IV – SEMESTER

STUDY MATERIAL

COURSE-5

INORGANIC& PHYSICAL CHEMISTRY

PREPARED BY

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UNIT – I

CO ORDINATION CHEMISTRY

TERMS USED IN COORDINATION COMPOUNDS

Central ion or Central metal

The cation to which one or more anions or neutral molecules are attached is called the central ion.

Ex: In $K_4[Fe(CN)_6]$ iron is the central ion

1. Ligand

Any atom or ion or molecule which is capable of donating a pair of electrons to the central metal is called ligand or coordination group.

Types

The ligands containing one, two or more donor atoms are known as unidenate, bidenate or polydenate respectively.

Ex: F^-, Cl^-, NH_3 unidenate ligands

Ethylene diamine bidenate ligand

2. Coordination number

The total number of ligands attached to the central ion is called coordination number.

Ex: In $K_4[Fe(CN)_6]$ coordination number is 6

3. Oxidation number

It is the number which represents the electric charge on the central metal atom of a complex ion.

Ex: In $K_4[Fe(CN)_6]$ oxidation number of iron is +2

$4K + Fe + 6CN = 0$

$4x1 + Fe + 6x-1 = 0$

$Fe = +2$

4. Coordination sphere

The central atom and the ligands directly attached to it is called coordination sphere.

$[Fe(CN)_6]$

IUPAC NOMENCLATURE OF COORDINATION COMPOUNDS

RULES

1. In the naming of the complex first the names of the ligands are written in the order of English alphabets. Then only the metal name is to be written.
2. Names of ligands

a. Negative ligands: The names of ligands ends with –O

Ex :

$$Cl^{-} \longrightarrow \text{chloro}$$

$$CN^{-} \longrightarrow \text{cyano}$$

$$OH^{-} \longrightarrow \text{hydraxc}$$

b. Positive ligands: The names of positive ligands ends with –ium

Ex: $NO^{+} \longrightarrow$ nitrosonium

$N_2H_5^{+} \longrightarrow$ hydrazonium

c. Neutral ligands are named differently

$H_2O \longrightarrow$ Aqua

$CO \longrightarrow$ Carbonyl

$NH_3 \longrightarrow$ Amine

3. Order of naming ligands

   The ligands are named in the alphabetical of their names without using hyphen. If there are several ligands in the coordination sphere these are listed in alphabetical order.

   Ex: $[Co\,Cl\,CN\,NO_2\,(NH_3)_3]$ Triaminechlorocyanonitrocobalt(III)
4. In case of simple ligands (Cl^-, F^-), when they are present more than once their number is indicated by the prefixes di, tri, tetra etc.
5. If the complex compound is ionic in nature, the cation is named first and then anion is named.

   Ex: $K_4[Fe(CN)_6]$ Potassiumhexacyanoferrate(II)
6. If the complex compound is neutral or nonionic its name is written as a single word.

   Ex: $[Co\,(NH_3)_3Cl_3]$ triaminetrichlorocobalt(III)
7. If the complex ion is negatively charged, the name of the metal in the complex ends with –ate.

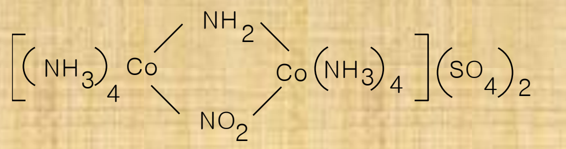
   Ex: $K_4[Fe\,(CN)_6]$ potassiumhexacyanoferrate(II)

   $K_3[Co\,(NO_2)_6]$ potassiumhexanitrocobaltate(III)
8. If the ligands have complex names their number is indicated by prefixes such as bis, tris, tetrakis etc. before the ligand and the ligand name is written in ( )

   Ex: $[Cr\,(en)_3]\,Cl_3$ Tris(ethylenediamine)chromium(III) chloride
9. The oxidation state or oxidation number of the metal in the complex is written besides the names of the metal in Roman numeral in brackets ( )

   Ex: $[Co\,(NH_3)_6]^{+3}$hexaaminecobalt(III)ion
10. In polycentric complex compounds before the names of the ligands which bind these centers the Greek letter (µ)

    Ex: Octamine-µ-amido-µ-nitrodicobalt(III)sulphate



11. If the ligands contain more than one donor atoms(ambidenate ligands) which can donate lonepairs the symbol of the hetero atom through which coordination occurs is written after the name of ligand.

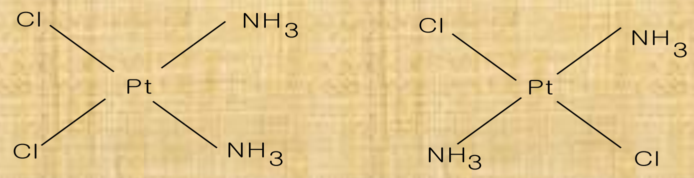
    Ex: $[Zn(NCS)_4]^{2-}$ Tetrathiocyanato-N-zincate(II)ion

    $[Cr(SCN)_6]^{3-}$ Hexathiocyanato-S-chromate(III)ion

12. Geometrical isomers are named as cis and trans depending upon whether the similar groups are on the same side or on the opposite sides.

Ex: cis-dichlorodiamineplatinum (II)

trans-dichlorodiamineplatinum (II)



ISOMERISM IN COORDINATION COMPOUNDS

Compounds are having the same chemical formula but different in structure or arrangements are called isomers and the phenomenon is known as isomerism.

Types

A. Structural isomerism
B. Stereo isomerism

Structural isomerism

1. Ionization isomerism
2. Hydration isomerism
3. Linkage isomerism
4. Coordination isomerism
5. Coordination position isomerism
6. Polymerization isomerism

1. **Ionization isomerism**The complex compounds having the same molecular formula but in solution gives different ions are called ionization isomers. This phenomenon is called ionization isomerism.

The exchange occurs between the ions present outside the coordination sphere and inside the coordination sphere is responsible for this type of isomerism.

Ex: $[Co(NH_3)_5Br]\ SO_4$, $[Co(NH_3)_5\ SO_4]\ Br$

2. **Hydration isomerism**

This type of isomerism arises due to neutral water molecules exchange with negative ions.

.Ex: Hydrated Cr (III) chloride complexes

1. $[Cr(H_2O)_6]Cl_3$ violet
2. $[Cr(H_2O)_5Cl]Cl_2\ H_2O$ green
3. $[Cr(H_2O)_5Cl_2]Cl\ 2H_2O$ dark green

3. **Linkage isomerism**

This type of isomerism arises due to ligands possess more than one donar atom.

Ex: $[Co(NH_3)_5ONO]\ Cl_2$, $[Co(NH_3)_5NO_2]\ Cl_2$

4. **Coordination isomerism**

If a complex compound contains one complex cation and one complex anion there will be a possibility of exchange of ligands between them. This results in coordination isomerism.

Ex: $[Co(NH_3)_6]^{3+}\ [Cr(CN)_6]^{3-}$ and $[Cr(NH_3)_6]^{3+}\ [Co\ (CN)_6]^{3-}$

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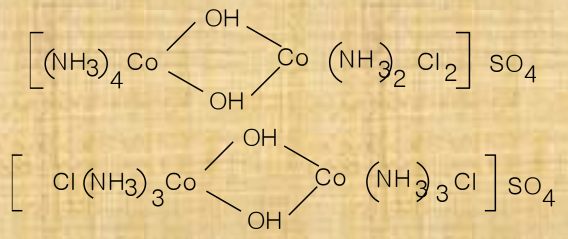
5. **Coordination position isomerism**

In multi center complexes if ligands get exchanges between the central metal ions, this type of isomerism is exhibited.



6. **Polymerization isomerism**

The coordination/complex compounds of different molecular weights but of same empherical formula are considered as polymerization isomers.

Ex: $[Pt(NH_3)_2Cl_2]$, $[Pt(NH_3)_4]$. $[PtCl_4]$. $[Pt(NH_3)_3Cl]$. $[PtCl_4]$.

Stereo isomerism

The difference in the three dimensional configuration of the coordination compounds is responsible for this type of isomerism even though the chemical composition is same.

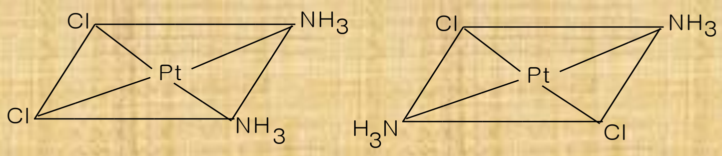
This is two types

1. Geometrical isomerism
2. Optical isomerism

Geometrical isomerism

The coordination compounds showing different physical and chemical properties because of the difference in three dimensional arrangements of the groups surrounding the central metal ion even though their chemical formulas are same or identical is called geometrical isomerism.

Ex: $[Pt(NH_3)_2Cl_2]$



cis trans

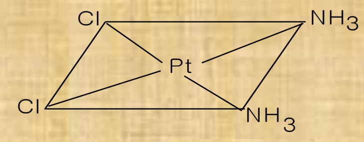
Tetra coordinate complexes may be in tetrahedral geometry or square planar geometry. Tetrahedral complexes are not exhibit geometrical isomerism.

Geometrical isomerism in square planar complexes:

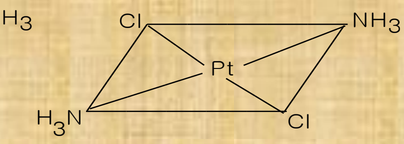
Square planar complexes general formulas MA_2B_2, MA_2BC and MABCD (A,B,Cand D are different monodenate ligands, M is metal ion) exhibit geometrical isomerism.

MA_2B_2(A= NH_3,Py, B=Cl^-,Br^-,NO_2^-)

Ex: $[Pt(NH_3)_2Cl_2]$



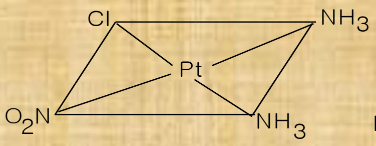
cis



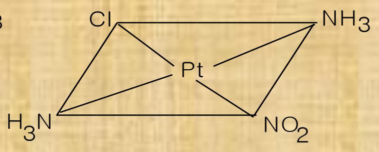
trans

MA_2BC

Ex: $[Pt(NH_3)_2Cl\ NO_2]$



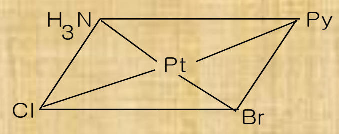
cis



trans

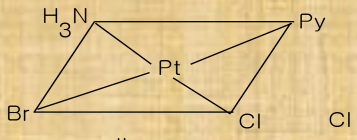
MABCDcomplexes of this type exist in three isomeric forms

Ex: $[Pt(Py)\ (NH_3)\ Br\ Cl]$



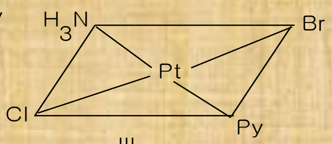
I

NH_3 group is trans to Br



II

NH_3 group is trans toCl



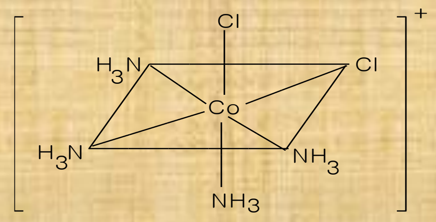
III

NH_3 groups in trans to Py

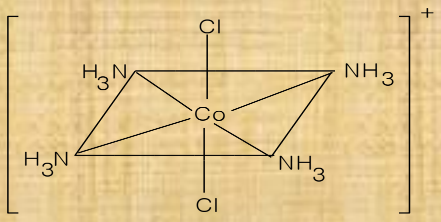
Geometrical isomerism in octahedral complexes:

General formulas $[MA_4X_2]$, $[M(A\text{-}A)_2X_2]$, $[MA_3X_3]$

Example for $[MA_4X_2] = [Co\ (NH_3)_4Cl_2]^+$

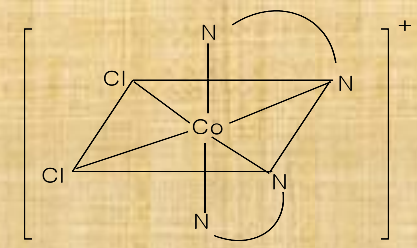


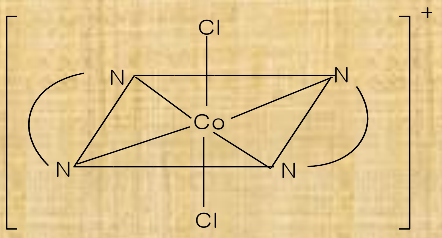
cis



trans

Example for $[M(A\text{-}A)_2X_2] = [Co(en)_2Cl_2]^+$





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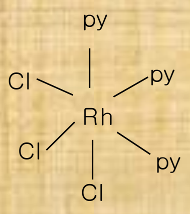
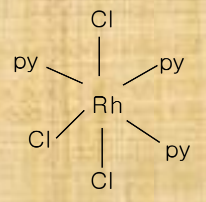
Example for [MA_3X_3] = [$Rh(Py)_3Cl_3$]



cis



trans

Optical isomerism

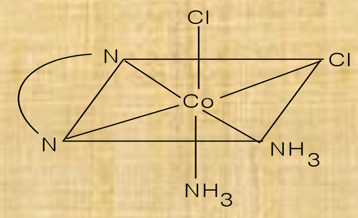
If a complex does not contain any element of symmetry it exhibits optical activity. These types of isomers are recognized as optical isomers. These isomers are called dextro (d) and laevo (l). If the plane of the polarized light is rotated clockwise towards right the isomer is called dextro isomer, if it is rotated towards left it is called laevo isomer. These forms are called enantiomers.

General formulas:

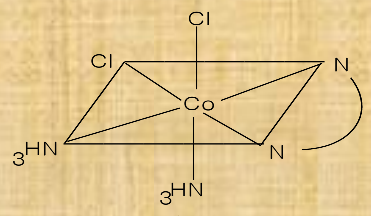
[$M(A\text{-}A)X_2Y_2$] =[$M(A\text{-}A)_2X_2$] =[$M(A\text{-}A)_3$] = [$M(A\text{-}B)_3$]

M= Metal atom
(A-A)= symmetrical bidenate ligand
(A-B) = unsymmetrical bidenate ligand
X,Y= mono denate ligands.

Example for [$M(A\text{-}A)X_2Y_2$] = [$Co(en)(NH_3)_2Cl_2$]

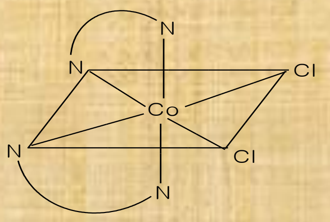


dextro

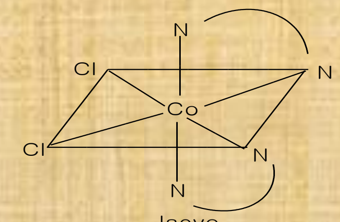


laevo

Example for [$M(A\text{-}A)_2X_2$] = [$Co(en)_2Cl_2$]$^+$



dextro



laevo

VALENCE BOND THEORY WITH SUITABLE EXAMPLES

Postulates

1. The metal atom or ion in the complex has a number of empty orbitals which can accommodate electrons donated by the ligands to form coordinate bonds.
2. Since the energy of the (n-1) d-orbitals is around energies of s and p orbitals of the nth orbit, these orbitals are together hybridized to give new equivalent orbitals called hybridized orbitals. which take part in bond formation with ligand orbitals
3. The hybridized metal orbitals overlap with ligand orbitals containing electron pairs to form strong bonds.
4. Each ligand donates a pair of electrons to the central metal ion.
5. If the complex contains unpaired electrons, it is paramagnetic in nature, whereas if it has paired electrons, the complex is diamagnetic.
6. Under the influence of a strong ligand, the electrons can be forced to pair up against the Hund's rule of maximum multiplicity. Either (n-1) d inner orbitals or outer nd orbitals may be used for hybridization.

Coordination number	Hybridisation	Geometry	Example
2	SP	Linearor diagonal	$[Ag(NH_3)_2]^+$
3	SP^2	Trigonal planar	$[Ag(PR_3)_3]^+$
4	SP^3	Tetrahedral	$[Ni(CO)_4]$
4	SP^2d	Square planar	$[Ni(CN)_4]^{2-}$
6	SP^3d^2	Octahedral	$[Fe(CN)_6]^{3-}$

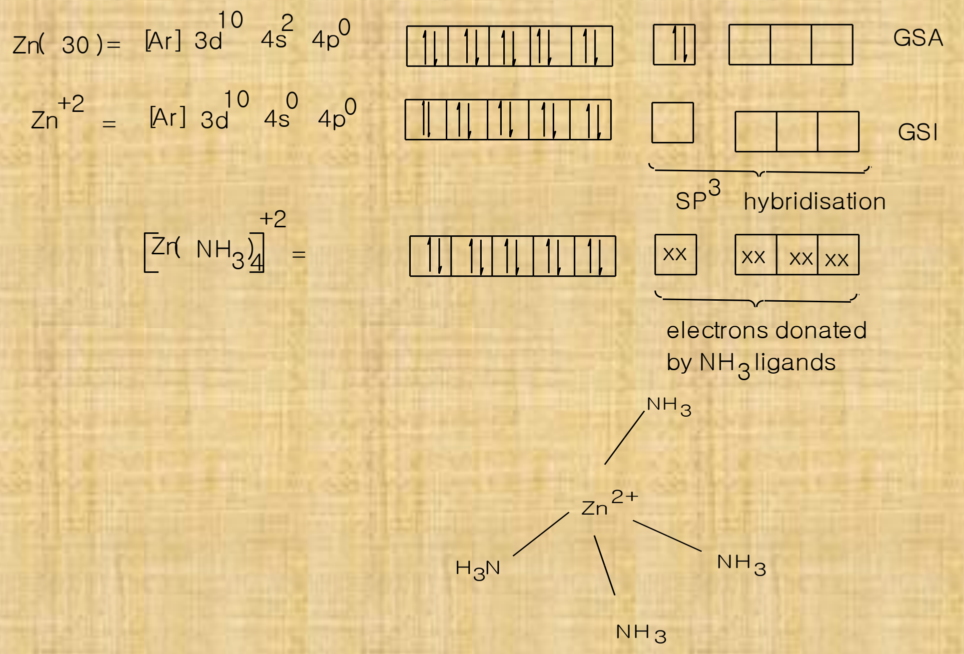
- According to this theory can be explained the magnetic properties and geometries of the coordination compounds.
  The formation of complex compounds occurs in the different stages as given below.
  .

1. The metal atom is considered to be in the ground state electronic configuration. This is called ground state of the atom..
2. As per the valence requirement the metal atom losses electrons and forms the ionic state. This is called ground state of the ion.
3. Depending on the need the ion in the ground state reaches the excited state. In this process the electrons in the metal orbitals get rearranged.
4. The necessary orbitals of the metal atom hybridise to get empty hybrid orbitals equal in number to the coordination number of the metal atom.
5. The orbitals of the ligands containing lone pair of electros overlap with these empty hybrid orbitals of the metal atoms. In this process electron pairs are transferred from the ligands to the empty hybrid orbitals of the metal. This helps in the formation of the metal ligand bond and results in the formation of complex compound.

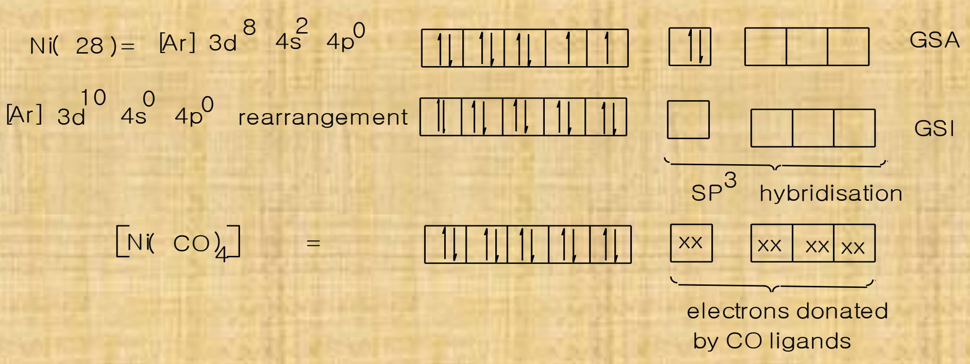
Example:
The geometries corresponding to coordination number 4 of the central metal atom.
The complex compounds with coordination number 4 for the central metal atom may possess either tetrahedral geometry or square planar geometry.

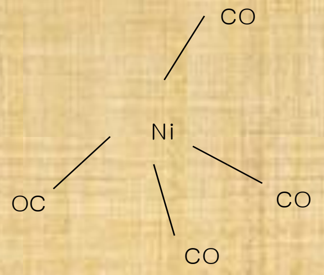
Tetrahedral complex compounds

Ex1: $[Zn(NH_3)_4]^{2+}$



Ex2: $[Ni(CO)_4]$

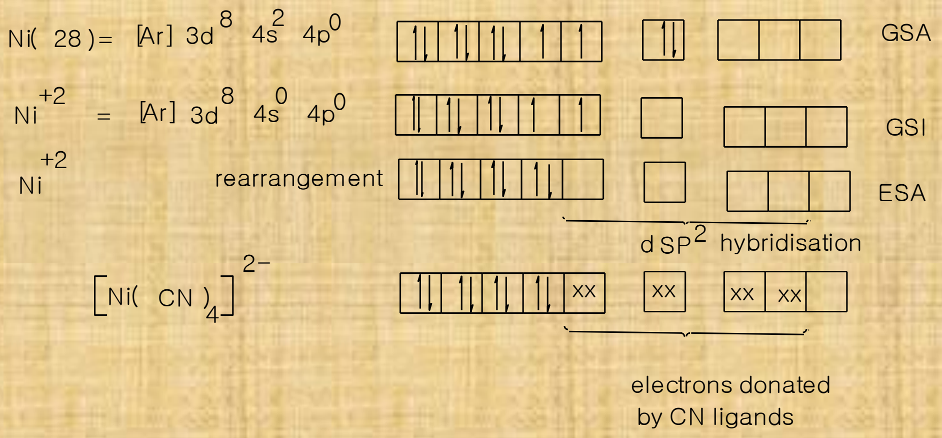


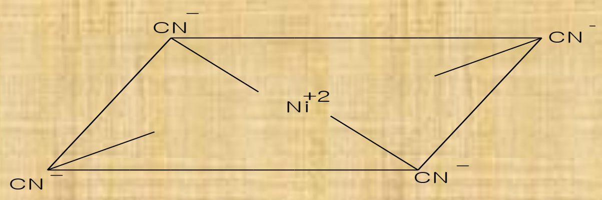


In these complexes the central metal atoms are in sp^3 hybridisation therefore these will have tetrahedral shape and since all the electrons are paired these are diamagnetic.

Square planar complex compounds

Ex: $[Ni(CN)_4]^{2-}$

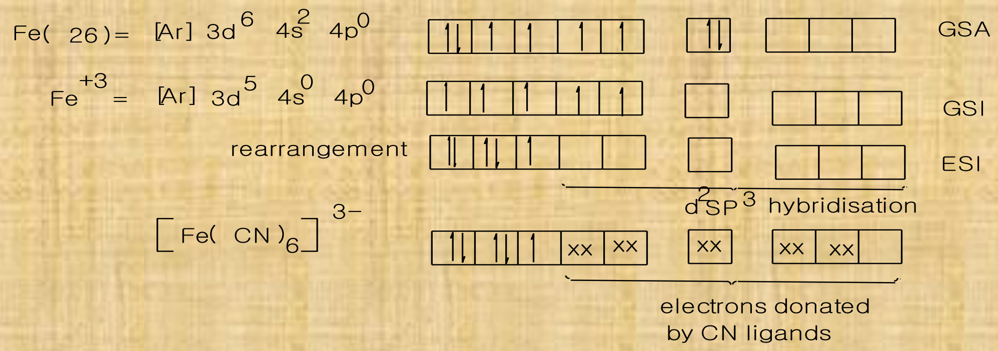




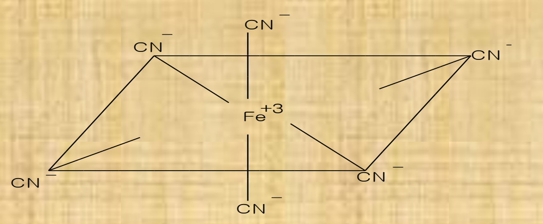
The shapes corresponding to the coordination number 6 of the central metal atom.

The coordination complexes with coordination number 6 of the central metal atom usuallyexhibit sp^3d^2 hybridization of the central metal atom and possess octahedral geometry.

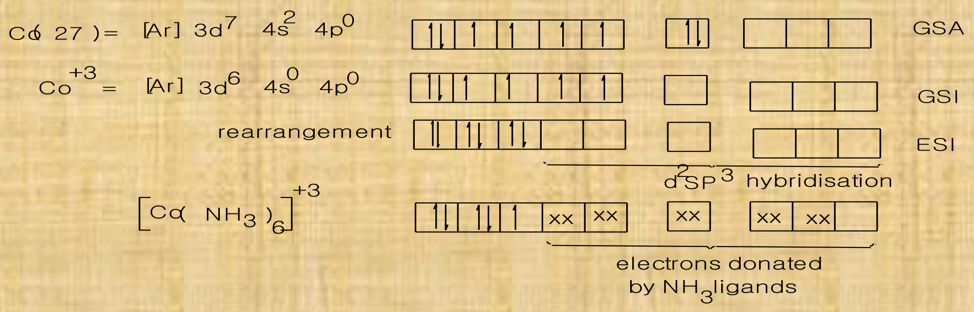
Ex1: $[Fe(CN)_6]^{3-}$

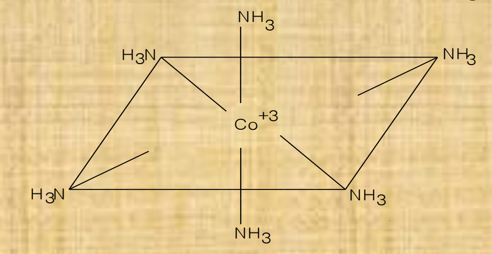


It is octahedral in shape and exhibits paramagnetism since it possessed one single electron.

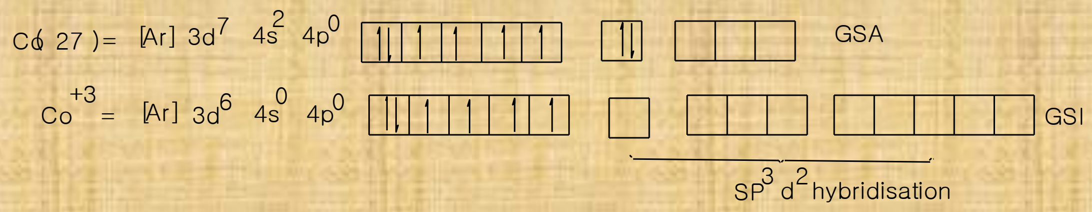


Ex2: [Co $(NH_3)_6$] $^{+3}$



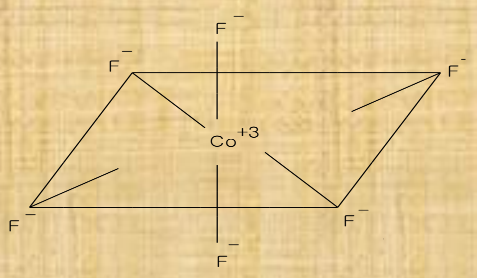


Ex3:$[CoF_6]^{3-}$



In this Co^{+3} ion is not transferred to excited state. The electrons are not redistributed. The four electrons remain unpaired. The sp^3d^2 hybridization is with outer d-orbitals (outer orbital complex).

$[CoF_6]^{3-}$



EXPLAIN CRYSTAL FIELD THEORY

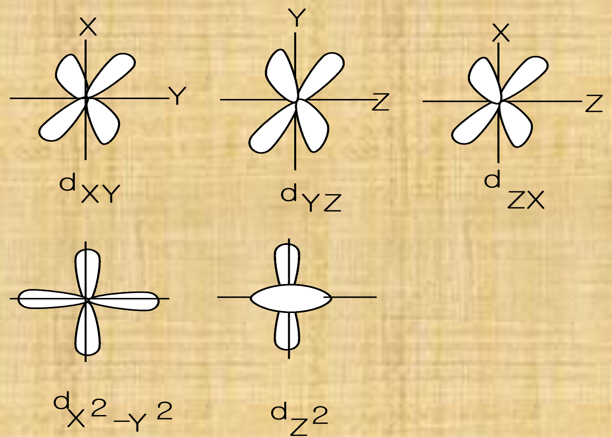
POSTULATES

- As per this theory the bond between the central metal atom and the ligand in the complex will have ionic character.
  This will be present as ion-ion attraction between the +ve metal ion and the –ve ligand ions and asion-dipole attraction between neutral ligand and the +ve metal ion.

- Ligands behave as point charges.
- This theory is based on the d-orbitals of the metal and the electrons present in it. The effect of ligands only on the d-orbitals of the metal is taken into consideration. The properties of the complexes depend on the distribution of electrons in the d-orbitals influenced by the ligands.
- The d-orbitals of free metal ion are degenerate. They all possess same energy.
  The d-orbitals are split as per energy by the influence of ligand field effect and they lose their degeneracy. This is known as crystal field splitting.This crystal field splitting of d-orbitals is the main basis of the crystal field theory.

Splitting of d-orbitals in octahedral, square planar and tetrahedral complexes:

- The five d-orbitals of a metal are designated as d_{xy},d_{yz},d_{zx},d_{x2-y2} and d_{z2}
- The first four d-orbitals contain double dumbell shaped electron clouds. For each of these d-orbitals there are four lobes. The last d-orbital has two vertical lobes and at the center, a saucer like structure.
- The four lobes of d_{xy},d_{yz},d_{zx} are spatially distributed in between the corresponding Cartesian axis (x,y) (y,z) (z,x). The groups of these three d-orbitals is named as t_{2g} group of orbitals. d_{xy},d_{yz},d_{zx}ఆర్బిటాల్లలోనాలుగులోబ్లువరుసగా(x,y) (y,z) (z,x)కార్టీజియన్నిరూపాక్షాలమధ్యThe lobes of d_{x2-y2} and d_{z2} orbitals are oriented or centered along the x, y and z axis. The group of these two d-orbitals is named as e_g group orbitals.



- The ligands in the coordination sphere of the metal ligand complex approach the metal ion. In this process an electric field is formed around the metal ion. This is called crystal field. The energy of the d-orbitals increases as aresult of this crystal field.
  Ex: $[TiF_6]^{2-}$

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In this complex ion Ti is present in +4 oxidation state. So the five d-orbitals in it are vacant but degenerate (orbitals possessing same energy are called degenerate orbitals). The energy of electron in any of these 5d-orbitals is the same. This is the free state of the metal. All the 5d orbitals are of same energy.

But if fluoride ions approach the Ti^{+4} ion the energy of the d-orbitals increases due to the crystal field produced by the ligands. Hence in the presence of ligands, the entry of electrons into d-orbitals of the metal ion is associated with higher energy than the entry of electrons into the free ion d-orbitals. This means that the energy of the d-orbitals of a metal increases in presence of ligands.

But the 5d-orbitals are degenerate in this higher energy state also. This is an imaginary state because all the d-orbitals of the metal cannot be of same energy in presence of the ligands. The reason for this is the different spatial orientation of the d-orbitals around the nucleus. Hence the ligands approach the metal ion the d-orbitals of the metal ion are not split energy wise.

Explain d-orbitals splitting in octahedral complexes

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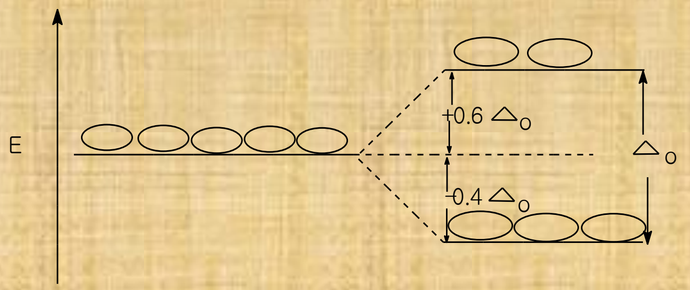
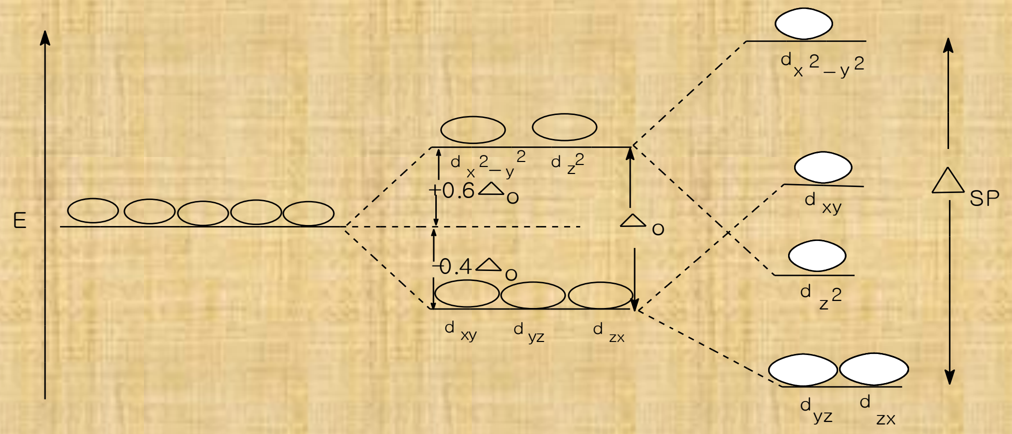
- In an octahedral complex the coordination number is 6. The six ligands approach the metal ion along the Cartesian coordinates x,y,z.
- Amongst these six ligands, 2 approach along x-axis, 2 approach along y-axis and the other 2 along z-axis.
- Two of the five d-orbitals (d_{x2-y2} and d_{z2}) oriented along the axis and they will be greatly repelled by ligand orbitals and reach higher energy state.
- Remaining 3d-orbitals (d_{xy},d_{yz},d_{zx}) have less repulsion orbitals of the ligands compared to d_{x2-y2} and d_{z2} Hence energy of dx, dy, dzx orbitals is lowered but less relatively.
- In this way the degenerate d-orbitals of the metal are split into higher energy e_g group of orbitals and lower energy t_{2g} group of orbitals.
- The splitting of degenerate d-orbitals into different groups of orbitals of different energies under the influence of crystal field is called crystal field splitting.
- The difference in the energy levels of these two groups of d-orbitals arising as a result of d-orbital splitting is called crystal field splitting energy (CFSE). This energy difference is denoted by delta (Δ)
- The difference in energy between t_{2g} and e_g in octahedral geometry is shown byΔ_o(o=octahedral)
- The energy of e_g orbitals after splitting is increased by 0.6 Δ_o and similarly the energy of t_{2g} orbitals is decreased by – 0.4 Δ_o compared to their energies before splitting.

Ex: $[CoF_6]^{3-}$, $[Fe(CN)_6]^{3-}$



Explain d-orbital splitting in square planar complexes

- By removing two vertically oriented ligands from the octahedral complex we get the square planar complex.
- By removing away the two ligands present on z-axis, the d_{z2} orbital oriented along z-axis is completely free from the repulsion by the ligand orbitals. Similarly d_{xz} , d_{yz} orbitals having z-axis orientation reduce their repulsion by the ligand orbitals to some extent. So the energy of these d-orbitals is reduced differently.



- The energy of d_{z2} orbital is highly reduced since this orbital is almost free from the repulsion by the ligand orbitals.
- d_{xz}, d_{yz} orbitals being oriented in the space between yz and xz axis, there will be small repulsion between these orbitals and the orbitals of the ligands present on x and y axis. So the decrease in the energy of these orbitals is greater than the decrease in d z^2obitals. This means d_{yz}, d_{zx} are lowest energy orbitals in this case.
- In contrast the repulsion between (d_{x2-y2} and d_{xy}) orbitals and the orbitals of the ligands present on x, y axis is relatively more. The energy therefore increases.
- The energy of d_{x2-y2} oriented on x,y-axis is very high since these orbitals are under high repulsion by the orbitals of the ligands present on x,y axis. The d_{xy} orbital which is oriented between the axis is under lesser repulsion by the ligands. Hence energyof $d_{xy}$is lower compare to that of d_{x2-y2}.
- The crystal field is shown by Δ_{sp}.
- The crystal field splitting energy of square planar(Δ_{sp}) is more than crystal field splitting energy of octahedral (Δ_o)
- These two are related by the equation $\Delta_{sp} = 1.3\ \Delta_o$

Examples: $[Ni(CN)_4]^{2-}$, $[PdCl_4]^{2-}$, $[PtCl_4]^{2-}$

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Explain d-orbital splitting in tetrahedral complexes

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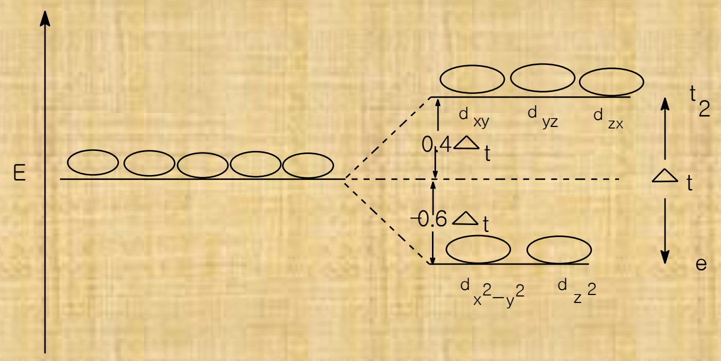
- As the ligands approach the central metal atom the d-orbitals of the metal oriented in between the axis are much more under repulsion by the orbitals of the ligands than the d-orbitals oriented along the axis.
- Therefore the energy of t $_2$orbitals increases. The enegy of e orbitals decreases. In this way the five degenerate d-orbitals are split into two groups of d-orbitals.
- The energy difference between these two groups of d-orbitals is denoted by Δ_t
- The energy of egroup of orbital is $-0.6\Delta_t$, lower than the enegy of unsplit degenerate d-orbitals. The energy of t_2 group of orbital is $0.4\ \Delta_t$higher than the energy of unsplit degenerate d-orbitals.
- In this way the d-orbital splitting in tetrahedral geometry is opposite to that present in octahedral geometry.
- Tetrahedral splitting Δ_t is found experimentally to be 4/9 of the octahedral

  $\Delta_t = 4/9\ \Delta_o$



Ex: $[NiCl_4]^{2-}$, $[CoCl_4]^{2-}$, $[Zn(NH_3)_4]^{2+}$

*** The relation between these three splitting’s are as follows

$\Delta_{sp} = 1.3\ \Delta_o$

$\Delta_t = 4/9\ \Delta_o$

Write a note on low spin – high spin complexes .

- The magnitude of the crystal field splitting (Δ) depends on the nature of metaland ligand
- The value of the Δ depends on the strength of the ligand.
- The ligands which produce higher division are called strong ligands. The ligands which produce smaller division are called weak ligands and intermediately division is called intermediate ligands.
- The splitting ability of the common ligands is experimentally determined and the ligands are arranged in an order on the basis of this ability. This is called spectro chemical series.

Strong ligands		Intermediate ligands		weak ligands
$CO > CN^- > NO_2^- > Phe$	>	$en > NH_3 > NCS^- > H_2O$	>	$OH^- > RCOO^- > F^-$

- The above series begin with strong ligands and ends with weak ligands.
- Strong ligands cause greater d-orbital splitting and help to form low spin complexes.If (n – 1) d-orbitals are involved in hybridization the complex is said to be inner orbital complex or low spin complex.
- Weak ligands cause low d-orbital splitting and help to form high spin complexes.If n d-orbitals are involved it is outer orbital complex or high spin complex.

What are the Factors affecting crystal field splitting energy?

1. Under the influence of crystal field the d-orbitals of the metal get split therefore the electrons enter selectively in d-orbitals of lower energy. The energy of the complex formed in this way is lowered, the complex attains stability.The stabilization energy thus attained by the complex is called crystal field splitting energy(CFSE)
   Ex: Ti $(H_2O)_6]^{3+}$
   There is one single electron in Ti $^{3+}$ ion. In free metal ion all the 5d orbitals are degenerate. Therefore this electron enters into any of these 5d orbitals. But whenTi $^{3+}$ ion forms a complex with 6 H_2O ligands. The crystal field influenced caused by 6 H_2O ligands makes the d-orbitals split into t_{2g} orbitals of lower energy 0.4 Δ_o and e_g Orbitals of higher energy 0.6 Δ_o. Now the single electron enters t_{2g} where by the energy decreases by 0.4 Δ_o attains stability to this effect. This is called CFSE.
   *** **The electronic arrangement, CFSE values of octahedral complexes**

number of electrons	electrons arrangement in presence of W F L					CFSE	electrons arrangement in presence of SFL					CFSE
	t_{2g}			e_g			t_{2g}			e_g		
1	↑					−0.4 Δ_o	↑					−0.4 Δ_o
2	↑	↑				−0.8 Δ_o	↑	↑				−0.8 Δ_o
3	↑	↑	↑			−1.2 Δ_o	↑	↑	↑			−1.2 Δ_o
4	↑	↑	↑	↑		−0.6 Δ_o	↑↓	↑	↑			−1.6 Δ_o
5	↑	↑	↑	↑	↑	0.0 Δ_o	↑↓	↑↓	↑			−2.0 Δ_o
6	↑↓	↑	↑	↑	↑	−0.4 Δ_o	↑↓	↑↓	↑↓			−2.4 Δ_o
7	↑↓	↑↓	↑	↑	↑	−0.8 Δ_o	↑↓	↑↓	↑↓	↑		−1.8 Δ_o
8	↑↓	↑↓	↑↓	↑	↑	−1.2 Δ_o	↑↓	↑↓	↑↓	↑	↑	−1.2 Δ_o
9	↑↓	↑↓	↑↓	↑↓	↑	−0.6 Δ_o	↑↓	↑↓	↑↓	↑↓	↑	−0.6 Δ_o
10	↑↓	↑↓	↑↓	↑↓	↑↓	0.0 Δ_o	↑↓	↑↓	↑↓	↑↓	↑↓	0.0 Δ_o

2. ΔValue depends on the strength of the ligand. ΔValue is great with strong ligands and low with weak ligands.
3. ΔValue depends on the oxidation state of the metal ion and the principle quantum number.

Tetragonal distortion of octahedral geometry

In a regular octahedron, all metal –ligand distances are equal. But in tetragonal omplex, metal – ligand bond lengths on z-axis are longer than the metal – ligand bond lengths on x,y-axis. Because of the longer metal – ligand lengths on z-axis, the repulsion experienced by t2g orbitals and eg orbitals is different from that of the octahedral geometry. Because of the presence of two ligands on z-axis at farther place, dz2-orbitals which is oriented along z-axis experience less repulsion compared to the octahedral. Where as the d $_{X}2 - _{Y}2$ orbitals experience more repulsion. Since four metal – ligand bond lengths on x,y – axis are same. The d $_{X}2 - _{Y}2$ orbitals of higher energy and dz2 orbitals of lower energy, similarly dxy, dyz, dzx also experience different repulsion. This is because the two ligands on z-axis are at a farther place. The dxy orbitals experience same repulsion as in octahedral geometry. dxy and dyz orbitals experienced less repulsion and so the t2g orbitals are also split into two sets. dxy orbitals of higher energy and dxy, dyz orbitals of lower energy.

JOHN-TELLER DISTORTION

John-Teler theorem states that any non-linear molecular system possessing electronic degeneracy will be unstable and will undergo distortion to form a system of lower symmetry as well as lower energy and thus the degeneracy will be removed.

This effect desctibes the geometrical distortion of molecules and ions that is associated with electronically degenerate configurations.

Orbitals of different configurations and distortions will be discussed as follows, types of orbitals.

$t_{2g}^{0} \quad t_{2g}^{3} \quad t_{2g}^{6} \longrightarrow$ Symmetrical

$t_{2g}^{1} \quad t_{2g}^{2} \quad t_{2g}^{4} \quad t_{2g}^{5} \longrightarrow$ unsymmetrical

$e_{g}^{0} \quad e_{g}^{4} \longrightarrow$ Symmetrical

$e_{g}^{1} \quad e_{g}^{3} \longrightarrow$ Unsymmetrical

$e_{g}^{2} \longrightarrow$ Low spin(SFL) Unsymmetrical

$e_{g}^{2} \longrightarrow$ High spin(WFL) Symmetrica

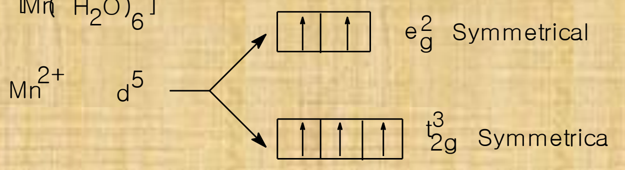
t_{2g}(S) + e_g(S) $\longrightarrow$ No distortion

t_{2g}(US) + e_g(S) $\longrightarrow$ Slight distortion

t_{2g}(S) + e_g(US) $\longrightarrow$ Strong distortion

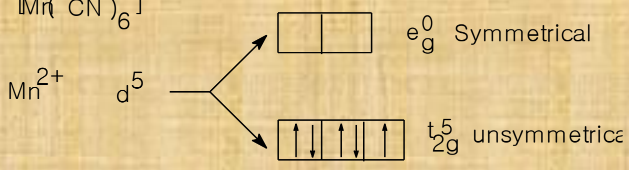
t_{2g}(US) + e_g(US) $\longrightarrow$ Strong distortion

Ex 1: $[Mn(H_2O)_6]^{2+}$



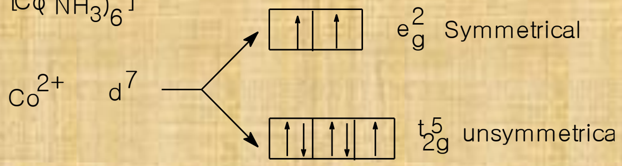
$t_{2g}(S) + e_g(S) \longrightarrow$ No distortion

Ex 2: $[Mn(CN)_6]^{4-}$



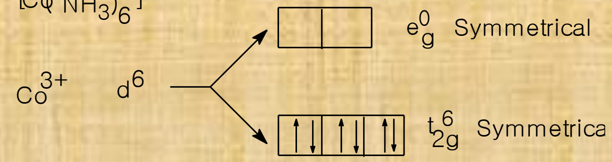
$t_{2g}(US) + e_g(S) \longrightarrow$ Slight distortion

Ex 3: $[Co(NH_3)_6]^{2+}$



$t_{2g}(US) + e_g(S) \longrightarrow$ Slight distortion

Ex 4: $[Co(NH_3)_6]^{3+}$



$t_{2g}(S) + e_g(S) \longrightarrow$ No distortion

UNIT – II
INORGANIC REACTION MECHANISM

Labile complexes

If the ligand substitution reaction in a complex occurs rapidly, the complex is known as labile complexes.

Taube proposed that those complexes that react completely within about one minute at 25^{0}C and 0.1M concentration should be considered labile and those which take longer time should be considered inert.

Inert complexes

If the ligand substitution reaction in a complex occurs slowly, the complex is known as labile complexes.

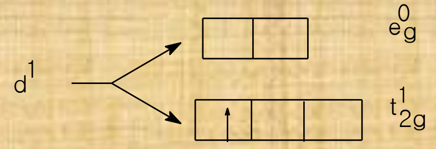
$$\left.\begin{array}{ccc} t_{2g}^0 & t_{2g}^1 & t_{2g}^2 \\ e_g^1 & e_g^2 & e_g^3 \end{array}\right\} \longrightarrow \text{Labile complexe}$$

Remaining are inert complexes

$d^0 \quad d^1 \quad d^2 \longrightarrow$ Labile complexes

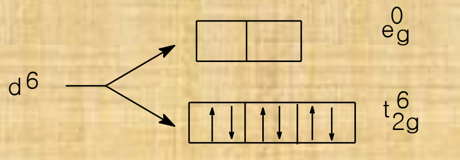
$d^3 \quad d^4 \quad d^5 \quad d^6 \longrightarrow$ Inert complexes

Ex 1: $[Sc(H_2O)_6]^{2+}$



Labile complexes

Ex 2: $K_4[Fe(CN)_6]$



Inert complexes

1. Ligand substitution reactions

In substitution reactions one ligand present in a metal complex is replaced by an external ligand through substitution process.

These are two types

1. Uni molecular nucleophilic substitution reactions SN^1 or Dissociation mechanism
2. Bi molecular nucleophilic substitution reactions SN^{2}or Association

Uni molecular nucleophilic substitution reactions SN^1

According to this mechanism, the complex first undergoes dissociation to lose the ligand to form an intermediate complex. In the second step the intermediate complex readily adds on the new ligand Y to form the final product.

$$\text{step I:}\quad \underset{\text{complex}}{ML_n} \xrightarrow{\text{slow}} \underset{\substack{\text{intermediate}\\ \text{complex}}}{ML_{n-1}} + L$$

$$\text{step II}\quad ML_{n-1} + \underset{\substack{\text{new}\\ \text{ligand}}}{Y} \xrightarrow{\text{fast}} ML_{n-1}Y$$

TheI step, losing of ligand, is slow process.

The II step, adding new ligand to reactive intermediate, is fast.

Rate of reaction depends on the slow process only. So, rate for such a reaction is

Rate = K [MLn]

As the rate depends only upon concentration of one specie MLn, it is known as Unimolecular nucleophilic substitution. Since the complex first gets dissociated in this mechanism it is also known as dissociation

Bi molecular nucleophilic substitution reactions SN^2

$$\text{step I:}\quad \underset{\text{complex}}{ML_n} + \underset{\substack{\text{new}\\ \text{ligand}}}{Y} \xrightarrow{\text{slow}} \underset{\substack{\text{intemediate}\\ \text{complex}}}{ML_nY}$$

$$\text{step II}\quad ML_nY \xrightarrow{\text{fast}} ML_{n-1}Y + L$$

The I step, adding new ligand to complex, is slow process.

The II step, losing the ligand, is fast.

Rate of reaction depend on the slow process only. So, rate for such a reaction is

Rate = K [MLn] [Y]

As the rate depends upon the concentration of two species, the mechanism is known as bimolecular nucleophilic substitution. Since the ligand is first associated with the complex, it is also known as Association.

Substitution in square planar complexes

Square planar complexes are formed by various metal ions, typically by Pt (II), Pd (II), Au (III) and Rh (I).

The metal ions with d^8 configuration generally form this type of complex compounds.

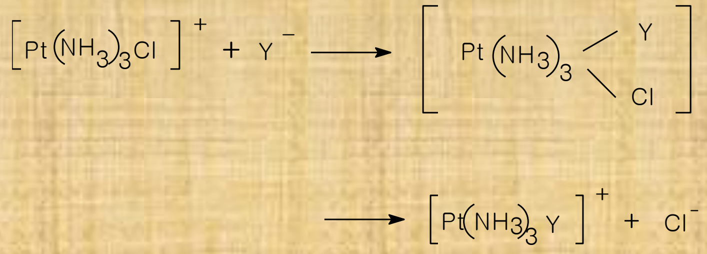
This reaction occurs in two ways

1. Solvent path

$$[Pt(NH_3)_3Cl]^{+} + H_2O \longrightarrow [Pt(NH_3)_3H_2O]^{2+} + Cl^{-}$$

$$[Pt(NH_3)_3H_2O]^{2+} + Y^{-} \longrightarrow [Pt(NH_3)_3Y]^{+} + H_2O$$

2. Displacement path

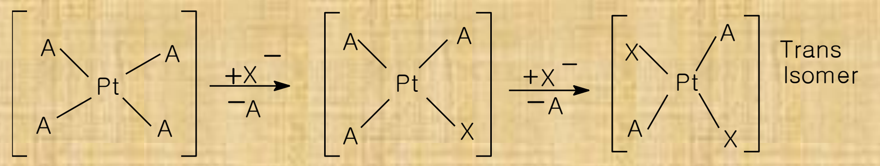


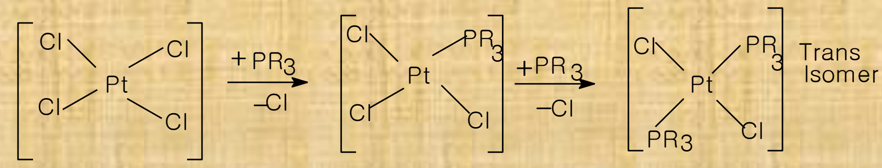
Trans affect

The kinetic effect of the trans-ligand in a square planar substitution is known as trans effect. The tendency of the group to direct the incoming group to occupy the position trans to that group in the complex.

Applications of Trans effect:

1. Synthesis of Pt(II) complexes





STABILITY OF METAL COMPLEXES

Stability constant(β):

The quantitative extent of the metal complex is expressed interms of the equilibrium constant of the metal complex formation reaction.

What are the factors affecting the stability of metal complexes?

Nature of metal ion

Charge ఆవేశం

As the charge of the ion increases, the stability of the complex formed by it increases.

Ex: $\beta_{(LiOH)}{}^{0}= 2$; $\beta_{(MgOH)}{}^{+}= 10^{2}$; $\beta_{[AlOH]}{}^{2+}=10^{7}$; $\beta_{[TiOH]}{}^{3+} =10^{10}$

$Li < Mg^{+2} < Al^{+3} < Ti^{+4}$

As the charge on the metal ion increases β value increases.

Size

As the size of the ion decreases, the stability increases.

$\beta_{[BeOH]}{}^{+}= 10^{7}$; $\beta_{[MgOH]}{}^{+}= 120$; $\beta_{[CaOH]}{}^{+}=30$; $\beta_{[BaOH]}{}^{+}=4$

$Be^{+2} < Mg^{+2} < Ca^{+2} < Ba^{+2}$

Charge-size ratio

As the value of the ratio increases, the stability increases.

$Cu^{+2} > Ni^{+2} > Co^{+2} > Fe^{+2} > Mn^{+2}$

$Be^{+2} > Mg^{+2} > Ca^{+2} > Sr^{+2} > Ba^{+2}$

Nature of the metalలోహస్వభావం

The metals and ligands which form the complexes are classified into two groups, a and b.

Class-a metals are high electro positive class-b metals are low electro positive.

Example for class-a metals

Na, Ca, Al, Ti etc.

Example for class-b metals

Pd, Pt, Hg, Pb etc

Example for class-a ligands

Ligands containing N, O, F elements

Example for class-b ligands

Ligands containing p, s elements.

class-a metals with class-a ligands and class-b metals with class-b ligands give stable complexes.

Nature of ligand

Basic nature If a ligand is more basic, the complex it forms is more stable.

Ex: NH_3 is more basic than H_2O. Therefore NH_3 forms with a metal more stable complex than water.

Chelating effect

If a ligand coordinates at more than one place with the metal and forms the complex, there will be rings in the complex. Such ligands which form the metal ligand complexes containing the rings are called chelating ligands. The complexes formed by such ligands are called chelates. This effect is known as chelating effect.

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Ex: $H_2N\ CH_2\ CH_2\ NH_2$ (en), $C_2O_4^{2-}$, EDTA etc.

DETERMINATION OF COMPOSITION OF A COMPLEX BY JOB'S METHOD

- Let us consider metal ion (M) reacts with ligand L to form a complex

  $$M + nL \rightleftharpoons ML_n$$

  n is the number of moles of ligands. The value of n is to be determined experimentally.
- In this method, equimolar solutions of the metal ion and the ligand solution are prepared separately. These solutions are mixed as shown below and the mixed solutions are prepared. The total volume is constant (10 mL).

Metal solution(mL)	0	1	2	3	4	5	6	7	8	9	10
Ligand solution(mL)	10	9	8	7	6	5	4	3	2	1	0

- In all the above mixed solutions the total number of moles is same.
- If the concentration of the mixed solution is 'C '.

  $C = C_M + C_L$

  C_M = concentration of metal ion solution

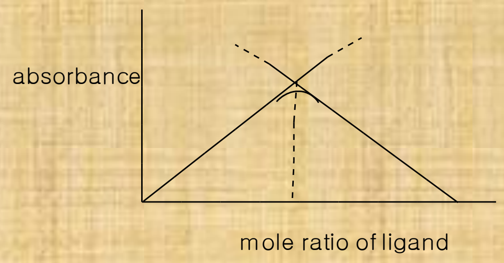
  C_L= concentration of ligand solution

The mole fraction of ligand= $\frac{C_L}{C} = X$

The mole fraction of metal ion, $\frac{C_M}{C} = 1 - X$

If the formula of the complex is MLn

$$n = \frac{\text{Mole fraction of ligand}}{\text{Mole fraction of metal ion}} = \frac{C_L}{C} \times \frac{C}{C_M} = \frac{C_L}{C_M} = \frac{X}{1-X}$$



The wave length at which the metal complex formed exhibits maximum absorbance must be first experimentally established. At this wave length the absorbance(A) of each of the mixed solution is measured with a spectrophotometer.

A graph is drawn between the absorbance(A) and the mole fraction of the ligand. The mole fraction of the ligand corresponding to the point of maximum absorbance is obtained from the graph by extrapolation method.

The mole fraction of ligand corresponding to this maximum point is identified and it denotes X.

$$\frac{X}{1-X} = n$$

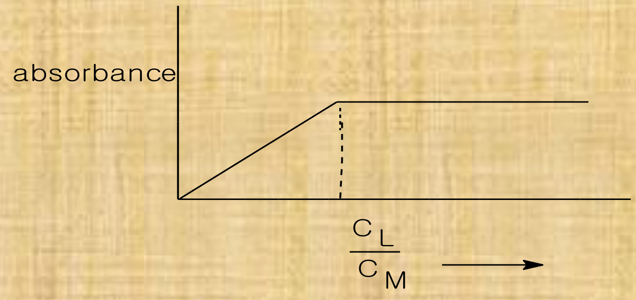
MOLE – RATIO METHOD

In this method the concentration of one of the two solutions, metal ion solution or ligand solution is kept constant and the second one is varied. By this method different mixed solutions of metal and ligand are prepared. The composition of mixed solutions is given below.

Metal ion solution mL	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Ligand solution mL	0.0	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0
Water mL	12.5	11.5	10.5	9.5	8.5	7.5	6.5	5.5	4.5	3.5

The absorbance of each mixed solution is measured spectro photometrically at the wave length corresponding to the maximum absorbance of the complex formed. A graph is drawn between the absorbance and C_L/C_M.

If only one complex is formed in the solution, the absorbance varies linearly with C_L/C_M and at a particular volume of C_L/C_M it becomes constant. The point corresponding to this point of intersection gives value of n.



BIO INORGANIC CHEMISTRY

The science that is concerned with all types of chemical reactions occurring in living organisms is called biochemistry.

The chemical elements are classified into two categories based on the chemical reactions and metabolic processes in living organisms.

These are 1. Essential elements

2. Non-essential elements

Essential elements

Those elements which are indispensable to maintain the normal living state of a tissue or the whole body.

Depending on their quantity again these are classified into

a) Macro elements b) Micro elements.

Chemical elements required in large amounts are called macro elements.

Ex: Na, K, Mg, Ca, S, P, Cl, Fe, C, H, O

Chemical elements required in small amounts are called micro elements.

Ex: Cu, Zn, Cr

The elements present in traces are called trace elements.

Explain the importance of elements in biological systems

Metals play important role in biochemical metabolisms.

For example Fe, Co, Mn, Cu, Mg is present in combination with proteins (metal-proteins are called chromo proteins). These are present as enzymes. The metal ion functions as activators in enzymes and help in group transfer, redox and hydrolysis reactions.

Biological significance of Na, K and Cl

These elements are obtained through food materials.

Sources: The important source of sodium and chlorine is common table salt(sodiumchloride). K is found in almost all foods, both plant and animal, coffee, tea, cocoa, dry beans, molasis, green leafy vegetables, milk, fish, chicken, pig meat, plantain and potatoes.

People suffering from blood pressure, kidney diseases, heart disease sodium deficiency is noticed. This is because these people are not allowed to consume common salt.

Functions: These are charge carriers. These are participating in the control of osmotic pressure. These preserve the sensory character of nerves. These control the muscular actions. These stabilize the P^H of bio fluids. These stabilize the viscosity of the blood. Na, K are useful in the formation of HCl that takes part in metabolism and also bile. These are also useful in preserving proteins and glycogens.

Absorption: Normally these three are completely absorbed from the gastrointestinal tract.

Biological significance of Mg and Ca:

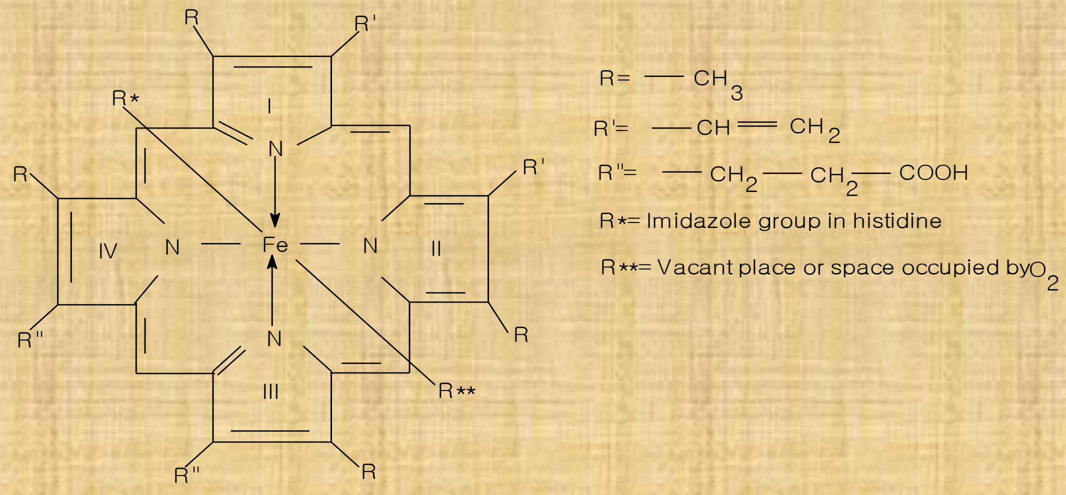
Mg^{2+} ion is present as the central ion in chlorophyll. This helps in the propagation of nerve impulses.
Ca^{2+} ions are useful in the building of cell wall. Deficiency of Ca^{2+} ions leads to rickets disease. In hormone reactions, it acts as messenger. In the contraction of muscles and in the clotting of blood, Ca^{2+} ions are very useful.

Biological significance of Fe

Fe^{2+} is the central metal ion present in hemoglobin, and other hemes. This is participating in the production of red blood cells/corpuscles. Iron is as important as blood in the body. Deficiency of this leads to anemia. This helps in the transport of O_2 in blood. It is also useful to store oxygen in muscles.

Give the structure and the functions of Hemoglobin.

Hemoglobin is responsible for the red colour of red blood corpuscles. Hemoglobin is a combination of the prosthetic group heme and the protein part globin. In heme, there is one porphyrin ring and one iron atom. Hemoglobin is bound with four heme units and four protein chains. So hemoglobin is tetramer. In respiration diamagnetic property changes to paramagnetic property.



Heme -b

Hemoglobin is of three type’s
Adult hemoglobin
Foetal hemoglobin
Sickle cell hemoglobin

Functions of hemoglobin

Hemoglobin transports oxygen in respiration. In respiration there will be exchange of O_2 and CO_2 between the body and the environment.
It takes oxygen to peripheral tissues from lungs. CO_2, H^+ ions are transported from peripheral tissues to respiratory organs and thereafter they are transported for excretion.
Oxygen is transported to myoglobin present in the peripheral tisues and oxygen is stored there.
If P^H decreases, hemoglobin loses affinity for oxygen.

CO binds with Fe^{2+} of hemoglobin and forms carboxy hemoglobin. This is symmetrical bond. This cannot be easily dissociated. Therefore CO molecule disrupts oxygen transport and acts as a poison.

Give the structure and the functions of chlorophyll

The green colouring matter of plants is chlorophyll.

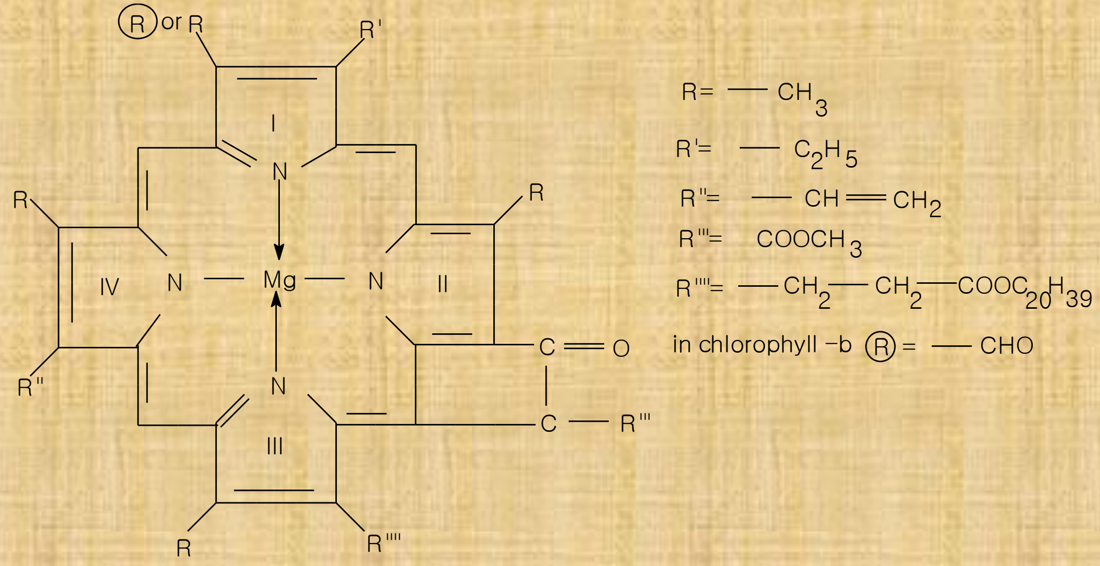
Chlorophyll is of two types. Chlorophyll- a, Chlorophyll-b

These are present in all species which contains parts that perform photosynthesis.

In chlorophyll-a, there will be at β-carbon a methyl group in pyrrole ring. In chlorophyll-b, there will be formyl group unlike CH_3 group in chlorophyll-a.

Chlorophyll-a absorbs light of wavelength 4300A^0(blue colour) while chlorophyll-b absorbs light of wave length 6800A^0(red).

It makes use of red light absorbed in photosynthesis. In photosynthesis CO_2 and H_2O vapour of the atmosphere react in presence of sunlight in green leaves and prepare carbohydrates.



Functions of Chlorophyll

Mainly responsible to photosynthesis.

Helps in maintaining O_2 and CO_2 balance in nature.

When chlorophyll absorbs light, the electrons are excited. These are moved from the molecule. The energy of the molecule increases. In photosynthesis there are two main light systems.

Light system – 1 in this process a reducing agent is formed leading to the formation of NADPH + H$^+$. This reaction occurs in chlorophyll-a.

Light system – 2 in this process an oxidant is formed. This leads to formation of oxygen. This takes place in chlorophyll-b.

Photo synthesis reaction

$$X\ CO_2 + X\ H_2O \xrightarrow{\text{Chlorophyll}} (CH_2O)_X + X\ O_2$$

It carries two stagesPS – I

1. PS – II

Primary product of PS – I is CO_2. CO_2 reduces to carbohydrate.

$$(CO_2)_n \longrightarrow (CH_2O)_n$$

Primary product of PS – II is energy in the form of two moles of ATP with oxygen as bi product(oxidation). In this process water is converted to oxygen.

$$ADP \longrightarrow ATP + O_2 + \text{Energy}$$

UNIT – III

PHASE RULE

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State Gibb’s Phase rule and explain the terms in it

“In a heterogeneous system in equilibrium the number of degrees of freedom and the sum of the phases are equal to the number of components plus 2.”

Mathematically it can be expressed as $P + F = C + 2$

Here P= Phase
F= Number of degrees of freedom
C=Number of components

Phase

“Phase is any part of a system which is homogeneous physically distinct and mechanically separable are termed as Phase.”

Ex: 1. Water system have three phases namely ice(S), Water (l), Vapor (g).

2. Mixture of two or more gases and mixture of two or more miscible liquids are having only phase.

Components

“The minimum number of independently variable constituents by means of which the composition of every possible phase in the system can be expressed with a chemical formula.”

Ex: Water system has three phases all these phases can be expressed by H_2O. So number of components of water system is one.

Number of degrees of freedom

“The minimum number of variable factors such as temperature, pressure and the composition of the phases which must be arbitrarily fixed in order to define condition of the system completely are termed as degrees of freedom.”

Ex: Water system has three phases all these three phases can be equilibrium at constant temperature and pressure. So the system has no degrees of freedom.

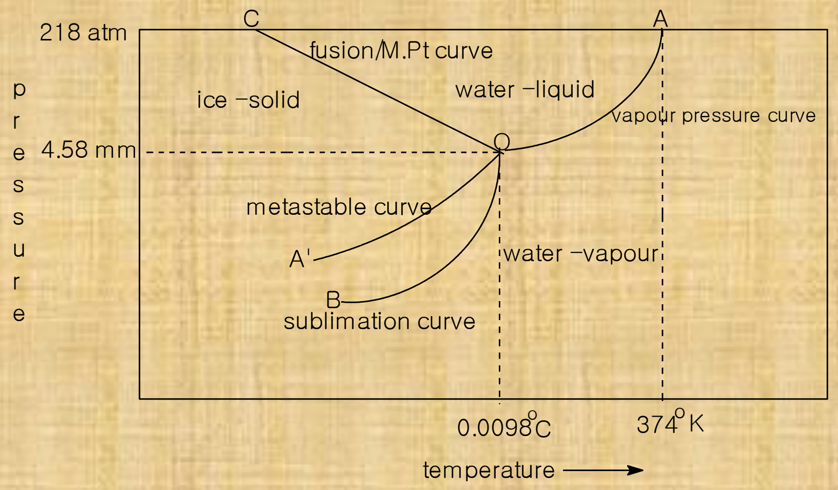
(If its temperature or pressure is changed one of the three phases will be disappear)

EXPLAIN THE PHASE DIAGRAM OF WATE SYSTEM (ONE COMPONENT SYSTEM)

The water system is one component system

- Water can exist mainly in three phases namely ice, water, and water vapor P=3

- The chemical formula of each phase is represented by H_2O. So number of components of water system is one. C=1
- The phase diagram consists of three curves OA, OB and OC. All these curves meet at point O
- These three curves divide the diagram into three areas AOB, AOC and BOC.



Curve OA (vaporisation curve)

water $\rightleftharpoons$ vapour

The curve OA starts from O. This is the freezing point of water. This curve ends at A. It represents the equilibrium between water and vapor. At any point on this curve the temperature is raised liquid phase will be disappear and if the temperature is decreased the vapor phase will be disappear. Any point on this curve two phases are coexist in equilibrium ie water and vapor.

P + F = C + 2 P=2, C=1
F= C + 2 – P
F= 1 + 2 – 2
F=1

∴The system is univariant

Curve OA' (metastable curve)

The curve OA' is a continuous curve of OA and represents the vapor pressure curve of super cooled water.This curve is known as metastable curve. When water vapor is cooled slowly it becomes solid at 0^0C. The super cooled water once changes into solid ice the curve merges into OB.

P + F = C + 2 P=2, C=1
F= C + 2 – P
F= 1 + 2 – 2
F=1

∴The system is univariant.

Curve OB (Sublimation curve)

ice $\rightleftharpoons$ vapour

The curve OB starts from O. This curve ends at B. It represents the equilibrium between ice and vapor. Below the triple point the solid phase can be changed into vapor phase. So at any point on this curve two phases are coexisting in equilibrium.

P + F = C + 2 P=2, C=1

F= C + 2 – P
F= 1 + 2 – 2
F=1

∴The system is univariant.

Curve OC (Fusion curve)

water $\rightleftharpoons$ ice

This curve shows the equilibrium between ice and liquid. The curve OC is having slope towards the pressure axis indicates the melting point of ice decreases with increase of pressure. At any point on this curve two phases are coexisting in equilibrium.

P + F = C + 2 P=2, C=1
F= C + 2 – P
F= 1 + 2 – 2
F=1

∴The system is univariant.

Triple point (O)

At this point all the three phases are in equilibrium. At this point the temperature and pressure are fixed at 0.00980^0 C and 4.58 mm.

P + F = C + 2 P=3, C=1
F= C + 2 – P
F= 1–3+ 2
F=0

∴The system is non-variant.

Areas) AOB, BOC, AOC

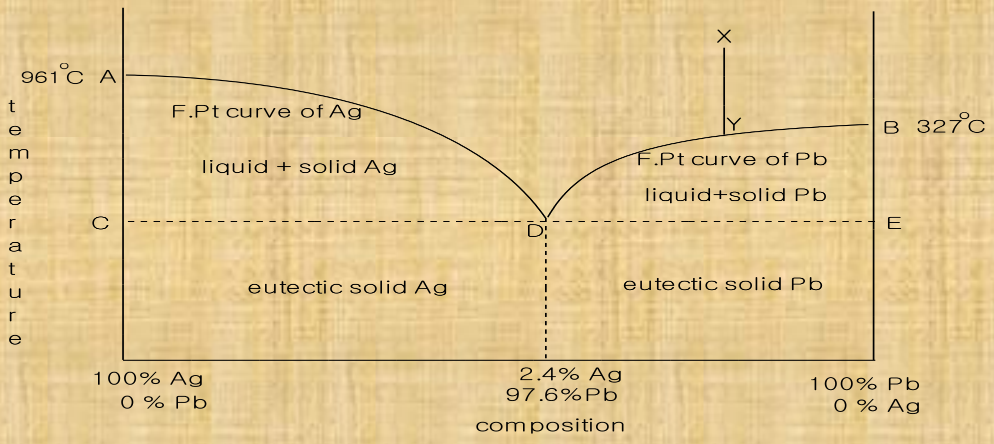
Any point on these areas only one phase is present.

P + F = C + 2 P=1, C=1 AOB= Vapor
F= C + 2 – P BOC= Ice
F= 1 + 2 – 1 AOC= Water
F=2

∴The system is bi variant.

Explain the phase diagram of Lead – Silver system

- Lead – Silver system is a two component system.
  This system has three phases namely
  1. Solid lead
  2. Solid Silver
  3. Solution of Silver and Lead in molten state.
- Phase diagram of this system consists of two curves AD and BD.
- These curves divide the diagram into one area i.e. ADB



Curve AD (Freezing point curve of Silver)

Point A is the melting point of pure Ag (961^0C). At this point small amount of lead is added gradually the melting point of Silver is decreased along AD curve. At point D no more lead goes into solution. At this point the solution becomes saturated with respect to Lead and any more lead is add to it separates out as a solid.Any point on this curve two phases are co-exist in equilibrium Solid Ag and Solution of Ag &Pb.

P=2, C=2

P + F' = C+1

F' = C – P + 1

F' = 2 – 2 + 1

= 1

∴The system is univariant

Curve BD (Freezing point curve of Lead)

Point B is the melting point of pure lead (327^0C). At this point small amount of Silver is added gradually the melting point of lead decreases along curve BD curve. At point D the solution becomes saturated with respect to Silver and any more Silver is added to it separates out as solid.Any point on this curve two phases are co-exist in equilibrium Solid Lead and Solution.

P=2, C=2

P + F' = C+1

F' = C – P + 1

F' = 2 – 2 + 1

= 1

∴The system is univariant.

Point D (Eutectic point)

At this point D two curves AD and BD are intersect and three phases are coexist in equilibrium. Those are Solid Ag, Solid Pb and Solution of Ag &Pb.

P + F' = C+1P=3, C=2

F' = C – P + 1

F' = 2 – 3 + 1

= 0

∴The system is nonvariant. At this point the composition of Ag is 2.4%, Pb is 97.6%.

Area above ADB

In this region only liquid phase is exist.

So $P=1$

$P=1, C=2$

$P + F' = C+1$

$F' = C - P + 1$

$F' = 2 - 1 + 1$

$= 2$

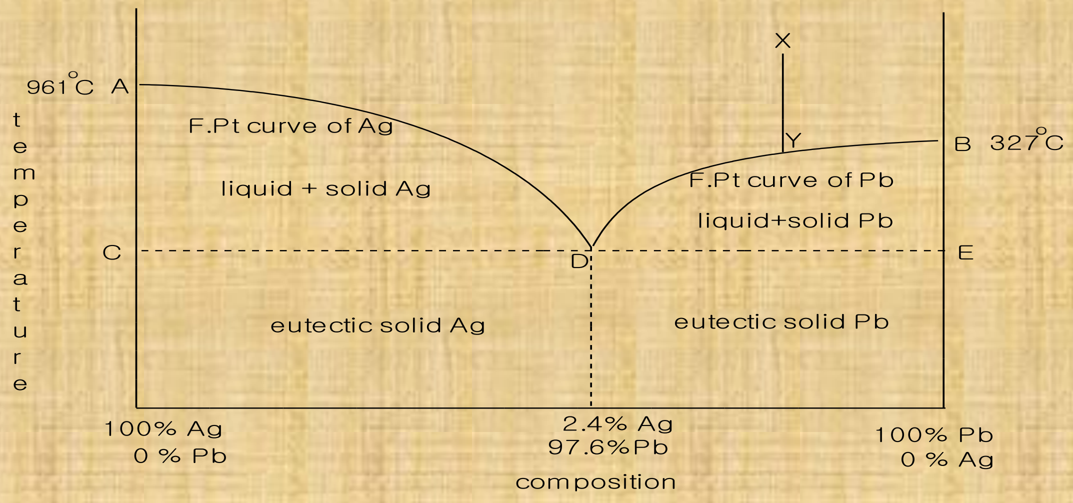
∴The system is bivariant.

Write the application of Lead – Silver system OR Desilverisation of Lead by Pattinson’s process

This process is based on the phase diagram of Pb-Ag system. The lead extracted from Galena contains traces (0.1%) of Silver. Lead is heated to a temperature above its melting point. So the system consists of only liquid phase.

Let X represents the molten lead containing a small amount of Ag. It is then allowed to cool. The temperature of the melt will fall along the line XY without change in composition till the Y is reached. When the point Y is reached lead will begin to crystallize out (it is removed with the help of ladels) and the solution will contain relatively increasing amount of Silver. Further cooling of the liquid takes place along the line YD. Lead continues to separate till the amount of Silver increases upto 2.6%.

“The process of increasing the concentration of Ag in Argentiferrous lead is known as Pattinson’s process.”



Incongruent melting point

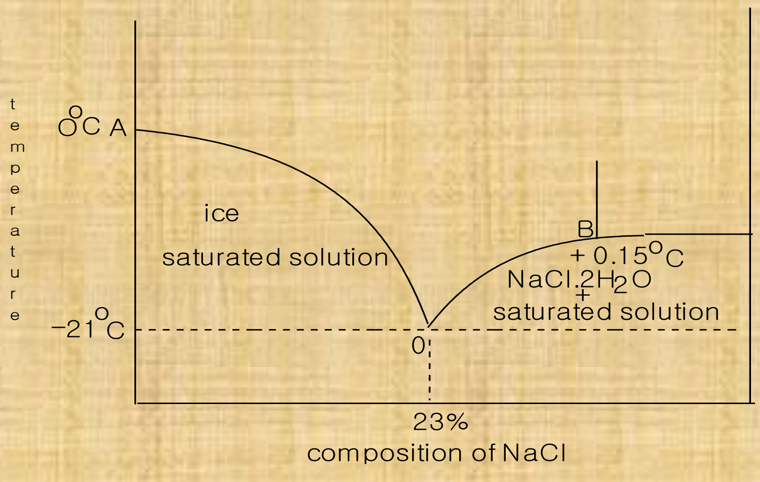
At which point the composition of solid and liquid are not in equilibriumis called incongruent melting point.

Explain NaCl – H_2O system (Sodium chloride – Water system)

This system has four phases namely

1. NaCl. $2H_2O$
2. NaCl
3. Ice
4. Solution

- It is two component system so C=2
- Phase diagram consists of two curves AO and BO. Both these curves meet at point O.
- This phase diagram consists of one incongruent melting point (B)



Curve AO

It is the freezing point curve of water (or) Point A is the melting point of ice. Sodium chloride is added to water the freezing point of water decreases along the curve AO.Along the curve AO two phases ice and solution are in equilibrium

P=2, C=2

P + F’ = C+1

F’ = C – P + 1

F’ = 2 – 2 + 1

= 1

∴The system is univariant.

Curve BO

It is the solubility curve of hydrated sodium chloride. The steep rise of the curve indicates the solubility of sodium chloride increases slowly with rise of temperature.At any point on this curve two phasesNaCl. $2H_2O$ and solution are in equilibrium

P=2, C=2

P + F’ = C+1

F’ = C – P + 1

F’ = 2 – 2 + 1

= 1

∴The system is univariant.

Point B

This is incongruent melting point. Temperature at this point is +0.15^{0}C. At this point dehydrate sodium chloride (NaCl. 2H_2O) changes to anhydrous NaCl. At this point three phases are present.   P=3, C=2

P=3, C=2

1. NaCl. 2H_2O
2. NaCl (anhydrous)
3. Solution

P=3, C=2

P + F' = C+1

F' = C – P + 1

F' = 2 – 3 + 1

= 0

∴The system is nonvariant.

At this point the composition of solid and liquid are in equilibrium is not identical. So point B is known as incongruent melting point.

Point O

At this point the solution becomes saturate and the NaCl.2H_2O separates out. So at this point three phases are coexist in equilibrium. At this point solid NaCl and solution contains 23% NaCl. Temperature at O is -21^{0}C.

P=3, C=2

P + F' = C+1

F' = C – P + 1

F' = 2 – 3 + 1

= 0

∴The system is nonvariant.

The eutectic point for salt – water system is called cryohydric point. The mixture present at cryohydric point is called cryohydrate. The composition of cryohydrate is called cryohydric composition.

Freezing mixtures

Mixture of salt and ice is called as freezing mixtures.

When a salt is added to ice its temperature will be decreased. As more and more amount of salt is added the temperature further until a lowest temperature is reached. At this temperature the salt, ice and solution are in equilibrium. This temperature is known as eutectic temperature. This temperature depends upon the nature of salt.

Ex: NH_4Cl + Ice = – 16.0
NH_4NO_3 + Ice = – 18.0
$NaNO_3$ + Ice = – 18.1
NaCl.2H_2O + Ice = – 21.0
KI + Ice = – 23.

ELECTRO CHEMISTRY

Conductance C

The reciprocal of resistance (R) is known as conductance.

$\frac{1}{R} = \frac{1}{\rho X \frac{l}{a}}$

C= $\frac{1}{\rho X \frac{l}{a}}$

Specific conductance K

The reciprocal of specific resistance (***ρ***) is known as specific conductance.

C= $\frac{1}{\rho X \frac{l}{a}}$

$\frac{CXl}{a} = \frac{1}{\rho}$

K= $\frac{CXl}{a}$

Equivalent conductance ∧

Conductance of a volume of a solution containing 1 g equivalent of solute between two parallel electrodes separated by unit length is called equivalent conductance.

KOHLRAUSCH'S LAW

The equivalent conductance at infinite dilution of an electrolyte ($\wedge\infty$) is equal to the algebraic sum of the equivalent conductance of mobilities of the cation ($\wedge\infty^{+}$) and the anion ($\wedge\infty^{-}$) of the electrolyte at infinite dilution.

$\wedge\infty = \wedge\infty^{+} + \wedge\infty^{-}$

Application of Kohlrausch's law

$\wedge\infty$ for CH_3COOH is obtained from the $\wedge\infty$ values of HCl, NaCl and CH_3COONa(sodium acetate)

$\wedge\infty$ HCl= $\wedge\infty$ H^{+} + $\wedge\infty$ Cl^{-}

$\wedge\infty$ NaCl = $\wedge\infty$ Na^{+} + Cl^{-}

$\wedge\infty$ CH_3COONa = $\wedge\infty$ CH_3COO^{-} + $\wedge\infty$ Na^{+}

From these equations

$\wedge\infty$ HCl + $\wedge\infty$ CH_3COONa - $\wedge\infty$ NaCl =

$\wedge\infty$ H^{+} + $\wedge\infty$ Cl^{-} + $\wedge\infty$ CH_3COO^{-} + $\wedge\infty$ Na^{+} – $\wedge\infty$ Na^{+}– $\wedge\infty Cl^{-}$

= $\wedge\infty$ H^{+} + $\wedge\infty$ CH_3COO^{-}

= $\wedge\infty$ CH_3COOH

It is equivalent conductance of the electrolyte CH_3COOH at infinite dilutions.

Degree of dissociation

The fraction of the total number of molecules present in the solution as ions is known as degree of dissociation.

OSTWALD DILUTION LAW

Consider one mole of the electrolyte AB dissolved in V liters of the solution. Let the degree of dissociation be α. According to the law of mass action.

$$AB \rightleftharpoons A^{+} + B^{-}$$

Equivalent concentrations are

$$\frac{1-\alpha}{V}\frac{\alpha}{V} \quad +\frac{\alpha}{V}$$

Equivalent constant (K) = $\frac{\frac{\alpha^2}{V^2}}{\frac{1-\alpha}{V}}$

$$= \frac{\alpha^2}{VX\,(1-\alpha)}$$

$$K = \frac{\alpha^2 C}{(1-\alpha)}$$

Debye – Huckel – Onsagar equation for strong electrolytes

1. All strong electrolytes are almost completely dissociated into ions at all dilutions.
2. Anions and cations are not uniformly distributed in the solution of an electrolyte. The ions of particular charge are surrounded by more of oppositely charged ions and solvent molecules.
3. As the concentration of the solution increases, the inter ionic attractive forces increases which prevent the mobilities of ions and hence equivalent conductivity decreases with increase of concentration.

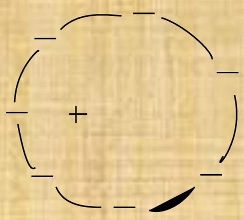
4. Strong electrolytes are not obeying Arhenius theory.

Asymmetry effect Or Relaxation effect

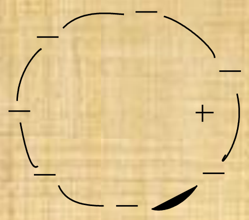
In the solution of strong electrolyte each ion is surrounded by oppositely charged ions due to inter ionic forces of attractions.

For example in an electrolyte a –ve ion is surrounded by several +ve ions and a +ve ion is surrounded by several –ve ions three dimensionally. These ionic spheres are symmetrical. So the forces of attraction exerted by the atmosphere on the central ion are uniform in all directions.

When current is passed through the electrolyte solution the ions move towards the oppositely charged electrodes. Thus the central ion moves in one direction and surrounding ions moves in the opposite direction. So symmetrical ionic atmosphere transforms into as asymmetric Due to this the +ve ion is much force of attraction from behind. Which is called retarding force. Thus the mobility of the ion is retarted and this effect is called asymmetric effect or relaxation effect.



symmetrical ionic atmosphere



asymmetric ionic atmospher

Electrophoretic effect In an electrolytic solution the ions are attracted by several water molecules such ions are called hydrated ions. When e. m. f is applied these hydrated ions move against a steam of solvent which is associated with opposite ionic atmosphere due to this the mobilities of ions (or) the velocities of ions will be deduced. This reduction depends on the thickness of the ionic atmosphere and viscosity of the solvent.

$\lambda_V = \lambda_0 - (A + B\,\lambda_0)\sqrt{C}$ A and B are constants

$A = \frac{82.4}{\sqrt{DTX\eta}}$ $B = \frac{8.2\ X\ 10^5}{\sqrt[3]{D}}$

TRANSPORT NUMBER

"The fraction of the total current carried by particular ion is called its transport number"

$= \frac{Current carried by cation}{Total current carried}$

$= \frac{U^+}{U^- + U^+}$ or $\frac{U_C}{U_a + U_C}$

Transport number of anion (ta)

$= \frac{U^-}{U^- + U^+}$ or $\frac{U_a}{U_a + U_C}$

$t_c + t_a = \frac{U^+}{U^- + U^+} + \frac{U^-}{U^- + U^+}$

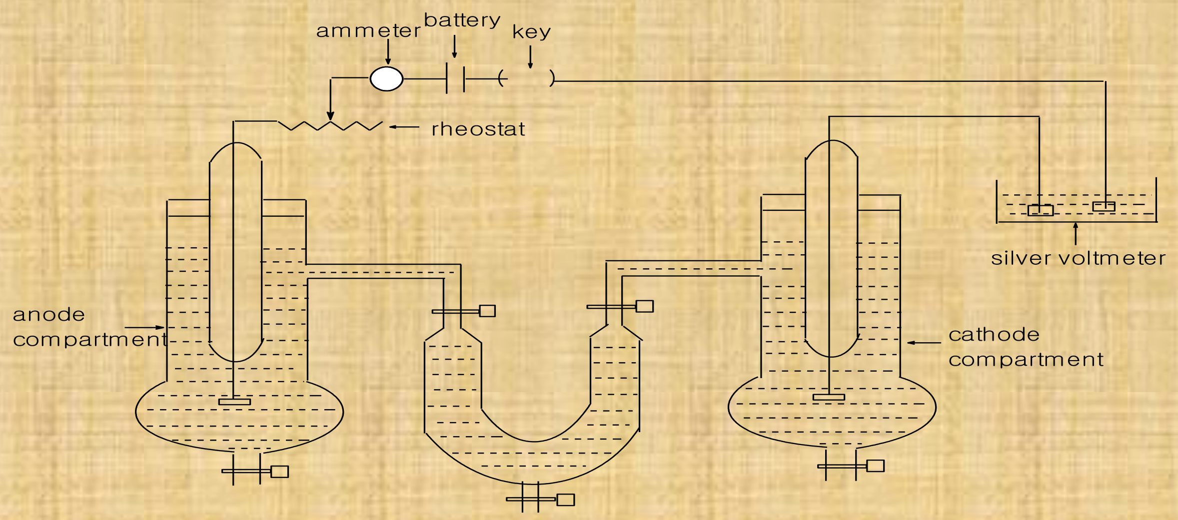
$t_c + t_a = 1$

Determination of transport number of Ag^+ ion or NO_3^- ion in the solution of $AgNO_3$ by using Hitorff's method.

The apparatus consists of two vertical glass tubes; these are connected through a U-tube. The left glass tube contains the anode so it is called as anode compartment. The right glass tube contains the cathode so it is called as cathode compartment.

DeterminationNO_3^- ion

In this method standard solution of $AgNO_3$ (0.1M) is used. In this method electrodes are made of pure silver. The apparatus are filled with standard $AgNO_3$ solution. A silver voltmeter or coulometer, adjustable resistance (rheostat) milli ammeter, key and battery are connected in series as shown in figure. For electrolysis 10 – 20 mA of current is passed for2 – 3 hours. In this time an appreciable change in concentrations around the electrodes takes place. The number of equivalents of Ag dipposited on cathode electrode in voltmeter gives the measure the total current passed. Solution from cathode and anode compartment is drained into a beaker and the weight of the solution is noted. The change in concentration is determined by using potassium or ammonium thiocyanate. Solution is again analyzed by titrating against the $AgNO_3$ solution by ammonium thiocyanate. Similarly the solution in middle compartment is analyzed there is no change in concentration. From the amount of the electrolyte in the same weight of water before and after electrolysis are weighed. The loss at the electrode compartment is obtained.



Calculations:

1. Concentration of anodic solution before electrolysis is X g
2. Concentration of anodic solution after electrolysis is Y g
3. Increase in the weight of Ag due to electrolysis = X – Y g = w g
4. If the no Ag had migrated from the anode, the increase in the weight should have been W g
5. Loss in concentration due to migration of Ag^+ ion= W – w g
6. Hence transport number of Ag^+ ion t_{Ag^+}

$$= \frac{Lossinconcentrationaroundanode}{Totalloss} = \frac{W-w}{W}$$

Transport number of NO_3^- ion t $_{NO3^-}$

$t_{NO3^-} = 1 - \frac{W-w}{W}$

Conductometric titrations

The titration in which end point or equivalent point is determined by means of conductance measurements is called conductometric titrations.

Principle

Electrical conductance depends upon the number and mobility of ions.

In these titrations alkali solution is taken in the burette and known volume (20ml) of the acid is taken into a beaker kept in thermostat. The conductivity cell is dipped in this beaker and connected to Conductivity Bridge. The conductance of the acid solution is noted initially. The acid solution contains the fastest moving H^+ ions. Its conductivity is very high. To the acid solution base is added from the burette with constant stirring of the solution. After the addition of each one ml of alkali the conductivity is noted. In this way conductivity is determined after the addition of one ml of alkali each time. A graph is drawn between the volume of alkali and conductivity.

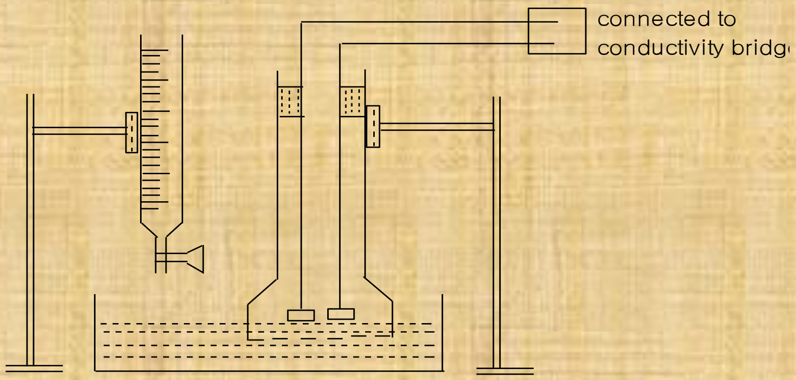
$N_1V_1 = N_2V_2$

N_1= Concentration of acid

V_1 = Volume of acid

N_2 = Concentration of base

V_2 = Volume of base

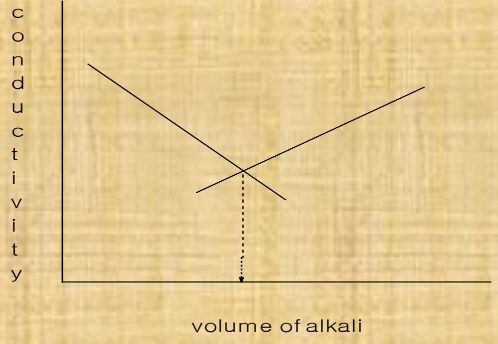


Ex: 1 Strong acid Vs Strong base

Ex: HCl Vs NaOH

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

Take 20 ml acid in a beaker kept in thermostat. The conductivity cell is dipped in this beaker and connected to Conductivity Bridge. NaOH solution is taken in the burette.The conductance of the HCl solution is noted initially. To the acid solution base is added gradually. The H^+ ions are replaced by Na^+ ions. Hence continued addition of NaOHthe conductance will go to decrease until the acid has been completely neutralized. The conductivity of the solution obtained on the addition of NaOH to this neutral solution increases and this will goes on increasing with addition of NaOH.On plotting the conductance against the volume of alkali the points will lie on two straight lines. The point of intersection gives the end point.



Nernst Equation = $E^0 + \frac{0.0591}{n} \log \frac{[Oxidation]}{[Reduction]}$

Number of electrons transfer = n

Standard electrode potential = E^0

Ex 2: Strong base Vs Weak acid

Ex: CH_3COOH Vs NaOH

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

Conductance of CH_3COOH is very low on account of its poor dissociation when alkali is added a salt forms which is a strong electrolyte and hence conductivity increases along line AB. When acid is completely neutralized further addition of alkali increases the number of OH^- ions and so the conductivity increases rapidly along line BC. B is the end point.

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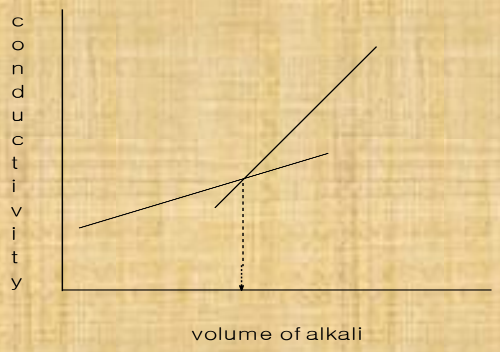
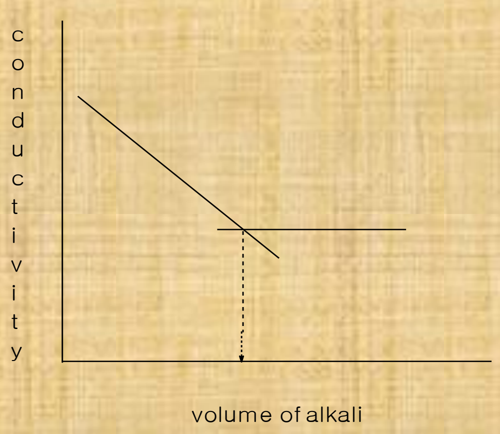


Ex 3: Strong acid Vs Weak base

HCl Vs NH_4OH

$$HCl + NH_4OH \longrightarrow NH_4Cl + H_2O$$

Conductivity of the HCl is initially high. Because HCl is a strong electrolyte and it dissociates to give the fast moving H^+ ions. When NH_4OH solution is added to the HCl solution the fast moving H^+ ions are replaced by NH_4^+ ions and hence the conductivity of the solution decreases along AB curve. After the end point has further addition of NH_4OH will not cause any appreciable change in conductivity because it is a weekly ionized substance.



REVERSIBLE ELECTRODES / CELLS

Some of the cell reactions may be restored by applying some external e. m. f slightly higher than the cell e. m. f in opposite direction. Such cells are said to be reversible.

Ex: Galvanic cell

IRREVERSIBLE ELECTRODES/CELLS

If it is not possible to restore the cell reaction, it is said to be irreversible.

Ex: Daniel Cell

Classification of reversible electrodes

1. Metal – Metal ion electrodes
2. Gas electrodes
3. Metal – Metal salt ion electrodes
4. Oxidation reduction electrodes

Electrode: it consists of a metal rod dipping into a solution containing its own ions.

1. **Metal – Metal ion electrode**

   This cell consists of Cu)copper) rod dipped in a solution of $CuSO_4$. This is separated with the help of pours diaphragm from the solution of ZnSO4 in which Zn rod is dipped.

   $$Zn \mid Zn^{++} \parallel Cu^{++} \mid Cu$$

Metal electrode

Zinc electrode $Zn^{++}(aqu) \mid Zn$

Non-metal electrode

Hydrogen electrode $H^{+}(aqu) \mid H_2(g), Pt$

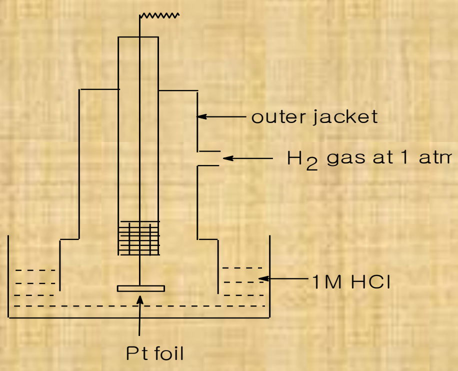
Single electrode potential

Cell is made up of two electrodes. One of the electrode oxidation takes place (electrons are evolved) at the other electrode reduction takes place(electrons are consumed) ‘The tendency of an electrode to loss or gain electrons is called electrode potential’. ‘The potential of a half cell is known as single electrode potential’. ‘single electrode potential is the difference of potential between a metal and that of the aqueous solution of its salt’.

Standard Hydrogen Electrode (SHE)

It is the primary standard electrode. It consists of a Pt foil coated with finely divided Pt black. This foil is fixed in a glass tube. The tube is enclosed in an outer jacket which is widened at the bottom and provided with holes through which excess of hydrogen gas can escape out.

The electrode is dipped into a solution of 1 M acid(HCl) pure and dry H_2 gas is continuously bubbled at a pressure of one atmosphere and at 25 ^{0}C. The potential of this electrode is arbitrarily fixed as zero (E^0). This half-cell is known as standard hydrogen electrode (or) Reference electrode (or) Normal hydrogen electrode.



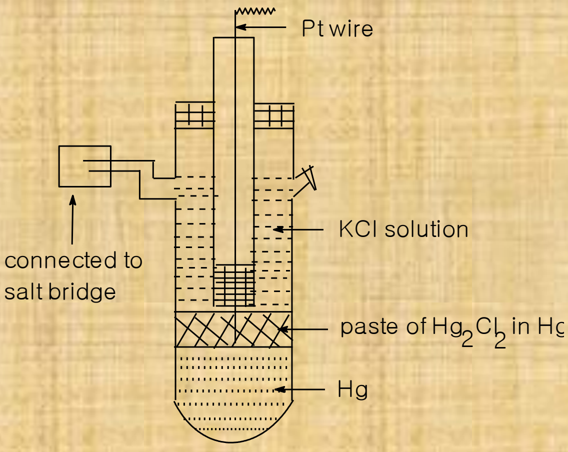
Half-cell reactions are

$$H_2(g) \longrightarrow 2H^+ + 2e$$
$$2H^+ + 2e \longrightarrow H_2(g)$$

Calomel electrode (metal – metal salt ion electrode)

It is secondary standard electrode. It consists of a glass tube provided with a side tube to connect salt bridge. There is another side tube is provided for the introduction of required chemicals.

Highly purified Hg metal is taken into this tube. It is then covered with a paste of calomel (Hg_2Cl_2) in Hg. A Pt wire sealed in a glass tube is dipped in this paste. The remaining part of the electrode is covered with a solution of KCl and Hg_2Cl_2. This electrode is connected to hydrogen electrode and the e.m.f of the cell is determined. This gives the electrode potential of calomel electrode. The potential of calomel electrode depends upon the concentration of KCl solution.



Electro chemical series

The table indicating the standard electrode potentials of different metals is called electro chemical series.

CHEMICAL KINETICS

Rate of reaction

The decrease of concentration of the reactants or increase in concentration of the products per unit time.

Rate of reaction = $\frac{Amount\ of\ reactant\ consumed}{Time\ interval}$

Or

= $\frac{Amount\ of\ product\ produced}{Time\ interval}$

Ex: $Zn + 2HCl \longrightarrow ZnCl_2 + H_2$

Rate of reaction = $\frac{Amount\ of\ Zn\ consumed}{Time\ interval}$

= $\frac{Amount\ of\ hydrogen\ produced}{Time\ interval}$

Velocity of a reaction: The change in the concentration per unit time

$\frac{dX}{dt}$ = rate

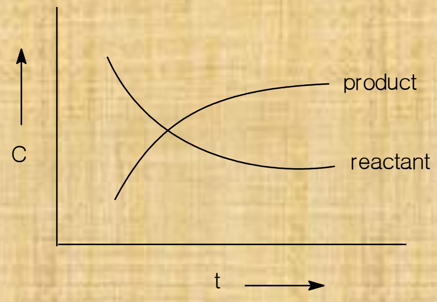
Units: mole liter $^{-1}$time $^{-1}$

Factors influencing the rate of reaction

1. Concentration
2. Temperature
3. Pressure
4. Solvent
5. Light
6. Catalyst

Concentration

Rate of reaction is proportional to the concentration of the reacting substance or inversely proportional to the time.



Rate of reaction α product of concentration of the reactant.

$A + B \longrightarrow$ produc

$V \quad C_A C_B$

$V = K\ C_A C_B$

Temperature

In general increase in temperature increases the rate of reaction.

"If the temperature of the reactant is increased by 10ºC the rate of reaction is increases by two

Or three times."

Temperature coefficient = $\frac{K_{t+10℃}}{K_t}$

**Relation between rate constant (K) and temperature of the reaction in Kelvin scale. It was proposed by Arrhenius.

K= A $e^{\frac{-Ea}{RT}}$

A= Arrhenius frequency factor

T= Temperature in Kelvin scale

Ea=Activation energy of the reaction

K_1= A $e^{\frac{-Ea}{RT1}}$ ---1

K_2= A $e^{\frac{-Ea}{RT2}}$ ---2

ln K_1= ln A $e^{\frac{-Ea}{RT1}}$

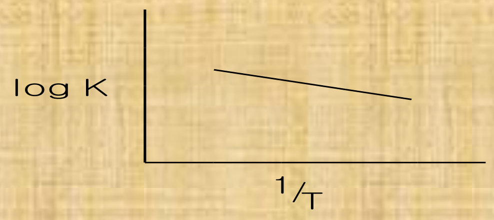
ln K_2= ln A $e^{\frac{-Ea}{RT2}}$

$$\ln K_2 - \ln K_1 = \ln A - \frac{Ea}{RT2} - \ln A + \frac{Ea}{RT1}$$

$$= -\frac{Ea}{RT2} + \frac{Ea}{RT1}$$

$$\ln\frac{K2}{K1} = -\frac{Ea}{R}\ \left[\frac{1}{T2} - \frac{1}{T1}\right]$$

The graph drawn between the rate constant and the reciprocal of the temperature is shown in figure.



Pressure

Pressure has little effect on the rate of reaction involving solid or liquid. However reaction involving gases are much affected by pressure. If the pressure increases the rate of reaction increases towards the direction of the side having less number of molecules (or moles).

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

Solvent

Solvent does not affect the rate of reaction.

Catalyst

The substance other than the reactants present in small amounts in the reaction and participates in the reaction and increases the rate of reaction without itself being consumed in the reaction is known as catalyst.

*The reaction that occurs fast in the presence of catalyst is called catalysed reactions.

*The catalyst and the reactants are in the same physical state the reactions are called homogeneous catalysed reactions.

*If the catalyst is in solid state and the reactants are in gaseous or liquid states that reactions are called heterogeneous catalysed reactions.

Light

Some reactions take place only in presence of light.

Ex: In presence of sunlight plants perform the reaction between CO_2 and H_2O present in the atmosphere in their green leaves and prepare carbohydrates. This is called photosynthesis.

$$CO_2 + H_2O \xrightarrow[\text{chlorophyll}]{} \text{carbohydrates} + O_2$$

Molecularity of a reaction

The number of reacting species (total number of molecules or ions) as represented by balanced equation which collide simultaneously to bring chemical reaction.

Ex: 1 If the reaction involves the decomposition of a single species. It is known as unimolecular reaction.

$$N_2O_5 \longrightarrow N_2O_4 + 1/2\ O_2$$

Ex 2: If the reaction involves two species of reactants it is known as bi molecular reaction.

$$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$$

Order of a reaction

The sum of the power of the concentration terms in rate equation is called order of a reaction.

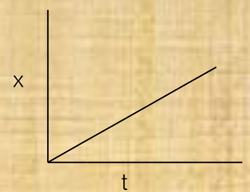
Distinguish between molecularity and order of reaction

Molecularity	Order of reaction
1. The number of molecules taking part in the rate determing step of a reaction is known as molecularity.	1.The order of reaction is given by the number of atoms or molecules whose concentrations alter during the chemical change.
2. It is a whole number and is never zero.	2.it may be whole number, zero and even fraction.
3. It is theoretical value from balanced single step reaction.	3.It is to be determined from the experiment.
4. It is equal to the number of molecules of the reactants which are taking part in a single step chemical reaction.	4.Order of reaction is the total sum of power of the concentration terms in the rate equation.

Ex 1: **Zero order reactions**

The rate of reaction is independent of the concentration of reactants are called zero order reaction.

$$H_2 + Cl_2 \xrightarrow{light} 2HCl$$



zero order

Units: moles liter^{-1} sec^{-1}

Ex2: **First order reaction**

Rate of reaction depends on the concentration of only one molecule is called first order reaction.

$$A \longrightarrow product$$

$\frac{dX}{dt}$= K[A]’

Ex:

$$N_2O_5 \longrightarrow N_2O_4 + 1/2\ O_2$$

Ex3: **Second order reactions**

Rate of reaction depends on the concentrations of two molecule is called first order reaction.

$$A + B \longrightarrow \text{product}$$

$$2A \longrightarrow \text{products}$$

$\frac{dX}{dt}$= K[A]^2 or $\frac{dX}{dt}$= K[A][B]

Pseudo molecular reactions

Reactions in which order is different from the molecularity are said to be pseudo molecular reactions.

Ex:

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

Derivation of equation for rate constant for first order reaction

$$\underset{a}{A} \longrightarrow \underset{x}{\text{products}}$$

V α C

Initial concentration is → a (t=0)

After t time the concentration is (a – x),

According to law of mass action

Rate of reaction α [A]

[A] after t time is (a – x)

$\frac{dx}{dt}$α (a – x)

$\frac{dx}{dt}$ = K (a – x)

$\frac{dx}{a-x}$ = K dt 1

On integration

$\int \frac{dx}{a-x} = \int K\,dt$

– ln (a – x) = Kt + C 2

When t=0, x=0

– ln (a – 0) = C

C= – ln a 3

Substituting the value of C in the equation 2

– ln (a – x) =Kt – ln a

$$\ln a - \ln (a - x) = Kt$$

$$\ln\frac{a}{(a-x)} = Kt$$

$$K=\frac{1}{t}\ln\frac{a}{(a-x)} \qquad \text{or}$$

$$K=\frac{2.303}{t}\log\frac{a}{(a-x)}$$

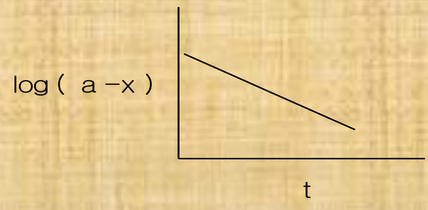
Units of K_1= Sec $^{-1}$

$$K_1 = \frac{\frac{dx}{dt}}{\text{concentration}}$$

$$K_1 = \frac{\text{mole liter}^{-1}\ \text{sec}^{-1}}{\text{mole liter}^{-1}}$$

$$K_1 = \text{Second}^{-1}$$

The graph drawn between log (a – x) Vs t is a straight line as shown in figure.



** Half life period of first order reaction is independent of initial concentration.

$$\underset{a}{A} \longrightarrow \underset{x}{\text{products}}$$

Initial concentration of A is → a

Let the time required for half of this amount is t/2

(a – x) = a/2

Substituting the value in the first order reaction

$$K_1=\frac{2.303}{t_{\frac{1}{2}}}\log\frac{a}{a/2}$$

$$=\frac{2.303}{t_{\frac{1}{2}}}\log\ 2$$

$$K_1 =\frac{0.693}{t_{\frac{1}{2}}}$$

So first order reaction is independent of initial concentration.

Examples:

1. Gaseous state reactions:
   The thermal decomposition reactions of H_2O vapour, SO_2Cl_2, N_2O_5
2. Liquid state reactions
   a) The decomposition reaction of aqueous solution of H_2O_2
   $H_2O_2(aq) \longrightarrow H_2O(l) + 1/2\ O_2(g)$
   b) The decomposition reaction of NH_4NO_3 in aqueous solutions
   $NH_4NO_3(aq) \longrightarrow 2\,H_2O + N_2(g)$
   c) Ester hydrolysis in acid solutions
   d) The hydrolysis of diazonium salts

Derivation of equation for rate constant for second order reaction.

$$2A \longrightarrow \text{products}$$

Initial concentration is → a (t=0)

After t time the concentration is (a – x)

According to law of mass actionRate of reaction α $[A]^2$

[A] after‘t’ time is (a – x)

$\frac{dx}{dt} \alpha\ (a - x)^2$

$\frac{dx}{dt} = K_2\,(a - x)^2$

$\frac{dx}{a-x} = K_2dt$ 1

On integration

$\int \frac{dx}{(a-x)} = \int Kdt$

$\frac{1}{(a-x)} = K_2t + C$ 2

When t=0, x=0

$\frac{1}{(a-0)} = C$

$\frac{1}{a} = C$ 3

Substituting the value of C in the equation 2

$\frac{1}{(a-x)} = K_2t + 1/a$

$$\frac{1}{(a-x)} - \frac{1}{a} = K_2t$$

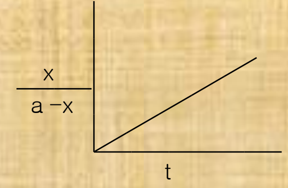
$$\frac{a-a+x}{a(a-x)} = K_2t$$

$$\frac{x}{a(a-x)} = K_2t$$

$$K_2 = \frac{1}{t}\frac{x}{a(a-x)}$$

Units: mol^{-1} time^{-1}liter

The graph drawn between $\frac{x}{(a-x)}$ Vs t is a straight line as shown in the figure.



OR

$A + B \longrightarrow \text{products}$

$$\frac{dx}{dt} \alpha\ (a-x)(b-x)$$

$$\frac{dx}{dt} = K_2\,(a-x)(b-x)$$

$$\frac{dx}{(a-x)(b-x)} = K_2dt \quad ..... 1$$

Integrating equ 1

$$\int \frac{dx}{(a-x)(b-x)} = K_2 \int dt$$

$$\frac{1}{(a-b)} \int \frac{dx}{(b-x)} - \int \frac{dx}{(a-x)} = K_2t + C \quad .....2$$

$$\frac{1}{(a-b)}\ -\ln(b-x) - (-\ln(a-x) = K_2t + C$$

$$\frac{1}{(a-b)} \ln\frac{(a-x)}{(b-x)} = K_2t + C \quad ....3$$

t=0, x=0

$$\frac{1}{(a-b)}\ln\frac{(a)}{(b)} = C \qquad ....4$$

Substitute C value in equation 3

$$\frac{1}{(a-b)}\ln\frac{(a-x)}{(b-x)} = K_2t + \frac{1}{(a-b)}\ln\frac{a}{b}$$

$$K_2t = \frac{1}{(a-b)}\ln\frac{(a-x)}{(b-x)} - \ln\frac{a}{b}$$

$$K_2 = \frac{1}{t}\frac{1}{(a-b)}\ln\frac{b(a-x)}{a(b-x)}$$

$$K_2 = \frac{2.303}{t}\frac{1}{(a-b)}\log\frac{b(a-x)}{a(b-x)}$$

**Half life value

In second order reaction half life value is inversely proportional to the initial concentration.

$K_2 = \frac{1}{t}\frac{x}{a(a-x)}$ $\qquad$ $x = a/2$

$t_{1/2}\ \alpha \frac{1}{a}$

Examples for second order reactions

1. The decomposition of O_3 at 100^0C

   $$2O_3(g) \xrightarrow{100^0C} 3O_2(g)$$

2. Thermal decomposition of chlorine monoxide at 200^0C to chlorine and oxygen.

   $$2Cl_2O(g) \xrightarrow{200^0C} 2Cl_2(g) + O_2(g)$$

Kinetics of complex reactions

1. Opposing reactions
2. Consecutive reactions
3. Parallel reactions
4. Chain reactions

Opposing reactions (reversible reactions)

$$A \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} B$$

In this reaction A is converted to B by first order kinetics. But B is converted back to A at the same time also by first order kinetics.

$$A \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} B$$

Let the initial concentrations be

a 0

Concentration after reaction ‘t’ time

(a – x) x

Rate of forward reaction $\frac{dx}{dt} = K_1(a - x)$

Rate of reverse reaction $\frac{dx}{dt} = K_{-1}\, x$

Net rate of reaction $\frac{dx}{dt} = \left(\frac{dx}{dt}\right)_{\text{forward}} - a \left(\frac{dx}{dt}\right)_{\text{reverse}}$

$\left(\frac{dx}{dt}\right)_{\text{net}} = K_1(a - x) - K_{-1}x$

At equilibrium

Rate of forward reaction = Rate of reverse reaction

$\left(\frac{dx}{dt}\right)_{\text{net}} = 0$

$\left(\frac{dx}{dt}\right)_{\text{net}} = K_1(a - x_e) - K_{-1}x_e = 0$

At equilibrium [B]= x_e

$K_{-1} = \frac{K1(a - xe)}{xe}$

x_e= equilibrium concentration

$\left(\frac{dx}{dt}\right) = K_1 \frac{a}{xe}(X_e - x)$

On integration we have

$\ln \frac{xe}{(xe - x)} = \frac{t\, K1\, a}{xe}$

$K_1 + K_{-1} = \frac{1}{t} \ln \frac{xe}{(xe - x)}$

Consecutive reactions:

in these reactions products are formed through the formation of one or more intermediates.

Parallel or side reactions

The reactions giving smaller amount of products are called side reactions.

Chain reactions Some reactions (photochemical reactions) continue to take place unendingly so long as the reacting substances are present in the reaction.

Ex: Nuclear fission reaction of Uranium – 235 with slow neutrons.

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LECTURER INCHEMISTRY

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Explain Collision theory

1. A chemical reaction is possible when the reaction molecules must collide with each other.
2. All collisions do not lead to chemical reactions.
3. The colliding molecules must possess minimum energy in order that their collision leads to the formation of the products. It is called threshold energy.
4. The additional energy required by the molecules to attain threshold energy is called activation energy.
5. The collisions which result in the formation action of product are called effective collisions.
6. Activation energy = Threshold energy – Energy of normal colliding molecules.
7. When temperature increases, the collision frequency increases, so effective collisions increases.
8. Concentration increases, collision frequency increases.

Activation Energy

The energy which the reactants have to absorb to form the activated complex is known as energy of activation.

Threshold energy

The colliding molecules must possess minimum energy in order that their collision leads to formation of the products. It is called threshold energy.

Describe various methods used for determining the order of a reaction

1. Half life method or Fractional change method
2. Graphical method
3. Integration or substitution method

- **Half life method or Fractional change method**

The time for 50% change in concentration of the reactants is called time for half change.

1. The time required to complete half of the reaction is independent of initial concentration for a first order reaction.

   $t \alpha \frac{1}{a^0}$ …….first order
2. The time required to complete half of the reaction is inversely proportional to the initial concentration for a second order reaction.

   $t \alpha \frac{1}{a}$ ….. second order
3. The time required to complete half of the reaction is inversely proportional to the square of initial concentration for a third order reaction.

   $t \alpha \frac{1}{a^2}$ …… third order

In general, the time required to complete for n th order reaction can be put as t $\alpha \frac{1}{a^{n-1}}$ ….. n th order.

Suppose we consider two experiments with initial concentrations a_1 and a_2. Let t_1 and t_2 be the times to complete for half change.

Then

$t_1 \alpha \frac{1}{{a_1}^{n-1}}$ and $t_2 \ \alpha \frac{1}{{a_2}^{n-1}}$

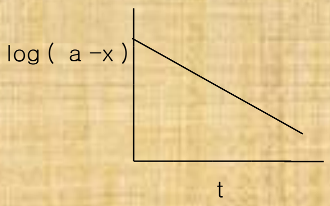
$$\frac{t_1}{t_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

Where n is the order of reaction. By using the equation, the order of the reaction can be determined.

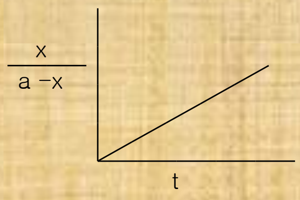
- **Graphical method**

  If a straight line is obtained by plotting log(a – x) against time indicates first order reaction.

  If a straight line is obtained by plotting $\frac{x}{a-x}$ against time indicates second order reaction.



first order



second order

- **Integration or substitution method**

  In this method, known amounts of reactants are mixed and the progress of the reaction is determined time to time by analysis. The data thus obtained the values of t,a, a – x, x are substituted in the kinetic equations of first, second and third orders.

  The equation which gives constant value of rate constant indicates the appropriate order of the reaction.