

**(i) Concepts in chemistry for engineering****Course Objective**

- To understand the terminologies of atomic and molecular structure
- To study the basics of Periodic properties, Intermolecular forces
- To study about spectroscopic technique
- To understand the thermodynamic functions
- To comprehend the basic organic chemistry and to synthesis simple drug.

**Course Outcomes**

1. Analyse microscopic chemistry in terms of atomic and molecular orbitals and intermolecular forces.
2. Rationalise periodic properties such as ionization potential, electronegativity, oxidation states and electronegativity.
3. Distinguish the ranges of the electromagnetic spectrum used for exciting different molecular energy levels in various spectroscopic techniques
4. Rationalise bulk properties and processes using thermodynamic considerations.
5. List major chemical reactions that are used in the synthesis of molecules.
6. Integrate the chemical principles in the projects undertaken in field of engineering and technology

**UNIT I - Atomic and molecular structure**

Schrodinger equation. Particle in a box solutions and their applications. Equations for atomic and molecular orbitals. Energy level diagrams of diatomic molecules. Pi-molecular orbitals of butadiene and benzene and aromaticity. Introduction to Crystal field theory.

**UNIT II - Periodic properties, Intermolecular forces and potential energy surfaces**

Effective nuclear charge, penetration of orbitals, variations of s, p, d and f orbital energies of atoms in the periodic table, electronic configurations, atomic and ionic sizes, ionization energies, electron affinity and electronegativity, polarizability, oxidation states, coordination numbers. Ionic, dipolar and van Der Waals interactions. Equations of state of real gases and critical phenomena.

**UNIT III - Spectroscopic techniques and applications**

Spectroscopy (Principles and Instrumentation only). Electronic spectroscopy. Vibrational and rotational spectroscopy. Applications. Surface characterization techniques SEM and TEM. Fluorescence and its applications in medicine.

#### **UNIT IV - Use of free energy in chemical equilibria**

Thermodynamic functions: energy, entropy and free energy. Significance of entropy and free energies. Free energy and emf. Cell potentials, the Nernst equation and applications. Acid base, oxidation, reduction and solubility equilibria. Use of free energy considerations in metallurgy through Ellingham diagrams.

#### **UNIT V - Organic reactions and synthesis of a drug molecule**

Introduction to organic reactions and its mechanism involving substitution, addition, elimination, oxidation, reduction, cyclization and ring opening. Synthesis of a commonly used drug molecule.

#### **SUGGESTED READINGS**

1. B. H. Mahan, (2010). University chemistry, Pearson Education,
2. M. J. Sienko and R. A. Plane, Chemistry: Principles and Applications.
3. C. N. Banwell, (1994) Fundamentals of Molecular Spectroscopy, McGraw-Hill,.
4. B. L. Tembe, Kamaluddin and M. S. Krishnan, Engineering Chemistry (NPTEL Web-book)
5. P. W. Atkins, (2009). Physical Chemistry, Oxford University Press,
6. K. P. C. Volhardt and N. E. Schore, (2014). 5th Edition, Organic Chemistry: Structure and Function, W.H. Freeman,
7. P C Jain & Monica Jain, (2015). Engineering Chemistry, Dhanpat Rai Publishing Company,



**KARPAGAM**  
ACADEMY OF HIGHER EDUCATION  
(Deemed to be University)  
(Established Under Section 3 of UGC Act, 1956)

# KARPAGAM ACADEMY OF HIGHER EDUCATION

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(Established Under Section 3 of UGC Act, 1956)

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## Department of Science and Humanities

### LECTURE PLAN

### CHEMISTRY I

**TOTAL HOURS: 50**

#### UNIT I Atomic and molecular structure

NUMBER OF HOURS REQUIRED 10

S. No.	Topics	Hours
1	Introduction	1
2	Schrodinger equation - Particle in a box solutions	1
3	Equations for atomic and molecular orbitals	1
4	Energy level diagrams of diatomic molecules	1
5	Tutorial	1
6	Pi-molecular orbitals of butadiene	1
7	Pi-molecular orbitals of benzene	1
8	Aromaticity	1
9	Introduction to Crystal field theory	1
10	Tutorial	1

#### UNIT II Periodic properties, Intermolecular forces and potential energy surfaces

NUMBER OF HOURS REQUIRED 10

S. No.	Topics	Hours
1	Introduction	1
2	Effective nuclear charge, penetration of orbitals,	1
3	Variations of s, p, d and f orbital energies of atoms in the periodic table	1
4	Electronic configurations, atomic and ionic sizes	1
5	Tutorial	1
6	Ionization energies, electron affinity and electronegativity	1
7	Polarizability, oxidation states, Coordination numbers	1
8	Ionic, dipolar and van Der Waals interactions	1
9	Equations of state of real gases and critical phenomena	1
10	Tutorial	1



## UNIT III Spectroscopic techniques and applications

NUMBER OF HOURS REQUIRED 10

S. No.	Topics	Hours
1	Electronic spectroscopy - Principles	1
2	Electronic spectroscopy - Instrumentation	1
3	Vibrational spectroscopy - Principles	1
4	Vibrational spectroscopy - Instrumentation	1
5	Tutorial	1
6	Rotational spectroscopy - Principles	1
7	Rotational spectroscopy - Instrumentation	1
8	Surface characterization techniques	1
9	Fluorescence and its applications in medicine	1
10	Tutorial	1

## UNIT IV Use of free energy in chemical equilibria

NUMBER OF HOURS REQUIRED 10

S. No.	Topics	Hours
1	Thermodynamic functions: energy, entropy and free energy	1
2	Significance of entropy and free energies	1
3	EMF and Cell potentials	1
4	Nernst equation and applications	1
5	Tutorial	1
6	Acid base concepts	1
7	Oxidation and reduction	1
8	solubility equilibria	1
9	Use of free energy considerations in metallurgy through Ellingham diagrams.	1
10	Tutorial	1



## UNIT V Organic reactions and synthesis of a drug molecule

NUMBER OF HOURS REQUIRED 10

S. No.	Topics	Hours
1	Substitution Reactions and its mechanism	1
2	Addition Reactions and its mechanism	1
3	Elimination Reactions and its mechanism	1
4	Oxidation - Reactions	1
5	Tutorial	1
6	Reduction - Reactions	2
7	Cyclization - Reactions	1
8	Ring opening - Reactions	1
9	Synthesis of a commonly used drug molecule	1
10	Tutorial	1

### Suggested Text Books

S. No.	Author(s) Name	Title of the book	Publisher	Year of Publication
1	B. H. Mahan	University chemistry	Pearson Education	2010
2	M. J. Sienko and R. A. Plane	Chemistry: Principles and Applications		
3	C. N. Banwell	Fundamentals of Molecular Spectroscopy	McGraw-Hill	1994
4	B. L. Tembe, Kamaluddin and M. S. Krishnan	Engineering Chemistry (NPTEL Web-book)		
5	P. W. Atkins	Physical Chemistry	Oxford University Press	2009
6	K. P. C. Volhardt and N. E. Schore, 5th Edition	Organic Chemistry: Structure and Function	W.H. Freeman	2014
7	P C Jain & Monica Jain	Engineering Chemistry	Dhanpat Rai Publishing Company	2015

### **Atom**

An atom is defined as the very smallest particle of an element that can take part in a chemical reaction. An atom of an element which cannot breakup during chemical reactions. An atom is made up of subatomic particles which are protons, neutrons and electrons.

### **Subatomic particles:**

The particles present in an atom are called sub atomic particles. They are protons, neutrons and electrons. Protons and neutrons are found in the nucleus. The electrons revolve round the nucleus in different shells.

### **Protons:**

Protons are present in the nucleus. It is positively charged particles with the mass equal to  $1.672 \times 10^{-27}$  kg. Protons were discovered by Goldstein in 1886. Charge of proton is +1.

### **Neutrons:**

Neutrons are found in the nucleus. Neutrons are neutral particles with mass almost equal to that of a proton. Neutrons were discovered by James Chadwick in 1932. It is neutral charge. Charge of neutrons is zero.

### **Electrons:**

Electrons are moving around the nucleus. It is negatively charged particles with negligible mass. The charge of electron is  $1.60 \times 10^{-19}$  coulombs. Its mass is equal to  $9.1 \times 10^{-31}$  kg/electron. Electron were discovered by J.J.Thomson. Charge of proton is -1.

### **Atomic number:**

Atomic number of an element is defined as the number of protons or number of electrons present in an atom. The atomic number is denoted by Z.

### **Mass number:**

The total number of protons and neutrons in an atom is called its mass number. It is represented as Z.

### **Molecules:**

Two or more atoms of the same elements and different elements combine to form molecules. Molecules can exist freely. They are the smallest particles of elements or compounds, which can exist in free state.

Molecules are classified as given below

- (1) Mono atomic molecules
- (2) Diatomic molecules
  - (a) Homo diatomic molecules
  - (b) Hetero diatomic molecules
- (3) Poly atomic molecules

(1) Mono atomic molecules

The molecules which contain only one atom are called mono atomic molecules

Ex: He, Ag, C, Ne, Cu.

(2) Diatomic molecules

The molecules which are made up of two atoms are called diatomic molecules.

There are two types of diatomic molecules. Based on the elements present, diatomic molecules are classified as follows

- (a) Homo diatomic molecules: These are diatomic molecules that contain two atoms of the same element. Ex:  $H_2$ ,  $Cl_2$ ,  $O_2$ ,  $N_2$ ,  $F_2$ ,  $Br_2$ .
- (b) Hetero diatomic molecules: These are diatomic molecules that contain two atoms of different elements. Ex:  $HCl$ ,  $HBr$ ,  $CO$ ,  $NaCl$ ,  $NO$
- (c) Poly atomic molecules: These are molecules that contain more than two atoms of one element or different elements. Ex:  $O_3$ ,  $H_2O$ ,  $CO_2$ ,  $NH_3$ ,  $H_2SO_4$ .

**Wave number:** The number of waves in a unit distance.

**Wave length:** The distance between peaks (high points) is called wavelength.

**Wave function:** A function that satisfies a wave equation and describes the properties of a wave.

**Amplitude:** The amplitude of a periodic variable is a measure of its change over a single period (such as time or spatial period).

**Difference between a particle and a wave**

- A particle occupies a well defined position in space i.e a particle is localized in space. Eg. grain of a seed, a ball etc.
- ✓ A wave is spread out in space. Ex: Throwing a stone in a pond of water. The sound of the speaker reaches everybody in the audience. A wave is delocalized in space.

- When a particular space is occupied by one particle. The same space cannot be occupied simultaneously by another particle. In other words, particles don't interfere.

✓ Two or more waves can exist in the same region of space. Hence interfere.

### **Difference between orbit and orbital**

(i) **Orbit** is a well defined circular path around the nucleus in which an electron revolves. The number of electrons that can be accommodated in each shell or orbit is given by the formula  $2n^2$  where  $n$  is the number of the shell or orbit.

First shell  $n=1 = 2 \times 1^2 = 2$  electrons (K shell or K orbit)

Second shell  $n=2 = 2 \times 2^2 = 8$  electrons (L shell or L orbit)

Third shell  $n=3 = 2 \times 3^2 = 18$  electrons (M shell or M orbit)

Fourth shell  $n=4 = 2 \times 4^2 = 32$  electrons (N shell or N orbit)

**Orbital** -represents the region in the space around the nucleus in which the probability of finding- the electron is maximum. Ex: shape of s orbital that orbital present electron cloud where the probability of electron is zero.

(ii) Orbit represents the planar motion of the electron.

Orbital represents the 3-D motion of an electron around the nucleus.

(iii) Orbit gives a definite path of an electron

Orbital does not specify definite path.

(iv) All the orbits are circular

Orbitals have different shapes e.g. s-orbitals is spherical while p-orbital is dumb bell shaped.

(v) Orbits do not have directional characteristics. So they can not explain the shape of the molecules.

Except s-orbitals, all the other orbitals have directional characteristics. So they can explain the shape of molecules.

(vi) An orbit can accommodate electrons equal to  $2n^2$ . An orbital can not accommodate more than two electrons.

(vii) Orbit concept is not accordance with uncertainty principle

Orbital concept is in accordance with the uncertainty principle.



### Heisenberg's Uncertainty Principle

Werner Heisenberg's in 1927 pointed out that "we can never measure simultaneously and accurately both the position and velocity of an electron"

This principle states that "It is impossible to determine exactly both the position and the momentum (velocity) of an electron or any other moving particle at the same time.

Mathematically, Uncertainty principle can be put as

$$\Delta x \cdot \Delta p \geq h / 4\pi$$

$\Delta x$  is the uncertainty in the position of the particle.

$\Delta p$  is the uncertainty in the momentum of the particle.

If the momentum (velocity), he measured accurately, a measurement of the position of the particle corresponding less accuracy.

On other hand, if the position is determined with the accuracy, the momentum becomes less accuracy known as uncertain. Thus certainty determination of one property introduces uncertainty of determination of the other.

### De-Broglie's equation:

De-broglie derived the relationship between the magnitude of the wavelength associated with the mass 'm' of a moving body and its velocity.

Planks Quantum theory

$$E = h\nu \quad (1)$$

Einstein relationship

$$E = mc^2 \quad (2)$$

$$\text{Equ (1) = (2)}$$

$$h\nu = mc^2 \quad \nu = c/\lambda$$

$$h \times c/\lambda = mc^2$$

$$\lambda = h/mc$$

Here 'c' is the velocity of photon which is replaced by velocity of particle 'v'.

$$\lambda = h/mv \text{ or } \lambda = h/mp$$

$$\text{Here } mv = p$$

The above equation is called as de Broglie's equation. De Beoglie equation explained electrons behave as dual character i.e., both particle and wave nature.

**Schrodinger wave equation:**

Calculation of the probability of finding the electron at various points in an atom was the problem before schrodinger. Schrodinger equation is the basic law in Quantum mechanics and is based upon the idea of a electron as “standing wave” around the nucleus.

The wave equation of stationary wave associated with particle in terms of coordinate system is

$$\psi = A \sin 2\pi x/\lambda \quad (1)$$

Where  $\psi$  is the amplitude of wave function, A is the constant (maximum value of  $\psi$ ), x is the displacement in the given direction and  $\lambda$  is the wave length.

Differentiate equation (1) with respect to ‘x’, we get

$$d\psi / dx = A \cos 2\pi x/\lambda \quad (2\pi/\lambda) \quad (2)$$

Differenciate again equation (2) with respect to ‘x’, we get

$$\begin{aligned} d^2\psi/dx^2 &= - (2\pi/\lambda)^2 A \sin 2\pi x/\lambda \\ d^2\psi/dx^2 &= - 4\pi^2/\lambda^2 A \sin 2\pi x/\lambda \end{aligned} \quad (3)$$

Equation 1 and 3, we get

$$d^2\psi/dx^2 = - 4\pi^2/\lambda^2 \psi$$

Rearrange the above equation

$$\lambda^2 = - 4\pi^2\psi / d^2\psi/dx^2 \quad (4)$$

According to de-Broglies equation

$$\lambda = h/mv$$

Square in both side

$$\lambda^2 = h^2 / m^2v^2$$

Rearrange the above equation

$$m^2v^2 = h^2/\lambda^2$$

$$(m \times m) \times v^2 = h^2/\lambda^2$$

$$mv^2 = h^2/\lambda m \quad (5)$$

The kinetic energy of particle of mass ‘m’ and velocity ‘v’ is given by

$$K.E = \frac{1}{2} mv^2 \quad (6)$$

Put the value of equation (5) in equation (6), we get

$$K.E = \frac{1}{2} h^2/m\lambda^2$$

Put the value of  $\lambda^2$  from equation (4)

$$K.E = -\frac{1}{2} \times \frac{h^2}{m} \times \frac{1}{4\pi^2} \psi \times \frac{d^2\psi}{dx^2}$$

$$K.E = -\frac{h^2}{8\pi^2 m} \psi \times \frac{d^2\psi}{dx^2}$$

As we know that

$$\text{Total Energy (E)} = K.E + P.E$$

$$E - P.E = K.E$$

$$E - P.E = -\frac{h^2}{8\pi^2 m} \psi \times \frac{d^2\psi}{dx^2}$$

Rearrange this equation

$$\frac{d^2\psi}{dx^2} = -\frac{8\pi^2 m}{h^2} \times \psi (E - P.E)$$

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} \times \psi (E - P.E) = 0$$

This is schrodinger wave equation in one dimension (x). If it is written for a particle whose motion is described by three space coordinates (x,y,z)

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2 m}{h^2} \times \psi (E - P.E) = 0$$

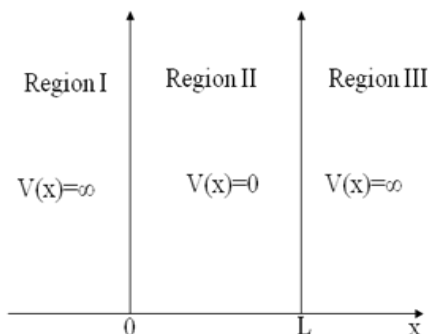
This equation is called the schrodinger wave equation.

$$\Delta^2\psi + \frac{8\pi^2 m}{h^2} \times \psi (E - P.E) = 0$$

$\Delta$  is known as Laplacian operator.

### **Schrodinger wave equations for a particle in one dimensional box**

One dimensional box is the main application of Schrodinger wave equation.



Consider a one dimensional box with long walls. A particle is placed inside it. The length of the base be 'L'. A particle that is constrained to move only in X direction from  $x=0$  to  $x=L$

In X direction where a particle is moving in the x-direction only. The boundary of this box is  $X=0$ ,  $X=L$  where a particle is moving two boundaries only along the x-axis.

A particle is moving inside a box. It cannot come outside a box. So the probability of finding the particle outside the box will be '0'. The particle is moving inside the box, the potential energy  $V=0$ .

Therefore, the potential energy in outside a box is infinitive.

$$V = \infty$$

The Schrodinger equation in one dimension is (i.e., a particle is moving x-direction only)

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2} (E-PE) \times \psi = 0 \quad \text{Where PE} = V$$

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2} (E-V) \times \psi = 0$$

Now, there are two conditions

(i) Outside the box  $V = \infty$

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2} (E-\infty) \times \psi = 0$$

This is possible only when  $\psi = 0$  i.e., probability of finding particle is not present outside the box.

(ii) Inside the box  $V=0$

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2} (E-0) \times \psi = 0$$

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2} \times E\psi = 0 \quad (1)$$

Now we can replace  $\frac{8\pi^2m}{h^2} \times E$  by  $k^2$   $K^2 = \frac{8\pi^2m}{h^2} \times E$

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0$$

The above equation (1) has the general solution (i.e., wave function ( $\psi$ ) can be represented in terms of trigonometric function.

$$\Psi(x) = A\sin kx + B\cos kx \quad \text{Where A \& B is arbitrary constants}$$

Here, there are two conditions

(i) When  $x=0$   $\psi(0)=0$

The probability of finding electrons at the boundaries ( $x$ ) is '0'.

Now put the values of  $x$ ,  $\psi$  (in general solution equation)

$$\Psi(x) = A\sin kx + B\cos kx$$

$$0 = A\sin 0 + B\cos 0 \quad \sin 0 = 0 \quad \cos 0 = 1$$

$$B = 0$$

Hence,  $\Psi(x) = A \sin kx$  (2)

(ii) When  $x=L$

$$\Psi(L) = 0$$

Put the value of  $x$ ,  $\psi(L)$  in equation

$$\begin{aligned} 0 &= A \sin KL + B \cos KL \\ &= A \sin KL + 0 \end{aligned}$$

$$A \sin KL = 0 \quad (3)$$

The equation (3) is satisfied if either

(i)  $A=0$

(ii)  $KL = n\pi$

However, if  $A$  &  $B$  become zero  $\psi = 0$  at all values of  $x$ . other solution i.e  $KL = n\pi$

$$K = n\pi/L$$

$n$  values  $n=1,2,3$  but not 0

Now we know  $k^2$  value  $K^2 = 8\pi^2m/h^2E$

$$8\pi^2m/h^2E = n^2\pi^2/L^2$$

$$E = n^2\pi^2/L^2 \times h^2/8\pi^2m$$

$$E = n^2 h^2 / 8mL^2$$

Where  $n$  is the quantum number i.e principle quantum number.  $E$  depends on  $n^2$  which results increased spacing between energy levels as  $n$  increases.

## Forms of wave function

If  **$n=1$**

$$E = h^2 / 8mL^2$$

Similarly  **$n=2$**

$$E = 4h^2 / 8mL^2$$

Similarly  **$n=3$**

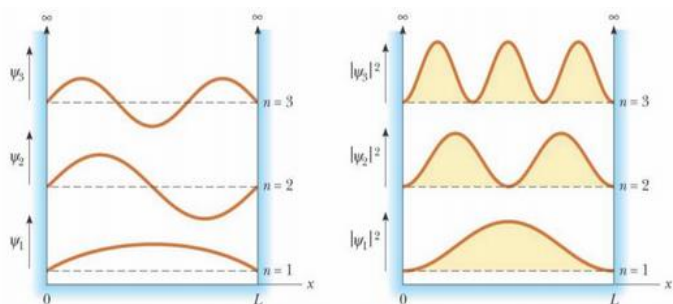
$$E = 9 h^2 / 8mL^2$$

Similarly  **$n=4$**

$$E = 16 h^2 / 8mL^2$$

## Electronic configuration of atoms

The distribution of electrons in different orbitals of the atom of an element is called the electron configuration. The electrons are filled in according to a scheme known as the

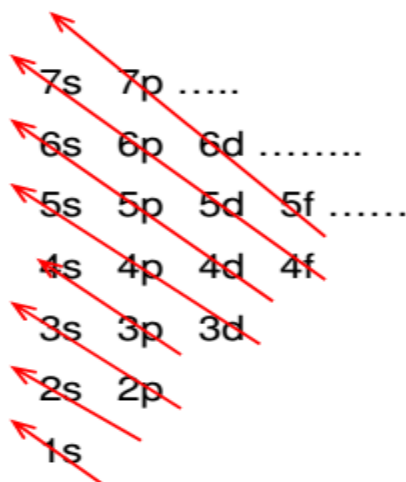


**Aufbau principle** (“building-up”), which corresponds (for the most part) to increasing energy of the subshells:

**“Electrons are filled in the increasing order of energy level.”** i.e., electrons are filled lowest energy level than highest energy level.

**1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f**

The **electron configuration** of an element shows how electrons are distributed in orbitals— which ones are filled and which ones remain vacant. We can predict the electron configuration of most elements, and we can use electron configurations to predict physical and chemical properties of the elements.



## The Pauli -Exclusion Principle

To predict the electron configuration for an atom’s ground state, the lowest energy state for an atom, electrons are put into the orbitals with the lowest energy possible, placing no more than two electrons in an orbital.

*“No more than two electrons can occupy the same orbital, and, if there are two electrons in the same orbital, they must have opposite spins.”*

The order of sub shell filling is related to  $n$ , the principal quantum number, and the angular momentum quantum number. In general, electrons fill orbitals in order of increasing  $(n + l)$  and when two or more subshells have the same  $(n + l)$  value, electrons fill the orbital with the lower  $n$  value.

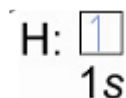
These general rules result in the following orbital filling order:

**1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p, 8s, ...**

The Pauli exclusion principle states that no two electrons within an atom can have the same set of four quantum numbers ( $n$ ,  $l$ ,  $m_l$ , and  $m_s$ ). The limits on possible values for the four quantum numbers means that a single orbital can accommodate no more than two electrons, and when an orbital contains two electrons, those electrons must have opposite spins

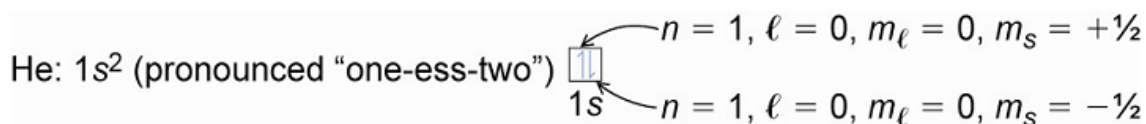
**Hydrogen and Helium** Hydrogen has a single electron that occupies the orbital with the lowest energy, the  $1s$  orbital. Two methods are used to represent this electron configuration. The ***spdf* notation** (also called *spectroscopic notation*) has the general format  $n\Box\#$ , where subshells are listed in the order in which they are filled and the number of electrons occupying each subshell is shown to the right of the subshell as a superscript. The *spdf* notation for hydrogen is

H:  $1s^1$  (pronounced “one-ess-one”)



**Orbital box notation** uses boxes or horizontal lines to represent orbitals and arrows to represent electrons. The electron configuration of hydrogen in orbital box notation is

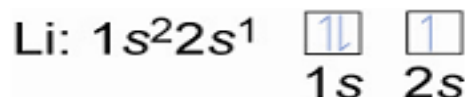
**Helium** has two electrons, and both occupy the lowest-energy  $1s$  orbital. The electron configuration of helium in *spdf* notation and orbital box notation is therefore



Each electron in helium has a unique set of four quantum numbers, as required by the Pauli exclusion principle. Notice that hydrogen and helium are in the first row of the periodic table and both elements fill orbitals in the first energy level ( $1s$ ). Orbital box notations provide information about the number of paired and unpaired electrons in an atom, and that information can be used to determine whether the atoms are paramagnetic or diamagnetic. Hydrogen has one unpaired electron and is a paramagnetic species, whereas helium’s electrons are paired and it is diamagnetic.

## UNIT I-ATOMIC AND MOLECULAR STRUCTURE

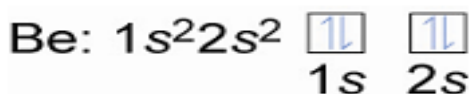
**Lithium to Neon** Lithium has three electrons, two in the  $1s$  orbital and one that is in an orbital in the second energy level. As shown previously, the  $2s$  orbital is lower in energy than the  $2p$  orbitals, so the electron configuration of lithium in *spdf* notation and orbital box notation is



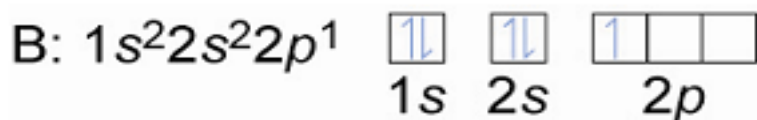
Notice that it would be more correct to draw the orbital box notation electron configuration of lithium as shown below because the  $2s$  orbital is higher in energy than the  $1s$  orbital.



However, it is common to show all orbitals on a horizontal line when writing orbital box notation electron configurations in order to make more efficient use of space. Beryllium has two electrons in the  $1s$  and the  $2s$  orbitals.



Boron has five electrons. Four electrons fill the  $1s$  and  $2s$  orbitals, and the fifth electron is in a  $2p$  orbital. Notice that the orbital box diagram shows all three  $2p$  orbitals even though only one of the  $2p$  orbitals is occupied.

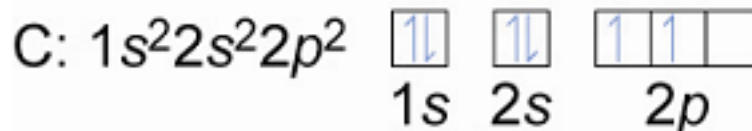


Carbon has six electrons, four in the  $1s$  and  $2s$  orbitals and two in the  $2p$  orbitals. When electrons occupy a subshell with multiple orbitals such as  $2p$ ,

**Hund's rule of maximum multiplicity** applies. This rule states that the filling the orbitals of same energy, pairing of electron does not takes place until all these orbitals are singly filled with electron having parallel spins.

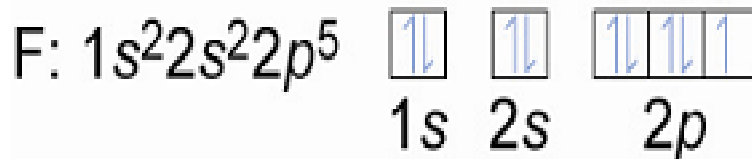
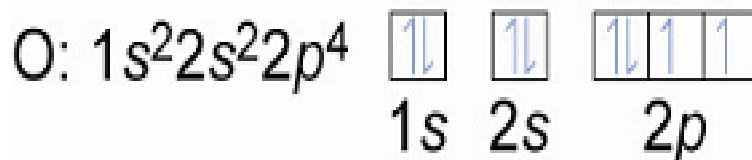
In the case of carbon, this means that the two  $2p$  electrons each occupy a different  $2p$  orbital.



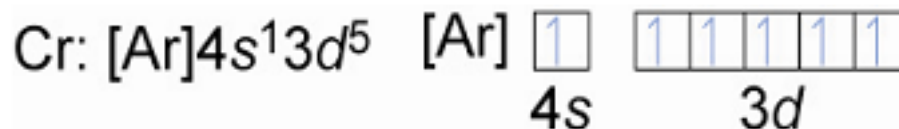


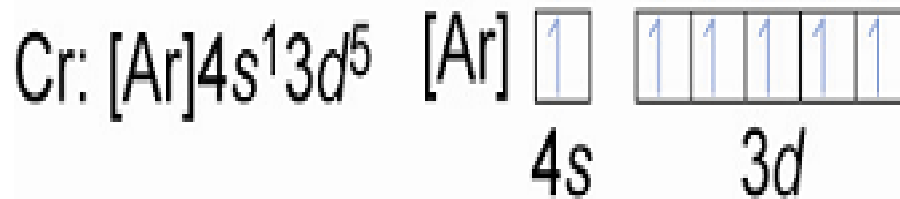
Carbon's electron configuration has two unpaired electrons in the 2p orbitals.

The electron configurations of nitrogen, oxygen, fluorine, and neon are shown here. Notice that the highest-energy orbital for all second-row elements is in the second energy level (2s or 2p).



Both chromium and copper have electron configurations that do not follow the general filling order, for reasons that are complex and related to the similar energies of the 4s and 3d orbitals in multielectron atoms. The electron configurations for these elements should be memorized. The electron configurations for all elements are shown. There are a few exceptions to the general filling order in the heavier elements, but most elements follow the general guidelines that we have used to write electron configurations.





**Chromium:**

- Chromium has 24 electrons so we expect:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$
- $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$  .....Why?
- This gives us two half-filled orbitals (the others are all still full)
- Half full is slightly lower in energy.
- The same principal applies to copper. Copper's electron

**Copper's electron configuration:**

- Copper has 29 electrons so we expect:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^9$
- But the actual configuration is:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$
- This change gives one more filled orbital and one that is half filled.
- Remember these exceptions:  $d^4$  and  $d^9$

## UNIT I-ATOMIC AND MOLECULAR STRUCTURE

Z	Element	Configuration	Z	Element	Configuration	Z	Element	Configuration
1	H	1s <sup>1</sup>	41	Nb	[Kr]5s <sup>1</sup> 4d <sup>4</sup>	81	Tl	[Xe]6s <sup>2</sup> 5d <sup>10</sup> 4f <sup>14</sup> 6p <sup>1</sup>
2	He	1s <sup>2</sup>	42	Mo	[Kr]5s <sup>1</sup> 4d <sup>5</sup>	82	Pb	[Xe]6s <sup>2</sup> 5d <sup>10</sup> 4f <sup>14</sup> 6p <sup>2</sup>
3	Li	[He]2s <sup>1</sup>	43	Tc	[Kr]5s <sup>2</sup> 4d <sup>5</sup>	83	Bi	[Xe]6s <sup>2</sup> 5d <sup>10</sup> 4f <sup>14</sup> 6p <sup>3</sup>
4	Be	[He]2s <sup>2</sup>	44	Ru	[Kr]5s <sup>1</sup> 4d <sup>7</sup>	84	Po	[Xe]6s <sup>2</sup> 5d <sup>10</sup> 4f <sup>14</sup> 6p <sup>4</sup>
5	B	[He]2s <sup>2</sup> 2p <sup>1</sup>	45	Rh	[Kr]5s <sup>1</sup> 4d <sup>8</sup>	85	At	[Xe]6s <sup>2</sup> 5d <sup>10</sup> 4f <sup>14</sup> 6p <sup>5</sup>
6	C	[He]2s <sup>2</sup> 2p <sup>2</sup>	46	Pd	[Kr] 4d <sup>10</sup>	86	Rn	[Xe]6s <sup>2</sup> 5d <sup>10</sup> 4f <sup>14</sup> 6p <sup>6</sup>
7	N	[He]2s <sup>2</sup> 2p <sup>3</sup>	47	Ag	[Kr]5s <sup>1</sup> 4d <sup>10</sup>	87	Fr	[Rn]7s <sup>1</sup>
8	O	[He]2s <sup>2</sup> 2p <sup>4</sup>	48	Cd	[Kr]5s <sup>2</sup> 4d <sup>10</sup>	88	Ra	[Rn]7s <sup>2</sup>
9	F	[He]2s <sup>2</sup> 2p <sup>5</sup>	49	In	[Kr]5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>1</sup>	89	Ac	[Rn]7s <sup>2</sup> 6d <sup>1</sup>
10	Ne	[He]2s <sup>2</sup> 2p <sup>6</sup>	50	Sn	[Kr]5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>2</sup>	90	Th	[Rn]7s <sup>2</sup> 6d <sup>2</sup>
11	Na	[Ne]3s <sup>1</sup>	51	Sb	[Kr]5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>3</sup>	91	Pa	[Rn]7s <sup>2</sup> 6d <sup>1</sup> 5f <sup>2</sup>
12	Mg	[Ne]3s <sup>2</sup>	52	Te	[Kr]5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>4</sup>	92	U	[Rn]7s <sup>2</sup> 6d <sup>1</sup> 5f <sup>3</sup>
13	Al	[Ne]3s <sup>2</sup> 3p <sup>1</sup>	53	I	[Kr]5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>5</sup>	93	Np	[Rn]7s <sup>2</sup> 6d <sup>1</sup> 5f <sup>4</sup>
14	Si	[Ne]3s <sup>2</sup> 3p <sup>2</sup>	54	Xe	[Kr]5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>6</sup>	94	Pu	[Rn]7s <sup>2</sup> 5f <sup>6</sup>
15	P	[Ne]3s <sup>2</sup> 3p <sup>3</sup>	55	Cs	[Xe]6s <sup>1</sup>	95	Am	[Rn]7s <sup>2</sup> 5f <sup>7</sup>
16	S	[Ne]3s <sup>2</sup> 3p <sup>4</sup>	56	Ba	[Xe]6s <sup>2</sup>	96	Cm	[Rn]7s <sup>2</sup> 6d <sup>1</sup> 5f <sup>7</sup>
17	Cl	[Ne]3s <sup>2</sup> 3p <sup>5</sup>	57	La	[Xe]6s <sup>2</sup> 5d <sup>1</sup>	97	Bk	[Rn]7s <sup>2</sup> 5f <sup>9</sup>
18	Ar	[Ne]3s <sup>2</sup> 3p <sup>6</sup>	58	Ce	[Xe]6s <sup>2</sup> 5d <sup>1</sup> 4f <sup>1</sup>	98	Cf	[Rn]7s <sup>2</sup> 5f <sup>10</sup>
19	K	[Ar]4s <sup>1</sup>	59	Pr	[Xe]6s <sup>2</sup> 4f <sup>3</sup>	99	Es	[Rn]7s <sup>2</sup> 5f <sup>11</sup>
20	Ca	[Ar]4s <sup>2</sup>	60	Nd	[Xe]6s <sup>2</sup> 4f <sup>4</sup>	100	Fm	[Rn]7s <sup>2</sup> 5f <sup>12</sup>
21	Sc	[Ar]4s <sup>2</sup> 3d <sup>1</sup>	61	Pm	[Xe]6s <sup>2</sup> 4f <sup>5</sup>	101	Md	[Rn]7s <sup>2</sup> 5f <sup>13</sup>
22	Ti	[Ar]4s <sup>2</sup> 3d <sup>2</sup>	62	Sm	[Xe]6s <sup>2</sup> 4f <sup>6</sup>	102	No	[Rn]7s <sup>2</sup> 5f <sup>14</sup>
23	V	[Ar]4s <sup>2</sup> 3d <sup>3</sup>	63	Eu	[Xe]6s <sup>2</sup> 4f <sup>7</sup>	103	Lr	[Rn]7s <sup>2</sup> 6d <sup>1</sup> 5f <sup>14</sup>
24	Cr	[Ar]4s <sup>1</sup> 3d <sup>5</sup>	64	Gd	[Xe]6s <sup>2</sup> 5d <sup>1</sup> 4f <sup>7</sup>	104	Rf	[Rn]7s <sup>2</sup> 6d <sup>2</sup> 5f <sup>14</sup>
25	Mn	[Ar]4s <sup>2</sup> 3d <sup>5</sup>	65	Tb	[Xe]6s <sup>2</sup> 4f <sup>9</sup>	105	Db	[Rn]7s <sup>2</sup> 6d <sup>3</sup> 5f <sup>14</sup>
26	Fe	[Ar]4s <sup>2</sup> 3d <sup>6</sup>	66	Dy	[Xe]6s <sup>2</sup> 4f <sup>10</sup>	106	Sg	[Rn]7s <sup>2</sup> 6d <sup>4</sup> 5f <sup>14</sup>
27	Co	[Ar]4s <sup>2</sup> 3d <sup>7</sup>	67	Ho	[Xe]6s <sup>2</sup> 4f <sup>11</sup>	107	Bh	[Rn]7s <sup>2</sup> 6d <sup>5</sup> 5f <sup>14</sup>
28	Ni	[Ar]4s <sup>2</sup> 3d <sup>8</sup>	68	Er	[Xe]6s <sup>2</sup> 4f <sup>12</sup>	108	Hs	[Rn]7s <sup>2</sup> 6d <sup>6</sup> 5f <sup>14</sup>
29	Cu	[Ar]4s <sup>1</sup> 3d <sup>10</sup>	69	Tm	[Xe]6s <sup>2</sup> 4f <sup>13</sup>	109	Mt	[Rn]7s <sup>2</sup> 6d <sup>7</sup> 5f <sup>14</sup>
30	Zn	[Ar]4s <sup>2</sup> 3d <sup>10</sup>	70	Yb	[Xe]6s <sup>2</sup> 4f <sup>14</sup>	110	Ds	[Rn]7s <sup>2</sup> 6d <sup>8</sup> 5f <sup>14</sup>
31	Ga	[Ar]4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>1</sup>	71	Lu	[Xe]6s <sup>2</sup> 5d <sup>1</sup> 4f <sup>14</sup>	111	Rg	[Rn]7s <sup>2</sup> 6d <sup>9</sup> 5f <sup>14</sup>
32	Ge	[Ar]4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>2</sup>	72	Hf	[Xe]6s <sup>2</sup> 5d <sup>2</sup> 4f <sup>14</sup>	112	Cn	[Rn]7s <sup>2</sup> 6d <sup>10</sup> 5f <sup>14</sup>
33	As	[Ar]4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>3</sup>	73	Ta	[Xe]6s <sup>2</sup> 5d <sup>3</sup> 4f <sup>14</sup>	113	—	[Rn]7s <sup>2</sup> 6d <sup>10</sup> 5f <sup>14</sup> 7p <sup>1</sup>
34	Se	[Ar]4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>4</sup>	74	W	[Xe]6s <sup>2</sup> 5d <sup>4</sup> 4f <sup>14</sup>	114	—	[Rn]7s <sup>2</sup> 6d <sup>10</sup> 5f <sup>14</sup> 7p <sup>2</sup>
35	Br	[Ar]4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>5</sup>	75	Re	[Xe]6s <sup>2</sup> 5d <sup>5</sup> 4f <sup>14</sup>	115	—	[Rn]7s <sup>2</sup> 6d <sup>10</sup> 5f <sup>14</sup> 7p <sup>3</sup>
36	Kr	[Ar]4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>6</sup>	76	Os	[Xe]6s <sup>2</sup> 5d <sup>6</sup> 4f <sup>14</sup>	116	—	[Rn]7s <sup>2</sup> 6d <sup>10</sup> 5f <sup>14</sup> 7p <sup>4</sup>
37	Rb	[Kr]5s <sup>1</sup>	77	Ir	[Xe]6s <sup>2</sup> 5d <sup>7</sup> 4f <sup>14</sup>	117	—	[Rn]7s <sup>2</sup> 6d <sup>10</sup> 5f <sup>14</sup> 7p <sup>5</sup>
38	Sr	[Kr]5s <sup>2</sup>	78	Pt	[Xe]6s <sup>1</sup> 5d <sup>9</sup> 4f <sup>14</sup>	118	—	[Rn]7s <sup>2</sup> 6d <sup>10</sup> 5f <sup>14</sup> 7p <sup>6</sup>
39	Y	[Kr]5s <sup>2</sup> 4d <sup>1</sup>	79	Au	[Xe]6s <sup>1</sup> 5d <sup>10</sup> 4f <sup>14</sup>			
40	Zr	[Kr]5s <sup>2</sup> 4d <sup>2</sup>	80	Hg	[Xe]6s <sup>2</sup> 5d <sup>10</sup> 4f <sup>14</sup>			

### Molecular Orbital Theory

Molecular orbital theory was put forward by Hund and Mullikan in 1932. M.O.Theory is also based on quantum mechanics, but its approach to bond formation is quite different from V.B. approach. In V.B. theory, when atoms are combined to form molecules, only the outermost atomic orbitals of the combining atoms lose their identity and all the remaining inner atomic orbitals of the combining atoms remain undisturbed.

The nucleus of each atom is also localized in the atom itself even when the atoms are chemically bonded. But in M.O. theory, when atoms are combined to form molecule, all the atomic orbitals in the outer shell or valence shell of the participating atoms are disturbed and lose their individual identity. These valence shell atomic orbitals are mixed up to form a new set of orbitals known as *molecular orbitals*.

Brief outline of this theory is given below:

- (1) In a molecule, electrons are present in new orbitals called molecular orbitals.
- (2) Molecular orbitals are formed by combination of atomic orbitals of equal energies (in case of homonuclear molecules) or of comparable energies (in case of heteronuclear molecules).
- (3) The number of molecular orbitals formed is equal to the number of atomic orbitals undergoing combination.
- (4) Two atomic orbitals can combine to form two molecular orbitals. One of these two molecular orbitals one has a lower energy and the other has a higher energy. The molecular orbital with lower energy is called bonding molecular orbital and the other with highest energy is called anti bonding molecular orbital.
- (5) The shapes of molecular orbitals depend upon the shapes of combining atomic orbitals.
- (6) The bonding molecular orbitals are represented by  $\sigma$  (sigma),  $\pi$  (pi),  $\delta$  (delta) and the antibonding molecular orbitals are represented by  $\sigma^*$ ,  $\pi^*$ ,  $\delta^*$ .

Thus, the molecular orbitals are **polycentric** in nature. Some important basic concepts of M.O. theory are explained below.

### 1) Linear Combination of Atomic Orbitals (LCAO)

The formation of M.O. from atomic orbitals is governed by quantum mechanical principles. According to this, every atomic orbital is associated with a **wave function** given as  $\psi$  (Psi). This can be explained by considering the simplest diatomic molecule, hydrogen ( $H_2$ ).  $H_2$  is made up of two hydrogen atoms –  $H_A$  and  $H_B$  and their atomic orbitals are given by wave function,  $\psi_A$  and  $\psi_B$  respectively.

According to M.O. theory, the wave function of the atomic orbitals are combined in a linear fashion (i.e. either added or subtracted) so as to obtain a new wave function for the molecular orbital.

*The method of obtaining a wave function for the molecular orbital from the wave function of atomic orbitals is known as linear combination of atomic orbitals (LCAO) method.*

## 2) Bonding and Anti-bonding molecular orbitals

According to LCAO method, the number of molecular orbitals that are obtained will be equal to the number of atomic orbitals that are combined. In the case of hydrogen molecule, we obtain only two molecular orbitals-

- (i) The first molecular orbital is obtained by adding the wave function of the two atomic orbitals and is known as *bonding molecular orbital* (BMO) and is represented as  $\sigma_{1s}$

$$\Psi = \Psi_A + \Psi_B \dots\dots\dots(1)$$

- (ii) The second molecular orbital is obtained by subtracting the wave functions of the two atomic orbitals and is known as *anti-bonding molecular orbital* (ABMO). This is represented as  $\sigma^*_{1s}$ :

$$\Psi^* = \Psi_A - \Psi_B \dots\dots\dots(2)$$

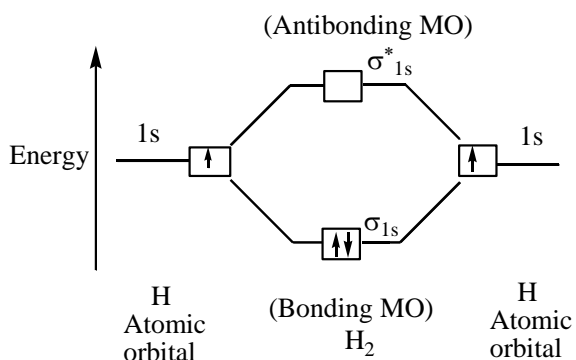
It is to be noted that in the bonding ( $\sigma_{1s}$ ) orbitals, the electron charge is concentrated in the region between two nuclei. This increases the electrostatic attraction and holds the nuclei together. On the other hand, in an anti-bonding ( $\sigma^*_{1s}$ ) orbitals, the electron charge is drifted from the region between the nuclei. This increases the electrostatic repulsion between the nuclei. The differences between Bonding molecular orbitals and Antibonding molecular orbitals are given in the following table:

No.	Bonding Molecular orbitals	Anti-bonding molecular orbitals
1.	A bonding molecular orbital is formed by the combination of electron waves of the same sign.	An Anti-bonding molecular orbital is formed by the combination of electron waves of the opposite sign.
2.	It is formed by the addition overlap of atomic orbitals. $\Psi = \Psi_A + \Psi_B$	It is formed by the subtraction overlap of atomic orbitals. $\Psi^* = \Psi_A - \Psi_B$

3.	It possesses lower energy than the atomic orbitals from which it is formed.	It possesses higher energy than the atomic orbitals from which it is formed.
4.	The electron density in between the nuclei is high.	The electron density in between the nuclei is low.
5.	As the attraction between the nuclei is high, a bond between the atoms is formed.	As the repulsion between the nuclei is high, a bond is not formed between the atoms.
6.	It stabilizes the molecule.	It destabilizes the molecule.

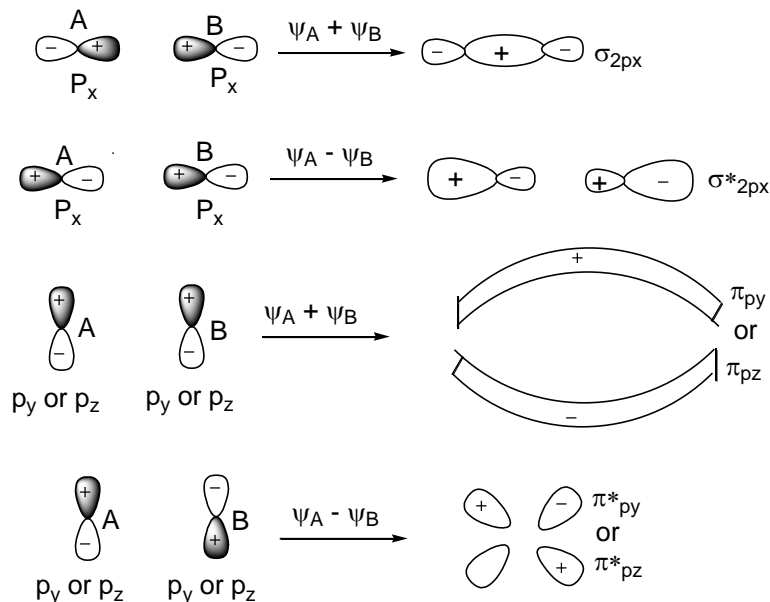
### 3) Energy level diagram

Based on energy consideration, the bonding orbital (due to attraction) has lesser energy and anti-bonding orbital (due to repulsion) has more energy than the individual atomic orbitals from which they are obtained as shown in the figure:



### 4) Formation of molecular orbitals from p-orbitals

Like s orbital,  $P_x$ ,  $p_y$  and  $p_z$  atomic orbitals also combine linearly to form molecular orbitals as shown below.



As seen from the figures, it is evident that  $p_x$  atomic orbitals overlap to give sigma bonding ( $\sigma_{2px}$ ) and sigma anti-bonding ( $\sigma^*_{2px}$ ) orbitals. But,  $p_y$  or  $p_z$  atomic orbitals overlap in sideways to give only pi-bonding ( $\pi_{2py}$  or  $\pi_{2pz}$ ) and pi anti-bonding ( $\pi^*_{2py}$  or  $\pi^*_{2pz}$ ) orbitals.

### (5) Sequence of energy of various molecular orbitals

The energies of various molecular orbitals are determined from spectroscopic methods. Based on this, the sequence of energy of various molecular orbitals is as follows:

$$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \sigma_{2pz} < \pi_{2py} = \pi_{2pz} < \pi^*_{2px} = \pi^*_{2py} < \sigma^*_{2pz}$$

The sequence of energy of various molecular orbitals for lighter elements (B, C, N) is as follows:

$$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \pi_{2px} = \pi_{2py} < \sigma_{2pz} < \pi^*_{2px} = \pi^*_{2py} < \sigma^*_{2pz}$$

### (6) Distribution of electrons in various, molecular orbitals

The electrons are now distributed in the above molecular orbitals following *Aufbau principle*, *Pauli Exclusion Principle* and *Hund's rule* of maximum multiplicity. These are explained below:

The electrons are now placed in the various molecular orbitals in the increasing order of energy (*Aufbau principle*) – the molecular orbital with lowest energy is filled first. Each molecular orbital can accommodate only a maximum number of two electrons (*Pauli principle*) and these two electrons must have opposite spin (*Hund's principle*).

### (7) Bond Order

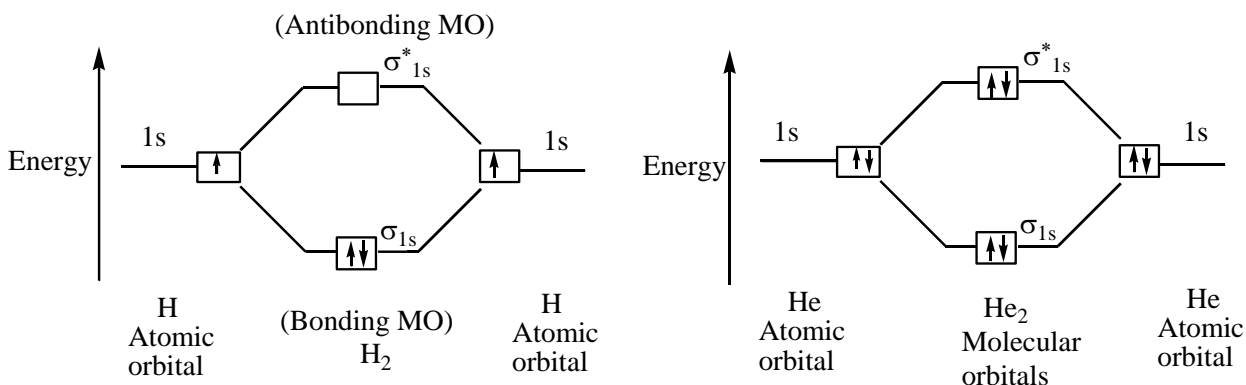
The actual number of bonds present in the molecule is known as bond order and is calculated using the formula:

$$\text{Bond order} = \frac{\text{No. of electrons in bonding orbitals} - \text{No. of electrons in the antibonding orbitals}}{2}$$

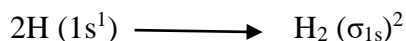
### APPLICATION OF M.O THEORY

#### a) Hydrogen molecule, H<sub>2</sub>

Hydrogen molecule is made by two hydrogen atoms. It contains two electrons and two molecular orbitals namely  $\sigma_{1s}$  and  $\sigma^*_{1s}$ . Both the electrons of the molecule will occupy the low energy  $\sigma_{1s}$  orbital and  $\sigma^*_{1s}$  orbital is vacant as in the figure.



Thus, the electronic configuration of hydrogen molecule is:

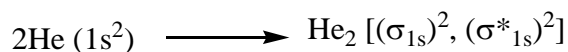


The bond order is  $(2-0) / 2 = 1$ . There is a strong sigma bond between two hydrogen atoms with bond energy 432 kJ/mol. The molecule is *diamagnetic*.

#### b) Helium molecule He<sub>2</sub>

The atomic number of helium is 2 and its electronic configuration is  $1s^2$ . Hence, a diatomic helium molecule will contain four electrons. Among them, two electrons enter the bonding  $\sigma_{1s}$  orbital and the remaining two electrons enter the antibonding  $\sigma^*_{1s}$ .

The electronic configuration of helium (He<sub>2</sub>) molecule is:





Two electrons in the bonding orbitals stabilise the molecule while two electrons in the antibonding orbital will destabilise the molecule making the bond order zero,  $(2-2) / 2 = 0$ . Hence,  $\text{He}_2$  does not exist. *Helium will exist only as monoatomic species.*

**c) Nitrogen molecule,  $\text{N}_2$**

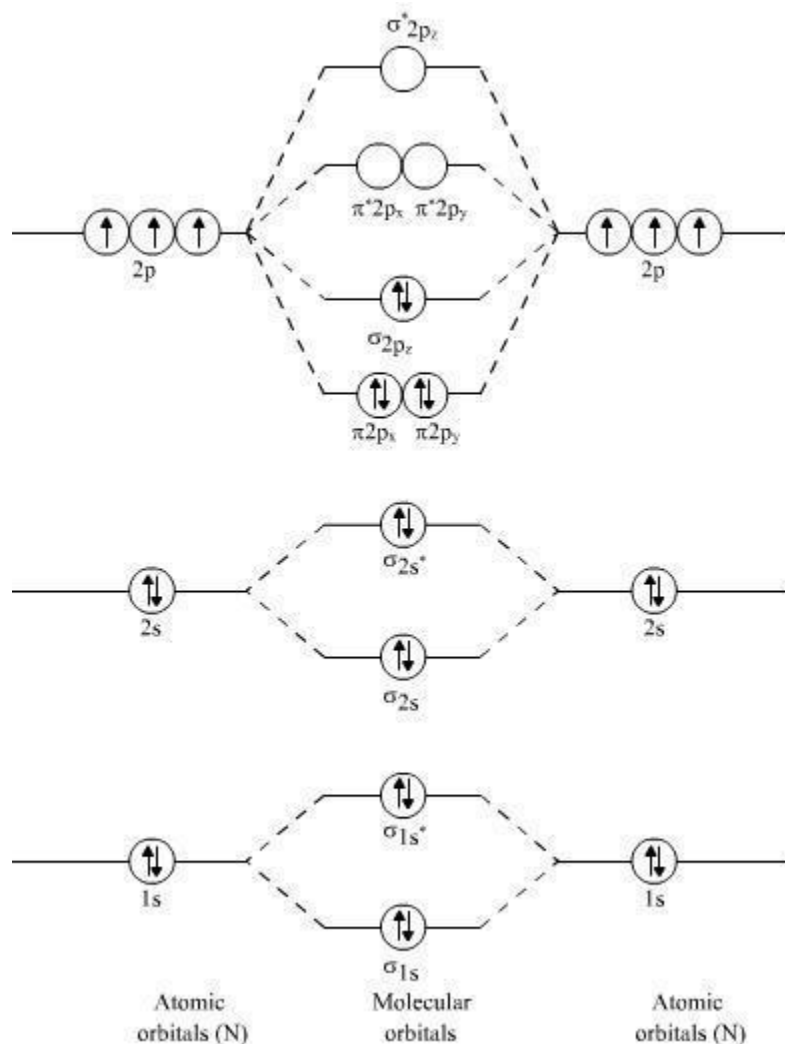
The atomic number of nitrogen is 7 and its electronic configuration is  $1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$ . The outer shell or valence atomic orbitals ( $2s$  and  $2p$ ) in each nitrogen atom combine to form the following eight molecular orbitals:

*Overlap of -*

- |       |                         |  |
|-------|-------------------------|--|
| (i)   | 2s and 2s gives         | $\sigma_{2s}$ and $\sigma_{2s}^*$ M.O.     |
| (ii)  | $2p_z$ and $2p_z$ gives | $\sigma_{2p_z}$ and $\sigma_{2p_z}^*$ M.O. |
| (iii) | $2p_x$ and $2p_x$ gives | $\pi_{2p_x}$ and $\pi_{2p_x}^*$ M.O.       |
| (iv)  | $2p_y$ and $2p_y$ gives | $\pi_{2p_y}$ and $\pi_{2p_y}^*$ M.O.       |

Each nitrogen atom has five electrons in the valence shell. Hence, in nitrogen molecule ( $\text{N}_2$ ), there are ten electrons. These electrons are to be accommodated in the above eight molecular orbitals. Four electrons will enter low energy,  $\sigma_{2s}$  and  $\sigma_{2s}^*$  M.Os. The remaining six electrons will enter the  $\sigma_{2p_z}$ ,  $\pi_{2p_x}$  and  $\pi_{2p_y}$  M.Os. which are lying at the next higher energy level as in the energy level diagram. The electronic configuration of nitrogen molecule is:





Here, KK represents completely filled inner shells which do not take part in the molecular orbitals formation.

The bond order of the molecule is,  $(8-2) / 2 = 3$ . Out of this, one is a sigma bond and the remaining two are pi-bonds.

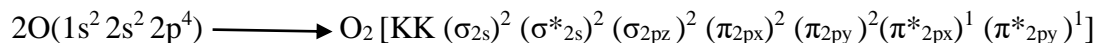
Out of ten electrons, eight electrons occupy the bonding orbitals. This makes the nitrogen molecule a highly stable molecule with high bond energy of 942 kJ/mol.

Nitrogen molecule is experimentally found to be diamagnetic. This is due to the absence of odd electrons in any one of the molecular orbitals, i.e., all electrons are paired.

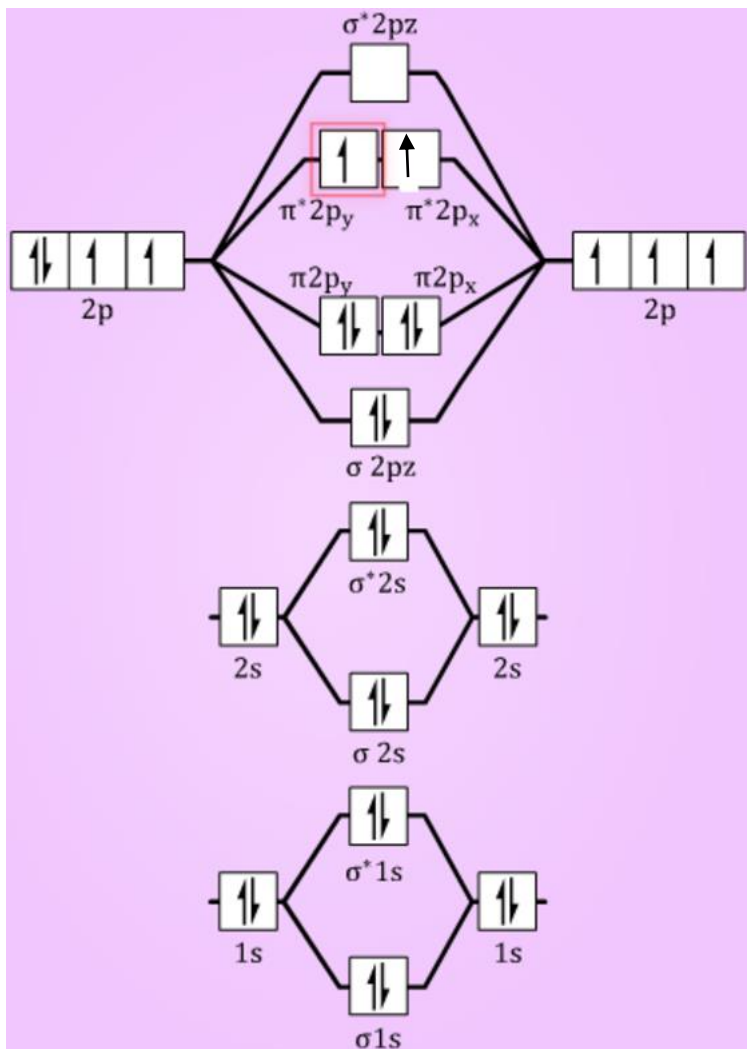
#### d) Oxygen Molecule, O<sub>2</sub>

The atomic number of oxygen is eight and its electronic configuration is  $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$ . The outer, valence shell atomic orbitals (i.e., 2s and 2p) in each oxygen atom combine to form a total of eight molecular orbitals.

Each oxygen atom has six valence electrons. Hence, in oxygen molecule ( $O_2$ ), twelve electrons are to be accommodated in the eight molecular orbitals that are formed. Four electrons will enter  $\sigma_{2s}$  and  $\sigma^*_{2s}$  molecular orbitals. Six electrons will enter  $\sigma_{2pz}$ ,  $\pi_{2px}$  and  $\pi_{2py}$  molecular orbitals. The remaining two electrons will occupy  $\pi^*_{2px}$  and  $\pi^*_{2py}$  i.e., **one electron will go to each of the antibonding orbitals**, as these orbitals are of same energy, to give two unpaired electrons. The distribution of electrons in various molecular orbitals is given in the figure. The electronic configuration of  $O_2$  molecule is:



The bond order is  $(8 - 4) / 2 = 2$ . The two oxygen atoms are bonded by a double bond. This double bond consists of one sigma bond and one pi bond. The formation of these bonds is explained as follows:



Two electrons in the  $\sigma_{2s}$  and two electrons in the  $\sigma_{2s}^*$  cancel each other. Two electrons in the  $\sigma_{2pz}$  will form a sigma bond. Out of four electrons in the pi bonding orbitals, two electrons are cancelled by the two electrons in the pi anti-bonding orbitals. Hence, two pi-electrons form a pi bond.

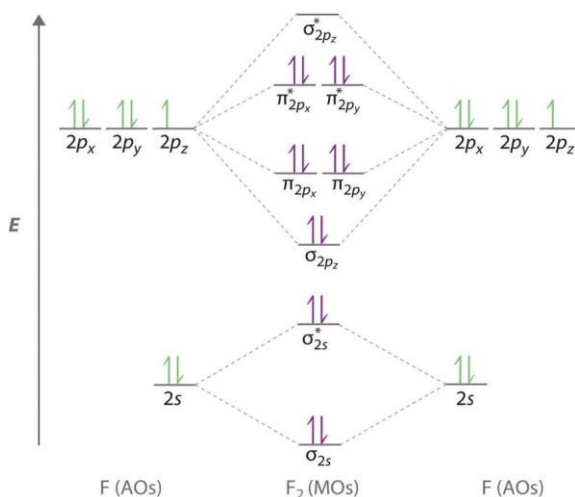
Comparison of the molecular orbitals of oxygen molecule with nitrogen molecule reveals that oxygen has more number of anti-bonding (4) electrons than nitrogen molecule (2). Hence, oxygen is less stable than nitrogen with low bond energy of 494 kJ/mol.

Various experiments show that oxygen molecule is paramagnetic having one or more odd electrons and M.O theory, clearly indicates the presence of two unpaired electrons as  $(\pi_{2px}^*)^1$  and  $(\pi_{2py}^*)^1$ .

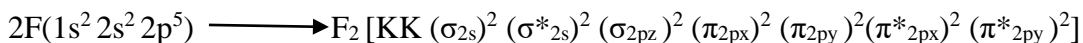
#### e) Fluorine molecule, $F_2$

The atomic number of fluorine is nine and its electronic configuration is  $(1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1)$ . The valence shell atomic orbitals (2s and 2p) in each fluorine atom combine to form a total of eight molecular orbitals.

Each fluorine atom has seven valence electrons. Hence, in fluorine molecule ( $F_2$ ), fourteen electrons are to be accommodated in the eight molecular orbitals. Four electrons will enter,  $\sigma_{2s}$  and  $\sigma_{2s}^*$  M.Os. Six electrons will enter  $\sigma_{2pz}$ ,  $\pi_{2px}$  and  $\pi_{2py}$  orbitals. The remaining four electrons will occupy  $\pi_{2px}^*$  and  $\pi_{2py}^*$  orbitals. The distribution of electrons in various M.Os is given in the figure.



The electronic configuration of fluorine molecule is:

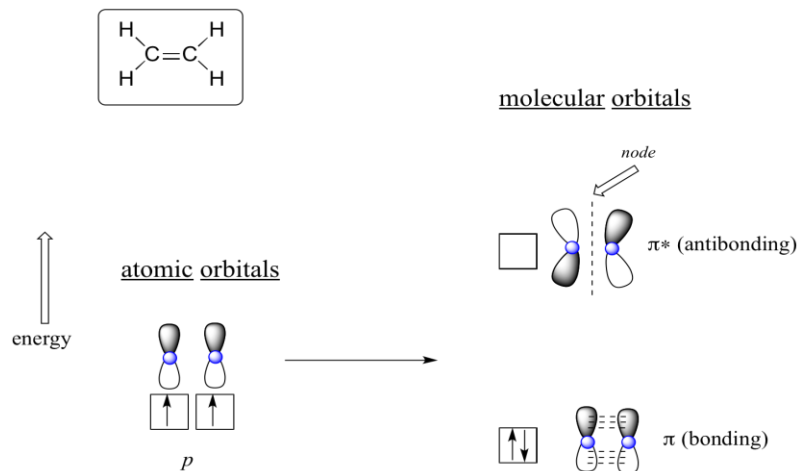


The bond order is  $(8-6) / 2 = 1$  and this single bond is a sigma bond. As all the bonding electrons are cancelled by the corresponding antibonding electrons except the two electrons present in  $\sigma_{2px}$  orbital, a sigma bond is formed between two fluorine atoms. Fluorine molecule has more numbers of anti-bonding electrons (6) than in nitrogen (2) and in oxygen (4) molecules. Hence, fluorine is less stable than nitrogen and oxygen, with low bond energy of 155 kJ/mol. It is evident from the molecular orbitals that fluorine molecule is *diamagnetic*.

### Pi-molecular orbital's of butadiene

Pi molecular orbitals are formed by side side overlap atomic orbitals. 1,3 butadiene consists of 4p orbitals of carbon. Each carbon  $sp^2$  hybridized in 1,3 butadiene. Four atomic orbitals of carbon combine to form four pi molecular orbitals. 1,3 butadiene is constructed by two ethylene molecule.

The structure of Ethylene molecule



### Possible combination for formation of Pi molecular orbitals

- (i)  $\pi + \pi$
- (ii)  $\pi - \pi$
- (iii)  $\pi^* + \pi^*$
- (iv)  $\pi^* - \pi^*$
- (v)  $\pi + \pi^*$
- (vi)  $\pi - \pi^*$

But quantum mechanics concept, same energy level of atomic orbitals combine to form stable molecular orbitals.

(i)  $\pi + \pi$

(ii)  $\pi - \pi$

(iii)  $\pi^* + \pi^*$

(iv)  $\pi^* - \pi^*$

This will not combine to form stable pi molecular orbitals

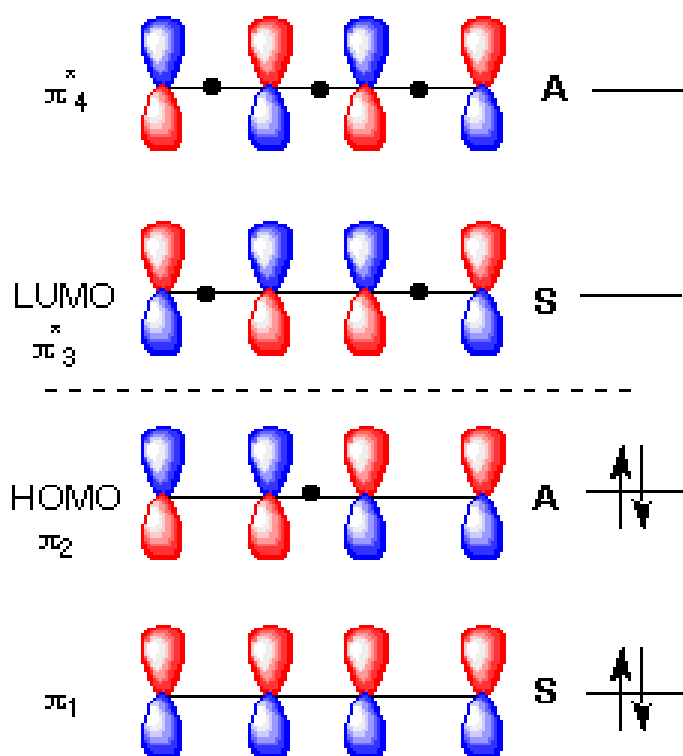
(v)  $\pi + \pi^*$

(vi)  $\pi - \pi^*$

## Energy Level diagrams of 1,3 butadiene

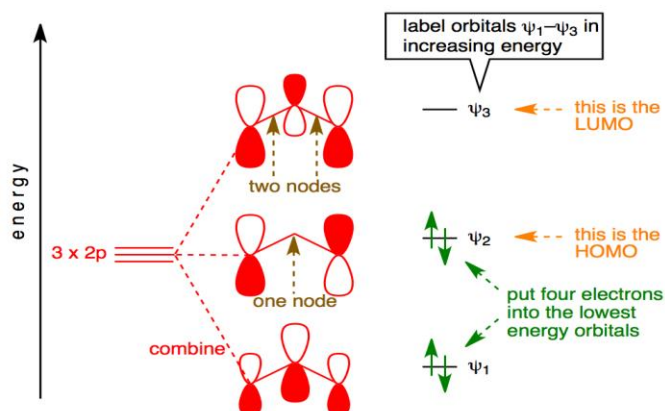
The number of nodes increases with each successive energy levels

$$n \propto E$$

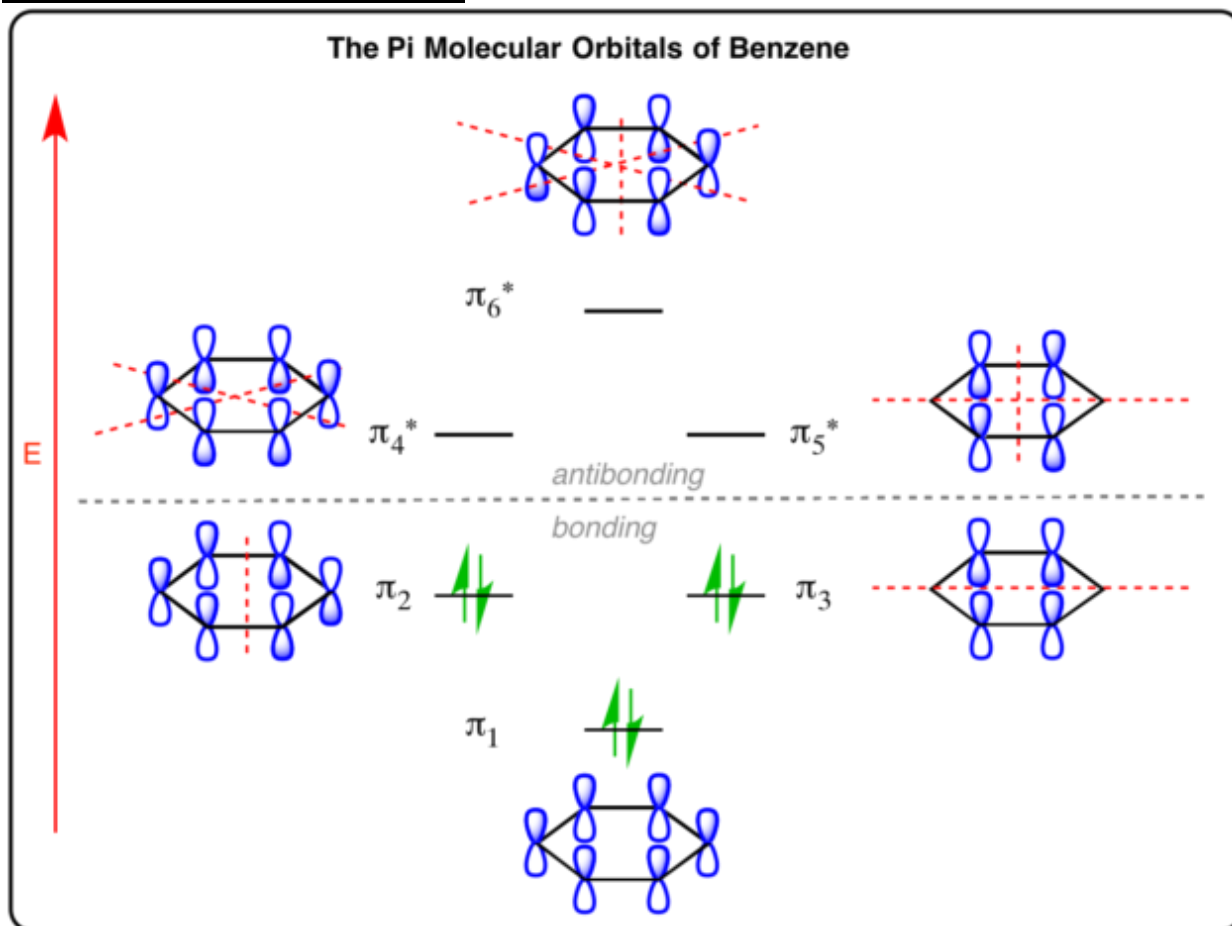


## Pi molecular orbitals of Benzene

Benzene has 6 carbon atoms and 6 hydrogen atoms. It has alternative double bond in the molecule. Each carbon is  $sp^2$  hybridized in benzene. Generally, six p atomic orbitals (6 p electrons) combine to form six pi molecular orbitals ( $6\pi$  electrons). Pi molecular orbitals of benzene is constructed by combination of  $\pi$  molecular orbitals of propene.



## Energy level diagrams of Benzene



Benzene has  $3\pi$  bonds which contains 6 electrons. Hence six electrons occupied in bonding molecular orbital. So Benzene are stable.

### Aromaticity:

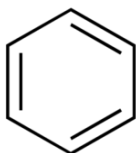
Organic compounds which resemble benzene in their chemical behavior are called aromatic compounds. They exhibit certain characteristic properties which are quite different from aliphatic and alicyclic compounds. These characteristic properties are collectively referred to as aromaticity or aromatic character.

### Characteristics:

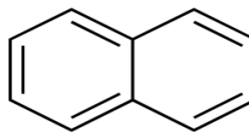
- The compounds must be cyclic in nature
- The molecular formula suggest a high degree of unsaturation due to presence of one or more double bonds in the ring. But it must behave as an saturated compound.
- The compounds must be flat in nature. (confirmation of X-ray & electron diffraction studies)
- The compounds must resist addition. But should readily take part in the electrophilic substitution reactions.
- High value of resonance.
- The compounds must follow Huckels rule or  $(4n+2)$  rule. This rule is based upon molecular orbital treatment which is used for predict aromaticity.
- $4n+2$  rule where  $n=2,6,10,14 \dots$   $\pi$  e- will be aromatic and others will be non-aromatic. ( $n$  is the no.of  $\pi$ e- in molecule or ion)

### **Aromatic compounds**

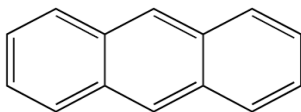
(i) Benzene ( $6\pi$  electrons)



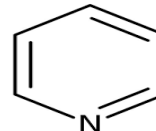
(ii) Naphthalene ( $10\pi$  electrons)



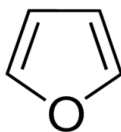
(iii) Anthracene ( $14\pi$  electrons)



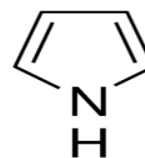
(iv) Pyridine ( $6\pi$  electrons)



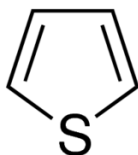
(v) Furan ( $6\pi$  electrons)



(vi) Pyrrole ( $6\pi$  electrons)



(vii) Thiophene ( $6\pi$  electrons)

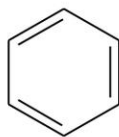




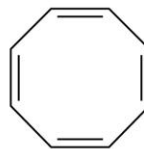
### Similar aromatic compounds- Annulenes



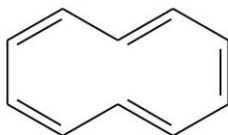
cyclobutadiene  
[4]annulene



benzene  
[6]annulene



cyclooctatetraene  
[8]annulene



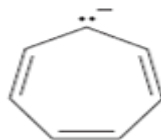
cyclodecapentaene  
[10]annulene

### **Aromatic ions**

(i) Cyclopropenyl anion ( $2\pi$  electrons) (ii) Cyclopentadienyl anion ( $6\pi$  electrons)

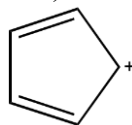


(i) Cycloheptatrienyl anion ( $6\pi$  electrons)

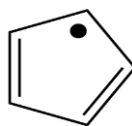


### **Non aromatic Species**

(i) Cyclopentadienyl cation ( $4\pi$  electrons)



(ii) Cyclopentadienyl radical ( $5\pi$  electrons)



### Crystal Field Theory (CFT)

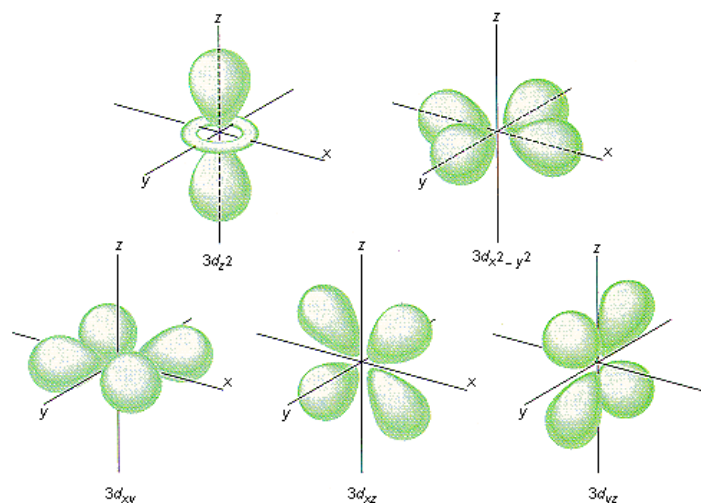
This theory advanced by Bethe, John Van Vleck was originally applied to ionic crystals and is therefore called crystal field theory. It is mainly concerned with the interaction of a orbitals of central metal with the surrounding ligands that produce crystal field effects. Crystal field theory was developed by considering two compounds: manganese (II) oxide, MnO, and copper(I) chloride, CuCl.

#### Salient Features:

- (i) A complex is considered to be a combination of central metal ion surrounded by various ligands.
- (ii) The interaction between the metal ion and the ligands is purely electrostatic (ionic).
- (iii) It does not consider any orbital overlap.
- (iv) The ligands are either negatively charged ions e.g., F<sup>-</sup> and CN<sup>-</sup> or neutral molecules e.g., H<sub>2</sub>O and NH<sub>3</sub>. The ligands approach the central metal ion with negative poles closest to the metal ion. Neutral molecules are polarized by the positive charge of the cation.
- (v) The interaction between the electrons of the metal ion and those of the ligands is purely repulsive. It is these repulsive forces that are responsible for causing the splitting of the d orbital of the metal into two groups t<sub>2g</sub> and e<sub>g</sub>. This effect is known as crystal field splitting.
- (vi) The number of ligands and their arrangement around the central ion will determine the crystal field. (vii) Different crystal fields will have different effects on the relative energies of the five d orbitals.

### Crystal Field splitting of d-orbitals

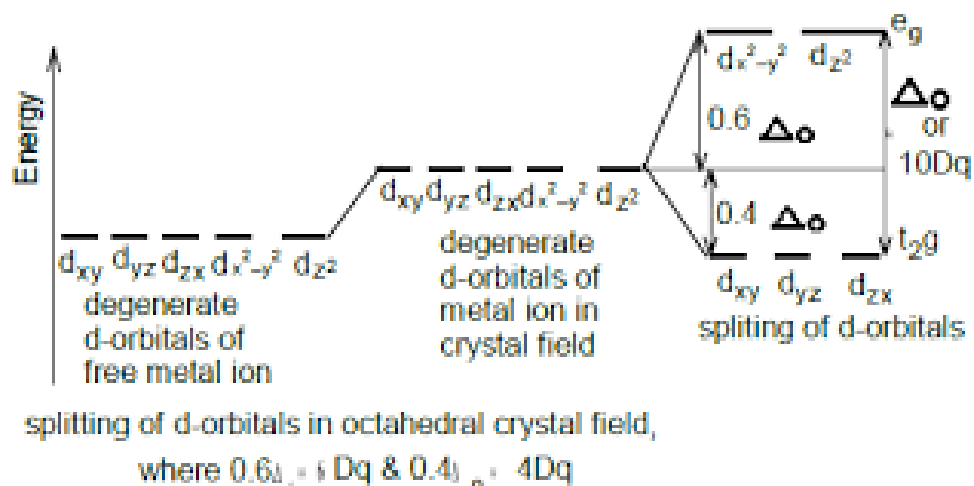
The outcome of crystal field theory is that the degeneracy of the d-orbitals of the central metal ion is when ligands approach it consequently the d-orbitals split into two groups e<sub>g</sub> and t<sub>2g</sub>. The shape of d-orbitals is given in figure. In a free (transition) metal ion all the five d-orbitals are degenerate i.e., have the same energy. An electron is free to occupy any of five d-orbitals d<sub>xy</sub>, d<sub>yz</sub>, d<sub>xz</sub>, d<sub>z</sub><sup>2</sup> and d<sub>x</sub><sup>2</sup>-y<sup>2</sup>.



$d_{xy}$ ,  $d_{yz}$ , and  $d_{xz}$  orbitals lie between  $xy$ ,  $yz$  and  $xz$  axes respectively. They are known as  $t_{2g}$  set of orbitals.  $d_{z^2}$  orbital is oriented along the  $z$ -axis,  $d_{x^2-y^2}$  orbital is oriented along the  $x$ -axis and  $y$ -axis. They are axials and are called  $e_g$  set of orbitals.

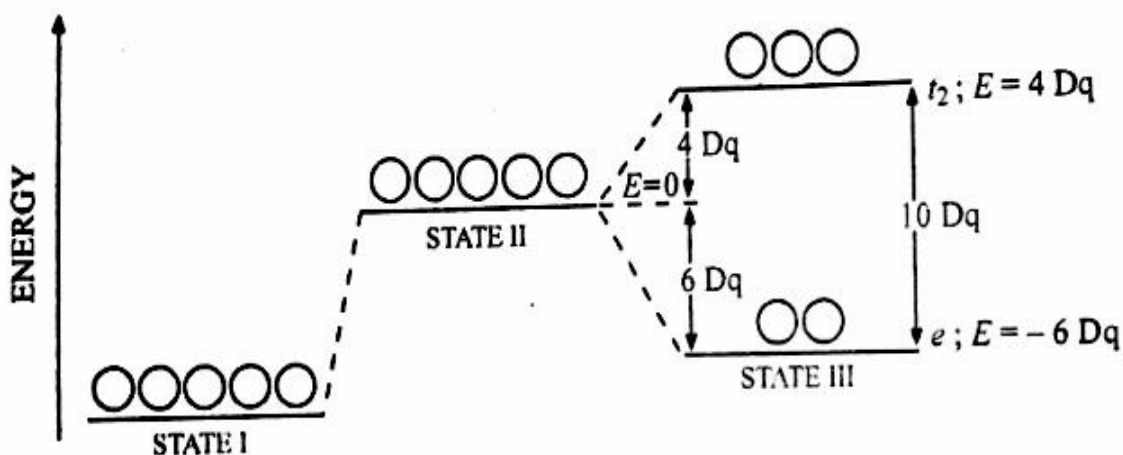
When the approach of the ligands, the electrons in the  $d$ -orbitals of the central metal ion are repelled by the lone pairs of the ligands. As a result, the energy of the entire system will be raised. If the electric field arising from the ligands is spherically symmetrical, the energy of all the  $d$ -orbitals would be raised to the same extent, and they will still be degenerate. But the  $d$ -orbitals differ in their orientation. As a result, the energies of the orbitals lying in the direction of the ligands are raised to a larger extent than those of the orbitals lying in between the ligands. The five degenerate  $d$ -orbitals of the metal ion split up into two sets of orbitals having different energies. This splitting of five degenerate  $d$ -orbitals of the metal ion under the influence of approaching ligands. The energy difference between  $t_{2g}$  and  $e_g$  sets of orbitals is called crystal field stabilization energy (CFSE). The crystal field splitting depends on the number and the arrangement of ligands around the central metal ion.

**Crystal field splitting in octahedral complex:** In octahedral complex, the six ligands are arranged octahedrally around a central metal ion. In this arrangement, the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals lie along the  $x$ ,  $y$  and  $z$  axes and point towards the ligands. So, they experience much more repulsion than the remaining  $d$  orbitals  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$  which are directed in between the  $x$ ,  $y$  and  $z$  axes. Consequently the energies of  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals increased much more in comparison to other  $d$ -orbitals.



### Crystal field splitting in tetrahedral complex:

The tetrahedral arrangement of a central metal ion surrounded by four ligands. No d orbital points exactly towards the ligand  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$  are pointing approximately by in the directions of the approaching ligands.  $dx^2-y^2$  and  $dz^2$  are lying in between approaching ligands. So the energies of  $d_{xy}$ ,  $d_{yz}$ , and  $d_{xz}$  increase more than those of  $dx^2-y^2$  and  $dz^2$ .



## UNIT II- PERIODIC PROPERTIES, INTERMOLECULAR FORCES AND POTENTIAL ENERGY SURFACES

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**Mendeleeff** – had arranged elements in the periodic table on basis of increasing atomic weights.

**Moseley**- modified Mendeleeff's periodic table and stated that the basis of classification of elements be according to increasing atomic numbers and not atomic weights.

Arrange elements in increasing order of atomic numbers in horizontal rows called '**periods**' and vertical columns called '**groups**'

Modern periodic table has **seven horizontal rows** called periods which are numbered from 1 to 7 starting from top and going downwards. Each period begins with an alkali metal and ends with an inert gas element.

The first three periods are called short periods because they contain small number (2 or 8) of elements. The next four periods are called long periods because they contain large number (18 or 32) of elements. The seventh period is a long period but is incomplete.

Modern periodic table has **eighteen vertical columns** called groups and are numbered as I to VII, VIII and zero groups. Groups I to VII subdivided into A and B.

Groups IA to VIIA are called 'normal or representative elements'.

Groups IB to VIIB and VIII are called 'transition elements'

Group zero at extreme right contains ' noble or inert gases'

**Reactive metals** are placed in group IA and IIA.

**Transition elements** (metals) are placed in the middle.

**Non metals** are placed in the upper right corner of the periodic table.

**PERIODIC PROPERTIES** The properties which appear at regular intervals in the periodic table are called '**periodic properties**' and the phenomenon '**periodicity of elements**'

Properties in which periodicity is observed are

- Atomic radii
- Ionisation Potential
- Electron affinity
- Electronegativity
- Non-metallic and metallic character.
- Density
- Melting and boiling point
- Nature of oxides, oxy acids, hydrides.

### **REASON FOR PERIODICITY IN PROPERTIES IN PERIODS AND GROUPS**

- (i) After definite intervals of atomic number, similar valence shell electronic configuration occurs.
- (ii) Properties of elements depend on the number and arrangement of electrons in various shells including valence shell.
- (iii) In the same period or subgroup, increase or decrease in a particular property is due to the gradual change in electronic configuration in the arranged elements.

## UNIT II- PERIODIC PROPERTIES, INTERMOLECULAR FORCES AND POTENTIAL ENERGY SURFACES

### ATOMIC RADII

The distance between the centre of the nucleus of an atom and its outermost shell. If the atom is assumed to be spherical, it is the radius of the sphere. The atomic radii are calculated from the covalent bond length. They are also called covalent radii.

Atomic radius is a periodic property. It varies regularly with increase in the atomic number. In general, the atomic radius decreases as we go from left to right in a period in the periodic table. This is due to increase in the nuclear charge and the additive electrons are added to the same electronic level. As we move down a group, the atomic radius increases from top to bottom in a group. This is due to the fact that as we go down a group, the additive electrons are accommodated in new electronic level.

Factors	Effect on Atomic size	Reason for effect on Atomic size
<b>Number of Shells</b> ➤ In an atom increases	<b>Atomic size</b> -increases	With increase in number of shells the distance of the outermost shell from the nucleus increases.
<b>Nuclear charge</b> ➤ Of an atom increases	<b>Atomic size</b> -decreases	Increase in nuclear charge attracts electrons in the outermost shell with increasing force.

### IONISATION POTENTIAL

The energy required to remove a loosely bound electron from outermost shell of an gaseous atom.

Energy required to remove 1<sup>st</sup> electron is called first Ionisation Potential.

$M \longrightarrow M^+ + 1e^-$  (First Ionisation potential is less)

Energy required to remove 2<sup>nd</sup> electron is called Second Ionisation Potential.

$M^+ \longrightarrow M^{++} + 1e^-$  (Second Ionisation potential is more)

Ionisation energy is a periodic property. As we go down a group, the ionization energy decreases due to the fact that the additive electrons occupy new shell and the atomic size increases.

Factors	Effect on Ionization Potential	Reason for effect on Ionization Potential
<b>Atomic Size</b> ➤ In an atom increases	<b>Ionization Potential</b> -decreases	With increase in atomic size the nuclear attraction on the outermost electrons decreases. Hence the outer electrons are loosely held.
<b>Nuclear charge</b> ➤ Of an atom increases	<b>Ionization Potential</b> -increases	With increase in nuclear charge the nuclear attraction on the outer electrons increases. Hence the outermost electrons are more firmly held.

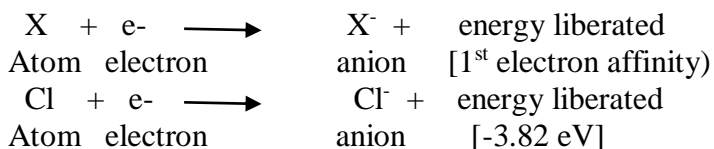
## UNIT II- PERIODIC PROPERTIES, INTERMOLECULAR FORCES AND POTENTIAL ENERGY SURFACES

The ionization energy generally increases as we go from left to right of the periodic table. This is due to increase in the nuclear charge and the additive electrons added to the same shell.

As we move down a group, the ionisation energy decreases from top to bottom in a group. This is due to increase in nuclear charge but the effect is dominated by increase in atomic radii.

### ELECTRON AFFINITY

The amount of energy released when an atom in the gaseous state accepts an electron to form an anion.



Generally, electron affinity decreases as we go down a group and it increases as we move from left to right in a period. As we go down the group, the atomic size increases and hence the electron affinity decreases. But as we go from left to right in a period, the nuclear charge increases and hence the electron affinity also increases.

Factors	Effect on Electron affinity	Reason for effect on Electron affinity
<b>Atomic Size</b> ➤ Increases	<b>Electron affinity</b> -decreases	Electron affinity is the tendency of an atom to accept electrons. A small atom takes up electrons more readily than a large atom since nucleus has greater attraction on the electrons.
<b>Nuclear charge</b> ➤ Increases	<b>Electron affinity</b> -increases	Increase in nuclear charge similarly increases the tendency of the atom to accept electrons.

### ELECTRONEGATIVITY

The tendency of an atom to attract electrons to itself when combined in a compound. It increases with increase in atomic number as we move from left to right in a period. But it decreases as we go from top to bottom in a group.

Factors	Effect on Electron negativity	Reason for effect on Electron affinity
<b>Atomic Size</b> ➤ Increases	<b>Electron negativity</b> -decreases	Factors and reasons affecting electronegativity are the same and in the same order as electron affinity
<b>Nuclear charge</b> ➤ Increases	<b>Electron negativity</b> -increases	

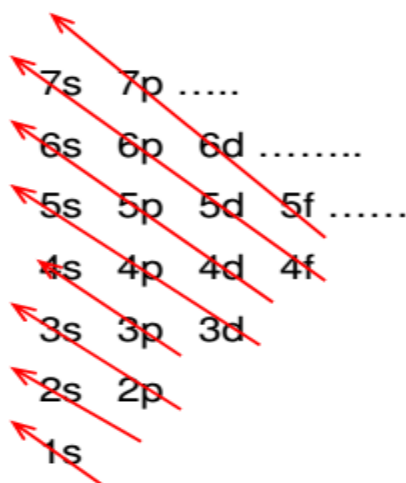
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### ELECTRONIC CONFIGURATION

The distribution of electrons among the orbitals of an atom is called the electron configuration. The electrons are filled in according to a scheme known as the **Aufbau principle** (“building-up”), which corresponds (for the most part) to increasing energy of the subshells:

**1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f**

The **electron configuration** of an element shows how electrons are distributed in orbitals—which ones are filled and which ones remain vacant. We can predict the electron configuration of most elements, and we can use electron configurations to predict physical and chemical properties of the elements.



### The Pauli -Exclusion Principle

To predict the electron configuration for an atom's ground state, the lowest energy state for an atom, electrons are put into the orbitals with the lowest energy possible, placing no more than two electrons in an orbital.

*“No more than two electrons can occupy the same orbital, and, if there are two electrons in the same orbital, they must have opposite spins.”*

The order of subshell filling is related to  $n$ , the principal quantum number, and the angular momentum quantum number. In general, electrons fill orbitals in order of increasing  $(n + l)$  and when two or more subshells have the same  $(n + l)$  value, electrons fill the orbital with the lower  $n$  value.

These general rules result in the following orbital filling order:

**1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p, 8s, ...**

The Pauli exclusion principle states that no two electrons within an atom can have the same set of four quantum numbers ( $n$ ,  $l$ ,  $m_l$ , and  $m_s$ ). The limits on possible values for the four quantum numbers means that a single orbital can accommodate no more than two electrons, and when an orbital contains two electrons, those electrons must have opposite spins

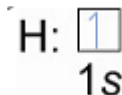
**Hydrogen and Helium** Hydrogen has a single electron that occupies the orbital with the lowest energy, the 1s orbital. Two methods are used to represent this electron configuration. The **spdf notation** (also called *spectroscopic notation*) has the general format  $n\Box\#$ , where



## UNIT II- PERIODIC PROPERTIES, INTERMOLECULAR FORCES AND POTENTIAL ENERGY SURFACES

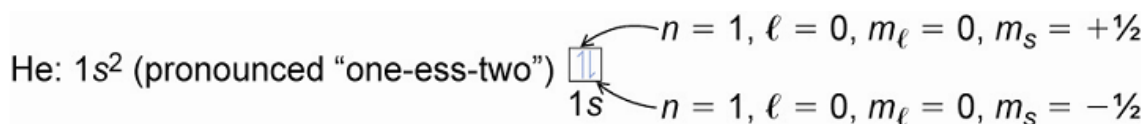
subshells are listed in the order in which they are filled and the number of electrons occupying each subshell is shown to the right of the subshell as a superscript. The *spdf* notation for hydrogen is

H:  $1s^1$  (pronounced “one-ess-one”)



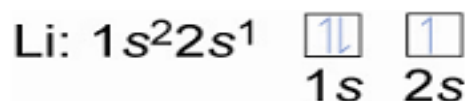
**Orbital box notation** uses boxes or horizontal lines to represent orbitals and arrows to represent electrons. The electron configuration of hydrogen in orbital box notation is

**Helium** has two electrons, and both occupy the lowest-energy  $1s$  orbital. The electron configuration of helium in *spdf* notation and orbital box notation is therefore



Each electron in helium has a unique set of four quantum numbers, as required by the Pauli exclusion principle. Notice that hydrogen and helium are in the first row of the periodic table and both elements fill orbitals in the first energy level ( $1s$ ). Orbital box notations provide information about the number of paired and unpaired electrons in an atom, and that information can be used to determine whether the atoms are paramagnetic or diamagnetic. Hydrogen has one unpaired electron and is a paramagnetic species, whereas helium’s electrons are paired and it is diamagnetic.

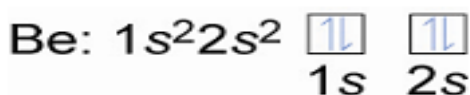
**Lithium to Neon** Lithium has three electrons, two in the  $1s$  orbital and one that is in an orbital in the second energy level. As shown previously, the  $2s$  orbital is lower in energy than the  $2p$  orbitals, so the electron configuration of lithium in *spdf* notation and orbital box notation is



Notice that it would be more correct to draw the orbital box notation electron configuration of lithium as shown below because the  $2s$  orbital is higher in energy than the  $1s$  orbital.

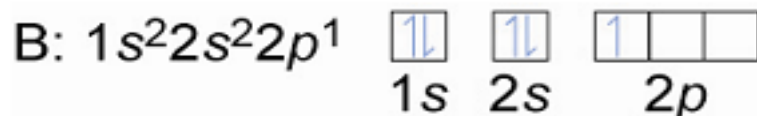


However, it is common to show all orbitals on a horizontal line when writing orbital box notation electron configurations in order to make more efficient use of space. Beryllium has two electrons in the  $1s$  and the  $2s$  orbitals.



## UNIT II- PERIODIC PROPERTIES, INTERMOLECULAR FORCES AND POTENTIAL ENERGY SURFACES

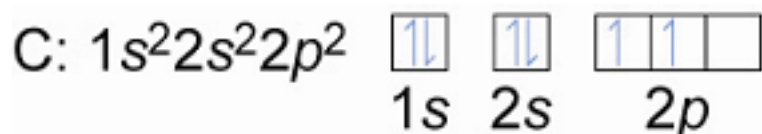
Boron has five electrons. Four electrons fill the  $1s$  and  $2s$  orbitals, and the fifth electron is in a  $2p$  orbital. Notice that the orbital box diagram shows all three  $2p$  orbitals even though only one of the  $2p$  orbitals is occupied.



Carbon has six electrons, four in the  $1s$  and  $2s$  orbitals and two in the  $2p$  orbitals. When electrons occupy a subshell with multiple orbitals such as  $2p$ ,

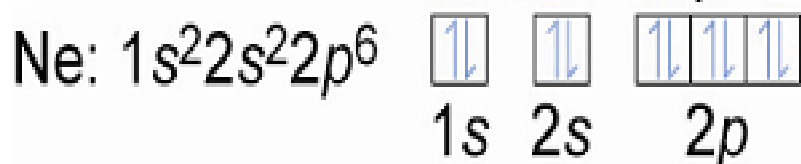
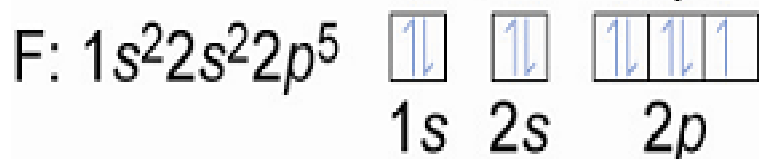
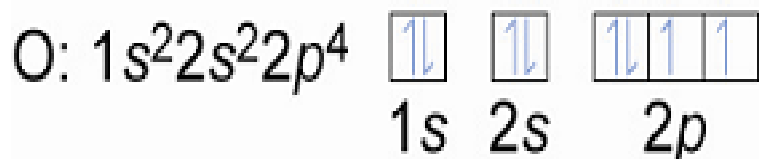
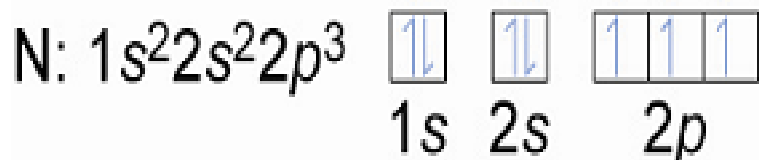
**Hund's rule of maximum multiplicity** applies. This rule states that the filling the orbitals of same energy, pairing of electron does not takes place until all these orbitals are singly filled with electron having parallel spins.

In the case of carbon, this means that the two  $2p$  electrons each occupy a different  $2p$  orbital.



**Carbon's electron configuration has two unpaired electrons in the  $2p$  orbitals.**

The electron configurations of nitrogen, oxygen, fluorine, and neon are shown here. Notice that the highest-energy orbital for all second-row elements is in the second energy level ( $2s$  or  $2p$ ).



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Chromium has 24 electrons so we expect:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$

Copper has 29 electrons so we expect:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^9$

# UNIT II- PERIODIC PROPERTIES, INTERMOLECULAR FORCES AND POTENTIAL ENERGY SURFACES

Z	Element	Configuration	Z	Element	Configuration	Z	Element	Configuration
1	H	1s <sup>1</sup>	41	Nb	[Kr]5s <sup>1</sup> 4d <sup>4</sup>	81	Tl	[Xe]6s <sup>2</sup> 5d <sup>10</sup> 4f <sup>14</sup> 6p <sup>1</sup>
2	He	1s <sup>2</sup>	42	Mo	[Kr]5s <sup>1</sup> 4d <sup>5</sup>	82	Pb	[Xe]6s <sup>2</sup> 5d <sup>10</sup> 4f <sup>14</sup> 6p <sup>2</sup>
3	Li	[He]2s <sup>1</sup>	43	Tc	[Kr]5s <sup>2</sup> 4d <sup>5</sup>	83	Bi	[Xe]6s <sup>2</sup> 5d <sup>10</sup> 4f <sup>14</sup> 6p <sup>3</sup>
4	Be	[He]2s <sup>2</sup>	44	Ru	[Kr]5s <sup>1</sup> 4d <sup>7</sup>	84	Po	[Xe]6s <sup>2</sup> 5d <sup>10</sup> 4f <sup>14</sup> 6p <sup>4</sup>
5	B	[He]2s <sup>2</sup> 2p <sup>1</sup>	45	Rh	[Kr]5s <sup>1</sup> 4d <sup>8</sup>	85	At	[Xe]6s <sup>2</sup> 5d <sup>10</sup> 4f <sup>14</sup> 6p <sup>5</sup>
6	C	[He]2s <sup>2</sup> 2p <sup>2</sup>	46	Pd	[Kr]4d <sup>10</sup>	86	Rn	[Xe]6s <sup>2</sup> 5d <sup>10</sup> 4f <sup>14</sup> 6p <sup>6</sup>
7	N	[He]2s <sup>2</sup> 2p <sup>3</sup>	47	Ag	[Kr]5s <sup>1</sup> 4d <sup>10</sup>	87	Fr	[Rn]7s <sup>1</sup>
8	O	[He]2s <sup>2</sup> 2p <sup>4</sup>	48	Cd	[Kr]5s <sup>2</sup> 4d <sup>10</sup>	88	Ra	[Rn]7s <sup>2</sup>
9	F	[He]2s <sup>2</sup> 2p <sup>5</sup>	49	In	[Kr]5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>1</sup>	89	Ac	[Rn]7s <sup>2</sup> 6d <sup>1</sup>
10	Ne	[He]2s <sup>2</sup> 2p <sup>6</sup>	50	Sn	[Kr]5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>2</sup>	90	Th	[Rn]7s <sup>2</sup> 6d <sup>2</sup>
11	Na	[Ne]3s <sup>1</sup>	51	Sb	[Kr]5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>3</sup>	91	Pa	[Rn]7s <sup>2</sup> 6d <sup>1</sup> 5f <sup>2</sup>
12	Mg	[Ne]3s <sup>2</sup>	52	Te	[Kr]5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>4</sup>	92	U	[Rn]7s <sup>2</sup> 6d <sup>1</sup> 5f <sup>3</sup>
13	Al	[Ne]3s <sup>2</sup> 3p <sup>1</sup>	53	I	[Kr]5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>5</sup>	93	Np	[Rn]7s <sup>2</sup> 6d <sup>1</sup> 5f <sup>4</sup>
14	Si	[Ne]3s <sup>2</sup> 3p <sup>2</sup>	54	Xe	[Kr]5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>6</sup>	94	Pu	[Rn]7s <sup>2</sup> 5f <sup>6</sup>
15	P	[Ne]3s <sup>2</sup> 3p <sup>3</sup>	55	Cs	[Xe]6s <sup>1</sup>	95	Am	[Rn]7s <sup>2</sup> 5f <sup>7</sup>
16	S	[Ne]3s <sup>2</sup> 3p <sup>4</sup>	56	Ba	[Xe]6s <sup>2</sup>	96	Cm	[Rn]7s <sup>2</sup> 6d <sup>1</sup> 5f <sup>7</sup>
17	Cl	[Ne]3s <sup>2</sup> 3p <sup>5</sup>	57	La	[Xe]6s <sup>2</sup> 5d <sup>1</sup>	97	Bk	[Rn]7s <sup>2</sup> 5f <sup>9</sup>
18	Ar	[Ne]3s <sup>2</sup> 3p <sup>6</sup>	58	Ce	[Xe]6s <sup>2</sup> 5d <sup>1</sup> 4f <sup>1</sup>	98	Cf	[Rn]7s <sup>2</sup> 5f <sup>10</sup>
19	K	[Ar]4s <sup>1</sup>	59	Pr	[Xe]6s <sup>2</sup> 4f <sup>3</sup>	99	Es	[Rn]7s <sup>2</sup> 5f <sup>11</sup>
20	Ca	[Ar]4s <sup>2</sup>	60	Nd	[Xe]6s <sup>2</sup> 4f <sup>4</sup>	100	Fm	[Rn]7s <sup>2</sup> 5f <sup>12</sup>
21	Sc	[Ar]4s <sup>2</sup> 3d <sup>1</sup>	61	Pm	[Xe]6s <sup>2</sup> 4f <sup>5</sup>	101	Md	[Rn]7s <sup>2</sup> 5f <sup>13</sup>
22	Ti	[Ar]4s <sup>2</sup> 3d <sup>2</sup>	62	Sm	[Xe]6s <sup>2</sup> 4f <sup>6</sup>	102	No	[Rn]7s <sup>2</sup> 5f <sup>14</sup>
23	V	[Ar]4s <sup>2</sup> 3d <sup>3</sup>	63	Eu	[Xe]6s <sup>2</sup> 4f <sup>7</sup>	103	Lr	[Rn]7s <sup>2</sup> 6d <sup>1</sup> 5f <sup>14</sup>
24	Cr	[Ar]4s <sup>1</sup> 3d <sup>5</sup>	64	Gd	[Xe]6s <sup>2</sup> 5d <sup>1</sup> 4f <sup>7</sup>	104	Rf	[Rn]7s <sup>2</sup> 6d <sup>2</sup> 5f <sup>14</sup>
25	Mn	[Ar]4s <sup>2</sup> 3d <sup>5</sup>	65	Tb	[Xe]6s <sup>2</sup> 4f <sup>9</sup>	105	Db	[Rn]7s <sup>2</sup> 6d <sup>3</sup> 5f <sup>14</sup>
26	Fe	[Ar]4s <sup>2</sup> 3d <sup>6</sup>	66	Dy	[Xe]6s <sup>2</sup> 4f <sup>10</sup>	106	Sg	[Rn]7s <sup>2</sup> 6d <sup>4</sup> 5f <sup>14</sup>
27	Co	[Ar]4s <sup>2</sup> 3d <sup>7</sup>	67	Ho	[Xe]6s <sup>2</sup> 4f <sup>11</sup>	107	Bh	[Rn]7s <sup>2</sup> 6d <sup>5</sup> 5f <sup>14</sup>
28	Ni	[Ar]4s <sup>2</sup> 3d <sup>8</sup>	68	Er	[Xe]6s <sup>2</sup> 4f <sup>12</sup>	108	Hs	[Rn]7s <sup>2</sup> 6d <sup>6</sup> 5f <sup>14</sup>
29	Cu	[Ar]4s <sup>1</sup> 3d <sup>10</sup>	69	Tm	[Xe]6s <sup>2</sup> 4f <sup>13</sup>	109	Mt	[Rn]7s <sup>2</sup> 6d <sup>7</sup> 5f <sup>14</sup>
30	Zn	[Ar]4s <sup>2</sup> 3d <sup>10</sup>	70	Yb	[Xe]6s <sup>2</sup> 4f <sup>14</sup>	110	Ds	[Rn]7s <sup>2</sup> 6d <sup>8</sup> 5f <sup>14</sup>
31	Ga	[Ar]4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>1</sup>	71	Lu	[Xe]6s <sup>2</sup> 5d <sup>1</sup> 4f <sup>14</sup>	111	Rg	[Rn]7s <sup>2</sup> 6d <sup>9</sup> 5f <sup>14</sup>
32	Ge	[Ar]4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>2</sup>	72	Hf	[Xe]6s <sup>2</sup> 5d <sup>2</sup> 4f <sup>14</sup>	112	Cn	[Rn]7s <sup>2</sup> 6d <sup>10</sup> 5f <sup>14</sup>
33	As	[Ar]4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>3</sup>	73	Ta	[Xe]6s <sup>2</sup> 5d <sup>3</sup> 4f <sup>14</sup>	113	—	[Rn]7s <sup>2</sup> 6d <sup>10</sup> 5f <sup>14</sup> 7p <sup>1</sup>
34	Se	[Ar]4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>4</sup>	74	W	[Xe]6s <sup>2</sup> 5d <sup>4</sup> 4f <sup>14</sup>	114	—	[Rn]7s <sup>2</sup> 6d <sup>10</sup> 5f <sup>14</sup> 7p <sup>2</sup>
35	Br	[Ar]4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>5</sup>	75	Re	[Xe]6s <sup>2</sup> 5d <sup>5</sup> 4f <sup>14</sup>	115	—	[Rn]7s <sup>2</sup> 6d <sup>10</sup> 5f <sup>14</sup> 7p <sup>3</sup>
36	Kr	[Ar]4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>6</sup>	76	Os	[Xe]6s <sup>2</sup> 5d <sup>6</sup> 4f <sup>14</sup>	116	—	[Rn]7s <sup>2</sup> 6d <sup>10</sup> 5f <sup>14</sup> 7p <sup>4</sup>
37	Rb	[Kr]5s <sup>1</sup>	77	Ir	[Xe]6s <sup>2</sup> 5d <sup>7</sup> 4f <sup>14</sup>	117	—	[Rn]7s <sup>2</sup> 6d <sup>10</sup> 5f <sup>14</sup> 7p <sup>5</sup>
38	Sr	[Kr]5s <sup>2</sup>	78	Pt	[Xe]6s <sup>1</sup> 5d <sup>9</sup> 4f <sup>14</sup>	118	—	[Rn]7s <sup>2</sup> 6d <sup>10</sup> 5f <sup>14</sup> 7p <sup>6</sup>
39	Y	[Kr]5s <sup>2</sup> 4d <sup>1</sup>	79	Au	[Xe]6s <sup>1</sup> 5d <sup>10</sup> 4f <sup>14</sup>			
40	Zr	[Kr]5s <sup>2</sup> 4d <sup>2</sup>	80	Hg	[Xe]6s <sup>2</sup> 5d <sup>10</sup> 4f <sup>14</sup>			

## UNIT II- PERIODIC PROPERTIES, INTERMOLECULAR FORCES AND POTENTIAL ENERGY SURFACES

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### COORDINATION NUMBERS

It is defined as the number of coordinate bonds formed by central metal atom with the ligands.

In otherwords, the maximum number of atoms or groups which can be co-ordinated with the central metal ion is known as its co-ordination number (C.N). The co-ordinated groups are called ligands. Each metal has a fixed co-ordination number. Co-ordination number is sometimes called Werner's co-ordination number. E.g:

Coordination number	Examples
2	$[\text{Ag}(\text{NH}_3)_2]^+$ , $[\text{Ag}(\text{CN})_2]^-$
4	$[\text{Ni}(\text{CO})_4]$ , $[\text{CuCl}_4]^{3-}$ , $[\text{Pd}(\text{NH}_3)_2\text{Cl}_2]$ , $[\text{Pt}(\text{NH}_3)_4]^{2+}$
5	$[\text{Fe}(\text{CO})_5]$
6	$[\text{Cr}(\text{NH}_3)_6]^{3+}$ , $[\text{Cr}(\text{NH}_3)_3\text{Cl}_3]$ , $[\text{Co}(\text{NO}_2)_6]^{3-}$ , $[\text{Fe}(\text{CN})_6]^{3-}$ , $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$ , $[\text{PtCl}_6]^{2-}$

The co-ordination number of metals vary from 2 to 10, but the most common co-ordination numbers are 4 and 6.

Coordination number	Examples
4	$\text{Zn}^{2+}$ , $\text{Ni}^{2+}$ , $\text{Cu}^{2+}$ , $\text{Pd}^{2+}$ , $\text{Pt}^{2+}$ , $\text{Cd}^{2+}$
6	$\text{Cr}^{3+}$ , $\text{Co}^{3+}$ , $\text{Fe}^{3+}$ , $\text{Pt}^{4+}$ , $\text{Fe}^{2+}$

### Neutral Complexes

Coordination number	Examples
5	$[\text{Fe}(\text{CO})_5]$
4	$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
6	$[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3]$
6	$[\text{Co}(\text{NH}_3)_3\text{NO}_2(\text{CN})\text{Cl}]$

### Cationic complexes

Coordination number	Examples
6	$[\text{Pt}(\text{NH}_3)_4\text{Cl}_2] \text{Br}_2$
6	$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$
2	$[\text{Ag}(\text{NH}_3)_2]\text{Cl}$

## UNIT II- PERIODIC PROPERTIES, INTERMOLECULAR FORCES AND POTENTIAL ENERGY SURFACES

### Anionic Complexes

Coordination number	Examples
6	$[\text{Fe}(\text{CN})_6]^{3-}$
4	$[\text{Ni}(\text{CN})_4]^{2-}$
4	$\text{K}_4[\text{Ni}(\text{CN})_4]$

### EFFECTIVE NUCLEAR CHARGE (SLATER'S RULE)

In a multielectron atom, the electron of the inner-shell decrease the force of attraction exerted by the nucleus on the valence electrons. This is called shielding effect. Due to this, the nuclear charge ( $Z$ ) actually present on the nucleus, reduces and is called effective nuclear charge ( $Z_{\text{eff}}$ ). It is calculated by using the formula

The relation between energy and energy shell for an electron in hydrogen atom is given by expression

$$Z_{\text{eff}} = Z - \sigma$$

Where  $\sigma$  is screening constant. The magnitude of  $\sigma$  is determined by Slater's Rule.

#### Slater's Rule

- Write the electronic configuration in the following order and groups (1s) (2s, 2p) (3s, 3p) (3d) (4s, 4p) (4d) (4f) (5s, 5p) (6s, 6p) etc.
- Electrons of (n+1) shell (shell higher than considering electrons) do not contribute in shielding i.e.  $\sigma = 0$
- All other electrons in (ns, np) group contribute  $\sigma = 0.35$  each
- All electrons of (n-1) s and p shell contribute  $\sigma = 0.85$  each
- All electrons of (n-2) s and p shell or lower shell contribute  $\sigma = 1.00$  each.
- All electrons of nd and nf orbital contribute  $\sigma = 0.35$  and those of (n-1) and f or lower orbital contribute  $\sigma = 1.00$  each.
- Be (At.no: 4) =  $1s^2 2s^2$   
 $\sigma = 0.35 + 2 \times 0.85$   
 $= 2.05$   
 $Z_{\text{eff}} = Z - \sigma$   
 $= 4 - 2.05$   
 $= 1.95$

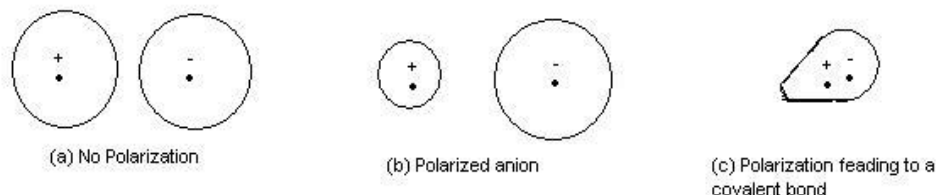
### POLARIZABILITY

Anions are larger in size than cations and therefore, their electron clouds are less lightly held. A small highly charged cation shall, therefore, distort the electron cloud of the large anions in a manner that it increases the electron density between the nuclei. For example, the large iodide ion by itself is perfectly symmetrical. However when a small positively charged lithium ion comes close to the iodide ion, the electron cloud on the anion is pulled towards the positive lithium ion. The iodide ion is said to be polarized and the process is called polarization.

The polarization effect produces covalence in LiI molecule because there is some electron density in between the nuclei as in the sharing of electrons in a covalent bond. The power of an ion to distort the other ion is known as its polarizing power and the

## UNIT II- PERIODIC PROPERTIES, INTERMOLECULAR FORCES AND POTENTIAL ENERGY SURFACES

tendency of the anion to distort is known as its polarizability. The polarizing power and the tendency of the anion to distort is known as its polarizability. The polarizing power of a cation is proportional to its charge/radius ratio. When a large and soft anion comes under the influence of a small cation, the cation is able to polarize the anion. (Fig.).



This results in deformation of electron cloud on anion, called the polarization of anion. Due to small size of the cation, polarization of the cation is not much. Extensive polarization would be witnessed when cation penetrates the anionic electron cloud giving a covalent. In compound consisting of large negative ions and small positive ions, the polarization leads to partial covalent character in ionic compounds. Examples of such ionic covalent compounds are  $\text{FeCl}_3$ ,  $\text{AlCl}_3$ ,  $\text{LiBr}$  etc.

The partial covalent character of ionic bonds was discussed by Fajan's in terms of following rules:

The smaller the size of cation and the larger the size of the anion, the greater the covalent character of an ionic bond.

The greater the charge on the cation or anion, the greater the covalent character of the ionic bond.

### OXIDATION STATE

It is oxidation number that denotes the charge, explaining the number of electrons it has lost to form the ion.

An element may have different values of oxidation number depending upon the nature of compound in which it is present.

Oxidation number of an element may be a whole number (Positive or negative) or fractional or zero.

#### Important Points for Determining Oxidation number:

- ✓ The algebraic sum of the oxidation numbers of all the atoms in an uncharged (neutral) compound is zero. In an ion, the algebraic sum is equal to the charge on the ion.
- ✓ The elements in the elementary state have oxidation number zero, e.g.  $\text{He}$ ,  $\text{Cl}_2$ ,  $\text{S}_8$ ,  $\text{P}_4$  etc.
- ✓ As fluorine is the most electronegative element, it always has an oxidation number of -1 in all of its compounds.
- ✓ In compounds containing oxygen, the oxidation number of oxygen is -2 except in peroxides (-1) such as  $\text{Na}_2\text{O}_2$ , in  $\text{OF}_2$  and in  $\text{O}_2\text{F}_2$  (+2 and +1 respectively).
- ✓ In all compounds, except ionic metallic hydrides, the oxidation number of hydrogen is +1. In metal hydrides like  $\text{NaH}$ ,  $\text{MgH}_2$ ,  $\text{CaH}_2$ ,  $\text{LiH}$  etc., the oxidation number of hydrogen is -1.
- ✓ Oxidation number for alkali metals is +1 and for alkaline earth metals is +2.
- ✓ Oxidation number of metal in amalgams is zero.

## UNIT II- PERIODIC PROPERTIES, INTERMOLECULAR FORCES AND POTENTIAL ENERGY SURFACES

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- ✓ In case of coordinate bond, it gives +2 value of oxidation number to less electronegative atom and -2 values to more electronegative atom when coordinative bond is directed from less electronegative atom to more electronegative atom.
- ✓ If coordinate bond is directed from more electronegative to less electronegative atom then its contribution be zero for both the atoms.
- ✓ For p-block elements (Except F and O), the highest oxidation number is equal to their group number and lowest oxidation number is equal to the group number minus eight.
- ✓ In transition elements the lowest oxidation number is equal to the number of ns electrons and highest oxidation number is equal to number of 'ns' and (n-1)d unpaired electrons.

### Determination of Oxidation number of underlined Element

(i)  $K_2\underline{Cr}_2O_7$

$$K = +1$$

$$Cr = x$$

$$O = -2$$

$$2 + 2x + (7 \times -2) = 0$$

$$2 + 2x - 14 = 0$$

$$2x = 14 - 2$$

$$X = 12/2$$

$$X = 6$$

(ii)  $[\underline{Fe}(CN)_6]^{4-}$

$$Fe = x$$

$$CN = -1$$

$$X + (6 \times -1) = -4$$

$$X - 6 = -4$$

$$X = 2.$$

### **INTERMOLECULAR FORCES**

The forces of attraction existing among the molecules of a substance (gaseous, liquid or solid) are called intermolecular forces.

Greater the intermolecular forces, higher is the melting and boiling point. Attractive intermolecular forces are known as van der Waals forces.

The different types of intermolecular forces are briefly explained below

(i) Dispersion forces or London forces: Dispersion forces or London forces are present among non-polar atoms and molecules, e.g. among the atoms or chlorine molecules. These are the weakest intermolecular forces. These forces increases with

(a) increase in number of electrons in molecules

(b) increase in molecular size.

(ii) Dipole-dipole interactions: Dipole-dipole forces act between the molecules possessing permanent dipoles.

The interaction is stronger than London forces and weaker than ion-ion interaction. The intensity of these forces is generally hampered by increase in temperature.



## UNIT II- PERIODIC PROPERTIES, INTERMOLECULAR FORCES AND POTENTIAL ENERGY SURFACES

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(iii) Dipole-induced dipole forces: Dipole-induced dipole forces act between the polar molecules having permanent dipole and the molecules lacking permanent dipole.

(iv) Hydrogen bond: It is special case of dipole-dipole interaction. This is found in the molecules in which highly polar is determined by the coulombic interaction between the lone-pair of electrons of the electronegative atom of one molecule and H-atom of other molecule.

### IONIC (OR) ELECTROVALENT BOND

An ionic bond is formed by the complete transference of one or more electrons from the outermost energy shell (called, valency shell) of one atom to outermost energy shell of another dissimilar atom.

The atom which loses the electrons becomes a positive ion (cation); while the other atom which gains electrons becomes a negative ion (anion). These two oppositely charged ions combine, due to electrostatic forces of attraction, to form an electrovalent or ionic compound. It may be pointed here that electrostatic attraction always tends to decrease the potential energy.

Conditions for the formation of ionic bonds:

Formation of an ionic bond depends upon ionization energy and electron affinity involved. One of the atoms should have a low ionization energy, so that only a small amount of energy is required to pull out an electron from its outermost energy level. On the other hand, the other atom should have a high electron affinity, so that it can readily accept an electron in its outermost energy level.

### REAL GAS

A real gas is one which obeys the gas laws fairly well under low pressure or high temperature. All gases are real gas. They show more and more deviations from the gas laws as pressure increased or the temperature is decreased.

#### (i) At low Pressure:

At extremely low pressure, volume (V) is very large. Hence the correction term  $a/V^2$  is very small. Similarly, the correction term b is also very small as compared to V. Thus both the correction terms can be neglected so that the van der Waals equation reduces to  $PV=RT$ . This is why at extremely low pressures, the gases obey the ideal gas equation.

#### (ii) At moderate pressure:

As the pressure is increased, the volume decreases and hence the factor  $a/V^2$  increases. Thus the factor  $a/V^2$  can no longer be neglected. However, if the pressure is not too high, the volume V is still sufficiently large so that b can be neglected in comparison with V. Thus the van der Waals equation reduces to

$$\{P + a/V^2\} V = RT$$

(or)

$$PV + a/V = RT$$

(or)

$$PV = RT - a/V$$

Thus PV is less than RT by a factor  $a/V$ . As the pressure increases, V decreases, so that the factor  $a/V$  increases. Thus PV decreases as the pressure is increased. This explains why a dip the plots of PV vs P of real gases is obtained.

#### (iii) At high Pressure

## UNIT II- PERIODIC PROPERTIES, INTERMOLECULAR FORCES AND POTENTIAL ENERGY SURFACES

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As the pressure is increased further so that it is fairly high,  $V$  is so small that  $b$  can no longer be neglected in comparison with  $V$ . Although under these conditions the factor  $a/V^2$  is quite large but since  $P$  is very high so  $a/V^2$  can be neglected in comparison with  $P$ . Thus the van der Waals equation reduces to

$$P(V-b) = RT$$

(or)

$$PV - Pb = RT$$

(or)

$$PV = RT + Pb$$

Thus  $PV$  is greater than  $RT$  by a factor  $Pb$ . Now as the pressure is increased, the factor  $Pb$  increases more and more. This explains why after the minima in the curves, the product  $PV$  increases continuously as the pressure is increased more and more.

(iv) At high temperature

At any given pressure, if the temperature is sufficiently high,  $V$  is very large so that as in case (i), the van der Waals equation reduces to  $PV=RT$ . Hence at high temperature, real gas behaves like the ideal gas.

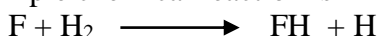
**CRITICAL PHENOMENON:**

Andrews studied the pressure-temperature conditions for liquefaction of several gases. He concluded that for each gas there is a temperature above which the gas cannot be liquefied, however high pressure we may apply. This temperature is called critical temperature which is different for different gases.

At critical temperature and pressure, the gas becomes indistinguishable with its liquid and is said to be in critical state. The smooth merging of the gas with its liquid state is referred to as the critical phenomenon.

### REACTION SURFACES

In recent years we have been able to combine quantum mechanical equations and the power of digital computers to determine the electronic energy of many molecules. Examples of simple chemical reaction is

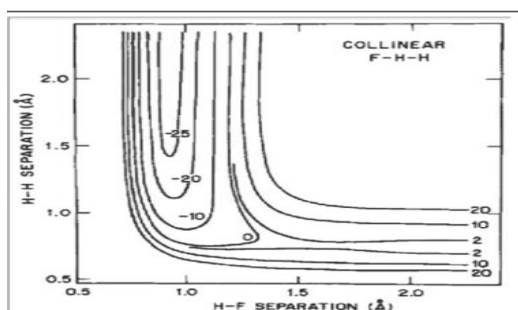


### POTENTIAL ENERGY SURFACES OF $H_2F$

$H_2F$  ( $F-H\cdots H$ ) has a linear molecule. The potential energy of this system is determined by the two distances  $F-H$  and  $H-H$ . This potential energy is equal to the electronic energy of the  $F-H-H$  molecule.

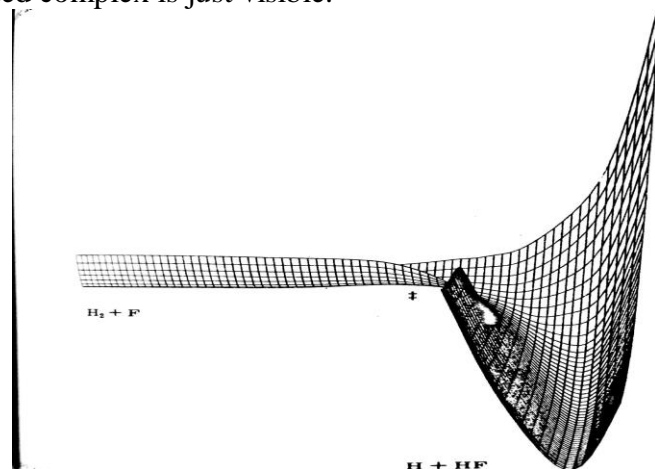
At the start of the reaction the  $F-H$  distance is large, and the  $H-H$  distance will have its normal  $H\cdots H$  bond distance of  $0.74 \text{ \AA}$ . At end of the reaction the  $H-H$  is large, and the  $F-H$  distance will have its normal  $F-H$  bond distance of  $0.92 \text{ \AA}$ . At intermediate values of these two distances, various states of the system form, including the activated complex. There will also be a unique, lowest energy path that forms by special combinations of the two distances. The potential energy for this system forms a surface; Figure 1 shows a contour diagram of this potential energy surface.

## UNIT II- PERIODIC PROPERTIES, INTERMOLECULAR FORCES AND POTENTIAL ENERGY SURFACES



In this figure the reaction as written starts in the lower right side and moves to the upper left of the diagram. The energy of the system is assumed to be zero for separated F and H<sub>2</sub>, and the very start of the reaction is off the diagram on the lower right. When F—H reaches only 4.8 Å, the energy of the system rises to 1 kJ mol<sup>-1</sup>, but the first contour shown in figure 1 is for 6.7 kJ mol<sup>-1</sup>. Since it is easier to calculate energies associated with long H—H distance, more detail is shown in Fig.1 for the end of the reaction than for its start. The activated complex forms at the saddle point corresponding to an F—H distance of 1.54 Å, an H—H distance of 0.77 Å, and an energy of 7.0 kJ mol<sup>-1</sup>. The experimental activation energy is 4.7 kJ mol<sup>-1</sup>, but it is uncertain by at least  $\pm 1$  kJ mol<sup>-1</sup>.

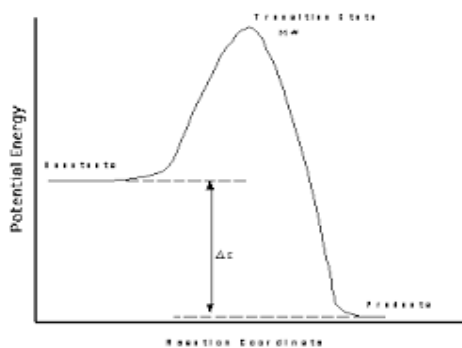
After the activated complex forms, the reaction proceeds across the contours in Fig.1 until the upper left corner of the diagram is reached at which point the products have stabilized. The calculated  $\Delta E^\circ$  value for this reaction is -144 kJ mol<sup>-1</sup>, and the experimental value is -133 kJ mol<sup>-1</sup>. Fig.2 shows the same potential energy surface looking down the “valley” formed by the product. The low saddle at the area of the activated complex is just visible.



In Fig.3 we used line to represent the most probable reaction path. That path corresponds to the bottom of the valley in Fig.2 or lowest energy path (dashed line) in Fig.1.

## UNIT II- PERIODIC PROPERTIES, INTERMOLECULAR FORCES AND POTENTIAL ENERGY SURFACES

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The reaction coordinate in Fig.3 is the combination of F—H and H—H distances that result from this lowest energy path from reactants to products. The reaction surface diagrams can also have paths in which the reactants have excess kinetic energy. In this case the system would appear to vibrate against the “sides” of the valleys. The lowest energy path is the most important, for it requires the least amount of activation energy.

## UNIT III- SPECTROSCOPIC TECHNIQUES AND APPLICATIONS

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### **Spectroscopy:**

It is the branch of science dealing with the study of interaction of electromagnetic radiation with matter. During the interactions, the energy is absorbed or emitted by the matter. The measurement of this radiation frequency (absorbed or emitted) are made using spectroscopy.

Spectroscopy is one of the most powerful tool available for the study of atomic and molecular structure, and is used in the analysis of most of the samples.

### **Types of spectroscopy:**

The study of spectroscopy can be carried out under the following headings.

1. Atomic spectroscopy
2. Molecular spectroscopy

1. Atomic spectroscopy: It deals with the interaction of the electromagnetic radiation with atoms. During which the atoms absorb radiation and gets excited from the ground state electronic energy level to another.

2. Molecular spectroscopy: It deals with the interaction of the electromagnetic radiation with molecules. This results in transition between rotational, vibrational and electronic energy levels.

### **Differences between molecular spectra and atomic spectra**

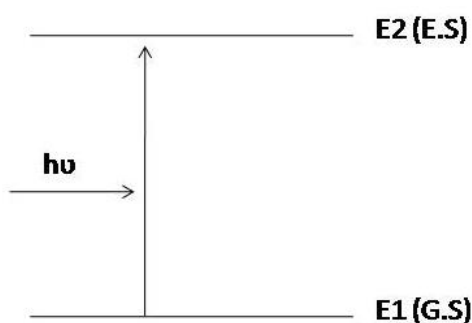
<u>S.No</u>	Atomic spectra	Molecular spectra
1	It occurs from the interaction of atoms with electromagnetic radiation	It occurs from the interaction of molecules with electromagnetic radiation
2	Atomic spectra is a line spectra	Molecular spectra is a complicated spectra
3	It is due to electronic transition in an element	It is due to vibrational, rotational and electronic transition in a molecule.

## UNIT III- SPECTROSCOPIC TECHNIQUES AND APPLICATIONS

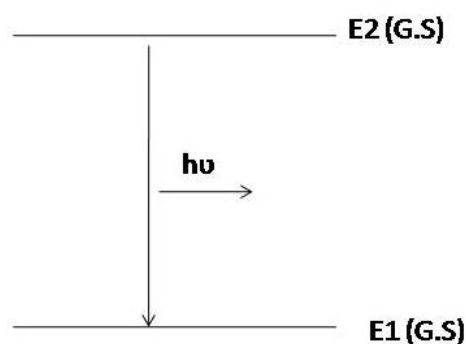
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### How does a spectrum arise?

1. Absorption spectrum: Consider molecule having only two energy levels E1 and E2. When a beam of electromagnetic radiation is allowed to fall on a molecule in the ground state, the molecule absorbs photon of energy  $h\nu$  and undergoes a transition from the lower energy level to the higher energy level. The measurement of this decrease in the intensity of radiation is the basis of absorption spectroscopy. Thus spectrum obtained is called the absorption spectrum.
2. Emission spectrum: If the molecules come down from the excited state to the ground state with the emission of photons of energy  $h\nu$ , the spectrum obtained is called emission spectrum.



**(a) Absorption Spectrum**



**(b) Emission Spectrum**

### Electromagnetic radiation

Electromagnetic radiation is a form of energy that is transmitted through space at an enormous velocity. As the name implies, an electromagnetic radiation has an electric component and a magnetic component.

Electromagnetic radiation consists of waves of energy is characterized by the following parameters

1. Wave length ( $\lambda$ ): It is the distance between two successive peaks (or) crests on an electromagnetic wave.
2. Frequency ( $\nu$ ): It is number of wave length passing through a point per second.
3. Wave number ( $\tilde{\nu}$ ): It is the number of waves per centimeter.
4. Velocity (C) : It is the product of wavelength and frequency.

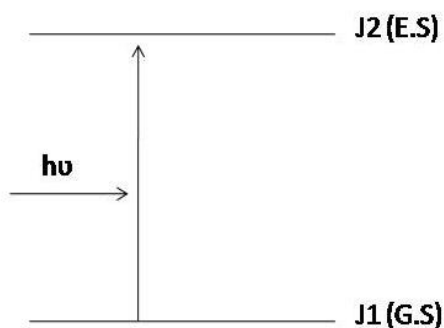
## UNIT III- SPECTROSCOPIC TECHNIQUES AND APPLICATIONS

### MICROWAVE SPECTROSCOPY (OR) ROTATIONAL SPECTROSCOPY

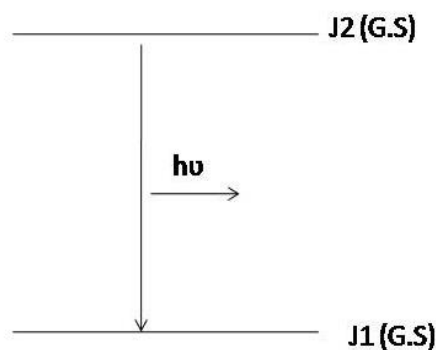
Microwave is an electromagnetic wave with a wave length 1cm-0.01cm. Frequency range : 200 MHz to 100 GHz. Wave number :  $1\text{-}100\text{cm}^{-1}$ . Microwave spectroscopy deals with the pure rotation motion of molecules and is also known as rotational spectroscopy.

The condition for observing resonance in that region is that a molecule must possess permanent dipole moment.

When a molecule having dipole moment rotates, it generates an electric field which can interact with the electric component of the microwave radiation. During interaction, energy can be absorbed or emitted and thus rotation of the molecule gives rise to a spectrum.



**(a) Absorption Microwave Spectrum**



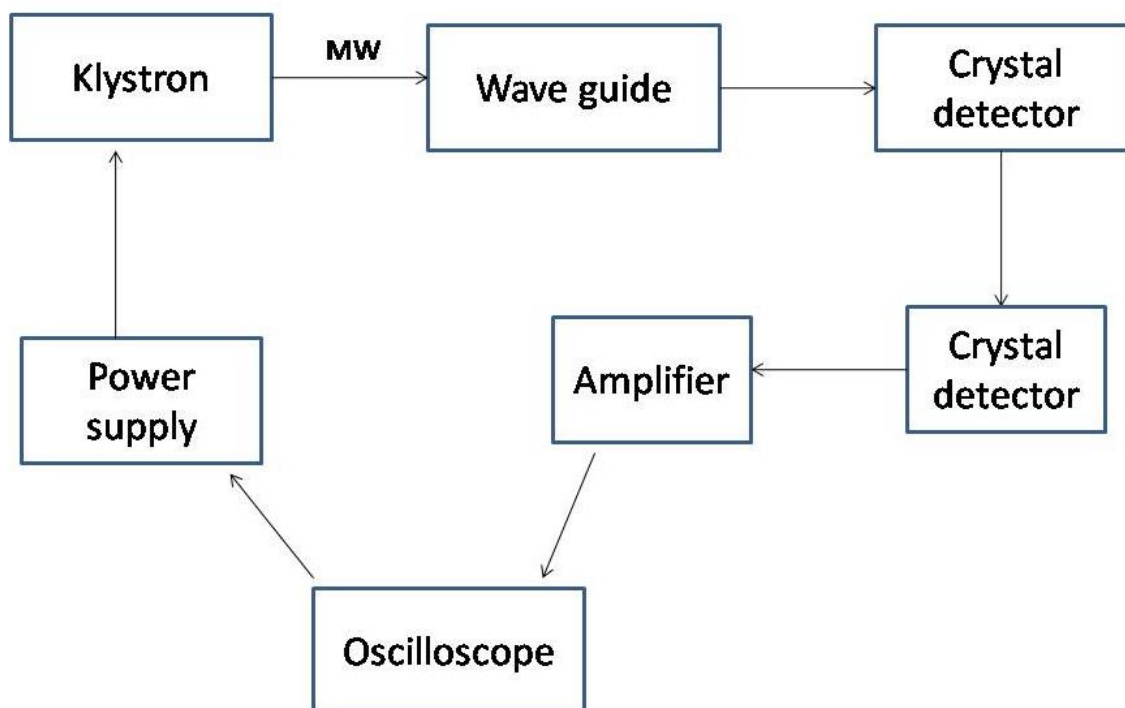
**(b) Emission Microwave Spectrum**

#### **Instrumentation:**

##### **Components of microwave spectrometer**

1. Source and monochromator: Klystron – Power supply
2. Wave guide (Hollow metallic conductors)
3. Crystal detector (quartz, Rochelle salt, barium titanate)
4. Amplifier and Oscilloscope

**Block diagram of Microwave spectrometer:**



**Working:**

Monochromatic radiations of various wavelengths in the microwave region emitted by klystron valve are allowed to pass through the sample space containing the gaseous sample of the substance under investigation. Then, the radiations are made to conduct along a rectangular tube called a waveguide. After receiving the radiations from the wave guide it vibrates and produces an electrical signal which is amplified by amplifier and then displayed either as a recording on a chart or as a pattern on an oscilloscopic screen. The pattern obtained on the chart or on the screen of the oscillograph enables one to determine the frequency or the range of frequencies of the detected microwave radiation.

The microwave spectrometer described above is usually used for the measurements of the highest accuracy because the absorption lines are narrow and fairly faithful in shape and relative intensities. The use of oscilloscope poses a serious problem that the amplifier bandwidth cannot be narrowed to remove noise and thus, the sensitivity is not exceptionally high. At the same time the new lines for unknown substances cannot be obtained very easily unless their frequencies are known within narrow limits.



## UNIT III- SPECTROSCOPIC TECHNIQUES AND APPLICATIONS

### Applications:

- (i) Determination of bond length of gaseous polar molecules with great precision.
- (ii) Ascertaining of symmetry of a gaseous molecule.
- (iii) Determinations of bond angle
- (iv) Determination of dipole moments
- (v) Calculation of free constant.

### ULTRAVIOLET AND VISIBLE (UV-VIS) SPECTROSCOPY (OR) ELECTRONIC SPECTROSCOPY

#### Principle

Transition of valency electrons within a molecule or ion from a lower electronic energy level (ground state)  $E_1$  & to higher electronic energy level (excited state)  $E_0$ .  
Amount of energy =  $E_1 - E_0 = h\nu$

#### Instrumentation:

Radiation source (Hydrogen (or) deuterium lamps)

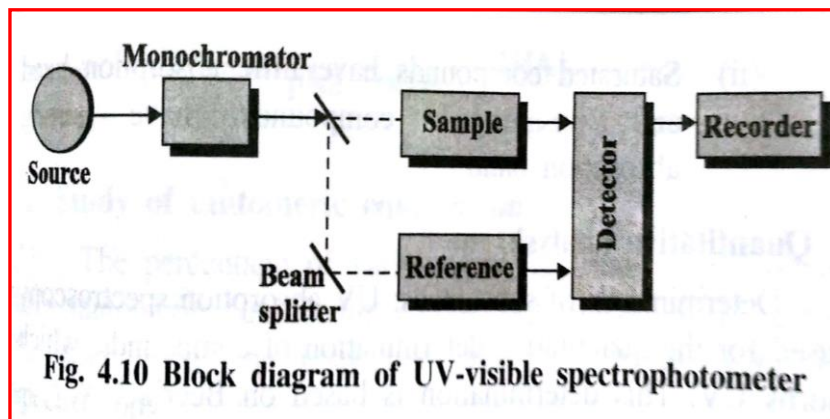
↓  
Monochromators - Disperse the radiation

↓  
Cells a) sample      b) reference (analysis)  
                                Uniform  
                                Inert to solvents  
                                ↓  
                                Transmit light

↓  
Detector (converts radiation into current)

↓  
Recording system. (signal received)

#### Working:



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Radiation source (Hydrogen (or) deuterium lamps.



Monochromators- Disperse the radiation



½ of a beam pass through to transparent cell  
Other ½ pass through cell contains solvents

Cells a) sample b) reference (analysis)



Compare the intensities of two beams.

Intensity of sample beam < Intensity of reference beam

Graph plotted wavelength Vs absorption of light.

### Applications:

❖ Predicting relationship between different groups:

- a) between two or more c-c multiple bonds
- b) between c-c & c-o double bonds
- c) between c-c double bonds & aromatic benzene ring.
- d) Structure of several vitamins.

### ❖ QUALITATIVE ANALYSIS

- for aromatic compounds
- comparing UV absorption spectrum of sample with known compounds.

### ❖ DETECTION OF IMPURITIES

- impurities present intense band appear

### ❖ QUANTITATIVE ANALYSIS

- using Beer's law  $A = -\log T = \log I_0 / I_t = \epsilon C \times$
- Plotting graph between absorbance vs concentration

### ❖ DETERMINATION OF MOLECULAR WEIGHT

- Compound converted in to suitable derivative and determined.

### ❖ DISSOCIATION CONSTANTS OF ACIDS AND BASES

$$pK_a = pH + \log [HA] / [A^-]$$

### ❖ STUDY OF TAUTOMERIC EQUILIBRIUM

- from the strength of the respective absorption bands
- eg. Keto & enol form

-

## UNIT III- SPECTROSCOPIC TECHNIQUES AND APPLICATIONS

### ❖ STUDYING KINETICS OF CHEMICAL REACTION

- Change in concentration of a product or a reactant with time.

### ❖ DETERMINATION OF CALCIUM IN BLOOD SERUM

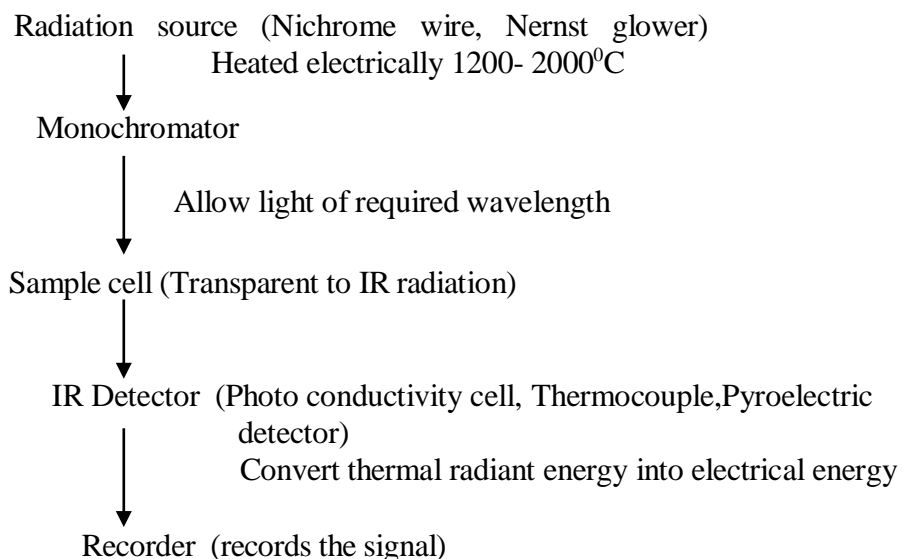
Ca (its oxalate)  $\longrightarrow$  redissolving in  $\text{H}_2\text{SO}_4$   $\longrightarrow$  treating with  
Dil. Ceric sulphate solution  $\longrightarrow$  absorption of solution (315 nm)

## INFRARED SPECTROSCOPY (OR) VIBRATIONAL SPECTROSCOPY:

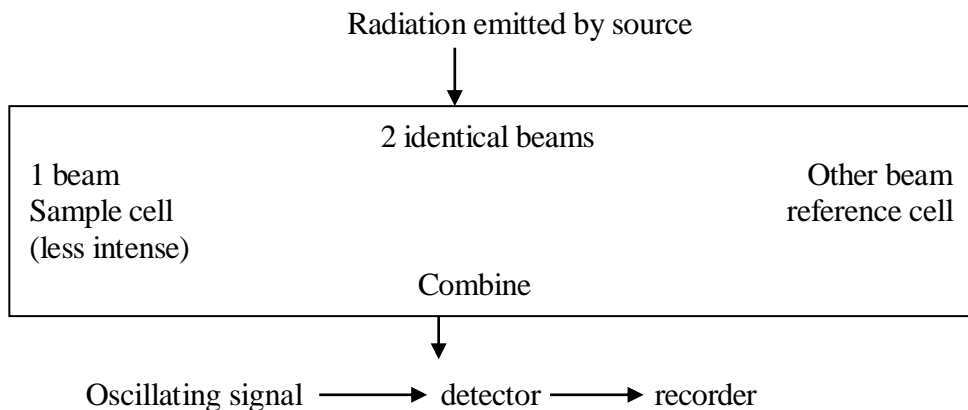
### Principle

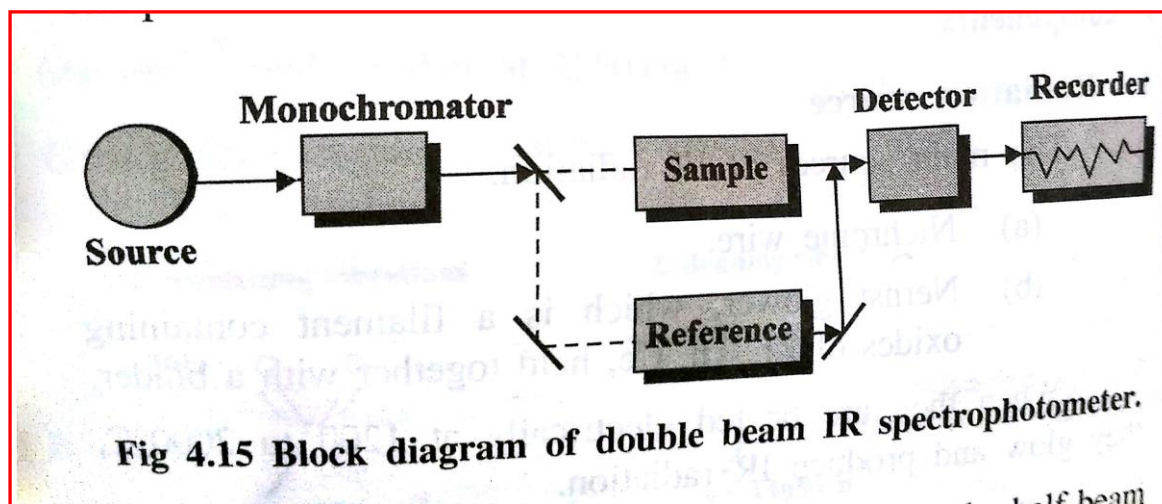
Absorption of energy by a molecule in the infrared region and transition occur between vibrational levels.

### Instrumentation



### Working





#### Applications of IR Spectroscopy

- ❖ Identity of the compound can be established  
Particular group of atoms - characteristic absorption band.
- ❖ Detection of functional groups  
functional groups absorb IR energy nearly same wavelength.
- ❖ Testing purity of sample  
Pure sample - Sharp, well resolved absorption bands  
Impure sample - Broad, poorly resolved absorption bands
- ❖ Study of progress of a chemical reaction  
Examining IR spectra at different time intervals
- ❖ Determination of shape or symmetry of a molecule  
For non-linear molecule =  $3n - 6$   
For linear molecule =  $3n - 5$
- ❖ To study tautomerism  
Keto-enol ( $\text{C}=\text{O}, \text{OH}$ ), lacto-lactum ( $-\text{NH}$ ), Mercapto-thioamide ( $\text{C}=\text{S}$ )  
Groups show a characteristic absorption band.
- ❖ Industrial applications
  - a) Determination of structure of chemical products
  - b) Determination of molecular weight
  - c) Crystallinity.

### **SURFACE CHARACTERIZATION TECHNIQUES** **SCANNING ELECTRON MICROSCOPE**

#### **Principle**

When the accelerated primary electron strikes the sample, it produces secondary electrons. These secondary electrons are collected by a positively charged detector which gives the three dimensional image of the sample or object.

#### **Construction**

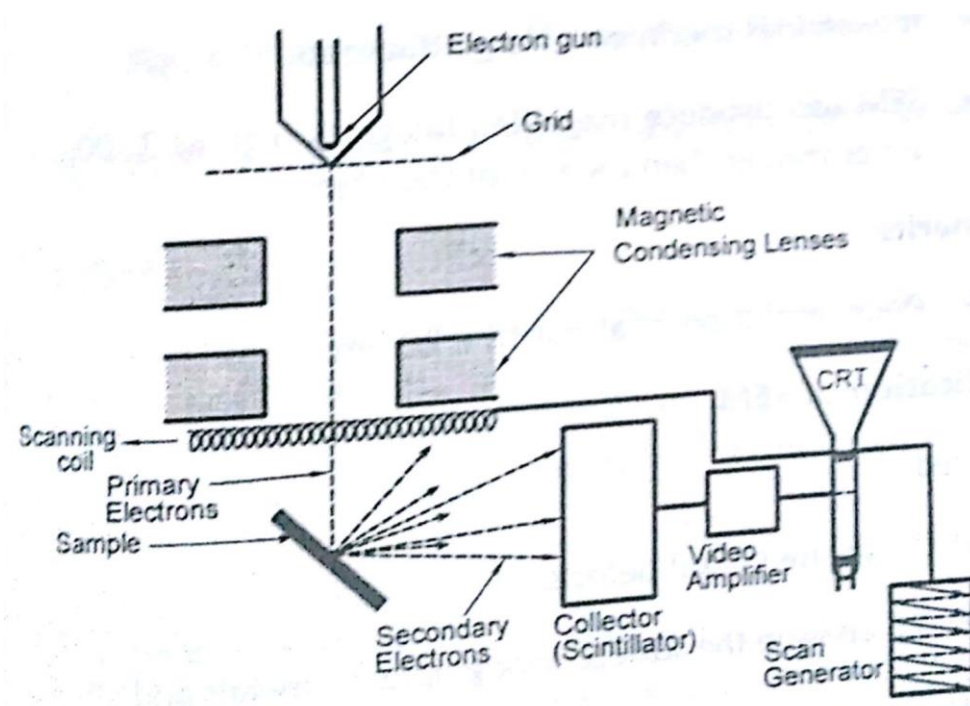
The basic components of SEM are

- (i) Electron gun is used to produce high energy electron beam.
- (ii) Magnetic condensing Lens is used to condense the electron beam.
- (iii) A scanning coil connected to scan generator.
- (iv) Scintillator / detector is used to collect the secondary electrons to convert them in to electrical signals.
- (v) Video amplifier
- (vi) CRO

#### **Working**

Electron gun produces stream of electrons and these electrons are accelerated by grid. They pass through the condensing lenses and scanning coil. Then they fall over the sample and scan it. Here low energy secondary electrons are produced. These low energy secondary electrons are collected by giving high voltage. The detector detects them and converts them into electrical signals. These electrical signals are amplified by the video amplifier and are fed to the CRO. Thus the whole picture of the line by line scanned sample is obtained in CRO by the similar procedure.

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### Advantages:

- It gives 3- dimensional images of the object
- Its focusing depth is large
- It examines specimen of large thickness.
- SEM can produce magnified image as high as 3,00,000 times greater than the size of the object

### Demerits:

Poor resolution of about 10-20nm.

### Application of SEM

It is used

- ✓ To locate crystal defects.
- ✓ To analyze the surface topography of metals and alloys.
- ✓ To study about the colloidal particles.
- ✓ Resolution is 0.1nm (or)  $1\text{\AA}$

In biology: To study virus, bacteria.

In physics: To study atomic structure of crystal in detail.

## **TRANSMISSION ELECTRON MICROSCOPE (TEM)**

### **Principle:**

Initially the electrons are accelerated up to high energy levels (in keV) and focused on the specimen. They pass through the specimen and the two dimensional image is formed on the

## UNIT III- SPECTROSCOPIC TECHNIQUES AND APPLICATIONS

fluorescent screen. For this transmitted or diffracted beam is used.

### Specimen preparation

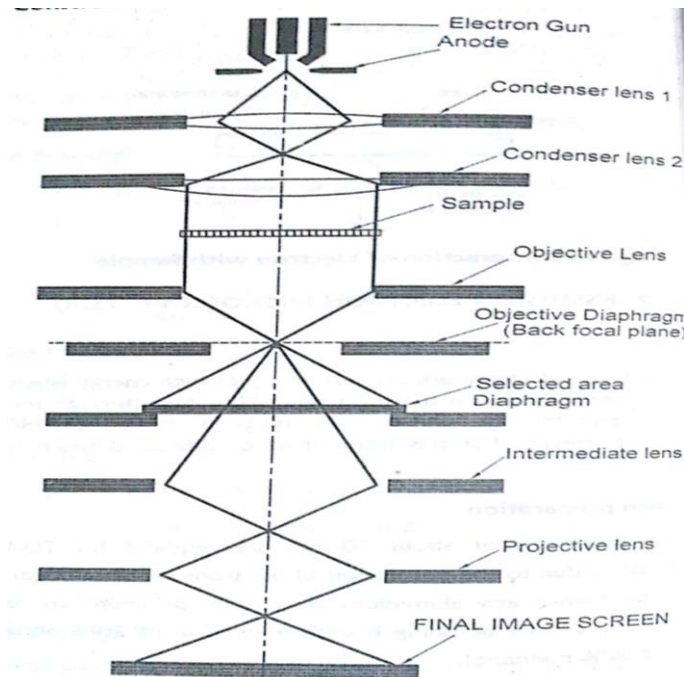
Thin specimens of about 60 nm are required for TEM observations due to the absorption of electrons in the material. If the specimen is any aluminium alloy, thin specimen can be obtained by electro polishing it with a solution of 20% nitric acid and 80% methanol.

TEM consists of the following components

- 1) Electron gun is used to produce stream of electrons.
- 2) Electromagnetic condensing lenses is used to focus the electrons on the specimen.
- 3) An objective lens to form diffraction
- 4) Some intermediate lenses to magnify the image/ diffraction pattern on the screen.
- 5) If the specimen thickness is of about 200 nm and if the specimen contains chemical elements slightly, low constant image will be obtained. To obtain amplitude contrasted image, an objective diaphragm is inserted in the back focal plane.
- 6) The crystalline parts appear dark and the amorphous parts appear bright. This imaging mode is called bright field mode.

### Working:

Electron gun produces stream of electrons. These electrons are made to fall on the object / sample using magnetic condensing lens. Based on the angle of incidence, the beam is partly transmitted and partly diffracted. Both the transmitted and diffracted beams recombine to form the image called phase contrast image. Then this resultant beam is passed through the magnetic objective lens and the aperture.



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The aperture is adjusted so that the diffracted image is eliminated from the resultant beam. Thus the final image obtained is due to the transmitted beam alone i.e., due to elastic scattering (no energy change). Then it is further magnified using projector lens. The magnified image is recorded in the fluorescent screen and this high contrast image is called bright field image. If the image obtained is due to the diffracted beam alone (by eliminating transmitted beam). i.e., due to inelastic scattering. That image after magnification is called as dark field image.

### Merits:

- TEM can produce magnified image as high as 10,00,000 times greater than the size of the object.
- High resolution.
- Resolving power is  $1\text{\AA}^\circ$  to  $2\text{\AA}^\circ$
- Can produce high contrast image.

### Demerits

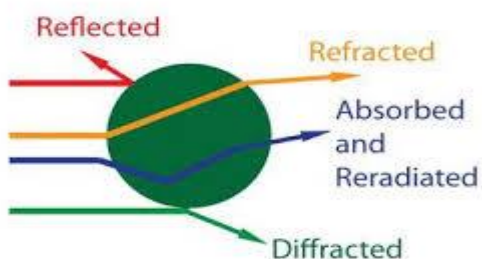
- Thin specimen should be used, not thick samples.
- Chances for structural change.
- No three dimensional image.

### Uses:

- ✓ In Nano sciences, it is used to study the internal structure of nano tubes, materials.
- ✓ To detect atomic scale defects.

### Scattering

When a Light beam Strikes a Particle, Some of the light is diffracted, Reflected, Refracted, Absorbed and Reradiated



Scattering can be broadly defined as the redirection of radiation out of the original direction of propagation, usually due to interactions with molecules and particles

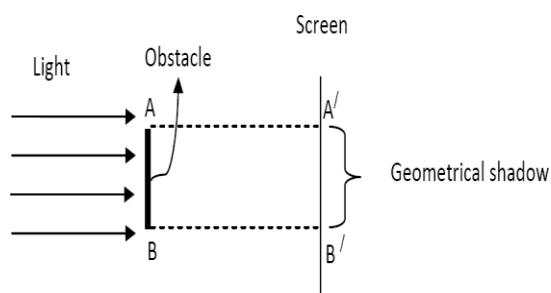
- Reflection, refraction, diffraction etc. are actually all just forms of scattering
- Matter is composed of discrete electrical charges (atoms and molecules – dipoles)
- Light is an oscillating EM field – excites charges, which radiate EM waves
- These radiated EM waves are scattered waves, excited by a source external to the scatterer
- The superposition of incident and scattered EM waves is what is observed



### **Diffraction**

**When the light falls on the obstacle whose size is comparable with the wavelength of light then the light bends around the obstacle and enters in the geometrical shadow. This bending of light is called diffraction.**

When the light is incident on an obstacle AB, their corresponding shadow is completely dark on the screen. Suppose the width of the slit is comparable to the wavelength of light, then the shadow consists of bright and dark fringes. These fringes are formed due to the superposition of bended waves around the corners of an obstacle. The amount of bending always depends on the size of the obstacle and wavelength of light used.



### **FLUORESCENCE**

A large number of substances are known which can absorb UV or light energy. But these substances lose excess energy as heat through collisions with neighbouring atoms or molecules. However, a number of important substances are also known which lose only part of this excess energy as heat and emit the remaining energy as electromagnetic radiation of a wavelength longer than that absorbed. This process of emitting radiation is collectively known as luminescence.

In luminescence, light is produced at low temperatures. Therefore, the light produced by this process is regarded as light without heat or cold light.

Luminescence is of two types:

- (a) Fluorescence: When a beam of light is incident on certain substances, they emit visible light or radiations. This phenomenon is known as fluorescence and the substances showing this phenomenon are known as fluorescent substances.
- (b) Phosphorescence: When light radiation is incident on certain substances, they emit light continuously even after the incident light is cut off. This type of delayed fluorescence is called phosphorescence and the substances are called phosphorescent substances.

### **PRINCIPLE**

Fluorescence and phosphorescence are photon emission processes that occur during molecular relaxation from electronic excited states. These photonic processes involve transitions between electronic and vibrational states of polyatomic fluorescent molecules (fluorophores). Fluorophores play the central role in fluorescence spectroscopy. Fluorophores are the components in molecules that cause them to fluoresce. Majorly

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fluorophores are the molecule which contain aromatic rings such as Tyrosine, Tryptophan, Fluorescein etc

The Jablonski diagram offers a convenient representation of the excited state structure and the relevant transitions. Molecules that have become electronically excited subsequent to the absorption of visible (400~700nm), UV (200~400nm), or NIR(700~1100 nm) radiation. Excitation process to the excited state from the ground state is very fast, on the order of  $10^{-15}$  s. After excitation, the molecule is quickly relaxed to the lowest vibrational level of the excited electronic state. This rapid vibrational relaxation process occurs on the time scale of femto seconds to picoseconds. Fluorescence emission occurs as the fluorophore decay from the singlet electronic excited states to an allowable vibrational level in the electronic ground state. The fluorescence excitation and emission spectra reflect the vibrational level structures in the ground and the excited electronic states, respectively.

**Fluorescence: Prompt fluorescence:**  $S_1 \rightarrow S_0 + h\nu$

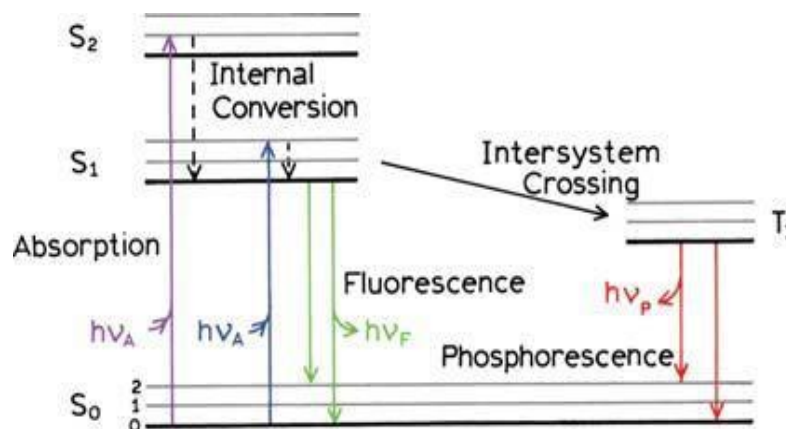
The release of electromagnetic energy is immediate or from the singlet state.

**Delayed fluorescence:**  $S_1 \rightarrow T_1 \rightarrow S_1 \rightarrow S_0 + h\nu$

This results from two intersystem crossings, first from the singlet to the triplet, then from the triplet to the singlet.

**Phosphorescence:**  $T_1 \rightarrow S_0 + h\nu$

Delayed release of electromagnetic energy from the triplet state.



**Figure. Jablonski Diagram**

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### Instrument

The instruments used for the measurement of fluorescence are known as fluorophotometers. In these, filters are used to isolate the wavelength of excitation.

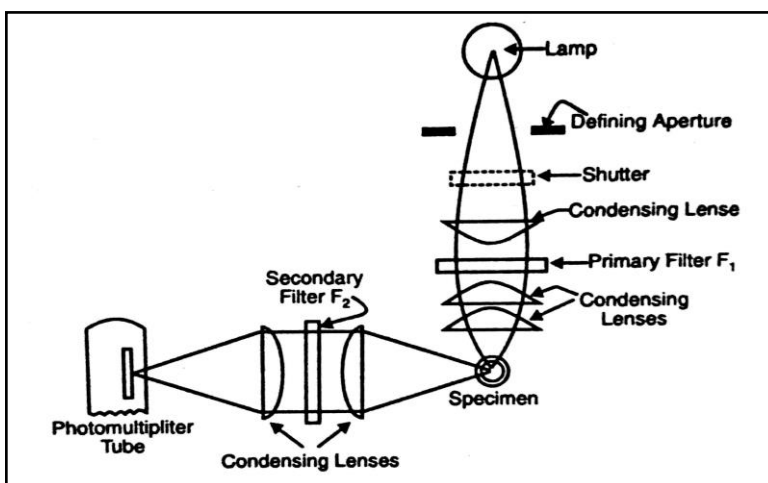
Fluorimeter consists of various components

1. A mercury vapour lamp
2. A condensing lens
3. A primary filter
4. A sample container
5. A secondary filter
6. A receiving photocell.

### **Working:**

The light from a mercury vapour lamp is allowed to pass through a condensing lens followed by its passage through a primary filters. The primary filter select only UV radiation but absorbs Visible radiation. The UV from the primary filter is passed through a sample container. From the sample, ultraviolet and fluorescent radiations are obtained which are passed through a secondary filter which absorbs the primary radiant energy but transmits the fluorescent radiation. This is received by a photocell placed in a position at right angles to the incident beam. The output of the photocell is measured by a sensitive galvanometer or other device.

### **Block diagram of Fluorimeters:**



The light source must be stable because fluorescence intensity is proportional to the intensity of irradiation. For most of the fluorimeters, fluctuations in the intensity of irradiation are not compensated for. In such instruments, two photocells are used and the readings are recorded on a potentiometer in balancing the photocells against each other.

### **APPLICATIONS OF FLUORESCENCE SPECTROSCOPY**

- Fluorescence processes find application in the following:
  - Fluorescent lamps
  - Biological detectors
  - Spectroscopy/chemical sensors

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- Fluorescent labeling
  - Mineralogy
  - Forensic applications
- Fluorescence Imaging
- – Physics and Terminology of Fluorescence
  - – Life Induced Fluorescence Imaging
    - Fluorescence Endoscopy
  - – Lifetime Imaging
    - Portable FLIM system & Glioma Imaging
- Photodynamic Therapy (PDT)
- Commonly used as a marker or for cell staining; Differentiating structures •
- In biomedical applications we can use these properties of fluorescence to increase the specificity and sensitivity in imaging diagnosis – i.e. Early Cancer Detection
- Systems can be made small and portable
- Photobleaching
- **Laser induced fluorescence spectroscopy of human tissues for cancer diagnosis:** Cancer is one of the most dreaded diseases of our time and has a very high incidence. Early tumours often arise from tissue which have a rapid turnover of cells and are active in repair like transformed mucosa on the surface of hollow organs (oral cavity, gastrointestinal tract, female reproductive organs etc.). Laser spectroscopic techniques have the potential for in-situ, near real time diagnosis and the use of non-ionizing radiation ensures that the diagnosis can be made repeatedly without any adverse side effects.
- Laser Induced Fluorescence (LIF) has been used for diagnosing cancer in two ways. One approach involves systemic administration of a drug like hematoporphyrin derivative (HpD) which is selectively retained by the tumour. When photo excited with light of appropriate wavelength the drug localized in the tumour fluoresces. This fluorescence is used for detection and imaging of the tumour. Photo excitation also leads to populating the triplet state via intersystem crossing. The molecule in excited triplet state can directly react with bio-molecules or lead to generation of singlet oxygen which is toxic to the host tissue. The resulting destruction of the host tissue is exploited for photodynamic therapy of tumour.
- **Study of Marine Petroleum Pollutants:** Fluorescence spectroscopy is one of the good technique to detection of oil slicks on the water surface, determination of petroleum contaminants in seawater and determination of particular petroleum derivative compounds as well as identification of pollution sources. Main components of any oil are hydrocarbons. The other components are primarily derivatives of hydrocarbons containing single atoms of sulfur, oxygen or nitrogen. Only a few of hydrocarbons fluoresce, while the major of them show no ability to luminescence. The content of compounds able to fluorescence rarely exceeds 10% of the oil mass. At the same time the petroleum strongly absorbs radiation, especially the ultraviolet and blue light. In spite of this petroleum is a luminescent

### UNIT III- SPECTROSCOPIC TECHNIQUES AND APPLICATIONS

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medium and fluorescence is a phenomenon which allows testing oils. Fluorescence of oils has wavelength over then 260 nm and covers a spectral area of ultraviolet and visible light. The phenomenon is most significant in the 270–400 nm range.

- **Accurate determination of glucose:** Glucose is considered as a major component of animal and plant carbohydrates in biological systems. Furthermore, blood glucose levels are also an indicator of human health conditions: the abnormal amount of glucose provides significant information of many diseases such as diabetes or hypoglycemia. Fluorophotometry was used widely owing to its operational simplicity and high sensitivity. Recently bio-molecule-stabilized Au nanoclusters were demonstrated as a novel fluorescence probe for sensitive and selective detection of glucose.

## UNIT IV- USE OF FREE ENERGY IN CHEMICAL EQUILIBRIA

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### THERMODYNAMIC FUNCTIONS

Thermo means heat and dynamics means motion or mechanical work. Hence thermodynamics means that branch of science which deals with the conversion of heat into mechanical work and vice versa.

Thermodynamics is a branch of science that deals with quantitative relationships between heat and other forms of energy.

### TERMS USED IN THERMODYNAMICS

1. **System:** Any specific part of the universe
2. **Surroundings:** The regions outside the boundaries of the system.
3. **Boundary:** The region (or) interface separating the system from the surroundings

### TYPES OF SYSTEM

1. **Isolated system**
2. **Closed system**
3. **Open system**

### PROPERTIES OF THERMODYNAMIC SYSTEM

1. **Intensive Properties:** Those properties which do not depend on the amount of substance present in the system. But it depend only on nature of the substance. Eg: Temperature, Pressure, density, concentration, viscosity, refractive index, surface tension, boiling point and freezing point.
2. **Extensive Properties:** Properties which depend on the amount of substance present in the system. E.g: Mass, Volume, Internal energy (E), Enthalpy (H), Entropy (S), Free energy (G).

### INTERNAL ENERGY ( $\Delta E$ )

Internal energy is defined as the total amount of energy associated with the given substance. It is made up of the following components

(i) Translational energy (ii) Rotational energy (iii) Vibrational energy of the molecules (iv) Coulombic energy of interaction of nuclei in atoms and (v) Interaction energy of constituent particles of the system.

It is represented as

## UNIT IV- USE OF FREE ENERGY IN CHEMICAL EQUILIBRIA

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$$E = E_V + E_r + E_t + E_C + E_I$$

Internal energy of a system depends on the number of particles present in it and hence it is an extensive property. It is generally expressed in  $\text{kJ mol}^{-1}$ . Whereever there is change in the state, there is change in the internal energy, ( $\Delta E$ ) is given by

$$E = E_2 - E_1$$

Where  $E_1$  and  $E_2$  are the internal energies of the system in the initial and final states repectively. If the system absorbs heat energy  $E_2 > E_1$  and hence  $\Delta E > 0$  (i.e., +ve), such reactions are called endothermic reactions. On the other hand, in exothermic reactions the system liberates heat energy and  $E_2 < E_1$  and accompanied by decrease in internal energy ( $\Delta E < 0$ ) i.e.,  $\Delta E$  is negative.

### ENTHALPY (H)

Enthalpy is the sum of internal energy (E) and pressure – volume energy (PV) of a system at a particular set of conditions. This function is defined by the relation.

$$H = E + PV$$

Where P and V are the pressure and volume of the system. It is generally expressed in  $\text{kJ mol}^{-1}$ .

Change of Enthalpy: Generally in chemical reactions instead of enthalpy, enthalpy change is used. The change in enthalpy of the system when it changes its state is given by

$$\Delta H = H_2 - H_1$$

Where  $H_1$  and  $H_2$  are enthalpy of the system in the initial and final states respectively. Let a chemical system has internal energy  $E_1$ , pressure  $P_1$  and volume  $V_1$ . Let it undergo change at constant temperature to give another chemical state with internal energy  $E_2$ , Pressure  $P_2$  and volume  $V_2$ . Let  $H_1$  be the enthalpy of the initial state and  $H_2$  the enthalpy of the final state, then

$$H_1 = E_1 + P_1 V_1$$

And

$$H_2 = E_2 + P_2 V_2$$

Substituting the values of  $H_1$  and  $H_2$  in the  $\Delta H$  equation, we get

$$\Delta H = (E_2 + P_2 V_2) - (E_1 + P_1 V_1)$$

## UNIT IV- USE OF FREE ENERGY IN CHEMICAL EQUILIBRIA

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$$= (E_2 - E_1) + (P_2 V_2 - P_1 V_1)$$

$$= \Delta E + (P_2 V_2 - P_1 V_1)$$

When the pressure remaining constant  $P_1 = P_2 = P$

$$\Delta H = \Delta E + P(V_2 - V_1)$$

$$\Delta H = \Delta E + P\Delta V$$

Thus, the change in enthalpy at constant pressure is equal to the increase in internal energy plus any pressure – volume work done.

### ENTROPY

The thermodynamic state quantify which is a measure of the degree of disorderness or randomness in a system. It is represented by S. It is generally expressed in  $\text{JK}^{-1}$ . It is mathematically expressed as

$$\Delta S = q_{\text{ev}} / T$$

#### Entropy change in Reversible Process

$$\Delta S_{\text{Total}} = 0$$

i.e., In a reversible isothermal process, there is no net change in entropy.

#### Entropy change in an Irreversible (Spontaneous) Process

$$\Delta S_{\text{Total}} = \text{Positive}$$

$$\Delta S_{\text{Total}} > 0$$

i.e., In an irreversible process, the entropy of the system increases.

#### Entropy change in an Isothermal Expansion of an Ideal gas

$$\Delta S = 2.303nR \log V_2/V_1$$

(Or)

$$\Delta S = 2.303nR \log P_1/P_2$$

#### Entropy change in Physical Transformations

$$\Delta S = L \times M / T$$

Where L is latent heat in calories, M is the molecular weight in grams and T is the temperature.



## UNIT IV- USE OF FREE ENERGY IN CHEMICAL EQUILIBRIA

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### FREE ENERGY (G)

Free energy of system (denoted by the symbol 'G') is thermodynamic state function, which is related to enthalpy and entropy as

$$G = H - TS$$

Free energy change ( $\Delta G$ ) of a system (or reaction) a measure of energy available for doing useful work. Thus

Energy available as useful work = Total energy available – Non available form of energy

$$G = H - TS$$

### CELL TERMINOLOGY

#### 1. Current

Current is the flow of electrons through a wire or any conductor.

#### 2. Electrode

Electrode is a material (or) a metallic rod/bar/strip which conducts electrons.

#### 3. Anode

Anode is the electrode at which oxidation occurs.

#### 4. Cathode

Cathode is the electrode at which reduction occurs.

#### 5. Electrolyte

Electrolyte is a water soluble substance forming ions in solution, and conduct an electric current.

#### 6. Anode Compartment

Anode compartment is the compartment of the cell in which oxidation half-reaction occurs. It contains the anode.

#### 7. Cathode Compartment

Cathode compartment is the compartment of the cell in which reduction half reaction occurs. It contains the cathode.

#### 8. Half-cell

Half cell is a part of a cell, containing electrode dipped in an electrolytic solution. If oxidation occurs at the electrode that is called oxidation half cell. If reduction occurs at the electrode that is called reduction half cell.

## UNIT IV- USE OF FREE ENERGY IN CHEMICAL EQUILIBRIA

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### 9. Cell

Cell is a device consisting two half cell. The two half cells are connected through one wire.

#### **CELLS**

A cell is a device which converts electrical energy into chemical energy (or) chemical energy into electrical energy. Generally a cell consists of two half cells. Each half cell consists of an electrode dipped in an electrolytic solution. These two half cells are connected through one wire.

#### ***Types of cells***

Based on the type of reaction, occurring in a cell, cells are classified into two types

1. Electrolytic cells
2. Electrochemical cells (or) voltaic cell (or) galvanic cells

#### **1. Electrolytic cells**

Electrolytic cells are the cells in which electrical energy is used to bring about the chemical reaction.

**Example:** Electrolysis, electroplating, etc.

#### **2. Electrochemical cells (or) Galvanic cells**

Electro chemical cells are the cells in which chemical energy is converted into electrical energy.

**Example:** Daniel cell

#### **REDOX REACTIONS**

Reactions in which oxidation and reduction takes place simultaneously are known as redox reactions.

#### **Oxidation**

It is a process, which involves loss of electrons by a substance.

#### **Reduction**

It is a process, which involves gain of electrons by a substance.

It is known that if a substance loses electrons, another substance must accept these electrons. Similarly, if a substance accepts electrons, another substance must supply these electrons. Thus, redox (oxidation and reduction) reactions always go side-by-side.

## UNIT IV- USE OF FREE ENERGY IN CHEMICAL EQUILIBRIA

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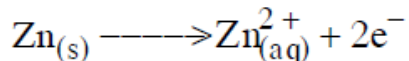
### Illustration

#### Zinc metal in copper sulphate solution

If zinc metal is placed in a copper sulphate solution, the following oxidation and reduction reactions takes place.

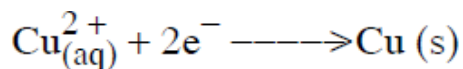
#### Oxidation

Zinc atom (Zn) loses two electrons and gets oxidized to zinc ion  $\text{Zn}^{2+}$



#### Reduction

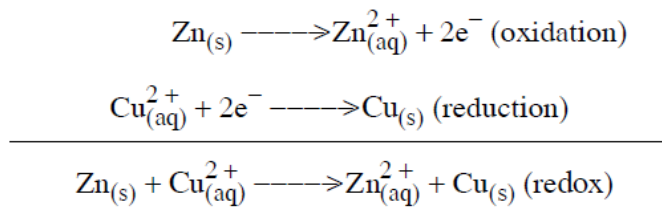
Copper ion  $\text{Cu}^{2+}$  gains two electrons, liberated by Zn and gets reduced to copper (Cu).



Each of the above reactions is known as half reaction. The reaction, in which loss of electrons takes place, is called oxidation half-reaction, while the reaction, in which gain of electrons takes place is called reduction half-reaction.

#### Overall redox reaction

It is obtained by adding the two half-reactions. Thus,

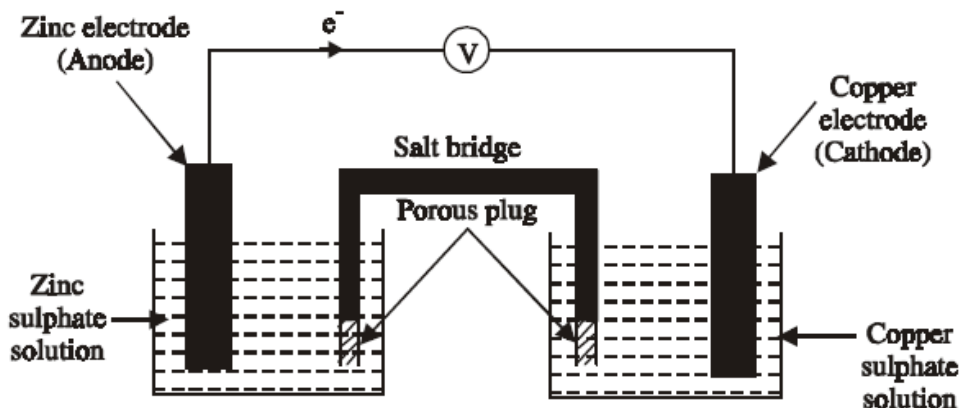


### ***ELECTROCHEMICAL CELLS***

Galvanic cells are electrochemical cells in which the electrons, transferred due to redox reaction, are converted into electrical energy.

#### Cell device (Construction)

Galvanic cell consists of a zinc electrode dipped in 1M  $\text{ZnSO}_4$  solution and a copper electrode dipped in 1M  $\text{CuSO}_4$  solution. Each electrode is known as a half cell. The two solutions are inter connected by a salt bridge and the two electrodes are connected by a wire through a voltmeter.



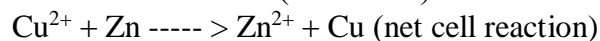
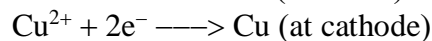
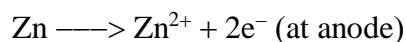
### Reactions occurring in the cell

#### *At anode*

Oxidation takes place in the zinc electrode by the liberation of electrons, so this electrode is called negative electrode or anode.

#### *At cathode*

Reduction takes place in the copper electrode by the acceptance of electrons, so this electrode is called the positive electrode or cathode.



The electrons liberated by the oxidation reaction flow through the external wire and are consumed by the copper ions at the cathode.

### *Salt bridge*

It consists of a U-tube containing saturated solution of KCl or  $\text{NH}_4\text{NO}_3$  in agar-agar gel. It connects the two half cells of the galvanic cells.

### *Functions of salt bridge*

- (i) It eliminates liquid junction potential.
- (ii) It provides the electrical continuity between the two half cells.

### Conditions for a cell to act as standard cell

The conditions for an electrochemical cell to act as a standard cell are

- (i) The e.m.f of the cell is reproducible.
- (ii) The temperature-coefficient of e.m.f (change in e.m.f with temperature) should be very low.

## UNIT IV- USE OF FREE ENERGY IN CHEMICAL EQUILIBRIA

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### ***Representation of a galvanic cell (or) Cell diagram***

- (i) A galvanic cell consists of two electrodes anode and cathode.
- (ii) The anode is written on the left hand side while the cathode is written on the right hand side.
- (iii) The anode must be written by writing electrode metal first and then electrolyte. These two are separated by a vertical line or a semicolon. The electrolyte may be written by the formula of the compound (or) by ionic species.

#### **Examples**

- (a)  $\text{Zn}/\text{Zn}^{2+}$  (or)  $\text{Zn}/\text{ZnSO}_4$  (or)  $\text{Zn}; \text{Zn}^{2+}$
- (b) Standard hydrogen electrode  
 $\text{Pt}, \text{H}_2 (1 \text{ atm}); \text{H}^+ (1 \text{ M})$
- (iv) The cathode must be written by writing electrolyte first and then the electrode metal. These two are separated by a vertical line or a semicolon.

#### **Example:**

- $\text{Cu}^{2+}/\text{Cu}$  (or)  $\text{CuSO}_4/\text{Cu}$  (or)  $\text{Cu}^{2+}; \text{Cu}$
  - (v) The two half cells are separated by a salt bridge, which is indicated by two vertical lines.
- Using the above representation, the galvanic cell is represented as follows.

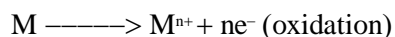
$\text{Zn} / \text{ZnSO}_4 (1 \text{ M}) // \text{CuSO}_4 (1 \text{ M}) / \text{Cu}$   
(or)  $\text{Zn} / \text{Zn}^{2+} (1 \text{ M}) // \text{Cu}^{2+} (1 \text{ M}) / \text{Cu}$   
(or)  $\text{Zn}; \text{Zn}^{2+} (1 \text{ M}) // \text{Cu}^{2+} (1 \text{ M}); \text{Cu}$

## ***ELECTRODE POTENTIAL***

### **Origin of Electrode Potential**

A metal (M) consists of metal ions  $\text{M}^{n+}$  with valence electrons. When the metal (M) is placed in a solution of its own salt, any one of the following reactions will occur.

- (i) Positive metal ions may pass into the solution.



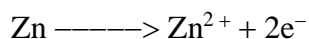
- (ii) Positive metal ions from the solution may deposit

#### ***Illustration***

In order to understand the origin of electrode potential, the following two examples are considered.

#### **Example-1      *Zn electrode dipped in $\text{ZnSO}_4$ solution***

When Zn electrode is dipped in  $\text{ZnSO}_4$  solution, Zn goes into the solution as  $\text{Zn}^{2+}$  ions due to oxidation.

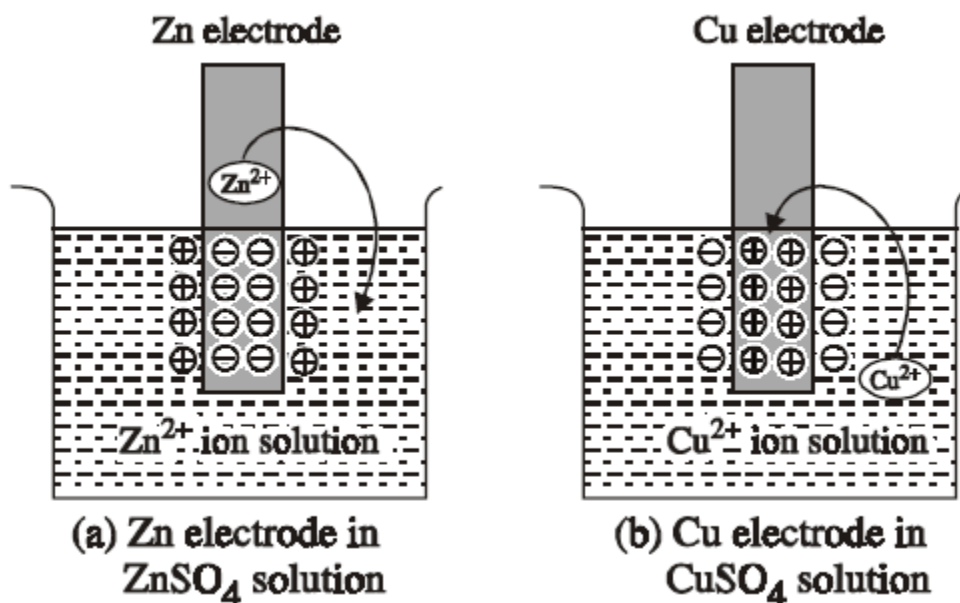
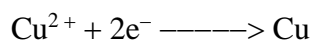


## UNIT IV- USE OF FREE ENERGY IN CHEMICAL EQUILIBRIA

Now, the Zn electrode attains a negative charge, due to the accumulation of valence electrons on the metal. The negative charges developed on the electrode attract the positive ions from solution. Due to this attraction the positive ions remain close to the metal.

### *Example -2 Cu electrode dipped in CuSO<sub>4</sub> solution*

When Cu electrode is dipped in CuSO<sub>4</sub> solution, Cu<sup>2+</sup> ions from the solution deposit over the metal due to reduction.



Now, the Cu electrode attains a positive charge, due to the accumulation of Cu<sup>2+</sup> ions on the metal. The positive charges developed on the electrode attract the negative ions from solution. Due to this attraction, the negative ions remain close to the metal. Thus, a sort of layer (positive (or) negative ions) is formed all around the metal. This layer is called Helmholtz electrical double layer. This layer prevents further passing of the positive ions from or to the metal. A difference of potential is consequently set up between the metal and the solution. At equilibrium, the potential difference becomes a constant value, which is known as the electrode potential of a metal.

### **Factors affecting electrode potential**

The rate of the above reactions depend on

- (i) The nature of the metal.
- (ii) The temperature.
- (iii) The concentration of metal ions in solution.

## UNIT IV- USE OF FREE ENERGY IN CHEMICAL EQUILIBRIA

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### Single electrode potential

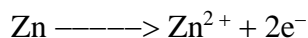
It is the measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt.

### Standard electrode potential

It is the measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt of 1 molar concentration at 25°C.

### Oxidation potential

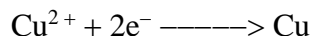
If oxidation occurs at the electrode, at equilibrium, the potential of the electrode is oxidation potential.



Thus, the tendency of an electrode to lose electrons is called the oxidation potential.

### Reduction potential

If reduction occurs at the electrode, at equilibrium, the potential of the electrode is reduction potential.



Thus, the tendency of an electrode to gain electrons is called the reduction potential.

## NERNST EQUATION FOR ELECTRODE POTENTIAL

Consider the following redox reaction



For such a redox reversible reaction, the free energy change ( $\Delta G$ ) and its equilibrium constant (K) are inter related as

$$\begin{aligned}\Delta G &= -RT \ln K + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]} \\ &= \Delta G^{\circ} + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]} \quad \text{..... (1)}\end{aligned}$$

where,

$\Delta G^\circ$  = Standard free energy change

The above equation (1) is known as *Van't Hoff isotherm*.

The decrease in free energy ( $-\Delta G$ ) in the above reaction will produce electrical energy. In the cell, if the reaction involves transfer of 'n' number of electrons, then 'n' faraday of electricity will flow. If E is the emf of the cell, then the total electrical energy ( $nEF$ ) produced in the cell is

$$\begin{aligned} -\Delta G &= nEF \\ \text{(or)} \\ -\Delta G^\circ &= nE^\circ F \end{aligned} \quad \text{..... (2)}$$

where,

$-\Delta G$  = decrease in free energy change.

(or)  $-\Delta G^\circ$  = decrease in standard free energy change.

Comparing equation 1 and 2, it becomes

$$-nEF = -nE^\circ F + RT \ln \frac{[M]}{[M^{n+}]} \quad \text{.....(3)}$$

Dividing the above equation (3) by  $-nF$

[  $\therefore$  the activity of solid metal  $[M] = 1$  ]

$$E = E^\circ - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$$

$$\text{In general, } E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{Product}]}{[\text{Reactant}]}$$

(or)

$$E = E^\circ + \frac{RT}{nF} \ln [M^{n+}]$$



(or)

$$E = E^{\circ} + \frac{2.303 RT}{nF} \log [M^{n+}] \quad \text{.....(4)}$$

When,  $R = 8.314 \text{ J/K/mole}$ ;  $F = 96500 \text{ coulombs}$  ;  
 $T = 298 \text{ K (25}^{\circ}\text{C)}$ , the above equation becomes

$$E = E^{\circ}_{\text{red}} + \frac{0.0591}{n} \log [M^{n+}] \quad \text{.....(5)}$$

$$\text{In general, } E = E^{\circ}_{\text{red}} + \frac{0.0591}{n} \log C$$

Similarly for oxidation potential

$$E = E^{\circ}_{\text{oxi}} - \frac{0.0591}{n} \log [M^{n+}] \quad \text{..... (6)}$$

The above equation 5&6 are known as “Nernst equation for single electrode potential”.

### Applications of Nernst equations

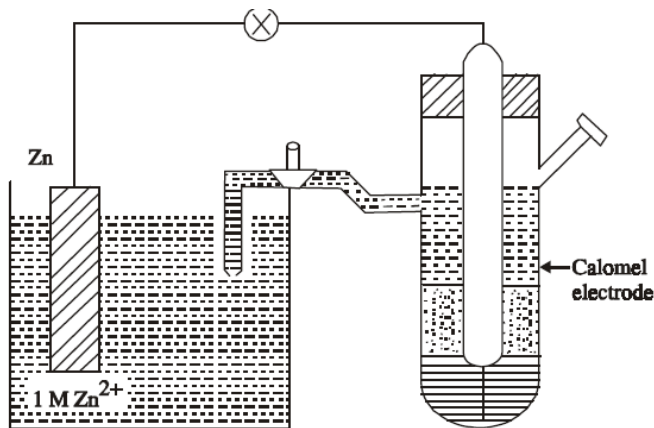
#### (Electrode Potential)

1. Nernst equation is used to calculate electrode potential of unknown metal.
2. Corrosion tendency of metals can be predicted.
3. It is used to calculate the EMF of a cell.
4. Concentration of the reactant can be calculated using the electrode potential.
5. Concentration of the solution in galvanic cell can be determined.
6. pH of a solution can be calculated by measuring the emf.
7. Applications of emf series

### MEASUREMENT OF SINGLE ELECTRODE POTENTIAL

It is impossible to determine the absolute value of a single electrode potential. But, we can measure the potential difference between two electrodes potentiometrically, by combining them to form a complete cell. For this purpose, 'reference electrode' is used. Standard hydrogen electrode(SHE) is the commonly used reference electrode, whose potential has been arbitrarily fixed as zero. The emf of the cell is measured and it is equal to the potential of electrode.

It is very difficult to set up a hydrogen electrode. So other electrodes called secondary reference electrodes like calomel electrodes are used.



#### Example

To measure the electrode potential of Zn, a cell is made by combining the saturated calomel electrode with Zn electrode, the potential of which is to be determined. Since the reduction potential of the coupled Zn electrode is less than of calomel electrode  $\approx 0.2422 \text{ V}$ , the calomel electrode will act as cathode and zinc electrode will act as anode.

The following cell reaction will occur in the above cell

## UNIT IV- USE OF FREE ENERGY IN CHEMICAL EQUILIBRIA

At anode:  $\text{Zn} \rightleftharpoons \text{Zn}^{2+} + 2\text{e}^-$  (oxidation)

At cathode:  $\text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{e}^- \rightleftharpoons 2\text{Hg}(\text{l}) + 2\text{Cl}^-$   
(reduction)

Cell reaction:  $\text{Zn} + \text{Hg}_2\text{Cl}_2(\text{s}) \rightleftharpoons \text{ZnCl}_2 + 2\text{Hg}(\text{l})$

The emf of the above cell is measured and the electrode potential is calculated from the emf as follows

$$E_{\text{cell}} = E_{\text{right}}^{\circ} - E_{\text{left}}^{\circ}$$

$$E_{\text{cell}} = E_{\text{cal}}^{\circ} - E_{\text{Zn}}^{\circ}$$

$$\begin{aligned} E_{\text{Zn}}^{\circ} &= E_{\text{cal}}^{\circ} - E_{\text{cell}} \\ &= +0.2422 - 1.0025 \end{aligned}$$

$$E_{\text{Zn}}^{\circ} = -0.7603 \text{ volt .}$$

ie., the reduction potential of Zn electrode = -0.7603 volt .

### EMF OF A CELL

Electromotive force is defined as, "the difference of potential which causes flow of current from one electrode of higher potential to the other electrode of lower potential.

$$\text{EMF} = \left\{ \begin{array}{l} \text{Standard reduction} \\ \text{potential of right hand} \\ \text{side electrode} \end{array} \right\} - \left\{ \begin{array}{l} \text{Standard reduction} \\ \text{potential of left} \\ \text{hand side electrode} \end{array} \right\}$$

### Factors affecting EMF of a cell

Nature of the electrolytes and electrodes.  
Concentration and composition of the electrolytes.  
pH and temperature of the solution.

### Acid and Base

## UNIT IV- USE OF FREE ENERGY IN CHEMICAL EQUILIBRIA

**Acid** is Latin word, it comes from Acidus (sour). All the sour taste things that found out that is same taste at same time. They have similar chemical properties. Some naturally occurring compound which contains acid are vinegar, citrus fruits (orange and lemons), Gastric juice, sour milk, tomatoes, grapes, tamarind & apples.

Base is bitter taste and slippery in nature. Bases are baking soda, washing soda, Quick lime.

**Concept of Acid and Base:** Earlier concept:

Acid		Base
1	Sour in taste	Bitter in taste
2	Litmus test: Acid turns Blue into Red	Litmus test: It turns Red into Blue

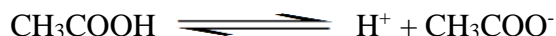
**Modern Concept of Acid and Base:**

1. Arrhenius concept
2. Bronsted Lowry Concept
3. Lewis Concept

### 1. Arrhenius concept

According to it ‘‘ an acid is a substance which when dissolved in water gives  $H^+$  ions in aqueous solution

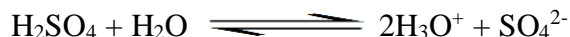
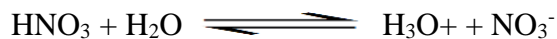
Example:



On the other hand, a base is substance which gives  $OH^-$  ions in aqueous solution.



According to Arrhenius concept, the strength of an acid depends upon to extent to which it ionizes to produce  $H^+$  ions, i.e., an acid is strong, when it produces a high concentration of hydrogen ( $H^+$ ) ions (or  $H_3O^+$  ions). On the basis  $HCl$ ,  $HNO_3$ ,  $H_2SO_4$  and  $H_3PO_4$  are all strong acid (dissociates almost completely in aqueous solution)



On the other hand, Acid which dissociates only partially in aqueous solution thereby producing a low concentration of hydrogen ( $H^+$ ) ions (or  $H_3O^+$  ions). This is known as weak acid.

Example:  $CH_3COOH$ ,  $HCN$ , Oxalic acid

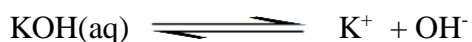
## UNIT IV- USE OF FREE ENERGY IN CHEMICAL EQUILIBRIA

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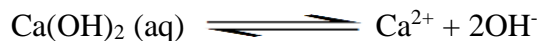


According to Arrhenius concept, the strength of alkali depends on the concentration of the hydroxyl ions ( $\text{OH}^-$ ) present in an aqueous solution of the alkali.

**Strong Alkali:** Is an alkali which dissociates almost completely in aqueous solution thereby producing a high concentration of hydroxyl ( $\text{OH}^-$ ) ions.

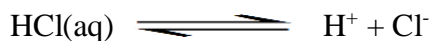


**Weak Alkali:** Is an alkali which dissociates only partially in aqueous solution thereby producing a low concentration of hydroxyl ( $\text{OH}^-$ ) ions.



### 2. Bronsted Lowry Concept

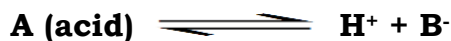
The major essentials of the Bronsted –Lowry theory (1923) are: Acid is a substance which donate proton ( $\text{H}^+$ ) to any other substance. An acid is a proton donor.



Base is a substance which accept proton from any other substance. A base is a proton acceptor.



The relationship between an acid and a base is thus summarized by



Proton donor                      Proton      Base (Proton acceptor)

### 3. Lewis Concept

According to Lewis theory, “ An acid is a substance which can accept a pair of electrons to form a covalent bonds. An acid is called as electron pair acceptors.

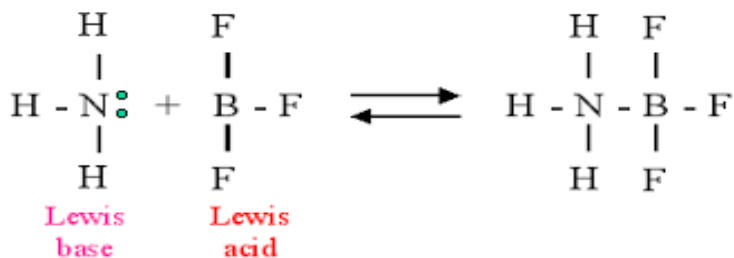
Examples of electron pair acceptors:  $\text{H}^+$ ,  $\text{Na}^+$ ,  $\text{Fe}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{ZnCl}_2$ ,  $\text{BH}_3$ ,  $\text{BF}_3$ ,  $\text{FeBr}_3$ ,  $\text{AlCl}_3$

On the other hand, base is a substance that can donate a pair of electrons to form a covalent bond. For example:  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{OH}^-$ ,  $\text{I}^-$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_3$ ,  $\text{NH}_3$



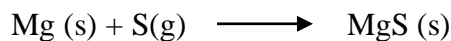
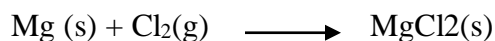
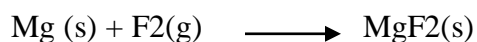
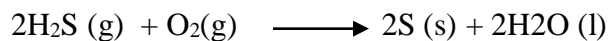
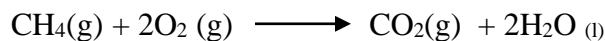
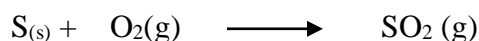
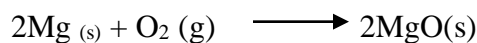
Acid      Base                      Covalent compound

## UNIT IV- USE OF FREE ENERGY IN CHEMICAL EQUILIBRIA

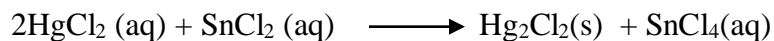
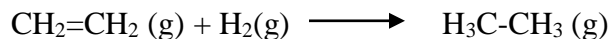
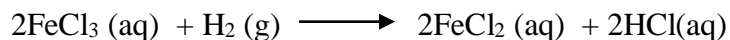


### Oxidation and Reduction

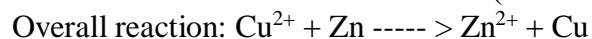
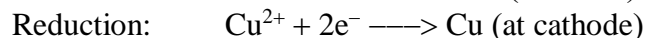
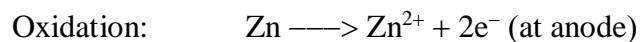
**Oxidation** is defined as the addition of oxygen/ electronegative element to a substance or removal of hydrogen/ electropositive element from a substance. The following reactions represent oxidation process according to the limited definition of oxidation:



**Reduction** is defined as the removal of oxygen/ electronegative element from a substance or addition of hydrogen/ electropositive element to a substance. The following reactions represent reduction processes:



Reaction in Galvanic cell



## UNIT IV- USE OF FREE ENERGY IN CHEMICAL EQUILIBRIA

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### Solubility Equilibria

Solubility product is the equilibrium constant for a reaction in which a solid dissolves into its constituent ions in solution.

The corresponding equilibrium constant is called solubility product constant ( $K_{sp}$ )

Exercise: Write the  $K_{sp}$  expression for the reaction:



### USE OF FREE ENERGY CONSIDERATIONS IN METALLURGY THROUGH ELLINGHAM DIAGRAMS

The free energy change ( $\Delta G$ ) occurring during the reduction processes help in deciding the suitable method for reduction.

For the spontaneous reduction of an oxide, halide or sulphide by an element, the essential condition is that there is a decrease in the free energy of the system (-ve  $\Delta G$ ). More the negative value of  $\Delta G$ , the higher is the reducing power of an element.  $\Delta G$  is given as

$$\Delta G = \Delta H - T\Delta S$$

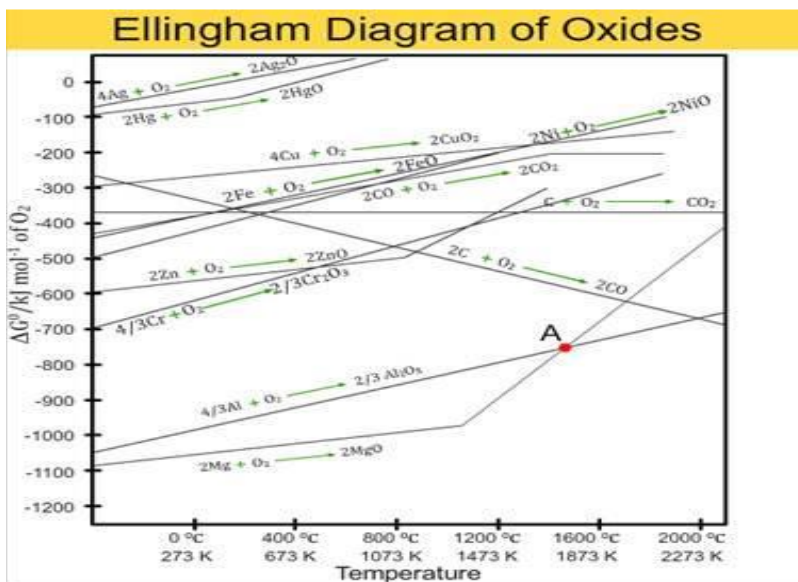
Where  $\Delta H$  is the enthalpy change,  $\Delta G$  is the Gibbs free energy,  $T$  is the temperature and  $\Delta S$  is the entropy change.

For the reduction of a metal oxide with a reducing agent. The plot of  $\Delta G$  versus temperature is studied which is called **Ellingham diagram**.

#### Characteristics of Ellingham Diagram

1. All the plots slope upwards since  $\Delta G^\circ$  becomes more positive when temperature increases, i.e., stability of oxides decreases.
2. A metal will reduce the oxide of other metals which lie above it in Ellingham diagram, i.e. the metals for which the free energy of formation ( $\Delta G^\circ_f$ ) of their oxides is more negative can reduce those metal oxides which has less negative  $\Delta G^\circ_f$ .

## UNIT IV- USE OF FREE ENERGY IN CHEMICAL EQUILIBRIA



3. The decreasing order of the negative values of  $\Delta G^\circ_f$  of metal oxides is

$\text{Ca} > \text{Mg}$  (below 1773 K)  $> \text{Al} > \text{Ti} > \text{Cr} > \text{C} > \text{Fe} > \text{Ni} > \text{Hg} > \text{Ag}$

Thus, Al reduces FeO, CrO and NiO in thermite reduction but it will not reduce MgO at temperature below 1773K.

Mg can reduce  $\text{Al}_2\text{O}_3$  below 162K but above 1023 K. Al can reduce MgO.

4. CO is more effective reducing agent below 1073 K and above 1073, coke is more effective reducing agent. E.g. CO reduces  $\text{Fe}_2\text{O}_3$  below 1073 K but above it, coke reduces  $\text{Fe}_2\text{O}_3$ . Coke reduces ZnO above 1270K.

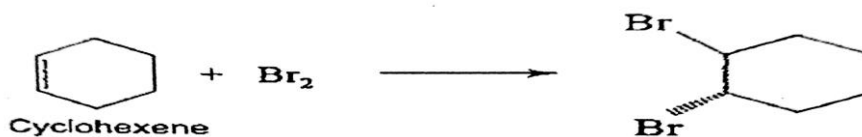


## UNIT V- ORGANIC REACTIONS AND SYNTHESIS OF A DRUG MOLECULE

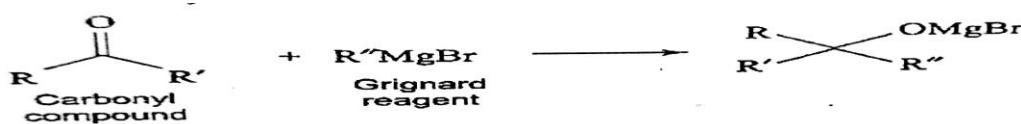
### ADDITION REACTIONS

In these reactions, a reagent adds to a substrate, all reagents and the substrates are consumed during the reaction.

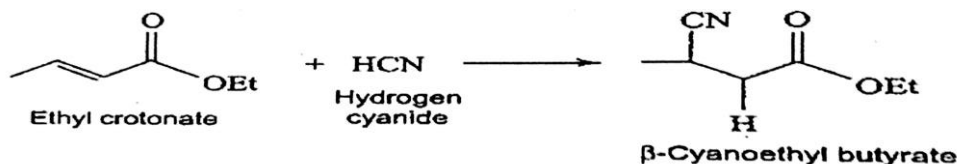
(a) Addition of bromine to an olefin



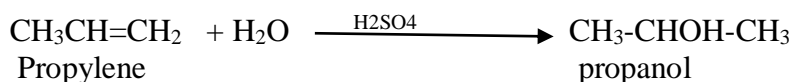
(b) Addition of Grignard reagent to a carbonyl compound



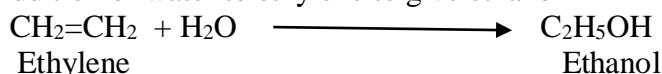
(c) Addition of hydrogen cyanide to an  $\alpha,\beta$ -unsaturated carbonyl compounds



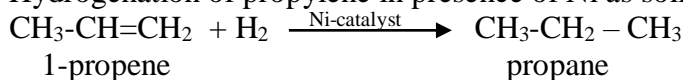
(d) Addition of water to olefins in presence of dilute sulphuric acid



(e) Addition of water to ethylene to give ethanol



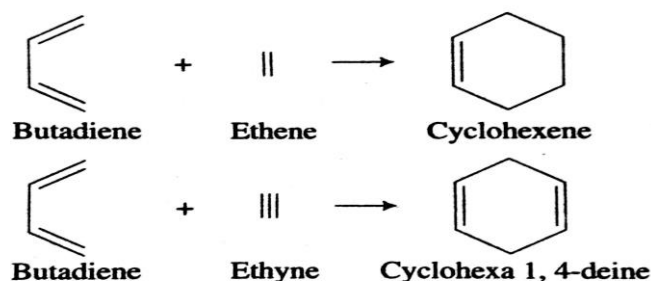
(f) Hydrogenation of propylene in presence of Ni as solid catalyst



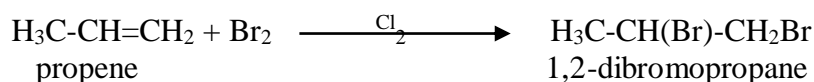
(g) **Diels-Alder reactions:**

It is a (4+2) cycloaddition reaction between a conjugated diene ( $4\pi$ -electron system) and a compound having a double or triple bond called the dienophile ( $2\pi$ -electron system) to form an adduct. In this reaction, the two components are either heated alone or in an inert solvent.

## UNIT V- ORGANIC REACTIONS AND SYNTHESIS OF A DRUG MOLECULE

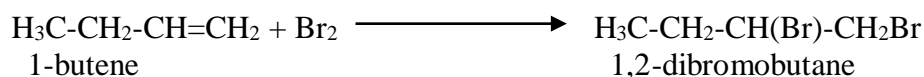


(h) Bromination of propene



Here, reactants (propene and bromine) are incorporated into the final product (1,2 dibromopropane).

(i) Bromination of Butene

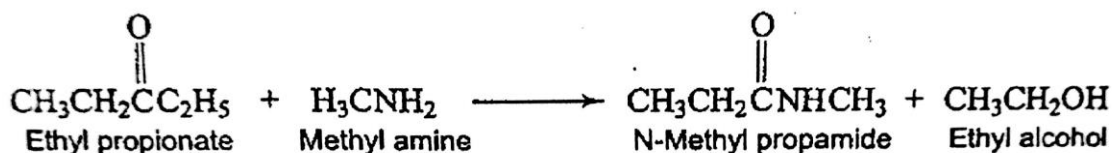


### SUBSTITUTION REACTION

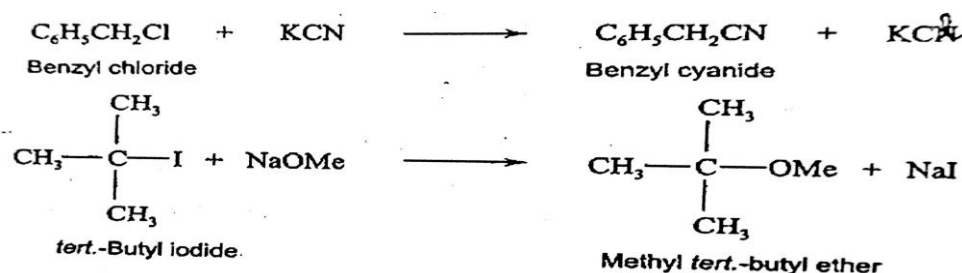
In these reactions, one atom (or group of atoms) is replaced by another atom (or group of atoms). The atom or group that is replaced is not utilized in the final product.

(a) The reaction of ethyl propionate with methyl amine.

In the above reaction, the leaving group ( $\text{OC}_2\text{H}_5$ ) is not incorporated in the formed amide and also, one hydrogen atom of the amine is not utilized. The remaining atoms of the reactants are incorporated into the final product.

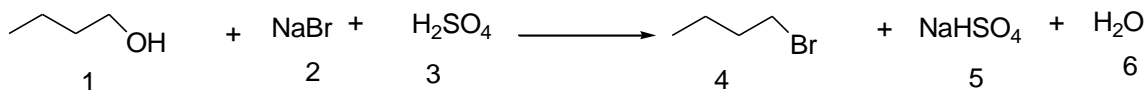


Typical examples include the well known  $\text{S}_{\text{N}}1$  and  $\text{S}_{\text{N}}2$  reactions. In these reactions, nucleophilic reagents displace a leaving group in an aliphatic carbon atom, the product formed incorporates the nucleophile with removal of the leaving group.



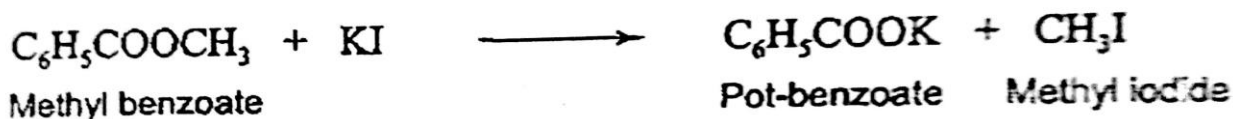
## UNIT V- ORGANIC REACTIONS AND SYNTHESIS OF A DRUG MOLECULE

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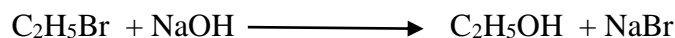


In some cases, the leaving group is the desired product. For example:

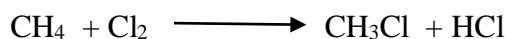
(b) Potassium iodide demethylation of a carboxylic acid methyl ester to give free carboxylate salt and methyl iodide.



(c) Alkyl halides undergo the nucleophilic substitution reaction. Thus alkyl halides are converted to alcohols by aqueous alkaline solution in water.



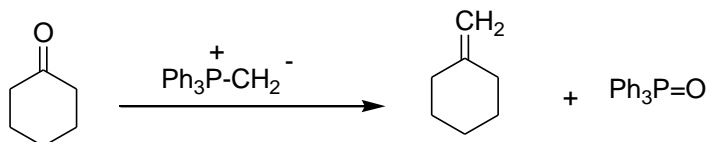
(d) Chlorination of methane



(e) Substitution of sodium methoxide



(f) Wittig reaction



$$\text{Atom economy} = \frac{96}{98 + 276} = 25.7\%$$

### ELIMINATION REACTION:

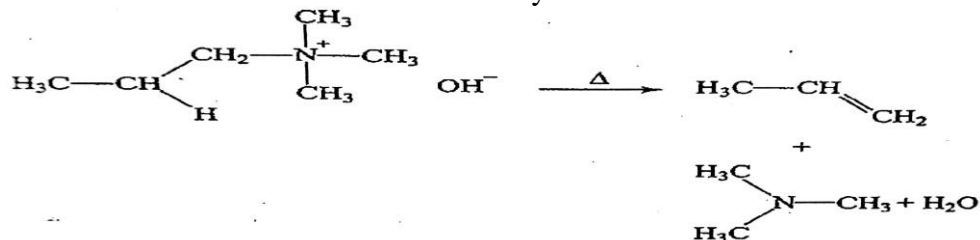
In an elimination reaction, two atoms or groups of atoms are lost from the reactant to form a  $\pi$  bond. The atom or group that is lost and is not utilized in the final product. So

## UNIT V- ORGANIC REACTIONS AND SYNTHESIS OF A DRUG MOLECULE

the elimination reactions are less atom economical than rearrangement or addition reactions.

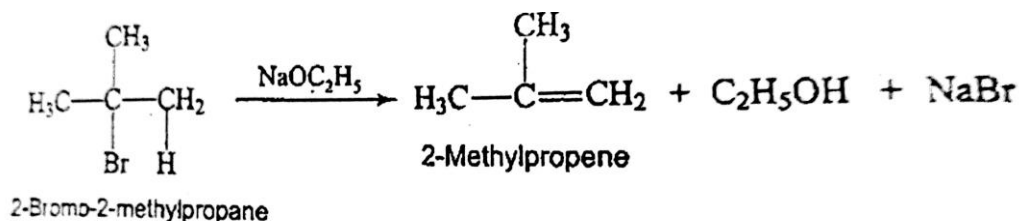
### (a) Hoffmann elimination

The above elimination reaction is not very atom economical.



### (b) Dehydrohalogenation of 2-bromo-2-methylpropane.

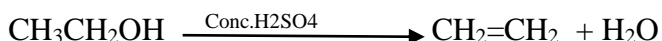
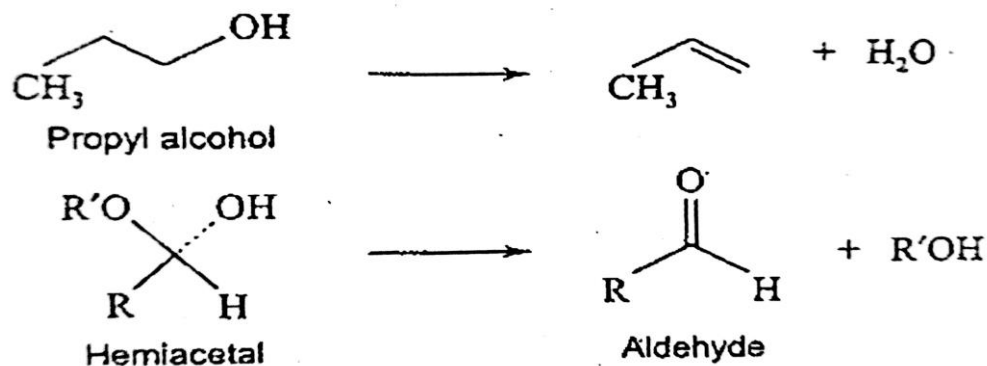
In an elimination reaction, dehydrohalogenation of 2-bromo-2-methylpropane with base to give 2-methylpropene.



The above dehydrohalogenation reaction is also not very atom economical.

### (c) Dehydration of an alcohol

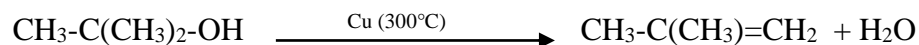
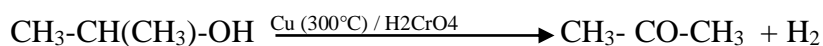
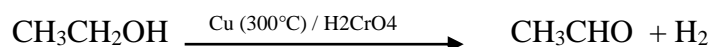
This type of reaction include dehydration of an alcohol to give an olefin and loss of an alcohol from a hemiacetal to give an aldehyde.



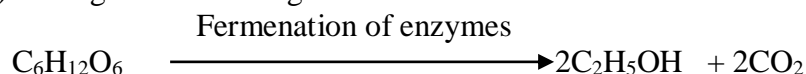
### (d) Dehydrogenation of alcohols

In an elimination reaction, dehydrogenation of alcohols to give aldehyde, ketone and Olefine.

## UNIT V- ORGANIC REACTIONS AND SYNTHESIS OF A DRUG MOLECULE



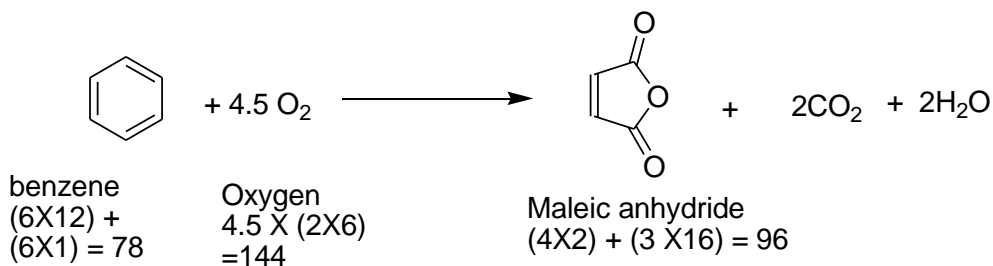
(e) Making ethanol from glucose:



### OXIDATION REACTION

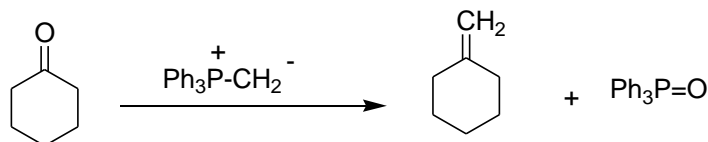
Benzene can be oxidised to make maleic anhydride, an important intermediate chemical.

Maleic anhydride from benzene



### REDUCTION REACTION

Wittig reaction



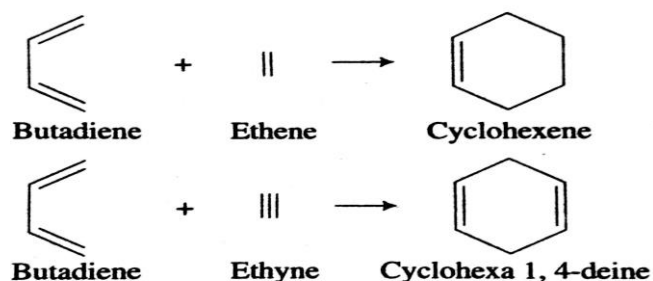
$$\text{Atom economy} = \frac{96}{98 + 276} = 25.7\%$$

### CYCLIZATION REACTION

(a) **Diels-Alder reactions:**

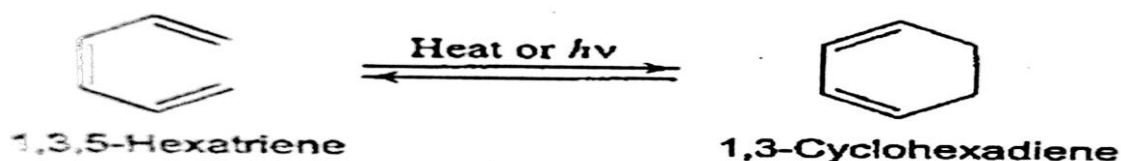
It is a (4+2) cycloaddition reaction between a conjugated diene (4 $\pi$ -electron system) and a compound having a double or triple bond called the dienophile (2 $\pi$ -electron system) to form an adduct. In this reaction, the two components are either heated alone or in an inert solvent.

## UNIT V- ORGANIC REACTIONS AND SYNTHESIS OF A DRUG MOLECULE



(b) Electrocyclic reactions:

These are reversible reactions in which a compound with two  $\pi$  electrons are used to form a sigma bond.



### SYNTHESIS OF COMMONLY USED DRUG MOLECULE

#### Analgesics (Pain relievers)

Analgesics are medications designed to relieve the symptoms of pain. There are a number of different groups of analgesics.

- Simple analgesics
- Non steroidal anti inflammatory drugs
- Opioids

There are many different drugs in each group as well as frequent additions, but examples of the most commonly used are:

Simple analgesics such as

- ✓ Aspirin
- ✓ Paracetamol

Antipyretics are substances that reduce fever. Antipyretics cause the hypothalamus to override a prostaglandin induced increase in temperature. The body then works to lower the temperature, which results in a reduction in fever.

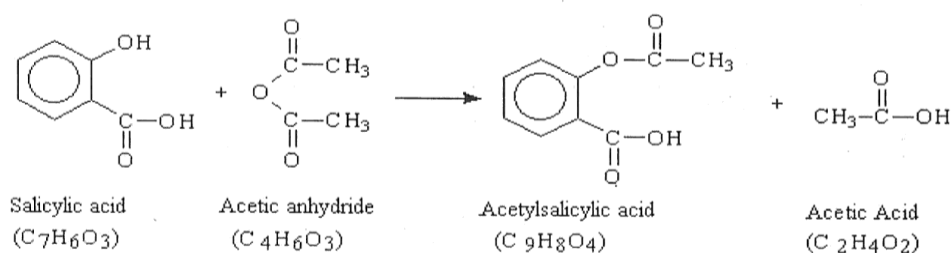
#### ASPIRIN

## UNIT V- ORGANIC REACTIONS AND SYNTHESIS OF A DRUG MOLECULE

Aspirin is the common name for the compound acetylsalicylic acid, widely used as a fever reducer and as a pain killer. Salicylic acid, whose name comes from Salix, the willow family of plants, was derived from willow bark extracts. In folk medicine, willow bark teas were used as headache remedies and other tonics. Now a days, salicylic acid is administered in the form of aspirin which is less irritating to the stomach than salicylic acid.

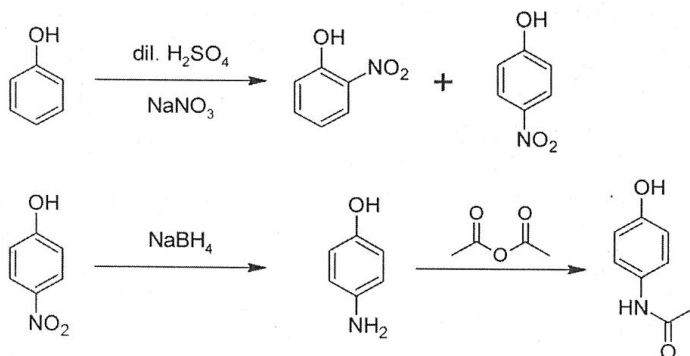
### Synthesis:

To synthesize the common pain killer **aspirin** via an esterification reaction between Salicylic acid and Acetic Anhydride in the presence of concentrated sulfuric acid acting as a catalyst. If salicylic acid is reacted with an excess of acetic anhydride, a small amount of a strong acid is used as a catalyst which speeds up the reaction. Phosphoric acid will be used as the catalyst. The excess acetic acid will be quenched with the addition of water. The aspirin product is not very soluble in water so the aspirin product will precipitate when water is added. The synthesis reaction of aspirin is shown below:



### PARACETAMOL

It is made by reacting 4-aminophenol with acetic anhydride. When the reaction is complete the paracetamol is then isolated and purified.

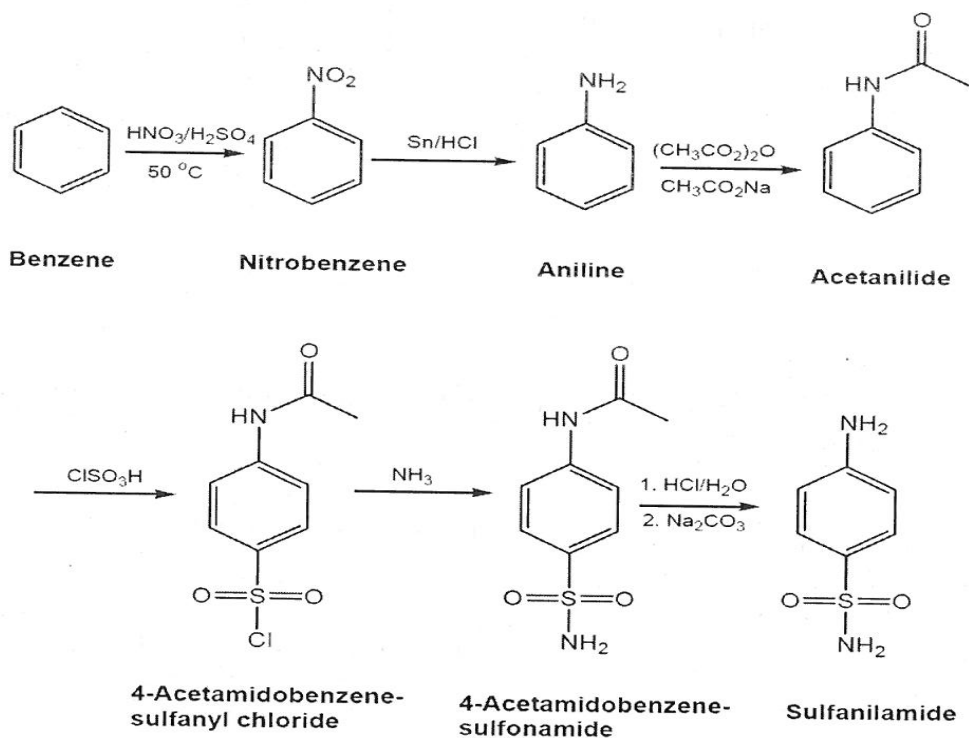


## UNIT V- ORGANIC REACTIONS AND SYNTHESIS OF A DRUG MOLECULE

### SULFONAMIDES

Sulfonamides can be prepared in the laboratory in many ways. The classic approach entails the reaction of sulfonyl chlorides with an amine. A base such as pyridine is typically added to absorb the HCl that is generated. A readily available sulfonyl chloride source is tosyl chloride.

The total synthesis of sulfonamide from benzene can be carried out in six steps using reactions that are very familiar to intermediate level organic chemists.





**UNIT I ATOMIC AND MOLECULAR STRUCTURE**

Questions	opt1	opt2	opt3	opt4	Answer
Which of the following is known as the Schrodinger equation?	$E = h\nu$	$E = mc^2$	$h = p$	$h\nu = E - E_0$	$h\nu = E - E_0$
For the hydrogen atom, which of the following orbitals has the lowest energy?	4s	4p	4d	They all have the same energy	<b>They all have the same energy</b>
Number of lobes in fifth d-orbital are	1	2	3	4	<b>2</b>
Size of 2s-orbital as compared to 1s-orbital is	large	small	medium	very large	<b>large</b>
Planck proposed that energy travels in	discontinuous manner	continuous manner	slow manner	general manner	<b>discontinuous manner</b>
Energy is absorbed by body in form of	photons	quantas	waves	energy	<b>photons</b>
Size of s-orbital increases when value of principal quantum number	Decreases	increases	remains constant	fluctuates	<b>increases</b>
The s-orbital does not show preference to any direction because	It is the smallest orbital	It is present in every atom	It is spherically symmetric	It is the first orbital	<b>It is spherically symmetric</b>
The p-orbital is in the shape of a	Sphere	Dumbbell	Pear-shaped lobe	No shape	<b>Dumbbell</b>
Schrodinger's equation described the	complement of the wave function	behavior of "matter" waves	motion of light	procedure for splitting an atom	<b>behavior of "matter" waves</b>
Which subatomic particles contribute to the mass number of an atom?	protons and neutrons	protons and electrons	neutrons and electrons	protons, neutrons, and electrons	<b>protons and neutrons</b>
Where are the neutrons located in an atom?	outside the nucleus	the electron cloud	they are not found in an atom	inside the nucleus	<b>inside the nucleus</b>
What is the shape of the s orbital?	dumbbell	spherical	flower	flat	<b>spherical</b>
What is the shape of a p orbital?	peanut	spherical	flower	flat	<b>peanut</b>
What is the shape of the d orbitals?	peanut	spherical	flower or four leaf clover	flat	<b>flower or four leaf clover</b>
How many electrons can occupy any one orbital?	2	4	6	8	<b>2</b>
Using 2n <sup>2</sup> calculate how many electrons could occupy the 6th energy level of an atom.	6	36	24	72	<b>72</b>
How many orbitals are there in the "d" sublevel?	1	3	5	7	<b>5</b>
The smallest particle of an element or matter	Proton	Atom	Electron	Electron Cloud	<b>Atom</b>
The central part of an atom that is made up of neutrons and protons	Protons	Neutrons	Nucleus	Reactivity	<b>Nucleus</b>
The region around the nucleus where the electrons may be found.	Electron Cloud	Reactivity	Neutron	Atom	<b>Electron Cloud</b>
Positively charged particle located in the nucleus of an atom.	Electrons	Protons	Subatomic Particles	Neutrons	<b>Protons</b>
Negatively charged particle found outside the nucleus of an atom	Electrons	Protons	Subatomic Particles	Neutrons	<b>Electrons</b>
What are valence electrons?	electrons on the first orbital always	nucleus	the outermost shell	the number of electrons on the outermost orbital	<b>the number of electrons on the outermost orbital</b>
Which particles make up the nucleus of an atom?	protons and neutrons	electrons and protons	electrons, protons, and neutrons	electrons and neutrons	<b>protons and neutrons</b>
Max Planck's great discovery was that radiation energy is emitted in packets that he called what?	wave function	photon	quanta	gamma ray	<b>quanta</b>
In the Heisenberg uncertainty principle, which two measurable properties of a particle cannot be observed precisely at the same time?	Energy and torque	Size and speed	Position and momentum	Spin and color	<b>Position and momentum</b>
Niels Bohr used quantum mechanics to describe which element?	Zinc	Hydrogen	Carbon	Helium	<b>Hydrogen</b>

The square of a particle's wave function describes the probability of what about the particle?	That it will decay	That it is at a particular place	That it has a specific spin	That it will disappear	<b>That it is at a particular place</b>
Simultaneous determination of exact position and momentum of an electron is	Possible	Impossible	Sometimes possible sometimes impossible	always Possible	<b>Impossible</b>
Uncertainty principle gave the concept of	Probability	An orbital	Physical meaning of $\Psi$	Physical meaning of $\Psi^2$	<b>Probability</b>
Orbital is	Space around the nucleus where the probability of finding the electron is maximum	Circular path around the nucleus in which the electron revolves	Amplitude of electrons wave	square of electrons wave	<b>Space around the nucleus where the probability of finding the electron is maximum</b>
The electronic energy levels of the hydrogen atom in the Bohr's theory are called	Rydberg levels	Orbits	Ground states	Orbitals	<b>Orbits</b>
When two atomic orbitals combine they form	One molecular orbital	two molecular orbital	three molecular orbital	four molecular orbital	<b>two molecular orbital</b>
In a double bond connecting two atoms, there is a sharing of	2 electrons	1 electron	4 electrons	All electrons	<b>4 electrons</b>
$\pi$ bond is formed	By overlapping of atomic orbitals on the axis of nuclei	By mutual sharing of pi electron	By sidewise overlapping of half filled p-orbitals	By overlapping of s-orbitals with p-orbitals	<b>By sidewise overlapping of half filled p-orbitals</b>
In a sigma bond	Sidewise as well as end to end overlap of orbitals take place	Sidewise overlap of orbitals takes place	End to end overlap of orbitals takes place	No overlapping	<b>End to end overlap of orbitals takes place</b>
Which of the following is not correct	A sigma bond is weaker than $\pi$ bond	A sigma bond is stronger than $\pi$ bond	A double bond is stronger than a single bond	A double bond is shorter than a single bond	<b>A sigma bond is weaker than <math>\pi</math> bond</b>
Bond created by overlapping of one modified orbit on another orbit is known as	Sigma bond ( $\sigma$ -bond)	Pi bond ( $\pi$ -bond)	Covalent bond	Dative bond	<b>Sigma bond (<math>\sigma</math>-bond)</b>
The paramagnetic nature of oxygen molecule is best explained on the basis of	Valence bond theory	Resonance	Molecular orbital theory	Hybridization	<b>Molecular orbital theory</b>
Complete transfer of one or more electrons between atoms constitutes in forming	ionic bond	covalent bond	co-ordinate covalent bond	dative bond	<b>ionic bond</b>
The bond order of NO molecule is	1	2	2.5	3	<b>2.5</b>
Molecular orbital theory was developed mainly by	Pauling	Pauling and Slater	Mulliken	Thomson	<b>Pauling and Slater</b>
Paramagnetism is exhibited by molecules	Not attracted into a magnetic field	Containing only paired electrons	Carrying a positive charge	Containing unpaired electrons	<b>Containing unpaired electrons</b>
The difference in energy between the molecular orbital formed and the combining atomic orbitals is called	Bond energy	Activation energy	Stabilization energy	Destabilization energy	<b>Stabilization energy</b>
With increasing bond order, stability of a bond	Remains unaltered	Decreases	Increases	None of these	<b>Increases</b>
The total number of electron that takes part in forming bonds in $N_2$	2	4	6	10	<b>6</b>
Which molecule is linear	$NO_2$	$ClO_2$	$CO_2$	$H_2S$	<b><math>CO_2</math></b>
Compound formed by $sp^3d$ hybridization will have structure	Planar	Pyramidal	Angular	Trigonal bipyramidal	<b>Trigonal bipyramidal</b>

Octahedral molecular shape exists in ..... hybridisation	sp <sup>3</sup> d	sp <sup>3</sup> d <sup>2</sup>	sp <sup>3</sup> d <sup>3</sup>	sp	<b>sp<sup>3</sup>d<sup>2</sup></b>
Shape of methane molecule is	Tetrahedral	Pyramidal	Octahedral	square planer	<b>Tetrahedral</b>
Which species do not have sp <sup>3</sup> hybridization	Ammonia	Methane	Water	Carbon dioxide	<b>Carbon dioxide</b>
As compared to pure atomic orbitals, hybrid orbitals have	Low energy	Same energy	High energy	None of these	<b>Low energy</b>
The number of unpaired electrons in O <sub>2</sub> molecule is	0	1	2	3	<b>2</b>
When two pairs of electrons are shared, bond is	Single covalent bond	Double covalent bond	Dative bond	Triple bond	<b>Double covalent bond</b>
Hybridisation involves	Addition of an electron pair	Mixing up of atomic orbitals	Removal of an electron pair	Separation of orbitals	<b>Mixing up of atomic orbitals</b>



**UNIT II PERIODIC PROPERTIES, INTERMOLECULAR FORCES AND POTENTIAL ENERGY SURFACES**

Questions	opt1	opt2	opt3	opt4	Answer
The valency of carbon is four. On what principle it can be explained in a better way	Resonance	Hybridization	Electron transfer	cannot be explained	<b>Hybridization</b>
Hybridization is due to the overlapping of	Orbitals of different energy levels	Orbitals of different energy content	Orbitals of same energy content	atoms	<b>Orbitals of same energy content</b>
The coordination number of a metal in coordination compounds is	Same as primary valency	Sum of primary and secondary valencies	Same as secondary valency	difference of primary and secondary valencies	<b>Same as secondary valency</b>
A group of atoms can function as a ligand only when	It is a small molecule	It has an unshared electron pair	It is a negatively charged ion	It is a positively charged ion	<b>It has an unshared electron pair</b>
The coordination number of a central metal atom in a complex is determined by	The number of ligands around a metal ion bonded by sigma and pi-bonds both.	The number around a metal ion bonded by pi-bonds	The number of ligands around a metal ion bonded by sigma bonds	The number of only anionic ligands bonded to the metal ion	<b>The number of ligands around a metal ion bonded by sigma bonds</b>
That ion or molecule which forms a complex compound with transitional metal ion is called	Recipient	Ligand	Coordinate ion	No special name	<b>Ligand</b>
Generally, a group of atoms can function as a ligand if	They are positively charged ions	They are free radicals	They are either neutral molecules or negatively charged ions	They have no charge	<b>They are either neutral molecules or negatively charged ions</b>
Ligands, in complex compounds	Accept e <sup>-</sup> -pair	Donate e <sup>-</sup> -pair	Neither accept nor donate e <sup>-</sup> -pair	All of these happen	<b>Donate e<sup>-</sup>-pair</b>
The number of neutral molecules or negative groups attached to the central metal atom in a complex ion is called	Atomic number	Effective atomic number	Coordination number	Primary valency	<b>Coordination number</b>
In complex compounds, metal ligand bond is	Coordinate bond	Hydrogen bond	Ionic bond	Covalent bond	<b>Coordinate bond</b>
A molecule which contains unpaired electrons is	carbon monoxide	Molecular nitrogen	Molecular oxygen	Hydrogen peroxide	<b>Molecular oxygen</b>

Which type of overlapping results the formation of a $\pi$ bond	Axial overlapping of s-s orbitals	Lateral overlapping of p-p orbitals	Axial overlapping of p-p orbitals	Axial overlapping of s-p orbitals	Lateral overlapping of p-p orbitals
Coordination compounds have great importance in biological systems. In this context which of the following statements is incorrect	Cyanocobalamin is B12 and contains cobalt.	Haemoglobin is the red pigment of blood and contains iron.	Chlorophylls are green pigments in plants and contains calcium.	Carboxypeptidase-A is an enzyme and contains zinc.	<b>Chlorophylls are green pigments in plants and contains calcium.</b>
In the case of small cuts, bleeding is stopped by applying potash alum. Here alum acts as	Fungicide	Disinfectant	Germicide	Coagulating agent	<b>Coagulating agent</b>
The complex used as an anticancer agent is	trans -[Co(NH <sub>3</sub> ) <sub>3</sub> Cl <sub>3</sub> ]	cis-[PtCl <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]	cis-K <sub>2</sub> [PtCl <sub>2</sub> B <sub>r</sub> <sub>2</sub> ]	Na <sub>2</sub> CO <sub>3</sub>	<b>cis-[PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]</b>
Which among the following chemical bond were described by Kossel and Lewis?	Metallic bond	Polar covalent bond	Coordinate bond	Ionic and Covalent bond	<b>Ionic and Covalent bond</b>
Which among the following is not a property of Ionic bond?	Losing of electrons	Gain of electrons	Sharing of electrons	Transfer of electrons	<b>Sharing of electrons</b>
Which among the following formation is not an example of Covalent bond?	LiF	NH <sub>3</sub>	CF <sub>4</sub>	HF	<b>LiF</b>
If a bond is made up of a large number of organic compound, then the bond is termed as?	Ionic bond	Metallic bond	Covalent bond	Dipolar bond	<b>Covalent bond</b>
Which among the following is not an example of hydrogen	H <sub>2</sub> O	Liquid HCl	NH <sub>3</sub>	CHCl <sub>3</sub>	<b>Liquid HCl</b>
Atoms undergo bonding in order to ?	Attain stability	Lose stability	Move freely	increase energy	<b>Attain stability</b>
An atom differs from its ion in which among the following?	Mass number	Atomic number	Neutrons	Number of protons	<b>Number of protons</b>
The filling of molecular orbital takes place according to	The Aufbau Principle	Pauli exclusion Principle	Hund's rule of maximum multiplicity	All of the mentioned	<b>All of the mentioned</b>
Arrange the following molecules in decreasing bond length.	O <sub>2</sub> > O <sub>2</sub> <sup>-</sup> > O <sub>2</sub> <sup>+</sup> > O <sub>2</sub> <sup>2-</sup>	O <sub>2</sub> <sup>2-</sup> > O <sub>2</sub> <sup>-</sup> > O <sub>2</sub> > O <sub>2</sub> <sup>+</sup>	O <sub>2</sub> <sup>2-</sup> > O <sub>2</sub> <sup>-</sup> > O <sub>2</sub> <sup>+</sup> > O <sub>2</sub>	O <sub>2</sub> <sup>-</sup> > O <sub>2</sub> <sup>+</sup> > O <sub>2</sub> <sup>2-</sup> > O <sub>2</sub>	<b>O<sub>2</sub><sup>2-</sup> &gt; O<sub>2</sub><sup>-</sup> &gt; O<sub>2</sub> &gt; O<sub>2</sub><sup>+</sup></b>
Arrange the following molecules in the order of increasing stability.	N <sub>2</sub> <sup>+</sup> < N <sub>2</sub> < N <sub>2</sub> <sup>-</sup> < N <sub>2</sub> <sup>2-</sup>	N <sub>2</sub> <sup>2-</sup> < N <sub>2</sub> <sup>-</sup> < N <sub>2</sub>	N <sub>2</sub> <sup>2-</sup> < N <sub>2</sub> <sup>-</sup> = N <sub>2</sub> <sup>+</sup> < N <sub>2</sub>	N <sub>2</sub> < N <sub>2</sub> <sup>+</sup> = N <sub>2</sub> <sup>-</sup> < N <sub>2</sub> <sup>2-</sup>	<b>N<sub>2</sub><sup>2-</sup> &lt; N<sub>2</sub><sup>-</sup> &lt; N<sub>2</sub> &lt; N<sub>2</sub><sup>+</sup></b>
Which of the following molecule does not exist due to its zero bond order?	H <sub>2</sub> <sup>+</sup>	He <sub>2</sub> <sup>+</sup>	He <sub>2</sub>	H <sub>2</sub> <sup>-</sup>	<b>He<sub>2</sub></b>
Which of the following is a microscopic property?	Reactivity	Inter-molecular force	Boiling point	Kinetic energy	<b>Inter-molecular force</b>

Which of the following has the highest bond dissociation	Covalent bond	Vander waals force	Dipole-dipole	Hydrogen bond	<b>Covalent bond</b>
The strength of Vander waals forces depends upon	Size of the molecule	Molecular structure	Number of electrons present in the molecule	All of the mentioned	<b>All of the mentioned</b>
Nitrogen has the electronic configuration $1s^2, 2s^2 2p^1 x^2 p^1 y^2 p^1 z$ and not $1s^2 2s^2 2p^2 x^2 2p^1 y^2 2p^1 z$ , which is determined by	Aufbau's principle	Pauli's exclusion principle	Hund's rule	Uncertainty principle	<b>Hund's rule</b>
Electronic configuration of H <sup>+</sup> is	$1s^0$	$1s^1$	$1s^2$	$1s^1 2s^1$	<b><math>1s^2</math></b>
An element has the electronic configuration $1s^2, 2s^2 2p^6, 3s^2 3p^2$ . Its valency electrons are	6	2	3	4	<b>4</b>
Which orbital is dumb-bell shaped	s-orbital	p-orbital	d-orbital	f-orbital	<b>p-orbital</b>
The total number of unpaired electrons in d- orbitals of atoms of element of atomic number 29 is	10	1	0	5	<b>0</b>
The following has zero valency	Sodium	Beryllium	Aluminium	Krypton	<b>Krypton</b>





### UNIT III SPECTROSCOPIC TECHNIQUES AND APPLICATIONS

Questions	opt1	opt2	opt3	opt4	Answer
The different types of energies associated with a molecule are	Electronic energy	Vibrational energy	Rotational energy	All of the mentioned	<b>All of the mentioned</b>
During the motion, if the centre of gravity of molecule changes, the molecule possess	Electronic energy	Rotational energy	Translational energy	Vibrational energy	<b>Translational energy</b>
The correct order of different types of energies is	Eel >> Evib >> Erot >> E tr	Eel >> Erot >> Evib >> E tr	Eel >> Evib >> Etr >> E rot	Etr >> Evib >> Erot >> E el	<b>Eel &gt;&gt; Evib &gt;&gt; Erot &gt;&gt; E tr</b>
The region of electromagnetic spectrum for nuclear magnetic resonance is	Microwave	Radio frequency	Infrared	UV-rays	<b>Radio frequency</b>
Which of the following is an application of molecular spectroscopy?	Structural investigation	Basis of understanding of colors	Study of energetically excited reaction products	All of the mentioned	<b>All of the mentioned</b>
Select the correct statement from the following option.	Spectroscopic methods require less time and more amount of sample than classical methods	Spectroscopic methods require more time and more amount of sample than classical methods	Spectroscopic methods require less time and less amount of sample than classical methods	Spectroscopic methods require more time and less amount of sample than classical methods	<b>Spectroscopic methods require less time and less amount of sample than classical methods</b>
The electronic spectra in the visible range span	25000-72000 cm <sup>-1</sup>	25000-50000 cm <sup>-1</sup>	12500-25000 cm <sup>-1</sup>	15000-30000 cm <sup>-1</sup>	<b>12500-25000 cm<sup>-1</sup></b>
Which of the following transitions are of weak intensities and lie in the visible region?	n to n*	sigma to sigma*	pi to pi*	n to sigma*	<b>n to n*</b>
What is the position of band of alkanes?	190 nm	185 nm	217 nm	150 nm	<b>150 nm</b>
Which of the following organic compound shows transition due to conjugation?	Alkenes	Saturated aliphatic ketones	Conjugated dienes	Alkanes	<b>Conjugated dienes</b>
Which of the following is an application of electronic spectroscopy?	Detection of impurities	Control of purification	Study of kinetics of chemical reaction	All of the mentioned	<b>All of the mentioned</b>
Vibrational spectroscopy involves the transitions falling in the spectral range of	100-1000 cm <sup>-1</sup>	300-3000 cm <sup>-1</sup>	400-4000 cm <sup>-1</sup>	500-5000 cm <sup>-1</sup>	<b>400-4000 cm<sup>-1</sup></b>
Which of the region of IR spectra appears between (1400-600) cm <sup>-1</sup> ?	Functional group region	Fingerprint region	Low-frequency region	None of the mentioned	<b>Fingerprint region</b>
Select the correct statement from the following option.	Infrared spectra can identify the unknown materials	It can determine the amount of components in a mixture	It can also determine the quality of a sample	All of the mentioned	<b>All of the mentioned</b>
Which of the following molecule have infrared active vibrations?	NO	CH <sub>4</sub>	H <sub>2</sub>	All of the mentioned	<b>NO</b>
Which of the following cannot show a vibrational absorption spectrum?	OCS	H <sub>2</sub> O	CO <sub>2</sub>	C H <sub>2</sub> = C H <sub>2</sub>	<b>C H<sub>2</sub> = C H<sub>2</sub></b>

Which of the following is not a type of bending molecular vibration?	Twisting	Stretching	Wagging	Rocking	Stretching
Presence of functional group in a compound can be established by using	Chromatography	IR spectroscopy	Mass spectroscopy	X-ray diffraction	IR spectroscopy
Select the incorrect option from the following option.	IR spectroscopy helps in determination of purity	IR spectroscopy helps in determination of force constant from vibrational spectrum	IR spectroscopy helps in identifying an unknown compound	None of the mentoned	None of the mentoned
A quantum of energy is also called as	electron	Photon	proton	neutron	
Energy associated with rotation of atoms is _____	Electronic energy	Vibrational energy	Rotational energy	Translational energy	Rotational energy
Energy associated with streching and bending of atoms is _____	Electronic energy	Vibrational energy	Rotational energy	Translational energy	Vibrational energy
Energy associated with exitation of atoms is _____	Electronic energy	Vibrational energy	Rotational energy	Translational energy	Electronic energy
The distance between two successive amplitude maxima or minima is called as	wave number	wavelength	frequency	None of these	wavelength
The number of wavelength passes in a given point per second id called as	wave number	wavelength	frequency	None of these	frequency
UV spectroscopy is associated with	excitation of elctron	vibration of electron	Rotation of electron	None of these	excitation of elctron
IR spectroscopy is associated with	excitation of elctron	vibration of electron	Rotation of electron	None of these	vibration of electron
Nuclear Maganetic Resonance spectroscopy is associated with	excitation of elctron	vibration of electron	Rotation of electron	None of these	Rotation of electron
Reference used in NMR is	TMS	TMF	Benzen	Tolune	TMS
Chemical shift of TMS proton is assigned a value of	7	0	10	3	0
Chemical shift of the compund for More shielding of proton _____ from TMS	more downfield	More upfield	Does not change	None of these	more downfield
Chemical shift of the compund for less shielding of proton _____ from TMS	more downfield	More upfield	Does not change	None of these	More upfield
The radiation used in NMR is _____ waves	UV	IR	Micro	Radio	Radio
The radiation used in Electronic spectroscopy is _____ waves	UV	IR	Micro	Radio	UV
The radiation used in Vibrational spectroscopy is _____ waves	UV	IR	Micro	Radio	IR
The range of UV radiation is	10 to 400 nm	400 to 750 nm	750 to 40000 nm	30cm to 100000 m	10 to 400 nm
The range of Visible radiation is	10 to 400 nm	400 to 750 nm	750 to 40000 nm	30cm to 100000 m	400 to 750 nm
The range of IR radiation is	10 to 400 nm	400 to 750 nm	750 to 40000 nm	30cm to 100000 m	750 to 40000 nm
The range of Radio waves is	10 to 400 nm	400 to 750 nm	750 to 40000 nm	30cm to 100000 m	30cm to 100000 m

The source used in UV Spectroscopy is	Hydrogen Lamp	rod of alkali oxides	Gold Plate	None of these	<b>Hydrogen Lamp</b>
The source used in IR Spectroscopy is	Deuterium lamp	rod of alkali oxides	Zinc Plate	None of these	<b>rod of alkali oxides</b>
Mono chromator used in UV Spectroscopy is	Prism	Glass	Calcium oxide film	All of these	<b>Prism</b>
Mono chromator used in IR Spectroscopy is	Prism	Grating	Glass	None of these	<b>Prism</b>

#### UNIT IV USE OF FREE ENERGY IN CHEMICAL EQUILIBRIA

Questions	opt1	opt2	opt3	opt4	Answer
The type of reaction taking place in anode	Redox	Oxidation	Reduction	Precipitation	<b>Oxidation</b>
An example for strong electrolyte is	Hydrochloric acid	Acetic acid	Sugar	Glucose	<b>Hydrochloric acid</b>
An example for weak electrolyte is	Hydrochloric acid	Acetic acid	Sugar	Glucose	<b>Acetic acid</b>
Sodium chloride is called an electrolyte, because	Its molecule is made up of electrically charged particles.	It is decomposed, when an electric current is passed through it.	It breaks up into ions, when a current is passed through it.	It ionizes, when fused or dissolved in a proper solvent	<b>It ionizes, when fused or dissolved in a proper solvent</b>
Electrolyte can conduct electricity, because	Their molecules contain unpaired electrons, which are mobile	Their molecules contain loosely held electrons, which become free under the influence of voltage.	The molecules break up into ions, when a voltage is applied	The molecules are broken up into ions, when the electrolyte is fused or dissolved in the solvent.	<b>The molecules are broken up into ions, when the electrolyte is fused or dissolved in the solvent.</b>
Which one of the following is an electrolyte?	C <sub>6</sub> H <sub>6</sub>	CHCl <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> Cl	NaCN	<b>NaCN</b>
Reduction takes place in -----	Anode	Cathode	Electrolyte	Cell	<b>Cathode</b>
Electrolytic cell in which electrical energy is converted into	Chemical energy	Light energy	Heat energy	Sound energy	<b>Chemical energy</b>
Electrochemical cell is a device which is used to get _____ energy.	Thermal	Electrical	Chemical	Mechanical	<b>Electrical</b>
The emf of the daniel cell	1.1 V	2 V	0 V	10 V	<b>1.1 V</b>
The emf of the daniel cell can be calculated by the formula	$E_{\text{CELL}} = E^{\circ}_{\text{Zn}} - E^{\circ}_{\text{Cu}}$	$E_{\text{CELL}} = E^{\circ}_{\text{Cu}} - E^{\circ}_{\text{Zn}}$	$E_{\text{CELL}} = E^{\circ}_{\text{Pb}} - E^{\circ}_{\text{Cu}}$	$E_{\text{CELL}} = E^{\circ}_{\text{Cu}} - E^{\circ}_{\text{Pb}}$	<b><math>E_{\text{CELL}} = E^{\circ}_{\text{Zn}} - E^{\circ}_{\text{Cu}}</math></b>
An electrochemical cell converts chemical energy into	Electrical energy	Heat energy	light energy	Solar energy	<b>Electrical energy</b>
In galvanic series, a metal high in series is more _____.	Anodic	Cathodic	Corroded	Neutral	<b>Anodic</b>
Electrical energy is converted into chemical energy in	Electrolytic cell	Daniel cell	Fuel cell	Electroplating	<b>Electrolytic cell</b>
A galvanic cell converts	electrical energy into chemical energy	chemical energy into electrical energy	electrical energy into heat energy	chemical energy into heat energy	<b>chemical energy into electrical energy</b>
In the galvanic cell electrical energy is generated at the expense of	Free energy	Chemical energy	Heat energy	Heat energy	<b>Chemical energy</b>
Chemical energy is converted directly into electrical energy in	a battery.	an electrical power plant	an electrolytic cell.	an automobile's engine.	<b>a battery.</b>
Tendency of an electrode to gain electron is	Oxidation potential	Reduction potential	Redox potential	Single electrode potential	<b>Reduction potential</b>
Tendency of an electrode to lose electron is	Oxidation potential	Reduction potential	Redox potential	Single electrode potential	<b>Oxidation potential</b>
The passage of electricity in the daniel cell, when zinc and copper electrode are connected to form	Cu to Zn in the cell	Cu to Zn outside the cell	Zn to Cu in the cell	Zn to Cu outside the cell	<b>Zn to Cu outside the cell</b>
The electrode potential is the tendency of metal	to gain the electron	loss the electron	either to loss or gain the electron	reactive	<b>either to loss or gain the electron</b>

In the electrochemical series elements are arranged in the	decreasing order of standard electrode potential	increasing order of standard electrode potential	increasing order of oxidation potential	increasing order of equivalent weight	<b>increasing order of standard electrode potential</b>
Zinc is above the copper in electrochemical series. So if standard zinc electrode and standard copper electrode are coupled to form a cell, in such cell	zinc is oxidized	copper is oxidized	zinc gain electron	copper losses electron	<b>zinc is oxidized</b>
Which one of the following is a reversible cell	Daniel cell	Dry cell	Zinc -silver cell	Lead -cadmium cell	<b>Daniel cell</b>
The standard free energy $-\Delta G =$	$nFE$	$RT/nF$	$\ln k$	$K$	<b><math>nFE</math></b>
The gas constant $R =$	8.314 J/K/mol	2.888 J/K/mol	96500 C	298 K	<b>8.314 J/K/mol</b>
The pH of the given solution can be measured by using	Zinc electrode	Calomel electrode	Standard hydrogen electrode	Glass electrode	<b>Glass electrode</b>
Emf is measured in	Ampere	Volts	ev	mho	<b>Volts</b>
If the emf of the cell is positive, The reaction is	Spontaneous	Feasible	Exothermic	Endothermic	<b>Spontaneous</b>
In the combination of metals Zn and Ag which will be acting as anode	Zn	Ag	Au	Fluoride	<b>Zn</b>
Which one of the following is used in measuring emf of a solution	Potentiometer	Ph meter	Thermometer	Voltmeter	<b>Potentiometer</b>
The principle in which potentiometer works is	Poggendorff compensation principle	Heisenberg principle	Pauli exclusion principle	Aufbau principle	<b>Poggendorff compensation principle</b>
Anode used in lead acid battery is	Lead	Lead oxide	Iron	Lithium	<b>Lead</b>
Storage cells are otherwise called	Accumulators	Fuel cells	Flow cells	Primary cells	<b>Accumulators</b>
An example for redox titration is	$Fe^{2+}/K_2Cr_2O_7$	$AgCl/NaOH$	$HCl/NaOH$	$NaCl/NaOH$	<b><math>Fe^{2+}/K_2Cr_2O_7</math></b>
Battery is a type of _____ cell.	Electrolytic	Electrochemical	Chemo electric	Thermal	<b>Electrochemical</b>
Dry cell is an example of _____ cell.	Primary	Secondary	Electrochemical	Electrolytic	<b>Primary</b>
Internal energy is denoted by	E	H	G	A	<b>E</b>
Heat content is denoted by	G	A	S	H	<b>H</b>
Free energy is denoted by	E	H	G	S	<b>G</b>
Work function is denoted by	S	E	H	A	<b>A</b>
Entropy is denoted by	S	E	H	A	<b>S</b>
Which one is correctly matched?	Acids – pH range above 7	Acids – pH range below 7	Acids – pH range 7 (neutral)	Acids – pH range 8-9	<b>Acids – pH range below 7</b>
Select the one which is neither an acid nor base	$CH_3COOH$	$HCl$	$KCl$	$CH_3OH$	<b><math>KCl</math></b>
Which one will change from red litmus to blue?	$NaCl$	$HCl$	$KOH$	$LiOH$	<b><math>HCl</math></b>
What will be the product when $HNO_3$ reacts with $NH_4OH$ ?	$NH_4NO_3$	$2NH_4NO_3$	$NH_4(NO_3)_2$	$NH_2NO_3$	<b><math>NH_4NO_3</math></b>
Find the odd one out:	Neutral salt : $NaCl$	Acid salt : $CuSO_4 \cdot 5H_2O$	Basic salt: $CuCO_3 \cdot Cu(OH)_2$	Nonhydrated salt: $KNO_3$	<b>Acid salt : <math>CuSO_4 \cdot 5H_2O</math></b>

### UNIT V ORGANIC REACTIONS AND SYNTHESIS OF A DRUG MOLECULE

Questions	opt1	opt2	opt3	opt4	Answer
_____ a reaction in which one molecule combines with another to form a larger molecule with no other products.	Addition	Substitution	Elimination	ring opening	<b>Addition</b>
_____ is a chemical reaction during which one functional group in a chemical compound is replaced by another functional group.	Addition	Substitution	Elimination	ring opening	<b>Substitution</b>
_____ a class of organic chemical reactions in which a pair of atoms or groups of atoms are removed from a molecule	Addition	Substitution	Elimination	ring opening	<b>Elimination</b>
Formation of a ring compound from a chain by formation of a new bond	Ring opening	reduction	oxidation	Cyclization	<b>Cyclization</b>
Formation of a linear compound from a cyclic compound	Ring opening	reduction	oxidation	Cyclization	<b>Ring opening</b>
Addition of Hydrogen	oxidation	reduction	ring opening	Cyclization	<b>reduction</b>
Removal of Hydrogen	oxidation	reduction	ring opening	Cyclization	<b>oxidation</b>
Addition of Oxygen	oxidation	reduction	ring opening	Cyclization	<b>oxidation</b>
Removal of Oxygen	oxidation	reduction	ring opening	Cyclization	<b>reduction</b>
Addition reaction takes place in	saturated compounds	Unsaturated compounds	Both Saturated & Unsaturated compounds	Not in Saturated & Unsaturated compounds	<b>Unsaturated compounds</b>
Elimination reaction takes place in	saturated compounds	Unsaturated compounds	Both Saturated & Unsaturated compounds	Not in Saturated & Unsaturated compounds	<b>saturated compounds</b>
Substance in treating disease	Drug	Medicine	Medication	None of these	<b>Medicine</b>
Medicine used for relieving anxiety, stress, worry, and fear	Anesthetics	Anxiolytics	Analgesics	Antibiotics	<b>Anxiolytics</b>
Medicine used for the loss of sensitivity	Anesthetics	Anxiolytics	Analgesics	Antibiotics	<b>Anesthetics</b>
_____ is a medicine that eliminate or alleviate the feeling of pain	Anesthetics	Anxiolytics	Analgesics	Antibiotics	<b>Analgesics</b>
_____ is a medicine treating infectious diseases	Anesthetics	Anxiolytics	Analgesics	Antibiotics	<b>Antibiotics</b>
addition of hydrogen halides to alkenes take place in the absence of peroxide medium	Markovnikov's Rule	Anti Markovnikov's Rule	aldol condensation	Clemmensen Reduction	<b>Markovnikov's Rule</b>
addition of hydrogen halides to alkenes take place in the peroxide medium	Markovnikov's Rule	Anti Markovnikov's Rule	aldol condensation	Clemmensen Reduction	<b>Anti Markovnikov's Rule</b>
Valance of carbon is	2	3	4	6	<b>4</b>

Free radicals are produced by	heterolytic bond fission	homolytic bond fission	Both	None of these	<b>homolytic bond fission</b>
Ions are produced by	heterolytic bond fission	homolytic bond fission	Both	None of these	<b>heterolytic bond fission</b>
nucleophile is an _____ chemicals species	Electron rich	Electron deficient	Proton rich	Proton deficient	<b>Electron rich</b>
Electrophine is a _____ chemical species	Electron rich	Electron deficient	Proton rich	Proton deficient	<b>Proton rich</b>
KMnO <sub>4</sub> is used as	Oxidizing agent	Reducing agent	Antibiotic	Analegesic	<b>Oxidizing agent</b>
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> is used as	Oxidizing agent	Reducing agent	Antibiotic	Analegesic	<b>Oxidizing agent</b>
Zinc is used as	Oxidizing agent	Reducing agent	Antibiotic	Analegesic	<b>Reducing agent</b>
Platinum is used as	Oxidizing agent	Reducing agent	Antibiotic	Analegesic	<b>Reducing agent</b>
Paladium is used as	Oxidizing agent	Reducing agent	Antibiotic	Analegesic	<b>Reducing agent</b>
Paracetomal is an example for	Antibiotic	Analegesic	Anesthetics	Anxiolytics	<b>Analegesic</b>
Erythromycin is an example for	Antibiotic	Analegesic	Anesthetics	Anxiolytics	<b>Antibiotic</b>
cefexime is an example for	Antibiotic	Analegesic	Anesthetics	Anxiolytics	<b>Antibiotic</b>
Clemmensen reaction is an example for	Oxidation	Reduction	ring opening	Cyclization	<b>Reduction</b>
wolff kishner reaction is an example for	Cyclization	Oxidation	Reduction	ring opening	<b>Reduction</b>
Meerwein Ponderof reaction is an example for	Oxidation	Reduction	ring opening	Cyclization	<b>Reduction</b>
The minimum amount of energy required by the reactant to form a product is	gibbs free energy	Activation energy	Kinetic energy	All of these	<b>Activation energy</b>
SN <sub>2</sub> denotes	unimolecular substitution reaction	bimolecular substitution reaction	bimolecular addition reaction	unimolecular addition reaction	<b>bimolecular substitution reaction</b>
SN <sub>1</sub> denotes	unimolecular substitution reaction	bimolecular substitution reaction	bimolecular addition reaction	unimolecular addition reaction	<b>unimolecular substitution reaction</b>
SN <sub>1</sub> reaction takes place in _____ steps	1	2	3	4	<b>2</b>
SN <sub>2</sub> reaction takes place in _____ steps	1	2	3	4	<b>1</b>
E <sub>1</sub> reaction takes place in _____ steps	1	2	3	4	<b>2</b>

E1 reaction takes place in _____ steps	1	2	3	4	<b>1</b>
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