

H E N D Y E X

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S. No.	Date	Title	Page No.	Teacher's Sign / Remarks
		<u>Inorganic chemistry</u> <u>Notes</u>		

"kipher publications"

04-04-2020 : Saturday.

My own Notes.

- m.R. kipf

put me to the Bottom

And

I'll work in my way to
Reach Top

- kiccha kipher
[m.R. kipf]

Coordination Compounds



These are the complex salts in which the metal ion accepts a pair of electron from which a molecule (or) ion ligand involved in the formation of co-ordinated co-valent bond.

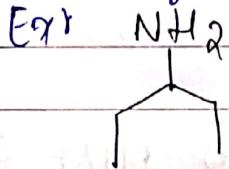
Ligands: The molecule (or) ion containing lone pair of electron forming co-ordinate with the central metal atom.

Classification.

1) **monodentate Ligand:** It contains a pair of electron forming one co-ordinate bond.
Ex:- $\text{C}_6\text{H}_5\text{mg}^{\text{+}}$.

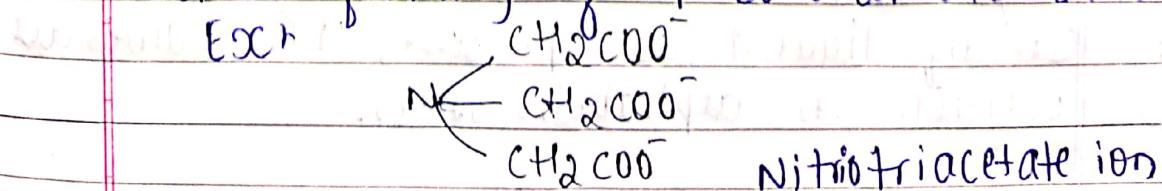
2) **Bidentate Ligand:** It contains 2 pair of electron forming 2 co-ordinate bond.
Ex:- $\text{H}_2\text{N}-\text{CH}_2-\text{COO}^-$
Glycinate ion.

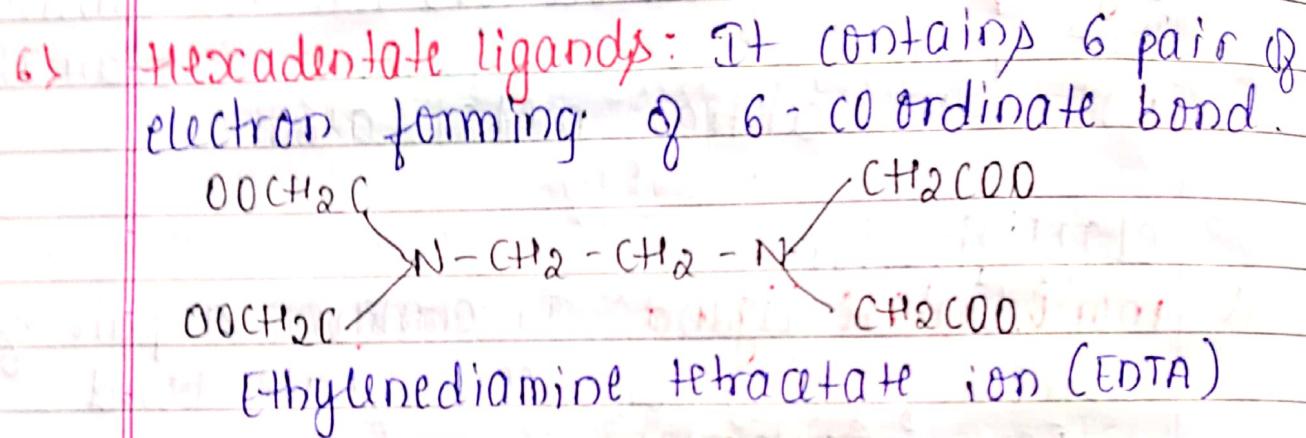
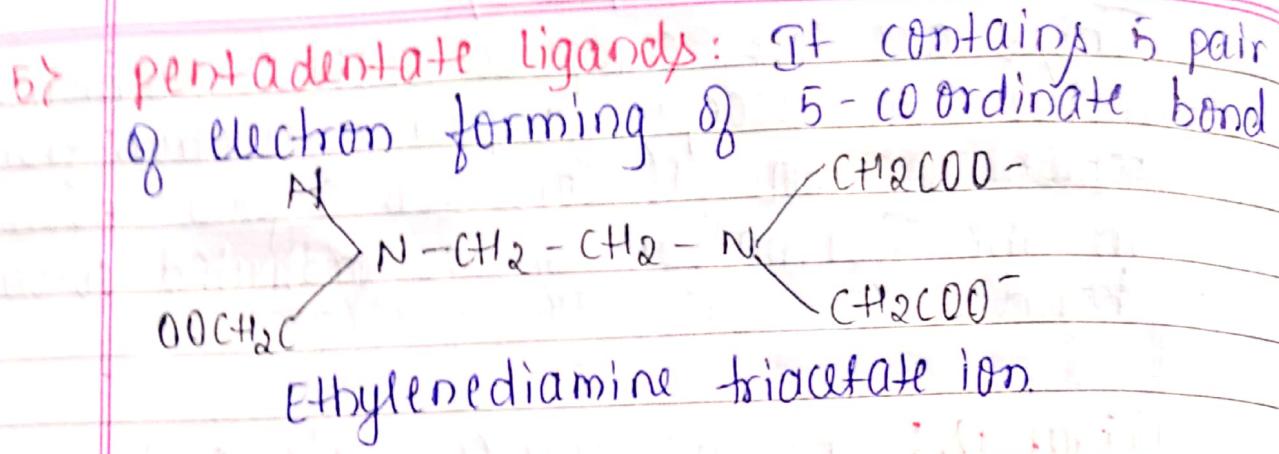
3) **Tridentate Ligand:** It contains 3 pair of electron forming 3 co-ordinate bond.



$\text{NH}_2 \text{ NH}_2$ 1,2,3-triaminopropane.

4) **Tetridentate Ligand:** It contains 4 pair of electron forming 4 co-ordinate bond.





7) **Ambidentate ligands:** A ligand which can bond with a metal atom through more than one site.
 Ex: NO_2 & ONO^- :

→ **Coordination no.:-** The number of ligands attached to central metal ion through co-ordinate bonds.

Nomenclature

- * Name of cation is written first then name of anion is written first & then name of metal ion is written.
- * In complex ion, name of ligand is written first & then name of metal is written.
- * If ligand are present, their names are written in alphabetic order.

- * When complex is anionic, name of metal ion is ended with 'ate'
- * Bridging ligand is represented by symbol ' μ ' before the name.
- * Geometrical isomers are indicated by writing *cis* or *trans* before the name.
Ex:- Dimethylglyoximate - DMG.

$[\text{Ag}(\text{NH}_3)_2]^+$ = diammine silver(I) chloride.

$[\text{Co}(\text{NH}_3)_6]^{2+}$ = hexaaamine (II) chloride.

$\text{K}_3[\text{Fe}(\text{CN})_6]$ = potassium chromium(III) chloride.

$[\text{Ni}(\text{CO})_4]$ = Tetra carbonyl nickel (0)

$[\text{Ni}(\text{NH}_3)_6]^{2+}$ = hexaaminenickel (II) chloride.

$\text{K}[\text{BF}_4]$ = potassium tetra fluoroborate (III).

$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ = hexaaquaferron (II) sulphate.

$\text{Na}[\text{Au}(\text{CN})_2]$ = Sodium dicyanocaurate (I)

$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ = hexaaquachromium (III) chloride.

→ Werner's theory.

Postulates:

- * The metal consists of 2 type of valencies as i) 1° valency (or) ionisable valency
ii) 2° valency (or) non-ionisable valency.
- * In a complex both valencies of metal are satisfied.
- * Each metal has fixed no. of 2° valencies.
- * Neutral molecules or anions satisfy 2° valency & are oriented in define direction of space.

Merits

- * It explains the formation of co-ordination compounds
- * It explains the geometry of complex.

Demerits

- * It doesn't give explanation for existence of 2 type of valencies
- * It couldn't be justified in light of electronic theory.

→ Sidgwick theory / Effective atomic number [EAN rule].

According to this rule the central atom of co-ordination compounds accepts lone pair of electron donating by ligands till the total number of electron is equal to the atomic numbers of that period.

calculation of EAN of central metal atom

$$\text{EAN} = Z - X + Y$$

where, Z = Atomic no.

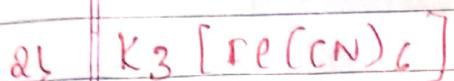
X = odd? state of metal ion

Y = Total number of electrons donated by ligand.



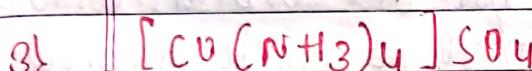
$$\begin{aligned}Z - X + Y \\= 26 - 2 + (6 \times 2) \\= 24 + 12 \\= 36\end{aligned}$$

- * Hence it obeys EAN rule
- * The molecule is diamagnetic



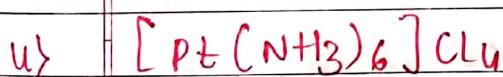
$$\begin{aligned}Z - X + Y \\= 26 - 3 + (6 \times 2) \\= 23 + 12 \\= 35\end{aligned}$$

- * The complex doesn't obey EAN rule
- * The molecule is paramagnetic



$$\begin{aligned}Z - X + Y \\= 29 - 2 + (4 \times 2) \\= 27 + 8 \\= 35\end{aligned}$$

- * The complex doesn't obey EAN rule
- * The molecule is paramagnetic



$$\begin{aligned}Z - X + Y \\= 78 - 4 + (6 \times 2) \\= 74 + 12 \\= 86\end{aligned}$$

- * Hence it obeys EAN rule
- * The molecule is diamagnetic.

Valence bond theory

These theory was mainly due to pauling & slater (1935)

It deals with electronic configuration of CM⁺ in its ground state, kind of bonding, geometry & magnetic properties of complex.

Postulates of VBT:

- * CM⁺ must contain number of empty s, p & d-orbitals equal to its co-ordinator numbers
- * These vacant orbitals undergo hybridisation to form hybrid orbitals.
- * Vacant hybrid orbitals are equivalent in energy & have definite geometry.
- * Each ligand has atleast one orbital containing lone pair of \bar{e} to donate to empty hybrid orbital of CM⁺ to form co-ordinate bond.
- * The geometry of the molecule is decided by the characters of the hybrid orbitals.
- * metal cation are formed by loss of valence electron.

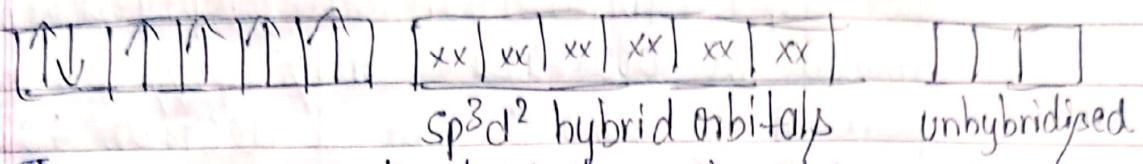
Octahedral complexes.

1) Hexafluorocobaltate (III) ion $[CoF_6]^{3-}$.

The element Co. has the outer electronic configuration $3d^7 4s^2$ & Co^{3+} ion has the outer electronic configuration $3d^6 4s^0$ which may be represented as.

$\uparrow\downarrow$	\uparrow	\uparrow	\uparrow	\uparrow									

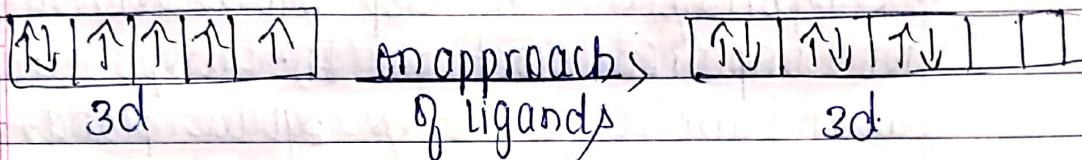
A ligand orbital containing a pair of e overlaps with an empty orbital of the metal ion to form a co-ordinate bond which is shown diagrammatically below & the e from ligands are shown as xx.



These are unpaired electron in the complex. hence it is paramagnetic in nature.

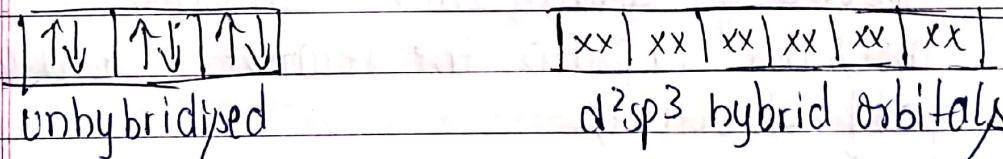
2) Hexaamine cobalt (III) $[\text{Co}(\text{NH}_3)_6]^{3+}$

The pairing of 3d orbital electrons take place at the approach of ligands as shown



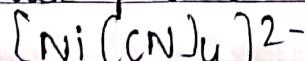
for octahedral arrangement the 6 empty orbitals needed are made available by hybridisation.

of two 3d, us & three up orbitals this is called $d^2\text{sp}^3$ hybridisation.



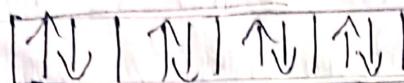
There are no unpaired electron in the ion & its diamagnetic nature.

- Square planar complexes.

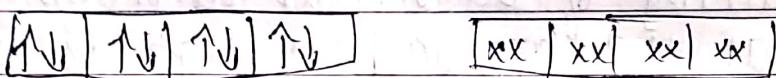
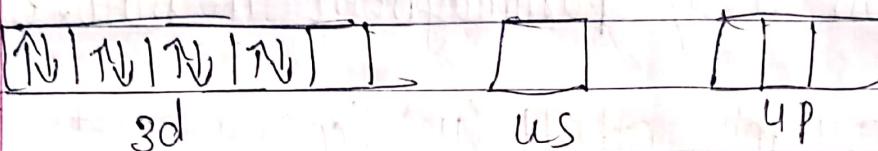


Ni(II) complex ions generally have (N 4). Nickel has atomic number 28 & Ni^{2+} ion has

out electronic configuration $3d^8$ which may be represented as



for dsp^2 hybridization, an empty d orbital should be available. This is possible if pairing of two of the d electrons takes place.



unhybridized dsp^2 hybrid orbital.

No unpaired electron, the complex ion is diamagnetic. & it is square planar.

Limitations of VBT:

- * It can not be extended quantitatively.
- * Does not explain characteristic absorption spectra of coordination compounds.
- * Does not explain the relative stabilities of d₁f structures.
- * fails to account for the thermodynamic properties of coordination compounds.
- * It cannot interpret the colour of complexes.
- * It does not explain magnetic behaviour of complexes.

Crystal field theory

The CFT is an electrostatic model which considered the metal-ligand bond to be ionic arising purely from electrostatic interactions b/w the metal ion & the ligand.

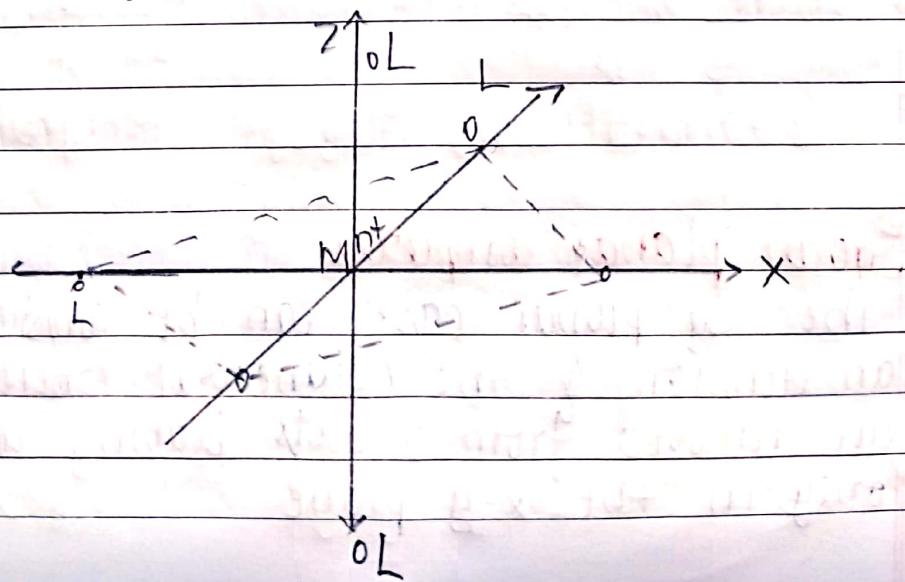
Ligands are treated as point charges in case of anion (or) dipole in case of neutral molecules.

Features

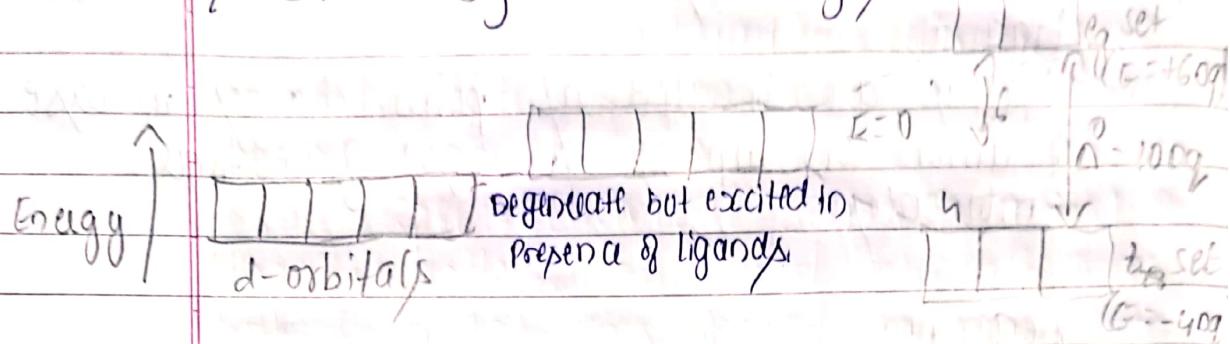
- * CM is surrounded by ligands which contain one or more lone pair of e.
- * Ionic ligand are treated as point charges. Neutral ligands are treated as point dipoles.
- * Bonding b/w CM & ligands arises from purely electrostatic interactions.
- * Metal ion & ligands do not mix their orbitals to share e.

Octahedral complex ($CN=6$)

In this, metal ion is the centre of octahedron & 6 ligands occupy the 6 corners of octahedron

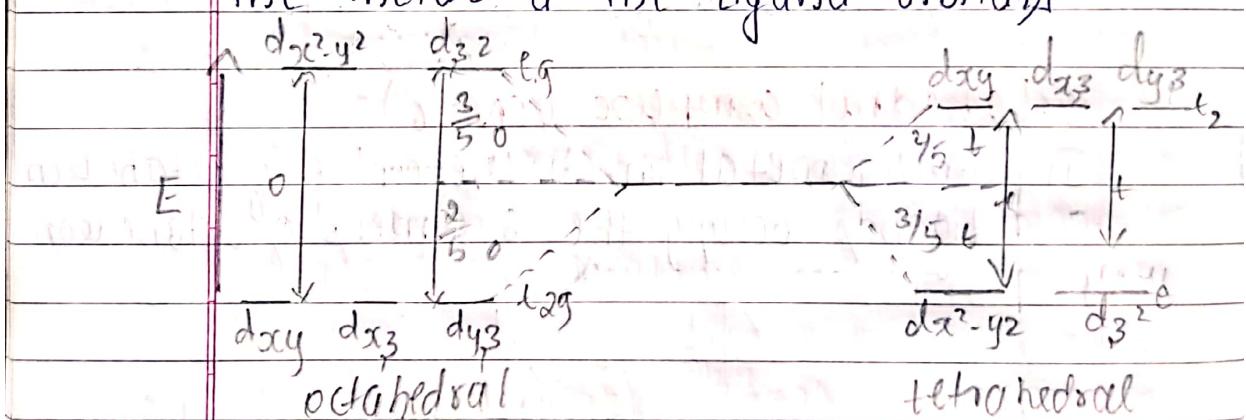


The energy is set 4 Dq less than that of hypothetical degenerate d-orbitals. The energy of eg set is 6 Dq greater than of hypothetical degenerate d-orbitals. Loss & gain of energy is shown by (-) & (+) signs.



Tetrahedral Complex

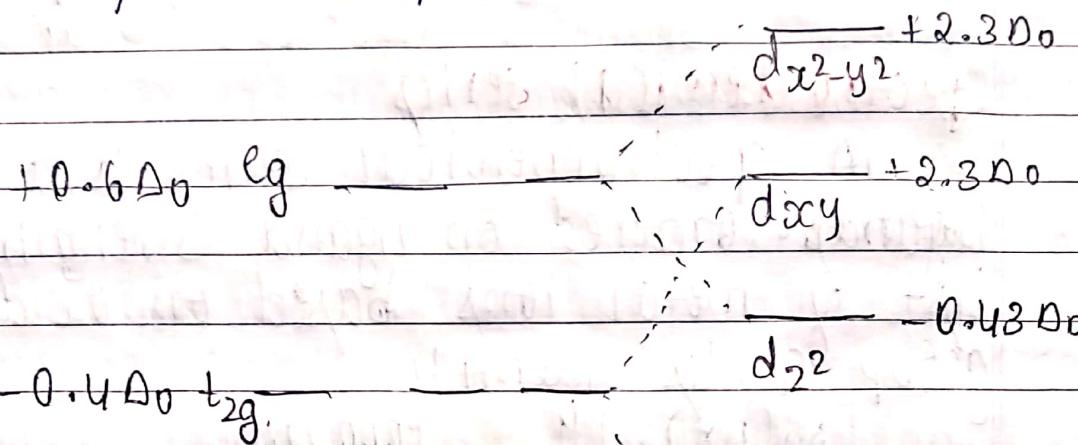
In this, there are 4 ligands attached to the central metal. The d orbitals also split into different energy levels. The top 3 consist of d_{xy} , d_{yz} , d_{zx} orbitals. The bottom 2 consist of $d_{x^2-y^2}$ & d_{z^2} orbitals. The reason is poor orbital overlap b/w the metal & the ligand orbitals.



Square planar complexes

The Sq planar case can be considered as an extension of the octahedral, where 2 ligands are removed from 2 axial leaving ligands only in the x-y plane.

- * Consequently, repulsion of an \bar{e} in the d_{x^2} orbital will no longer be equivalent that experienced by an \bar{e} in $d_{x^2-y^2}$ orbital its energy falls down.
- * The d_{z^2} & d_{y^2} orbitals also drop in energy, but not as much. the energy of $(d_{x^2-y^2})$ & d_{xy} orbitals increases.

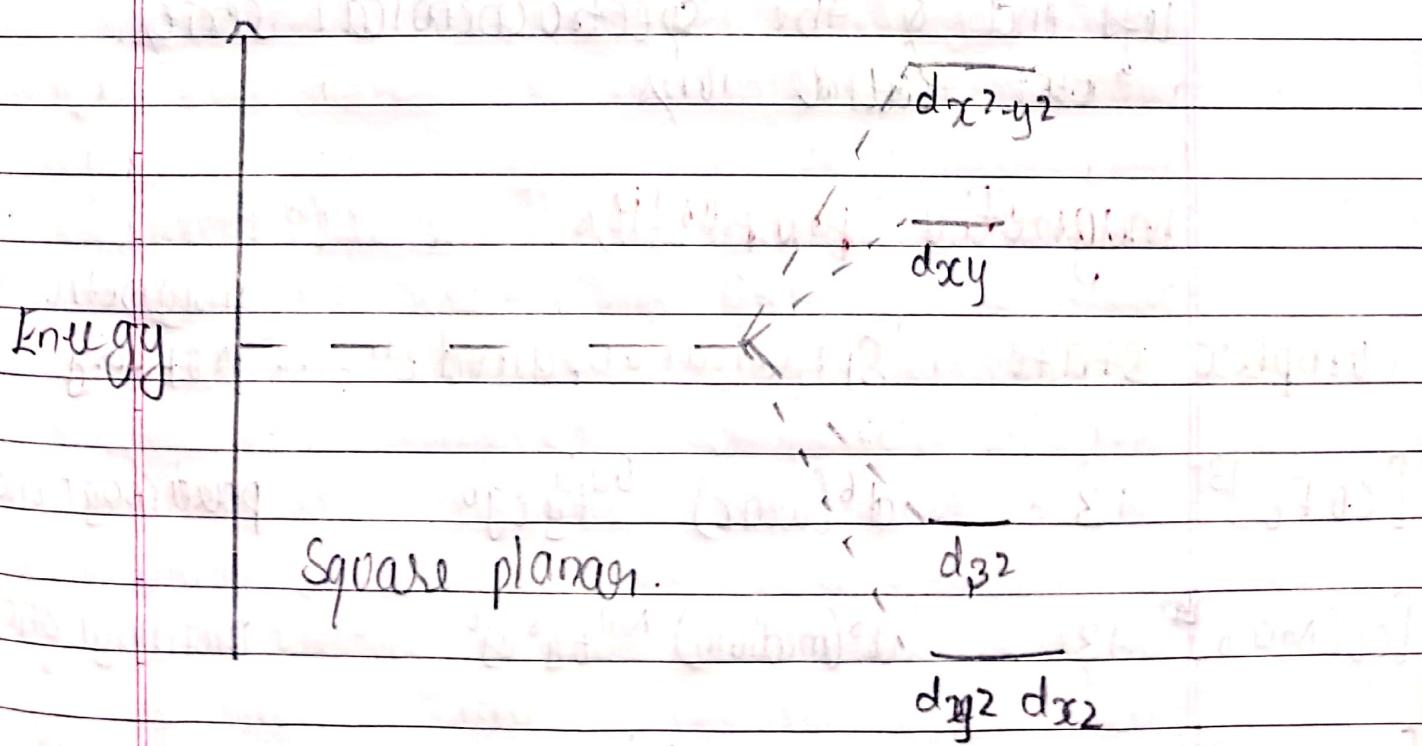


Octahedral co-ordination \therefore

$$\frac{d_{xy}}{d_{x^2-y^2}} - 0.51 \Delta_0$$

Square planar co-ordinator

Simply the splitting of d-orbitals in sq planar complexes is shown as below:



Crystal field stabilisation energy.

It is defined as the energy of the electronic configuration in the ligand field minus the energy of the electronic configuration in the isotropic field.

$$CSFE = DE = \text{Ligand field} - \text{Isotropic field}$$

Spectrochemical series

A spectrochemical series is a list of ligands ordered on ligand strength & a list of metal ions based on oxidation state & its identity.

$$[\text{Ni}(\text{Br})_6]^{4-} = 4000 \text{ cm}^{-1}$$

$$[\text{Ni}(\text{Cl})_6]^{4-} = 7200 \text{ cm}^{-1}$$

$$[\text{Ni}(\text{en})_3]^{2+} = 11500 \text{ cm}^{-1}$$

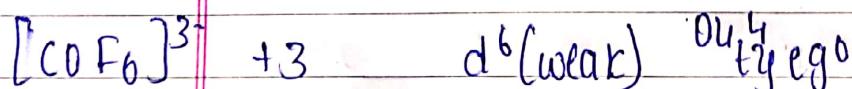
weak field ligands: Ligands that produce a small Δ are called WFL & lie at the left end of the spectrochemical series.

Ex:- halide ions.

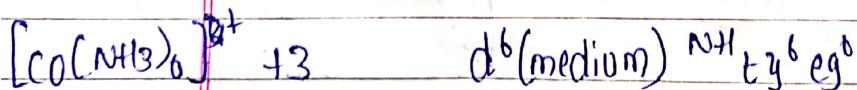
Magnetic properties

magnetic property.

Complex state Spherical unpaired eⁿ



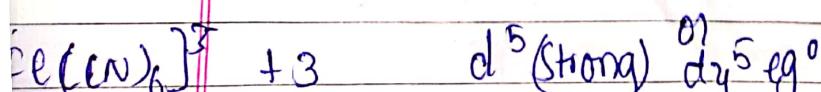
paramagnetic



diamagnetic

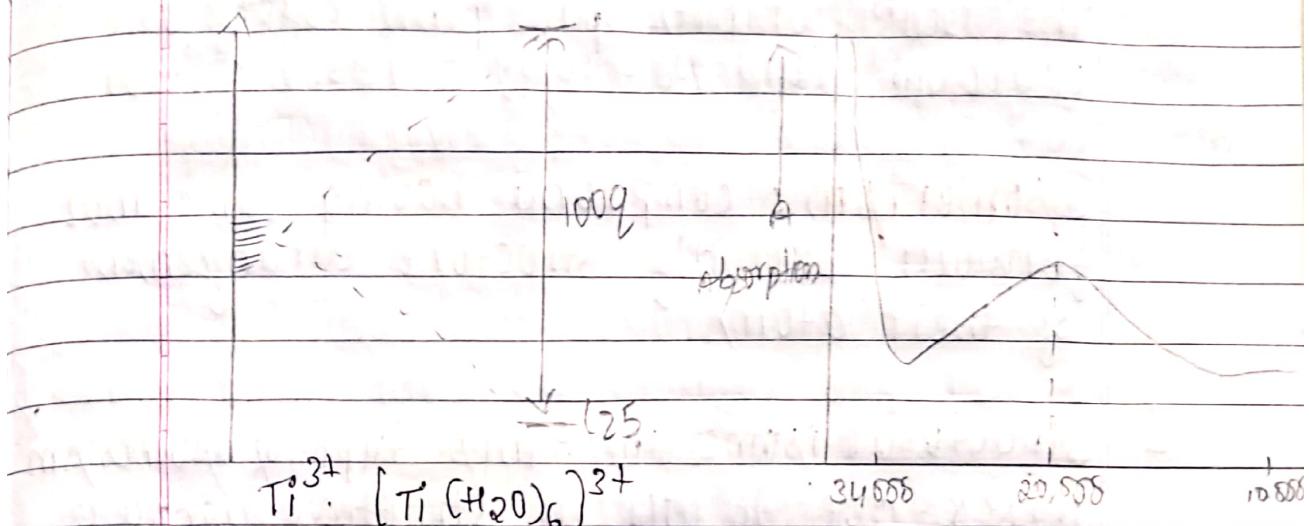
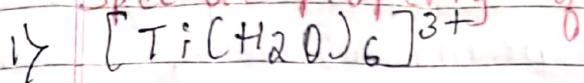


diamagnetic



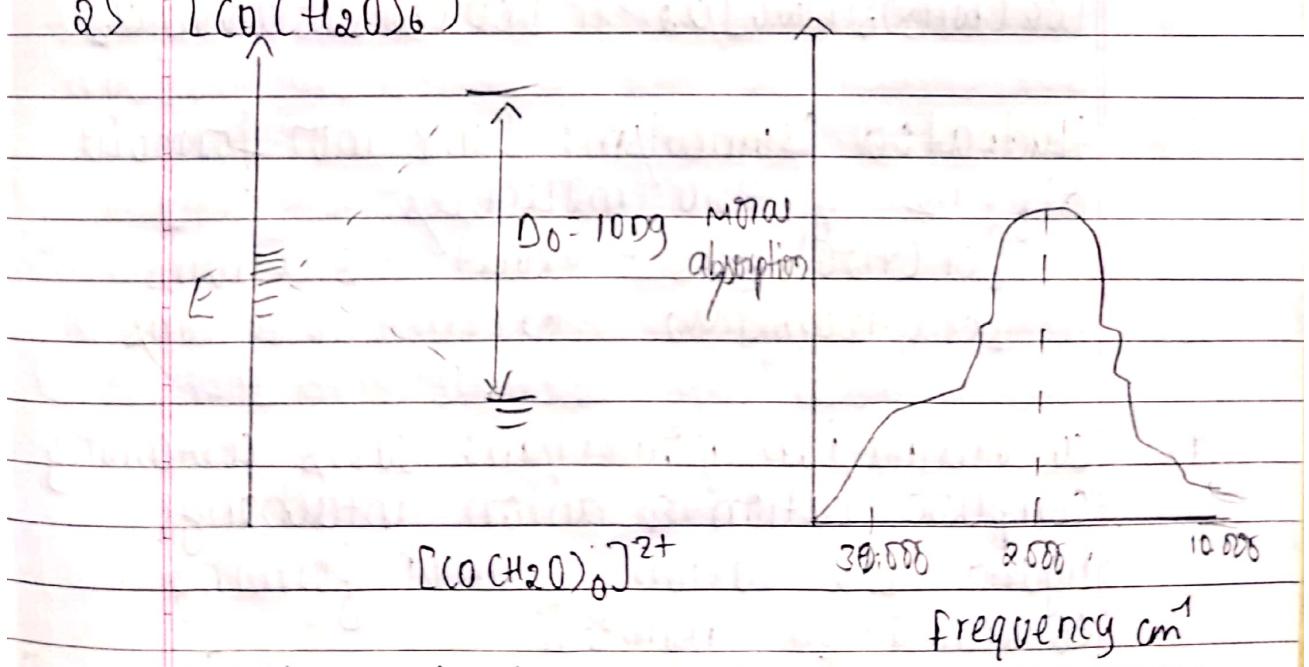
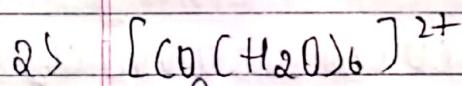
para

SPECIAL PROPERTY 8



A single broad peak is frequency cm^{-1} observed at $20,300 \text{ cm}^{-1}$ (or) at 493 nm corresponding to the transition $t_{2g} \rightarrow e_g$.

The crystal field splitting energy = 10 dy = $D_0 = 20,300 \text{ cm}^{-1}$. the SO^+ exhibits purple color because of absorption of yellow green & blue colour.



Because unpaired e in t_{2g} set has the same spin as paired e in e_g level set. Hence to the

paired \bar{e} . In the opposite spin to $\bar{e}g$ level can only be promoted. The SO_4^{2-} exhibits pale pink colour at 19000 cm^{-1} (or) $\Delta_0 = 1009 = 185.4 \text{ kJ/mol}$

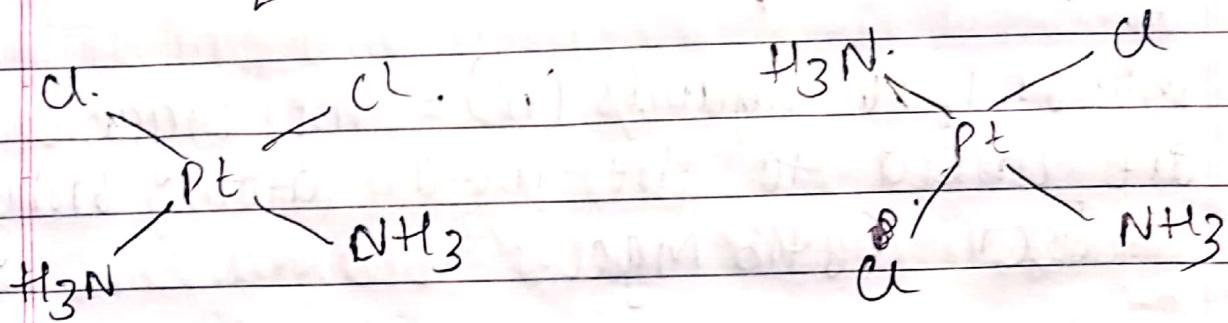
Isomerism: compound having same mol formula but diff structure arrangement of their atoms.

- Structural isomerism: This type of isomerism arises due to diff in structure complex
 - a) Ionization isomerism: Compounds have same mol formula but produce diff ion.
 $[\text{Co}(\text{NH}_3)_5\text{Br}]^{\text{SO}_4^-}$ & $[\text{Co}(\text{NH}_3)_5\text{SO}_4]^- \text{Br}$
 - b) Linkage isomerism: Same mol formula, same ligands but diff in linkage b/w donor atom & ligand.
 $[\text{Co}(\text{NH}_3)_5\text{ONO}]^{\text{Cl}_2^-}$ & $[\text{Co}(\text{NH}_3)_5\text{OONO}]^{\text{Cl}_2^-}$.
 - c) Hydrated isomerism: Same mol formula diff no. of H_2O molecules.
 $[\text{Cr}(\text{H}_2\text{O})_6]^{\text{Cl}_3^-}$ - violet - 3 Cl^- ions
 $[\text{Cr}(\text{H}_2\text{O})_5]^{\text{Cl}_2^-}$ - green - 2 Cl^- ions
 - d) co-ordination isomerism: salts containing complex cation & anion interchange ligand b/w cation & anion forming co-ordination isomers
 $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ & $[\text{Cr}(\text{CN})_6][\text{Co}(\text{NH}_3)_6]$

Stereoisomerism

as geometrical isomerism: compounds have same mol formula but diff in their position of ligands about central metal atom.

Ex: Sq planar complex:



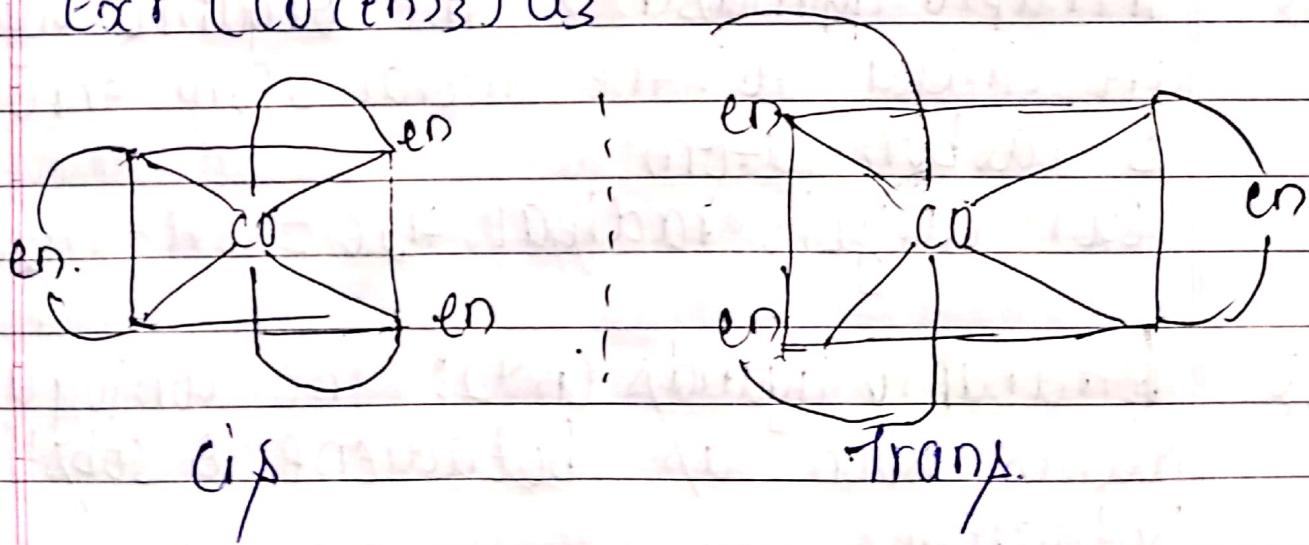
mf 0 cis

mf 0, trans

$[Pt(NH_3)_2Cl_2]$ = diamine dichloro platinum

b) optical isomerism: compounds have same mol formula, same chemical properties but different rotation of plane polarized light.

Ex: $[Co(en)_3]Cl_3$



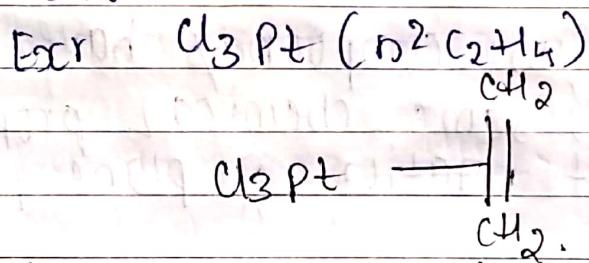
Organometallic compounds

Compounds containing carbon metal bond & carbon atom of organic group is directly attached to metal atom
Ex: Grignard reagent (RMgX)

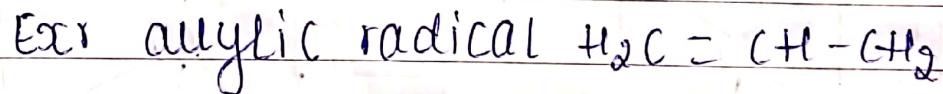
Classification:

1) Monohapto ligands (n^1): The organic ligands are linked to the metal atom only.
Ex: $\text{C}_6\text{H}_5\text{MgCl}$

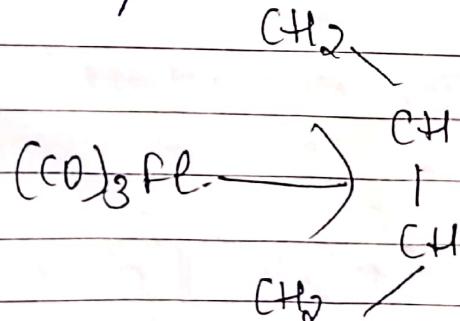
2) Dihapto ligands (n^2): The organic ligands are linked to the metal atom only at carbon atom.



3) Trihapto ligands (n^3): The organic ligands are linked to the metal atom through 3 carbon atoms.

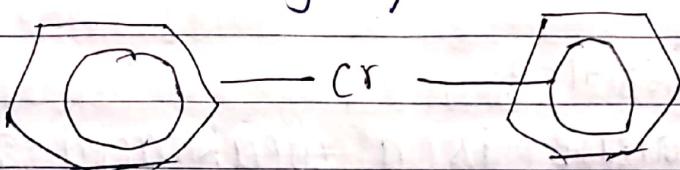


4) Tetrahapto ligands (n^4): The conjugated dienes such as butadiene & substituted butadienes.



5 Σ pentahapto ligands (n^5): cyclopentadienyl radical links to iron atom in ferrocene through all its 5 carbon atom
 Ex) $\text{Fe}(\gamma^5(\text{C}_5\text{H}_5)_2)$ ferrocene.

6 λ Hexahapto ligands (n^6): The benzene rings in dibenzene chromium $\text{Cr}[\gamma^6(\text{C}_6\text{H}_6)_2]$ is a hexahapto ligands



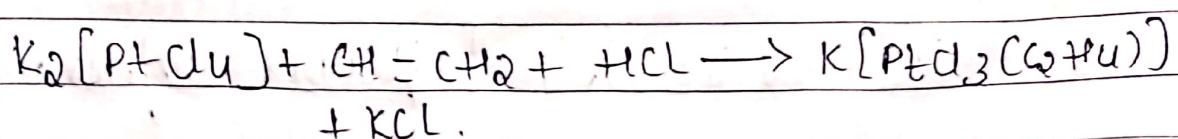
→ Hapticity of ligands:- The number of carbon atoms through which an organic ligand is attached to the central atom.
 It is denoted by symbol "n".

→ Synthesis & Structure

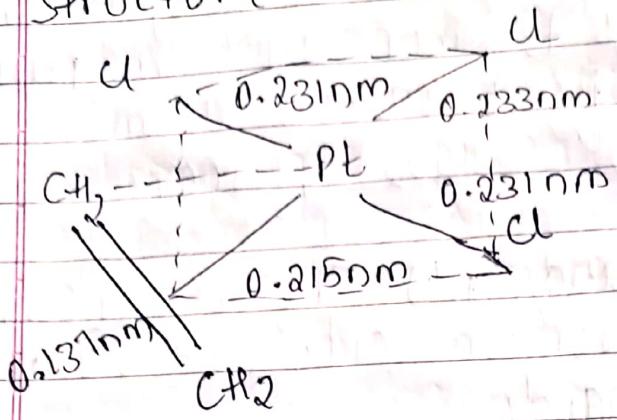
1) $\text{K}[\text{PtCl}_3(\text{n}^2\text{C}_2\text{H}_4)]$

This was 1 λ^2 organometallic compound of transition metal to be prepared. it is called Zeise's salt.

It is prepared as a yellow crystalline solid by displacing one of the chloride ions in the complex $\text{K}_2[\text{PtCl}_4]$ by ethylene molecule.

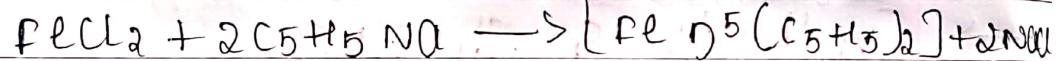
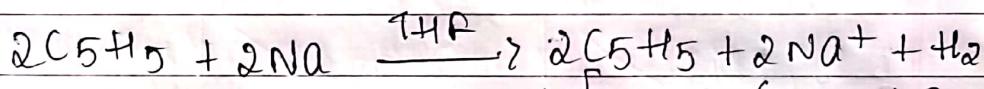


Structure

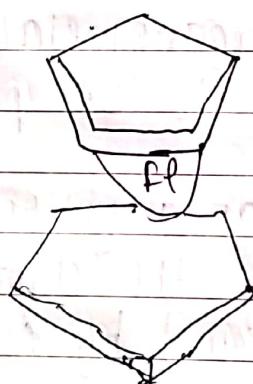


2) $[\text{Fe}(\eta^5(\text{C}_5\text{H}_5)_2)]$

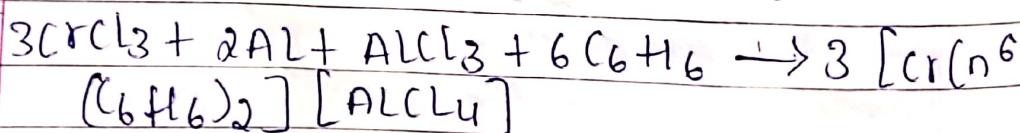
- cyclopentadiene is a weak acid & form salts with strong base containing the symmetrical cyclopentadienide ion.
- cyclopentadiene reacts with Na/Na⁺ in THF to form sodium salt. this salt is treated with metal halides. etc



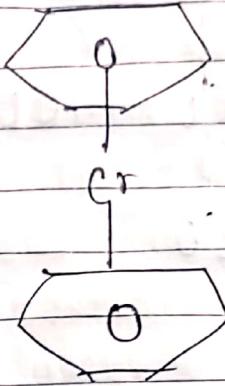
Structure



3) $\text{Cr}(\eta^6(\text{C}_6\text{H}_6)_2)$. [Fischer-Hafner method]



Structure:

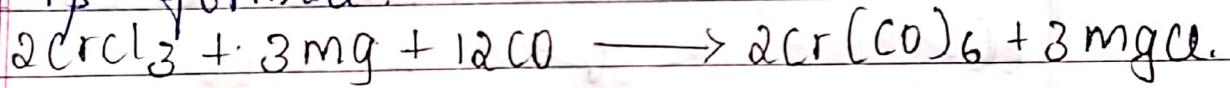


Dibenzene chromium.

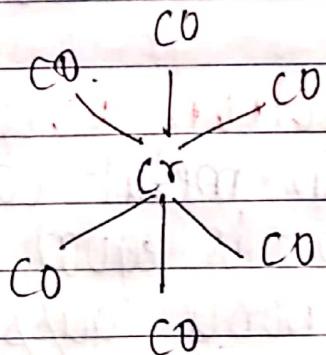
Metal carbonyls :- A compound in which metal is linked to a CO molecule is called metal carbonyls.

Ex:- $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, $\text{Cr}(\text{CO})_6$

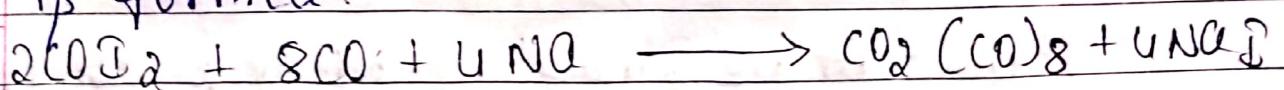
1) $\text{Cr}(\text{CO})_6$:- When CrCl_3 & Mg mixture is heated in a current of CO, hexacarbonyl is formed.



Structure:

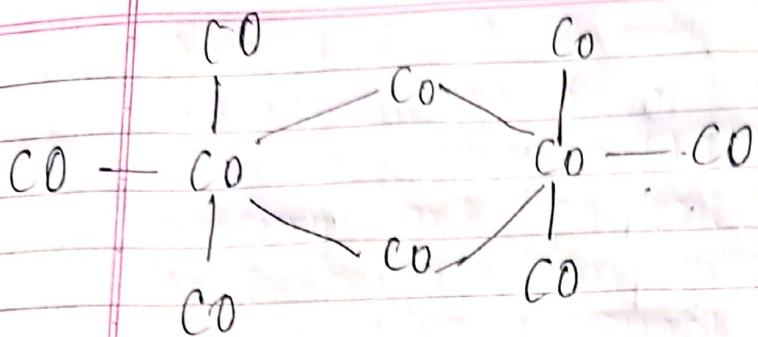


2) $\text{Co}_2(\text{CO})_8$:- When CoI_2 & sodium is heated in a current of CO, octa carbonyl dicobalt is formed.

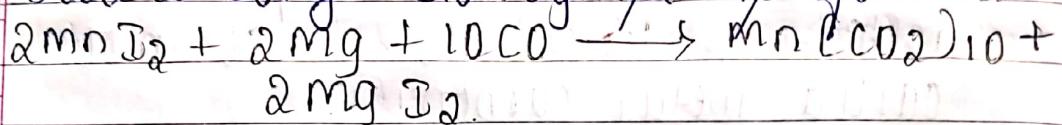


Structure:

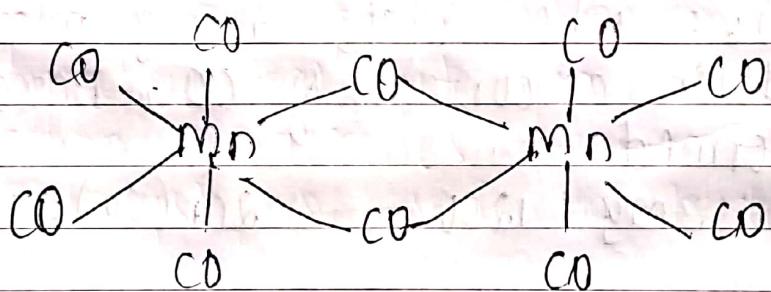
P.T.O.



3) $Mn_2(CO)_{10}$: When a mixture of Mn_3O_4 + Mg is heated in a current of CO, deca carbonyl diamagnesie is formed.



Structure:



→ Eighteen Electron rule.

In metal carbonyls EAN of metal atom is equal to the atomic no of nearest noble gas element which contains 18 electrons in outermost shell.

In mononuclear metal carbonyles

$$EAN = \text{At. no. of metal} + \text{No. of e}^- \text{ donated by CO (ligands)}$$

$$\begin{aligned} \text{1} & \text{ Ni(CO)}_4 = \text{EAN} \\ & = 28 + 4 \times 2 = 36. \end{aligned}$$

$$\text{2} \text{ Cr(CO)}_6^+ = 24 + 6 \times 2 = 36$$

$$\text{3} \text{ Fe(CO)}_5 = 26 + 5 \times 2 = 36$$

$$\text{4} \text{ V(CO)}_6 = 23 + 6 \times 2 = 35$$

In polynuclear metal carbonyls

EAN = At. no. of metal + no. of e⁻ donated, no. of e⁻ by CO (ligand) contributed to M-M bond.

$$\text{5} \text{ CO}_2\text{-}(\text{CO})_8 = 27 + 8 \times 2 + 2 = 45$$

$$\text{6} \text{ Mn}_2\text{(CO)}_{10} = 50 + 10 \times 2 + 2 = 72.$$

Applications of complex compounds & organometallic compounds.

Cis - platin in cancer therapy.

Cis platin is $[\text{Pt}(\text{NH}_3)_2\text{Cl}]$. Cis platin can be used as anticancer drug for various type of tumours. When it is introduced to blood stream, the chlorine atom is lost. The platinum bonds to nitrogen bonds of two guanine units of DNA.

Cis platin decreases the production of WBC & RBC. Hence calculated amt of cis - platinum to be introduced.

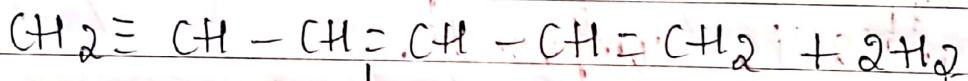
Nasca EDTA in the treatment of heavy metal.

Heavy metals like lead, mercury are poisonous & presence of these metals in biological system caused adverse effect.

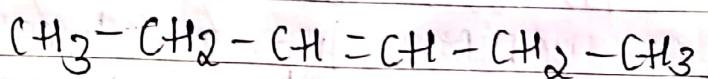
Heavy metal poisiony can be treated by oral consumption of Nasca EDTA which forms complexes with heavy metals are soluble in water, which enables excretion through urine.

Wilkinson's catalyst in alkene hydrogenation

It is a monochlorotriphenyl phosphine Rhodium (I). It is an effective catalyst for selective hydrogenation of alkenes. When Wilkinson's catalyst is used in hydrogenation.



↓
Wilkinson's catalyst $[\text{RhCl}(\text{PPh}_3)_3]$

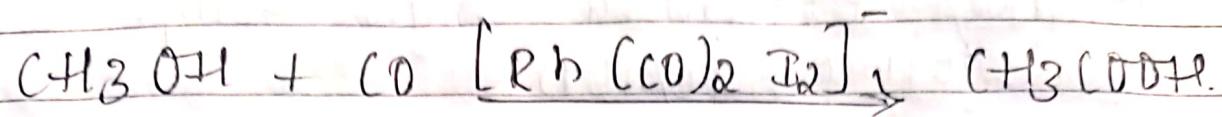


Monsanto acetic acid process.

Monsanto developed a process for large scale production of acetic acid from methyl alcohol.

When methyl alcohol reacts with CO in a presence of catalyst

Rb(CO)₂I₂ ion gives acetic acid.



Industrial materials - I.

Refractories: A material which withstands extremely high temp^o without undergoing fusion.

Uses:

- * construction of furnaces, ovens, metal melting
- * Atomic powerplant, rockets & jet
- * Generally refractories used in form of bricks like Blast + furnace.

Properties

- 1) Refractoriness:- It is ability of material withstand high temp^o without melting.
 - * It is expressed in terms of pyrometric value [PCE].
- 2) Spalling: cracking of refractory due to uneven expansion of sudden variation of temp^o.
- 3) Thermal conductivity: usually refractory have low thermal conductivity bcoz of prevent loss of heat
Ex: r. Alumina, magnesite.
- 4) Chemical resistance: It is imp to select appropriate refractories to withstand the chemical action of slags, fuel ashes.

furnace glasses

classification:

1) Acidic refractories: These are acidic in nature & thus resistant to acidic material but attacked by basic materials.

Ex: SiO_2 , Al_2O_3 , SiO_3

2) Basic refractories: These are basic in nature & thus resistant to basic material but attacked by acidic materials.

Ex: CaO , MgO , Al_2O_3 , ZrO_2

3) Neutral refractories: slightly acid or base if acts as both acidic (or) basic slags.

Ex: Cr_2O_3 , FeO , ZrO_2 , SiC .

→ char[±] of refractory.

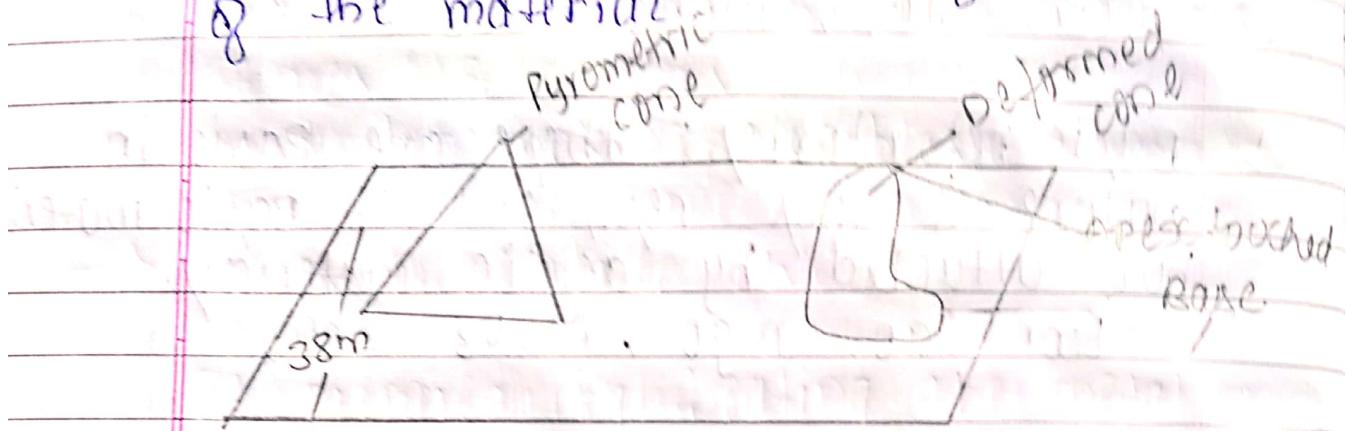
- * Be able to withstand very high temp.^r
- * Have resistance to withstand temp.^r fluctuations.
- * Have low porosity
- * Be able to withstand sudden changes in pressure, spalling ; cracking.
- * preferably have low electrical conductivity.

determination of PCE value

It is determined by comparing the

EFFECT OF TEMP^o ON STANDARD ONE (or) PYROMETRIC CONE.

In this method a test cone is prepared from the refractory material, then its reformation end point is compared to standard PCE cone. The resultant PCE value is a measure of refractories of the material.



Significance:

- * The end point of deformation of a cone correspond to certain heat work cond?
- * The PCE value are utilized for separation purposes.

→ Abrasives.

It is a material having the ability to cut / grind a surface (or) finish other materials.

Classification:

Natural Abrasives.

Artificial Abrasives.

1) Natural Abrasives:

a) Hard abrasives:

Ex:- diamond, corundum, emery

b) Siliceous abrasives

Ex:- quartz, flint, pumice, sandstone

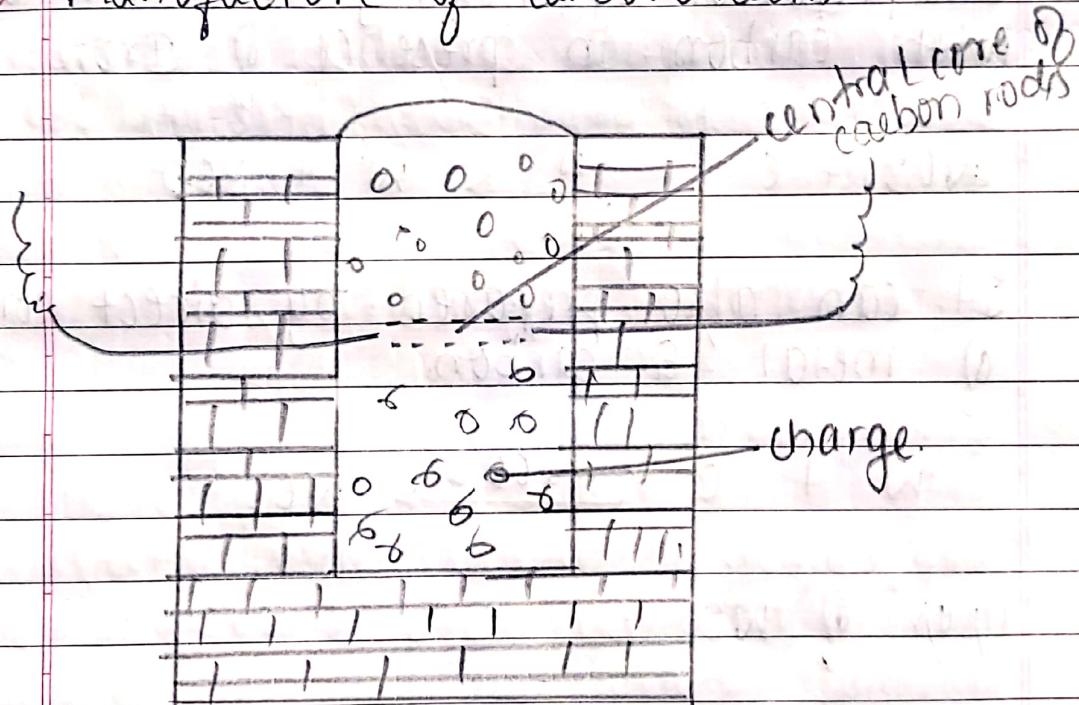
c) Soft abrasives

Ex:- Iron oxide, Tin & chromium oxide

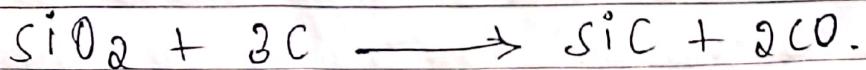
2) Artificial Abrasives:

Ex:- carborundum, boron carbide,
Tungsten carbide.

→ Manufacture of carborundum / sic:



If the mfg. of heating sand with carbon along with a small quantity of saw dust in an electric furnace at about 2500K.



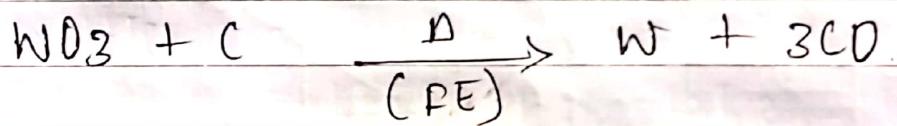
- furnace made up of fire bricks & provide carbon electrons.
- saw dust make the charge porous & escape CO.

uses of sic.

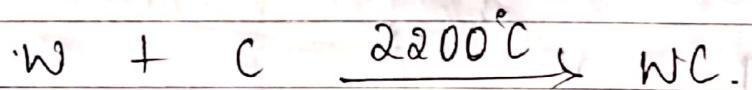
- * used for making grinding machines, stones & crushes.
- * used for making crucibles

→ Tungsten carbide [WC].

It prepared by heating the metal oxide with carbon in presence of Iron



It can also prepared by direct comb. of metal & carbon.



uses of WC.

They are used as coating on paper, Grinding wheels or as loose stones

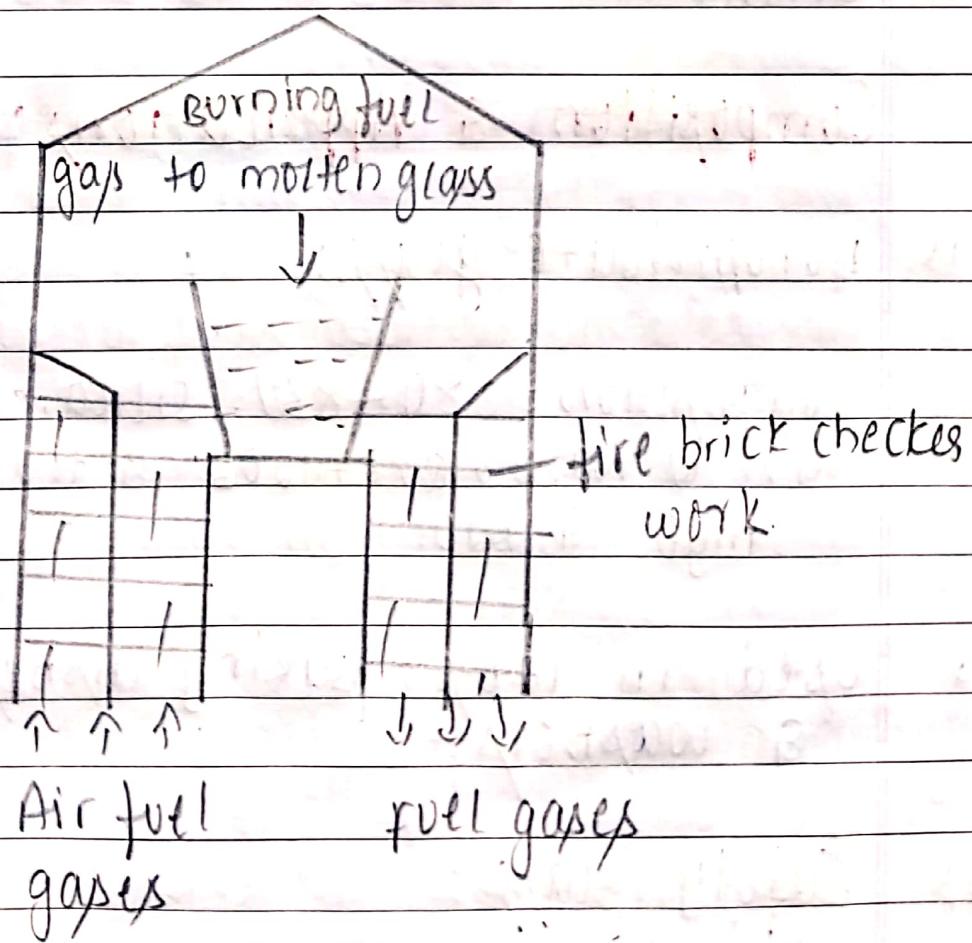
GLASS

It is a rigid supercooled liquid having no definite m.p & a hight viscosity that prevent crystallisation.

properties.

- * It is a non-crystalline, transparent solid & it is insoluble in water.
- * It is very hard. it comes next to diamond.
- * It has no definite m.p.
- * It can contain vacuum.
- * It is bad conductor of electricity.

Manufacture of soda glass.



Stage I: Fusion of raw materials

Raw materials are ground & through repeated grinding then it heated to 1400°C by burning fuel gas. It becomes transparent & cooled. Undecomposed impurities are removed. Then glass is ready to make article.

Stage II: Shaping

Molten glass is poured into dif mould to get desired shape. If colored, glass is required.

Stage III: Annealing

Finishing article should be cooled very slowly. Otherwise glass becomes very brittle.

Composition & Applications:

1) Borosilicate glass:

Composition: 80-83% silica, 10-12% B_2O_3 , 4% Na_2O , 2% Al_2O_3 & traces of CaO , MgO & K_2O .

- * Used in labs, baking dishes, pipelines & washers.

2) Safety glass:

Laminated safety glass made by bonding two sheets of ordinary glass with a

thin layer of vinyl plastic blow them

rough
8
Tempered safety glass: it obtained by heating a single sheet of glass to just below its fusion point & then quenching in oil, air (or) molten salt.

* used in mfg for doors & windows/bheels of automobiles, ships, aeroplanes & furnaces.

to
A 3) fibre glass: It used in textiles. this makes the cloth ap fire proof.

4) silica glass: obtained from pure silica.

* used in mfg of lab wares such as condensers, crucibles etc.

5) soft glass:

composition: $\text{SiO}_2 = 70 - 74\%$.

$\text{Na}_2\text{O} = 13 - 16\%$.

$\text{CaO} = 10 - 13\%$

* used for window glass, bottles, tobe wares.

6) potash glass:-

composition: $\text{SiO}_2 = 71\%$.

$\text{K}_2\text{O} = 18\%$.

$\text{CaO} = 11\%$.

* used for making hard glass apparatus

7) lead potash glass:-

composition: $\text{SiO}_2 = 53\%$.

$\text{K}_2\text{O} = 14\%$, $\text{PbO} = 33\%$.

* used for making prisms, lens & other optical glasses

Ceramics.

Raw materials & their roles
clay, feldspar, sand.

i) clay: It defined as finely grinded rock which is highly plastic when wet, hard when dried & rock-like permanent when fired & unaffected by water.

The composition of clay varies widely clay are generally impure, hydrated aluminium silicate.

Some of the common clays are.

i) kaolinite = $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$.

ii) illite = $\text{K}_2\text{O} \cdot \text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$

iii) montmorillonite = $\text{CaO} \cdot \text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot \text{H}_2\text{O}$

ii) feldspar: It serve as a flux & binder in ceramic article & also provide glassy appearance to article. sand particles provides necessary skeletal structure to ceramic ware.

Production of ceramic ware.

i) preparation of slip.

The raw materials are ground to a fine powder separately. they are mixed together with water in the material tank

A cream like paste is obtained which is called the slip.

2) Filtering: The paste is then passed through a filter paper to remove excess of H₂O.

3) Casting: The soft mass obtained above is kneaded well to get off air bubbles. This is then cast into desired shape. Other methods of casting are known as plaster of paris mould (or) banding. Some method of casting.

The articles are dried slowly & fired in an oven to get a porous called Bisque.

4) Glazing: Ceramic ware obtained above is hard, translucent & porous.

The ingredients required for glazing are quartz, feldspar, a little boric acid & metallic oxide of Zn, Pb & tin. These are finely powdered & mixed in required portion.

A homogeneous paste is made with water called slurry. It is applied on ceramic ware by dipping, spraying or using a brush. The ceramic ware is dried & then fired.

Glaze provides a non-porous, hard, glossy surface.

Purpose of glazing.

- * To produce a decorative effect
- * To make the surface impervious to H₂O.
- * To increase the durability of ceramic ware.
- * To provide a smooth glossy surface.

during firing, after applying glaze, it
not allowed to come indirect contact with
fire as dust & soot may discolour them.

- 5) Firing. It done at high temp^o & under
controlled cond^o. depending upon the temp^o
of firing the pores get covered up.

Ceramic Insulators

Insulators are materials, the
transfer of heat as well as prevent con-
duction of electricity.

Properties:

- * Ceramics are hard & rigid hence proved mechanical strength
- * They are thermally stable
- * chemically inert & restricted transfer of heat to electricity.

Applications of ceramic ware.

- * used to make lab items like crucibles,
furnaces etc
- * used in making kitchen wares
- * used in making sanitary pipes & toilet
articles
- * used for making electrical insulators etc.

Cement

Raw materials & grades

Lime:- It provides strength to the cement

Silica: Imparts strength to cement

Alumina: Reduces the setting time of cement

Gypsum: Helps to retard the setting of cement

Iron oxide: provide strength, hardness & colour to the cement

Manufacture of cement

The chief raw material used for mfg of portland cement are limestone & clay.

There are 2 methods of mfg:

a) wet process: It used in India & Europe

The crushed limestone mixed with slurry of clay about 60% of H₂O in proportion & pulverised in ball mill & further ground in tube mills & thoroughly homogenised by making of compressed air & then stored in tank. Where after analysis, addition are made to adjust the proportion.

* It is superior quality.

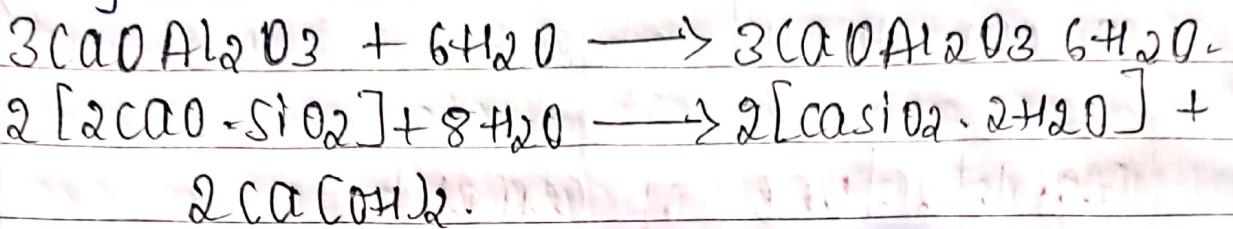
b) dry process: Here raw materials are separately crushed & ground in suitable machine & dried then mixed in proper proportion pulverised in ball mills & homogenised. Then it dried, powdered & stored.

* It is low quantity & slow process.

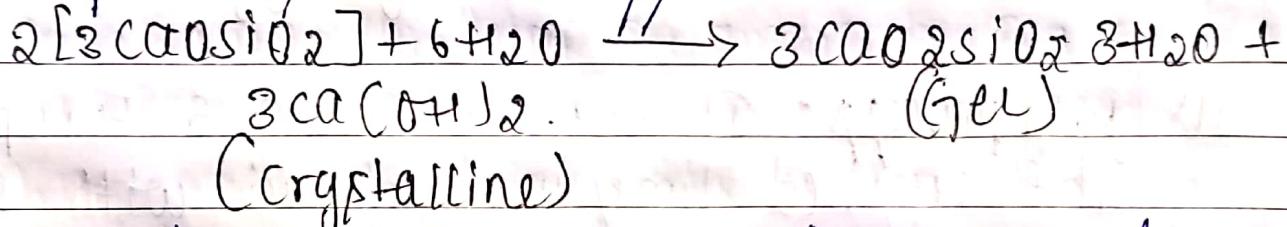
Setting of cement

It is defined as stiffening of original plastic mass due to initial gel formation.

Initial setting of cement is due to hydration.



Final setting involves formation of colloidal gel & crystalline. There is interlacing of crystals as well as with sand grains to previous hard mass.



As hydrolysis & crystallization proceed, the strength & hardness of the set mass increases. The entire process requires about 28 days.

Industrial Materials-II

Date _____
Page _____

paints & varnishes

paint defined as a homogenous fluid containing suspension of finely divided solids that dries up when applied on a surface.

constituents of oil.

1) pigment:

- * It provide color & to impart an aesthetic appeal to the film.
- * To reduce gloss & weathering property.

2) Binders: Non-volatile liquid portion of the paint is Binders.

- * Give Adhesion to the surface
- * provide moisture - progress.

3) Thinner: It are volatile liquid part of the paint

- * used in benzene, cyclohexane, ethyl alcohol etc

4) Driers: These are the substance added to accelerate the drying of the film

- * Suppress the action of antioxidants
- * catalyze the drying of the film through oxidation.

5) other compounds: water based: also require dispersing agent (casein) antifoam agent (pine oil) & preservative (chlorophenol)

constituents of Emulsion paints.

1) pigments & extenders.
These are water dispersible such as
 TiO_2 , ZnS etc.

2) Binders:
The oils & resins used as binders
are water dispersible, linseed oil polythene
estegum are commonly used.

3) Emulsifying agents:
It help to form an emulsion
depending on type of pigments & vehicles
used.

4) Stabilizers: It added to increase the
stability of the paints. They serves as
thickening agent for the H_2O phase.

5) preservatives: It added to prevent decompos-
ition of any protein & eliminate the growth
of fungus on paints.

6) Anti-foaming agent: Added to check form-
of foam during the agitation of emulsion
paints

Varnishes: It are transparent viscous
liquids & contain no pigment. It is a
homogenous colloidal dispersion of resins
in drying oil.

Constituents of varnishes.

- 1) Resins: It used may be synthetic like phenolic alkyl, urea formaldehyde, vinyl (or) silicone.
* It provide glossy, adhesive, durable film
- 2) Drying oils: It used in linseed, tung oil, dehydrated castor oil, soyabean oil.
- 3) Thinners: Turpentine, kerosene, xylene, acetone, ethanol, amylacetate etc., are used as thinners
- 4) Driers: It help in accelerating the drying rate.

- 5) Anti-skimming agents: It used in tert-amyl phenol, guaiacol, etc.

Fuels.

A fuel is any substance which on combustion produces heat (or) power.

characteristics:

- * It should be easily available
- * It should be economical.
- * It contain low % of non combustible matter
- * It should have proper ignition temp.
- * It should leave less ash

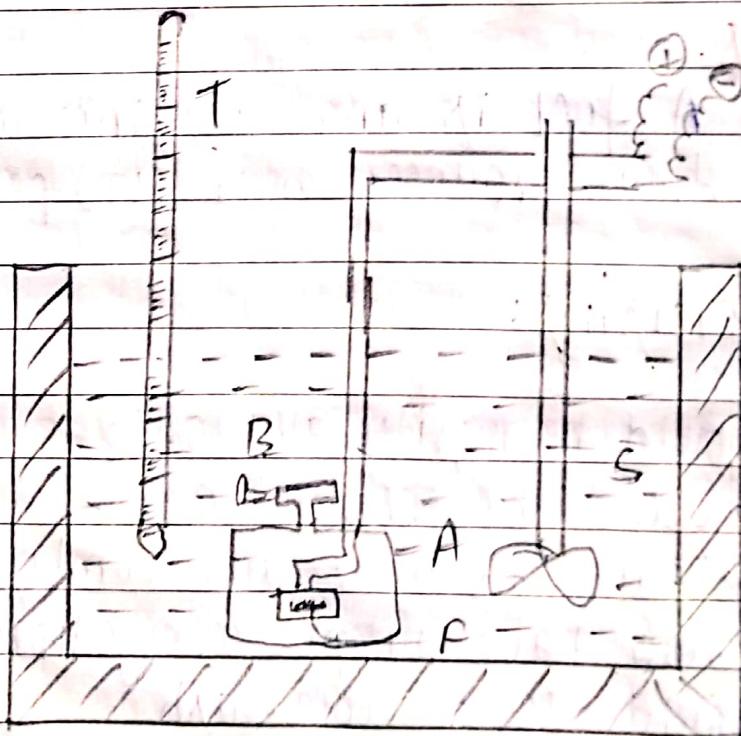
Calorific value of fuel: Amount of heat produced on complete combustion of a unit

quantity of the fuel
s.i unit is J/kg .

calorific value also be expressed in term
of British thermal unit (BTU).

Determination of calorific value of fuel
by using bomb calorimeter.

- * The bomb is made of a strong cylindrical steel container 'A' in which known amount of fuel is burnt
- * It is provided with air tight lid 'B' & an inlet valve for passing oxygen.
- * The bomb is placed inside a calorimeter filled with definite mass of H_2O this is provided with a precision thermometer T & a stirrer S.



A known mass of fuel is taken in a silica crucible F & kept inside the bomb.
A thin mg wire is projecting from crucible

connected to terminal rods. O_2 filled into bomb
the initial temp^r of H_2O in meter is down.
The fuel in Bomb is ignited by connecting
the terminal rods to source of electric current
The water is kept stirred & the maximum
temp^r attained by H_2O is noted.

Calorific value of the fuel is calculated by
the equation : $Q = WSAT/m$.

(Coal): It is a combustible black (or) brownish
black sedimentary rock usually occurring in rock
strata in layers of veins.

Varieties of coal.

1) peat: This is initial semi carbonized stage in
the formation of coal. It content 30 - 40% of
C & its calorific value about 16.2 MJ/kg.

2) Lignite: Brown coal & it is woody. 46 - 60% of
C & calorific value about 12.8 - 19.3 MJ/kg.

3) Sub-bituminous coal: Black & denser, harder
than lignite. It content 46 - 60% of C & calorific
value 19.2 - 30.2 MJ/kg.

4) Bituminous coal: Black coals which burn with
a smoky yellow flame.

a) High volatile: carbon contains 46 - 69% &
calorific value of 25.5 - 34.8 MJ/kg.

b) Low volatile: carbon contains 69 - 86% & calorific
value of 23.6 - 36.2 MJ/kg.

5) Anthracite: Black, hard & lustrous. carbon contains 86% to 98% & calorific value about 31.2 - 36.2 MJ/kg.

→ Gaseous fuels: It include the fuel natural gas & secondary fuels like H₂O, gas, producer gas, coal gas, Biogas, LPG etc.

fuel	composition	calorific value in kJ/m ³
natural gas	CH ₄ (80%), C ₂ H ₆ (12.5%)	30000 - 35000
	N ₂ (4%), CO, CO ₂ , He, Ar.	
coal gas	CH ₄ (30%), H ₂ (40%)	20000
	CO(7%), C ₂ H ₆ (4%)	
	N ₂ , He.	
producer gas	H ₂ (10%), CO(30%)	5500
	N ₂ (55%)	
water gas	H ₂ (50%), CO(40-50%)	12000
	N ₂ (5%)	
liquid petroleum gas	n-butane (27%) isobutane (30%)	120000
	butane (10%)	
	ethane, propane	

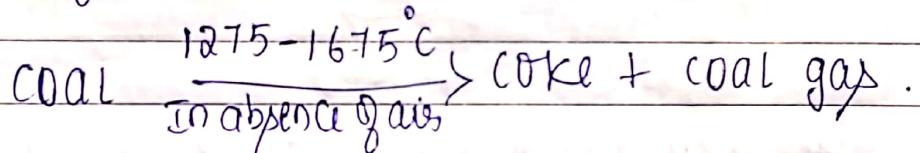
Biogas CH_4 (55%), H_2 (8%), 18000-20000.
 CO_2 (35%)

Advantages of gaseous fuel.

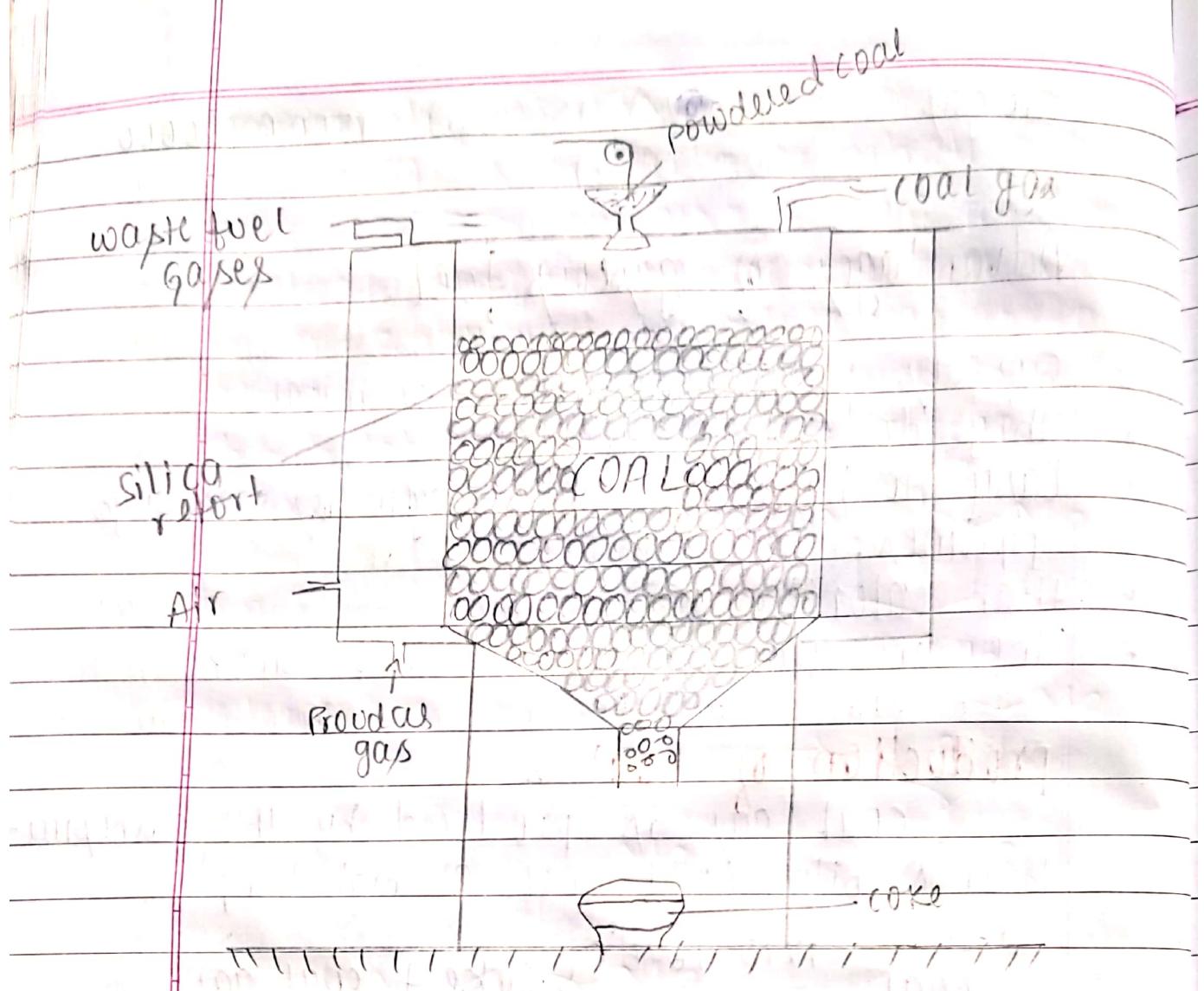
- * Gaseous fuels are more economical.
- * They do not produce ash.
- * Easy to handle, carried in cylinders & through pipelines.
- * High calorific value.
- * They are clean i.e. burn without smoke.

Production of coal

coal gas is produced by the carburation of bituminous coal at high temp.



In vertical process as shown in above diagram the bituminous coal is feed into closed silica retorts. It is heated by burning mixture of producer gas & air heating jackets surrounding the retorts. An outlet is provided at the top of the retort through which coal gas is collected. The resulting outgoing gas contains H_2N , CO_2 , H_2S & CS_2 . These impurities are removed by passing through a scrubber containing H_2O . When H_2O vapour, coal tar & little ammonia condense.



After removing the final traces of NH_3 , the mixture is passed through ferric oxide followed by an alkaline soln of ferrous sulphate to remove hydrogen sulphide & HCl . Finally dehydrated by passing through anhydrous CaCl_2 . The purified gas is stored in cylinders.

Octane number: The standard measurement of an engine of fuel is called octane number.

Significance: It is used to determine the quality of fuel (or) Engine.

Explosives: Those materials which under the influence of thermal decomposes rapidly chemical rxns with large volume of gases liberating a lot of heat energy.

Classification:

a) High explosive: produce high amt of heat with rapid chemical rxns

at primary explosive: These are highly sensitive explosive which explode by a slight shock

Ex:- DDNP, Hg(CNO)₂, Lead azide.

b) 2^o explosive: These are quite sensitive to fire & mechanical shock but they have high energy content.

Ex:- TNT, Picric acid, dynamite.

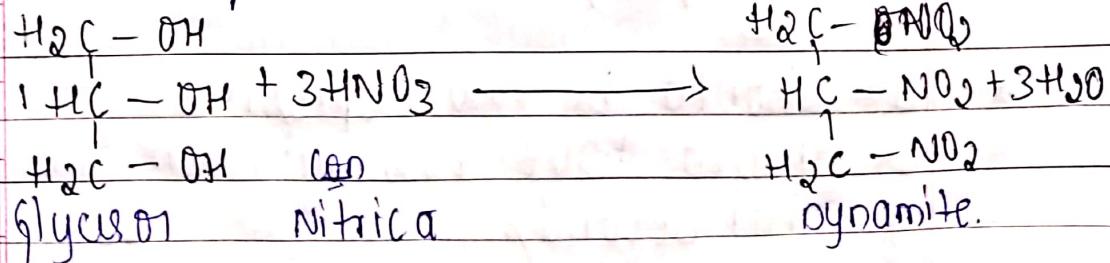
c) Low explosives: These are simply burns but do not explode suddenly.

Ex:- dinitrotoluene, gunpowder, nitrocellulose

Preparation of dynamite.

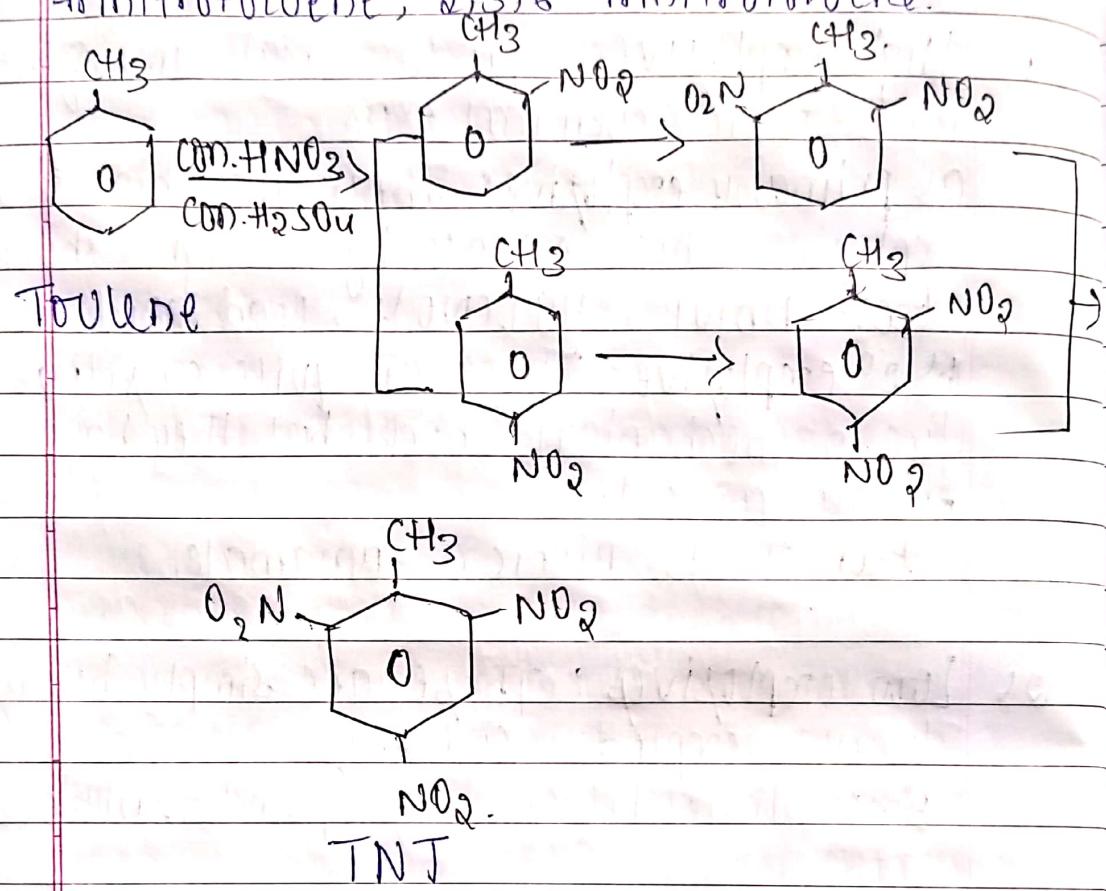
The major component of dynamite is glycer trinitrate which known as nitroglycerine.

Dynamite is prepared by subjecting glycerol to the nitration using nitrating mixture at 10°C temp.



Preparation of TNT

TNT is prepared by nitration of toluene using conc HNO_3 & conc H_2SO_4 mixture at moderate temp. The product is washed with water & followed by dilute Na_2SO_3 to remove unsymmetrical TNT such as 2,3,4-trinitrotoluene, 2,3,6-trinitrotoluene.



Propellants: A material containing a fuel & an oxidizer, which on combustion produces large volume of gases & high temp. of about 3273K.

Characteristics:

- * It should be low explosive
- * It should have low ignition time order of milli seconds

- * It should have high calorific value
- * It should have higher impulse.
- * The product of combustion should have low mol wt.
- * It should not leave behind any solid residue after combustion.

Classification of propellants.

a) Solid propellants: propellants are solid in state.

as Homogeneous s.p.: It contain both fuel & oxidizer in the same compound

Ex:- Nitroglycerine, Ballistite.

b) Heterogeneous s.p.: It contain solid fuel, solid oxidizer & a binder mixed together.

Ex: A mixture of sodium nitrate ammonium picrate & polybutadiene

c) Liquid propellants: propellants are liquid in state.

a) Monopropellants: It contain both fuel & oxidizers in the same molecule
Ex: Hydrazine, Ethyl oxide

b) Bipropellants: It consists of a liquid fuel & liquid oxidizer which are stored separately & pumped into the combustion chamber at required rates

Ex: common liquid fuel are kerosene, liquid H_2 , dimethyl hydrazine etc,

common liquid oxidizer are liquid H_2O_2 , fuming nitric oxide, nitrogen pentoxide etc.

Appⁿ of propellants

- * used as rocket fuel
- * used as propulsion unit for missiles, target drones & supersonic shields.

Bio Inorganic Chemistry

Date _____
Page _____

Essential (or) major elements: These are elements which involve in major biological processes to maintain the existence & survival of the living organism.
Ex: Na, K, Ca, Mg, P, S, Cl.

Trace elements: These are elements which contributes quantity is very much less i.e., in tens of micrograms. They play an important role in biological processes.
Ex: Fe, Cu, I, Mn, Co, Zn, F, Cr, Ni.

Functions. Sodium.

- * provides 92% of ECF osmolarity & maintains internal environment
- * maintenance of electrolyte & fluid balance
- * Exocrine secretion
- * maintenance of blood volume & B.P

2) Potassium.

- * It maintains intercellular osmotic pressure, acid base balance.
- * It helps in contraction of heart
- * involved in proper transmission of nerve impulses.
- * involved in biosynthesis of proteins

3) Calcium

- * It helps in blood coagulation
- * It present in bones & teeth as salt along with Mg & P.
- * It required for normal function of heart,

- * muscles & nerves
- * It helps in oocyte activation & building strong bones & teeth

4) Iron.

- * It helps in formation of hemoglobin
- * regulation of body temp
- * Brain development
- * Binding O₂ to RBC & transport
- * Immune system.

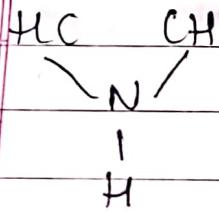
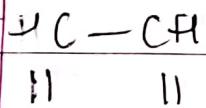
5) phosphorous.

- * It gives structural support to the body
- * It has active in enzyme system
- * It takes part in energy generation & storage of ATP
- * It takes part in cell growth

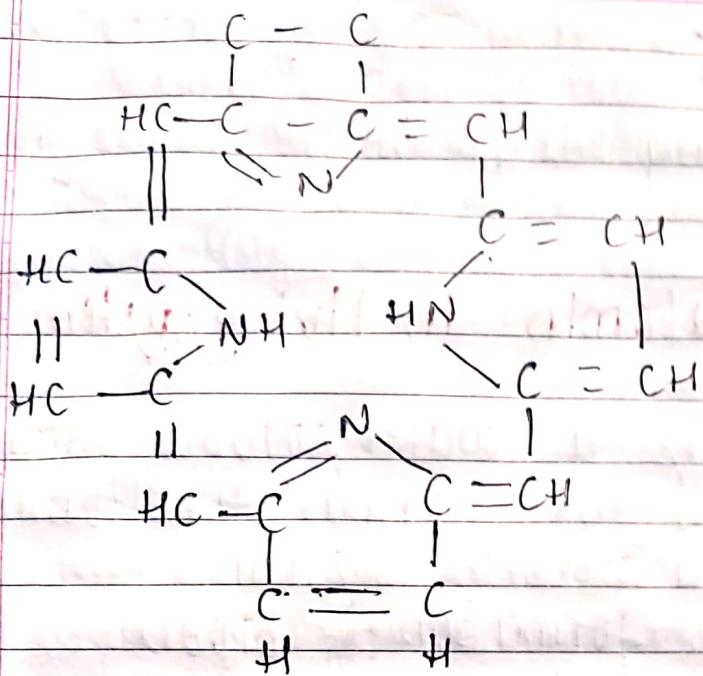
METALLO - porphyrins.

These are cyclic compounds formed by the linkage of 4 pyrrole rings through methylene bridges.

It acts as cheating ligands 4 N₂ atoms of 4 pyrrole ring form coordinate bond with metal cation to form metal porphyrins.



Pyrrole.



porphyrin ring

1. **Haemoglobins:** Iron porphyrins are attached to protein globin. They possess the ability to combine reversibly with oxygen.

Haemoglobins serve as O_2 transporters in blood.

* It also helps in transporting CO_2 from the tissues to the lungs.

2. **Myoglobin:** These occur in muscle cells of vertebrates & invertebrates.

* They serve as oxygen transporters within the muscle tissue.

* It is present in flight muscles of birds.

3. **Chlorophyll:** It makes the entire molecule rigid so that energy is not easily lost thermally.

If increases the rate of short lived singlet excited is transformed into corresponding triple state, hence it trans its excitation energy into the redox chain

Role of cobalamin in living system

Cobalamin is a water soluble vitamin with a key role in the normal functioning of the brain & nervous system.

It helps in formation of blood.

It especially affecting DNA synthesis & regulation but also fatty acid synthesis & energy production.

It can be produced industrially only through bacterial fermentation synthesis.

This is used in the treatment of pernicious anemia, it is isolated from liver.

Cobalamin is changed human cells to a principal cobamide coenzyme viz methyl cobalamin in cytosol in mitochondria.

Chemistry of Newer Materials.

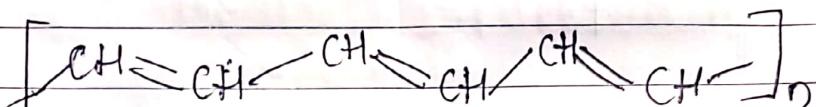
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Conducting polymers

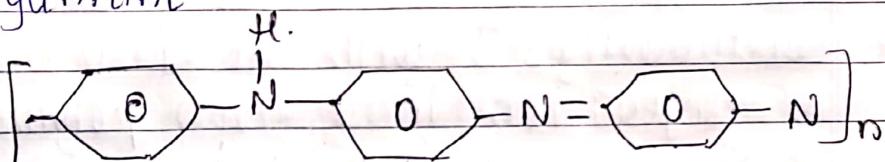
A polymer with highly delocalized π -system having electrical conductance.

Ex:-

Polyacetylene



Polyaniline



Mechanism of conduction

conducting polymers have backbone of conjugated sp^2 hybridised carbon centres. one valence \bar{e} on each carbon centre resides in a p_z orbital which is orthogonal to the other 3 sigma bond. All the p_z orbitals combine with each other in a molecule to form set of delocalised orbitals. When it is partially emptied this leads to conducting property to the polymer. Similarly polymer can be doped to reduction which adds \bar{e} to an unfilled electron bands. In most of the organic polymers are doped by either oxidation or reduction.

Quantitative treatment of doping

In principle, objective of doping of polymer is to enhance their electrical

conductivity. In most cases, phenomenal increase in conductivity of the order $10^8 - 10^{12}$ results. The dopants used, the process of doping & doping level of the dopant in the polymer & temp.

properties:

- * Conductivity \propto with the \uparrow in the extent of conjugation in a given polymer.
- * Increase in doping level of the polymer conductivity is found to increase but after sometime it can be saturated
- * Some of the properties can be varied by the change in the doping material they are:
 - 1) Conductivity
 - 2) Ability to store a charge
 - 3) Ability to ion exchange
 - 4) Coloured products
- * Elasticity with high electrical conductivity

Applications:

- Engineering field:

- * Mfg of organic solar cells
- * Printing electronic circuits
- * Chemical sensors
- * Electro magnetic shielding
- * Flexible transparent displays

2) Biological applications:

- * Bio actuators
- * used in tissue
- * Neural applications
- * phy & che modifications of bio molecules can be done
- * used as biosensor

Super conductors:

The phenomenon of electrical resistance becoming zero at low tempⁿ is called super conductivity. the material with zero electrical resistance is called Super conductors

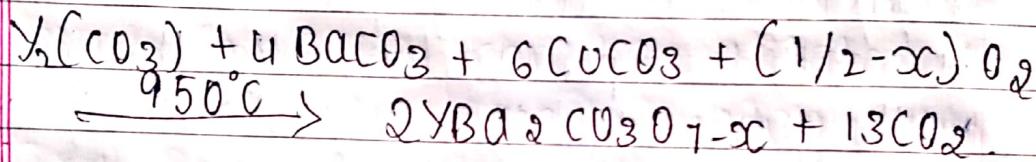
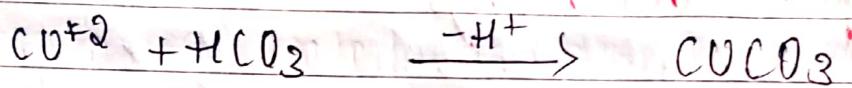
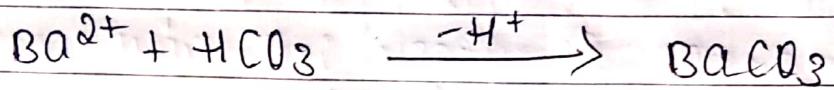
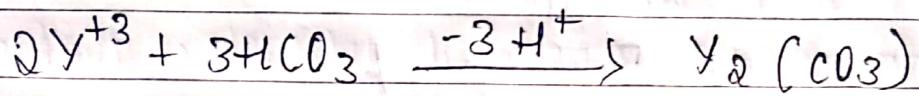
Type - I :- Superconductors are those super conductors which lose their superconductivity very easily or abruptly when placed in the external magnetic field.

Type - II :- Superconductors are those super conductors which lose their superconductivity gradually but not easily (or) abruptly when placed in external magnetic field

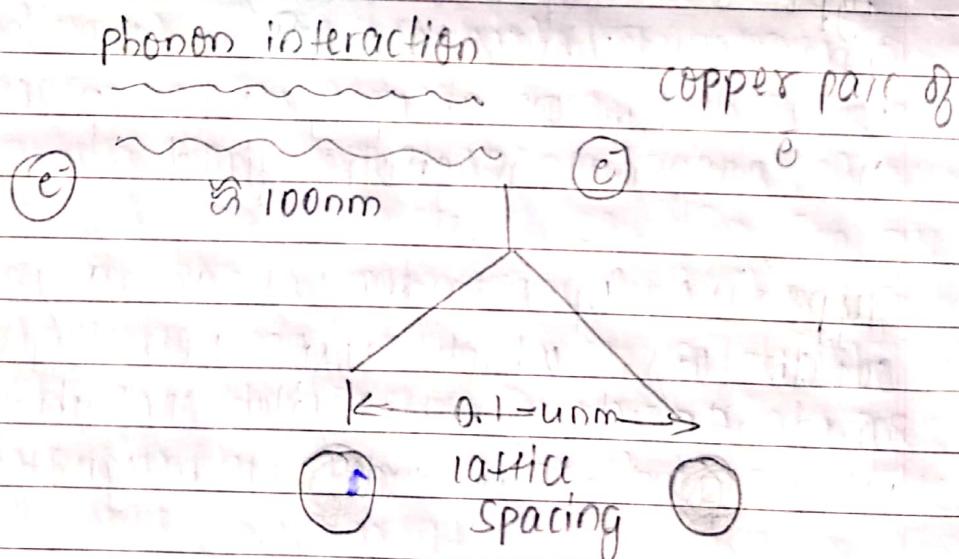
Preparation of high tempⁿ Super conductor.

The $\text{YBa}_2\text{Cu}_3\text{O}_7 \cdot x$ compound is prepared by calcination & sintering of homogeneous mixture of Y_2O_3 , BaCO_3 & CuO in the

appropriate atomic ratio.
At the time sintetizing, the semiconductor tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_6$ compound is formed, which on slow cooling in O_2 atmosphere turns into superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\text{x}}$.



BCS Theory.



According to BCS theory, . . .

- * A metal in which the conduction electrons inside the Fermi sphere. the electrons are repelled to each other. But these electrons attractive to ions towards it. Hence

these e^- are screened by ve ions & the screening effect reduces the repulsion b/w these electrons.

- * In equilibrium condition, A balance ~~exists~~ b/w attraction & repulsion is established & two e^- combine to form pair called copper pair.
- * At low temp. $T \ll T_c$ the e^- lattice interaction are stronger than e^-e^- repulsion & cup pair will move in lattice without any exchange of energy.
- * In electric field the e^- gain additional K.E & gives rise to current. But they do not transfer this energy to lattice. hence they do not get slow down. so the substance does not possess any electrical resistivity & behave like superconductor.

General applications of high temp. super conductors.

- * To make high strength super magnets which are used in MRI & NMR Spectroscopy
- * Used in the energy related areas such as production of magnetic fusion.
- * In the transport field, high speed trains based on magnetic limitations
- * Used in chemical industries
- * Used in large synchronical generations & motors.

Fullerenes:

fullerenes is an allotrope of carbon.

Excr BUCKY ball (C_{60}).

preparation & Isolation C_{60} .

A graphite disc was heated by a high intensity laser beam that produces a hot vapour of carbon. A burst of helium gas than the vapour of carbon out through an opening where the beam expands, the expansion, cooled the atoms & they condense into clusters (or) C_{60} molecules i.e fullerenes. pure C_{60} & G_0 can be isolated by column chromatography using alumina column.

Structure & chemical reaction of C_{60}

C_{60} consists of arrays of 60 carbon atoms with geometry of icosahedron having 20 hexagons & 12 pentagons, A geometry typical of a soccer ball. In C_{60} all the carbon atoms are equivalent by symmetry but there are both single & double bonds with C-C distances of 1.453 \AA & 1.383 \AA respectively. C_{60} is a strained molecule but it shows great K.E. However they are thermodynamically less stable than diamond & graphite.

Uses :

* It used as superconductors at low temp. of

10 - 40 K

- * It is used as doped with metal like Na & K occupy the interstices b/w adjacent C_{60}
- * It is also used as lubricants due to their spherical st^r.
- * It is also used in high energy fuels & medical materials.

Carbon nanotubes.

A form of carbon in which atoms are linked by a cylindrical frame with diameter of only a few nanometers is called carbon nanotubes.

Ex:- Single walled CNT, cylindrical CNT & multiwalled CNT.

Structure:- CNT st^r consist of a single sheet of graphite, rolled into a tube both ends of which are capped with C_{60} fullerenes hemispheres. The tubes can be either open at their ends or capped at one (or) both ends with half a spherical fullerenes.

Nanomaterials:

A material as a set of substances where at least one dimension is less than approximately 100 nm.

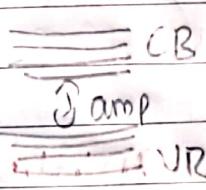
Electronic structure.

In terms of bulk material & their electronic structure. In case of nano materials

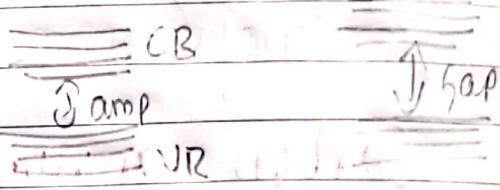
energy gap b/w conduction band & valence bond is different from bulk material, material having few hundred atoms. the continuous density of states in the conduction band is replaced by a set of discrete energy levels



BULK material



large metal clusters



nano materials having 4 atoms

for zero dimension, nano materials the ϵ are fully confined. on other hand, for 3D materials. the ϵ are fully delocalised. In 1-D & 2-D nanomaterials ϵ confinement & delocalization co-exist.

Different methods of production.

They are having widely 5 methods.

1. Sol-gel synthesis
2. Inert gas condensation
3. mechanical alloying
4. plasma synthesis
5. Electro-deposition

Sol-gel synthesis:

The method involves the formation of a conc suspension of a metallic oxide(s) hydroxide(s) which is dehydrated by solvent extraction resulting in a semi-rigid mass. this process gives a good

control over composition & particle size.
Almost nano size metal nanocrystal can
be produced in water but this method
is limited in applicability.

Inter-gas condensation.

In this technique, A inorganic material is vapourized using thermal evaporation (or) e-beam evaporation. In the method an atm of 1-50⁰m bar of inert gas due to high pressure of inert gas molecules & their collision with the ultra fine particles having 10-100nm.

Eg:- Fe is evaporated into an inert gas atm through collision with the atoms the evaporated Fe atoms K.E & condense in the form of small crystallite crystals.

Mechanical alloying (Ball milling)

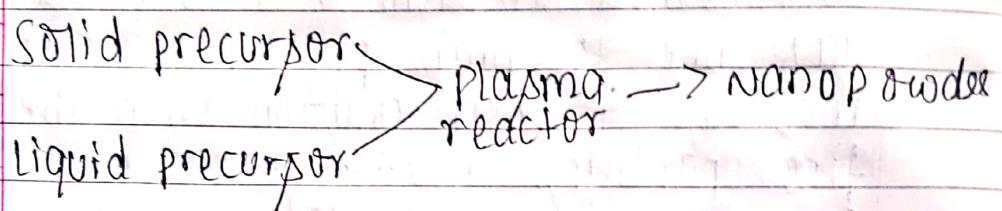
In this method, the milling is carried out at room temp for up to 150 hrs. following the milling, the produced is annealed under inert gas at flow at temp = at 1400⁰C for 6 hrs. mechanism of process is not known.

But in the process forms nanotube nuclei & the annealing process activates nanotube growth. In this method more multi walled nanotubes & few single walled nanotubes. Mechanical alloying leads to the formation of alloys which cannot produce in conventional process.

plasma synthesis:

This method has been successfully used in the synthesis of advanced materials such as new ceramics, nano metric metallic powders, biomaterials & superconductors.

The typical size of the nanoparticles produced by this method ranges from 20 to 100nm depending on the quenching conditions employed.



Ex:- Size of nano powder: Al powder (60nm)
Silicon Carbide (50nm)

Electro deposition:

In this method consists of an electrochemical cell & accessories for applying controlled current at a certain voltage. the cell contain cathode & anode. the cathode is made from non-metallic & metallic material.

using this surface of the cathode as a template, various desired nano str^c (or) morphologies synthesized for a specific applications. the electro deposition process involves the formation of either instantaneously (or) progressive nucleation. Template-assisted electron deposition is an important techniques

for synthetic metallic nano-materials
with controlled shaped & size.

General application

- * It used in medicines.
- * Used in making of high energies density batteries
- * Used to mfg of next generation computers technologies
- * Used in high sensitivity sensor.
- * Used in H₂O purification process
- * In food science.
- * Used in aerospace
- * Used in automobiles.
- * Used in veterinary application.
- * Used in high power magnets