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# XII CHEMISTRY QUESTION BANK (2019-2020)

# **UNIT – 1 METALLURGY**

#### 1. What are the various steps involved in extraction of pure metals from their ores?

i) Concentration of the oreii) Extraction of the crude metal.iii) Refining of the crude metal.

#### 2. Which type of ores can be concentrated by froth flotation method? Give two examples for ores.

Sulphide ores can be concentrated by froth flotation method.

(eg) Galena (PbS), Zinc blende (ZnS)

#### 3. What is the role of Limestone in the extraction of Iron from its oxide Fe<sub>2</sub>O<sub>3</sub>?

Lime stone (CaO<sub>3</sub>) is used as a basic flux in the extraction of iron from its oxide Fe<sub>2</sub>O<sub>3</sub>.

Limestone decomposes to form CaO

$$CaCO_3 \longrightarrow CaO + CO_2$$

Impurity silica (SiO2)react with CaO form fusible slag calcium silicate.

$$CaO(s) + SiO_2(s) \longrightarrow CaSiO_3(s)$$
  
Flux Gaugue Slag

#### 4. Out of coke and CO, which is better reducing agent for the reduction of ZnO? Why?

Out of coke and CO, coke is better reducing agent than CO for the reduction of ZnO.

$$ZnO(s)+C \longrightarrow Zn(s)+CO(g)$$

In Ellingham diagram formation ZnO line lies above the formation  $C \longrightarrow CO$  at low temperature  $(T_1)$ , ZnO line also lies above the  $CO \longrightarrow CO_2$  but at high temperature.

Hence carbon can be used as a better reducing agent than CO for the reduction of ZnO. Below the temperature T<sub>1</sub> both Coke and CO cannot reduce ZnO.

#### 5. Describe a method for refining nickel. (OR) Mond's process.

Impure nickel is heated in a stream of carbon monoxide at around 350K. Nickel reacts with CO to form a highly volatile nickel tetracarbonyl. The solid impurities are left behind.

$$Ni(s) + 4CO(g)$$
 350 K  $Ni[CO]$  4(g)

On heating nickel tetra carbonyl around 460K, decomposes to give pure nickel.

$$Ni[CO]_{4(g)} \xrightarrow{460 \text{ K}} Ni_{(s)} + 4CO_{(g)}$$

#### 6. Give the basic requirement for vapour phase refining.

The metal is treated with a suitable reagent to form a volatile compound.

Then the volatile compound is decomposed to give the pure metal at high temperature.

#### 7. Explain the principle of electrolytic refining with an example.

Crude metal is refined by electrolysis carried out in an electrolytic cell.

Cathode : Thin strips of pure metal.
Anode : Impure metal to be refined.

Electrolyte: Aqueous solution of the salt of the metal with dilute acid.

As current is passed, metal ions from the electrolytic solution will be deposited at the cathode. Less electro positive impurities in the anode settle down as anode mud.

#### **Example: Electro refining of silver**

Cathode : Pure silver

Anode : Impure silver rods.

Electrolyte: Acidified aqueous solution of silver nitrate.

#### 8. Give the limitations of Ellingham diagram.

- 1. It gives information about the thermodynamic feasibility of a reaction.
- 2. It does not tell anything about the rate of the reaction.
- 3. More over it does not give any idea about the possibility of other reactions that might be taking place.
- 4. The interpretation of  $\Delta G$  is based on the assumption that the reactants are in equilibrium with the product which is not always true.

#### 9. What is leaching?

In this method crushed ore is allowed to dissolve in a suitable solvent to form a soluble metal salt or complex leaving the gangue undissolved is called leaching.

#### 10. What is auto reduction of metallic ores?

Simple roasting of some of the metallic ores give the crude metal.

Use of reducing agent is not necessary because of low thermal stability

(eg) Cinnabar is roasted to give mercury.

$$HgS(s) + O_2(g) \longrightarrow Hg(l) + SO_2(g) \uparrow$$

#### 11. Write about calcination.

Calcination is the process in which the concentrated ore is strongly heated in the absence of air.

During this process water of crystallisation present in the hydrated oxide escapes as moisture. This method can also be carried out with a limited supply of air.

$$\begin{array}{ccc} PbCO_3 & \longrightarrow & PbO + CO_2 \uparrow \\ CaCO_3 & \longrightarrow & CaO + CO_2 \uparrow \end{array}$$

#### 12. What is cementation?

Gold can be recovered by reacting the deoxygenated leached solution with Zinc. In this process Gold is reduced to its elemental state (zero oxidation state) and the process is called cementation.

$$Zn (s) + 2[Au (CN)_2]^-(aq) \rightarrow [Zn(CN)_4]^2(aq) + 2Au (s)$$

# 13. Explain the following terms with suitable examples. i) Gangue ii) Slag

#### i) Gangue:

The non metallic impurities, rocky materials and siliceous matter present in the ores are called gangue. (eg): SiO2 is the gangue present in the iron ore Fe2O3.

#### ii) Slag:

Slag is a fusible chemical substance formed by the reaction of gangue with a flux.

$$CaO(s) + SiO_2(s) \longrightarrow CaSiO_3(s)$$
  
Flux gangue slag

#### 14. What are the steps involved in the extraction of crude metal?

- 1. Conversion of the ore into metal oxide either by roasting or calcination.
- 2. Reduction of the metal oxide into metal.

#### 15. Write about distillation process of refining a metal?

This method is used for low boiling volatile metals like zinc and mercury. In this method impure metal is heated to evaporate and the vapours are condensed to get pure metal.

# <u>UNIT 2 p – Block element I</u>

# 1. Write a short note on anamolous properties of the first element of p-block.

- (i) Small size of the first member.
- (ii) High ionization enthalpy and high electronegativity.
- (iii) Absences of d-orbital in their valence shell.

### 2. Boron does not react directly with hydrogen. Suggest one method to prepare diborane from BF3.

#### 3. Give the uses of borax.

- (i) Borax is used for the identification of coloured metal ions.
- (ii) It is used as a flux in metallurgy.
- (iii) It act as a preservative.

#### 4. Write a note on Fisher tropsch synthesis.

The reaction of carbon monoxide with hydrogen at pressure of less than 50 atm using metal catalysts at 500 - 700K yields saturated and unsaturated hydrocarbons

$$\begin{array}{ll} nCO + (2n+1)H_2 \longrightarrow & C_nH_{(2n+2)} + nH_2O \\ nCO + 2nH_2 & \rightarrow & C_nH_{2n} + nH_2O \end{array}$$

Carbon monoxide forms complex compounds with transition metals. **Eg**: Nickel tetracarbonyl.

# 7. Give the structure of CO and CO<sub>2</sub>. Structure of CO

#### • It has a linear structure.

• The C-O bond distance is 1.128A<sub>o</sub>.

$$c \stackrel{+}{\overset{\frown}{\circ}} \stackrel{\frown}{\overset{\frown}{\circ}} \stackrel{\frown}{\longleftrightarrow} c \stackrel{-}{\Longrightarrow} c \stackrel{+}{\overset{\frown}{\Longrightarrow}} c \stackrel{+}{\overset{\frown}{\longleftrightarrow}} c \stackrel{-}{\Longrightarrow} c \stackrel{+}{\overset{\frown}{\longleftrightarrow}} c \stackrel{+}{\Longrightarrow} c \stackrel{-}{\Longrightarrow} c \stackrel{+}{\longleftrightarrow} c \stackrel{-}{\longleftrightarrow} c \stackrel{+}{\longleftrightarrow} c \stackrel{+}{\longleftrightarrow$$

#### Structure of CO<sub>2</sub>

- It has a linear structure.
- It has equal bond distance for both C-O bonds.

$$: \overset{-}{\circ} \overset{-}{\circ} \overset{-}{\circ} \overset{+}{\circ} \overset{+}{\circ} \overset{-}{\circ} \overset{+}{\circ} \overset{$$

#### 8. Give the uses of silicones.

- (i) Silicones are used for low temperature lubrication.
- (ii) Silicones are used for making water proofing clothes.
- (iii)Silicones are used as insulating material in electric motor.

#### 9. AlCl3 behaves like a lewis acid. Substantiate this statement.

AlCl<sub>3</sub> is electron deficient. Al forms three bonds with chloride and hence outer shell has six electron. It needs two more electrons to complete its octet. So readily accept a pair of electrons. Hence AlCl<sub>3</sub> is a Lewis acid and forms addition compounds with ammonia and phosphate.

#### 10. Describe the structure of diborane.

In diborane two BH<sub>2</sub> units are linked by two bridged hydrogens. Therefore, it has eight B-H bonds. However, diborane has only 12 valence electrons and are not sufficient to form normal covalent bonds.

The four terminal B-H bonds (**two centre – two electron bond or 2c-2e bond**) are normal covalent bonds.

The remaining four electrons have to be used for the bridged bonds. i.e. **two** three centred B-H-B bonds utilize two electrons each. **Hence, these bonds are three centre –two electron bonds (3c-2e)** 

The bridging hydrogen atoms are in a plane. In diborane, the boron is **sp**<sub>3</sub> hybridised.

#### 11. Write a short note on hydroboration.

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Diborane adds on alkenes and alkynes in ether solvent at room temperature. This reaction is called hydroboration.

$$B_2H_6 + 6RCH = CHR \rightarrow 2B(RCH - CH_2R)_3$$
  
Diborane trialkyl borane

#### 12. Write a note on zeolites

Zeolites are three dimensional crystalline solids containing aluminium, silicon and oxygen.

The general formula NaO.(Al2O3).x(SiO2).yH2O.

The Si and Al atoms are tetrahedrally coordinated with each other through shared oxygen atoms.

#### 13. CO is a reducing agent. Justify with an example.

Carbon monoxide is a strong reducing agent. It reduce the oxides of the less active metals to their respective metals and itself gets oxidised to carbon dioxide in the process.

Eg: 
$$3CO + Fe_2O_3 \xrightarrow{\text{Heat}} 2Fe + 3CO_2$$

#### 14. What is Inert pair effect?

The outer s-electrons (ns) have a tendency to remain inert and show reluctance to take part in the bonding is known as inert pair effect.

#### 15. How borax is prepared from Colemanite ore?

$$2Ca_2B_6O_{11} + 2Na_2CO_3 + H_2O$$

heat

 $3Na_2B_4O_7 + 3CaCO_3 + Ca(OH)_2$ 

borax

#### 16. Why Borax solution is basic in nature?

Borax solution in hot-water is alkaline as it dissociates into boric acid and sodium hydroxide

$$Na_2B_4O_7 + 7H_2O \rightarrow 4H_3BO_3 + 2NaOH$$

#### 17. Explain McAfee process

Aluminium chloride is obtained by heating a mixture of alumina and coke in a current of chlorine

 $Al_2O_3 + 3C + 3Cl_2 \xrightarrow{heat} 2AlCl_3 + 3CO_2$ 

On industrial scale it is prepared by chlorinating aluminium around 1000K 2Al + 3Cl<sub>2</sub> 2AlCl<sub>3</sub>

#### 18. Explain the types of silicates

(i) Ortho silicates (or) Neso silicates: Discrete [SiO4]4-tetrahedral units. Eg: Phenacite (Be2SiO4)

(ii)Pyro silicate (or) Soro silicates: Silicates which contain [Si2O7]6-ions, Eg: Thortveitite (Sc2Si2O7)

(iii) Cyclic silicate (or) Ring silicates: Silicates which contain (SiO<sub>3</sub>)<sub>n2n</sub>-ions. Eg: Beryl [Be<sub>3</sub>Al<sub>2</sub> (SiO<sub>3</sub>)<sub>6</sub>]

(iv)Inosilicates: Silicates which contain 'n' number of silicate units liked by two or more oxygen atoms.

(v)Chain silicates (or) Pyroxenes: These silicates contain [SiO<sub>3</sub>)]<sub>2n-1</sub> ions Eg: Spodumene - LiAl(SiO<sub>3</sub>)<sub>2</sub>.

(vi) Double chain silicates(or) amphiboles: These silicates contain [Si4O11]6n-ions. Eg: Asbestos.

(vii) Sheet (or) phyllo silicates: Silicates which contain (Si2O5)n2n-ions. Eg: Talc, Mica etc...

(viii) Three dimensional silicates (or) tecto silicates: [SiO4]4- tetrahedral are shared with other tetrahedralto form three-dimensional network are called three dimensional silicate.

They have general formula (SiO<sub>2</sub>) n. **Eg**: Quartz.

# <u>UNIT - 3. p - Block Elements II</u>

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#### 1. Explain why fluorine always exhibit an oxidation state of -1?

- 1. Since fluorine is the most electronegative element, it exhibits only a negative oxidation state of -1.
- 2. Due to the absence of d-orbital, fluorine does not show positive oxidation state.

# 2. Give the oxidation state of halogen in the following

#### a) OF2, b) O2F2, c) Cl2O3, d) I2O4

Fluorine shows only -1 oxidation state. Hence

- a) Oxidation state of F' in OF2 is-1
- b) Oxidation state of 'F' in O<sub>2</sub>F<sub>2</sub> is -1
- c) Cl<sub>2</sub>O<sub>3</sub> Oxidation state of Cl is +3
- d) I<sub>2</sub>O<sub>4</sub> Oxidation state of Iodine is +4

#### 3. What are interhalogen compounds? Give example?

Each halogen combines with other halogen to form a series of compounds called interhalogen compounds. Eg: ClF, BrCl, IF7

#### 4. What is the hybridisation of iodine in IF7? Give its structure?

Hybridisation of IF7 is sp3d3

Structure of IF<sub>7</sub> - Pentagonal Bipyramidal (7 Bond pairs and No lone pair)

#### 5. How will you prepare chlorine in the laboratory?

In the laboratory, chlorine is prepared by the oxidation of hydrochloric acid by KMnO<sub>4</sub>.

$$2KMnO_4$$
 + 16HCl→ 2 KCl + 2 MnCl<sub>2</sub> +8H<sub>2</sub>O + 5Cl<sub>2</sub>↑

### 6. Write the reason for the anamolous behaviour of nitrogen?

- 1. Small size
- 2. High ionisation enthalpy and high electronegativity.
- 3. Absence of d-orbitals in their valence shell.
- 4. Nitrogen is a diatomic gas unlike the other members of the group.

#### 7. How is ammonia prepared in the laboratory?

Ammonia is prepared in the laboratory by heating ammonium salts with a base.

$$2NH_{4+} + OH^{-} \rightarrow 2NH_3 + H_2O$$
  
 $2NH_4Cl + CaO \rightarrow CaCl_2 + 2NH_3 + H_2O$ 

#### 8. Illustrate the reducing property of ammonia with an example

When Ammonia is passed over heated lead oxide, it is reduced into lead  $3PbO + 2NH_3 \rightarrow 3Pb + N_2 + 3H_2O$ 

#### 9. Why H<sub>2</sub>SO<sub>4</sub> is used as a dehydrating agent?

It is highly soluble in water and has strong affinity towards water and hence it can be used as a dehydrating agent.

#### 10. Illustrate the reducing property of phosphine.

Phosphine precipitates some metal from their salt solutions. It illustrates the reducing property of phosphine.  $3AgNO_3 + PH_3 \rightarrow Ag_3P + 3HNO_3$ 

### 11. Give an account on bleaching action of SO<sub>2</sub>.

In the presence of water, SO<sub>2</sub> bleaches coloured wool, silk, sponges & straw into colourless product due to its reducing property.

$$SO_2 + 2H_2O \rightarrow H_2SO_4 + 2[H]$$

#### **UNIT – 4.TRANSITION AND INNER TRANSITION ELEMENTS**

#### 1. What are transition metals? Give four examples

Transition metal as an element whose atom has an incomplete d sub shell or which can give rise to cations with an incomplete d sub shell. Example: Iron, Cobalt, Nickel, Copper.

#### 2. What are inner transition elements?

The elements in which the extra electron enters (n-2)f orbitals are called f-block elements.

These elements are also called as inner transition elements because they form a transition series within the transition elements.

In the inner transition elements there are two series of elements.

1) Lanthanoids (Previously called lanthanides) 2) Actinoids (Previously called actinides)

### 3. Why Gd<sup>3+</sup> is colourless?

Electronic configuration of Gd is [Xe]4f<sup>7</sup>5d<sup>1</sup>6s<sup>2</sup>

Electronic configuration of Gd<sup>3+</sup> is [Xe] 4f<sup>7</sup>5d<sup>0</sup>6s<sup>0</sup>

In Gd<sup>3+</sup>, no electrons are there in outer 5d orbitals.d-d transition is not possible. So Gd<sup>3+</sup> is colourless.

# 4. Explain why compounds of Cu<sup>2+</sup> are coloured but those of Zn<sup>2+</sup> are colourless.

 $Cu^{2+}$ : 3d  $^4$ : 4 unpaired electrons, so coloured.

 $\mathbf{Zn}^{2+}$ : 3d <sup>10</sup>: No unpaired electrons, so colourless.

#### 5. What is lanthanoid contraction and what are the effects of lanthanoid contraction?

As we move across 4f series, the atomic and ionic radii of lanthanoids show gradual decrease with increase in atomic number. This decrease in ionic size is called lanthanoid contraction.

#### **Consequences of lanthanoid contraction:**

- 1) As we move from Ce3+ to Lu3+, the basic character of Ln3+ ions decreases. Due to the decrease in the size of Ln3+ ions, the ionic character of Ln-OH bond decreases (covalent character increases) which results in the decrease in the basicity.
- 2) Because of this very small change in radii of lanthanoids, their chemical properties are quite similar.
- 3) The elements of the second and third transition series resemble each other more closely than the elements of the first and second transition series.

#### 6. What are interstitial compounds?

An interstitial compound or alloy is a compound that is formed when small atoms like hydrogen, boron, carbon or nitrogen are trapped in the interstitial holes in a metal lattice. Example: TiC, ZrH<sub>1.92</sub>,Mn<sub>4</sub>N.

# 7. Which is stronger reducing agent $Cr^{2+}$ or $Fe^{2+}$ ?

If the standard electrode potential (Eo) of a metal is large and negative, the metal is a powerful reducing agent, because it loses electrons easily.

$$Cr^{2+} + 2e^{-}Cr E_{0} = -0.91V$$
  
 $Fe^{2+} + 2e^{-}Fe E_{0} = -0.44V$ 

Since Cr<sup>2+</sup> has larger negative value of E<sub>0</sub>, Cr<sup>2+</sup> is a stronger reducing agent than Fe<sup>2+</sup>.

# 8. Why iron is more stable in +3 oxidation state than in +2 and the reverse is true for manganese? Electronic Configuration.

 $Fe^{3+}$ : [Ar]  $3d^5 Fe^{2+}$ : [Ar]  $3d^6$ 

 $Mn^{2+}$ :[Ar]  $3d^5Mn^{3+}$ : [Ar]  $3d^4$ 

Fe<sup>3+</sup> ion has half filled d orbital which is more sable than partially filled d orbital of Fe<sup>2+</sup>. Mn<sup>2+</sup> ion has half filled d orbital which is more stable than partially filled d orbital of Mn<sup>3+</sup>.

### 9. Why transition metals form number of alloys?

Atomic sizes of transition metals are similar and one metal atom can be easily replaced by another metal atom from its crystal lattice to form an alloy.

#### 10. Why transition metal and its compound act as good catalyst?

Transition metal has energetically available d orbitals.

d-orbitals can accept electrons from reactant molecule and form bond with reactant molecule using its d electron.

#### 11. Why transition elements form complexes?

- i. Transition metal ions are small and highly charged
- ii. They have vacant low energy orbitals to accept an electron pair donated by other group.

#### 12. Under what oxidation state do transition metals form ionic oxide and covalent oxides?

Metals in lower oxidation state form ionic oxides.

Metals in higher oxidation state form covalent oxides

Example Mn<sub>2</sub>O<sub>7</sub> is covalent. Oxidation state is +7.

# 13. Zn, Cd and Hg do not have partially filled d-orbitals why they are treated as transition elements?

They are treated as transition elements because their properties are an extension of the properties of the respective transition elements.

#### 14. What are the properties of Interstitial compound?

- i. They are hard and show electrical and thermal conductivity
- ii. They have high melting points higher than those of pure metals
- iii. Transition metal hydrides are used as powerful reducing agents
- iv. Metallic carbides are chemically inert.

#### 15. What is Hume- Rothery rule to form a substitute alloy?

- i. The difference between the atomic radius of solvent and solute is less than 15%
- ii. Both the solvent and solute must have the same crystal structure and valence.
- iii. The eletronegativity difference between solvent and solute must be close to zero.

#### **UNIT-5 COORDINATION CHEMISTRY**

#### 1. Write the IUPAC names for the following complexes.

- Sodium 2,2',2'',2'''-(ethane-1,2-diyldinitrilo)tetraacetatoNickelate(II) i) Na<sub>2</sub>[Ni (EDTA )]
- ii) [Ag (CN) 2] - dicyanidoargentate(I) ion
- iii) [Co (en)3]2(SO4)3 tris(ethane1,2-diamine)cobalt(III)sulphate
- iv) [Co (ONO) (NH<sub>3</sub>)<sub>5</sub>]<sup>2+</sup> pentaamminenitrito-K-O-cobalt(III)ion
- v) Pt (NH<sub>3</sub>)<sub>2</sub>Cl(NO<sub>2</sub>)] - diamminechloridonitrito- K-N-platinum(II)

#### 2. Write the formula for the following coordination compounds.

- a) potassiumhexacyanidoferrate(II) - K4[Fe(CN)6] b) pentacarbonyliron(0) - [Fe(CO)5]
- c) pentaamminenitrito- K -N-cobalt(III)ion  $- [Co(NH_3)_5(NO_2)]^{2+}$ d) hexaamminecobalt(III)sulphate - [Co(NH3)6]2(SO4)3
- e) sodiumtetrafluoridodihydroxidochromate(III) - Na<sub>3</sub>[CrF<sub>4</sub>(OH)<sub>2</sub>]

#### 3. Arrange the following in order of increasing molar conductivity

i) Mg [Cr(NH<sub>3</sub>)(Cl)<sub>5</sub>] ii) [Cr(NH<sub>3</sub>)<sub>5</sub>Cl]<sub>3</sub>[CoF<sub>6</sub>]<sub>2</sub> iii) [Cr(NH<sub>3</sub>)<sub>3</sub>Cl<sub>3</sub>]

On ionisation,

- i) Mg [Cr(NH<sub>3</sub>)(Cl)<sub>5</sub>]  $\longrightarrow$  Mg<sup>2+</sup> + [Cr(NH<sub>3</sub>)(Cl)<sub>5</sub>]<sup>2-</sup>
- ii)  $[Cr(NH_3)sCl]_3[CoF_6]_2 \longrightarrow 3[Cr(NH_3)sCl]^{2+} + 2[CoF_6]^{3-}$ iii)  $[Cr(NH_3)sCl_3] \longrightarrow$  does not ionize

As the number of ions in solution increases, their molar conductivity also increases.

Therefore [Cr(NH<sub>3</sub>)<sub>3</sub>Cl<sub>3</sub>]<Mg [Cr(NH<sub>3</sub>)(Cl)<sub>5</sub>]<[Cr(NH<sub>3</sub>)<sub>5</sub>Cl]<sub>3</sub>[CoF<sub>6</sub>]<sub>2</sub>

# 4. [CuCl4]<sup>2</sup>-exists while [CuI4]<sup>2</sup>-does not exist why?

Both the species contains Cu<sup>2+</sup>ions

In [CuCl4]<sup>2</sup>- the chloride ion does not reduce Cu<sup>2+</sup> to Cu<sup>+</sup>

In [CuI4]<sup>2</sup> complex iodide ion reduces Cu<sup>2+</sup> to Cu<sup>+</sup> therefore the complex is unstable.

# 5. Give an example of coordination compound used in medicine and two examples of biologically important coordination compounds.

Coordination compound used in medicine:

Ca- EDTA chelate radioactive poisoning removing lead and radioactive metal ions from body.

Cis- Platin antitumour drug cancer treatment

Biologically important coordination compounds:

<b>Coordination Complex</b>	Centralmetalion	Uses
RBC Composed Of Heme Group	$\mathrm{Fe}^{2+}$	Carrying oxygen from lungs to tissue,
		CO <sub>2</sub> from tissue to lungs

Chlorophyll Photosynthesis

# 6. Based on VB theory explain why $[Cr(NH_3)_6]^{3+}$ is paramagnetic, while $[Ni(CN)_4]^{2-}$ is diamagnetic. **Complex**

 $[Cr(NH_3)_6]^{3+}$ Central metal ion Cr(III): 3d<sup>3</sup>4s<sup>0</sup>

Outer orbitals of metal atom/ion: 3d<sup>3</sup>4s<sup>1</sup>4p

Nature of ligand: NH3 is a weak ligand

Magnetic property

The number of unpaired electron n=3

Therefore the magnetic moment is

$$\mu s = \sqrt{n(n+2)}$$
 $\mu s = \sqrt{3(3+2)}$ 
=3.87 BM

 $[Ni(CN)_4]^2$ 

CN-is a strongfield ligand causes the pairing of 3d electrons in the metal

The number of unpaired electron n=0 Therefore the magnetic moment is

$$\mu s = 0 BM$$

#### 7. Draw all possible geometrical isomers of the complex [Co(en)2Cl2]+and identify the optically active isomer.

Trans isomer [Co(en)2Cl2] does not show optical isomerism because of plane of symmetry Cis isomer shows optical isomerism because it lacks symmetry

# 8. $[Ti(H_2O)_6]^{3+}$ is coloured, while $[Sc(H_2O)_6]^{3+}$ is colourless- explain.

$[\mathrm{Ti}(\mathrm{H}_2\mathrm{O})_6]^{3+}$		[Sc(H2O)6]3
Central metal ion	: Ti <sup>3+</sup>	$\mathrm{Sc}^{3+}$
Electronic Configuration	: 3 d <sup>1</sup>	$3d^0$
Number of unpaired electron	:1	0

Ti<sub>3+</sub> has one unpaired electron for d-d transition, No unpaired electron, so d-d transition is not possible hence it is not coloured

hence it is coloured

#### 9. What is linkage isomerism? Explain with an example.

This type of isomers arises when an ambidentate ligand is bonded to the central metal atom/ion through either of its two different donor atoms.(-NO2/-ONO-) Example:

 $[Co(NH_3)5(NO_2)]^{2+}$  &  $[Co(NH_3)5(ONO)]^{2+}$ 

#### 10. Classify the following ligand based on the number of donor atoms.

a) NH3	b) en c) ox <sup>2</sup> d) triaminotrie	thylamine e) pyridine
Ligand	Number of donoratom	Type of ligand
NH <sub>3</sub>	1 ( N-donor)	Monodentate
en	2 (2N-donor)	Bidentate
ox <sup>2</sup> - (oxalato)	2 (2 –O- d <mark>on</mark> or)	Bidentate
Triam <mark>ino</mark> trieth <mark>yla</mark>	mine 3 (3N-don <mark>or</mark> )	Tridentate
	Central nitrogen atom cannot be coor	ridnated
Pyridine	1 (N-donor)	Monodentate

#### 11. What is crystal field splitting energy?

The splitting of five d-orbitals of the metal ion in the presence of ligand field into two sets having different energies is called crystal field splitting or energy level splitting. The difference in the energy of the two sets is called crystal field splitting energy.

#### 12. What is crystal field stabilization energy (CFSE)?

The crystal field stabilization energy is defined as the energy difference of electronic configurations in the ligand filed (ELF) and the isotropic field/barycentre (Eiso).

```
CFSE (\DeltaEo) = {ELF} - {Eiso}
               = {[nt_{2g}(-0.4) + n_{eg}(0.6)] \Delta o + n_{p}P} - {n'_{p}P}
nt_{2g} = the number of electrons in t_{2g} orbitals
neg = number of electrons in eg orbitals
np = number of electron pairs in the ligand field
n'p = number of electron pairs in the isotropic field (barycentre).
```

### 13. On the basis of VB theory explain the nature of bonding in $[C_0(C_2O_4)_3]^{3-}$ $[Co(C_2O_4)_3]^{3}$

Central metal /atom : Co(III) Electronic configuration : Co:  $3d^7 4s^2 4p$ Geometry : Octahedral  $: d^2sp^3$ Hybridization

: n = 0; Diamagnetic Number of unpaired electron

C<sub>2</sub>O<sub>4</sub><sup>2</sup>- is a strong field ligand.

 $3d^{6}4s^{0}4p$ Inner orbital (low spin) complex.

#### 14. What are the limitations of VB theory?

- 1. It does not explain the colour of the complex
- 2. It considers only the spin only magnetic moments and does not consider the other components of magnetic moments.
- 3. It does not provide a quantitative explanation as to why certain complexes are inner orbital complexes and the others are outer orbital complexes for the same metal.

#### 15. Explain optical isomerism in coordination compounds with an example.

Co-ordination compound solutions rotate the plane of the plane polarised light either clockwise or anticlockwise and the corresponding isomers are called 'd' (dextro rotatory) and 'l' (levo rotatory) forms respectively.

The octahedral complexes of type  $[M(xx)_3]_{n\pm}$ ,  $[M(xx)_2AB]_{n\pm}$  and  $[M(xx)_2B_2]_{n\pm}$  exhibit optical isomerism.

#### 16. What is linkage isomerism? Explain with an example.

Isomers arises when an ambidentate ligand is bonded to the central metal atom/ion through either of its two different donor atoms.(-NO2/-ONO-)

Example:

 $[Co(NH_3)5(NO_2)]^{2+}$  &  $[Co(NH_3)5(ONO)]^{2+}$ 

#### 17. What are hydrate isomers? Explain with an example.

The exchange water molecules in the crystal lattice with a ligand in the coordination entity will give different isomers. These type of isomers are called hydrate isomers.

#### Example:

CrCl<sub>3.6</sub>H<sub>2</sub>O has three hydrate isomers as shown below.

[Cr(H<sub>2</sub>O)<sub>6</sub>]Cl<sub>3</sub> *violet colour*, gives three chloride ions in solution [Cr(H<sub>2</sub>O)<sub>5</sub>Cl]Cl<sub>2</sub>H<sub>2</sub>O *pale green colour*, two chloride ions in solution [Cr(H<sub>2</sub>O)<sub>5</sub>Cl<sub>2</sub>]Cl<sub>2</sub>H<sub>2</sub>O *dark green colour*, one chloride ion in solution.

#### **UNIT 6 SOLID STATE**

#### 1. Define unit cell.

A basic repeating structural unit of a crystalline solid is called a unit cell.

#### 2. Give any three characteristics of ionic crystals.

Ionic solids have high melting points.

They do not conduct electricity in solid state.

They conduct electricity in molten state (or) when dissolved in water.

They are hard and brittle.

#### 3. Explain briefly seven types of unit cell.

S.NO	NAME OF THE UNIT CELL	EDGE LENGTH	<b>ANGLES</b>
1	Cubic	a=b=c	$\alpha = \beta = \gamma = 90^{\circ}$
2	Rhombohedral	a=b=c	$\alpha = \beta = \gamma \neq 90^{\circ}$
3	Hexagonal	a=b≠c	$\alpha = \beta = 90^{\circ}, \gamma = 120^{\circ}$
4	Tetragonal	a=b≠c	$\alpha = \beta = \gamma = 90^{\circ}$
5	Orthorhombic	a≠b≠c	$\alpha = \beta = \gamma = 90^{\circ}$
6	Monoclinic	a≠b≠c	$\alpha = \gamma = 90^{\circ}, \beta \neq 90^{\circ}$
7	Triclinic	a≠b≠c	$\alpha \neq \beta \neq \gamma \neq 90^{o}$

#### 4. Calculate the number of atoms in an fcc unit cell.

Number of atoms in fcc unit cell = Nc/8 + Nf/2 = 8/8+6/2 = 1+3=4

#### 5. Why ionic crystals are hard and brittle?

Ionic crystal are hard due to strong electrostatic force of attraction between cations and anions. They are brittle because ionic bonds are non directional.

# 6. Atoms X and Y form bcc crystalline structure. Atom X is present at the corners of the cube and Y is at the centre of the cube. What is the formula of the compound?

Number of corner atoms (X) =  $N_c / 8 = 8 / 8 = 1$ Number of body centre atoms(Y) =  $N_b / 1 = 1 / 1 = 1$ 

Formula of the compound = X Y.

#### 7. What are point defects?

Point defects are the deviations from ideal arrangement that occurs at some points or atoms in a crystalline substance.

#### 8. Explain Schottky defect.

Schottky defect arises due to the missing of equal number of cations and anions from the crystal lattice .Hence stoichiometry of the crystal is not changed.

Ionic solids in which the cation and anion are of almost of similar size show schottky defect. Example: **NaCl**. Presence of large number of schottky defects in a crystal lowers its density.

#### 9. Explain Frenkel defect

Frenkel defect arises due to the dislocation of ions from its crystal lattice.

The ion which is missing from the lattice point occupies an interstitial position.

This defect occurs when cation and anion differ in size.

Unlike Schottky defect, this defect does not affect the density of the crystal.

Ex: AgBr

#### 10. What are primitive and non-primitive unit cell?

A unit cell that contains only one lattice point is called a primitive unit cell,

A unit cell that contains additional lattice points, either on a face or within the unit cellis called a non-primitive unit cells.

#### 11. What are isotropy and anisotropy?

Isotropy means having identical values of physical properties (refractive index, electrical conductance) in all directions. Ex-amorphous solids.

Anisotropy means having different values of physical properties when measured along different directions. Ex- crystalline solids

#### 12. Give a note on covalent solids?

The constituents (atoms) are bound together in a three dimensional network entirely by covalent bonds.

Such covalent network crystals are very hard, and have high melting point.

They are usually poor thermal and electrical conductors

**Examples:** Diamond, silicon carbide etc.

#### .13. What are molecular crystals?

In molecular solids, the constituents are neutral molecules.

They are held together by weak Vanderwaals forces.

Generally, molecular solids are soft and they do not conduct electricity.

Example: Ice

### 14. Explain metallic solids.

The lattice points are occupied by positive metal ions and a cloud of electrons pervades the space.

They are hard, and have high melting point.

Metallic solids possess excellent electrical and thermal conductivity. They possess bright lustre.

**Examples:** Metals and metal alloys belong to this type of solids, for example Cu,Fe,Zn,Ag, Au, Cu- Zn etc.

#### 15. State Bragg's Equation

 $n \lambda = 2 d \sin \theta$ 

where,

- $\lambda$  wavelength of X-ray
- $\theta$  angle of diffraction
- n order of refraction
- d Inter planar distance

#### 16. How electrical neutrality is maintained in stoichiometric ionic crystals?

In stoichiometric ionic crystals, a vacancy of one ion must always be associated with either by the absence of another oppositely charged ion (or) the presence of same charged ion in the interstitial position so as to maintain the electrical neutrality.

#### 17. What is meant by the term "coordination number"?

The neighbouring atoms surrounded by each atom is called coordination number.

In BCC is 8.

#### 18. Barium has a body centered cubic unit cell with a length of 508pm along an edge. What is the density of barium in g cm-3?

Given: M=137.3 gmol<sup>-1</sup>, a= 508pm = 5.08x 10<sup>-8</sup>cm, Z=2  $\rho = n \text{ M} / \text{ a}^3 \text{ N}_{\text{A}} = 2 \text{ x } 137.3 / (5.08 \text{ x } 10^{-8})^3 \text{ x } 6.023 \text{ x } 10^{23} = 3.478 \text{ g cm}^{-3} = 3.5 \text{ g cm}^{-3}$ 

# **UNIT-7 CHEMICAL KINETICS**

#### 1. Define rate law

$$aA + bB \longrightarrow products$$
  
 $rate \ \alpha \ [A]^x [B]^y$   
 $rate = k [A]^x [B]^y$ 

Rate is given in terms of molar concentration of reactants raised to the power which may or may not equal to stoichiometric coefficient.

#### 2. Define Rate constant

Rate constant is same as rate of reaction when concentration of all the reactants is unity.

#### 3. What are Zero order reactions?

Rate is independent of the concentration of reactant is called zero order reaction.

$$A \longrightarrow Product$$
  
rate =  $k[A]^0$ , rate =  $k$ 

#### 4. What is pseudo first order reaction?

A second order reaction can be altered to a first order reaction by taking one of the reactants in large excess, such reaction is called pseudo first order reaction.

Example : Acid hydrolysis of ester 
$$CH_3COOCH_3 + H_2O \xrightarrow{H_+} CH_3COOH + CH_3OH$$

#### 5. Explain the effect of catalyst on reaction rate with an example.

- 1. A catalyst is a substance which alters the rate of a reaction without itself undergoing any chemical change.
- 2. It may participate in a reaction but regenerated at the end of reaction.
- 3. A catalyst increases rate of reaction by lowering the activation energy.

Example: 
$$2KClO_3$$
  $MnO_2$   $2KCl + 3O_2$   $MnO_2$  acts as catalyst.

#### 6. Define molecularity.

It is the total number of reactant speciesthat are involved in an elementary step.

#### 7. Define order of a reaction.

$$aA + bB \longrightarrow products$$
  
 $rate = k [A]^x [B]^y$   
overall order = x + y

It is the sum of the powers of concentration terms involved in the experimentally determined rate law.

#### 8. Give examples of first order reaction.

(iv) All radioactive decay

(v) Isomerisation of cyclopropane to propene

#### 9. Give two examples of zero order reaction.

(i) 
$$H2(g) Cl2(g) \longrightarrow 2HCl(g)$$

(ii) Decomposition of N2O on hot platinum surface

$$N_2 \ O_{(g)} \ \underline{\hspace{1cm} Pt \hspace{1cm}} \ N_{2 \ (g)} \ + \ {}^{1}\!\!/_{2} \ O_{2 \ (g)}$$

(iii) Iodination of acetone in acid medium is zero order with respect to iodine.

#### 10. What is collision frequency?

Number of collisions per second per unit volume is called collision frequency.

#### 10. Give units of rate constant of (a) first order reaction (b) zero order reaction

(a) First order reaction : sec<sup>-1</sup>

(b) **Zero order reaction** :  $mol L^{-1}s^{-1}$ 

#### 11. Define activation energy?

In order to react, the colliding molecules must possess a minimum energy called activation energy.

#### 12. Write Arrhenius equation.

$$K = A. e^{-Ea/RT}$$

K = Rate constant

A = Frequency Factor

Ea= Activation energy

R = Gas constant

T = Temperature

#### 13. Define Half life period of a reaction:

The half life of a reaction is defined as the time required for the reactant concentration to reach one half its initial value.

$$t_{1/2} = 0.693 / k$$

#### 14. What are the factors that affects rate of reaction?

- 1. Nature and state of the reactant
- 2. Concentration of the reactant
- 3. Surface area of the reactant
- 4. Temperature of the reaction
- 5. Presence of a catalyst

#### 15. State collision theory

Chemical reactions occur as a result of collisions between the reacting molecules.

#### 16. What is Rate and Instantaneous rate of reaction?

#### Rate:

The change in the concentration of the species involved in a chemical reaction per unit time gives the rate of a reaction.

#### **Instantaneous rate:**

The rate of the reaction, at a particular instant during the reaction is called the instantaneous rate.

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