p-Block Elements (N, O, Hologen and Inert Gases)
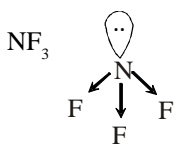
<div align="center">EXERCISES</div>

ELEMENTARY

Q.1 (4)

In N_2 N≡N there are one sigma & two π bonds so N exists in diatomic form which has high bond enthalpy making it inert.

Q.2 (4)

$$\underbrace{N \qquad P}_{\text{Non-metals}} \quad \underbrace{As \qquad Sb}_{\text{Metalloids}} \quad \underbrace{Bi}_{\text{Metal}}$$

Q.3 (1)

Phosphorus is kept in water due to it burt at $30°C$.

Q.4 (1)

Atmospheric nitrogen is inert and unreactive because of very high bond energy .

Q.5 (1)

Nitrogen does not form complexes because of the absence of d-orbitals.

Q.6 (4)

Q.7 (2)

$$Ba(N_3)_2 \rightarrow Ba + 3N_2$$

Q.8 (2)

$$FeSO_4 + NO \rightarrow \underset{\text{(Brown)}}{FeSO_4.NO}$$

Q.9 (1)

$P_4 + 5O_2 \rightarrow P_4O_{10}$; white phosphorus gets easily oxidized because it is highly reactive.

Q.10 (4)

N_2O is itself non-combustible but supports combustion.
$$S + 2N_2O \rightarrow SO_2 + 2N_2$$

Q.11 (2)

P_2O_3, B_2O_3 are acedic
As_2O_3 is amphoteric
Bi_2O_3 is Alkaline

Q.12 (4)

NO_2 brown coloured gas.

Q.13 (2)

$$\overset{*}{P}_4O_8$$
$$4x + (-2 \times 8) = 0$$
$$4x - 16 = 0$$
$$x = \frac{16}{4} = +4$$

Q.14 (3)

Q.15 (4)

In upper atmosphere NO is formed by lightning flash.
$$N_2 + O_2 \rightleftharpoons 2NO$$

Q.16 (3)

$$2NO + O_2 \rightarrow 2NO_2$$

Q.17 (2)

$$NH_3 + Cl_2 \longrightarrow NCl_3 + HCl$$

Q.18 (1)

Q.19 (1)

NCl_5 is not known because of absence of d-orbitals in nitrogen.

Q.20 (4)

NH_3 when dissolved in water forms
$$NH_3 + H_2O \rightarrow NH_3^+ + OH^- \rightleftharpoons NH_4OH$$

Q.21 (1)

NF_3

It is least basic because of the high electronegativity of 3F atoms. The lone pair present on nitrogen atom is not easily available for donation.

Q.22 (1)

$PH_3 > AsH_3 > SbH_3 > BiH_3$ order of bond energy
On moving down the group bond energy decreases. Hence, stability decreases.

Q.23 (4)

Due to absence of d-orbitals in N atom, it cannot accept electrons from H_2O for hydrolysis of NF_3.

Q.24 (1)
NH$_3$ is a strongest base because Lone pair is easily available for donation.

Q.25 (1)
NCl$_3$ is highly reactive and unstable. Hence it is explosive.

Q.26 (2)

Q.27 (1)
Paramagnetism because of two unpaired electrons in the antibonding molecular orbitals.

Q.28 (4)

Q.29 (4)

Q.30 (3)
$$2H_2O + 2F_2 \rightarrow 4HF + O_2$$
2 unpaired electrons

Q.31 (3)
SO$_2$ is soluble in water
$$H_2O + SO_2 \rightarrow \underset{\text{Sulpurus acid}}{H_2SO_3}$$

Q.32 (4)
Ozone O$_3$ is an allotropic form of oxygen.

Q.33 (3)
$$S + O_2 \rightarrow SO_2$$

Q.34 (1)
The minimum and maximum oxidation number of S are -2 and $+6$ respectively. Since the oxidation number of S in SO$_2$ is $+4$, therefore it can be either increased or decreased. Therefore SO$_2$ behaves both as an oxidising as well as reducing agent.
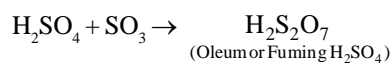
Q.35 (4)
$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \rightarrow K_2SO_4 + \underset{\text{Green}}{Cr_2(SO_4)_3} + 3H_2O$$

Q.36 (1)
$$2H_2O + SO_2 \rightarrow H_2SO_4 + 2[H] \text{ (Nascent hydrogen)}$$
Coloured flower $+ 2[H] \rightarrow$ Colourless flower

Q.37 (1)
$$H_2O + SO_3 \rightarrow H_2SO_4$$

Q.38 (2)

Q.39 (4)

$$H_2SO_4 + SO_3 \rightarrow \underset{\text{(Oleum or Fuming H}_2\text{SO}_4)}{H_2S_2O_7}$$

Q.40 (1)

Q.41 (1)
$$2H_2S + O_2 \rightarrow 2H_2O + 2S$$

Q.42 (3)
The bond between (H$_2$Te) is weakest hence it gives H$^+$ ion easily.

Q.43 (3)
V$_2$O$_5$ catalyst are used for the manufacture of H$_2$SO$_4$ by Contact process.

Q.44 (2)
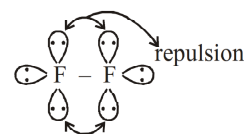O$_2$F$_2$ is similar to that of H$_2$O$_2$
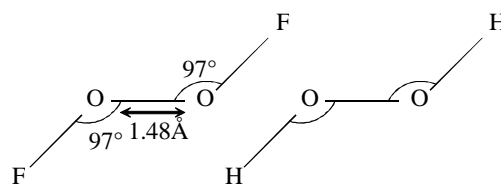
Q.45 (2)
Lose of electron.

Q.46 (4)

Q.47 (1)

Q.48 (1)

Q.49 (4)

Q.50 (4)

Q.51 (1)

Q.52 (1)

Q.53 (4)

Q.54 (4)
Reactivity order
$$I^- > Br^{3-} > Cl^- > BF^-$$

Q.55 (4)
Iodine has the least affinity for water and is only slightly soluble in it. However, it dissolves in 10% aq. solution of KI due to the formation of a complex ion i.e. I_3^-
$I_2 + KI \rightleftharpoons KI_3$ or $I_2 + I^- \rightleftharpoons I_3^-$ (complex ion)

Q.56 (1)
HI is the strongest reducing agent among halogen acids because of lowest bond dissociation energy.

Q.57 (1)
HF is liquid because of intermolecular H-Bonding.

Q.58 (1)

$$\underset{\text{Weak acid}}{HClO} \rightleftharpoons H^+ + \underset{\substack{\text{Strong conjugate} \\ \text{base}}}{ClO^-}$$

Q.59 (1)

Q.60 (4)
In HF the molecules aggregate because of intermolecular hydrogen bonding. Hence, it has highest boiling point and highest heat of vaporisation.

Q.61 (4)
HI is strongest acid because H – I bond is weakest among halogen acids.

Q.62 (1)
In HF the molecules aggregate because of intermolecular hydrogen bonding. Hence, it has highest boiling point.

Q.63 (1)

Q.64 (1)
$HClO_4 > HCl > H_2SO_4 > HNO_3$
Decreasing order of acidic character.

Q.65 (1)
$CaOCl_2 \longrightarrow CaCl_2^+ + OCl^-$

Q.66 (1)
Pseudohalide ions and Pseudohalogens
There are certain monovalent negative ions made up of two or more electronegative atoms which exhibit properties similar to these of halide ions. Such ions are known as pseudo halide ions just as halide ions, pseudo halide ions have also corresponding dimoric molecules. These are called pseudo halogens and show properties similar to those of halogens.

Pseudohalide	Pseudohalogens
CN^- cyanide	$(CN)_2$ Cyanogen
SCN^- Thiocyanate	$(SCN)_2$ Thiocyanogen

Q.67 (2)

Q.68 (1)
Gas – H_2 O_2 He N_2
Mol. mass – 2 32 4 28

Q.69 (3)

Q.70 (4)
All the noble gases are monoatomic, colourless and odourless gases. Their monoatomic nature is due to the stable outer configuration $ns^2\, np^6$ of their atoms. As a result, they do not enter into chemical combination even amongst themselves.

Q.71 (1)

Q.72 (3)
Neon $\rightarrow$ Ne is monoatomic and others are diatomic N_2, F_2 and O_2.

Q.73 (2)
$Ne_{10} \rightarrow 1s^2\, 2s^2\, 2p^6$

Q.74 (2)

Q.75 (2)
Zero group element are show less chemically activity because this group element have 8 electron.

Q.76 (4)

Q.77 (4)
He, Ne, and Kr all are found in very little amount in atmosphere, so all are called rare gas.

Q.78 (4)

Q.79 (3)
$XeF_2, XeOF_2, XeF_4, XeOF_4, XeF_6, XeO_3$

Q.80 (4)
XeF_2 has sp^3d -hybridization with linear shape
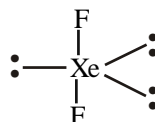
Q.81 (4)

Q.82 (1)

XeO_3 shows sp^3 hybridization.

Q.83 (1)

Zero group element are attached with weak intermolecular force.

Q.84 (2)

XeF_2, XeF_4 and XeF_6 are formd.

Q.85 (4)

In the formation of XeF_4, sp^3d^2 hybridisation occurs which gives the molecule an octahedral structure. The xenon and four fluorine atoms are coplanar while the two equatorial positions are occupied by the two lone pairs of electrons.
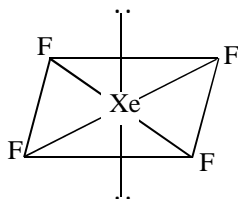
JEE-MAIN
OBJECTIVE QUESTIONS

Q.1 (4)

Black phosphorus is thermodynamically most stable form of phosphorus as it is a highly polymerised form of phosphorus. Hence it is least reactive.

Q.2 (2)

Has one lone pair of electrons on central atom which they can donate to lewis acid.

Q.3 (1)

The basic strength of the hydrides of group 15 elements down the group decreases because down the group as electronegativity decreases p-orbital take part in the bond and lone pair present in s-orbital :
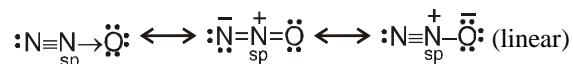s-orbital is larger and non directional hence it has less effective tendency of bond formation.

Q.4 (3)

Q.5 (4)

NH_4Cl gives NH_3, NH_4NO_3 gives N_2O and $AgNO_3$ gives NO_2.

(1) $NH_4Cl \xrightarrow{\Delta} NH_3 + HCl$

(2) $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$

(3) $AgNO_3 \xrightarrow{\Delta} Ag + NO_2 + \frac{1}{2}O_2$

(4) $NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$

Q.6 (1)

Q.7 (3)

$$:N\equiv\underset{sp}{N}\rightarrow\overset{..}{\underset{..}{O}}: \longleftrightarrow :\overset{-}{\underset{..}{N}}=\overset{+}{\underset{sp}{N}}=\overset{..}{\underset{..}{O}} \longleftrightarrow :N\equiv\overset{+}{\underset{sp}{N}}-\overset{..}{\underset{..}{O}}: \text{ (linear)}$$

Q.8 (4)

$4HNO_3 + P_4O_{10} \xrightarrow{250K} 4HPO_3 + N_2O_5$ (anhydride of HNO_3)
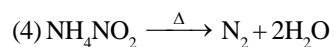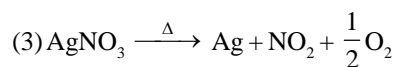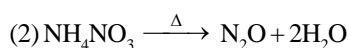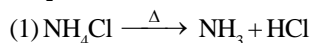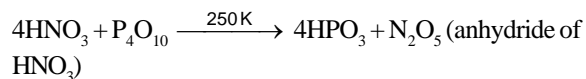
Q.9 (4)

Q.10 (4)

Q.11 (1)

Q.12 (2)

Q.13 (1)
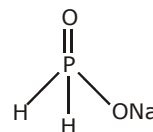
Q.14 (1)

Q.15 (3)
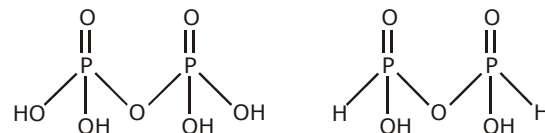
Q.16 (2)

Q.17 (1)

Q.18 (1)
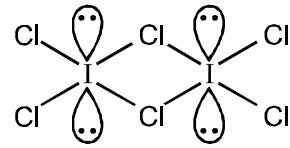
A moelcular weight of molecule increase it convert to gas → liquid → solid

Q.19 (2)

S–S, $:\overset{..}{\underset{..}{O}}=\overset{..}{\underset{..}{O}}:$ — more l.p. repultion in O due to smaller size.

Q.20 (3)

Q.21 (4)

Q.22 (4)

Allotrope of oxygen.

Q.23 (4)

Q.24 (3)

SO_2 & Cl_2

$Cl_2 + H_2O \longrightarrow 2HCl + O$

Cl_2 is a powerful bleaching agent bleaching action is due to oxidation

$Cl_2 + H_2O \longrightarrow 2HCl + [O]$

Q.25 (2)

$$\text{Acidic properties} \propto \frac{\text{Non metallic character}}{\text{metallic character}}$$

Q.26 (1)

$\overset{+4}{S}O_2 \xrightarrow{\text{reduction}} S^o$

oxidising agent.

Q.27 (3)

$3O_2 \xrightarrow{U.V.} 2O_3$

Q.28 (1)

$2O_3 \quad 3O_2$

Q.29 (3)
Q.30 (3)
Q.31 (2)

Q.32 (2)

Ripole moment $\propto \Delta EN$ of atom.

Q.33 (1)

Q.34 (1)

Q.35 (4)

Amongst halogens fluorine is the strongest oxidising agent on account of low bond dissociation energy and high enthalpy of hydration.

Q.36 (2)

Fluorine, being most electronegative element, always show the oxidation state of –1. Other halogens can show higher positive oxidation state in addition to negative oxidation of –1.

Q.37 (2)

$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$

Q.38 (4)

Standard reduction potential (in volts) of the perhalate ions are gives as below –

$ClO_4^- + 2H^+ + 2e^- \longrightarrow ClO_3^- + H_2O;\ E° = 1.19V$

$BrO_4^- + 2H^+ + 2e^- \longrightarrow BrO_2^- + H_2O;\ E° = 1.74V$

$IO_4^- + 2H^+ + 2e^- \longrightarrow IO_3^- + H_2O;\ E° = +1.65V$

more the standard reduction potential, the more is tendency of perhalite ion to undergo reduction and more stronger it will be an oxidizing agent.

Q.39 (3)

It's bleaching action is due to nascent oxygen.

Q.40 (2)

Pseudohalides contain at least one N atom and their properties are similar to halides.

Q.41 (1)

e.g. CN^-

Q.42 (1)

NCCN is pseudohalogen but CN^- and N_3^- are pseudohalide but I_3^- is only polyhalide.

Q.43 (1)

ICl_3, exist as dimer in **solid state**.

Planar molecule

and

$ICl_3 + 2H_2O \longrightarrow HIO_2$ (iodous acid) + 3HCl (Hydrochloric acid)

Q.44 (3)

In March 1962, Neil Bartlett, then at the University of British Columbia, observed the reaction of a noble gas. First , he prepared a red compound which is formulated as $O_2^+ [PtF_6]^-$ and it is already know that the first ionisation enthalpy of molecular oxygen (1175 kJ mol $^{-1}$) is almost similar with that xenon (1170 kJ mol $^{-1}$). Then he made efforts to prepare same type of compound by mixing Pt F_6 and Xenon $Xe^+ [PtF_6]^-$. After this discovery, a number of xenon compounds mainly with most electronegative elements like fluorine and oxygen, have been synthesised.

Q.45 (2)

Noble gases exist as monoatomic molecules.

Q.46 (1)

All the noble gases except radon occur in the atmosphere. Xenon and radon are the rarest elements of the group. Radon is obtained as a decay product of 226Ra.

$$_{88}^{226}Ra \longrightarrow {}_{86}^{222}Rn + {}_{2}^{4}He$$
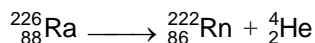
Q.47 (1)

Most abundant element in air is Ar. Order of abundance in the air is $Ar > Ne > Kr > He > Xe$.

Q.48 (2)

XeF_5 does not exist at all.

Q.49 (2)

Xenon form maximum number of compounds like XeF_2, XeF_4, XeF_6, XeO_3, XeO_4 etc.

JEE-ADVANCED
OBJECTIVE QUESTIONS

Q.1 (D)

Q.2 (A)

Q.3 (D)

Allotropes differ in their crystal structures and physical properties but have same chemical properties.

Q.4 (D)

Q.5 (D)

$$P_4 \xrightarrow[\text{low tempt./sunlight}]{250°C \text{ or}} \text{Red phosphorus.}$$

Q.6 (B)

Q.7 (A)

White phosphorus is obtained by heating a mixture of phosphorite mineral, $Ca_3(PO_4)_2$ with sand and coke in an electric furnace in inert atmosphere.

$$2Ca_3(PO_4)_2 \text{ (from bone-ash)} + 10C + 6SiO_2 \xrightarrow{\Delta}$$
$$6CaSiO_3 + 10CO + P_4(s)$$

Q.8 (C)

In P_4O_6 each phosphorus is linked to three oxygen atoms; whereas in P_4O_{10} each phosphorus atom is linked to four oxygen atoms.

Q.9 (C)
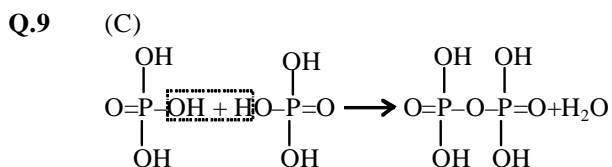
Q.10 (C)

Q.11 (C)

$$2Pb\ (NO_3)_2 \xrightarrow{673K} 2PbO + 4NO_2 + O_2$$

$NaNO_3$ and KNO_3 gives their nitrites and O_2 where as NH_4NO_3 gives N_2O.

Q.12 (B)

$$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$$

Q.13 (D)

Q.14 (A)

The difference of electronegativities between nitrogen (V) and oxygen is least as compared to that of in the other oxides. On moving down the group acidic strength decreses.

Q.15 (C)

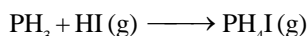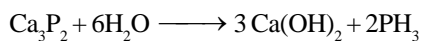Structure of Hypophosphorus acid. As it contains only one replaceable H atom. it is mono basic.
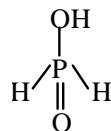
Q.16 (C)

Q.17 (B)

Q.18 (A)

Q.19 (A)

Q.20 (C)

$$NH_4Cl + KNO_2 \longrightarrow NH_4NO_2;$$
$$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$$

Q.21 (B)

Q.22 (A)

Q.23 (B)

Down the group the X–H bond length increases with increase in size of atom. So bond dissociation energies decrease and thererfore, thermal stability decrease. Hence the correct decreasing order is
$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$.

Q.24 (C)

According to the following reaction, one mole of Ca_3P_2 gives 2 mole of PH_3

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3.$$

Q.25 (B)

Q.26 (A)

$$Ca_3P_2 + 6H_2O \longrightarrow 3\,Ca(OH)_2 + 2PH_3$$

$$PH_3 + HI\,(g) \longrightarrow PH_4I\,(g)$$

Q.27 (B)

Q.28 (B)

Q.29 (C)

Q.30 (A)

$PF_3 \rightarrow$ surronding atms does not have vacantal orbital.

Q.31 (C)

Q.32 (D)

$$CaC_2 + N_2 \xrightarrow{\;\Delta\;} CaCN_2 + C \quad \text{nitrolim}$$
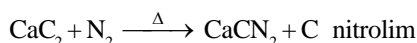
Q.33 (C)

When sulphur is heated, firstly S_8 rings break, diradicals are formed, polymerisation takes place. On further $\uparrow$T viscosity increase and then viscosity decrease at very high temperature ($\sim 600^\circ$C) rings are formed and in vapour phase S_2 (paramagnetic) molecules are present.

Q.34 (C)

Stability (Mono clinic < Rhombic)

Monoclinic and Rhombic sulphur have same puckered ring structure but they differs in crystalline structure.

Q.35 (B)

H_2S acts as strong reducing agent with nitric acid and acidified $KMnO_4$.

$$2HNO_3 + H_2S \longrightarrow 2H_2O + NO_2 + S.$$

Q.36 (B)

$$H_2S + O_2 \longrightarrow H_2O + SO_2$$
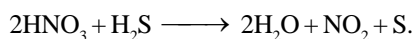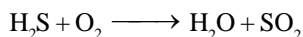
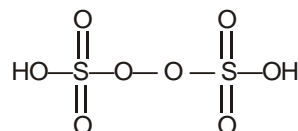**Q.37** (C)

Q.38 (B)

O.S. of S in $SO_3^{2-} = +4$

O.S. of S in $S_2O_4^{2-} = +3$

O.S. of S in $S_2O_6^{2-} = +5$

(None of these contains peroxide linkage).

The correct order of increasing O.S. is ;
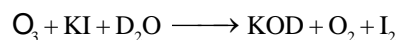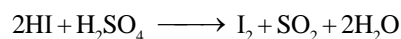
$S_2O_4^{2-} < SO_3^{2-} < S_2O_6^{2-}$

Q.39 (A)

Q.40 (A)

$$O_3 + KI + D_2O \longrightarrow KOD + O_2 + I_2$$

Q.41 (C)

SO_2Cl_2

Q.42 (B)

Q.43 (B)

Q.44 (D)

$$\overset{-1}{2HI} + \overset{+6}{H_2SO_4} \longrightarrow \overset{0}{I_2} + \overset{+4}{SO_2} + 2H_2O$$
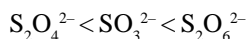
Thus H_2SO_4 oxidises HI to I_2.

$$\overset{-1}{2HI} + \overset{+6}{H_2SO_4} \longrightarrow \overset{0}{I_2} + \overset{+4}{SO_2} + 2H_2O$$

Q.45 (C)

Q.46 (B)

$$Na_2S_2O_3 + 4Cl_2 + 5H_2O \longrightarrow 2NaHSO_4 + 8HCl$$
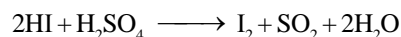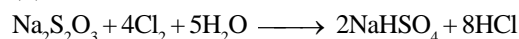
Q.47 (D)

It is sodium sulphite containing sulphite, SO_3^{2-}.
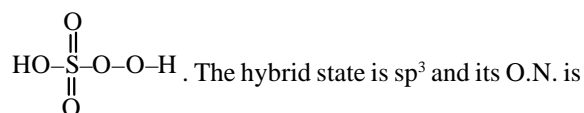
Q.48 (B)

$$H_2SO_5 + H_2O \longrightarrow H_2O_2 + H_2SO_4.$$
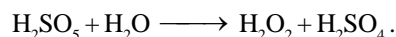
Q.49 (C)

Q.50 (D)

The structure of Caro's acid is

. The hybrid state is sp^3 and its O.N. is

+6.

Q.51 (B)

$H_2S_2O_6$, $H-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$ – 4π bonds;

H_2SO_3, $HO-\overset{\overset{O}{\|}}{S}-OH$ –one π bond ;

$H_2S_2O_5$, $H-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-\overset{\overset{O}{\|}}{\underset{\underset{O}{}}{S}}-OH$ – 3π bonds ;
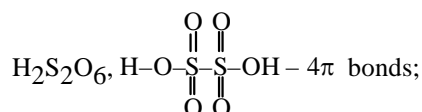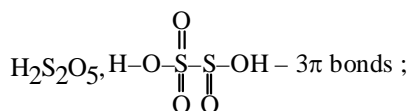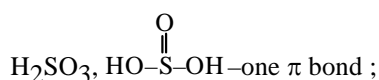
Q.52 (B)

It has d- and f-orbitals so it can show higher positive oxidation states with highly electronegative fluorine and oxygen.

Q.53 As the size of anion increases the distance between the nucleus and valence shell electrons increases resulting into weak force of attraction between them. This leads to increase in the ease of the donation of electrons in the order $F^- < Cl^- < Br^- < I^-$. Hence I^- acts as a strongest reducing agent.

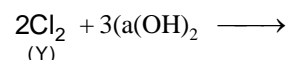**Q.54** (A)

$SRP = 2.87$ V (highest)

Q.55 (C)

Chlorine gas reacts with CaO, NaOH and NH_3 ; so chlorine gas cannot be dried by passing over these compounds. H_2SO_4 have great affinity for water and therefore it is used for drying Cl_2.
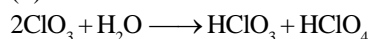
Q.56 (C)

$F_2 + \underset{(X)}{HCl} \longrightarrow HF + \underset{(Y)}{Cl_2}$

Cl_2 is grenish yellow gas

$\underset{(Y)}{2Cl_2} + 3(a(OH)_2 \longrightarrow$

$Ca(OCl)_2 \cdot \underset{(Z)}{Ca(OH)_2} \cdot CaCl_2.2H_2O$
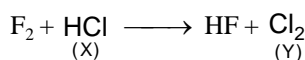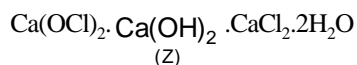
Z is bleaching powder it turns red litmus paper to white.

Q.57 (A)

AgF is soluble in water.

Q.58 (B)

$2ClO_3 + H_2O \longrightarrow HClO_3 + HClO_4$

Q.59 (D)

HI is the strongest acid so I^- is the weakest base.

Q.60 (D)

$H_2SO_4 + HI \longrightarrow I_2 + SO_2 + H_2O$

Q.61 (D)

$2ClO_2 + H_2O \longrightarrow HClO_2 + HClO_3$

Q.62 (B)

$Cl_2 + H_2O \longrightarrow 2HCl + [O]$.
Bleaching is due to oxidation.
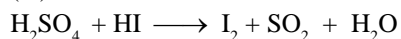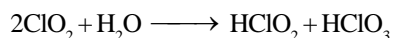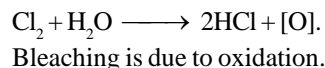
Q.63 (C)

I_4O_9 is actually $I(IO_3)_3$ which gets ionised.
$I(IO_3)_3 \rightleftharpoons I^{3+} + 3(IO_3-)$

Q.64 (A)

$\Delta H_{vaporisation}$ order : $HF > HI > HBr > HCl$

Q.65 (D)

$\overset{H-F-H}{\underset{2.26\ \text{Å}}{\longleftrightarrow}}$
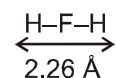
Average. HF bond length $= \dfrac{2.26}{2} = 1.13$Å

stretching $= 1.13 - 0.92 = 0.21$ Å

Q.66 (D)

$IO^- \xrightarrow[\text{Hot and conc.}]{OH^-} \underset{P}{I^-} + \underset{Q}{IO_3^-}$
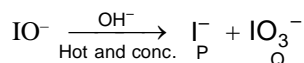
Q is more stable anion its conjugate acid is $\underset{X}{HIO_3}$

$\underset{X}{2HIO_3} \overset{240°C}{\rightleftharpoons} \underset{Y}{I_2O_5} + H_2O$
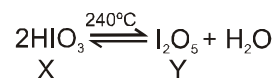
$\underset{Y}{I_2O_5} + 5CO \longrightarrow I_2 + 5CO_2 \longrightarrow$ Useful in fire extinguishing

Q.67 (B)

H_2SO_4 oxidises HBr to Br_2
$H_2SO_4 + 2HBr \longrightarrow SO_2 + Br_2 + 2H_2O$.

Q.68 (D)

$\underset{\text{Cold and dil.}}{Cl_2 + 2NaOH \longrightarrow NaCl + NaClO + H_2O}$ (A)

$\underset{\text{Hot and conc.}}{3Cl_2 + 6NaOH \longrightarrow 5NaCl + NaClO_3 + 3H_2O}$ (B)
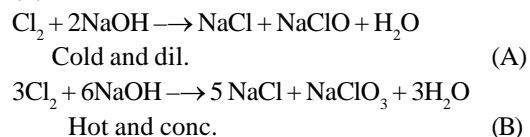
Q.69 (B)

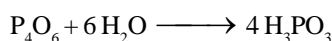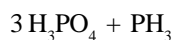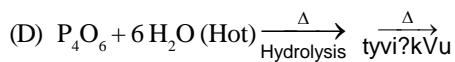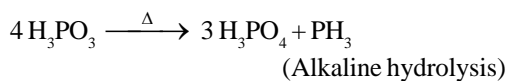If Helium is compressed and liquified it forms He(I) liquid at 4.2 K. This liquid is a normal liquid like any other liquid. But if it is further cooled then He(II) is obtained at 2.2 K, which is known as super fluid, because it is a liquid with properties of gases. It climbs through the walls of the container & comes out. It has very high thermal conductivity and very low viscosity.
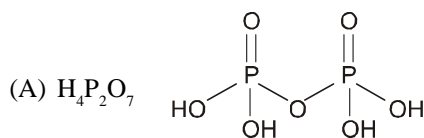
Q.70 (A)

It is factual.

Q.71 (D)

Very weak, Vander Waals forces.

Q.72 (A)

As size increases, Vander Waals forces also increases.

Q.73 (B)

(I) They do not form compounds readily as they are chemically inert on account of stable electron configuration.

(II), (III) & (IV) are correct statement.

Q.74 (C)

Coconut charcoal possess characteristic property for adsorbing different noble gases at different temperatures.

Q.75 (D)

Both Xe and O_2 have comparable ionisation energies.

$Xe \longrightarrow Xe^+ + e^-$ ionisation energy = 1,170 kJ/mol

$O_2 \longrightarrow O_2^+ + e^-$ ionisation energy = 1,175 kJ/mol

Q.76 (D)

Inert gas can not be electrolysed, due to complete octate, they don't gain electron or release electrons.

Q.77 (A)

$6\,XeF_4 + 12\,H_2O\ 4\,Xe + 2XeO_3 + 24\,HF + 3O_2$

$CaCN_2 + 3H_2O\ CaCO_3 + 2NH_3.$

Q.78 (C)

$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$

Q.79 (A)

$2[HXeO_4]^- + 2OH^- \longrightarrow [XeO_6]^{4-} + Xe + O_2 + 2H_2O$

Q.80 (C)

$\overset{\cdot\cdot}{\underset{\cdot\cdot}{Xe}}-F$, $\sigma = 1$, l.p. 3, 4, sp^3d.

JEE-ADVANCED

MCQ/COMPREHENSION/COLUMN MATCHING

Q.1 (AB)

Down the group the size of atoms increases and so electronegativity decreases ; but electropositive character increases on account of increase in size of atoms. Hence they form positive ions i.e. cation not M^{3-}.

Q.2 (AB)

Apart from NH_3 other hydrides also form stable complexes.

Q.3 (AB)

$2NaNO_2 \xrightarrow{800^\circ C} Na_2O + N_2 + \dfrac{3}{2}O_2$

$NaNO_2 + NH_4Cl \longrightarrow NaCl + N_2 + 2H_2O$

Q.4 (ACD)

Red phosphorus is inert towards sodium hydroxide but white phosphorus reacts according to following reaction.

$P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$

Q.5 (ABC)

(A) $4NH_3 + 5O_2 \xrightarrow[5\,atm, 850^\circ C]{Pt/Rh} 4NO\,(g) + 6H_2O\,(g)$; principal reaction of Ostwald's method of HNO_3 manufacturing.

(B) HNO_2 is weak oxidising agent and oxidises Fe^{2+} to Fe^{3+} and I^- to I_2 and it self reduced to N_2O or NO. In contrary HNO_2 is oxidised by $KMnO_4$ and Cl_2 forming NO_3^-.

(C) $2NO_2 + O_3 \longrightarrow N_2O_5 + O_2$

Q.6 (ACD)

(A) $Sb + 5HNO_3 \longrightarrow H_3SbO_4 + 5NO_2 + H_2O$

(B) $Mn + 2HNO_3 \longrightarrow Mn(NO_3)_2 + H_2$

(C) $3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O$

(D) $4HNO_3 + P_4O_{10} \xrightarrow{250K} 2N_2O_5 + 4HPO_3$

Q.7 (BCD)

$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$

N_2O is a colourless neutral gas. It produces laughter so it is called as laughing gas.

Note : Picrin (CCl_3NO_2) is tear gas.

Q.8 (AD)

$A \Rightarrow P_4O_6$; $B \Rightarrow H_3PO_3$;

$C \Rightarrow H_3PO_4$; $D \Rightarrow PH_3$

Q.9 (ABCD)

(A) $PCl_5 + 6LiF \longrightarrow LiPF_6 + 5LiCl$

(B) $6PCl_5 + P_4O_{10} \longrightarrow 10POCl_3$

(C) $PCl_3 + NaH \longrightarrow PH_3$

(D) $PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$
     (equimolar amount)

9

Q.10 (ABCD)
Fact.

Q.11 (ABCD)
Factual

Q.12 (BD)
All acts as reducing agent and the increasing order of reducing character is $NH_3 < PH_3 < AsH_3 < BiH_3$ on account of decreasing M–H bond dissociation energies with increasing size of central atoms.
NH_3 is only a mild reducing agent.

Q.13 (ACD)
(A) $NaNO_2 + NH_4Cl \longrightarrow NaCl + NH_4NO_2$

$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$

(B) $H_2O_2 \longrightarrow H_2O + [O]$; $NaNO_2 + [O]$

$\longrightarrow NaNO_3$

(C) $2NH_3 + 3CuO \longrightarrow 3Cu + N_2 + 3H_2O$

(D) $2KMn^{+7}O_4^- + 2NH_3 \longrightarrow 2KOH + 2MnO_2 + N_2 + 2H_2O$

Q.14 (ABCD)
$Ca_3N_2, Ca_3P_2 , Na_3As_2 , Mg_3Bi_2$

Q.15 (ABC)
$AgNO_3 \xrightarrow{\Delta} Ag + NO_2 + \frac{1}{2}O_2$;

$2BaO_2 \xrightarrow{800°C} 2BaO + O_2$.

$Pb(NO_3)_2 \xrightarrow{\Delta} PbO + 2NO_2 + 1/2O_2$;

$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$

Q.16 (BCD)
Cu, Ag and Zn ions dissolve in excess of aq. NH_3 to form complex.

Q.17 (BCD)
(A) In PH_3 the lone pair of electrons is present in spherical non directional more concentrated s-orbital where as lone pair of electrons is present in directional sp^3 hybrid orbital. As a result, the ease of donation of lone pair of electron is more in NH_3 as compare to PH_3.
(B) It is incorrect statement.
(C) $3CuSO_4 + 2PH_3 \longrightarrow Cu_3P_2$ (black ppt) $+ H_2SO_4$
(D) $PH_3 + O_2 \longrightarrow$ Dense white fumes of P_4O_{10}. H_3PO_4 is negligibly formed.

Q.18 (ABCD)

Q.19 (ABCD)
$NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$;

$NH_4^+ + OH^- \rightleftharpoons NH_3.H_2O$

Q.20 (ABD)
$3X_2 + 8NH_3 \longrightarrow N_2 + 6NH_4X$
(X : F, Cl, Br)

Q.21 (C)
$H_2O + 2NO_2 \longrightarrow HNO_3 + HNO_2$

Q.22 (B)
(A) $N_2O_3 + 2KOH \longrightarrow 2KNO_2 + H_2O$
(B) $H_2O + 2NO_2 \longrightarrow HNO_2$ (reducing agent) $+ HNO_3$ (oxidising agent)
(C) Neutral to litmus as neutral oxide
(D) In the liquid state, N_2O_4 tends to ionise
$N_2O_4 \rightleftharpoons NO^+ + NO_3^-$

Q.23 (C)
$A = PH_4I$; $B = PH_3$; $C = HI$; $D = PI_3$

Q.24 (B)

Q.25 (B)
(A) is PH_4I. The given changes are :

(i) $PH_4I (A) \xrightarrow{\Delta} HI (C) + PH_3 (B)$

(ii) $PH_4I (A) + H_2O \longrightarrow PH_3 (B) \uparrow + H_3O^+ + I^-$

(iii) $PH_3 (B) + I_2 \longrightarrow PI_3 (D) + HI$

(iv) $PI_3 (D) + H_2O \longrightarrow H_3PO_3 + HI$

(v) $HI + AgNO_3 \longrightarrow AgI \downarrow + HNO_3$

(vi) $4PH_3 (B) + 8O_2 \longrightarrow P_4O_{10}$ (C) (dense white fumes) $+ 6H_2O$

Q.26 (P) - 3 ; (Q) − 4 ; (R) − 2 ; (S) − 1

Q.27 (A) p, q, s ; (B) p, q, r, s ; (C) q, r, s ; (D) p, q, r, s

(A) $PCl_5 + H_2O \xrightarrow{\text{Hydrolysis}} POCl_3 + 2\,HCl$
sp^3

$POCl_3 + 3\,H_2O \longrightarrow H_3PO_4 + 3\,HCl$;
sp^3

$$HO - \overset{\overset{\displaystyle O}{\|} \ p\pi - d\pi}{\underset{\underset{\displaystyle OH}{|}}{P}} - OH$$

(B) $P_4 + 3 \ NaOH + 3 \ H_2O \xrightarrow[CO_2]{\Delta}$

$\underset{sp^3}{3 \ PH_3} + \underset{sp^3}{3 \ NaH_2PO_2}$ or $H_2PO_2^-$

$$H - \overset{\overset{\displaystyle O}{\|} \ p\pi - d\pi}{\underset{\underset{\displaystyle H}{|}}{P}} - O^- \ ; \text{Disproportionation reaction}$$

(C) Disproportionation reaction

$4 \ H_3PO_3 \xrightarrow{\Delta} 3 \ H_3PO_4 + PH_3$
(Alkaline hydrolysis)

(D) $P_4O_6 + 6 \ H_2O \ (Hot) \xrightarrow[\text{Hydrolysis}]{\Delta} \xrightarrow{\Delta}$ tyvi?kVu

$3 \ H_3PO_4 + PH_3$

$P_4O_6 + 6 \ H_2O \longrightarrow 4 \ H_3PO_3$

$4 \ H_3PO_3 \xrightarrow{\Delta} 3 \ H_3PO_4 + PH_3$

Q.28 (A) - q, s ; (B) - q, r ; (C) - q, s ; (D) - q

(A) $H_4P_2O_7$
$$\underset{OH \quad\quad OH}{HO - P - O - P - OH}$$
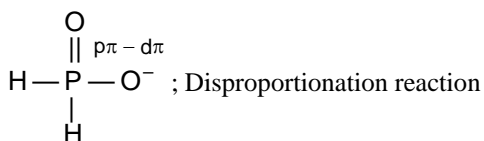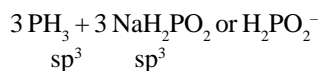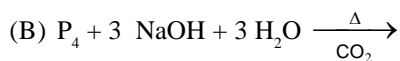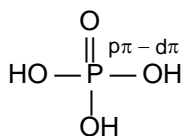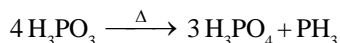
One P—O—P bond and four P—OH bonds

(B) $H_4P_2O_5$
$$\underset{H \quad\quad\quad H}{HO - P - O - P - OH}$$
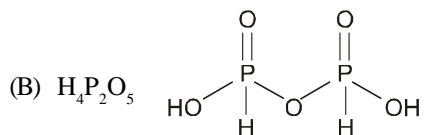
Two P—H bond and one P—O—P bond

(C) $(HPO_3)_3$ (cyclic)

Q.29 (A) - p,q ; (B) - p,r ; (C) - q,s ; (D) - p,q,r,s
$2NH_3 + 3F_2 \longrightarrow N_2 + 6HF$
$8NH_3 \text{ (excess.)} + 3Cl_2 \longrightarrow N_2 + 6NH_4Cl$
$NH_3 + 3Br_2 \text{ (excess.)} \longrightarrow NBr_3 + 3HBr$
$NH_3 \text{ (aq.)} + I_2 \longrightarrow NI_3 . NH_3 + 3HI$

$8NI_3 . NH_3 \longrightarrow 5N_2 + 9I_2 + 6NH_4I$
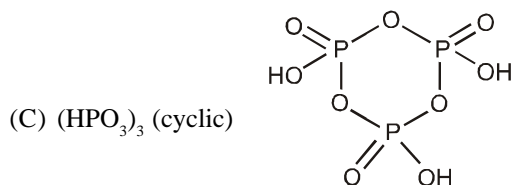
Q.30 (AC)
$FeS + \text{dil.HCl or } H_2SO_4 \longrightarrow H_2S$
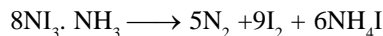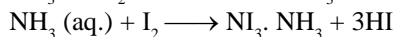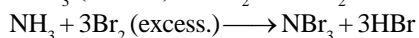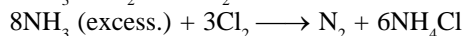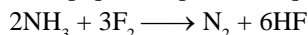
Q.31 (ABCD)
Factual

Q.32 (BCD)
(B) Group 16 elements form oxides of type EO_2 and EO_3.
(D) SO_2 works both as oxidising and reducing agent.

Q.33 (ABCD)
SO_2 acts as reducing agent only in presence of strong oxidising agent.
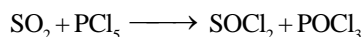
Q.34 (CD)
$SO_2 + PCl_5 \longrightarrow SOCl_2 + POCl_3$
No change in oxidation number of any element. So, not a redox reaction.
$SOCl_2$ is thionylchloride; SO_2Cl_2 is sulphuryl chloride.

$$\left.\begin{array}{l} POCl_3 + H_2O \longrightarrow H_3PO_4 + HCl \\ SOCl_2 + H_2O \longrightarrow H_2SO_3 + HCl \end{array}\right\} \text{strongly acidic solutions}$$
$$\downarrow$$
$$SO_2$$
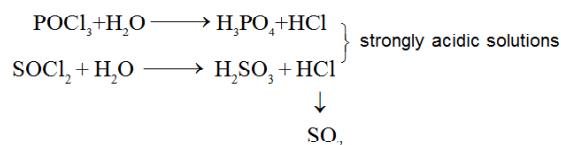
Both the products have sp^3 hybridisation of central atom.

$SO_2 + PCl_5 \longrightarrow SOCl_2 + POCl_3$
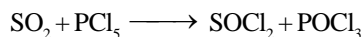
Q.35 (ABCD)
(A) In alkaline solution, its reducing character is more than in acidic medium.

$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$
$2OH^- + H_2O_2 \longrightarrow O_2 + 2H_2O + 2e^-$
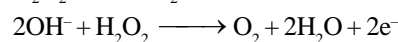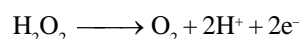
(B) Correct statements.
(C) Due to H- bonding it forms a hydrate $H_2O_2.H_2O$ (melting point 221 K).
(D) $K_2MnO_4 + O_3 + H_2O \longrightarrow$
$\quad\quad\quad KMnO_4 + 2KOH + O_2$
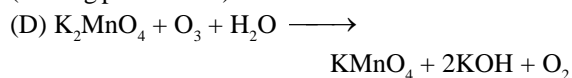
Q.36 (ABCD)

(D)
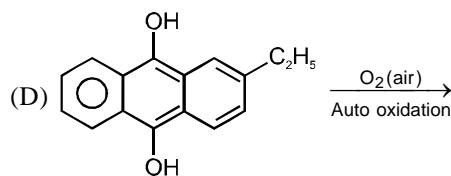
2-ethyl anthraquinol

$+ H_2O_2$
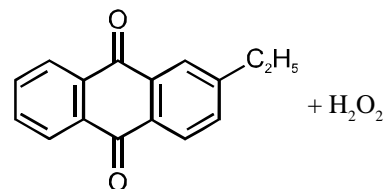
Q.37 (ACD)

All allotropes of sulphur which are less stable gradually changes to most stable allotropic form.

$\Rightarrow$ Monoclinic sulphur is soluble in CS_2 but insoluble in water.

Q.38 (ABD)

(A) $2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$

(B) He is insoluble in blood at higher pressure.

(C) O_2 has two unpaired electrons in antibonding π molecular orbitals.
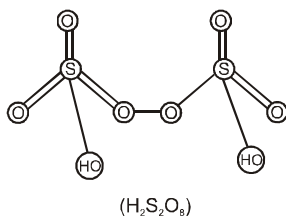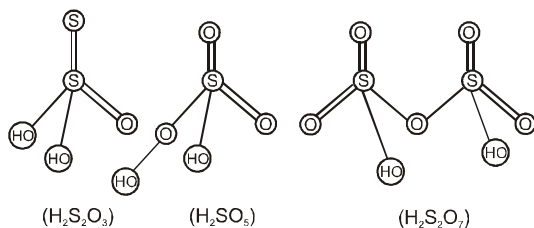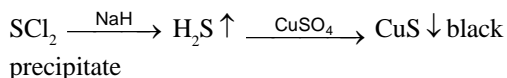
Q.39 (ABCD)

Factual

Q.40 (ABD)

Sulphuric acid has very high affinity towards water and that is why it is used as dehydrating agent. Concentrated H_2SO_4 + concentrated HNO_3 acts as a sulphonating agent for the sulphonation of various aromatic compounds.

It acts as oxidising agent and oxidises HBr to Br_2 and HI to I_2.

Q.41 (D)

$(H_2S_2O_3)$ (H_2SO_5) $(H_2S_2O_7)$

$(H_2S_2O_8)$

Q.42 (AB)

$SCl_2 \xrightarrow{NaH} H_2S \uparrow \xrightarrow{CuSO_4} CuS \downarrow$ black precipitate

Q.43 (ABCD)

(A) It removes the chlorine from the surface of fibres (while dyeing) according to following reaction.

$Na_2S_2O_3 + 4Cl_2 + 5H_2O \longrightarrow 2NaHSO_4 + 8HCl$
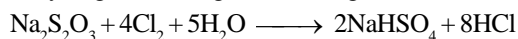
Therefore, it is known as antichlor.

(B) $I_3^- + S_2O_3^{2-} \longrightarrow 3I^- + S_4O_6^{2-}$
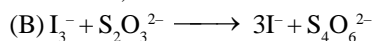
This reaction finds application in the iodometric and iodimetric methods of titrimetric analysis.

(C) $S_2O_3^{2-} + H^+ \longrightarrow S\downarrow$ (white) $+ SO_2 + H_2O$ (disproportionation reaction).

(D) $2S_2O_3^{2-} + Ag^+ \longrightarrow [Ag(S_2O_3)_2]^{3-}$ (soluble complex) or $[Ag(S_2O_3)_3]^{5-}$
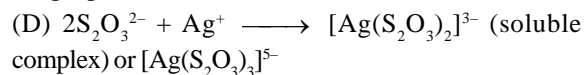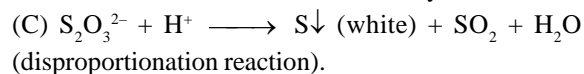
This reaction is utilized in photography where hypo is used as fixer.

Q.44 (ABCD)
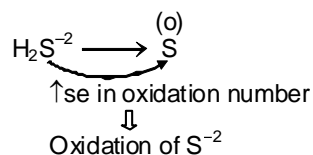
All the above are example of reducing nature of H_2S.

Q.45 (C)

(A) It is true because of effective $p\pi$-$d\pi$ overlapping owing to small size of sulphur as compared to phosphorus and silicon.
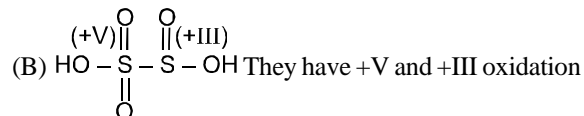
(B) They have +V and +III oxidation state.

(C) HNO_3 oxidises sulphur to H_2SO_4 (+VI) but only oxidises selenium to H_2SeO_3 (+IV). The higher oxidation states become less stable on descending the group.

(D) In M – O electronegativity difference is large while in X – O, it is comparatively smaller (< 1.4).

M = metal and X = non-metal

Q.46 (A)

(A) As bond (H – E) dissociation enthalpy decreases down the group, the acidic character increases from H_2O to H_2Te.

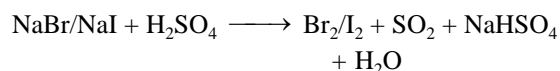(B) Order of thermal stability is $H_2O > H_2S > H_2Se > H_2Te$.

(C) H_2O does not have reducing property and this character increases from H_2S to H_2Te.

(D) Water has highest boiling point because of H-bonding and thus the correct order is $H_2S < H_2Se < H_2Te < H_2O$.

Q.47 (P) 2 ; (Q) 3, (R) 1, (S) 4

Q.48 (AB)

Q.49 (BC)

$NaBr/NaI + H_2SO_4 \longrightarrow Br_2/I_2 + SO_2 + NaHSO_4 + H_2O$

Q.50 (BD)

Smaller halogen (i.e., stronger oxidising agent) displaces bigger halogen (i.e. weaker oxidising agent) from solution of its halide. e.g., $Br^- + Cl_2 \longrightarrow Br_2 + 2Cl^-$.

Q.51 (AC)

$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$

Q.52 (ABCD)

All the given reactions are correct and all are preparation methods of halogens.

Q.53 (BC)

Q.54 (ACD)

all statement are correct.

Q.55 (ACD)

X is HCl.

HCl has lowest boiling point used is the most volatile.

$X + NaHCO_3 \longrightarrow NaCl + H_2O \mid CO_2 \uparrow$

Q.56 (ABC)

In I_2 opposite reaction of F_2 occurs

$HI + O_2 \longrightarrow I_2 + H_2O$

Q.57 (ABC)

(A) As O.N. increases, acidic strength increases.

(B) As non-metalic character increases, acid strength increases

Oxyacid	No. of $p\pi - p\pi$ bond
$HClO_4$	3
$HClO_3$	2
(C) $HClO_2$	1
HClO	0

(D) All are sp^3 hybridised, therefore same percentage s-character :

Q.58 (ABD)

FCl_3 is not possible due to unavailability of d-orbitals in fluorine.

Q.59 (ABCD)

(A) Thermal stability of AB type compounds increases with increase in electronegativity difference between A and B.

So order is IF > BrF > ClF, true

(B) True

$IF_7 + 6H_2O \longrightarrow 7HF + H_5IO_6$

(C) True, All the electrons, bonding or non-bonding, are present in pairs. Hence interhalogen molecules are dianagmatic in nature.

(D) True
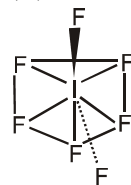
Pentagonal bipyramidal.

Q.60 (A)

HF has high bond dissociation energy ; so removal of H becomes difficult.

Q.61 (B)

It is not polar and carbon does not have empty d-orbital. There is also least difference in electronegativity.

Q.62 (A)

Because its conjugate acid, H_2O is weakest acid.

Q.63 (D)

(A) $Br_2 + 2e^- \longrightarrow 2Br^-$; SRP = +1.09 V

(B) Being covalent in nature sparingly soluble in water.

(C) Fluorescein + $Br_2 \longrightarrow$ tetrabromo fluorescein(I) (red)

Q.64 (D)

(A) $AgNO_3 + NaBr \longrightarrow NaNO_3 + AgBr\downarrow$ (pale yellow)

(B) $Pb(NO_3)_2 + NaBr \longrightarrow PbBr_2 \downarrow$ (white) + $NaNO_3$

(C) $NaBr + H_2SO_4 \longrightarrow Br_2 + SO_2 + SO_4^{2-} + 2Na^+ + 2H_2O$

Q.65 (C)

(A) $3Br_2 + 3Na_2CO_3 \longrightarrow 5NaBr + NaBrO_3 + 3CO_2$

$\quad$ (A) $\quad$ (B) $\quad\quad$ (C)

(B)
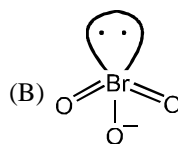
$3Br_2 + 3Na_2CO_3 \longrightarrow 5NaBr + NaBrO_3 + 3CO_2$

$5NaBr + NaBrO_3 + 3H_2SO_4 \longrightarrow 5HBr + HBrO_3 + 3Na_2SO_4$

$5HBr + HBrO_3 \longrightarrow 3Br_2 + 3H_2O$

Q.66 (D)

F is more electronegative than Cl.

Q.67 (A)

IF_7

Q.68 (C)

$: \overset{..}{\underset{..}{Cl}} F_3$, l.p. $= 2$

Q.69 (B)

it is 1, 3, 5, 7

Q.70 (C)

Q.71 (A)

Q.72 (C)

Q.73 (A)

Q.74 (A) - q,s ; (B) - s ; (C) - p ; (D) - r

(A) $Cl_2O_6 + H_2O \rightarrow HClO_3 + HClO_4$

(B) $NaClO_4(s) + HCl(conc.) \rightarrow HClO_4 + NaCl$

(C) $2KClO_3 + 2(COOH)_2 \rightarrow K_2C_2O_4 + 2H_2O + 2CO_2 + 2ClO_2$

(D) $2HgO + 2Cl_2 \xrightarrow{573K} HgO.HgCl_2 + Cl_2O$

Q.75 (BC)

Xe and Kr being bigger in size trapped in the cavities formed by the water molecules while He and Ne being smaller escape from the cavities.

Q.76 (AB)

$A \rightarrow XeF_2$
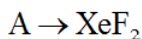
$\mu = 0$

planner

Xe-F

Bond length   2.00 Å

$B \rightarrow XeF_6$

$\mu - 0$
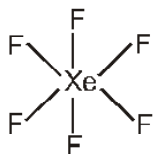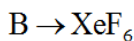
non-planner

1.89 Å
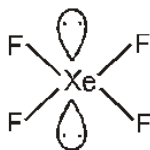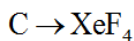
$C \rightarrow XeF_4$

$\mu - 0$

planner

1.95 Å

Q.77 (ABCD)

(A) $XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$

(B) $2XeF_6 + SiO_2 \longrightarrow 2XeOF_4 + SiF_4$

(C) $XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$

(D) $XeO_3 + 2XeF_6 \longrightarrow 3XeOF_4$
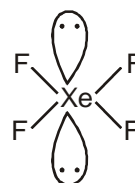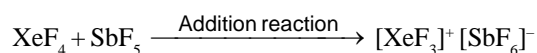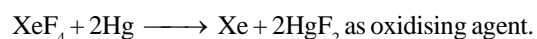
Q.78 (B)

Q.79 (D)

Q.80 (C)

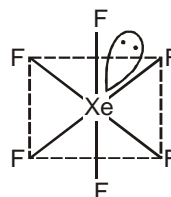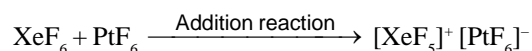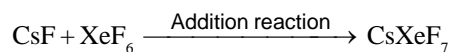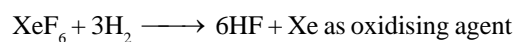**Q.81** (A) - p,q,r,s ; (B) - p,q,r,s,t; (C) - p,q,r,s ; (D) - q,s,t

(A) $XeF_2 + 2H_2O \xrightarrow{Hydrolysis} 2Xe + 4HF + O_2$

$XeF_2 + 2HCl \longrightarrow Xe + 2HF + Cl_2$

as oxidising agent

$XeF_2 + PF_5 \xrightarrow{Addition\ reaction} [XeF]^+ [PF_6]^-$
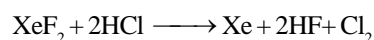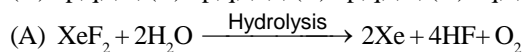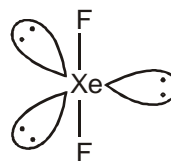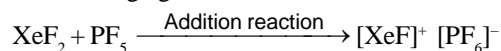
(B) $6XeF_4 + 12H_2O \xrightarrow[Disproportionation]{Hydrolysis} 4Xe + 2XeO_3 + 24HF + 3O_2$

$XeF_4 + 2Hg \longrightarrow Xe + 2HgF_2$ as oxidising agent.

$XeF_4 + SbF_5 \xrightarrow{Addition\ reaction} [XeF_3]^+ [SbF_6]^-$

(C) $XeF_6 + 3H_2O \xrightarrow{Hydrolysis} XeO_3 + 2HF$

$XeF_6 + 3H_2 \longrightarrow 6HF + Xe$ as oxidising agent

$CsF + XeF_6 \xrightarrow{Addition\ reaction} CsXeF_7$

$XeF_6 + PtF_6 \xrightarrow{Addition\ reaction} [XeF_5]^+ [PtF_6]^-$

(D) $XeO_3 + OH^- \rightleftharpoons HXeO_4^-$

$2HXeO_4^- + 2OH^- \longrightarrow XeO_6^{4-} + Xe + O_2 + 2H_2O$

$XeO_3 + 6H^+ + 6e^- \longrightarrow Xe + 3H_2O$ (E = 2.10 V)

acts as oxidising agent.
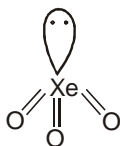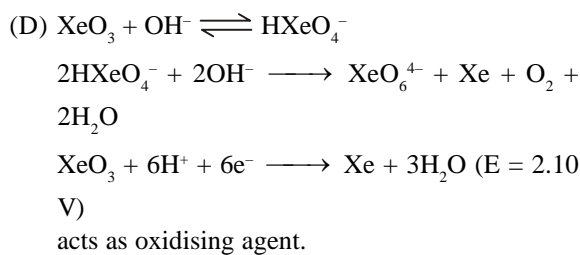
NUMERICAL VALUE BASED

Q.1 [5]

(1, 2, 3, 5, 6) are correct.

Q.2 [3]

a, d and f are correct.

Q.3 [4]

Statement (b), (d), (e), (f) are correct and remaining are false.

Q.4 [3]

$a = 1$; $b = 2$; $c = 1$; $d = 4$

$2a + b + 3c - d = 2 \times 1 + 2 + 3 \times 1 - 4 = 3$

Q.5 [7]

Yellow coloured crystalline element is sulphur.

$S_8 + 24F_2 \longrightarrow 8SF_6$ (x)

SF_6 is octahedral geometry & thermally stable.

Q.6 [8]

$SF_4 + 2H_2O \longrightarrow SO_2 + 4HF$

$2SF_2 + 2H_2O \longrightarrow S + SO_2 + 4HF$

$SF_6 + H_2O \longrightarrow$ no reaction

Q.7 [5]

$4BF_3 + 3H_2O \longrightarrow B(OH)_3 + 3HBF_4$

$BCl_3 + 3H_2O \longrightarrow B(OH)_3 + 3HCl$

$NCl_3 + 4H_2O \longrightarrow NH_3.H_2O + 3HOCl$

$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$

$AsCl_3 + 3H_2O \longrightarrow H_3AsO_3 + 3HCl$

Q.8 [9]

Favourite NCERT reactions except 3 and 4.

Q.9 [6]

$PH_3, H_2S, AsH_3, SbH_3, H_2Se, H_2Te$

Follow drago's rule.

Q.10 [4]

$2NH_3 + NaOCl \longrightarrow NH_2Cl + NaOH$ (fast)

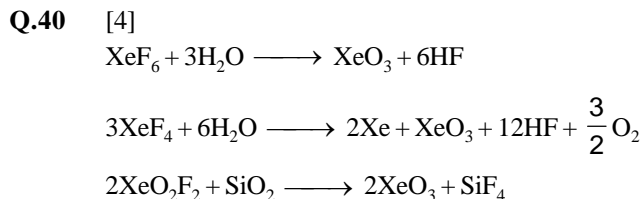$2NH_3 + NH_2Cl \longrightarrow \mathbf{NH_2-NH_2}$ (strong nucleophile) $+ NH_4Cl$ (slow)
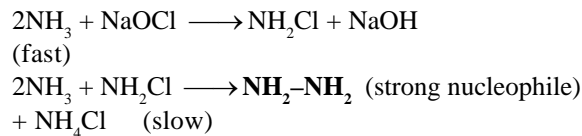
Q.11 [7]

a, b, j are only neutral, all others acidic.

Q.12 [5]

a, b, d, h, i are gases.

Q.13 [10]
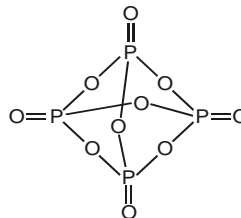
Experimental P–O–P bond angle in P_4O_{10} is 127°.

Q.14 [12]

(a) $N_2O_4, H_2CO_3, SO_2, SO_3, N_2O_3, HNO_3$

$x = 6$

(b) $(HPO_3)_3, SO_2, SO_3, P_4O_{10}, H_2SO_4, H_3PO_3$

$y = 6$

Q.15 [3]

a, d, f have +3 oxidation state.

Q.16 [6]

Except HCl, it will react with all other compounds, replacing OH–group by Cl–group.

Q.17 [6]

Pb, Sn, Mg, MgO, Hg, Ag dissolve in cold conc. HNO_3. Pb_3O_4 (dissolves partially, PbO_2 remains undissolved), Fe (passivated), Au (insufficient oxidising power of HNO_3), Pt (insufficient oxidising power of HNO_3).

Q.18 [6]

Pb, Cu, $SrCO_3$ (fail to dissolve). Remaining can dissolve Fe_3O_4, Fe, Mg, MgO, $CoCO_3$, $CuCO_3$.

Q.19 [3]

(iii, viii, ix)

Q.20 [10]

$P_4 + 10 SO_2Cl_2 \longrightarrow 4 PCl_5 + 10 SO_2$

Q.21 [24]

$SOCl_2 + H_2O \longrightarrow 2HCl + SO_2$

Total 4 moles required (2 for HCl & 2 for SO_2)

$SO_2Cl_2 + 2H_2O \longrightarrow H_2SO_4 + 2HCl$

Total 4 moles required (2 for HCl & 2 for H_2SO_4)

$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$

Total 5 moles required (3 for HCl & 2 for H_3PO_3)

15

$PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$
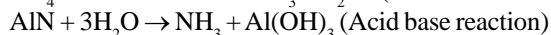
Total 8 moles required (5 for HCl & 3 for H_3PO_4)

$NCl_3 + 3H_2O \longrightarrow NH_3 + 3HOCl$

Total 3 moles required for HOCl

Q.22 [10]

(i) Produces SO_2 and HF

(ii) Produces H_3PO_3 and HCl

(iii) Neutral gas

(iv) Produces HNO_3 and HCl

(v) No hydrolysis

(vi) Produces H_2SeO_4 + HF

(vii) Produces H_3AsO_3 + HCl

(viii) Produces H_3PO_4 + HCl

(ix) Produces H_2SO_3

(x) Produces H_2SO_4 and HCl

(xi) Produces H_2SO_3 and HCl

(xii) Produces H_2CO_3 ($H_2O + CO_2$) and HCl

(xiii) No hydrolysis

Q.23 [3]

$Cl_2 + Na_2S_2O_3 + H_2O \rightarrow 2HCl + S + Na_2SO_4$

Q.24 [5]

In $Na_2S_4O_6 \rightarrow$ 2S atoms in +5 oxidation state & 2S atoms in 0 oxidation state.

Q.25 [4]

$\overset{+3}{As}O_3^{-3} \longrightarrow \overset{+5}{As}O_4^{-3}$;

$NH_2–NH_2 \longrightarrow N_2$

$H_2S \longrightarrow S$;

$PbS \longrightarrow PbSO_4$

Q.26 [9]

$3S + 6NaOH \longrightarrow Na_2S_2O_3\,(A) + 2Na_2S\,(B) + 3H_2O$

$Na_2S + CdCl_2 \longrightarrow 2NaCl + CdS\,(C)$

$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6\,(E) + 2NaI\,(D)$

$2Na_2S_4O_6\,(E) + 4HCl \longrightarrow 4NaCl + 2H_2O + 5SO_2\,(F) + 3S$

$2 + 1 + 1 + 0 + 4 + 1 = 9$

Q.27 [32]

O_2

Q.28 [43]

$P = Cl_2$

$Q = N_2$

$71 - 28 = 43$

Q.29 [6]

Q.30 [2]

Aquaregia :

$3HCl + \overset{5}{H}NO_3 \longrightarrow \overset{3}{N}OCl + 2H_2O + 2Cl$

(Conc.) (Conc.)

Q.31 [5]

HCl will be obtained is a, b, c, d, e.

Q.32 [3]

ClO_2 ; Cl_2O_6 and NO_2 are mixed anhydride.

Q.33 [13]

$Br_2 + F_2(\text{excess}) \longrightarrow \underset{(A)}{BrF_5} \xrightarrow{\text{Hydrolysis}} \underset{(B)}{HF} + \underset{(C)}{HBrO_3}$

Q.34 [2]

Cl is excited state ↑↓ | ↑↓ ↑ ↑ | ↑ _ _ _ (3d)

Q.35 [32]

Electonic configuration of

$$_{85}At = \begin{array}{c|c|c|c|c|c} 2 & 8 & 18 & 32 & 18 & 7 \\ \hline K & L & M & N & O & P \end{array}$$

Q.36 [4]

Boiling point, Atomic volume, Density at STP, critical temp.

Q.37 [7]

XeF_2 is a strong oxidising agent with SRP = +2.64.

$XeF_2 + Cl^- \longrightarrow Cl_2 + Xe$

$Br^- \longrightarrow Br_2$

$I^- \longrightarrow I_2$

$XeF_2 + NH_3 \longrightarrow N_2 + NH_4F + Xe$

$XeF_2 + CrF_2 \longrightarrow CrF_3 + Xe$

$Pt + XeF_2 \longrightarrow PtF_6 + Xe$

$S_8 + XeF_2 \longrightarrow SF_6 + Xe$

Q.38 [8]

XeO_6^{4-}

O.S. = +8

Q.39 [20]

$Xe + O_2F_2 \longrightarrow \underset{(A)}{Xe_2F_2} + \underset{(B)}{O_2}$

↓ Hydrolysis

$\underset{(C)}{O_2 + HF + Xe}$

No. of lone pair in XeF_2 : 9 , σ bonds in XeF_2 : 2

No. of lone pair in HF : 3 , σ bond : 1

No. of lone pair in O_2 : 4 , σ bonds in O_2 : 1

Q.40 [4]

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

$$3XeF_4 + 6H_2O \longrightarrow 2Xe + XeO_3 + 12HF + \frac{3}{2}O_2$$

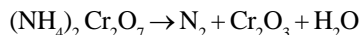$$2XeO_2F_2 + SiO_2 \longrightarrow 2XeO_3 + SiF_4$$

KVPY
PREVIOUS YEAR'S

Q.1 (D)

So, H_3PO_2, H_3PO_3 and H_3PO_4 contains 2,1 and zero P–H bonds.

Q.2 (D)

$$2KBr + Cl_2 \rightarrow 2KCl + Br_2(\text{brown})$$

Q.3 (D)

$$(NH_4)_2Cr_2O7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + 4H_2O$$

Q.4 (C)

$NH_4Cl + KOH \rightarrow KCl + NH_3 + H_2O$ (Acid base reaction)
$AlN + 3H_2O \rightarrow NH_3 + Al(OH)_3$ (Acid base reaction)
$2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2NH_3 + H_2O$
(Acid base reaction)
$NH_4Cl + NaNO_2 \rightarrow NaCl + NH_4NO_2$
(Double decomposition reaction)
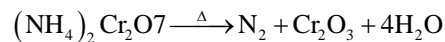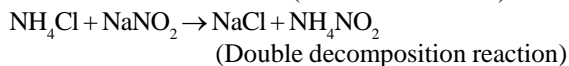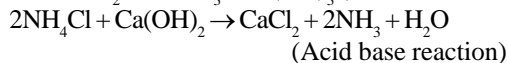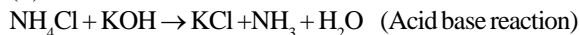
Q.5 (D)
Due to steric hinderance SF_6 is not hydrolysed by H_2O at 25ºC.

Q.6 (D)

$(NH_4)_2Cr_2O_7 \rightarrow N_2 + Cr_2O_3 + H_2O$
$2NaN_3 \rightarrow 2Na + 3N_2$
$NH_4NO_2 \rightarrow N_2 + H_2O$
$(NH_4)_2C_2O_4 \rightarrow 2NH_3 + H_2C_2O_4$
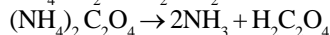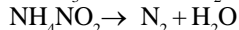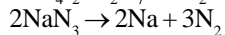
Q.7 (B)
H_3PO_2 is has strong reducing property because of smaller oxidation state = +1 and due to 2 P – H bond

Q.8 (D)

$C + H_2SO_4 \rightarrow CO_2 + SO_2 + H_2O$
$S + H_2SO_4 \rightarrow SO_2 + H_2O$
$P_4 + H_2SO_4 \rightarrow H_3PO_4 + SO_2 + H_2O$

Q.9 (D)

$$(NH_4)_2Cr_2O_7 \rightarrow \underset{+6}{N_2} + \underset{+3}{Cr_2O_3} + 4H_2O$$

+ 6 to + 3

Q.10 (B)

$2NA[BH_4] + I_2 \rightarrow B_2H_6(X) + 2NaI + H_2$
$3B_2H_6 + 6NH_3 \xrightarrow{\Delta} 2B_3N_3H_6(Y) + 12H_2(Z)$
$X = B_2H_6$
$Y = B_3N_3H_6$
$Z = 12 H_2$
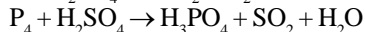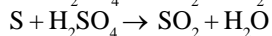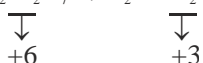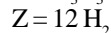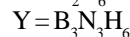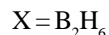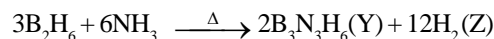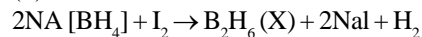
JEE-MAIN
PREVIOUS YEAR'S

Q.1 (3)
Q.2 (2)
Q.3 (3)
Q.4 (2)
Q.5 (1,3)
Q.6 (3)
Q.7 (1)
Q.8 (1)
Q.9 (5)
Q.10 (2)
Q.11 (1)
Q.12 (1)
Q.13 (1)
Q.14 (4)
Q.15 (2)
Q.16 (4)
Q.17 (3)
Q.18 (4)
Stability of oxides of Halogens is
$I > Cl > Br$

Q.19 (3)
(Bonus)
No option contains all species that show disproportionation reaction.

MnO_4^-

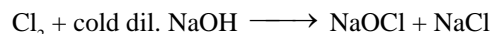Mn is in +7 oxidation state (highest) hence cannot be simultaneously oxidized or reduced.

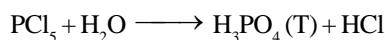**Q.20** (4)
Q.21 (2)

JEE-ADVANCED
PREVIOUS YEAR'S

Q.1 (A)
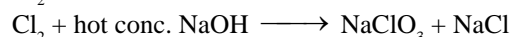
Q.2 (A)
(1 & 2)
Cl_2 + cold dil. NaOH $\longrightarrow$ NaOCl + NaCl
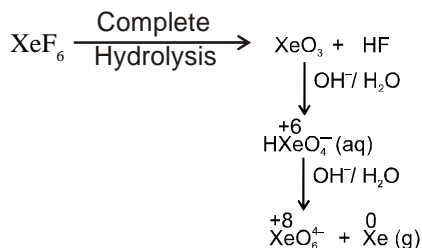Cl_2 + hot conc. NaOH $\longrightarrow$ NaClO_3 + NaCl
NaOCl is salt of hypochlorous acid = P.
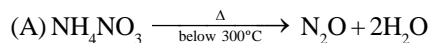$NaOCl_3$ is salt of chloric acid = Q.

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$$Cl_2 + SO_2 \xrightarrow{\text{Charcoal}} SO_2Cl_2 \text{ (R)}$$

$$SO_2Cl_2 + P_4 \longrightarrow PCl_5 \text{ (S)} + SO_2$$

$$PCl_5 + H_2O \longrightarrow H_3PO_4 \text{ (T)} + HCl$$

Q.3 (C)

$$XeF_6 \xrightarrow[\text{Hydrolysis}]{\text{Complete}} XeO_3 + HF$$

$\downarrow OH^-/H_2O$

$\overset{+6}{H}XeO_4^- \text{ (aq)}$

$\downarrow OH^-/H_2O$

$\overset{+8}{Xe}O_6^{4-} + \overset{0}{Xe} \text{ (g)}$

Q.4 (B, C)

(A) $NH_4NO_3 \xrightarrow[\text{below 300°C}]{\Delta} N_2O + 2H_2O$

(B) $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + 4H_2O$

(C) $Ba(N_3)_2 \xrightarrow{\Delta} Ba + 3N_2$

(D) Mg_3N_2 (it does not decompose into N_2)
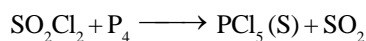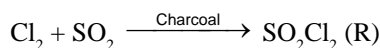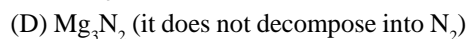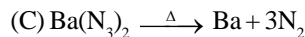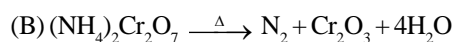
Q.5 (A,B,C)

(A) Bi_2O_5 is metallic oxide but N_2O_5 is non metallic oxide therefore Bi_2O_5 is basic but N_2O_5 is acidic.

(B) In NF_3, N and F are non metals but BiF_3, Bi is metal but F is non metal therefore NF_3 is more covalent than BiF_3.

(C) In PH_3 hydrogen bonding is absent but in NH_3 hydrogen bonding is present therefore PH_3 boils at lower temperature than NH_3.

(D) Due to small size in N–N single bond l.p. – l.p. repulsion is more than P–P single bond therefore N–N single bond is weaker than the P–P single bond.

Q.6 (288.00)

$S_8 + 48HNO_3 \rightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$

1 mole of rhombic sulphur produce 16 mole of H_2O i.e. 288 gm of H_2O

Q.7 (A,B,D)

Hypochlorite ion : $ClO^{\ominus}$
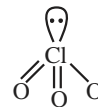
Chlorate ion : $ClO_3^{\ominus}$

Per chlorate ion : $ClO_4^{\ominus}$
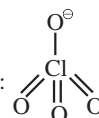
(A) Acidic order : $H\overset{+1}{Cl}O < H\overset{+5}{Cl}O_3 < H\overset{+7}{Cl}O_4$

Conjugate base order : $ClO^- > ClO_3^- > ClO_4^-$

(B) Hypochlorite ion $(ClO^{\ominus})$: $\ddot{\overset{..}{Cl}}-\overset{\ominus}{\ddot{O}}:$ Linear shape
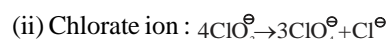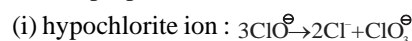
Chlorate ion $(ClO_3^{\ominus})$: Trigonal pyramidal shape

Perchlorate ion $(ClO_4^{\ominus})$: Perfect tetrahedral shape
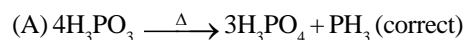
due to resonance

In chlorate ion bond angle changes due to presence of lone pair on chlorine atom. While hypochlorite ion is linear and perchlorate ion is tetrahedral and there is no effect of lone pair on hypochlorite ion.
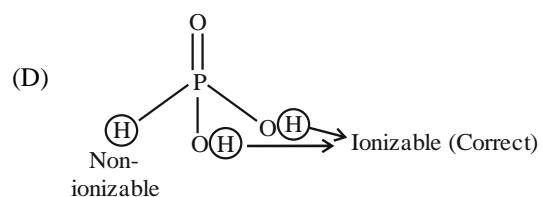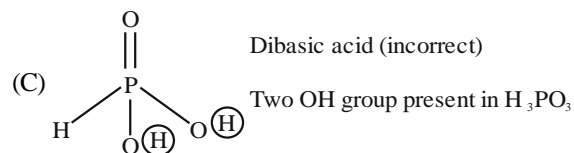
(C) Disproportionation reaction of

(i) hypochlorite ion : $3ClO^{\ominus} \rightarrow 2Cl^- + ClO_3^{\ominus}$

(ii) Chlorate ion : $4ClO_3^{\ominus} \rightarrow 3ClO_4^{\ominus} + Cl^{\ominus}$

(D) $ClO^- + SO_3^{2-} \rightarrow SO_4^{2-} + Cl^{\ominus}$

Q.8 (6)

Q.9 (A, B, D)

(A) $4H_3PO_3 \xrightarrow{\Delta} 3H_3PO_4 + PH_3$ (correct)
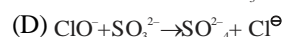
(B) H_3PO_4 has "P" in its highest oxidation state, hence cannot act as a reducing agent (correct)

(C) Dibasic acid (incorrect)

Two OH group present in H_3PO_3

(D) Non-ionizable / Ionizable (Correct)

The hydrogen which is directly attached to phosphorous does not ionized in water.

$\xrightarrow{\text{aq.}}$ $+ 2H^+$
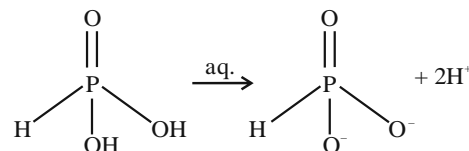
d and f Block Elements

<div align="center">

EXERCISES

</div>

ELEMENTARY

Q.1 (3)

$$3d^5 \qquad 4s^1$$

Cr | 1 | 1 | 1 | 1 | 1 | | 1 |
|---|---|---|---|---|---|---|
| 1 | 1 | 1 | 1 | 1 | | |
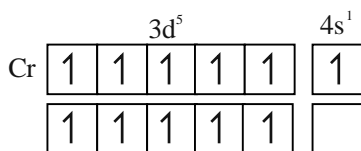
Q.2 (4)
There are 6 electrons in its ultimate and penultimate shell.

Q.3 (4)

Q.4 (1)
$_{30}Zn = [Ar]\, 4s^2\, 3d^{10}$
$Zn^{+2} = [Ar]\, 3d^{10}$ (No. unpaired electron so diamagnetic in nature).

Q.5 (1)

$$\boxed{\mu = \sqrt{n(n+2)}}$$ where n = No. of unpaired electrons

Magnetic moment.

Q.6 (3)
d-block elements; because
(i) Small atomic size
(ii) High nuclear charge
(iii) Presence of vacant d-orbitals.

Q.7 (3)
Cu, because last electron enters d-orbital ($3d^{10}\, 4s^1$).

Q.8 (2)
Cu due to the presence of vacant d-orbital.

Q.9 (3)

Q.10 (4)
Cu^+ do not have any unpaired electron.

Q.11 (1)
Availability of empty d-orbital to accept lone pair of electrons.

Q.12 (3)
Diamagnetism is not a characteristic property of transition metal as they have unpaired electron in d-subshell.

Q.13 (2)

Q.14 (4)
Transition elements act as catalyst as they show variable oxidation state.

Q.15 (1)
In $KMnO_4$, Mn is in +7 oxidation state having no unpaired electrons but posses colour due to charge transfer.

Q.16 (1)
Permanganic Acid $\rightarrow HMnO_4$

Q.17 (2)
Mn is in higher oxidation state of +7 so acidic in nature.

Q.18 (4)
General electronic configuration of lanthanides
$\qquad (n-2)\, f^{1-14}\, (n-1)\, d^{0-1}\, ns^2$
$\Rightarrow (n-2)f^{1-14}\, (n-1)s^2\, p^6\, d^{0-1}\, ns^2$

Q.19 (3)
As the atomic number increases in lanthanides due to very weak sheilding effect, Zeff increases and radius decreases.

Q.20 (3)
Oxidation state of Mn changes from +7 to +2 in acidic medium i.e. one mole of it accepts 5 mole of electrons.

Q.21 (2)
Ag^+ forms a complex ion with NH_3
$AgCl + 2NH_3 \rightarrow [Ag(NH_3)_2]Cl$

Q.22 (1)
MnO is ionic due to lower oxidation state.

Q.23 (1)

Q.24 (1)

Q.25 (4)

**Q.26** (1)

JEE-MAIN
OBJECTIVE QUESTIONS

Q.1 (3)
General electronic configuration of transition elements is [Noble gas] $(n – 1) d^{1–10} ns^{1–2}$.

Q.2 (3)
Along the period the atomic radius decreases with the increase in nuclear charge (as atomic number increases), whereas the shielding effect of d-electrons added in inner orbitals is small.

Q.3 (2)
(1) The order of penetration of the electrons present in different sub-shells of same energy level is s > p > d > f.
(2) The decrease in size is small after mid way. In the begining, the atomic radius decreases with the increase in nuclear charge (as atomic number increases), where as the shielding effect of d-electrons is small. After mid way as the electrons enters the last but one shell, the added d-electron shields the outer most electrons. Hence with the increase in the d-electrons screening effect increases. This counter balances the increased nuclear charge. As a result, the atomic radii remain practically same after chromium.
(3) The filling of 4f before 5d orbital results in a regular decrease in atomic radii called **Lanthanoid contraction** which essentially compensates for the expected increase in atomic size with increasing atomic number. The net result of the lanthanoid contraction is that the second and the third d series exhibit similar radii (e.g., Zr 160 pm, Hf 159 pm).
(4) In transition elements, the atomic volumes are large because the increased nuclear charge is poorly screened and so attracts all the electrons more strongly. In addition, the extra electrons added occupy inner orbitals. Consequently the densities of the transition metals are high. The densities of the second row are high and third row values are even higher because of lanthanoid contraction.

Q.4 (1)
Strong metallic bonds between the atoms of transition elements attribute to their high melting and boiling points. Zinc has all electrons paired ([Ar] $3d^{10} 4s^2$) and thus do not participate in metallic bonding. So accordingly its melting point is least.

Q.5 (2)

Q.6 (3)

20

Energy of ns & (n–1)d have comparable energy so both participates in bonding

Q.7 (2)
The order of shielding effect of various orbital electrons is s > p > d > f. Due to the poor shielding effect of 4f-electrons in 5d-series elements, there is enhanced increase in effective nuclear charge. As a result of this the valence electrons are tightly bound with the nucleus and thus their removal require higher energy.

Q.8 (3)
The lesser number of oxidation states in the begining of series can be due to the presence of smaller number of electrons to lose or share (Sc, Ti). On the other hand, at the extreme right hand side end (Cu, Zn), lesser number of oxidation state is due to large number of d electrons so that only a fewer orbitals are available in which the electron can share with other for higher valence.

Q.9 (1)
Os shows + 8 oxidation state in its compound with oxygen i.e., in OsO_4.

Q.10 (1)
Cr^{3+} is most stable because in aqueous solution it has higher CFSE on account of half filled t^3_{2g} energy level of 3d orbitals in octahedral spliting.

Q.11 (1)
Anode involves oxidation or loss of electron.

Q.12 (4)
(1) Greater the number of valence electrons, stronger is the resultant bonding and thus greater is the enthalpies of atomization.
(2) Cr^+ has half-filled valence shell electron configuration $3d^5$, so it has higher second ionisation energy. Similarly Cu^+ has completely filled stable valence shell electron configuration, $3d^{10}$, so it has higher second ionisation energy.
(3) Sum of first two ionisation energies $(IE_1 + IE_2)$ of Ni(II) is less than that of Pt(II). Similarly sum of first four ionisation energies of Pt(IV) is less than that of Ni(IV).

Q.13 (2)
$_{30}$Zn $[Ar]^{18}$ $3d^{10}$, so n = 0, Fe^{2+} $[Ar]^{18}$ $3d^6$, so n = 4 ; Ni^{2+} $[Ar]^{18}$ $3d^8$, so n = 2 ; Cu^{2+} $[Ar]^{18}$ $3d^9$, so n = 1.

Q.14 (1)
$\mu = \sqrt{n(n+2)}$; $3d^5$ has maximum, 5 unpaired electrons so it will have highest magnetic moment.

Q.15 (3)

$3.87 = \sqrt{n(n+2)}$; n = number of unpaired electrons.

So n = 3.

Q.16 (4)

n ; Cr^{2+} $[Ar]^{18}$ $3d^4$; so n = 4 ; Mn^{2+} $[Ar]^{18}$ $3d^5$ so n = 5 ;

Fe^{2+} $[Ar]^{18}$ $3d^6$ so n = = 4

n = Number of unpaired electron(s).

Q.17 (3)

$\sqrt{15} = \sqrt{n(n+2)}$; n = 3, and three unpaired electrons are found when Mn is in Mn^{4+} i.e., $3d^3$ $4s^0$ configuration as its metal electron configuration is $[Ar]^{18}$ $3d^5$ $4s^2$.

Q.18 (2)

(1) $Cu^+ [Ar]^{18}$ $3d^{10}$, so n = 0 ; Zn^{2+} $[Ar]^{18}$ $3d^{10}$, so n = 0 ; Sc^{3+} $[Ar]^{18}$ $3d^0$, so n = 0

(2) Mn^{2+} $[Ar]^{18}$ $3d^5$, so n = 5 ; Fe^{3+} $[Ar]^{18}$ $3d^5$, so n = 5 ; Ni^{2+} $[Ar]^{18}$ $3d^8$, so n = 2

(3) Cr^{2+} $[Ar]^{18}$ $3d^4$, so n = 4 ; Mn^{3+} $[Ar]^{18}$ $3d^4$, so n = 4 ; Sc^{3+} $[Ar]^{18}$ $3d^0$, so n = 0

(4) Cu^{2+} $[Ar]^{18}$ $3d^9$, so n = 1 ; Ni^{2+} $[Ar]^{18}$ $3d^8$, so n = 2; Ti^{4+} $[Ar]^{18}$ $3d^0$, so n = 0

Q.19 (3)

The colour of the compounds of transition metals may be attributed to the presence of incomplete (n – 1) d-sub-shell. Under the influence of approaching ions towards the central metal ion, the d-orbitals of the central metal split into different energy levels. This phenomenon is called **crystal field splitting**. In the case of the transition metal ions, the electron can be easily promoted from one energy level to another in the same d-sub-shell. These are called **d-d transitions**. The amount of energy required to excite some of the electrons to higher energy states within the same d-sub-shell corresponds to energy of certain colours of visible light. Therefore, when white light falls on a transition metal compound, some of its energy corresponding to a certain colour, is absorbed and the electron gets raised from lower energy set of orbitals to higher energy set of orbitals.

Q.20 (1)

Complex pormation α (Zeff = Z – σ) tendency

Q.21 (2)

Fully pilled d-subshell

$Zn \rightarrow Zn^{2+} + 2e^-$

$3d^{10}4s^2$ $3d^{10}$

Q.22 (2)

$HgCl_2$ is volatile is reffered as corrosive sublimate.

Q.23 (1)

Mo is used become of its high melting point.

Q.24 (1)

Mn^{2+} acts as autocatalyst

Q.25 (2)

Q.26 (4)

In Ti^{4+}, Cu^+ and Zn^{2+}, all have electrons paired so all are diamagnetic. Cr^{3+} with electron configuration $[Ar]^{18}$ $3d^3$ has three unpaired electrons. So it undergoes d-d transition of electrons in presence of ligands according to CFT and thus it is coloured.

Q.27 (3)

As there is no unpaired electron in Mn(VII) – $[Ar]^{18}$ $3d^0$; so d-d transition of electrons does not take place. The colour is due to charge transfer spectrum from O^{2-} to empty d-orbitals of Mn(VII).

Q.28 (3)

$2CrO_4^{2-}$ (yellow) $+ 2H^+ \longrightarrow Cr_2O_7^{2-}$ (organge) $+ H_2O$.

Q.29 (1)

$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$

$5SO_3^{2-} + 2MnO_4^- + 6H^+ \rightarrow 2Mn^{2+} + 3H_2O + 5SO_4^{2-}$

Q.30 (1)

$2CrO_4^{2-} + H^+ \rightleftharpoons Cr_2O_7^{2-} + {}^-OH$

yellow   Orange

Q.31 (2)

$CrO_3 + NaOH \rightarrow Na_2CrO_4 + H_2O$

ruby solid

Q.32 (2)

MnO_4^- has purple colour due to change transfer

$Mn^{7+}, O^{2-} \underset{CTML}{\overset{CTLM}{\rightleftharpoons}} Mn^{6+}, O^-$

Q.33 (2)

Mn_2O_7 is an acid anhydride of $HMnO_4$ and thus MnO_4^- is oxo-salt of Mn_2O_7.

$Mn_2O_7 + H_2O \longrightarrow 2HMnO_4$;

$2HMnO_4 + 2KOH \longrightarrow 2KMnO_4 + 2H_2O$.

Q.34 (1)
$KMnO_4$ acts as self indicator.

Q.35 (1)
$H_2CrO_4 + H_2O_2 \rightarrow CrO_5 + H_2O$
chromic   acid
Blue   Blue in ether.
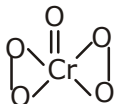
Q.36 (2)
$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$ (weak alkaline medium).

Q.37 (2)
(1) $2MnO_4^- + 16H^+ + 10Cl^- \longrightarrow 2Mn^{2+} + 8H_2O + 5Cl_2$
(2) Chromyl chloride test ; $Cr_2O_7^{2-} + 4Cl^- + 6H^+ \longrightarrow$
$2CrO_2Cl_2 \uparrow$ (deep red) $+ 3H_2O$
(3) $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$
(4) $2Cl^- + F_2 \longrightarrow Cl_2 + 2F^-$

Q.38 (1)
$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O.$

Q.39 (3)
$4FeO. Cr_2O_3$ (chromite ore) $+ 8Na_2CO_3 + 7O_2$
$\xrightarrow{\text{Roasting in air}} 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$
$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$;
$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$

Q.40 (1)
$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + H_2O + Cr_2O_3$
      (green)

Q.41 (1)
$2KMnO_4 + 3H_2SO_4 \longrightarrow 2KHSO_4 + (MnO_3)_2SO_4 + 2H_2O$
$(MnO_3)_2SO_4 + H_2O \longrightarrow Mn_2O_7 + H_2SO_4$

Q.42 (4)
$4FeSO_4 + 2H_2O + O_2 \longrightarrow 4Fe(OH).SO_4$ (basic ferric sulphate)

Q.43 (3)
Cold dilute alkaline $KMnO_4$ is Bayer's neagent.

Q.44 (1)
(A) Cr^{2+} is reducing as it involves change from d^4 to d^3, the latter is more stable configuration (t^3_{2g}) Mn(III) to Mn(II) is from $3d^4$ to $3d^5$ again $3d^5$ is an extra stable configuration.
(B) Due to higher CFSE of d^6 configuration in presence of ligands which more than compensates the 3rd IE.
(C) The hydration or lattice energy more than compensates the ionisation enthalpy involved in removing electron from d^1.

Q.45 (3)
Cu^{2+} ion ($3d^9$) absorbs red light from the visible region, for the promotion of 3d electrons, the ions reflect blue light and appear blue.

Q.46 (4)
Ni^{2+} , Fe^{2+} and Cu^{2+} has 2, 4 and 1 unpaired electrons respectively. So in presence of ligands d-d transition takes place and these hydrated ions produce colour in aqueous solutions. Cu^+ is diamagnetic with $3d^{10}$ configuration; so no d-d transition is possible and thus colourless.

Q.47 (2)
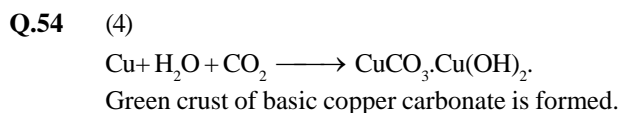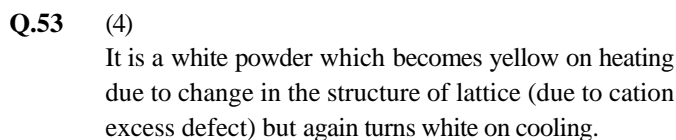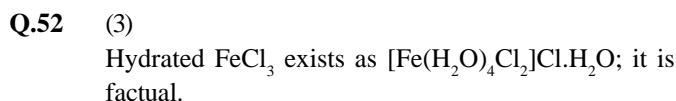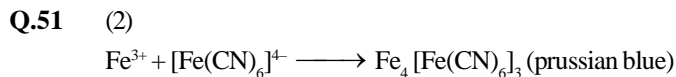MO is catalytic promoter & it improves catalytic properties as catalyst.

Q.48 (4)
The catalytic property of transition metals is due to their tendency to form reaction intermediates with suitable reactants. These intermediates give reaction paths of lower activation energy and, therefore, increase the rate of the reaction.
These reaction intermediates readily decompose yielding the products and regenerating the original substance. The transition metals form these reaction intermediates due to the presence of vacant orbitals or their tendency to form variable oxidation states.
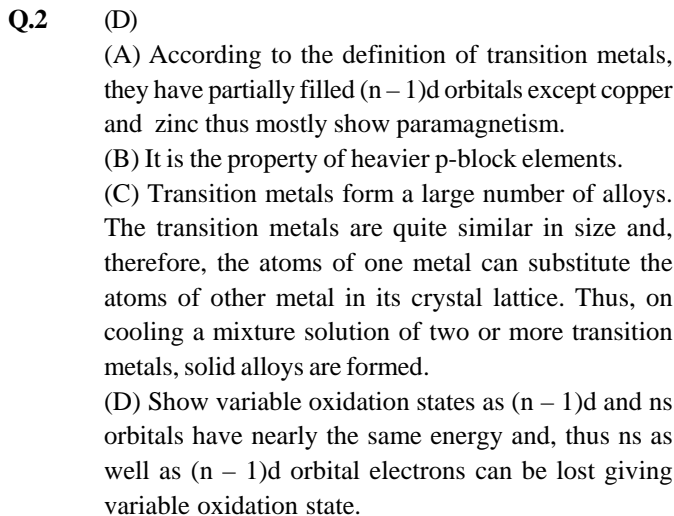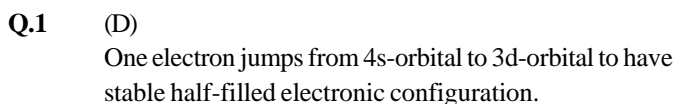
Q.49 (4)
The transition metals form a large number of interstitial compounds in which small atoms like hydrogen, carbon, boron and nitrogen occupy interstitial sites in their lattices

Q.50 (4)
(A) This activity is ascribed to their ability to adopt multiple oxidation state and to form complexes.
(B) Because of having larger number of unpaired electrons in their atoms, they have stronger interatomic interaction and hence stronger bonding between the atoms.

(C) Transition metals like Fe, Co, Ni, Cu etc. form interstitial compounds with elements such as hydrogen, boron, carbon and nitrogen. The small atoms of these non-metallic elements (H, B, C, N, etc.) get trapped in vacant spaces of the lattices of the transition metal atoms.

Q.51 (2)

$Fe^{3+} + [Fe(CN)_6]^{4-} \longrightarrow Fe_4[Fe(CN)_6]_3$ (prussian blue)

Q.52 (3)

Hydrated $FeCl_3$ exists as $[Fe(H_2O)_4Cl_2]Cl.H_2O$; it is factual.

Q.53 (4)

It is a white powder which becomes yellow on heating due to change in the structure of lattice (due to cation excess defect) but again turns white on cooling.

Q.54 (4)

$Cu + H_2O + CO_2 \longrightarrow CuCO_3.Cu(OH)_2.$
Green crust of basic copper carbonate is formed.

Q.55 (2)

$CuSO_4 + KI \rightarrow Cu_2I_2 + I_2\uparrow + K_2SO_4$
$CuSO_4 + dilH_2SO_4 \rightarrow [Cu(H_2O)_4]SO_4$

Q.56 (4)

Mixture of $CuSO_4$ and lime is called Bordeaux mixture which is used as fungicides.

Q.57 (4)

Dissolves in both ether and water forming solvated/hydrated monomeric species,

$[Fe(H_2O)_4Cl_2]Cl.2H_2O$
    solvated $FeCl_3$
    hydrated $FeCl_3$

Q.58 (4)

Cu, Ag, Au, are coinage metal used in coin in older days.

Q.59 (2)

$5AgNO_3 + 3I_2 (excess) + 3H_2O \longrightarrow HIO_3 + 5AgI + 5HNO_3.$

Q.60 (2)

Q.61 (1)

100% – 24 carat

$1\% = \dfrac{24}{100}$

$75\% = \dfrac{24}{100} \times 75 = 18$

Q.62 (2)

$ZnCl_2 . 2H_2O \xrightarrow{\Delta} Zn(OH)Cl + HCl + H_2O.$

Q.63 (4)

$Ag^+ + 2S_2O_3^{2-} \longrightarrow [Ag(S_2O_3)_2]^{3-}$

Q.64 (1)

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OBJECTIVE QUESTIONS

Q.1 (D)

One electron jumps from 4s-orbital to 3d-orbital to have stable half-filled electronic configuration.

Q.2 (D)

(A) According to the definition of transition metals, they have partially filled (n – 1)d orbitals except copper and zinc thus mostly show paramagnetism.
(B) It is the property of heavier p-block elements.
(C) Transition metals form a large number of alloys. The transition metals are quite similar in size and, therefore, the atoms of one metal can substitute the atoms of other metal in its crystal lattice. Thus, on cooling a mixture solution of two or more transition metals, solid alloys are formed.
(D) Show variable oxidation states as (n – 1)d and ns orbitals have nearly the same energy and, thus ns as well as (n – 1)d orbital electrons can be lost giving variable oxidation state.

Q.3 (B)

After mid way i.e. after Cr as the electrons enters the last but one shell, the added d-electron shields the outer most electrons. Hence with the increase in the d-electrons screening effect increases. This counter balances the increased nuclear charge. As a result, the atomic radii remain practically same after chromium.

Q.4 (D)

The atomic radii of the transition metals lie in-between those of s- and p-block elements. In the begining, the atomic radius decreases with the increase in nuclear charge (as atomic number increases), whereas the shielding effect of d-electrons is small and orbital electrons are added to the penultimate d–subshell rather than to the outer shell of the atom.

Q.5 (A)

This phenomenon is associated with the intervention of the 4f orbitals which must be filled before the 5d series of elements begin. The filling of 4f before 5d orbital results in a regular decrease in atomic radii called **Lanthanoid contraction.** This is because of poor shielding of one of the 4 f-electrons by another in the sub-shell.

Q.6 (C)

(A) = 8.95   (B) = 8.91
(C) = 3.0   (D) = 7.14.

Across the period atomic volumes decreases upto copper due poor shielding of d-orbital electrons and addition of extra electrons in inner orbitals and then increases in zinc due to interelectronic repulsions in completely filled d- and s-orbitals. Consequently densities increase from Sc to Cu and then decreases in Zn.

Q.7 (A)

Valence shell electron configuration of $_{30}Zn^{2+}$ is $3d^{10}$ $4s^o$. As there is no unpaired electrons for d–d transition, the solution of ions will be colourless.

Valence shell electron configuration of $_{28}Ni^{2+}$ is $3d^8$ $4s^o$. As there are 2 unpaired electrons, there is d–d transition of electron, so the solution of ions will be coloured.

Valence shell electron configuration of $_{24}Cr^{3+}$ is $3d^3$ $4s^o$. As there are 3 unpaired electrons, there is d–d transition of electron, so the solution of ions will be coloured.

Q.8 (A)

(A) Zn^{+2} has $3d^{10}$ configuration so it is more stable than Zn^{+3} ($3d^9$).

Q.9 (A)

It is an amphoteric in nature and it reacts with alkalies as well as with acids to give $V_4O_9^{2-}$ and VO^{2+} respectively.

Q.10 (A)

Electron configuration of Mn is $[Ar]^{18}$ $3d^5$ $4s^2$ and thus it contains five unpaired electrons. Hence it can show the highest oxidation state equal to $+7$.

Q.11 (A)

$Cr^{3+} + e^- \longrightarrow Cr^{2+}$, $E^\Theta = -0.41$ volts and

$Mn^{3+} + e^- \longrightarrow Mn^{2+}$, $E^\Theta = +1.51$ volts

This shows that Cr^{2+} is unstable and has a tendency to acquire more stable Cr^{3+} state by acting as a reducing agent. On the other hand Mn^{3+} is unstable and is reduced to more stable Mn^{2+} state.

Q.12 (C)

(A) Valence shell electron configuration of V^{3+} is $[Ar]^{18}$ $3d^2$; so n = 2
(B) Valence shell electron configuration of Cr^{3+} is $[Ar]^{18}$ $3d^3$; so n = 3
(C) Valence shell electron configuration of Fe^{3+} is $[Ar]^{18}$ $3d^5$; so n = 5
(D) Valence shell electron configuration of Co^{3+} is $[Ar]^{18}$ $3d^6$; so n = 4

Q.13 (B)

(A) $MnSO_4.4H_2O$; valence shell electron configuration of Mn^{2+} is $[Ar]^{18}$ $3d^5$; so n = 5
(B) $CuSO_4.5H_2O$; valence shell electron configuration of Cu^{2+} is $[Ar]^{18}$ $3d^9$; so n = 1
(C) $FeSO_4.6H_2O$; valence shell electron configuraiton of Fe^{2+} is $[Ar]^{18}$ $3d^6$; so n = 4
(D) $NiSO_4.6H_2O$; valence shell electron configuration of Ni^{2+} is $[Ar]^{18}$ $3d^8$; so n = 2

Paramagnetism increases with increasing number of unpaired electrons. Thus Cu^{2+} has lowest degree of paramagnetism.

Q.14 (D)

(A) Valence shell electron configuration of Cu^+ is $[Ar]^{18}$ $3d^{10}$; so n = 0
(B) Valence shell electron configuration of Zn^{2+} is $[Ar]^{18}$ $3d^{10}$; so n = 0
(C) Valence shell electron configuration of Sc^{3+} is $[Ar]^{18}$ $3d^0$; so n = 0
(D) Valence shell electron configuration of V^{4+} is $[Ar]^{18}$ $3d^1$; so n = 1

As V^{4+} has one unpaired electron and so in presence of water as ligand it will undergo d-d transition of

electron. Hence V^{4+} ions will produce colour in the solution.

Q.15 (B)

(B) In CuF_2 the valence shell electron configuration of Cu^{2+} is $3d^9$ and thus it has one unpaired electron. So d-d transition possible and compound is coloured in aqueous solution.

Q.16 (C)

(I) Show variable oxidation states as $(n-1)d$ and ns orbitals have nearly the same energy and, thus ns as well as $(n-1)d$ orbital electrons can be lost giving variable oxidation state.

(II) Colour of the compounds may be attributed to the incomplete $(n-1)d$ subshell which may involved in d-d transition of electrons in presence of ligands.

(III) They have low volatility because of high enthalpies of atomization on account of strong metallic bonding.

Q.17 (C)

Zn^{2+}, Li^+, K^+ and Al^{3+} are diamagnetic and, therefore, do not have unpaired electrons. So compounds containing these ions are colourless. But Co^{2+} contains three unpaired electrons and, therefore, d-d transition of electrons takes place and thus its compound is coloured.

Q.18 (B)

(A) Associated with d-d transition of electron.

(B) The transition metals form the reaction intermediates due to the presence of vacant orbitals or their tendency to form variable oxidation states.

(C) Associated with the number of unpaired electrons participating in metallic bonding.

(D) As $\mu = \sqrt{n(n+2)}$, so it is associated with number of unpaired electron.

Q.19 (A)

(I) $[Cr(H_2O)_6]Cl_3$, $x + 6(0) = +3$; so $x = +3$

(II) CrO_5,

; so $x = +6$
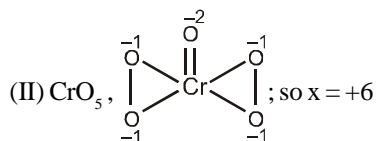
(III) $K_3[CrO_8]^{3-}$ or $[Cr(O_2)_4]^{3-}$, here ligand is peroxo i.e. O_2^{2-} ; $x + 4(-2) = -3$; so $x = +5$.

(IV) $(NH_3)_3CrO_4$ or $[Cr(O_2)_2]$, here ligand is peroxo i.e. O_2^{2-} ; $x + 2(-2) = 0$; so $x = +4$.

Q.20 (C)

(A) In $Cr_2O_7^{2-}$, the valence shell electron configuration of $Cr(VI)$ is $3d^0$. Thus $Cr(VI)$ is diamagnetic but coloured due to the charge transfer spectrum.

(B) In $(NH_4)_2$ $[TiCl_6]$, the valence shell electron configuration of $Ti(IV)$ is $3d^0$. Thus $Ti(IV)$ is diamagnetic and colourless.

(C) In $VOSO_4$, the valence shell electron configuration of $V(IV)$ is $3d^1$. Thus $V(IV)$ is paramagnetic and blue coloured due to d-d transition.

(D) In $K_3[Cu(CN)_4]$, the valence shell electron configuration of $Cu(I)$ is $3d^{10}$. Thus $Cu(I)$ is diamagnetic and colourless.

Q.21 (A)

$3MnO_4^{2-} + 2H_2O \longrightarrow 2MnO_4^- + MnO_2 + 4OH^-.$

Q.22 (C)

$Cr_2O_7^{2-} + 2H^+ + 4H_2O_2 \longrightarrow 2CrO(O_2)_2$ (blue coloured) $+ 5H_2O.$

Q.23 (A)

$2MnO_4^- + 5SO_3^{2-} + 6H^+ \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O.$

$\therefore \dfrac{2}{5}$ mole of MnO_4^- for one mole SO_3^{2-}.

Q.24 (B)

$(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O.$

green coloured powder blown in air is Cr_2O_3 .

Q.25 (A)

$6KMnO_4 + 10FeC_2O_4 + 24H_2SO_4 \longrightarrow 3K_2SO_4 + 6MnSO_4 + 5Fe_2(SO_4)_3 + 20CO_2 + 24H_2O.$
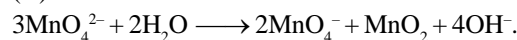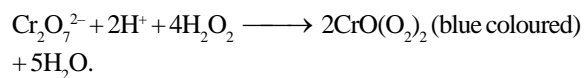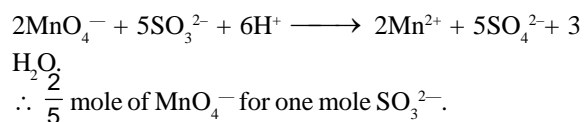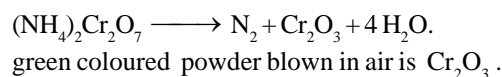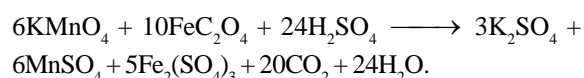
$\therefore \dfrac{3}{5}$ mole of $KMnO_4$ for one mole ferrous oxalate.

Q.26 (B)

(A) Coloured due to charge transfer from ligand to metal ion.

(B) Valence shell electron configuration of $Cu(I)$ is $3d^{10}$ and, therefore, all electrons are paired ; Valence shell electron configuration of $Cu(II)$ is $3d^9$ and, therefore, one electron is unpaired.

(C) CrO_3 is an acid anhydride of chromic acid.

(D) Valence shell electron configuration of Ti^{3+} is $3d^1$ and, therefore, has one unpaired electron; so it is coloured. But valence shell electron configuration of Sc^{3+} is $3d^0$ and, therefore, it has no unpaired electron; so it is colourless.

25

Q.27 (A)

(A) $Na_2Cr_2O_7$ is not used as primary standard because it is hygroscopic in nature.

(B) $2KMnO_4 + 3H_2SO_4 \longrightarrow 2KHSO_4 + (MnO_3)_2SO_4 + 2H_2O$

$(MnO_3)_2SO_4 + H_2O \longrightarrow Mn_2O_7 + H_2SO_4$

(C) $PH_3 + 6AgNO_3 + 3H_2O \longrightarrow 6Ag + 6HNO_3 + H_3PO_3$

$AsH_3 + 6AgNO_3 + 3H_2O \longrightarrow 6Ag + 6HNO_3 + H_3AsO_3$

(D) $3FeS_2 + 2H_2O + 11O_2 \longrightarrow 2FeSO_4 + Fe_2(SO_4)_3 + 2H_2SO_4$

Q.28 (C)

$Fe_2(SO_4)_3 \longrightarrow Fe_2O_3 + 3SO_3.$
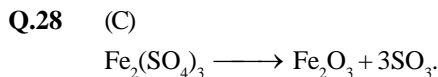
Q.29 (C)

(A), (B) and (D) given hydrated $FeCl_3$ and (C) yields anhydrous $FeCl_3$ according to the reaction,

$2Fe + 3Cl_2 \xrightarrow{\Delta} 2FeCl_3$ (anhydrous).

Q.30 (D)

$2FeCl_3 \longrightarrow$

(gas)
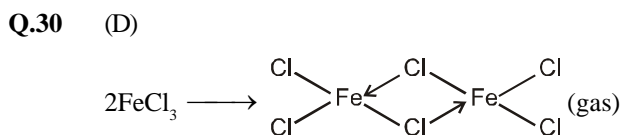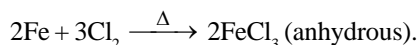
Q.31 (D)

HNO_3 being strong oxidising agent oxidises iron to its oxides (Fe_3O_4) which forms a thin protective layer over the metal. This makes the iron passive.

Q.32 (A)

Cu(I) thiocyanate is used for the gravimetric estimation of Cu(II).

Q.33 (A)

$2CuCl_2 + SO_2 + 2H_2O \longrightarrow Cu_2Cl_2 + 2HCl + H_2SO_4.$
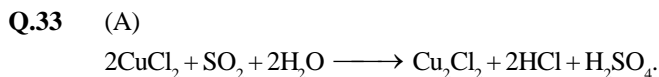
Q.34 (D)

It is factual.

Q.35 (C)

Zn has great tendency to oxidise to Zn^{2+} because of the negative value of SRP. So it is taken as anode in electro-chemical cell.

Q.36 (A)

German silver contains Cu = 60% ; Zn = 20% ; and Ni = 20%.

Q.37 (A)

Mixture of anhydrous zinc chloride and concentrated HCl is called Lucas reagent. It is used for the distinction between primary, secondary and tertiary alcohols.

Q.38 (B)

$Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2$
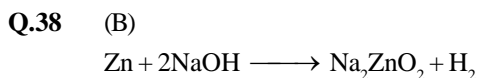
Q.39 (C)

$Ag^+ + 2S_2O_3^{2-} \longrightarrow [Ag(S_2O_3)_2]^{3-}$; soluble complex is formed.

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MCQ/COMPREHENSION/COLUMN MATCHING

Q.1 (ABC)

Q.2 (AB)

This ion Mc aorther forrest cyanide process used for Ag, Au (Refer metallurgy)

Q.3 (BC)

Covalent character α polarisity power α charge

Q.4 (ABC)

(A) The great tendency of transition metal ions to form complexes is due to : (i) small size of the atoms and ions, (ii) high nuclear charge and (iii) availability of vacant d-orbitals of suitable energy to accept lone pairs of electrons donated by ligands.
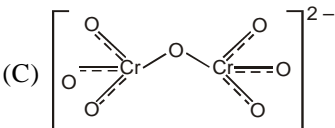
(B) The existence of the transition elements in different oxidation states is due to the participation of inner (n – 1) d-electrons in addition to outer ns-electrons because, the energies of the ns and (n – 1) d-sub-shells are nearly same.

(C) The transition metals show magnetic properties due to presence of number of unpaired electrons in d-orbitals.

(D) Most the transition metal ions are coloured, because they have unpaired electrons which can undergo d-d- transition in presence of ligands.

Q.5 (AB)

+2	+4	+8/3	+7
MnO	MnO_2	Mn_3O_4	Mn_2O_7
Basic oxide	amphoteric oxide		acidic oxide

Q.6 (AB)

Zr & Hf have same atomic sizes as in Hf weak shielding of both d & f electron contracts its size & make it comparable with Zr

Q.7 (ABC)

$K_2SO_4 .Al_2(SO_4)_3.24\ H_2O + H_2O$

potash alum $\rightarrow K^+_{aq.} + Al^{3+}_{aq.} + SO_4^{2-}$

Q.8 (ABC)

The great tendency of transition metal ions to form complexes is due to : (i) small size of the atoms and ions, (ii) high nuclear charge and (iii) availability of vacant d-orbitals of suitable energy to accept lone pairs of electrons donated by ligands.

Q.9 (ABD)

$4\ Cl^- + Cr_2O_7^{2-} + 6H^+ \longrightarrow 2CrO_2\ Cl_2 \uparrow$ (deep red) + $3H_2O$

$CrO_2Cl_2 + 4OH^- \longrightarrow CrO_4^{2-}$ (yellow) $+ 2H_2O + 2Cl^-$

$CrO_2Cl_2 + H_2O \longrightarrow H_2CrO_4 + HCl$

Q.10 (BCD)

Interstitial compound results in
(A) hardness increses
(B) Malleability (decreases)
(C) Ductality (decreases)

Q.11 (AB)

Weak metallic bond as due to poor shielding of d & f orbital its ionisation energy became high & kernel formation becomes difficult.

Q.12 (ABC)

All statements are comeet
$[Ni(CO)_4], [Fe(CO)_5]\ [Cr(CO)_5]$

Q.13 (AB)

Ionisation energies are between s & p-block.

Q.14 (ABD)

O.S. different by 1 unit

Q.15 (ABC)

oxide of Be, Al, Zn, Cr, Pb, Sn, As, are amphoteric

Q.16 (ABC)

Transition element froms intershtial compound.

Q.17 (ABCD)

(A) $2Ag^+ + S_2O_8^{2-} \longrightarrow 2Ag^{2+} + 2SO_4^{2-}$

$Ag^{2+} + 4py \longrightarrow [Ag(py)_4]^{2+}$ (red).

(B) $3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$.

(C) $\left[\begin{array}{c} O \\ \Vert \\ O=Cr-O-Cr=O \\ \vert \qquad \vert \\ O \qquad O \end{array} \right]^{2-}$

(D) Ti^{2+} has two unpaired electrons; So d-d transition is possible while Ti^{4+} has no electrons in d-orbitals.

Q.18 (AB)

(A) and (B) reactions separately comprise the iodometric titration.

Q.19 (ABD)

(A) The colour of the transition metal ions / compounds is attributed to d-d transition of electrons e.g. in $[Cu(NH_3)_4]^{2+}$.
(B) Charge transfer spectrum e.g. in MnO_4^- (no d electrons present).
(C) The colour change is not because of change in the geometry of the molecules.
(D) Yellow colour of the AgI is due to the polarisation of I^- by Ag^+.

Q.20 (AC)

$Cr_2O_7^{2-} + O_2^{2-} \rightarrow CrO_5 + O^{2-}$
blue
$CrO_5 + H^+ \rightarrow Cr^{3+} + O_2$
Green

Q.21 (ABC)

(A) $2MnO_4^- + 5SO_2 + 2H_2O \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+$
(B) $2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 5O_2 + 2Mn^{2+} + 8H_2O$
(C) $5Fe^{2+} + 5MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

Q.22 (AB)

$2\ MnO_2 + 4KOH + O_2(KNO_3) \longrightarrow 2K_2MnO_4 + 2H_2O$.

$MnO_4^{2-} \xrightarrow[\text{oxidation}]{\text{electrolytic}} MnO_4^- + e^-$.

Q.23 (ABC)

$(NH_4)_2Cr_2O_7 \xrightarrow{\ \Delta\ } Cr_2O_3 + N_2 + H_2O$
exothermic reaction
(volcanic reaction)

Q.24 (ABC)

(A) Acidified $K_2Cr_2O_7$ solution reacts with H_2O_2 to give a deep blue solution due to the formation of CrO_5.
$Cr_2O_7^{2-} + 2H^+ + 4H_2O_2 \longrightarrow 2CrO_5 + 5H_2O$
(B) In alkaline medium with 30% H_2O_2, a red-brown K_3CrO_8 (diperoxo) is formed. It is tetra peroxo species $[Cr(O_2)_4]^{3-}$ and thus the Cr is in +V oxidation state.
(C) In ammoniacal solution a dark red-brown compound, $(NH_3)_3CrO_4$ - diperoxo compound with Cr(IV) is formed.
(D) In CrO_4^{2-} the Cr is in its highest +6 oxidation state. So it can not be further oxidised.

Q.25 (AB)

(A) $CO_2 + H_2O \longrightarrow H_2CO_3 \longrightarrow 2H^+ + CO_3^{2-}$
$CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$
(B) $3K_2MnO_4 + 2CO_2 \longrightarrow 2KMnO_4 + MnO_2 + 2K_2CO_3$.
(C) No colour change.
(D) No colour change.

27

Q.26 (BC)

Q.27 (AB)

F^- has low polarisbility & hence CuF is ion but Br^- & Cl^- ion has high polarisibity & $CuCl_2$ & $CuBr_2$ are ionic in nature.

Q.28 (ABCD)

$$Cu(SO_4) + NH_3 \longrightarrow [Cu(NH_3)_4]SO_4$$

dsp^2 1 unpaired electron

Q.29 (AD)

(A) Anhydrous ; (B) Hydrated ; (C) Hydrated ; (D) Anhydrous

Q.30 (AB)

Fe, Pt Refer metallurgy

Q.31 (AD)

Quinol is acting as an acid as it is donating H^+ ions and also as a reducing agent due as it reduces Ag^+ to Ag

Q.32 (AB)

(A) $6AgNO_3 + 3I_2 (excess) + 3H_2O \longrightarrow HIO_3 + 5AgI + 5HNO_3$

(B) $AgNO_3 (excess) + KCN \longrightarrow AgCN(white) + KNO_3$.

Q.33 (AB)

(A) Used in developing of photography plate. i.e. to reduce Ag^+ to $Ag\downarrow$.

(B) Fixing of photography plate i.e. to remove unreduced AgBr.

(C) & (D) reactions are not involved in photography.

Q.34 (ABC)

(A) $PH_3 + 6AgNO_3 + 3H_2O \longrightarrow 6Ag + 6HNO_3 + H_3PO_3$

(B) It possesses powerful corrosive action on organic tissues, which it turns black especially in presence of light. The blackening is due to finely divided metallic silver, reduced by organic tissue.

(C) $AgCN (s) + CN^- (aq) \longrightarrow [Ag(CN)_2]^-$ (soluble complex).

(D) Zr is the element of the 4d series 4th group while Ta is a element of 5d series 5th group so have differ atomic sizes.

Q.35 (C)

$\mu = 1.73$ indicates that the titanium ion has one unpaired electron. The valence shell electron configuration of titanium is $[Ar]^{18} 3d^2 4s^2$. So it will lose three electrons to have one unpaired electron and thus the oxidation state of titanium is +3.

Q.36 (C)

(A) In VCl_3, the vanadium(III) has valence shell electron configuration $3d^2$. So its aqueous solution will be coloured due to d-d-transition of electron.

(B) In $VOSO_4$, the vanadium(IV) has valence shell electron configuration $3d^1$. So its aqueous solution will be coloured due to d-d-transition of electron.

(C) In Na_3VO_4, the vanadium(V) has valence shell electron configuration $3d^0$. So its aqueous solution will be colourless as there will be no d-d-transition.

(D) In $[V(H_2O)_5SO_4]2H_2O$, the vanadium(II) has valence shell electron configuration $3d^3$. So its aqueous solution will be coloured due to d-d-transition of electron.

Q.37 (D)

(A) Mn^{2+} has five unpaired electrons in 3d-sub shell as its valence shell configuration is $3d^5$. (B) It is a obvious fact (C) Number of unpaired electrons first increases from one(Sc) to five(Mn) and then pairing from(Fe) begins so number of unpaired electrons decreases. As a consequence, the paramagnetism first increases and then decreases.

Q.38 (D)

(A) $2MnO_4^- + 2NH_3 \longrightarrow 2MnO_2 + N_2 + 2OH^- + 2H_2O$

(B) It is due to charge transfer from O^{2-} to empty d-orbital of Mn(VII).

(C) MnO_4^- is in highest oxidation state i.e. +VII and thus can not be oxidised further.

(D) $MnO_2 + OH \longrightarrow MnO_2^{2-} \xrightarrow{[e^-]} MnO_4^-$

Q.39 (A)

(A) In $MnSO_4, = +II$; (B) $MnO_4^{2-} = +VI$; (C) $MnO_4^- = +VII$

Q.40 (D)

(III) Electron configuration of Mn(VI) in MnO_4^{2-} is $[Ar]^{18} 3d^1$. So it is paramagnetic and tetrahedral. Electron configuration of Mn(VII) in MnO_4^- is $[Ar]^{18} 3d^0$. So it is diamagnetic and tetrahedral.

(IV) $3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$.

(Solution : 52 to 54)

$A = MnSO_4$, $B = K_2MnO_4$, $C = KMnO_4$, $D = MnO_2$, $E = HMnO_4$, $F = BaSO_4$.

$MnSO_4(A) + 2KNO_3 + K_2CO_3 \longrightarrow K_2MnO_4(B) + 2KNO_2 + 2CO_2 + K_2SO_4$

$2MnO_4^{2-} + 4H^+ \longrightarrow MnO_4^- (C) + MnO_2 + 2H_2O$.

$Mn^{2+} + 2OH^- \longrightarrow Mn(OH)_2\downarrow$; $Mn(OH)_2 + Br_2 + 2NaOH \longrightarrow MnO_2(D) + 2NaBr + 2H_2O$

$MnO_2 + 4HNO_3 \longrightarrow 2Mn(NO_3)_2 + 2H_2O + O_2$

$Mn(NO_3)_2 + 5PbO_2 + 6HNO_3 \longrightarrow 2HMnO_4(E) + 5Pb(NO_3)_2 + 2H_2O$

$SO_4^{2-} + Ba^{2+} \longrightarrow BaSO_4\downarrow$ (white) (F)

Q.41 (A) - q, s ; (B) - r, s ; (C) - p, s ; (D) - p, s

(A) $3 \overset{+6}{Mn}O_4^{2-} + 2CO_2 \longrightarrow 2 \overset{+7}{Mn}O_4^{-} + \overset{+4}{Mn}O_2 + 2CO_3^{2-}$
. The nature of the reaction is thus disproportionation and in the product, MnO_4^{-}, Mn showed the highest oxidation state of +7.

(B) $2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$
The nature of the reaction is redox only and in the product, CrO_4^{2-}, Cr showed the highest oxidation state

of + 6. O$=$Cr$-$O$-$Cr$=$O (structure) $^{2-}$; hence,
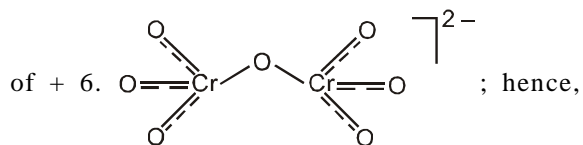
$Cr_2O_7^{2-}$ has dimeric bridged tetrahedral metal ion.

(C) $2FeSO_4 \longrightarrow Fe_2O_3 + SO_2 + SO_3$. SO_2 and SO_3 are pungent smelling colourless gases. In SO_3, the sulphur is present in its highest oxidation state of + 6.

(D) $\overset{2+}{Cu}Cl_2.2H_2O \longrightarrow \overset{2+}{Cu}O + \overset{1+}{Cu_2}Cl_2 + 2HCl + Cl_2 +$
$5H_2O$. HCl and Cl_2 are pungent smelling gases. In CuO, Cu is present in its highest oxidation state of +2.

Q.42 (A) - s ; (B) - q, r ; (C) - q ; (D) - p
(A) Cu(I) and Zn (II) have valence shell electron configuration $3d^{10}$; all electrons are paired so the complexes are diamagnetic and colourless.
(B) Mn(+7) and Cr(+6) have valence shell electron configuration $3d^0$. There is no electron in d-orbitals but they are coloured due to charge transfer spectrum. Mn and Cr showed their highest oxidation state of +7 and +6 respectively.
(C) Cu(I) and Hg (II) have valence shell electron configuration $3d^{10}$; all electrons are paired so the compound are diamagnetic but they are coloured due to charge transfer spectrum.
(D) V (IV) and Cu(II) have valence shell electron configuration $3d^1$ and $3d^9$ respectively. Both have one unpaired electrons, so undergo d-d-transition of electron and have similar colour.

Q.43 (A) - r ; (B) - s ; (C) - p ; (D) - q.
(A) Mixture of $BaSO_4$ (white) and ZnS (white) is called lithopone and is used as white paint.
(B) Double salt, $FeSO_4(NH_4)_2SO_4.6H_2O$ is called Mohr's salt.
(C) Silver nitrate is commercially named as lunar caustic.
(D) $[Cu(NH_3)_4]SO_4$ is a blue colour compound and is called as Schwitzer`s regent.

NUMERICAL VALUE BASED

Q.1 [3]

CrO_4^{2-}, MnO_4^{-}, $Cr_2O_7^{2-}$

$\downarrow$ $\downarrow$ $\downarrow$

d^0 d^0 d^0 type

Q.2 [4]

$Fe^{2+} : [Ar]4s^0 3d^6$

4

Q.3 [3]

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

Q.4 [2]

$(A) = SnCl_2 ; (B) = Sn(OH)Cl ; (C) = Sn(OH)_2$

$\underset{(A)}{SnCl_2} + H_2O \rightarrow \underset{(B)}{Sn(OH)Cl} + HCl$

$SnCl_2 + NaOH \rightarrow \underset{(C)}{Sn(OH)_2} + 2NaCl$

$Sn(OH)_2 + 2NaOH \rightarrow Na_2SnO_2 + 2H_2O$

$3SnCl_2 + 2AuCl_3 \rightarrow 3SnCl_4 + 2Au$

$SnCl_2 + 2HCl + I_2 \rightarrow SnCl_4 + 2HI$
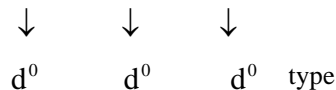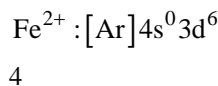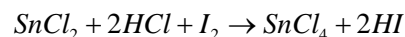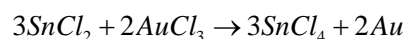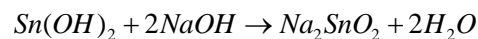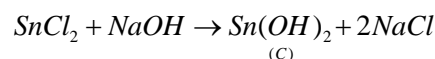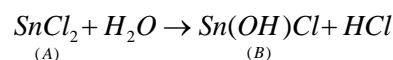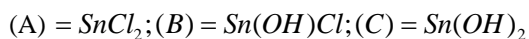
Q.5 [3]
$\mu = 1.73$ BM corresponds to 1 unpaired electron which is possible when Ti is in Ti^{3+} state $(3d^1)$
3

Q.6 [0]
sp^3 hybridisation

Q.7 [6]

(structure showing Cr with O atoms)
$\overset{-1}{O}$, $\overset{+6}{Cr}$, $\overset{-1}{O}$, $\overset{-1}{O}$, $\overset{-2}{O}$
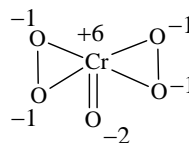
Q.8 [8]
Osmium forms an oxide, OsO_4

Q.9 [2]

(A) is $Pb(CH_3COO)_2$

$Pb(CH_3COO)_2 + H_2S \rightarrow \underset{Black}{PbS} + 2CH_3COOH$

$$Pb(CH_3COO)_2 + 2HCl \rightarrow PbCl_2 + 2CH_3COOH$$
<div style="text-align:center">Soluble in
hot water</div>

$$Pb(CH_3COO)_2 \rightarrow PbO + CO_2 + CH_2COCH_3$$
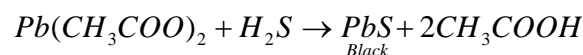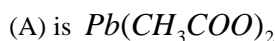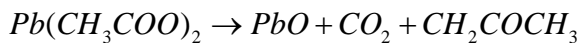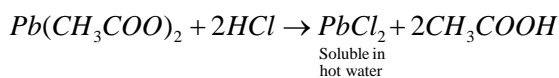
Q.10 [4]

$$E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{498 \times 10^{-9}} = 3.99 \times 10^{-19} \text{ J}$$

Q.11 [3]

$Sc \rightarrow [Ar]3d^1, 4s^2$

$Cr \rightarrow [Ar]3d^5, 4s^1$

$Cu \rightarrow [Ar]3d^{10}, 4s^1$
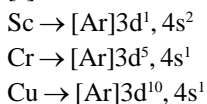
Q.12 [4]

Cr, Cu, Fe, Hg

Q.13 [2]

For 4.90 BM magnetic moments total number of unpaired electron in it is 4

$$\therefore \text{ total spin} = \frac{4}{2} = 2$$

Q.14 [34]

Ions	no. of unpaired electrons
Cu^{2+}, Ti^{+3}	1
Ni^{2+}, V^{+3}	2
Co^{2+}, Cr^{+3}	3
Fe^{2+}, Cr^{+2}, Mn^{3+}	4
Mn^{3+}, Fe^{3+}	5

Q.15 [39]

X is $\underset{26}{Fe}$ $X^{+2} = Fe^{+2} \cdot t_{2g}^{2,2,2} \text{ eg}^{0,0}$ low spin

$X^{+3} = Fe^{+3} \text{ } 3d^5 \text{ ro } t_{2g}^{1,1,1} \text{ eg}^{1,1}$ high spin

a + b + 2c = 25 + 4 + 2×5 = 39

but free state $X^{+2} = Fe^{+2} \equiv 3d^6$

(4 unpaired)

$X^{+3} = Fe^{+3} = 3d^5$ (5 unpaired)

Q.16 [6]

$$FeC_2O_4 \xrightarrow{\Delta} FeO + CO + CO_2$$
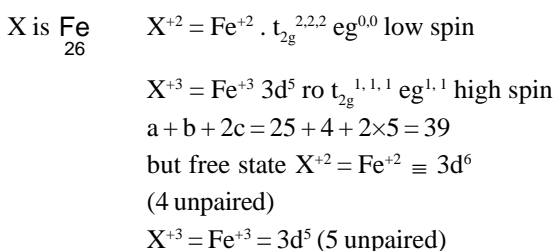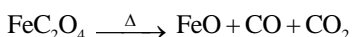
Number of diamagnetic products = 2 (CO & CO_2) = x ; (CO & CO_2)

and Number of unpaired electrons in paramagnetic products $FeO = 4$ ($3d^6$) = y ; ($3d^6$)

Q.17 [4]

Q.18 [4]

$SO_4^{2-} \cdot H_2O$

Q.19 [8]

1. $FeSO_4 + (NH_4)_2 SO_4 + 6H_2O \longrightarrow FeSO_4 \cdot (NH_4)_2 SO_4 \cdot 6H_2O$ (Mohr salt)
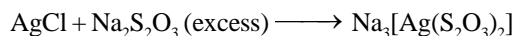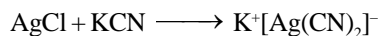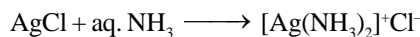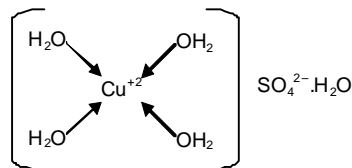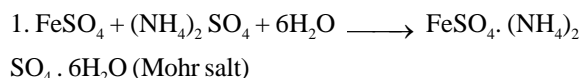
2. Green vitriol is $FeSO_4 \cdot 7H_2O$ & its anhydrous form ($FeSO_4$) is white.

3. $2 \overset{(+2)}{Fe}\overset{(+6)}{SO_4} \xrightarrow{\Delta} \overset{(+3)}{Fe_2} O_3 + \overset{(+4)}{SO_4} + SO_3$ (Redox)
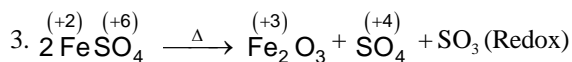
4. Fact (Fenton's reagent = $FeSO_4 + H_2O_2$)

5. $\underset{(aq)}{FeSO_4} + \underset{(aq)}{6KCN} \longrightarrow K_4[Fe(CN)_6]$
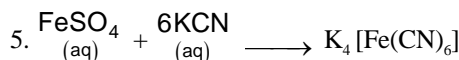
6. White vitriol is $ZnSO_4 \cdot 7H_2O$ & Blue vitriol is $CuSO_4 \cdot 5H_2O$

7. Due to its oxidation to Fe^{3+}.

8. $Fe^{2+} + 2H_2O \rightleftharpoons Fe(OH)_2 \downarrow + 2H^+$ (acidic solution)

9. Only SO_2 can turn acidified $K_2Cr_2O_7$ solution green.

Q.20 [3]

$FeCr_2O_4 \xrightarrow[\text{Fuse}]{Na_2O_2} \{NaFeO_2 + Na_2CrO_4\} \xrightarrow[H_2O]{\text{Boil}} (Na_2CrO_4)$

aq. $\xrightarrow{\text{excess } H^+} Na_2Cr_2O_7$

<div style="text-align:center">(B)   (C)
(Yellow)   (Orange)</div>

$\downarrow H_2O_2$

$Na_2CrO_4 \xleftarrow{H_2O_2} NaCrO_2 \xleftarrow[\text{excess}]{NaOH} Cr(OH)_3 \xleftarrow{NH_3 \text{ little}}$

$Cr^{3+} \xleftarrow[-O_2]{\text{warm } H^+} CrO_5$
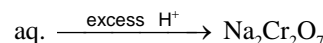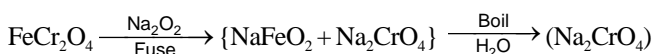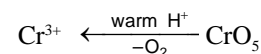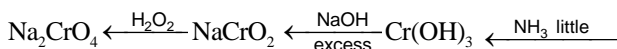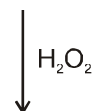
(H)	(G)	(F)	(E)	(D)
(Yellow)	(green)	(green)	(green)	(Violet)

(i)   (ii)   (iii)   (iv)

$AgCl + aq. \text{ } NH_3 \longrightarrow [Ag(NH_3)_2]^+Cl^-$

$AgCl + KCN \longrightarrow K^+[Ag(CN)_2]^-$

$AgCl + Na_2S_2O_3 \text{ (excess)} \longrightarrow Na_3[Ag(S_2O_3)_2]$

$AgCl + \text{conc. } HCl \longrightarrow [AgCl_2]^-$

$AgCl + aq. \text{ } NaOH \longrightarrow Ag_2O \downarrow$

Q.21 [12]

$$KMnO_4 \xrightarrow[\text{R.A.}]{H^+} Mn^{2+} \qquad x = 2$$

$$KMnO_4 \xrightarrow[\text{R.A.}]{OH^-} Mn^{4+} \qquad y = 4$$

$$K_2Cr_2O_7 \xrightarrow{OH^-} CrO_4^{2-} \qquad z = 6$$
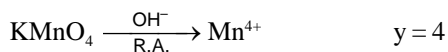
Q.22 [15]

Outer electronic configuration of Lu is $4f^{14}5d^16s^2$

$\therefore$ No. of electrons = 15

Q.23 [11]

	Atomicity
$Ln \xrightarrow[\Delta]{N_2} LnN$	2
$\xrightarrow[\Delta]{S} Ln_2S_3$	5
$\xrightarrow{\text{Halogen}} LnX_3$	4
	11
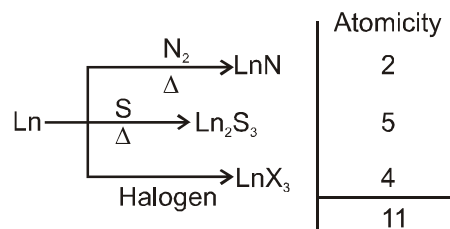
KVPY
PREVIOUS YEAR'S

Q.1 (D)

Q.2 (B)
Fact

Q.3 (A)

$$MnO_2 + KO_2 \xrightarrow[\text{In Air}]{\text{Oxidized}} \text{dark green compound}$$

(X) MnO_4^{-2} & K_2MnO_4

Disproportionation $\downarrow$

$\text{Purple colour(Y)} + \overset{+4}{Mn}O_2$

$\overset{+7}{K Mn O_4}$

(X) $\rightarrow K_2MnO_4$
(Y) $\rightarrow KMnO_4$

Q.4 (C)
$$4NaCl + K_2Cr_2O_7 + 6H_2SO_4 \rightarrow 4NaHSO_4 + 2KHSO_4$$
$$\qquad\qquad\qquad + 2CrO_2Cl_2(X) + 6H_2O$$
$$CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4(Y) + 2NaCl + 2H_2O$$
$X = CrO_2Cl_2$
$Y = Na_2CrO_4$

Q.5 (C)
$$KI + 2KMnO_4 + H_2O \rightarrow KIO_3 + 2MnO_2 + 2KOH$$
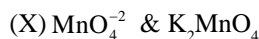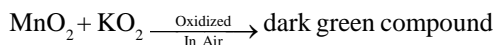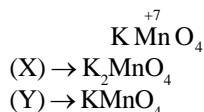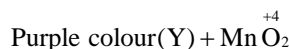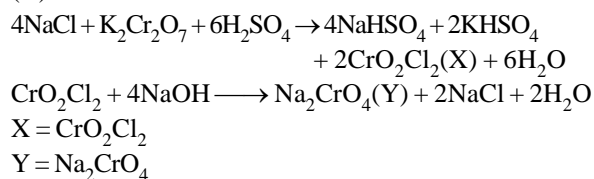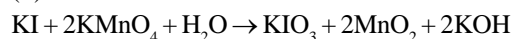
JEE-MAIN
PREVIOUS YEAR'S

Q.1 (6)

$$MnOH_4^- + S_2O_3^{2-} \xrightarrow{OH^-} MnO_2 + SO_4^{2-}$$
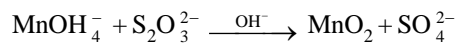
Oxidation state of 'S' in SO_4^{2-} is 6

Q.2 (1)
$Cr^+ \Rightarrow [Ar]3d^5$
$Mn^{2+} \Rightarrow [Ar]3d^5$
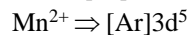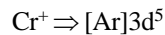
Q.3 (1)

Q.4 (2)
Yb shows +2 & +3 only

Q.5 (1)

Q.6 (4)
Size of $_{97}Bk^{3+}$ ion is less than that of $_{93}Np^{3+}$ due to actinoid contraction.
As we know that in a period from left to right ionic radius decreases and in actinide series it is due to actinoid contraction.

Q.7 (4)

Q.8 (49)

Fe $\rightarrow$ [Ar] $4s^23d^6$ $\boxed{\uparrow\downarrow|\uparrow|\uparrow|\uparrow|\uparrow}$
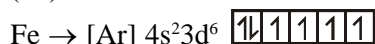
Number of unpaired $e^- = 4$

$\mu = \sqrt{4(4+2)}$ B.M.

$\mu = \sqrt{24}$ B.M.
$\mu = 4.89$ B.M.
$\mu = 48.9 \cdot 10^{-1}$ B.M.
Nearest integer value will be 49.

Q.9 (1)
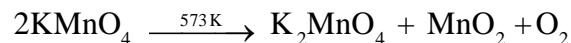
$$2KMnO_4 \xrightarrow{573\,K} K_2MnO_4 + MnO_2 + O_2$$
Potassium $\qquad$ Potassium
permanganate $\qquad$ manganate

Tetrahedral unit diamagnetic $\qquad$ Tetrahedral unit paramagnetic
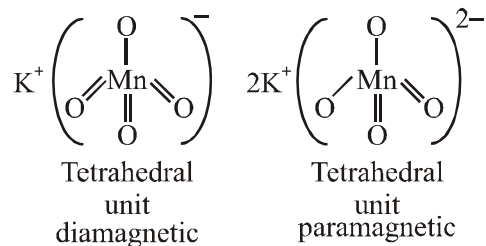
Statement-I is correct.
Statement-II is incorrect.

Q.10 (1)

$$2FeI_3 \longrightarrow 2FeI_2 + I_2$$

(Unstable)   (Stable)

Due to strong reducing nature of I^-

$$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$$

remaining halides of Fe^{2+} & Fe^{3+} are stable.

Q.11 (3)

Urea $-HCHO$ resin is used in manufacture of wood laminates.

Q.12 (16)

Writting the half reaction

oxidation half reaction

$$MnO_4^- \to Mn^{2+}$$

balancing oxygen

$$MnO_4^- \to Mn^{2+} + 4H_2O$$

balancing Hydrogen

$$8H^+ + MnO_4^- \to Mn^{2+} + 4H_2O$$

balancing charge

$$5e^- + 8H^+ + MnO_4^- \to Mn^{2+} + 4H_2O$$

Reduction half

$$C_2O_4^{2-} \to CO_2$$

Balancing carbon

$$C_2O_4^{2-} \to 2CO_2$$

Balancing charge

$$C_2O_4^{2-} \to 2CO_2 + 2e^-$$

Net equation

$$16H^+ + 2MnO_4^- + 5C_2O_4^{2-} \to 10CO_2 + 2Mn^{2+} + 8H_2O$$

So $c = 16$

Q.13 (1)

Electronic configuration of divalent metal ion having atomic number 25 is

$$Mn^{+2}_{(aq)} \Rightarrow \quad 1s^2 \; 2s^2 \quad 2p^6 \quad 3s^2 \quad 3p^6 \quad 3d^5$$
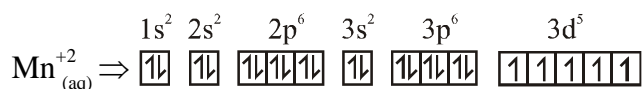
Total number of unpaired electrons = 5

μ (Magnetic moment) $= \sqrt{n(n+2)}$ BM

where n = number of unpaired e^-

$\therefore \mu = \sqrt{5(5 \quad 2)} = \sqrt{35}$ BM = 5.92 BM

Q.14 (2)

Mn3O4 shows magnetic properties.

Q.15 (2)

Q.16 (1)

Q.17 (2)

Q.18 (3)

Q.19 (1)

Q.20 (3)

Q.21 (2)

Q.22 (5)

Q.23 (4)

Q.24 (4)

Q.25 (3)

Q.26 (2)

Q.27 (2)

Q.28 (4)

Q.29 (4)

JEE-ADVANCED PREVIOUS YEAR'S

Q.1 (A, C, D) / (A, D)

In acidic medium,

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \quad (v.f.=5)$$
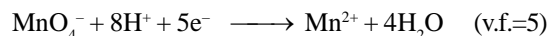
In neutral / faintly alkaline medium,

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^- \quad (v.f.=3)$$
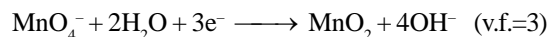
In strongly alkaline medium,

$$MnO_4^- + e^- \longrightarrow MnO_4^{2-} \quad (v.f.=1)$$
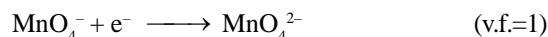
Q.2 (A)

$CuSO_4$ will be absorbing orange-red colour & hence will be of blue colour.

Q.3 (ACD)

$$AgNO_2 + HCl \longrightarrow AgCl \downarrow$$
$$AgNO_3 + HBr \longrightarrow AgBr \downarrow$$
$$AgNO_3 + HI \longrightarrow AgI \downarrow$$

All these precipitates will get dissolved in hypo forming complex $Na_3[Ag(S_2O_3)_2]$

Q.4 [7]

I^- to I_2 oxidation can be done by acidified $K_2Cr_2O_7$, $CuSO_4$, H_2O_2

$$K_2Cr_2O_7 + KI + H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + I_2 + H_2O$$

$2CuSO_4 + 4KI \longrightarrow 2CuI \downarrow + I_2 + 2K_2SO_4$

$H_2O_2 + 2KI \longrightarrow 2KOH + I_2$

$2KI + Cl_2 \longrightarrow 2KCl + I_2$

$H_2O + 2KI + O_3 \longrightarrow 2KOH + O_2 + I_2$

$FeCl_3 + 2KI \longrightarrow 2KCl + FeCl_2 + I_2$

$HNO_3 + KI \longrightarrow KNO_3 + I_2 + NO \uparrow$

$Na_2S_2O_3 + KI \longrightarrow$ no reaction.
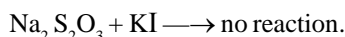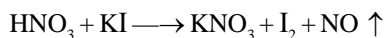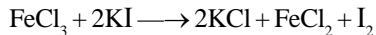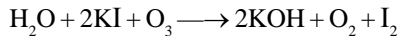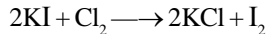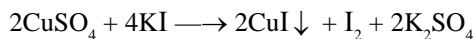
Note : In H_2O_2 & O_3, I^- to I_2 oxidation will occur initially.

Q.5 (ABC)

$Cr^{2+} + Mn^{3+} \rightleftharpoons Cr^{3+} + Mn^{2+}$
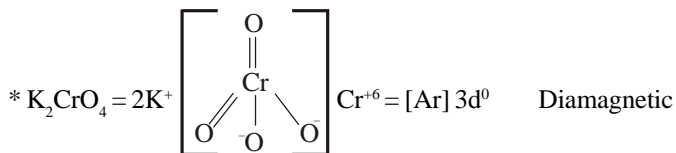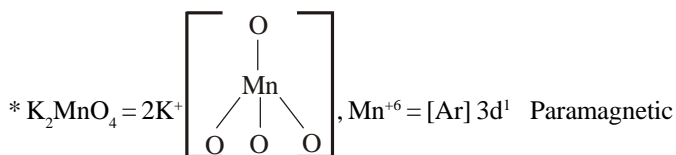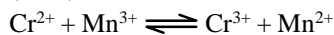
Cr^{2+} is a reducing agent Mn^{3+} is an oxidising agent both Cr^{2+} & Mn^{3+} exhibit d^4 electronic configuration.

Q.6 (CD)

In Basic medium, Fe^{3+} will be precipitated as $Fe(OH)_3$.

Q.7 (A)

$X \longrightarrow \left[Ag(S_2O_3)_2 \right]^{3-}$ $Y \longrightarrow Ag_2S_2O_3$ (white)

$Z \longrightarrow Ag_2S$ (Black)

Q.8 [1]

* H-atom = $\boxed{\uparrow}$ Paramagnetic
$1s^1$

* $NO2 =$ odd electron species   Paramagnetic

* $O_2^- =$ (superoxide) = One unpaired electrons in π^* M.O.

                                           Paramagnetic

* S_2 (in vapour phase) = same as O_2, two unpaired e^-s are present in π^* M.O.   Paramagnetic

* $Mn_3O_4 = 2\overset{+2}{Mn}O . \overset{+4}{Mn}O_2$ Paramagnetic

* $(NH_4)_2[FeCl_4] = Fe^{+2} = 3d^6 \ 4s^0$

         Cl^- Cl^- Cl^- Cl^- Paramagnetic
      sp^3 - hybridisation

* $(NH_4)_2[NiCl_4] = Ni = 3d^8 \ 4s^2$
                  $Ni^{+2} = 3d^8 \ 4s^0$

         Cl^- Cl^- Cl^- Cl^- Paramagnetic
      sp^3 - hybridisation

* $K_2MnO_4 = 2K^+$, $Mn^{+6} = [Ar]\ 3d^1$ Paramagnetic

* $K_2CrO_4 = 2K^+$ $Cr^{+6} = [Ar]\ 3d^0$ Diamagnetic

Q.9 (B,C,D)

$Zn + 2H_2SO_4$ (HOT and conc.)

$$\rightarrow ZnSO_4 + SO_2 \uparrow + 2H_2O$$
     (G)   (R)   (X)

$Zn + 2NaOH$ (conc.) $\rightarrow Na_2ZnO_2 + H_2 \uparrow$
                     (T)   (Q)

$ZnSO_4 + H_2S + 2NH_4OH$

$$\rightarrow ZnS \uparrow + 2H_2O + (NH_4)_2SO_4$$
     (Z)   (X)   (Y)

Q.10 [6]

$KMnO_4 + KI \rightarrow MnO_2 + I_2$

Eq of $KMnO_4$ = Eq of I_2

$4 \times 3 = n \times 2$

$n = 6$

Q.11 [4]

$K_2CrO_4 + H_2O_2 \xrightarrow[\text{(In acidic medium)}]{\text{Amyl alcohol}} \underset{\underset{\text{(Blue liquid)}}{(X)}}{CrO_5}$

Here the structure of CrO_5 is :
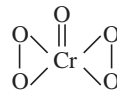
Here, single bonded O-atoms with Cr is = 04

Co-Ordination Compounds

ELEMENTARY

Q.1 (4)

Pyridine is monodestate ligand, so it is not chelating ligand.

Q.2 (4)

$K_4[Fe(CN)_6]$ Complex salt

Q.3 (2)

$Ag_2S + 4NaCN \rightleftharpoons 2Na[Ag(CN)_2] + Na_2S$

(Sodium dicyno argentate)

$2Na[Ag(CN)_2] + Zn \rightarrow Na_2[Zn(CN)_4 + 2Ag \downarrow$

(Sodium Tetracyno Zincate (ppt))

Q.4 (4)

In $K_4Fe(CN)_6$, the species retains its identity in solid as well as in solution state.

Q.5 (2)

The complexes can be written as follows

$[Co(NH_3)_6]Cl_3$ $[Co(NH_3)_5Cl]Cl_2$

$[Co(NH_3)_4Cl_2]Cl$

(A)   (B)   (C)

Hence, number of primary valencies are 3, 2 and 1 respectively.

Q.6 (2)

$K_3[Fe(CN)_6]$ because in it CN^- donats a lone pair of electron.

Q.7 (2)

Al has 6 co-ordination number.

Q.8 (2)

Q.9 (4)

Q.10 (2)

Negative ligands end in $- O$ eg. SO_4^{2-} (sulphato).

Q.11 (2)

Q.12 (4)

Alum acts as coagulating agent.

Q.13 (2)

As there is no direct bonding between the metal atom and the carbon atom.

Q.14 (2)

C_2H_5Li is an organo-metallic compound.

Q.15 (3)

$x + 5 \times 0 - 1 - 3 = 0$

$x = + 4$

Q.16 (4)

$$\overset{bi}{\uparrow} \quad \overset{bi}{\uparrow}$$

$[E(en)_2(C_2O_4)]NO_2 \rightarrow$ C.N. $= 2 \times 2 + 2 = 6$

$x + 2 \times 0 + (-2) - 1 = 0$

$x = +3$

Q.17 (2)

$$K_3[Fe(CN)_6]$$
$$\downarrow$$
$$Fe^{3+}$$
$$\hookrightarrow 23 + 12 = 35$$

EAN rule $\Rightarrow$ violates.

Q.18 (2)

$[Co(H_2O)_6]Cl_2 \rightleftharpoons [Co(H_2O)_6]^+ + 2Cl^-$

Q.19 (2)

$$[\underset{x}{Pt}(\underset{0}{C_2H_4})\underset{-1}{Cl_3}]^-$$

$x + 0 + 3x(-1) = -1$, $x - 3 = -1$, $x = +2$

Q.20 (1)

$[Co(NH_3)_6]Cl_3 \rightarrow [Co(NH_3)_6]^{3+} + 3Cl^-$

$x + 6(0) = +3 \Rightarrow x = +3$

Q.21 (2)

$[Ni(CN)_4]^x$, (Ni $= +2$) (CN $= -1$)

$x = 2 + 4(-1) \Rightarrow x = -2$

Q.22 (4)

Q.23 (1)

$[Pt(NH_3)_4Cl_2][PtCl_4]$

Tetraammine dichloro platinum (IV) tetrachloroplatinate (II).

Q.24 (3)

Q.25 (1)

Q.26 (1)

In the compounds $[Co(NH_3)_5 NO_2]Cl_2$, the oxidation state of cobalt is +3 and here 5 NH_3 ligand, a NO_2 ligand are attached to the central atom. therefore its name is pentaamminecobalt (III) chloride.

Q.27 (3)

I. $[Cu(NH_3)_4] [PtCl_4]$

II. $[Cu(NH_3)_3Cl] [Pt(NH_3)Cl_3]$

III. $[Pt(NH_3)_4] [CuCl_4]$

IV. $[Pt(NH_3)_3Cl] [Cu(NH_3)Cl_3]$

Q.28 (1)

$[Pt(NH_3)_2Cl_2]$
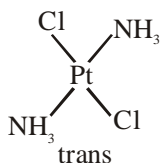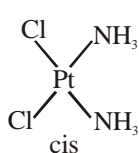
Q.29 (2)

In $[Ag(NH_3)_2]Cl$, Ag^+ contains d^{10} configuration. All others contain unpaired electrons.

Q.30 (4)

Generally strong field ligand $\Rightarrow$ Isomer orbital

$[Ni(NH_3)_6]^{2+} \rightarrow Ni^{2+} \rightarrow 3d^8 \rightarrow sp^3d^2$.

Q.31 (4)

$[PtCl_4]^{2-} \rightarrow dsp^2 \Rightarrow$ square planer.

Q.32 (3)

W.F. $\rightarrow$ outer orbital complex.

$[FeF_6]^{3-} \longrightarrow [FeF_6]^{3-}$
$\downarrow$
$+3$
$3d^5 45°$
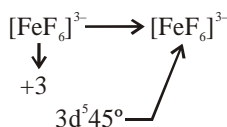
Q.33 (1)

Q.34 (1)

Q.35 (2)

JEE-MAIN
OBJECTIVE QUESTIONS

Q.1 (2)

$\overset{..}{N}H_2 - CH_2 - CH_2 - \overset{..}{N}H_2$. It contains two donor atoms i.e. nitrogen. So it is a bidentate ligand.

Q.2 (3)

It attaches to the central metal ion through four carboxylate group oxygen atoms and the two amine nitrogens.

EDTA^{4-}, Ethylenediaminetetraacetate ion
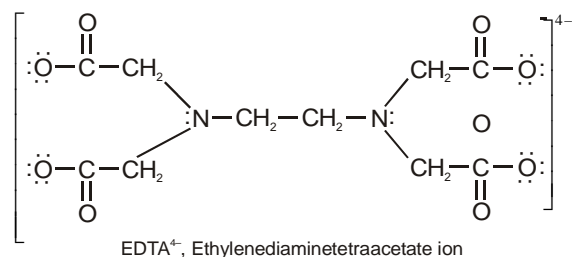
Q.3 (1)

$Fe(CN)_2 + 4KCN \longrightarrow Fe(CN)_2.4 KCN \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$

It gives test of K^+ but does not give test of Fe^{2+}. These type of salts which do not lose their identity when dissolved in water are called complexes.

Q.4 (2)

All ligands are Lewis bases as they donate lone pair of electrons to the metal ion to form coordinate covalent bonds.

Q.5 (2)

(1) Let x be the oxidation state of Mo in $[Mo_2O_4(C_2H_4)_2(H_2O)_2]^{2-}$. So $2x - 8 = -2$ or $x = +3$.

Q.6 (4)

H_2O is neutral, chromium oxidation state i.e. charge is +3 and oxalato anion has –2 charge; due to two $C_2O_4^{2-}$ it will be – 4 and net charge on the complex is algebraic sum of the charge on metal ion and ligands present in the coordination sphere. So $3 + 2 \times (-2) = -1$. So the formulae of complex is $[Cr(C_2O_4)(H_2O)]^-$.

Q.7 (2)

Higher the value of K higher will be strength of ligand & more will be thermodynamic stability of complex produced.

Q.8 (1)

$NH2 - \overset{\uparrow}{N} H2$
Monodentate
rest are bidentate legands.

Q.9 (3)

Ethylene diamine triacetate ion

35

Q.10 (2)

NH_4^+ has no lone pair, rest has lone pair.

Q.11 (2)

Refrence theory

Q.12 (4)

Ca^{2+} & Mg^{2+} ions forms complex with Na_2H_2EDTA.

Q.13 (4)
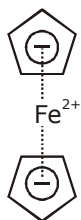
Q.14 (2)

$Al(C_2H_5)_3$	σ - complex
$Fe(C_5H_5)_2$	π - complex
$Zn(C_2H_5)_2$	σ - complex
$[Ni(CO)_4]$	σ - complex

Q.15 (2)

$[Fe(CO)_5]$ TBP
CO is strong field ligand
Fe - $3d^6 4s^2$
Pairing
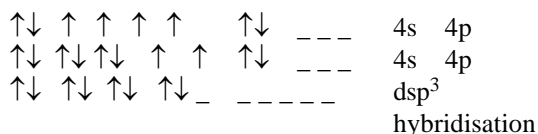
Q.16 (3)

Zeise's salt
$K [Pt^{II}Cl_3(\pi–C_2H_4)]$

$x_3 \neq x_1 = x_2$
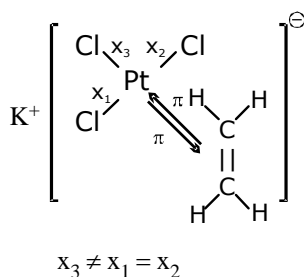
Q.17 (4)

In organometallic compounds, the metal is directly attached to the carbon atom. In $C_2 H_5ONa$, the Na is attached to oxygen atom.

Q.18 (1)

Relative to free ethylene the C — C bond is Incresed (from 133.77 pm to 137.5 pm). The bonding scheme is analogous to that in carbon monoxide complexes in which there is a ligand metal σ donation and a reciprocal metal to ligand π bonding.
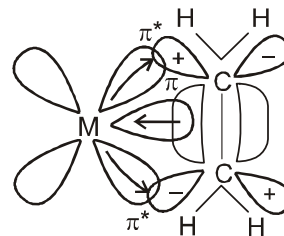
Q.19 (4)

$[Cu^{2+}(NH_3)_4]^{2+}$ $Cu^{2+} = d^9$
NH_3 is strong field ligand electration
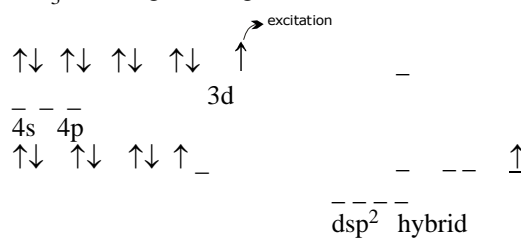
1 unpaired electron

$\mu = \sqrt{1(1+2)} = \sqrt{3} = 1.73$ B.M.

Q.20 (4)

$(C_2H_5)_4$ Pb is a σ-bonded complex.

Q.21 (3)

$X + 3(-1) = 1 \therefore X = +2$.

Q.22 (1)

Consider werner's theroy

Q.23 (4)

$[Co(CO)_4]$
EAN = 27 –(0)+ 4 × 2 = 35
$2[Co(CO)_4] \longrightarrow Co_2(CO)_8$
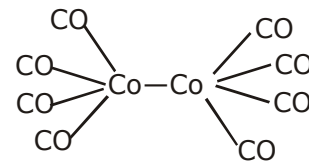
EAN = 27 + 1 + 4 ×2 = 36

Q.24 (3)

$[Pt(NH_3)_5Cl]Cl_3 \rightarrow [Pt(NH_3)_5Cl]^{3+} + 3Cl^-$

4 ions

$[Pt(NH_3)_4]Cl_4 \rightarrow$ 5 ions
$[Pt(NH_3)_2Cl_4] \rightarrow$ 0 ions
$[Pt(NH_3)_4Cl_2]Cl_2 \rightarrow$ 3 ions

Q.25 (3)

x is number of lone pairs of electrons donated to central metal ion.

So, $26 + 2x = 36$ or $x = \dfrac{10}{2} = 5$

Q.26 (2)

$K_2 [PtCl_6]$; Platinum is in $+ 4$ oxidation state.
Atomic number of Pt $= 78$.
So EAN Pt(IV) $= 78 - 4 + 12 = 86$

Q.27 (3)

$[Fe(CO)_x]^0$
EAN $= 26 + 2x = 36$
$x = 5$

Q.28 (1)

Conductivity α number of ions in the solution.
(1) $K_4[Fe(CN)_6] \xrightleftharpoons{aq.} 4K^+ (aq) + [Fe(CN)_6]^{4-}$ (aq)

4 : 1 electrolyte.

It contains maximum number of ions i.e. 5.
(2) $[Co(NH_3)_6] Cl_3 \xrightleftharpoons{aq.} [Co(NH_3)_6]^{3+} (aq) + 3Cl^-$ (aq)

1 : 3 electrolyte.

(3) $[Cu(NH_3)_4] Cl_2 \xrightleftharpoons{aq.} [Cu(NH_3)_4]^{2+} (aq) + 2Cl^-$ (aq)

1 : 2 electrolyte.

(4) $[Ni (CO)_4] \xrightleftharpoons{aq.} [Ni (CO)_4]$ (aq) (neutral).

Q.29 (1)

Molar conductance depends not only on the number of ions in aqueous solution but also on the electrical charges on the ions.
(A) $[Co(NH_3)_6]Cl_3 \xrightleftharpoons{aq.} [Co(NH_3)_6]^{3+} (aq) + 3Cl^-$ (aq). It has 4 ions and six electrical charges.
(B) $[Co(NH_3)_3Cl_3] \xrightleftharpoons{aq.} [Co(NH_3)_3Cl_3]$ (aq) (neutral)
(C) $[Co(NH_3)_4 Cl_2] Cl \xrightleftharpoons{aq.} [Co(NH_3)_4 Cl_2]^+ (aq) + Cl^- (aq)$. It has 2 ions and two electrical charges.
(D) $[Co(NH_3)_5Cl]Cl_2 \xrightleftharpoons{aq.} [Co(NH_3)_5Cl]^{2+} (aq) + 2Cl^- (aq)$. It has 3 ions and four electrical charges.

Q.30 (2)

$PtCl_4.2KCl \equiv K_2[PtCl_6] \xrightleftharpoons{aq.} 2K^+ + [PtCl_6]^{2-}$.
So, it has three ions per formula unit. The Cl^- is present in coordination sphere so it will not give white precipitate with silver nitrate solution. So in the compound the coordination number of platinum is 6.

Q.31 (2)

The counter ion present out side the coordination sphere can give test. Here Cl^- is present in the ionization sphere as counter ion so it will give the test.
$Ag^+ + Cl^- \longrightarrow AgCl \downarrow$ (white).

Q.32 (4)

(4) $[Cr(H_2O)_6]Cl_3 \xrightleftharpoons{aq.} [Cr(H_2O)_6]^{3+} (aq) + 3Cl^- (aq)$.
Cl^- present in ionisation sphere will give precipitate with $AgNO_3$.
$3Cl^- + 3Ag^+ \longrightarrow 3AgCl$
So, one mole of complex will give three moles of AgCl precipitate.

Q.33 (4)

$PtCl_4.4NH_3 \equiv [Pt(NH_3)_4Cl_2]Cl_2 \xrightleftharpoons{aq.} [Pt(NH_3)_4Cl_2]^{2+}$ (aq) $+ 2Cl^- (aq)$.
$2Ag^+ + 2Cl^- \longrightarrow 2AgCl \downarrow$ (white)

Q.34 (4)

$K_4[Ni(CN)_4]$ Let O.S of Ni $= x$
$4 + x - 4 = 0$
$x = 0$
(1) Co^{3+} (2) Fe^{2+} (3) Co^{-1}

Q.35 (4)

$[Pt(NH_3)_3Cl_3]Cl \xrightleftharpoons{aq.} [Pt(NH_3)_3Cl_3]^+ (aq) + Cl^- (aq)$
Out of four Cl^- only one Cl^- (i.e. 25%) present in ionization sphere will give preciptate.
$Ag^+ + Cl^- \longrightarrow AgCl \downarrow$ (white).

Q.36 (3)

$[Co(NH_3)_5(NO_2)]Cl_2 \xrightleftharpoons{aq.} [Co(NH_3)_5(NO_2)]^{2+} (aq) + 2Cl^-(aq)$ (no. of ions $= 3$)
$2Ag^+ + 2Cl^- \longrightarrow 2AgCl \downarrow$ (white).

Q.37 (3)

Anhydrous binary compound will have all water molecules in coordination sphere so its formula will be $[Co(H_2O)_4Cl_2]Cl$. Two Cl^- will have dual behaviour i.e. they will act as primary valency as well as the secondary valency and third Cl^- will satisfy only primary valency.

Q.38 (3)

Coordination no. of Cr $= 6$
$1/3 \times 3 = 1$ Chloride ion is outside the coordination sphere.

Q.39 (2)

$K_2^{+4}[PtCl_6]$

At No. Pt = 78

EAN = 78 – 4 + 6 × 2 = 86

Q.40 (2)

Coordination no. of Co = 6

$[Co(NH_3)_5Cl]Cl$

eq. of complex = eq AgCl

$$\frac{0.1\times100}{1000}\times2 = \text{Mol. AgCl} \times 1$$

0.02 = mol. AgCl

Q.41 (1)

$[CO(NH_3)Cl_3]$ is neutral complex

Q.42 (2)

(I) $[Pt(NH_3)_5Cl]Cl_3 \rightarrow 4$ ions

(II) $[Pt(NH_3)_4Cl_2]Cl_2 \rightarrow 3$ ions

(III) $[Pt(NH_3)_3Cl_3]Cl \rightarrow 2$ ions

(IV) $[PtCl_4(NH_3)_2] \rightarrow$ no ions

Q.43 (4)

eq. of complex = eq. of AgCl

$$\frac{10\times1}{1000}\times n \qquad \frac{4.305}{108+35.5}\times1$$

n = 3

So three ions out side the coordination sphere.

Q.44 (3)

$K_2[Ni^{2+}(CN)_4]$ — EAN = 28 –2 + 4 × 2 = 34

$[Cu^{2+}(NH_3)_4]SO_4$ — EAN = 29 – 2 + 8 = 35

$K_2[Pt^{4+}Cl_6]$ — EAN = 78 – 4 + 6 × 2 = 86

Q.45 (4)

$[Cu(NH_3)_4]SO_4$ — EAN = 35

$K_3[Fe(CN)_6]$ — EAN = 35

$K_4[Fe^{2+}(CN)_6]$ — EAN = 36

$[Co^{3+}(NH_3)_6]Cl_3$ — EAN = 36

$K_3[Cr^{3+}(C_2O_4)_3]$ — EAN = 33

$Cr^{3+}(NH_3)_6]Cl(NO_2)_2$ — EAN = 33

Q.46 (3)

A → $K_4[Fe(CN)_6]$ — EAN = 36

B → $[Co(NH_3)_6]Cl_3$ — EAN = 36

C → $[Cu(NH_3)_4]SO_4$ — EAN = 35

D → $K_3[CoCl_2(C_2O_4)_2]$ — EAN = 36

Q.47 (3)
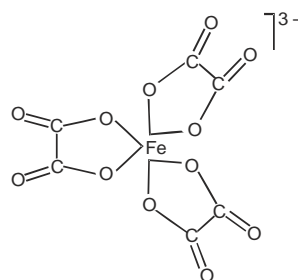
It is a chelate complex having three five -membered rings. It attains extra stability through chelation.

Q.48 (2)

$CaCl_2$ has 3 ion

$CoCl_3\ 5NH_3 = [Co(NH_3)_5Cl]Cl_2$

also has 3 - ions

In complex assume C. N. = 6

Q.49 (3)

Transition metal & ligand present in the complex does not furnishes their analytical test.

Q.50 (4)

Assuming complex follows EAN rule

EAN of Co = 27 + 4 × 2 + x = 36

x = 1

EAN of Fe = 26 – 2 + 2x + 6 = 36

x = 3

Q.51 (1)

$[Cr(NH_3)_5C\ell]\ so_4$ will form

$BaSO_4$ (white ppt) on treatment with $BaCl_2$.

Q.52 (2)

Q.53 (3)

O. N. of Al = +3

O. N. of B = + 3

$[BF_4]^-$

$[Al(C_2O_3)_3]^{3-}$

Q.54 (4)

As there are six σ-bonds between metal atom /ion and ligands, the coordination number of Pt(IV) in this complex is six.

Q.55 (2)

Let x be the oxidation state of copper in $[Cu(CN)_4]^{3-}$. So, x + 4(–1) = – 3 or x = 1. In (1) and (3) the oxidation state of copper is +2.

Q.56 (1)

Let x be the oxidation state of cobalt in $[CoCl_2(en)_2]^+$. So, x + 2(–1) + 0 = +1 or x = + 3.

As there are six σ-bonds between cobalt and ligands, it coordination number is 6 (here 'en' is a bidentate ligand).

Q.57 (2)

$[Ni^0(CO)_4]$

$[Cr^{3+}(NH_3)_6]_2[Ni^{4+}F_6]_3$

$[Ni^{2+}(NH_3)_6][B^{+3}F_4]_2$

$K_4[Ni^{+2}(CN)_6]$

Q.58 (1)

Correct name is dichloridodimethylglyoximatecobalt (II)

Q.59 (3)

(1) Coordination number of platinum is generally six when its oxidation state is (IV). So it is incorrect name.

(2) With type of ligand and +4 oxidation state of platinum, the complex should be cationic not anionic. So it is also incorrect name.
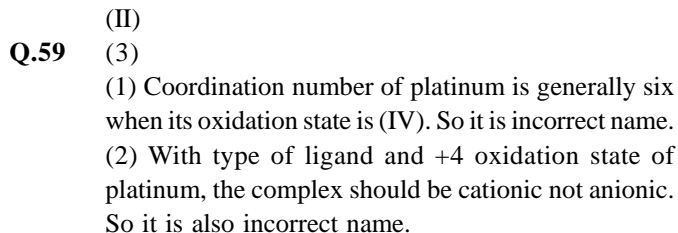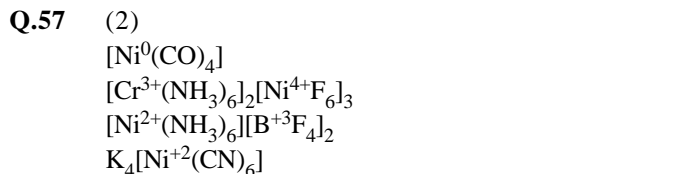
not anion but IUPAC name is given as anion.

(3) For coordination number six, the oxidation state of Pt is +IV. So the probable formulae of the complex may be $[Pt(NH_3)_2(en)(SCN)_2]^{2+}$. So its correct IUPAC name is Diammineethylenediaminedithiocyanato-S-platinum (IV).

(4) With two NH_3, two en and two SCN^- ligands, the coordination number of Pt becomes eight, which is incorrect according to the question.

Q.60 (1)

Compound $[Cr^{VI}F_4^{-4}O^{-2}]$ (CN = 5) is a neutral molecule so there should not be potassium cation.

Q.61 (4)

(i) The central atom, Co is placed first.

(ii) The ligands are then placed in alphabetical order.

(iii) The formula for the entire coordination entity, whether charged or not, is enclosed in square brackets.

Q.62 (4)

Cation is named first followed by anion. In coordination sphere the ligands are named alphabetically followed by name of metal ion and then its oxidation state in Roman numeral.

In $[Co(NH_3)_4Cl(ONO)]^+Cl^-$, cobalt is in +3 oxidation state and the complex is cationic. ONO ligand attach to metal ion through O atom ; so — O — is used while naming as nitrito before the name of metal ion. So IUPAC name given in option (4) is correct.

Q.63 (3)

Metal, Co is placed first followed by ligands in alphabetical order as ammine > aqua > chlorido i.e. $[Co(NH_3)_3(H_2O)_2Cl]Cl_2$.

Q.64 (1)

$[Co(en)_2Cl_2]^+$
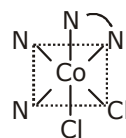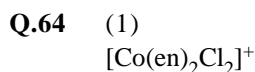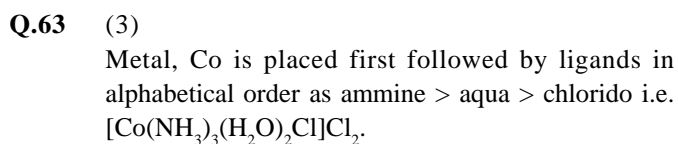
Optically active (cis) (trans)

Mirror image

Q.65 (3)

$Co(NO_2)_3 + 3KNO_2 \longrightarrow K_3[Co(NO_2)_6] \underset{aq.}{\rightleftharpoons} 3K^+$ + $[Co(NO_2)_6]^{3-}$ (total six electric charge)

3 : 1 electrolyte.

Q.66 (2)

$CH_3 - C = N - O^-$

$CH_3 - C = N - OH$

Dimethyl glyoximato ligand.

Q.67 (2)

O. N of Br = x $\Rightarrow + 2 +2x - 8 = 0$

$\Rightarrow x = + 3$

Q.68 (3)

Q.69 (2)

Let the O. N. of Fe = x $\Rightarrow 4 + x + (-1) \times 5 + (-1) = 0$ $\Rightarrow x = + 2$

Q.70 (2)

CNS SCN

NO_2^- ONO^-

CN^- CN^- } Ambident ligand

Q.71 (3)

cis

Trans
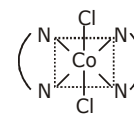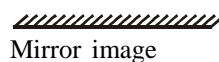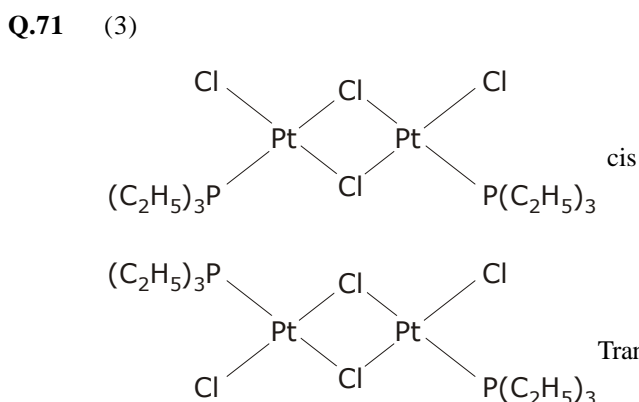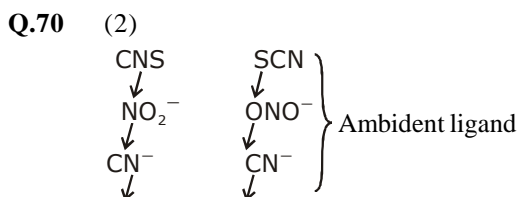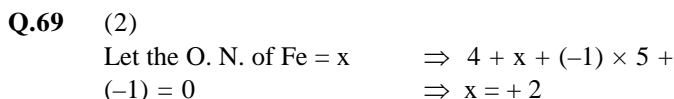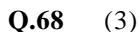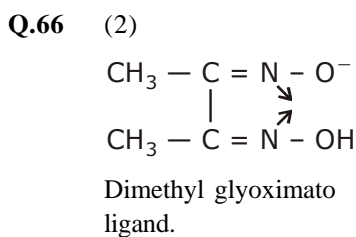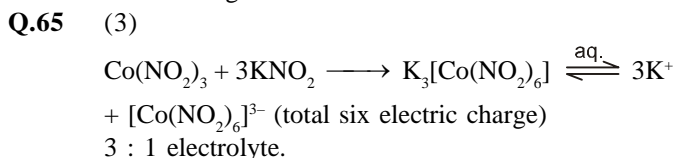
Q.72 (4)

⁻OCN is ambident ligand & it shows linkage isomerism.

Q.73 (3)

[PtBrCl NH$_3$ Py] Pt^{2+} is dsp^2 hybridised & hence geometry is square planner & sq. planner complex with four different ligands shows geometrical isomerism.

Q.74 (3)

[Cu^{2+}(NH$_3$)$_4$]	[PtCl$_4$]
[Cu(NH$_3$)$_3$Cl]$^+$	[PtCl$_3$NH$_3$]$^-$
[Cu(NH$_3$)$_2$Cl$_2$]^0	[PtCl$_2$(NH$_3$)$_2$]^0 [it is not]
[Cu(NH$_3$)Cl$_3$]$^-$	[PtCl(NH$_3$)$_3$]$^+$
[CuCl$_4$]$^{2-}$	[Pt(NH$_3$)$_4$]$^{2+}$

Total four

Q.75 (4)

Trans

Cis (optically active)
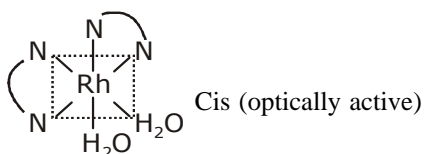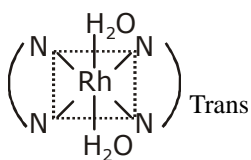
Q.76 (3)

Cis [Co(NH$_3$)$_2$(en)$_2$]$^{3+}$

cis
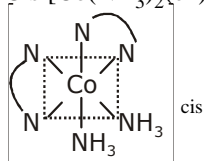
No POS optically active rest compound has POS.

Q.77 (3)

Concentrated H$_2$SO$_4$ is dehydrating agent. It will not dehydrate the complex in which H$_2$O molecule is inside the coordination sphere.

Q.78 (4)

Different molecular mass, so no isomerism

Q.79 (4)

Br$^-$ + Ba^{2+} → x

SO$_4$$^{2-}$ + Ba^{2+} → BaSO$_4$(s) (white ppt)

Br$^-$+ Ag$^+$ → AgBr(s) Pale yellow ppt

SO$_4$$^{2-}$ + Ag$^+$ → x

2 - ions form both the complex but magnitude of conductance is different, second complex is more electrically conducting.

Q.80 (2)

NO$_2$$^-$ is an ambidentate ligand and thus it can linkage to metal ion through O as well as through N. Hence show linkage isomerism.

Q.81 (2)

[Co(NH$_3$)$_3$(NO$_3$)$_3$] exists in following to isomeric forms.

fac–   mer–

Q.82 (4)

Geometrical isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands. Geometrical isomerism is common among coordination compounds with coordination numbers 4 having square planar geometry and 6 having octahedral geometry.

Q.83 (3)

Cis   Trans

Q.84 (3)

(1) Linear geometry

(2) Ma$_4$b has one form Ma$_4$b

(3)

cis –

trans –

(4) Ma$_3$b and Ma$_4$ both have one form each.

Q.85 (2)

(I) NH$_3$T NO$_2$, (II) NH$_3$T NH$_2$OH ,

(III) NH$_3$T py.

Q.86 (4)

cis

Trans

Q.87 (1)

Mirror | No super impossable mirror image

Q.88 (2)

trans | cis

cis | Trans

No isomerism

Q.89 (4)

Ambient ligand

Since both cation & anion constitute coordination sphere so it exhibit coordination isomerism and contains ambident ligand so, it shows linkage isomerism.

Q.90 (4)

$[Ag^+F_4]^-$ sp^3 sp^3
T.H.
$[Hg^{2+}T_4]^{2-}$ sp^3
T.H.
$[Ni^{2+}Cl_4]^{2-}$ sp^3
T.H.(weak field ligand)
$[Ni(CN)_4]^{2-}$ dsp^2
Square planer

Q.91 (1)

Order of strength of lighand en > H_2O > Br

$\therefore$ Order of Δ_0 is $\Delta_{en} > \Delta_{H_2O} > \Delta_{Br}$

$$\Delta = \frac{hc}{\lambda_{absorbed}}$$

Q.92 (1)

H_2O is weak field ligand
Fe^{2+} $3d^6$

↑ ↓ ↑ ↑ ↑ ↑ _   _ _ _   _ _ _ _ _
3d   4s   4p   4d
4 unpaired   _ _ _ _ _ _
electron   sp^{3}d^2

Q.93 (1)
exception

Q.94 (1)

$5d^8$ configuration have higher CFSE and the complex is thus square planar and diamagnetic.

Pt^{2+}, $[Xe]4f^{14} 5d^8$

$[Pt(NH_3)_4]^{2-}$

dsp^2 hybrid orbitals

Q.95 (3)

Trigonalbipyramidal ;

(sp^{3}d)

being symmetrical molecule $\mu = 0$.
As it is symmetrical molecule, therefore, its dipole moment (μ) is zero.

Q.96 (4)

In complex nickel is in zero oxidation state. The CO is strong field ligand and therefore compels for the pairing of electrons. The hybridisation scheme is as shown in figure.

$Ni^0([Ar] 3d^8 4s^2)$

$[Ni(CO)_4]$

sp^3 hybrid orbitals

Four pairs of electrons from four CO.
It is tetrahedral and as all electrons are paired so diamagnetic.

Q.97 (4)

In d^6, 'low spin' octahedral complex all electron will be paired because of higher CFSE.

Q.98 (2)

S_1 Mn^{3+}, 3d^4 ;

Fe^{3+} , 3d^5 ;

Co^{3+}, 3d^6 [CoF$_6$]$^{3-}$

S_2 VBT does not give a quantitative interpretation of the thermodynamics stabilities of coordination compounds and (its short coming).

S_3 is correct statement as $\Delta_o \propto$ strength of ligand and oxidation state of central metal ion.

Q.99 (3)

Low spin complex utilizes $(n - 1)$ d-orbital for hybridisation and thus low spin complex is formed with d^2sp^3 hybridisation.

Q.100 (4)

The complex [FeF$_6$]$^{4-}$ is paramagnetic and uses outer orbital (4d) in hybridisation (sp^{3}d^2) ; it is thus called as outer orbital or high spin or spin free complex. So :

Fe^{2+}, [Ar]3d^6

[FeF$_6$]$^{4-}$

sp^{3}d^2 hybrid orbitals
Six pairs of electrons
from six F$^-$ ions.

Q.101 (3)

(3) Mn^{2+}, 3d^5 configuration has 5 unpaired electrons.

In (4) Fe^{2+} (3d^6) has no unpaired electrons because of strong field ligand (CN$^-$), all electrons are paired.

In (1) and (2) Cu^{2+}(3d^9) has one unpaired electron.

Q.102 (1)

Fe^{3+}, 3d^5 configuration has 5 unpaired electrons because F$^-$ is a weak field ligand.

Q.103 (1)

(1) This may attributes to the following two reasons. (i) There are only four ligands instead of six, so the ligand field is only two thirds the size ; as the ligand field splitting is also the two thirds the size and (ii) the direction of the orbitals does not concide with the direction of the ligands. This reduces the crystal field splitting by roughly further two third. So $\Delta_t = \dfrac{2}{3} \times \dfrac{2}{3} = \dfrac{4}{9}\Delta_o$.

Q.104 (3)

(1), (2) and (4) all have tetrahedral geometry except (3) which has square planer geometry.

Q.105 (4)

d^0 & d^{10} system are colourless

Q.106 (1)

(1) [FeCl(CN)$_4$(O$_2$)]$^{4-}$; O$_2$ is O$_2^{2-}$; CN$^-$ is strong field ligand, so compels for the pairing of electrons.
Fe^{3+} → 3d^5;

d^2sp^3

(2) K$_4$[Fe(CN)$_6$];
CN$^-$ is strong field ligand so compels for the pairing of electrons.
Fe^{2+} → 3d^6:

d^2sp^3

(3) [Co(NH$_3$)$_6$]Cl$_3$;
NH$_3$ is strong field ligand and 3d^6 configuration has higher CFSE compelling for the pairing of electrons.
Co^{3+} → 3d^6:

d^2sp^3

(4) [Fe(CN)$_5$(O$_2$)]$^{5-}$;
O$_2$ is O$_2^{2-}$; CN$^-$ is strong field ligand so compels for the pairing of electrons.
Fe^{2+} → 3d^6:

d^2sp^3

Q.107 (2)

Ag$^+$ has 4d^{10} configuration and thus all electrons are paired in 4d-orbitals.

Q.108 (3)

(1) Mo^{3+}, 4d^3

4d^3 contains three unpaired electrons with strong field as well as with weak field ligand.

(2) It is inner orbital complex (d^{2}sp^3) and all six electrons are paired as 3d^6 configuration has higher CFSE.

Q.109 (3)

In complex, [Ni(CO)$_4$] nickel is in zero oxidation state. The CO is strong field ligand and, therefore compels for the pairing of electrons. The hybridisation scheme is as shown in figure.

Ni^0([Ar] 3d^8 4s^2)

[Ni(CO)$_4$]

sp^3 hybrid orbitals

Four pairs of electrons from four CO.

It is tetrahedral and as all electrons are paired so diamagnetic.

In the diamagnetic and square planar complex [Ni(CN)$_4$]$^{2-}$, the nickel is in +2 oxidation state and the ion has the electronic configuration 3d^8. The hybridisation scheme is as shown in figure.

Ni^{2+}, [Ar]3d^8

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

dsp^2 hybrid orbitals

In the paramagnetic and tetrahedral complex [NiCl$_4$]$^{2-}$, the nickel is in +2 oxidation state and the ion has the electronic configuration 3d^8. The hybridisation scheme is as shown in figure.

Ni^{2+}, [Ar]3d^8

[NiCl$_4$]$^{2-}$

sp^3 hybrid orbitals

Q.110 (4)

[Co^{3+}(NH$_3$)$_6$]$^{3+}$	Co^{3+}	d^6
[Fe^{3+}(CN)$_6$]$^{3-}$	Fe^{3+}	d^5
[Cr^{3+}(H$_2$O)$_6$]$^{3+}$	Cr^{3+}	d^3
[Mn^{7+}O$_4$]$^-$	Mn^{7+}	d^0

Q.111 (3)

(3) Coordination compounds made up of cationic and anionic coordination entities show coordination isomerism due to the interchange of ligands between the cation and anion entities.

Q.112 (1)

[Ni(CO)$_4$]	[Ni(NH$_3$)$_4$]$^{2+}$
O.N. Ni = 0	O.N. Ni = +2
sp^3(T.H.)	dsp^2 (square planer)
μ_{spin} = 0	μ_{spin} = 0

Q.113 (3)

d^0 & d^{10} complex are colourless

Q.114 (3)

In [Ni(PPh$_3$)$_2$Cl$_2$] complex PPh$_3$ & Cl are weak field ligand
so it does not cause pairing.
In Ni(CO)$_4$
Ni 3d^8 4s^2
Pairing 3d^{10} so
↑↓ ↑↓ ↑↓ ↑↓ ↑↓   _ _ _ _
4s   4p
4-sp^3 hybrid orbital

Q.115 (4)

[Mn^{+6}O$_4$]$^{2-}$ d^{3}s paramagnetic, contains one unpaired electron.

Q.116 (3)

$^-$CN is very strong field ligand causes high splitting & makes the complex thermodynamically more stable

Q.117 (3)

F$^-$ is weak field ligand
[Fe^{3+} F$_6$]$^{3-}$ Fe^{3+} 3d^5
↑ ↑ ↑ ↑ ↑   _ _ _ _   _ _   4d
3d   4s   4p
_ _ _ _ _
6sp^{3}d^2 hybrid orbital

Q.118 (3)

[Fe^0(CO)$_5$]^0
Co is strong field ligand
Fe   3d^8

Q.119 (3)

Cl$^-$ weak field ligand (High spin complex)
CN$^-$ strong field ligand (Low spin complex)
Br$^-$ weak field ligand (High spin complex)
PPh$_3$ weak field ligand (High spin complex)

JEE-ADVANCED
OBJECTIVE QUESTIONS

Q.1 (C)

$Pb^{2+} + CaH_2\,EDTA \rightarrow [Pb(EDTA)]^{2-} + Ca^{2+} + H^+$

Q.2 (D)

$Cu^{2+} + KCN \rightarrow CuCN + (CN)_2$

$\downarrow KCN$

$K_3[Cu(CN)_4]$

Q.3 (D)

$K_4[Zn^{II}(CN)_4(O_2)_2]^{4-}$ $\xrightarrow{\text{oxidised}}$

$K_2[Zn^{II}(CN)_4(O_2)_2]^{2}.$

O_2^- (has 1unpaired electron in antibonding MO)

$\xrightarrow{\text{oxidised}}$ O_2 (has 2 unpaired electrons in antibonding MO).

So, paramagnetic moment increases.

Q.4 (B)

$$\frac{1}{\text{bond strength}} \; \alpha \;\; CO \;\; \text{bond length} \; \alpha \; \frac{e}{p}$$

e- electron

p - ptoron

$[V(CO)_6]^- \; \dfrac{e}{p} = \dfrac{24}{28} > 1$

$[Cr(CO)_6] \; \dfrac{e}{p} = \dfrac{24}{24} = 1$

$[Mn(CO)_6]$

$^+ \dfrac{e}{p} = \dfrac{24}{25} < 1$

Q.5 (B)

Using MOT determine bond order of O_2^{2-}, & O_2^- ion

Q.6 (A)

As + ve charge on the central metal atom increases, the less readily the metal can donate electron density into the π^* orbitals of CO ligand to weaken the C – O bond.

Hence order of C – O bond strength is : $[Mn(CO)_6]^+ > [Cr(CO)_6] > [V(CO)_6]^- > [Ti(CO)_6]^{2-}$.

Q.7 (B)

(I) $[Cr(NH_3)_6]^{3+}\,[Cr(NO_2)_6]^{3-}$

(II) $[Cr(NO_2)_2(NH_3)_4]^+\,[Cr(NO_2)_4(NH_3)_2]^-$

Same no. of ions but different magnitude of charge I^{st} complex, is more electrically conduction than II.

Q.8 (D)

(A) $K_4[Fe(CN)_6]$; $3d^6$,

CN^-

is strong field ligand and thus compels for the pairing of electrons.

$K_3\,[Fe(CN)_6]$; $3d^5$,

CN^- is

strong field ligand and thus compels for the pairing of electrons.

(B) SO_4^{2-} (aq) + Ba^{2+} (aq) $\longrightarrow$ $BaSO_4\!\downarrow$ (white);

Br^- (aq) + Ba^{2+} (aq) $\longrightarrow$ no visible change.

(C) Cl^- (aq) + Ag^+ (aq) $\longrightarrow$ $AgCl\!\downarrow$ (white); Br^- (aq) + Ag^+ (aq) $\longrightarrow$ $AgBr\!\downarrow$ (pale yellow)

Q.9 (C)

$[Co(NH_3)_6]^{3+}\,[Cr(NO_2)_6]^{3-}$

on electrolysis: At cathode

$[Co(NH_3)_6]^{3+} + 3e \rightarrow Co + 6NH_3$

$[Cr(NH_3)_6]^{3+}\,[Co(NO_2)_6]^{3-}$

On electrolysis : At cathode

$[Cr(NH_3)_6]^{3+} + 3e \rightarrow Cr + 6NH_3$

Different metal at cathode are obtained

Q.10 (C)

$$Ni^{2+} + 4\,NH_3 \rightleftharpoons [Ni(NH_3)_4]^{2+}$$

$\therefore \; k = \dfrac{[Ni(NH_3)_4]^{2+}}{[Ni^{2+}][NH_3]^4}$

But $\dfrac{[Ni^{2+}]}{[Ni^{2+}] + [Ni(NH_3)_4]^{2+}} = 1.6 \times 10^{-6}$

or $\dfrac{Ni^{2+}}{[Ni(NH_3)_4]^{2+}} \approx 1.6 \times 10^{-6}$

$\therefore \; k = \dfrac{10^6}{1.6 \times (0.5)^4} = 10^7$

Hence instability constant $= 10^{-7}$

Q.11 (D)

VO_2^{2+} let O. N. as V is x

$x + (-2) \times 2 = + 2$

$x = + 6$ (which is not possible)

as

$V = 3d^3\,4s^2$

so maximum O.N. is + 5

Q.12 (C)

EAN of Fe $= 26 + 2 \times 2 + 3 \times 2 = 36$

EAN of Co $= 27 + 1 + 4 \times 2 = 36$

Q.13 (C)

$x/2 \times 2 + 27 + 1 = 36$

$x = 8$

Q.14 (C)

Q.15 (D)

NO is three electron donating ligand

6×2 for CO $= 4 \times 3$ for NO

$=$ total 12 electron for donation

Q.16 (A)

Brown complex

Let O. N. of Co is x

$0 \times 5 + x + (-2) + x + 0 \times 5 = +4$

$x = +3$

$Co^{3+} d^6$ in strong field ligand

↓↑ ↓↑ ↓↑ _ _

(d^6)

μ spin $= 0$

In given complex one Co^{3+} losses electron & form Co^{4+} as nature of ligand remain same & Co^{4+} gains d^5

configuration in strong field with 1 upe μspin $= \sqrt{3}$

$= 1.73$ BM

Q.17 (C)

Complex contains only one Cl^- out side the coordination sphere which gives one mole white ppt. $AgNO_3$

Q.18 (B)

Trans   Cis

Optically inactive   Optically active

Q.19 (C)

Q.20 (C)

Q.21 (C)

 has POS

can be written as

 So it is optically inactive

Q.22 (A)

It is polar in nature. The chelate rings require the cis structure, because the chelating ligand is too small to span the trans positions.

Q.23 (D)

Option has no POS next has POS (plane of symmetry)

Q.24 (B)

dsp^2 sq. planer

Tetrahedral complex does not show geometrical isomerism

Q.25 (D)

$[CoBr(NH_3)_5]SO_4 \rightarrow [Co(NH_3)_5Br]^{2+} + SO_4^{2-}$

$[Co(NH_3)_5SO_4]Br \rightarrow [Co(NH_3)_5SO_4]^+ + Br^-$

Q.26 (C)

(A) $[NiBr_2 (PEt_3)_2]$ having $3d^8$ configuration with strong field ligand PEt_3 (not so bulkier as PPh_3), the complex is square planar and diamagnetic.

$[Cu(NH_3)_4]^{2+}$ having $3d^9$ configuration is square planar in which one electron jumps to 4p orbital. It contains one unpaired electron; so it is paramagnetic.

(B) $[Co(NH_3)_6]^{3+}$ having $3d^6$ configuration has greater CFSE and thus favours pairing of electrons. So it has d^2sp^3 hybridisation and is diamagnetic.

In $[Cr(CN)_6]^{4-}$, the CN^- is strong field ligand. So,

$$\overset{II}{[Cr(CN)_6]^{4-}}$$

(Source; sharpe)

d^2sp^3 and paramagnetic with two unpaired electrons.

(CITCI)

(NH₃TNH₃)

(NH₃TCI)   Mirror

(D) Have $[\overset{II}{Pt}(NH_3)_4] [\overset{IV}{Pt}Cl_6]$ and

$[\overset{IV}{Pt}(NH_3)_4 Cl_2] [\overset{II}{Pt}Cl_4]$ isomeric forms.

Q.27   (C)

Ma_3b, Ma_4 and $M(AA)_2$ (symmetrical bidentate ligand) have only one form; they does not show geometrical isomerism. But $M(AB)(CD)$ shows two geometrical isomerism.

ATD   ATC

Q.28   (A)

Only cis isomer as trans isomer replacement induces strain.

$+ C_2O_4^{2-} \rightarrow$ not possible

trans

not possible

Q.29   (B)

Ma_2b_4 has two geometrical isomers one cis- and one trans. Similarly Ma_2b_2 also has one cis- and one trans-forms.

Q.30   (B)

As trans isomer has symmetry elements it does not show optical isomerism.

(A), (C) and (D) are correct statements.

Q.31   (A)

Q.32   (C)

(1) cis - $[Co(NH_3)_4 Cl_2]^+$ has plane of symmetry as well as centre of symmetry ; so optically inactive.

(2) trans - $[Co(en)_2 Cl_2]^+$ has plane of symmetry as well as centre of symmetry ; so optically inactive.

(3) cis - $[Co(en)_2 Cl_2]^+$ lacks plane of symmetry as well as centre of symmetry ; so optically active.

(4) $[Co(en)_3]^{3+}$ lacks axis of internal rotation ; so optically active.

Q.33   (B)

(B) Exhibits linkage isomerism as it has ambidentate ligand, NO_2^-.

Q.34   (A)

(A) $[Co(en)_2 Cl_2]^+$ show geometrical isomerism and its only cis-form show optical isomerism.

trans

cis

(B) $[Co(NH_3)_5Cl]^{2+}$ exists only in one form.

trans

(C)

cis

It does not shows optical isomerism because of the presence of plane of symmetry and centre of symmetry.

(D) $[Cr(OX)_3]^{3-}$ shows optical isomerism but does not show geometrical isomerism because of the same type of ligands.

Q.35 (C)

In both complexes the oxidation state of cobalt is +3 with $3d^6$ configuration. Except $[CoF_6]^{3-}$, all other complexes of cobalt with weak field and strong field ligands are inner orbital complexes and diamagnetic because of higher CFSE.

$[CoF_6]^{3-}$

sp^3d^2

$[Co(C_2O_4)_3]^{3-}$

d^2sp^3

Q.36 (B)

$[Co(H_2O)_6]^{3+}$ diamagnetic ; CFSE $= -0.4 \times 6\Delta_0 + 2P$,
CFSE $= -0.4 \times 6 \times 10dq + 2P = -24dq + 2P$
$[CoF_6]^{3-}$ paramagnetic ; CFSE $= -0.4 \times 4 + 0.6 \times 2 \times 10dq = -4.0\ dq$
$\Delta_0 = 10\ dq$ (arbitrary value of crystal field splitting energy)

Q.37 (A)

S_1 :

chelate complex,

diamagnetic and has d^2sp^3 hybridisation.

$[Co(ox)_3]^{3-}$ $3d^6$

d^2sp^3

S_2 : NO_2^- is strong field ligand and thus it is inner orbital complex and paramagnetic with one unpaired electron present in higher 4d-orbital
$[Co(NO_2)_6]^{4-}$
$3d^7$

d^2sp^3

S_3 : $5d^8$ configuration; thus diamagnetic and dsp^2 hybridisation ($5d^8$ has higher CFSE so that $\Delta_0 > p$)

Q.38 (B)

If strong field ligand is used then pairing causes dsp^3 hybridisation which is thermodynamically not allowed so only possible hybridisation is sp^3d^2.

Q.39 (A)

(B) $[FeCl_4]^{2-}$ - sp^3 with four unpaired electrons. It is paramagnetic with four unpaired electrons (valence shell electron configuration, $3d^6$).

(C) $[Fe(CN)_6]^{3-}$ - d^2sp^3 with one unpaired electron. 'CN$^-$ is a strong field ligand and, therefore, it compels for pairing of electrons to have d^2sp^3 hybridisation. It is paramagnetic with one unpaired electron (valence shell electron configuration, $3d^5$)

47

(D) $[Fe(CO)_2(NO^+)_2]$ - sp^3 and diamagnetic. Iron is in –II oxidation state. So,

$[Fe(CO)_2(NO^+)_2]$

3d					4s	4p		
↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

sp^3 hybridisation

Q.40 (C)

Q.41 (B)

Br^- is weak field ligand cannot for inner d-orbital complex & square planer geometry is produced by dsp^2 hybidisation

Q.42 (B)

(I) FaC wrt. Cl

(II) Mer wrt. Cl

(III) Mer wrt OH^- & NH_3

Q.43 (C)

Fe^{2+} d^6

d^6 in weak field

↑↓ ↑ ↑ ↑ ↑

4 unpaired electrons

$\mu = \sqrt{4 \times 6}$ BM

μ_{spin} = 4.91 BM

d^6 in strong field

↑↓ ↑↓ ↑↓ _ _

$\mu = 0$

spin

Q.44 (C)

H_2O is weak field ligand & Br^- is strong field ligand for transition metal belonging to II & III transition series.

Q.45 (D)

Cl^- is weak field ligand for transition metal belonging to the first transition series but strong field ligand for 2nd & 3rd transition series metal so for C.N. = 4

$[NiCl_4]^{2-}$ is

sp^3 hybridised

CN^- is strong field ligand

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

$[PdCl_4]^{2-}$

are dsp^2

hybridised.

Q.46 (D)

(i) It is tetrahedral (sp^3) because there is no (n–1)d orbital vacant for dsp^2 hybridisation.

(ii) Ag with +3 oxidation state and $4d^8$ configuration

has square planar geometry.

(iii) It is tetrahedral (sp^3) because there is no (n–1)d orbital vacant for dsp^2 hybridisation.

(iv) Pt with +2 oxidation state and $5d^8$ configuration has square planar geometry.

(v) Rh with +1 oxidation state and $4d^8$ configuration has square planar geometry.

When we place these complexes in a magnetic balance, then there is decrease in their weights. This indicates that the complexes are dimagnetic.

Q.47 (A)

All electrons are paired ; so diamagnetic and has d^2sp^3 hybridisation.

$[RhCl(PPh_3)_3]$ + H_2 $\longrightarrow$ $[RhCl(H)_2(PPh_3)_3]$

Wilkinsons's catalyst

New complex chloridodihydridotris(triphenyl phosphine)rhodium(III)

$Rh(III) \rightarrow 4d^6$

4d					5s	5p		
↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

d^2sp^3

Q.48 (C)

$[Cu(CN)_4]^{3-}$	Square planner & dsp^2
$[Ni(CN)_6]^{4-}$	Octahedral & sp^3d^2
$[ZnBr_4]^{2-}$	Tetrahedral & sp^3
$[Cr(NH_3)_6]^{3+}$	Ocatahedral & d^2sp^3

Q.49 (B)

d^3	$[Cr(H_2O)_6]^{3+}$	3 upe
d^6	$[Fe(H_2O)_6]^{2+}$	4 upe
d^8	$[Cu(H_2O)_6]^{2+}$	2 upe
d^{10}	$[Zn(H_2O)_6]^{2+}$	0 upe

H_2O is weak field ligand

Q.50 (D)

$[Fe(I) (H_2O)_5 NO^+]$

3d					4s	4d						

Three unpaired electrons

six – sp^3d^2 hybrid orbital

So μ = 3.87.

Q.51 (C)

(I) $_{26}Cr(-IV) - 3d^8 \, 4s^2$; $[Cr(CO)_4]^{4-}$

3d					4s	4p		
↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

sp^3 hybridisation

CO is strong field ligand; so complex is diamagnetic and tetrahedral.

(II) $_{28}$Ni(+II) - 3d^8 ; [Ni(DMGH)$_2$]

3d | 4s | 4p

↑↓ ↑↓ ↑↓ ↑↓ | ↑↓ | ↑↓ | ↑↓ ↑↓

dsp^2 hybridisation

DMGH is a chelating lignad; so complex is diamagnetic and square planar.

(III) $_{78}$Pt(+II) - 5d^8 ; [PtHBr(PEt$_3$)$_2$]

5d | 6s | 6p

↑↓ ↑↓ ↑↓ ↑↓ | ↑↓ | ↑↓ | ↑↓ ↑↓

dsp^2 hybridisation

5d^8 configuration has greater CFSE, so complex is diamagnetic and square planar.

(IV) $_{47}$Ag(+I) - 4d^{10} ; [Ag(SCN)$_4$]$^{3-}$

4d | 5s | 5p

↑↓ ↑↓ ↑↓ ↑↓ ↑↓ | ↑↓ | ↑↓ ↑↓ ↑↓

sp^3 hybridisation

No empty d-orbital is available for dsp^2 hybridisation and SCN$^-$ is weak field ligand, so complex is tetrahedral and diamagnetic.

(V) $_{79}$Au(+III) - 5d^8 ; [AuBr$_4$]$^-$

5d | 6s | 5p

↑↓ ↑↓ ↑↓ ↑↓ | ↑↓ | ↑↓ | ↑↓ ↑↓

dsp^2 hybridisation

5d^8 configuration has greater CFSE, so complex is diamagnetic and square planar.

Q.52 (C)

Paramagnetic complexes are coloured d^0 & d^{10} complexes are colourless K$_2$Cr$_2$O$_7$ Cr^{+6} is diamagnetic but coloured due to charge transfer.

Q.53 (D)

[Co(H$_2$O)$_4$]$^{2+}$ 3upe sp$_3$ T. H.

[CoCl$_4$]$^{2+}$ 3upe sp$_3$ T. H.

[Co(Dmg)$_2$]   1upe dsp^2 square planner

Q.54 (C)

Let O.N. of Os be x

$X - 1 + (-2)\times2 + (-1) + (-1) = +1$

$X = +8$

[Os(ONO)$^{-1}$(O)$_2$$^{-2}$(O$_2$)$^{-1}(SCN)^{-1}$ H$_2$O]$^+$OH$^-$
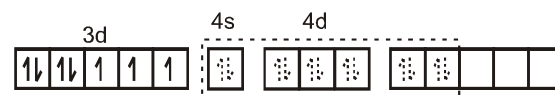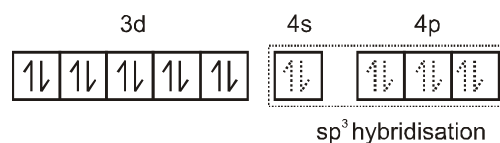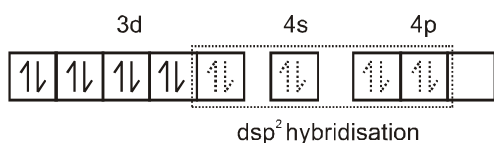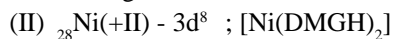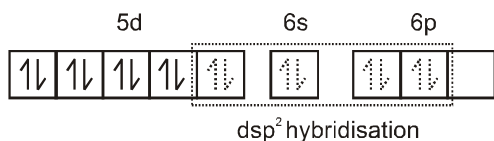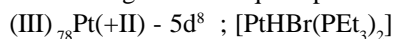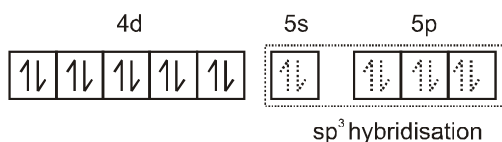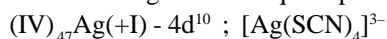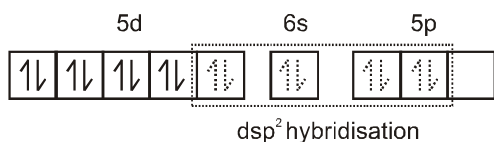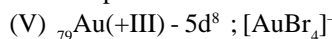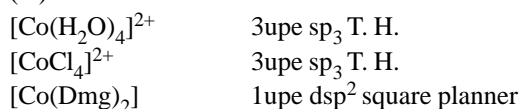
↘ superoxide ion

C.N. = 6

Os belongs to IIIrd transition series so all ligands acts as strong field ligand so d^{2}sp^3

Os^{8+} has d^0 congifuration.

Q.55 (D)

Maximum unpaired electron possible are five

↑ ↑ ↑ ↑ ↑

d^5

$\mu_{spin} = \sqrt{5 \times 7}$ B. M. $= \sqrt{35}$ B. M $= 5.92$ BM

Q.56 (D)

[Mn(H$_2$O)$_6$]$^{2+}$ $= 3 \times (-0.4) + 2 \times (0.6) = 0$

[Cr(H$_2$O)$_6$]$^{2+}$ $= 3 \times (-0.4) + 1 \times (0.6) = 0.6\ \Delta_0$

[Mn(H$_2$O)$_6$]$^{3+}$ $= 3 \times (-0.4) + 1 \times (0.6) = 0.6\ \Delta_0$

[Cr(H$_2$O)$_6$]$^{3+}$ $= 3 \times (-0.4) + 0 \times (0.6) = 1.2\ \Delta_0$

Q.57 (C)

Cis   Trans

Q.58 (A)

[Fe(CN)$_6$]$^{4-}$ Fe^{2+} 3(t$_2$g)^6 3(eg)^0 No upe

[Cu(NH$_3$)$_4$]$^{2+}$ dsp^2 sq. palnner 1 upe

[Ti(H$_2$O)$_6$]$^{3+}$ d^{2}sp^3 1 upe

[Fe(CN)$_6$]$^{3-}$ d^{2}sp^3 1 upe

Q.59 (A)

↑ ↑   e$_g$

↑↓ ↑↓ ↑↓   t$_{2g}$

M.M. $= \sqrt{n(n+2)}$

$= \sqrt{2(2+2)} = \sqrt{8}$ B. M. $= 2.83$ BM

Q.60 (C)

$\mu spin = 2.83 = \sqrt{n(n+2)}$

n = 2 (upe)

d^3 [Cr(H$_2$O)$_6$]$^{3+}$ 3upe

d^{10} [Cu(CN)$_4$]$^{3-}$ 0upe

d^7 [V(H$_2$O)$_6$]$^{3+}$ 2upe

d^7 [Co(H$_2$O)$_6$]$^{2+}$ 3upe
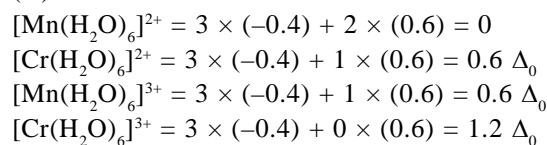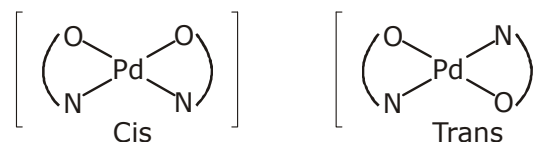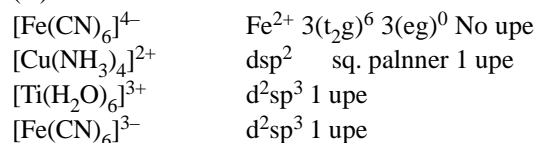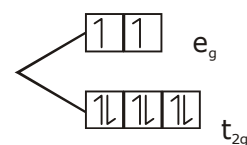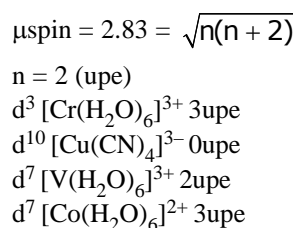
Q.61 (B)

$^-$CN strong field ligand

Q.62 (A)

[NiF$_6$]$^{2-}$ 0 upe

[Cu(NH$_3$)$_4$]$^{2+}$ 1 upe

[CoF$_6$]$^{3-}$ 4 upe (F$^-$ acts as weak field ligand)

[Fe(EDTA)]$^-$ 1 upe (EDTA^{4-} acts as strong field ligand)

Q.63 (B)

In both complexes the oxidation state of Ni is +2. In [NiCl$_4$]$^{2-}$ the Cl$^-$ is a weak field ligand, so it does not compel for pairing. Then,

[NiCl$_4$]$^{2-}$

sp^3-hybridisation
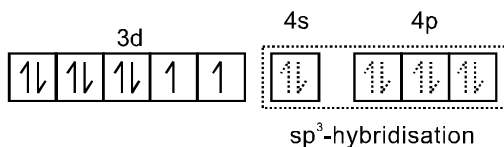
Hence NiCl$_4$ is paramagnetic and tetrahedral.

In [NiCl$_2$ (PMe$_3$)$_2$] the trimethyl phosphine is a strong field ligands; so it compels for the pairing of electrons. Then,

[NiCl$_2$ (PMe$_3$)$_2$]

dsp^2
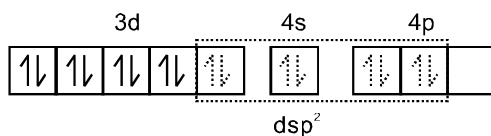
Hence [NiCl$_2$ (PMe$_3$)$_2$] is diamagnetic and square planar.

JEE-ADVANCED

MCQ/COMPREHENSION/COLUMN MATCHING

Q.1 (ABD)

$$\left[C_5H_5 \underset{\pi}{\overset{\pi}{\rightleftharpoons}} Ni \underset{\pi}{\overset{\pi}{\rightleftharpoons}} C_5H_5 \right] \quad C_2H_5MgI$$
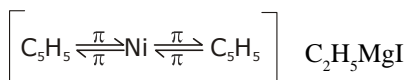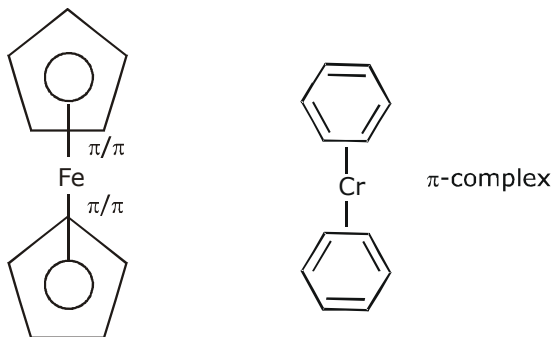
Q.2 (BD)

Applying law of equivalence

eq of complex = eq of Ag NO$_3$

[Cr(H$_2$O)$_5$Cl]Cl$_2$

$200 \times 0.01 \times 2 = 0.1 \times v$

= 40 mL

[Cr(H$_2$O)$_4$Cl$_2$]Cl. H$_2$O

$200 \times 0.01 \times 1 = 0.1 \times V$

V = 20 ml

Q.3 (BD)

(B) [Cr(H$_2$O)$_5$Cl]Cl$_2$ + 2AgNO$_3$ $\longrightarrow$ 2AgCl + [Cr(H$_2$O)$_5$Cl] (NO$_3$)$_2$

number of mole of complex = 200 × 0.01 = 2

required milli mole of AgNO$_3$ = 4

milli mole = M × V$_{ml}$ $\Rightarrow$ 4 = 0.1 × V$_{ml}$ = 40 ml

(D) [Cr(H$_2$O)$_5$Cl$_2$]Cl + AgNO$_3$ $\longrightarrow$ AgCl + [Cr(H$_2$O)$_5$Cl$_2$] (NO$_3$)

number of mole of complex = 200 × 0.01 = 2

required milli mole of AgNO$_3$ = 2

milli mole = M × V$_{ml}$ $\Rightarrow$ 2 = 0.1 × V$_{ml}$ = 20 ml.
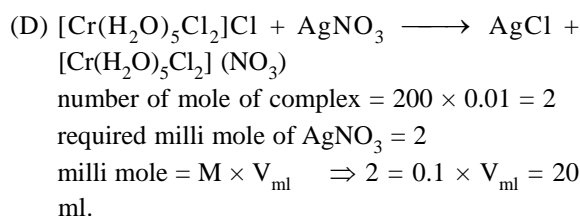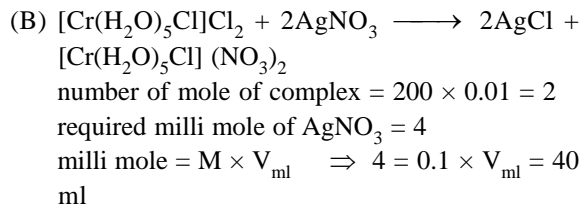
Q.4 (BCD)

Q.5 (ABC)

(A) For a given metal and ligand the stability is greater when the charge on the metal ion is greater; as oxidation state increases size of cation decreases.

(B) F$^-$ forms strongest complex. Smaller the size of the anion, greater the charge density on the atom and hence greater the sability of complex.

(C) Smaller the size of the metal ion, greater is the stability of the complex.

(D) Complex having chelate rings is more stable.

Q.6 (ACD)

(A) EAN of Cr = 24 + 12 = 36

and   EAN of Fe = 26 + 10 = 36.

(B) EAN of Co^{3+} = 25 + 12 = 37

and   EAN of Ni^{2+} = 26 + 12 = 38.

(C) EAN of Cu$^+$ = 28 + 12 = 36

and   EAN of Ni = 28 + 8 = 36.

(D) EAN of V$^-$ = 24 + 12 = 36

and   EAN of Co^{3+} = 24 + 12 = 36.

Q.7 (ABCD)

Let O.N. of Co be x

O×2+x+(−1)+(−1)+x+O×2=+4

x = +3

Q.8 (ABD)

(C) It is not correct formula because the Fe is in +3 oxidation state and as such formula should be $[Fe^{3+}(CN)_6]^{3-}$ or $K_3[Fe(CN)_6]$.

Q.9 (AD)

Cl^- ions are present in ionisation spheres in complexes (A) and (D) and thus react with $AgNO_3$ to form the white precipitate of AgCl.

Q.10 (A)

(A) Ma_2b_2 : – 2 (aa)(bb)
(ab)(ab)

(B) Ma_2b_4 – 2 (aa)(bb)(bb)
(ab)(ab)(bb)

(C) & (D) Ma_5b and Ma_6, have only one form.

Q.11 (ACD)

$[COCl_2(OH)_2(NH_3)_2]$ Br & $[CoClBr(OH)_2 (NH_3)_2]Cl$ are ionisation isomers.

cis   trans
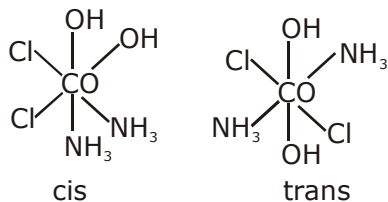
NO POS so optically active

Q.12 (ACD)

(A) $[CoCl_2(OH_2)_2(NH_3)_2$]Br and $[CoClBr(OH_2)_2(NH_3)_2$]Cl are ionisation isomers.
(B) Does not have ambidentate ligand; so does not show linkage isomerism.
(C) It is $Ma_2b_2c_2$ type.

$Ma_2b_2c_2$ – 5   (aa)(bb)(cc) (optically inactive)
(aa)(bc)(bc) (optically inactive)
(bb)(ac)(ac) (optically inactive)
(cc)(ab)(ab) (optically inactive)
(ab)(ac)(bc) (optically active)

Q.13 (BD)

II & III are Non super mirror image
I & II are geometrical isomers
I is cis wrt Cl
II is trans wrt Cl

Q.14 (ABCD)

$[Pt(bn)_2]^{2+}$ has square planner complex & hence molecular plane is the plane of symmetry
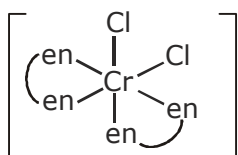
cis is optically active where as trans form is optically inactive
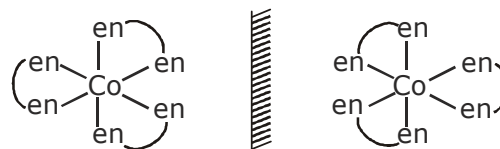
Non super imposable mirror image
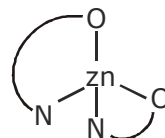
No plane of symmetry

Q.15 (BD)

optically active   trans
cis   optically active

Diastereomer

Q.16 (AB)

fac   Mer

Two optical isomers

Trans   cis   (optically active)
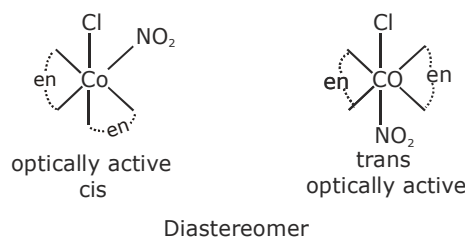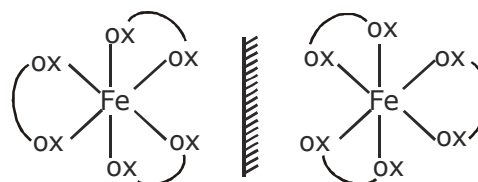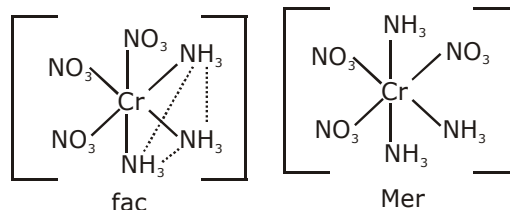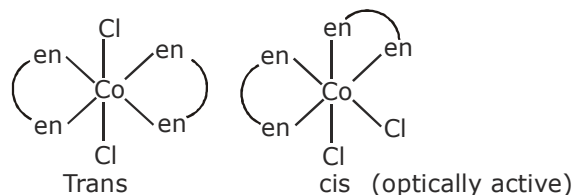
$[CoBrCl(Ox)_2]^{3-}$ more than three stereosiomers

Q.17 (AC)

(A) $[IrCl(CO)(PPh_3)_2]$
carbonylchloridobis(triphenylphosphine)iridium(I).
(B) Coordination number of Ir is four. Ir is in (+1) oxidation state with $4d^8$ configuration. It is trans isomer, so its geometry should be square planar.

$[IrCl(CO)(PPh_3)_2]$

dsp^2 hybridisation
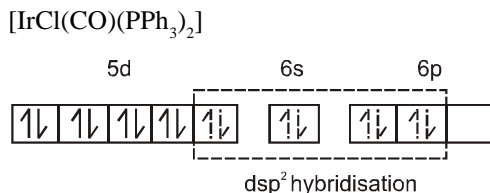
(C) All electrons are paired ; so magnetic moment is zero.

(D)

trans-form

cis-form
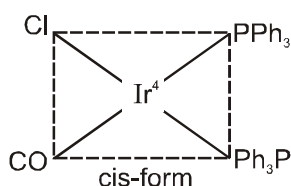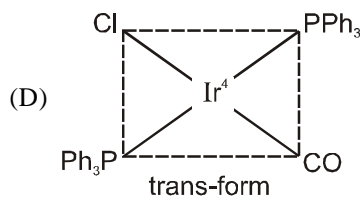
The complex has plane of symmetry, so it does not show optical isomerism.

Q.18 (AC)

$Na[CoCl_2(NO_2)(\sigma–C_3H_5)(NH_3)_2]$
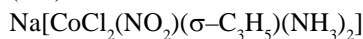
Let O.N. of cobe x

x–2-1–1=−1

x=+3

Q.19 (ABC)

Ambidentate ligands can attach to metal ion through two coordination sites giving linkage isomerism. All are ambidentate ligands.

Q.20 (ABCD)

(A) $[\overset{II}{Co}(NH_3)_5(NO_2)]Cl$ and $[\overset{II}{Co}(NH_3)_5(ONO)]Cl$ - linkage isomerism

$[\overset{II}{Co}(NH_3)_5(NO_2)]Cl$ and $[\overset{II}{Co}(NH_3)_5Cl]NO_2$ - ionization isomerism

(B) $[\overset{III}{Co}(NH_3)_5(H_2O)](NO_2)_3$ and

$[\overset{III}{Co}(NH_3)_5(NO_2)](NO_2)_2.H_2O$ - hydrate isomerism

$[\overset{III}{Co}(NH_3)_5(NO_2)](NO_2)_2.H_2O$ and

$[\overset{III}{Co}(NH_3)_5(ONO](NO_2)_2.H_2O$

(C) $[\overset{II}{Pt}(NH_3)_4]^{2+}[\overset{II}{Pt}(SCN)_4]^{2-}$ and

$[\overset{II}{Pt}(NH_3)_3(SCN)]^+[\overset{II}{Pt}(NH_3)(SCN)_3]^-$ - coordination isomerism

$[\overset{II}{Pt}(NH_3)_4]^{2+}[\overset{II}{Pt}(SCN)_4]^{2-}$ and $[\overset{II}{Pt}(NH_3)_4]^{2+}$

$[\overset{II}{Pt}(NCS)_4]^{2-}$ - linkage isomerism

(D) $[Cr(NH_3)_4(NO_2)_2](NO_3)_2$ and $[Cr(NH_3)_4(NO_3)_2](NO_2)_2$ - ionization isomerism

$[Cr(NH_3)_4(NO_2)_2](NO_3)_2$ and $[Cr(NH_3)_4(ONO)_2](NO_3)_2$ - linkage isomerism

Q.21 (ABCD)

(A) $[Ag(NH_3)_2]^-$

$Ag(I) \rightarrow 4d^{10}5s^0$ $H_3N \xrightarrow{\hspace{1.5cm}} Ag^+ \xrightarrow{\hspace{1.5cm}} NH_3$

Linear

sp hybridisation

(B) $NiCl_4^{2-}$, VO_4^{3-} and MnO_4^- have tetrahedral geometries.

$Ni^{2+} \rightarrow 3d^8$
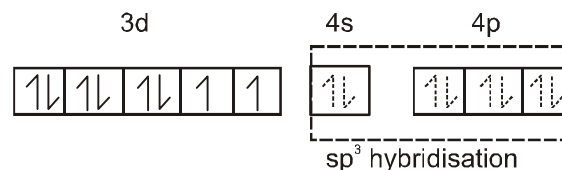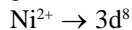
sp^3 hybridisation

(C) $[Cu(NH_3)_4]^{2+}$, $[Pt(NH_3)_4]^{2+}$ and $[Ni(CN)_4]^{2-}$ have square planar geometries.

$[Cu(NH_3)_4]^{2+}$

dsp^2 hybridisation

Pt^{2+}, $[Xe]4f^{14}5d^8$

$[Pt(NH_3)_4]^{2+}$
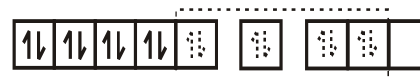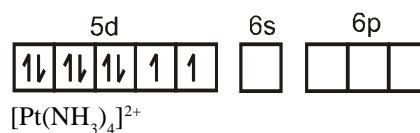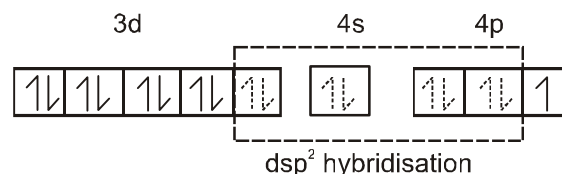
dsp^2 hybrid orbitals

Similarly the hybridisation scheme for $[Ni(CN)_4]^{2-}$ (CN$^-$ is a strong field ligand) is as shown in figure.

Ni^{2+}, $[Ar]3d^8$

3d   4s   4p

$[Ni(CN)_4]^{2-}$
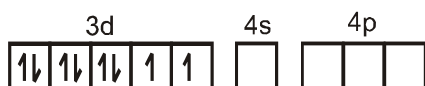
dsp² hybrid orbitals

(D) $[Fe(CO)_5]$ is diamagnetic and has dsp³ hybridisation. So it has trigonal bipyramidal geometry.

Q.22 (AD)

$[Ir(H_2O)_6]^{3+}$ d²SP³ It is Inner orbital complex, dimagnetic

$[Ni(NH_3)_6]^{2+}$ SP³d² Outer orbital complex, Para Magnetic

$[Cr(NH_3)_6]^{3+}$ d²SP³ Inner orbital complex, Para Magnetic

$[CO(NH_3)_6]^{3+}$ d²SP³ Inner orbital complex, di Magnetic

Q.23 (ACD)

$[Cu^{2+}(NH_3)_4]SO_4$
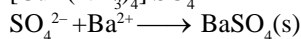
$SO_4^{2-} + Ba^{2+} \longrightarrow BaSO_4(s)$
　　　　　　　　(White ppt)

Conductivity corresponds to two ions

Q.24 (ACD)

$[TiCl_4]$ - $3d^0 4s^0 \rightarrow$ tetrahedral diamagnetic.

$[FeCl_4]^-$ - $3d^5 \rightarrow$ tetrahedral with five unpaired electrons, so paramagnetic ?

Q.25 (BCD)

$[Cu(NH_3)_4]^{2+}$ dsp² square planner paramagnetic

$[Ni(CO)_4]$ sp³ Tetrahedral Dimagnetic

$[Ni(CO)_4]$ sp³ Tetrahedral Dimagnetic

$[Zn(NH_3)]_4^{2+}$ sp³ Tetrahedral Dimagnetic

Q.26 (AC)

$[Ru(H_2O)_6]^{3+}$ d²sp³ 1 unpaired electron (upe) octahedral

$[Mn(CO)_5]^-$ dsp³ 0 upe TBP

$[Fe(NH_3)_6]^{2+}$ sp³d² 4 upe octahedral

$Cr_2O_7^{2-}$ sp³ 0 upe dimagnetic

Q.27 (B)

(A) $[Co(ox)_3]^{3-}$; $3d^6$ configuration, all electrons are paired and hybridisation is d²sp³–diamagnetic with μ = 0.

(B) $[Cr(NH_3)_6]^{3+}$; $3d^3$ configuration, all electrons are unpaired and paramagnetic with μ (approximately)3.78 B.M and hybridisaion is d²sp³ (NH_3 strong field ligand).

(C) $[Fe(H_2O)_5NO]^{2+}$; $3d^6 4s^1$ configuration, hybridisation is sp³d² and is paramagnetic with three unpaired electrons (μ ≈ 3.78 B.M.)

(D) $[Zn(NH_3)_6]^{2+}$; $3d^{10}$ configuration, all electrons are paired so diamagnetic with μ = 0 and hybridisation is sp³d².

Q.28 (BD)

$[Fe(CN)_6]^{4-}$ d^6 No upe d²sp³ dimagnetic

$[Ni(CN_4)]^{2-}$ d^8 No upe dsp² dimagnetic

$[Zn(OH_4)]^{2-}$ Tetrahyroxido zincate (II), en is a bidentate ligand

$[Cr(NH_3)_2(en)_2]^{3+}$ C.N. = 6

Q.29 (ABD)

$[Co(ox)_3]^{3-}$ involves chelation

$[Co(NH_3)_6]^{2+}$ d²sp³ 1 upe by excitaion in d-orbital

$[Cu(NH_3)_4]$ dsp² 1 upe by excitation in P-orbital

Colour due to charge transfer is more intense than d-d transition

$(Mn_2(CO)_{10}$
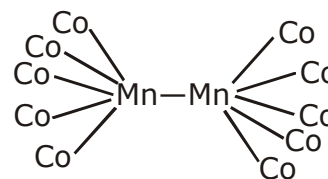
Q.30 (ABD)

$Na_2[Fe(CN)_5](NO)]$

Let O.N. of iron

$2 + x - 5 + 1 = 0$ be x

$x = +2$

$[Ag(NH_3)_2]^+$ Ag+ $4d^{16}$ sp hybridised Linear dimagnetic, 0 upe

$[Fe^{3+}(H_2O)_6]^{3+}$ sp³d² 5 upe paramagnetic

$[Ni(Co)_4]$ Let O.N. of Ni =x

$x + 0 \times 4 = 0$

$x = 0$

Q.31 (D)

(A) $[Fe(CN)_6]^{4-}$ d^6

CN^- is strong field lignad.

(B) $[Ni(CO)_4]$ d^{10}
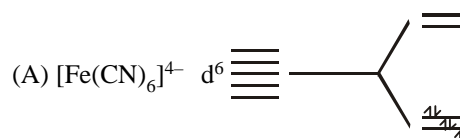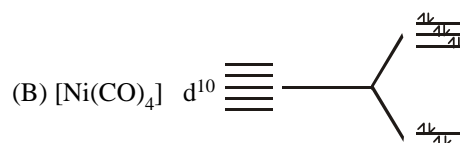
CO is strong field lignad.

(C) $[Ni(CN)_4]^{2-}$; Ni^{2+} has $3d^8$ configuration and CN^- is strong field lignad. So, complex is square planar and diamagnetic.

(D) $[CoF_6]^{3-}$

d^6 F⁻ being weak field
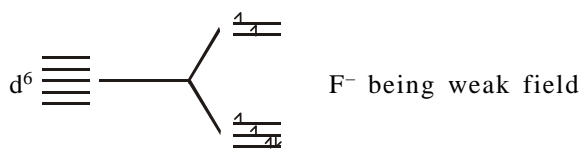
ligand does not allow pairing.

Q.32 (ABD)

[⁺¹Cu(CN)₄]³⁻ sp³ Tetrahedral No upe

[²⁺Cd(CN)₄]²⁻ sp³ Tetrahedral No upe

[²⁺Cu(NH₃)₄]²⁺ dsp² square planner 1 upe

[Cd(CN₄)]²⁻ complex is thermodynamicaly unstable & hence it gets decomposed after passing through H_2S

[Cd(CN)₄]²⁻+H_2S→ Cds +CN⁻+H⁺

        (yellow ppt)

[Cu(CN)₄]³⁻+H_2S ⟶No reaction

Q.33 (BCD)

Pt^{2+} $5d^8$

Pd^{2+} $4d^8$

for 2ⁿᵈ & 3ʳᵈ transitaian series all ligand acts as strong field ligand so for C.N.=4 the prefreble geometry is square planer

[Ni(CN)₄]² dsp² square planner, dimagnetic

[Ni(CO)₄] Sp³ tetrahedral, dimagnetic

(3d⁸) Ni^{2+} when tends to form inner d-orbital complex the hybridisatioan in dsp³d in which one d comes from 4d so the energy difference is so high is mixing is not possible

Q.34 (AC)

(i) $_{25}$Mn is in + II oxidation state. The electronic configuration of Mn^{2+} is [Ar]¹⁸ 3d⁵ 4s⁰. The CN⁻ is strong field ligand. So,

[Mn(CN)₆]⁴⁻

d^2sp^3 hybridisation

It is inner orbital / low spin octahedral complex with one unpaired electron.

Similarly for [Fe(CN)₆]⁴⁻

d^2sp^3 hybridisation
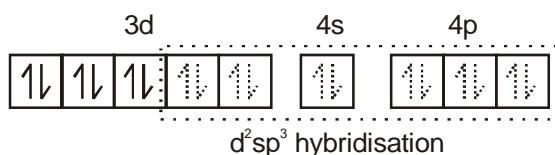
It is inner orbital / low spin octahedral complex with no unpaired electron.

(ii) As the negative charge on the metal increases from the manganese complex to vanadium complex, it is

delocalised on to the ligands by the π back bonding. This strengthens the metal-carbon bond and weakens the C – O bond (as bond order of CO decreases). Hence order of C – O bond strength is : [Mn(CO)₆]⁺> [Cr(CO)₆] > [V(CO)₆]⁻ > [Ti(CO)₆]²⁻ and M – C bond strength is : [Mn(CO)₆]⁺< [Cr(CO)₆] < [V(CO)₆]⁻ < [Ti(CO)₆]²⁻.

(iii) [RhCl(PPh₃)₃] is Wilkinson's catalyst. Because of 4d⁸ configuration its higher CFSE favours square planar low spin complex (i.e. dsp²). It is used as homogeneous catalyst for the hydrogenation of alkenes.

(iv) False statement : trans [Co(en)₂Cl₂]⁺ has a centre and several planes of symmetry but the cis-form has neither, and (+) and (–) forms of cis [Co(en)₂Cl₂]⁺ have been separated.
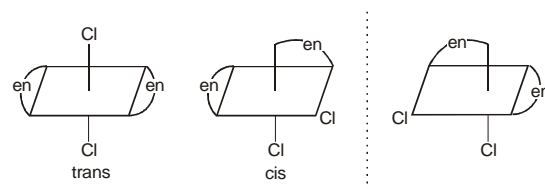
(v) In Ni(CO)₄, the Ni is in zero oxidation state. The CO is strong field ligand, so

[Ni (CO)₄]

sp³ hybridisation
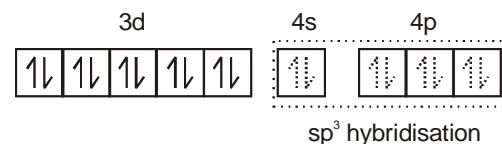
It is outer orbital complex with μ$_s$ = 0. EAN = 28 + 8 = 36

In [NiCl₂(PPh₃)₂] the Ni is in + II oxidation state. Ligand triphenyl phosphine in spite of strong field ligand favours tetrahedral geometry on account of its bulkier nature. So,

[NiCl₂(PPh₃)₂]
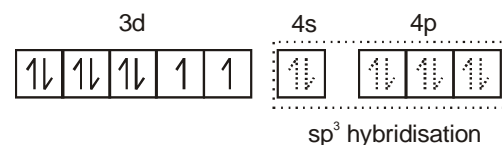
sp³ hybridisation

It is also outer orbital complex with μ$_s$ = $\sqrt{8}$ ~ 2.73 B.M.

EAN = 26 + 8 = 34.

Q.35 (BCD)

In complex nickel is in zero oxidation state. The CO is strong field ligand and therefore compels for the pairing of electrons. The hybridisation scheme is as shown in figure.

$Ni^0([Ar] 3d^8 4s^2)$

[Ni(CO)$_4$]

sp^3 hybrid orbitals

Four pairs of electrons from four CO.

It is tetrahedral and as all electrons are paired so diamagnetic.

Q.36 (ABD)

(A) [Co(PMe$_3$)$_4$]

sp^3 hybridisation

(B) [Ni(en)$_3$]$^{2+}$

sp^{3}d^2 hybridisation

(C) [V (NH$_3$)$_6$]$^{3+}$

d^{2}sp^3 hybridisation

(D) [Mn^{3-} (NO$^+$)$_3$ (CO)]
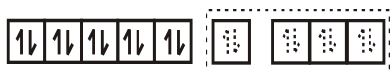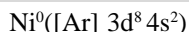
sp^3 hybridisation
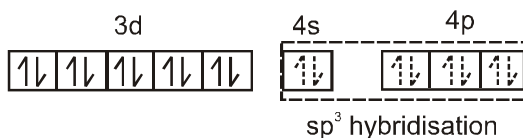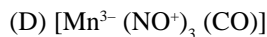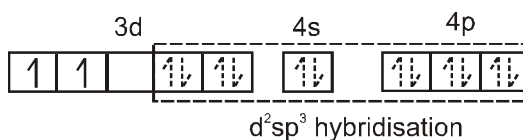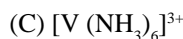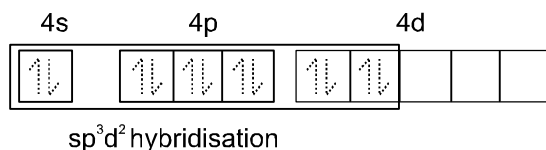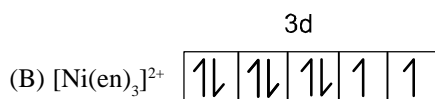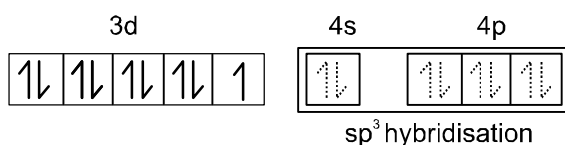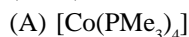
Q.37 (BD)

Ni (dmg)$_2$ complex is square planar and dimagnetic.

(B) Mn in [MnO$_4$]$^-$ is in + 7 oxidation state having [Ar]^{18} 3d^0 configuration. Complex ion is tetrahedral and diamagnetic

(D) Pt (II) – 5d^8 configuration. Complex is square planar and therefore, dimagnetic.

So, $\mu = 0$

Q.38 (D)

It is homogeneous catalyst for hydrogenation of alkenes.

Q.39 (D)
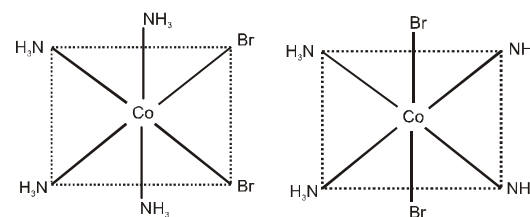
cis -   trans -

It shows geometrical isomerism but not optical isomerism due to the presence of at least one plane of symmetry.

[Co(NH$_3$)$_4$Br$_2$]NO$_2$ and [Co(NH$_3$)$_4$BrNO$_2$]Br are ionisation isomers and later complex reacts with AgNO$_3$ solution to give pale yellow precipitate. [Co(NH$_3$)$_4$BrNO$_2$]Br and [Co(NH$_3$)$_4$BrONO] Br are linkage isomers.

Q.40 (C)
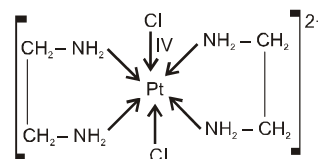
trans-form is optically inactive because it is achiral.

Q.41 (D)

Q.42 (B)

$t^3_{2g}e^2_g$ outer orbital

$t^3_{2g}e^0_g$ inner orbital

$t^4_{2g}e^2_g$ outer orbital

$t_{2g}6e^1_g$ inner orbital by excitation of electron.

Q.43 (B)

[Co(H$_2$O)$_6$]$^{3+}$ Δ> P as for

Co^{3+} Cl$^-$, I$^-$, Br$^-$, F$^-$ are only weak field ligands, rest are strong field ligands.

Q.44 (D)

Water present in ionisation sphere is absorbed by conc. H$_2$SO$_4$ (dehydrating agent). If Cl$^-$ present as counter ion then reacts with, AgNO$_3$ to give white precipitate of AgCl.

Q.45 (C)

With F^- ligand, metal ion has electron configuration, $t_{2g}^{2,1,1} e_g^{1,1}$.

So, $\mu = \sqrt{4(4+2)} \approx 4.9$ BM ; where n = number of unpaired electrons.

Q.46 (B)

With NO_2^- ligand, electron configuration in crystal field splitting for Co^{3+} will be $t_{2g}^{2,2,2} e_g^0$ i.e. no unpaired electrons.

Q.47 (A)

Complex contains one Cl^- as counter ion.

One mole of complex = one mole of Cl^-

As two mole of Cl^- gives one mole of $PbCl_2$.

∴ One mole of Cl^- will give ½mole of $PbCl_2$.

Q.48 (A)

Only two geometrical isomers are possible of $[CoBrCl(en)_2]^+$.
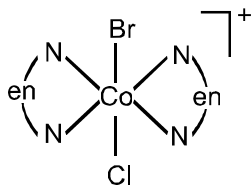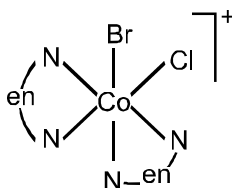
Q.49 (A)

(A) dsp^2 no unpair e^-
(B) experimental
(C) sp^3d^2 2 unpair e^-
(D) experimental

Q.50 (C)

$2\sqrt{2} = \sqrt{n(n+2)}$

n = 2 unpaired electron.
(A) dsp^2 no unpair e^-
(B) dsp^2 no unpair e^-
(C) sp^3d^2 2 unpair e^-
(D) sp^3d^2 2 unpair e^- but no ion

Q.51 (B)

Higher value of magnetic moment indicates that more no of unpaired electron so weak field ligand and outer orbital complex are formed whereas low value indi-

cates pairing & hence strong field ligand & inner orbital complex are formed.

Q.52 (D)

Ti^{3+} have same electronic configuration i.e., $[Ar]3d^1 4s^0$ with low as well as with high crystal field ligand. Ti^{3+} with high crystal field stabilization energy on account of higher oxidation state favours the formation of inner orbital complex i.e., d^2sp^3 hybridisation.

Q.53 (D)

Both are strong field ligands but complex with PPh_3 is tetrahedral due to its bulkier nature.

Q.54 (A)

Q.55 (B)

complex contain ambident ligand

Q.56 (A)
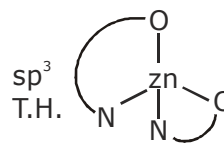
Rest complex has square planner geometry & hence molecular plane is plane of symmetry.

Q.57 (A)

Q.58 (B)

(X) = $[Co(SCN)_4]^{2-}$; (Y) = $[Co(dmg)_2]$.

Q.59 (A)

X = $[Co(SCN)_4]^{2-}$, cobalt is in + 2 oxidation state and SCN^- is weak field ligand. So,
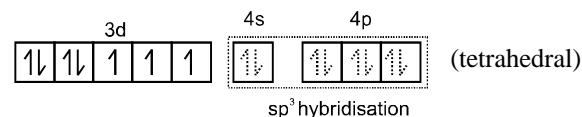
$[Co(SCN)_4]^{2-}$:

Y = $[Ni(dmg)_2]$: Nickel is in +2 oxidation state and dmg is chelating ligand. So,
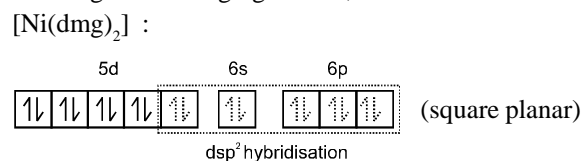
$[Ni(dmg)_2]$:

Q.60 (C)

X = $[Co(SCN)_4]^{2-}$, cobalt is in + 2 oxidation state and SCN^- is weak field ligand. So,
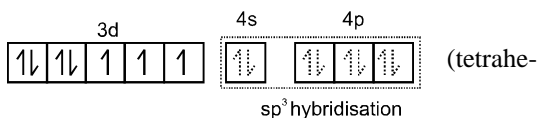
$[Co(SCN)_4]^{2-}$:

(tetrahedral)

sp³ hybridisation

$Y = [Ni(dmg)_2]$: Nickel is in +2 oxidation state and dmg is chelating ligand. So,

$[Ni(dmg)_2]$:

(square planar)

dsp² hybridisation
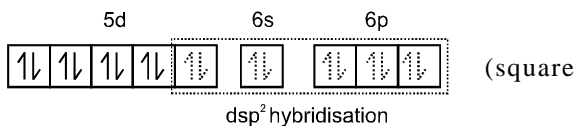
$[Ni(dmg)_2]$ shows intra moelcular H-bonding as shown below.

Reactions involved :

$Co^{2+}(aq) + 4SCN^-(aq) \longrightarrow [Co(SCN)_4]^{2-}(aq.)$ blue colour complex.

$Ni^{2+}(aq) + 2$
$CH_3 — C = N — OH$
$\quad\quad\quad\quad |$
$CH_3 — C = N — OH$
$\xrightarrow{NH_4OH}$

red precipitate
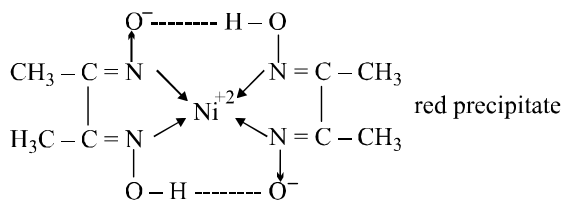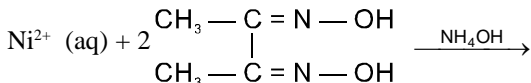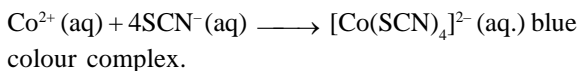
Q.61 (B)

+6

$[CrO_4^{2-}]$ d^0 sp³ tetrahedral dimagnetic & coloured due to charge transfer

2+
$[NiCl_4]^{2-}$ 2 unpair e⁻ sp³ tetrahedral paramagnetic
$[Cd(CN)_4]^{2-}$ 0 unpair e⁻ sp³ tetrahedral dinagnetic colourless.

Q.62 (B)

0
$[Ni(CO)_4]$
Ni ↑↓ ↑↓ ↑↓ ↑ ↑
pairing
↑↓ ↑↓ ↑↓ ↑↓ ↑↓ 4-sp³ hybrid orbital
synergic bonding increases CO bond length

Double bond char.
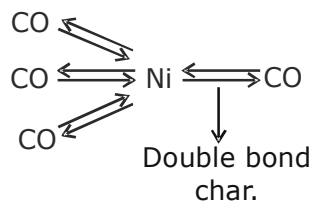
EAN = 28 + 4 × 2 = 36
It cannot acts as oxidising & reducing agent

Q.63 (A) - q, r, t ; (B) - q, r, t ; (C) - p, s ; (D) - q, r

(A) $[Co(en)_3]^{3+}$; Co^{3+} has d^6 configuration which has higher CFSE ; so hybridisation is d^2sp^3 and complex is diamagnetic. 'en' is a bidentate chelate ligand.

(B) $[Co(ox)_3]^{3-}$; Co^{3+} has d^6 configuration which has higher CFSE ; so hybridisation is d^2sp^3 and complex is diamagnetic. 'ox' is a bidentate chelate ligand.

(C) $[Co(H_2O)_6]^{2+}$; Co^{2+} has d^7 configuration ; H_2O is a weak field monodentated ligand, so it is paramagnetic with three unpaired electrons having sp^3d^2 hybridisation.

(D) $[Co(NO_2)_6]^{3-}$; Co^{3+} has d^6 configuration which has higher CFSE ; so hybridisation is d^2sp^3 and complex is diamagnetic. 'NO_2^-' is a monodentate ligand.

Q.64 (A) – s ; (B)– p ; (C) – q

Q.65 (A) - p, r, t; (B) - p, s, t; (C) - p, r, t; (D) - q, r

(A) $[\overset{III}{Fe}(en)_3]^{3+}$ -

d²sp³ hybridisation
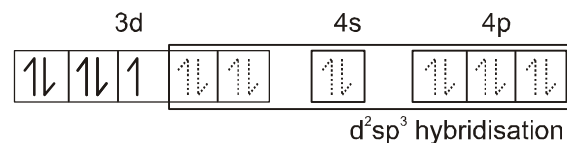
Number of unpaired electrons = 1; so paramagnetic

(B) $[\overset{III}{Co}(ox)_3]^{3-}$ -

d²sp³ hybridisation
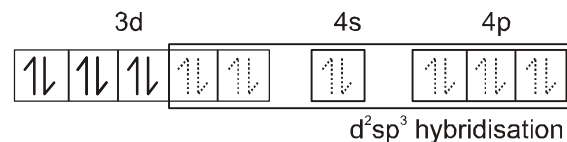
Number of unpaired electrons = 0; so diamagnetic.

(C) $[\overset{III}{Cr}(CN)_6]^{3-}$ -

d²sp³ hybridisation
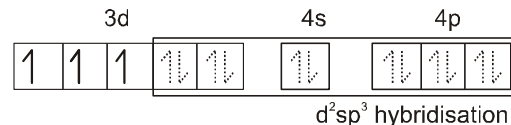
Number of unpaired electrons = 3 ; so paramagnetic.

(D) $[\overset{II}{Ni}Cl_6]^{4-}$ -

sp³d² hybridisation
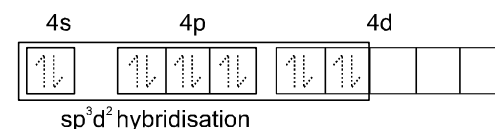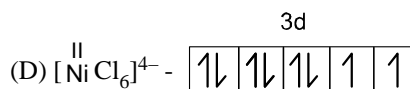
Number of unpaired electrons = 2; so paramagnetic.

57

Q.66 (A) – r, s ; (B) – p, q ; (C) – p ; (D) – p, q

$$\left[\overset{2+}{Ni(H_2O)_6}\right]Cl_2 \; d^8$$

3d | 4s — 4p — 4d |
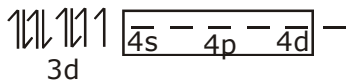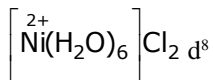
2unpair e⁻ 6-sp³d² hybrid orbital

$\mu = \sqrt{2 \times 4} = \sqrt{8} = 2.83BM.$

$$\left[\overset{3+}{Co(CN)_2(NH_3)_4}\right]^{+1-} OC_2H_5$$
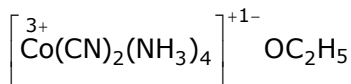
CN^- & NH_3 are strong field ligand

$CO^{3+}d^6$

| 3d — 4s — 4p |

6–d²sp³ hybrid orbital

$[\overset{3+}{IrCl_6}]^{3-}$ d²sp³ No unpair e⁻

4+

$[PtCl_2(NH_3)_4]Br_2$ d²sp³ No unpair e⁻

Q.67 (A) – p, q, r ; (B) – q, r, s ; (C) – p, q, r, s ; (D) p, q.

(A) $[\overset{III}{Co(en)_2}(NH_3)Cl]^{2+}$ SO_4^{2-} and

$[\overset{III}{Co(en)_2}(NH_3)SO_4]^+$ Cl^- ionisation isomerism.

trans–

cis–
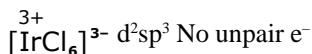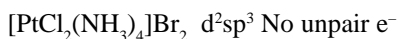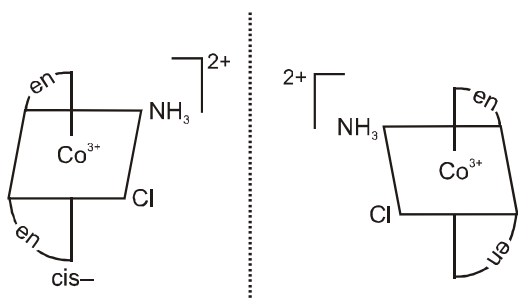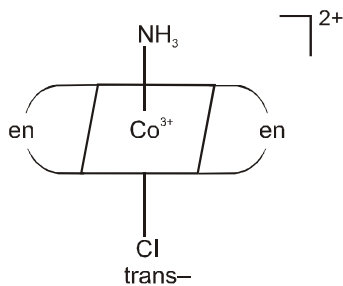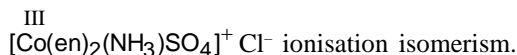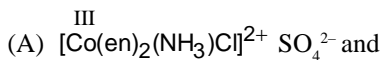
Note : trans-form has a centre of symmetry and several planes of symmetry, but the cis-form has neither.

(B) Has total 12-isomeric forms including linkage (NO_2 - ambidentate ligand), ionisation (exchange of NO_2^- and NO_3^-), geometrical isomers (cis- and trans-).

Compound is optically inactive as cis- as well as trans-forms possess at least one plane of symmetry.

(C) Exchange of NO_2^- and Cl^- gives rise to ionisation isomerism.

Linkage through either O – and N – gives rise to linkage isomerism.

cis –   mirror plane

cis –   mirror plane

trans–   trans–
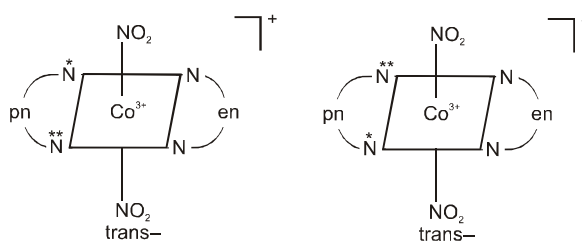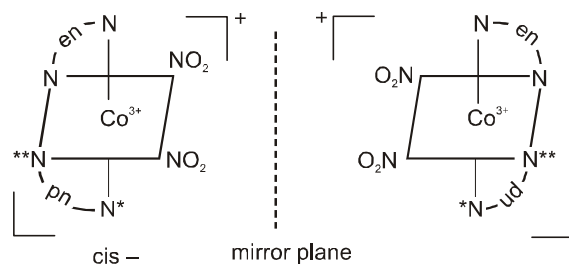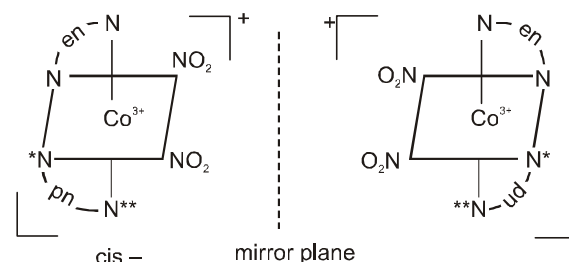
Thus exists in two trans – and two cis-isomers and each of cis-isomers show optical isomerism.

$$\overset{1}{C}H_2 - \overset{2}{C}H - \overset{3}{C}H_3 \; (1, 2\text{-diaminopropane(pn)})$$
$$H_2N \qquad NH_2$$

(D)

cis –   trans –
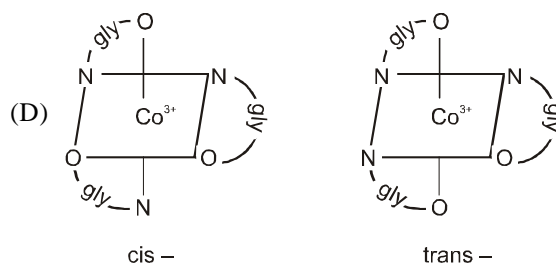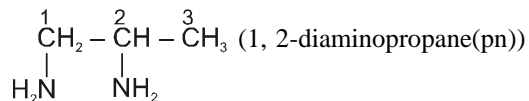
Both cis– and trans – isomers have each a pair of optical isomers because of absence of any one of symmetry elements.

Q.68 (A) – p, s ; (B) – p,s ; (C) – q ; (D) – r,q

$[Cu(NH_3)_4]^{2+} SO_4^{2-}$ dsp^2 square planer

$[Pt(NH_3)_2Cl_2]$ dsp^2 square planer

$K_4[Fe(CN)_6]$ d^2sp^3 octahedral

$[Fe(H_2O)_6]Cl_3$ sp^3d^2 octahedral

CN^- in strong field ligend but H_2O is weak field ligand.

Q.69 (A) – p ; (B) – p ; (C) – q ; (D) – r

en is bidentate

$EDTA^{4-}$ is hexadentate

NH_3 is monodentate

CO is monodentate

Q.70 (A) – p,r,s ; (B) – t ; (C) – q,r,t ; (D) – p,r,s
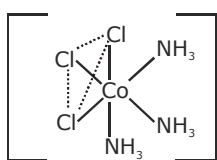
facial
(opticallyinactive)
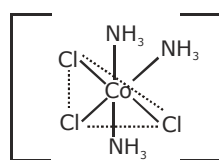
Meridonial(optically inactive)
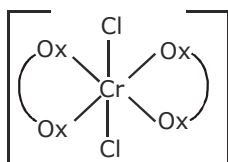
trans
(optically inactive)
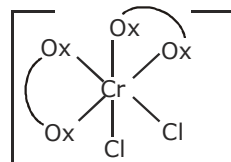
cis
(optically active)

$[Cr(Ox)_3]^{3-}$ is non super imposable on its mirror image

$[RhCl_3(Py)_3]$ show facial & Meridonial form which are optically active

Q.71 (A) – r ; (B) – r ; (C) – p ; (D) – q

$[Fe(CO)_4]^{2-}$ EAN = 26 + 2 + 4 × 2 = 36

$\left[\overset{3+}{CO}(NH_3)_5\right]Cl_2$ EAN = 27 – 3 + 5 ×2+2=36

$K_2\left[\overset{2+}{Ni}(CN)_4\right]$ EAN = 28 – 2 + 4 × 2 = 34

$[Cu(NH_3)_4]^{2+}$ EAN = 29 – 2 + 4 × 2 = 35

Q.72 (A) – q,s,t ; (B) – p,r ; (C) – p,r ; (D) – p, r

Para $[Fe(NH_3)_6]^{2+}$ sp^3d^2 4 unpair e⁻ outer orbital complex

Dimagnetic $\left[\overset{4+}{NiF_6}\right]^{2-}$ d^2sp^3 0 unpair e⁻ Inner orbital complex

Dimagnetic $[Co(H_2O)_6]^{3+}$ d^2sp^3 0 unpair e⁻ Inner orbital complex

Dimagnetic $\left[PtCl_2(NH_3)_4\right]Cl_2$ d^2sp^3 0 unpair e⁻ Inner orbital complex

Q.73 (A) – q ; (B) – p, q ; (C) – r, s ; (D) – r, s

$[\overset{4+}{Mn}Cl_6]^{2-}$ d^3 in weak field
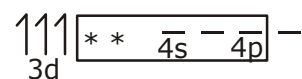
3 unpair e⁻ — — — — —

6-d^2sp^3 hybrid orbital

$[Fe(CN)_6]^{3-}$ d^2sp^3 1 unpair e⁻

$[CoF_6]^{3-}$ sp^3d^2 4 unpair e⁻

$[Fe(H_2O)_6]^{2+}$ sp^3d^2 4 unpair e⁻

Q.74 (A) – p,q,r,s ; (B) – r, q ; (C) – p, q ; (D) – p,q,r,s

$\left[\overset{2+}{Cu}(NH_3)_4\right]^{2+}$ dsp^2 1 unpair e⁻ μ=1.73BM Inner orbital complex

$\left[\overset{2+}{Cu}(Cl)_4\right]^{2-}$ sp^3 2 unpair e⁻ μ=2.82B.M.

$K_2\left[\overset{+1}{Cr}(CN)_4(NH_3)(N\overset{+}{O})\right]$ d^2sp^3

1 unpair e⁻ μ =1.73

$K_4[Co(NO_2)_6]$ d^2sp^3 1 unpair e⁻ μ = 1.73

excitation of 1 unpair e⁻ to vacant d-orbital
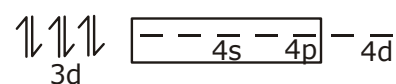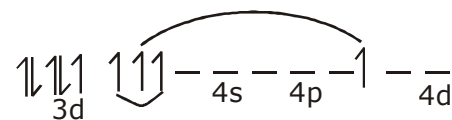
6-d^2sp^3 hybrid orbital

Q.75 (A) – p, q ; (B) – p, r ; (C) – r, s

NUMERICAL VALUE BASED

Q.1 [0]

Q.2 [13]

All are bidentate except diethylenetriamine which is tridentate.

Q.3 [6]

$$P_4O_{10} + 6H_2O \longrightarrow H_3PO_4$$

Q.4 [05]

$Na_2[Cr(edta)] - 2Na^+$

$Na_3[Co(NO_2)_6] - 3Na^+$
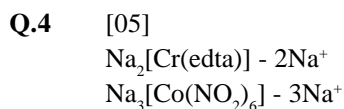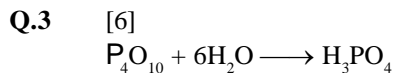
Q.5 [26]

Q.6 [6]

only

Q.7 (40 + 20) ml = [60] ml

Q.8 [4]

Q.9 [4]

True statements : (i), (iii), (iv), (vii).

Q.10 [6]

Q.11 [6]

Q.12 [3]

Correct options are (1), (3) & (4).

Q.13 [6]

Q.14 [3]

Paramagnetic $\times$ Inner orbital complexes are $[Cr(NH_3)_6 Cl_3$, $[Co(NH_3)_6](NO_3)_2$, $[V(H_2O)_6]SO_4$

Q.15 [4]

Q.16 [5]

Hapticity is the number of atoms of the pi donor ligand directly attached to the metal ion. In C5H5 the electron cloud is delocalized over all the five carbon atoms. Hence all the five carbon atoms are attached to the metal ion and make the hapticity 5.

Q.17 [4]

For $CoCl_2Br_2 \rightarrow$ No. of G.I. = 0

For $[Rh(en)_3]^{3+} \rightarrow$ No. of G.I. = 0

For $[Cr(en)_2Br_2]^+ \rightarrow$ No. of G.I. = 2

For $[Pt (en) Cl_2] \rightarrow$ No. of G.I. = 0

For $[Co(NH_3)_3 (NO_2)_3] \rightarrow$ No. of G.I. = 2

Hence sum of Geometrical isomers = 4.

Q.18 [4]

Q.19 [5]

$[Fe(n^5 - C_5H_5)_2]$

Q.20 [12]

It shows linkage, geometrical and optical isomerism.

(1) cis-NO_2 / SCN ⎫

(2) cis-ONO / SCN ⎬ Mirror images of

(3) cis-NO_2 / NCS ⎪ (1), (2), (3), (4)

(4) cis-ONO / NCS ⎭

(5) trans-NO_2 / SCN (9)

(6) trans-ONO / SCN(10)

(7) trans-NO_2 / NCS (11)

(8) trans-ONO/ NCS (12)

Q.21 [4]

$Be(4) = 1s^2 2s^2$

$Be^* =$
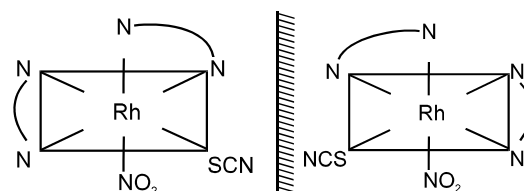
Four orbital can be used by Be for bond formation.

KVPY
PREVIOUS YEAR'S

Q.1 (A)

$Co^{+3} = [Ar] 3d^6 s^0$

NH_3 is a strong field ligand

(ii) $Ni^{+2} = [Ar] 3d^8 4s^0$

NH_3 is a strong field ligand

(iii) $Cr^{+3} = [Ar] 3d^3 4s^0$

H_2O is a weak field ligand

(iv) $Fe^{+2} = [Ar] 3d^6 4s^0$

H_2O is a weak field ligand.

So, $[Co(NH_3)_6]Cl_3$ will be diamagnetic.

Q.2 (C)

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

$Mn^{+2} \rightarrow 3d^5 4s^0 4p$

CN^- is strong ligands so creates back paring effect of

(n – 1) d obritals configuration

So, umpaired e⁻ = 1

$$\mu = \sqrt{5(5+2)}$$

μ = 1.73 B.M   and in $[MnBr_4]^{-2}$

Br is a weak ligands so no back pairng effect on (n – 1) d orbital so, unpaired e⁻ is = 5

$$\mu = \sqrt{5(5+2)} = \sqrt{35} = 5.92 \text{ B.M}$$

Q.3   (A)
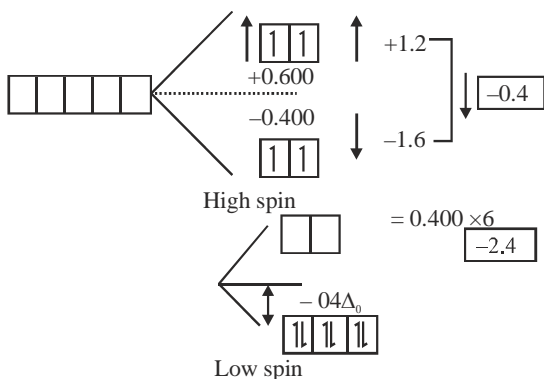
Q.4   (C)

Ni (CO)₄

$Ni^0 = 3d^8 4s^2$
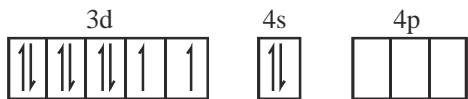
By effect of S.F.L.CO.
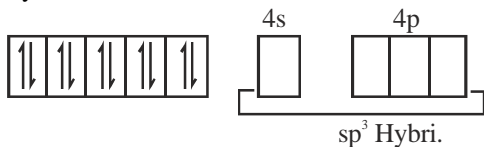
sp^3 Hybri.

$[Cr(H_2O)_6]^{+2}$ $Cr+2 = 3d^4 4s^0 4p^0$

d^2sp^3
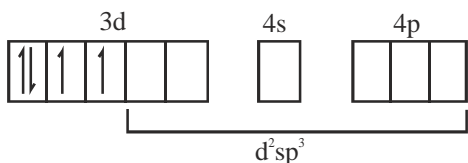
Q.5   (A)

$[MCl_4]^{2-}$ Tetrahedral = sp^3 hybridisation

M^{+2}

$$\because \mu = \sqrt{n(n+2)} \text{B.M.} = 3.83$$

n = 3

Means configuration of $M^{+2} = 3d^7$ So, M $= 3d^7 4s^2 = ^{27}Co$

Q.6   (A)

$Zn + 2OH^- + 2H_2O \rightarrow [Zn(OH_4)]^{2-} + H_2$

2gm (1 mole) H_2 is given by 65.4 gm of Zn
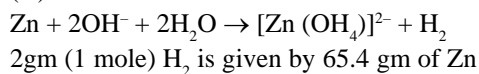
1 gm is given by $\dfrac{65.4}{2}$ gm of Zn

Q.7   (B)

Coordination number = 6

$[Co(NH_3)_4Cl_2]Cl \rightarrow [Co(NH_3)_4 Cl_2]^+ + Cl^-$

Q.8   (C)
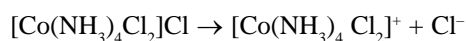
$Fe^{3+} = 3d^5$
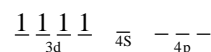
$\overset{\ominus}{F}$ is WFL so μ = 5.92 while NH_3 is SFL & pairing of electrons takes place so μ = 1.73

Q.9   (B)

$[Co(H_2O)_6]^{2+}$ 6NH₃ $\longrightarrow [Co(NH_3)_6]^{2+}$
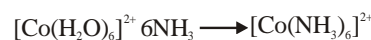
Paramagnetic O_2 –e⁻(oxidation)
n = 3; μ = 3.9
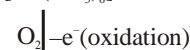
$[Co(NH_3)_6]^{3+}$
Diamagnetic
μ = 0; n = 0

Q.10   (C)

Energy of d_{z^2} is greater than d_{xy} in case of octahedral crystal field while energy of d_{z^2} is less then d_{xy} in case of tetrahedral splitting
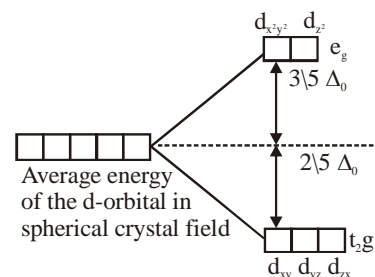
[Spliting in octahedral crystal field]
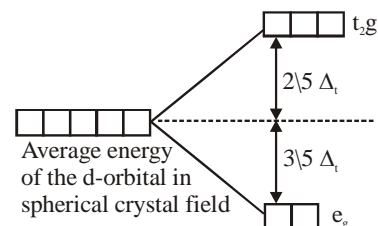
[Spliting in tetrahedral crystal field]

61

Q.11 (C)

Ni exist in zero oxidation state of its configuration is- its configuration is -

$_{28}$Ni = [Ar] 3d^8 4s^2

3d^8 4s^2 4p^0
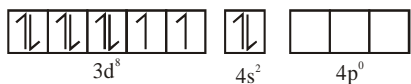
Co is strong ligand so pairing of electrons possible and configuration will be
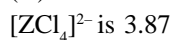

3d^8 4s^2 4p^0

sp^3/Tetrahedral
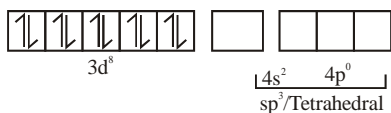
– Number of unpaired electrons are zero hence it is diamagnetic in nature.
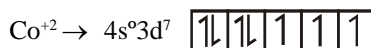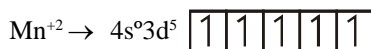
Q.12 (B)

Total 3 geometrical isomers are possible -

(1) Cis

(2) Trans

(3) Trans

Q.13 (C)

[ZCl$_4$]$^{2-}$ is 3.87

$x + (-1)4 = 2$ $u = \sqrt{n(n+2)}$

$x = +4 -2$

$x = +2$

Mn$^{+2} \rightarrow$ 4s^{o}3d^5

Ni$^{+2} \rightarrow$ 4s^{o}3d^8

Co$^{+2} \rightarrow$ 4s^{o}3d^7

Cu$^{+2} \rightarrow$ 4s^{o}3d^9

Q.14 (C)

$\left[Mn\, Br_4 \right]^{-2}$

$x + (-1)4 = -2$

$x = +2$

Mn $\rightarrow$ 4S^{2}3d^5

Mn$^{+2} \rightarrow$ 4s^o 3d^5
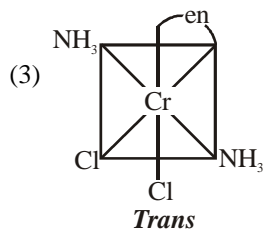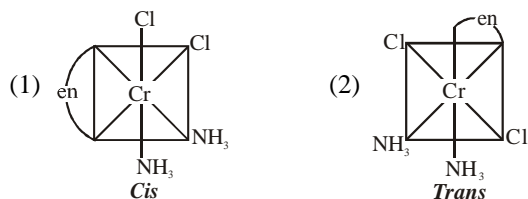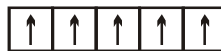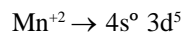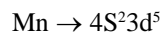
We know that Br is weak field ligand so Hund's Rule is applicable then

4s   4p

Br   Br Br Br
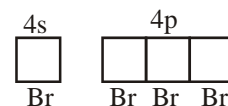
Hybridization is $\rightarrow$ sp^3
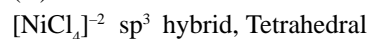and N$_0$ of unpaired = 5 electron.

Q.15 (C)

Q.16 (B)

optically active   optically active

Q.17 (A)

[NiCl$_4$]$^{-2}$ sp^3 hybrid, Tetrahedral
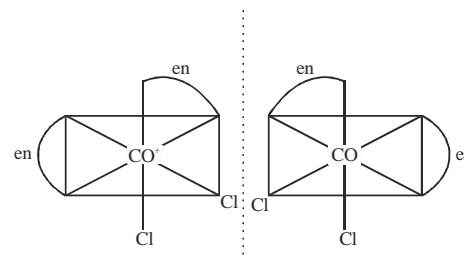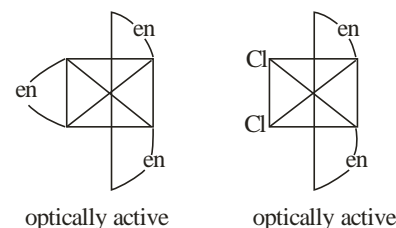
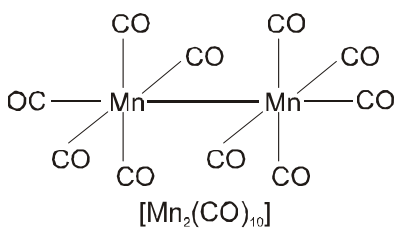**Q.18** (B)

–NO$_2$ is ambidentate ligand as it connect with metal by N or O atom.

Q.19 (C)

(A) [Fe(CN)$_6$]$^{3-}$ d^5 Low spin   n = 1 $\mu = \sqrt{2}$

(B) [Fe(H$_2$O)$_6$]$^{2+}$ d^6 High spin   n = 4 $\mu = \sqrt{24}$

(C) [MnF$_6$]$^{4-}$ d^5 High spin   n = 5 $\mu = \sqrt{35}$

(D) [NiCl$_4$]$^{2-}_{Tetrahedral}$ d^8 High spin   n = 2 $\mu = \sqrt{8}$

Q.20 (A)
$K_3[Fe(CN)_6] \Rightarrow Fe_3^{+3} = d_5 = t_{2g}^{2,2,1}, eg^{0,0}$
$K_3[CoF_6] \Rightarrow Co^{+3} = 3d^6 \Rightarrow t_{2g}^{2,1,1}, eg^{1,1}$
Both are paramagnetic

Q.21 (A)
$CoSO_4Cl.5NH_3 \Rightarrow ON = +3 \ \& \ CN = 6$

$[Co(NH_3)_5(SO_4)]Cl \xrightarrow{AgNO_3} AgCl\downarrow$
'X' _White_

$[Co(NH_3)_5Cl]SO_4 \xrightarrow{BaCl_2} BaSO_4\downarrow$
'Y' _White_

X & Y show ionisation Isomerism.

Q.22 (B)
MX_4Y_2 have 2 geometrical isomers both are achiral.

cis form   trans form

Q.23 (D)
$[Co(NH_3)_3Cl_3]$

fac
optically inactive

mer
optically inactive

GI = 2
Total steroisomer = 2

d

cis

Trans (optically inactive)
G.I. = 2
Optical isomer = 3
stereo isomer = 3

Q.24 (C)
Complex Shape Hybridisation.
$[CdCl_4]^{2-}$ Tetrahedral sp^3
$[Zn(CN)_4]^{2-}$ Tetrahedral sp^3
$[PdCl_4]^{2-}$ Square Planar dsp^2
$[Cu(CN)_4]^{3-}$ Tetrahedral sp^2

Q.25 (A)

Q.26 (B)
$[Ni(dmg)_2]$
Ni^{2+}
dmg^{-1} SFL

No unpaired electron present in splited 'd' obirtal
∴ dimagnetic ($\mu_B = 0$).

JEE-MAIN
PREVIOUS YEAR'S
Q.1 (4)
$[Mn(CN)6]^{4-}$
$Mn^{2+} = 3d^5 \xrightarrow{Strong\ field\ ligand} t_{2g}^{2,2,1} eg^{00}$
Hybridisation = d^2sp^3
$[Fe(CN)_6]^{3-}$
$Fe^{3+} = 3d^5 \xrightarrow{Strong\ field\ ligand} t_{2g}^{2,2,1} eg^{00}$
Magnetic nature → paramagnetic

Q.2 (1)
$[FeF_6]^{3-} \Rightarrow sp^3d^2 \ \& \ n = 5$; $[NiCl_4]^{2-} \Rightarrow sp^3 \ \& \ n = 2$
$[Cu(NH_3)_4]^{2+} \Rightarrow dsp^2 \ \& \ n = 1$; $[Co(NH_3)_6]^{3+} \Rightarrow d^2sp^3$
& n = 0

Q.3 (1)
Both are correct

Q.4 [0]

63

$[Mn_2(CO)_{10}]$

Q.5 [3]

Cis
optically active
having two stereoisomers d & ℓ

Trans
optically inactive

Therefore total three stereoisomers are possible

Q.6 (1)

$[FeCl_4]^{2-}$ Contain Fe^{+2} in tetrahedral complex. Its configuration is $e_g^{2,1} t_{2g}^{1,1,1}$ it have 4 unpaired electron in $[CO(ox)_3]^{3-}$ Co^{+3} have configuration $t_{2y}^{2,2,2}$ $eg^{0,0}$

$Mn O_4^{2-}$ have Mn in +6 oxidation state and configuration of Mn is $e_g^{1,0} t_{2g}^{0,0,0}$

Q.7 (2)
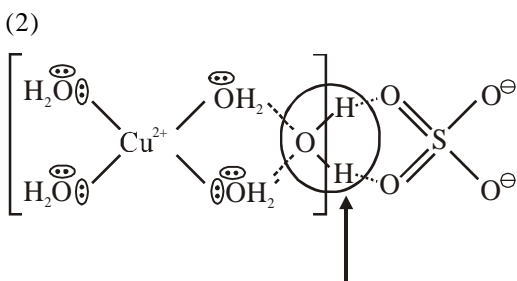
Hydrogen bonded
water molecule = 1
Secondary valency = 4

Q.8 [3]

$K_3[Cr(oxalate)_3]$
Chromium is in +3 oxidation state.
Number of unpaired electrons in Cr^{+3} will be 3.

Q.9 (4)

trans-$[Ni Br_2(PPh_3)_2]$ is
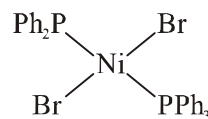
meridional - $[Co(NH_3)_3(NO_2)_3]$ is
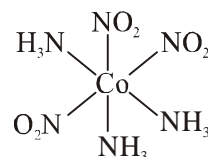
Q.10 (2)

Chlorophyll is a coordination compound of magnesium.

Vitamin B-$_{12}$, cyanocobalamine is a coordination compound of cobalt.

Cisplatin is used as an anti-cancer drug and is a coordination compound of platinum.

Grubbs catalyst is a compound of Ruthenium.

Q.11 [6]

$$Fe^{3+} + 3K^+ + 3C_2O_4^{2-} \rightarrow K_3[Fe(C_2O_4)_3]$$
$$\text{(A)}$$

Secondary valency of Fe in 'A' is 6.

Q.12 (1)

Complex	Type of Isomerism
(a) $[Co(NH_3)_6] [Cr(CN)_6]$	Co-ordination isomerism
(b) $[Co(NH_3)_3 (NO_2)_3]$	Linkage isomerism
(c) $[Cr(H_2O)_6]Cl_3$	Solvate isomerism
(d) cis-$[CrCl_2(ox)_2]^{3-}$	Optical isomerism

Q.13 (4)

(a) $_{58}Ce \rightarrow [Xe]4f^2 5d^0 6s^2$
In complex $Ce \rightarrow [Xe]4f^2 5d^0 6s^2$
there is no unpaired electron so $\mu_m = 0$

(b) $_{64}Gd^{3+} \rightarrow [Xe]4f^2 5d^0 6s^0$
contain seven unpaired electrons so,

$\mu_m = \sqrt{7(7+2)} = \sqrt{63}$ B.M.

(c) $_{63}Eu^{3+} \rightarrow [_{54}Xe]4f^6 5d^0 6s^0$
contain six unpaired electron

so, $\mu_m = \sqrt{6(6+2)} = \sqrt{48}$ B.M.

Hence, order of spin only magnetic movement

$\boxed{b > c > a}$

Q.14 [2]

trans - $CoCl_3.4NH_3$

or

trans-$[Co(NH_3)_4Cl_2]Cl$

$\downarrow$ -4NH$_3$
+ 2en
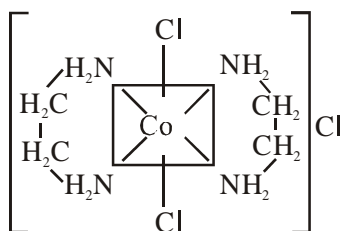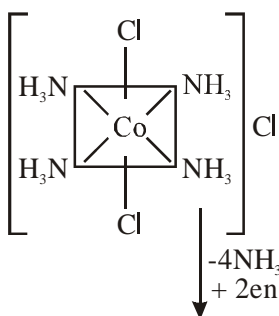
As we know that ethylene diamine is a bidentate ligand and ammonia is a mono dentate ligand.

It means overall two ethylene diamine is required to replace the all neutral ligands (four ammonia) from the coordination sphere of this complex.

Q.15 [4]

$\lambda_{absorbed}$ = 498 nm (given)

The octahedral splitting energy

$$\Delta_0 \text{ or } E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{498 \times 10^{-9}}$$

= 0.0399 × 10–17 J

= 3.99 × 10–19 J

= 4.00 × 10–19 J (round off)

Q.16 [6]
Q.17 (4)
Q.18 (4)
Q.19 (3)
Q.20 (2)
Q.21 [0]
Q.22 (1)
Q.23 (3)
Q.24 [2]
Q.25 (3)
Q.26 (2)

Q.27 (2)
Q.28 (4)
Q.29 [2]
Q.30 (4)
Q.31 (1)
Q.32 (4)
Q.33 [2]
Q.34 (4)
Q.35 (2)

JEE-ADVANCED PREVIOUS YEAR'S

Q.1 (C)

K–$[Fe(CN)_6]^{3-}$: $3d^5$ electron configuration after pairing of electrons for d^2sp^3 hybridisation it contains one unapaired electrons.

L–$[Co(NH_3)_6]^{3+}$: $3d^6$ electron configuration, d^2sp^3, diamagnetic.

M–$[Co(ox)_3]^{3-}$: $3d^6$ electron configuration, d^2sp^3, diamagnetic.

N–$[Ni(H_2O)_6]^{2+}$: $3d^8$ electron configuration, sp^3d^2, with two unpaired electrons paramagnetic.

O–$[Pt(CN)_4]^{2-}$: $5d^8$ electron configuration, dsp^2, diamagnetic.

P–$[Zn(H_2O)_6]^{2+}$: $3d^{10}$ electron configuration, sp^3d^2, diamagnetic.

Q.2 (6)

m moles of $[Cr(H_2O)_5Cl]Cl_2$ = 0.01 × 30 = 0.3.

$\Rightarrow$ mmole of Cl^- = 0.3 × 2 = 0.6

$\Rightarrow$ mmole of Ag^+ = mmoles of Cl^-

$\Rightarrow$ 0.1 × V = 0.6

$\Rightarrow$ V = 6 mL.

Q.3 (D)

$[Co(H_2O)_4 (NH_3)_2]Cl_3$

= diamminetetraaquacobalt (III) chloride

Q.4 (C)

$[NiCl_2 \{PEt_2Ph\}]$ contains Ni^{2+} with electronic configuration

Ni^{2+} = [Ar] $3d^8 4s^0$
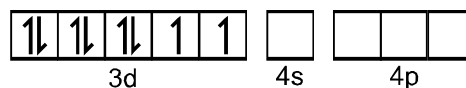
In high spin state, it is paramagnetic, sp^3 hybridised, tetrahedral.

In low spin state, it is diamagnetic, dsp^2, square planar.

Q.5 (B)

P = $[FeF_6]^{3-}$ ox. no. of Fe = +3 ,   configuration : - $3d^5 4s^0$

As F^- is weak ligand, pairing does not take place.

so it has 5 unpaired electron

$Q = [V(H_2O)_6]^{2+}$ ox. no. of V = + 2, configuration 3d^3 4s^0

It has 3 unpaired electrons.

$R = [Fe(H_2O)_6]^{2+}$, ox. no. of Fe = +2, configuration 3d^6, 4s^0

As H$_2$O is weak ligand, pairing does not take place, so it has 4 unpaired electron

$\Rightarrow$ order of spin only magnetic moment

$\Rightarrow$ Q < R < P so, answer is (B).

Q.6 (BD)

(A) $[Cr(NH_3)_5Cl]Cl_2$ and $[Cr(NH_3)_4Cl_2]Cl$, both compounds will not show either structural or stereoisomerism.

(B) $[Co(NH_3)_4Cl_2]^+$ and $[Pt(NH_3)_2(H_2O)Cl]^+$, Ma$_4$b$_2$ type (octahedral), Ma$_2$bc type (square planar) and both will show geometrical isomerism.

(C) $[CoBr_2Cl_2]^{2-}$ and $[PtBr_2Cl_2]^{2-}$, Ma$_2$b$_2$ type (tetrahedral), Ma$_2$b$_2$ (square planar).

(D) $[Pt(NH_3)_3(NO_3)]Cl$ and $[Pt(NH_3)_3Cl]Br$ both will show ionisation isomerism.

Q.7 (8)
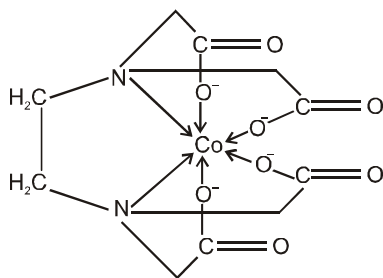
Q.8 P-3, Q-1, R- 4, S-2

(P) $[Cr(NH_3)_4Cl_2]Cl$ $\rightarrow$ Cr^{+3} is d^3. It is paramagnetic and it shows cis-trans isomerism.

(Q) $[Ti(H_2O)_5Cl](NO_3)_2$ $\rightarrow$ Ti^{+3} is d^1. It is paramagnetic and it show ionisation isomerism.

(R) $[Pt(en)(NH_3)Cl]NO_3$ $\rightarrow$ Pt^{+2} is d^8. But this complex is square planar and all electron are paired. So it is diamagnatic. It exhibit ionisation isomerism.

(S) $[Co(NH_3)_4(NO_3)_2]NO_3$ $\rightarrow$ Co^{+3} is d^6. Since ligands are strong, so electron are paired. it is diamagnetic.

It exhibit cis-trans isomerism.

Q.9 (4)

SCN$^-$ is weak field effect (WFE) ligand whereas CN$^-$ is strong field effect (SFE) ligand.

$_{26}$Fe^{+3} in $[Fe(SCN)_6]^{3-}$ = [Ar]
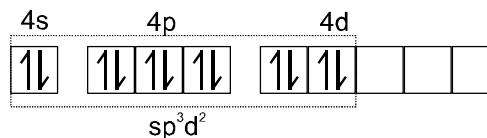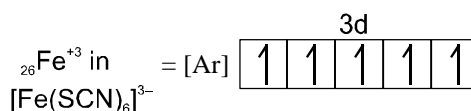
Spin only magnetic moment = $\sqrt{5(5+2)}$ = $\sqrt{35}$ BM

$_{26}$Fe^{+3} in $[Fe(CN)_6]^{3-}$ = [Ar]
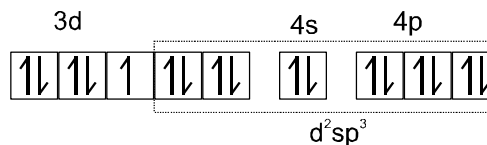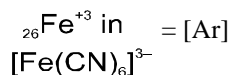
Spin only magnetic moment = $\sqrt{1(1+2)}$ = $\sqrt{3}$ BM

Difference = $\sqrt{35}$ $-$ $\sqrt{3}$ $\simeq$ 4

Q.10 (3)

$[Fe(CH_3CO)Br(CO)_2\{P(C_2H_5)_3\}_2]$

$CH_3-C^{\ominus}$ Ligand $\longrightarrow$ One Fe–C bond

$\overset{\|}{O}$

CO Ligand $\longrightarrow$ two Fe–C bond

Q.11 (6)

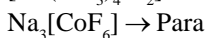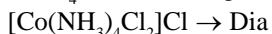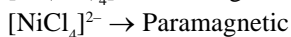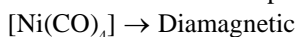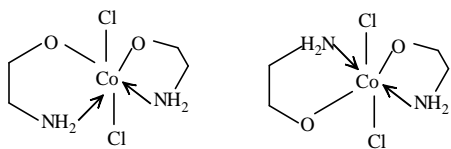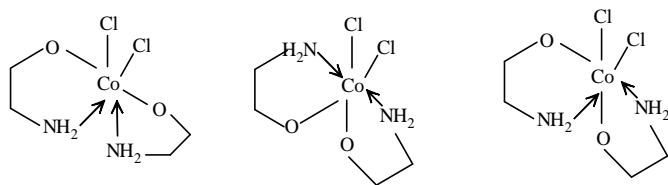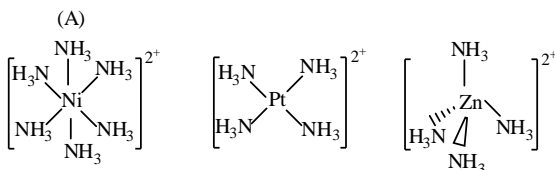All the complexes given show cis-trans isomerism

$[Co(NH_2-CH_2-CH_2-NH_2)Cl_2]^+$

$[(CrCl_2(C_2O_4)_2]^{3-}$

$[Fe(H_2O)_4(OH)_2]^+$

$[Fe(NH_3)_2(CN)_4]^-$

$[Co(NH_2–CH_2–CH_2–NH_2)_2(NH_3)Cl]^{2+}$

$(CO(NH_3)_4(H_2O)Cl]^{2+}$
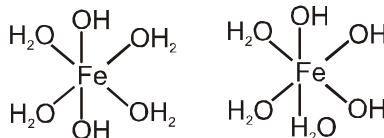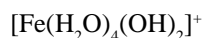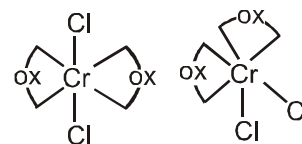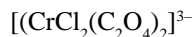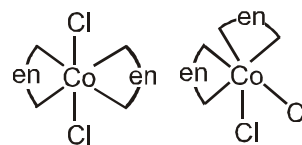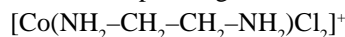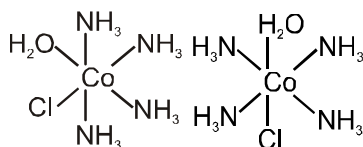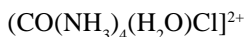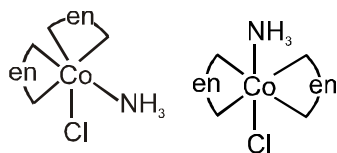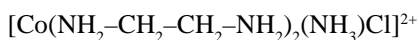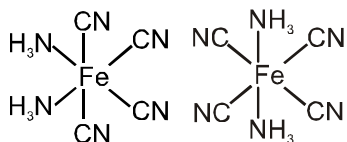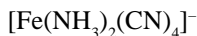
Q.12 (B)

CO and NH_3 are strong ligands which compel Ni and Co^{3+} to make electrons paired. Hence,

$[Ni(CO)_4] \rightarrow$ Diamagnetic

$[NiCl_4]^{2-} \rightarrow$ Paramagnetic

$[Co(NH_3)_4Cl_2]Cl \rightarrow$ Dia

$Na_3[CoF_6] \rightarrow$ Para

$Na_2O_2 \rightarrow$ Dia (O_2^{2-} is diamagnetic, MOT)

$CsO_2 \rightarrow$ Para (O_2^- is para according to MOT)
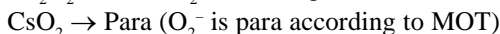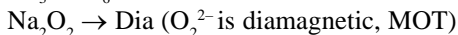
Q.13 (5)

Q.14 (A)

Q.15 (B,C)

(A) $[Fe(CO_5)]$ & $[Ni(CO)_4]$ complexes have 18-electrons in their valence shell.

(B) Carbonyl complexes are predominantly low spin complexes due to strong ligand field.

(C) As electron density increases on metals (with lowering oxidation state on metals), the extent of synergic bonding increases. Hence M–C bond strength increases
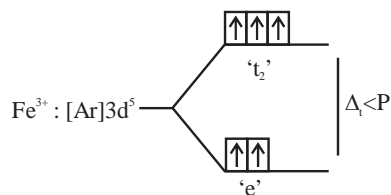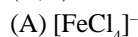
(D) While positive charge on metals increases and the extent of synergic bond decreases and hence C¡VO bond becomes stronger.

Q.16 (6.00)
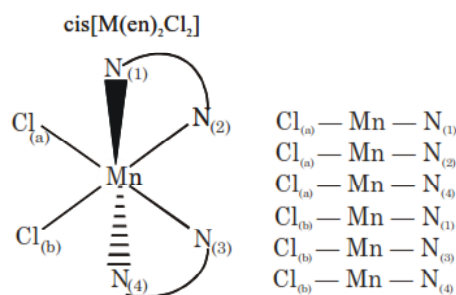
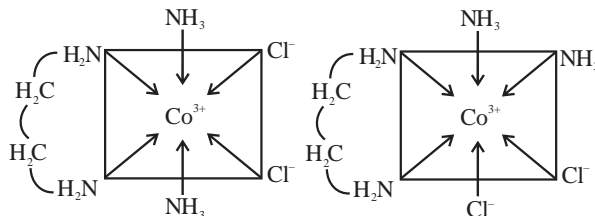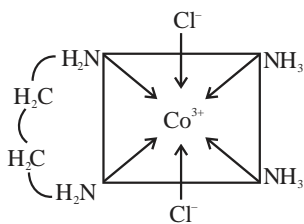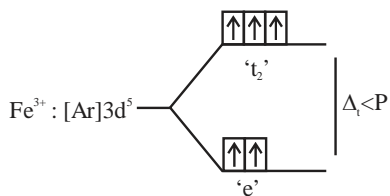Number of cis (Cl—Mn—N) = 6

Q.17 (A,C)

(A) $[FeCl_4]^-$

$[FeCl_4]^-$ is sp^3 hybridised and has tetrahedral geometry with 5 unpaired electrons.

(B) $[Co(en)(NH_3)_2Cl_2]^+$ has three geometrical isomers.

(C) $[FeCl_4]^-$

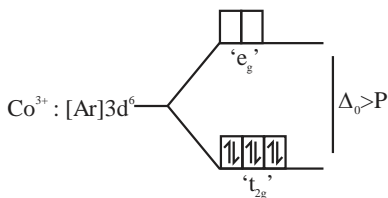Number of unpaired electrons (n)=5

Spin only magnetic moment = $\sqrt{n(n+2)}$ B.M.

$$=5.92 \text{ B.M.}$$

$[Co(en)(NH_3)_2Cl_2]^+$
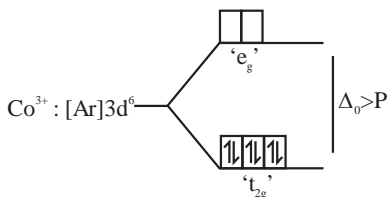

Number of unpaired electrons (n)=0

Spin only magnetic moment = $\sqrt{n(n+2)}$ B.M.

$$= 0$$

(D) $[Co(en)(NH_3)_2Cl_2]^+$

$[Co(en)(NH_3)_2Cl_2]^+$ is d^2sp^3 hybridised and has octahedral geometry with 0 unpaired electron.

Q.18   (A,B,C)

Paramagnetic compound (X) are attracted towards magnetic field and the pan is deflected downwards.

While the Diamagnetic compound (X) are repelled by magnetic field and pan is deflected upward.

(A) $X \Rightarrow H_2O \rightarrow$ Diamagnetic (correct)

(B) $X \Rightarrow K_4[Fe(CN)_6](s) \rightarrow$ Diamagnetic (correct)

Here Fe^{2+} + Strong field ligand $\rightarrow 3d^6 \Rightarrow [t_2g^6, eg^0]$

(C) $X \Rightarrow O_2 \rightarrow$ Paramagnetic (correct)

Here $O_2(g)$ is paramagnetic due to two-unpaired electrons present in $\pi*$ (antibonding orbitals).

(D) $X \Rightarrow C_6H_6(\ell) \rightarrow$ Diamagnetic (Incorrect)

It is due to presence of 0 unpaired electrons.

Q.19   A, B ,D

(A)

$[FeCl_4]^-$

$Fe \longrightarrow [Ar] 3d^6 4s^2$

$Fe^{+3} \longrightarrow [Ar]3d^5 4s^0$

Cl^- is W.F.L. and does not pair up the unpaired electron of central metal atom.

$\therefore Fe^{3+}$ (d^5) in $[FeCl_4]^-$
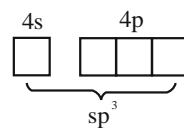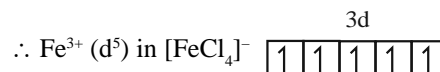
$[Fe(CO)_4]^{2-}$

$Fe \longrightarrow [Ar]3d^6 4s^2$

$Fe^{2-} \longrightarrow [Ar]3d^8 4s^2$

$\therefore Fe^{2-}$ (d^{10}) in $[Fe(CO)_4]^{2-}$

(B)

$[CO(CO)_4]-$

$CO \longrightarrow [Ar] 3d^7 4s^2$

$CO^{-1} \longrightarrow [Ar] 3d^8 4s^2$

$\therefore Co^-$ (d^{10}) in $[Co(CO)_4]^-$
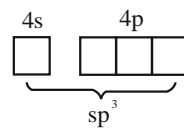
$[CoCl_4]^{2-}$

$Co \longrightarrow [Ar]3d^7 4s^2$

$Co^{+2} \longrightarrow [Ar] 3d^7 4s^0$

Cl^- is W.F.L. and does not pair up the unpaired electron of central metal atom.

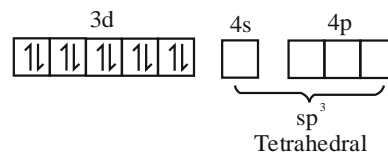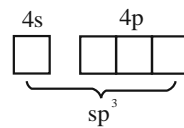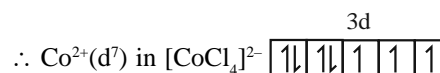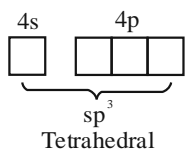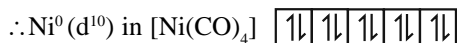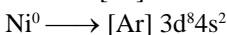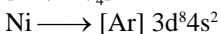$\therefore Co^{2+}(d^7)$ in $[CoCl_4]^{2-}$

(C)

$[Ni(CO)_4]$

$Ni \longrightarrow [Ar] 3d^8 4s^2$

$Ni^0 \longrightarrow [Ar] 3d^8 4s^2$

$\therefore Ni^0 (d^{10})$ in $[Ni(CO)_4]$ | ⇅ | ⇅ | ⇅ | ⇅ | ⇅ |

3d

4s   4p

sp^3
Tetrahedral

(C)

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

$Ni^{+2} \longrightarrow [Ar] 3d^8 4s^2$

$Ni^{+2} \longrightarrow [Ar] 3d^8 4s^0$

CN^- is S.F.L. and pair up the unpaired electron of central metal atom.

$\therefore Ni^0 (d^{10})$ in $[Ni(CO)_4]$

$\therefore Ni^0 (d^8)$ in $[Ni(CN)_4]^{2-}$

| ⇅ | ⇅ | ⇅ | ⇅ | |

4s   4p

dsp^3
Square planar

(D) $[Cu(py)_4]^+$

$Cu \longrightarrow [Ar] 3d^{10} 4s^1$

$Cu^{+1} \longrightarrow [Ar] 3d^{10} 4s^0$

$\therefore Cu^{+1} (d^{10})$ in $[Cu(py)_4]^+$

| ⇅ | ⇅ | ⇅ | ⇅ | ⇅ |

4s   4p

sp^3
Tetrahedral

$[Cu(CN)_4]^{3-}$

$Cu \longrightarrow [Ar] 3d^{10} 4s^1$

$Cu^{+1} \longrightarrow [Ar] 3d^{10} 4s^0$

$CN-$ is S.F.L. and pair up the unpaired electron of central metal atom.

$\therefore Cu^{+1} (d^{10})$ in $[Cu(CN)_4]^{3-}$

| ⇅ | ⇅ | ⇅ | ⇅ | ⇅ |

4s   4p

sp^3
Tetrahedral

Q.20 (6)

Isomers

(I) $[Pt (NH_3)_4 Cl_2]Br_2 \Rightarrow G.I. = 2$

(II) $[Pt (NH_3)_4 Br_2] Cl_2 \Rightarrow G.I. = 2$

(III) $[Pt (NH_3)_4 BrCl] Br.Cl \Rightarrow G.I. = 2$
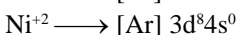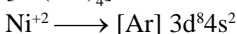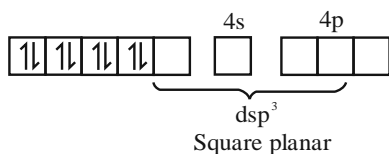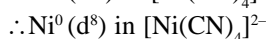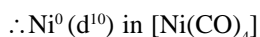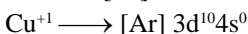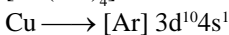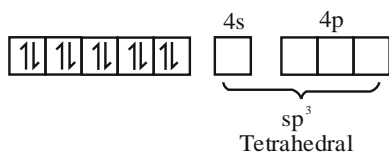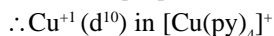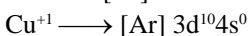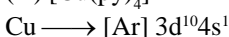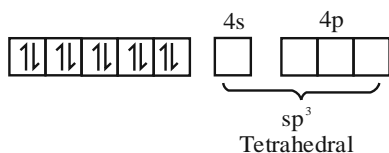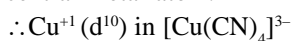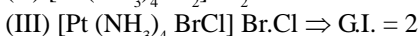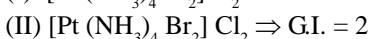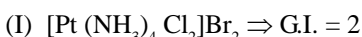
I, II, III are ionisation isomers of each other, each having 2 geometrical isomers.

Total possible isomers will be 6

Q.21 (A)

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

$Cr^{3+} \Rightarrow [Ar]3d^3$
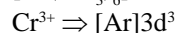
In presence of NH_3 ligand ☐☐ eg

| 1 | 1 | 1 | t_{2g}
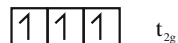
Number of unpaired electrons = 3

$\mu = \sqrt{n(n+2)}$ B.M.

$\mu = \sqrt{3(3+2)}$ B.M.

$\mu = \sqrt{15}$ B.M.

$\Rightarrow 3.87$ B.M.

$[CuF_6]^{3-}$

$Cu^{3+} \Rightarrow [Ar]3d^8$
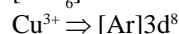
In presence of F^- Ligand

$Cu^{3+} \Rightarrow$ | 1 | 1 | eg

| ⇅ | ⇅ | ⇅ | t_{2g}
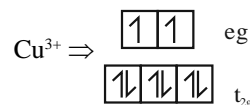
Number of unpaired electrons = 2

$\mu = \sqrt{n(n+2)}$ B.M.

$\mu = \sqrt{2(2+2)} \Rightarrow \sqrt{8}$ B.M.

$\Rightarrow 2.84$ B.M.

Mettalurgy

EXERCISES

ELEMENTARY

Q.1 (1)
Mineral is called an ore is a metal can be economically obtained from it.

Q.2 (4)
Flux is added to remove impurities.

Q.3 (2)
All mineral are not ore.

Q.4 (3)

Q.5 (4)

Q.6 (3)

Q.7 (1)
Na is alkali metal highly reactive. Hence present in combined state.

Q.8 (4)

Q.9 (2)
Sulphide ore is concentrated by Froath floatation process.

Q.10 (2)
Plam oil function $\longrightarrow$ frother.

Q.11 (2)
Heating below it melting point & in absence of air.

Q.12 (1)
Fe is more reactive than Cu.

Q.13 (4)
Ag is less reactive, So it is found in native state in nature.

Q.14 (1)

Q.15 (3)
Chemical separation or Leaching.
In this powdered ore is treated with a suitable reagent which can dissolve the ore but not the impurities.

Q.16 (3)

Q.17 (1)

70

Froth floatation because it is sulphide ore (ZnS)

Q.18 (1)
$CaCO_3 \rightarrow CaO + CO_2$
Heating the ore in absence of air is calcination.

Q.19 (2)
Smelting is a process of reducing metal oxide to metal by means of coke or CO.
$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$
$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

Q.20 (1)

Q.21 (3)
Flux is added during smelting it combines with infusible gangue present in the ore to form a fusible mass known as slag.
Flux + Gangue $\rightarrow$ Slag

Q.22 (2)

Q.23 (2)
Al forms thin filmofoxide
$\Rightarrow$ So Al becomes possive in nitric acid.

Q.24 (3)
Van Arkel method *Ti* and *Zr* are refined by this method. It is used for obtaining ultra pure metals.

Q.25 (1)
Metals are electropositive elements because they have tendency to loose e^- and forms $+$ve ions
$Na \rightarrow Na^+ + e^-$

Q.26 (2)

Q.27 (3)
Zone refining is employed for preparing extremely pure metals.
It is based on the principle that when a molten solution of the impure metal is allowed to cool the pure metal crystallises out while the impurities remain in the melt. Ex : Semiconductors like Si, Ge and Ga are purified by this method.

Q.28 (2)

Q.29 (2)

Q.30 (3)
Sodium $\rightarrow$ Highly reactive metal

Q.31 (1)

In thermite process a mixture of aluminium powder and ferricoxide in the rate of 1 : 3 is used.

Q.32 (2)

Blister copper $\longrightarrow$ Cu with 2% Impurity.

Q.33 (2)

$Zn + 2[Ag(CN)_2]^- \longrightarrow [Zn(CN)_4]^{2-} + 2Ag$
$\downarrow$
reducing agent

Q.34 (2)

Carbonates ore
Siderire & malachite.

JEE-MAIN
OBJECTIVE QUESTIONS

Q.1 (1)

Calamine is $ZnCO_3$.

Q.2 (3)

Aluminothermite process, Al act as reducing agent.
e.g. $Mn_3O_{4(s)} + 8Al \rightarrow Mn_{(\ell)} + Al_2O_3(s)$
$Cr_2O_{3(s)} + Al \rightarrow Cr_{(\ell)} + Al_2O_3$

Q.3 (1)

Hydrometallurgy

Q.4 (2)

Zinc blende (ZnS) ; copper glance (Cu_2S) ; Galena (PbS).
Therefore, (B) option is correct.

Q.5 (4)

(4) Feldspar is $K_2O.Al_2O_3.6SiO_2$. beryl is $Be_3Al_2Si_6O_{18}$.

Q.6 (2)

Some transition metal can form poly nuclear metal carbonyls also.

Q.7 (2)

Carnalite ($KCl. MgCl_26H_2O$)
It does not contain Ca.

Q.8 (1)

Sea water contains 0.13% Mg as salt and extracted by Dow's process and also from ore magnesite found in earth crust.

Q.9 (1)

NaCl and $CaCl_2$ both being ionic compounds ionise to give ions which lowers the melting point and increase the conductivity of the mixture.

Q.10 (2)

(1) Calamine $\rightarrow ZnCO_3$ Siderite $\rightarrow FeCO_3$
(2) Argentite $\rightarrow Ag_2S$ Cuprite $\rightarrow Cu_2O$
(3) Zinc blende $\rightarrow Zns$ Pyrite $\rightarrow$ Sulphide
(4) Malackite (green) $CuCO_3 . Ca(OH)_2$
Azurite $2CuCO_3 . Cu(OH)_2$
                              (Blue)

Q.11 (3)

Siderite $FeCO_3$

Q.12 (1)

Q.13 (1)

German silver in an alloy of Cu, Ni and Zn. It does not contain silver.

Q.14 (1)

Fool's gold is Iron pyrite.

Q.15 (4)

Enthalpy of formation of Al_2O_3
is very high and it can not be changed into Al by the use of C.

Q.16 (A)

Froth floatation is an example of adsorption process.

Q.17 (C)

$Ti_{(impulse)} + 2I_2 \xrightarrow{250^\circ C} TiI_4 \xrightarrow{1400^\circ C}$
Ti (pure) $+ 2I_2$
if Van-Arel process

Q.18 (2)

Due to volatile nature.

Q.19 (3)

Process is known as self reduction or autoreduction.

Q.20 (3)

Sulphide ore is roasted in presence of excess of air or O_2 below its melting point to convert into the oxide and to remove the impurities of S, P, Sb etc., as their volatile oxides. In some cases roasting of certain sulphide ores provide directly the metals.

Q.21 (C)

Van-Arkel process

Q.22 (2)

$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \longrightarrow$
                $2Na[Al(OH)_4](aq)$
$2Na[Al(OH)_4] (aq) + CO_2(g) \rightarrow Al_2O_3.xH_2O(s)$
                $+ 2NaHCO_3(aq)$

$Al_2O_3.xH_2O(s) \xrightarrow{1470K} Al_2O_3(s) + xH_2O(g)$

Q.23 (4)

Low grade sulphide ores are concentrated by froth floatation process and it is based on the fact that gangue and ore particles have different degree of wetability with water and pine oil.

Q.24 (4)

Carnalite

$KCl . MgCl_2 . 6H_2O$

$\downarrow$

Mg and Cl_2

Q.25 (C)

(A) Calamine $\rightarrow ZnCO_3$

　　Siderite $\rightarrow FeCO_3$

(B) Argentile $\rightarrow Ag_2S$

　　Cuperite $\rightarrow Cu_2S$

(C) Zinc blende $\rightarrow ZnS$

　　Iron pyrite $\rightarrow FeS_2$

(D) Malachite $\rightarrow CuCO_2 . Cu(OH)_2$

　　Azurite $\rightarrow CuCO_3 . 2Cu(OH)_2$

Q.26 (B)

Self reduction process

$Cu_2S + \dfrac{3}{2} O_2 \rightarrow Cu_2O + SO_2$

$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$

Q.27 (C)

Q.28 (2)

$ZnS + 4NaCN \rightarrow Na_2[Zn(CN)_4] + Na_2S$

$PbS + NaCN \rightarrow$ No such complex formation.

Q.29 (3)

Carbonate ores are calcined in absence of air to obtain the metal oxides.

Q.30 (2)

Magnete seperation $\rightarrow FeCr_2O_4$

froath floatation $\rightarrow Ag_2S$

gravity separation $\rightarrow Al_2(SiO_3)_2$

Q.31 (4)

Smelting is not a process of $conc^n$ of ore.

Q.32 (2)

An infusible acidic impurity is removed by reacting with basic oxide, e.g., SiO_2 forming fusible slag.

$CaCO_3 \rightarrow CaO + CO_2$; SiO_2 (acidic oxide) + CaO (basic oxide) $\rightarrow CaSiO_3$ (slag).

Q.33 (3)

Q.34 (A)

Q.35 (2)

$PbS + NaCN/KCN \rightarrow$ No. reaction

$ZnS + NaCN/KCN \rightarrow [Zn(CN)_4]^{2-} + S^{2-} + 4Na^+/4K^+$

Q.36 (2)

(Y) PbS reduces PbO to Pb ; it is called self reduction.

Q.37 (B)

Palm oil function as frother. It decreases the surface tension of the total solution, by which the formation of froth becomes easier.

Q.38 (1)

Sodium ethyl xanthate acts as collector.

Q.39 (2)

Q.40 (2)

Q.41 (2)

$FeO + SiO_2 \rightarrow FeSiO_3$ (slag)

Q.42 (3)

$Ag_2S + 2NaCN \underset{Air}{\rightleftharpoons} 2AgCN + Na_2S$

$4Na_2S + 5O_2 + 2H_2O \longrightarrow 2Na_2SO_4 + 4NaOH + 2S.$

Q.43 (1)

$FeCr_2O_4$ due to magnetic nature is separated by magnetic seperation

Q.44 (2)

$4Ag + 8CN^- + 2H_2O \longrightarrow 4[Ag(CN)_2]^-$ (soluble complex) $+ 4OH^-$

$2[Ag(CN)_2]^- + Zn \longrightarrow 2Ag + [Zn(CN)_4]^{2-}$

Q.45 (3)

Cathode : Al^{3+} (melt) $+ 3e^- \longrightarrow Al$

Anode : $C + O^{2-}$ (melt) $\longrightarrow CO + 2e^-$; $C + 2O^{2-}$ (melt) $\longrightarrow CO_2 + 4e^-$

Q.46 (3)

(i) $Cu_2O + FeS \rightarrow Cu_2S + FeO$

(ii) $AsFeCrO_4$ is magnetic in nature.

(iii) True

(iv) Cassiterite $\Rightarrow SnO_2$

　　　Rutile $\Rightarrow TiO_2$ 　　　True

Q.47 (4)

Benficiation $\rightarrow$ concentration

sulphide ore $\rightarrow$ Froth floatation process

Q.48 (B)

Q.49 (D)

Q.50 (1)

Bessermerisatioin process is
used for Fe and Cu

Q.51 (1)

For a reduction process the change in the free energy, ΔG must be negative and to make ΔG negative temperature should be high enough so that $T\Delta S > \Delta H$.

Q.52 (4)

When the oxide undergoes a phase change, there will be an increase in the entropy of the oxide.

(2) It is true statements, $HgO \xrightarrow{\Delta} Hg + 1/2O_2$

(3) For a reduction process the change in the free energy, ΔG^0 must be negative and to make ΔG^0 negative temperature should be high enough so that $T\Delta S^0 > \Delta H^0$.

Q.53 (1)

Reduction of oxides of Mn, Cr etc., by electropositive aluminium metal is called as alumino thermite process.

Q.54 (3)

Mercury from cinnarbar (HgS)

(Auto reductant and self reduction)

(Cu_2S, PbS, HgS)

Q.55 (4)

Aluminium oxide could be extracted by electrolysis phenomenon.

Q.56 (3)

Cu and Ag are found in anode mud.

Q.57 (1)

$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$;

$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$.

Q.58 (1)

Matte is obtained in blast furnace and that contains mostly Cu_2S and FeS. It is transferred to bessemer converter where self reduction takes place according to the following reactions.

$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$;

$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$.

Q.59 (3)

As PbS on self reduction with PbO and $PbSO_4$ gives metallic lead.

Q.No.60 to Q.62 are based on following reactions

(I) $FeCr_2O_4 + NaOH + air \longrightarrow (A) + Fe_2O_3$

(II) $(A) + (B) \longrightarrow Na_2Cr_2O_7$

(III) $Na_2Cr_2O_7 + X \xrightarrow{\Delta} Cr_2O_3$

(IV) $Cr_2O_3 + Y \xrightarrow{\Delta} Cr$

Q.60 (A)

$A \rightarrow Na_2CrO_4$

$B \rightarrow H_2SO_4$

Ans. (A)

Q.61 (A)

$X \rightarrow CO$

$Y \rightarrow Al$

Q.62 (C)

Q.63 (2)

Zone refining is based on the principle of fractional crytallisation.

Q.64 (4)

Sulphide ore of Hg, Cu, Pb are heated in air, a part of these is changed in to oxides or sulphate that then react with the remaining part of the sulphide ore to give its metal and SO_2. This is called self reduction, auto reduction or air reduction method.

Q.65 (3)

Aluminium is extracted by electrolytic reduction of mixture of molten $Al_2O_3 + Na_3AlF_6 + CaF_2$.

Due to very high energy of dissociation of Al_2O_3 , the reduction at such high temperature will give carbide in place of metallic Al according to the following

reaction. $2Al_2O_3 + 6C \xrightarrow{\Delta} Al_4C_3 + 3CO_2$.

Q.66 (3)

$Na_3[AlF_6] \longrightarrow 3NaF + AlF_3$

NaF and AlF_3 both are ionic compounds and so ionise to give ions. This increases the electrical conductivity and lowers the melting point of Al_2O_3 .

At cathode : Al^{3+} (melt) $+ 3e^- \longrightarrow Al$.

At anode : $C(s) + O^{2-}$ (melt) $\longrightarrow CO$ (g) $+ 2e^-$;

$C(s) + 2O^{2-}$ (melt) $\longrightarrow CO_2$ (g) $+ 4e^-$.

Q.67 (1)
Si and Ge is used for semiconductors are required to be high purity and hence purified by zone refining.

Q.68 (2)
Reactive metal can not be reduced by carbon hence process of electrolysis is used.

Q.69 (C)
Cathode (reduction) Cu^{2+} (aq) + 2e$^-$ $\longrightarrow$ Cu(s).

Q.70 (1)

Q.71 (2)

Q.72 (4)
Electrolyte contains $PbSiF_6$ containing 8-12% of H_2SiF_6.

Q.73 (D)
Zone refining method is based on the principle that an impure molten metal on gradual cooling will deposit crystals of the pure metal, while the impurities will be left in the remaining part of the molten metal.

Q.74 (1)

Q.75 (1)
CaO and K_2O can not be reduced by C.

Q.76 (C)
Al-powder reduces the metallic oxides to metal.

$3MnO_2 + 4Al \xrightarrow{\Delta} 3Mn + 2Al_2O_3$.

Q.77 (2)
The process mention is rxn is known as Mc. Arthur forest
Method :
$Ag_2S + 4NaCN \rightarrow 2[Ag\,(CN)_2]^- + 2Na^+ + S_2^{2-}$
$[Ag\,(CN)_2]^- + Zn \rightarrow (Zn\,(CN)_4)^{2-} + 2Ag\downarrow$

Q.78 (3)
By cupellation
it is used for the removal of Pb
from Ag and Au

Q.79 (4)

Q.80 (C)
Blister copper is 98 % pure Cu

Q.81 (3)
Iron obtained from blast furnace is pig iron

Q.82 (2)

Thermal decomposition : $Ni(s) + 4CO \dfrac{3}{2}$

$[Ni(COl_4)] \xrightarrow{150-180^o} Ni(s) + 4(i)$
                                    (pure)

Q.83 (D)
Q.84 (3)
The solidified copper obtained after bessemerisation is impure and contains Fe, Ni, Zn, Ag, Au etc., as impurity. It has blistered like appearance due to the evolution of SO_2 and so it is called blister copper.

Q.85 (3)
$Ni + 4CO \xrightarrow{T_1} Ni\,(CO)_4 \xrightarrow{T_2} Ni + 4CO$
$T_1 = 50^oC$
$T_2 = 230^oC$

Q.86 (3)
$FeO + SiO_2 \rightarrow FeSiO_3$ (Slag) (In extraction of Cu)
$CaO + SiO_2 \rightarrow CaSiO_3$ (In extraction of Fe)

Q.87 (B)
$2[Ag(CN)_2]^- + Zn \rightarrow [Zn(CN)_4]^{2-}$
                                              $\downarrow$
                               reducing agent

Q.88 (3)
It is obtained by electrolytic reduction of molten anhydrous $KCl.MgCl_2$ (other methods are not economical/ feasible for the extraction of Mg metal).

Q.89 (3)
Electrolyte used is $Al_2O_3 + Na_3AlF_6 + CaF_2$

Q.90 (4)

Q.91 (B)

Q.92 (2)
$Ni + 4CO \rightarrow Ni(CO)_4$
                    volatile

Q.93 (1)
The Hooper process is a process for the electrolytic refining of aluminium. Impure Al forms the anode and pure Al forms the cathode of the Hooper's cell which contains three liquid layers. The bottom layer is molten impure Al, the middle is a fused salt layer containing sodium fluoride, aluminum fluoride and barium fluoride, and the top layer is pure Al. At the anode (bottom layer), Al passes with solution as aluminium ion (Al^{3+}), and at the cathode (top layer), these ions are reduced to the pure metal. In operation, molten metal is added to the bottom of the cell and pure aluminium is drawn off the top.

At anode : $\qquad$ Al $\longrightarrow$ Al^{3+} + 3e$^-$

At cathode : $\qquad$ Al^{3+} + 3e$^-$ $\longrightarrow$ Al.

Q.94 (3)

Anode mud obtained in electrolytic refining of lead contains, Sb, Cu, Ag and Au.

Therefore, (C) option is correct.

Q.95 (4)

Anode mud contains the impurity of Au only.

Q.96 (4)

Due to low discharge potential of Na$^+$, it will deposited first.

Q.97 (3)

$Na_2SO_4 \Rightarrow 2Na^+ + SO_4^{2-}$

SO_4^{2-} will not oxidised as

S is an maximum O.S.,

In this oxidation and reduction process will happen with H_2O only and H_2 and O_2 would produced.

Q.98 (1)

Slag is lighter and Lower melting than metal.

JEE-ADVANCED
OBJECTIVE QUESTIONS

Q.1 (B)

Carnallite is the important ore of aluminium and it has chemical composition $KCl.MgCl_2.6H_2O$.

Q.2 (D)

Dolomite is mixed carbonate of calcium and magnesium i.e. $CaCO_3.MgCO_3$.

Q.3 (C)

It is used to separate haematite ore as it is attracted by electromagnet.

Q.4 (C)

Ore bauxite, $Al_2O_3 . 2H_2O$ of aluminium occurs as oxide ore in nature.

Q.5 (D)

H_2O + C(red hot) $\longrightarrow$ CO (g) + H_2 (g) ; Ni(s) +

4CO (g) $\xrightarrow{50^\circ C}$ [Ni(CO)$_4$] (g) ;

[Ni(CO)$_4$] (g) $\xrightarrow{200^\circ C}$ Ni(s) + 4CO (g). So Mond process is used for the purification of nickel.

Q.6 (C)

Al_2O_3 (bauxite) + 2NaOH (aq) + H_2O (l) $\xrightarrow{leaching}$ 2Na[Al(OH)$_4$] (aq).

Q.7 (A)

The process is truly adsorption as gangue particles are wetted with water and sulphide ore particles are wetted with pine oil.

Q.8 (D)

Options (A), (B) and (C) comprise the froth floatation process.

Q.9 (A)

As their is difference in the densities of the gangue and ore particles (i.e. Fe_2O_3).

Q.10 (B)

For examples SiO_2 + CaO $\longrightarrow$ CaSiO$_3$ (metal silicate) or FeO + SiO_2 $\longrightarrow$ FeSiO$_3$.

Q.11 (D)

Potassium or sodium ethyl xanthate get attached with the particle of the sulphide ore and thus make them water repellant i.e. hydrophobic.

Q.12 (D)

Ore is heated below its melting point in a reverberatory furnace in the presence of air to convert it into its oxides. It removes easily oxidisable volatile impurities like arsenic as As_2O_3, antimony as Sb_2O_3 and sulphur as SO_2. Roasting is an exothermic process; once started it does not require additional heating.

Q.13 (D)

In Hoope's electrolytic cell, there are three different layers of liquids; upper most layer of molten pure aluminium, middle one of the fluorides of Na$^+$, Ba^{2+} and Al^{3+} and bottom most layer of molten impure aluminium. To make the lower most layer heavier silicon and copper are added.

Q.14 (B)

$4NaCN + Ag_2S \xrightarrow{O_2} 2Na[Ag(CN)_2] + Na_2S.$

Q.15 (A)

The free energy change that occurs when 1 mol of common reactant (in this case O_2) is used may be plotted graphically against temperature for a number of reactions. This is called an Ellingham diagram.

Q.16 (C)

At lower temperature following reactions occur in blast furnace.

$3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$;

$Fe_3O_4 + CO \longrightarrow 3Fe + 4CO_2$;
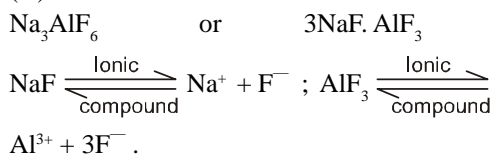
$Fe_2O_3 + CO \longrightarrow 2FeO + CO_2$

Q.17 (C)

The Gibb's free energy of most sulphides are greater than that for CS_2. In fact, CS_2 is an endothermic compound. Therefore, the $\Delta_f G^0$ of M_xS is not compensated. So reduction of M_xS is difficult. Hence it is common practice to roast sulphide ores to corresponding oxides prior to reduction.
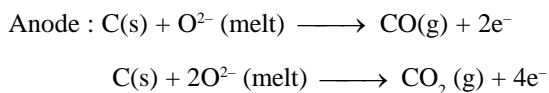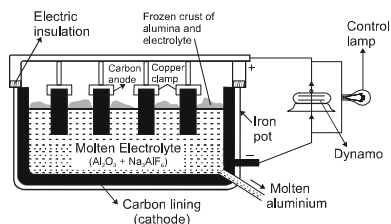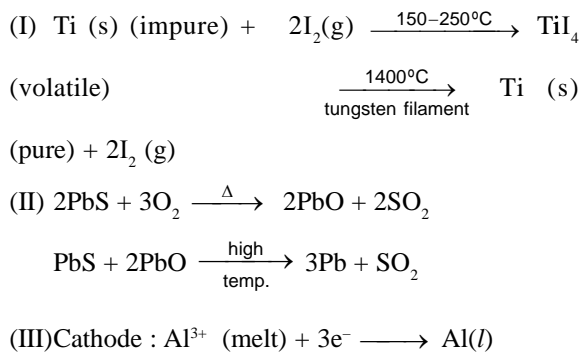
Q.18 (D)

Zone refining method is based on the principle that an impure molten metal on gradual cooling will deposit crystals of the pure metal, while the impurities will be left in the remaining part of the molten metal.
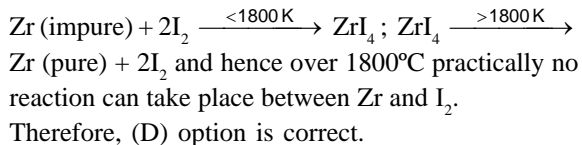
Q.19 (B)
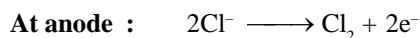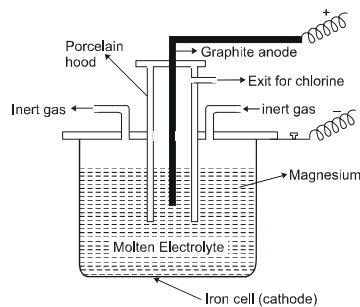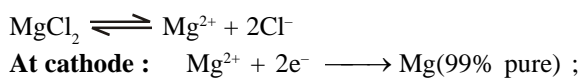
$$Na_3AlF_6 \qquad or \qquad 3NaF. AlF_3$$

$NaF \xrightleftharpoons[\text{compound}]{\text{Ionic}} Na^+ + F^-$; $AlF_3 \xrightleftharpoons[\text{compound}]{\text{Ionic}}$

$Al^{3+} + 3F^-$.

Q.20 (C)

(I) Ti (s) (impure) + $2I_2$(g) $\xrightarrow{150-250^\circ C}$ TiI_4

(volatile) $\xrightarrow[\text{tungsten filament}]{1400^\circ C}$ Ti (s)

(pure) + $2I_2$ (g)

(II) $2PbS + 3O_2 \xrightarrow{\Delta} 2PbO + 2SO_2$

$PbS + 2PbO \xrightarrow[\text{temp.}]{\text{high}} 3Pb + SO_2$

(III) Cathode : Al^{3+} (melt) + $3e^- \longrightarrow Al(l)$

Anode : $C(s) + O^{2-}$ (melt) $\longrightarrow CO(g) + 2e^-$

$C(s) + 2O^{2-}$ (melt) $\longrightarrow CO_2$ (g) $+ 4e^-$

Q.21 (D)

Zr (impure) + $2I_2 \xrightarrow{<1800 K} ZrI_4$; $ZrI_4 \xrightarrow{>1800 K}$ Zr (pure) + $2I_2$ and hence over $1800^\circ C$ practically no reaction can take place between Zr and I_2. Therefore, (D) option is correct.

Q.22 (C)

$MgCl_2 \rightleftharpoons Mg^{2+} + 2Cl^-$

At cathode : $Mg^{2+} + 2e^- \longrightarrow$ Mg(99% pure) ;

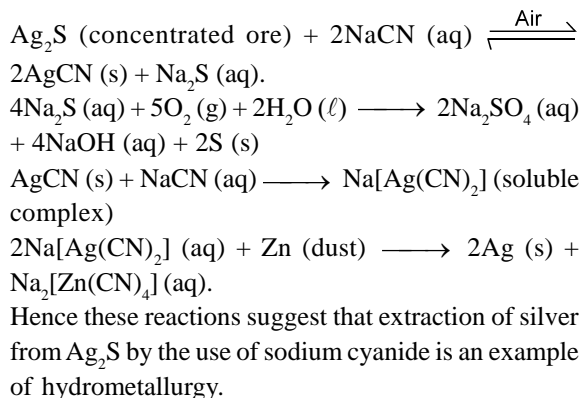**At anode :** $2Cl^- \longrightarrow Cl_2 + 2e^-$

Q.23 (A)

$CaO + SiO_2 \longrightarrow CaSiO_3$ (slag) (Haematite ore contains silica as impurities).
Slag being lighter and insoluble in molten metal floats over and thus forms upper layer.

Q.24 (C)

Iron contains the impurity of SiO_2 (acidic) which is removed by basic flux i.e., CaO forming a slag.

Q.25 (B)

Ag_2S (concentrated ore) + 2NaCN (aq) $\xrightleftharpoons{\text{Air}}$ 2AgCN (s) + Na_2S (aq).
$4Na_2S$ (aq) $+ 5O_2$ (g) $+ 2H_2O$ (ℓ) $\longrightarrow$ $2Na_2SO_4$ (aq) $+ 4NaOH$ (aq) + 2S (s)
$AgCN$ (s) + NaCN (aq) $\longrightarrow$ $Na[Ag(CN)_2]$ (soluble complex)
$2Na[Ag(CN)_2]$ (aq) + Zn (dust) $\longrightarrow$ 2Ag (s) + $Na_2[Zn(CN)_4]$ (aq).
Hence these reactions suggest that extraction of silver from Ag_2S by the use of sodium cyanide is an example of hydrometallurgy.

Q.26 (D)

(A) Cupellation is used when lead is present in traces.
(B) In argentiferous lead the silver is removed by Parke's process because silver has higher solubility in molten zinc than lead.
(C) Silver has higher solubility in molten zinc than lead and thus forms zinc-silver alloy from which zinc can be distilled off leaving behind the silver.
(D) Silver has higher solubility in molten zinc and thus forms zinc-silver alloy from which zinc can be distilled off leaving behind the silver.

Q.27 (C)

Anode mud contains Ag, Au as impurities.

Q.28 (A)

Q.1 (CD)
Common impurites in the
bauxite are Fe_2O_3, SiO_2

Q.2 (ACD)
(A) Cu_2O and ZnO
(B) $MgCO_3$ and $KCl.MgCl_2.6H_2O$
(C) Cu_2S and $2CuCO_3.Cu(OH)_2$.
(D) $K_2O.Al_2O_3.6SiO_2$ & $Na_3AlSi_3O_8$.

Q.3 (ABD)
Argentite $\rightarrow Ag_2S$
Galena $\rightarrow PbS$
Anglesite $\rightarrow PbSO_4$
Copper glance $\rightarrow Cu_2S$

Q.4 (ABC)
(A) Haematite $\rightarrow Fe_2O_3$
(B) Magnetite $\rightarrow FeO_4$
(C) Limonite $\rightarrow Fe_2O_3 . 3H_2O$
(D) Copper pyrite $\rightarrow CuFeS_2$

Q.5 (BD)
(A) KCl, KNO_3 (B) SnO, PbO
(C) $FeCO_3$, Al_2O_3 (D) Cu_2O, SnO_2
Therefore, (B, D) options are correct.
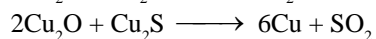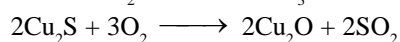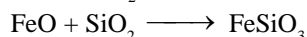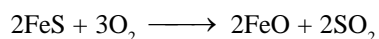
Q.6 (AC)
Egg shell is made up of $CaCO_3$.
Dolomite : $CaCO_3.MgCO_3$; Calamine : $ZnCO_3$
Lime stone : $CaCO_3$; Feldspar : $K_2O.Al_2O_3.6SiO_2$.

Q.7 (ABC)
(A) Sulphides ores are generally concentrated by froth
floatation.

(B) $2CuFeS_2 + 4O_2 \xrightarrow{\text{roasting}} Cu_2S + 2FeO + 3SO_2$
$Cu_2S + FeO + SiO_2 \longrightarrow FeSiO_3$ (fusible slag) $+ Cu_2S$
(matte)
(C)   Bessemerisation
   $2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$
   $FeO + SiO_2 \longrightarrow FeSiO_3$
   $2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$
   $2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$
(self reduction).

Q.8 (BC)
Poling is used for the purification of those metals
which contain the impurities of their own oxides like
CuO in Cu and SnO in Sn.

Q.9 (AB)
The Crude metallic Zn can be purified by elctrolysis
process or by distillation.

Q.10 (ABCD)

Q.11 (AB)

Q.12 (ABC)

Q.13 (BD)
Liquation process is used for the purification of those
metals which are less fusible than impurities present.

Q.14 (BC)
Sulphides ores concentration by frother floatation
process.

Q.15 (AC)

Q.16 (AC)
During calcination
Carbonates $\rightarrow$ Oxides
Hydroxide $\rightarrow$ Oxide

Q.17 (AC)

Q.18 (ABD)
(C) is incorrect statement as $2CuFeS_2 + 4O_2 \xrightarrow{\Delta}$
$Cu_2S + 2FeO + 3SO_2$.

Q.19 (AB)
Carbon reduction is used for Fe, Sn, Zn; Pb
$\Rightarrow$ Fe_2O_3 & SnO_2

Q.20 (AB)
$CuFeS_2$ and PbS are
concentrated by froth floatation process.

Q.21 (AC)

Q.22 (CD)

Q.23 (ACD)
leaching is used for red bauxite, gold ore and silver
ore.

Q.24 (BC)

Q.25 (AC)
(A) Roasting. It is a process of heating the
concentrated ore (generally sulphide ore) strongly in

the excess of air or O_2 below its melting point.

Roasting at high temperature. The sulphide ores of some of the metals like Cu, Pb, Hg, Sb etc., when heated strongly in the free supply of air or O_2 are reduced directly to the metal rather than to the metallic oxides.

(C) Calcination. It is a process of heating the concentrated ore strongly in a limited supply of air or in the absence of air.

Q.26 (BC)
Poling is applied for Cu and Sn.

Q.27 (ABC)
In poling process of purification of Cu, O_2 oxidises S, Sb, As and Fe into their oxides.

Q.28 (ABC)
smelting of iron in a blast furnace does not involve sublimation.

Q.29 (BC)
$Na_3[AlF_6]$ being ionic provides ions, thus increases the conductivity of the mixture and lowers its melting point (impurity lowers the melting point of the melt).

Q.30 (AB)
Fe and Pt does not form amalgam.

Q.31 (ABC)
For ultrapure semiconductor
materials Ge, Si, Ga

Q.32 (AC)
Ba, Potassium can not be obtained by the electrolysis of their aq. solution because. At cathode, $2H_2O + 2e^-$ $\rightarrow H_2 + 2OH^-$
At anode, $2H_2O \rightarrow 4H^+ + O_2 + 4e^-$

Q.33 (ABCD)
All processes are correct.
(A) $Fe_2O_3 + 4CO \xrightarrow{\Delta} 3Fe + 4CO_2$
(B) $ZnO + C \xrightarrow{\Delta} Zn + CO$
(C) $2Cu_2O + Cu_2S \xrightarrow{\Delta} 6Cu + SO_2$
(D) $PbO + C \xrightarrow{\Delta} Pb + CO$

Q.34 (BCD)

(A) $\dfrac{\Delta G}{T} = -\Delta S$, $\dfrac{\Delta G}{T}$ is slope in Ellingham diagram.

Which is same below the boiling point.
(B) Below the boiling point slope is same as factor $T\Delta S$ is same.
(C) Above $\Delta G = 0$ line free energy becomes positive

so oxide decomposes.
(D) Random increases i.e. ΔS increases, so slope also increases.

Q.35 (ABD)
Cynide process used for Au and Ag comlexes formed in this, are : $Na[Au(CN)_2]$, $Na[Ag(CN)_2]$, $Na_2[Zn(CN)_4]$.

Q.36 (AD)
Gold is not attacked by sulphuric acid, nitric acid and Cl_2 use to separate it from borax so, parting of gold can be done with these.

Q.37 (BCD)

Q.38 (ACD)
The reaction which takes place in Besseiner converter during extration of Cu

$Cu_2S + \dfrac{3}{2}O_2 \rightarrow Cu_2O + SO_2 \uparrow$

$Cu_2S + Cu_2O \rightarrow Cu + SO_2 \uparrow$

$FeS + \dfrac{3}{2}O_2 \rightarrow FeO + SO_2 \uparrow$

Ans. $\rightarrow$ A, C, D

Q.39 (AB)
$CaCl_2$ is added to improve electrical conductivity and it also decrease the m.p. of NaCl.

Q.40 (ABCD)
(i) Slag is a fusible mass. (ii) It has low melting point. (iii) It is lighter than and immiscible with the molten metal. It is due to these impurities that the slag floats as a separate layer on the molten metal and can thus be easily separated from the metal. The layer of the slag on the molten metal prevents the metal from being oxidised. It is used as one of the constituent of cement and in building material.

Q.41 (ABC)
Semlting $\rightarrow$ C-reduction

Q.42 (BC)

Q.43 (AD)

Q.44 (AB)

Q.45 (BC)
Cyanide process is applied for extraction of Ag and Au.

Q.46 (AD)

$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

$CaO + SiO_2 \rightarrow CaSiO_3$

Q.47 (ABD)

Cathode $\rightarrow$ graphite material

Anode $\rightarrow$ graphite material

$\rightarrow$ anode react away forming CO_2

Q.48 (BD)

Molten matte $\rightarrow Cu_2S + FeS$

It is treated with a blast

of air and sand.

Q.49 (CD)

Q.50 (BD)

Sodium and Aluminium reacts with water so often extracted from their fuses salts.

Q.51 (AC)

(A) true;

(C) small amount of Mn is added to molten steel to remove sulphur and oxygen.

Q.52 (A)

Dissolution of gold in NaCN forming soluble complex is reversible, so it is carried out in presence of air bubbling. Oxygen contained in air oxidises Au to Au^+ which then complexes with CN^- to form soluble complex.

Q.53 (B)

(B) HCN produced with water by NaCN and KCN is poisonous and have carcinogenic activity.

Q.54 (C)

The process which involves the dissolution of ore in to a suitable reagent and then extraction of metal from the solution by more electropositive element is called hydrometallurgy.

Q.55 (A)

[X] = $CuCO_3$. $Cu(OH)_2$ or $2CuCO_3$. $Cu(OH)_2$; [Y] = Cu_2S or $CuFeS_2$

$CuCO_3.Cu(OH)_2 \xrightarrow{\Delta} CuO$ (S) + $CO_2 + H_2O$;

[Y] = Cu_2S or $CuFeS_2$

$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$; $Cu_2S + 2Cu_2O$

$\longrightarrow 6Cu$ (M) + SO_2(g)

$5SO_2 + 2IO_3^- + 4H_2O \longrightarrow I_2 + SO_4^{2-} + 8H^+$

I_2 + strach $\longrightarrow$ blue colour

Q.56 (D)

It is sulphide ore (Cu_2S or $CuFeS_2$) & is called as copper glance or copper pyrite ; S^{2-} gives yellow ppt. of CdS with $CdCO_3$ suspension.

Q.57 $G_1 = SO_2$; It can increase its oxidation state from +4 to +6 & decrease from +4 to 0 or –2.

Q.58 $CuCO_3 + 2HCI \longrightarrow CuCl_2 + CO_2 + H_2O$; $CuCl_2 +$

$2KI \longrightarrow CuI_2 + 2KCI$; $2CuI_2 \longrightarrow Cu_2I_2 \downarrow + I_2$

Q.59 $CuCO_3.Cu(OH_2) \xrightarrow{\Delta} CuO \downarrow$ (black) + $CO_2 + H_2O$

$CuCO_3 . Cu(OH)_2 + 4HCl \longrightarrow 2CuCl_2 + 3H_2O + CO_2$;

$2CuCl_2 + 4KI \longrightarrow Cu_2I_2 \downarrow$ (white) + I_2 + 4KCl

Q.60 (C)

Since the mixture is soluble in water to give strong alkaline solution, if must contain NaOH as one of the constituent. Since the aqueous solution gives precipitate with diluted HCl. Which dissolves in excess of diluted HCl. It must contain Zinc salt. Then the mixture consists of

$ZnSO_4 + 4NaOH \rightarrow Na_2ZnO_2 + NaSO_4 + 2H_2O$

$Na_2ZnO_2 + 2HCl \rightarrow 2NaCl + Zn(OH)_2 \downarrow$

$Zn(OH)_2 + 2HCl \rightarrow ZnCl_2 (Soluble) + 2H_2O$

Q.61 (B)

$BaCl_2 + K_2SO_4 \rightarrow BaSO_4 \downarrow$ (White ppt.)+2KCl

Q.62 (B)

$AgNO_3 + 2NH_4OH \rightarrow [Ag(NH_3)_2]Cl$(Soluble)+$2H_2O$

Q.63 (A $\rightarrow$ p, r) ; (B $\rightarrow$ p, r) ; (C $\rightarrow$ q) ; (D $\rightarrow$ s)

(A) Extraction of gold is a hydrometallurgical process in which gold ore is leached with NaCN solution and then precipitated by zinc scrap.

(B) Extraction of copper is a hydrometallurgical process in which copper ore is leached with H_2SO_4 solution and then precipitated by iron scrap.

(C) Slag formation process is smelting.

(D) Drying of hydrated $MgCl_2$ in presence of dry HCl gas is a calcination process.

Q.64 (A) $\rightarrow$ Q, B $\rightarrow$ R, C $\rightarrow$ S, D $\rightarrow$ P

Calamine $\rightarrow ZnCO_3$

Cryolite $\rightarrow Na_3AlF_6$

Malachite $\rightarrow CuCO_3$. $Cu(OH)_2$

Carnaite $\rightarrow KCl.MgCl_2$ $6H_2O$

Q.65 $(A \to r, t)$; $(B \to s)$; $(C \to t)$; $(D \to p)$; $(E \to q)$.

(A) $FeO + SiO_2 \longrightarrow FeSiO_3$ (slag) ; this reaction occurs in extraction of copper from copper pyrites in smelting as well as in bessemerisation processes.

(B) Reduction of oxides of Mn, Cr with electropositive metal aluminium is called thermite process.

(C) Self reduction generally occurs in bessemer converter in extraction of copper from copper pyrites.

(D) Conversion of $Al(OH)_3$ into Al_2O_3 by heating in absence of air represents the calcination.

(E) Displacement of silver from its salt solution by more electropositive zinc.

Q.66 (B)

Cyanide process $\to$ Ag and Au

floatation process $\to$ Dressing of Hgs

Electrolytic reduction $\to$ Extraction of Al

Zone refining $\to$ Ultrapure of Ge,

Ans. $\to$ (B)

Q.67 $(A \to q,s)$; $(B \to r)$; $(C \to s)$; $(D \to p)$

(A) **Poling :** Impure molten metal is stirred with green wood poles. The reducing gases liberated reduce the oxide of the metal to free metal. This method is used for the purification of those metals which contain the impurities of their own oxides. For example CuO in Cu and SnO_2 in tin.

(B) **Cupellation :** It is used when impurities are of other metals and is mainly used for the removal of lead from silver.

(C) **Liquation :** This process is used for the purification of the metal, which it self is readily fusible but the impurity present in it are not i.e. impurities are non-fusible. This process is used for purification of Sn and Zn.

(D) **Van Arkel method :** (vapour phase refining) Metals like titanium, zirconium, thorium and uranium are purified by this method.

Q.68 (D)

(I) Iron and Cu $\to$ Bessemerisation

(II) Zirconium & $\xrightarrow{\text{titanium}}$ Van Arkel

(III) Lead and Sn $\longrightarrow$ Liquation

(IV) Cu & Sn $\longrightarrow$ Poling

Q.69 (B)

(A) Tin-cassiterite (SnO_2)

(B) Zinc - calamine ($ZnCO_3$)

(C) Iron - siderite ($FeCO_3$)

(D) Lead - Cerrusite ($PbCO_3$)

Therefore, (B) option is correct.

Q.70 (A)

(a) $C + CO_2 \longrightarrow 2CO \longrightarrow 1000°C$

(b) $FeO + CO \longrightarrow Fe + CO_2 \longrightarrow 800°C$

(c) $CaO + SiO_2 \longrightarrow CaSiO_3 \longrightarrow 1800°C$

(d) $Fe_3O_4 + 4CO \longrightarrow 3Fe + 4CO_2 \longrightarrow 400°C$

Q.71 (B)

Q.72 (A)

Down cell $\to$ Fused (40 % NaCl + 60 % $CaCl_2$)

Dow seawater process $\to$ fused $NaCl_2$

Hall-heroult $\Rightarrow$ fused ($Al_2O_3 + Na_3AlF_6 + CaF_2$)

Moissan $\to$ Fused KHF_2

Q.73 (C)

(a) Van Arkel method $\to$ Purification of Ta

(b) Solvay process $\to$ Manufacture of Na_2CO_3

(c) Cupellation $\to$ Refining of silver
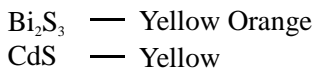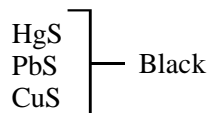
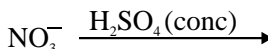(d) polling $\to$ Purification of Cu.
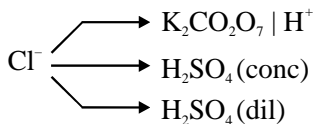
NUMERICAL VALUE BASED

Q.1 (7)

Q.2 (2)

Q.3 (4)

Q.4 (4)

$\left.\begin{array}{l} HgS \\ PbS \\ CuS \end{array}\right]$ — Black

Bi_2S_3 — Yellow Orange

CdS — Yellow

Q.5 (4)

$Cl^- \Big\langle$
$\longrightarrow K_2CO_2O_7 \mid H^+$
$\longrightarrow H_2SO_4 (conc)$
$\longrightarrow H_2SO_4 (dil)$

$NO_3^- \xrightarrow{H_2SO_4 (conc)}$

Q.6 (7)

$FeSO_4.7H_2O \xrightarrow[-720]{300°C} 2FeSO_4 \xrightarrow[\text{temp}]{\text{High}}$

$Fe_2O_3 + SO_2 + SO_3$
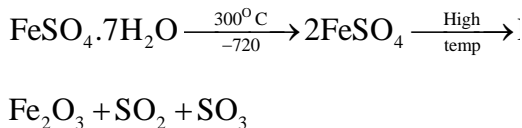
Q.7 (5)

$Ag_2SO_3, AgCl, Ag_2C_2O_4, AgNO_2 \& CH_3COOAg$ are white ppts, while Ag_3PO_4 is yellow and Ag_2CrO_4 is red.

Q.8 (3)

AgCl, $Zn(OH)_2$, $Cu(OH)_2$ will dissolve in excess of NH_4OH.

Q.9 (4)

$Na(NH_4)HPO_4 . 4H_2O$

Q.10 Benitoite is represented as BaTi $[Si_3O_n]$, the value of n is ……..

Ans. (9)

Q.11 (3) (ii, iii, iv)

Name of ore	Composition of ore
(i) Carnallite $\longrightarrow$	$KCl.MgCl_2.6H_2O$
(ii) Cuprite $\longrightarrow$	Cu_2O
(iii) Cassiterite $\longrightarrow$	SnO_2
(iv) Chromite $\longrightarrow$	$FeO.Cr_2O_3$
(v) Cinnabar $\longrightarrow$	HgS
(vi) Calamine $\longrightarrow$	$ZnCO_3$
(vii) Cerussite $\longrightarrow$	$PbCO_3$
(viii) Chalcopyrite $\longrightarrow$	$CuFeS_2$
(ix) Chalcocite $\longrightarrow$	Cu_2S

So, answer is (ii), (iii) & (iv)

Q.12 (75)

Fe^{2+} and Fe^{3+}

Number of Fe^{3+} = 2 × Number of Fe^{2+}

∴   EF = $2Fe^{3+} . Fe^{2+}O_4^{2-} = Fe_{0.75}O$

Q.13 (4) (i, ii, iii & vii)

(i) Dolomite	$CaCO_3.MgCO_3$
(ii) Malachite	$CuCO_3.Cu(OH)_2$
(iii) Calcite	$ZnCO_3$
(iv) Copperpyrites	$CuFeS_2$
(v) Sylvine	KCl
(vi) Cryolite	Na_3AlF_6
(vii) Siderite	$FeCO_3$
(viii) Iron pyrite	FeS_2
(ix) Argentite	Ag_2S

So, answer is (i), (ii), (iii) and (vii)

Q.14 (4)

$Al_2O_3 + 2NaOH + 2H_2O \xrightarrow{\Delta} 2NaAlO_2 + 3H_2O$

; $Ag_2S + 2CN^- \longrightarrow [Ag(CN)_2]^- + S^{2-}$

$Au + 2CN^- + 2H_2O + O_2 \longrightarrow [Au(CN)_2]^- + 4OH^-$

; $CuFeS_2 \longrightarrow$ No leaching

$PbS \longrightarrow$ No leaching ; $MgCl_2 \longrightarrow$ No leaching ; $FeCO_3 \longrightarrow$ No leaching

$2Cu_2O$ (s) + $4H_2SO_4$ (aq) + O_2 (g) $\longrightarrow$

$4CuSO_4$ (aq) + $4H_2O$ (ℓ) ; $HgS \longrightarrow$ No leaching

Q.15 (3)

$2HgS + 3 O_2 \longrightarrow 2HgO + 2SO_2$; $2HgO + HgS \longrightarrow 3Hg + SO_2$

$Cu_2S + 3O_2 \longrightarrow 3Cu_2O + 2 SO_2$; $2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$

$2PbS + 3O_2 \longrightarrow 2PbO + 2 SO_2$; $2PbO + PbS \longrightarrow 3Pb + SO_2$

Q.16 (6)

The metals which are more electropositive than Al (Li → Al). They are extracted by electrolysis of their molten metalchlorides.

Li, Ba, Na, Al, Ca, Mg

Q.17 (2)

At 500 – 800 K (lower temperature range in the blast furnace)

$3 Fe_2O_3 + CO \longrightarrow 2 Fe_3O_4 + CO_2$

$Fe_3O_4 + CO \longrightarrow 3Fe + 4 CO_2$

$Fe_2O_3 + CO \longrightarrow 2FeO + CO_2$

At 900 – 1500 K (higher temperature range in the blast furnace):

$C + CO_2 \longrightarrow 2 CO$;

$FeO + CO \longrightarrow Fe + CO_2$

Q.18 (5) (a, b, d, e, f)

In NaCl metallurgy $CaCl_2$ and KF are added. Carnellite firstly converted into anhydrous $MgCl_2$ then undergo process.

Q.19 (7)

(1) $B_2O_3 + 2Al \xrightarrow{\Delta} 2B + Al_2O_3$ (aluminothermic process-extraction of boron)

81

(2) $Cr_2O_3 + Al \xrightarrow{\Delta} 2Cr + Al_2O_3$ (extraction of chromium)

(2) $TiCl_4 + 2Mg \xrightarrow{\Delta} Ti + 2MgCl_2$ (Kroll process-extraction of titanium)

(4) $PbS + 2PbO \xrightarrow{\Delta} 3Pb + SO_2$ (extraction of lead)

(5) $3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$ (Indirect reduction)

(6) $Fe_3O_4 + CO \longrightarrow 3FeO + CO_2$ (Indirect reduction)

(7) $2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$ (Self reduction)

Q.20 (16)

Net reaction in Hall-Heroult process is :

$$3C + 2Al_2O_3 \longrightarrow 4Al + 3CO_2$$
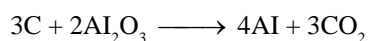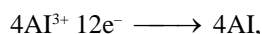
or $4Al^{3+} 12e^- \longrightarrow 4Al$,
number of electrons (n) = 12
$\Delta G° = 3\Delta G°_f (CO_2) - 2\Delta G°_f (Al_2O_3)$
   $= 3 \times 394 - 2(-1520) = 1858$ kJ

$$\Delta G° = -nFE°_{cell}$$

$$-E°_{cell} = \frac{\Delta G°}{nF} = \frac{1858 \times 1000}{12 \times 96500} =$$

1.60 V

Ans. 1.60 × 10 = 16

Q.21 (65)

$$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag$$
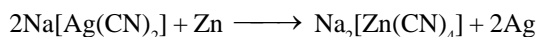
$$\frac{0.5 \times 500}{1000} = 0.25 \text{ moles}$$

$$\text{moles of Zn} = \frac{0.25}{2}$$

$$\text{moles of Zn} = \frac{0.25}{2} \times 65 = \frac{65}{8} \times 8 = 65$$

Q.22 (39)

$\Delta G° = +nFE°_{cell}$ $MgCl_2 \longrightarrow Mg + Cl_2$

$$= \frac{2 \times 96500 \times 2.02}{1000} = 390 \text{ kJ/mole}$$

Q.23 (60)
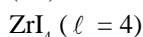
ZrI_4 ($\ell = 4$)
Gas involved in Mond's process is CO (m = 3).
Thomas slag is $Ca_3(PO_4)_2$ (n = 3 + 2 = 5)

Q.24 (5)
Physical Method : I, II, III, IV
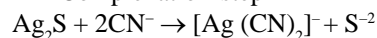Chemical Method : V, VI, VII, VIII, IX

KVPY
PREVIOUS YEAR'S
Q.1 (C)

$$2ZnS + 3O_2 \xrightarrow{950°C} 2ZnO + 2SO_2$$

$$ZnS + 2O_2 \xrightarrow{950°C} ZnSO_4$$

then $2ZnSO_4 \xrightarrow{950°C} 2ZnO + 2SO_2 + O_2$

Q.2 (A)
   Complexation step
$Ag_2S + 2CN^- \rightarrow [Ag(CN)_2]^- + S^{-2}$
   $\downarrow$ + Zn Reduction step
   $[Zn(CN)_4]^{-2} + Ag$

Q.3 (A)
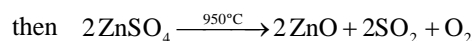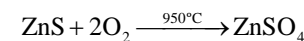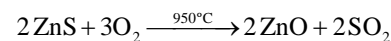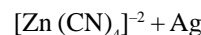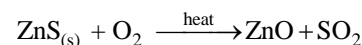
$$ZnS_{(s)} + O_2 \xrightarrow{heat} ZnO + SO_2$$
Roasting

JEE-MAIN
PREVIOUS YEAR'S
Q.1 (1)

Theory based

Q.2 (1)
Q.3 (2)
Q.4 (1)

Q.5 (3)
(a) Mercury $\rightarrow$ Distillation refining
(b) Copper $\rightarrow$ Electrolytic refining
(c) Silicon $\rightarrow$ Zone refining
(d) Nickel $\rightarrow$ Vapour phase refining

Q.6 (1)
To reduce the melting point of reaction mixture, cryolite is added.

Q.7 (4)
Ore Formula
(a) Haematite Fe_2O_3
(b) Bauxite $Al_2O_3.xH_2O$
(c) Magnetite Fe_3O_4
(d) Malachite $CuCO_3.Cu(OH)_2$

Q.8 **(1)**

At intersection point $\Delta G = 0$ and sudden increase in slope is due to melting or boiling point of the metal.

Q.9 **(1)**

Reduction of $Al_2O_3 \rightarrow Al$ is carried out by electrolytic reduction of its fused salts.

ZnO, Fe_2O_3 & Cu_2O can be reduce by carbon.

Q.10 **(2)**

In roasting process, metal sulphide (MS) ore are converted into metal oxide and sulphur is remove in the form of SO_2 gas.

H_2O
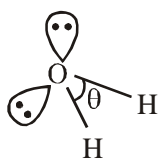
$\theta = 104.5°$

the hybridisation of oxygen is water molecule is sp^3.

So electron geometry of water molecule is tetrahedral and the bond angle should be 109°28" but as we know that lone pair-lone pair repulsion of electrons is higher than the bond pair-bond pair repulsion because lone pair is occupied more space areound central atom than that of bond pair.

$$2MS + 3O_2 \xrightarrow{\Delta} 2MO + 2SO_2\uparrow$$
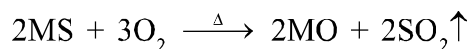
Q.11 (2)

Q.12 (1)

Q.13 (4)

Q.14 (1)

Q.15 (1)

Q.16 (2)

Q.17 (2)

Q.18 (1)

Q.19 (4)

Q.20 [6]

Anode mud contains Sb, Se, Te, Ag, Au and Ot

Q.21 (2)

Q.22 (2)

JEE-ADVANCED

PREVIOUS YEAR'S

Q.1 (AD)

Important ore of tin is cassiterite (SnO_2). SnO_2 is reduced to metal using carbon at 1200 – 1300°C in an electric furnace. The product often contains traces of Fe, which is removed by blowing air through the molten mixture to oxidise FeO which then floats to the surface.

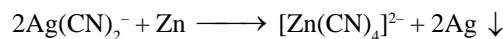$$SnO_2 + 2C \longrightarrow Sn + 2CO$$

$$Fe + O_2 \longrightarrow FeO$$
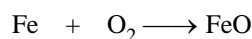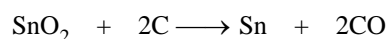
Q.2 (D)

In haematite(Fe_2O_3), Fe is present in (III) oxidation state and in magnetite (Fe_3O_4) which is a mixed oxide of FeO and Fe_2O_3, Fe is present in (II) and (III) oxidation state.

Q.3 (B)

In extraction of silver, Ag_2S is leached with KCN in presence of air :

$$Ag_2S + NaCN + O_2 \rightleftharpoons Na\,[Ag(CN)_2] + Na_2S_2O_3$$

Thus, O_2 is oxidant.

$$2Ag(CN)_2^- + Zn \longrightarrow [Zn(CN)_4]^{2-} + 2Ag \downarrow$$
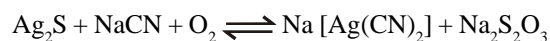
Q.4 (A)

Common ore of $Ag – Ag_2S$, $Cu – CuFeS_2$,

$Pb – PbS$, $Sn – SnO_2$, $Mg – KCl$. $MgCl_2$. $6H_2O$, $Al – Al_2O_3$. xH_2O
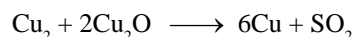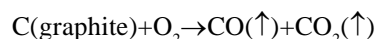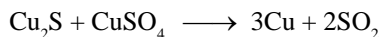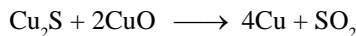
So answer is (A)

Q.5 (CD)

SnO_2 and Fe_2O_3 are reduced by C reduction method.

Al_2O_3 and $MgCO_3$. $CaCO_3$ are reduced by electrolytic reduction.

Q.6 (BCD)

$$Cu_2 + 2Cu_2O \longrightarrow 6Cu + SO_2$$

$Cu_2S + 2CuO \longrightarrow 4Cu + SO_2$

$Cu_2S + CuSO_4 \longrightarrow 3Cu + 2SO_2$

$C(graphite) + O_2 \rightarrow CO(\uparrow) + CO_2(\uparrow)$

(D) The steel vessel with a lining of carbon acts as cathode.

Q.7 (BCD)

Impure Cu is used as anode pure Cu deposited at cathode. Electrolyte is acidified solution of $CuSO_4$. impurities settle as anode mud.

Q.8 (A - P,Q,S) ; (B - T) ; (C - Q,R) ; (D - R)

Q.9 (ABC)

Q.10 (B)

Ore	Formula
Calamine	$ZnCO_3$
Malachite	$CuCO_3.Cu(OH)_2$
Magnetite	Fe_3O_4
Cryolite	Na_3AlF_6

So correct answer is option (B)

Q.11 (A,C,D)

$4Au(s) + 8CN^-(aq) + 2H_2O(aq) + O_2(g) \rightarrow 4[Au(CN)_2]^-(aq) + 4OH^-(aq)$

$$(Q)$$

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

$\quad$ (R) $\qquad$ (T) $\qquad$ (Z)

Q.12 (B,C,D)

(A)

$$Au + HNO_3 + 4HCl \rightarrow AuCl_4^{\ominus} + H_3O^+ + NO + H_2O$$

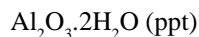(B) Aqua regia $= 3HCl$ (cons.) $+ HNO_3$(cons.)

(C) $AuCl_4^{\ominus}$ is produced

(D) Yellow colour of aqua regia is due to it's decomposition into NOCl (orange yellow) and Cl_2 (greenish yellow).

Q.13 (A,B,C,D)
(A) $2Na[Al(OH)_4]_{(aq.)}$
$+ CO_2 \rightarrow Na_2CO_3 + H_2O + 2Al(OH)_3 (\downarrow)$
$\qquad$ or
$\qquad Al_2O_3.2H_2O$ (ppt)
(B) Function of Na_3AlF_6 is to lower the melting point of $\quad$ electrolyte.
(C) During electrolysis of Al_2O_3, the reactions at anode are :

$$\left[2Al^{3+}(\ell) + 3O^{2-}(\ell) \xrightarrow{\text{At anode}} O_2(gas) + 2e^- \right]$$

Q.14 (A , C, D)
(A) $PbS + 2PbO \rightarrow 3Pb + SO_2$ (self reduction)
(B) Silica is added to remove impurity of Fe in the form of slag $FeSiO_3$
(C) $CuFeS_2$ ore is partially oxidized first by roasting and then self reduction of Cu takes place to produce blister copper.
(D)

$$4\,Na[\overset{+1}{Au}(CN)_2] + 2Zn \rightarrow 2Na_2[\overset{+2}{Zn}(CN)_4] + 4\,\overset{0}{Au}$$

Qualitative Analysis

JEE-MAIN
OBJECTIVE QUESTIONS

Q.1 (2)

(i) $Cr_2O_7^{2-} + 3SO_2 + 2H^+ \longrightarrow 2Cr^{3+}$ (green) + $3SO_4^{2-} + H_2O$; CO_2 and O_2 do not give reactions with acidified $K_2Cr_2O_7$

(ii) $Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 \downarrow$ (white) + H_2O ; O_2 does not give reaction with acidified $K_2Cr_2O_7$.

(iii) O_2 dissolves in pyrogallol.

Q.2 (4)

$CH_3COO^- + H^+ \longrightarrow CH_3COOH \uparrow$ (smells like vinegar).

Q.3 (3)

$SO_3^{2-} + Ba(OH)_2 \longrightarrow BaSO_3 \downarrow$ (white) + $2OH^-$.

$3SO_2 + Cr_2O_7^{2-} + 2H^+ \longrightarrow 2Cr^{3+}$ (green colour solution) + $3SO_4^{2-} + H_2O$.

Q.4 (3)

Q.5 (3)

H_2S + Any strong oxidising agent
$\rightarrow S \downarrow + H_2O$
(yellow - white turbidity)

Q.6 (1)

$PbSO_4 + 2CH_3COONH_4 \longrightarrow (NH_4)_2SO_4 + (CH_3COO)_2Pb$.

Q.7 (3)

$Pb^{2+} + H_2S \longrightarrow PbS \downarrow$(black) $+2H^+$; $3PbS + 8HNO_3 \longrightarrow 3Pb(NO_3)_2 + 2NO \uparrow + 3S \downarrow + 4H_2O$.

$Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4 \downarrow$ (white).

Q.8 (3)

$H_2S \rightleftharpoons 2H^+ + S^{2-}$; $HCl \rightleftharpoons H_2^+ + Cl^-$.
Due to common ion effect, the ionisation of H_2S is suppressed and thus low concentration of S^{2-} ions is obtained. This much of S^{2-} ions concentration is enough to precipitate only IInd group cations (because of the low K_{SP} of IInd group sulphides).

Q.9 (4)

Yellow precipitate of CdS is insoluble in yellow ammonium sulphide where as yellow precipitate of As_2S_3 is soluble forming $(NH_4)_3 AsS_4$.

Q.10 (4)

AS_2S_3 is insoluble in dil. acids but soluble in alkalie.

Q.11 (4)

$Zn^{2+} + NH_4OH \longrightarrow Zn(OH)_2$

$Zn(OH)_2 \xrightarrow{\text{excess}(NH_4OH)} [Zn(NH_3)_4]^{2+}$
soluble Imperfect complex

$\Big\Vert H_2S$
ZnS (white PPt)

Q.12 (1)

PbS, Bi_2S_3 and CuS dissolve in dilute HNO_3 forming nitrates but HgS dissolves in aquaregia forming $HgCl_2$.

Q.13 (1)

(1) $Cu^{2+} + S^{2-} \longrightarrow CuS \downarrow$ (black) ,

(2) $Cd^2 + S^{2-} \longrightarrow CdS \downarrow$ (yellow) ,

(3) $Zn^{2+} + S^{2-} \longrightarrow ZnS \downarrow$ (white) ,

(4) $2Fe^{3+} + H_2S \longrightarrow 2Fe^{2+} + 2H^+ + S \downarrow$ (milky white)

Q.14 (1)

Q.15 (2)

CH_3COONa is mild basic and P^H is about 9

Q.16 (2)

$S_2O_3^{2-} + H^+ \longrightarrow SO_2 \uparrow + S \downarrow$ yellow ppt
$BaS_2O_3 + K_2CrO_4 \longrightarrow BaCrO_4 \downarrow$ yellow ppt

Q.17 (1)

HgS is soluble in aquaregia

Q.18 (2)

$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 \downarrow$
(while PPt)

Base   Acid.

85

Q.19 (2)

Q.20 (2)

Q.21 (2)

Q.22 (4)

Q.23 (1)

$$SO_3^{2-} + 2H^+ \longrightarrow SO_2 \uparrow + H_2O$$

$$SO_2 + 2IO_3^- + 4H_2O \longrightarrow I_2 + 5SO_4^{-2} + 8H^+$$

Thus the gas B and compound A are SO_2 and Na_2SO_3 respectively.

Q.24 (3)

Q.25 (1)

Q.26 (2)

$$3AgCl + Na_3AsO_3 \longrightarrow Ag_3AsO_3 \downarrow (yellow) + 3Cl^- + 3Na^+.$$

$$AsO_4^{3-} + 3Ag^+ \longrightarrow Ag_3AsO_4 \downarrow (brownish\text{-}red).$$

Q.27 (4)

$$AgCl + 2NH_3 \longrightarrow [Ag(NH_3)_2]^+ \ Cl^- \ (soluble \ complex).$$

Q.28 (4)

$$Br^- + H_2SO_4 \longrightarrow HBr + HSO_4^- \ ; \ HBr + H_2SO_4$$
$$\longrightarrow Br_2 + SO_2 + 2H_2O$$

$$Br_2 + 2I^- \longrightarrow 2Br^- + I_2 \ ; \qquad I_2 + starch \ (स्टार्च)$$
$$\longrightarrow blue \ colour \ (नीला \ रंग)$$

Q.29 (4)

$$Ag^+ + Br^- \longrightarrow AgBr \downarrow (pale \ yellow) \ ; \ NaBr +$$
$$Na_2CO_3 \longrightarrow No \ reaction.$$

$$2NaBr + 2H_2SO_4 \longrightarrow Br_2 \uparrow (reddish \ brown) + SO_2$$
$$+ 2Na^+ + 2H_2O.$$

Q.30 (2)

$[Fe(H_2O)_5(NO)]SO_4$
(brownring complex) $\Rightarrow$ nitroso ferrous sulphate

Q.31 (1)

$PbCl_2$ is soluble in hot water

86

Q.32 (1)

$$Br^- + Cl_2 \uparrow \longrightarrow Br_2 + 2 \ Cl^- ; \ Br_2 \uparrow + Cl_2 \uparrow \longrightarrow$$
$$2BrCl \ (pale \ yellow).$$

Q.33 (3)

$$OCl^- + 3I^- + H_2O \longrightarrow I_3^- + 2OH^- + Cl^-.$$

$I_3^- + starch \longrightarrow$ blue -black spot on starch paper due to the formation of iodine-starch adsorption complex.

Q.34 (1)

$$2I^- + Cl_2 \longrightarrow I_2 \ (violet) + 2Cl^-$$

$$5Cl_2 \ (excess) + I_2 + 6H_2O \longrightarrow 2HIO_3$$
$$(colourless) + 10HCl$$

Q.35 (3)
All nitrates are soluble in water but nitrates of mercury and bismuth gives their insoluble basic salts on treatment with water.

Q.36 (2)
$$AgCl + NH_4OH \rightarrow [Ag(NH_3)_2]Cl + H_2O$$
$$\qquad\qquad\qquad\qquad soluble$$

Q.37 (2)

$$Pb(NO_3)_2 + 2NH_4OH \longrightarrow Pb(OH)_2 \downarrow (white) +$$
$$2NH_4NO_3$$

$$Pb(NO_3)_2 + 2NaCl \longrightarrow PbCl_2 \downarrow (white) + 2NaNO_3$$

$$Pb(NO_3)_2 + H_2S \longrightarrow PbS \downarrow (black) + 2NaNO_3$$

Q.38 (3)

$$Pb^{2+} + 2Cl^- \longrightarrow PbCl_2 \downarrow (soluble \ in \ hot \ water) \ ;$$

$$PbCl_2 + CrO_4^{2-} \longrightarrow PbCrO_4 \downarrow (yellow) + 2Cl^-.$$

Q.39 (2)
$HgCl_2$ does not give chromyl chloride test due to less extent of ionisation because of high polarising power of cation.

Q.40 (4)
$AgCl \downarrow (white) \ ; \ PbCl_2 \downarrow (white) \ ; \ Hg_2Cl_2 \downarrow (white) \ ;$ $CuCl_2$ soluble.

Q.41 (4)
$$Sn^{2+} + Hg^{2+} \longrightarrow Sn^{4+} + Hg_2^{2+}$$
$$Hg_2^{2+} + Sn^{2+} \longrightarrow Sn^{4+} + Hg$$
$$(excess) \qquad\qquad (grey)$$

Q.42 (2)

$$2AgNO_3 \longrightarrow 2Ag + 2NO_2 + O_2 \uparrow$$

Q.43 (4)

$AgCl + Ag.\ NH_3 \longrightarrow [Ag(NH_3)_2]$ Cl souble

Q.44 (2)

Q.45 (4)

SO_4^{2-} show no effect with Dil or Conc. acid. It give its test with PPt reaction only.

Q.46 **(2)**

(1) $Bi^{3+} + 3I^- \longrightarrow BiI_3 \downarrow$ (black)

(2) $2Cu^{2+} + 5I^- \longrightarrow Cu_2I_2 \downarrow + I_3^-$ (brown solution)

(3) $Pb^{2+} + 2I^- \longrightarrow PbI_2 \downarrow$ (yellow)

(4) $Hg_2^{2+} + 2I^- \longrightarrow HgI_2$ (red/scarlet)

Q.47 (4)

solid mix +Con. $H_2SO_4 + C_2H_5OH \longrightarrow (C_2H_5)_3 BO_3$
Taken as past   green edge from on touching

Q.48 (4)

AgF is most soluble in water due to its highest ionic character.

Q.49 (1)

$NaCl + AgNO_3 \longrightarrow AgCl(s) \downarrow$ (white PPt)
$AgCl + NH_4OH \longrightarrow [Ag(NH_3)_2]$ Cl
$[Ag(NH_3)_2]Cl + dil\ HNO_3 \longrightarrow AgCl$ (s)
                    (white ppt)

Q.50 (1)

$B(OH)_3 + H_2O \longrightarrow [B(OH)_4]^- + H^+\ BO_2^- + 2H_2O + H^+$

(cis-1,2-diol)

$\Rightarrow$ facilitates the rex in forward direction.

Q.51 (2)

Q.52 (3)

All produce insoluble carbonates with K_2CO_3 except Na_2SO_4 that forms soluble Na_2CO_3.

Q.53 (3)

$BaCl_2 + 2AgNO_3 \longrightarrow 2AgCl \downarrow$ (white) $+ BaNO_3$

$BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 \downarrow$ (white) $+ 2HCl$

Q.54 (3)

$2NO_2^- + 3I^- + 4CH_3COOH \longrightarrow I_3^- + 2NO \uparrow + 4CH_3COO^- + 2H_2O$.

$I_3^- + $ starch $\longrightarrow$ blue colouration.

Q.55 (1)

$4Cl^- + Cr_2O_7^{2-} + 6H^+ \longrightarrow 2CrO_2Cl_2 \uparrow$ (deep red) $+ 3H_2O$.

Q.56 (4)

Ni^{2+} requires large conc. of S^{2-} for ppt as K_{sp} of Ni is large. So it can not be precipitated by H_2S and HCl because   here $[S^{2-}]$ is quiteless due to common ion effect.

Q.57 (4)

$Ba^{2+} + CrO_4^{2-} \longrightarrow BaCrO_4 \downarrow$ (yellow) ; $Ag^+ + Cl^-$
$\longrightarrow AgCl \downarrow$ (white)

Q.58 (3)

$Ag_3PO_4 + NH_4OH \rightarrow [Ag(NH_3)_2]_3PO_4 + H_2O$
yellow ppt

Q.59 (3)

$Ba^{2+} + CrO_4^{2-} \rightarrow$ yellow ppt of $BaCrO_4$
$Ba^{2+} + SO_4^{2-} \rightarrow$ white ppt of $BaSO_4 \downarrow$

Q.60 (4)

$Pb^{2+} + CrO_4^{2-} \longrightarrow PbCrO_4 \downarrow$ (yellow) ; $PbCrO_4 \downarrow$
$+ 4OH^- \longrightarrow [Pb(OH)_4]^{2-} + CrO_4^{2-}$.

Q.61 (3)

$BaCrO_4$ has least Ksp
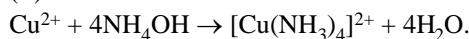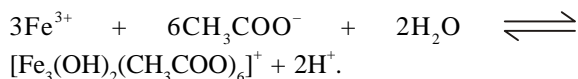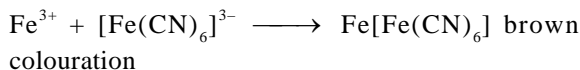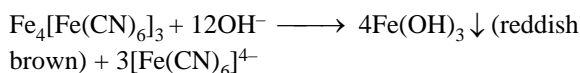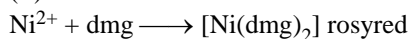$\Rightarrow Ba^{2+} + CrO_4^{2-} \longrightarrow BaCrO_4 \downarrow$ (yellow ppt)

Q.62 (3)

solid mix + solid $K_2Cr_2O_7$ + Conc. H_2SO_4

$\xrightarrow{\text{warming}}$ CrO_2Cl_2 ↑

Reddish brown fumes

Q.63 (2)

$CrO_3 + NaOH \longrightarrow Cr(OH)_3$

Green PPt

↓ xs of NaOH

$[Cr(OH)]_4$

(soluble)

Q.64 (4)

$Ba^{2+} + CrO_4^{2-} \longrightarrow BaCrO_4$ ↓ (yellow) ; $Ag^+ + Br^-$

$\longrightarrow AgBr$ ↓ (pale yellow).

Q.65 (1)

Q.66 (1)

Q.67 (2)

Q.68 (4)

K_2HgI_4 /KOH

Nesseler reagent

used for detection of NH_4^+

Q.69 (3)

(1) $Hg^{2+} + Co^{2+} + 4SCN^- \longrightarrow Co[Hg(SCN)_4]$↓
(deep blue) ;

(2) $2Hg^{2+} + Sn^{2+} + 2Cl^- \longrightarrow Hg_2Cl_2$↓ (white) + Sn^{4+}

; $Hg_2Cl_2 + Sn^{2+} \longrightarrow Hg$ ↓ (black) + $Sn^{4+} + 2Cl^-$

(3) $2Hg^{2+} + NO_3^- + 4NH_3 + H_2O \longrightarrow$
$HgO.Hg(NH_2)NO_3$↓ (white)

(4) KCN no effect i.e. no reaction.

Q.70 (4)

$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$; $NH_4OH \rightleftharpoons NH_4^+ + OH^-$.

Because of common ion effect, the ionisation of NH_4OH is suppressed.

Q.71 (3)

$[Al(OH)_4]^- + NH_4^+ \xrightarrow{\Delta} Al(OH)_3$↓ + NH_3↑ + H_2O

Hydroxide ion concentration is reduced owing to the formation of ammonia (a weak base) which escapes on boiling.

Q.72 (3)

Q.73 (1)

Ca salts impart brick red colour to the flame.

Q.74 (4)

(1) titan yellow is absorbed by magnesium hydroxide producing a deep-red colour or precipitate.

(2) $Mg^{2+} + NH_3 + HPO_4^{2-} \longrightarrow Mg(NH_4)PO_4$ ↓ (white).

(3) Blue lake is formed by the adsorption of reagent on $Mg(OH)_2$.

Q.75 (2)

As the concentration of CO_3^{2-} ions provided by $(NH_4)_2CO_3$ in presence of NH_4Cl and ammonia is not just sufficient to precipitate the Mg as $MgCO_3$ because of its high K_{SP} value.

Q.76 (1)

Mg^{2+} doo not show flame test because of its High I.E.

Q.77 (3)

Q.78 (4)

$Hg_2Cl_2 + NH_3 \longrightarrow 2Hg$↓ + HgO. $Hg(NH_2)$ x
(Black)

x=Cl, Br $\longrightarrow$ white

x=I $\longrightarrow$ Brown

Q.79 (2)

$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7 + 10H_2O$;

$Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + B_2O_3$

$CuO + B_2O_3 \xrightarrow{\Delta} Cu(BO_2)_2$ (copper (II) metaborate) - red and opaque bead in oxidising flame.

Q.80 (4)

$Pb^{2+} + HCl \longrightarrow PbCl_2$
(white ppt.)

↓ Hot water

PbS↓ $\xleftarrow{H_2S}$ Soluble $PbCl_2$
(black)

Q.81 (3)

Q.82 (2)

Strontium chloride gives crimson colour flame in Bunsen burner.

$BaCl_2$ -apple green, $CaCl_2$ - brick red, KCl - lilac(violet).

Q.83 (2)

$Fe^{2+} + NO + 5H_2O \longrightarrow [Fe(H_2O)_5NO]^{2+}$ (brown complex)

Q.84 (2)

Q.85 (2)

Q.86 (3)
$Fe(OH)_3$ is not soluble in NaOH solution but $Al(OH)_3$ is soluble in NaOH solution

Q.87 (2)
$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \xrightarrow[\text{NaOH}]{\text{Excess of}} [Zn(OH)_4]^{2-}$
white ppt.

$\Rightarrow$ Zn exist in anionic part

Q.88 (4)
$NiCl_2 \rightarrow$ green colour

Q.89 (3)
Na_2CO_3 produces large $[CO_3^{2-}]$ which may ppt other cations along with Ba^{2+}, Sr^{2+} and Ca^{2+} which interfere the detection of group V cation.

Q.90 (2)
$Cu^{2+} + KCN \rightarrow Cu(CN)_2 \rightarrow CuCN + (COO)_2$

yellow ppt

excess of KCN

$3K^+ + [Cu(CN)_4]^{3-} \rightleftharpoons$

$K_3[Cu(CN)_4]$

colourless

Q.91 (1)
As, Bi^{3+}, Sn^{4+}, Both will give ppt
with H_2S and dil. HCl

Q.92 (4)

$NH_4^+ + [PtCl_6]^{2-} \longrightarrow (NH_4)_2[PtCl_6] \downarrow$ (yellow).

$[Co(NO_2)_6]^{3-} + 3NH_4^+ \longrightarrow (NH_4)_3 [Co(NO_2)_6] \downarrow$ (yellow).

Q.93 (4)

$NH_4^+ + OH^- \xrightarrow{\Delta} NH_3 \uparrow + H_2O.$

(1) NH_3, alkaline in nature turns red litmus blue;
$NH_3 + HCl \longrightarrow NH_4Cl$ (white fumes)

(2) $2Hg\ NO_3 + 2NH_3 \longrightarrow \underbrace{Hg(NH_2)NO_3 + Hg}_{black} +$

NH_4NO_3 ; $CuSO_4 + 4NH_3 \longrightarrow [Cu(NH_3)_4]\ SO_4$
(intense blue)

(3) $2K_2\ (HgI_4) + NH_3 + 3KOH \longrightarrow HgOHgNH_2I$
$\downarrow$ (brown) $+ 7KI + 2H_2O$

Q.94 (2)
$[Fe(H_2O)_5(NO)]SO_4$

brown ring complex

Q.95 (3)

$Pb^{2+} + I_2 \longrightarrow Pb\ I_2 \downarrow$ (yellow)
$Pb\ I_2 + 2\ I^- \rightleftharpoons [Pb\ I_4]^{2-}$ (soluble complex)

Q.96 (2)

$Ag^+ + HCl \longrightarrow AgCl \downarrow$ (white) $+ H^+$; $Cu^{2+} +$

$2HCl \longrightarrow CuCl_2$ (soluble) $+ 2H^+.$

Q.97 (2)
$Fe^{3+} + K_4[Fe(CN)_6] \rightarrow Fe_4[Fe(CN)_6]_3$

prussian blue

Q.98 (2)
same as above solution

Q.99 (2)
(1)$Cu^{2+} + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{2+}$
Blue colour
(2) $Cu^{2+} + K_4\ [Fe(CN)_6)] \longrightarrow Cu_2\ [Fe(CN)_6]$
Chocolate Brown PPt
(3) $Fe^{3+} + K_4\ [Fe(CN)_6] \longrightarrow Fe_4[Fe(CN)_6]_3$

prussian blue

(4) $CuSO_4 \xrightarrow{H_2O} CuSO_4 + H_2O$

(Blue)

Q.100 (1)
$2Hg^{2+} + SnCl_2 \rightarrow Hg_2Cl_2 \downarrow$ (silky white) $+ Sn^{4+}.$

Q.101 (4)

89

Q.102 (2)

$$3Fe^{2+} + 2k_3[Fe(CN)_6] \longrightarrow Fe_3[Fe(CN)_6]_2$$
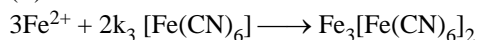
turn bull's blue
ferroferri cyanide

Q.103 (3)

$$Cu^{2+} + 4NH_4OH \rightarrow [Cu(NH_3)_4]^{2+} + 4H_2O.$$

Q.104 (2)

$Fe^{3+} + [Fe(CN)_6]^{3-} \longrightarrow Fe[Fe(CN)_6]$ brown colouration

$$3Fe^{3+} + 6CH_3COO^- + 2H_2O \rightleftharpoons [Fe_3(OH)_2(CH_3COO)_6]^+ + 2H^+.$$

Q.105 (2)

$Fe_4[Fe(CN)_6]_3 + 12OH^- \longrightarrow 4Fe(OH)_3\downarrow$ (reddish brown) $+ 3[Fe(CN)_6]^{4-}$

Q.106 (1)

$Ni^{2+} + dmg \longrightarrow [Ni(dmg)_2]$ rosyred

Q.107 (3)

Cu^{2+} Cd^{2+} Cr^{3+} Fe^{3+} Fe^{3+} Al^{3+}

$\Rightarrow H_2S$ in presence of dil. HCl is gp. reagent for group II cation.

$\Rightarrow Cu^{2+}, Cd^{2+}$. will PPt in form of their suphide

$\Rightarrow$ filtrate is ready for the test of $Fe^{3+}, Cr^{3+}, Al^{3+}$

Q.108 (3)

Both dissolves in acids. $Cr(OH)_3$ is partially soluble while $Fe(OH)_3$ is not soluble in aqueous NH_3. Only $Cr(OH)_3$ not $Fe(OH)_3$ is soluble by $NaOH/H_2O_2$ according to the reaction.

$Cr(OH)_3\downarrow$ (green) $\xrightarrow{NaOH/H_2O_2} CrO_4^{2-}$ (yellow solution) $+ H_2O$.
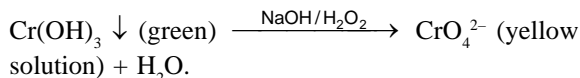
Q.109 (3)

Ferric alum contains Fe^{3+} ions ; $Fe^{3+} + 3SCN^- \rightarrow Fe(SCN)_3$ (deep red colouration).

Q.110 (4)

$Fe^{3+} + 3SCN^- \longrightarrow Fe(SCN)_3$ (deep red colouration)

$Co^{2+} + 4SCN^- \xrightarrow{amyl\ alcohol} [Co(SCN)_4]^{2-}$ (blue colouration)

$Cu^{2+} + 2SCN^- \longrightarrow Cu(SCN)_2 \downarrow$ (black) ;

$2Cu(SCN)_2 \longrightarrow 2CuSCN\downarrow$ (white) $+ (SCN)_2$.
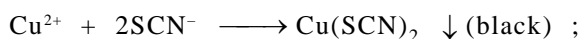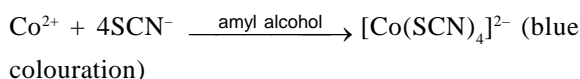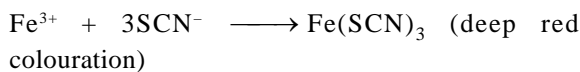
Q.111 (4)

$Fe^{2+} + [Fe(CN)_6]^{4-} \rightarrow$ white precipitate ; $Fe^{3+} + [Fe(CN)_6]^{4-} \rightarrow$ Prussian blue precipitate.

$Zn^{2+} + [Fe(CN)_6]^{4-} \rightarrow$ Bluish white/white precipitate ; $Cu^{2+} + [Fe(CN)_6]^{4-} \rightarrow$ chocolate brown precipitate
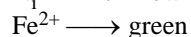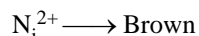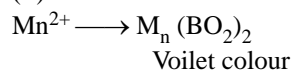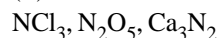
$Ag^+ + [Fe(CN)_6]^{4-} \rightarrow$ white precipitate ; $Ca^{2+} + K_4[Fe(CN)_6]^{4-} \rightarrow$ white precipitate.

Q.112 (2)

On adding HCl the equilibrium will shift in backward direction.

Q.113 (3)

Q.114 (1)

$Ni^{2+} + DMG \xrightarrow{NH_4OH} [Ni(DMG)_2]\downarrow$ (red).

Q.115 (4)

$Zn^{2+} + 2NH_4OH \longrightarrow Zn(OH)_2\downarrow$ (white) $+ 2NH_4^+$;

$Zn(OH)_2 + 4NH_4OH \longrightarrow Zn(NH_3)_4 + 6H_2O$

$Zn^{2+} + S^{2-} \longrightarrow ZnS$ (white)
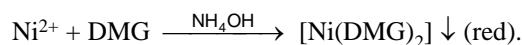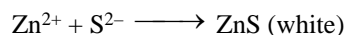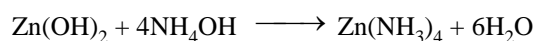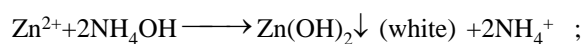
Q.116 (4)

Zn^{2+} is colourless and borax bead test is given by coloured ions such as $Cu^{2+}, Mn^{2+}, Fe^{3+}$ ect.

Q.117 (3)

Q.118 (3)

Q.119 (4)

$Mn^{2+} \longrightarrow M_n(BO_2)_2$
Voilet colour

$N_i^{2+} \longrightarrow$ Brown

$Fe^{2+} \longrightarrow$ green

Q.120 (3)

NCl_3, N_2O_5, Ca_3N_2

NCl_5 is not possible because of absence of vacant d orbitall

JEE-ADVANCED
OBJECTIVE QUESTIONS

Q.1 (B)

$BaCO_3 + dil\ HCl \longrightarrow BaCl_2$
(soluble)

$ZnS + dil\ HCl \longrightarrow ZnCl_2$
(soluble)
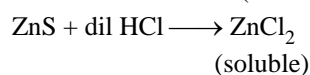
Q.2 (C)

(A) $2Fe^{3+} + H_2S \longrightarrow 2Fe^{2+} + 2H^+ + S\downarrow$ (white-yellow)

(B) $2Fe^{3+} + 3S^{2-} \longrightarrow 2FeS\downarrow$ (black) $+ S\downarrow$

(C) $Fe^{3+} + 3SCN^- \longrightarrow Fe(SCN)_3$ deep red colouration

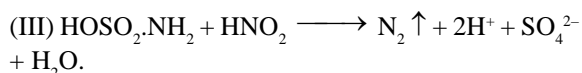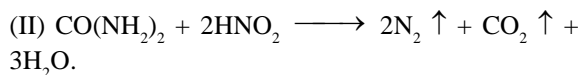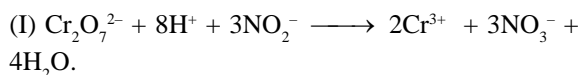**Q.3** (C)

The one with highest value of Ksp will have highest value of solubility because for each given salt the expression of ksp

$ksp = S^2$

Q.4 (D)

$Na_2S > ZnS > CuS$
(Solubility in water)

Q.5 (D)

H_2S in acidic medimum is group reagent for 2nd group cation and hence they will be ppted only in the form of their sulphides

Q.6 (D)

Q.7 (C)

(I) $Cr_2O_7^{2-} + 8H^+ + 3NO_2^- \longrightarrow 2Cr^{3+} + 3NO_3^- + 4H_2O.$

(II) $CO(NH_2)_2 + 2HNO_2 \longrightarrow 2N_2 \uparrow + CO_2 \uparrow + 3H_2O.$

(III) $HOSO_2.NH_2 + HNO_2 \longrightarrow N_2 \uparrow + 2H^+ + SO_4^{2-} + H_2O.$

(IV) NO_2^- and NO_3^- both on reduction with Zn/NaOH on warming gives ammonia gas.

Q.8 (B)

$2\,AgCl \xrightarrow{h\nu} 2\,Ag \downarrow$ (black) $+ Cl_2 \uparrow.$
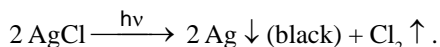
Q.9 (C)

$2I^- + Cl_2 \longrightarrow I_2 + 2Cl^-.$ I_2 being covalent dissolves in chloroform giving purple or violet solution.

$Ba^{2+} + SO_4^{2-} \longrightarrow BaSO_4 \downarrow$ (white).

Q.10 (B)

$Pb^{2+} + 2Cl^- \longrightarrow PbCl_2 \downarrow$
(white ppt)

$Pb^{2+} + S^{2-} \longrightarrow PbS \downarrow$
(Black ppt)
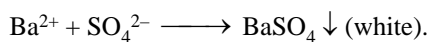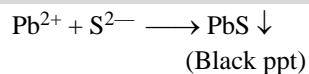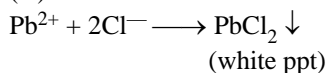
Q.11 (D)
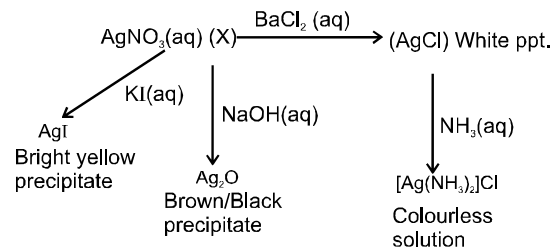
Q.12 (D)

$BaSO_4$ is not dissolved in dil. HCl.

Q.13 (B)

$NH_4 NO_3 \longrightarrow N_2 \uparrow + 2H_2O \uparrow$
(no residue)

$\Rightarrow$ all are gases

Q.14 (D)

Q.15 (B)

$Fe^{3+} + KCNS \longrightarrow [Fe(CNS)_3]$
Blood red colour

Q.16 (C)

$CoO + B_2O_3 \longrightarrow Co(BO_2)_2$
cobalt (II) metaborate
(Blue)

Q.17 (C)

Q.18 (D)

(A) $Pb^{2+} + H_2S \longrightarrow PbS \downarrow$ (black) $+ 2H^+.$

(B) $Cr_2O_7^{2-} + 3H_2S + 8H^+ \longrightarrow 2Cr^{3+}$ (green colour solution) $+ 3S \downarrow + 7H_2O.$

(C) $S^{2-} + [Fe(CN)_5NO]^{2-} \longrightarrow [Fe(CN)_5NOS]^{4-}$ (purple colouration).

Reactions : $Na_2SO_4 + BaCl_2 \longrightarrow BaSO_4 \downarrow + NaCl.$

$BaSO_4 + 4C + Na_2CO_3 \xrightarrow{Fuse} Na_2S + BaCO_3 \downarrow + 4CO \uparrow.$

$Na_2S + H_2SO_4 \longrightarrow Na_2SO_4 + H_2S.$

Q.19 (C)

$$NaCl + AgNO_3 \longrightarrow AgCl \text{ (white)}$$

(pH=7) $\qquad$ Q $\Big\downarrow$ dil.HNO$_3$

not soluble
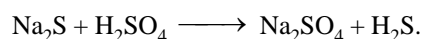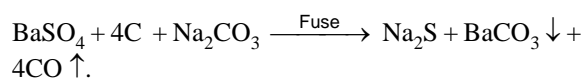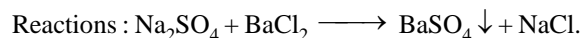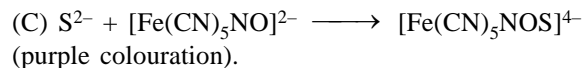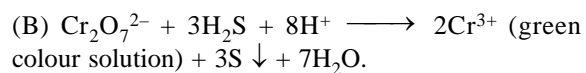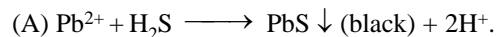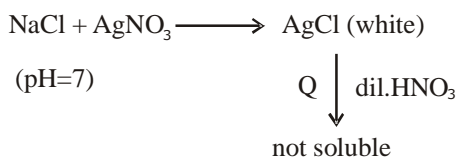
Q.20 (C)

PbSO$_4$ (while ppt) is insoluble in water

Q.21 (A)

MnO$_4^-$ in acidic medium oxidises Fe^{2+} to Fe^{3+}.

Q.22 (A)

$HPO_4^{2-} + Mg^{2+} + NH_4OH + NH_4Cl \longrightarrow Mg\,(NH_4)$
$PO_4\downarrow$

(white ppt)

Q.23 (A)
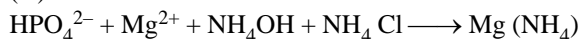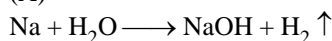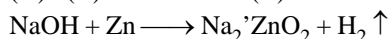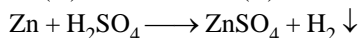
$Na + H_2O \longrightarrow NaOH + H_2\uparrow$
(A) (C) $\qquad$ (B)
$NaOH + Zn \longrightarrow Na_2'ZnO_2 + H_2\uparrow$
  (D) $\qquad\qquad$ (B)
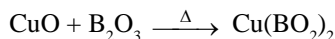$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2\downarrow$
$\Rightarrow$ Na impats a deep golden yellow colour.

Q.24 (A)
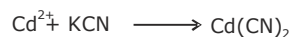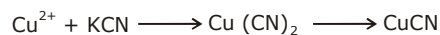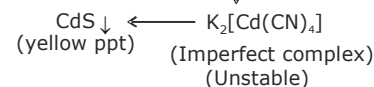
$2\,CuS\downarrow + 8\,CN^- \longrightarrow 2\,[Cu(CN)_4]^{3-} + S_2^{2-}$

Q.25 (C)

$Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + B_2O_3$

$CuO + B_2O_3 \xrightarrow{\Delta} Cu(BO_2)_2$

$2Cu(BO_2)_2 + 4NaBO_2 + 2C \xrightarrow{\Delta} 2Cu$ (red and opaque) $+ 2Na_2B_4O_7 + 2CO\uparrow$

Q.26 (A)

$Cd^{2+}+ KCN \longrightarrow Cd(CN)_2$

$\Big\downarrow$ Xs of KCN

$CdS\downarrow \longleftarrow K_2[Cd(CN)_4]$
(yellow ppt)   (Imperfect complex)
     (Unstable)

$Cu^{2+} + KCN \longrightarrow Cu\,(CN)_2 \longrightarrow CuCN$
         (yellow ppt) $\quad$ Xs $\Big|$ +(CN)$_2$
            of
            KCN $\downarrow$

$X \xleftarrow{H_2S} [Cu(CN)_4]^{3-}$
     (Perfect complex)
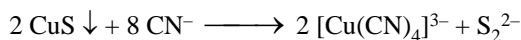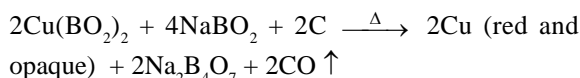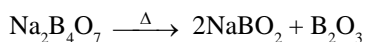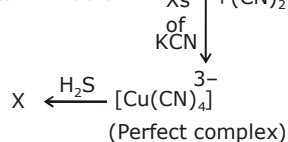
Q.27 (A)

All are soluble except
AgCl which is sparingly soluble
$\Rightarrow$ Low solubility $\Rightarrow$ Low value of Ksp

Q.28 (B)

$$Mg + N_2 \longrightarrow Mg_3N_2$$
$$(y)$$
$$\Big\downarrow H_2O$$
$$NH_3$$
$$NH_3 + CuSO_4 \longrightarrow [Cu(NH_3)_4]^{2+}$$
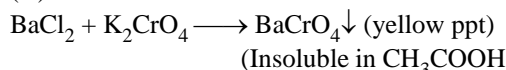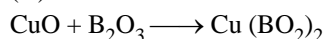$$\text{Blue}$$
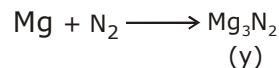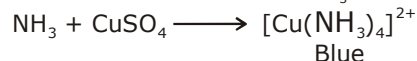
Q.29 (A)

Hg$_2^{2+}$

Q.30 (C)

H$_2$S in acidic medium is group reagent for 2nd group cation and hence they will be ppted only in the form of their sulphides

Q.31 (B)

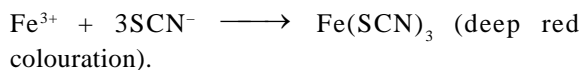$BaCl_2 + K_2CrO_4 \longrightarrow BaCrO_4\downarrow$ (yellow ppt)
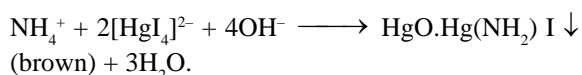   (Insoluble in CH$_3$COOH
Ba imparts apple green colour to the flam

Q.32 (C)

$CuO + B_2O_3 \longrightarrow Cu\,(BO_2)_2$

Q.33 (A)

$Fe^{3+} + 3SCN^- \longrightarrow Fe(SCN)_3$ (deep red colouration).

Q.34 (D)

$Cr^{3+} + H_2O \longrightarrow Cr(OH)_3\downarrow$
        (green)
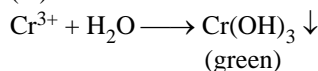
Q.35 (B)

The gas must be NH$_3$, so can give brown precipitate of iodide of millon's base with potassium mercuric iodide.
NH$_4$NO$_3$ is compound (A)

$NH_4^+ + OH^- \longrightarrow NH_3\uparrow + H_2O.$

$NH_4^+ + 2[HgI_4]^{2-} + 4OH^- \longrightarrow HgO.Hg(NH_2)\,I\downarrow$
(brown) $+ 3H_2O.$

$NH_4NO_3 \longrightarrow N_2O + 2H_2O.$
N$_2$O supports combustion.

$2N_2O \longrightarrow 2N_2 + O_2\,.$

Q.36 (D)

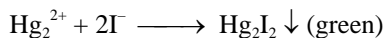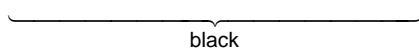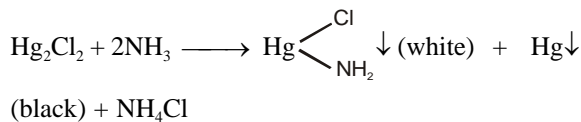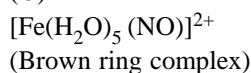(A) Hg_2^{2+} $\xrightarrow{\text{Dil HCl}}$ $Hg_2Cl_2 \downarrow$ (white)

$\xrightarrow{NH_3(aq)}$

$\underbrace{Hg \downarrow \text{(black)} + Hg(NH_2)Cl \downarrow \text{(white)}}_{\text{Black}}$.

Q.37 (C)

$Hg_2Cl_2 + 2NH_3 \longrightarrow$ $Hg\overset{Cl}{\underset{NH_2}{<}} \downarrow$ (white) + $Hg\downarrow$

(black) + NH_4Cl

$\underbrace{\qquad\qquad\qquad\qquad}_{\text{black}}$

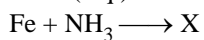$Hg_2^{2+} + 2I^- \longrightarrow Hg_2I_2 \downarrow$ (green)
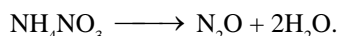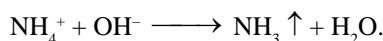
Q.38 (C)
$[Fe(H_2O)_5(NO)]^{2+}$
(Brown ring complex)
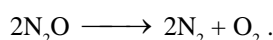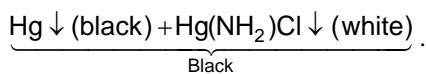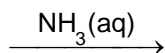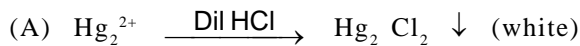
Q.39 (B)
Nessler's reagent
K_2HgI_4 / KOH
$\downarrow$
HgI_4^{2-}
(anion)

Q.40 (B)
After Add^n of NH_3
$Zn^{2+} + NH_3 \longrightarrow [Zn(NH_3)_4]^{2+}$
(Aq.)
$Cu^{2+} + NH_3 \longrightarrow [Cu(NH_3)_4]^{2+}$
(Aq.)
$Fe + NH_3 \longrightarrow X$
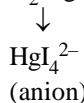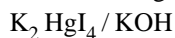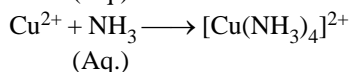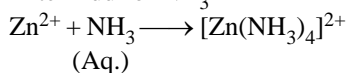
Q.41 (A)
Both belong to same group i.e. IInd group and their K_{SP} values are low ; so both are precipitated according to the following reactions.

$2Bi^{3+} + 3S^{2-} \longrightarrow Bi_2S_3 \downarrow$ (black).

$Sn^{4+} + 2S^{2-} \longrightarrow SnS_2 \downarrow$ (yellow).

Q.42 (B)
The K_{SP} of $Al(OH)_3$ is low as compared to that of the hydroxides of other metals. The OH^- concentration provided by ammonium hydroxide in presence of NH_4Cl is just sufficient to precipitate Al^{3+} as $Al(OH)_3$.

$Al^{3+} + NH_3 + H_2O \xrightarrow{NH_4Cl} Al(OH)_3 \downarrow$ (gelatinous white) + NH_4^+ .

Q.43 (D)
$Al_2O_3.CoO$ formed in the test is blue in colour. It is called as thenard's blue.
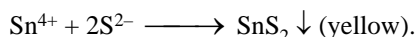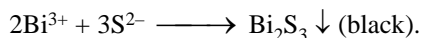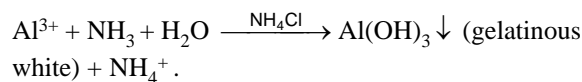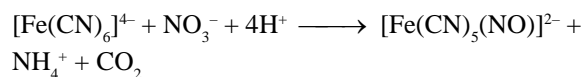
Q.44 (C)
$Fe^{3+} + [Fe(CN)_6]^{3-} \longrightarrow Fe[Fe(CN)_6]$ (brown colouration).

Q.45 (D)
$[Fe(CN)_6]^{4-} + NO_3^- + 4H^+ \longrightarrow [Fe(CN)_5(NO)]^{2-} + NH_4^+ + CO_2$

Q.46 (D)
$Fe^{2+} + 2K^+ + [Fe(CN)_6]^{4-} \longrightarrow K_2Fe[Fe(CN)_6] \downarrow$ (white).

Q.47 (C)

$Al(OH)_3 \xrightarrow[\text{NaOH}]{\text{excess of}} [Al(OH)_4]^-$
(Soluble colour less)

$Cr(OH)_3 \xrightarrow[\text{NaOH}]{\text{Xs of}} [Cr(OH)_4]^-$
(Soluble)

$Fe(OH)_3 \xrightarrow[\text{NaOH}]{\text{Xs of}}$ not soluble

$Zn(OH)_2 \xrightarrow[\text{NaOH}]{\text{Xs of}} [Zn(OH)_4]^{2-}$
(Soluble)

Q.48 (A)
$2\,Cr(OH)_3 + 3\,Na_2O_2 \longrightarrow 2Na_2CrO_4$ (yellow colour solution) + $2NaOH + H_2O$.
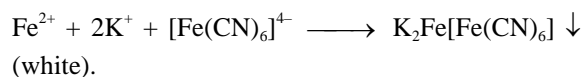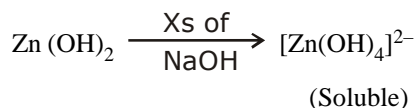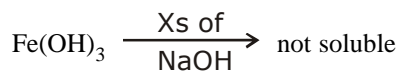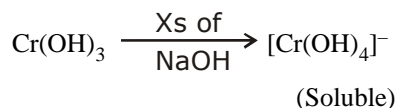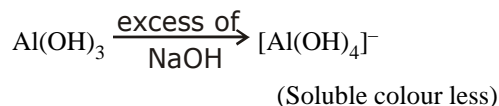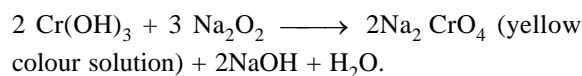
Q.49 (A)
Cr^{3+} forms dark green chromium metaborate $Cr(BO_2)_3$ in oxidising flame (in cold).

Q.50 (A)
Ni^{2+} and Fe^{2+} both on reaction with alkaline solution of dimethyl glyoxime give red precipitate and red solution respectively but not zinc.

Q.51 (D)

$Ag_2S + 2HCl \longrightarrow AgCl \downarrow + 2H_2S$; HgS is also insoluble in 2N HCl so silver and mercury do not pass into filtrate while ZnS, MnS and FeS dissolve in 2N HCl forming their soluble chlorides and thus pass into filtrate.

Q.52 (B)

Brown ring test is a confirmating test

Q.53 (A)

In excess of NH_4OH, precipitate of $Zn(OH)_2$ gets dissolved.
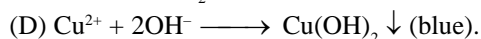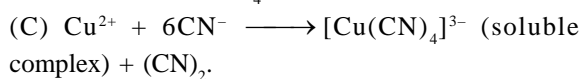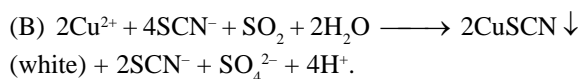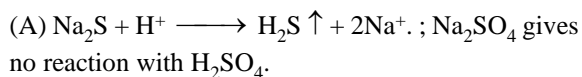
$Zn(OH)_2 + 4NH_3 \rightleftharpoons [Zn(NH_3)_4]^{2+} + 2OH^-$.
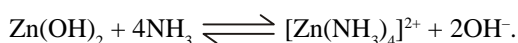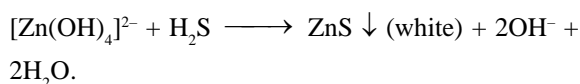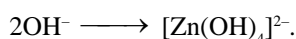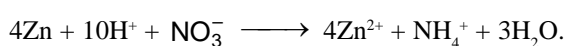
Q.54 (C)

$4Zn + 10H^+ + NO_3^- \longrightarrow 4Zn^{2+} + NH_4^+ + 3H_2O$.

$Zn^{2+} + 2OH^- \longrightarrow Zn(OH)_2 \downarrow$ (white) ; $Zn(OH)_2 + 2OH^- \longrightarrow [Zn(OH)_4]^{2-}$.

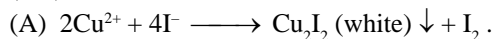$[Zn(OH)_4]^{2-} + H_2S \longrightarrow ZnS \downarrow$ (white) + $2OH^- + 2H_2O$.
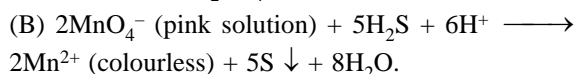
JEE-ADVANCED

MCQ/COMPREHENSION/COLUMN MATCHING

Q.1 (AB)

(A) $2Cu^{2+} + 4I^- \longrightarrow Cu_2I_2$ (white) $\downarrow + I_2$.

(B) $2Cu^{2+} + 4SCN^- + SO_2 + 2H_2O \longrightarrow 2CuSCN \downarrow$ (white) + $2SCN^- + SO_4^{2-} + 4H^+$.

(C) $Cu^{2+} + 6CN^- \longrightarrow [Cu(CN)_4]^{3-}$ (soluble complex) + $(CN)_2$.

(D) $Cu^{2+} + 2OH^- \longrightarrow Cu(OH)_2 \downarrow$ (blue).

Q.2 (ABCD)

(A) $Na_2S + H^+ \longrightarrow H_2S \uparrow + 2Na^+$. ; Na_2SO_4 gives no reaction with H_2SO_4.

(B) $2MnO_4^-$ (pink solution) + $5H_2S + 6H^+ \longrightarrow 2Mn^{2+}$ (colourless) + $5S \downarrow + 8H_2O$.

No colour change is observed with Na_2SO_4.

(C) $S^{2-} + [Fe(CN)_5NO]^{2-} \longrightarrow [Fe(CN)_5NOS]^{4-}$ (purple or violet colouration).

No colour change is observed with Na_2SO_4.

(D) $S^{2-} + Cd^{2+} \longrightarrow CdS \downarrow$ (yellow).
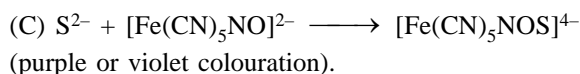
Na_2SO_4 forms $CdSO_4$ which is water soluble.

Q.3 (ACD)

CuS, PbS and Bi_2S_3 are black precipitates while Sb_2S_3 is orange coloured precipitate.

Q.4 (AD)

Sulphides of Cu, Zn and Cd will be precipitated as if the solution is aqueous/alkaline (i.e., it is does not contain any acid). S^{2-} ion concentration obtained by H_2S in aqueous/alkaline solution is sufficient to precipitate all these metals as their sulphides.

Q.5 (ABC)

Carbonates of alkali metals and ammonium are soluble in water. All other carbonates are insoluble in water.

Q.6 (AD)

$SO_3^{2-} + Zn + 8H^+ \longrightarrow H_2S \uparrow + 3Zn^{2+} + 3H_2O$
$Pb^{2+} + S^{2-} \longrightarrow PbS \downarrow$ (black)
$Ag^+ + S^{2-} \longrightarrow Ag_2S \downarrow$ (black)

$2MnO_4^- + 5H_2S + 6H^+ \longrightarrow 2Mn^{2+} + 5S + 8H_2O$

Q.7 (BC)

(A) Cd^{2+} (aq) + H_2S (g) $\longrightarrow CdS \downarrow$ (yellow) + $2H^+$ (aq)

(B) $Co_3^{2-} + 4Hg^{2+} + 3H_2O \longrightarrow Hg_4O_3CO_3 \downarrow$ (reddish-brown) + $6H^+$
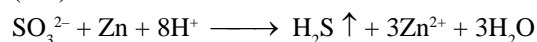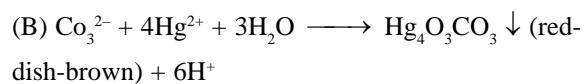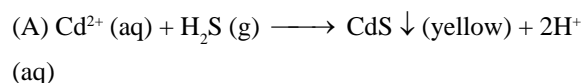
HCO_3^- (aq) does not give precipitate.
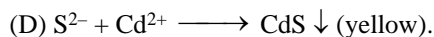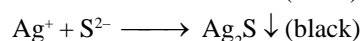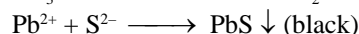
(C) $SO_3^{2-} + 3Zn + 8H^+ \longrightarrow H_2S \uparrow + 3Zn^{2+} + 3H_2O$

(D) $5SO_2 + 2IO_3^- + 4H_2O \longrightarrow I_2 + 5SO_4^{2-} + 8H^+$

Q.8 (ABD)

(A) $2Pb^{2+}$ (aq) + $2CO_3^{2-}$ (aq) + H_2O (ℓ) $\longrightarrow$ $Pb(OH)_2 \downarrow$ (white) + $PbCO_3 \downarrow$ (white) + $CO_2 \uparrow$

(B) Pb^{2+} (aq) + $2Br^-$ (aq) $\longrightarrow PbBr_2 \downarrow$ (white)

(C) $2Ag^+$ (aq) + $2NH_3$ (aq) + H_2O (ℓ) $\longrightarrow Ag_2O \downarrow$ (brown) + $2NH_4^+$

(D) Ag^+ (aq) + Cl^- (aq) $\longrightarrow AgCl \downarrow$ (white)

Q.9 (AB)

(A) $Br^- + H^+ \longrightarrow HBr \uparrow$; $2HBr + 2H_2SO_4 \longrightarrow Br_2 \uparrow$ (reddish brown) + $SO_2 \uparrow + SO_4^{2-} + H_2O$.

(B) $4NO_3^- + 2H_2SO_4 \longrightarrow 4NO_2 \uparrow$ (reddish brown) + $O_2 \uparrow + 2SO_4^{2-} + 2H_2O$.

(C) $SO_3^{2-} + 2H^+ \longrightarrow SO_2 \uparrow$ (colourless) $+ H_2O$.

(D) $3I^- + 2H_2SO_4 \longrightarrow I_3^- \uparrow$ (violet/purple) $+ SO_4^{2-}$ $+ 2H_2O + SO_2$.
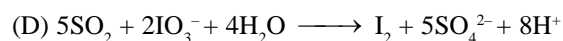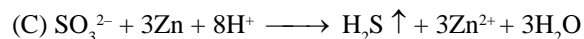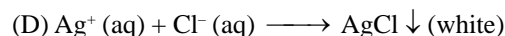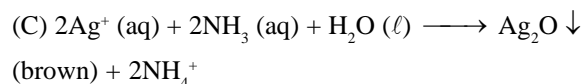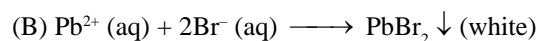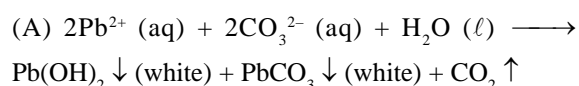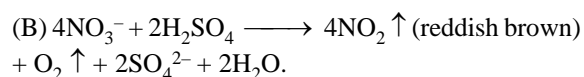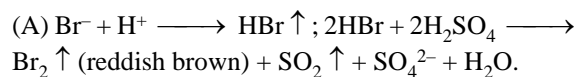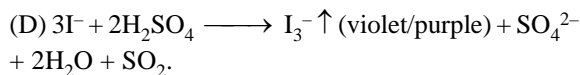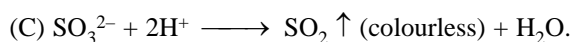
Q.10 (ABC)

(A) AgCl dissolves completely forming $[Ag(NH_3)_2]Cl$; $AgCl + 2NH_4OH \longrightarrow [Ag(NH_3)_2]Cl + 2H_2O$.

(B) AgBr dissolves completely forming $[Ag(NH_3)_2]$ Br soluble complex.

$$AgBr + 2NH_4OH \longrightarrow [Ag(NH_3)_2]Br + 2H_2O.$$

(C) $Ag_2CrO_4 + 4NH_3 \longrightarrow 2[Ag(NH_3)_2]^+ + CrO_4^{2-}$
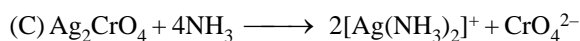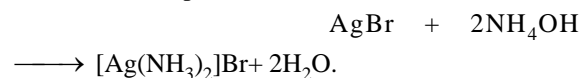
(D) AgI is insoluble in concentrated aqueous NH_3.

Q.11 (CD)

$$Hg_2I_2\downarrow \text{ (green)} \xrightarrow[\text{with } H_2O]{\text{boiled}} HgI_2\downarrow \text{ (red)} + Hg$$
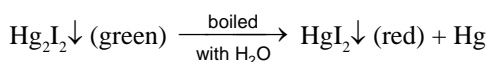
Disproportionation reaction occurs.

Q.12 (AD)

$Co^{2+} + 7NO_2^- + 3K^+ + 2H^+ \longrightarrow K_3[Co(NO_2)_6] \downarrow$ (yellow) $+ NO \downarrow + H_2O$.
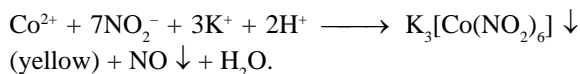
So [X] is $K_3[Co(NO_2)_6]$. It is called Fischer's reagent ; $[Co(III)(NO_2)_6]^{3-}$ has d^2sp^3 hybridisation and is diamagnetic. It's IUPAC name is potassium hexanitrito – N – cobaltate(III).

Q.13 (ACD)

$2CuSO_4 + 4KI \longrightarrow 2CuI \downarrow$ (white) $+ 2K_2SO_4 + I_2$

$3SCN^- + Cu^{2+} \longrightarrow CuSCN \downarrow$ (white) $+ (SCN)_2$

$6CN^- + Cu^{2+} \longrightarrow [Cu(CN)_4]^{3-} + (CN)_2$

Q.14 (ABCD)

$AgCl + 2CN^- \longrightarrow [Ag(CN)_2]^- + Cl^-$;

$AgCl + 2S_2O_3^{2-} \longrightarrow [Ag(S_2O_3)_2]^{3-} + Cl^-$.
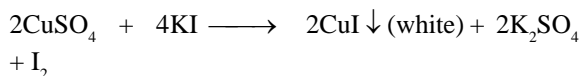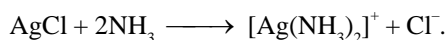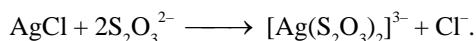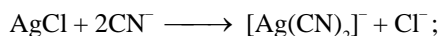
$AgCl + 2NH_3 \longrightarrow [Ag(NH_3)_2]^+ + Cl^-$.
AgCl is soluble in concentrated solution of KCl.

$AgCl + Cl^- \longrightarrow [AgCl_2]^-$ (soluble complex)

Q.15 (AC)

(A) $HPO_4^{2-} + 3NH_4^+ + 12\ MoO_4^{2-} + 23H^+ (HNO_3)$ $\longrightarrow (NH_4)_3[P(Mo_3O_{10})_4] \downarrow$ (canary yellow/ yellow) $+ 12H_2O$.

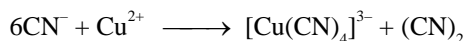(C) $AsO_4^{3-} + 12\ MoO_4^{2-} + 3NH_4^+ + 24H^+(HNO_3)$ $\longrightarrow (NH_4)_3AsMo_{12}O_{40} \downarrow$ (yellow) $+ 12H_2O$.

Q.16 (BCD)

(A) $Ag+ 2CrO_4^{2-} \longrightarrow Ag_2CrO_4 \downarrow$ (red) [X].

(B) $Ag_2CrO_4\downarrow + 4NH_3 \longrightarrow 2[Ag(NH_3)_2]^+ + CrO_4^{2-}$.

(C) $Cr^{3+} + 3OH^- \longrightarrow Cr(OH)_3 \downarrow$ (green).
$Cr(OH)_3 + OH^- \longrightarrow [Cr(OH)_4]^-$ (green coloured soluble complex).

(D) $3\overset{+4}{S}O_2 + \overset{+7}{C}r_2O_7^{2-} + 2H^+ \longrightarrow 2Cr^{3+}[Y] + 3\overset{+6}{S}O_4^{2-} + H_2O$.

Q.17 (AB)

(A) $3AgCl \downarrow + AsO_3^{3-} \longrightarrow Ag_3AsO_3 \downarrow$ (yellow) $+ 3Cl^-$
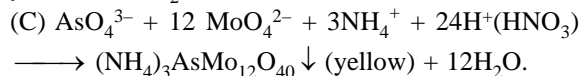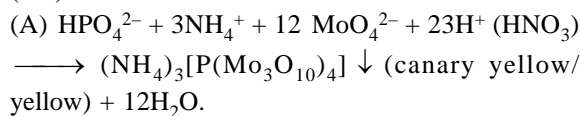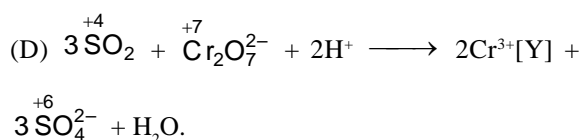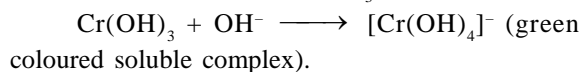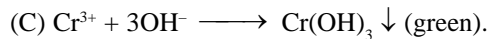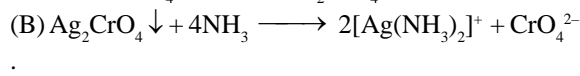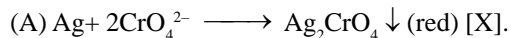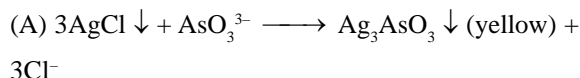
AgI is unaffected by this treatment.

(B) $AgCl + 2NH_3 \longrightarrow [Ag(NH_3)_2]Cl$
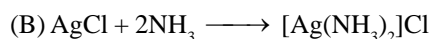
AgI is not soluble in dilute ammonia solution.
(C) Both soluble in potassium cyanide, forming soluble complexes.
(D) Both insoluble in dilute HNO_3.

Q.18 (ABC)

(A) $Mn^{2+} + NH_3 + HPO_4^{2-} \longrightarrow Mn(NH_4)PO_4 \downarrow$ (pink)

(B) $Mn^{2+} + 2OH^- \longrightarrow Mn(OH)_2 \downarrow$ (white)

$2Mn(OH)_2 + O_2 \longrightarrow 2MnO(OH)_2 \downarrow$ (brown)

(C) $5PbO_2 + 2Mn^{2+} + 4H^+ \longrightarrow 2MnO_4^- + 5Pb^{2+} + 2H_2O$

(D) $Mn^{2+} + S^{2-} \longrightarrow MnS \downarrow$ (pink)

Q.19 (BC)

(A) $Pb(NO_3)_2 + 2NaCl \longrightarrow PbCl_2\downarrow$ (white) $+ 2NaNO_3$
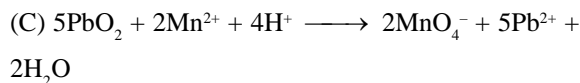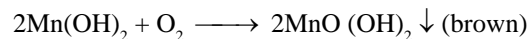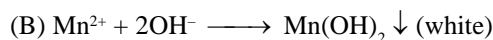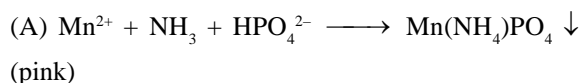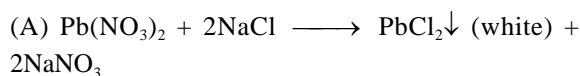
$Ba(NO_3)_2 + 2NaCl \longrightarrow BaCl_2 + 2NaNO_3$;
$BaCl_2$ is soluble in water
(B) Na_2SO_4 gives white precipitate of $PbSO_4$ and $BaSO_4$ with $Pb(NO_3)_2$ and $Ba(NO_3)_2$ respectively.

(C) Disodium hydrogen phosphite gives white precipitate with both salts.

$$HPO_3^{2-} + Ba^{2+} \longrightarrow BaHPO_3 \downarrow \text{ (white)} ; HPO_3^{2}$$

$$+ Pb^{2+} \longrightarrow PbHPO_3 \downarrow \text{ (white)}$$

(D) $Pb^{2+} + CrO_4^{2-} \longrightarrow PbCrO_4 \downarrow$ (yellow) ; $Ba^{2+} +$

$CrO_4^{2-} \longrightarrow BaCrO_4 \downarrow$ (yellow)

Q.20 (ABCD)

(A) $Ag^+ + Cl^- \longrightarrow AgCl \downarrow$

; $AgCl + Cl^- \longrightarrow [AgCl_2]^-$ (soluble complex).

(B) $Cu^{2+} + 2CN^- \longrightarrow Cu(CN)_2 \downarrow$ (yellow). ;

$Cu(CN)_2 \downarrow \longrightarrow 2 CuCN \downarrow$ (white) + $(CN)_2$.

(C) $(CH_3COO)_2Co + 2NH_4SCN \longrightarrow Co(SCN)_2 + 2CH_3COONH_4$.

$\qquad Hg^{2+} + Co^{2+} + 4SCN^- \longrightarrow Co[Hg(SCN)_4] \downarrow$ (deep-blue).

(D) $BiI_3 \downarrow + H_2O \longrightarrow BiOI \downarrow$ (orange) + $2H^+ + 2I^-$.

Q.21 (ABCD)

(A) $Hg^{2+} + 2I^- \longrightarrow HgI_2 \downarrow$ (red).

(B) $Pb^{2+} + 2I^- \longrightarrow PbI_2 \downarrow$ (yellow).

(C) $Ag^+ + I^- \longrightarrow AgI \downarrow$ (bright yellow).

(D) $Cu^{2+} + 4I^- \longrightarrow Cu_2I_2 \downarrow$ (white) + I_2

Q.22 (AC)

$2As^{3+} + 3S^{2-} \xrightarrow{H^+} As_2S_3 \downarrow$ (yellow) ; $2Sn^{4+} + 2S^{2-}$

$\xrightarrow{H^+} SnS_2 \downarrow$ (yellow).

SnS is brown and Sb_2S_3 is orange coloured precipitates.

Q.23 (ACD)

Coloured transition metal salts which are mostly paramagnetic, give coloured meta borates with borax on heating in oxidising flame.

Q.24 (AD)

(A) Fe^{2+} responds to this test but not Fe^{3+}; Fe(II) gives soluble red iron(II) dimethylglyoxime in alkaline solution.

(D) $Ag_2O \downarrow + 4NH_3 + H_2O \longrightarrow 2[Ag(NH_3)_2]^+ + 2OH^-$

$\quad Ag_2O \downarrow + 2H^+ \longrightarrow 2Ag^+ + H_2O$
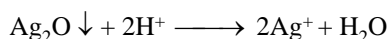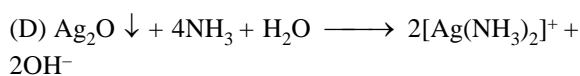
(B) and (C) are correct statements.

Q.25 (AD)

(B) $Cd^{2+} + 2OH^- \longrightarrow Cd(OH)_2 \downarrow$ (white). ; $Cd(OH)_2$ is insoluble in excess reagent.

(D) $Mn^{2+} + 2OH^- \longrightarrow Mn(OH_2) \downarrow$ (white) ; $Mn(OH)_2$ is insoluble in excess reagent but precipitate turns to brown slowly on exposure to air forming hydrated manganese dioxide. ;

$2Mn(OH)_2 \downarrow + O_2 \longrightarrow 2MnO(OH)_2 \downarrow$ (brown).
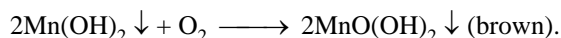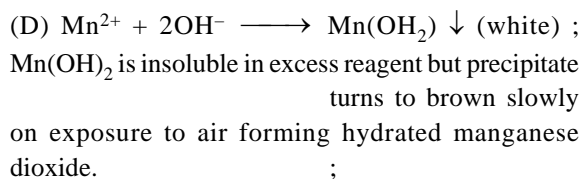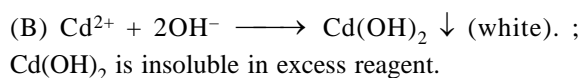
Q.26 (BD)

(A) Red colour solution or precipitate is produced when reagent reacts in alkaline solution.

(B) $HO.SO_2.NH_2 + HNO_2 \longrightarrow N_2 + 2H^+ + SO_4^{2-} + H_2O$.

(C) $Fe^{2+} + [Fe(CN)_6]^{3-} \longrightarrow Fe^{3+} + [Fe(CN)_6]^{4-}$.

$\quad 4Fe^{3+} + [Fe(CN)_6]^{4-} \longrightarrow Fe_4[Fe(CN)_6]_3 \downarrow$ (Turnbull's blue).
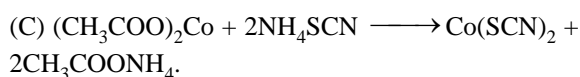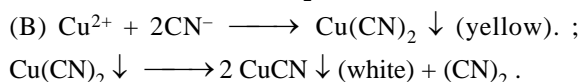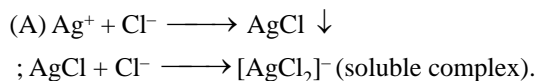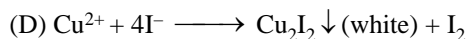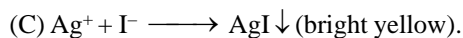
(D) $4Cr(OH)_3 \downarrow + 5O_2^{2-} \longrightarrow 4CrO_4^{2-}$ (yellow solution) + $6H_2O$.

Q.27 (ABC)

(A) $Cu^{2+} + [Fe(CN)_6]^{4-} \longrightarrow Cu_2[Fe(CN)_6] \downarrow$ (brown).

(B) $Ca^{2+} + 2K^+ + [Fe(CN)_6]^{4-} \longrightarrow 2K^+ Ca^{2+}[Fe(CN)_6] \downarrow$ (white).

(C) $3Zn^{2+} + 2K^+ + 2[Fe(CN)_6]^{4-} \longrightarrow K_2Zn_3[Fe(CN)_6]_2 \downarrow$ (white/bluish-white).

(D) $Fe^{3+} + [Fe(CN)_6]^{4-} \longrightarrow Fe_4[Fe(CN)_6]_3$ (prussian blue).

Q.28 (ABCD)

(A) $Zn(OH)_2 \downarrow + 2OH^- \longrightarrow [Zn(OH)_4]^{2-}$

(B) $Zn(OH)_2 \downarrow + 2H^+ \rightleftharpoons Zn^{2+} + 2H_2O$
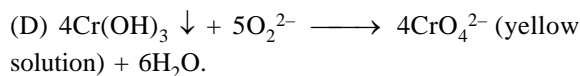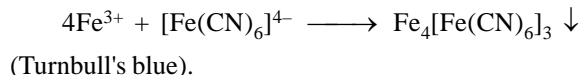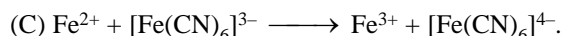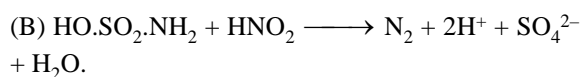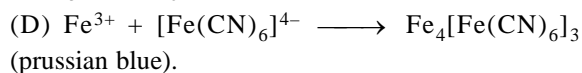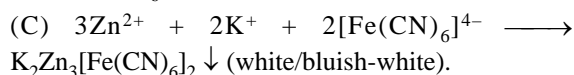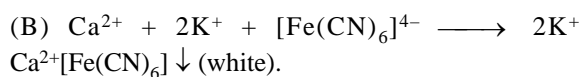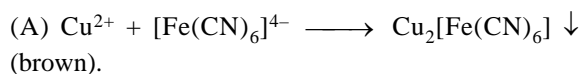
(C) & (D) White precipitate of $Zn(OH)_2$ dissolves in excess of ammonia solution and in solutions of ammonium salts owing to the production of tetraamminezincate(II).

$\qquad Zn(OH)_2 \downarrow + 4NH_3$

$\rightleftharpoons [Zn(NH_3)_4]^{2+} + 2OH^-$
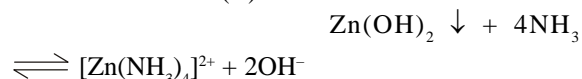
Q.29 (D)

As bottle 2 + bottle 3 give colourless, odourless gas, it may be carbon dioxide. Generally carbonates are decomposed by acids giving CO_2 gas.It suggests bottle

2 and 3 contain sodium carbonate and HCl.

Bottle 3 + 4 gives blue precipitate which confirms the Cu^{2+} in either of bottles. $CuSO_4$, $CuCl_2$ and $Cu(NO_3)_2$ are soluble and $CuCO_3$ is insoluble in water as evident from the reaction.

$Cu^{2+} + CO_3^{2-} \longrightarrow CuCO_3 \downarrow$ (blue). Thus blue precipitate must be of copper carbonate.

Hence, bottle 4 is $CuSO_4$, 3 is Na_2CO_3, 2 is HCl (from above) and 1 is $Pb(NO_3)_2$ as it gives white precipitate of $PbCl_2$ with bottle (2).

Note : $PbNO_3$, Na_2CO_3 and HCl solutions are colourless but $CuSO_4$ is blue colour solution.

Q.30   (A)

(A) $2Cu^{2+} + 4I^- \longrightarrow Cu_2I_2 \downarrow$ (white) + I_2

(B) $2Cu^{2+} + [Fe(CN)_6]^{4-} \longrightarrow Cu_2[Fe(CN)_6] \downarrow$ (chocolate brown)

(C) $Pb^{2+} + 4OH^- \longrightarrow [Pb(OH)_4]^{2-}$ (colourless soluble complex); $Cu^{2+} + 2OH^- \longrightarrow Cu(OH)_2 \downarrow$ (blue).

(D) $Pb^{2+} + 4Cl^- \longrightarrow [PbCl_4]^{2-} \downarrow$ (colourless soluble complex).

Q.31   (D)

Bottle 4 is $CuSO_4$ and that gives deep blue colouration with excess of ammonia solution.

$Cu^{2+}(aq) + 4NH_3(aq) \longrightarrow [Cu(NH_3)_4]^{2+}$ (intensive deep blue colour) (aq)

Q.32   (D)

$Pb^{2+} + CO_3^{2-} \longrightarrow PbCO_3 \downarrow$ (white)

$Pb^{2+} + 2Cl^- \longrightarrow PbCl_2 \downarrow$ (white)

$Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4 \downarrow$ (white)
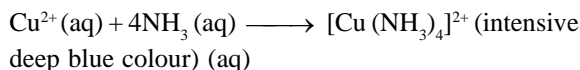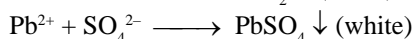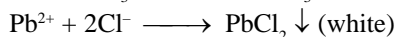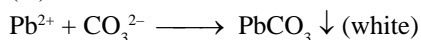
Comprehension # 2 (Q. No. 33 to 35)

Q.33   (C)

Q.34   (C)

Q.35   (D)

Comprehension # 3 (Q. No. 36 to 38)

Q.36   (C)

$Bi^{3+} + 3I^- \to BiI_3 \downarrow$ (black) ; $BiI_3 \downarrow$ (black) + $I^- \to [BiI_4]^-$ (orange colour solution)
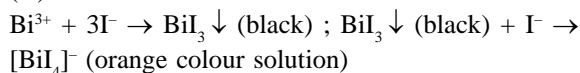
Q.37   (B)

Black precipitate of BiI_3 on heating with water turns orange

$BiI_3 \downarrow + H_2O \longrightarrow$ $BiOI \downarrow + 2H^+ + 2I^-$

Q.38   (D)

(A) $Cl^- + Ag \longrightarrow AgCl \downarrow$ (white) ; $3AgCl + AsO_3^{3-} \longrightarrow Ag_3AsO_3 \downarrow$ (yellow) + $3Cl^-$

(B) $Bi^{3+} + 3OH^- \longrightarrow Bi(OH)_3$ (white) ; $Bi(OH)_3 \xrightarrow{\Delta} BiO.OH\downarrow$ (yellowish-white) + H_2O

(C) $BiOCl \downarrow$ (white) + $2H^+ \longrightarrow Bi^{3+} + H_2O + Cl^-$
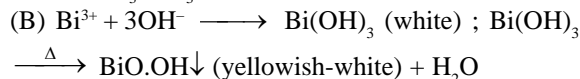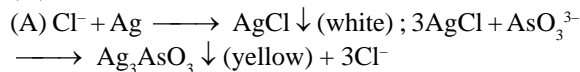
Reaction involved in comprehension :

$2Bi^{3+}$ (A) + $3H_2S \xrightarrow{H^+} Bi_2S_3 \downarrow$ (black) (B) + 6 H^+

$Bi_2S_3 + 8HNO_3 \longrightarrow 2Bi(NO_3)_3$ (C) + 2NO + 3S + $4H_2O$

$Bi^{3+} + 3OH^- \xrightarrow{NaOH} Bi(OH)_3 \downarrow$ (white) ; $2Bi(OH)_3 \downarrow$ (white) + $3[Sn(OH)_4]^{2-} \longrightarrow 2Bi \downarrow$ (D) + $3[Sn(OH)_6]^{2-}$
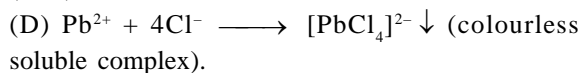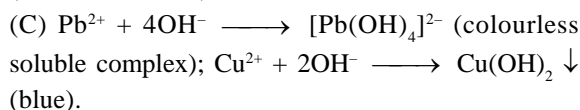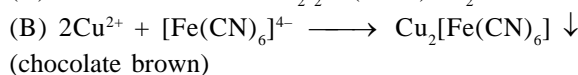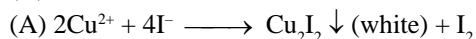
$Bi^{3+} + 3OH^- \xrightarrow{NH_4OH} Bi(OH)_3 \downarrow$ (white) ; $Bi(OH)_3 \downarrow$ (white) + $3HCl \longrightarrow BiCl_3 + 3H_2O$

$BiCl_3 + H_2O \longrightarrow BiOCl \downarrow$ (bismuth oxychloride) (E) + 2HCl

$4NaCl + K_2Cr_2O_7 + 3H_2SO_4$ (conc.) $\longrightarrow 2CrO_2Cl_2$ (deep red vapours) + $2Na_2SO_4 + K_2SO_4 + 3H_2O$

$CrO_2Cl_2 + 4OH^- \longrightarrow CrO_4^{2-} + 2Cl^- + 2H_2O$

$CrO_4^{2-} + Ba^{2+} \longrightarrow BaCrO_4 \downarrow$ (yellow).

Q.39   (C)

Q.40   (B)

Q.41   (D)

Q.42   (B)

Sample $\xrightarrow{NaCl}$ Precipitate 'A' **insoluble chloride** (AgCl) + Filtrate (Ba^{2+} and Zn^{2+})

$\Bigg| Na_2SO_4$

ppt. 'C' insoluble hydroxide $(Zn(OH)_2)$

$\xleftarrow[NH_3]{\text{aqueous}}$ Filtrate (Zn^{2+}) + **ppt. 'B' insoluble sulphate** ($BaSO_4$)

$Ag^+ + Cl^- \longrightarrow AgCl\downarrow$ (white) ; $3AgCl + Na_3AsO_3 \longrightarrow Ag_3AsO_3\downarrow$ (yellow) + 3NaCl

$Ba^{2+} + SO_4^{2} \longrightarrow BaSO_4\downarrow$ (white) ; Ba^{2+} salts give apple gree colour to the Bunsen flame.

$Zn^{2+} + 2NH_3 + 2H_2O \longrightarrow Zn(OH)_2\downarrow$ (white) $+ 2NH_4\uparrow$

$Zn(OH)_2\downarrow + 4NH_4 \rightleftharpoons [Zn(NH_3)_4]^{2+} + 2OH^-$
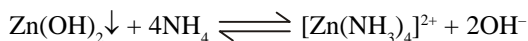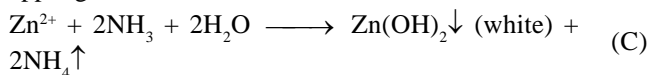
Q.43 (B)

(A) $AgCl + 2NH_3 \longrightarrow [Ag(NH_3)_2]Cl$ soluble complex

(B) 2M HCl is group reagent of 1st group but in concentrated HCl AgCl dissolves forming $[AgCl_2]^-$ complex

(C) $AgCl + 2CN^- \longrightarrow [Ag(CN)_2]^-$ (soluble complex) $+ Cl^-$

(D) $AgCl + 2S_2O_3^{2-} \longrightarrow [Ag(S_2O_3)_2]^{3-}$ (soluble complex) $+ Cl^-$

Q.44 (D)

(A) $CoO . ZnO$ = Rinmann's green reagent used as green pigment.

(B) $BaSO_4\downarrow + H_2SO_4$ (conc.) $\longrightarrow Ba^{2+} + HSO_4^-$

(C) $2AgCl\downarrow$ (white) $\xrightarrow{h\nu} 2Ag\downarrow$ (black) $+ Cl_2\uparrow$

Q.45 (A - p,r) ; (B - p,q) ; (C - p,s) ; (D - q,s)

(A) $2Bi^{3+} + 3H_2S \longrightarrow Bi_2S_3\downarrow$ (black) $+ 6H^+$
$Bi^{3+} + 3I^- \longrightarrow BiI_3\downarrow$ (black)

(B) $Cu^{2+} + H_2S \longrightarrow CuS\downarrow$ (black) $+ 2H^+$
$Cu^{2+} + 2SCN^- \longrightarrow Cu(SCN)_2\downarrow$ (black)
$2Cu(SCN)_2 \longrightarrow 2 CuSCN\downarrow$ (white) $+ (SCN)_2\uparrow$.
$2Cu^{2+} + 4I^- \longrightarrow Cu_2I_2\downarrow$ (white) $+ I_2\uparrow$.
$2Cu^{2+} + [Fe(CN)_6]^{4-} \longrightarrow Cu_2[Fe(CN)_6]\downarrow$ (brown).

(C) $Zn^{2+} + H_2S \longrightarrow ZnS\downarrow$ (white) $+ 2H^+$
$2K^+ + 2[Fe(CN)_6]^{4-} + 3Zn^{2+} \longrightarrow K_2Zn_3 [Fe(CN)_6]_2\downarrow$ (white)
$ZnI_2 \longrightarrow$ soluble

(D) $4Ag^+ + [Fe(CN)_6]^{4-} \longrightarrow Ag_4 [Fe(CN)_6]\downarrow$ (white)
$Ag^+ + SCN^- \longrightarrow AgSCN\downarrow$ (white)
$Ag_2S\downarrow$ black ; $AgI\downarrow$ (yellow)

Q.46 (A - p,q,r ; B - r,s ; C - p,q,s,t ; D - p,s)

(A) $AgCl\downarrow + Cl^- \longrightarrow [AgCl_2]^-$ soluble complex.
$AgCl\downarrow + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ + Cl^-$
$AgCl\downarrow + 2CN^- \rightleftharpoons [Ag(CN)_2]^- + Cl^-$
AgCl is insoluble in dilute HNO_3.

(B) $2CuS\downarrow + 8CN^- \longrightarrow 2[Cu(CN)_4]^{3-} + S_2^{2-}$.
$3CuS\downarrow + 8HNO_3 \longrightarrow 3Cu^{2+} + 6NO_3^- + 3S\downarrow + 2NO\uparrow + 4H_2O$

$S\downarrow + 2HNO_3 \xrightarrow[\text{longer time}]{\text{boiled for}} 2H^+ + SO_4^{2-} + 2NO\uparrow$

(C) $Zn(OH)_2\downarrow + 2H^+ \rightleftharpoons Zn^{2+} + 2H_2O$
$Zn(OH)_2\downarrow + 4NH_3 \rightleftharpoons [Zn(NH_3)_4]^{2+} + 2OH^-$
$Zn(OH)_2\downarrow + 2OH^- \longrightarrow [Zn(OH)_4]^{2-}$

(D) $BaCO_3 + 2H^+ \rightleftharpoons Ba^{2+} + CO_2 + H_2O$
$BaCO_3$ is slightly soluble in solution of ammonium salts of strong acids only.

Q.47 (A) p,q; (B) r; (C) p,q,s; (D) p,q,s

Q.48 (A) - p,q ; (B) - p,s ; (C) - s ; (D) - p,r

(A) Mn^{2+} meta borate $\longrightarrow$ Amethyst red
$Mn^{2+} + 2OH^- \longrightarrow Mn(OH)_2\downarrow$ (white)
$Mn(OH)_2\downarrow$ (white) $+ O_2$ (air) $\longrightarrow 2MnO(OH_2)\downarrow$ (brown)

(B) Cr^{3+} metaborate $\longrightarrow$ Green
$Cr^{3+} + 3OH^- \longrightarrow Cr(OH)_3\downarrow$ (green)
$Cr(OH)_3 + OH^- \longrightarrow [Cr(OH)_4]^-$ (green coloured soluble complex).
$[Cr(OH)_4]^- + H^+ \longrightarrow Cr(OH)_3\downarrow + H_2O$
$Cr(OH)_3\downarrow + 3H^+\downarrow \longrightarrow Cr^{3+} + 3H_2O$

(C) $Al^3 + 3OH^- \longrightarrow Al(OH)_3\downarrow$ (white)
$Al(OH)_3 + OH^- \longrightarrow [Al(OH)_4]^-$ (colourless soluble complex).
$[Al(OH)_4]^- + H^+ \longrightarrow Al(OH)_3\downarrow + H_2O$
$Al(OH)_3 + 3H^+\downarrow \longrightarrow Al^{3+} + 3H_2O$

(D) Fe^{3+} metaborate $\longrightarrow$ Pale yellow
$Fe^{3+} + 3CN^- \longrightarrow Fe(CN)_3\downarrow$ (reddish brown)
$Fe(CN)^3\downarrow + 3CN^- \longrightarrow Fe(CN)_6]^{3-}$ (yellow colour soluble complex).
$Fe^{3+} + 3OH^- \longrightarrow Fe(OH)_3\downarrow$ (reddish brown).

Q.49 (A–t), (B–r), (C–p,s), (D–p,q), (E–s).

(A) $Fe^{3+} + 3NH_3 + 3H_2O \longrightarrow Fe(OH)_3\downarrow$ (reddish brown) ;
$Cu^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+}$ (deep blue solution)
$3Zn^{2+} + 2NH_3 + 2H_2O \rightleftharpoons Zn(OH)_2\downarrow$ (white) $+ 2NH_4^+$.
$Zn(OH)_2\downarrow + 4NH_3 \rightleftharpoons [Zn(NH_3)_4]^{2+}$ (colourless) $+ 2OH^-$.

(B) All dissolves in 50% HNO_3 forming soluble nitrates, $Pb(NO_3)_2$, $Cu(NO_3)_2$ and $Cd(NO_3)_2$.

(C) $Pb^{2+} + 2 KI \rightarrow PbI_2\downarrow$ (yellow) $+ 2 K^+$; $Pb^{2+} + K_2CrO_4 \rightarrow PbCrO_4\downarrow$ (yellow) $+ 2 K^+$

(D) $Bi^{3+} + 3 KI \rightarrow BiI_3\downarrow$ (black) $+ 3K^+$
$BiCl_3 + 3 Na_2SnO_2 + 6 NaOH \rightarrow 2 Bi\downarrow$ (black) $+ 3$

$Na_2SnO_3 + 6\,NaCl + 3\,H_2O$

(E) $\quad Ag^+ + I^- \longrightarrow AgI \downarrow$ (yellow) ; $Ag^+ + Na_2SnO_2$

$\xrightarrow{OH^-}$ Black or brown precipitate.

$2Ag^+ + CrO_4^{2-} \longrightarrow Ag_2CrO_4 \downarrow$ (red)
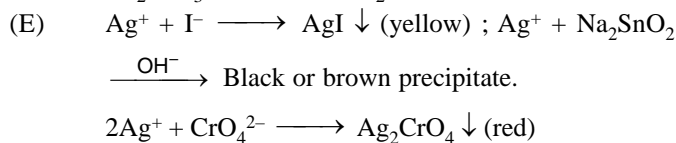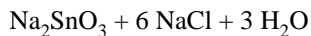
Q.50 (A) s; (B) p,q,r,s ; (C) p,s; (D) p

JEE-ADVANCED
INTEGER TYPE

Q.1 (3)

$Pb^{2+} + 2Cl^- \longrightarrow PbCl_2 \downarrow$ (white) ; $Hg_2^{2+} + 2Cl^-$

$\longrightarrow Hg_2Cl_2 \downarrow$ (white)

$Ag^+ + Cl^- \longrightarrow AgCl \downarrow$ (white)
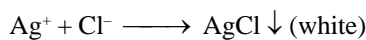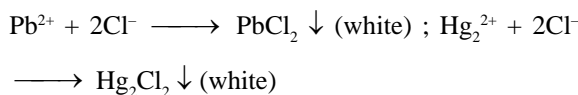
K_{sp} of chlorides of Pb^{2+} and Hg_2^{2+} is low as compared to K_{sp} of Hg^{2+} and Cd^{2+}. Chloride ion concentration provided by dilute HCl is just enough to exceed the K_{sp} of $PbCl_2$ and Hg_2Cl_2. Thus Pb^{2+} and Hg_2^{2+} are precipitated as their chlorides.

Q.2 (4)

$Hg^{2+} + [Co(SCN)_4]^{2-} \longrightarrow Co[Hg(SCN)_4]\downarrow$

deep blue crystalline precipitate

Q.3 (3)

$As^{3+} + 3H_2S \longrightarrow As_3S_3\downarrow$

yellow

$As_2S_3 + S_2^{2-} \longrightarrow AsS_4^{3-} + S_3^{2-}$

Oxidation state of sulphur –2, –1, 0.

Q.4 (4)

$FeSO_4 + \underset{(excess)}{6KCN} \xrightarrow{\Delta} \underset{(X)}{K_4[Fe(CN)_6]} + K_2SO_4$

$K_4[Fe(CN)_6] + \underset{(Conc.)}{6H_2SO_4} + 6H_2O \longrightarrow 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + \underset{(Y)}{6CO}\uparrow$

$K_4[Fe(CN)_6] + \underset{(dilute)}{3H_2SO_4} \longrightarrow 2K_2SO_4 + FeSO_4 + \underset{(Z)}{6HCN}\uparrow$

Gas(Y) – $C^+ \equiv O^- \longrightarrow 2p\pi\text{-}p\pi$ bond

Gas(Z) – $H - C \equiv N \longrightarrow 2p\pi\text{-}p\pi$ bond

Sum of $p\pi\text{-}p\pi$ bonds $= 4$

Q.5 (2)

$Ni^{2+} + 2dmg \xrightarrow{NH_4OH} [Ni(dmg)_2] \downarrow$ (bright red).

rosy red ppt

Q.6 (3)

(a) $Ba^{2+} + CrO_4^{2-} \longrightarrow BaCrO_4\downarrow$ (yellow

(b) $NH_4^+ + PtCl_6^{2-} \longrightarrow (NH_4)_2[Pt(Cl_6)]\downarrow$ (yellow)

(c) $NH_4^+ + [Co(NO_2)_6]^{3-} \longrightarrow (NH_4)_3[Co(NO_2)_6]\downarrow$ (yellow)

(d) $Ca^{2+} + [Fe(CN)_6]^{4-} + K^+ \longrightarrow K_2Ca[Fe(CN)_6]\downarrow$ (white)

(e) $Sr^{2+} + CO_3^{2-} \longrightarrow SrCO_3\downarrow$ (white)

Q.7 (3)

$Ag^+ + 2NH_3(aq) \longrightarrow [Ag(NH_3)_2]^+$
Colourless solution

• $\quad Pb^{2+} + 2NH_4OH \longrightarrow Pb(OH)_2\downarrow$
White ppt

• $\quad Cu^{2+} + 4NH_3(aq) \longrightarrow [Cu(NH_3)_4]^{2+}$
(excess) Dark blue solution

$Cd^{2+} + 2NH_3(aq) \longrightarrow [Cd(NH_3)_4]^{2+}$
Colourless solution

$Zn^{2+} + 4NH_3 \longrightarrow [Zn(NH_3)_4]^{2+}$
Colourless solution

• $\quad Ni^{2+} + 6NH_3 \longrightarrow [Ni(NH_3)_6]^{2+}$
Dark blue solution

Q.8 (20)

$Aq.CuSO_4(blue) + KCN \longrightarrow Cu(CN)_2 \downarrow + K_2SO_4$

$Cu(CN)_2\downarrow \longrightarrow CuCN \downarrow + (CN)_2 \uparrow$

$CuCN \downarrow + CN^- \longrightarrow [Cu(CN)_4]^{3-}$ (colourless soluble complex)

$A = [Cu(CN)_4]^{3-}$ (colourless soluble complex)

$a = 0$ (sp^3); $c = 4$

$8a + 5c = 20$

Q.9 (9)

$Co^{2+} + CN^- \longrightarrow Co(CN)_2$

$Co(CN)_2 + 4CN^- \longrightarrow [Co(CN)_6]^{4-}$

$[Co(CN)_6]^{4-} + O_2 \longrightarrow [Co(CN)_6]^{3-}$

$Co^{3+} \Rightarrow d^6$

Q.10 (5)

(i), (ii), (iv), (v), (vi)

(i) $NaBr + AgNO_3 \longrightarrow AgBr\downarrow + NaNO_3$

Pale Yellow

(ii) $NaI + AgNO_3 \longrightarrow AgI\downarrow + NaNO_3$

Yellow

(iii) $NaBr + Pb(NO_3)_2 \longrightarrow PbBr_2\downarrow + NaNO_3$

Brown

(iv) $NaI + Pb(NO_3)_2 \longrightarrow PbI_2\downarrow + NaNO_3$

Yellow

(v) $Na_2S + Cd(CH_3COO)_2 \longrightarrow CdS\downarrow + CH_3COONa$

Yellow

(vi) $K_2CrO_4 + Pb(CH_3COO)_2 \longrightarrow PbCrO_4\downarrow + CH_3COOK$

Yellow

(vii) $K_2CrO_4 + AgNO_3 \longrightarrow Ag_2CrO_4\downarrow + KNO_3$

Brick red

(viii) $NaBr + $ Chlorine water $\longrightarrow 2BrCl$

(excess)   reddish brown gas

Q.11 (3)

$(NH_4)_2SO_4 \xrightarrow{\Delta} NH_3\uparrow$

$(NH_4)_2CO_3 \xrightarrow{\Delta} NH_3\uparrow + CO_2 + H_2O$

$NH_4Cl \xrightarrow{\Delta} NH_3\uparrow + HCl$

$NH_4NO_3 \xrightarrow{\Delta} N_2O\uparrow + H_2O$

$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2\uparrow + Cr_2O_3 + 4H_2O$

Q.12 (9)

Q.13 (6)

$CO_3^{2-}, SO_3^{2-}, HCO_3^{-}, S_2O_3^{2-}, NO_2^{-}, CH_3COO^{-}$

Q.14 (3)

$NO_2^{-}, NO_2^{-}, SO_3^{2-}, HCO_3^{-}$

Q.15 (3)

$X \equiv Na_4[Fe(CN)_5 NOS]$

Stereoisomer = 0 [no G.I. and no O.I]

NOS has three donar atom (O,N,S).

Q.16 (0)

$X \equiv \overset{VI}{CrO_2Cl_2}$ "sp³"

Q.17 (4)

$X \equiv [Fe(H_2O)_5 NO]^{2+}$

$Fe^{+1} \Rightarrow d^7$

$\mu = \sqrt{3(3+2)} = \sqrt{15} = 3.87 \approx 4$

Q.18 (1)

$NO_2^{-} \xrightarrow{H^+} [HNO_2] \longrightarrow HNO_3 + NO\uparrow$

$2NO(\text{Colorless}) + O_2 (\text{air}) \longrightarrow 2NO_2 (\text{reddish brown})$

Q.19 (5)

$Ag_2CO_3, AgCl, AgNO_2, Ag_2SO_3, CH_3COO\,Ag \Rightarrow$ white

$AgBr \rightarrow$ yellow

Q.20 (3)

$A \equiv (C_2H_5)_3BO_3$

Q.21 (14)

$X = Cl_2$

$Y = CrO_2Cl_2$

$a = 1 - 0 - (-1) = 1, b = 2 + 5 = 7$

$c = 6$

$a + b + c = 14$

KVPY PREVIOUS YEAR'S

Q.1 (D)

H_2S gas is passed through a hot acidic aqueous solution containing $Al^{+3}, Cu^{+2}, Pb^{+2}$ and Ni^{+2}

II group elements give ppt $\rightarrow$ CuS, PbS

$Pb^{2+}\ Cu^{2+}\ Cd^{2+}\ Bi^{2+}\ Hg^{2+}\ \ As^{3+}\ Sb^{3+}\ Sn^{2+}\ Sn^{4+}$

Q.2 (C)

$MnO_2 + \underset{conc.}{HCl} \rightarrow Cl_2(g)(x)$

$Ca(OH)_2 + Cl_2 \rightarrow CaOCl_2 (y)$

$CaOCl_2 + dil.\ HCl \rightarrow Cl_2 + CaCl_2 + H_2O$

Q.3 (C)

$2\,KI + 4\,HNO_3 \rightarrow I_2 + 2\,NO_2 + 2KNO_3 + 2\,H_2O$

Iodide ion is a strong reducing agent and reduces HNO_3 vapours to NO_2 (Brown gas)

JEE MAIN

PREVIOUS YEAR'S

Q.1   (3)

Q.2   (1)

Q.3   (2)

Q.4   (3)

Q.5   (1)

Q.6   (2)

Q.7   **[4]**

Q.8   (2)
$Mn^{2+} \rightarrow$ IV group
$As^{3+} \rightarrow$ II B group
$Cu^{2+} \rightarrow$ II A group
$Al^{3+} \rightarrow$ III group

Q.9   (3)
Oxides of nitrogen and sulphur are acidic and settle down on ground as dry deposition.
 Ammonium salts in rain drops result in wet deposition

Q.10   (4)

JEE-ADVANCED

PREVIOUS YEAR'S

Q.1   (A)

Q.2   (C)
$Cu(M) + AgNO_3(N)$ (aqueous colourless solution) $\longrightarrow$ Resultant solution contains $Cu(NO_3)_2$ (blue solution) and $AgNO_3$

(colourless solution)

(N)
Note : Here it is considered that complete $AgNO_3$ is not utilized in the reaction.
$AgNO_3$ (aq)+ NaCl (aq) $\longrightarrow$ AgCl $\downarrow$ (white) (O) + $NaNO_3$
Solution containing white ppt. of AgCl also contains $Cu(NO_3)_2$ which developed deep blue colouration with aqueous NH_3 solution
AgCl $\downarrow$ (white) + $2NH_3$ (aq.) $\longrightarrow [Ag(NH_3)_2]^+$
$Cu(NO_3)_2$ (aq.) + $4NH_3$ (aq.) $\longrightarrow [Cu(NH_3)_4] (NO_3)_2$
(deep blue solution)

So, Metal rod M is Cu.
The compound N is $AgNO_3$ and the final solution contains $[Ag(NH_3)_2]^+$ and $[Cu(NH_3)_4]^{2+}$

Q.3   (B)
Metal rod M is Cu

Q.4   (A)
In presence of acidic medium, ionisation of H_2S is supressed so less number of S^{2-} ions are produced. So only those sulphides are precipitated which have low solubility product (K_{SP}) value, For example CuS and HgS.

Q.5   (ACD)

$$KI \text{ (aq)} + K_3[Fe(CN)_6](aq) \longrightarrow \underset{\text{Brownish - yellow}}{KI_3 \text{ (aq)}} + K_4[Fe(CN)_6] \text{ (aq)}$$

$\downarrow$ + $ZnSO_4$ (aq)

$\underset{\text{white ppt}}{K_2Zn_3[Fe(CN)_6]_2\downarrow}$ + KI_3 (aq)
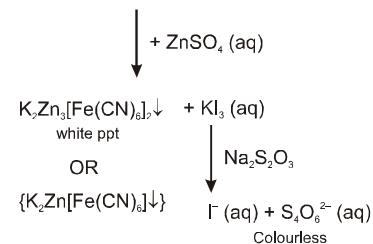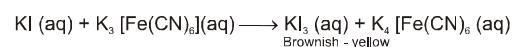
OR $\downarrow$ $Na_2S_2O_3$

$\{K_2Zn[Fe(CN)_6]\downarrow\}$ $\underset{\text{Colourless}}{I^- \text{ (aq)} + S_4O_6^{2-} \text{ (aq)}}$

(D) with NaOH
$K_2Zn[Fe(CN)_6] + NaOH \longrightarrow [Zn(OH)_4]^{2-}$ (aq) + $[Fe(CN)_6]^{4-}$ (aq)
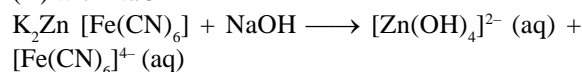
Q.6   (B)
HNO_3 decomposes by giving NO_2, O_2, H_2O
$4HNO_3 \longrightarrow 2H_2O + 2NO_2 + 3O_2$
So, Ans is (B).
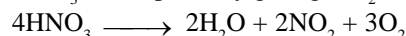
Q.7   (D)
Ammoniacal H_2S is group reagent of fourth group cationic radicals. Fe^{3+} & Al^{3+} will precipitate $Fe(OH)_3$ and $Al(OH)_3$ respectively. Only Zinc will form white precipitate of ZnS.

Q.8   (A)
$Pb^{2+} + 2Cl^- \longrightarrow PbCl_2$ (white ppt)
                soluble in hot water

Q.9   (D)

$\underset{\text{(P)   (Q)}}{Pb^{2+} / Cr^{3+}} \xrightarrow{\text{HCl}} \underset{\text{White ppt}}{PbCl_2}$ + $\underset{\text{Filtrate}}{CrCl_3}$

(Dissolve in Hot water)   (H$_2$S / mineral acid)

$\downarrow$ $\downarrow$

$\underset{\text{(R) Cr(OH)}_3}{\text{Green ppt.}} \xleftarrow{\text{(H}_2\text{S / ammonical medium)}}$ No effect

$\downarrow$

$\underset{\text{(S)}}{\underset{\text{yellow solution}}{Na_2CrO_4}}$
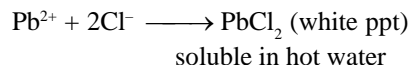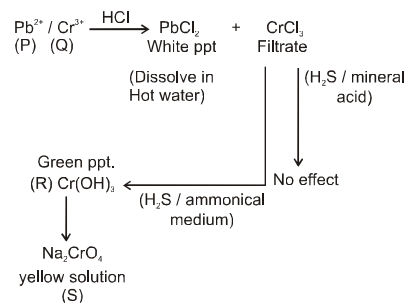
Q.10 [7]

Pbs , CuS , HgS , Ag_2S , NiS , CoS , Bi_2S_3, are black (7)

MnS : buff. colored, SnS_2 : yellow.

Q.11 (C,D)

Precipitate is formed on passing H_2S in acidic medium

i.e. ion must be of group II.

Cu^{2+} , Pb^{2+} , Hg^{2+} , Bi^{3+}

Q.12 (D)

Q.13 (A)

$$KClO_3 \xrightarrow[MnO_2]{\Delta} KCl + \underset{(W)}{O_2}$$

$$\underset{(white)}{P_4} + \underset{(excess)}{O_2} \longrightarrow \underset{(X)}{P_4O_{10}}$$

$$P_4O_{10} + HNO_3 \longrightarrow \underset{(Y)}{N_2O_5} + \underset{(Z)}{HPO_3}$$
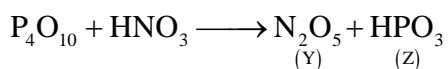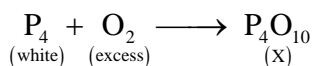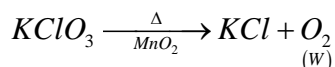
Q.14 (B)

Process involved in Q → R reaction is alkylation

Q.15 (A)

Chromium (III) salt $\xrightarrow{\Delta}$ Cr_2O_3

Borax $\xrightarrow{\Delta}$ $B_2O_3 + NaBO_2$

$2Cr_2O_3 + 6B_2O_3 \rightarrow 4Cr(BO_2)_3$
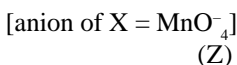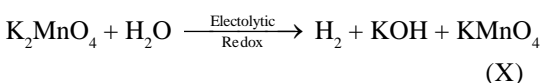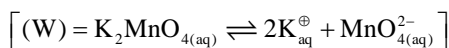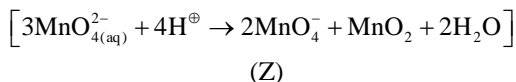
So correct answer is option (1)

Q.16 (2,3,4)

$$MnO_2 + 2KOH + \frac{1}{2}O_2 \xrightarrow{\Delta} K_2MnO_4 + H_2O$$

$$\left[(W) = K_2MnO_{4(aq)} \rightleftharpoons 2K^{\oplus}_{aq} + MnO^{2-}_{4(aq)} \right]$$

$$K_2MnO_4 + H_2O \xrightarrow[Redox]{Electolytic} H_2 + KOH + KMnO_4$$
$$(X)$$

[anion of X = MnO^-_4]
$$(Z)$$

$$\left[\because \underset{(Y)}{MnO^{2-}_4} \xrightarrow[Oxidation]{Electrolytic} \underset{(Z)}{MnO^-_4} + e^- \right]$$
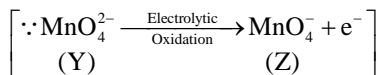
$\because$ In acidic solution ; Y undergoes disproportionation reaction

$$\left[3MnO^{2-}_{4(aq)} + 4H^{\oplus} \rightarrow 2MnO^-_4 + MnO_2 + 2H_2O \right]$$
$$(Z)$$

Q.17 (A)

X:Ag   P:AgCl

Y:Pb   Q:$PbCl_2$

$$\underset{Pb(NO_3)_2}{\overset{AgNO_3}{+}} \xrightarrow{+NaCl\downarrow} \underset{white\ ppt}{AgCl\downarrow} + \underset{white\ ppt}{PbCl_2\downarrow}$$

Aquesous suspension is heated and then filtered

Residue   Filtrate
AgCl↓(P) $PbCl_2$(Q)
white ppt   Hot solution

$AgCl + 2NH_3$ solution → $[Ag(NH_3)_2Cl]$
(P)   (excess)   clear solution
$AgCl + 2Na_2S_2O_3$ solution → $Na_3[Ag(S_2O_3)_2] + NaCl$
(P)   (excess)   clear solution
$PbCl_2$ +   2KI   → $PbI_2\downarrow + 2KCl$
Hot solution   (yellow ppt)
(Q)

Q.18 (C)

Q.19 (D)

Q.20 (A , B)

$$Pb(NO_3)_2 \xrightarrow{dil.HCl} \underset{\substack{White \\ ppt}}{PbCl_2 \downarrow}$$

$$Bi(NO_3)_3 \xrightarrow{dil.HCl} \underset{\substack{Water \\ Soluble}}{BiCl_3}$$

$$Hg(NO_3)_2 \xrightarrow{dil.HCl} \underset{\substack{Water \\ Soluble}}{HgCl_2}$$

$$AgNO_3 \xrightarrow{dil.HCl} \underset{White\ PPt}{AgCl \downarrow}$$

$$An(NO_3)_2 \xrightarrow{dil.HCl} \underset{Water\ Soluble}{ZnCl_2 \downarrow}$$

$$Pb(NO_3)_2 \xrightarrow{NaOH(dil)} \underset{Water\ PPt}{Pb(OH)_2 \downarrow}$$

$$Zn(NO_3)_2 \xrightarrow{NaOH(dil)} \underset{Water\ PPt}{Zn(OH)_2 \downarrow}$$

$$Bi(NO_3)_3 \xrightarrow{NaOH(dil)} \underset{White\ PPt}{Bi(OH)_3 \downarrow}$$

$$AgNO_3 \xrightarrow{NaOH(dil)} \underset{Brown\ PPt}{Ag_2O}$$

$$Hg(NO_3)_2 \xrightarrow{NaOH(dil)} \underset{Yellow\ PPt}{HgO \downarrow}$$