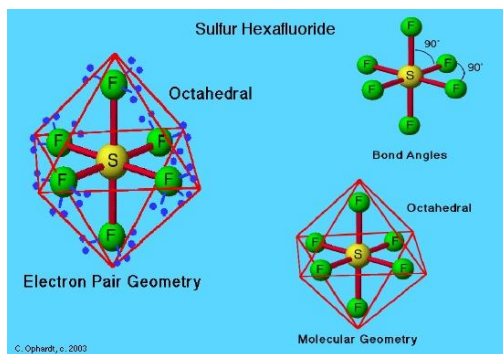
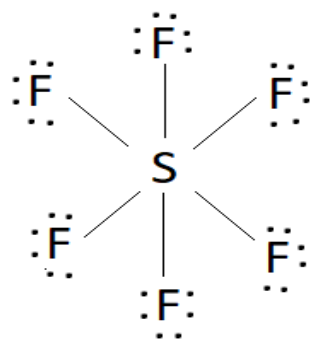


5. The central atom has six electron pair $\text{SN} = 6$

There are five possibilities.

i. AX_6 — six bonding pair

The Lewis dot structure of SF_6 is



The six bonding pairs arrange themselves with four equatorial bond pairs and one more pair at each of the polar locations. The shape is called octahedral. Every F-S-F bond angle is 90° .

ii. AX5E — five bonding pairs and one lone pair

The Lewis dot structure of IF_5 is

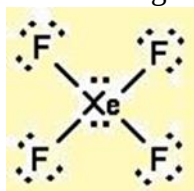


The electron pairs arrange themselves at the corners of an octahedron with a lone pair occupying one of these positions. Four of the F atoms are at the corners of a square, and one is directly above the I atom. Lines connecting the F atoms form a pyramid with a square base, so the shape is **square pyramidal**. The F-I-F angles between neighbouring F atoms are 90° .

ii. AX4E2 — four bond pairs and two lone pairs

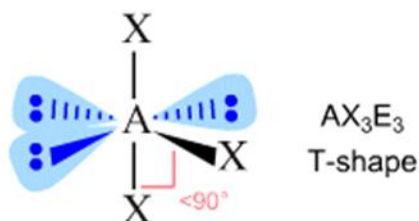
What is the molecular shape of XeF_4 ?

The electron pairs arrange themselves at the corners of an octahedron. The four bonding pairs point toward the corners of a square, and the lone pairs occupy the axial positions above and below the plane of the square. Since the four F atoms are at the corners of a square, the molecular shape is **square planar**. The F-Xe-F bond angles between neighbouring F atoms are 90° .

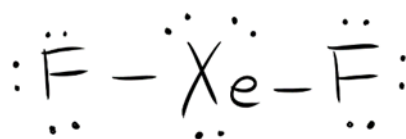


iv. AX₃E₃ — three bonding pairs and three lone pairs

There are no molecules that belong to the AX₃E₃ system. However, the electron geometry is octahedral, with the three lone pairs occupying equatorial positions. The remaining bond pairs are arranged in a T-shape with bond angles of 90°.

**v. AX₂E₄ — two bonding pairs and four lone pairs**

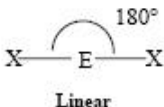
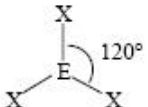
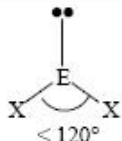
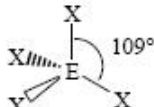
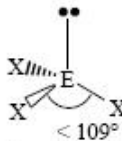
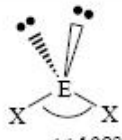
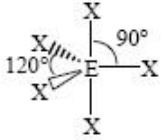
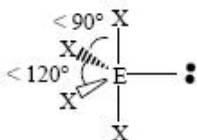
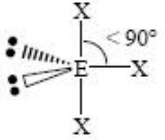
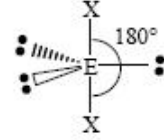
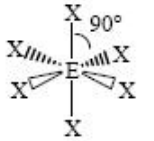
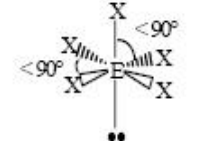
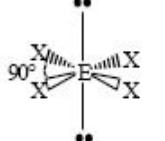
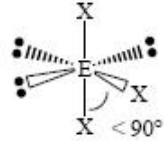
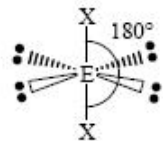
No stable AX₂E₄ molecules are known. However, we predict the molecular shape to be linear with bond angles of 180°.

**SUMMARY**

To predict the shape of a molecule:

1. Write the Lewis dot structure for the molecule.
2. Determine the steric number of the central atom.
3. Decide on the electron pair orientation based on the steric number.
4. Consider the placement of lone pairs and any distortions from "regular" shapes.
5. Name the shape based on the location of atoms attached to the central atom

The table below summarizes all the molecular shapes

VSEPR Geometries					
Steric No.	Basic Geometry 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 Linear				
3	 Trigonal Planar	 Bent or Angular			
4	 Tetrahedral	 Trigonal Pyramid	 Bent or Angular		
5	 Trigonal Bipyramid	 Sawhorse or Seesaw	 T-shape	 Linear	
6	 Octahedral	 Square Pyramid	 Square Planar	 T-shape	 Linear

Bond angle

Bond angle: The angle formed between the central and terminal atoms in a molecule is called as the bond angle or inter orbital angle. It is represented as θ .

Factors affecting bond angle

Repulsion between atoms or groups attached to the central atom may increase or decrease the bond angle.

- 1- In hybridisation as the s character of the s hybrid bond increases, the bond angle increases.

Bond type	sp^3	sp^2	sp
Bond angle	$109^\circ 28'$	120°	180°

- 2- By increasing lone pair of electron, bond angle decreases approximately by 2.5%.

Bond type	CH_4	NH_3	H_2O
Bond angle	109°	107°	105°

3- If the electronegativity of the central atom decreases, bond angle decreases.

	H_2O	$> H_2S$	$> H_2Se$	$> H_2Te$
Bond angle	104.5°	92.2°	91.2°	89.5°

4- In case the central atom remains the same, bond angle increases with the decrease in electronegativity of the surrounding atom.

	PCl_3	PBr_3	PI_3	$AsCl_3$	$AsBr_3$	AsI_3
Bond angle	100°	101.5°	102°	98.4°	100.5°	101°

Note

a higher bond order results in a shorter bond length and a higher bond energy.

Localized and delocalized electrons

Localized and delocalized electrons generally refer to electrons in atoms and molecules. Localized bonding refers to sharing electron pairs between two atoms in a molecule. In this context, electrons are considered localized or confined to the region between the bonded atoms. When two atoms come together to form a covalent bond, they share electrons to achieve a more stable electron configuration. The electrons involved in the bond are typically derived from overlapping atomic orbitals. The most common example is the sharing of electron pairs between nonmetal atoms (Example HCl).

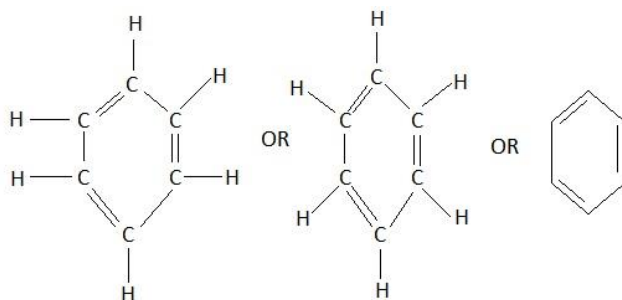
Delocalized bonding occurs when electrons are not confined to the region between two specific atoms but are spread out over multiple atoms or regions within a molecule. This phenomenon arises from the concept of electron delocalization, wherein electrons have the freedom to move through a larger portion of the molecule, resulting in unique bonding properties and behaviors. One classic example of delocalized bonding is found in the benzene molecule. Benzene consists of a ring of six carbon atoms, with each carbon atom bonded to one hydrogen atom and one adjacent carbon atom. The π -electrons in the p-orbitals of the carbon atoms undergo delocalization, freely moving throughout the entire ring. This delocalized electron cloud gives rise to the exceptional stability and aromatic properties exhibited by benzene. Delocalized bonding extends beyond organic compounds and encompasses inorganic and coordination compounds, as well as various functional groups. Examples include carbonyls, conjugated systems, and even inorganic ions like the nitrate ion (NO_3^{-1} , SO_4^{2-} and CO_3^{2-}). Delocalized bonding significantly impacts molecular structure, stability, reactivity, and optical properties. It enhances stability by spreading electron density, reduces electron-electron repulsion, and influences charge distribution. Furthermore, delocalized bonding affects acidity and basicity in organic compounds.

Kekule Structure of Benzene

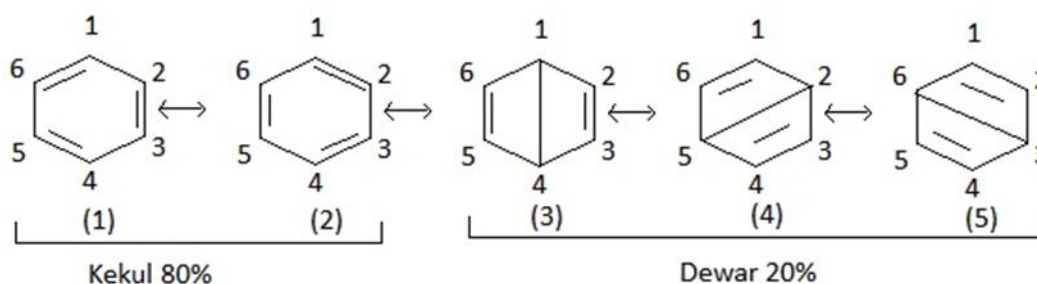
Kekulé was the first to suggest a sensible structure for benzene. The carbons are arranged in a hexagon, and he suggested alternating double and single bonds between them. Each carbon atom has a hydrogen attached to it. Kekule suggested that:

- 1- The benzene molecule is made up of a hexagon of six carbon atoms.

2- There are alternate single and double bonds and one hydrogen is attached to each carbon atom.



Benzene has five resonance structures. They are Two Kekule's and Three Dewar's structure.



in addition to these two resonance structures, three other structures have been proposed by Dewar. They are called Dewar structures. The five structures are joined by double-headed arrows: Dewar structure is also called para-bond structures. The π -bonds between C1 – C4, C2 – C5, C3 – C6 are least favorable. For this reason, these structures III, IV, and V are least Contribution, i.e., 7% each towards the resonance hybrid. The contribution of Kekule structure (I) and (II) is 80 % and that of Dewar structures (III), (IV), (V) is 20 % to the actual or real structure of benzene.

Resonance energy

The Kekulé structure has problems with the shape. Benzene is a planar molecule (all the atoms lie in one plane), and that would also be true of the Kekulé structure. The problem is that C-C single and double bonds are different lengths.

C-C (0.154 nm)

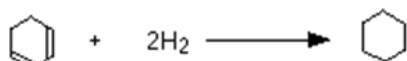
C=C (0.134 nm)

That would mean that the hexagon would be irregular if it had the Kekulé structure, with alternating shorter and longer sides. In real benzene all the bonds are exactly the same - intermediate in length between C-C and C=C at 0.139 nm. Real benzene is a perfectly regular hexagon.

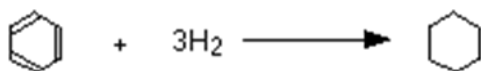
In order to do a fair comparison with benzene (a ring structure) we're going to compare it with cyclohexene. Cyclohexene, C_6H_{10} , is a ring of six carbon atoms containing just one $C=C$. In the cyclohexane case, for example, The hydrogenation equation could be written:



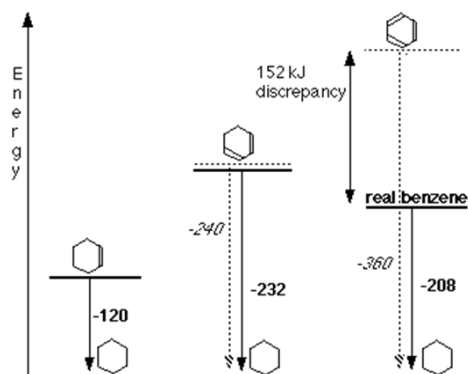
The enthalpy change during this reaction is -120 kJ mol^{-1} . In other words, when 1 mole of C_6H_{10} had two double bonds in it initially (cyclohexa-1,3-diene), exactly twice as many bonds would have to be broken and exactly twice as many made. In other words, you would expect the enthalpy change of hydrogenation of cyclohexa-1,3-diene to be exactly twice that of cyclohexene - that is, -240 kJ mol^{-1} .



In fact, the enthalpy change is -232 kJ mol^{-1} - which isn't far off what we are predicting. Applying the same argument to the Kekulé structure for benzene (what might be called cyclohexa-1,3,5-triene), you would expect an enthalpy change of -360 kJ mol^{-1} , because there are exactly three times as many bonds being broken and made as in the cyclohexene case.



In fact what you get is -208 kJ mol^{-1} - not even within distance of the predicted value! This is very much easier to see on an enthalpy diagram. Notice that in each case heat energy is released, and in each case the product is the same (cyclohexane).



The most important point to notice is that real benzene is much lower down the diagram than the Kekulé form predicts. The lower down a substance is, the more energetically stable it is. This means that real benzene is about 150 kJ mol^{-1} more stable than the Kekulé structure gives it credit for. This increase in stability of benzene is known as the delocalization energy or resonance energy of benzene.