PART-A

1 **Give the IUPAC name of the following complexes**:
i) $[(Cu(NH_3)_4]SO_4$- Tetramminecopper(ii) sulphate
i) $[Co(H_2O)_3(NH_3)_3]Cl_3$- Tetrammine triaquacobalt
(iii) chloride

2 **Write the optical isomers of $[CoC1_2(en)_2]^+$**

3. **What is spectrochemical series?**
The arrangement of various ligands in the increasing order of their ability to split d-arbitals (increasing order of crystal field splittling $10D_q$) is called spectrochemical series.

4. **Cis-platin is used in cancer therapy but not transplatin. Why?**
Cisplatin and its related bis (amine) complexes are used in treatment of cancer. When cisplatin is injected in low concentrations platin binds to DNA in place of chloro ligands to the nitrogen atoms of guanine by co-ordination. Due to intrastand linking of Pt with two adjacent guanine bases of DNA, normal reproduction of DNA is impaired and the cell division is prevented. The trans-isomer is not inactive.

5. **Define hardness of an abrasive. On what scale is it expressed?**
It is the ability of the abrasive to scratch other substances or to get scratched.
Mohs' scale

6. **What is spalling in refractories and how can it be minimized?**
It is defined as the breaking or flaking of a refractory due to uneven expansion or contraction as a result of sudden variation in temperature (or wide differences in the temperature) is called spalling (thermal spalling).

It can be minimized by proper design of the bricks, construction and operation of the furnace (bricks should be properly baked or fired).

7. **Mention any two characteristics of a propellant.**

a) It should have high heat of combustion. b) It should yield low molecular weight combustion products c) It should not detonate when subjected to thermal or mechanical shock d) It should not leave behind poisonous, corrosive, toxic or solid products after combustion.

8. **Define calorific value of a fuel**

It is defined as the amount of heat evolved when unit mass (or unit volume at one atmosphere pressure in the case of a gas) of a fuel is burnt completely in excess of air and the products of combustion cooled at 298K.

Or

It is the amount of heat produced on complete combustion of unit quantity (mass/vol) of the fuel in the presence of air/oxygen.

9. **Explain the role of Vitamin – B12 in living systems.**

a) Vitamin B12 reacts with ATP, results coenzyme which involves in effecting unusual rearrangement reaction. b) Cobalamine along with folic acid required for the development of red blood cells.
c) Vitamin containing co (1) plays an important role in the function of vitamin B12 and readily under goes alkylation via reductive oxidation d) Deficiency of vitamin B12 causes pernicious anemia in humans.

10. **How is high temperature super conductor-Yttrium Barium Copper oxide (YBCO) synthesized Give equation.**

By heating a mixture of the metal carbonates at temperature between 1000Kand 1300K.

$4\ BaCO_3 + Y_2(CO_3)_3 + 6\ CuCO_3 + (½ - X)O_2 \rightarrow 2YBa_2Cu_3O_{7-X} + 13CO_2$

11. **Give any two engineering applications of conducting polymers.**

a) They are useful in discharge large quantity of static electricity of computer industries and in chemical industries. This can be accomplished by coating the conducting polymer over an insulating surface b) Conducting polymer can observe harmful electromagnetic radiations. So these can be used to coat on the cases of computer monitors and cell phones c) They are useful as corrotion inhibitors d) They can applied in flat panel displays which are thinner than liquid crystals displays or plasma displays. e) They are also useful as flexible display devices for mobile phones. f) As artificial intelligent materials.

12. **What are fullerenes? Give an example**

They are the allotropic forms of carbons which are the forms of hollow sphere, ellipsoid and many other shapes
C_{60}, C_{70}, C_{72}, C_{74}, C_{80}……

PART-B

13 **a) Give the postulates of Werner's theory of co-ordination compounds.**

1. Central metal atom in a complex exhibits two types of valencies-Primary valency and secondary valency. b) The primary valency is ionisable and non directional. The primary valency is variable and it is satisfied by negative ions. c) Secondary valency is non ionisable and it is satisfied by negative ions or neutral molecules. d) Secondary valencies have directional characteristics and directed towards fixed position in three dimensional space. This results in definite geometry in the complex ions.

b)Calculate the EAN of Ni in the complex tetracarbonylnickel (O) (Atomic No. of Ni=28)

EAN = Z-X+Y
28-0+4x2 = 36

14. **a) Explain the magnetic properties of $[CoF_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$ ions based on CFT.**

The oxidation state of cobalt is +3, in both the complexes. The electronic configuration is $[Ar]3d^6\ 4S^0$. In $[CoF_6]^{3-}$, the F- is weak ligand. It is a high spin complex. ($P > \Delta o$) Therefore the d electron configuration is $t_2g^4\ eg^2$. Hence there are four unpaired electrons. Therefore it is paramagnetic.

In $[Co(NH_3)_6]^{3+}$ is a low spin complex, where ($P < \Delta o$). Hence the d electron configuration is is $t_2g^6\ eg^0$. And there are no unpaired electrons. Therefore it is diamagnetic.

b) Mention the type of isomerism exhibited by the following pair of co-ordination compounds:

i) $[PtCl_2(NH_3)_2]Br_2$ and $[Pt\ Br_2\ (NH_3)_2]Cl_2$.- ionization

ii) $[Cu\ (NH_3)_4]\ [PtCl_4]$ and $[Pt(NH_3)_4]\ [CuCl_4]$. - coordination

15. a) Discuss the splitting of d-orbitals in tetrahedral complexes.

In a tetrahedral complex, the metal ion is situated at the center of tetrahedron and each of the four ligands are positioned at the corners of tetrahedron. The splitting of d-orbitals in a tetrahedral field is reverse of that of octahedral field. In this case t_{2g} set of orbitals (d_{xy}, d_{yz}, d_{zx}) which are oriented in between the coordinate axes are more repelled by the ligands and there is a raise in their energies. The e_g set of orbitals ($dx^{2-}y^2$ and dz^2) are oriented along the coordinate axes and are less repelled by the ligands (Note that the angle between the ligand and an eg orbital is large and experience a small repulsion. The angle between the ligand and a t_{2g} orbital is large and experience a small repulsion). Therefore t_{2g} orbitals have a higher energy compared to e_g orbitals. The magnitude of crystal field splitting energy in a tetrahedral field (Δ_t) is lower than in an octahedral field. Because, the orbitals in a tetrahedral field are surrounded by only four ligands instead of six. Further, the direction of ligands and-orbitals does not coincide to the same extent as in an octahedral field. For the same metal ion and ligands, it can be shown that $\Delta_t = 4/9\ \Delta_o$. An electron occupying e_g orbitals stabilizes the complex to an extent of $0.6\Delta_t$ while an electron occupying higher t_{2g} orbital destabilizes to an extent of $0.4\ \Delta_t$

b) What are ligands? Give one example for a bidentate neutral ligand.

Ligands are the molecular or ions which can donate one or more lone pairs of electrons to the central metal or ion farming coordinate bonds.
Ethylenediamine (en), 2-21 dipyridine.

16. **a) What are metal carbonyls? Write the structure of $Mn_2(CO)_{10}$**

These are complexes in which metal atom or atmos attached to CO ligands.

b) Explain Monsanto acetic acid process

When methanol is treated with CO, carbonylation takes place in presence of $[RhI_2(CO)_2]^-$ complex farming ethanoic acid.

$$CH_3OH + CO \xrightarrow[HI]{[RhI_2(CO)_2]^-} CH_3COOH$$

17. **a) Based on VBT, explain the geometry and magnetic property of $[Co(NH_3)_6]^{3+}$.**

Coordination number and oxidation state of cobalt in the complex are 6 and 3 are respectively. The outer orbital configuration of Co^{3+} is $3d^6$ and the ion has four unpaired electrons. During formation of the complex, electrons in the 3d orbitals undergo pairing and two d-orbitals became empty. These two d-orbitals along with the 4s and three 4p orbitals mix together forming six d^2sp^3-hybrid orbitals of equal energy. These are directed towards the corners of a regular octahedron and receive the lone pair of electrons donated by ammonia ligands forming six sigma coordinate bonds. Obviously the complex is expected to be diamagnetic due to absence of unpaired electrons and has octahedral structure due to involvement of d^2sp^3 hybrid orbitals.

b) Calculate the effective atomic number of $Cr(CO)_6$ based on 18-electron rule.

Electrons from Cr = 6
Electrons from 6 (Co) = 6 x 2 = 12

Total electrons equal 18

18. **a) Describe the manufacture of Portland cement by wet process.**

Raw materials (i) Lime stone (ii) Clay (iii) Gypsum (iv) Powder coal
Process:
Grinding : The raw materials are separately ground to a fine powder in a ball mill and

then mixed in proper proportions to obtain homogenized mix called dry meal.
Burning: The dry meal is introduced into a rotary kiln which is a steel tube lined with refractory bricks and kept in a slanting position. The charge moves down slowly. A blast of burning saw dust is sent in from the other end. A maximum temperature of 1750^{o}c is reached. At the other end of the kiln where the temperature is highest, lime and clay undergo chemical fusion resulting in calcium aluminates and silicates.
$CaCO_3 \rightarrow CaO + CO_2$, $2CaO + SiO_2 \rightarrow 2CaO.SiO_2$
$3CaO + SiO_2 \rightarrow 3CaO.SiO_2$ $3CaO + Al_2O_3 \rightarrow 3CaO.Al_2O_3$
The product is in the form of hard, grayish stones called cement clinker.
Grinding of clinker : After cooling, the clinkers are ground to a fine powder. During this process 2-3% gypsum is added to reduce the setting time of cement. The cement is packed in air tight bags.

b) Mention any two characteristics of a fuel.

1. It should high calorific value.
2. Posses moderate ignition temperature.
3. It should have low ash residue.
4. It should be dry or should have least moisture content.
5. It should not produce obnoxious byproducts like smoke, CO, NO_2, SO_2 etc during combustion.
6. It should have no or minimal fire hazard and should not occupy too much space and should be safe to transport.
7. A fuel must be readily and cheaply available in large quantity.

19. **a) Give the composition and one application each for (i) borosilicate glass (ii) optical glass**

(i) Borosilicate glass :
Composition : 80-83% silica, 10-12% B_2O_3, 4% Na_2O, 2% Al_2O_3, and traces of oxides of sodium and calcium
Uses : Making quality glass apparatus, baking utensils, thermometers, pipelines for corrosive liquids in chemical industries, TV tubes, electrical insulator.

ii) Optical glass :
B_2O_3, BaO, ZnO, P_2O_5, and silica, traces of rare earth oxides like CeO_2.
Uses: for making lenses, prisms, decorative articles, imitation diamonds, cathode ray tubes etc.

b) Mention the constituents of varnishes.

Resins, drying oils, solvents, driers, plastisizers.

20. **a) Mention the raw materials and their roles in the manufacture of ceramic wares.**

Clay
It imparts plasticity which helps in moulding the materials to a desired shape without deformation.
Feldspar
It serves as flex and binder in ceramic articles. Also provides glossing appearance in the ceramic articles.
Sand (or quartz)
It provides necessary skeletal structure to the ceramic wave. Sand added during firing helps in reducing the shrinkage and induces regitity.

b) Define octane number.

It is the percentage of iso-octane (2, 2, 4 – trimethylpentane) in a mixture of iso-octane and n-neptane which gives equivalent knock performance.

Or

It is a number that provides a measure of the ability of a fuel to resist knocking when it is burnt in a spark-ignition engine.

21. **a) What are explosives? How are they classified? Give one example for each type.**

A material, which under the influence of thermal or mechanical shock decomposes rapidly and spontaneously with evolution of large volume of gases liberating a lot of heat.
Classification : **Low explosive or propellants.**
Eg: Gun powder (or black powder), dinitrotoluene, nitrocellulose.
Primary or initiating explosives or detonators.
Eg: Leadazide, Mercury fulminate, diazonitrophenol.
High explosive : Eg: Trinitrotoluene (TNT), glycerol trinitrate (GTN), ammonium nitrate, cellulose nitrate (CN) RDX (trimethylene trinitriamine).
b) Why preservatives are added to emulsion paints? Give one example.

To prevent decomposition of any protein and to eliminates the growth of fungus on paints.
Ex: Thymol, mercuric chloride, sodium trichlorphenate.

22. **a) Describe the manufacture of silicon carbode.**
It is manufactured by heating sand with carbon (coke) with a small quantity of saw dust in an electric furnace to about 2500K.
$SiO_2 + 3C \rightarrow SiC + 2CO$.

The furnace is made of fire bricks and provided with carbon electrodes. The charge (sand + coke + saw dust + salt) is placed inside the furnace. The salt serves as a flux i.e., a binding for materials and also helps in converting impurities as volatile chlorides. Saw dust make the charge porous and facilitates the escape of gaseous products. An electric arc is struck between the electrodes and heated for nearly 36 hours. Silica reacts with coke farming silicon carbide. After the reaction is completed, the product is further allow to cool for 24 Hrs. a brilliant black layer of SiC gets formed at the centre core. It is removed, crushed and washed with dilute H_2SO_4 followed by dilute NaOH to remove impurities. It is finally washed with water and dried in a kiln.

b) Write any two applications of high temperature super conductors.

1. Magnetic shielding devices, medical imaging systems
2. Superconducting quantum interference devices (Squids) Infrared sensors analog signal processing devices and microwave devices.
3. power transmission, superconducting magnets in generators, energy storage devices, particle accelerators, levitated vehicles transportation.

23. **a) What is myoglobin? Discuss its biological functions.**

It is a conjugated protein containing heme (often called muscle hemoglobin) .
It is one of the important protein in the human body. Generally it is found in muscle tissue where it binds oxygen, helping to provide extra oxygen to release to power muscle contraction. It is a relatively small oxygen binding heme protein in muscle cells. Myoglobin contains a heme group which is responsible for its main function of carrying, molecules to muscle tissues. In man, myoglobin is present in significant quantities only in cardiac muscles. However in diving mammals like dolphins and seals, the muscle contain a higher proportion of myoglobin. This might help these animals to remain submerged for long periods.

b) Mention the role of Ni and V in biological systems.

Ni – Stabilises coiled ribosome and activates hydrogenase reaction.
V – Essential to chicks and rats. Deficiency causes impaired took and bone formation and feather development.

24. **a) Describe the conversion of polyacetylene to conducting polymer by doping method.**

Intrinsically conducting polymer (ICP) has low conductivity. Their conductivity can be improved by creating either positive or negative charges on polymer backbone by oxidation or reduction which can be facilitated by their property of low ionization energy and electron affinity that favors early oxidation or reduction. This technique of adding small quantities of oxidant or reductant to increase the conductance of polymer is called doping.

p-doping : Intrincally conducting polymer-polyacetylene is treated with a lewis acid like iodine or bromine. Oxidation takes place, positive charges on the polymer backbone is created.

n-doping : ICP is treated with a lewis base like N or Li or Ca that creates negative charges on the polymer backbone and make it conducting polymer.

b) Write a note on carbon nanotubes.

A carbon nanotube (CNT) is a tube shaped material, made of carbon having diameter measuring on the nanometer scale. A nanometer is about 10,000 times smaller than a human hair. CNT are unique because the bonding the between the atmos is very strong and the tubes can have extreme aspect ratios. A CNT can be as thin as as few nanometer yet be as long as hundred of microns. A CNT is a sheet of carbon atoms joined in pattern hexagons and rolled into a cylinder. The conducting property of nanotube depends upon how the two ends of sheet meet long. For particular way of arrangement of atoms along the meeting line makes the entire tube conducting like a metal and for another type of arrangement, the tube behave like a semiconductor. CNT or non reactive and with stand high temperature.

25. **a) Explain mechanical alloying method of synthesis of nanomaterials.**

In ball milling process the powder mixture placed in the ball mill is subjected to high energy collision from the balls. It was found that this method, termed mechanical alloying, could successfully produce fine, uniform dispersions of oxide particles (Al_2O_3, Y_2O_3, ThO_2) in nickel-base superalloys that could not be made by more conventional powder metallurgy methods. Their innovation has changed the traditional method in which production of materials is carried out by high temperature synthesis. Besides materials synthesis, high energy ball milling is a way of modifying the conditions in which chemical reactions usually take place either by changing the reactivity of as-milled solids (mechanical activation) increasing reaction rates, lowering reaction temperature of the ground powders) or by inducing chemical reactions during milling (mechanochemistry). It is, furthermore, a way of inducing phase transformations in starting powders whose particles have all the same chemical composition : amorphization or polymorphic transformations of compounds, disordering of ordered alloys, etc.

During the high-energy ball milling process, the powder particles are subjected to high energetic impact. Microstructurally, the mechanical alloying process can be divided into

four stages : (a) initial stage, (b) intermediate stage, (c) final stage, and (d) completion stage.

High energy ball milling process has attracted much attention and inspired numerous research interests because of its promising results, various applications and potential scientific values. The synthesis of nanostructured metal oxides for gas detection is one of the most promising applications of high energy ball milling.

Ex: Metastable a-Fe_2O_3-MO_2 (M: Ti and Sn) solid solutions by high energy milling for C_2H_5OH detection.

b) Write a note on electrophilic aromatic substitution reaction with respect to fullerenes.

Reaction of $C_{60}Cl_6$ and ferric chloride with aromatic compounds gives the corresponding C_s-symmetric aryl derivatives $C_{60}Ar_5Cl$, where Ar = phenyl, tolyl, anisyl, tert-butylphenyl, fluorophenyl, tri-methylsilylphenyl and thienyl. The derivatives arising from exclusive para substitution in anisole and fluorobenzene, together with $C_{60}(4\text{-}FC_6H_4)_5H$ have been isolated and fully characterized. Toluene undergoes substitution in the ortho as well as the para position. Traces of octaaryl derivatives are obtained in the reaction with toluene and anisole.

PART – A

Answer any eight of the following questions. Each question carries two marks.(8 × 2 = 16)

1. **Give the IUPAC names of the following complexes :**
   i) Li[AlH4] : lithiumtetrahydridoaluminate(III)
   ii) $[Co(H_2O)_6]^{3+}$: hexaaquacobalt(III) ion (1+1)
2. **Calculate the EAN of copper in $[Cu(NH_3)_4]SO_4$ (atomic number of Cu = 29)**
   EAN of Cu = Z – L + G = 29 – 2 + 8 = 35 (1+1)
3. **State Eighteen electron rule.**
   "It states that the effective atomic number of the metal carbonyls is equal to the atomic number of the nearest noble gas which has eighteen electrons in the outermost orbit."
4. **Mention two limitations of valence bond theory.**
   Valence bond theory fails to explain,
   i) Characteristic absorption spectra of co-ordination compounds and their colours (spectral properties)
   ii) Thermodynamic properties of co-ordination compounds
   iii) Relative stabilities of different structures (complexes)
   iv) Variation of magnetic moments of complexes with temperature
   v) Formation of outer orbital and inner orbital complexes (any two 2M)
5. **Name the raw materials used in the manufacture of glass.**
   The raw materials used in the manufacture of glass are,
   i) Network formers : Sand SiO_2, Boron trioxide B_2O_3
   ii) Network modifiers : Soda Na_2O, potash K_2O
   iii) Others ingredients : Feldspars, colouring agents decolourising agents, cullets (1+1)
6. **Give any two advantages of gaseous fuels.**
   The advantages of gaseous fuels are,
   i) High calorific value
   ii) Rate of burning can be controlled easily
   iii) Do not produce ash
   iv) Can be distributed through pipelines
   v) Less air required for complete combustion
   vi) Pollution due to smoke is avoided
   vii) High thermal efficiency can be obtained
   viii) Burn easily and instantaneously (any two. 2M)

7. **Define Spalling. How do you minimise it?**
   "Spalling is defined as the breaking of the refractory brick (Material)in service to such an extent that pieces fall away leaving a new surface of the brick (Material)exposed.
   " Spalling is due to sudden changes in temperature or change in composition due to the action of molten metals and slags. It can be minimised by proper (design) baking of the bricks, construction and proper operation of the furnace. (1+1)

8. **Write a note on annealing of glass**.
   If the glass after giving the shape is rapidly cooled, internal strain is developed and becomes brittle. Even with slightest shock it may break. "The process of cooling glass under controlled conditions is called annealing". For this purpose the glass article is passed through a long chamber called "LEHR ". It is hot at one end and at room temperature at the other

end.On passing through the LEHR glass is cooled gradually and internal strain is not developed and the glass becomes more durable.

9. Write any two applications of Superconductors.

Superconductors find applications in,

I) The manufacture of superconducting magnets
II) Magnetic levitation
III) Superconducting quantum interference device
IV) As magnetic shielding devices and medical imaging systems
V) In power transmission, superconducting magnets in generators, energy storage devices, particle accelerators, rotating machinery (any two)

10. Write a note on carbon nanotubes.

A carbonnanotube (CNT) is a tube shaped material, made of carbon having a diameter measuring on the nanometer scale. A nanometer is about 10,000 times smaller than human hair. CNT are unique because the bonding between the atoms is very strong and the tubes can have extreme aspect ratios. A CNT can be thin as few nanometer yet be as long as hundred of microns. This is a sheet of carbon atoms joined in pattern of hexagons and rolled in to a cylinder. The conducting property of nanotubes depends upon how the two ends of the sheet meet along. For particular way of arrangement of atoms along the meeting line makes the entire tube conducting like a metal and for another type of arrangement, the tube behave like a semiconductor. CNT are nonreactive and withstand high temperature. When one type of nanotube is rolled inside another tube we get a multi-walled nanotube.

11. What is the role of Cobalamine in living systems?

Cobalamine (Vitamin B12) reacts with ATP to form a co-enzyme which involves in effecting unusual rearrangement reaction. Cobalamine along with folic acid is required for the development of RBC 's. Deficiency of vitamin B12 causes pernicious anaemia in humans.

12. Give any two examples of conducting polymers.

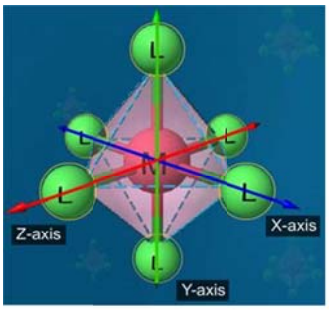
Examples: Polyacetylene, Polypyrrole, Polythiophene, Polyaniline. (Any two)

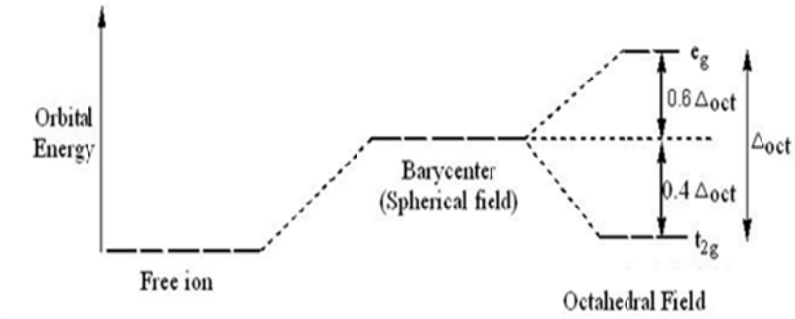
PART - B

Answerany nine of the following questions. Each question carries six marks. (9 × 6 = 54)

13. a) Explain the crystal field splitting pattern in octahedral complexes.

According to the crystal field theory, the ligands are considered as point charges. In an octahedral complex, the metal ion is considered to be at the centre of an octahedron and the six ligands approach it along the three axes. (1m)





(1m)

The ligands exert an electrostatic force of repulsion on the outer d-electrons. This repulsion raises the energy of the degenerate d orbitals to give five excited degenerate orbitals which is hypothetical. The lobes of the two orbitals d x^2-y^2 and dz^2(e_g) are more concentrated on the axes along which the ligands are approaching. Hence the electrons in these orbitals suffer a greater repulsion than the t_{2g} set of orbitals that is d_{xy}, d_{yz}, and d_{zx}which lie in between the axes. Thus in an octahedral field, the d-subshell is split into two sets of e_g has higher energy and the other set t_{2g} has lower energy as shown in the diagram.

The splitting of five degenerate d-orbitals of metal ion under the influence of approaching ligands, into two sets of orbitals having different energies is called crystal field splitting. The magnitude of difference in energy between the two sets of orbitals is designated as Δ_o. The energy of the eg orbital is 0.6Δo higher than the hypothetical degenerate d-orbitals. (2m)

b) What are metal carbonyls? Give an example.

The transition metals form complexes with carbon monoxide (CO) as ligands are called metal carbonyls. Examples :$V(CO)_6$, $Fe(CO)_5$, $Ni(CO)_4$.(1+1)

14. a) Give the postulates of Werner's theory of co-ordination compounds.

i) Central metal atom in a complex exhibits two types of valencies-Primary valency and secondary valency

ii) The primary valency is ionisable and non-directional. The primary valency is variable and it is satisfied by negative ions.

iii) Secondary valency is non-ionisable and it is satisfied by negative ions or neutral molecules.

iv) Secondary valencies have directional characteristics and directed towards fixed position in three dimensional space. This results in definite geometry in the complex ions. (1 mark each)

b) What is Spectrochemical series?

"When the ligands are arranged in the increasing order of their crystal field splitting the series obtained is called Spectrochemical series.

15. a) Based on valence bond theory explain the geometry and magnetic property of $[Co(NH_3)_6]^{3+}$.

Coordination number and oxidation state of cobalt in the complex are 6 and 3 are respectively. The outer orbital configuration of Co^{3+} is $3d^6$ and the ion has four unpaired electrons. During formation of the complex, electrons in the 3d orbitals undergo pairing and two d-orbitals became empty. These two d-orbitals along with the 4s and three 4p orbitals mix together forming six d^2sp^3-hybrid orbitals of equal energy. These are directed towards the corners of a regular octahedron and receive the lone pair of electrons donated by ammonia ligands forming six sigma coordinate bonds. Obviously the complex is expected to be diamagnetic due to absence of unpaired electrons and has octahedral structure due to involvement of d^2sp^3 hybrid orbitals.

Co^0

Co^{3+}

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

(Value as a whole)

b) Define crystal field splitting energy.

The splitting of five degenerate d-orbitals of the metal ion into two sets of d- orbitals possessing different energies is known as crystal field splitting. The energy difference between the two sets of d-orbitals is referred to as crystal field splitting energy.

16. a) Explain the following with a suitable example.

i) Co-ordination isomerism: This type of isomerism is observed in complexes containing both cationic and anionic complexes. An interchange of the ligands linked to two metal ions is observed.
Example: $[Co(NH_3)_{6][}Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$ (1+1)

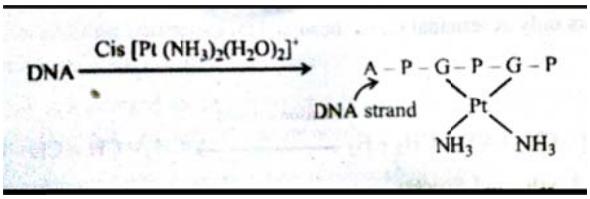
ii) Hydrate isomerism: This type of isomerism exists in complexes associated with water molecules. These complexes differ in number of water molecules inside and outside co-ordination sphere. In such cases the water molecules will be directly linked to metal ion in one species and they lie outside the co-ordination sphere in the other.
Example: $[Cr(H_2O)_6]Cl_3$ violet, $[CrCl(H_2O)_5]Cl_2H_2O$ pale yellow and $[CrCl_2(H_20)_4]Cl\ 2H_2O$ dark green (1+1)

b) What are high spin complexes? Give an example.

The complexes in which the number of unpaired electrons in the free ion and in the complex is same, such complexes are known as high spin complexes.
OR When Δ-Crystal field splitting energy (Δ) is small (weak field ligand), the electrons will fill in which all the t_{2g} and e_g orbitals are singly occupied before any pairing occurs.It is then classified as high **spin** because there is maximum number of unpaired electrons.
Example : $[CoF_6]^{3-}$. (1+1)

17. a)Explain the applications of :

i) Cis platin in cancer therapy: The cis isomer of $[Pt(NH_3)_2Cl_2]$ is used as anticancer drug for the treatment of many type of malignant tumours. The exact mechanism of action is not known. It is believed that the chloride ions are replaced by water molecules to form diaquo complex. The diaquo complex ion reacts with DNA molecules. The platinum atom can bond to nitrogen of two guanosine units and form a bridge between them. This prevents the normal reproduction of DNA. In other words cell division is prevented.



ii) Wilkinson's catalyst in the hydrogenation of oils : Wilkinson's catalyst is $[RhCl(PPh_3)_3]$. This catalyst is very useful for the catalytic hydrogenation of unsaturated molecules at room temperature and pressure. The major advantage of this catalyst is that during hydrogenation using this catalyst only the double bonds at the end of a chain are hydrogenated (terminal) and those elsewhere in the chain are not hydrogenated. This selective hydrogenation is very usefull in pharmaceutical industry.

$CH_3\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH_2 + H_2 \rightarrow CH_3\text{-}CH{=}CH\text{-}CH_2\text{-}CH_2\text{-}CH_2$(2+2)

b) Explain the application of co-ordination compounds in Monsanto acetic acid process.

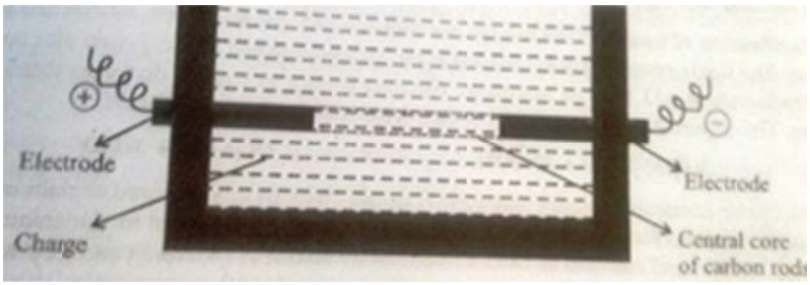
The Process involves the production of acetic acid from Methyl alcohol with carbon monoxide in presence of the rhodium salt and iodine at atmospheric pressure and temperature. The catalyst $[RhI_2(CO)_2]^-$ is formed which converts methyl alcohol to acetic acid.

$CH_3OH + CO$ ----------> CH_3COOH ⟶

18. a) Describe the manufacture of Carborandum.

Silicon Carbide is called Carborandum, it is an abrasive. The Charge consists of 56% SiO_2, 35% Coke, 7% saw dust and 2% salt. The charge is powdered and fed into the furnace where carbon electrodes are kept horizontally at the centre leaving a gap in between as shown in the diagram .

$$SiO_2 + 3\,C \xrightarrow[+\,618.5\ kJ]{} SiC + 2\,\overrightarrow{CO}$$



An electric arc is struck between the electrodes which produces a heat of 3000K for 36hrs.SiC formed at the gap of two electrodes. The saw dust keeps the mass porous and facilitates easy escape of gaseous products. Salt acts as a flux and makes the mass easily fusible. The black strip is cooled for 24 hours. Washed repeatedly with sulphuric acid and sodium hydroxide to remove the impurities and then dried and graded.
(Fig 1+eqn 1 + Expn- 2)

b) Define hardness of an abrasive. On what scale it is expressed?

Hardness of an abrasive is its ability to scratch or get scratched. Hardness is expressed in terms of an arbitrary scale called MOH'S scale. (1+1)

19. a) Mention the raw materials and their role in the production of ceramic wares.

i) **CLAY:** Clay has the property of plasticity which enables to mould them in desired shape. On adding water the plasticity of clay increases and at a certain stage it becomes sticky. 10 to 15% of water produces maximum plasticity in clay.

ii) **FELDSPAR :** Are the main constituents of granite. Feldspars has a low fusion temperature. They serve as a flux and binder in the body of ceramic articles. They give glossy surface to the ceramic articles.

iii) **SAND :** Sand provides skeletal structure to ceramic articles. Unlike clay it does not undergo shrinkage on heating. Sand is characterised by non-plastic, non-shrinkable and refractory.

iv) **OTHEER INGREDIENTS :** Fluxing agents like Borax, soda ash… , refractory ingredients like alumina, chromite, magnesite, are used for the production of specific type of ceramics. Old bricks in finely divided form known as "GROG" is used to reduce porosity and prevent shrinkage. (1+1+1+1)

b) What is the role of gypsum in the setting of cement?

The addition of 3-5% gypsum during the grinding of clinker cement helps retarding the process of setting of cement. It is found that slower the setting process greater is the strength of hardened cement. Gypsum retards the setting process by removing fast setting tricalcium aluminate content of the cement by forming calcium sulfoaluminate.

20. a) How is calorific value of a fuel is determined by bomb calorimeter?

The calorific value of a solid or liquid fuel is determined using a bomb copper calorimeter. The bomb is made of a strong cylindrical steel container 'A' in which the known amount of Fuel is burnt. It is provided within air tight lid 'B' and an inlet value for passing oxygen. The Bomb is placed inside a copper calorimeter filled with a definite mass of water this provided with a precision thermometer T and a stirrer S.

A known mass of the fuel is taken in a silica crucible F and kept inside the bomb. A thin magnesium wire is projecting from the crucible which is connected to the terminal rods.