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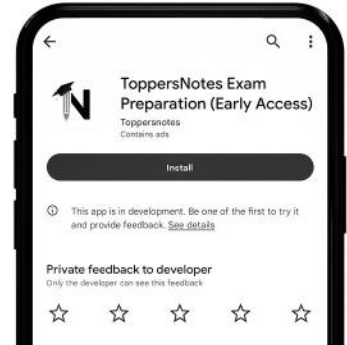## Physical Chemistry - 2

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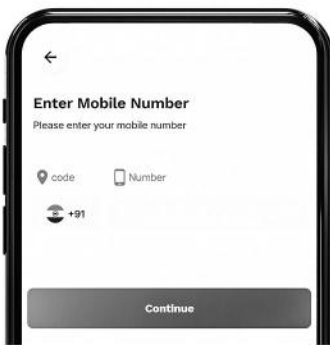To use the QR codes in the book, Please follow the below steps :-

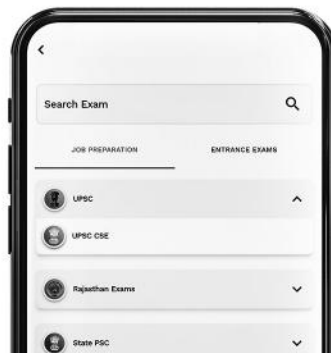**To install the app, scan the QR code with your mobile phone camera or Google Lens**
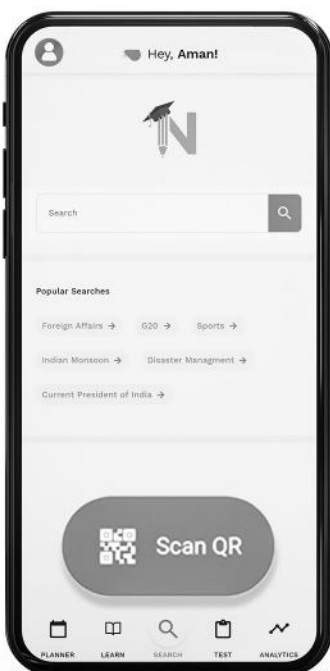
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CHAPTER 1

Chemical Bonding and Molecular Structure

<div style="text-align:center">

CHAPTER OUTLINE

</div>

- Valency
- Ionic or Kernel Bond
- Valence Bond Theory (VBT)
- Hydrogen Bond
- Resonance
- VSEPR (Valence Shell Electron Pair Repulsion Theory)

- Chemical Bond
- Covalent Bond
- Coordinate or Semi-polar Bond
- Metallic Bonding
- Hybridization
- Molecular Orbital Theory

VALENCY

- **Valency** is a property of atoms that allows them to create chemical bonds with one another.
- **Frankland** coined the term valency, which meaning "ability to combine."
- As a result, it is an atom's ability to join with another atom.
- Atoms do this by either releasing or receiving electrons in their outermost shell.
  Valency (V) = the number of valence electrons
- Example:
  The electronic configuration of the element sodium (Na) in group IA is 2,8,1.
  The number of valence electrons is one, hence the valency is one.
- If the number of valence electrons is greater than four, the valency is determined using the following relationship: V=Ve⁻—8 (number of valence electrons minus 8) (number of valence electrons minus 8)
  For example, the nitrogen (N) arrangement is 2, 5.
  Its valency is V=5-8=-3 (negative sign signifies the tendency to accept electrons)

Kossel-Lewis Theory: Octet Theory

- **Lewis** proposed the **covalent bond**, whereas **Kossel** proposed the **electrovalent bond**.
- Atoms join to form molecules in order to lower their internal energy and gain an octet in their valence shell, similar to inert gases. This is referred to as the **octet rule**.
- As atoms unite, they obtain a stable inert gas configuration in their valence shell by losing, acquiring, or exchanging electrons.

Octet Rule

- Each atom attempts to achieve the octet state, that is, a state with eight valence electrons, according to this rule.
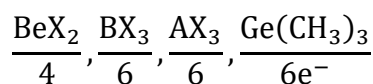
Exceptions:

- Transition metal ions like $Cr^{+3}, Mn^{+2}, Fe^{+2}$.
- Pseudo inert gas configuration cations like Zn^{2+}, Cd^{2+}.

Contraction of octet state

- Here central atom is electron deficient or does not have an octet state.
- Example:
  $$\frac{BeX_2}{4}, \frac{BX_3}{6}, \frac{AX_3}{6}, \frac{Ge(CH_3)_3}{6e^-}$$

Expansion of octet state

- Here central atom has more than $8e^-$ due to empty d orbital.
  Examples: $PCl_5, SF_6, OsF_8, ICl_3$
- Odd electronic species like NO, NO_2, ClO_2
- Inter halogens compounds like IF_7, BrF_3
- Compounds of xenon such as XeF_2, XeF_4, XeF_6

CHEMICAL BOND

A chemical bond is the attractive force that holds two atoms together. At a specific distance, a chemical connection balances the forces of attraction and repulsion.

A chemical bond is formed to:

- Attain the octet state
- Minimize energy
- Gain stability
- Decrease reactivity
- As two atoms come close together, forces of attraction and repulsion interact.
- **Bond distance** is the distance at which attractive forces overpower repulsive forces.
- The bond is established because the system's potential energy is lowest here.
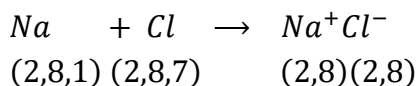
Types of Bonds

There are total 6 types of chemical bonds which are listed in a decreasing order of their respective bond strengths.

1. Ionic bond
2. Covalent bond
3. Coordinate bond
4. Metallic bond
5. Hydrogen bond
6. Van der Waals bond

- Metallic bond, hydrogen bond and van der Waals bond are interactions.

IONIC OR ELECTROVALENT BOND

- The complete transfer of valence electrons from a metal to a non-metal results in the formation of an ionic bond.

For example:

$$Na + Cl \rightarrow Na^+Cl^-$$
$$(2,8,1) \ (2,8,7) \qquad (2,8)(2,8)$$
$$Mg + O \rightarrow Mg^{+2}O^{-2}$$
$$(2,8,2) \ (2,6) \qquad (2,8)(2,8)$$
$$Al + N \rightarrow A^{+3}N^{-3}$$
$$(2,8,3)(2,5) \qquad (2,8)(2,8)$$
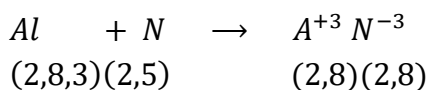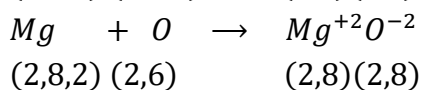
- **Electrovalency** is equal to the **number of electrons exchanged**.
- As in the case of AlF$_3$, the maximum number of electrons transferred by a metal to a nonmetal is three (Al metal transfers three electrons to F).
- The outermost orbit of metal is destroyed during electron transfer, and the remaining piece is known as the core or kernel, hence this bond is also known as a **kernel bond.**
- Ionic bonds have an **electrostatic or coloumbic force of attraction**.
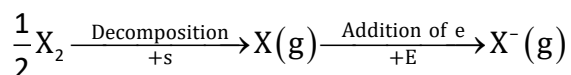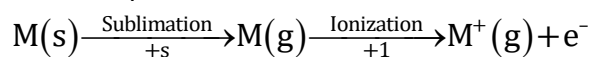- It is a **non-directional bond**.

Conditions for the Formation of an Ionic Bond

- The bond formation process must be exothermic (H = -ve), and the necessary parameters are-
  o **Metals** with **low ionisation energies** must be used.
  o **Non-metal** materials must have a **strong electron affinity**.
  o **Ions** must have **high lattice energy**.
  o The **cation** should be **large** and have a **low electronegativity**.
  o An **anion** must be **small** and have a **high electronegativity.**

Born-Haber Cycle

- The **Born-Haber cycle** can be applied to demonstrate the energy requirements for the formation of an ionic molecule.
- It may also be used to calculate the lattice energy, ionisation energy, and electron affinity.

For example:

$$M(s) \xrightarrow[+s]{\text{Sublimation}} M(g) \xrightarrow[+1]{\text{Ionization}} M^+(g) + e^-$$

$$\frac{1}{2}X_2 \xrightarrow[+s]{\text{Decomposition}} X(g) \xrightarrow[+E]{\text{Addition of e}} X^-(g)$$

$$M^1(g)1X^-(g) \xrightarrow[-U]{\text{Crystal formation}} MX(g)$$

$$\Delta H_f = S + \frac{1}{2}D + I - E - U$$

where,

S = Heat of sublimation

D = Heat of dissociation

I = Ionization enthalpy

E = Electron gain enthalpy or electron affinity

U = Lattice energy

- For the formation of an ionic solid, **energy must be released** during its formation, that is, ΔH **must be negative** for it.
$$-E - U > S + 1/2D + I$$

Properties of Ionic Compounds

1. Ionic compounds have **solid crystalline structures** (flat surfaces), comprising of definite geometry.
2. Due to **strong electrostatic force of attraction** as constituents are arranged in a **definite pattern.**
3. These compounds are **hard** in nature.

    Hardness $\propto$ **Electrostatic force of attraction**

    $\propto$ **Charge on ion**

    $\propto \dfrac{1}{\textbf{Ionic radius}}$

4. Ionic compounds have **high boiling point, melting point and density** due to strong electrostatic force of attraction.

    Boiling point, melting point $\propto$ **Electrostatic force of attraction**

    Volatile nature $\propto$

    $\dfrac{1}{\textbf{Electorstatic force of attraction}}$

5. Ionic compounds exhibit **isomorphism**, which means they have the same crystalline structure.

    For instance, all alums, NaF, and MgO.

6. Because of the existence of free ions, they are **conductors** in the **fused, molten, or liquid states.** Because there are no free ions in **the solid state**, they are **non-conductors.**

7. They exhibit **quick ionic reactions** because the **activation energy for ions** is **zero**.
8. Because of the **non-directional nature** of the ionic connection, they do not exhibit **spatial isomerism**.
9. When an ionic solid molecule is formed from its constituent ions, **lattice energy (U)** is released.

Lattice Energy

- The energy required to split an ionic solid molecule into its constituent ions is also known as lattice energy.
- It is denoted by U.

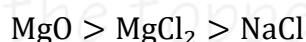 $U \propto$ **Charge on ion** $\propto \dfrac{1}{\textbf{Size of ion}}$

    Hence, lattice energy for the following compounds increases in the order shown below:

    $NaCl < MgCl_2 < AlCl_3 < SiCl_4$
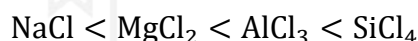
- **As charge on a metal atom increases, its size decreases.**
- In case of univalent and bivalent ionic compounds, lattice energy decreases in the following order:

    $Bi - bi > Uni - bi$ or $Bi - uni > Uni - uni$

    For example:

    $MgO > MgCl_2 > NaCl$

10. Because of the high dielectric constant of polar solvents like water, ionic compounds are soluble in these solvents, destroying the force of attraction between ions and causing them to dissolve in the solvent.

Facts Related to Solubility

- If ΔH (hydration) $>$ Lattice energy then ionic compound is soluble.
- If ΔH (hydration) $<$ Lattice energy then ionic compound is insoluble
- If ΔH (hydration) = Lattice energy then the compound is at equilibrium state

Some Solubility Orders

a. $LiX < NaX < KX < RbX < CsX$
b. $LiOH < NaOH < KOH < RbOH < CsOH$
c. $BeX_2 < MgX_2 < CaX_2 < BaX_2$

---

d. $Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Ba(OH)_2$
e. $BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$
f. $AIF_3 > AlCl_3 > AlBr_3 > AII_3$

- Crystals of high ionic charges are less soluble. For example, compounds of $CO_3^{-2}, SO_4^{-2}, PO_4^{-3}$ are less soluble.

   Compounds Ba^{+2}, Pb^{+2} are insoluble as lattice energy $> \Delta H_{hy}$

   Compounds of Ag (salt) are insoluble as lattice energy $> \Delta H_{hy}$

- Presence of common ions decrease solubility. For example, solubility of AgCl decreases in presence of $AgNO_3$ or KCl, due to presence of common ions that is, Ag^+ and Cl^- respectively.

COVALENT BOND

A covalent bond is established by the equal sharing of electrons between two atoms that are either identical or dissimilar.

- If the atoms are the same or have the same electronegativity, the covalent bond between them is non-polar.
  - Example: $X - X, O = O, N \equiv N$
- If the atoms are dissimilar or have distinct electronegativity values, the covalent bond formed between them is polar.
  - Example: $\overset{+\delta}{H} - \overset{-\delta}{O} - \overset{+\delta}{H}, \overset{+\delta}{H} - \overset{-\delta}{X}$
- **Covalency** is represented here by the number of electrons shared or covalent bonds.
- A single atom can share a maximum of three electrons with another.
- **Heitler-valence London's bond theory, Pauling-overlapping Slater's theory, and Hund-theory Mullikan's** are used to describe the nature of covalent bonds.
- Heitler and London introduced the orbital notion of covalent bonding. "*Covalent bonds are created due to half-filled atomic orbitals containing electrons with opposing spin to one other,*" according to this theory.

- The potential energy of the system diminishes due to overlapping.
- **Bond length** is defined as the internuclear distance with the greatest overlap and the greatest drop in potential energy.

Covalent bond energy consideration

As two hydrogen atoms H_A and H_B, each with its own electron e_A and e_B, approach each other, the following attraction and repulsive forces begin to operate.
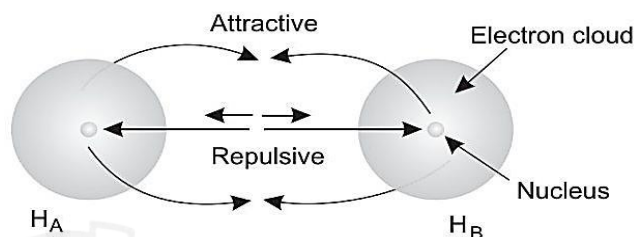

Figure: Formation of Covalent bond

Here, attractive forces between $H_A e_A$ and $H_B e_B$ and $H_B e_A$ and $H_A e_B$.

Repulsive forces are between e_A and e_B and between nucleus of H_A and H_B.

- It is noticed that attractive forces outnumber repulsive forces, resulting in lower energy, and so the potential energy of the system drops.
- The minimum energy point refers to the critical distance between two nuclei, at which maximal energy reduction occurs. This distance is known as bond length.
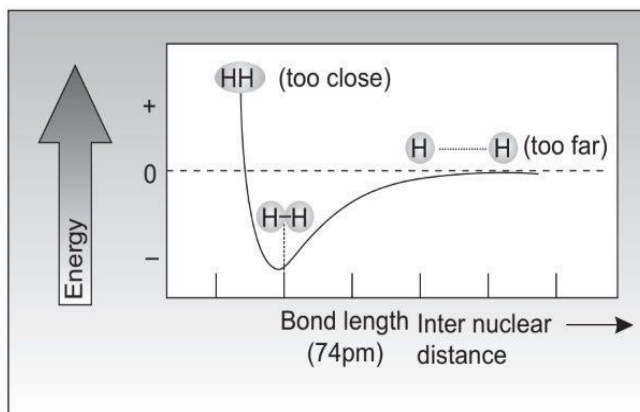- **Example:** Bond length in H-H is 74pm.

Figure : Variation of Energy and Bond length

Features of Covalent Compounds

1. Covalent compounds are mainly found in liquids and gases, but if the molecular weight of the chemical is large enough, they can also be found in solids.

   Example:

Molecular wt	Glucose	Sugar
	180	342
	(less solid)	(more solid)

2. **Non-polar solute dissolves in non-polar solvent because "like dissolves like."**

   Example, CCl_4 dissolves in organic solvents. Similarly, polar solutes dissolves in polar solvent. For example, alcohol and ammonia dissolve in water.

3. The boiling and melting points of covalent compounds are lower than those of ionic ones. This is due to the fact that covalent bonds have a weak van der Waals force in nature.

Comparable to	KOH	>	HX
	Strong		Weak
	ionic force		van der
	of attraction		Walls forces

   Boiling point and melting point $\propto$ Hydrogen bonding $\propto$ Molecular weight

   For example,

HF	>	HI	>	HBr	>	HCl
Due to				As molecular		
H-bonding				weight decreases		

4. Covalent compounds are non-conductors due to the lack of free ions, whereas graphite is a conductive due to the availability of free electrons in its hexagonal sheet-like structure. Diamond has a tetrahedral structure, hence free electrons are not available. As a result, it is not a conductor.

5. Since covalent bonds are directional, these compounds can exhibit spatial isomerism.

6. Polarization occurs when a cation and an anion are near to one other and the anion's form is twisted by the cation. As a result, an ionic molecule obtains covalent nature.

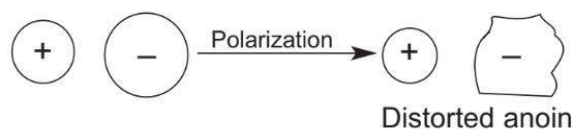$$\text{Polarization} \propto \text{Covalent nature} \propto \frac{1}{\text{Ionic nature}}$$

Figure : Effect of Polarization

Fajan's rule

Polarization or covalent nature is explained by the following rules:

- **Charge on cation**
  - Polarization, covalent character, or polarising force of cation charge. That is, the bigger the charge on a cation, the stronger its polarising force and the greater its covalent nature.

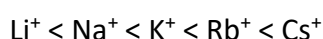   Example: $SiCl_4$ > $AlCl_3$ > $MgCl_2$ > $NaCl$

- **Size of Cation**
  - When charge is same and anion is common, covalent nature $\propto \frac{1}{\text{Size of cation}}$ i.e. smaller cation has more polarizing power.

  For example,

  $LiCl$ > $NaCl$ > KCl > $RbCl$ > $CsCl$

Max. covalent	Max. ionic
Least ionic	Least covalent

  Li^+ < Na^+ < K^+ < Rb^+ < Cs^+

Smallest	Largest
in size	in size

Size of anion

- This feature is considered when the charges are the same and the cation is common.

- Polarization or covalent nature $\propto$ size of anion.

- Therefore, larger anions are more polarized

  Example: LiF, $LiCl$, $LiBr$, LiI

  As F^-, Cl^-, Br^-, I^-

- A **cation** with **18 valence electrons** has **more polarizing power** than a **cation** with **8 valence electrons**.

Examples:

group IB	>	group IA
Cu^+	>	Na^+
Ag^+	>	K^+
group IIB	>	group IIA
Zn^{+2}	>	Mg^{+2}
ZnO	>	MgO
Zn^{+2}		Mg^{+2}
2, 8, 18		2, 8

Facts to Remember

The intensity of the colour increases as the covalent nature increases.

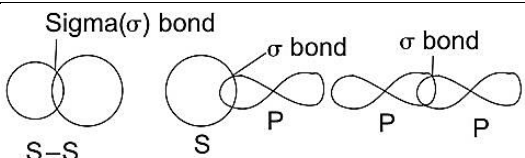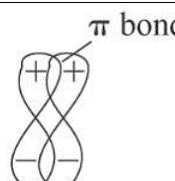Example: $FeCl_3$ is reddish-brown, whereas $FeCl_2$ is greenish-yellow.

VALENCE BOND THEORY (VBT)

- This theory is founded on the knowledge of atomic orbitals, electronic configurations of elements, overlap criteria of atomic orbitals, hybridisation of atomic orbitals, and variation and superposition principles.

- According to the orbital overlap idea, the creation of a covalent bond between two atoms comes from the pairing of electrons with opposing spins in the valence shell. The bigger the overlap, the stronger the bond between atoms.

- **Co-axial overlapping → extent of overlapping more → high bond strength**

- **Collateral overlapping → extent of overlapping less → low bond strength**

- In Co-axial overlapping, extent of overlapping is-
  p-p < s-p < s-s

- In terms of overlap and hybridisation of atomic orbitals, the VBT explains the formation and directional features of bonds in polyatomic compounds such as CH_4, NH_3, etc.

- Two types of bonds are formed on account of overlapping-
  (a) Sigma (σ) bond
  (b) Pi (π) bond

Sigma (σ) Bond and Pi (π) bond

	Sigma (σ) Bond	Pi (π) bond
Formation	The axial or head to head or linear overlap between two $s-s$ or $s-p$ or $p-p$ orbitals and form a sigma bond.	Lateral or sidewise overlapping between two p orbitals results in the formation of pi bond.
Properties	1 Sigma bonds are stronger and hence less reactive than pi bonds due to more effective and stronger overlapping. 2 Between two bound atoms, the lowest and maximum number of sigma bonds is one. 3 **Stability $\propto$ Number of sigma bonds.** 4 **Reactivity $\propto \frac{1}{\sigma}$** 5 Free rotation of the atoms is possible in sigma bond. 6 The shape of molecule is determined by Sigma bond.	1 Because of less effective overlapping, it is a weaker or less stable binding, and hence more reactive. 2 The minimum and greatest number of pi bonds that may exist between two bound atoms is 0 and 2, respectively. 3 **Stability $\propto \frac{1}{\text{Number of pi bonds}}$** 4 **Reactivity $\propto$ Number of pi bonds.** 5 Free rotation is not possible. 6 It does not determine the shape of a molecule but shortens bond length.

Pictorial Representation	 **Figure:** Formation of Sigma Bond	 **Figure :** Formation of pi bond

To Find the Number of Sigma and Pi Bonds in a Molecule
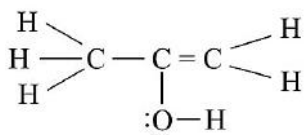
(Single bond) $= 1\sigma$

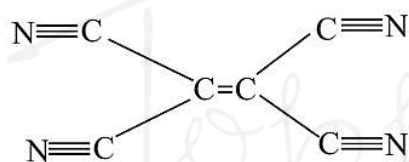(Double bond) $= 1\sigma, 1\pi$

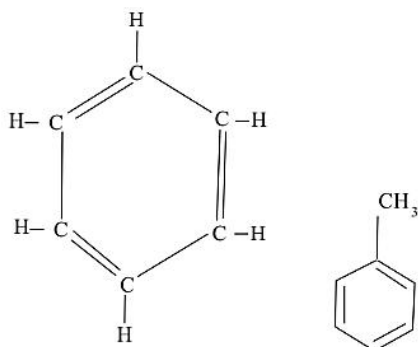(Triple bond) $= 1\sigma, 2\pi$

Examples:

1. Enolic form of acetone

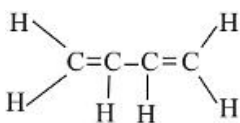It has 9σ and 1π bond, and 2 lone pairs of electrons.

2. $C_2(CN)_4$

It has 9σ and 9π bond, and 4 lone pairs of electrons.

3.

It has 12σ and 3π bonds.   It has 15σ and 3π bonds

4. Buta-1, 3-diene

It has 9σ and 2π bonds

COORDINATE OR SEMI-POLAR BOND

- A coordinate bond is a type of bond created by the donation of an electron pair from the donor to the recipient, implying a partial transfer or uneven distribution of electrons.

- It is denoted as ($\rightarrow$) from donor to receiver.

$$A: \qquad +B \longrightarrow (A \rightarrow B)$$
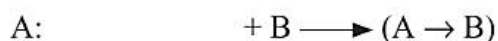
Donor or   Receiver

Lewis base   Lewis acid

Example: Formation of $NH_3.BF_3$ Molecule
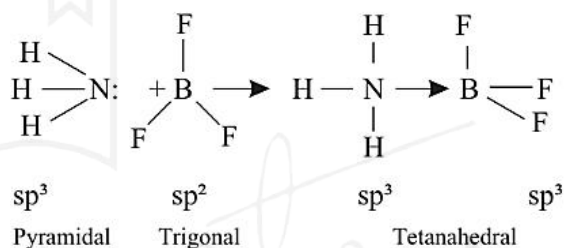
- Coordinate bonds are intermediate between ionic and covalent bonds, but resemble covalent bonds more closely.

- Coordinate compounds have features that are more similar to covalent compounds.

 Example: Properties of ligands like NH_4^+, H_3O^+, NH_3 resemble BF_3 (a covalent compound) and complexes like $K_3Fe(CN)_6$.

- Singlet linkage is formed by donation of one electron and denoted by ($\neg$).

 It was studied by Lorry and Sidwick.

 Examples: PCl_5, SF_6, IF_7.
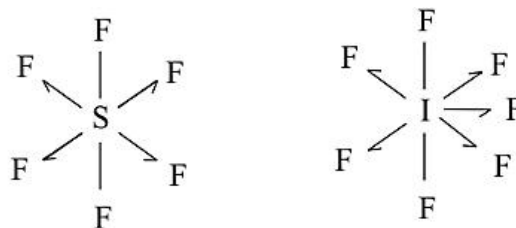
HYDROGEN BOND

- Latimer and Rodebush invented the hydrogen bond.
- It is a weak contact between hydrogen and a very electronegative and tiny atom such as F, O, or N, symbolised by dotted (-) lines.
- The hydrogen atom is covalently bound to any of them in this case.
- A hydrogen bond might be dipole-dipole, ion-dipole, or dipole-induced dipole in nature. Since chlorine is so large, it has no H-bonding.
- H-bond strength for the following order = $HF > H_2O > NH_3$

Types of Hydrogen Bonding

a) **Intermolecular H-bonding**

- Intermolecular H-bonding is formed between two or more different molecules of the same or different types.
- Examples: HF, H_2O, NH_3, R-OH, R-COOH, $R - NH_2$, Glucose, Sucrose etc.
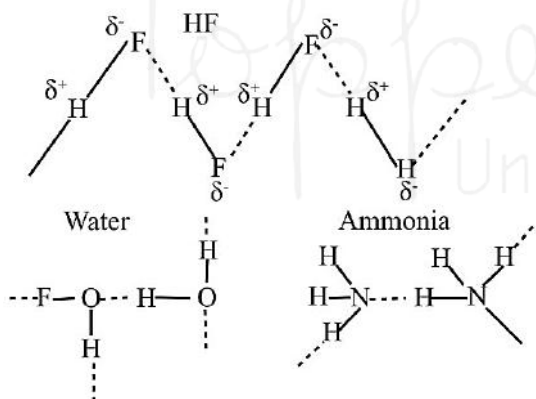
Figure: Intermolecular H-bonding in Water and Ammonia

Facts Related to Intermolecular Hydrogen Bonding

- One water molecule may make hydrogen bonds with up to four other water molecules.
- As a result of hydrogen bonding in water, the water molecules are densely packed, giving water a smaller volume but greater density than ice, which has an open cage-like shape.
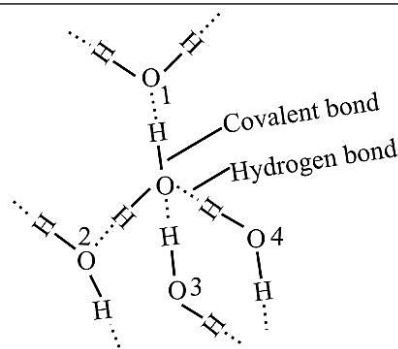
- Water has **maximum density at $4°C$** as above $4°C$ some hydrogen bonds are broken leading to a decrease in the density.
- Two ice cubes when pressed against each other can form one block **due to hydrogen bonding.**

Effects of Intermolecular H-bonding

- Intermolecular H-bonding causes an **increase** in the boiling point, melting temperature, solubility, thermal stability, viscosity, surface tension, and occurrence of liquid state as molecules become more intimately connected.
- HF is a liquid with a greater boiling point than other HX molecules, which at normal temperature are gases (here X = halogens).
- **Alcohols** are **extremely soluble** in **water** in any proportion, and their boiling temperatures are greater than those of substances that are significantly less soluble in water. **Glycerol has a high boiling point and a high viscosity.**
- The boiling point and solubility of acids are greater than those of their acid derivatives.
- The **complementary strands of DNA and RNA** are kept together by H-bonding between the nitrogenous bases of the two strands.
- **Proteins and nucleic acids** are bound together by **hydrogen bonds.**
- KHF$_2$ or HF_2^- exist owing to hydrogen bonding, however synthesis of other HX_2^- (such as HCl$_2$) is not conceivable due to the lack of hydrogen bonding between the halogen atoms and their huge sizes.

- The amount of hydrogen bonding in water is more than in H_2O, hence its boiling point is greater than that of HF.

$$H_2O > HF > NH_3$$

- Acids can dimerize due to intermolecular hydrogen bonding.
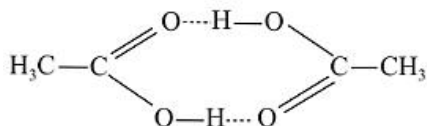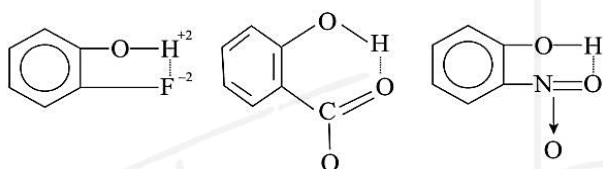
  Example: Acetic acid dimerizes in benzene.

Figure: Dimerization of Acetic Acid

b) Intramolecular H-bonding or Chelation

- Intramolecular H-bonding or chelation is formed within a molecule.
- Examples: Pyridine-2-carbonaldoxime, o-hydroxybenzoic acid,

Effects of Intramolecular H-bonding

- Owing to this bonding, the molecule's boiling point and acidity decrease, but its volatility increases.
- o-nitrophenol has a low boiling point and a less acidic character than p-nitrophenol, but it is more volatile. The combination of these two substances can be separated using steam distillation.

METALLIC BONDING

- Drude and Lorenz proposed the notion of metallic bonding in the form of the electron-sea model.
- Metallic bond is the contact force between the mobile electrons and positively charged nuclei of metal atoms that binds the atom together.
- **Metallic bond strength $\propto$ Number of valence electrons or charge on nucleus**

Conditions for Formation of Metallic Bond

- The metal must possess a low ionisation energy.
- A sufficient amount of empty orbitals should exist in the metal.

Properties Related to Metallic Bond

- On the surface of a metal, mobile electrons oscillate back and forth, giving the metal a brilliant sheen.
- Metals are **ductile** (can be dragged into wires) and **malleable** (may be pounded into sheets) due to their non-directional metallic bond and slippery atomic kernels.
- Due to the existence of mobile electrons, metals exhibit **high thermal** and **electrical conductivities**. **The conductivity reduces** as **the temperature rises** because the increase in temperature causes the kernels to vibrate, which in turn pushes the mobile electrons away from the kernels.
- **Boiling point, melting point, hardness, density of metal α Metallic bond strength.**
  Therefore, alkali metals are soft and can be cut with a knife due to weak metallic bonding.
  Hg is liquid possessing the lowest melting point $-38.5°$ (among metals) due to very weak metallic bond.
- Iridium and osmium have extremely high densities as a result of their metallic bonds.
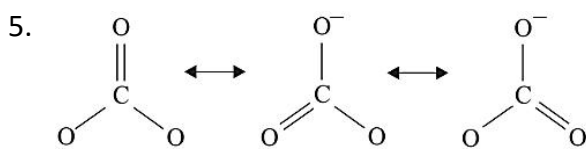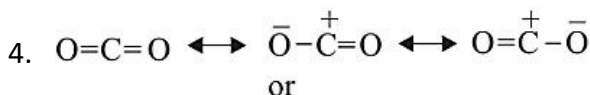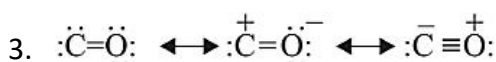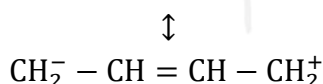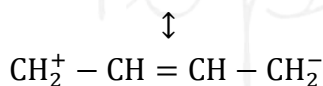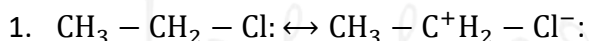- Strong metallic bonds give tungsten its extremely high melting point.

Demerits of Electron-Sea Model

- The Electron-Sea model cannot adequately explain the heat of atomization, heat of fusion, hardness, and melting point.
- It cannot explain why Cu is 50 times more conductive than Bi or why Na is softer than Os.
- Mercury's melting point is 234K, while tungsten's is 3275 K.

RESONANCE

- Since a single structural formula cannot describe all the features of a molecule, such molecules are represented by many structural formulae that are canonical structures, contributing structures, or resonating structures.
- Due to the delocalization of electrons, it is noticed.
- Atoms in canonical structures for a particular molecule are arranged identically.
- In canonical structures, position and arrangement of atoms are same; only the distribution of electrons differs.
- Canonical structures are depicted by the symbol ($\leftrightarrow$) between them.
- Canonical structures should be planar or nearly planar.
- The total number of paired and unpaired electrons in canonical structures is the same
  Examples:
  1. $CH_3 - CH_2 - Cl: \leftrightarrow CH_3 - C^+H_2 - Cl^-:$
  2. $CH_2 = CH - CH = CH_2$
     $\updownarrow$
     $CH_2^+ - CH = CH - CH_2^-$
     $\updownarrow$
     $CH_2^- - CH = CH - CH_2^+$

  3. $:\ddot{C}=\ddot{O}: \longleftrightarrow :\overset{+}{\ddot{C}}=\overset{-}{\ddot{O}:} \longleftrightarrow :\overset{-}{C} \equiv \overset{+}{O}:$

  4. $O=C=O \longleftrightarrow \bar{O}-\overset{+}{C}=O \longleftrightarrow O=\overset{+}{C}-\bar{O}$
     or
     $:\overset{+}{O} \equiv C-\overset{-}{\ddot{O}:} \longleftrightarrow :\overset{-}{\ddot{O}}-C \equiv \overset{+}{O}:$

  5.

- Resonance changes bond length.
  Example: In benzene $C - C = 1.39$ Å, i.e. an intermediate value between $(C - C) = 1.54$ Å, $(C = C) = 1.34$ Å

Resonance Energy

- Resonance energy = Energy of most stable canonical structure - Resonance hybrid energy.
- Resonance energy $\propto$ Number of canonical structure
  Resonance energy $\propto$ Stability
- Resonance energy $\propto \dfrac{1}{\text{Reactivity}}$
- Resonance energy = Expected heat of hydrogenation
  o Actual heat of hydrogenation.
- Benzene is highly stable and conducts electrophilic substitution reactions due to its high resonance energy. It does not conduct addition reactions while possessing double bonds (due to delocalization of π electrons or resonance).
- Benzene has 36 kcal/mole of resonance energy.
- Resonance energy of CO_2 is 154.9 kJ.
- In tautomerism, the arrangement of atoms is distinct for its many configurations, but in resonance, the arrangement of atoms is same.

Stability of Different Canonical Structures

1. A non-polar structure is always more stable than a polar structure.
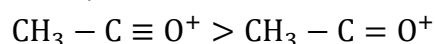   Example: The following structures are arranged in a decreasing order of stability.
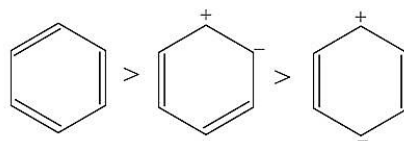
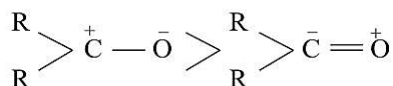   In the last two structures, the charges are apart so they are less stable.
2. More the number of covalent bonds, more will be the stability.
   Therefore,
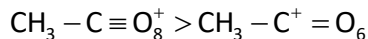 $$CH_3 - C \equiv O^+ > CH_3 - C = O^+$$
3. The canonical structure in which electropositive atoms have positive charges and electronegative atoms have negative charges is more stable.
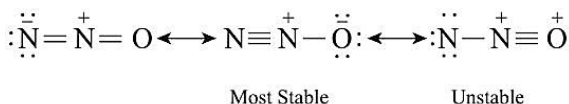
Therefore,

$$\underset{R}{\overset{R}{>}} \overset{+}{C} - \bar{O} > \underset{R}{\overset{R}{>}} \bar{C} = \overset{+}{O}$$

4. The canonical structure when every atom has an octet state is more stable. Therefore,

$$CH_3 - C \equiv \overset{+}{O_8} > CH_3 - \overset{+}{C} = O_6$$

5. If like charges are closer then the structure will be unstable.

$$:\overset{..}{\underset{..}{N}} = \overset{+}{N} = O \longleftrightarrow N \equiv \overset{+}{N} - \overset{..}{\underset{..}{O}}: \longleftrightarrow :\overset{..}{N} - \overset{+}{N} \equiv \overset{+}{O}$$

Most Stable   Unstable

Types of Resonance

Isovalent Resonance	Heterovalent Resonance
The canonical structures have same number of bonds and same type of charges.	The canonical structures have different number of bonds and charges.
Examples: SO_2, NO_2, CO_3^{-2}	Examples: Buta- 1, 3-diene, vinyl cyanide

HYBRIDIZATION

- Pauling says that the atomic orbitals combine to generate a new set of equivalent orbitals called hybrid orbitals. These hybrid orbitals are utilised in the creation of bonds. The term for this phenomenon is **hybridisation**.
- It is the intermixing or redistribution of energy between two or more half-filled, fully filled, incompletely filled, or vacant orbitals of equivalent energy, resulting in the formation of the same number of hybrid orbitals. Hybrids possess same energy and shapes.
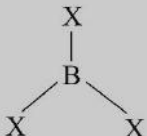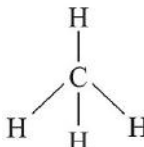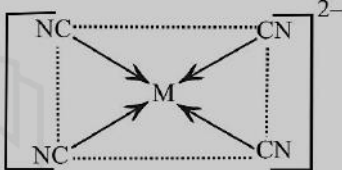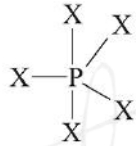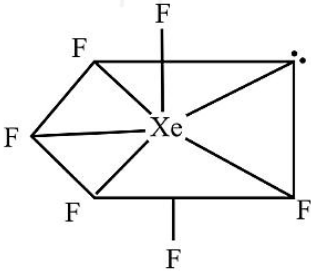
Features of Hybridization

- **Equal to the number of atomic orbitals** involved in hybridization, hybrids are produced.
- **Electrons** do not undergo hybridization.
- **A hybrid bond** is always a **sigma bond**.
- A **hybrid bond** is **always stronger** than a non-hybrid bond.
- Hybridization happens during the formation of bonds.
- **Hybridization $\propto$ Overlapping** (for enough overlapping, orbitals must be at an appropriate distance from each other, that is, neither very close nor very far).
- The hybridization of molecules enhances their stability and diminishes their reactivity and energy.
- Molecular hybridization occurs at the centre atom (NH_3, H_2O, CH_4). Here, the central atoms are N, O, and C.
- Hybridization does not occur between independent atoms, but rather between atoms that are bound together.

Shapes, Hybridisation, atomic orbitals, bond angle along with examples

Shape of molecule ion	Hybridisation Type	Atomic orbitals	Examples
Linear	sp	$s + p$	$BeCl_2, C_2H_2, CO_2, HgCl_2,$
Trigonal planar	sp^2	$s + p(2)$	$SnCl_2, CO_3^{2-}$
Tetrahedral	sp^3	$s + p(3)$	CH_4, H_2O, NH_3
Square planar	dsp^2	$d + s + p(2)$	$[Ni(CN)_4]^{2-}, [PtCl_2]^{2-}$
Trigonal bipyramidal	sp^3d	$s + p(3) + d$	PF_5, PCl_5
Square pyramidal	sp^3d^2	$s + p(3) + d(2)$	BrF_5

| Octahedral | sp^3d^2, d^2sp^3 | $s + p(3) + d(2), d(2) + s + p(3)$ | $SF_6 [CrF_6]^{3-}$ |
| Pentagonal bipyramidal | sp^3d^3 | $s + p(3) + d(3)$ | IF_7 |

Hybridisation	Bond Angle	Pictorial Representation
sp	180°	$H - C_{sp} \equiv C_{sp} - H$
sp^2	120°	
sp^3	109°28′.	
dsp^2	90°	
sp^3d	90 ,120°	
sp^3d^2	90°	
sp^3d^3	72° to 90°	

Rules to Find the Type of Hybridization

For covalent compounds and ions:

1. Count the total number of valence electrons and ($\pm$) charge

   Examples:

   a) PO_4^{-3}, the number of valence electrons is $5 + 4 \times 6 + 3 = 32$.

   b) For NH_4^+, the number of valence electrons is $5 + 4 - 1 = 8$

2. Divide the total value of electrons to get the quotient X (number of bond pair electrons)
   - If total value of X is between **2 to 8**, divide it by 2
   - If total value is between **10 to 56** divide it by 8
   - If total value is **58 or more**, divide it by 18.

3. If any remainder is left, divide again as above to get another quotient Y (number of lone pair electrons).

12

4. If X or X + Y = 2 = sp

3 = sp^2

4 = sp^3

5 = sp^3d

6 = sp^3d^2

7 = sp^3d^3

Examples:

a) $PCl_5 = 5 + 5 \times 7 = 40/8 = 5$ i.e. hybridizationis sp^3 d

b) $SF_6 = 6 + 6 \times 7 = 48/8 = 6$ i.e. sp^3 d^2 hybridization.

Rule to find the geometry of covalent compounds

Using the following equation, one may determine the form or geometry of a molecule or ion by determining the kind of hybridization, number of bond pairs, and lone pair of electrons.

$$P = 1/2(V + M - C + A)$$

where, P = total numbers of pairs of electrons around the central atom which gives the present hybridization as calculated above.

A = Charge on anion

C = Charge on cation

M = Number of monovalent atoms

V = Number of electrons in the valence shell of the central atom.

To find lone pair of electrons

Lone pair = P – N

Here,

P = Total numbers of pairs of electrons around the central atom which gives hybridization as above.

N = Number of atoms surrounding the central atom or number of bond pairs of electrons.

Examples:

SO_2

$P = \frac{1}{2}(6 + 0 - 0 + 0)$

$= \frac{6}{2} = 3(sp^3)$

$lp = (3 - 2) = 1$

SF_6

$= \frac{1}{2}(6 + 6 - 0 + 0)$

$= \frac{12}{2} = 6sp^3d^2$

$lp = (6 - 6) = 0$

Hybridization in complexes Coordination number of ligands is used to find the hybridization.

TABLE: Hybridization

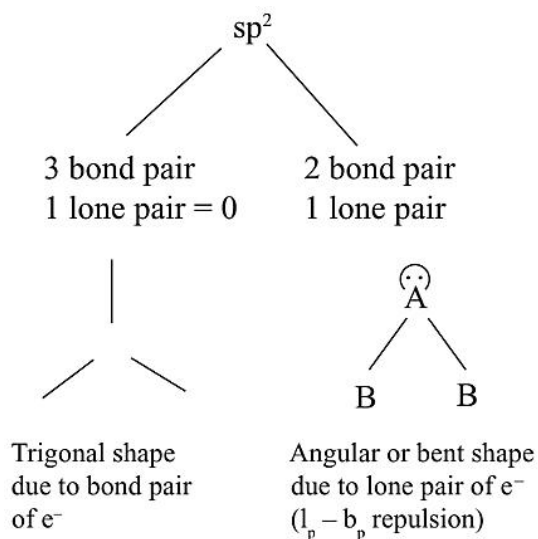| Coordination Number	Hybridization		
2	sp		
3	sp^2		
4	sp^3	or	dsp^2
5	sp^3d	or	dsp^3
6	sp^3d^2	or	d^2sp^3
	When ligands Are weak like H_2O, F, Cl, Br, I	When ligands are strong like CO, CN, NH_3	

Examples:

a) $[Fe(CN_6)]^{-3}$ the coordination number is 6 and ligand is strong, so the hybridization is d^2sp^3.

b) $[Fe(H_2O)_6]^{+3}$ the coordination number is 6 and ligand is weak, so hybridization is sp^3 d^2.
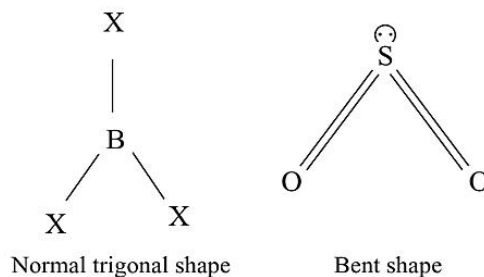
VSEPR (VALENCE SHELL ELECTRON PAIR REPULSION THEORY)

- Valence shell electron pair repulsion theory was introduced to **predict the shape of polyatomic molecules and ions**.

- In accordance with this hypothesis, the form of molecules is also determined by the type of electrons around the core atom, in addition to hybridization.

- There are two possible types of electrons surrounding the core atom: bond pair and lone pair.

- These electrons undergo electron-electron repulsion and the decreasing order of electronic repulsion is: $lp - lp >$ lp-bp $> bp - bp$

- Owing to this electronic repulsion, the molecule's structure is deformed and the bond angle is altered.

  Distortion in shape α $e^- - e^-$ repulsion

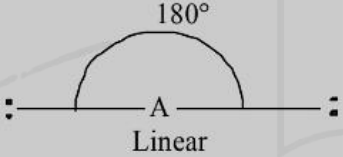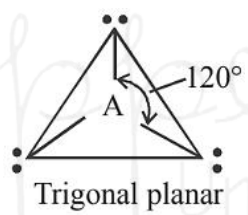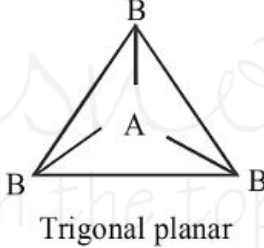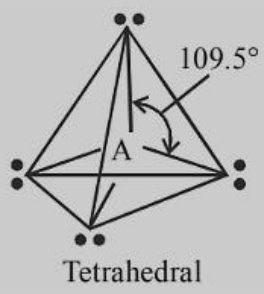 Distortion in shape or change in bond angle α electronic repulsion

Examples:

3 bond pair
1 lone pair = 0

Trigonal shape
due to bond pair
of e⁻

2 bond pair
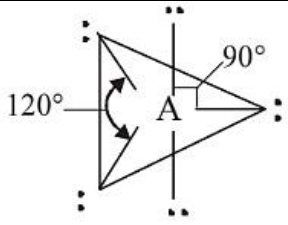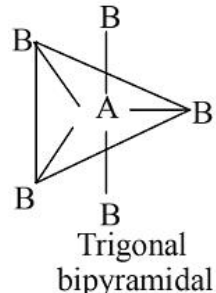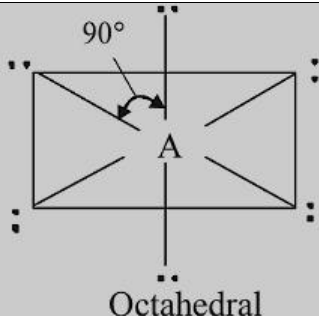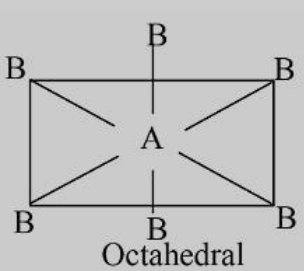1 lone pair

$\overset{\cdot\cdot}{A}$

Angular or bent shape
due to lone pair of e⁻
($l_p - b_p$ repulsion)

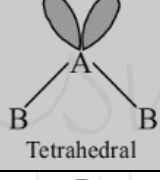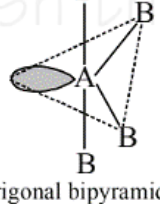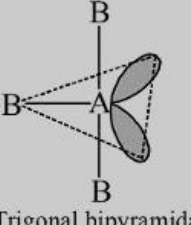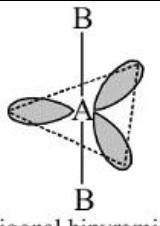Examples: BX_3, BH_3, SO_3

Normal trigonal shape   Bent shape
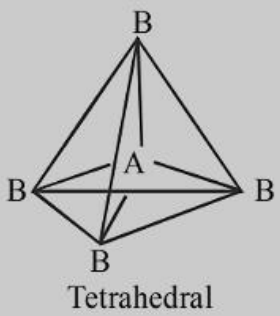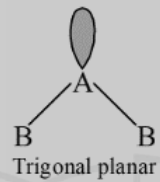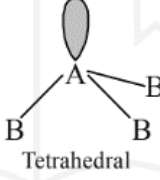
Here, the S atom contains two bond pairs and one lone pair of electrons, therefore the lp-bp kind of repulsion alters the form by bending and altering the bond angle, resulting in an angular shape. The same applies to $SnCl_2$ and $PbCl_2$.

Geometry of molecules when central atom has no lone pair of electrons.

No. of electron pairs	Arrangement of electron pairs	Molecular Geometry	Examples
2	180° Linear	B—A—B Linear	BeF_2, $HgCl_2$
3	120° Trigonal planar	Trigonal planar	BF_3, $AlCl_3$
4	109.5° Tetrahedral	Tetrahedral	CH4, SiF4
5	120° 90° Trigonal bipyramidal	Trigonal bipyramidal	PCl_5, AsF_5

6	Octahedral	Octahedral	SF_6

Geometry of molecules when central atom has one or more lone pair of electrons

Molecule type	No. of bonding pairs	No. of lone pairs	Total electron pairs	Arrangement of electron pairs	Shape (geometry)	Example
AB_2L	2	1	3	Trigonal planar	Bent or V shaped	SO_2, O_3, $SnCl_2$
AB_3L	3	1	4	Tetrahedral	Pyramidal	NH_3
AB_2L_2	2	2	4	Tetrahedral	V shaped	H_2O
AB_4L	4	1	5	Trigonal bipyramidal	See saw	SF_4
AB_3L_2	3	2	5	Trigonal bipyramidal	T shaped	ClF_3
AB_2L_3	2	3	5	Trigonal bipyramidal	Linear	XeF_2