

**SRINIVASAN COLLEGE OF ARTS AND SCIENCE****PERAMBALUR - 621 212****(Affiliated to Bharathidasan University, Tiruchirappalli)****COURSE MATERIAL****DEPARTMENT OF CHEMISTRY****B. Sc. Chemistry*****General Chemistry - II***

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**SYLLABUS****UNIT I CHEMICAL BONDING**

1.1 Ionic bond – formation, variable electrovalency – Lattice energy, Born – Haber Cycle. Covalent bond - formation, variable covalency, maximum covalency, covalent character in ionic bond – Fajans Rule. Polarisation – partial ionic character of a covalent bond.

1.2 VB theory, MO theory – Basic principles of bonding and antibonding orbitals, applications of MOT to H<sub>2</sub>, He<sub>2</sub>, N<sub>2</sub> & O<sub>2</sub> – molecular orbital sequence, comparison of VB & MO Theories.

1.3 Hybridisation – Formation of BeCl<sub>2</sub> & BCl<sub>3</sub>. VSEPR theory of simple inorganic molecules – BeCl<sub>2</sub>, SiCl<sub>4</sub>, PCl<sub>5</sub>, SF<sub>6</sub>, IF<sub>7</sub>, XeF<sub>6</sub>, BF<sub>3</sub> & H<sub>2</sub>O.

1.4 Hydrogen bonding – Intermolecular & Intramolecular H<sub>2</sub> – bonding and consequences.

**UNIT II CHEMISTRY OF s-BLOCK & ZERO GROUP ELEMENTS AND METALLURGY**

2.1 General characteristics of s-block elements – comparative study of elements – alkali metals and their hydroxides, oxides and halides, alkaline earth metals and their oxides, carbonates and sulphates.

2.2 Diagonal relationship of Li & Mg, Be & Al, chemistry of NaOH, KI & Mg(NH<sub>4</sub>)PO<sub>4</sub>.

2.3 Metallurgy : Occurrence of metals – concentration of ores – froth floatation, magnetic separation, calcination, roasting, smelting, flux, aluminothermic process, purification of metals – electrolysis, zone refining, van Arkel de-Boer process.

2.4 Zero group elements – position in the periodic table, occurrence, isolation, applications, compounds of Xe – XeF<sub>6</sub> & XeOF<sub>4</sub>.

**UNIT III CHEMISTRY OF BENZENE AND BENZENOID COMPOUNDS**

3.1 Aromaticity – Huckle's rule - structure of benzene – Benzene-preparation, chemical properties and uses. Aromatic electrophilic substitution reactions and mechanism – Orientation and reactivity in substituted benzenes.

3.2 Polynuclear aromatic hydrocarbons – Nomenclature, Naphthalene from coal tar and petroleum – Laboratory preparation, Structure of Naphthalene, Aromatic character, Physical properties, Chemical properties, Uses. Mechanism of Aromatic electrophilic substitution – Theory of orientation and reactivity.

3.3 Anthracene, Phenanthrene from coal tar and petroleum, Laboratory preparation, Molecular Orbital structures, Aromatic Characters, Physical Properties, Chemical properties and uses. Preparation of biphenyls, Physical and Chemical properties and uses.

**UNIT IV ALKYL AND ARYL HALOGENS**

4.1 Nomenclature of haloalkanes – structure - general preparations of haloalkanes - physical and chemical properties and uses.

4.2 Nucleophilic aliphatic substitution reaction mechanisms (SN1 and SN2) – Stereochemical aspects.

4.3 Halobenzenes: Theory of orientation and reactivity - general preparation – properties - uses. Electrophilic and nucleophilic aromatic substitution reaction mechanisms.

**UNIT V ATOMIC STRUCTURE AND BASIC QUANTUM MECHANICS**

5.1. Rutherford's and Bohr's model an atom- Bohr's theory and origin of hydrogen spectrum. Sommerfield's extension of Bohr's theory.

5.2. Electromagnetic radiation- definitions for  $\Psi$ ,  $\nu$  and velocity.

5.3. Dualism of light -Particle nature of radiation- black body radiation and Planck's quantum theory, photoelectric effect and Compton effect of matter.

5.4. De Broglie hypothesis and Davisson and Germer experiment. Heisenberg's uncertainty principle. Schrodinger wave equation (Derivation not needed). Physical significance of  $\Psi$  and  $\Psi^2$ .

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## UNIT I CHEMICAL BONDING

### What is Chemical Bonding?

Chemical Bonding refers to the formation of a chemical bond between two or more atoms, molecules, or ions to give rise to a chemical compound. These chemical bonds are what keep the atoms together in the resulting compound.

The attractive force which holds various constituents (atom, ions, etc.) together and stabilizes them by the overall loss of energy is known as chemical bonding. Therefore, it can be understood that chemical compounds are reliant on the strength of the chemical bonds between its constituents; The stronger the bonding between the constituents, the more stable the resulting compound would be.

The opposite also holds true; if the chemical bonding between the constituents is weak, the resulting compound would lack stability and would easily undergo another reaction to give a more stable chemical compound (containing stronger bonds). To find stability, the atoms try to lose their energy.

Whenever matter interacts with another form of matter, a force is exerted on one by the other. When the forces are attractive in nature, the energy decreases. When the forces are repulsive in nature, the energy increases. The attractive force that binds two atoms together is known as the chemical bond.

### Important Theories on Chemical Bonding

Albrecht Kössel and Gilbert Lewis were the first to explain the formation of chemical bonds successfully in the year 1916. They explained chemical bonding on the basis of the inertness of noble gases.

#### *Lewis Theory of Chemical Bonding*

An atom can be viewed as a positively charged 'Kernel' (the nucleus plus the inner electrons) and the outer shell. The outer shell can accommodate a maximum of eight electrons only. The eight electrons present in the outer shell occupy the corners of a cube which surround the 'Kernel'. The atoms having octet configuration, i.e. 8 electrons in the outermost shell, thus symbolize a stable configuration. Atoms can achieve this stable configuration by forming chemical bonds with other atoms. This chemical bond can be formed either by gaining or losing an electron(s) (NaCl, MgCl<sub>2</sub>) or in some cases due to the sharing of an electron (F<sub>2</sub>).

Only the electrons present in the outer shell, also known as the valence electrons take part in the formation of chemical bonds. Gilbert Lewis used specific notations better known as Lewis symbols to represent these valence electrons.

Generally, the valency of an element is either equal to the number of dots in the corresponding Lewis symbol or 8 minus the number of dots (or valence electrons).

Lewis symbols for lithium (1 electron), oxygen (6 electrons), neon (8 electrons) are given below:



#### Lewis dot structure in Chemical Bonding

Here, the number of dots that surround the respective symbol represents the number of valence electrons in that atom.

#### ***Kossel's theory of Chemical Bonding***

Noble gases separate the highly electronegative halogens and the highly electropositive alkali metals.

Halogens can form negatively charged ions by gaining an electron. Whereas alkali metals can form positively charged ions by losing an electron.

These negatively charged ions and positively charged ions have a noble gas configuration that is 8 electrons in the outermost shell. The general electronic configuration of noble gases (except helium) is given by  $ns^2np^6$ .

As unlike charges attract each other these unlike charged particles are held together by a strong force of electrostatic attraction existing between them. For example,  $\text{MgCl}_2$ , the magnesium ion, and chlorine ions are held together by force of electrostatic attraction. This kind of chemical bonding existing between two unlike charged particles is known as an electrovalent bond.

#### ***Explanation of Kossel Lewis Approach***

In 1916 Kossel and Lewis succeeded in giving a successful explanation based upon the concept of an electronic configuration of noble gases about why atoms combine to form molecules. Atoms of noble gases have little or no tendency to combine with each other or with atoms of other elements. This means that these atoms must be having stable electronic configurations.

Due to the stable configuration, the noble gas atoms neither have any tendency to gain or lose electrons and, therefore, their combining capacity or valency is zero. They are so inert that they even do not form diatomic molecules and exist as monoatomic gaseous atoms.

### ***Types of Chemical Bonds***

When substances participate in chemical bonding and yield compounds, the stability of the resulting compound can be gauged by the type of chemical bonds it contains.

The type of chemical bonds formed vary in strength and properties. There are 4 primary types of chemical bonds which are formed by atoms or molecules to yield compounds. These types of chemical bonds include:

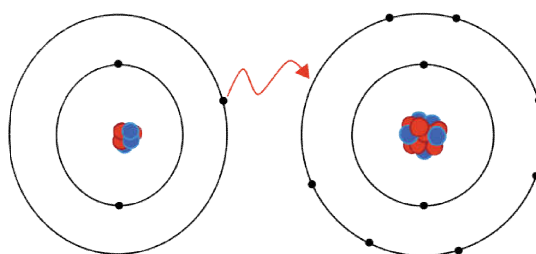
- Ionic Bonds
- Covalent Bonds
- Hydrogen Bonds
- Polar Bonds

These types of bonds in chemical bonding are formed from the loss, gain, or sharing of electrons between two atoms/molecules.

### ***Ionic Bonding***

Ionic bonding is a type of chemical bonding which involves a transfer of electrons from one atom or molecule to another. Here, an atom loses an electron which is in turn gained by another atom. When such an electron transfer takes place, one of the atoms develops a negative charge and is now called the anion.

The other atom develops a positive charge and is called the cation. The ionic bond gains strength from the difference in charge between the two atoms, i.e. the greater the charge disparity between the cation and the anion, the stronger the ionic bond.



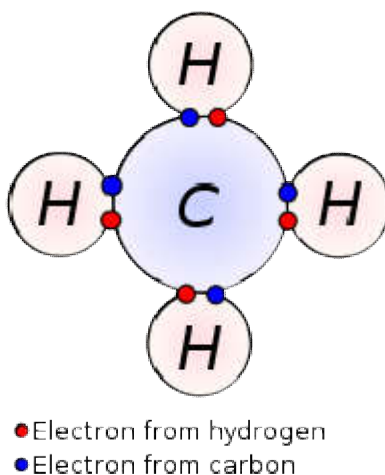
### ***Covalent Bonding***

A covalent bond indicates the sharing of electrons between atoms. Compounds that contain carbon (also called organic compounds) commonly exhibit this type of chemical bonding.

The pair of electrons which are shared by the two atoms now extend around the nuclei of atoms, leading to the creation of a molecule.

### Covalent Bonding in CH<sub>4</sub>

#### Covalent Bonding



#### ***Polar Covalent Bonding***

Covalent bonds can be either be Polar or Non-Polar in nature. In Polar Covalent chemical bonding, electrons are shared unequally since the more electronegative atom pulls the electron pair closer to itself and away from the less electronegative atom. Water is an example of such a polar molecule.

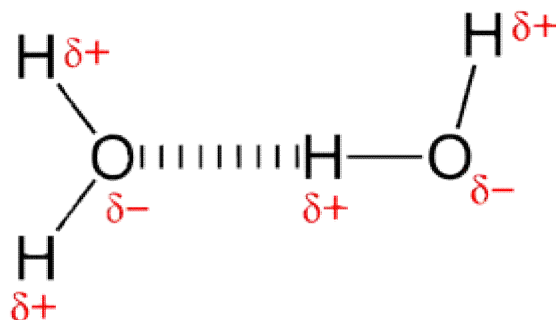
A difference in charge arises in different areas of the atom due to the uneven spacing of the electrons between the atoms. One end of the molecule tends to be partially positively charged and the other end tends to be partially negatively charged.

#### ***Hydrogen Bonding***

Compared to ionic and covalent bonding, Hydrogen bonding is a weaker form of chemical bonding. It is a type of polar covalent bonding between oxygen and hydrogen wherein the hydrogen develops a partial positive charge. This implies that the electrons are pulled closer to the more electronegative oxygen atom.

This creates a tendency for the hydrogen to be attracted towards the negative charges of any neighbouring atom. This type of chemical bonding is called a hydrogen bond and is responsible for many of the properties exhibited by water.

#### *Hydrogen bonding in water*



### *What is Ionic Bond?*

The bond formed as a result of strong electrostatic forces of attraction between a positively and negatively charged species is called an electrovalent or ionic bond. The positively and negatively charged ions are aggregated in an ordered arrangement called the crystal lattice which is stabilized by the energy called the Lattice enthalpy.

### ***Conditions for the formation of an Ionic Bond***

The low ionization energy of the atom forming the cation.

High electron gain enthalpy of the atom forming the anion.

High negative lattice enthalpy of the crystal formed.

Generally, the ionic bond is formed between a metal cation and non-metal anion.

### **Lattice Energy**

Lattice Energy is a type of potential energy that may be defined in two ways. In one definition, the lattice energy is the energy required to break apart an ionic solid and convert its component atoms into gaseous ions. This definition causes the value for the lattice energy to always be positive, since this will always be an endothermic reaction. The other definition says that lattice energy is the reverse process, meaning it is the energy released when gaseous ions bind to form an ionic solid. As implied in the definition, this process will always be exothermic, and thus the value for lattice energy will be negative. Its values are usually expressed with the units kJ/mol.

Lattice Energy is used to explain the stability of ionic solids. Some might expect such an ordered structure to be less stable because the entropy of the system would be low. However, the crystalline structure allows each ion to interact with multiple oppositely charged ions, which causes a highly favorable change in the enthalpy of the system. A lot of energy is released as the oppositely charged ions interact. It is this that causes ionic solids to have such



high melting and boiling points. Some require such high temperatures that they decompose before they can reach a melting and/or boiling point.

### ***Born-Haber Cycle***

There are several important concepts to understand before the Born-Haber Cycle can be applied to determine the lattice energy of an ionic solid; ionization energy, electron affinity, dissociation energy, sublimation energy, heat of formation, and Hess's Law.

***Ionization Energy*** is the energy required to remove an electron from a neutral atom or an ion. This process always requires an input of energy, and thus will always have a positive value. In general, ionization energy increases across the periodic table from left to right, and decreases from top to bottom. There are some exceptions, usually due to the stability of half-filled and completely filled orbitals.

***Electron Affinity*** is the energy released when an electron is added to a neutral atom or an ion. Usually, energy released would have a negative value, but due to the definition of electron affinity, it is written as a positive value in most tables. Therefore, when used in calculating the lattice energy, we must remember to subtract the electron affinity, not add it. In general, electron affinity increases from left to right across the periodic table and decreases from top to bottom.

***Dissociation energy*** is the energy required to break apart a compound. The dissociation of a compound is always an endothermic process, meaning it will always require an input of energy. Therefore, the change in energy is always positive. The magnitude of the dissociation energy depends on the electronegativity of the atoms involved.

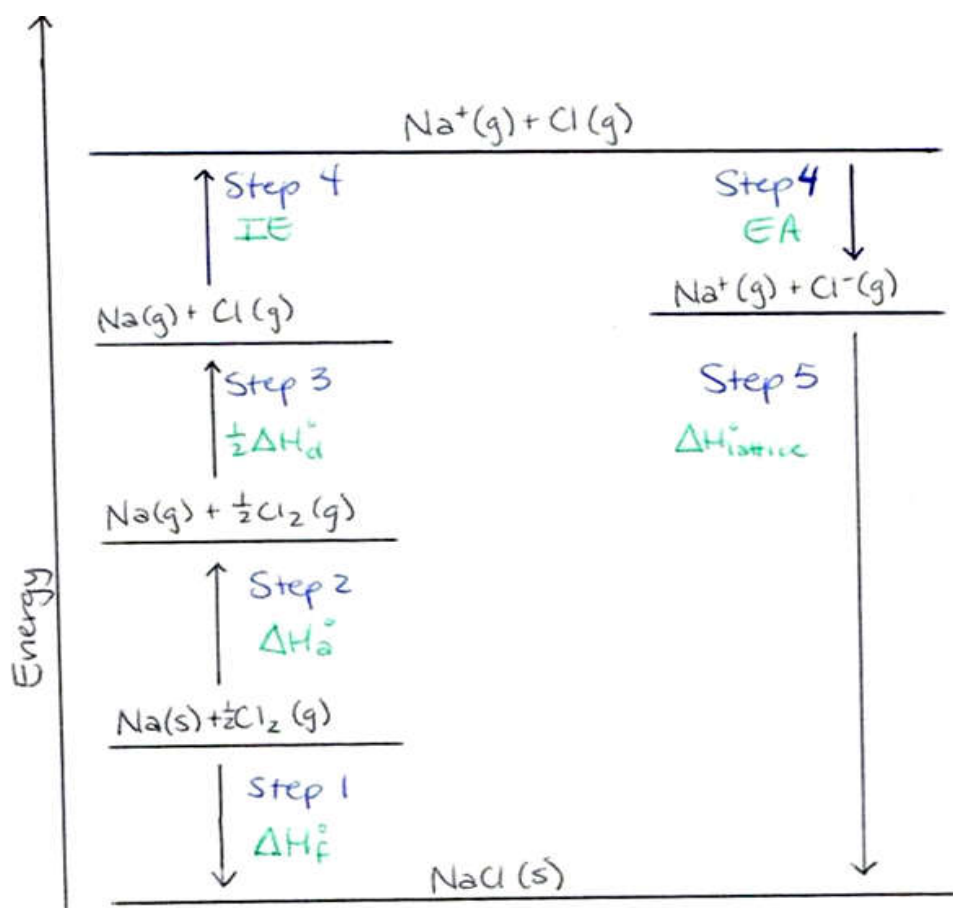
Sublimation energy is the energy required to cause a change of phase from solid to gas, bypassing the liquid phase. This is an input of energy, and thus has a positive value. It may also be referred to as the energy of atomization.

***The heat of formation*** is the change in energy when forming a compound from its elements. This may be positive or negative, depending on the atoms involved and how they interact.

***Hess's Law*** states that the overall change in energy of a process can be determined by breaking the process down into steps, then adding the changes in energy of each step. The Born-Haber Cycle is essentially Hess's Law applied to an ionic solid.

### ***Using the Born-Haber Cycle***

The values used in the Born-Haber Cycle are all predetermined changes in enthalpy for the processes described in the section above. Hess' Law allows us to add or subtract these values, which allows us to determine the lattice energy.



### Step 1

Determine the energy of the metal and nonmetal in their elemental forms. (Elements in their natural state have an energy level of zero.) Subtract from this the heat of formation of the ionic solid that would be formed from combining these elements in the appropriate ration. This is the energy of the ionic solid, and will be used at the end of the process to determine the lattice energy.

### Step 2

The Born-Haber Cycle requires that the elements involved in the reaction are in their gaseous forms. Add the changes in enthalpy to turn one of the elements into its gaseous state, and then do the same for the other element.

### Step 3

Metals exist in nature as single atoms and thus no dissociation energy needs to be added for this element. However, many nonmetals will exist as polyatomic species. For example, Cl exists as Cl<sub>2</sub> in its elemental state. The energy required to change Cl<sub>2</sub> into 2Cl atoms must be added to the value obtained in Step 2.

**Step 4**

Both the metal and nonmetal now need to be changed into their ionic forms, as they would exist in the ionic solid. To do this, the ionization energy of the metal will be added to the value from Step 3. Next, the electron affinity of the nonmetal will be subtracted from the previous value. It is subtracted because it is a release of energy associated with the addition of an electron.

\*This is a common error due to confusion caused by the definition of electron affinity, so be careful when doing this calculation.

**Step 5**

Now the metal and nonmetal will be combined to form the ionic solid. This will cause a release of energy, which is called the lattice energy. The value for the lattice energy is the difference between the value from Step 1 and the value from Step 4.

**Fajan Rule**

Covalent character developed in an ionic compound may be determined by Fajan's rule. According to this rule covalent character is more, when :

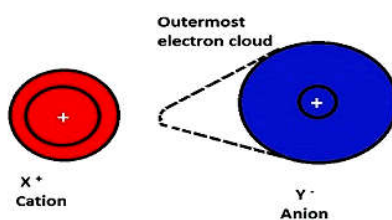
- a) Ions have high charge i.e cation has greater positive charge and anion has greater negative charge.
- b) Cation has small ionic radius.
- c) Anion has large ionic radius.
- d) Compounds of cation having  $s^2, p^6, d^{10}$  configuration of outer most shell are largely covalent as compared to cation having the same size and charge but outer electronic configuration of  $s^2p^6$  type.

***Explanation:***

In ionic compound, cation attracts the electrons of anion towards itself. The ability of cation to attract the electrons of anion is called polarizing power. The electrons of anion get attracted towards the cation. This is called polarizability of the anion. Due to this, anion is distorted. It is called polarization. Due to polarization sharing of electrons takes place and ionic compound has some covalent character.

***“Greater is the polarization, greater is the covalent character.”***

## Fajan's Rules



## VSEPR

VSEPR Theory is used to predict the shape of the molecules from the electron pairs that surround the central atoms of the molecule. The theory was first presented by Sidgwick and Powell in 1940. VSEPR theory is based on the assumption that the molecule will take a shape such that electronic repulsion in the valence shell of that atom is minimized.

### *What is VSEPR Theory?*

The Valence Shell Electron Pair Repulsion Theory abbreviated as VSEPR theory is based on the premise that there is a repulsion between the pairs of valence electrons in all atoms, and the atoms will always tend to arrange themselves in a manner in which this electron pair repulsion is minimalized. This arrangement of the atom determines the geometry of the resulting molecule.

The different geometries that molecules can assume keeping with VSEPR theory can be seen in the illustration provided below.

Number of Electron Dense Areas	Electron-Pair Geometry	Molecular Geometry				
		No Lone Pairs	1 lone Pair	2 lone Pairs	3 lone Pairs	4 lone Pairs
2	Linear	Linear				
3	Trigonal planar	Trigonal planar	Bent			
4	Tetrahedral	Tetrahedral	Trigonal pyramidal	Bent		
5	Trigonal bipyramidal	Trigonal bipyramidal	Sawhorse	T-shaped	Linear	
6	Octahedral	Octahedral	Square pyramidal	Square planar	T-shaped	Linear

According to the VSEPR theory, the repulsion between two electrons is caused by the Pauli exclusion principle that has greater importance than electrostatic repulsion in the determination of molecular geometry.

***Postulates of VSEPR Theory:***

- The postulates of the VSEPR theory are listed below
- 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.
- The total number of valence shell electron pairs decides the shape of the molecule.
- 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.
- 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.
- Should the central atom of the molecule be surrounded by bond pairs of electrons, then, the asymmetrically shaped molecule can be expected.
- Should the central atom be surrounded by both lone pairs and bond pairs of electrons, the molecule would tend to have a distorted shape.
- The VSEPR theory can be applied to each resonance structure of a molecule.
- The strength of the repulsion is strongest in two lone pairs and weakest in two bond pairs.
- 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.
- If the electron pairs lie far from each other, the repulsions between them will be less and eventually, the energy of the molecule will be low.

***Limitations of VSEPR Theory:***

Some significant limitations of the VSEPR theory include:

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.

The VSEPR theory does not shed any light on the compounds of transition metals. The structure of several such compounds cannot be correctly described by this theory. This is because the VSEPR theory does not take into account the associated sizes of the substituent groups and the lone pairs that are inactive.

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.

***Predicting the Shapes of Molecules:***

The following steps must be followed in order to decide the shape of a molecule.

- The least electronegative atom must be selected as the central atom (since this atom has the highest ability to share its electrons with the other atoms belonging to the molecule).
- The total number of electrons belonging to the outermost shell of the central atom must be counted.
- The total number of electrons belonging to other atoms and used in bonds with the central atom must be counted.
- These two values must be added in order to obtain the valence shell electron pair number or the VSEP number.

***Linear Shape of Molecule:***

In this type of molecule, we find two places in the valence shell of the central atom. They should be arranged in such a manner such that repulsion can be minimized (pointing in the opposite direction).

Example:  $\text{BeF}_2$

***Trigonal Planar Shape of Molecule:***

In this type of molecule, we find three molecules attached to a central atom. They are arranged in such a manner such that repulsion between the electrons can be minimized (toward the corners of an equilateral triangle).

Example:  $\text{BF}_3$

***Tetrahedral Shape of Molecule:***

In two-dimensional molecules, atoms lie in the same plane and if we place these conditions on methane, we will get a square planar geometry in which the bond angle between H-C-H is  $90^\circ$ . Now, if we consider all these conditions for a three-dimensional molecule, we will get a tetrahedral molecule in which the bond angle between H-C-H is  $109^\circ 28'$  (toward the corners of an equilateral triangle)  $\text{CH}_4$

***Trigonal Bipyramid Shape of Molecule:***

Let's take an example of  $\text{PF}_5$ . Here, repulsion can be minimized by even distribution of electrons towards the corner of a trigonal pyramid. In trigonal bipyramid, three positions lie along the equator of the molecule. The two positions lie along an axis perpendicular to the equatorial plane.

## Valence Bond Theory

Electrons in a molecule occupy atomic orbitals rather than molecular orbitals. The atomic orbitals overlap on the bond formation and the larger the overlap the stronger the bond.

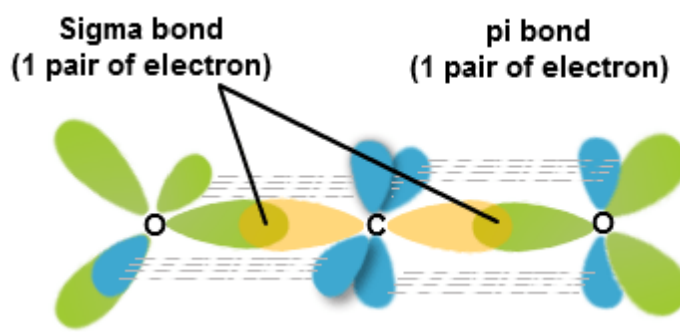
### *Postulates of Valence Bond Theory*

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

Covalent bonds are formed when two valence orbitals (half-filled) belonging to two different atoms overlap on each other. The electron density in the area between the two bonding atoms increases as a result of this overlapping, thereby increasing the stability of the resulting molecule.

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. Covalent chemical bonds are directional and are also parallel to the region corresponding to the atomic orbitals that are overlapping.

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.



## UNIT- II

The elements of Group 1 and Group 2 of the modern periodic table are called s block elements. The two types of s block elements are possible i.e. the elements with one electron (s<sup>1</sup>) or the elements with two electrons (s<sup>2</sup>) in their s-subshell.

s block comprises of 14 elements: hydrogen (H), lithium (Li), helium (He), sodium (Na), beryllium (Be), potassium (K), magnesium (Mg), rubidium (Rb), calcium (Ca), cesium (Cs), strontium (Sr), francium (Fr), barium (Ba), and radium (Ra).

## What are S Block Elements?

The s block elements having only one electron in their s-orbital are called group one or alkali metals whereas the s block elements having two electrons filling their s-orbital are called group two or alkaline earth metals.

The electrons present in an atom occupy various sub-orbitals of available energy levels in the order of increasing energy. The last electron of an atom may find itself in either of the s, p, d and f subshells. Accordingly, the elements of the atom having their last valence electron present in the s-suborbital are called the s block elements.

The image shows a periodic table with the first two columns (Groups 1 and 2) highlighted in red. A blue box labeled "S-block elements" has arrows pointing to these columns. The table includes element symbols, names, and atomic numbers. The elements in the s-block are: Hydrogen (H), Lithium (Li), Sodium (Na), Potassium (K), Rubidium (Rb), Cesium (Cs), Francium (Fr), Helium (He), Beryllium (Be), Magnesium (Mg), Calcium (Ca), Strontium (Sr), Barium (Ba), Radium (Ra).

## List of S Block Elements

The position of S Block Elements in Periodic Table

Electronic Configuration of S Block Elements

The electronic configuration of S block elements is explained below,

The alkali elements in s block consist of a single valence electron in their outermost shell. This outermost electron is loosely held which makes these metals highly electropositive. Due



to which they are not available in the free state in nature. The general electronic configurations of s block elements – group 1 are as shown in the table below:

Element	Symbol	Electronic configuration
Lithium	Li	1s <sup>2</sup> 2s <sup>1</sup>
Sodium	Na	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>1</sup>
Potassium	K	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 4s <sup>1</sup>
Rubidium	Rb	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>6</sup> 5s <sup>1</sup>
Cesium	Cs	[Xe]6s <sup>1</sup>
Francium	Fr	[Rn]7s <sup>1</sup>

The electronic configurations of elements included in group 2 of S block elements is shown below:

Elements	Symbols	Electronic configuration
Beryllium	Be	[He]2s <sup>2</sup>
Magnesium	Mg	[Ne]3s <sup>2</sup>
Calcium	Ca	[Ar]4s <sup>2</sup>
Strontium	Sr	[Kr]5s <sup>2</sup>
Barium	Ba	[Xe]6s <sup>2</sup>
Radium	Ra	[Rn]7s <sup>2</sup>

### ***Properties of S Block Elements***

Both alkali and alkaline earth elements show a regular gradation in their properties among their respective group elements. But the first member of both S block elements, namely,

Lithium and Beryllium differ much from the rest of their members but at the same time, they resemble more with the diagonal element present in the next column.

*The anomaly of these S block elements is due to;*

Low atomic and ionic size

Greater charge density (charge/volume of the atom)

Greater polarization

Absence of d-orbitals.

- Greater polarization of s block elements makes the first element more covalent and differentiates them from the rest which are ionic.
- The similarity in size and charge density makes them resemble the element diagonally placed in the next group (diagonal relationship).
- It is observed that the physical and chemical properties of these s block elements changes in a particular trend as the atomic number of the elements increases. Changes in the various properties of the group are as mentioned below:

### ***Chemical Properties of S Block Elements***

#### **Atomic and Ionic Radii**

When the s block elements of the modern periodic table are observed it is seen that the size of the alkali metals is larger compared to other elements in a particular period. As the atomic number increases the total number of electrons increases along with the addition of shells. On moving down the group the atomic number increases. As a result, the atomic and ionic radius of the alkali metals increases.

**Sizes of atoms and their ions in pm**

Group 1		Group 2		Group 13		Group 16		Group 17	
Li <sup>+</sup> 90	Li 134	Be <sup>2+</sup> 59	Be 90	B <sup>3+</sup> 41	B 82	O 73	O <sup>2-</sup> 126	F 71	F <sup>-</sup> 119
Na <sup>+</sup> 116	Na 154	Mg <sup>2+</sup> 86	Mg 130	Al <sup>3+</sup> 68	Al 118	S 102	S <sup>2-</sup> 170	Cl 99	Cl <sup>-</sup> 167
K <sup>+</sup> 152	K 196	Ca <sup>2+</sup> 114	Ca 174	Ga <sup>3+</sup> 76	Ga 126	Se 116	Se <sup>2-</sup> 184	Br 114	Br <sup>-</sup> 182
Rb <sup>+</sup> 166	Rb 211	Sr <sup>2+</sup> 132	Sr 192	In <sup>3+</sup> 94	In 144	Te 135	Te <sup>2-</sup> 207	I 133	I <sup>-</sup> 206

### Properties of S-block Elements

Atomic and ionic radii of S block Elements

#### Ionization Enthalpy

As we go down the group the size of the atoms increases due to which the attraction between the nucleus and the electrons in the outermost shell decreases. As a result, the ionization enthalpy decreases. The ionization enthalpy of the alkali metals is comparatively lesser than other elements.

#### Hydration Enthalpy

As the ionic sizes of the elements increase, the hydration enthalpy decreases. Smaller the size of the ion the hydration enthalpy is high as the atom has the capacity to accommodate a larger number of water molecules around it due to high charge/radius ratio and hence gets hydrated.

#### Physical Properties of S block elements

In the S block elements, the density of the alkali metals increases down the group. Exception: the density of potassium is less than the density of sodium. The alkali metals have a low melting and boiling point due to the weak metallic bonding. Alkali metals and its respective salts have the capability to impart colour to the oxidizing flame due to the heat generated from the flame which excites the valence electrons from one energy level to another energy level. This helps in the detection of alkali metals during the flame test.

#### Diagonal Relationship within S Block Elements

The Diagonal Relationship Within S-Block Elements

**THE DIAGONAL RELATIONSHIP WITHIN S-BLOCK ELEMENTS**

	GROUP 1	GROUP 2	GROUP 13	GROUP 14
SECOND PERIOD	Li	Be	B	C
THIRD PERIOD	Na	Mg	Al	Si

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- A diagonal relationship in S block elements exists between adjacent elements which are located in the second and third period of the periodic table. For example, Lithium of group 1A and second period shows similarities with the properties of magnesium which are located in the 2nd group and 3rd period.
- Similarly, properties of beryllium which are located in the 2nd group and 2nd period show a likeness with properties of aluminium which is located in the third period and third group. The two elements which show similarities in their properties can be called a diagonal pair or diagonal neighbours.
- The properties of S block elements vary significantly when compared to the other elements of the sub-group they belong to. The diagonal neighbours show a lot of similarities. Such a relationship is exhibited as you move left to right and down the group; the periodic table has opposing factors.
- For example, the electronegativity of the S block elements increases as we go across the period and decreases as we go down the group. Therefore when it is moved diagonally the opposite tendencies cancel out and the value of electronegativity almost remains the same.

***Similarities between Lithium and Magnesium***

- The hardness of lithium and magnesium is higher than the other elements in their respective groups.
- Chlorides of lithium and magnesium have the capability to be soluble in ethanol.
- They are lighter when compared to other elements in their groups.
- Lithium and magnesium react gently with water. The oxides and hydroxides are less soluble.
- In the presence of nitrogen, lithium and magnesium form their respective nitrides.
- Superoxides are not formed when lithium and magnesium react with excess oxygen.

- Carbon dioxide and their respective oxides are formed when carbonates of magnesium and lithium are heated.
- Similarities between Beryllium and Aluminum
- Aluminum hydroxide and beryllium hydroxide react with excess alkali to form their respective ions.
- Both these elements have the capacity to withstand the acid attack due to the presence of an oxide film on the surface of the metal.
- Both these metals have the tendency to form complexes.
- Chlorides of both these metals possess the capacity to be soluble in organic solvents.

## **ZERO GROUP ELEMENTS**

### ***Group 18 elements of the modern periodic table***

Group 18 of the modern periodic table consists of noble gases. Helium, neon, argon, krypton, xenon, and radon are noble gases. These gases are monoatomic and chemically inert under normal conditions and hence are also named as inert gases. These gases are present in very small quantities in the atmosphere and so they are also called rare gases. Radon possesses radioactive characteristics. These gases were not discovered at Mendeleev's time, so he did not specify any place for them in the periodic table. Later on, a new group known as zero groups were created to place them in the modern periodic table. According to the IUPAC conventions, group zero has been renamed to group 18.

### ***Physical and chemical properties of group 18 elements***

The noble gases do not react under normal conditions. The non- reactivity of noble gases is due to the following reasons:

- The valence shell of the noble gases is completely filled. The next available shell is of much higher energy.
- Noble gases have very high ionization enthalpies.
- They have large positive values of electron gain enthalpy.
- Noble gases have no tendency to gain or lose electrons under ordinary conditions. This is the only reason due to which they do not participate in chemical reactions and remain inert. According to modern researchers, it has been seen that noble gases can be compelled to take part in a chemical reaction under certain specific conditions.
- A scientist named Neil Bartlett found that  $\text{PtF}_6$  reacts with oxygen and forms  $\text{O}_2^+ [\text{PtF}_6]^-$ . The ionization energy of oxygen and xenon is comparable, and so  $\text{PtF}_6$  should react with xenon to form  $\text{Xe}^+ [\text{PtF}_6]^-$ . This assumption was proved to be correct and hence he succeeded in isolating the orange-yellow compound,  $\text{XePtF}_6$ . This compound was obtained at room temperature by the interaction of  $\text{PtF}_6$  with xenon. This discovery of Neil Bartlett led to the further discovery of several other xenon compounds, mainly those formed with electronegative elements such as fluorine and oxygen. There are only a few compounds of Krypton. Some compounds

of radon have been prepared and identified by radiotracer techniques, but their isolation has not been possible. The true chemical nature of compounds of helium, neon, and argon are still unknown.

## **Metallurgy**

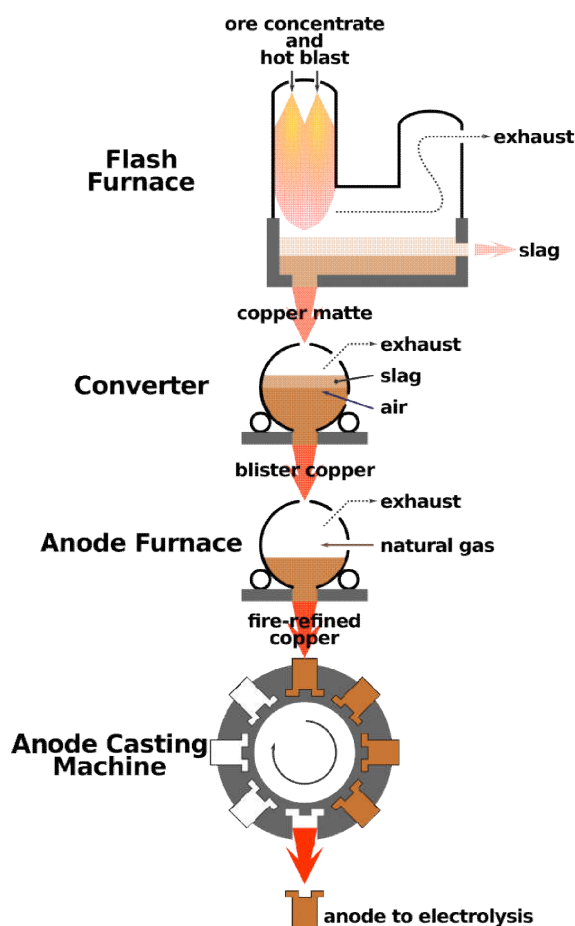
Metallurgy is defined as a process that is used for the extraction of metals in their pure form. The compounds of metals mixed with soil, limestone, sand, and rocks are known as minerals. Metals are commercially extracted from minerals at low cost and minimum effort. These minerals are known as ores. A substance which is added to the charge in the furnace to remove the gangue (impurities) is known as flux. Metallurgy deals with the process of purification of metals and the formation of alloys.

### *Copper Flash Smelting Process*

#### **Principles of Metallurgy:**

The metallurgical process can be classified as the following:

1. **Crushing and grinding:** The first process in metallurgy is crushing of ores into a fine powder in a crusher or ball mill. This process is known as pulverization.
2. **The concentration of ores:** The process of removing impurities from ore is known as a concentration of minerals or ore dressing. In metallurgy, we concentrate the ores mainly by the following methods.



3. Hydrolytic method: In this method, we pour the ore over a sloping, vibrating corrugated table with grooves. A jet of water is allowed to flow over the surface. The denser ore particles settle in the grooves, and the impurities are washed away by water.

4. Magnetic separation: In this case, the crushed ore is placed on a conveyor belt. This belt rotates around two wheels in which one of the wheels is magnetic, and therefore the magnetic particles get attracted to the magnetic wheel and fall apart from the non-magnetic particles.

5. Froth floatation: In this process, we take the crushed ore in a large tank which contains oil and water. A current of compressed air is passed through it. The ore gets wet by oil and is separated from the impurities in the form of froth. Ore is lighter, and so it comes on the surface and impurities are left behind.

6. Roasting and calcination: In metallurgy, the process of heating a concentrated ore in the presence of oxygen is known as roasting. This process is applied in a case of sulfide ores. For ores containing carbonate or hydrated oxides, heating is done in the absence of air to melt the ores, and this process is known as calcination.

### UNIT – III

## CHEMISTRY OF BENZENE AND BENZENOID COMPOUNDS

In the organic chemistry, Aromaticity describes the cyclic and planar molecules having resonance bonds exhibiting more stability than the connective or geometric arrangements within the same kind of atoms.

#### **What is Aromaticity?**

Aromaticity is defined as a property of the conjugated cycloalkenes which enhances the stabilization of a molecule due to its ability of electrons present in the  $pp$  orbitals for the purpose of delocalization.

Aromatic molecules are said to be very stable and they do not break so easily and also reacts with other types of substances. The organic compounds which are not said to be aromatic are known as aliphatic compounds. These might be in cyclic form, but only the aromatic rings have a special kind of stability.

#### ***Aromaticity Rules***

Aromatic compounds are less stable compounds and they have many kinds of chemical as well as synthetic uses. In fact, the nucleic acids and the amino acids that make up our cell structure make use of these aromatic compounds. But, the main thing is what makes aromatic compounds? The aromatics compounds are said to exhibit some of the special characteristics or called as rules which are given below-

- The aromatic compounds are always cyclic structures.
- Each element of the ring within the structure must and should have a  $p$ -orbital ring which is in a perpendicular form to the ring, and this makes it a planar molecule
- All the compounds obey the Huckel's Rule, i.e all the aromatic compounds should have the  $(4n+2)$   $\pi$  number of electrons.
- The last one is that the organic compound has to be flat.

#### **HUCKEL'S RULE**

##### ***What is Huckel's Rule?***

Huckel's Rule is used in order to estimate the aromatic qualities of any planar ring-shaped molecule in the field of organic chemistry. The supporting quantum mechanics required for the formulation of this rule was solved first by the German physical chemist and physicist Erich Armand Arthur Joseph Huckel in the year 1931.

*The Huckel  $4n + 2$   $\pi$  Electron Rule*



A ring-shaped cyclic molecule is said to follow the Huckel rule when the total number of pi electrons belonging to the molecule can be equated to the formula '4n + 2' where n can be any integer with a positive value (including zero).

Examples of molecules following Huckel's rule have only been established for values of 'n' ranging from zero to six. The total number of pi electrons in the benzene molecule depicted below can be found to be 6, obeying the 4n+2 electron rule where n=1.

## BENZENE

Benzene is a cyclic hydrocarbon with a chemical formula C<sub>6</sub>H<sub>6</sub>, that is, each carbon atom in benzene is arranged in a six-membered ring and is bonded to only one hydrogen atom. According to molecular orbital theory for benzene structure, benzene ring involves the formation of three delocalized  $\pi$  – orbitals spanning all six carbon atoms, while the valence bond theory describes two stable resonance structures for the ring. Benzene is one of the most fundamental compounds used in the manufacturing of various plastics, resins, synthetic fibers, rubber lubricants, dyes, detergents, drugs, and pesticides. Benzene is found to exhibit a unique set of physical and chemical properties. Some physical and chemical properties of benzene are mentioned below:

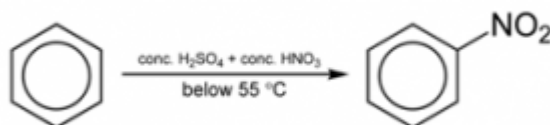
### *Physical and chemical properties of benzene:*

Benzene belongs to the family of aromatic hydrocarbons which are nonpolar molecules and are usually colorless liquids or solids with a characteristic aroma. Benzene being non-polar is immiscible with water but is readily miscible with organic solvents. Upon combustion of benzene sooty flame is produced.

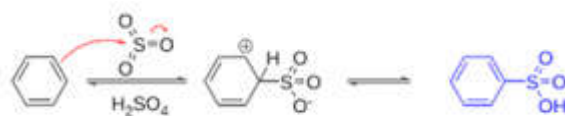
### *Chemical properties of benzene:*

#### *Electrophilic substitution reaction:*

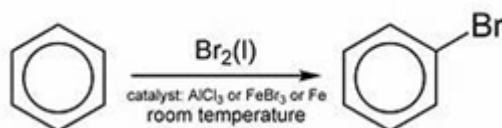
**Nitration of Benzene:** Benzene reacts with nitric acid at 323-333 K in the presence of sulphuric acid to form nitrobenzene. This reaction is known as nitration of Benzene.



**Sulfonation of Benzene:** Sulfonation of benzene is a process of heating benzene with fuming sulphuric acid ( $\text{H}_2\text{SO}_4 + \text{SO}_3$ ) to produce Benzene sulfonic acid. The reaction is reversible in nature.



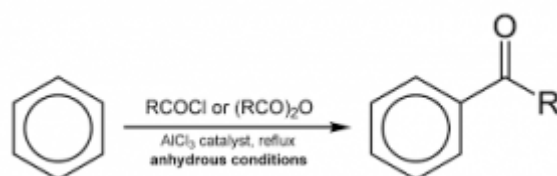
**Halogenation of Benzene:** Benzene reacts with halogens in the presence of Lewis acids like  $\text{FeCl}_3$ ,  $\text{FeBr}_3$  to form aryl halides. This reaction is termed as halogenation of benzene.



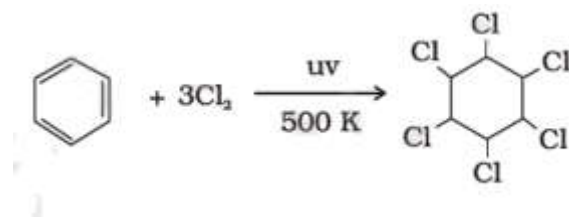
**Friedel Craft's alkylation reaction:** When benzene is treated with an alkyl halide in the presence of a Lewis acid such as anhydrous aluminum chloride, alkyl benzene is formed. This reaction is popularly known as Friedel Craft's alkylation reaction.



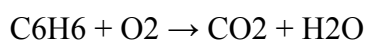
**Friedel Craft's acylation reaction:** When benzene is treated with an acyl halide in the presence of Lewis acid such as anhydrous aluminum chloride, acyl benzene is formed. This reaction is popularly known as Friedel Craft's acylation reaction.



**Addition reactions:** Addition of chlorine in the presence of ultraviolet light produces benzene hexachloride better known as gammaxene.



Combustion of benzene: Upon combustion of benzene, benzene burns with a sooty flame along with the evolution of  $\text{CO}_2$  gas.

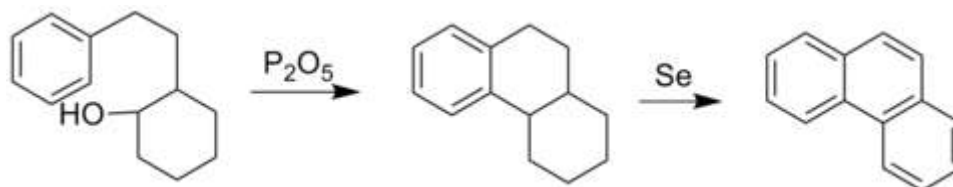


### Polycyclic Aromatic Hydrocarbons

These are the hydrocarbons which comprise of aromatic rings in fused form. These are found in coal, tar, oil and some of the cooked foods such as smoked fish, burnt toast, etc. One common example of these polycyclic hydrocarbons is naphthalene. These compounds are said to be pollutants. Some of the examples of aromatic hydrocarbons are Methylbenzene, Naphthalene, Phenanthrene, Trinitrotoluene, and o-dihydroxybenzene.

#### Phenanthrene

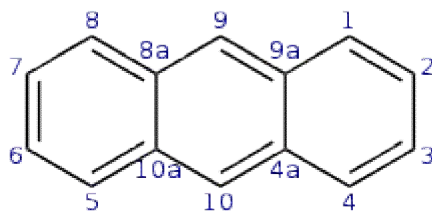
Phenanthrene is used to make dyes, plastics and pesticides, explosives and drugs. It has also been used to make bile acids, cholesterol and steroids. Phenanthrene is nearly insoluble in water but is soluble in most low polarity organic solvents such as toluene, carbon tetrachloride, ether, chloroform, acetic acid and benzene. This process involves electrophilic aromatic substitution using a tethered cyclohexanol group using diphosphorus pentoxide, which closes the central ring onto an existing aromatic ring. Dehydrogenation using selenium converts the other rings into aromatic ones as well. The aromatization of six-membered rings by selenium is not clearly understood, but it does produce  $\text{H}_2\text{Se}$ .



#### Anthracene

Anthracene is a solid polycyclic aromatic hydrocarbon (PAH) of formula  $\text{C}_{14}\text{H}_{10}$ , consisting of three fused benzene rings. It is a component of coal tar. Anthracene is used in

the production of the red dye alizarin and other dyes. Anthracene is colorless but exhibits a blue (400–500 nm peak) fluorescence under ultraviolet radiation.

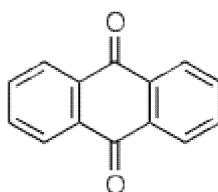


### Reduction

Reduction of anthracene with alkali metals yields the deeply colored radical anion salts  $M^+[anthracene]^-$  ( $M = Li, Na, K$ ). Hydrogenation gives 9,10-dihydroanthracene, preserving the aromaticity of the two flanking rings.

### With electrophiles

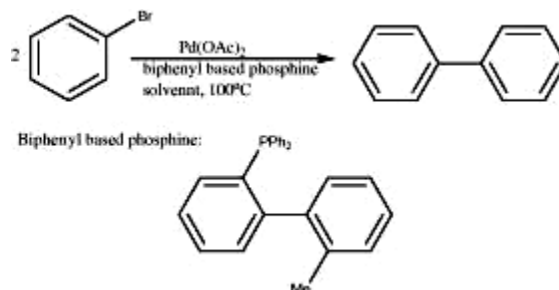
Chemical oxidation occurs readily, giving anthraquinone,  $C_{14}H_{8}O_2$  (below), for example using hydrogen peroxide and vanadyl acetylacetonate



Electrophilic substitution of anthracene occurs at the 9 position. For example, formylation affords 9-anthracenecarboxaldehyde. Substitution at other positions is effected indirectly, for example starting with anthraquinone.

### Biphenyl

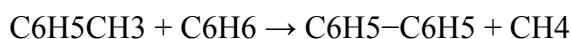
Biphenyl is an aromatic hydrocarbon with a molecular formula  $(C_6H_5)_2$ . It is notable as a starting material for the production of polychlorinated biphenyls (PCBs), which were once widely used as dielectric fluids and heat transfer agents.



It has a distinctively pleasant smell. Biphenyl is an aromatic hydrocarbon with a molecular formula  $(C_6H_5)_2$ . It is notable as a starting material for the production of polychlorinated biphenyls (PCBs), which were once widely used as dielectric fluids and heat transfer agents.

Biphenyl is also an intermediate for the production of a host of other organic compounds such as emulsifiers, optical brighteners, crop protection products, and plastics. Biphenyl is insoluble in water, but soluble in typical organic solvents. The biphenyl molecule consists of two connected phenyl rings.

Biphenyl occurs naturally in coal tar, crude oil, and natural gas and can be isolated from these sources via distillation. It is produced industrially as a byproduct of the dealkylation of toluene to produce benzene:



The other principal route is by the oxidative dehydrogenation of benzene:



In the laboratory, biphenyl can also be synthesized by treating phenylmagnesium bromide with copper(II) salts.

## UNIT - IV

### ALKYL AND ARYL HALOGENS

#### ALKYL HALOGENS:

The **haloalkanes** (also known as **halogenoalkanes** or **alkyl halides**) are a group of [chemical compounds](#) derived from [alkanes](#) containing one or more [halogens](#). They are a subset of the general class of [halocarbons](#), although the distinction is not often made.

#### NOMENCLATURE:

#### IUPAC:

The formal naming of haloalkanes should follow IUPAC nomenclature, which put the halogen as a prefix to the alkane.

For example, ethane with bromine becomes bromoethane, methane with four chlorine groups becomes tetrachloromethane.

However, many of these compounds have already an established trivial name, which is endorsed by the IUPAC nomenclature, for example chloroform (trichloromethane) and methylene chloride (dichloromethane).

## CLASSIFICATION:

From the structural perspective, haloalkanes can be classified according to the connectivity of the carbon atom to which the halogen is attached.

In **primary (1°) haloalkanes**, the [carbon](#) that carries the halogen atom is only attached to **one** other alkyl group.

An example is [chloroethane](#) ( $\text{CH}_3\text{CH}_2\text{Cl}$ ).

In **secondary (2°) haloalkanes**, the carbon that carries the halogen atom has **two C–C bonds**.

In **tertiary (3°) haloalkanes**, the carbon that carries the halogen atom has **three C–C bonds**.

Haloalkanes can also be classified according to the type of **halogen on group 7** responding to a specific halogenoalkane. Haloalkanes containing carbon bonded to [fluorine](#), [chlorine](#), [bromine](#), and [iodine](#) results in [organofluorine](#), [organochlorine](#), [organobromine](#) and [organoiodine](#) compounds, respectively.

Compounds containing more than one kind of halogen are also possible. Several classes of widely used haloalkanes are classified in this way [chlorofluorocarbons](#) (CFCs), [hydrochlorofluorocarbons](#) (HCFCs) and [hydrofluorocarbons](#) (HFCs).

These abbreviations are particularly common in discussions of the environmental impact of haloalkanes.

## PROPERTIES:

### Physical Properties:

Haloalkanes generally resemble the parent alkanes in being **colorless**, relatively **odorless**, and **hydrophobic**.

The melting and boiling points of chloro-, bromo-, and iodoalkanes are higher than the analogous alkanes, scaling with the atomic weight and number of halides. This is due to the increased strength of the [intermolecular forces](#)—from [London dispersion](#) to dipole-dipole interaction because of the increased polarizability.

Thus [carbon tetraiodide](#) ( $\text{CI}_4$ ) is a **solid** whereas [carbon tetrachloride](#) ( $\text{CCl}_4$ ) is a **liquid**. Many fluoroalkanes, however, go against this trend and have lower melting and boiling points than their nonfluorinated analogues due to the decreased polarizability of fluorine.

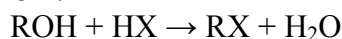
For example, [methane](#) ( $\text{CH}_4$ ) has a melting point of  $-182.5\text{ }^\circ\text{C}$  whereas [tetrafluoromethane](#) has a melting point of  $-183.6\text{ }^\circ\text{C}$ .

## PREPARATION ALKYL HALIDES

### PREPARING ALKYL HALIDES BY ALCOHOLS

Alkyl halide can be prepared by the reaction of halogen acids with alcohols. Hydrochloric ( $\text{HCl}$ ), hydrobromic acid ( $\text{HBr}$ ), Hydrogen iodide acid ( $\text{HI}$ ) are halogen acids. Alcohols react with these acids and give alkyl halides. In this reaction, a halogen is substituted instead of

OH.

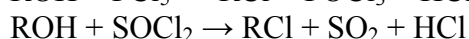
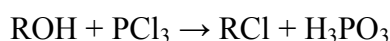


### Reaction rate of alcohols with HX



### Preparing alkyl halides by alcohols with inorganic acid chlorides:

Alkyl chlorides are formed by the reaction of alcohols and inorganic acid chlorides. Phosphorus(III) chloride ( $\text{PCl}_3$ ) or Phosphorus(V) chloride ( $\text{PCl}_5$ ) or thionyl chloride ( $\text{SOCl}_2$ ) are used as inorganic acid chlorides.



### From alkanes:

Alkanes react with halogens by free radical halogenation. In this reaction a hydrogen atom is removed from the alkane, then replaced by a halogen atom by reaction with a diatomic halogen molecule. The reactive intermediate in this reaction is a free radical and the reaction is called a *radical chain reaction*.

Free radical halogenation typically produces a mixture of compounds mono- or multihalogenated at various positions. It is possible to predict the results of a halogenation reaction based on bond dissociation energies and the relative stabilities of the radical intermediates. Another factor to consider is the probability of reaction at each carbon atom, from a statistical point of view.

Due to the different dipole moments of the product mixture, it may be possible to separate them by distillation.

### From alkenes and alkynes:

In [hydrohalogenation](#), an [alkene](#) reacts with a dry hydrogen halide (HX) like [hydrogen chloride](#) (HCl) or [hydrogen bromide](#) (HBr) to form a mono-haloalkane. The double bond of the alkene is replaced by two new bonds, one with the halogen and one with the hydrogen atom of the hydrohalic acid. [Markovnikov's rule](#) states that in this reaction, the halogen is more likely to become attached to the more substituted carbon. This is an [electrophilic addition](#) reaction. Water must be absent otherwise there will be a [side product](#) of a [halohydrin](#). The reaction is necessarily to be carried out in a dry inert solvent such as  $\text{CCl}_4$  or directly in the gaseous phase. The reaction of alkynes are similar, with the product being a geminal dihalide; once again, [Markovnikov's rule](#) is followed.

Alkenes also react with halogens ( $\text{X}_2$ ) to form haloalkanes with two neighboring halogen atoms in a [halogen addition reaction](#). Alkynes react similarly, forming the tetrahalo compounds. This is sometimes known as "decolorizing" the halogen, since the reagent  $\text{X}_2$  is colored and the product is usually colorless and odorless.

### From alcohols:

Alcohol undergoes nucleophilic substitution reaction by halogen acid to give Haloalkanes. Tertiary alkanol reacts with hydrochloric acid directly to produce tertiary chloroalkane (alkyl chloride), but if primary or secondary alcohol is used, an activator such as zinc chloride is needed. This reaction is exploited in the Lucas test.

The most popular conversion is effected by reacting the alcohol with thionyl chloride (SOCl<sub>2</sub>) in the "Darzens halogenation", which is one of the most convenient laboratory methods because the byproducts are gaseous. Both phosphorus pentachloride (PCl<sub>5</sub>) and phosphorus trichloride (PCl<sub>3</sub>) also convert the hydroxyl group to the chloride.

Alcohols may likewise be converted to bromoalkanes using hydrobromic acid or phosphorus tribromide (PBr<sub>3</sub>). A catalytic amount of PBr<sub>3</sub> may be used for the transformation using phosphorus and bromine; PBr<sub>3</sub> is formed *in situ*.

Iodoalkanes may similarly be prepared using red phosphorus and iodine (equivalent to phosphorus triiodide). The Appel reaction is also useful for preparing alkyl halides. The reagent is tetrahalomethane and triphenylphosphine; the co-products are haloform and triphenylphosphine oxide.

### From carboxylic acids:

Two methods for the synthesis of haloalkanes from carboxylic acids are the Hunsdiecker reaction and the Kochi reaction.

### Biosynthesis:

Many chloro and bromoalkanes are formed naturally. The principal pathways involve the enzymes chloroperoxidase and bromoperoxidase.

### By Rydons method:

An alcohol on heating with halogen in presence of triphenyl phosphate produces haloalkanes or alkyl halides.

## CHEMICAL PROPERTIES:

### Preparing alkenes by alkyl halides

Alkenes are prepared by the reactions of alcoholic alkali (NaOH, KOH) and alkyl halides with heating. Halogen atom in the alkyl halide and a hydrogen atom in adjacent two carbon atoms are removed in this reactions to give the alkene, H<sub>2</sub>O and the salt (NaBr, KBr, NaCl).

### Reaction of chloroethane, alcoholic KOH to prepare ethene



### Reaction of 1-bromopropane, alcoholic KOH to prepare propene

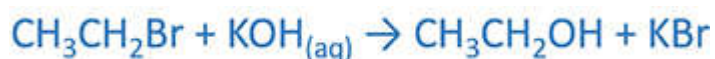




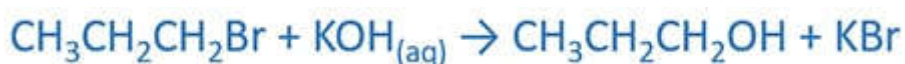
### Prepare alcohols by alkyl halides

Alcohols are prepared by the reaction of alkyl halides and **aqueous alkali**. The halogen group is substituted by hydroxyl ion. In this reaction hydroxyl group behaves as a nucleophile.

#### Ethyl bromide and aqueous KOH



#### 1-bromopropane and aqueous KOH



### Prepare Grignard reagent by alkyl halides

Magnesium and dry ether is mixed with alkyl halide to prepare Grignard reagent. For keep Grignard stable, dry ether is essential. These Grignard reagents are used to extend carbon chains. In aqueous medium, grignard reagent slowly hydrolyzes and give hydrocarbons.

Bromoethane, Mg and dry ether



Bromobenzene, Mg and dry ether



### USES:

As they contain fewer C–H bonds, halocarbons are less flammable than alkanes, and some are used in **fire extinguishers**.

Haloalkanes are better [solvents](#) than the corresponding alkanes because of their increased polarity.

Haloalkanes containing halogens other than fluorine are more reactive than the parent alkanes—it is this reactivity that is the basis of most controversies.

Many are [alkylating agents](#), with primary haloalkanes and those containing heavier halogens being the most active (fluoroalkanes do not act as alkylating agents under normal conditions). The ozone-depleting abilities of the CFCs arises from the [photolability](#) of the C–Cl bond.

## NUCLEOPHILIC SUBSTITUTION REACTIONS OF ALKYL HALIDES:

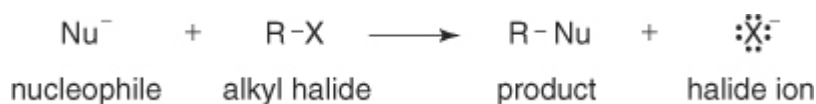
Carbon halogen bond (C-X) is polarized in alkyl halides. Therefore carbon atom gets a small positive charge ( $\delta^+$ ). Hence, [nucleophilic reagents](#) react with that carbon atom.

When nucleophile attacks to the carbon atom, halogen atom is removed as a [halide ion\(X\)](#). Therefore these reactions are defined as nucleophilic substitution reaction. When eliminated aqueous halide anion becomes more stable, the reaction gets easier to occur.

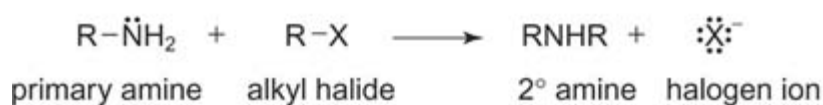
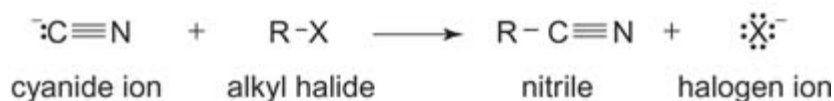
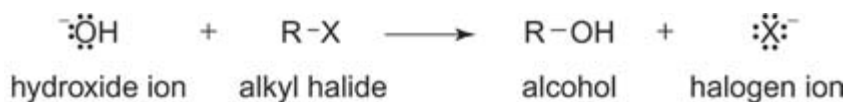
- Aqueous dilute alkaline(NaOH, KOH) and alkyl halides
- Aqueous cyanide(CN<sup>-</sup>) ions and alkyl halides.

## Nucleophilic Substitution Common Reactions

Alkyl halides undergo many reactions in which a nucleophile displaces the halogen atom bonded to the central carbon of the molecule. The displaced halogen atom becomes a halide ion.



Some typical nucleophiles are the hydroxy group ( $\text{OH}^-$ ), the alkoxy group ( $\text{RO}^-$ ), and the cyanide ion ( $\text{C}\equiv\text{N}^-$ ). Reaction of these nucleophiles with an alkyl halide (R–X) gives the following reactions and products:



The halogen ion that is displaced from the carbon atom is called the **leaving group**, and the overall reaction is called a **nucleophilic substitution reaction**.

## TYPES:

It is divided into Two types:

SN1 Reactions

SN2 Reactions

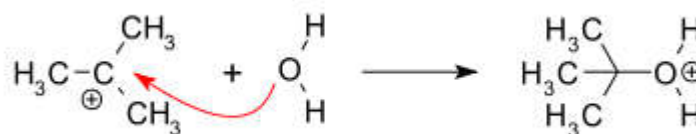
### SN1 Reactions:

In SN1 reactions, 1 indicates that the rate determining step is unimolecular. Thus, the reaction has a first-order dependence on [electrophile](#) and zero-order dependence on [nucleophile](#). A carbocation is formed as an intermediate in this reaction and this type of reactions commonly occur in secondary and tertiary [alcohols](#). SN1 reactions have three steps.

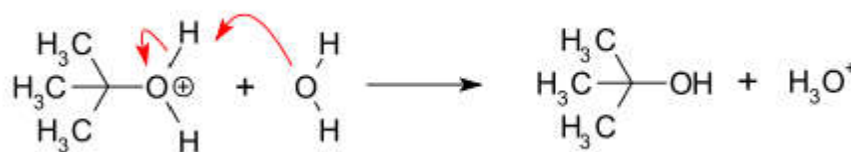
1. Formation of the carbocation by removing the leaving group.



2. The reaction between the carbocation and the nucleophile (Nucleophilic attack).



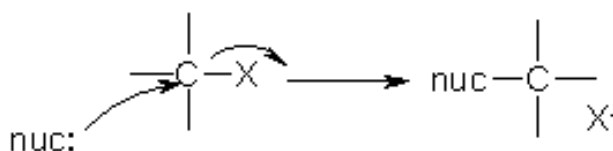
3. This happens only when the nucleophile is a neutral compound (a solvent).



## SN2 Reactions:

In SN2 reactions, one bond is broken, and one bond is formed simultaneously. In other words, this involves the displacement of the leaving group by a nucleophile. This reaction happens very well in [methyl](#) and primary alkyl halides whereas very slow in tertiary alkyl halides since the backside attack is blocked by bulky groups.

The general mechanism for SN2 reactions can be described as follows.

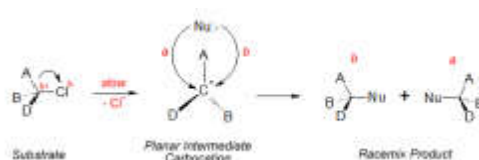


## The Reaction Pathway – Sn1 and Sn2 Reactions

There are two main pathways that a nucleophilic substitution reaction can follow:

### Sn1 (Substitution, Nucleophilic, Unimolecular):

- Substrate ionises to form a planar intermediate carbocation in the rate determining step.
- The intermediate cation then rapidly reacts with the nucleophile. This means there are two transition states.
- This is a 1st order reaction as rate =  $k[\text{substrate}]$ . It is a unimolecular process.
- Favoured in polar solvents – this aids ionisation.
- Favoured Tertiary > Secondary > Primary as the two state process allows access to the carbon centre without steric hindrance (see Sn2 below).

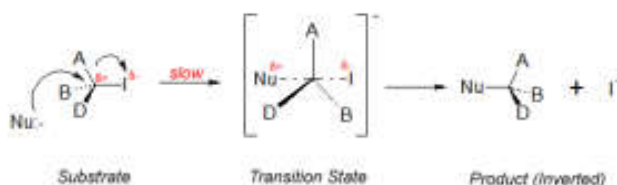


*Sn1 Substitution*

Sn1 creates a racemic product (an equal amount of left and right enantiomers) which as a result is optically inactive. This means it will not rotate polarised light.

### Sn2 (Substitution, Nucleophilic, Bimolecular):

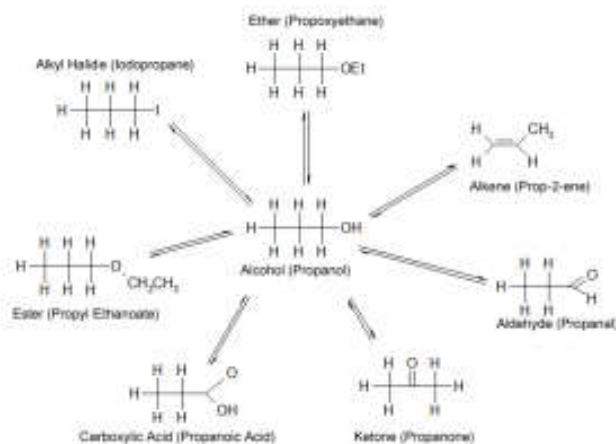
- Reaction occurs completely within one transition state.
- This is a second order reaction as rate =  $k[\text{substrate}][\text{nucleophile}]$
- Reaction favoured in polar aprotic solvents (solvents which have high polarity but cannot dissociate a  $\text{H}^+$ ) such as DMF (Dimethylformamide) and DMSO (Dimethyl Sulfoxide).
- Steric hindrance slows or stops reaction progression in tertiary systems as steric crowding stops attack by the nucleophile (aka there isn't room!) and tertiary cations are quite stable. In this case we would expect  $\text{S}_{\text{N}}1$ . Note that the "back route" must be clear else the reaction will proceed by  $\text{S}_{\text{N}}1$ .
- Favoured Primary > Secondary > Tertiary.



$\text{S}_{\text{N}}2$  creates a product with an inverted stereo structure to that of the substrate. Essentially the Nucleophile attaches to the opposite side from the leaving group, inverting the molecule's original stereochemistry.

### Alcohols:

Alcohols are extremely important for synthesising new molecules:



### *Synthesising new molecules from Alcohols (In this case Propanol)*

It is especially useful when you consider that we can already use the Alkyl Halide table from above to form a variety of molecules that way.

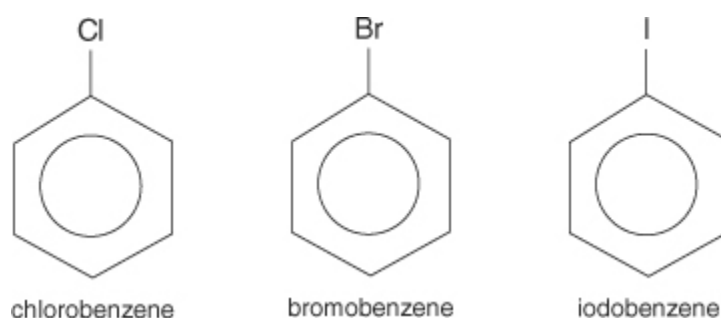
### ARYL HALIDE:

In [organic chemistry](#), an **aryl halide** (also known as **haloarene** or **halogenoarene**) is an aromatic compound in which one or more hydrogen atoms directly bonded to an [aromatic](#) ring are replaced by a [halide](#).

The haloarene are distinguished from [haloalkanes](#) because they exhibit many differences in methods of preparation and properties. The most important members are the aryl chlorides, but the class of compounds is so broad that many derivatives enjoy niche applications.

### Nomenclature:

Aryl halides are named by prefixing the name of the halogen to benzene. For example:



### Physial Properties of aryl halides

The physical properties of unsubstituted aryl halides are much like those of the corresponding alkyl halides. Thus, boiling points, melting points, and solubilities of aryl halides are very similar to those of alkyl halides containing the same number of carbon atoms.

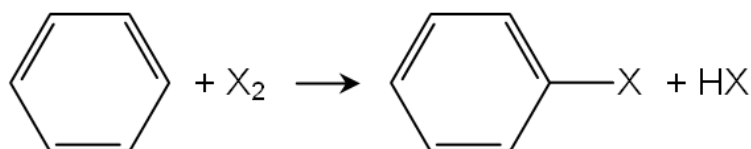
### PREPARATION:

#### Direct halogenations:

In the [Friedel-Crafts halogenation](#), [Lewis acids](#) serve as catalysts. Many metal chlorides are used, examples include [iron\(III\) chloride](#) or [aluminium chloride](#). The most important aryl halide, [chlorobenzene](#) is produced by this route. Monochlorination of benzene is always accompanied by formation of the dichlorobenzene derivatives.

Arenes with electron donating groups react with halogens even in the absence of Lewis acids. For example, phenols and anilines react quickly with chlorine and bromine water to give multiple halogenated products. The decolouration of bromine water by electron-rich arenes is used in the [bromine test](#).

Direct halogenation of arenes are possible in the presence of light or at high temperature. For alkylbenzene derivatives, the alkyl positions tend to be halogenated first in the free radical halogenation. To halogenate the ring, Lewis acids are required, and light should be excluded to avoid the competing reaction.

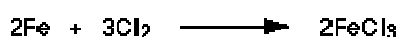


### Making chlorobenzene:

Benzene reacts with chlorine in the presence of a catalyst, replacing one of the hydrogen atoms on the ring by a chlorine atom.

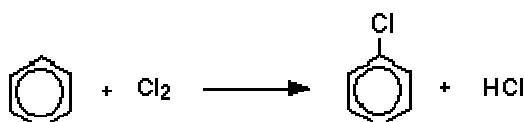
The reaction happens at room temperature. The catalyst is either aluminium chloride or iron.

Strictly speaking iron isn't a catalyst, because it gets permanently changed during the reaction. It reacts with some of the chlorine to form iron(III) chloride,  $FeCl_3$ .



This compound acts as the catalyst and behaves exactly like aluminium chloride,  $AlCl_3$ , in this reaction.

The reaction between benzene and chlorine in the presence of either aluminium chloride or iron gives chlorobenzene.

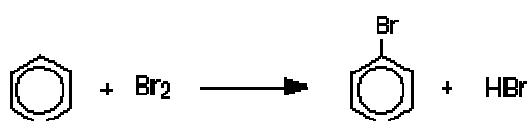


or, written more compactly:

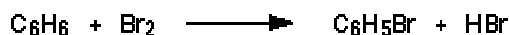


### Making bromobenzene:

The reaction between benzene and bromine in the presence of either aluminium bromide (rather than aluminium chloride) or iron gives bromobenzene. Iron is usually used because it is cheaper and more readily available. If you use iron, it is first converted into iron(III) bromide by the reaction between the iron and bromine.



or:

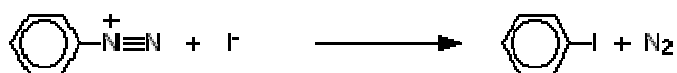


### Making iodobenzene:

Iodobenzene can be made from the reaction of benzene with iodine if they are heated under reflux in the presence of concentrated nitric acid, but it is normally made from benzenediazonium chloride solution. That's what we will concentrate on here.

If you add cold potassium iodide solution to ice-cold benzenediazonium chloride solution, nitrogen gas is given off, and you get oily droplets of iodobenzene formed.

There is a simple reaction between the diazonium ions present in the benzenediazonium chloride solution and the iodide ions from the potassium iodide solution.



### Reactions of Haloarenes:

Reactions of haloarenes or reactions of aryl halides are mainly of 3 types:

- Nucleophilic Substitution Reactions
- Electrophilic Substitution Reactions
- Reaction with [Metals](#)

#### I. Nucleophilic Substitution Reactions:

Nucleophilic Substitution Reactions are difficult in case of haloarenes. However, haloarenes undergo nucleophilic substitution reaction under certain conditions. Key reasons for decreased or unreactive nature of haloarenes towards nucleophilic substitution reactions are as below:

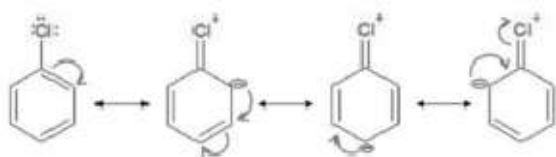
#### Resonance Effect:

In case of haloarenes,  $\pi$  – electrons present in the benzene ring undergo

conjugation with the [halogen](#) atom present in the haloarene structure. This results in [resonance](#) and [development](#) of partial double bond in the C-X bond. The partial double bond cleavage of a haloarene is more difficult than a haloalkane. Thus, haloarenes cannot be cleaved by a



nucleophile easily and they are less reactive towards a nucleophilic substitution reaction.



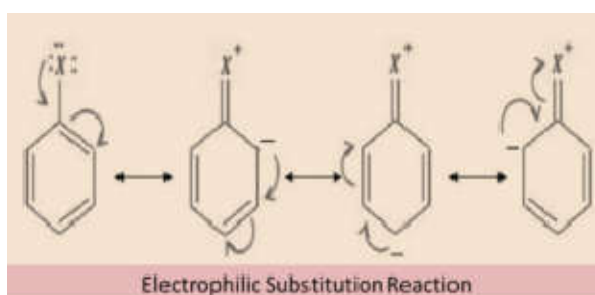
Example of Resonance Effect

## Electrophilic Substitution Reactions:

The type of reactions in which an electrophile substitutes another electrophile in any organic compound is known as electrophilic substitution reaction. An electrophile means an electron seeking species. Haloarenes will undergo the usual benzene ring reactions such as nitration, halogenation, Friedel-Crafts reactions and sulphonation.

We know that haloarenes are electron-rich compounds. Therefore, they can undergo electrophilic substitution reaction and the attacking species, in this case, will be an electrophile. The +M effect will result in the concentration of electron density at ortho –and para –positions.

However, electrophilic substitution reactions with respect to the haloarene reactions are slow in comparison to benzene reactions. This is because the halogen group present in haloarenes are deactivating because of the –I effect. Hence, electrons withdraw from the benzene ring.

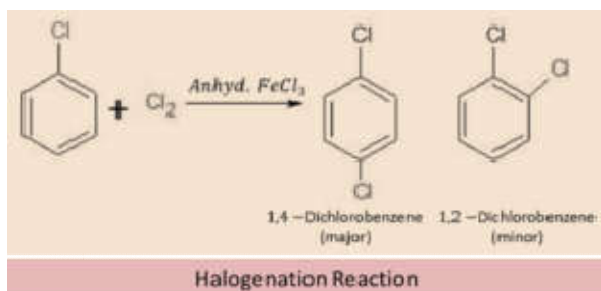


Electrophilic Substitution Reaction

## Halogenation:

The reactions of haloarenes take place when haloarene react with chlorine in the presence of a solvent (say ferric chloride). The chlorine molecule tends to become polar in nature and develops a slightly positive charge. Thus, the chlorine acts as an electrophile and will attack the electron-rich Ortho and Para position of the compound.

The reaction will result in the formation of both Ortho and Para compounds. However, Para isomer will be the major product and Ortho isomer will be the minor product of the reaction. In the below example chlorobenzene reacts in the presence of Lewis acid and form ortho and para substitutes of dihalobenzenes.



### Nitration:

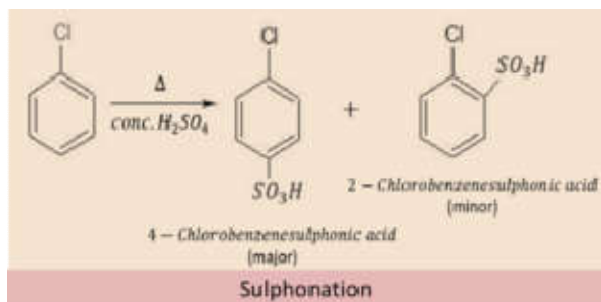
The reaction starts with the formation of  $\text{NO}_2^+$  from nitric acid on initiation with sulphuric acid.  $\text{NO}_2$  contains an electrophilic centre because of the electronegative oxygen atoms present in the molecule itself. Again, the electrophile will attack the electron-rich ortho and para positions. The reaction will result in the formation of Para isomer and Ortho isomer as the major and the minor product respectively.

In the below example, nitration of halobenzene will result in the formation of ortho and para substituted products in the presence of nitric and sulphuric acid. The electrophile, in this case, is  $\text{NO}_2^+$ .



### Sulphonation:

In sulphonation  $\text{SO}_3$  acts as an electrophile. It attacks the electron-rich haloarene at Ortho and Para positions. The reaction results in the formation of Para and Ortho Chlorobenzenesulphonic acids, where Para isomer forms the major product and Ortho isomer forms the minor product.



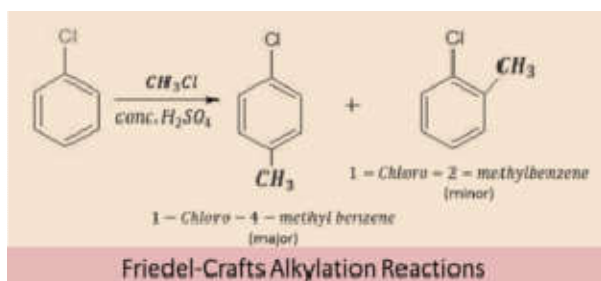
### Friedel-Crafts Reaction:

There are generally two types of Friedel-Crafts reaction

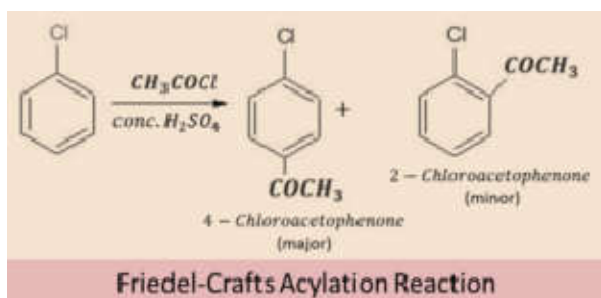
- Friedel-Crafts Alkylation Reactions
- Friedel-Crafts Alkylation Reactions
- Friedel-Crafts Acylation Reactions

In this case, the electrophile is the alkyl and acetic group because of the positive charge present in the carbon atom.

### Friedel-Crafts Alkylation Reactions:



### Friedel-Crafts Acylation Reactions:



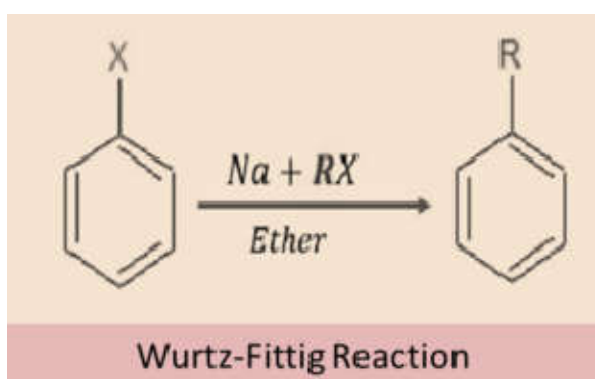
## Reactions with Metals:

Haloarenes undergo few reactions with metals. Two primary reactions are:

- Wurtz-Fittig Reaction
- Fittig Reaction

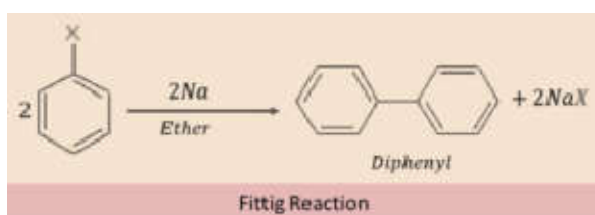
### Wurtz-Fittig Reaction:

In this reaction, a mixture of alkyl halide reacts with an aryl halide in the presence of dry ether and sodium. The resultant product is alkyl arene.



### Fittig Reaction:

In this reaction, a mixture of haloarenes reacts with sodium in the presence of dry ether. The resultant product is diaryl.

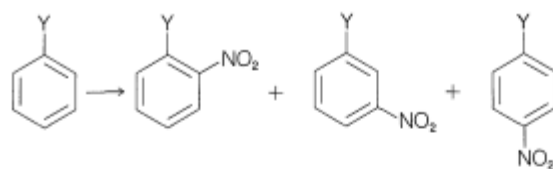


## The Pattern of Orientation in Aromatic Substitution:

The reaction most studied in connection with the orientation problem is nitration, but the principles established also apply for the most part to the related reactions of halogenation, sulfonation, alkylation, and acylation. Some illustrative data for the nitration of a number of mono-substituted benzene derivatives are given in Table. The table includes the percentage of ortho, meta, and para isomers formed, along with their reactivities relative to benzene. We see that there is a wide range of reactivity according to the nature of the substituent, and that

the ortho, meta, and para positions are *not* equally reactive. Although these substituent effects may appear complex, they are related closely to substituted alkenes

*orientation and Rate Data for Nitration of Some Monosubstituted Benzene Derivatives[Math Processing Error]*

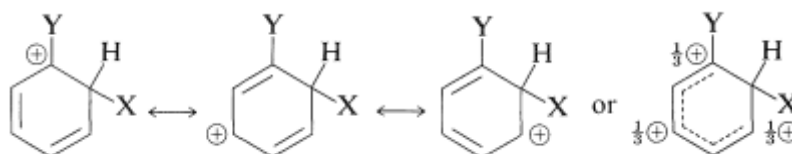


Substituent, Y	Orientation			Relative reactivity
	% ortho	% meta	% para	
—H	—	—	—	1
—CH <sub>3</sub>	56.5	3.5	40	24
—C(CH <sub>3</sub> ) <sub>3</sub>	12.0	8.5	79.5	15.7
—CH <sub>2</sub> Cl	32.0	15.5	52.5	0.302
—Cl	29.6	0.9	68.5	0.033
—Br	36.5	1.2	62.4	0.030
—NO <sub>2</sub>	6.4	93.2	0.3	~ 10 <sup>-7</sup>
—CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	28.3	68.4	3.3	0.003
—CF <sub>3</sub>		100		
⊕ —N(CH <sub>3</sub> ) <sub>3</sub>		89	11	

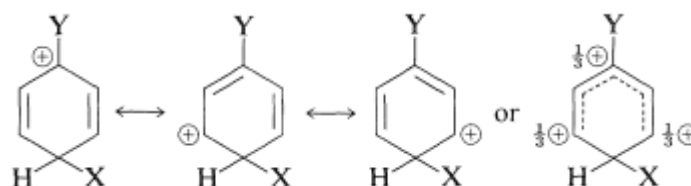
\*The data are representative but will vary to some extent with the reaction conditions and nature of the substituting agent.

We now can examine the structures of the three substitution intermediates with a view to deciding how the substituent might affect their stability. According to the valence-bond method, the positive charge in the ring is dispersed mainly on alternate carbons, as shown below.

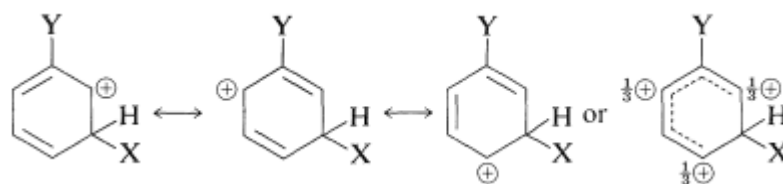
***ortho substitution:***



***para substitution:***



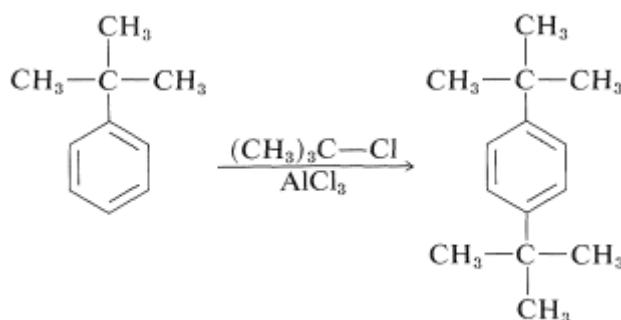
***meta substitution:***



### Steric Effects:

Thus far we have made no distinction between the reactivities of the ortho and the para positions, yet they clearly are not equal. If they were equal, the ortho:para ratio would be 2:1, thereby reflecting the fact that there are two ortho positions but only one para position in monosubstituted benzenes. Most substitution reactions favor the para product, sometimes by a considerable amount (see Table).

A reasonable explanation is that ortho substitution is subject to steric hindrance between the substituent and the entering group. *tert*-Butylbenzene, for example, gives much less ortho nitration than methylbenzene (Table), thereby suggesting that the size of the substituent is important. Also, *tert*-butylbenzene gives no ortho alkylation with *tert*-butyl chloride, suggesting that the size of the entering group is also important:



### Applications:

The aryl halides produced on the largest scale are chlorobenzene and the isomers of dichlorobenzene. One major but discontinued application was the use of **chlorobenzene** as a **solvent** for dispersing the herbicide Lasso.

Overall, production of aryl chlorides (also naphthyl derivatives) has been declining since the 1980s, in part due to environmental concerns. [Triphenylphosphine](#) is produced from chlorobenzene:



**Aryl bromides** are widely used as **fire-retardants**. The most prominent member is [tetrabromobisphenol-A](#), which is prepared by direct bromination of the diphenol.

## UNIT V

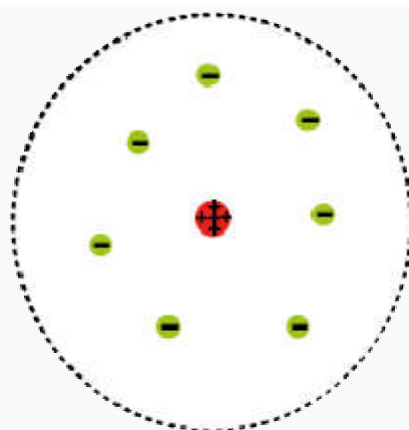
# ATOMIC STRUCTURE AND BASIC QUANTUM MECHANICS

### ATOMIC STRUCTURE:

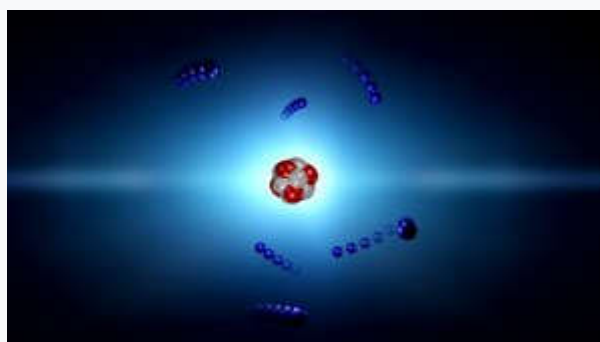
The structure of an atom, theoretically consisting of a positively charged nucleus surrounded and neutralized by negatively charged electrons revolving in orbits at varying distances from the nucleus, the constitution of the nucleus and the arrangement of the electrons differing with various chemical elements.

### RUTHERFORD MODEL:

The **Rutherford model** was devised by [Ernest Rutherford](#) to describe an [atom](#). Rutherford's new model for the atom, based on the experimental results, contained new features of a relatively high central charge concentrated into a very small volume in comparison to the rest of the atom and with this central volume also containing the bulk of the [atomic mass](#) of the atom. This region would be known as the "[nucleus](#)" of the atom.



Basic diagram of the atomic nuclear model: electrons in green and nucleus in red



3D animation of an atom incorporating the Rutherford model

### Experimental basis for the model:

Rutherford overturned Thomson's model in 1911 with his well-known [gold foil experiment](#) in which he demonstrated that the atom has a tiny and heavy nucleus.

Rutherford designed an experiment to use the [alpha particles](#) emitted by a radioactive element as probes to the unseen world of atomic structure.

Rutherford presented his own physical model for subatomic structure, as an interpretation for the unexpected experimental results. In it, the atom is made up of a central charge (this is the modern [atomic nucleus](#), though Rutherford did not use the term "nucleus" in his paper) surrounded by a cloud of (presumably) orbiting [electrons](#). In this May 1911 paper, Rutherford only committed himself to a small central region of very high positive or negative charge in the atom.

For concreteness, consider the passage of a high speed  $\alpha$  particle through an atom having a positive central charge  $Ne$ , and surrounded by a compensating charge of  $N$  electrons.

From purely energetic considerations of how far particles of known speed would be able to penetrate toward a central charge of  $100e$ , Rutherford was able to calculate that the radius of his [gold](#) central charge would need to be less (how much less could not be told) than  $3.4 \times 10^{-14}$  meters. This was in a gold atom known to be  $10^{-10}$  meters or so in radius—a very surprising finding, as it implied a strong central charge less than 1/3000th of the diameter of the atom.

#### These are the key indicators-

- The atom's electron cloud does not influence alpha particle scattering.
- Much of an atom's positive charge is concentrated in a relatively tiny volume at the center of the atom, known today as the nucleus. The magnitude of this charge is proportional to (up to a charge number that can be approximately half of) the atom's atomic mass—the remaining mass is now known to be mostly attributed to neutrons. This concentrated central mass and charge is responsible for deflecting both alpha and beta particles.
- The mass of heavy atoms such as gold is mostly concentrated in the central charge region, since calculations show it is not deflected or moved by the high speed alpha particles, which have very high momentum in comparison to electrons, but not with regard to a heavy atom as a whole.
- The atom itself is about 100,000 ( $10^5$ ) times the diameter of the nucleus. This could be related to putting a grain of sand in the middle of a football field.

#### BOHR THEORY:

A theory of atomic structure in which the hydrogen atom (Bohr atom) is assumed to consist of a **proton as nucleus**, with a single **electron moving in distinct circular orbits around it**, each **orbit** corresponding to a **specific quantized energy state**: the theory was extended to other atoms.

**Bohr model**, description of the structure of [atoms](#), especially that of [hydrogen](#), proposed (1913) by the Danish physicist [Niels Bohr](#).

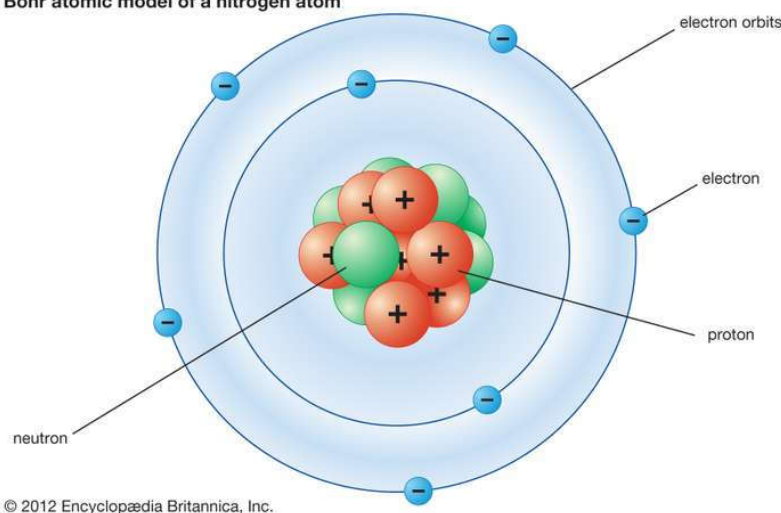


The Bohr model and all of its successors describe the properties of atomic [electrons](#) in terms of a set of allowed (possible) values. Atoms absorb or emit radiation only when the electrons abruptly jump between allowed, or stationary, states.

Direct experimental evidence for the existence of such discrete states was obtained (1914) by the German-born physicists [James Franck](#) and [Gustav Hertz](#).

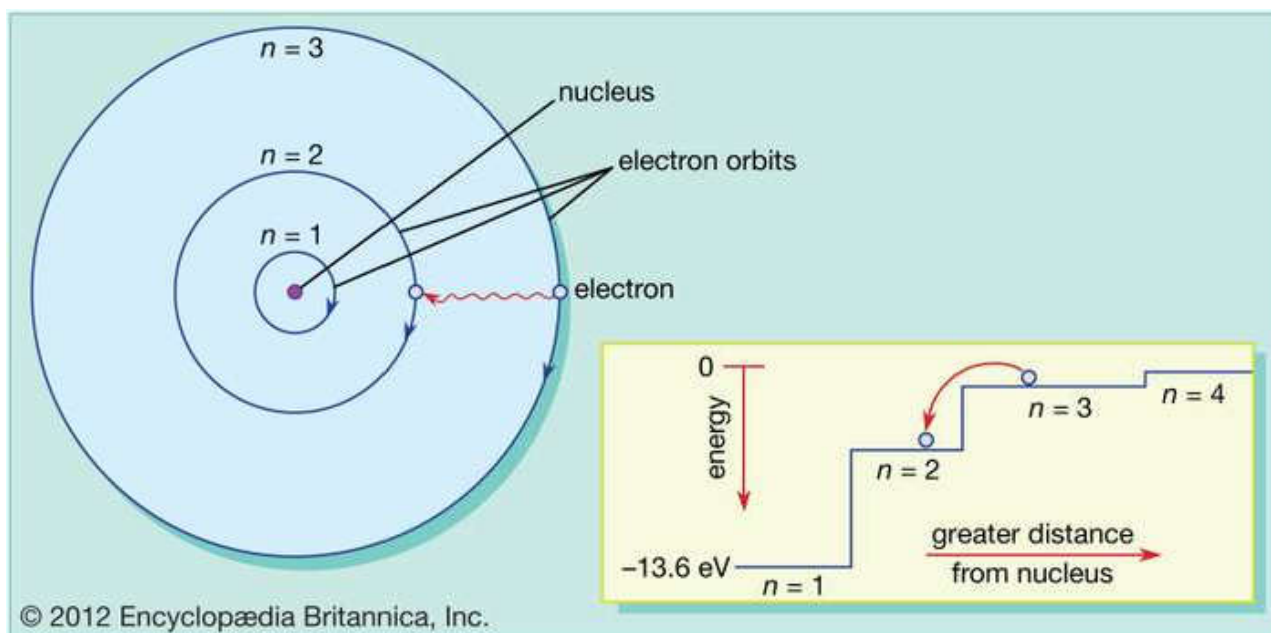
Physicists James Franck and Gustav Hertz.

Bohr atomic model of a nitrogen atom



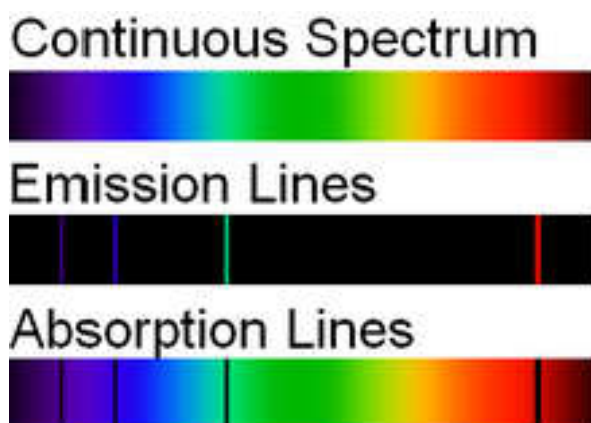
Immediately before 1913, an atom was thought of as consisting of a tiny positively charged heavy core, called a nucleus, surrounded by light, planetary negative electrons revolving in circular orbits of arbitrary radii.

Bohr amended that view of the motion of the planetary electrons to bring the model in line with the regular patterns (spectral series) of light emitted by real hydrogen atoms. By limiting the orbiting electrons to a series of circular orbits having discrete radii, Bohr could account for the series of discrete wavelengths in the emission spectrum of hydrogen. Light, he proposed, radiated from hydrogen atoms only when an electron made a transition from an outer orbit to one closer to the nucleus. The energy lost by the electron in the abrupt transition is precisely the same as the energy of the quantum of emitted light.



### Bohr's Theory of the Hydrogen Emission Spectrum

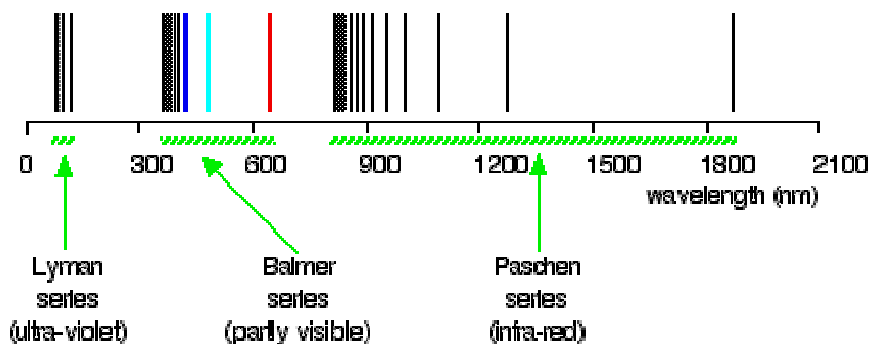
The spectrum of *hydrogen*, which turned out to be crucial in providing the first insight into atomic structure over half a century later, was first observed by Anders Angstrom in Uppsala, Sweden, in 1853.



The spectral lines are grouped into series according to  $n_1$  values. Lines are named sequentially starting from the longest wavelength/lowest frequency of the series, using Greek letters within each series. For example, the ( $n_1=1/n_2=2$ ) line is called "Lyman-alpha" (Ly- $\alpha$ ), while the ( $n_1=3/n_2=7$ ) line is called "Paschen-delta" (Pa- $\delta$ ). The first six series have specific names:

- Lyman series with  $n_1=1$
- Balmer series with  $n_1=2$
- Paschen series (or Bohr series) with  $n_1=3$

- Brackett series with  $n_1=4, n_2=5$
- Pfund series with  $n_1=5, n_2=6$
- Humphreys series with  $n_1=6, n_2=7$



### SOMMERFELD ATOM MODEL:

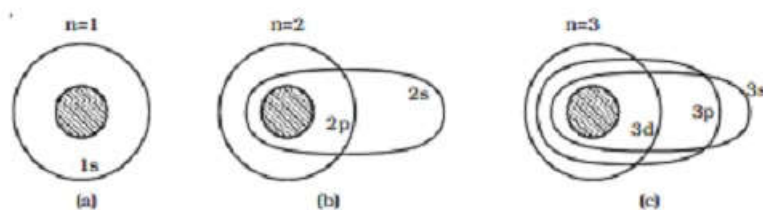


Fig. Various sub-shells for the electrons

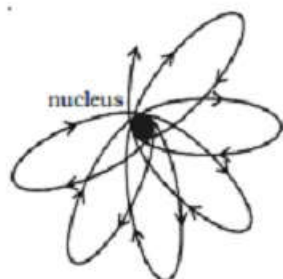


Fig. Rosette path of an electron

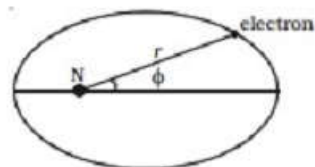


Fig. Sommerfeld atom model

In order to explain the observed fine structure of spectral lines, Sommerfeld introduced two main modifications in Bohr's theory.

- According to Sommerfeld, the path of an electron around the nucleus, in general, is an ellipse with the nucleus at one of its foci.

- (ii) The velocity of the electron moving in an elliptical orbit varies at different parts of the orbit. This causes the relativistic variation in the mass of the moving electron.

Now, when elliptical orbits are permitted, one has to deal with two variable quantities.

- (i) The varying distance of the electron from the nucleus ( $r$ ).
- (ii) The varying angular position of the electron with respect to the nucleus i.e the azimuthal angle  $\phi$ .

To deal with these two variables, two quantum numbers are introduced

- (i) The principal quantum number  $n$  of Bohr's theory, which determines the energy of the electrons, and
- (ii) a new quantum number called orbital (or azimuthal) quantum number ( $l$ ) which has been introduced to characterize the angular momentum in an orbit i.e., it determines the orbital angular momentum of the electron. Its values vary from zero to  $(n-1)$  in steps of unity.

This orbital quantum number ( $l$ ) is useful in finding the possible elliptical orbits. The possible elliptical orbits are such that

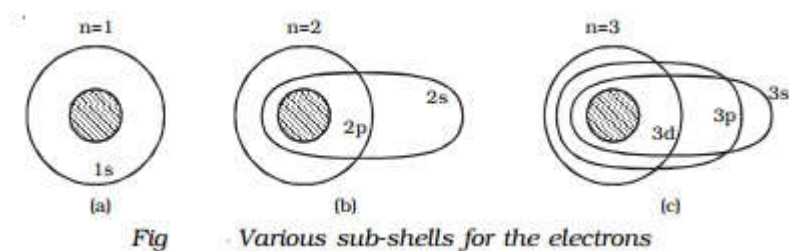
$$b/a = l+1/n$$

where  $a$  and  $b$  are semi-major and semi-minor axes respectively of the ellipse.

According to Sommerfeld's model, for any principal quantum number  $n$ , there are  $n$  possible orbits of varying eccentricities called sub-orbits or sub-shells. Out of  $n$  subshells, one is circular and the remaining (i.e.,  $n-1$ ) are elliptical in shape.

These possible sub-orbits possess slightly different energies because of the relativistic variation of the electron mass.

Consider the first energy level ( $n=1$ ). When  $n = 1, l = 0$  i.e., in this energy level, there is only one orbit or sub-shell for the electron. Also, when  $a = b$ , the two axes of the ellipse are equal. As a result of this, the orbit corresponding to  $n=1$  is circular. This subshell is designated as  $s$  sub-shell. Since, this sub-shell belongs to  $n=1$ , it is designated as  $1s$  (Fig).



Similarly, for the second energy level  $n=2$ , there are two permissible sub-shells for the electrons. For  $n=2, l$  can take two values, 0 and 1.

When  $n = 2, l = 0$ .

$$b/a = 0 + 1/2 = 1/2$$

or

$$b = a/2$$

This subshell corresponding to  $l = 0$  is elliptical in shape and is designated as  $2s$ .

when  $n = 2, l = 1$ .

$$b/a = 1 + 1/2 = 2/2 = 1$$

or

$$b = a$$

This sub-shell corresponding to  $l = 1$  is circular in shape and is designated as  $2p$  (Fig b).

For  $n = 3, l$  has three values 0, 1 and 2, i.e. there are three permissible sub-shells for the electrons.

when  $n = 3, l = 0$ .

$$b/a = (0+1)/3 = 1/3 = 1 \text{ or } b=a/3$$

when  $n = 3, l = 1$ .

$$b/a = (1+1)/3 = 2/3 = 1 \text{ or } b=2a/3$$

and when  $n = 3, l = 2$ .

$$b/a = (2+1)/3 = 3/3 = 1 \text{ or } b=a$$

The sub-shells corresponding to  $l = 0, 1$  and  $2$  are designated as  $3s, 3p$  and  $3d$  respectively. The circular shell is designated as  $3d$  and the other two are elliptical in shape (Fig c).

It is common practice to assign letters to  $l$ -values as given below:

Orbital quantum number $l$	:	0	1	2	3	4
electron state :		s	p	d	f	g

Hence, electrons in the  $l = 0, 1, 2, 3$  states are said to be in the  $s, p, d, f$  states.

### ***Fine structure of spectral line***

Based on Sommerfeld atom model, the total energy of an electron in the elliptical orbit can be shown as,

$$E_n = (-me^4 Z^2) / (8\epsilon_0^2 h^2 n^2)$$

This expression is the same as that obtained by Bohr. Thus the introduction of elliptical orbits gives no new energy levels and hence no new transition. In this way, the attempt of Sommerfeld to explain the fine structure of spectral lines failed. But soon, on the basis of variation of mass of electron with velocity, Sommerfeld could find the solution for the problem of the fine structure of the spectral lines.

According to Sommerfeld, the velocity of the electron is maximum when the electron is nearest to the nucleus and minimum when it is farthest from the nucleus, since the orbit of the electron is elliptical. This implies that the effective mass of the electron will be different at different parts of its orbit. Taking into account the relativistic variation of the mass of

the electron, Sommerfeld modified his theory and showed that the path of electron is not a simple ellipse but a precessing ellipse called a rosette.

## **ELECTROMAGNETIC RADIATION:**

**electromagnetic radiation (EM radiation or EMR)** refers to the waves (or their [quanta](#), [photons](#)) of the [electromagnetic field](#), propagating (radiating) through space, carrying electromagnetic [radiant energy](#). It includes [radio waves](#), [microwaves](#), [infrared](#), [\(visible\) light](#), [ultraviolet](#), [X-rays](#), and [gamma rays](#).

[Classically](#), electromagnetic radiation consists of **electromagnetic waves**, which are synchronized [oscillations](#) of [electric](#) and [magnetic fields](#). In a vacuum, electromagnetic waves travel at the [speed of light](#), commonly denoted  $c$

### **Examples of Electromagnetic Energy:**

- Radio waves
- Microwaves
- Infrared
- Visible light (red, orange, yellow, green, blue, indigo, violet)
  
- Ultraviolet
  
- X-ray
- Gamma-rays

### **Radio waves:**

Radio waves are at the lowest range of the EM spectrum, with frequencies of up to about 30 billion hertz, or 30 gigahertz (GHz), and wavelengths greater than about 10 millimeters (0.4 inches). Radio is used primarily for communications including voice, data and entertainment media.

### **Microwaves:**

Microwaves fall in the range of the EM spectrum between radio and IR. They have frequencies from about 3 GHz up to about 30 trillion hertz, or 30 terahertz (THz), and wavelengths of about 10 mm (0.4 inches) to 100 micrometers ( $\mu\text{m}$ ), or 0.004 inches. Microwaves are used for high-bandwidth communications, radar and as a heat source for microwave ovens and industrial applications.

### **Infrared:**

Infrared is in the range of the EM spectrum between microwaves and visible light. IR has frequencies from about 30 THz up to about 400 THz and wavelengths of about 100  $\mu\text{m}$  (0.004 inches) to 740 nanometers (nm), or 0.00003 inches. IR light is invisible to human eyes, but we can feel it as heat if the intensity is sufficient.

### **Visible light:**

Visible light is found in the middle of the EM spectrum, between IR and UV. It has frequencies of about 400 THz to 800 THz and wavelengths of about 740 nm (0.00003 inches) to 380 nm (.000015 inches). More generally, visible light is defined as the wavelengths that are visible to most human eyes.

### **Ultraviolet:**

Ultraviolet light is in the range of the EM spectrum between visible light and X-rays. It has frequencies of about  $8 \times 10^{14}$  to  $3 \times 10^{16}$  Hz and wavelengths of about 380 nm (.000015 inches) to about 10 nm (0.0000004 inches). UV light is a component of sunlight; however, it is invisible to the human eye. It has numerous medical and industrial applications, but it can damage living tissue.

### **X-rays:**

[X-rays](#) are roughly classified into two types: soft X-rays and hard X-rays. Soft X-rays comprise the range of the EM spectrum between UV and gamma rays. Soft X-rays have frequencies of about  $3 \times 10^{16}$  to about  $10^{18}$  Hz and wavelengths of about 10 nm ( $4 \times 10^{-7}$  inches) to about 100 picometers (pm), or  $4 \times 10^{-8}$  inches. Hard X-rays occupy the same region of the EM spectrum as gamma rays. The only difference between them is their source:



X-rays are produced by accelerating electrons, while gamma rays are produced by atomic nuclei.

### Gamma-rays:

Gamma-rays are in the range of the spectrum above soft X-rays. Gamma-rays have frequencies greater than about  $10^{18}$  Hz and wavelengths of less than 100 pm ( $4 \times 10^{-9}$  inches). Gamma radiation causes damage to living tissue, which makes it useful for killing cancer cells when applied in carefully measured doses to small regions. Uncontrolled exposure, though, is extremely dangerous to humans.

### LAMDA:

**Lambda** or **lamda** (uppercase  $\Lambda$ , lowercase  $\lambda$ ; [Greek](#): λάμ(β)δα *lám(b)da*) is the 11th letter of the [Greek alphabet](#), representing the sound /l/. In the system of [Greek numerals](#) lambda has a value of 30. Lambda is derived from the [Phoenician Lamed](#)  $\lambda$ . Lambda gave rise to the [Latin L](#) and the [Cyrillic El](#) (Л). The ancient [grammarians](#) and dramatists give evidence to the pronunciation as [la:bda:] (λάβδα) in Classical Greek times. In [Modern Greek](#) the name of the letter, Λάμδα, is pronounced [ˈlam.ða].

### Examples of the symbolic use of uppercase lambda include:

- The [lambda particle](#) is a type of [subatomic particle](#) in [subatomic particle physics](#).
- Lambda is the set of logical axioms in the [axiomatic method](#) of logical deduction in [first-order logic](#).
- Lambda was used as a [shield pattern](#) by the [Spartan army](#). This stood for [Lacedaemon](#) ([Λακεδαίμων](#), *Lakedaímōn*), the name of the [polis](#) of the Spartans, as opposed to the city itself.
- Lambda is the [von Mangoldt function](#) in mathematical [number theory](#).
- In [statistics](#), [Wilks's lambda](#) is used in multivariate analysis of variance ([MANOVA](#) analysis) to compare group means on a combination of dependent variables.
- In the [spectral decomposition of matrices](#), lambda indicates the [diagonal matrix](#) of the [eigenvalues](#) of the [matrix](#).

**Examples of the symbolic use of lowercase lambda include:**

- Lambda indicates the [wavelength](#) of any [wave](#), especially in [physics](#), [electronics engineering](#), and [mathematics](#).
- In [evolutionary algorithms](#),  $\lambda$  indicates the number of offspring that would be generated from  $\mu$  current population in each generation. The terms  $\mu$  and  $\lambda$  are originated from [Evolution strategy](#) notation.
- Lambda indicates the [radioactivity decay constant](#) in [nuclear physics](#) and [radioactivity](#). This constant is very simply related (by a multiplicative constant) to the [half-life](#) of any radioactive material.
- In probability theory, lambda represents the density of occurrences within a time interval, as modeled by the [Poisson distribution](#).

**VELOCITY:**

**Velocity** itself can be **described** as the vector, i.e. both a magnitude (speed) and direction, by which an object in motion moves. In EVE, **velocity** is almost always in units of meters per second (m/s).

- The **velocity** of an object is the [rate of change](#) of its [position](#) with respect to a [frame of reference](#), and is a function of time. Velocity is equivalent to a specification of an object's [speed](#) and direction of [motion](#) (e.g. 60 [km/h](#) to the north). Velocity is a fundamental concept in [kinematics](#), the branch of [classical mechanics](#) that describes the motion of bodies.
- Velocity is a physical [vector quantity](#); both magnitude and direction are needed to define it. The [scalar absolute value \(magnitude\)](#) of velocity is called *speed*, being a coherent derived unit whose quantity is measured in the [SI \(metric system\)](#) as [metres per second](#) (m/s) or as the SI base unit of ( $\text{m} \cdot \text{s}^{-1}$ ). For example, "5 metres per second" is a scalar, whereas "5 metres per second east" is a vector. If there is a change in speed, direction or both, then the object has a changing velocity and is said to be undergoing an [acceleration](#).

**DUALISM OF LIGHT:**

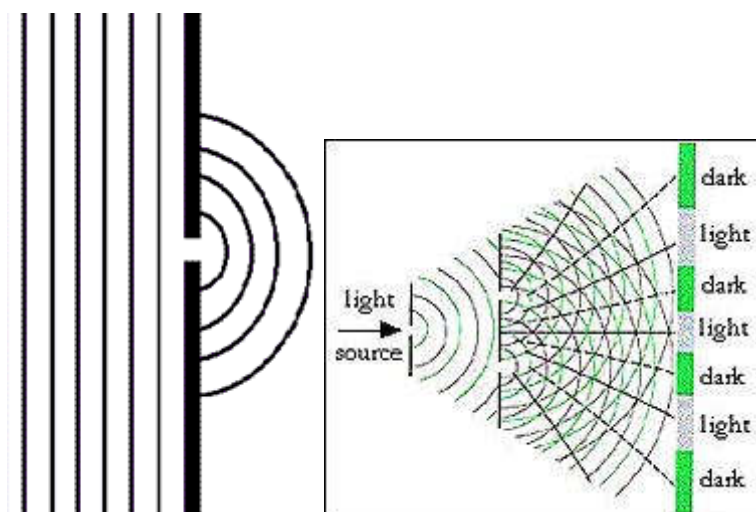
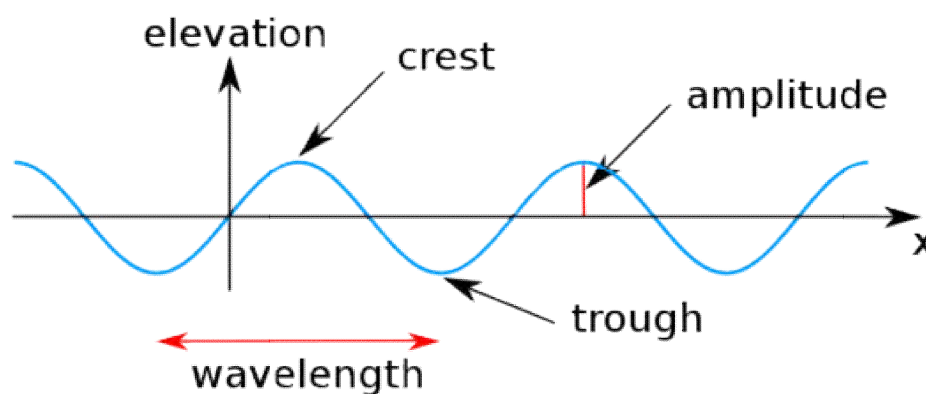
The behaviors of the electron does not allow for it to be observable as a particle and as a wave. The two sided nature of the electron is known as the Wave-Particle Duality: The property of particles behaving as waves and the property of waves behaving as particles as well as waves. Although the duality is not very effective in

large matter. The wave characteristic of the electron implicates many of the electron's particle behaviors.

Planck's Hypothesis of the Quantum Theory states that energy is emitted in quanta, little packets of energy, instead of a continuous emission. He stated that energy emitted is related to the frequency of the light emitted. Planck's hypothesis states that a quantum of energy was related to the frequency by his equation  $E=h\nu$

### Waves & Particles Behaviors of Light:

An easy way to prove the duality between a particle and a wave is to observe light. At the time, many scientists believed that light is a wave. Since light is like waves, it has the ability to diffract, reflect, refract, and interfere etc . . . Yet, light behaved strangely at certain times, and scientists were befuddled until . . .



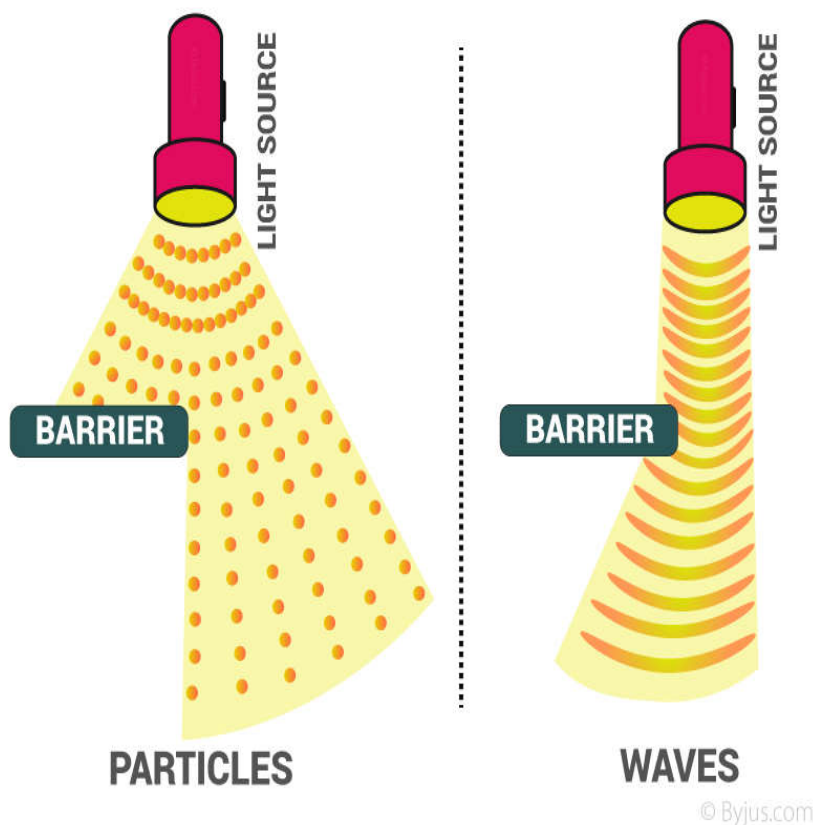
Diffraction Interference

### PARTICLE NATURE OF RADIATION:

Dual Behavior of Electromagnetic Radiation:

The photoelectric effect could be explained considering that radiations consist of small packets of energy called quanta. These packets of energy can be treated as particles. On the other hand, radiations exhibit a phenomenon of interference and diffraction which indicated that they possess wave nature. So it may be concluded that electromagnetic radiations possess dual nature.

1. [Particle nature](#)
2. [Wave nature](#)



Particle Nature of Electromagnetic Radiation:

**Planck's Quantum Theory** – It states, “One photon of light carries exactly one quantum of energy.” Wave theory of radiation cannot explain the phenomena of the photoelectric effect and black body radiation.

*Wave Nature of Electromagnetic Radiation:*

Due to a dispersion of white light, VIBGYOR appears. Vibgyor stands for – Violet, Indigo, Blue, Green, Yellow, Orange, and Red.

Emission & Absorption Spectrum:

Spectra can be divided into two types based on absorption by gas or vapor & white light emission:

1. **Emission Spectrum:** Spectrum due to the emission of white light by gas at high temperature is known as an emission spectrum. This kind of spectrum usually consists of bright lines on the dark background. Emission of energy by electrons generates emission spectrum.
2. **Absorption Spectrum:** The spectrum which occurs due to absorption of white light by gas and transmitted white light, it is termed as an absorption spectrum. Unlike emission spectrum, it consists of dark lines on the bright background. It is due to absorption of energy by electrons.

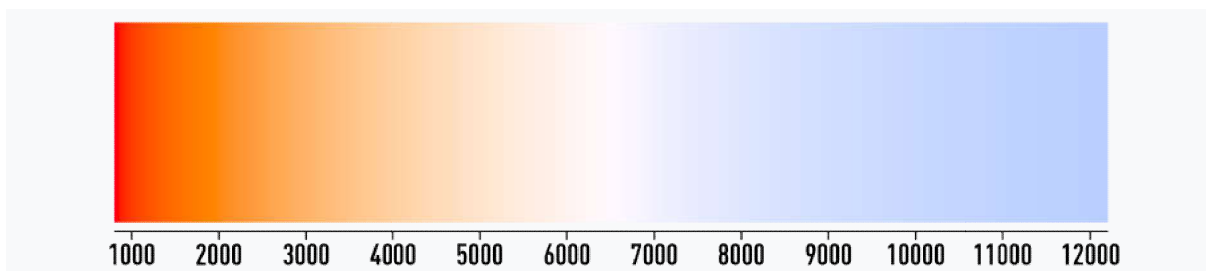
**Spectra can be divided into two types depending on the spectral lines:**

- **Line Spectrum or Atomic Spectrum** – This is made up of distinct lines. When an electron in an atom excites and de-excites, this spectrum occurs. Emission & absorption spectra show the line spectrum.
- **Band Spectrum** – It is a characteristic of a molecule. It consists of closely spaced lines called bands. In a molecule, the vibration & rotation of atoms generates such spectrum.

## BLACK-BODY RADIATION:

**Black-body radiation** is the [thermal electromagnetic radiation](#) within or surrounding a body in [thermodynamic equilibrium](#) with its environment, emitted by a [black body](#) (an idealized opaque, non-reflective body). It has a specific spectrum of wavelengths, inversely related to intensity that depend only on the body's temperature, which is assumed for the sake of calculations and theory to be uniform and constant

All normal ([baryonic](#)) matter emits electromagnetic radiation when it has a temperature above [absolute zero](#). The radiation represents a conversion of a body's internal energy into electromagnetic energy, and is therefore called [thermal radiation](#). It is a [spontaneous process](#) of radiative distribution of [entropy](#).



Color of a black body from 800 K to 12200 K. This range of colors approximates the range of colors of stars of different temperatures, as seen or photographed in the night sky.

Solids, when heated, emit radiation varying over a wide range of wavelengths. For example: when we heat solid color, changes continue with a further increase in temperature. This change in color happens from a lower frequency region to a higher frequency region as

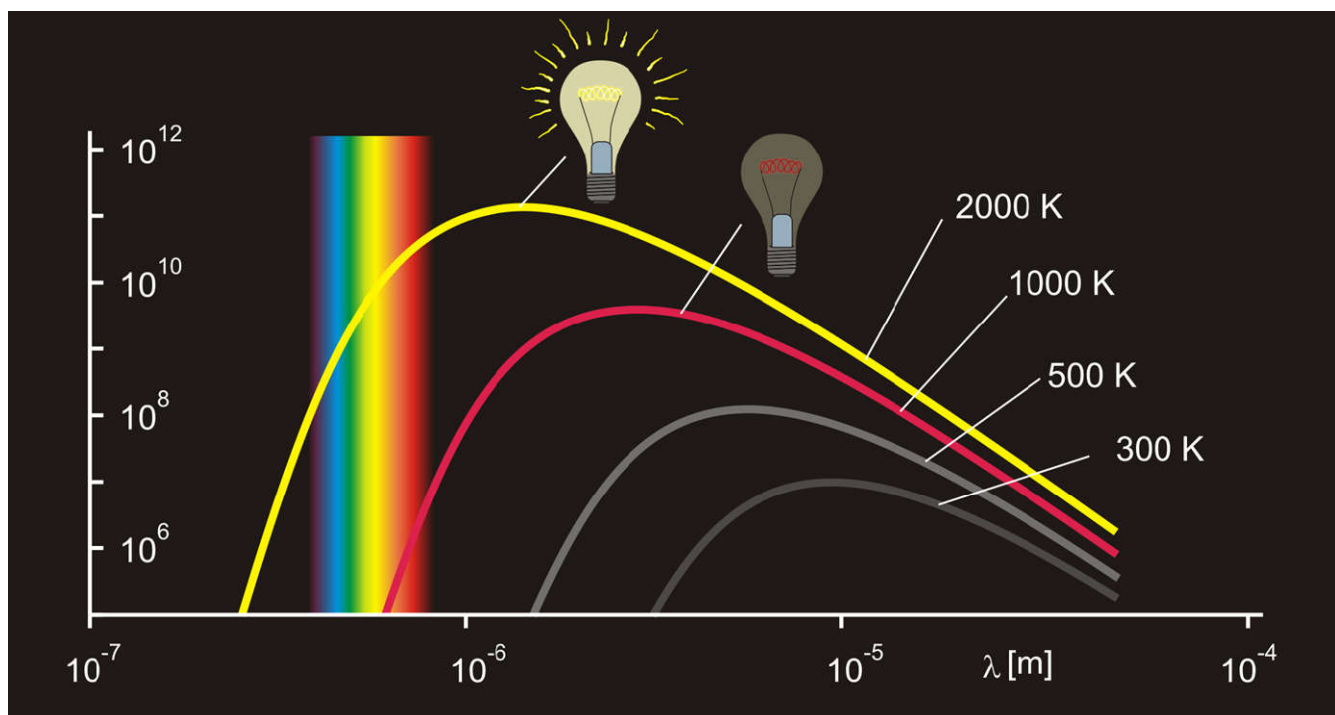
the temperature increases. For example, in many cases, it changes from red to blue. An ideal body which can emit and absorb radiation of all frequencies is called a black body. The radiation emitted by such bodies is called black body radiation.

Thus, we can say that variation of frequency for a black body radiation depends on the temperature. At a given temperature, the intensity of radiation is found to increase with an increase in the wavelength of radiation which increases to a maximum value and then decreases with an increase in the wavelength. This phenomenon couldn't be explained with the help of Maxwell's suggestions. Hence, Planck proposed the Planck's quantum theory to explain this phenomenon.

### PLANCK'S QUANTUM THEORY:

According to Planck's quantum theory,

1. Different atoms and molecules can emit or absorb energy in discrete quantities only. The smallest amount of energy that can be emitted or absorbed in the form of electromagnetic radiation is known as quantum.
2. The energy of the radiation absorbed or emitted is directly proportional to the frequency of the radiation.



Meanwhile, the energy of radiation is expressed in terms of frequency as,

$$E = h \nu$$

Where,

**E** = Energy of the radiation

$h$  = Planck's constant ( $6.626 \times 10^{-34}$  J.s)

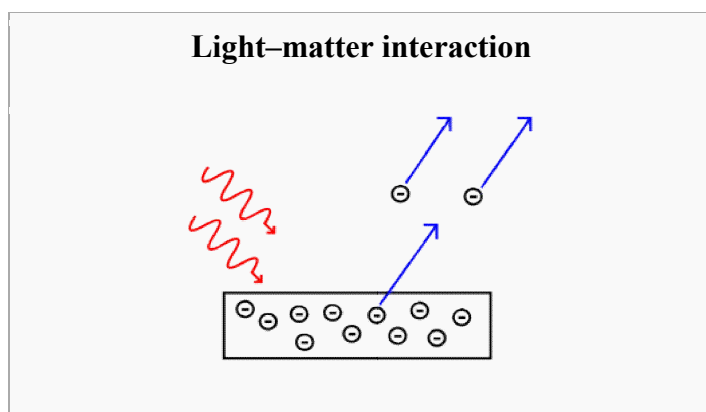
$\nu$  = Frequency of radiation

Interestingly, Planck has also concluded that these were only an aspect of the processes of absorption and emission of radiation. They had nothing to do with the physical reality of the radiation itself. Later in the year 1905, famous German physicist, Albert Einstein also reinterpreted Planck's theory to further explain photoelectric effect. He was of the opinion that if some source of light was focused on certain materials, they can eject electrons from the material. Basically, Planck's work led Einstein in determining that light exists in discrete quanta of energy, or photons.

## PHOTOELECTRIC EFFECT:

The **photoelectric effect** is the emission of [electrons](#) or other *free carriers* when [electromagnetic radiation](#), like [light](#), hits a material. Electrons emitted in this manner can be called *photoelectrons*. This phenomenon is commonly studied in [electronic physics](#) and in fields of [chemistry](#) such as [quantum chemistry](#) and [electrochemistry](#).

According to [classical electromagnetic](#) theory, the photoelectric effect can be attributed to the transfer of [energy](#) from the light to an electron. From this perspective, an alteration in the [intensity](#) of light induces changes in the kinetic energy of the electrons emitted from the metal. According to this theory, a sufficiently dim light is expected to show a time lag between the initial shining of its light and the subsequent emission of an electron.



### Experimental observations of photoelectric emission:

The theory of the source of photoelectric effect must explain the experimental observations of the emission of electrons from an illuminated metal surface.

For a given metal surface, there exists a certain minimum frequency of incident [radiation](#) below which no photoelectrons are emitted. This frequency is called the *threshold frequency*. Increasing the frequency of the incident beam, keeping the number of incident photons fixed (this would result in a proportionate increase in energy) increases the maximum [kinetic energy](#) of the photoelectrons emitted. Thus the stopping [voltage](#) increases (see the experimental setup in the figure). The number of [electrons](#) also changes because of the [probability](#) that each photon results in an emitted electron are a function of [photon energy](#). If

the intensity of the incident radiation of a given frequency is increased, there is no effect on the kinetic energy of each photoelectron.

Above the threshold frequency, the maximum kinetic energy of the emitted photoelectron depends on the frequency of the incident light, but is independent of the intensity of the incident light so long as the latter is not too high.

For a given metal and frequency of incident radiation, the rate at which photoelectrons are ejected is directly proportional to the intensity of the incident light. An increase in the intensity of the incident beam (keeping the frequency fixed) increases the magnitude of the photoelectric current, although the stopping voltage remains the same.

The time lag between the incidence of radiation and the emission of a photoelectron is very small, less than  $10^{-9}$  second.

The direction of distribution of emitted electrons peaks in the direction of [polarization](#) (the direction of the electric field) of the incident light, if it is linearly polarized.

## USES:

### Photomultipliers:

These are extremely light-sensitive vacuum tubes with a [photocathode](#) coated onto part (an end or side) of the inside of the envelope. The photo cathode contains combinations of materials such as cesium, rubidium, and antimony specially selected to provide a low work function, so when illuminated even by very low levels of light, the photocathode readily releases electrons. By means of a series of electrodes (dynodes) at ever-higher potentials, these electrons are accelerated and substantially increased in number through [secondary emission](#) to provide a readily detectable output current. Photomultipliers are still commonly used wherever low levels of light must be detected.

### Image sensors:

[Video camera tubes](#) in the early days of [television](#) used the photoelectric effect, for example, [Philo Farnsworth's "Image dissector"](#) used a screen charged by the photoelectric effect to transform an optical image into a scanned electronic signal.

## COMPTON EFFECT:

Compton scattering is an example of [inelastic scattering](#) of light by a free charged particle, where the wavelength of the scattered light is different from that of the incident radiation. In Compton's original experiment (see Fig. ), the energy of the X ray photon ( $\approx 17$  keV) was very much larger than the binding energy of the atomic electron, so the electrons could be treated as being free. The amount by which the light's wavelength changes is called the **Compton shift**. Although nuclear Compton scattering exists, Compton scattering usually refers to the interaction involving only the electrons of an atom.

The effect is significant because it demonstrates that light cannot be explained purely as a [wave](#) phenomenon. [Thomson scattering](#), the classical theory of an [electromagnetic wave](#) scattered by charged particles, cannot explain shifts in wavelength at low intensity: classically, light of sufficient intensity for the electric field to accelerate a charged particle to a relativistic speed will cause radiation-pressure recoil and an associated Doppler shift of the scattered light, but the effect would become arbitrarily small at sufficiently low light intensities *regardless of wavelength*.



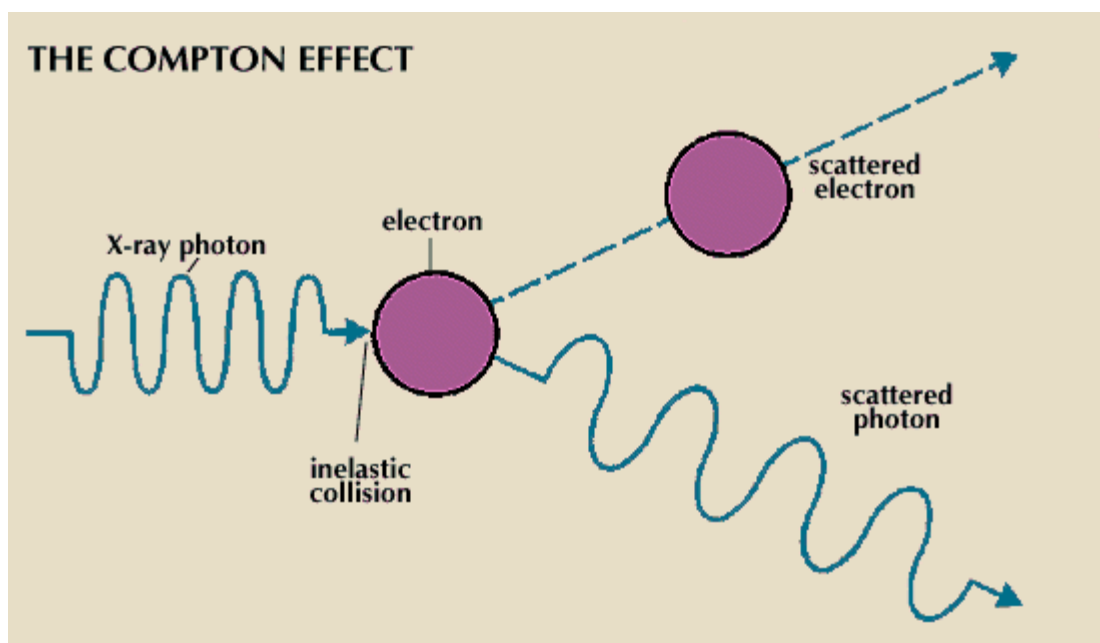
Thus, light behaves as if it consists of particles, if we are to explain low-intensity Compton scattering. Or the assumption that the electron can be treated as free is invalid resulting in the effectively infinite electron mass equal to the nuclear mass (see e.g. the comment below on elastic scattering of X-rays being from that effect). Compton's experiment convinced physicists that light can be treated as a stream of particle-like objects (quanta called photons), whose energy is proportional to the light wave's frequency.

As shown in Fig. , The interaction between an electron and a photon results in the electron being given part of the energy (making it recoil), and a photon of the remaining energy being emitted in a different direction from the original, so that the overall momentum of the system is also conserved.

If the scattered photon still has enough energy, the process may be repeated. In this scenario, the electron is treated as free or loosely bound. Experimental verification of momentum conservation in individual Compton scattering processes by [Bothe](#) and [Geiger](#) as well as by Compton and Simon has been important in disproving the [BKS theory](#).

Compton scattering is one of three competing processes when photons interact with matter. At energies of a few eV to a few keV, corresponding to [visible light](#) through soft X-rays, a photon can be completely absorbed and its energy can eject an electron from its host atom, a process known as the [photoelectric effect](#).

High energy photons of 1.022 MeV and above may bombard the nucleus and cause an electron and a positron to be formed, a process called [pair production](#). Compton scattering is the most important interaction in the intervening energy region.



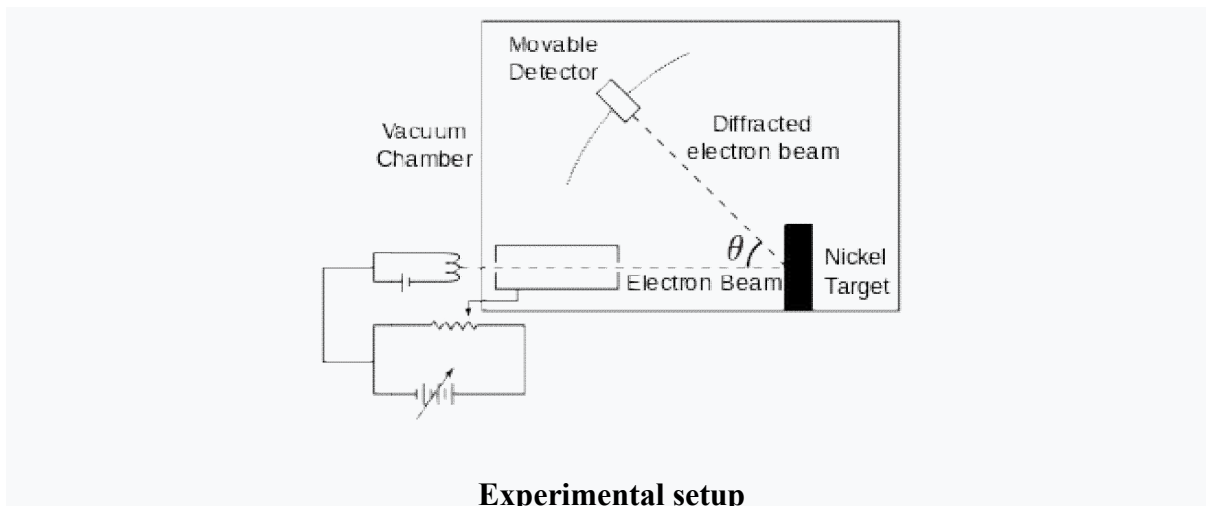
### DAVISSON–GERMER EXPERIMENT:

The **Davison–Germer experiment** was a 1923-27 experiment by [Clinton Davison](#) and [Lester Germer](#) at [Western Electric \(later Bell Labs\)](#), in which electrons, scattered by the surface of a crystal of nickel metal, displayed a diffraction pattern. This confirmed the

[hypothesis](#), advanced by [Louis de Broglie](#) in 1924, of wave-particle duality, and was an experimental milestone in the creation of [quantum mechanics](#).

## Experiments:

Davisson began work in 1921 to study electron bombardment and secondary electron emissions. A series of experiments continued through 1925.



Davisson and Germer's actual objective was to study the surface of a piece of nickel by directing a beam of electrons at the surface and observing how many electrons bounced off at various angles. They expected that because of the small size of electrons, even the smoothest crystal surface would be too rough and thus the electron beam would experience diffused reflection.

The experiment consisted of firing an electron beam (from an [electron gun](#), an [electrostatic particle accelerator](#)) at a nickel crystal, perpendicular to the surface of the crystal, and measuring how the number of reflected electrons varied as the angle between the detector and the nickel surface varied.

The electron gun was a heated tungsten filament that released thermally excited electrons which were then accelerated through an electric potential difference, giving them a certain amount of kinetic energy, towards the nickel crystal.

To avoid collisions of the electrons with other atoms on their way towards the surface, the experiment was conducted in a vacuum chamber. To measure the number of electrons that were scattered at different angles, a [faraday cup](#) electron detector that could be moved on an arc path about the crystal was used. The detector was designed to accept only [elastically scattered electrons](#).

During the experiment, air accidentally entered the chamber, producing an oxide film on the nickel surface. To remove the oxide, Davisson and Germer heated the specimen in a high temperature oven, not knowing that this caused the formerly polycrystalline structure of the nickel to form large single crystal areas with crystal planes continuous over the width of the electron beam.

When they started the experiment again and the electrons hit the surface, they were scattered by nickel atoms in crystal planes (so the atoms were regularly spaced) of the crystal. This, in 1925, generated a diffraction pattern with unexpected peaks.

## DE BROGLIE HYPOTHESIS:

Considering Einstein's relationship of wavelength  $\lambda$  to momentum  $p$ , de Broglie proposed that this relationship would determine the wavelength of any matter, in the relationship:

$$\lambda = h / p$$

recall that  $h$  is Planck's constant

This wavelength is called the *de Broglie wavelength*. The reason he chose the momentum equation over the energy equation is that it was unclear, with matter, whether  $E$  should be total energy, kinetic energy, or total relativistic energy. For photons, they are all the same, but not so for matter.

Assuming the momentum relationship, however, allowed the derivation of a similar de Broglie relationship for frequency  $f$  using the kinetic energy  $E_k$ :

$$f = E_k / h$$

### Alternate Formulations

De Broglie's relationships are sometimes expressed in terms of Dirac's constant,  $\hbar = h / (2\pi)$ , and the angular frequency  $\omega$  and wavenumber  $k$ :

$$p = \hbar * k E_k$$

$$= \hbar * \omega$$

## Experimental Confirmation:

In 1927, physicists Clinton Davisson and Lester Germer, of Bell Labs, performed an experiment where they fired electrons at a crystalline nickel target. The resulting diffraction pattern matched the predictions of the de Broglie wavelength. De Broglie received the 1929 Nobel Prize for his theory (the first time it was ever awarded for a Ph.D. thesis) and Davisson/Germer jointly won it in 1937 for the experimental discovery of electron diffraction (and thus the proving of de Broglie's hypothesis).

Further experiments have held de Broglie's hypothesis to be true, including the quantum variants of the [double slit experiment](#). Diffraction experiments in 1999 confirmed the de Broglie wavelength for the behavior of molecules as large as buckyballs, which are complex molecules made up of 60 or more carbon atoms.

## Significance of the de Broglie Hypothesis:

The de Broglie hypothesis showed that wave-particle duality was not merely an aberrant behavior of light, but rather was a fundamental principle exhibited by both radiation and matter. As such, it becomes possible to use wave equations to describe material behavior, so long as one properly applies the de Broglie wavelength. This would prove crucial to the

development of quantum mechanics. It is now an integral part of the theory of atomic structure and particle physics.

### HEISENBERG UNCERTAINTY PRINCIPLE :

Quantum mechanics is the discipline of measurements on the minuscule scale. That measurements are in macro and micro physics can lead to very diverse consequences. Heisenberg uncertainty principle or basically uncertainty principle is a vital concept in Quantum mechanics. Uncertainty principle says that both position and momentum of a particle cannot be determined at the same time and accurately. The result of position and momentum is at all times greater than  $h/4\pi$ . The formula for Heisenberg Uncertainty principle is articulated as,

$$\Delta x \Delta p \geq \frac{h}{4\pi}$$

$\Delta x =$  **Uncertainty of Position**

$\Delta p =$  **Uncertainty of Momentum**

### SCHRÖDINGER EQUATION:

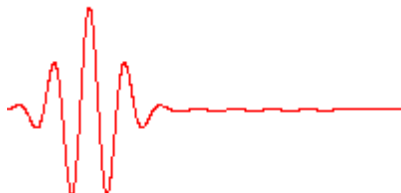
The **Schrödinger equation** is a [linear partial differential equation](#) that describes the [wave function](#) or state function of a quantum-mechanical system. It is a key result in [quantum mechanics](#), and its discovery was a significant landmark in the development of the subject. The equation is named after [Erwin Schrödinger](#), who postulated the equation in 1925, and published it in 1926, forming the basis for the work that resulted in his [Nobel Prize in Physics](#) in 1933

Schrodinger's equation describes the wave function of a quantum mechanical system, which gives probabilistic information about the location of a particle and other observable quantities such as its momentum. The most important thing you'll realize about quantum mechanics after learning about the equation is that the laws in the quantum realm are **very different** from those of classical mechanics.

The diagram shows the Schrödinger wave equation:  $\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2} (E - V)\psi = 0$ . Arrows point from text labels to parts of the equation: 'Second derivative with respect to X' points to  $\frac{\partial^2 \psi}{\partial x^2}$ ; 'Shrodinger Wave Function' points to  $\psi$ ; 'Position' points to  $x$ ; 'Energy' points to  $E$ ; and 'Potential Energy' points to  $V$ .

### Time-dependent equation:

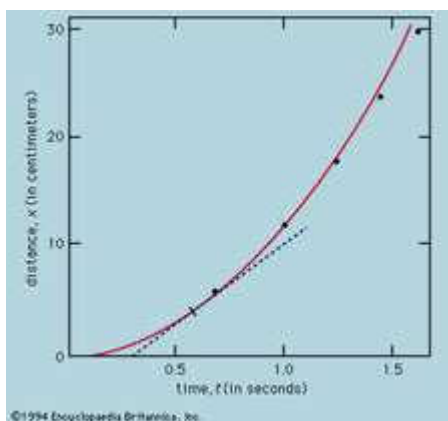
The form of the Schrödinger equation depends on the physical situation (see below for special cases). The most general form is the time-dependent Schrödinger equation (TDSE), which gives a description of a system evolving with time:



A [wave function](#) that satisfies the nonrelativistic Schrödinger equation with  $V = 0$ . In other words, this corresponds to a particle traveling freely through empty space. The [real part](#) of the [wave function](#) is plotted here.

Schrödinger expressed de Broglie's [hypothesis](#) concerning the wave behaviour of matter in a [mathematical form](#) that is adaptable to a variety of physical problems without additional arbitrary assumptions.. According to classical mechanics, if a particle of mass  $m_e$  is subjected to a force such that its [potential energy](#) is  $V(x, y, z)$  at position  $x, y, z$ , then the sum of  $V(x, y, z)$  and the [kinetic energy](#)  $p^2/2m_e$  is equal to a constant, the total [energy](#)  $E$  of the particle. Thus,

$$\frac{p^2}{2m_e} + V(x, y, z) = E. \quad (6)$$



principles of physical science: Rise of quantum mechanics

The idea of the quantum was introduced by the German physicist Max Planck in 1900 in response to the problems posed by the spectrum of radiation...

It is assumed that the particle is bound—i.e., confined by the potential to a certain region in [space](#) because its energy  $E$  is insufficient for it to escape. Since the potential varies with position, two other quantities do also: the momentum and, hence, by extension from the de Broglie relation, the wavelength of the wave. Postulating a [wave function](#)  $\Psi(x, y, z)$  that varies with position, Schrödinger replaced  $p$  in the above energy equation with a [differential operator](#) that embodied the de Broglie relation. He then showed that  $\Psi$  satisfies the [partial differential equation](#)

$$-\frac{\hbar^2}{2m_e} \left( \frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \right) + V(x, y, z)\Psi = E\Psi. \quad (7)$$

This is the (time-independent) [Schrödinger wave equation](#), which established [quantum mechanics](#) in a widely applicable form. An important advantage of Schrödinger's theory is that no further arbitrary quantum conditions need be postulated. The required quantum results follow from certain reasonable restrictions placed on the wave function—for example, that it should not become infinitely large at large distances from the centre of the potential.

### Physical significance of $\Psi$ and $\Psi^2$ :

Schrödinger applied his equation to the [hydrogen](#) atom, for which the potential function, given by classical electrostatics, is proportional to  $-e^2/r$ , where  $-e$  is the [charge](#) on the electron.

The nucleus (a [proton](#) of charge  $e$ ) is situated at the origin, and  $r$  is the distance from the origin to the position of the electron. Schrödinger solved the equation for this particular potential with straightforward, though not elementary, mathematics. Only certain discrete values of  $E$  lead to acceptable functions  $\Psi$ . These functions are characterized by a trio of integers  $n, l, m$ , termed [quantum numbers](#).

The values of  $E$  depend only on the integers  $n$  (1, 2, 3, etc.) and are identical with those given by the [Bohr theory](#). The quantum numbers  $l$  and  $m$  are related to the angular momentum of the electron; Square root of  $\sqrt{l(l+1)}\hbar$  is the magnitude of the angular momentum, and  $m\hbar$  is its component along some physical direction.

The square of the wave function,  $\Psi^2$ , has a physical interpretation. Schrödinger originally supposed that the electron was spread out in space and that its density at point  $x, y, z$  was given by the value of  $\Psi^2$  at that point. Almost immediately [Born](#) proposed what is now the accepted interpretation—namely, that  $\Psi^2$  gives the probability of finding the electron at  $x, y, z$ . The distinction between the two interpretations is important. If  $\Psi^2$  is small at a particular position, the original interpretation implies that a small fraction of an electron will always be detected there. In Born's interpretation, nothing will be detected there most of the time, but, when something is observed, it will be a whole electron. Thus, the concept of the electron as a point particle moving in a well-defined path around the nucleus is replaced in [wave mechanics](#) by clouds that describe the probable locations of electrons in different states.

**All the Best**