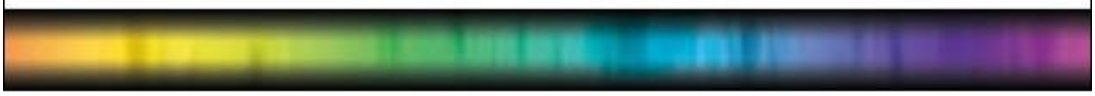
## Selection Rules for Electronic Spectra

- When the molecule absorbs electromagnetic radiation, it may be due to interaction of
  - electrical dipole or quadruple with the electrical field of emr – Electrical dipole transitions
  - the magnetic dipole of the molecule with the magnetic field of emr – Magnetic dipole transitions

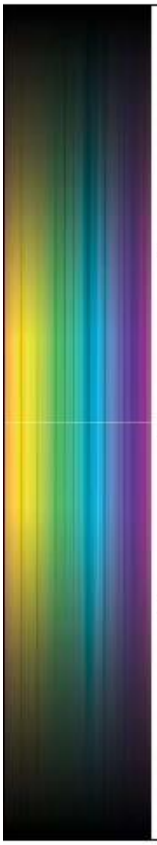
Electrical dipole >> Magnetic dipole > Electrical quadruple



## The Laporte Selection Rule

- All transitions within the d-shell, such as $^3A_{2g} \rightarrow {}^3T_{2g}$ are Laporte forbidden, because they are g→g.
- The intensity of the d-d transitions that give d-block metal ions their colors are not very intense.
- Charge transfer bands frequently involve p→d or d→p transitions, and so are Laporte-allowed and therefore very intense.

.



## Use of Electronic spectrum

- **Electronic spectrum – due to d-d transitions.**
- **From the transition energy – energy of d $e^-$ can be got.**
- **The energies of d levels affected by many complicated factors.**

## Terms, States and Microstates

- **Energy levels described by quantum numbers.**
  - **Principal quantum number – n**
  - **Azimuthal quantum number – l**
  - **Magnetic quantum number – $m_l$**
  - **Spin quantum number – $m_s$**
- **But actual conditions are complicated .**
- **Quantum numbers alone are not sufficient**

**Why ?**

## Spin-Orbit Coupling

So far we've considered only $e^-$-$e^-$ (orbital angular momentum) and spin-spin (spin angular momentum) interactions.

Orbitals and spins can also interact giving rise to spin-orbit coupling

- $J$ is the total angular momentum

$$J \Rightarrow L+S, L+S-1, L+S-2, \ldots, |L-S|$$

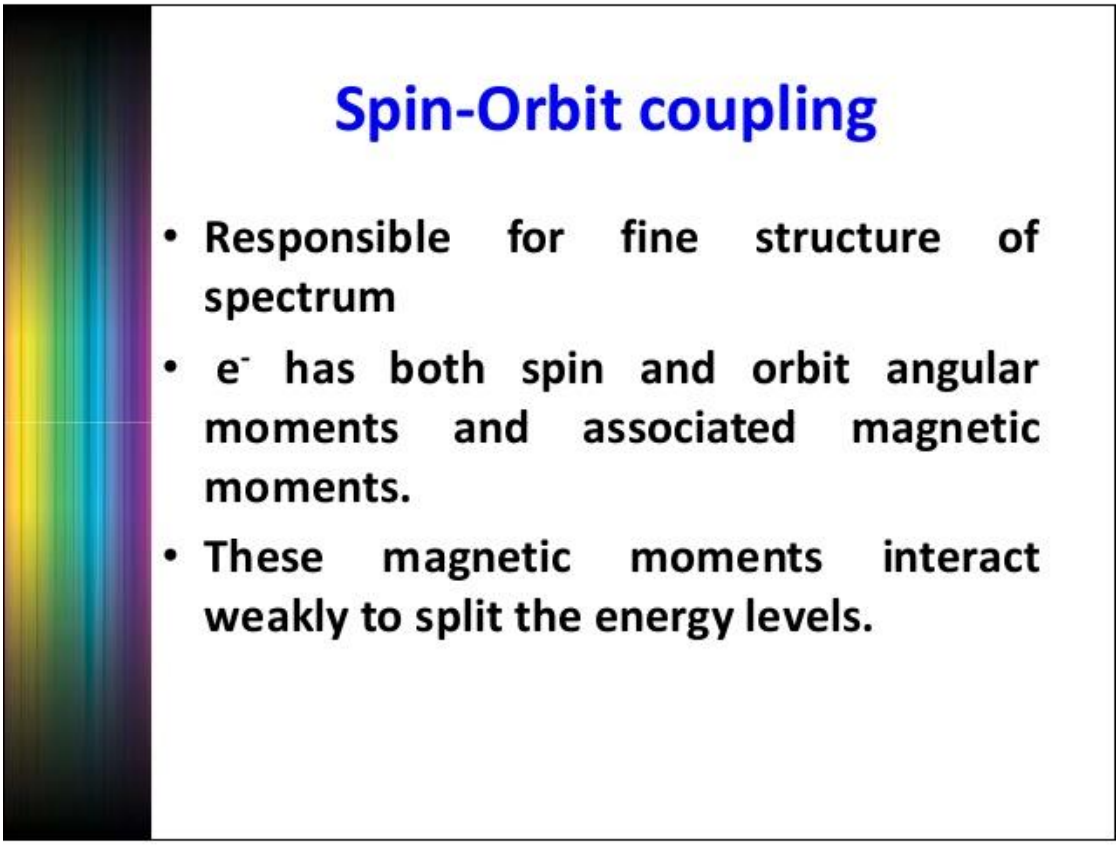
So for the $^3F$ ground state of a $d^2$ free ion, we have

$$J \Rightarrow |L+S| = 4$$
$$\Rightarrow L-S = 2$$
$$\text{so } J = 4, 3, 2$$

So the $^3F$ ground state electron configuration of a $d^2$ free ion splits into $^3F_4$, $^3F_3$, and $^3F_2$.

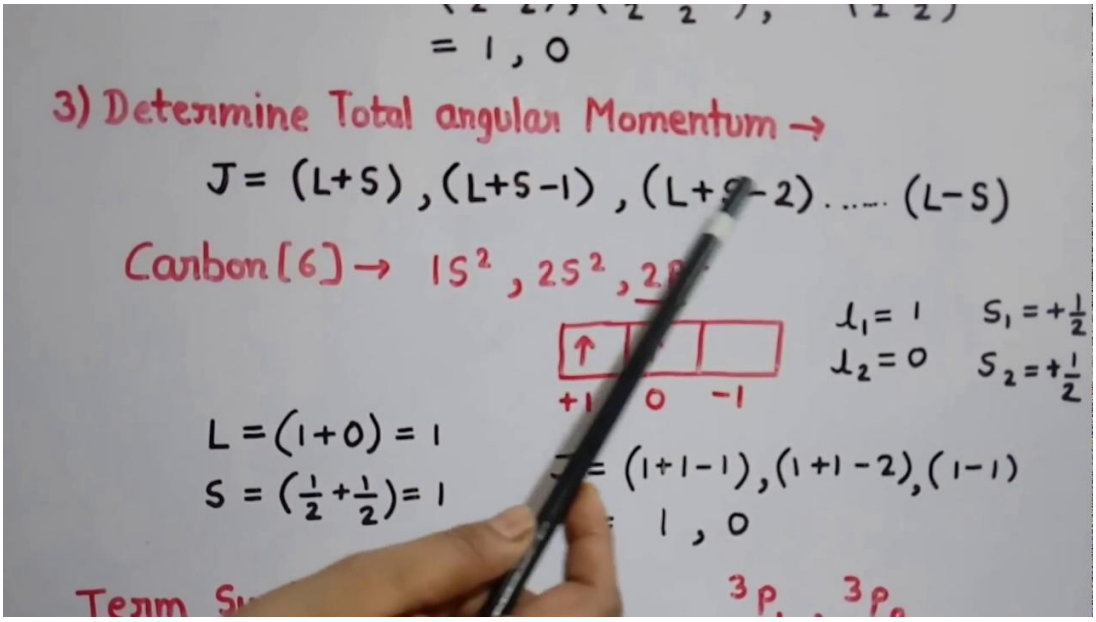
To determine the lowest energy spin-orbit coupled state:

1. For less than half-filled shells, the lowest $J$ is the lowest energy
2. For more than half-filled shells, the highest $J$ is the lowest energy
3. For half-filled shells, only one $J$ is possible



# Spin-Orbit coupling

- Microstates can be visualized through the *vector model* of the atom. The vector model associates angular momentum with energy.
- Each electron has an orbital angular momentum *l* and a spin angular momentum *s*.



## Configuration

- Arrangement of $e^-$s in an atom or ion
  - The electrons are filled in the increasing order of energy – Aufbau principle
  - If more than one orbital is having same energy, pairing of e- will not take place until all the orbitals are at least singly occupied – Hund's rule
  - No two electrons can have all the four quantum numbers same – Pauli's exclusion principle

## Terms

- Energy level of an atomic system specified by an electronic configuration.
- Many terms may arise from a configuration
- Depends on the intrinsic nature of cofig.
- Electrons from filled orbitals have no contribution to energy – Assumption
- Partially filled orbitals decide the energy terms.

## Terms ... Cont

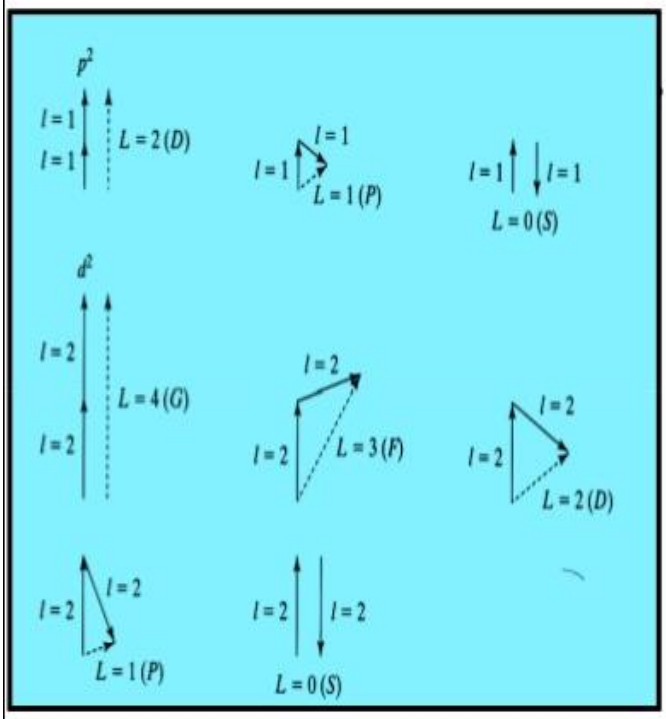
- **Partially filled orbitals have two perturbations**
  - **Inter Electronic Repulsions**
  - **Spin-Orbit coupling**

## Inter-electronic repulsions

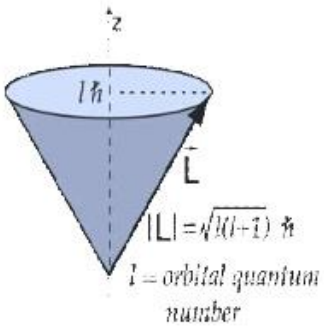
- **Energy depends on the arrangement of $e^-$**
- **The electrons in partially filled orbitals repel each other.**
- **Repulsion splits the energy levels resulting in many terms.**
- **Energies of electrons within an orbital itself are slightly different [ Pairing and Exchange energies].**

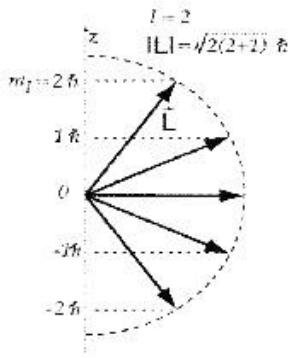
# Spin-Orbit coupling

- **Microstates can be visualized through the *vector model* of the atom. The vector model associates angular momentum with energy.**
- **Each electron has an orbital angular momentum *l* and a spin angular momentum *s*.**




The **total orbital angular momentum** ***L*** of a group of electrons in an atom is given by a vector sum of the individual orbital angular momenta *l*.




The **single electron orbital angular momentum *l*** (and hence the total orbital angular momentum *L*) can only have certain orientations quantization.

## Spin-orbit coupling / L-S coupling

*i) Russel-Saunders for light atoms*:

$J = L + S, L + S - 1, \ldots, |L - S|$

$L = l_1 + l_2, l_1 + l_2 - 1, \ldots, |l_1 - l_2|$

$S = s_1 + s_2, s_1 + s_2 - 1, \ldots, |s_1 - s_2|$

**Russel-Saunders coupling works well for the light elements up to bromine.**

- **Couple all individual orbital angular momenta *l* to give a resultant total orbital angular momentum *L*.** ($L = \Sigma\, l_i$)
- **Couple all individual spin angular momenta *s* to give a resultant total spin angular momentum *S*.** ($S = \Sigma\, s_i$)
- **Finally couple *L* and *S* to give the total angular momentum *J* for the entire atom.**

## Spin-orbit coupling / L-S coupling

- The extent to which L and S are coupling is called "Spin-Orbit Coupling constant" $(\zeta)$
- The perturbation created by L-S coupling is

$$\zeta\,(l.s)$$

*This value is for single electron of a configuration and always positive*

$$\zeta = \left[\frac{z_{eff}.e^2}{2.m^2c^2}\right]\left(\frac{1}{r^{-3}}\right)$$

## Spin-orbit coupling / L-S coupling

- For convenience, a parameter characteristic of a term is used.
- L-S coupling constant for a term is $\lambda$
- The perturbation of energy of a term is $\lambda(l.s)$

$$\lambda = \frac{\pm\zeta}{2.s}$$

- The $\lambda$ value is positive for less than half filled and negative if the orbital is greater than half filled.

# L-S Coupling continued

- Each term is split in to states by L-S coupling specified by J values, which differing by unity.
- Each L value will have (2L+1) $M_L$ components.
- Each S value will have (2S+1) $M_S$ components.
- So any term will have a degeneracy of

(2S+1).(2L+1)

## Spin-Orbit Coupling

So far we've considered only $e^-$-$e^-$ (orbital angular momentum) and spin-spin (spin angular momentum) interactions.

Orbitals and spins can also interact giving rise to spin-orbit coupling

- *J* is the total angular momentum

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To determine the lowest energy spin-orbit coupled state:

1. For less than half-filled shells, the lowest *J* is the lowest energy
2. For more than half-filled shells, the highest *J* is the lowest energy
3. For half-filled shells, only one *J* is possible

# *j-j coupling*

- Couple individual orbital *l* and spin *s* angular momenta first to the complete electron angular momentum *j*. ($j = l + s$)
- Couple all *j* to give the total angular momentum *J*. ($J = j$)
- j-j coupling is much more complicated to treat, but should be used for elements heavier than bromine.
- For 4d and 5d series of ions.

## Term Symbols for $d^2$

$l_1 = 2; l_2 = 2$

$L = |l_1+l_2|, |l_1+l_2-1|, |l_1+l_2-2| \ldots,0,\ldots, |l_1-l_2|$

**So the possible values for L are**

$L = 4, 3, 2, 1, 0$

$s_1 = ½ ; s_2 = ½$

**So the possible values for S are**

$S = 1, 0$

# Microstates of $d^2$

Maximum L value is 4

So the possible $M_L$ values are +4, +3, +2, +1, 0, -1, -2, -3, -4

Maximum S value possible is 0

So $M_s$ can be only 0

| $M_L$ | +4 | +3 | +2 | +1 | 0 | -1 | -2 | -3 | -4 |
|---|---|---|---|---|---|---|---|---|---|
| $M_S$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Term | $^1G$ (9) | | | | | | | | |

# Microstates of $d^2$

Next maximum L value is 2

So the possible $M_L$ values are +2, +1, 0, -1, -2

Maximum S value possible is 1

So $M_s$ can be +1, 0, -1

| $M_L$ | +2 | +1 | 0 | -1 | -2 |
|---|---|---|---|---|---|
| $M_S$ | 0 | 0 | 0 | 0 | 0 |
| Term | $^1D$ (5) | | | | |

# Microstates of $d^2$

Next maximum L value is 3

So the possible $M_L$ values are +3, +2, +1, 0, -1, -2, -3

Maximum S value possible is 1

So $M_s$ can be +1, 0, -1

| $M_L$ | +3 | | | +2 | | | +1 | | | 0 | | | -1 | | | -2 | | | -3 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $M_S$ | +1 | 0 | -1 | +1 | 0 | -1 | +1 | 0 | -1 | +1 | 0 | -1 | +1 | 0 | -1 | +1 | 0 | -1 | +1 | 0 | -1 |
| Term | $^3F$ (21) | | | | | | | | | | | | | | | | | | | | |

# Microstates of $d^2$

- Next maximum L value possible is 1
  - Possible $M_L$ values are +1 , 0 , -1
- Maximum S value possible is : 1
  - Possible $M_s$ value are +1 , 0 , -1
- Considering all possible combinations

| $M_S$ | +1 | | | 0 | | | -1 | | |
|---|---|---|---|---|---|---|---|---|---|
| $M_L$ | +1 | 0 | -1 | +1 | 0 | -1 | +1 | 0 | -1 |
| Term | $^3P$ (9) | | | | | | | | |

- Five terms obtained: $^1G$, $^3F$, $^1D$, $^3P$, $^1S$
- Hund's rule for ground state energy:
  - maximum spin multiplicity
  - maximum L value

  Ground Term: $^3F$

  Expected relative energies of microstates

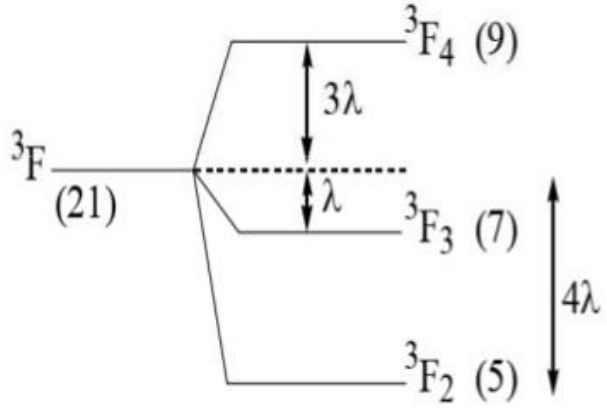
  $^3F < {}^3P < {}^1G < {}^1D < {}^1S$

  Actual order

  $^3F < {}^1D < {}^3P < {}^1G < {}^1S$

The splitting depends on the size of the spin-orbit coupling constant $\lambda$ or $\zeta$

Example $d^2$



| $d^n$ | 2 | 1 | 0 | -1 | -2 | L | S | Ground Term |
|---|---|---|---|---|---|---|---|---|
| $d^1$ | ↑ | | | | | 2 | 1/2 | $^2D$ |
| $d^2$ | ↑ | ↑ | | | | 3 | 1 | $^3F$ |
| $d^3$ | ↑ | ↑ | ↑ | | | 3 | 3/2 | $^4F$ |
| $d^4$ | ↑ | ↑ | ↑ | ↑ | | 2 | 2 | $^5D$ |
| $d^5$ | ↑ | ↑ | ↑ | ↑ | ↑ | 0 | 5/2 | $^6S$ |
| $d^6$ | ↑↓ | ↑ | ↑ | ↑ | ↑ | 2 | 2 | $^5D$ |
| $d^7$ | ↑↓ | ↑↓ | ↑ | ↑ | ↑ | 3 | 3/2 | $^4F$ |
| $d^8$ | ↑↓ | ↑↓ | ↑↓ | ↑ | ↑ | 3 | 1 | $^3F$ |
| $d^9$ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑ | 2 | 1/2 | $^2D$ |

**Terms for $3d^n$ free ion configurations**

| Configuration | # of quantum states | # of energy levels | Ground Term | Excited Terms |
|---|---|---|---|---|
| $d^1$,$d^9$ | 10 | 1 | $^2D$ | - |
| $d^2$,$d^8$ | 45 | 5 | $^3F$ | $^3P$, $^1G$, $^1D$, $^1S$ |
| $d^3$,$d^7$ | 120 | 8 | $^4F$ | $^4P$, $^2H$, $^2G$, $^2F$, 2 x $^2D$, $^2P$ |
| $d^4$,$d^6$ | 210 | 16 | $^5D$ | $^3H$, $^3G$, 2 x $^3F$, $^3D$, 2 x $^3P$, $^1I$, 2 x $^1G$, $^1F$, 2 x $^1D$, 2 x $^1S$ |
| $d^5$ | 252 | 16 | $^6S$ | $^4G$, $^4F$, $^4D$, $^4P$, $^2I$, $^2H$, 2 x $^2G$, 2 x $^2F$, 3 x $^2D$, $^2P$, $^2S$ |

## The Crystal Field Splitting of Russell-Saunders terms in weak $o_h$ crystal fields

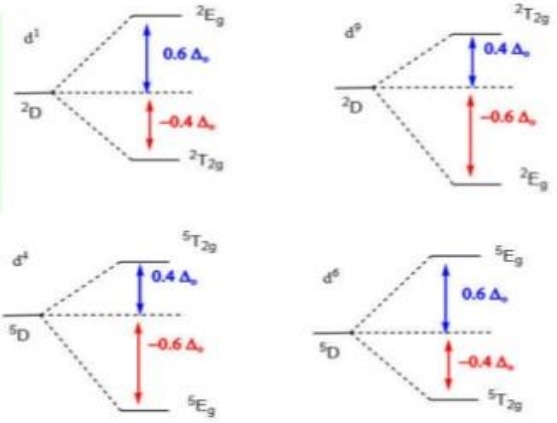
| Russell-Saunders Terms | Crystal Field Components |
|---|---|
| S (1) | $A_{1g}$ |
| P (3) | $T_{1g}$ |
| D (5) | $E_g + T_{2g}$ |
| F (7) | $A_{2g} + T_{1g} + T_{2g}$ |
| G (9) | $A_{1g} + E_g + T_{1g} + T_{2g}$ |
| H (11) | $E_g + T_{1g} + T_{1g} + T_{2g}$ |
| I (13) | $A_{1g} + A_{2g} + E_g + T_{1g} + T_{2g} + T_{2g}$ |

## Order of energies of crystal field terms

b) Determination of the energies of the upper ligand field terms

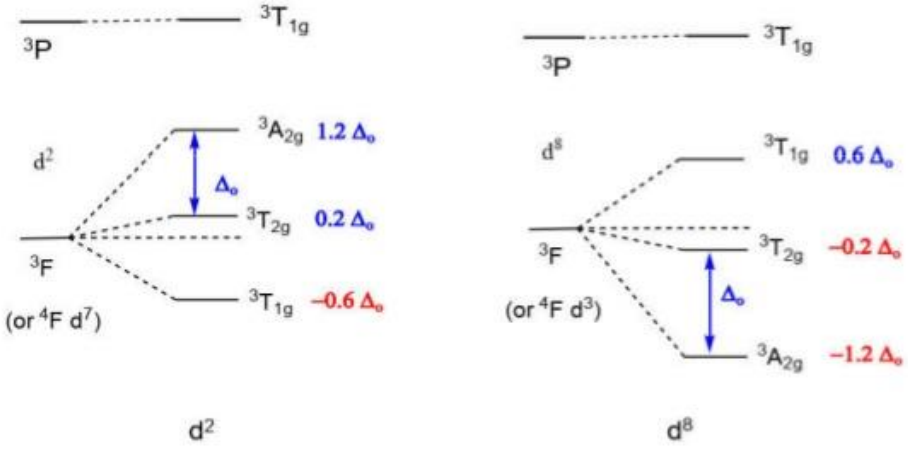
In case of $d^1$,$d^4$,$d^6$ and $d^9$ systems, the energies of the upper levels are relatively easy to calculate (from the degeneracies of the terms)

T: triply degenerate
E: doubly degenerate term



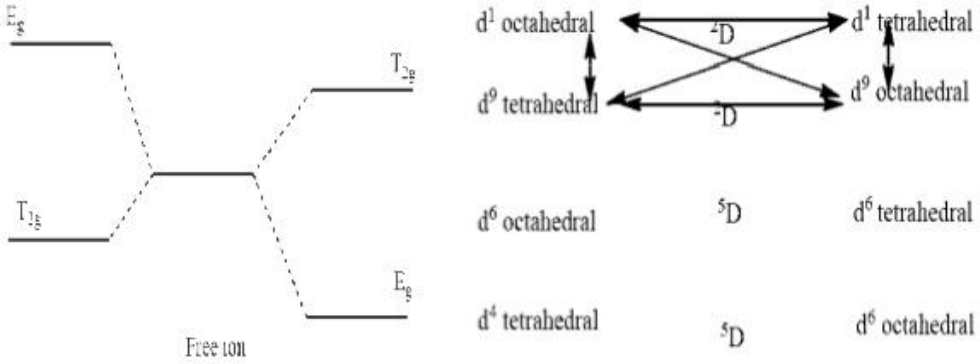
## Energies of the crystal field terms: $d^2$, $d^3$, $d^7$, $d^8$ configuration

- are more difficult to calculate (beyond the scope of this lecture)
- only the results are given here (splitting of the ground terms) (without consideration of the configuration interaction)



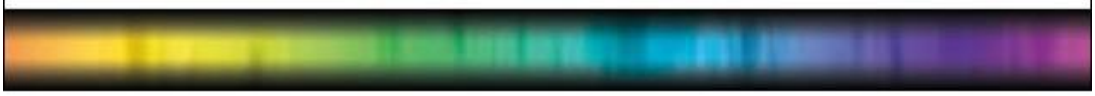

$d^2$ $d^8$

An inverse relation exists between $d^n$ and $d^{10-n}$ systems (hole formalism) and also between octahedral and tetrahedral symmetries. Considering these, the energy level diagrams for the $d^n$ system, strong field configuration is given below. These four diagrams can explain all the seven systems, viz., $d^2$ to $d^8$.



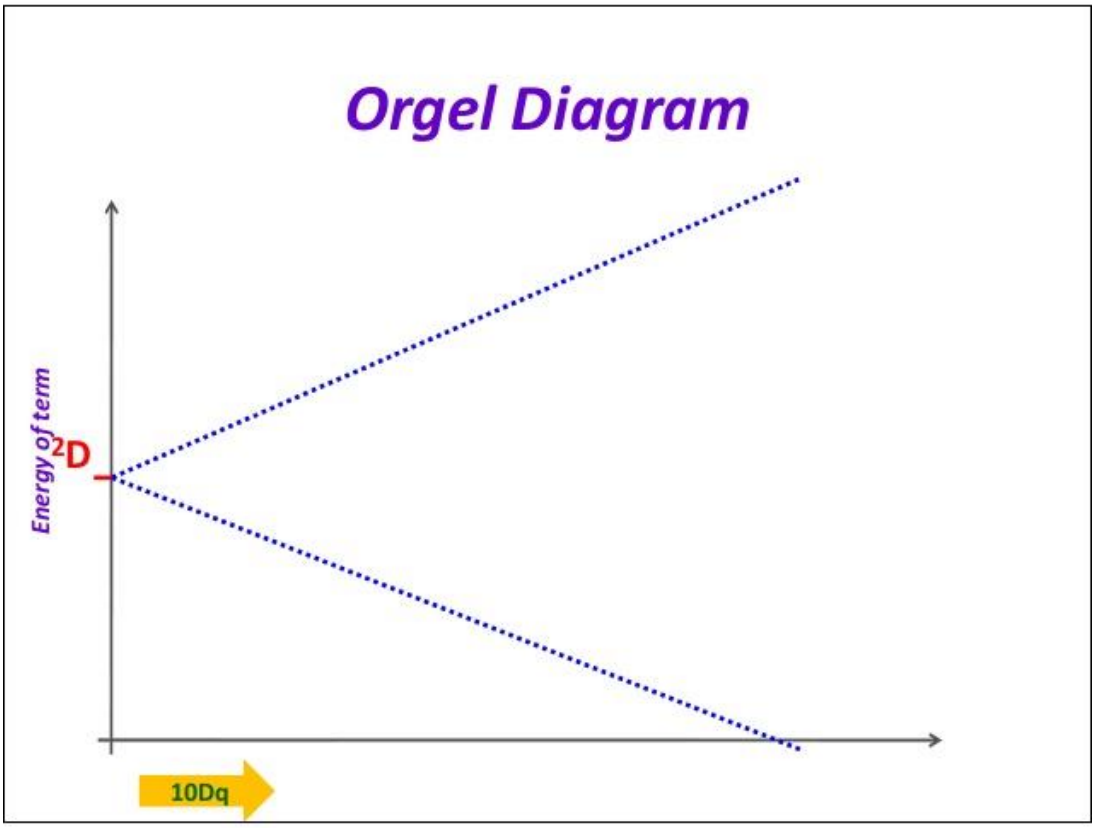
## Correlation Diagrams
## Relating Electron Spectra to Ligand Field Splitting

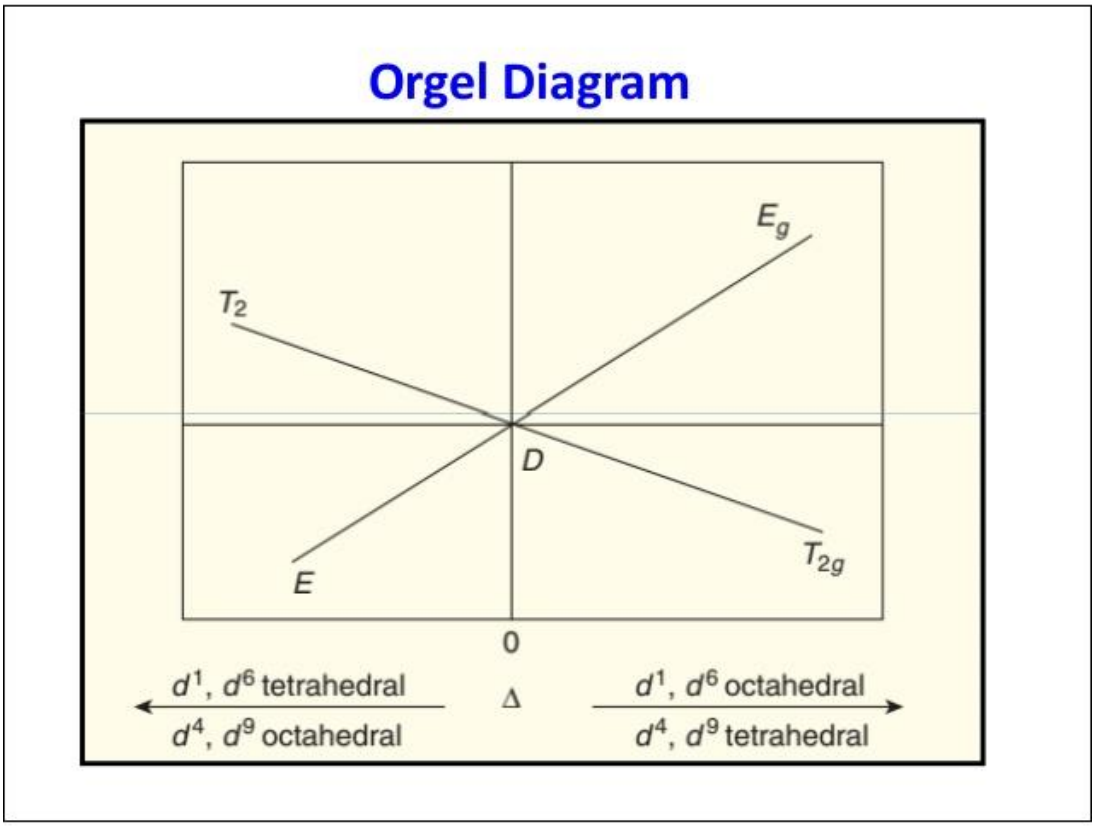
- Examine the correlation diagram for a $d^2$ configuration in an octahedral ligand field.
  - Far left (absence of ligand field) – the free-ion terms. On this side, the ligand field has very little influence.
  - Far right (strong ligand field) – the states are largely determined by the ligand field.
- In real compounds, the situation is somewhere in the middle.
- Correlating the states on both sides is done in accordance with the so called " non-crossing rule " .

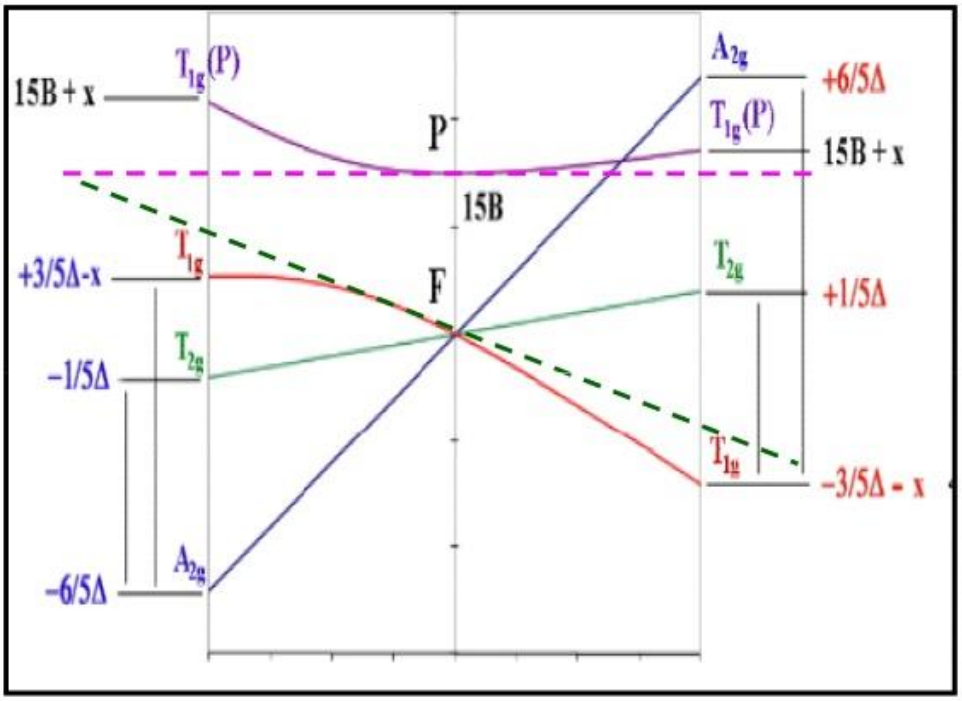


## *Orgel Diagram*

- Used for interpretation of electronic spectra of metal ion complexes.
- Got by plotting the energies of split levels of a term by increasing ligand field strength
- Only applicable for weak field cases.
- Can predict only spin-allowed transitions.
- Transitions are assumed to occur from the lowest energy level.


Orgel Diagram
Energy of term
$^2D$
10Dq


Orgel Diagram
$E_g$
$T_2$
D
$T_{2g}$
E
0
$d^1$, $d^6$ tetrahedral
$d^4$, $d^9$ octahedral
Δ
$d^1$, $d^6$ octahedral
$d^4$, $d^9$ tetrahedral




For metal ions having $d^2$, $d^3$, $d^7$, and $d^8$ configurations, the ground state is an *F* state, but there is an excited *P* state that has the same multiplicity. For $d^2$ and $d^7$ ions in an *octahedral* field, the spectroscopic states are the same (except for the multiplicity) as they are for $d^3$ and $d^8$ ions in *tetrahedral* fields. Therefore, the expected spectral transitions will also be the same for the two types of complexes. The three spectral bands are assigned as follows ($T_{1g}(F)$ means the $T_{1g}$ state arising from the *F* spectroscopic state):

$$\nu_1 T_{1g} \quad (F) \rightarrow T_{2g}$$
$$\nu_2 T_{1g} \quad (F) \rightarrow A_{2g}$$
$$\nu_3 T_{1g} \quad (F) \rightarrow T_{1g}(P)$$

$$E(\nu_1) = 5\mathrm{Dq} - 7.5B + (225B^2 + 100\mathrm{Dq}^2 + 180\mathrm{DqB})^{1/2}$$

$$E(\nu_2) = 15\mathrm{Dq} - 7.5B + (225B^2 + 100\mathrm{Dq}^2 + 180\mathrm{DqB})^{1/2}$$

$$E(\nu_3) = (225B^2 + 100\mathrm{Dq}^2 + 180\mathrm{DqB})^{1/2}$$

| Octahedral Field | | | |
|---|---|---|---|
| For *T* ground states: | | For *A* ground states: | |
| $\nu_1$ | $T_{1g} \rightarrow T_{2g}$ | $\nu_1$ | $A_{2g} \rightarrow T_{2g}$ |
| $\nu_2$ | $T_{1g} \rightarrow A_{2g}$ | $\nu_2$ | $A_{2g} \rightarrow T_{1g}$ |
| $\nu_3$ | $T_{1g} \rightarrow T_{1g}(P)$ | $\nu_3$ | $A_{2g} \rightarrow T_{1g}(P)$ |

| Tetrahedral Field | | | |
|---|---|---|---|
| For *T* ground states: | | For *A* ground states: | |
| $\nu_1$ | $T_1 \rightarrow T_2$ | $\nu_1$ | $A_2 \rightarrow T_2$ |
| $\nu_2$ | $T_1 \rightarrow A_2$ | $\nu_2$ | $A_2 \rightarrow T_1$ |
| $\nu_3$ | $T_1 \rightarrow T_1(P)$ | $\nu_3$ | $A_2 \rightarrow T_1(P)$ |

## Selection Rules for Electronic Spectra

- When the molecule absorbs electromagnetic radiation, it may be due to interaction of
  - electrical dipole or quadruple with the electrical field of emr – Electrical dipole transitions
  - the magnetic dipole of the molecule with the magnetic field of emr – Magnetic dipole transitions

Electrical dipole >> Magnetic dipole > Electrical quadruple

## The Laporte Selection Rule

- All transitions within the d-shell, such as $^3A_{2g} \rightarrow {}^3T_{2g}$ are Laporte forbidden, because they are g→g.
- The intensity of the d-d transitions that give d-block metal ions their colors are not very intense.
- Charge transfer bands frequently involve p→d or d→p transitions, and so are Laporte-allowed and therefore very intense.

.

## $T_d$ vs $O_h$

- A tetrahedron has no center of symmetry, and so orbitals in such symmetry cannot be *gerade*. Hence the d-levels in a tetrahedral complex are $e$ and $t_2$.
- This largely overcomes the Laporte selection rules, so that tetrahedral complexes tend to be very intense in color.
- Dissolving $CoCl_2$ in water produces a pale pink solution of $[Co(H_2O)_6]^{2+}$, but in alcohol forms, which is a tetrahedral $[CoCl_4]^{2-}$ having very intense blue color.

# Charge-Transfer Bands

- Charge-transfer band arise from the movement of electrons between orbitals that are predominantly ligand in character and orbitals that are predominantly metal in character.
- These transitions are identified by their high intensity and the sensitivity of their energies to solvent polarity.
- Absorption for charge transfer transition is more intense than d–d transitions.

*($\varepsilon_{d\text{-}d}$=20 L mol$^{-1}$ cm$^{-1}$ or less, $\varepsilon_{charge\text{-}transfer}$ =50,000 L mol$^{-1}$ cm$^{-1}$ or greater)*

**Charge-Transfer transition is classified into:**

- **Ligand-to-Metal Charge-Transfer transition.**
  *(LMCT transition)*

  If themigration of the electron is from theligand to the metal.

- **Metal-to-Ligand Charge-Transfer transition.**
  *(MLCT transition)*

  If themigration of the electron is from themetal to the ligand .

•*Ligands possess σ, σ*, π, π*, and nonbonding (n) molecular orbitals.*

•*If the ligand molecular orbitals are full, charge transfer may occur from the ligand molecular orbitals to the empty or partially filled metal d-orbitals.*

•*LMCT transitions result in intense bands. Forbidden d-d transitions may also take place giving rise to weak absorptions.*

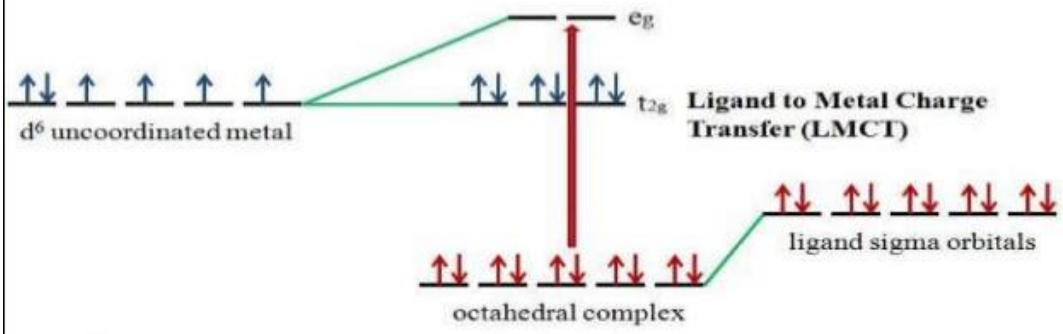



Figure 3. Ligand to Metal Charge Transfer (LMCT ) involving an octahedral $d^6$ complex. (Inspired by reference 3)

## MLCT

•*If the metal is in a low oxidation state (electron rich) and the ligand possesses low-lying empty orbitals (e.g., CO or CN − ).*

•*LMCT transitions are common for coordination compounds having π-acceptor ligands.*

• *Upon the absorption of light, electrons in the metal orbitals are excited to the ligand π* orbitals.*

•*MLCT transitions result in intense bands. Forbidden d – d transitions may also occur.*

• *This transition results in the oxidation of the metal.*

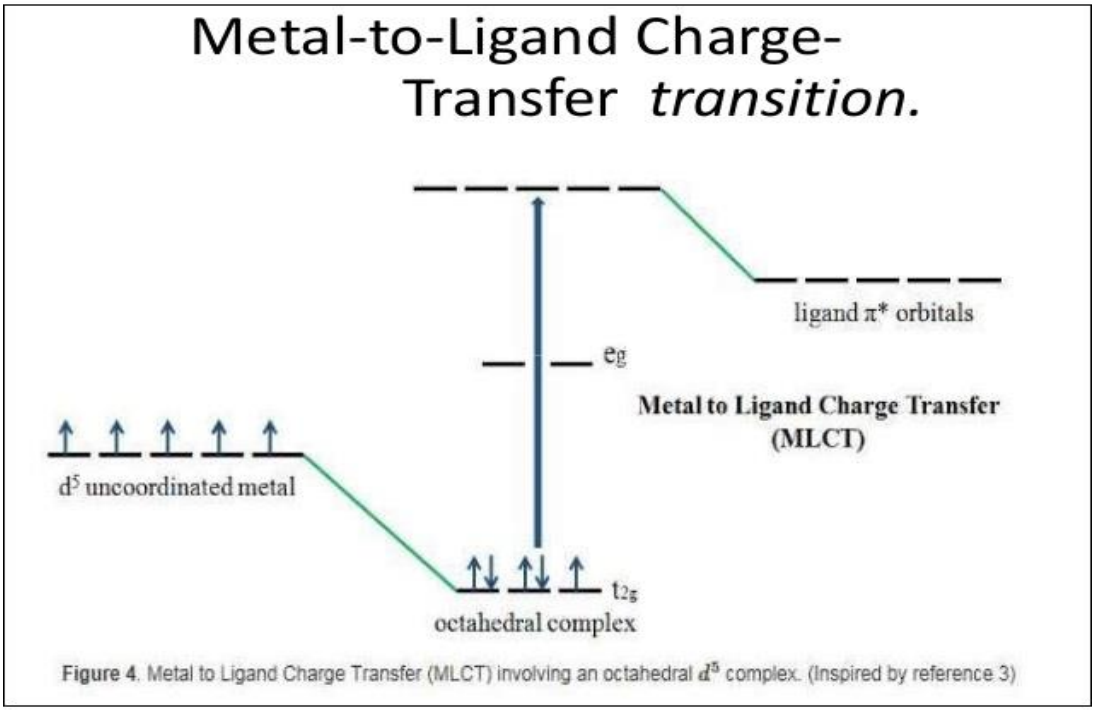
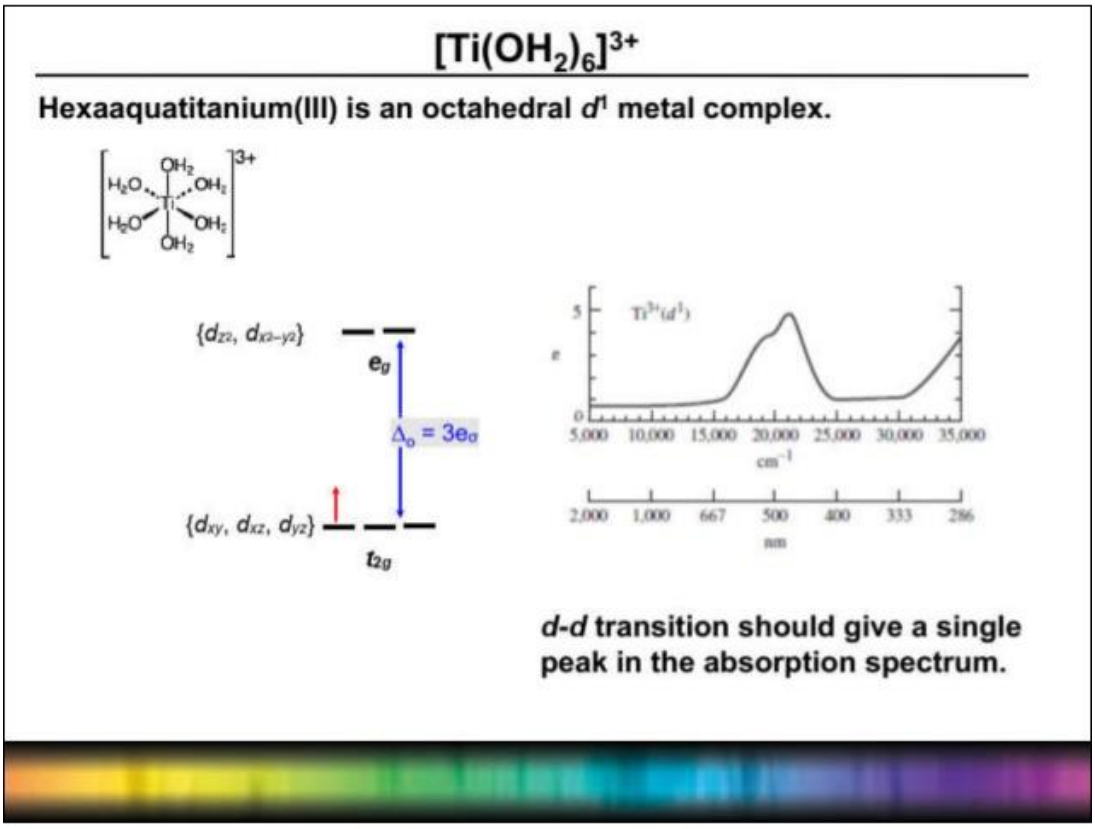



**Figure 4**. Metal to Ligand Charge Transfer (MLCT) involving an octahedral $d^5$ complex. (Inspired by reference 3)



By miss Laxmi R Ankalagi

# Chromatography

**Introduction** : Chromatography is a analytical chemistry technique which is used to separate the components present in a mixture. Thus analytical chemistry may be defined as the branch of chemistry which deals with the identification, separation and quantitative determination of composition of matter. Analytical methods can be divided into two types

1. Classical methods
2. Instrumental methods

1. Classical methods : Classical methods uses separations such as precipitation, extraction and distillation and qualitative analysis by odour,colour ,melting point and quantitative analysis is achieved by measurement of weight or volume.

2. Instrumental methods : Instrumental methods uses an apparatus to measure the physical quantities of the analyte such as conductivity, fluorescence etc.

Thus analytical chemistry is concerned with the identification of a substance, elucidation of its structure and quantitative analysis of its composition.It is an interdisciplinary branch of science which deals with various disciplines of chemistry such as inorganic-organic industrial and biochemistry.

**Chromatography** : chromatography is a separation process of components of molecular mixtures. Chromatography may be defined as a method of separating a mixture of components into individual components through equilibrium distribution between the two phases namely stationary phase and mobile phase. **Principleofchromatography :** chromatography is based on the principle of selective distribution of different components of a mixture between two phases namely stationary phase and mobile phase.

- The stationary phase is a substance which is fixed in its place for the chromatographic procedure and it may be a solid or liquid.
- The mobile face is the one which moves in a definite direction during the chromatographic procedure and it may be a liquid or gas.
- When the stationary phase is solid the selective distribution is based on adsorption and when the stationary phase is a liquid the selective distribution is based on partition.

**Types**: There are two types ,

1. Adsorption chromatography
2. Partition chromatography

1. Adsorption chromatography: The chromatographic technique ,which involves a solid as a stationary phase and a liquid or gas as the mobile phase is called as adsorption chromatography. Example is column chromatography.

2. Partition chromatography: The chromatographic technique, which involves a liquid supported on an inert solid as a stationary phase and a liquid or gas as a mobile phase is called as partition chromatography. Example is paper chromatography.

**Physicalfactors** or **stepsinvolvedinthechromatography :**

1. Adsorption or retention of substance on the stationary phase.
2. Separation of the adsorbed substances by the mobile phase.
3. Elution : Recovery of separated substances by the continuous flow of the mobile phase is termed as elution.
4. Qualitative and quantitative analysis of the eluted substances.

The basis of all forms of chromatography is partition or distribution coefficient ($K_d$) which describes the way in which a compound distributes itself between two immiscible phases. For a compound distributing itself between equal volumes of two immiscible solvents say A & B , the value for this coefficient is a constant at a given temperature and is given by the expression as follows

$$K_d = \frac{\text{Concentration of sub in solvent A}}{\text{Concentration of sub in solvent B}}$$

Partition coefficient of a substance between two immiscible solvents is the ratio of the concentration of substance in one solvent i.e mobile solvent to the concentration of the substance in another solvent i.e stationary solvent.

$$K_d = \frac{\text{Con of sub in mobile solvent}}{\text{Con of sub in stationary solvent}}$$

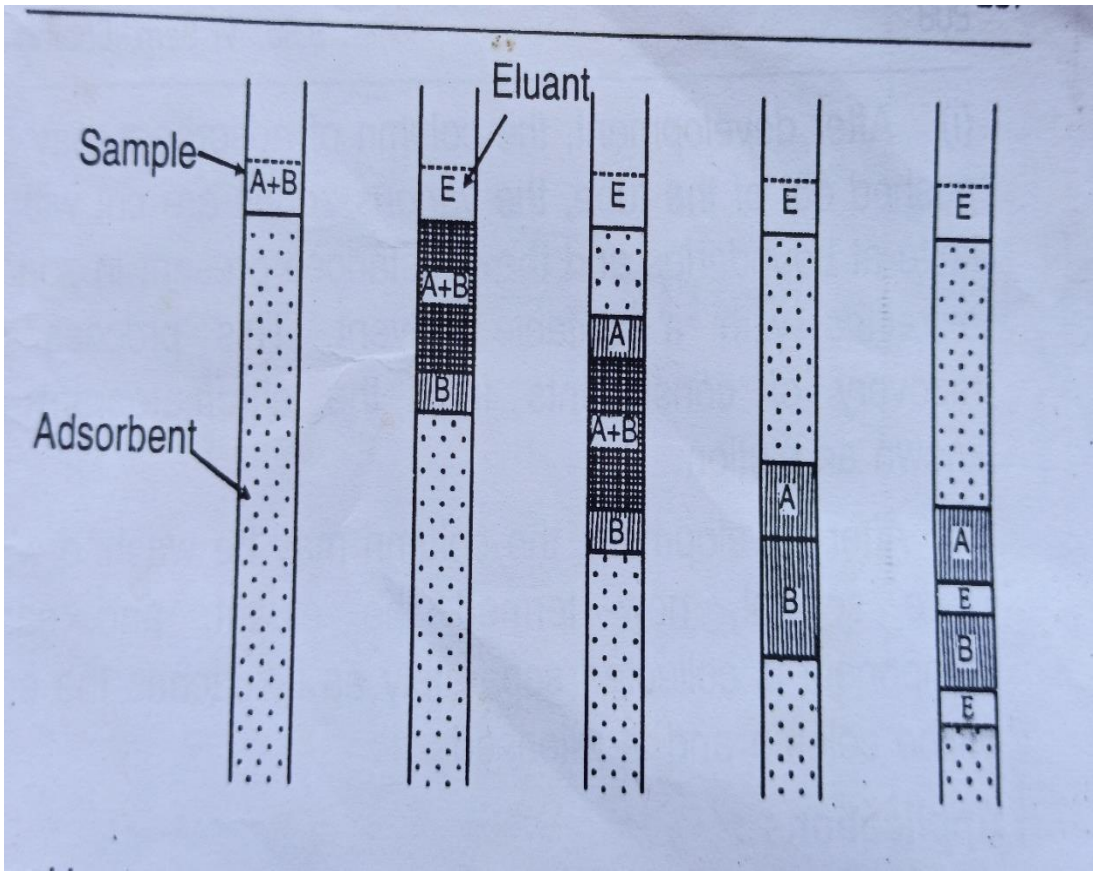
This is known as Nernst distribution law.

**Columnchromatography** :

Column chromatography may be defined as the separation process which involves the uniform percolation of a liquid solute through a column packet with finely divided material on which the adsorption takes place.This is based on the selective adsorption of different components of a mixture being analysed by using suitable adsorbents such as alumina, charcoal powder on which the adsorption takes place. In this technique the stationary phase is the solid that is nothing but the adsorbent and the mobile phase is a liquid mixture to be separated.

**Principleofcolumnchromatography** :

Column chromatography is based on the retention of solute by surface adsorption. It is known that the rate of adsorption varies with a given adsorbent for different materials and this principle of selective adsorption is used in the column chromatography.




**Procedure** :

1. In this method, the mixture to be separated is dissolved in a suitable solvent and allowed to pass through a tube which contains a suitable adsorbent.
2. The component which has a greater adsorbing power is absorbed first and in the upper part of the column while, the next component which is having the lower adsorbing power than the component one is adsorbed later and in the lower portion of the column so that this process is continued.
3. As a result the materials are partially separated and adsorbed in the various parts of the column. The initial separation of the various components can be improved by passing either the original or some other suitable solvent slowly through the columns.
4. The various bands present in the column become more defined. The banded column of adsorbent is now termed as chromatogram and the operation of forming is called as development of the chromatogram and a portion of a column which is occupied by a particular substance is called as its zone.
5. In order to separate or to estimate the various components that are present two important procedures may be adopted.

1. Elution
2. Washing with excess amount of solvent

1.**Elution** :

After the development the column of adsorbent may be pushed out of the tube, the various zones are cut with a sharp knife at boundaries and the substances present in the zones are extracted with the suitable solvent. This process of recovery of components from the chromatogram is known as elution.

2.**Washingwithexcessofsolvent** :

After the development, the column maybe washed with more amount of the solvent now it is termed as eluant,and the each component is collected separately as it reaches the end of the column and is released.

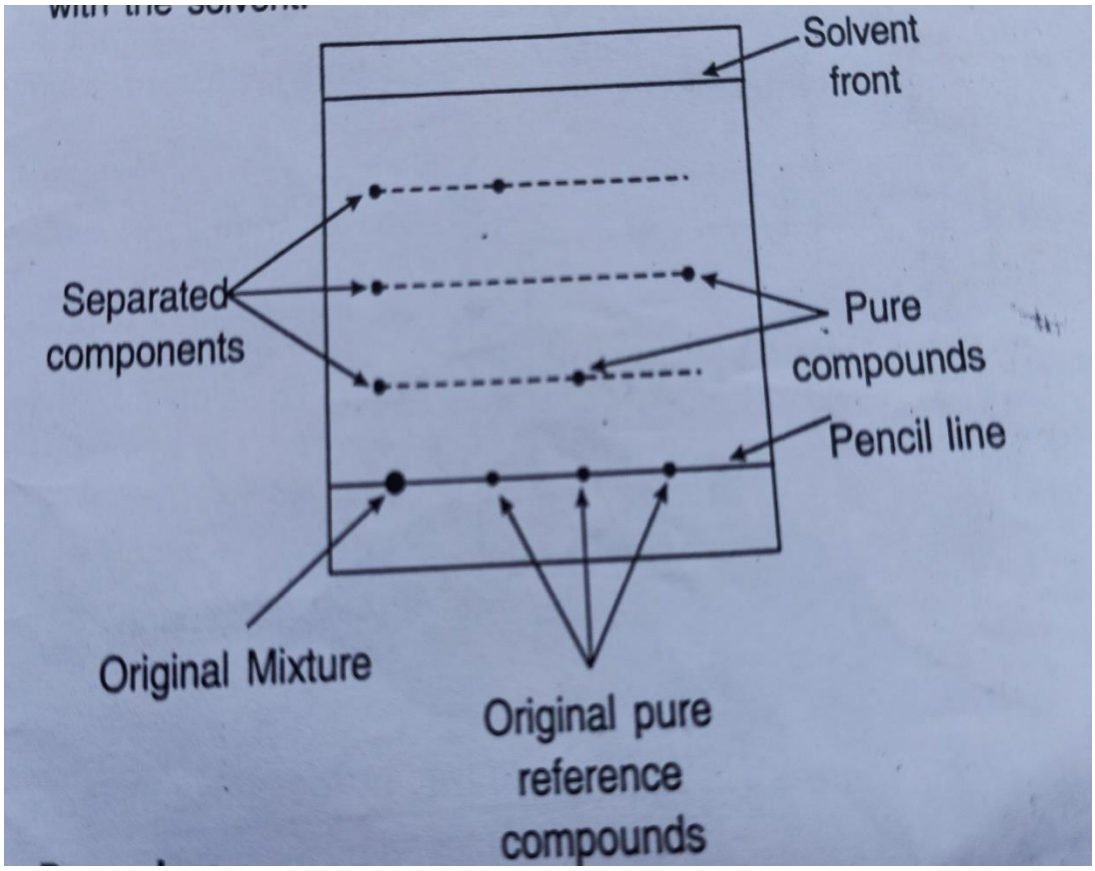
**Applicationsofcolumnchromatography** :

1. Column chromatography is used in the determination of homogeneity of the chemical substances.
2. Column chromatography is used in the separation of the mixtures into the pure individual components.
3. Column chromatography can also be used for the removal of impurities and purification of the compounds.
4. Column chromatography is used in the separation of geometrical isomers. For example cis- trans isomers of carboxylic acids have been separated on charcoal and silica gel.
5. Column chromatography can also be used in the separation of Tautomeric mixtures.
6. Column chromatography can also be used in the separation of Racemates and first successful separation of racemates using organic solvents were achieved on lactose.
7. The greatest application of column chromatography is it is used in the separation and identification of inorganic anions and cations.

**Paperchromatography** : Paper chromatography may be defined as a technique in which the separation of mixture of components is done by the flow solvents on a specially designed chromatographic filter paper. The stationary phase is water present in the cellulose of the filter paper and the mobile phase is a suitable organic solvent which is immiscible with the stationary phase.

**PrincipleofPaperchromatography** :

Paper chromatography is a type of partition chromatography in which the substances are distributed between the two liquids one a stationary liquid i.e water present in the cellulose of the filter paper and the other is mobile liquid i.e the organic solvent which is immiscible with the stationary liquid. The components of the mixture to be separated migrate at a different rates and appear as a spots at different points on the paper. This separation is achieved by the differential migration of the different components which occurs due to the differences in their partition coefficient values. The lower the value of partition coefficient the more the component will pass over into the mobile phase and move at a higher speed together with the solvent.




**Procedure** :

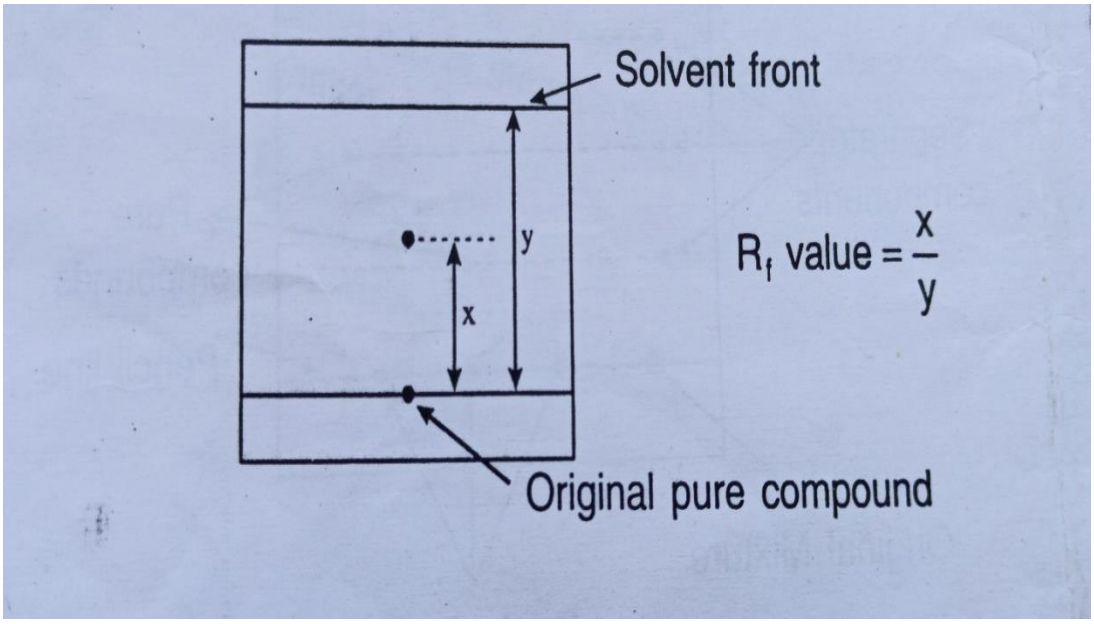
1. A pencil line is drawn near one edge of the rectangular piece of specially designed chromatographic filter paper parallel to it.
2. The mixture to be separated is applied as a small drop on the pencil line.
3. The filter paper is now hung vertically in a glass tank which contains a suitable organic solvent and the bottom of the filter paper is so positioned in the solvent that the pencil line should be clear .
4. The tank is now sealed with the lid to prevent the evaporation of the solvent
5. The solvent rises up by means of capillary action and the components of the solvent also rise of the paper at different rates and appears as a spots at a different points on the paper.
6. The paper is now removed from the tank and allowed to dry ,once the solvent had almost reached the top of the paper and the components of mixture are
   separated and identified based on their retardation factor values.

**Retardationfactor ($R_f$)** : Under carefully controlled condition, it is possible to characterize a particular component separated from a mixture by its retardation factor value.

Thus $R_f$ defines the movement of the substances relative to the solvent front in a given chromatographic system. The distance travelled by the solvent from the origin line is referred as solvent front. $R_f$ is a function of partition coefficient and it is constant for a given substance provided the conditions of chromatographic systems are kept constant.

Thus $R_f$ may be defined as the ratio of the distance travelled by the component from the origin line to the distance travelled by the solvent from the origin line i.e solvent front.

$$R_f = \frac{\text{Distance travelled by a component from origin line}}{\text{Distance travelled by the solvent from the origin line}}$$

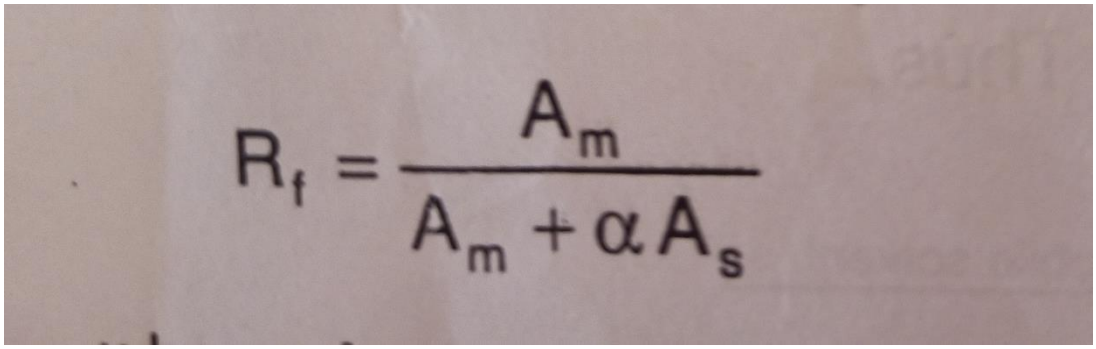



Factors affecting the retardation factor value : The retardation factor value of a substance depends upon a number of factors such as

- The solvent employed for the separation
- The nature of the mixture
- the medium used for the separation or the quality of paper.
- The temperature
- The size of The vessel in which the operation is done.

**CalculationofR$_f$value** :

The $R_{f\ value}$ can be calculated if the distribution coefficient of the system is known and the cross sectional areas of the two faces are measured then and the RF value can be calculated using the following relation



$$R_f = \frac{A_m}{A_m + \alpha A_s}$$

Where Am is cross sectional area of the mobile phase, As is cross sectional area of the stationary phase and Alpha is constant called as selectivity factor or selectivity coefficient. It is defined as the ability of the chromatographic system to chemically distinguish between the sample components.

For example let us consider chromatographic system in which the

- Distance travelled by the component A be 4 cm
- Distance travelled by the component B be 8 cm
- Distance travelled by the solvent is 10 cm Then the Retardation factor value can be calculated using the above data

$R_f$ =. Distance travelled by the component from the origin line

Distance travelled by the solvent from the origin line

Thus $R_f$ of component A = 4/10 = 0.4 cm

$R_f$ of component B = 8 / 10 = 0.8 cm respectively.

| SI no | Name of the compound | Rf value |
|---|---|---|
| 1 | X | 0.2 |

| | | |
|---|---|---|
| 2 | Y | 0.4 |
| 3 | Z | 0.8 |

By refering the above table it is concluded that the component A is compound Y with $R_f$ value of 0.4

& That of component B is compund Z with $R_f$ value of

0.8 Respectively

**Applicationsofpaperchromatography** :

1. Paper chromatography can be used for the separation of amino acids and the analysis of proteins and oligopeptides.
2. Several compounds of biological origin such as lipids, carbohydrates, hormones etc. can be studied with the help of paper chromatography
3. Pesticides and halogenated insecticides and organophosphorus insecticides can be identified with the help of paper chromatography.
4. The structural analysis of an unknown compound can be made with the paper chromatography.
5. Paper chromatography can also be used in the study of inorganic metal salts and complex ions.
6. Paper chromatography can also be used for the analysis of mixture of sugars.
7. The most important application of paper chromatography is it is used in the analysis of compounds from the biological origin such as hormones lipids etc.

**By Laxmi.R . Ankalagi**

# Electrogravimetry

## Introduction

In electrogravimetric analysis the element to be determined is deposited electrolytically upon a suitable electrode & amount of product is determined by weighing the electrode before and after analysis.

Electrogravimetry is defined as the quantitative analysis in which a product of an electrolytic reaction is deposited quantitatively on an electrode & the amount of product is determined by weighing the dry electrodes before & after the electrolysis.

Requirementsfor the electro gravimetric analysis

- The deposition of the substance of interest must be complete.
- The deposit must be inert in nature i.e it must not undergo any change in its weight during the process of electrolysis.
- The deposit must be of known composition.
- The deposit must adhere firmly so that the electrode can be rinsed & weighed without loss.

## *Principle*

Electrogravimetry is an electro- analytical method & involves the deposition of the desired constituent from its solution electrolytically. These are based on two laws

1.Ohm’s law
2. Faraday's laws of electrolysis

1. Ohm's law : It states that at constant temperature, the strength of the electric current through a metallic conducter is directly proportional to the potential difference across its ends provided the other physical conditions remain the same.

.

Thus if I is current strength in a conductor because of potential difference V across its ends ,then a cording to Ohm's law

$$V \propto I$$

Or

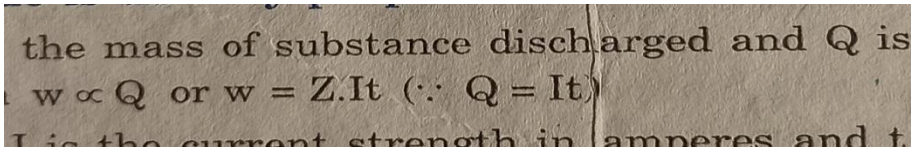
V= IR

Where R is a constant of proportionality & is called as resistance of the conductor.

2. Faraday’s laws of electrolysis

First law : During electrolysis the mass of the substance discharged at an electrode is directly proportional to the quantity of electricity passed.

If W is mass of substance discharged & Q is quantity of electricity passed then


the mass of substance discharged and Q is
$w \propto Q$ or $w = Z.It$ $(\because Q = It)$

Or

W= Z.It ( Q=It)

Wher I is current strength in amperes & t is time in seconds for which current has been passed.Z is constant of proportionality called as electrochemical equivalent of the element.When I= 1 ampere ,t= 1 second we can write

W=Z

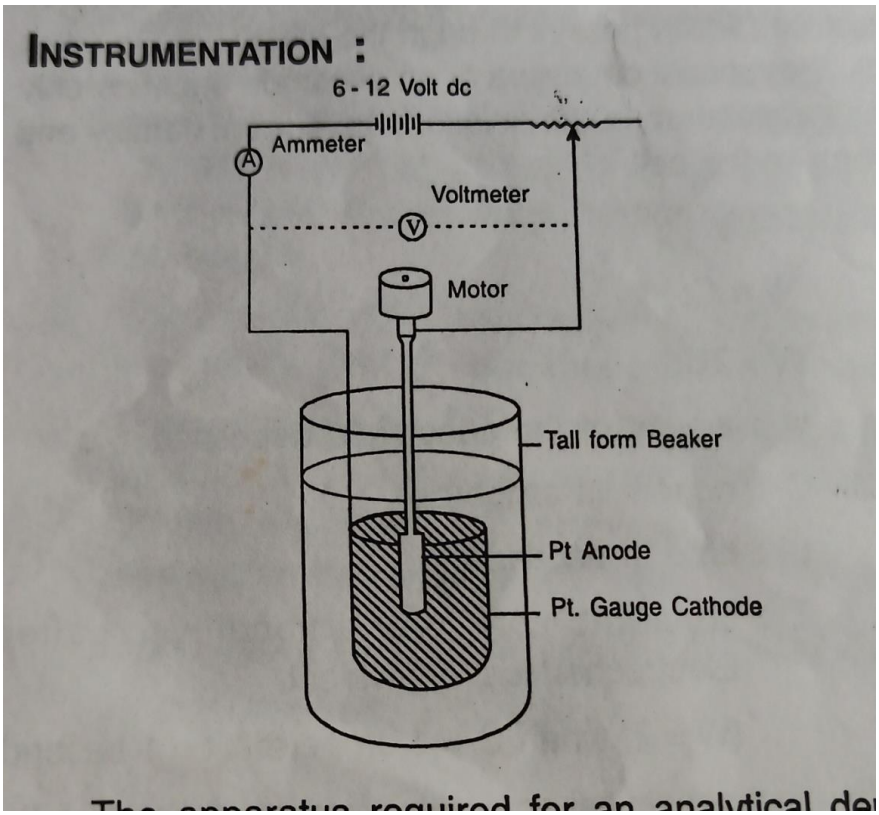
Thus electrochemical equivalent of an element is the mass of element discharged by passing one ampere of current for one second. It is expressed in g/C or kg / C .

Second law : when the same amount of electricity is passed through different electrolytes ,the masses of substances discharged at the electrode are directly proportional to their equivalent masses.

If the same amount of electricity is passed through two different electrolytes containing A and B

Mass of A / Mass of B = eq.mass of A / eq.mass

# Instrumentation:




The apparatus required for an analytical deposition consist of three components

1. Cell
2. Electrodes
3. Power supply

1.cell : a typical cell is as shown in the above figure. Tall form beakers which are provided with mechanical steering are usually employed for the deposition of a metal on a solid electrode. The anode is frequently rotated with the help of UN electric motor. Mechanical stirring is done to minimize concentration polarization.

2.Electrodes: Generally the electrodes made from platinum are used. Sometimes electrodes made from copper , brass and other metals can also be used. But the advantage of using the platinum electrodes over the other metal electrodes are as follows

- Platinum electrodes are relatively non reactive
- Platinum electrodes can be ignited to remove any grease organic matter or gases that could have changed the physical properties of the deposit.

## **Disadvantages** of **platinumelectrodes**

- One cannot use platinum electrodes for depositing metals like Bi,Zn,Ga etc. Because these metals cause permanent damage two platinum electrodes. Therefore a protective coating of copper should be done on a platinum electrodes before the electrolysis of these metals is carried out
- 2. One must avoid the use of platinum electrode as an anode in solutions having high concentrations of chloride ion, because chlorine may be evolved instead of oxygen there occurs oxidation of the electrode. If

one has to use platinum electrode in these cases, it should be protected by means of a depolarizer like hydrazine which is proportionally oxidized to nitrogen.

- Generally, gauze cylinders are used for making cathode. The cylinders are 2 to 3 cm in diameter and about 6 cm in length. The use of gauze cylinders minimises polarization effects by increasing surface area to which the solution can freely circulate. A gauze cylinder is also used for making the anode however it should be of smaller diameter so that it can be fitted inside the cathode.

3.Power supply : we need 6 to 12 volts of power supply and the electrolysis is done for 25 to 30 minutes.

# ElectrogravimetricestimationofCu

Principle : a known mass of copper is dissolved in the required amount of dil nitric acid and the solution is made up in a standard flask. A known volume of this solution is used for the analysis. The deposition is made from a sulphuric acid solution and the presence of small amount of nitric acid enables a good deposit on the electrode.

Procedure: the procedure involves three steps

1. Preparation of electrodes
2. Preparation of copper solution
3. Determination of copper

1.Preparation of electrodes.

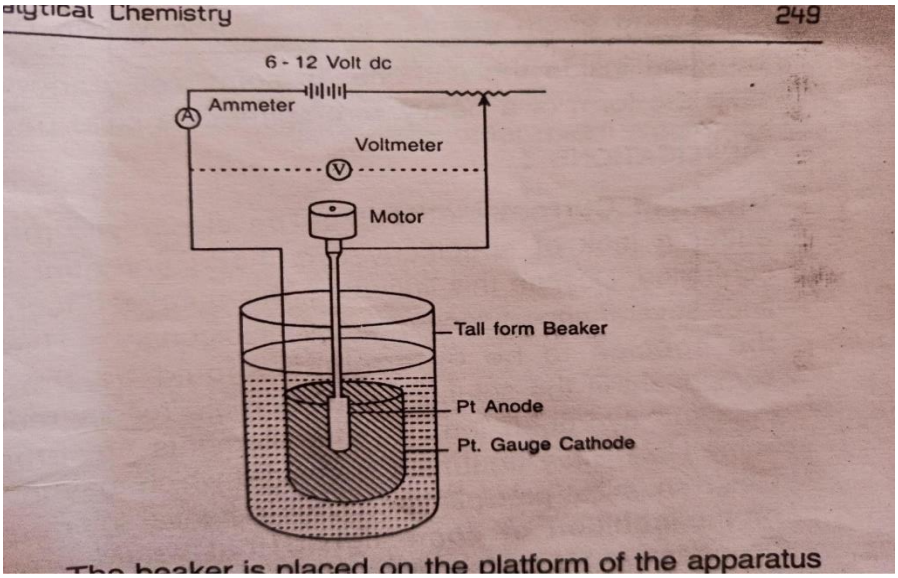
- The electrodes are first immersed in in con nitric acid for 1 minute followed by in dil nitric acid for 5 minutes.
- The electrodes are then rinsed with distilled water and acetone respectively the electrodes are now dried for 5 minutes at 110 to 120 °C in a desiccator and weighed accurately.

2. Preparation of copper solution:

About 1 gram of copper wire is weight accurately and dissolved in minimum amount of dilute nitric acid and the solution is transferred to 250 ml standard flask and the solution is is diluted to the mark and mixed thoroughly to get homogeneous solutions.

3.Determination of copper :

25 ml of standard copper solution is transferred into a clean speaker the solution is treated with 1.5 ml of nitric acid and 3 to 4 ml of sulphuric acid and small amount of urea. The mixture is diluted with about 100 ml of distilled water and the electrical circuit is assembled as shown in the figure.




- The beaker is placed on the platform of the apparatus & raised into position in such a way that the electrodes almost touch the bottom of the beaker .
- The stirring motor is started and connected to source of the current and the current is adjusted to 1 to amp and electrolysis is done for 25 to 30 minutes.
- After the deposition is complete the beaker is slowly lowered, without disconnecting the circuit and the cathode is washed with distilled water.
- When the beaker is completely removed the circuit is disconnected and the beaker is replaced by one having distilled water and the rotating motor is run for minute.
- The cathode is then rinsed with distilled water followed by acetone, dried at 110°ac for about 5 minutes.
- The amount of copper present in the sample is determined from the mass of copper deposited on the cathode.

Calculation

Mass of copper present in 25 ml of solution = x g
Mass of copper present in 250 ml of solution = X.10 g
If W g of sample contains X .10 g of copper then
100 ml of sample contains X .10.100 / w
Thus it gives percentage of copper present in given sample solution.

# ApplicationsofElectrogravimetry

- It is used for the determination of concentration of chemical elements very accurate and precisely in quantitative analysis.
- In a solution the different species are are separated by selectively plating out and removing out.
- It is used in in electrochemical methods for removing interferences.

# LimitationsofElectrogravimetry

- In the the given potential window only the analyte metal should be reduced.
- Sometimes hazardous side products maybe produced.
- The solution needs to be heated and stirred to decrease concentration polarization and make the conversion of analyte complete.

## THERMOGRAVIMETRY (VI Sem) by SRK

Thermogravimetric analysis

**Thermogravimetric analysis** or **thermal gravimetric analysis** (**TGA**) is a method of thermal analysis in which the mass of a sample is measured over time as the temperature changes. This measurement provides information about physical phenomena, such as phase transitions, absorption, adsorption and desorption; as well as chemical phenomena including chemisorptions, thermal decomposition, and solid-gas reactions (e.g., oxidation or reduction).[1]



Thermogravimetric analyzer

Thermogravimetric analysis (TGA) is conducted on an instrument referred to as a thermogravimetric analyzer. A thermogravimetric analyzer continuously measures mass while the temperature of a sample is changed over time. Mass, temperature, and time are considered base measurements in thermogravimetric analysis while many additional measures may be derived from these three base measurements.

A typical thermogravimetric analyzer consists of a precision balance with a sample pan located inside a furnace with a programmable control temperature. The temperature is generally increased at constant rate (or for some applications the temperature is controlled for a constant mass loss) to incur a thermal reaction. The thermal reaction may occur under a variety of atmospheres including: ambient air, vacuum, inert gas, oxidizing/reducing gases, corrosive gases, carburizing gases, vapors of liquids or "self-generated atmosphere"; as well as a variety of pressures including: a high vacuum, high pressure, constant pressure, or a controlled pressure.

The thermogravimetric data collected from a thermal reaction is compiled into a plot of mass or percentage of initial mass on the y axis versus either temperature or time on the x-axis. This plot, which is often smoothed, is referred to as a TGA curve. The first derivative of the TGA curve (the DTG curve) may be plotted to determine inflection points useful for in-depth interpretations as well as differential thermal analysis.

A TGA can be used for materials characterization through analysis of characteristic decomposition patterns. It is an especially useful technique for the study of polymeric materials, including thermoplastics, thermosets, elastomers, composites, plastic films, fibers, coatings, paints, and fuels.

**Type of TGA:**

There are three types of thermogravimetry.

1. **Isothermal or static thermogravimetry-** In this technique, the sample weight is recorded as a function of time at constant temperature.
2. **Quasistatic thermogravimetry-** In this technique, the sample is heated to a constant weight each of series of increasing temperatures.
3. **Dynamic thermogravimetry-** In this technique the sample is heated in an environment whose temperature is changed in a linear manner.

**Thermal stability**

TGA can be used to evaluate the thermal stability of a material. In a desired temperature range, if a species is thermally stable, there will be no observed mass change. Negligible mass loss corresponds to little or no slope in the TGA trace. TGA also gives the upper use temperature of a material. Beyond this temperature the material will begin to degrade.

TGA is used in the analysis of polymers. Polymers usually melt before they decompose, thus TGA is mainly used to investigate the thermal stability of polymers. Most polymers melt or degrade before 200 °C. However, there is a class of thermally stable polymers that are able to withstand temperatures of at least 300 °C in air and 500 °C in inert gases without structural changes or strength loss, which can be analyzed by TGA.[2] [3] [4]

**Oxidation and combustion**

The simplest materials characterization is the residue remaining after a reaction. For example, a combustion reaction could be tested by loading a sample into a thermogravimetric analyzer at normal conditions. The thermogravimetric analyzer would cause ion combustion in the sample by heating it beyond its ignition temperature. The resultant TGA curve plotted with the y axis as percentage of initial mass would show the residue at the final point of the curve.

Oxidative mass losses are the most common observable losses in TGA.[5]

Studying the resistance to oxidation in copper alloys is very important. For example, NASA (National Aeronautics and Space Administration) is conducting research on advanced copper alloys for their possible use in combustion engines. However, oxidative degradation can occur in these alloys as copper oxides form in atmospheres that are rich in oxygen. Resistance to oxidation is very important because NASA wants to be able to reuse shuttle materials. TGA can be used to study the static oxidation of materials such as these for practical use.

Combustion during TG analysis is identifiable by distinct traces made in the TGA thermograms produced. One interesting example occurs with samples of as-produced unpurified carbon nanotubes that have a large amount of metal catalyst present. Due to combustion, a TGA trace can deviate from the normal form of a well-behaved function. This phenomenon arises from a rapid temperature change. When the weight and temperature are plotted versus time, a dramatic slope change in the first derivative plot is concurrent with the mass loss of the sample and the sudden increase in temperature seen by the thermocouple. The mass loss could be the result of particles of smoke released from burning caused by inconsistencies in the material itself, beyond the oxidation of carbon due to poorly controlled weight loss.

**Thermogravimetric kinetics**

Thermogravimetric kinetics may be explored for insight into the reaction mechanisms of thermal (catalytic or non-catalytic) decomposition involved in the pyrolysis and combustion processes of different materials.[6][7][8][9][10][11][12]

Activation energies of the decomposition process can be calculated using Kissinger method.[13]

Though a constant heating rate is more common, a constant mass loss rate can illuminate specific reaction kinetics. For example, the kinetic parameters of the carbonization of polyvinyl butyral were found using a constant mass loss rate of 0.2 wt %/min.[14]

**Operation in combination with instruments**

The TGA instrument continuously weighs a sample as it is heated to temperatures of up to 2000 °C for coupling with FTIR and mass spectrometry gas analysis. As the temperature increases, various components of the sample are decomposed and the weight percentage of each resulting mass change can be measured.

Thermogravimetric analysis is often combined with other process or used in conjunction with other analytical methods. For example, a TGA is sometimes attached in line with a mass spectrometer.

**Types of Thermal gravimetric analysis:**

1) Isothermal or Static Thermogravimetry: In this technique, the sample weight is recorded as function of time at constant temperature.

2) Quasistatic Thermogravimetry: In this technique the sample is heated to a constant weight at each of increasing temperatures.

3) Dynamic Thermogravimetry: In this technique the sample is heated in an environment whose temperature is changed in linear manner.

**TGA of calcium oxalate monohydrate ($CaC_2O_4.H_2O$)**

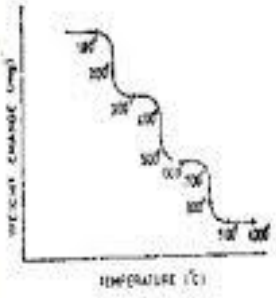
- The successive plateau corresponds to the formation of anhydrous salt, calcium carbonate and calcium oxide.

(a) $CaC_2O_4.H_2O \rightarrow CaC_2O_4 + H_2O$

(b) $CaC_2O_4 \rightarrow CaCO_3 + CO$

(c) $CaCO_3 \rightarrow CaO + CO_2$

- The thermogram indicates that the loss of water begins at 100°C and loss of CO at 400°C and $CO_2$ at 680°C



# We have TGA - only

- Heating a sample of Calcium oxalate

- $Ca(C_20_4)*xH_2O \leftrightarrow Ca(C_20_4)*H_2O + x\text{-}1\ H_2O$
- $Ca(C_20_4)*H_2O \leftrightarrow Ca(C_20_4) + H_2O$
- $Ca(C_20_4) \leftrightarrow CaCO_3 + CO$
- $CaCO_3 \leftrightarrow CaO + CO_2$

**Comparison of Thermal gravimetric analysis and Differential thermal analysis techniques:**

| Sr.No. | Thermal gravimetric analysis (TGA) | Differential thermal analysis (DTA) |
|---|---|---|
| 1 | In TGA the weight loss or gain is measured as a function of temperature or time. | In DTA the temperature difference between a sample and reference is measured as a function of temperature. |
| 2 | The TGA curve appears as steps involving horizontal and curved portions. | The DTA curve shows upward and downward peaks. |

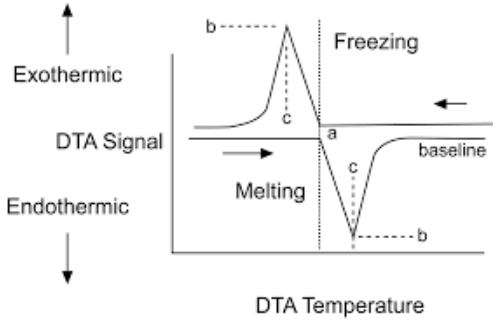
| | | |
|---|---|---|
| 3 | Instrument used in TGA is a thermobalance. | Instrument used in DTA is a DTA Apparatus. |
| 4 | TGA gives information only for substances which show a change in mass on heating or cooling. | DTA does not require a change in mass of the sample in order to obtain meaningful information.<br><br>DTA can be used to study any process in which heat is absorbed or liberated. |
| 5 | The upper temperature used for TGA is normally 1000 °C. | The upper temperature used for DTA is often higher than TGA (As high as 1600 °C). |
| 6 | Quantitative analysis is done from the thermal curve by measuring the<br><br>loss in mass m. | Quantitative analysis is done by measuring the peak areas and peak heights. |
| 7 | The data obtained in TGA is useful in determining purity and composition of materials, drying and ignition temperatures of materials and knowing the stability temperatures of compounds. | The data obtained in DTA is used to determine temperatures of transitions, reactions and melting points of substances. |

Differential thermal Analysis

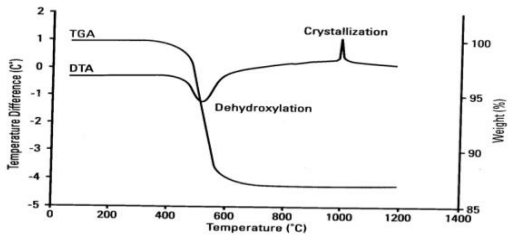
Principle:The basic principle involved in DTA is the temp difference b/w the test sample & an inert reference sample under controlled &identical conditions of heating or cooling is recorded continuously as a function of temp or time, thus the heat absorbed or emitted by a chemical system is determined.

1) If any reaction takes place in the sample, then the temp difference will occur b/w the sample & thevreference material.
2) In an endothermic change ( such as melting or dehydration of the sample) the temp of the sample is lower than that reference material. I,e $\Delta T$ = -ve ( for endothermic process)
3) In an exothermic change or process the sample temperature is higher than the reference material.
4) I,e $\Delta T$ = + ve (exothermic process)
5) The shape & size of the peak gives information about the nature of the test sample.
    1) Sharp endothermic peaks indicate phase change ( such as melting ,fusion etc) transion from one crystalline form to another crystalline form.
    2) Broad endothermic peaks are obtained from dehydration reactions.

3) Chemical reactions like oxidative reactions are exothermic reactions.




DTA + DTG




What are the uses of differential thermal analysis?

**Applications**. A DTA curve can be **used** only as a finger print for identification purposes but usually the **applications** of this method are the determination of phase diagrams, heat change measurements and decomposition in various atmospheres. DTA is widely **used** in the pharmaceutical and food in

## Applications of DTA

- **DTA curves for two substances are not identical. Hence they serve as finger prints for various substances.**
- **Used to study the characteristic of polymeric material.**
- **This technique is used for testing the purity of the drug sample and also to test the quality control of number of substances like cement, soil, glass,etc.**
- **Used for the determination of heat of reaction, specific heat and energy change occurring during melting etc.**
- **Trend in ligand stability (thermal stability of the ligands) gives the information about the ligands in the coordination sphere.**

Smt S.R.Kaladagi

# Notes on soil Analysis

Syllabus : Macronutrients, trace metals,& oraganic matter,in soil. Determination of $p^H$

Determination of nitrogen by alkaline permanganate method & phosphorous by Bray's Olsen's method present in the soil.

Introduction: Soil may be defied as a thin layer of earth's crust which serves as natural medium for the growth of plants.

It is the unconsolidated mineral matter that has been subjected to, &influenced by genetic & environmental factors, parent material,climate,organisms & topography all acting over aperiod of time. Rocks are the chief source for the parent materials over which siols are developed. There are three kinds of rocks 1) Igneous rocks 2) Sedimentary rocks & 3) Metamorphic stones

The rocks vary greatly in chemical composition & accordingly the soil differ in their properties because they are formed from the weathering of rocks. Weathering can be physical or chemical in nature. The agents of physical weathering are temp,water,wind, plant & animals & chemical processes of weathering are hydration,hydrolysis, carbonation, oxidation & reduction.

Plant nutrients : Although plants absorb a large number of elements, all of them are not essential for the growth of ropes. The elements are absorbed became they happen to be in the soil solution & those taking active part in the growth & development processes are called the essential ones. Some of these are required in large amounts & some in trace

What are nutrients?

The elements essential for the life & which are in constant circulation from environment to living organisms & back to environment are called nutrients.

Classification : Plants need water, air, light, suitable temp, & 16 nutrients to grow. Plants get carbon.hydrogn & oxygen from air & water . The 13 nutrints from soil /

Nutrients in soin are classified in two types

a) Macronutrients
b) Micronutrients Ex Fe,Mn, B, Zn, Cu, Mo, Cl
   Macronutrients again divided in two types 1) Primary macronutrient Ex N,P,K
   2) Secondary macronutrients Ex Ca, Mg, S
   Macronutrients : What are macronutrients?
   Nutrients present in soil required for the plant growth in large quantities are known as macronutrients
   Primary macronutrient : N,P,K are termed as primary macronutrients because of their larege requirements by the plants.
   Secondary macronutrients : Ca,Mg,S are termed as secondary macronutrients because of their moderate requirements
   Micronutrients : Nutrients presents in soil required for the plant growth in small quantities are known as micronutrients. These metals are also known as trace metals because these are required in trace quantities. If present I at higher levels exert a toxic effect. Mossy of these elements act as components of essential enzymes.

It has been found that the presence of some elements which are not considered essential for plant growth & are not directly concerned in the nutrition of the crop, but are present in the plants used as food & feed, are of vital importance to the health of man & animals. The elements within this gp are I2, Co & Na. In addition , there is another gp of elements which are toxic to the animals feeding on the plants containg them. These are Selenium , thallium, arsenic & fluorine. Elements such as Na, F, Ni ,Pb, Ar, Se, Al & Cr, when occurring in soils in high available amounts , may also prove toxic to the plants & restrict their growth.

Some elements, occurring freely in the soil, are absorbed by the plants as impurities. They may occasionally stimulate growth through they are not essential for plants growth. They include Li, Sr, Sn, Ra, Be, V, Ba, Hg, Ag, & Br.

Importance of each macronutrients( Function of nutrients )

1) Nitrogen: It is an essential ingredient of proteins. Other constituents of proteins are oxygen, hydrogen, nitrogen, usuallysulphur and sometimes phosphorous. When proteins decompose through hydrolysis they give out amino acids ,reversely, when proteins are formed or synthesized the basic substances are amino acids.Nitrogen is the basic nutrient & mkes up 1-4 /· Of day weight of plants & it forms chlorophiyll, amino acids ,proteins, alkloides & protoplasm. In the plant sap ammonia, nitrates & nitrities are found only in traces or very small quantities. When the plant takes up large Quantities of nitrogen from the soi the colour of the plant changes to dark green, indicating the increase of chlorophyll in the plant. Sice the amount of chlorophyll in the plant determines the carbohydrate synthesis.

When there is ales uptake of nitrogen , the leaves remain small & pale- yellow in color.

Nitrogen (N) Nitrogen analyses are not difficult to conduct, but interpreting results can be problematic. This is because a major portion of soil N is contained in the soil OM. Plant availability of organic N is dependent on OM breakdown, which is difficult to estimate. Therefore analyses of “total N”, a sum of all forms of soil N, including organic N, are not routinely conducted. Instead, N in the nitrate form (NO3 -N) is assayed. Nitrate is directly available to plants, so this test provides an indication of short term N availability. However, NO3 -N can be quickly lost from soil, either leached past the rooting zone, or lost to the atmosphere in gaseous forms. Nitrate analyses can provide an accurate determination of the N available to plants at the time of soil sampling, although this may not provide reliable information concerning N availability later in the growing season. If soil N analysis is to be used for making fertilizer recommendations, soil samples should be collected either shortly before planting time or during the growing season. The extractant used to remove NO3 -N from the soil is not particularly important because of its high solubility. Some laboratories extract NO3 -N from soil with a salt solution, such as potassium chloride (KCl). However, other laboratories in the southwestern U.S. measure NO3 -N in the same extract used to measure soil P (see below) to reduce analysis costs. Results from these two kinds of extractants are directly comparable. Phosphorus (P) Most soil P is tightly bound to soil particles or contained in relatively insoluble complexes. The P-containing complexes in alkaline soils are very different than those in neutral or acidic soils. The amount of P removed during soil extraction is very much dependent on the nature of P complexes and on the specific extractant used, so it is critical that P extractants be matched to soil properties. The Olsen or bicarbonate extractant, a dilute sodium bicarbonate solution, is used to extract P from calcareous, alkaline, and neutral soils, and is appropriate for Arizona soils. In contrast, most other P extractants, such as the Mehlich extractants, are suited for acidic soils, and may not be suitable for arid-region soils. If an appropriate extractant is selected, P analysis is a reliable and useful soil test. On a soil test report, the analysis may be reported as PO4 -P. Potassium (K), Calcium (Ca), Magnesium (Mg), and Sodium (Na) The four major exchangeable cations in arid-region soils are K, Ca, Mg, and Na. All except Na are essential plant nutrients; however Na is included here because it plays an important role in soil physical properties. Soil Na level is needed for calculations of cation exchange capacity (CEC) and exchangeable sodium percentage (ESP), discussed later. Element K Ca Mg Na Molecular Wt 39.1 40.1 24.3 23 Charge/molecule 1 2 2 1 4 The University of Arizona Cooperative Extension An ammonium acetate extractant is used to extract exchangeable K, Ca, Mg, and Na from arid-region soils, but it does not extract less plant-available forms. Some difficulty may be encountered in soils containing Ca or Mg carbonates (calcareous soils) because the ammonium acetate extraction may remove some Ca or Mg from these minerals along with the exchangeable forms. In these situations, the analytical results may indicate slightly elevated levels of these nutrients. Some laboratories adjust the pH of the ammonium acetate extractant to 8.5 to minimize this error. However, this is not usually a large problem and K, Ca and Mg tests generally provide excellent estimates of

plant available levels of these nutrients. Cation Exchange Capacity (CEC) Cation exchange capacity is often estimated by summing the major exchangeable cations (K, Ca, Mg, and Na) using units of cmolc /kg. Most laboratories do not routinely conduct a separate analysis for CEC, but use the ammonium acetate extractable levels of these elements (discussed above) for this calculation. Exchangeable Sodium Percentage (ESP) and Sodium Adsorption Ratio (SAR) ESP and SAR are measures of soil Na content relative to other soil cations. ESP is the concentration of Na divided by the CEC. As described above, the CEC is often estimated as the sum of the major exchangeable cations, so ESP = Na/(K+Ca+Mg +Na), in units of cmolc /kg. SAR is roughly comparable to ESP, but is a ratio of Na to Ca plus Mg. For this calculation, concentrations of Na, Ca, and Mg are measured in a saturated paste extract (see discussion of EC, above). The equation used for calculation of SAR is: where concentrations are in units of mmol/kg or mmol/L. SAR and ESP are both very useful measures of the influence of Na on soil properties. The choice between the two is based largely on the type of extraction used for cation analyses. SAR can be used with either soil or water samples, whereas ESP is applicable only with soils. Free Lime Free lime is a measure of soil carbonates (salts of CO3 2-). When combined with an acid, carbonates release gaseous CO2 . The test usually performed for soil carbonates is semi-quantitative. A weak acid solution is applied to the soil sample, and the degree of ‘fizzing’ or release of CO2 gas is determined visually and categorized as ‘none’, ‘low’, ‘medium’, or ‘high’. OPTIONAL SOIL TESTS Sulfur (S) Sulfur, like N, may be contained primarily in the soil OM, but plants absorb only the inorganic sulfate (SO4 2-) form. Measuring total soil S does not provide a good estimate of S plant availability because rates of release from OM cannot be accurately predicted. Instead, S in the sulfate form is a more common measure. Sulfate can be extracted from the soil with several extractants, including water or weak salt solutions. Analysis of SO4 -S is relatively easy, but it usually provides a measure of immediately available S, and not the soil’s long-term ability to provide S to a growing plant. Some desert soils contain large quantities of sulfates, in which case sulfate analysis gives a good indication of the soil’s ability to supply S. Micronutrients Copper (Cu), Iron (Fe), Manganese (Mn), and Zinc (Zn) — Micronutrient analysis is optional at most laboratories. Most laboratories in our region use a DTPA-TEA (diethylenetriamine pentaacetic acid - triethanolamine) extractant which uses the chelating agent DTPA to extract available Fe, Cu, Mn, and Zn from soils. Analyses of these micronutrients are probably less accurate for predicting the likelihood of plant deficiencies or of crop responses to supplemental application of these nutrients than analyses of macronutrients such as K, Ca, and Mg because of 1) the influence of dynamic soil conditions, and 2) the importance of genetically controlled plant micronutrient uptake mechanisms. For example, Mn availability can change substantially if soil drainage status is altered, becoming more available in waterlogged soils, and less available in dry soils. Iron availability is also affected by soil moisture and irrigation practices. Furthermore, availability of Cu, Fe, Mn, and Zn are greatly affected by soil pH, so soils may need to be re-tested if soil pH is significantly altered. Soil testing can not reliably predict the effects of altering management practices on availability of these nutrients. Additionally, plants vary considerably in their ability to extract metal micronutrients from soil. For example, it is not unusual for a tropical plant to exhibit iron deficiency while an adjacent desert adapted plant does not, even though soil conditions are identical for both plants. Boron (B) — The most common method of extracting B from soils is with hot water. This is an accurate test, but soil B levels can change rapidly. Boron is highly water soluble and can quickly be leached from the rooting zone, or moved laterally during monsoon rainfall events. Therefore, extractable soil B provides estimates of plant availability that are less reliable than those of many other nutrients, not because of shortcomings with the analytical method, but because of rapid B movement in the soil. Molybdenum (Mo)— Few laboratories conduct soil Mo analysis. Molybdenum is present at very low levels in most soils, much lower than most of the other nutrients, making an accurate determination difficult. Most plants have a low requirement for Mo, and slight differences in soil Mo levels can impact plant performance. Therefore soil tests for Mo are of limited use and are seldom conducted. Organic Matter (OM) The OM level of a soil can be determined by several analytical techniques which are quite accurate. All measure the amount of soil OM or the carbon it contains, but most do not determine its nature or how it will contribute to soil fertility. Levels of nutrient

What is soil organic matter ?

Soil organic matter (SOM) is the organic component of soil, consisting of three primary parts including small (fresh) plant residues and small living soil organisms, decomposing (active) organic matter, and stable organic matter (humus)

Functions of organic matter in soil : ♦ Supplies N,P,S & other secondary & micro-nutrients for plant growth

- ♦ Holds up to 20 times of their wt of soil
- ♦ Holds cations & anions & release them slowly
- ♦ The ratio of C:N:P:S is 1:0:5:1
- ♦ Effects the breaksdown of pesticides & weedicides

Determination of Soil $p^H$:

- The $p^H$ meter was calibrated using pH 7 buffer solution.
- Then the meter was adjusted with known $p^H$ of buffer solutions 4.0 and 9.2.
- 20 g of soil was weighed and transferred into 100 mL beaker.
- 40 mL distilled water was added and stirred well with a glass rod.
- This was allowed to stand for half an hour with intermittent stirring.
- To the soil water suspension in the beaker, the electrode was immersed and pH value was determined from the automatic display of the pH meter.

**Points to Remember while Performing the Experiment in a Real Laboratory:**

1. Always wear lab coat and gloves when you are in the lab. When you enter the lab, switch on the exhaust fan and make sure that all the chemicals and reagents required for the experiment are available. If it is not available, prepare the reagents using the components for reagent preparation.
2. Properly adjust the flame of the Bunsen burner. The proper flame is a small blue cone; it is not a large plume, nor is it orange.
3. Make sure to clean all your working apparatus with chromic acid and distilled water and ensure that all the apparatus are free from water droplets while performing the experiment.
4. Make sure to calibrate the electronic weigh balance before taking the measurements.
5. Ensure that the desiccator has sufficient amount of desiccant; Silica gel
6. Use chromic acid to clean the crucible, then heat it and make sure to cool it and before placing in the desiccators. Ensure that you are handling the crucible, with cleaned tongs or with tissue paper .Never touch it with your hand.
7. Switch on the oven and adjust the temperature to $130^0$ C. Make sure to use a cotton glove while working with a hot air oven.
8. Make sure to clean the Kipp's apparatus tube with water and ensure that it has sufficient solid material; iron sulfinide and acid, $H_2SO_4$ for producing $H_2S$ gas.
9. Clean all glass wares with soap and distilled water. Once the experiment completed recap the reagent bottles. Switch off the light, exhaust fan, hot air oven and Gas cylinder before leaving the lab.
10. Discard the used gloves in a waste bin.

Principle : The glass electrode in contact with hydrogen ions of the soil suspension accuires an electric potential (emf) & gives $H^+$ ion concentration or $P^H$ of the sample

Preparation of standard buffer solution: Buffer solutions may be of $P^H$ 4.0,7.0,9.2 in pure water. A buffer tablet is dissolved in 100 of water to obtain buffer solution. Saturated solution of potassium hydrogen tartarate ( formula is$KC_4H_5O_6$) may be used which gives a $P^H$ of 3.6 at $25^{0c}$

a) $P^H$ in saturated soil paste: Prepare a soil paste in distilled Water. On saturation, the soil pate glistens and flows slightly when the container is tilted. Allow it to stand for about of 4 hrs. There should be no free water on the soil surface & also paste should not stiffen. The glistening soil paste is ready to determine $P^H$.

b) $P^H$ in 1:2soil water suspension: weigh 40g of soil in 250ml flask & dissolve in 80ml of disttiled water. Shake the mixture on the reciprocating shaker for 1hr.

c) $P^H$ in 1:2 soil & $CaCl_2$ solution suspension: Weigh 10g of air dry soil in 100ml beaker. Add 20ml of 0.01M $CaCl_2$ solution . The $P^H$ should be b/w 5.0 to 6.5 adjust PH with $Ca(OH)_2$ or HCl. Allow the soil to absorb $CaCl_{l2}$ solution without stirring. Then thoroughly stir for 30 mins & allow to settle.

Determmination of nitrogen of soil by alkaline permanganate method

Outline: In case of soils , minerlizable N is estimated as ban index of available nitrogen content & not the total nitrogen content. The easily mineralizable nitrogen is estimated using $KMnO_4$, which oxidizes & hydrolysis the organic matter present in the soil. The liberated ammonia is condensed & absorbed in boric acid, which is titrated aganst standard acid. Te process of oxidative hydrolysis is, however, a progressive one & thus,a uniform time & heating temp should be allowed for best results. Usw of glass beads checks bumping while liquid paraffinchecks frothing during heating as recommended in total N estimation by kjeldahl method

Reqirements: a) Nitrogen distillation unit,( kjeldahl flask),conical flasks,pipettes,burette etc

b) Reagents :

- 0.32% $KMnO_4$ :→ dissolve 3.2g of $KMnO_4$ in water & make the volume to 1 litre
- 2.5% NaOH : Dissolve 25 g of NaOH pellets in water make the volume to 1 litre
- 2% $H_3BO_3$ (( Boric acid) : Dissolve 20 g of Boric acid powder in warm water by stirring & dilute to 1 litre
- Mixed indicator: Dissolve 0.066g of methyl red & 0.99 g of Bromocresol green in 100 ml of ethyl alcohol. Add 20 ml of this mixed indicator to each litre of 2% boric acid solution
- 0.1M Potassium hydrogen phthalate : Dissolve 20.422 g of the salt in water & dilute to1 litre. This is primary standared & does not require standardization
- 0.02M $H_2SO_4$ : Prepare approximately 0.1M $H_2SO_4$ by adding 5.6 ml of Conc.$H_2SO_4$ to about 1 litre of disilled water. From this , prepare0.02M $H_2SO_4$ by diluting a suitable volume (20 ml add to 100 ml) with distilled water.Standardize it against 0.1M NaOH solution.
- 0.1M NaOH : Dissolve 4 g of NaOH in 100 ml distilled water. Standardized against potassium hydrogen phphalate.
-

Procedure

- Weigh 20 g of soil sample in a800 ml kjeldahl flask
-
- Moisten the soil with about 10 ml of distilled water, wash down the soil,if any adhering to the flask.
-
- Add 100 ml of 0.32% of $KMnO_4$
-
- Add a few glass bids or broken pieces of glass rod
-
- Add2-3 ml of paraffin liquid, avoiding contact with upper part of the neck of the flask.
-
- Measure 20 ml of 2% boric acid containg mixed indicator in a250 ml conical flask & place it under the receiver tube. Dip the receiver tube in the boric acd.
-
- Run tap water through condenser.
-
- Add 100 ml of 2.5 % NaOH solution & immediately attach to the rubber stopper fitted in the alkali trap.
-
- Light up the burners on & continue distillation until about 100 ml of distillate is collected.
-
- First remove the conical flask containing distillate & then switch off the heater to avoid back solution.
-

- Titrate the distillate against 0.02M $H_2SO_4$ taken in burette until pink colour starts appearing.
- Run a blank without soil.
- Carefully remove kjeldalh flask after cooling & drain the contents in the sink.
-

Calculation : Volume of acid used to neutralize ammonia in the soil= A-B

N content in the test sample = (A-B) × 0.56mg

% of Nitrogen = (A-B) × 0.56 × 5

Where A= Volume of 0.02M H2SO4 used in titration against ammonia absorbed in boric acid.
B = Volume of 0.02M $H_2SO_4$ used in blank titration.
1 ml of 0.02M $H_2SO_4$ = 0.56mg N ( 1000ml of 1M $H_2SO_4$ =14 g N)
Wt of soil sample= 20 g
Thus factor for converting into % Nitrogen = 100÷20 = 5

RESULT = % of Nitrogen in the soil = ---------

Available nitrogen in the soil is calculated using the equation

1. Avaiale N ( 1bs/A) = 0.014×N of $H_2SO_4$ × B.R ×2 ×106 /Wt of the soil

.

1. Avaiale N ( Kg/ha) = 0.014×N of $H_2SO_4$ × B.R ×2 ×106 × 112 /Wt of the soil.

Determination of phosphorous of soil by Bbray's & Olsen's method

Outline: Two methods are most commonly used for determination of available phosphorous in soils.
Bray's Method ; It is used for acidic soils
Olsen's Method : It is used for neutral & alkaline soils.
In these methods, specific colored compounds are formed with the addition of approximate reagents in the solutions, T he intensity of which is proportionate to the concentration of the element being estimated. The colour intensity is measured spectrophoto metrically.
Principle: Phosphate bound on Al & Fe is released by fluoride contained in the Bray's extractant. Acidic medium stimulate field PH conditions. Phosphate reacts with ammonium molybdate forming a hetropoly complex which is then reduced by stannous chloride. The partially reduced compound gives blue color to the solution. The intensity of the color is read at 660m using red filter in spectrophotometer.
Bray's Method for Acid solution : Requirements: Apparatus: Spectrophotometers, pipette-2 ml,5 ml, 10 ml & 20 ml
Reagents: 1) Bray' Extractant: (0.03M $NH_4F$ in0.025MHCl) 2.22 g of $NH_4F$ in 220ml of distilled water, filter & add to the filtrate 1.8 litre of water containing 4 ml of Conc HCl make up the volume 2 liters with distilled water

2) Molybdate Reagent: Dissolve 1.5g $(NH_4)_2MoO_4$ in 300 ml distilled water. Add the solution to 350 ml HCl solution gradually with stirring. Dilute to 1 litre with distilled water.
3) Stannous Chloride Solution : ( Stock solution) Dissolve 10g $SnCl_2$ .2H2O in 25 ml of Conc HCl. Add a pinch of pure metallic tin & store the solution in a glass stopper bottle.
4) Stannous Chloride Solution : ( Working Solution) Dilute 1 ml of stock solution of stannous chloride to 66.0 ml with distilled water just before use. Prepare fresh dilute solution every working day.

Procedure: 1) Preparation of standared curve: Dissolve 0.1916 g of pure dry $KH_2PO_4$ in 1 litre distilled water. This solution contains 0.10 mg $P_20_5$ / ml. Preserve this as a stock solution of phosphate. Take 10 ml of this solution 7 dilute it to 1 litre with distilled water. This solution contains 1Mg $P_2O_5$ /ml. ( 0.001mg$P_2O_5$/ml) Take 1,2,4,6 & 10 ml of this in separate 25 ml flasks. Add to each 5 ml of the extractant solution,5 ml of molybdate reagent & dilute with distilled water to about 20 ml. 1ml dil $SnCl_2$ solution, shake again & dilute to the 25 ml mark. After 10 minutes, read the blue color of the solution on the specrophotometre at 660 nm wavelength. Plot the graph of absorbance reading against Mg $P_2O_5$ & join the points.

2) Extraction : Add 50 ml of the Bray's extractant to the 100 ml conical flask containing 5 gm soil sample. Shake for 5 minutes & filter.

3) Development of color : take 5 ml of the filtered soil extract with a bulb pipette in a 25 ml measuring flask, deliver, 5 ml of the molybdate reagent with an automatic pipette, dilute to about 20 ml with distilled water. Shake & add 1ml of dil $SnCl_2$ solution with a bulb pipette. Fill to the 25 ml mark & shake thoroughly. Read the blue color after 10 minutes on the spectrophotomrter at 660nm wavelength after setting the instrument to zero with the bulk prepared simileraly but without the soil.

Calculation : If A is the value of Mg $P_2O_5$ obtain from the standared curve then,

Avaailable P ( Kg $P_2O_5$/ha ) = $A \times 25 \times 50 \times 2 \times 10^6 \times 12/5 \times 5$.

Draw the gragh here (absorbance against % (Mg /ml) straight line passes through the origin)

Method 2 Olsen's Method : Requirements:Apparatus: spectrophotometer, pipettes: 2 ml , 5 ml , 10 ml , 20 ml Beakers, flasks: 25 ml ,50 ml ,& 500 ml

Reagents : 1) Bicarbonate extractant: Dissolve 42 g of $Na_2CO_3$ in 1 litre of distilled water 7 adjust the $P^H$ by addition of dil NaOH or HCl. Filterate, if necessary.

2) Molybdate Reagent : Dissolve 1.50 g $(NH_4)_2$ $MoO_4$ IN 300 ml distilled water. Add the solution to 350 ml of 10 M HCl solution gradually with stirring. Dilute to 1 litre with distilled water.

3) Stannous Chloride Solution : Dissolve 10g $SnCl_2.2H_2O$ in 250 ml of Conc HCl. Add a pinch of pure metallic tin & store solution in a stoppered bottle.

Procedure: 1) Preparation of standared curve: Dissolve 0.1916 g of pure dry $KH_2PO_4$ in 1 litre distilled water. This solution contains 0.10 mg $P_20^5$ / ml. Preserve this as a stock solution of phosphate. Take 10 ml of this solution 7 dilute it to 1 litre with distilled water. This solution contains 1Mg $P_2O_5$ /ml. ( 0.001mgP2O5/ml) Take 1,2,4,6 & 10 ml of this in separate 25 ml flasks. Add to each 5 ml of the extractant solution,5 ml of molybdate reagent & dilute with distilled water to about 20 ml. 1ml dil $SnCl_2$ solution, shake again & dilute to the 25 ml mark. After 10 minutes, read the blue color of the solution on the specrophotometre at 660 nm wavelength. Plot the graph of absorbance reading against Mg $P_2O_5$ & join the points.

2) Extraction : Add 50 ml of the bicarbonate extractant to the 100 ml conical flask containing2. 5 gm soil sample. Add1 g activated charcoal Shake for 30minutes on the mechanical shaker & filter.

3) Development of color : take 5 ml of the filtered soil extract with a bulb pipette in a 25 ml measuring flask, deliver, 5 ml of the molybdate reagent with an automatic pipette, dilute to about 20 ml with distilled water. Shake & add 1ml of dil $SnCl_2$ solution with a bulb pipette. Fill to the 25 ml mark & shake thoroughly. Read the blue color after 10 minutes on the spectrophotomrter at 660nm wavelength after setting the instrument to zero with the bulk prepared simileraly but without the soil.

Calculation : If A is the value of Mg P2O5 obtain from the standared curve then,

Avaailable P ( Kg $P_2O_5$/ha ) = $A \times 50 \times 50 \times 20{,}00{,}000/ 10{,}00{,}000 \times 5 \times 5$.

Where wt of the soil taken = 5 g

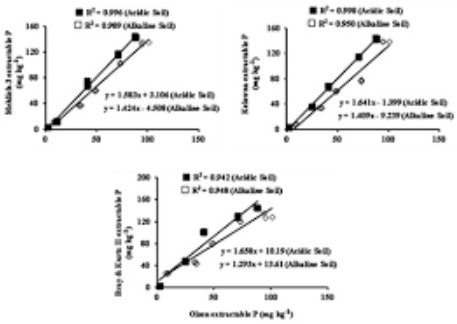
Volume of the extract = 50ml

Volume of the extract taken for the estimation = 5 ml

Volume made for estimation ( dilution = 5 times ) = 25 ml.

Amount of P observed in the sample on the standard curve =A (Mg) Wt of 1 hectare of soil up to a depth of 22 cm is taken as 2 million kg.

Nature of graph



**By Miss Laxmi.R.Ankalagi**

**FlamePhotometry**

Introduction

Flame Photometry is also called as flame emission spectroscopy and it is based on the measurement of intensity of light emitted when a metal is introduced into a flame. The wavelength of colour tells us what the element is and intensity of the colour tells us how much of the element is present.

Thus, Flame photometry is a spectral technique in which the excitation is caused by spraying is solution of the sample in a hot flame. A flame can serve effectively as a source of atomic emission lines and also so as an absorbing medium for the same lines. Thus flame photometry is concerned with the emission of characteristic radiation in flames by individual elements and correlation of the emission intensity with the concentration of the element introduced in the flame.

The technique is most widely acceptable for the analysis of sodium and potassium especially in fluids and tissues.

Thus flame photometry may be defined as spectral technique in which the excitation is caused by spraying a solution of the sample in a hot flame.

***Principle***:

When a sample is sprayed into the flame three phenomenon occurs

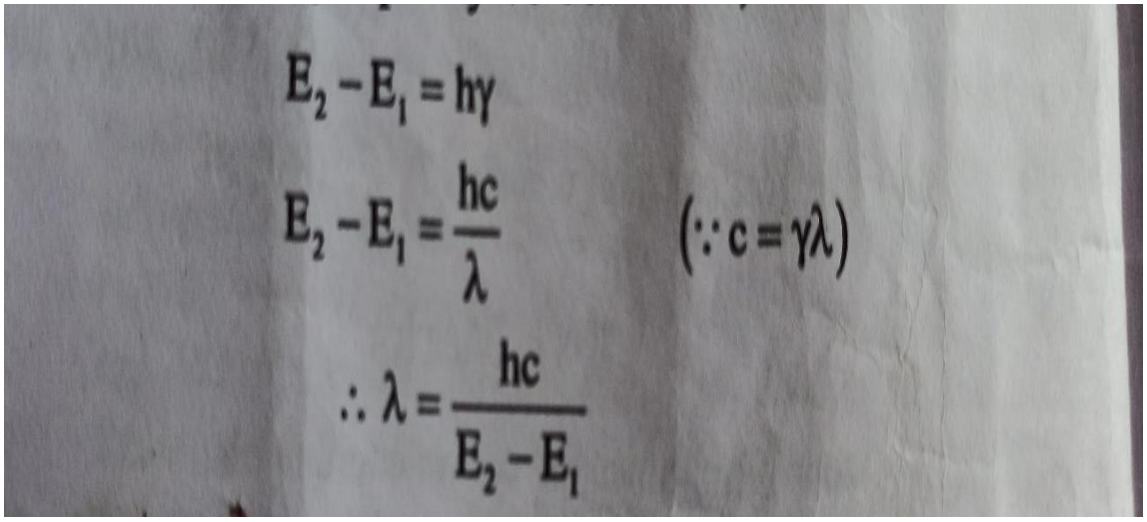
1.Evaporation of the solvent living a solid residue.

2.Vaporization of the solid with dissociation into its constituent atoms, which will be in the ground state.

3.Some atoms may be excited by the thermal energy of the flame to the higher energy levels and attain a condition in which radiate energy.

The resulting emission spectrum thus consist of lines originating from excited atoms or ions. The spectra due to these ions may be produced at high temperature and at high concentration of the atoms in the flame.

If $E_2$ and $E_1$ represent the energies of higher and lower levels then the radiation emitted during the jump may be defined as follows



$$E_2 - E_1 = h\gamma$$

$$E_2 - E_1 = \frac{hc}{\lambda} \qquad (\because c = \gamma\lambda)$$

$$\therefore \lambda = \frac{hc}{E_2 - E_1}$$

From the above equation it is possible to evaluate the wavelength of emitted radiation which is characteristic of the element which emits and the intensity of emitted radiation corresponding to the amount of element which is present in the flame.

***Instrumentation*** : A typical flame photometer is consists of the following components

1.Pressure Regulator and Flow meter

2.Atomizer

3.Burners

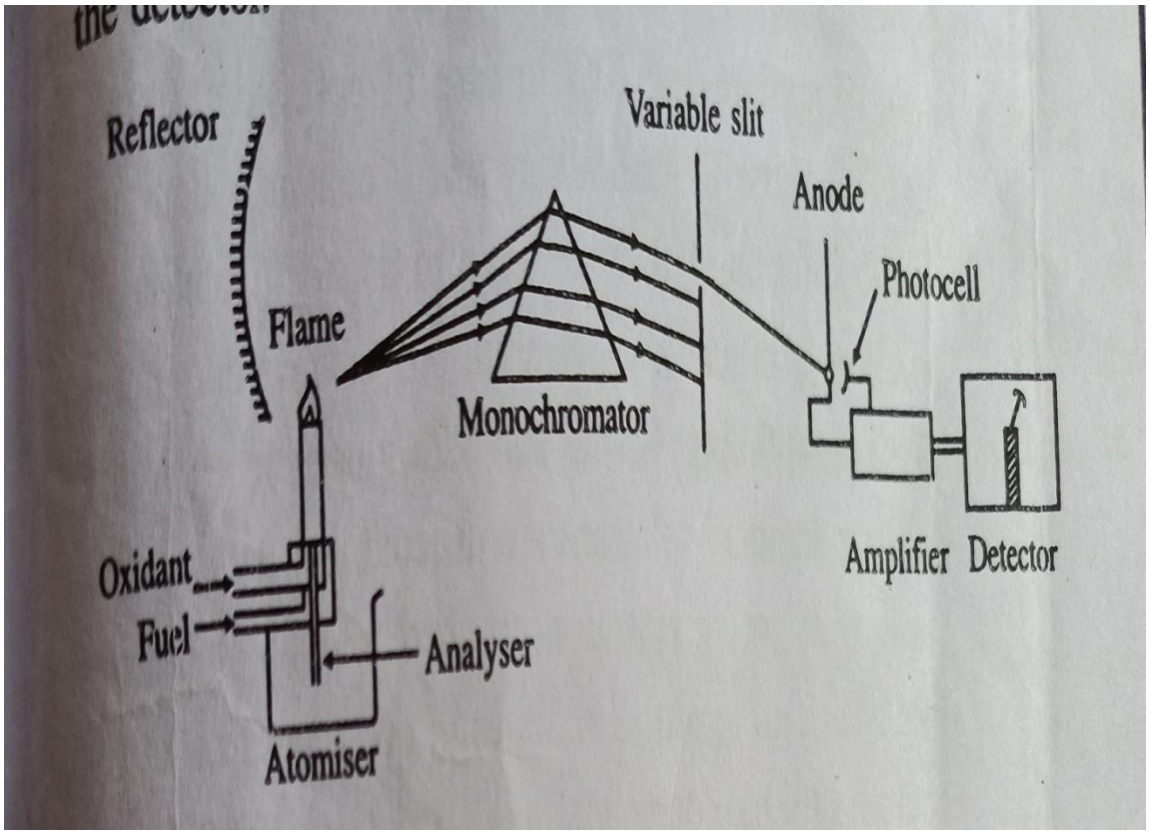
4.Mirrors

5.Slits

6.Optical system

7.Photosensitive detector and recording output of the detector

***Instrumentation:***




**1.PressureRegulator andflowmeter**: These are used for the proper adjustment of pressure and flow of gases usually double diaphragm and needle valves are used to control the pressure and to control the gas flow, a rotameter should be inserted in the gas line and a flow rate of 2to 10 feet per hour is best for good results.

**2.Atomizer**: The atomizer is used to introduce a liquid sample into the flame at a stable and reproducible rates. They are classified into two types

- Firstly those which introduce the spray into a condensing chamber for removing large droplets
- Secondly those which introduced the spray directly into the flame

One needs about 4 to 25 cm3 of the sample of which 5 percentage reaches the flame.

**3.Burners** : The flame used in flame photometer must process the following functions

- The flame should poses the ability to evaporate liquid droplets from the sample solution resulting in the formation of solid residue.
- The flame should decompose the solid into constituent atoms.
- The flame must have capacity to exit the atoms and cause them to emit radiant energy.

Thus in flame photometry the Berners such as Mecker burner , Total combustion burner, premix or laminar flow Burners have been employed.

**4.Mirrors**: the radiation from the flame is emitted in all directions in space thus major portion of emitted radiation will not be reaching at the detector. In order to increase the amount of radiation reaching at the detector a concave mirror is set behind the burner.

**5.Slits** : Two types of slits are used here. One is entrance slit and another one is exit slit. The entrance slit is kept between flame and optical system. This slit permits the radiation from the flame and the mirrored reflection of the flame to enter the optical system.

The exit slit is kept between monochromator and detector and this slit allows only a selected wavelength range from the radiation travelling from the monochromator the detector. It also prevents the entry of interfering lines.

**6.Opticalsystem**: The optical system functions both as as a collector and monochromator of light and focus the light on a photosensitive detector. The light is focused on the entire detector by a concave mirror by the adjustment of the flame.

**7.Photosensitivedetector**: Photosensitive detectors such as barrier layer cells are not useful because the response is not amplifiable. These detectors produce an electrical signal from the radiation falling on them. Thus the photoelectron multiplier tubes are best to use. The readout systems available include meters, charts, recorders and digital display.

**Determinationofsodium&potassiumbyflamephotometricmethod (electro photometricmethod)**

Determination of sodium and potassium by flame photometry involves two important steps,

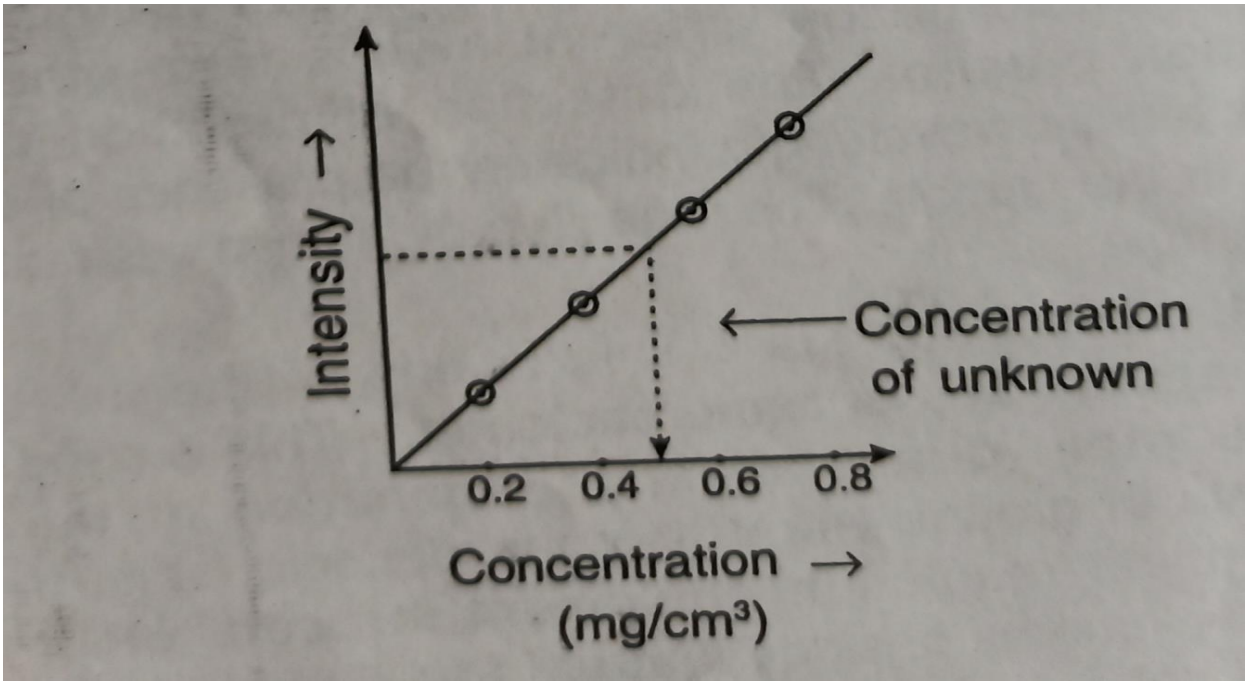
1.Construction of calibration curve

2.Determination of the metal

1. **Constructionof calibrationcurve**:

Calibration curve is a graph which is obtained by plotting a graph of intensity against concentration of the solutions. To plot this graph we need to prepare standard solutions. To prepare the standard solution a known mass of suitable salt,NaCl in case of sodium and KCl in case of

potassium is dissolved in a distilled water in such a way that it contains about 1 milligram per ml of the solution. This solution is referred as stocksolution and this is used to prepare the different concentrated solutions such as 0.2, 0.4, 0.6 and 0.8 mg per cm3 respectively. Each of these solutions starting with the least concentrated solution are injected into the flame photometer and the corresponding intensity of the emitted radiations are measured at 589 nm for sodium and 768 nm for potassium and a calibration graph is constructed by plotting the intensity against the concentration of the solutions which gives a straight line passing through origin.




2. **Determinationofconcentrationofmetal** :

The unknown solution whose concentration we need to find out is also injected into the flame photometer and the intensity of the emitted radiation is measured and the amount of metal is determined with the help of the calibration curve.

***Applicationsofflamephotometry***:

**1.Qualitative analysis**

Flame photometer is used to detect elements of group 1 and group 2 of the periodic table.(Na,K,Li,Mg,Ca etc.) Some of these elements can be detected visually by the colour in the flame. For example sodium produces golden yellow flame. But this method is not reliable. Best method is to use the flame photometer with the filter on monochromator to separate the radiation with the wavelengths characteristic of the different metals from other radiation present.

The detection of radiation of characteristic wavelength indicates the presence of a metal in the sample. The detection of elements is fast and simple.

1.**Quantitativeanalysis** :

This is one of the most useful application of flame photometry. This is used for the rapid quantitative determination of elements in group 1 and group 2 of the periodic table. If high optical resolution equipment is used, other metallic elements besides that of group 1 and 2 can also be determined.

***Some OtherApplications*** :

1.Flame photometry can also be used for the analysis of glass.

2.Analysis of water can also be done with the help of flame photometry.

3.Analysis of the blood and urine samples can also be done with the help of flame photometry.

4.The most important application of flame photometry is it is widely used for the analysis of sodium and potassium specially in the fluids and tissues.

***Limitationsofflamephotometry***

1.The analysis of noble gases cannot be done with the help of flame photometry.

2.Does not provide information about the molecular form of the metal present in the solution.

3.Only liquid samples can be used for the analysis .

4.Non radiating elements such as carbon hydrogen etc. cannot be analyzed with the help of flame photometry.

# CHEMOTHERAPY By DSL

## Introduction:

Chemotherapy is an aggressive form of chemical drug therapy meant to destroy rapidly growing cells in the body. The practice of using drugs to treat diseases and the drugs often used called chemotherapeutic agents. Drugs is any chemical substances used to kill or prevent the growth of infection caused by the microorganisms like bacteria without affecting the host cells such practice is known as chemotherapy and drugs used to treat this are called chemotherapeutic agents.

## Requirement of an ideal synthetic drug.

1. It is non toxic

2. Non reactive

3. It is physicochemical stable

4. It is metabolically stable

5. Chemically inert and free from microbial contamination

6. It gives both raped as well as sustained activity

7. It should be easily available

## Classification of chemical drugs

The most of common way of classification of drugs on the bases of their particular applications as follows

1. **Antimicrobials –antibacterial and antiviral drugs**
2. **Antimalarials**
3. **Symptomatic**
4. **Antibiotics**
5. **Anticancer**

**Antimicrobials –antibacterial and antiviral drugs**

Many diseases caused by the bacterial and viral infections such drugs are manly used to kill or prevent the growth of the antimicrobials

**Ex. Sulpha drugs, pencilline, tetracycline ete**

## Antimalarials

These are class of the drugs in which manly used to kill or prevent the growth of malarial (plasmodium) parasite are called as antimalarial drugs
Ex. Chloroqune, Paludrine ete

## *Antibiotic drugs*

*Antibiotics*, also known as antibacterials, are medications that destroy or slow down the growth of bacteria. They include a range of powerful drugs and are used to treat diseases caused by bacteria. *Antibiotics* cannot treat viral infections, such as cold, flu, and most coughs.
Ex. Pencillin, Tetracycline ete

## Symptomatic drugs

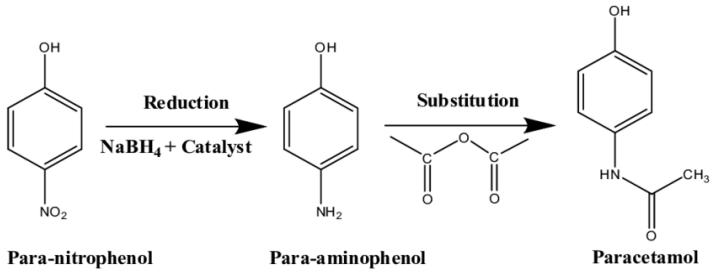
These are the class of chemical drugs manly used on the bases of the symptoms such drugs are known as symptomatic
Ex. Antipyratics, anaesthetics ete

# Synthesis and uses of chemotherapeutic drugs

# Antipyretics drugs.

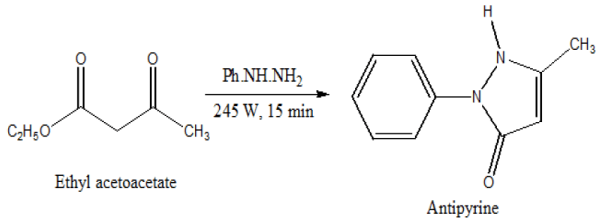
Synthesis of Paracetamol

Paracetamol can be prepared by reacting 4-aminophenol with ethanoic anhydride (more commonly called acetic anhydride). This reaction forms an amide bond and ethanoic acid as a by- product. Paracetamol manly used for the antipyretics




**Synthesis of antipyrine**

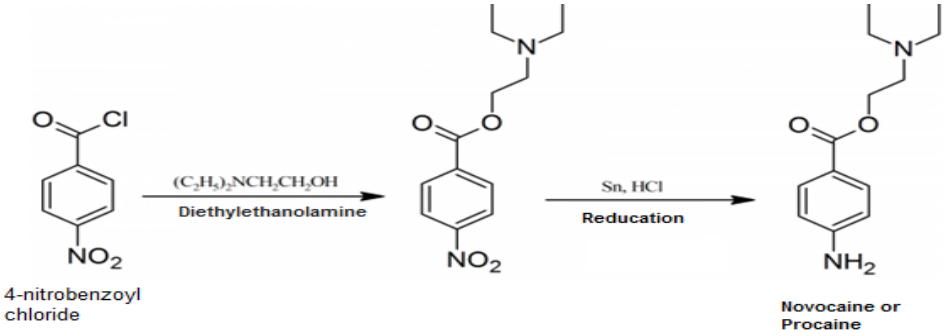
Antipyrine can be synthesized from ethylacetoacetate and phenyl hydrazine gives corresponding antipyrine which is generally used as antipyretics




Scheme 1: Reaction of synthesis of antipyrine

## Synthesis of Novocaine or Procaine

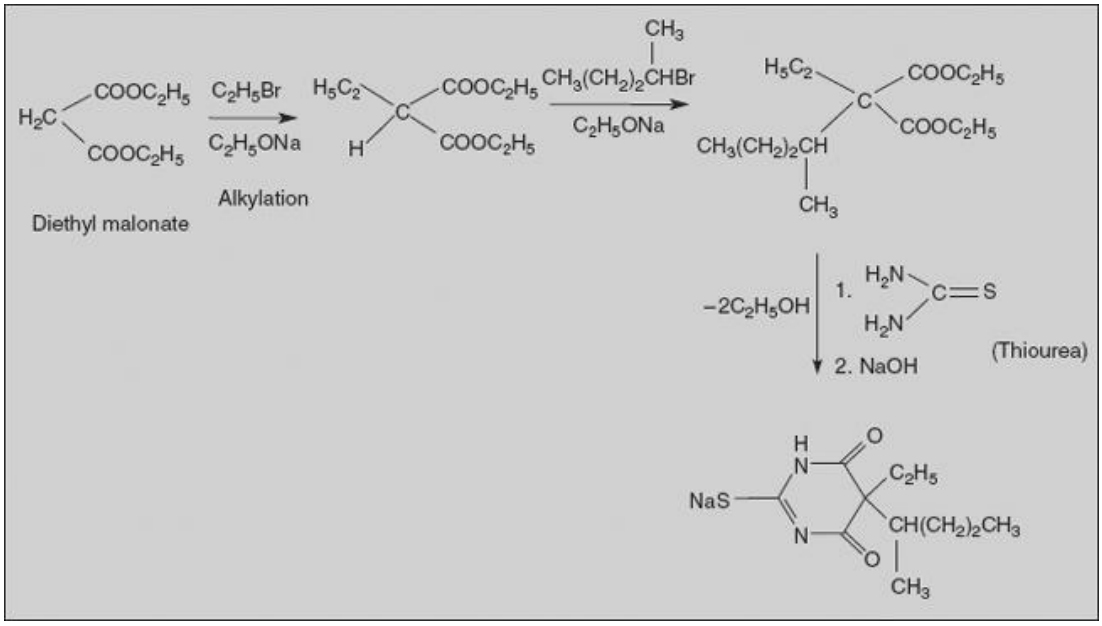
Procaine can be synthesized by the reaction between 4-nitrobenzoyl chloride and Diethylethanolamine followed by the reduction gives procaine with very good yield.




Procaine is a local anesthetic drug of the amino ester group. It is used primarily to reduce the pain of intramuscular injection of penicillin, and it is also used in dentistry. Procaine is referred to generically as novocaine. Today it is used therapeutically in some countries due to its sympatholytic, anti-inflammatory, perfusion-enhancing, and mood-enhancing effects.

## Synthesis of Pentathol sodium

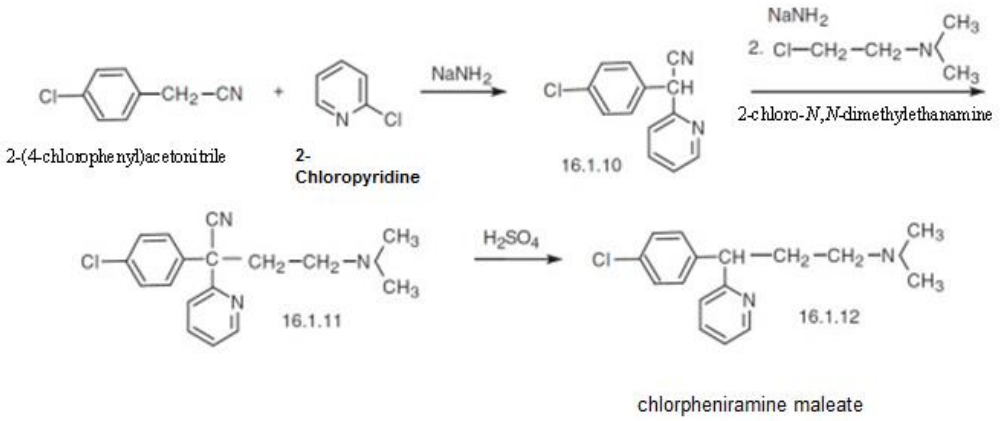
Pentathol sodium can be synthesized when the reaction between diethylmalonate is alkylation followed by the addition of thiourea and sodium hydroxide gives corresponding pentathol sodum salt




**Synthesis of chlorpheniramine maleate**

Chlorphenamine (CP, CPM), also known as chlorpheniramine, is an antihistamine used to treat the symptoms of allergic conditions such as allergic rhinitis (hay fever). It is taken by mouth. The medication takes effect within 6 hours and lasts for about a day.

It can be synthesized as following steps



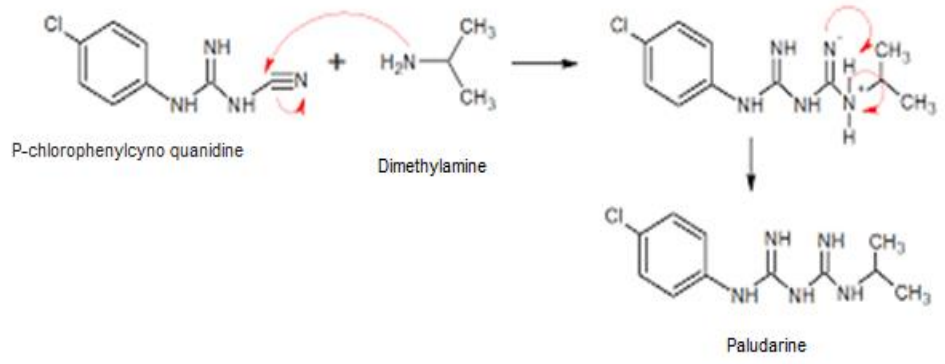

**Antimalarial Drugs.** These are the class of chemotherapeutic agents manly used to kill or prevent the growth of malarial (plasmodium) parasite are called as antimalarial drugs

Ex. Chloroqune, Paludrine ete

**Synthesis of Paludrine**

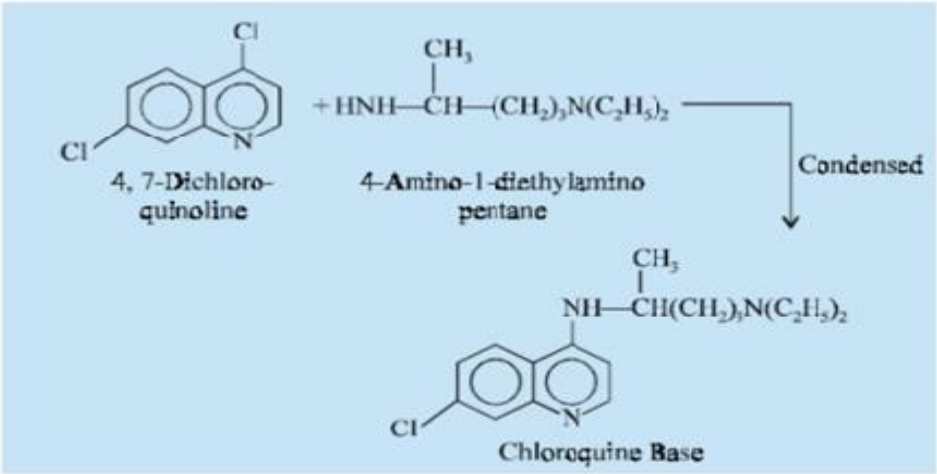
Paludrine or Proguanil is used for the prevention and treatment of malaria in both adults and children, particularly in areas where chloroquine-resistant *P. falciparum* malaria has been reported. It is usually taken in combination with atovaquone, another antimalarial drug.

It can be synthesized by the reaction between Dimethylamine and P-Chlorophenylcyno Guanidine leads to corresponding paludarine with quantitative yield.




**Synthesis of Chloroquine**

Chloroquine is a medication primarily used to prevent and treat malaria in areas where malaria remains sensitive to its effects.[1]Certain types of malaria, resistant strains, and complicated cases typically require different or additional medication. Chloroquine was discovered in 1934 by Hans Andersag. It's also used to for the treatment of Covid-19 in 2020.



It is on the World Health Organization's List of Essential Medicines, the safest and most effective medicines needed in a health system. It is available as a generic medication.It is synthesized by the reaction between 4-amino-1diethylaminopentane is condensed with heterocyclic 4, 7-dichloro-quinoline yield chloroquinoline.

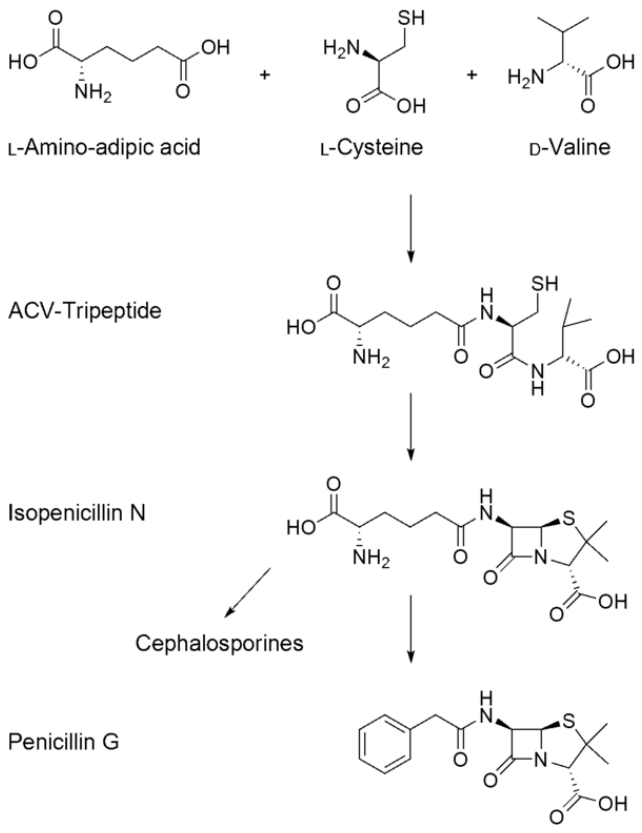
**Antibiotic drugs.** *Antibiotics*, also known as antibacterials, are medications that destroy or slow down the growth of infection caused by bacteria. They include a range of powerful drugs and are used to treat diseases caused by bacteria. *Antibiotics* cannot treat viral infections, such as cold, flu, and most coughs.

Ex. Pencillin, Tetracycline ete

**Synthesis of Pencillin**

Penicillin is a group of antibiotics, derived originally from common moulds known as Penicillium moulds; which includes penicillin G (intravenous use), penicillin V (use by mouth), procaine penicillin, and benzathine penicillin (intramuscular use).

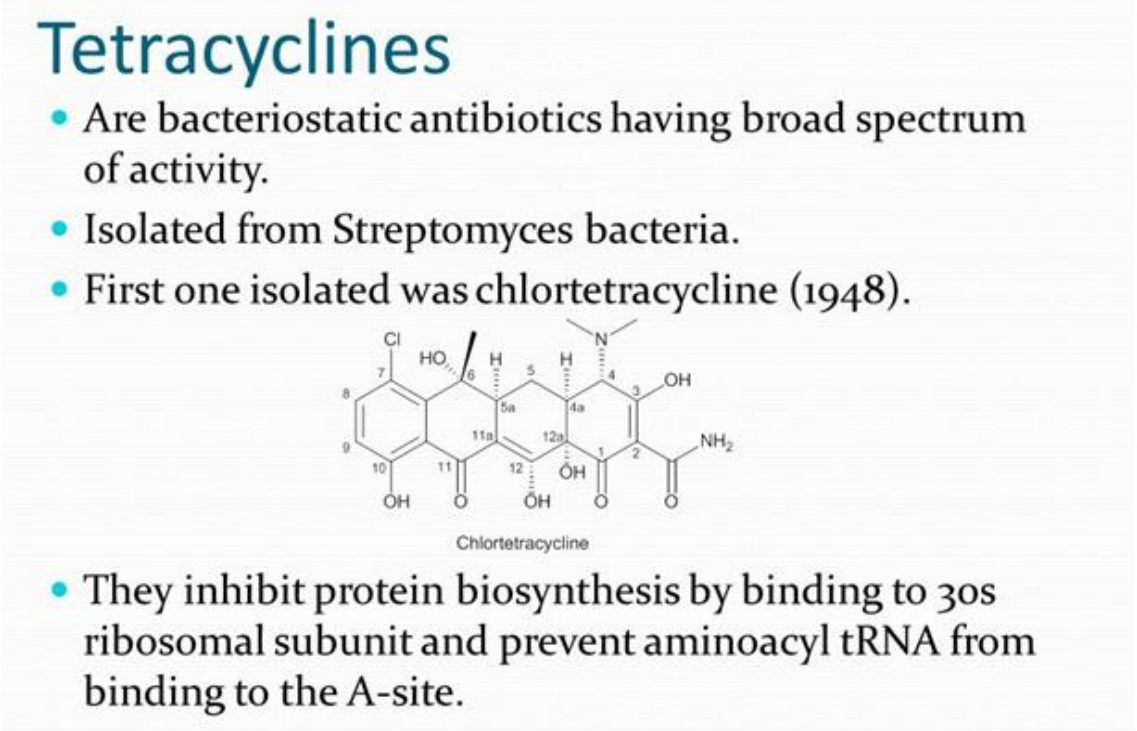
It can be synthesized in following steps



The term "penicillin" was used originally for benzyl penicillin, penicillin G. Currently, "Penicillin" is used as a generic term for antibiotics that contain the beta lactam unit in the chemical structure. Penicillin was discovered in 1928 by Scottish scientist Alexander Fleming. People began using it to treat infections in 1942.

**Tetracycline**

Tetracyclines are generally used in the treatment of infections of the urinary tract, respiratory tract, and the intestines and are also used in the treatment of chlamydia, especially in patients allergic to β-lactams and macrolides. Tetracyclines inhibit protein synthesis in both bacterial and human cells. Bacteria have a system that allows tetracyclines to be transported into the cell, whereas human cells do not. Human cells therefore are spared the effects of tetracycline on protein synthesis. Tetracyclines were discovered in the 1940s and exhibited activity against a wide range of microorganisms including gram-positive and gram-negative bacteria, and protozoan parasites.



**PARA PHARMACEUTICAL REAGENTS**

The substances used in medicine for storage of blood samples and their characterization, testing of urine and blood samples and different other pathological investigations are called para pharmaceutical reagents.

1) **Benedicts reagents:** This reagents is used to identify the presence of reducing sugar, benedicts reagent is prepared as follow.

Dissolve 173 grams of sodium citrate and 100 grams of anhydrous sodium carbonate in 750 ml of water by heating. Take 17.3 grams of crystalline coppersulphate and dissolve separately in 100ml of water. Mix these two solutions with stirring add water to make up the volume to 1000ml.

In the test take 5ml Benedict's reagents in a test tube and add 8 drops of the test material, boll for about 2minute. Appearance of colored precipitates indicates the percentage of reducing sugars as follows:

Green color - 0.1 to 0.5%

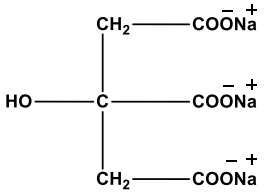
Yellow color - 0.5 to 1%

Orange color - 1 to 2%

Red color - above 2%

This is semi quantitative reagents to test reducing sugar.

2) **Sodium Citrate:** The structure of sodium citrate is,




Sodium citrate is system alkalising agent to adjust the pH of blood to slightly alkaline state in patients suffering from acidosis. Sodium citrate is also used as blood anti coagulant either alone or with other citrate. In acute dehydration and diarehaea there is loss of sodium ions hence sodium citrate is used as oral rehydrating agent.

3) **Barfoed's Reagent:** This reagent is used to find the presence of reducing sugars like glucose fructose, Galactose etc (monosaccharides) in body fluids like urine, blood etc.

Barfoed's reagent is prepared by dissolving 13.3 grams of crystalline coppersulphate in water to make 200ml of solution to which 1.8ml of glacial acetic acid is added to get the reagent.

During the test, to ml of test solution few drops of Barfoed's reagent is added and boiled for 30 seconds and allowed to cool. Formation of red ppt indicates the presence of reducing sugar i.e., monosaccharide.

# Nuclear Magnetic Resonance Spectroscopy

## Theoretical principles By DSL

### Introduction

Nuclear Magnetic Resonance spectroscopy is a powerful and theoretically complex analytical tool. Here, we will cover the basic theory behind the technique. It is important to remember that, with NMR, we are performing experiments on the **nuclei** of atoms, not the electrons. The chemical environment of specific nuclei is deduced from information obtained about the nuclei. **The Nuclear Magnetic Resonance Spectroscopy ($^{1}$H NMR) is a techniques manly based on the electromagnetic radiation of radiofrequency by the nuclear atoms.** It's manly used for organic structure determination and by studying a molecule by using NMR we will obtain following information.

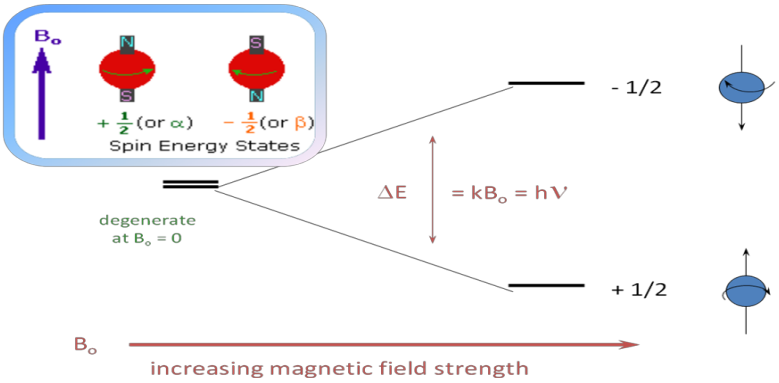
- **The numbers of signal:** How many different kinds of protons in molecules
- **Position of signal:** Electronic environment of each kind of protons
- **Intensity of signal:** Resolution of signal
- **Splitting patterns:** Numbers of peaks neighboring protons & its environments
- **Coupling constant:** molecular structure and its stereo chemical studies
- **E.M Purcel and F. Bloch the two physicists shared the noble prize 1952.**
- It is used to study a wide variety of nuclei:
  - $^{1}$H
  - $^{13}$C
  - $^{15}$N
  - $^{19}$F
  - --- $^{31}$P

### Nuclear spin and the splitting of energy levels in a magnetic field

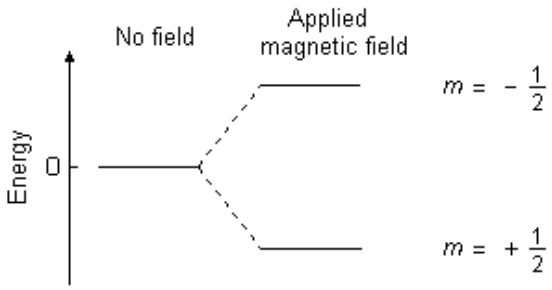
Subatomic particles (electrons, protons and neutrons) can be imagined as spinning on their axes. In many atoms (such as $^{12}$C) these spins are paired against each other, such that the nucleus of the atom has no overall spin. However, in some atoms (such as $^{1}$H and $^{13}$C) the nucleus does possess an overall spin. The rules for determining the net spin of a nucleus are as follows;

1. If the number of neutrons **and** the number of protons are both even, then the nucleus has **NO** spin.
2. If the number of neutrons **plus** the number of protons is odd, then the nucleus has a half-integer spin (i.e. 1/2, 3/2, 5/2)
3. If the number of neutrons **and** the number of protons are both odd, then the nucleus has an integer spin (i.e. 1, 2, 3)

The overall spin, *I*, is important. Quantum mechanics tells us that a nucleus of spin *I* will have 2*I* + 1 possible orientations. A nucleus with spin 1/2 will have 2 possible orientations. In the absence of an external magnetic field, these orientations are of equal energy. If a magnetic field is applied, then the energy levels split. Each level is given a *magnetic quantum number, m*.




**Energy levels for a nucleus with spin quantum number 1/2**

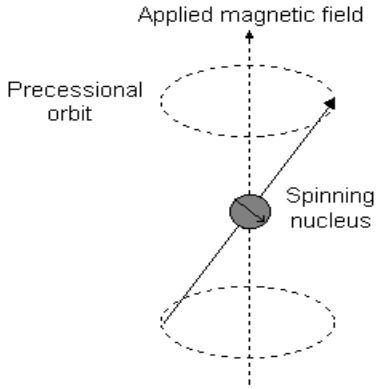



When the nucleus is in a magnetic field, the initial populations of the energy levels are determined by thermodynamics, as described by the Boltzmann distribution. This is very important, and it means that **the lower energy level will contain slightly more nuclei than the higher leve**l. It is possible to excite these nuclei into the higher level with electromagnetic radiation. The frequency of radiation needed is determined by the difference in energy between the energy levels.

## The absorption of radiation by a nucleus in a magnetic field

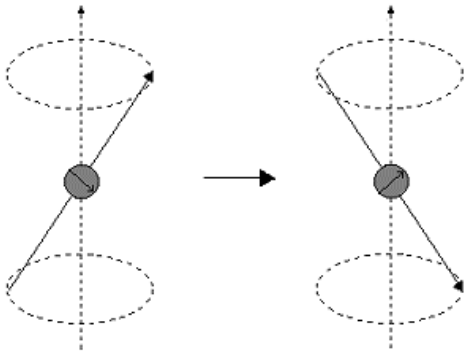
In this discussion, we will be taking a "classical" view of the behaviour of the nucleus - that is, the behaviour of a charged particle in a magnetic field.

Imagine a nucleus (of spin 1/2) in a magnetic field. This nucleus is in the lower energy level (i.e. its magnetic moment does not oppose the applied field). The nucleus is spinning on its axis. In the presence of a magnetic field, this axis of rotation will *precess* around the magnetic field;




The frequency of precession is termed the *Larmor frequency*, which is identical to the transition frequency.
The potential energy of the precessing nucleus is given by;
$E = -\mu B \cos\theta$

where $\theta$ is the angle between the direction of the applied field and the axis of nuclear rotation.
If energy is absorbed by the nucleus, then the angle of precession, $\theta$, will change. For a nucleus of spin 1/2, absorption of radiation "flips" the magnetic moment so that it **opposes** the applied field (the higher energy state).



It is important to realize that only a small proportion of "target" nuclei are in the lower energy state (and can absorb radiation). There is the possibility that by exciting these nuclei, the populations of the higher and lower energy levels will become equal. If this occurs, then there will be **no** further absorption of radiation. The spin system is *saturated*. The possibility of saturation means that we must be aware of the relaxation processes which return nuclei to the lower energy state.

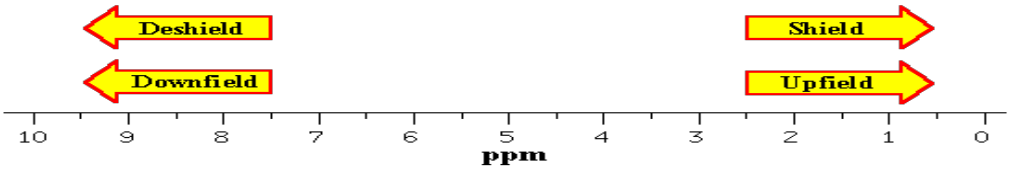
## Chemical shift (δ)

- An NMR spectrum is a plot of the *radio frequency applied* against *absorption*.
- A signal in the spectrum is referred to as a *resonance*.
- The frequency of a signal is known as its *chemical shift*.

The chemical shift in absolute terms is defined by the frequency of the resonance expressed with reference to a standard compound which is defined to be at 0 ppm. The scale is made more manageable by expressing it in parts per million (ppm) and is indepedent of the spectrometer frequency.

$$\text{Chemical shift, } \delta = \frac{\text{frequency of signal} - \text{frequency of reference}}{\text{spectrometer frequency}} \times 10^6$$

It is often convienient to describe the relative positions of the resonances in an NMR spectrum. For example, a peak at a chemical shift, δ, of 10 ppm is said to be *downfield* or *deshielded* with respect to a peak at 5 ppm, or if you prefer, the peak at 5 ppm is *upfield* or *shielded* with respect to the peak at 10 ppm.



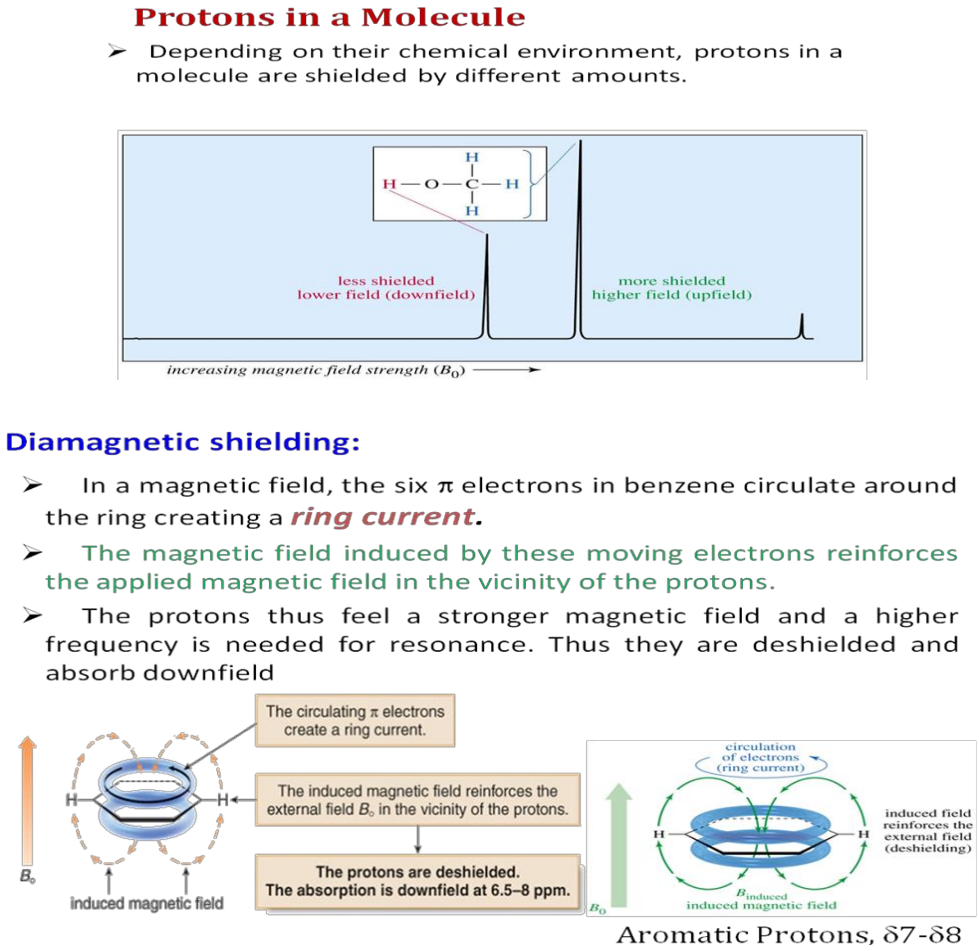

Typically for a field strength of 4.7T the resonance frequency of a proton will occur around 200MHz and for a carbon, around 50.4MHz. The reference compound is the same for both, tetramethysilane ($Si(CH_3)_4$ often just refered to as TMS).

*Chemical shift is defined the separation between the frequencies for the same nucleus in different chemical environments is known as chemical shift.* It can also refer the *nuclear shielding / applied magnetic field*. Chemical shift is a function of the nucleus and its environment. It is measured relative to a reference compound. For $^1H$ NMR, the reference is usually tetramethylsilane, $Si(CH_3)_4$.

Shielding in H-NMR

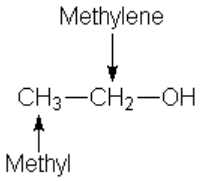
The magnetic field experienced by a proton is influenced by various structural factors. Since the magnetic field strength dictates the energy separation of the spin states and hence the radio frequency of the resonance, the structural factors mean that different types of proton

will occur at different chemical shifts. This is what makes NMR so useful for structure determination; otherwise all protons would have the same chemical shift.

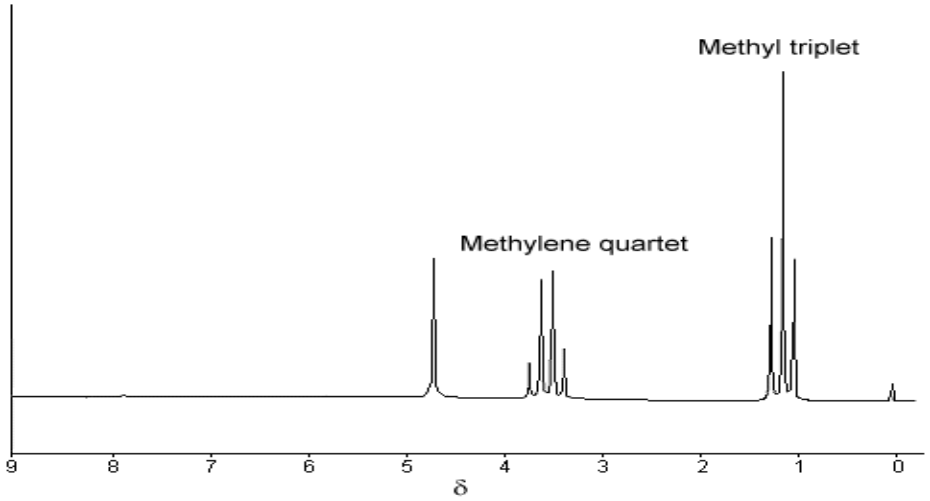



## Spin - spin coupling:

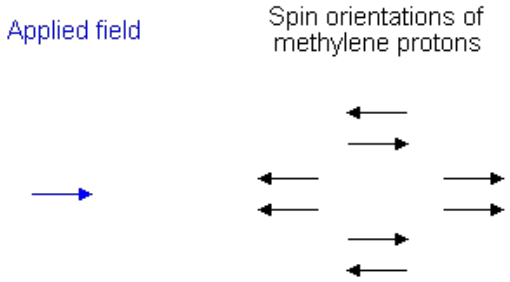
Consider the structure of ethanol;



The $^1$H NMR spectrum of ethanol (below) shows the methyl peak has been split into three peaks (a *triplet*) and the methylene peak has been split into four peaks (a *quartet*). This occurs because there is a small interaction (*coupling*) between the two groups of protons. The spacings between the peaks of the methyl triplet are equal to the spacings between the peaks of the methylene quartet. This spacing is measured in Hertz and is called the *coupling constant, J*.

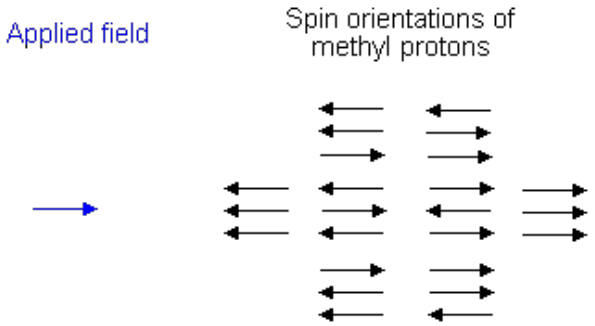



To see why the methyl peak is split into a triplet, let's look at the **methylene** protons. There are two of them, and each can have one of two possible orientations (aligned with or opposed against the applied field). This gives a total of four possible states;




In the first possible combination, spins are paired and opposed to the field. This has the effect of reducing the field experienced by the **methyl** protons; therefore a slightly higher field is needed to bring them to resonance, resulting in an upfield shift. Neither combination of spins opposed to each other has an effect on the methyl peak. The spins paired in the direction of the field produce a downfield shift. Hence, the methyl peak is split into three, with the ratio of areas 1:2:1.

Similarly, the effect of the methyl protons on the methylene protons is such that there are eight possible spin combinations for the three methyl protons;




Out of these eight groups, there are two groups of three magnetically equivalent combinations. The methylene peak is split into a quartet. The areas of the peaks in the quartet have the ration 1:3:3:1.

In a *first-order* spectrum (where the chemical shift between interacting groups is much larger than their coupling constant), interpretation of splitting patterns is quite straightforward;

- The multiplicity of a multiplet is given by the number of equivalent **protons** in **neighbouring** atoms plus one, i.e. *the n + 1 rule*
- Equivalent nuclei do not interact with each other. The three methyl protons in ethanol cause splitting of the neighbouring methylene protons; they do not cause splitting among themselves
- The coupling constant is not dependant on the applied field. Multiplets can be easily distinguished from closely spaced chemical shift peaks.

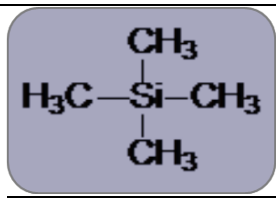
## Tetramethylsilane(TMS):

Tetramethylsilane is the accepted internal standard for calibrating chemical shift for $^{1}H$, $^{13}C$ and $^{29}Si$ NMR spectroscopy in organic solvents (where TMS is soluble). If compounds are insoluble in organic solvent and soluble in water, then used sodium salts of

DSS, 2,2-dimethyl-2-silapentane-5-sulfonate, are used instead. Because of its high volatility, TMS can easily be evaporated, which is convenient for recovery of samples analyzed by NMR spectroscopy. The following list of important advantages of TMS used as reference standard.

## Reference Std. Tetramethylsilane(TMS)

- Chemically inert
- Magnetically Isotopic
- Sharp single only one peak on NMR spectrum
- Molecule must be soluble in most of the organic solvent
- Must be relatively volatile
- High electronic density of H in TMS. (Almost all the H peaks of organic compounds appear on the left of the TMS peak.)
- Since silicon is less electronegative than carbon, TMS protons are highly shielded. Signal defined as zero.

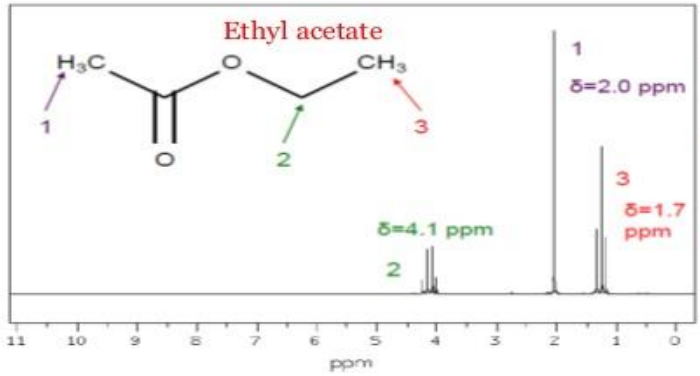



Tetramethylsilene

## Spin-spin coupling (splitting)

The interaction between the spins of neighbouring nuclei in a molecule may cause the splitting of NMR spectrum.This is known as spin-spin coupling or splitting.

The splitting pattern is related to the number of equivalent H-atom at the nearby nuclei.




**Spin-Spin Splitting patterns**

1. Singlet. 3 equivalent protons. Not coupled to any neighboring protons.
2. Quartet. 2 equivalent protons. Split (1:3:3:1) because coupled to the 3 $^1$Hs at the 2 position.
3. Triplet. 3 equivalent protons. Split (1:2:1) because coupled to the 2 $^1$Hs at the 3 position.

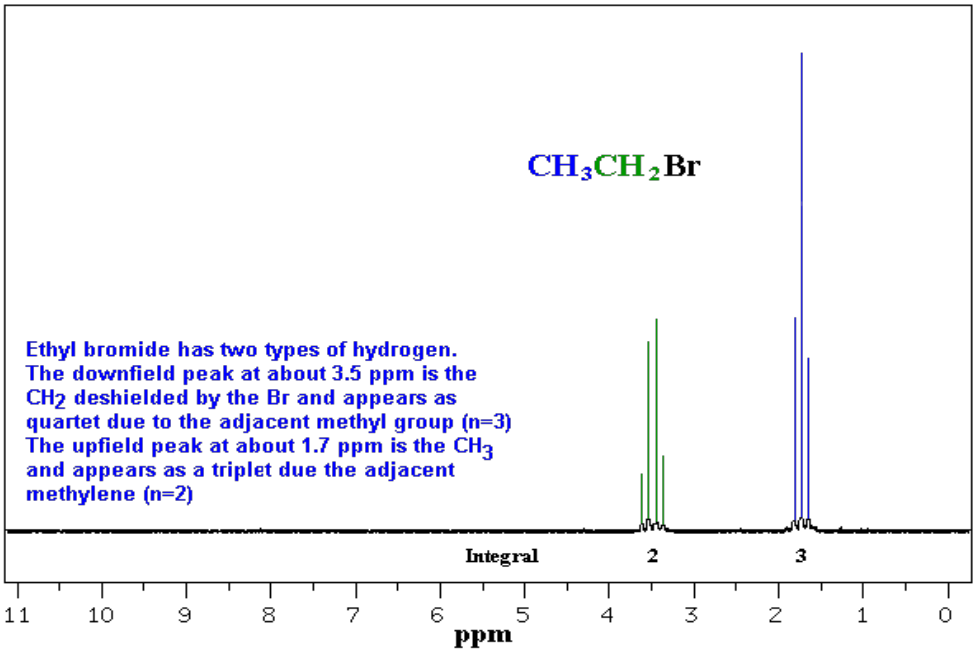
5

## n+1 rule:-

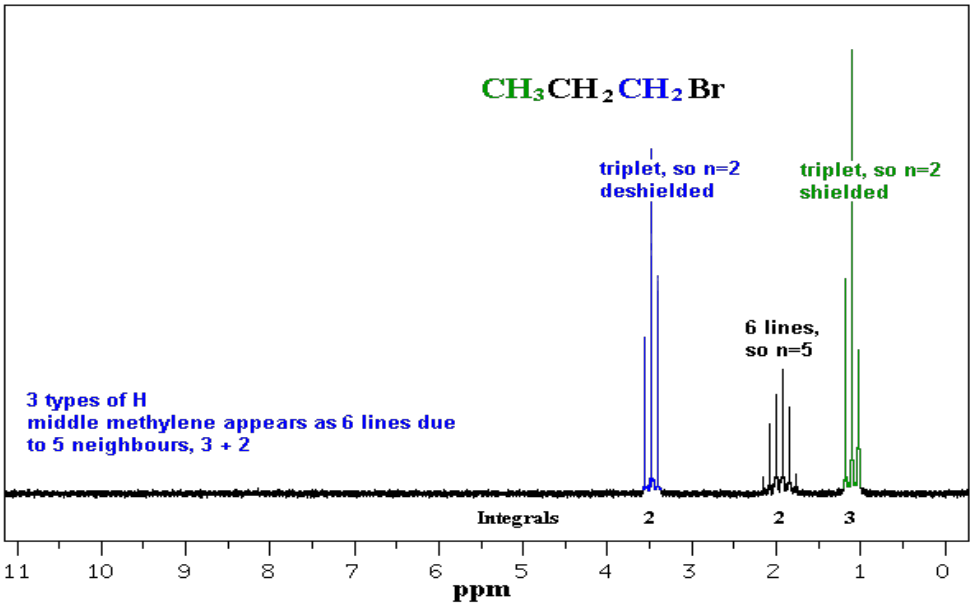
- The multiplicity of signal is calculated by using n+1 rule.
- This is one of the rule to predict the splitting of proton signals. This is considered by the nearby hydrogen nuclei.

Therefore, n= Number of protons in nearby nuclei

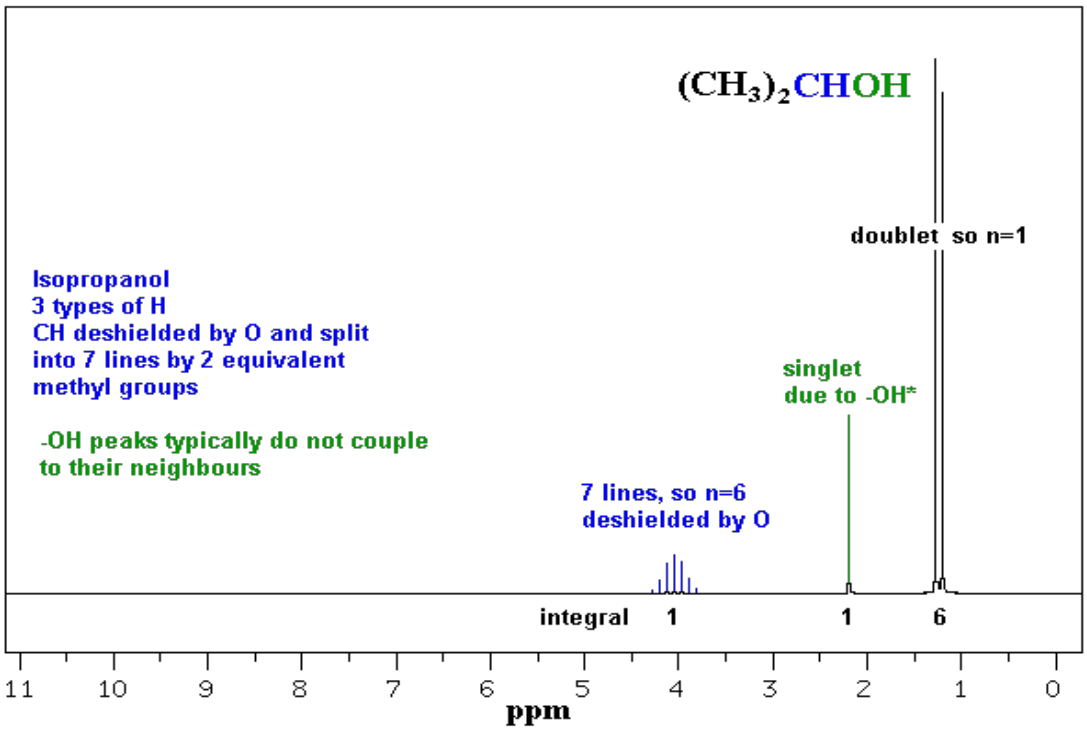
- Zero H atom as neighbour n+1=0+1=1(singlet)
- One H atom as neighbour n+1=1+1 = 2(doublet)
- Two H atom as neighbour n+1=2+1 =3(triplet)

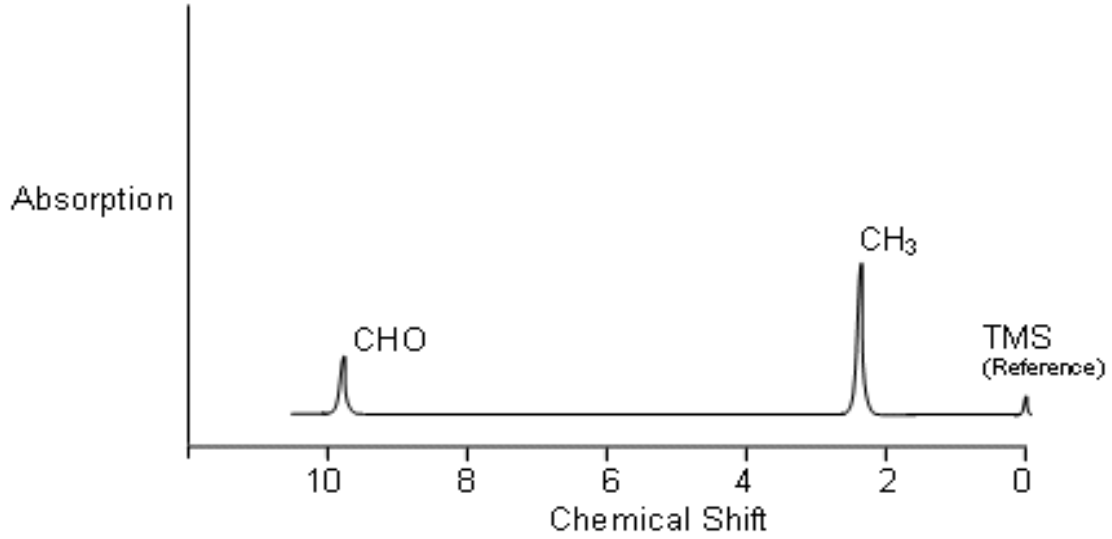



From the above NMR spectrum of ethyl bromide has two types of signals are two type protons that is methyl and methylene. A triplet signal at 1.70 ppm is due to the up field protons of methyl and a quartet peak appears at 3.5ppm is due to downfield of methylene protons

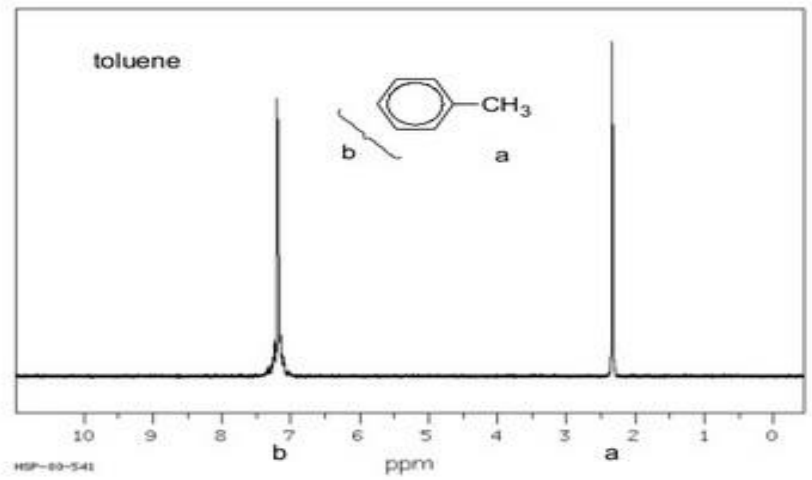


In case of 1-Bromopropane shows three types of signals that is triplet for methyl protons obtained a signal at 1.25ppm and methylene shows multiplates (6 lines )signals at 2.00ppm due to the neighbours 3+2 protons (middle CH2). The deshielded methylene signals shows peaks at 3.55ppm near to the Br group.

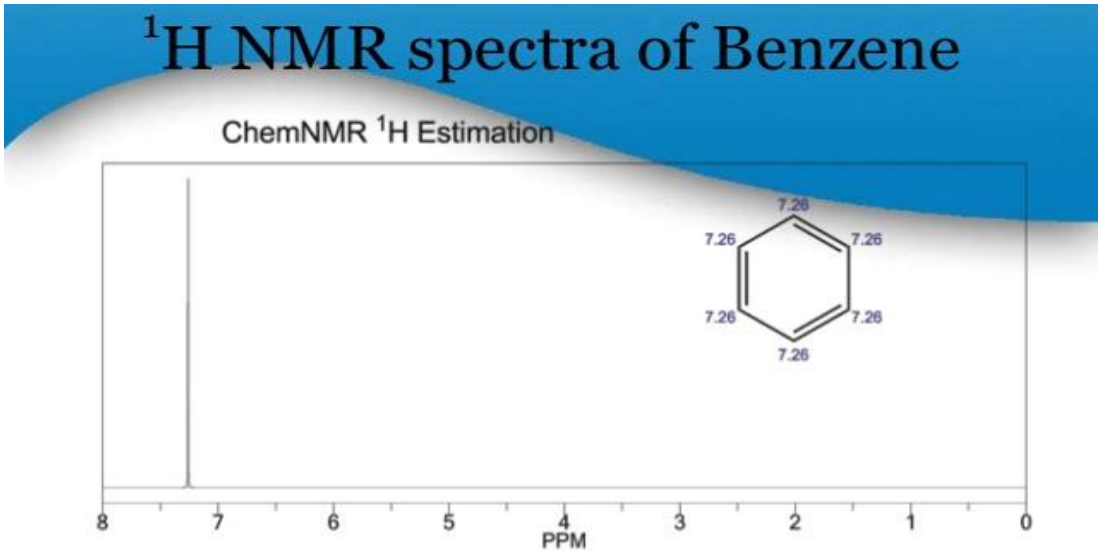


From the PMR spectra of Acetaldehyde have two types non equivalent proton a sharp signals of methyl at 2.32ppm and aldehyde signals at 9.92ppm.




From the NMR spectrum of toluene shows two type signals at 7.32ppm is due to the aromatic proton and a sharp signal at 2.45ppm in due the methyl proton these is due the non equivalent protons.




- Aromatic Hydrogen shows peak in the chemical shift scale 6.5-8.0 ppm.
- From the above spectrum Benzene has same type of protons and it shows single peak at 7.26

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**PPT**

# Introduction:-

Nuclear Magnetic Resonance (NMR) is a spectroscopy technique which is based on the absorption of electromagnetic radiation in the **radio frequency region 4 to 900 MHz** by nuclei of the atoms.

Proton Nuclear magnetic resonance spectroscopy is one of the most powerful tools for elucidating the number of hydrogen or proton in the compound.

It is used to study a wide variety of nuclei:

- $^{1}H$ $^{15}N$
- $^{19}F$ $^{19}F$
- $^{13}C$ $^{31}P$

Page 3

# Theory of NMR:-

Spin quantum number (I) is related to the atomic and mass number of the nucleus.

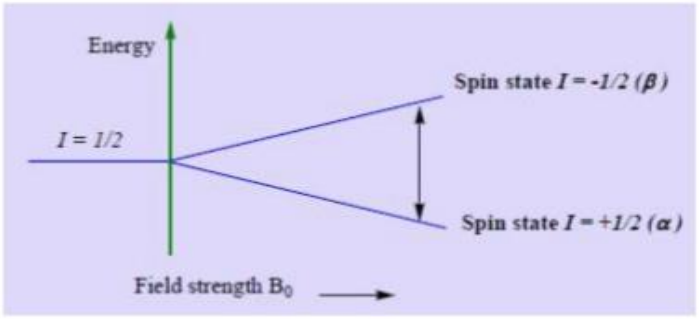
| I | Atomic Mass | Atomic Number | Examples | |
|---|---|---|---|---|
| Half-integer | Odd | Odd | $^{1}H$ (1/2) | NMR active |
| Half-integer | Odd | Even | $^{13}C$ (1/2) | |
| Integer | Even | Odd | $^{2}H$ (1) | |
| Zero | Even | Even | $^{12}C$ (0) | Not NMR active |

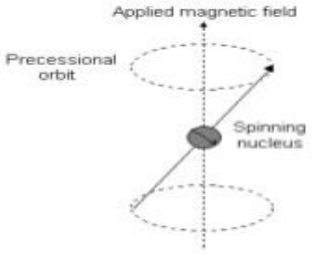
Elements with either odd mass or odd atomic number have the property of nuclear "spin".

Page 4

If an external magnetic field is applied, the number of possible orientations calculated by **(2I+1).**

Hydrogen has spin quantum number **I=1/2** and possible orientation is (2*1/2+1=2) two **+1/2** and **-1/2.**

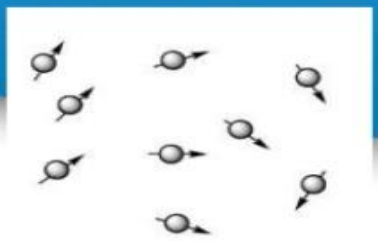



Page 5

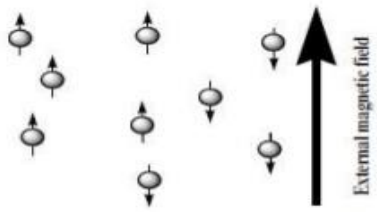
## Principles of NMR

The theory behind NMR comes from the spin of a nucleus and it generates a magnetic field. Without an external applied magnetic field, the nuclear spins are random in directions.



No external magnetic field

But when an external magnetic field($B_o$), is present the nuclei align themselves either with or against the field of the external magnet.

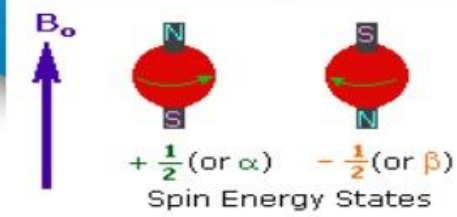


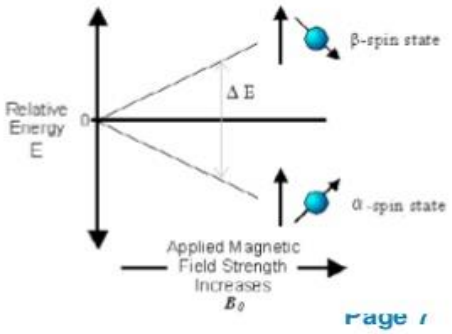

With external magnetic field

If an external magnetic field is applied, an energy transfer (ΔE) is possible between ground state to excited state.

when the spin returns to its ground state level, the absorbed radiofrequency energy is emitted at the same frequency level.

The emitted radiofrequency signal that give the NMR spectrum of the concerned nucleus.




Page 7

The emitted radio frequency is directly proportional to the strength of the applied field.

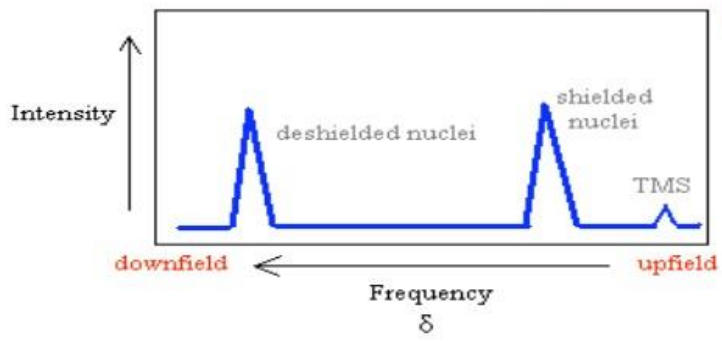
$$\nu = \frac{\gamma B_o}{2\Pi}$$

$B_o$ = *External magnetic field experienced by proton*

$\gamma$ = *Magnetogyric ratio ( The ratio between the nuclear magnetic moment and angular moment)*

Page 8

# NMR spectrum




The NMR spectrum is a plot of intensity of NMR signals VS magnetic field (frequency) in reference to TMS

Page 9

# Chemical shift

A **chemical shift** is defined as the difference in parts per million (ppm) between the resonance frequency of the observed proton and tetramethylsilane (TMS) hydrogens.

TMS is the most common reference compound in NMR, it is set at δ=0 ppm

$$\text{Chemical shift, } \delta = \frac{\text{frequency of signal} - \text{frequency of reference}}{\text{spectrometer frequency}} \times 10^6$$

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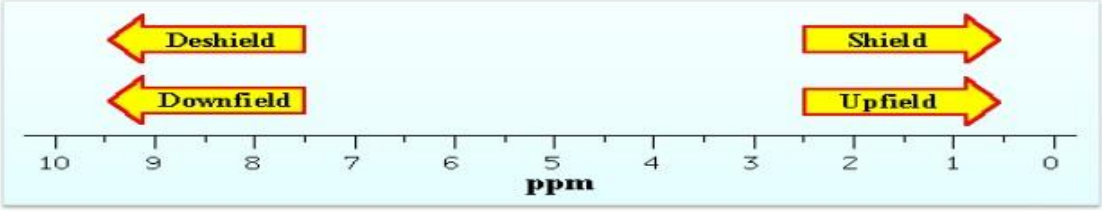
Shielding of protons:-

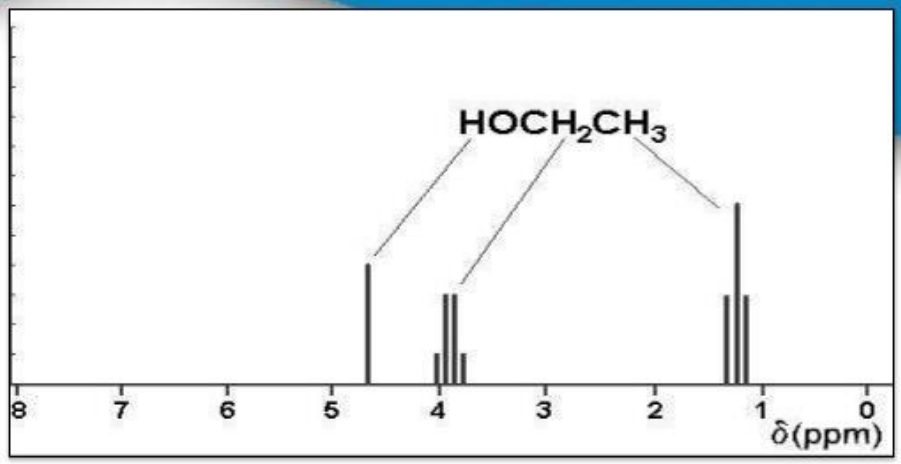
**High electron density** around a nucleus **shields** the nucleus from the external magnetic field and the signals are **upfield** in the NMR spectrum

Deshielding of protons:-

**Lower electron density** around a nucleus **deshields** the nucleus from the external magnetic field and the signals are **downfield** in the NMR spectrum




# Proton NMR spectra of Ethanol:-




$^1$H spectrum of Ethanol:-

3 types of proton

$CH_3, CH_2, OH$

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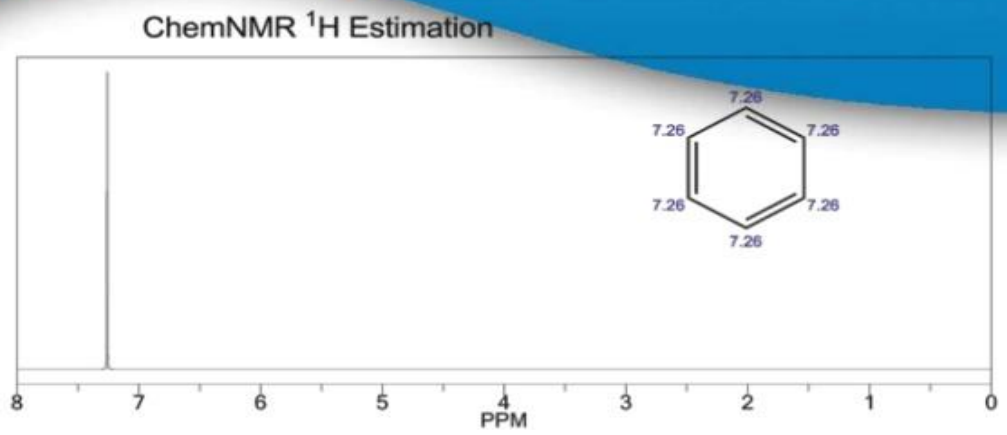
# $^1$H NMR spectra of Benzene




- Aromatic Hydrogen shows peak in the chemical shift scale 6.5-8.0 ppm.
- From the above spectrum Benzene has same type of protons and it shows single peak at 7.26

Page 22

# n+1 rule:-

❖ The multiplicity of signal is calculated by using n+1 rule.

❖ This is one of the rule to predict the splitting of proton signals. This is considered by the nearby hydrogen nuclei.

Therefore, n= Number of protons in nearby nuclei

➢ Zero H atom as neighbour n+1=0+1=1(singlet)

➢ One H atom as neighbour n+1=1+1 = 2(doublet)

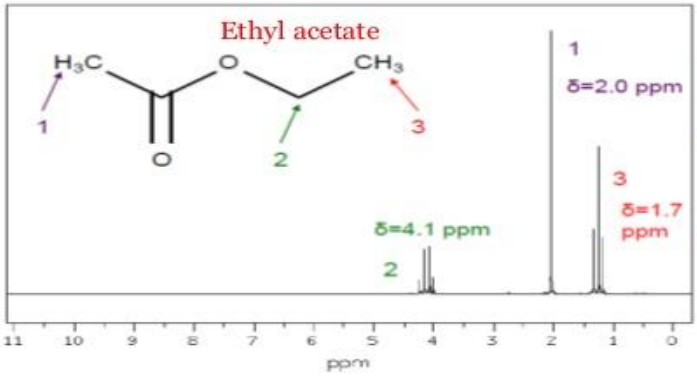
➢ Two H atom as neighbour n+1=2+1 =3(triplet)

Page 24

# Spin-spin coupling (splitting)

The interaction between the spins of neighbouring nuclei in a molecule may cause the splitting of NMR spectrum.This is known as spin-spin coupling or splitting.

The splitting pattern is related to the number of equivalent H-atom at the nearby nuclei.



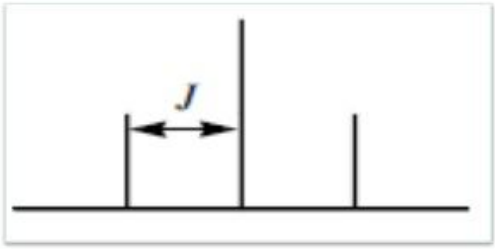

**Spin-Spin Splitting patterns**

1. Singlet. 3 equivalent protons. Not coupled to any neighboring protons.
2. Quartet. 2 equivalent protons. Split (1:3:3:1) because coupled to the 3 $^1$Hs at the 2 position.
3. Triplet. 3 equivalent protons. Split (1:2:1) because coupled to the 2 $^1$Hs at the 3 position.

5

# Coupling Constant

- The distance between the peaks in a given multiplet is a measure of the splitting effect known as coupling constant.
- It is denoted by symbol J, expressed in Hz.
- Coupling constants are a measure of the effectiveness of spin-spin coupling and very useful in $^1$H NMR of complex structures.

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## FACTORS INFLUENCING CHEMICAL SHIFT

➢ Both $^{1}H$ and $^{13}C$ Chemical shifts are related to the following major factors:

- ➢ Depends on Hydrogen bonding
- ➢ Depends on adjacent group
- ➢ Depends on carbon group attached
- ➢ Depends on hybridization
- ➢ Depends on anisotropy

# Location of Signals

**TABLE 13-2** Chemical Shifts of the Chloromethanes

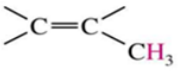
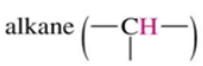
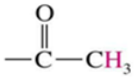
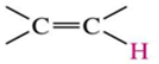
| Compound | Chemical Shift | Difference |
|---|---|---|
| $CH_4$ | $\delta 0.2$ | |
| | | 2.8 ppm |
| $CH_3Cl$ | $\delta 3.0$ | |
| | | 2.3 ppm |
| $CH_2Cl_2$ | $\delta 5.3$ | |
| | | 1.9 ppm |
| $CHCl_3$ | $\delta 7.2$ | |

*Note:* Each chlorine atom added changes the chemical shift of the remaining methyl protons by about 2 to 3 ppm. These changes are nearly additive.

- ➢ More electronegative atoms deshield more and give larger shift values.
- ➢ Effect decreases with distance.
- ➢ Additional electronegative atoms cause increase in chemical shift.

=>

# Typical Values

| Type of Proton | Approximate $\delta$ | Type of Proton | Approximate $\delta$ |
|---|---|---|---|
| alkane ($-CH_3$) | 0.9 |  | 1.7 |
| alkane ($-CH_2-$) | 1.3 | | |
| alkane  | 1.4 | Ph—H | 7.2 |
| | | Ph—$CH_3$ | 2.3 |
|  | 2.1 | R—CHO | 9–10 |
| | | R—COOH | 10–12 |
| —C≡C—H | 2.5 | R—OH | variable, about 2–5 |
| R—$CH_2$—X | 3–4 | Ar—OH | variable, about 4–7 |
| (X = halogen, O) | | R—$NH_2$ | variable, about 1.5–4 |
|  | 5–6 | | |

*Note:* These values are approximate, as all chemical shifts are affected by neighboring substituents. The numbers given here assume that alkyl groups are the only other substituents present. A more complete table of chemical shifts appears in Appendix 1.

**By SSK**

# Unit:Electromotive force

Electromotive force is the electrical action produced by a non-electrical source. A device that converts other forms of energy into electrical energy, such as a battery or generator, provides an emf as its output. Sometimes an analogy to water "pressure" is used to describe electromotive force.

Electromotive force (**emf**) is a measurement of the energy that causes current to flow through a circuit. It can also be **defined** as the potential difference in charge between two points in a circuit. Electromotive force is also known as voltage, and it is measured in volts.

**Irreversible cells** are those which require replacement of chemicals. when they give out electricity. ... **Reversible cells** are those in which **reversible** reactions are involved. these **cells** can brought back to their initial state by applying external potential difference. Example : Daniel **cell**.

- Irreversible cells are those which require replacement of chemicals.when they give out electricity. these cannot be recharged.

Examples :- Zinc cell

**Reversible cell**-a cell is said to be reversible if it satisfies three conditions:

1.If an opposing EMF equal to that of the cell is applied to the cell, no current should flow in the circuit and hence no chemical reaction should take place.

2.If an opposing EMF slightly (infinitesimally) smaller than that of the cell is applied,an infinitesimally small current should flow from the cell and infinitesimally small reaction should take place.

3. If an opposing EMF infinitesimally greater than that of the cell is applied, an infinitesimally small current should flow in the opposite direction and an infinitesimally small reaction in the reverse direction should occur.

For example: Daniell cell, consisting of a zinc electrode dipped in ZnSO4 solution and a copper electrode dipped in CuSO4 solution. When it is producting current,the reaction taking place in the cell is $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

**Irreversible cells**

Consider a cell consisting of a zinc rod and a silver rod dipped in dilute sulphuric acid. When the two rods are connected with a wire the reaction takes place.

$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$

i.e. zinc is oxidized to $Zn^{2+}$ ions and $H^+$ ions are reduced to $H_2$ gas. In other words, zinc dissolves at one electrode and $H_2$ gas is evolved at the other.

Now if the cell is connected to an external source of EMF whose EMF is slightly greater than that of the cell and is opposing the cell, silver dissolves at one electrode and $H_2$ gas is evoloved at the other.

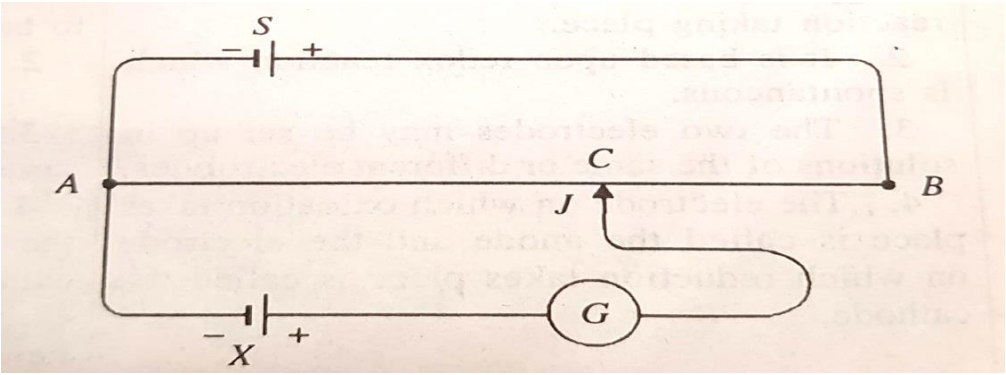
$2Ag + H_2SO_4 \rightarrow Ag_2SO_4 + H_2$

I,e.now oxidation takes place at the silver electrode and reduction takes place at the other. Thus condition of reversibility is not satisfied I,e the chemical change is not reversed instead, a new chemical reaction takes place. The cell is not reversible but it is irreversible.

**EMF of chemical cell and its measurement by potentiometer**.

Potentiometric method is based upon compensation principle,is used for the accurate measurement of EMF. In this method, the unknown EMF is opposed by another known EMF until the two are equal.The general principle involved may be explained with the help of beiow fig.

AB is a stretched wire of uniform thickness,S is a standard cell whose EMF is known. It is connected to the end A and B. X is a cell whose EMF is to be determined. One end of the cell X is connected to the end A and the other to the sliding contact J through the galvanometer G is such that it sends EMF in a direction opposite to that of the cell S. The sliding contact is moved along the wire AB till at a particular point, say C, no deflection is observed in the galvanometer. If $E_s$ represents the EMF of the standard cell S and $E_x$ that of the experimental cell,X then $E_x/E_s$=length AC/lengthAB or $E_x$ =length AC /length AB X $E_s$ Thus knowing $E_s$ , $E_x$ can be calculated.




**Weston standard cell**:

It consists of an H shaped glass vessel. One of the limbs contains mercury, covered with a paste of mercurous sulphate and mercury, crystals of solid $CdSO_4.8/3\ H_2o$ and saturated solution of cadmium sulphate. This limb acts as the anode. The other limb acts as the cathode contains cadmium amulgum covered with crystals of solid $CdSO_4.8\ /3\ H_2o$ and saturated $CdSO_4$ solution. Short Pt wires are sealed into the bottoms of the limbs to make contact with the active materials. Thelimbs are finally closed with corks and sealing wax. The purpose of placing solid crystals of $CdSO_4.8/3\ H_2o$ is to keep the $CdSO_4$ solution saturated at all temperatures.

The cell has a constant reproducible value of e. m. f. which does not change with time. Also the temperature coefficient of e. m. f. is very low.

The EMF of below cell is 1.0185 volt at $15^0$C and 1.0181 volt at $25^0$ C.

The reaction taking place in the cell is $Cd + Hg_2SO_4$ aq → $CdSO_4.8/3\ H_2o + 2Hg$

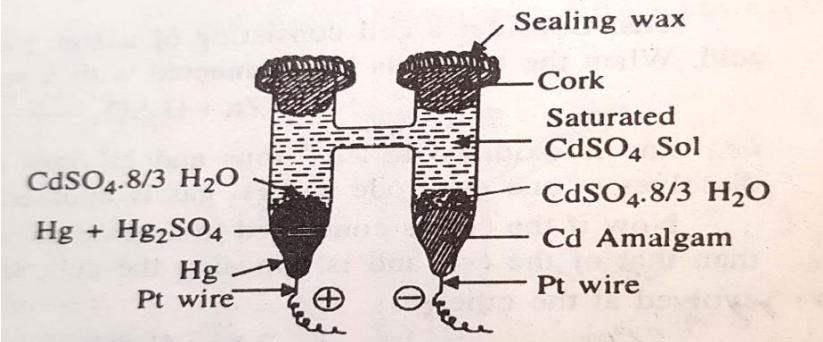



**Fig. 11·5.** Weston standard cell.

**Types of electrodes** ---------:**Reference electrode** : The potential of an unknown electrode can be obtained only by combining it with an electrode of known potential to make a cell. The EMF of this cell is determined and the potential of the unknown electrode is calculated. The electrode with a known potential used to determine the potential of unknown electrodes is called reference electrode. One of electrodes used as reference electrode is hydrogen electrode its electrode potential has been taken as zero.

But the use of hydrogen electrode as the reference electrode is not convenient because it involves the use of hydrogen gas. Hence the number of other electrodes have been used as reference electrodes. The most common out of these is the calomel electrode. The electrode potentials of the calomel electrode at$25^0$ C using 0.1N Kcl, 1.0N Kcl and saturated Kcl solution have been determined accurately. These are given as reduction potentials.

| Concentration of Kcl solution | Reduction potential |
|---|---|
| 0.1N | +0.3338volt |
| 1.0N | +0.2800volt |
| Saturated | +0.2415volt. |

To determine the electrode potential of any electrode , a cell using this as one of the electrode and calomel electrode as the second electrode is set up.

**Calomel Electrode** : (Hg- $Hg_2Cl_2$-kCl electrode): It is prepared as the pure mercury is placed at the bottom of a tube T (as shown in below fig.) It is covered with a paste of mercurous chloride (calomel) and then filled with either decinormal or normal or saturated solution of KCl from the side tube A such that the side tube B is also filled the KCl solution. A tube C having a piece of Pt wire sealed at its end

is fixed into the tube T Such that the Pt wire remains dipped into the mercury. A little mercury is placed in the tube C and a Cu wire put into it to make an electrical contact.

Oxidation can occur at this electrode through the following reactions:

$2Hg_{(l)} \rightarrow Hg_2^{2+} + 2e^{--}$

$Hg_2^{2+} + 2Cl^{--} \rightarrow - Hg_2Cl_{2(s)}$

Overall reaction is $2Hg_{(l} + 2Cl^{--} \rightarrow - Hg_2Cl_{2(s} + 2e^{--}$

Reduction can occur at this electrode as fllows:

$Hg_2Cl_{2(s)} \text{ ---.> } Hg_2^{2+} + 2Cl^{—}$

$Hg_2^{2+} + 2e^{--} \rightarrow 2Hg_{(l)}$

Overall reaction : $\text{--} \rightarrow - Hg_2Cl_{2(s} + 2e^{--} \rightarrow$ is $2Hg_{(l} + 2Cl^{--}$

This overall reaction is just the reverse of the overall reactin when oxidation takes place. Hence the calomel is reversible with respect to chloride ions.

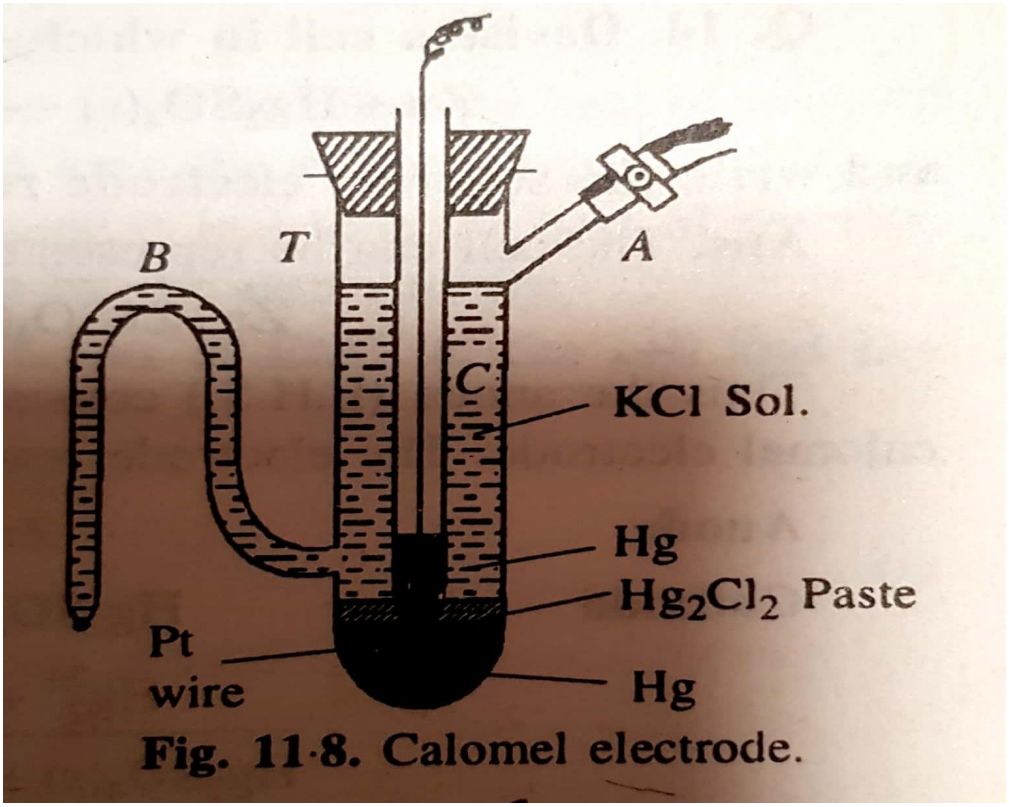


**Fig. 11·8. Calomel electrode.**

**Derivation of Nernst equation for emf of a cell** : Suppose the cell reaction in any reversible cell is represented by the general equation.

$aA + bB + - - - \text{----------} \rightarrow xX + yY + - - -$

The free energy change of this reaction is given by the equation

$$G = G^0 + RT \ln a^x_X \, . a^y_Y \ldots / a^a_A \, . \, a^b_B - - - \qquad \text{----------(1)}$$

Where $G^0$ represents the standard free energy change and $a_A$, $a_B$, $a_X$, and $a_Y$ represents the activities of A B X and Y respectively in any state other than the standard state at the state of equilibrium.

If the cell reaction involves transference of n moles of the electrons, this corresponds to the flow of nF faradays of electricity. If E is the EMF of the cell, then electrical energy produced in the cell = nFE. Since electrical energy produced is equal to the decrease in free energy of the cell reaction , we have

$$-G = nFE \qquad \text{----------(2)}$$

Similarly, for the standard state, we will have

$$-G^0 = nFE^0 \qquad \text{----------(3)}$$

Where $E^0$ is the standard EMF of the cell.

Substituting the values of G and $G^0$ from equations (2) and (3) in equation (1), we get

$$-nFE = -nFE^0 + RT \ln a^x_X \, . a^y_Y - - - / a^a_A \, . a^b_B - - -$$

$$\text{Or } E = E^0 - RT / nF \ln a^x_X \, . a^y_Y - - - / a^a_A \, . a^b_B - - - \qquad \text{----------(4)}$$

Thus knowing the cell reaction (so that n is known), and the standard EMF of the cell, the EMF of the cell for known activities of the various reactants and products can be calculated. Equation (4) is called Nernst equation for the calculation of EMF of cell.

When the concentrations are not very high, replacing activites by concentrations, equation (4) becomes

$$E = E^0 - RT / nF \ln [X]^x \, . [Y]^y - - - - / [A]^a \, . [B]^b - - - \qquad \text{----------(5)}$$

Substituting for R = 8.314 and F = 96500, at $25^0$ C I,e T = 298 K equation (5) changes to

$$E = E^0 - 0.0591 / n \ln [X]^x \, . [Y]^y - - - - / [A]^a \, . [B]^b - - - -$$

**Concentration cells**--- With and without transference.

Concentration cells –Cells in which the EMF produced is only due to the difference in the concentrations of the electrodes or that of the solutions of the electrolytes with which they are in contact are called

concentration cells. When the difference is in the concentration of the electrodes, the cells are called **electrode concentration cells**.When the difference is in the concentration of the electrolytes, the cells are called **electrolyte concentration cells**.

**electrolyte concentration cells are of two types**: 1.Electrolyte concentration cells without transference

2. Electrolyte concentration cells with transference

**Electrolyte concentration cells without transference**: Let us take the example of hydrogen concentration cell having different concentration of electrolytes

$H_2$(1atm) I $H^+$ (a1) II $H^+$ (a2) I $H_2$ (1atm)

On the left hand electrode, by convention, oxidation takes place I,e the electrode reaction is

½ $H_2$ (1atm) ----------→ $H^+$ (a1) + $e^-$ ----------(1)

To apply Nernst equation, this reaction may be written as reduction half cell reaction as

$H^+$ (a1) + $e^-$ ----------→½ $H_2$ (1atm) (n = 1)

Therefore electrode potential of the left hand electrode will be

$E_1 = E^0_{H^+,H2}$ -- RT / nF ln 1/ a1 [$a_{H2} = 1$ ]

= = $E^0_{H^+,H2}$ + RT / nF ln a1

= RT / F ln a1 [ $E^0_{H^+,H2} = 0$ ] --------(2)

On the right hand electrode, by convention, reduction takes place I,e the electrode reaction is

$H^+$ (a2) + $e^-$ ----------→ ½ $H_2$ (1atm) ----------(3)

By Nernst equation, the EMF of this electrode will be

E2 = 8 RT / F ln a2 ----------(4)

The overall reaction is obtained by adding the reactions (1) and (3) this gives

$H^+$ (a2) ----------→ $H^+$ (a1) ----------(5)

The EMF of the cell is given by the expression

E = E2 – E1

=RT / F ln a2 -- RT /F ln a1

E= RT / F ln a2 / a1 ---------- (6)

From equation 5 it is obvious that for 1 faraday of electricity to be produced. There is a transfer of 1 mol of $H^+$ ions from solution having activity a2 to the solution having activity a1 The transfer takes place through the salt bridge. Secondly from equation 6 it is clear that for EMF to be + ve a2 must be greater than a1.

**. Electrolyte concentration cells with transference**: Consider the cell

$H_2$ (1atm) IHCl (a1) : HCl( a2) l $H_2$ (1atm)

**Processes taking place at the electrodes** : By convention, oxidation takes place on the left hand electrode. ½ $H_2$ (1atm) ----------→ $H^+$ (a1) + $e^-$

Reduction takes place on the right hand electrode

$H^+$ (a2) + $e^-$ ----------→ ½ $H_2$ (1atm)

The sum of the two electrode reactions gives

$H^+$ (a2) ----------→ $H^+$ (a1) ----------(1)

**Processes taking place at the liquid junction** : Electrons flow in the external circuit from left to right. However as $H^+$ ions are produced in the left electrode and $Cl^-$ ions in right electrode, the inner circuit is completed by the transference of $Cl^-$ ions from right to left and the transference of of $H^+$ ions from

left to right across the liquid junction.

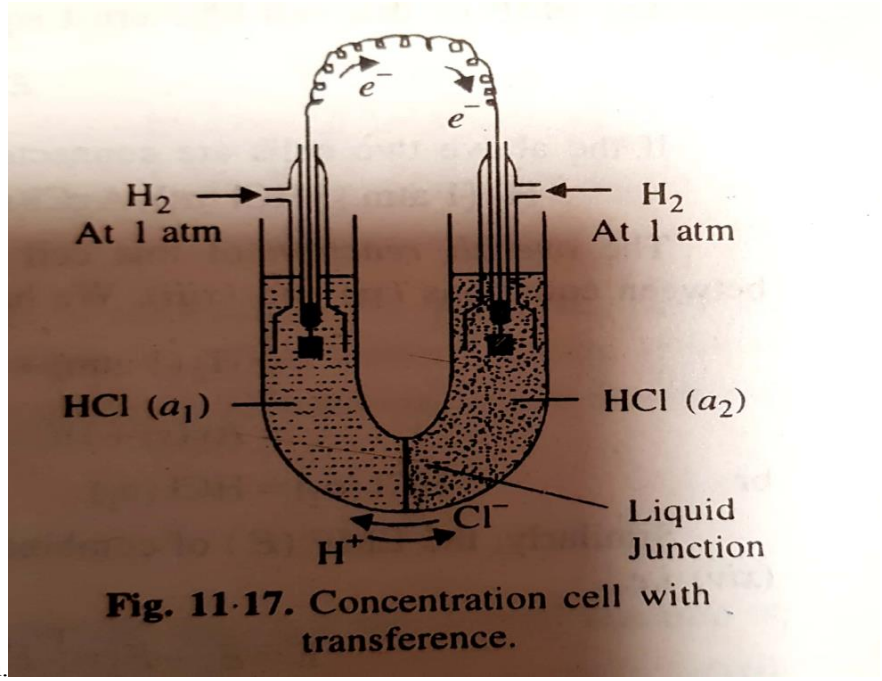



**Fig. 11·17. Concentration cell with transference.**

If the trancef0rt number of $CI^-$ is represented by $t^{--}$, then for one faraday of electricity passing through the cell, $t^-$ gram equivalents of the $CI^-$ ions will be transferred from right to left I,e.

$t_{---} Cl^{--} (a2)$ ----------→ $t_{---} Cl^{--} (a1)$ ----------(2)

Further transport number of $H^+$ ions = $1 - t_{--}$ . Therefore during the same time , $( 1 - t_{--} )$ gram equivalents of $H^+$ ions will be transferred from left to right.

$( 1 - t_{--} ) H^+ (a1)$ ----------→ $( 1 - t_{--} ) H^+ (a2)$ ----------(3)

The overall reaction is , Adding equations 1, 2 and 3 we get,

$$H^+ (a2) + t_{---} Cl^{--} (a2) + ( 1 - t_{--} ) H^+ (a1) = H^+ (a1) + t_{---} Cl^{--} (a1) + ( 1 - t_{--} ) H^+ (a2)$$

Or $H^+ (a2) + t_{---} Cl^{--} (a2)$ -- $( 1 - t_{--} ) H^+ (a2)$ = = $H^+ (a1)$ + $t_{---} Cl^{--} (a1)$ -- $( 1 - t_{--} ) H^+ (a1)$

Or $t_{--} HCl (a2) = t_{—}HCl (a1)$ ----------(4)

Applying Nernst equation to the process 4 , The EMF of the cell is given by

$E = --RT / F \ln a_1^{t--} / a_2^{t—}$

$= t_{—}RT /F \ln a2/a1$ ----------(5)

Here for EMF to be + ve, a2 must be greater than a1.

Replacing the activities of the electrolytes by the molalities and activity coefficients of the ions, we have

$$E = t_{--} RT/F \ln m_2^2 r_2^2 / m_1^2 r_1^2$$

$$= 2\, t_{--} RT/F \ln m_2 r_2 / m_1 r_1$$

Thus the EMF of such a cell can be calculated if we know molalities, activity coefficients and transport number of ions.

**Liquid junction potential** : The potential set up at the junction of the two solutions because of the difference in the speeds of the ions moving across the boundary is called liquid junction potential.

**Expression for liquid junction potential:** According to EMF of electrolyte concentration cell without transference $E_1 = RT/F \ln a2/a1$ or $E_1 = RT/F \ln m_2 r_2 / m_1 r_1$ ----------(1)

Acc0rding to EMF of electrolyte concentration cell with transference $E_2 = 2\, t_{--} RT/F \ln m_2 r_2 / m_1 r_1$ =

$$E_j = E_2 - E_1$$

$$= 2\, t_{--} RT/F \ln m_2 r_2 / m_1 r_1 - RT/F \ln m_2 r_2 / m_1 r_1$$

$$= (2t_{--} - 1)\, RT/F \ln m_2 r_2 / m_1 r_1$$

Also, since $t_+ + t_{--} = 1$

Therefore $(2t_{--} - 1) = t_{--} + (t_{--} - 1) = t_{--} + (-t_+)$

$= t_{--} - t_+$ ----------(2)

Hence equn 2 may be written in the form

$E_j = (t_{--} - t_+)\, RT/F \ln m_2 r_2 / m_1 r_1$

**Applications of EMF measurements:1.** Determination of $p^H$ using different electrodes.

1.Hydrogen electrode 2. Quinhydrone electrode 3. Glass electrode.

**1.Hydrogen electrode**: The electrode reaction, written as reduction reaction, is

$$H^+ + e^- \longrightarrow \tfrac{1}{2} H_2 \text{ (1atm)}$$

By Nernst equation, the potential of this electrode is given by

$$E_{H^+, H2} = E^0_{H+, H2} + RT/F \ln [H^+]$$

$$= E^0_{H+, H2} + 0.0591 \log [H^+] \text{ at } 25^0C$$

$= 0.0591 \log [H^+]$ [as $E^0_{H+,H2} = 0$ ]

$= -- 0.0591\ p^H$ [as $-\log[H^+] = pH$ ]

When the hydrogen electrode is combined with the calomel electrode, oxidation takes place at the hydrogen electrode and reduction at the calomel electrode. Hence by convention, the cell may be written as

Pt, $H_2$ (1atm) l $H^+$(unknown conc.) ll KCl(saturated) l$Hg_2 Cl_2$ (s) l Hg

EMF of this cell is given by

E = Electrode potential of R. H. S. electrode -- Electrode potential of L. H. S. electrode

$= 0.2415 -- (--0.0591P^H)$

$=0.2415 + 0.0591\ P^H$

Or $P^H = E - 0.2415 / 0.0591$

**2. Using quinhydrone electrode**: Quinhydrone is a equimolar amounts of quinine. and hydroquinone The working of the quinhydrone electrode is based upon the fact that quinine is reduced to hydroquinone ions I e, $C_6 H_4O_2 + 2e^{--}$ ----------→ $C_6 H_4O_2^{2--}$

Quinone Hydroquinone ion

And the hydroquinone ions combine reversibly with the $H^+$ ions to form hydroquinone I,e,

$C_6 H_4O_2^{2--} + 2H^+$ <----------→ $C_6 H_6O_2$

So that the overall reaction is , $C_6 H_4O_2 + 2e^{--} + 2H^+$ <----------→ $C_6 H_6O_2$

If quinine is represented by Q , and Hydroquinone is represented by $Q H_2$. So the above reaction may be written as $Q + 2 H^+ + 2e^{--}$ <----------→$QH_2$

Thus if a Pt wire is dipped in to a solution containing $H^+$ ions and a pinch of a quinhydrone , it can acts as a reversible electrode . The reaction as written above is reduction reaction. Applying Nernst equation, The electrode potential of the above electrode is given by

$E_Q = E^0_Q -- RT / 2F \ln [Q H_2] /[Q] [H^+]^2$ [ n = 2 for the above reaction]

Since quinhydrone is an equimolar mixture of Q and $QH_2$ , taking $[Q] = [QH_2]$ i.e,putting $[Q H_2] /[Q]=1$, in the above equation, we get

$E_Q = E^0_Q -- RT / 2F \ln [1 / [H^+]^2$

$E_Q = E^0_Q + RT / F \ln [H^+]$

$= E^0_Q + 2.303RT \log [H^+] / F$

$= E^0_Q + 0.0591 \log [H^+]$ at $25^0C$

$= E^0_Q - 0.0591\ P^H$

The Stnd electrode potential $E^0_Q$ of the quinhydrone electrode has found to be 0.6996 volt. Hence we may write $E_Q = 0.6996 - 0.0591\ P^H$

When the quinhydrone is combined with calomel electrode, oxidation takes place at the calomel electrode and reduction at the quinhydrone electrode. Hence by convention, the cell may be written as

Hg l $Hg_2\ Cl_2$ (s) l KCl (saturated) ll $H^+$ (unknown conc) l Q l Q $H_2$ l Pt

EMF of this cell is given by

E = Electrode potential of R. H. S. electrode -- Electrode potential of L H. S. electrode

$= (0.6996 - 0.0591\ P^H) - 0.2415$

$= 0.4581 - 0.0591\ P^H$

$P^H = 0.4581 - E / 0.0591$

After measuring the EMF (E) of the cell potentiometrically, the $P^H$ of the solution can be calculated.

**3. Using glass electrode** : If two solutions of different $P^H$ are present on the two sides of the glass surface, a potential is established across the glass membrane whose magnitude dependes upon the difference in the $P^H$ of the two solutions . For a particular variety of a glass, if on one side of the glass surface, a solution of fixed $P^H$ value is placed, the potential developed across the glass membrane will depend only upon the $P^H$ of the other solution, placed in contact with the other side of the glass surface. Thus the assembly obtained is called a glass electrode. As shown in fig.

A tube of special variety of glass is taken which has low melting point and high electrical conductivity. At the end of this tube is blown a glass bulb having a very thin wall . This is filled with a solution of constant $P^H$ . To make the electrical contact with the solution . a Pt wire is dipped into this solution, the other end of which is attached to a terminal.

The electrode potential of the glass electrode, is given by the equation

$E_G = E^0_G + 0.0591 \log [H^+]$ at $25^0C$

$= E^0_G - 0.0591\ P^H$ ----------(1)

Where $E^0_G$ is a constant depending upon the nature of the glass and the $P^H$ of the solution taken in side the glass tube . To determine the value of $E^0_G$ for a particular glass electrode, the value of $E_G$ is determined for a solution of known $P^H$ value.

To determine the value of $E_Q$ , the glass electrode is combined with the calomel electrode and the EMF of the resulting cell is measured.

The cell may be represented as

Glass electrode l Experimental solution l calomel electrode.

EMF of this cell will be

$$E = E_C - E_G \qquad \text{----------(2)}$$

Where $E_C$ is the electrode potential of the calomel electrode whose value depends upon the concentration of KCl solution used.

From equn 2 , $E_G = E_C - E$

Combining this result with equn 1, we get

$E_C - E = E^0_G - 0.0591\ P^H$

Or $P^H = E^0_G - E_C + E / 0.0591$

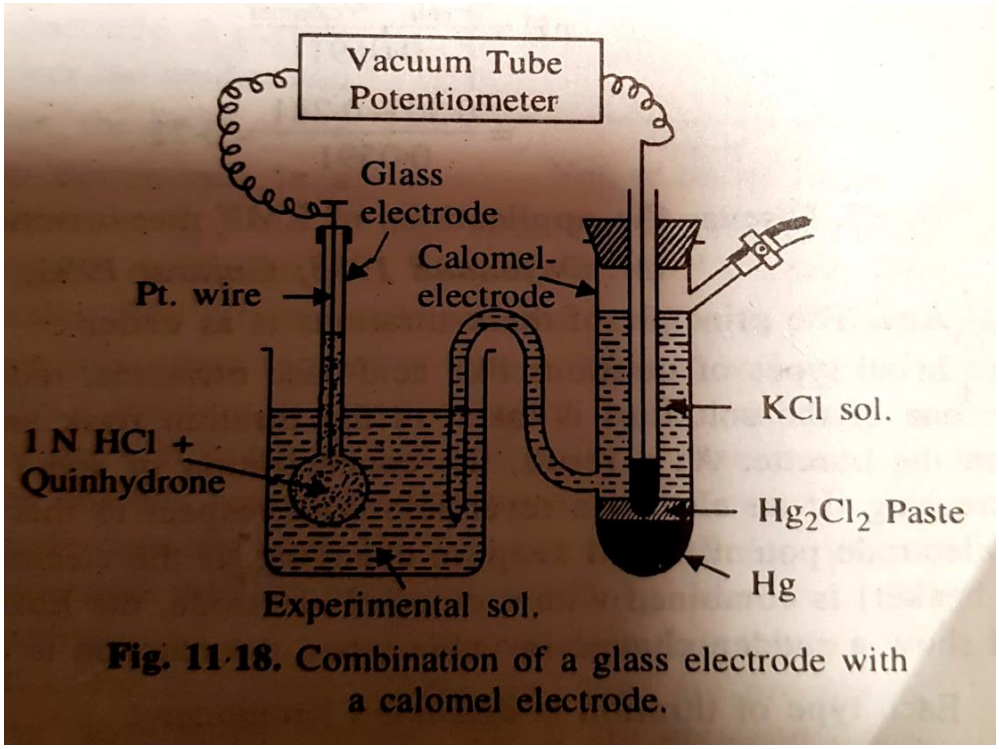



**Fig. 11·18. Combination of a glass electrode with a calomel electrode.**

**2. Potentiometric titrations** : (a) Acid Base titrations. (b) Redox titrations

(**a) Acid Base titrations** : the solution of HCl acid is to be titrated against NaOH solution The acid solution is taken in a beaker and a hydrogen electrode (quinhydrone or glass or hydrogen gas ) is set up into it. This electrode is then coupled with the calomel electrode. A burette containing the NaOH solution is fitted over the beaker. NaOH solution is added to the beaker first in the larger amounts and then in a very small amounts near the end point. EMF of the cell is noted after each addition. The EMF is then plotted against the volume of NaOH added when a maximum peak is obtained From this peak the volume of NaOH solution used corresponding to the equivalence point can be found.

(**b) Redox titrations :** Suppose a solution of ferrous sulphate is to be titrated against potassium dichromate ($K_2 Cr_2 O_7$ )solution. The ferrous sulphate solution is taken into a beaker and a Pt wire is inserted into it. The electrode thus formed is combined with the calomel electrode. A burette containing potassium dichromate solution is fixed over the beaker and after every addition of

potassium dichromate solution, the EMF of the cell is noted. The end point is then determined in a manner similar to that of acid base titrations.

By Laxmi R Ankalagi

## Photochemistry

Introduction:

Photochemistry is defined as that branch of chemistry which deals with the process involving emission or absorption of radiation. Two types of reactions are studied under photochemistry namely

1. Photo physical processes or reactions
2. Photochemical processes or reactions

1.**Phtophysicalprocessesorreactions** : These processes takes place in the presence of light but do not involve any chemical reactions. These processes takes place due to absorption of light by the substances followed by the emission of absorbed light. If there is instantaneous emission of the absorbed light the process is called as fluorescence. If high amount of energy is absorbed the electrons may leave the atoms completely such a process is called photoelectric effect. Photophysical processes include fluorescence, phosphorescence and photoelectric effect.

2. **Photochemicalprocessesorreactions**: These are the reactions that takes place by absorption of radiations of suitable wavelength. In such processes the absorbed light energy is first stored in the molecule and then it is further

used to bring about the reaction. Examples of photochemical reactions are

1. Reaction between hydrogen and chlorine

$H_2(g) + Cl_2(g) \xrightarrow{\text{light.}} 2HCl(g)$

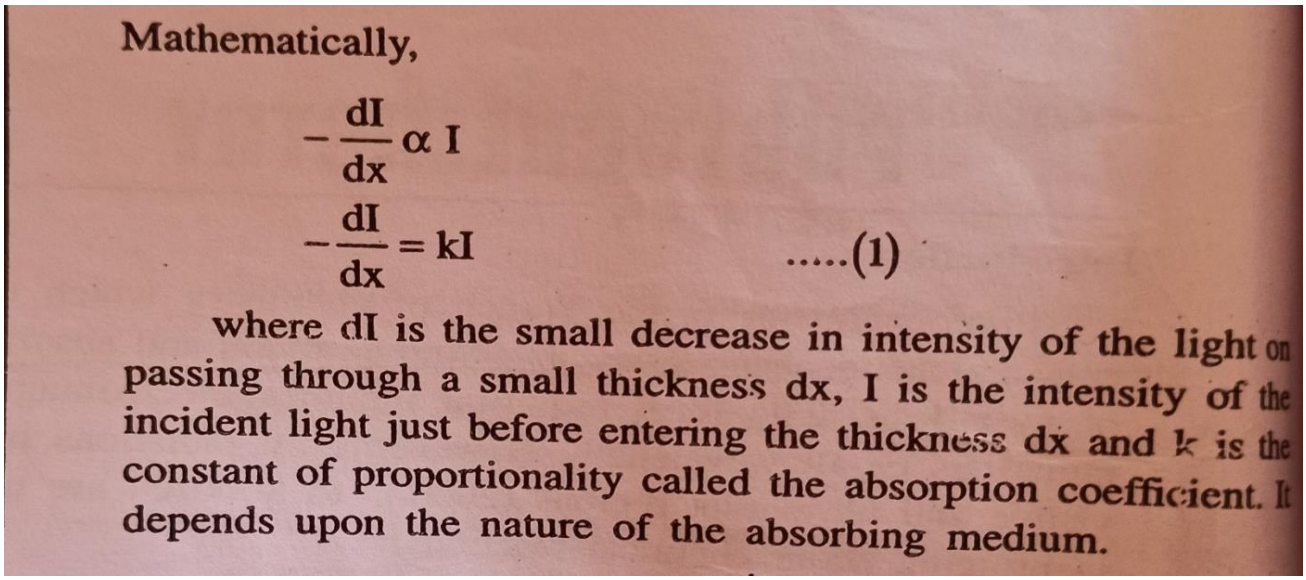
2. Photosynthesis of carbohydrates in plants taking place in presence of chlorophyll the green colouring matter present in the leaves

$6CO_2 + 6H_2O \xrightarrow{\text{light}} C_6H_{12}O_6 + 6O_2$

Glucose

**Lawsofphotochemistry**:

1.**Lambert's law** : This law states that when a monochromatic light is passed through a pure homogenous medium the decrease in the intensity of light with thickness of absorbing medium at any point x is proportional to the intensity of the incident light. Mathematically, the law can be represented as follows.



Mathematically,

$$-\frac{dI}{dx} \propto I$$

$$-\frac{dI}{dx} = kI \qquad \ldots\ldots(1)$$

where dI is the small decrease in intensity of the light on passing through a small thickness dx, I is the intensity of the incident light just before entering the thickness dx and k is the constant of proportionality called the absorption coefficient. It depends upon the nature of the absorbing medium.

2.**Beer'sLaw** : This law states when a monochromatic light is passed through a solution, the decrease in the intensity of the light with thickness of solution is directly proportional not only to the intensity of incident light but also to the concentration of the solution. mathematically we have ,

$$-\frac{dI}{dx} \propto I \times c \qquad \ldots(i)$$

or $$-\frac{dI}{dx} = \varepsilon Ic$$ ($\varepsilon$ is pronounced as epsilon)

where ε is a constant of proportionality and is called **molar absorption coefficient.** Its value depends upon the nature of the absorbing solute and the wavelength of the light used.

3. **Beer** – **Lambert'slaw** : This law states that when a beam of monochromatic light passes through a solution, the rate of decrease of intensity of radiation with thickness of absorbing solution is proportional to the intensity of incident radiation and the concentration of the solution.

   Mathematically this law can be represented as follows

x

ent.

Mathematically,

$$-\frac{dI}{dx} \propto Ic$$

$$-\frac{dI}{dx} = k' Ic \qquad \ldots\ldots\ldots(1)$$

where dI is the small decrease in intensity of the light on passing through a small thickness dx, I is the intensity of the incident light just before entering the thickness dx and c is the concentration of the solution. k' is the constant of proportionality called the molar absorption coefficient. Its value depends upon the nature of the absorbing solution and the wavelength of light used.

4 .**Grotthuslaw ( firstlawofphotochemistry**) : This law states that when a light falls on a body a part of it is reflected, a part of it is transmitted and the rest of is absorbed.it is only the absorbed light which is effective in bringing about a chemical reaction.

This law however does not imply that the absorbed light must always result into chemical reaction. The absorbed light may be simply bring about phenomenon such as fluorescence, phosphorescence etc. Similarly the absorbed light energy may be simply converted into thermal enenergy. for example in case of potassium permanganate solution, the light energy is absorbed strongly but no chemical effect is produced. Further in some cases it is observed that the light energy may not be absorbed by the reacting substance directly but may be absorbed by some other substances present along with the reacting substance. The energy thus absorbed is then passed on to the reacting substance which then starts reacting.This process is called photosensitisation.photosynthesis of carbohydrates in plants where chlorophyll acts as photosensitizer is a prominent example of photosensitization

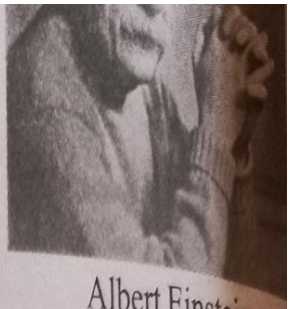
5.**Einsteinlawofphotochemicalequivalence**( **secondlawofphotochemistry**) : This law states that every atom or molecule that take part in a photochemical reaction absorbs one quantum of radiation to which the substance is exposed.

If v is frequency of absorbed radiation, then the energy absorbed by each reacting atom or molecule is one Quantum. I.e hv where h is planck's constant. The energy absorbed by one mole of the reactant molecule is given

$$E = Nhv \quad \ldots (i)$$

where $N$ is Avogadro's number

Putting $v = \frac{c}{\lambda}$, we can write $E = Nh\frac{c}{\lambda}$ ... (ii)



Albert Einstein

where $c$ is the velocity of light and $\lambda$ is the wavelength of the absorbed radiation.

*The energy possessed by one mole of photons or the energy absorbed by one mole of th reaching molecules is called one Einstein*

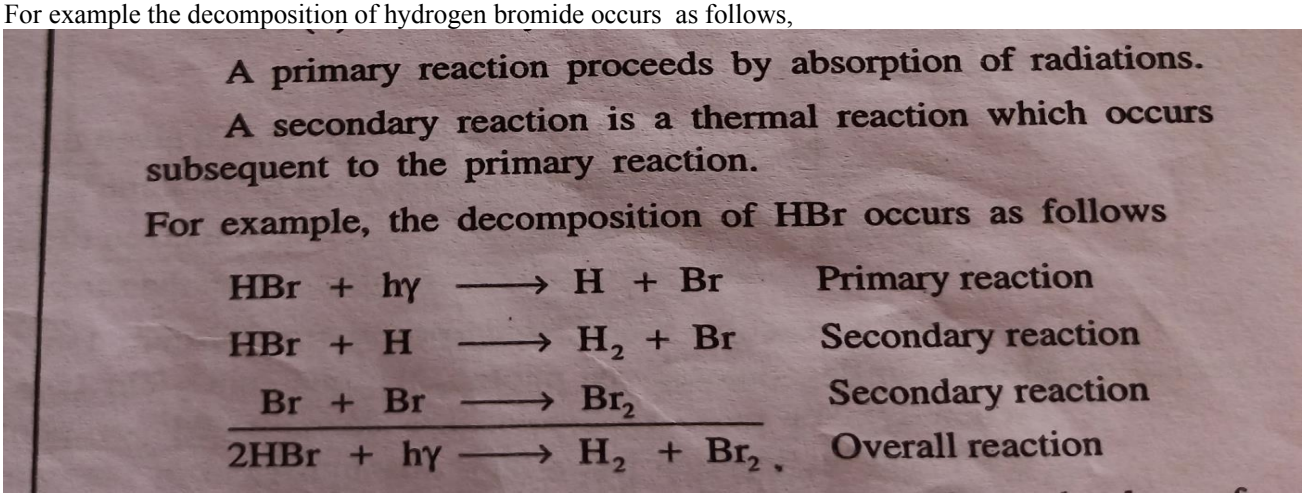
**Primaryandsecondaryreactions**.:

According to Einstein's law of photochemical equivalence, every reacting molecule absorbs one quantum of radiation and clearly the number of reactant molecules should be equal to the number of quanta absorbed.But it is not fully true and in many cases it has been observed that a small amount of light absorbed can bring about a large amount of reaction and in some cases a large amount of light absorbed brings about only a small amount of reaction this can be explained as follows the overall photochemical reaction main consists of.

1. Primary reaction
2. Secondary reaction

1. **Primaryreaction** : Primary reaction is a one which proceeds by absorption of radiation.
2. **Secondaryreaction** : secondary reaction is one which occurs subsequent to the primary reaction.

For example the decomposition of hydrogen bromide occurs as follows,



A primary reaction proceeds by absorption of radiations.

A secondary reaction is a thermal reaction which occurs subsequent to the primary reaction.

For example, the decomposition of HBr occurs as follows

$HBr + h\gamma \longrightarrow H + Br$ Primary reaction

$HBr + H \longrightarrow H_2 + Br$ Secondary reaction

$Br + Br \longrightarrow Br_2$ Secondary reaction

$2HBr + h\gamma \longrightarrow H_2 + Br_2$ Overall reaction

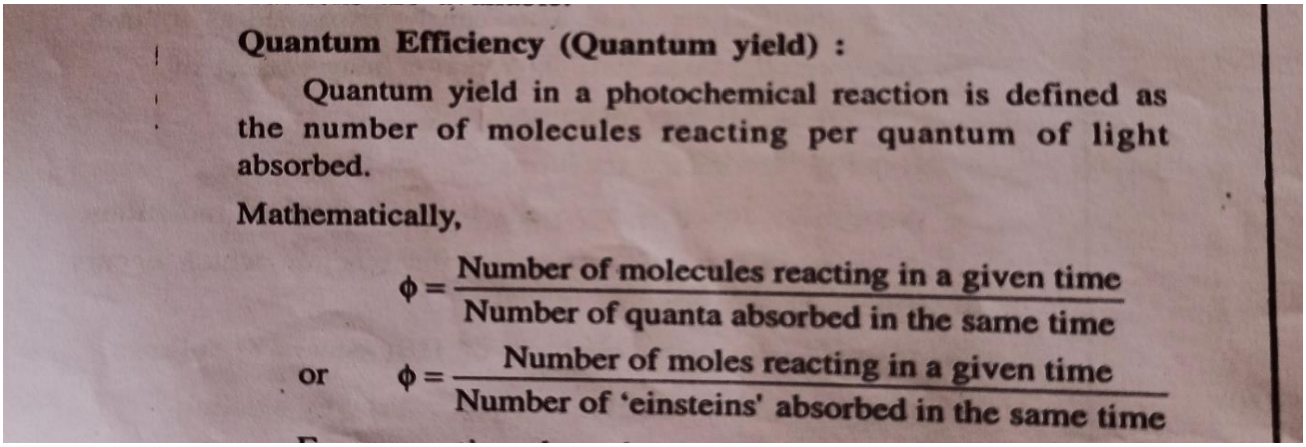
The primary reaction only obey the law of photochemical equivalence strictly but the secondary reactions have no concern with the law. In primary reaction ,the light radiation is absorbed by an atom mr1 a molecule to produce an excited atom or excited molecule. The formation of excited atom or molecule does not necessarily means that the reaction will takes place for only one molecule will react. In secondary reactions ,the excited molecule during the primary process may undergo one of the following changes to complete the reaction such as

- It me react to form the final product
- It can be partly or fully deactivated and no reaction occurs
- It may start a chine reaction.

It is important to note that secondary reactions may takes place in the dark provided the products of primary reactions are available.

**Quantumefficiency**or**Quantumyield** :

Quantum yield or Quantum efficiency in a photochemical reaction is defined as the number of molecules reacting per quantum of light absorbed. It is denoted by the symbol psi and can be mathematically expressed as



**Quantum Efficiency (Quantum yield) :**

Quantum yield in a photochemical reaction is defined as the number of molecules reacting per quantum of light absorbed.

Mathematically,

$$\phi = \frac{\text{Number of molecules reacting in a given time}}{\text{Number of quanta absorbed in the same time}}$$

or

$$\phi = \frac{\text{Number of moles reacting in a given time}}{\text{Number of 'einsteins' absorbed in the same time}}$$

For a reaction that o eye the Einstein'slaw.one molecule decomposes per photon ,the quantum yield is equal to 1. when two or more molecules are decomposes per photon then psi is greater then 1 and such reaction is said to be have high quantum efficiency or Quantum yield and if the number of molecules decompsed is less then 1 then the reaction is said to have low quantum efficiency.

**Highquantumefficiency** : In a photochemical reaction,if the no of molecules decompsed per photon of light absorbed is greater then 1 ,then the reaction is said to have high quantum efficiency.( If psi is greater then 1 )

Reasons for high quantum efficiency are

1.Reactions which takes place subsequent to the primary reactions.

2. A reaction chain forms many molecules per photon of light absorbed.

1. Reactions which takes place subsequent to primary reactions:

One photon absorbed in the primary reaction dissociates one molecule the reactant. But the excited atoms that results may start a subsequent secondary reaction in which a further molecule is decompsed. obviously ,one photon of radiation has decomposed two molecules,one in the primary reaction and another in the secondary reaction. Hence the two molecules are decompsed

for one photon of light absorbed hence the quantum efficiency or yield of the overall reaction is 2 hence it' results in high quantum efficiency.

$AB + hv \rightarrow A + B$ ( Primary reaction)

$AB + A \rightarrow A_2 + B$ ( secondary reaction)

2.A reaction chain forms many molecules per photon of radiation absorbed.:

When there are two or more reactants,a molecule of one of them absorbs a photon and dissociates causing primary reaction.The excited atom that is produced starts a secondary reaction chain so that it results in high quantum efficiency.

$A_2 + hv. \rightarrow 2A$

$A + B_2 \rightarrow AB + B$

$B + A_2 \rightarrow AB + A$

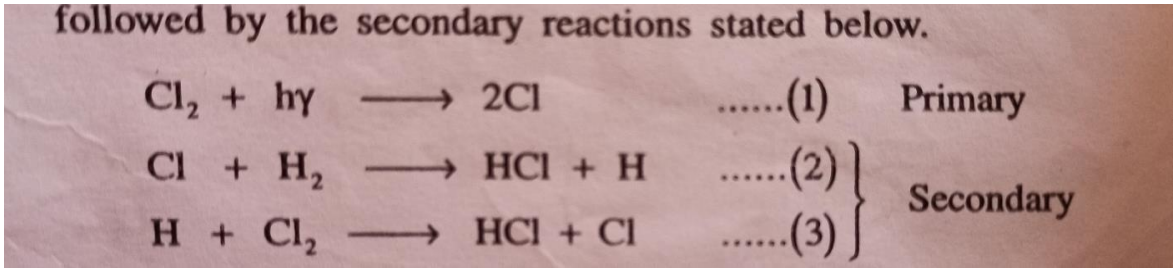
Examples

1.Decompostion of HI

In this case in the Primary reaction, a molecule of hydrogen iodide absobs a photon and dissociates to produce H and I .so that this is followed by secondary steps so that in a overall reaction,two molecules of hydrogen iodide are decompsed for one photon of light absorbed thus the quantum yield is 2 i.e it results in

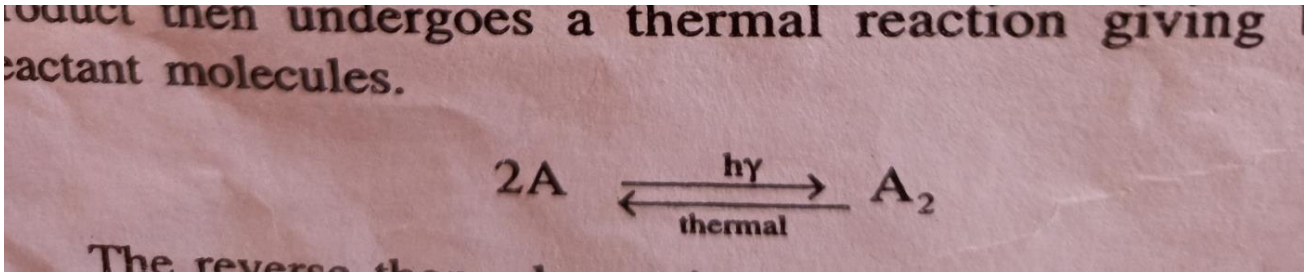
High quantum efficiency or yield

**Hydrogen chlorine reaction.** A mixture of hydrogen and chlorine is exposed to light of wavelength 4000 A° .The hydrogen and chlorine react rapidly to form hydrogen chloride. In the primary step, a molecule of chlorine absobs a photon and dissociates into two cl atoms. This is followed by the secondary reactions .The chlorine atom used in the step 2 is regenerated in step 3 Thus the steps 2& 3 constitute a self propagating chain.This produces two molecules of HCl in each cycle.Thus one photon of light absorbed in step 1 forms a large no of HCl molecules by repetition of the reaction sequence 2 & 3 .The chain reaction terminates when the Cl atoms recombine at the walls of the vessel where they lose their excess energy.The no of HCl molecules formed foe a photon of light absorbed is high and results in high quantum efficiency.



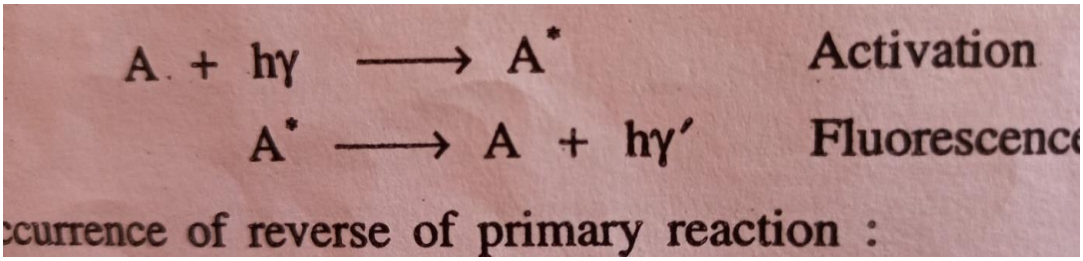

**Lowquantumefficiency** : In a photochemical

reaction if the no of molecules decompsed per photon of light absorbed is less than 1, then the




reaction is said to have low quantum efficiency.( Psi is less then 1) Reasons for low quantum efficiency:

1. Deactivation of reacting molecules.
2. Occurrence of reverse of primary reaction




3. Recombination of dissociated fragments

1.Deactivation of reacting molecules:

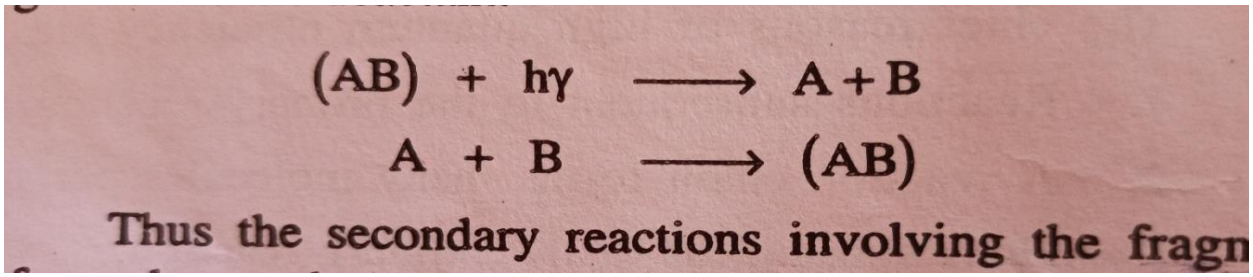
The excited molecules in the primary reaction may be deactivated before they get chance to react,this is caused by collisions with some inert molecules or by fluorescence and results in low quantum efficiency.

.

2.Occurrence of reverse of primary reaction: Here the primary reaction yields a polymer.theproduct then undergoes a thermal reaction giving back the reactant molecules. So that the reverse of thermal reaction proceeds till the equilibrium State us reached and results in low quantum efficiency.

3.Recombinationof dissociated fragments :

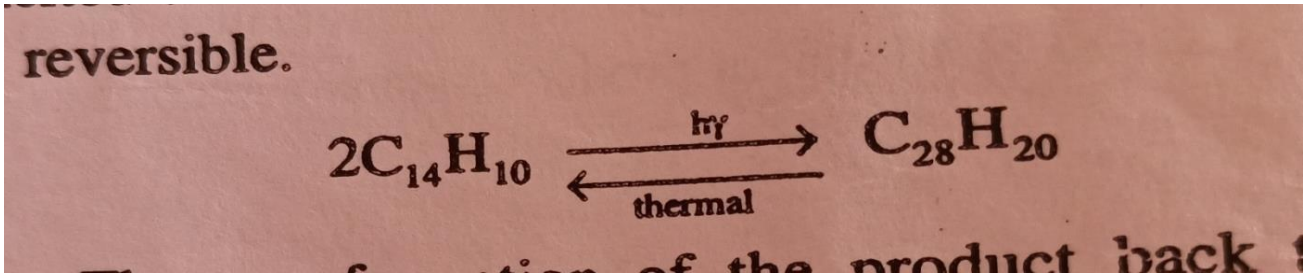
In a primary reaction the reactant molecules may dissociate to give smaller fragments.These fragments can recombine to give back the reactant mlocules.Thus the secondary reaction involving the fragments to form the product will not occur.This will greatly lower the yield and results in low quantum yield.




Examples

1. Dimerization of Anthracene.

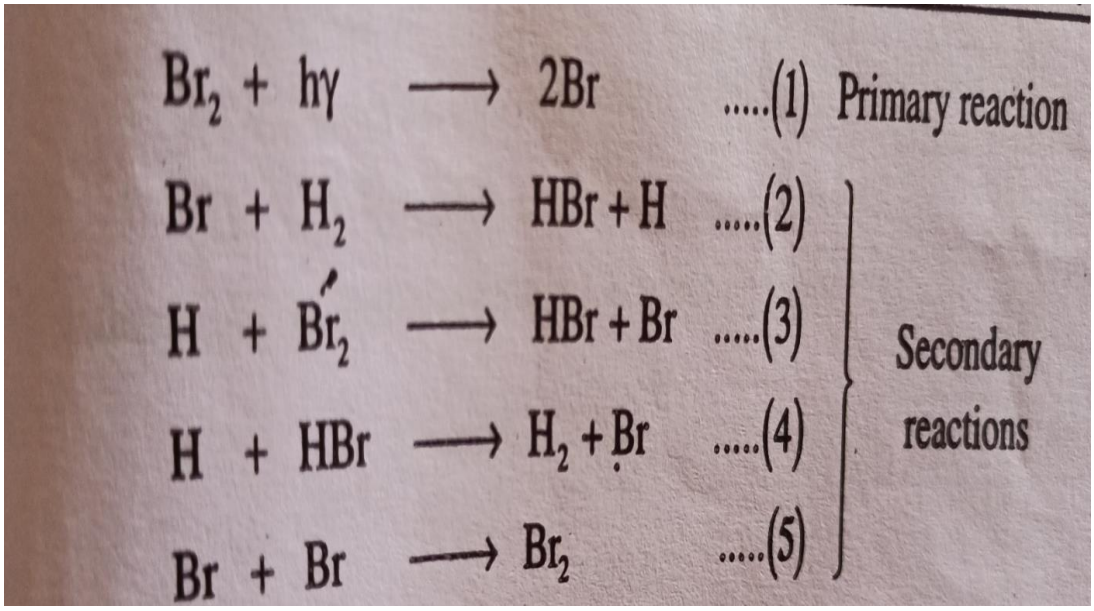
When Anthracene dissolved in benzene is exposed to uv Light,it is converted into dianthracene.obviously the quantum yield should be tow. But it is actually found to be




0.5 .The low quantum efficiency is explained as the reaction is accompanied by fluorescence which deactivates the excited Anthracene molecules.furthger the reaction is reversible. The transformation of the product back to reactant occurs till a equilibrium State is reached.this further lowers the quantum yield

2.Combination of $H_2$& $Br_2$ :

When a mixture of hydrogen and bromine are exposed to light, hydrogen bromide is formed the reaction occurs as follows,




The step2 is extremely slow.the reaction steps 3 ,4 & 5 depends directly or indirectly on step 2 and so are very slow. Therefore most of the Br atoms produced in the primary reaction recombine to give back $Br_2$ molecules. Thus the HBr molecules obtained per quantum light absorbed is extremely small thus results in low quantum efficiency and the quantum efficiency or yield of the reaction is found to be 0.01 at ordinary temperature.

**Luminescence**:

When a solid body is heated, it first becomes red hot and then becomes white hot and hence it begins to glow. The glue can be produced by methods other than the action of heat. The light does produces is called cold light. The glow produced in a body by methods other than the action of heat that is the production of cold light is called luminescence. The body emitting the cold light is called luminescent. In other words luminescence may be regarded as light without heat it is of the following types

1. Fluorescence
2. Phosphorescence
3. Chemiluminescence.

1. **Fluorescence** :

Certain substances which when exposed to light radiations of short wavelength or high frequency, immediately start remitting the light of different frequencies compared to those of the incident radiations. This process is called fluorescence and the substance that exhibits fluorescence is called fluorescent substance

- Fluorescence starts as soon as the substance is exposed to light it and it stops as soon as the light is cut off. Obviously the absorption of energy results into the excitation of the electrons followed by the immediately by the jumping back of excited electrons to the lower levels. As a result the absorbed energy is emitted back.

- It is interesting to observe that in the phenomenon of fluorescence, the wavelength of the emitted light is usually greater than that of the absorbed light. This is explained on the basis that the energy absorbed rises the electron to a sufficiently higher level but the return of excited electron to the original level takes place in steps through the intermediate levels,the energy thus produced in every jump is smaller and hence the wavelength of light emitted is larger than that of the absorbed light.
  Examples :

  Minerals like fluorite, petroleum and dyes like eosin, florescein, compounds like uranyl sulphate, vapours of sodium, Mercury and iodine etc. are some of the important examples for fluorescent substances. Application: fluorescent dyes are used in paints and fabrics to make them glow when bombarded with UV photons in sunlight.

**2.Phosphorescence** : certain substances

which when exposed to light radiations of short wavelength or high frequency continue to emit the light for sometime, even after the incident light is cut off. The afterglow may last for fractions of second to hours or even days depending on the type of material, temperature and other factors. This phenomenon is called phosphorescence and the substance which exhibits phosphorescence is called phosphorescent substance.

- Phosphorescence is caused by ultraviolet and visible light.

- Phosphorescence is found mostly in solids,as might be expected because in solids the molecules have least freedom of motion so that the excited electrons does keep on jumping back slowly for quite some time.

- When a molecule absorbs high energy radiation, cities excited to higher energy States. Then it emits light energy of longer wavelength while returning to the ground state. During this returning process,the excited molecule passes from one series of electronic States to another and gets trapped. This then emits the light which persists even after the removal of source of the light hence sometimes the phosphorescence can be designated as delayed fluorescence .
  Examples : examples for Phosphorus and substances are zinc sulphide, p alkaline earth sulphides, many dies when dissolved in a fused boric acid or glycerol and cooled until it forms a rigid glass also exhibits the phosphorescence.

**3.Chemiluminescence** : certain
substances emit the visible light as a result of chemical reaction at ordinary temperatures. This phenomenon is called chemiluminescence. The reaction is referred as chemiluminescent reaction.such a reaction is reverse of photochemical reaction in which the light absorption causes chemical reaction.the light emitted in a chemiluminescent reaction is called as cold light because it is produced at ordinary temperature.. According to Quantum theory,certain chemical reactions result in the formation of a products which are in the excited States. In such reactions, a part of the all of the energy change of the reaction instead of

appearing as a heat,goes to activate some molecules so that these activated or excited molecules emit there extra energy e in the form of visible radiations and constituted the chemiluminescence. Hence in this process the chemical energy is converted into the light energy. Examples for chemiluminescence are

- The glow of fireflies due to aerial oxidation of luciferin protein, in presence of enzyme luciferase is a good example for chemiluminescence.
- Auto oxidation of some grignard reagents also exhibit chemiluminescence
- the glow of phosphorus is due to chemiluminescence arising due to slow oxidation of phosphorus in air.
- Reaction of alkali metal with halogens aur halides also show chemiluminescence.

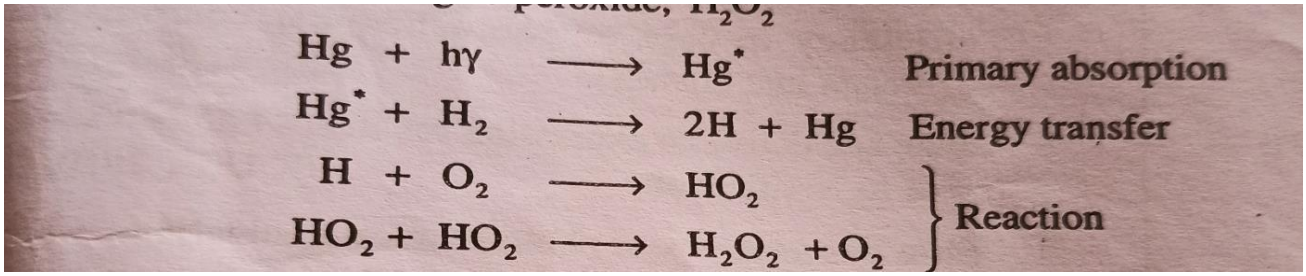
**.Photosensitization** : certain reactions are known which are not sensitive to light but these reactions can be made light sensitive by adding a small amount of foreign material which can absorb the light and stimulate the reaction without taking itself part in the reaction.Sachin added material is known as photosensitizer and the phenomenon is known as photo sensitization.

Commonly used photosensitizers are cadmium and mercury papers. The function of photosensitizer is to absorb the light,become excited and then pass on this energy to one of the reactants and thereby activate them for reactions without itself taking part in the reaction does a photosensitizer acts as a carrier of the energy.

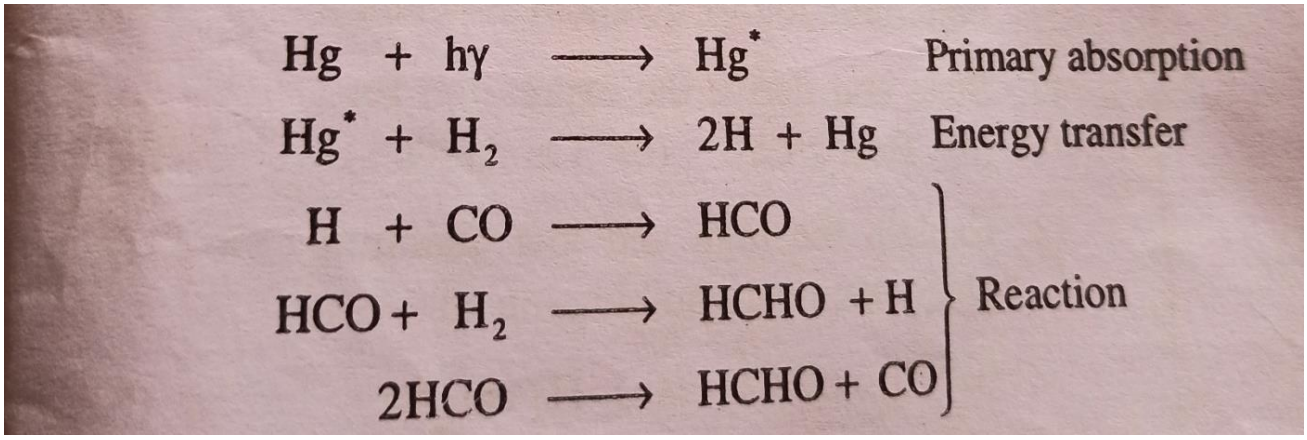
Examples of photosensitized reactions are

1. Reaction between $H_2$& $O_2$

This reaction is photosensitized by Mercury vapour and this reaction result in the formation of the hydrogen peroxide as the product.




2.Reaction between $H_2$& CO in this reaction the Mercury vapour is used as photosensitizer and the product is a formaldehyde.




3.Dissociation of hydrogen molecules in presence of mercury vapour.

Hydrogen molecules do not dissociates

When exposed to uv light.howeverwhen hydrogen gas is mixed with mercury vapour & then exposed to uv light, hydrogen molecules dissociate to give hydrogen atoms through the following reactions.

Hg + hv → Hg*

Hg* + H2 → Hg + 2H

Where Hg * represent the activated mercury vapour.Thus in the above reaction mercury acts as a photosensitizer.

Application: the photosensitisation plays a vital role in the photosynthesis of carbohydrates in plants in which the green coloured pigment called chlorophyll acts as the photosensitizer.

**Photoinhibition**: Presence of certain substances considerably reduces the quantum yield of some photochemical reactions.For example in the photosynthesis of HCl ,the presence of traces of oxygen reduces the quantum yield of this reaction substances like nitric oxide, sulphur oxide etc. also show the similar effects.It is believed that such substances react with chain propagating atoms or radicals resulting into the chain termination. The chain termination in the photosynthesis of HCl by the presence of traces of oxygen takes place as follows,

$$H + O_2 \quad HO_2$$

$$Cl + O_2 + HCl \quad HO_2 + Cl_2$$