Chemical Bonding and Molecular Structure Notes

Why do Atoms Combine?

Atoms combine to become stable. The more stable they are, the less energy they will have. Hence atoms combine with each other only if it leads to lowering of energy.

Since noble gases are the most stable elements, all atoms combine to **form an octet** so that they can also be the most stable.

Octet Rule

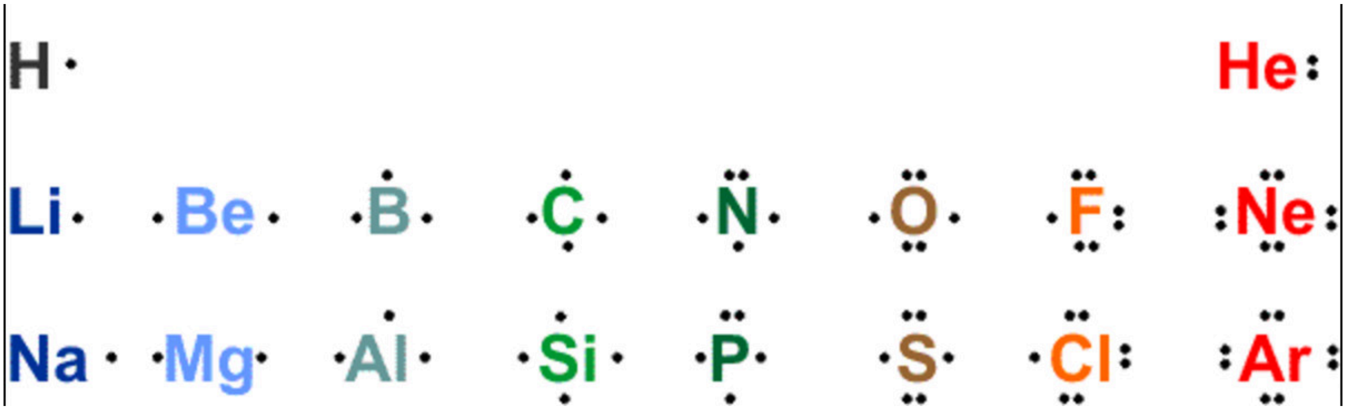
The principle of an atom acquiring 8 electrons in the valence shell is called octet rule.

However, for hydrogen and lithium, the nearest noble gas configuration consists of helium which can have only 2 electrons in the valence shell.

Lewis Symbols

In Lewis notation, each dot around an element represents an electron.

The valency of an element is either equal to the number of dots or 8 minus the number of dots.



How to Draw a Lewis Structure

1. Select the central atom
    a. The **central atom** is the **most electronegative** atom or the one which is present in the **least number**.
    b. Hydrogen and fluorine can never be central atoms.
    c. Some examples of central atoms are O, S, N, P, Cl, C, Si, etc.
2. The **octets of corner atoms** must be **complete**.
3. The central atom can have 8 or more electrons.
   The compounds in which atoms have more than 8 electrons are called *hypervalent* compounds.
4. If a **positive** charge is present on the compound, then it is placed on the **central atom**.
   If a **negative** charge is present on the compound, then it is placed on the **corner atom**.

Total number of electrons = Valence electrons of all atoms + negative charge - positive charge

Bond pair electrons = 2 × Number of bonds

Lone pair electrons = Total electrons − bond pair electrons

Formal Charge

The formal charge is assigned to each atom in a polyatomic ion.

Formal Charge = Total valence electrons in free atom - Lone Pair Electrons - Bond Pairs

⇒ FC = V - LPE - BP

The formal charges help to choose the Lewis structure with the lowest energy (and hence highest stability). The Lewis structure with the **least formal charge** has the **lowest energy**.

Drawbacks of Lewis Structures

- Some compounds have more or less than 8 electrons in their central atoms.
- Lewis structures are based on the inertness of inert gases, but some inert gases like Xe and Kr also form compounds.

- It cannot explain the shape or relative stability (in terms of energy) of compounds.

Types of Chemical Combination

There are two ways in which atoms can complete their octet. They can either transfer electrons, or share them with each other.

There are two main types of chemical bonds:

1. Ionic Bond or Electrovalent Bond
2. Covalent Bond

Ionic Bond or Electrovalent Bond

Ionic bond is formed by the **transfer of electrons** from one atom to another to complete their octets and become stable.

The atom which loses electrons becomes positively charged and the atom which gains electrons becomes negatively charged. The two oppositely charged atoms come closer due to an *electrostatic* force of attraction, called an *ionic bond*.

The compound thus formed is called an *ionic compound* or *electrovalent compound*.

The number of electrons lost or gained by an atom during the bond formation is called its *electrovalence* or *electrovalency*.

For example, sodium has electrovalency +1, calcium has electrovalency +2, chlorine has -1, etc.

Factors Affecting Formation of Ionic Bond

To form a strong ionic bond, the following conditions are required:

1. **Low ionization enthalpy** - Ionization enthalpy is the amount of energy required to remove the most loosely bound electron from an atom to form a cation.
2. **High electron gain enthalpy** - Electron gain enthalpy is the amount of energy released when an electron is added to an atom to form an anion.
3. **High lattice enthalpy** - Lattice enthalpy is the amount of energy released when free ions combine to form 1 mole of a salt crystal.

If the net effect of the above is a decrease in energy, only then will the ionic bond be formed (since bonds are only formed when there's a decrease in energy).

Lattice Enthalpy

Lattice enthalpy is the amount of energy released when **free ions combine to form** 1 mole of a **salt crystal**.

$M^+ + X^- \rightarrow MX$

ΔH = Lattice enthalpy = $-U$

But lattice enthalpy is also the amount of energy required to **completely separate** 1 mole of an **ionic compound** into its **constituents**.

$MX \rightarrow M^+ + X^-$

ΔH = Lattice enthalpy = $+U$

Factors Affecting Lattice Enthalpy

Stable compounds will need more energy to get separated. So lattice enthalpy is directly proportional to stability.

Since stable compounds are difficult to dissolve, stability is inversely proportional to solubility.

Smaller ions are more tightly packed and form stronger bonds. So lattice enthalpy is inversely proportional to the size of the ions.

Also, more charge on the ions leads to stronger attractions. So lattice enthalpy is directly proportional to the magnitude of charge on the ions.

In short:

- Lattice enthalpy $\propto$ Stability ⇒ Lattice enthalpy $\propto \frac{1}{Solubility}$
- Lattice enthalpy $\propto \frac{1}{Size\ of\ ions}$
- Lattice enthalpy $\propto$ Magnitude of charge on the ions

- Lattice enthalpy also increases with increase in valency as shown:

  Uni-univalent Compounds < Bi-univalent Compounds < Bi-bivalent compounds

  E.g.: $NaCl < CaF_2 < MgO$

Properties of Ionic Compounds

- **Solid state** - Ionic compounds don't exist as independent molecules, but as arrangements of ions.

  For example, in NaCl crystal, each Na^+ ion is surrounded by 6 Cl^- ions and each Cl^- ion is surrounded by 6 Na^+ ions. The number of oppositely charged atoms present around an ion is called its ***coordination number***. So the coordination number of NaCl is 6.

- **High melting and boiling points** - As more energy is required to break stronger bonds.

- **Soluble in polar solvents but insoluble in non-polar solvents** - ***Dielectric constant*** is the capacity of a solvent to neutralize an ionic compound.

  Polar solvents like water have high dielectric constants, so they dissolve ionic compounds easily.

- **Good conductors of electricity in aqueous state, but not in solid state** - As the ions are not free to move in solid state.

- **Ionic reactions** - When ionic compounds are dissolved in water, they split into cations and anions and show properties of their constituent ions.

- **Non-directional character** - In ionic compounds, each ion is uniformly surrounded by oppositely charged ions, so the electrical field is non-directional.

Covalent Bonds

Covalent bond is formed by the sharing of electrons between two atoms to form a *covalent compound*.

Properties of Covalent Compounds

- **Liquid/Gas state** - Covalent compounds don't exist as ions, but as independent molecules.

  There are weak intermolecular forces since covalent bonds are weak, and hence they exist as liquids and gases. Exceptions - Urea and sugar exist in solid state.

- **Low melting and boiling points** - As less energy is required to break weaker bonds.

- **Soluble in non-polar solvents but insoluble in polar solvents** - Covalent compounds don't dissolve in polar solvents like water, but they dissolve easily in non-polar solvents like benzene, carbon tetrachloride, etc.

- **Bad conductors of electricity** - As there are no ions.

- **Molecular reactions** - The reactions between covalent compounds occur between their molecules, and hence they are **slow** because energy is required to break these bonds and form new covalent bonds.

- **Directional character** - Covalent bonds are found between the nuclei of atoms, so they are directional.

Coordinate Covalent Bonds

In covalent bonds, both the atoms in a bond contribute one electron each to the bond.

A coordinate bond is a covalent bond in which **one atom contributes all the electrons**, while the other atom just participates in the bond without contributing anything.

The atom which contributes the electrons is called the *donor*, while the atom which accepts the electron is called the *acceptor*.

Examples of coordinate bonds: O_3 (ozone), H_3O^+ (hydronium ion), H_2SO_4 (sulphuric acid), etc.

Bond Parameters

1. Bond Order

Bond order is the *number of bonds* between two atoms in a molecule.

Isoelectronic species have the same bond order.

E.g.: The bond order of H_2 is 1, O_2 is 2, and N_2 is 3.

2. Bond Length

Bond length is the *internuclear distance* between 2 covalently bonded atoms.

Factors Affecting Bond Length

- **Bond order - Inversely proportional**

  Distance increases as bond order decreases.

  E.g.: Increasing order of bond lengths - $C\equiv C < C=C < C-C$

- **Atomic size - Directly proportional**

Larger the atoms, the bigger the distance between them.

E.g.: Increasing order of bond lengths - C-C < Si-Si < Ge-Ge

3. Bond Angle

Bond angle is the *average angle between the bonds* around the central atom in a molecule.

4. Bond Enthalpy

When bonds are formed, some amount of energy is **released**. This same amount of energy is required to **break** the bond and separate the atoms, and is called bond enthalpy or *bond dissociation enthalpy* or *bond energy*.

Bond enthalpy is the *amount of energy required to break one mole of bonds* of a particular type between two atoms in the gaseous state.

Factors Affecting Bond Enthalpy

Strong bonds have a high bond enthalpy.

- **Bond length - Inversely proportional**

  Shorter the bond length, stronger the bonds.

  As bond length is dependent on the atomic size and bond order, bond enthalpy also depends on them:

- Atomic size - Inversely proportional

  Smaller the atoms, stronger the bonds.

  E.g.: Bond enthalpy of H-H is more than Cl-Cl.

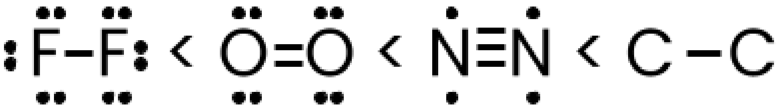
- Bond order - Directly proportional

Bond enthalpy increases as bond order increases.

E.g.: Bond enthalpy of C=C is more than C-C.

- **Number of Lone Pairs - Inversely proportional**

  E.g.: Increasing order of bond energies:

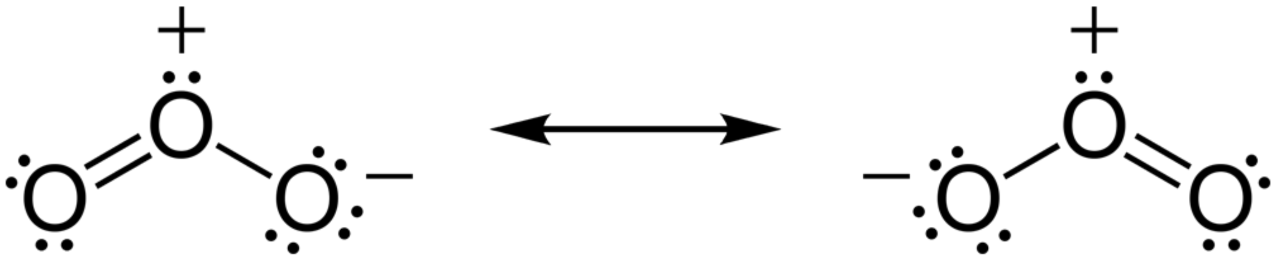


Resonance

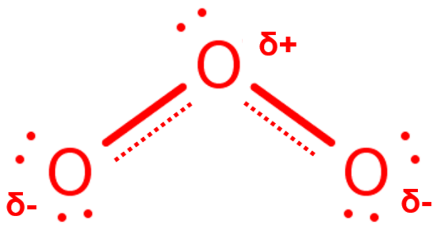
Sometimes, a single Lewis structure isn't enough to show a molecule.

Resonance structures are sets of Lewis structures which depict the same molecule. The actual structure is called the *resonance hybrid*, and the individual structures are called *resonance structures* or contributing structures.

For example, the ozone (O_3) molecule can be shown in the following 2 resonance structures:



The actual ozone molecule is a resonance hybrid of the above structures and is as shown:



Properties of Resonance

Resonance stabilizes the molecule, because the energy of the resonance hybrid is less than the energy of any resonance structure.

The bond lengths in a resonance hybrid are equal to each other.

Resonance is a theoretical concept and thus the resonance structures do not actually exist. Only the resonance hybrid exists.

Resonance Energy

Resonance energy = Actual bond energy − Energy of most stable (least energy) resonance structure

Greater the resonance and resonance energy, greater the stability of the molecule.

Bond Order in Resonance Structures

$$\text{Bond Order} = \frac{Total\ number\ of\ bonds\ between\ two\ atoms\ in\ all\ the\ resonance\ structures}{Total\ number\ of\ resonance\ structures}$$

It can also be calculated as:

$$\text{Bond Order} = \frac{Total\ number\ of\ bonds\ between\ central\ and\ surrounding\ atoms\ in\ one\ of\ the\ resonance\ structures}{Number\ of\ surrounding\ atoms\ in\ one\ of\ the\ resonance\ structures}$$

E.g.: The bond order of Ozone (O_3) is $\frac{2+1}{2} = 1.5$ according to the first formula or $\frac{3}{2} = 1.5$ according to the second formula.

Polarity of Bonds

No bond is completely ionic or completely covalent.

All ionic bonds have some covalent character and all covalent bonds have some ionic character.

In a bond between two different atoms, the atom which is more electronegative will pull the shared electrons towards it more. So, this will result in that atom having a slightly negative charge (−) and the less electronegative atom will have a slightly positive charge (+).

For example, in HCl, H is less electronegative than Cl. So H has a slightly positive charge H^{+} while Cl has a slightly negative charge Cl^{-}.

Such molecules having **two oppositely charged poles** are called **polar molecules** and the bond is called **polar covalent bond**.

Greater the electronegativity difference between the atoms, the **greater is the polarity** of the molecule.

More polarity means more ionic and less covalent, while **less polarity means less ionic** and more covalent.

If the electronegativity difference between two atoms is **1.7**, then the bond is **50% ionic** and **50% covalent**. If it is more than 1.7, then the bond is more ionic and if it is less than 1.7, then the bond is more covalent.

Dipole Moment

Dipole moment is the **measure of polarity** in a molecule.

Dipole moment is defined as the **product** of the **magnitude of charge** and the **distance between the charges**.

Dipole moment $\mu = q \times d$

Dipole moment is measured in Debyes (D).

$1\ D = 10^{-18}$ esu cm

$1\ esu = 3.33 \times 10^{-10}\ C$

Charge of an electron e = 1.6×10^{-19} C **= 4.8×10^{-10} esu**

Dipole moment is a vector quantity, and is represented by an arrow pointing from the positive to the negative atom.

E.g: The dipole of HCl is shown as, H  Cl

For diatomic molecules, (in which there's only one bond), the dipole moment of the molecule is the same as the dipole moment of the bond (also known as *bond dipole*).

For polyatomic molecules, (in which there is more than one bond), the **total dipole moment** of the molecule is the **vector sum** of **all the bond dipole moments**.

Therefore, the presence of polar bonds doesn't always mean that the molecule is polar, since if the polar bonds are arranged in such a way that they get canceled, then the polarity is zero.

To calculate the **fractional charge of an atom** in a molecule:

$$\text{Fractional Charge} = \frac{q}{e} = \frac{Charge\ present}{Charge\ of\ an\ electron}$$

To calculate the **% ionic character of a molecule**:

$$\text{Percentage Ionic Character} = \frac{\mu_{observed}}{\mu_{ionic}}$$

Here, μ_{ionic} is the dipole moment of that molecule if it were completely ionic, i.e.:

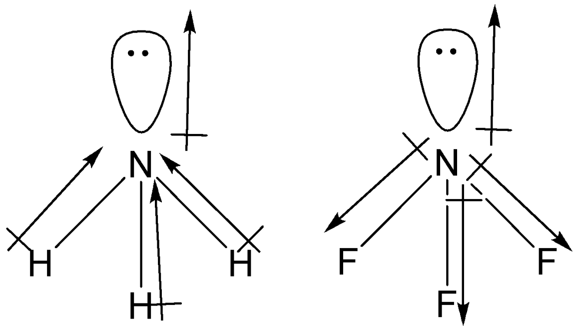
$\mu_{ionic} = q \times d = 4.8 \times 10^{-10}\ \text{esu} \times d\ \text{cm}$

Exception: NH_3 and NF_3

NH_3 and NF_3 both have a pyramidal shape with one lone pair on the nitrogen atom.

As F is more electronegative than H, NF_3 should have more polarity than NH_3. But in reality **NH_3 is more polar than NF_3**.

This is because in NH_3, **N is more electronegative than H**, so the dipole moments are from H to N, and in the **same direction** as the dipole moment of the lone pair. But in NF_3, **F is more electronegative than N**, so the dipole moments are from N to F, and they are **opposite** to the dipole moment of the lone pair. Thus, they get canceled and the polarity is less in NF_3.



Polarization

When two oppositely charged molecules A^+ and B^- come together, the cation attracts the electrons of the anion.

This results in *distortion* of the electron cloud around the anion towards the cation, and is called *polarization*.

- If there's **no polarization**, the bond is **completely ionic**.
- If there's **less polarization**, the bond is **mainly ionic** and **partially covalent**.
- If there's **more polarization**, the bond is **mainly covalent** and **partially ionic**.

So ***polarity is the opposite of polarization*** when it comes to **ionic and covalent character**.

The amount of polarization depends on:

- The power of the cation to polarize/distort the anion
- The tendency of the anion to get polarized by the cation

Fajans’ Rules

The amount of polarization can be found using Fajans’ rules. A molecule has **high polarization** if it has:

1. **Small cation**

   Smaller the cation, the greater its polarizing power.

   Small cations have high electron density and can polarize the anion more.

2. **Large anion**

   Larger the anion, the greater its tendency to get polarized .

   Large anions can’t attract electrons that easily.

3. **Large charge** on cation or anion

   Larger the charge on the cation, greater is its polarizing power, and larger the charge on the anion, greater is its tendency to get polarized.

4. **Cation with 18 electrons shell**

   Cations with 18 electrons have d shell, which can’t shield the nucleus as effectively as the s and p shells, leading to increased nuclear charge and hence more polarizing power.

Periodic Trends in Covalent Character

- Covalent character **increases across a period** as size decreases and charge increases.

  E.g.: Increasing covalent character: $NA^+ < Mg^{2+} < Al^{3+} < Si^{4+}$

- Covalent character **decreases down a group** as size increases.

  E.g.: Decreasing covalent character: $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

Valence Shell Electron Pair Repulsion Theory

This theory basically states that the **orbitals** containing **lone pairs or bond pairs** arrange themselves in the atom in such a way that they are **as far apart** as possible.

Decreasing order of repulsion:

Lone pair - Lone pair > Lone pair - Bond pair > Bond pair - Bond pair

This is because the **bond pair electrons** are under the influence of **two nuclei** simultaneously, but the **lone pair electrons** are under the influence of **one nuclei only** and hence are more **spread out**.

Shapes of Molecules

e^- Pairs	Formula	Shape	BP	LP	Actual Shape	Bond Angle	Examples
2	AB_2	Linear	2	0	Linear	180°	BeF_2, $BeCl_2$
3	AB_3	Trigonal Planar	3	0	Trigonal Planar	120°	BF_3
3	AB_2L		2	1	Bent	119.5°	SO_2, O_3
4	AB_4	Tetrahedral	4	0	Tetrahedral	109.5°	CH_4
4	AB_3L		3	1	Trigonal Pyramidal	107°	NH_3
4	AB_2L_2		2	2	Bent	104.5°	H_2O
5	AB_5	Trigonal Bipyramidal	5	0	Trigonal Bipyramidal	3-120°, 2-90°	PCl_5
5	AB_4L		4	1	See-Saw	3-117°, 2-89°	SI_4
5	AB_3L_2		3	2	T-shaped	87.6°	ClF_3
5	AB_2L_3		2	3	Linear	180°	XeF_2
6	AB_6	Octahedral (Square Bipyramidal)	6	0	Octahedral	90°	SF_6
6	AB_5L		5	1	Square Pyramidal	NA	BrF_5, $XeOF_4$
6	AB_4L_2		4	2	Square Planar	NA	XeF_4

In trigonal bipyramidal shape, **3 bonds** are called ***equatorial bonds*** and the other **2 bonds** are called ***axial bonds***. **Axial bonds are longer** than equatorial bonds due to **greater repulsion** from other bonds.

Although the VSEPR theory tells us about the shapes of molecules, it doesn't explain their bond formations.

Hence, two new theories based on quantum mechanics were made - *valence bond theory*, and *molecular orbital theory*.

How to Find The Shape of A Molecule

1. Find the total number of valence electrons in the entire molecule.
2. Divide it by 8 if it is greater than 8, else by 2.
3. The quotient is the number of bond pairs, and the remainder // 2 is the number of lone pairs.
4. Use the above table to figure out the shape.

Valence Bond Theory

The valence bond theory consists of the following:

1. Orbital overlapping
2. Hybridization

Orbital Overlapping

When two atoms come closer, their atomic **orbitals overlap each other** to form a *molecular orbital*, and this leads to the **pairing of electrons** and **formation of covalent bonds**.

More overlapping leads to **stronger bonds.**

Types of Covalent Bonds Based on Nature of Overlapping

Sigma Bond (σ)	Pi Bond (π)
It is formed by the **axial** (head to head) overlapping of atomic orbitals.	It is formed by the **sideways** overlapping of atomic orbitals.

It occurs in **s-s, s-p and p-p** orbitals.	It occurs only in **p-p** orbitals.
It is **stronger** due to more overlapping.	It is **weaker** due to less overlapping.
The molecular orbital formed is **symmetrical** about the internuclear axis and the charged electron cloud is present on this axis.	The molecular orbital formed is **discontinuous** and has **2 charged electron clouds above and below** the internuclear axis.
Free rotation is possible.	Free rotation is **not possible**.
It **may exist alone or with pi bonds**.	It **only exists with a sigma bond**.

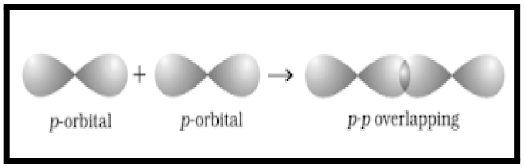
Sigma Bonds

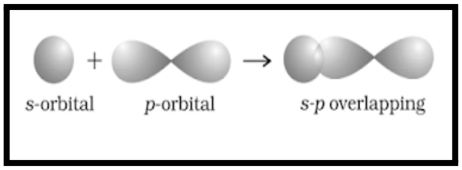
Within sigma bonds, as the value of **n increases**, the **bond strength decreases**.

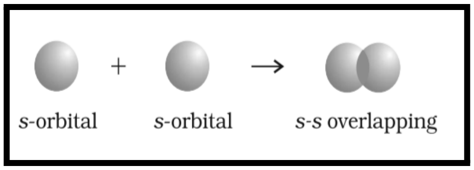
E.g.: Decreasing order of bond strength: 1s-1p > 2s-2p > 3s-3p

For the **same value of n**, the bond strength of p-p is more than s-p, which is more than s-s.

E.g.: Decreasing order of bond strength: **p-p > s-p > s-s**







Hybridization

The **intermixing** of **atomic orbitals** of **different shapes** and **slightly different energies**, where **redistribution of energy** takes place, to **form new orbitals** of the **same shape and energy** is called ***hybridization.***

The new orbitals formed are called ***hybrid***/***hybridized orbitals***.

Characteristics of Hybridization

- Hybrid orbitals are equal in energy and shape.
- Only valence shell electrons get hybridized.

- The **number of hybrid orbitals formed is equal to the number of orbitals that get hybridized.**
- Hybrid orbitals participate in bonding because they are more stable than atomic orbitals.
- **More the directional character** in a covalent bond, the **stronger is the bond**.

  Decreasing order of directional character: **sp^3-sp^3 > sp^3-sp^2 > sp^2-sp^2 > sp-sp**

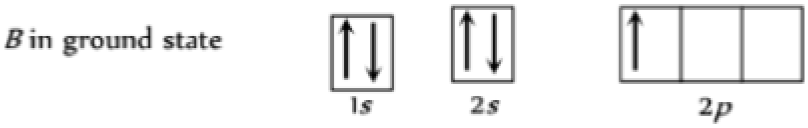
Types of Hybridization

1. sp Hybridization
2. sp^2 Hybridization
3. sp^3 Hybridization
4. sp^3d Hybridization
5. sp^3d^2 Hybridization
6. sp^3d^3 Hybridization

Example of sp^2 Hybridization

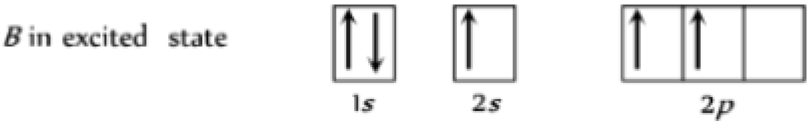
BCl_3 shows sp^2 hybridization.

The electronic configuration of B is $1s^2$ $2s^2$ $2p^1$.



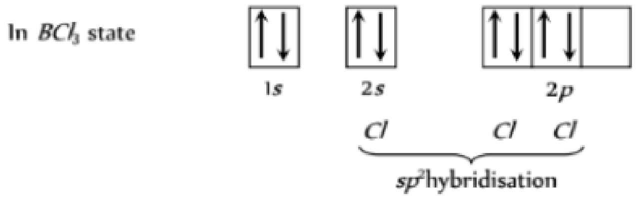
When it gets excited, one electron from the 2s orbital gets *promoted* to the 2p orbital.

The energy for this promotion comes from the bond formation (since we know that bond formation releases energy).



When this excited B atom combines with 3 Cl atoms, it creates 3 new sp^2 hybrid orbitals, and leads to the formation of BCl_3.

The 3 orbitals are at an angle of 120°, and hence are in the trigonal planar shape.



Type	Number of Orbitals	Shape	Bond Angle	Examples
sp	s + 1(p) = 2 sp	Linear	180°	BeF_2, C_2H_2
sp^2	s + 2(p) = 3 sp^2	Trigonal Planar	120°	BCl_3, C_2H_4
sp^3	s + 3(p) = 4 sp^3	Tetrahedral	109.5°	NH_3, H_2O, CH_4
sp^3d	s + 3(p) + d = 5 sp^3d	Trigonal Bipyramidal	3 - 120°, 2 - 90°	PCl_5, PF_5
sp^3d^2	s + 3(p) + 2(d) = 6 sp^3d^2	Octahedral (Square Bipyramidal)	90°	SF_6
sp^3d^3	s + 3(p) + 3(d) = 7 sp^3d^3	Pentagonal Bipyramidal	5 - 72°, 2 - 90°	IF_7

In case the compound contains lone pairs, then the same rules of VSEPR theory will apply, i.e. the shapes and angles will change accordingly.

Determination of Hybridization State

Number of hybrid orbitals =

$$\frac{Number\ of\ valence\ electrons\ in\ the\ central\ atom + Total\ number\ of\ monovalent\ atoms + Charge\ of\ anion - Charge\ of\ cation}{2}$$

We can then find the type of hybridization from the number of hybrid orbitals:

Number of Hybrid Orbitals	Type of Hybridization
2	sp
3	sp^2
4	sp^3
5	sp^3d

6	sp^3d^2
7	sp^3d^3

In carbon compounds,

- Single bond = 0 π bonds = sp^3
- Double bond = 1 π bond = sp^2
- Triple bond = 2 π bonds = sp

To determine the number of hybrid orbitals of a carbon atom in an organic compound, we need to **add** the **number of atoms attached to that carbon atom** and the **number of lone pairs on that carbon atom.**

After that we can use the above table to find the hybridization state.

Molecular Orbital Theory

Just like electrons of atoms are present in atomic orbitals, electrons in a molecule are present in molecular orbitals.

When two atomic orbitals combine, they form 2 molecular orbitals - *bonding molecular orbital*, and *antibonding molecular orbital*.

The **number of molecular orbitals formed is equal to the number of combining atomic orbitals**.

Atomic orbitals are affected by **one nucleus** and hence they are ***monocentric***, while molecular orbitals are affected by **2 or more nuclei** and hence they are ***polycentric***.

The molecular orbitals are filled according to the same rules as atomic orbitals - *Aufbau principle, Pauli's exclusion principle, and Hund's rule of maximum multiplicity.*

There are two types of molecular orbitals: σ molecular orbitals and π molecular orbitals.

The differences between them are the same as the differences between σ bonds and π bonds.

Formation of Molecular Orbitals

Atomic orbitals can be expressed as wave functions which are obtained from the solutions of Schrödinger's wave equation.

However, it is very difficult to solve Schrödinger's wave equation for molecular orbitals.

To solve it, an approximate method called ***Linear Combination of Atomic Orbitals*** is used.

According to the LCAO method, **molecular orbitals are formed by addition and subtraction of the atomic orbitals**.

For example, when two atoms A and B combine:

$\Psi_{MO} = \Psi_A \pm \Psi_B$

where Ψ_{MO} is the molecular orbital, and Ψ_A and Ψ_B are the atomic orbitals of A and B.

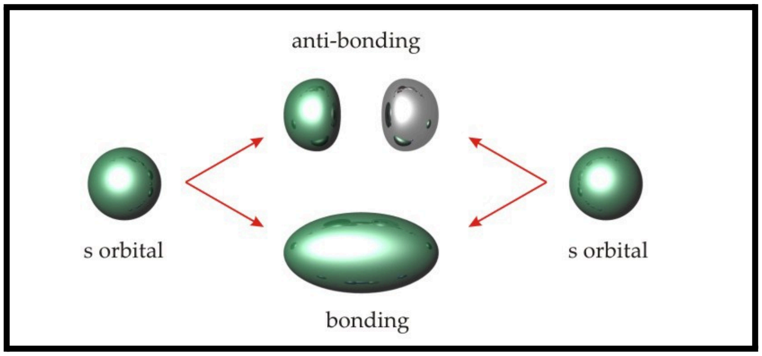
This will lead to formation of 2 molecular orbitals:

$\Psi_{MO} = \Psi_A + \Psi_B$

This is the bonding orbital and is formed by the addition of the atomic orbitals.

$\Psi^*_{MO} = \Psi_A - \Psi_B$

This is the antibonding orbital and is formed by the subtraction of the atomic orbitals.



In summary:

Bonding Molecular Orbitals	Antibonding Molecular Orbitals
Formed by the **addition** of atomic orbitals. $\Psi_{MO} = \Psi_A + \Psi_B$	Formed by the **subtraction** of atomic orbitals. $\Psi^*_{MO} = \Psi_A - \Psi_B$

Formed due to **constructive interference** of the waves. Hence, the waves get added up.	Formed due to **destructive interference** of the waves. Hence the waves get subtracted/canceled.
Formed when the **lobes** of the combining atomic orbitals have the **same sign**.	Formed when the **lobes** of the combining atomic orbitals have **opposite signs**.
They have **greater electron density** in between the nuclei of the atoms.	They have **lesser electron density** in between the nuclei of the atoms.
They are **more stable** and have **less energy**.	They are **less stable** and have **more energy**.

Conditions for Combination of Atomic Orbitals

1. The combining atomic orbitals must have the **same or nearly the same energies**.

   E.g.: A **2s orbital** of one atom **can combine with a 2s orbital** of another atom, but **not with a 1s orbital**.

2. The extent of overlapping between the two atomic orbitals must be large.
3. The combining atomic orbitals must have the same symmetry/orientation.

   E.g.: A **$2p_z$** orbital **can combine with another $2p_z$** orbital, but **not with a $2p_x$ or $2p_y$** orbital.

   Similarly, a **2s** orbital **can combine with a $2p_z$** orbital, but **not with a $2p_x$ or $2p_y$** orbital.

Orders of Energy

Order of Energy from H_2 to N_2

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \boldsymbol{\pi 2p_x = \pi 2p_y < \sigma 2p_z} < \pi^* 2p_x = \pi^* 2p_y < \sigma^* 2p_z$$

Order of Energy for O_2, F_2, etc.

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \boldsymbol{\sigma 2p_z < \pi 2p_x = \pi 2p_y} < \pi^* 2p_x = \pi^* 2p_y < \sigma^* 2p_z$$

Bond Order in Molecular Orbital Theory

Bond order = $\frac{N_b - N_a}{2}$

where N_b is the number of electrons in bonding orbitals,

and N_a is the number of electrons in antibonding orbitals.

If $\mathbf{N_b > N_a}$, then the molecule is **stable**. Otherwise if $\mathbf{N_b \leq N_a}$, then the molecule is **unstable**.

If bond order = 0, the molecule doesn't exist.

The bond orders of 1, 2, and 3 correspond to single, double, and triple bonds respectively.

The bond order can even be a fraction.

Magnetic Properties

If one or more electrons are **unpaired**, the molecule is **paramagnetic** (**repelled** by magnets).

If all electrons are **paired**, the molecule is **diamagnetic** (**attracted** by magnets).

Example: Molecular Orbital Diagram of O_2

The atomic number of oxygen is 8.

The electronic configuration of an **oxygen atom** is $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$.

The electronic configuration of an **oxygen molecule** is

$\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^2\ \pi 2p_x^2\ \pi 2p_y^2\ \pi^* 2p_x^1\ \pi^* 2p_y^1$.

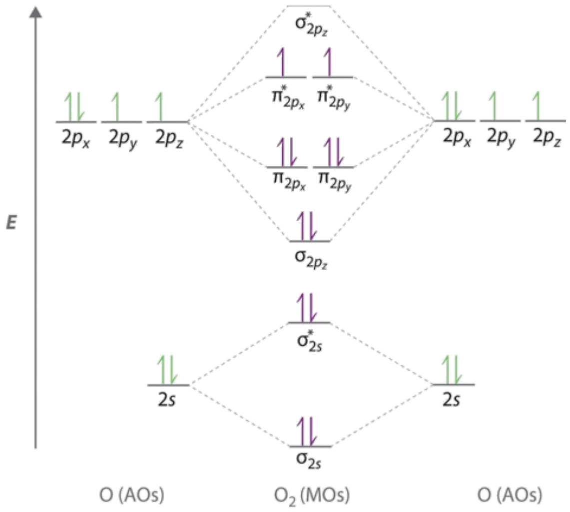
The 1s molecular orbitals don't participate in bonding and hence they can be denoted as KK.

So the electronic configuration of an oxygen molecule can also be written as

KK $\sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^2\ \pi 2p_x^2\ \pi 2p_y^2\ \pi^* 2p_x^1\ \pi^* 2p_y^1$.

Bond order of O_2 = $\frac{N_b - N_a}{2} = \frac{8-4}{2} = 2$

Since all electrons are paired, the oxygen molecule is diamagnetic.



Hydrogen Bond

When a **hydrogen atom** is bonded with a **highly electronegative atom** such as halogens, it forms a **weak bond** with **another electronegative atom** in the **same or different molecule**.

This bond is called a ***hydrogen bond***.

Some compounds which show hydrogen bonding are HF, H_2O, and NH_3.

Conditions of Hydrogen Bonding

- The atom should be **highly electronegative**.
- The **electronegative atom** should be **small**.

  E.g.: NH_3 shows hydrogen bonding but **HCl does not**, because N is smaller than Cl.

Types of Hydrogen Bonding

1. Intermolecular hydrogen bond
2. Intramolecular hydrogen bond

Intermolecular Hydrogen Bond

It occurs **between 2 molecules**.

It leads to the **association** of molecules, and hence **affects their physical properties**.

It is present in HF, H_2O, and alcohol.

Intramolecular Hydrogen Bond

It occurs in the **same molecule**.

It **prevents the association** of molecules, and hence **doesn't affect** their physical properties.

It is present in o-nitrophenol and o-nitrobenzoic acid.

Effects of Hydrogen Bonding

- **Increase in size and molecular mass** of the compound due to association
- **Higher melting and boiling points** due to increase in force of attraction in molecules
- **Less volatility** due to high boiling point

Why is Ice Lighter Than Water?

In ice, each oxygen atom is surrounded by 4 hydrogen atoms such that 2 are linked by covalent bonds and the other 2 are linked by hydrogen bonds.

Since **hydrogen bonds are longer than covalent bonds**, this leads to formation of **vacant spaces**.

So, ice has an **open cage-like structure** which **decreases its density** and makes it **lighter**.

Why Does Water Have Maximum Density at 4°C?

When ice is melted, the **cage-like structure** partially **breaks down**.

The water molecules start flowing into those vacant spaces in the ice, and this leads to **concentration of volume** and **increases the density of water**.

As it is further heated, the **kinetic energy** of the molecules **increases** and they start **moving away** from each other, and this **reduces the density of water**.