ACE YOUR WAY CBSE XII

Series 5

CHAPTERWISE PRACTICE PAPER : THE *d*-AND *f*-BLOCK ELEMENTS | COORDINATION COMPOUNDS

Time Allowed : 3 hours　　　　Maximum Marks : 70

GENERAL INSTRUCTIONS

(i) All questions are compulsory.
(ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
(iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
(iv) Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
(v) Q. no. 23 is a value based question and carries 4 marks.
(vi) Q. no. 24 to 26 are long answer questions and carry 5 marks each.
(vii) Use log tables if necessary, use of calculators is not allowed.

1. Explain why Cu^{2+} ion is stable in aqueous solution.

2. What is the type of isomerism shown by $[Co(en)_3]Cl_3$?

3. In which type of compounds transition metals show very low oxidation state?

4. Why outer octahedral complexes are called high spin complexes?

5. Ce(IV) is a good analytical reagent. Why?

6. Write the IUPAC names of the following :

(i) $[CoCl(NO_2)(NH_3)_4]Cl$

(ii) $[PtCl(NH_2CH_3)(NH_3)_2]Cl$

(iii) $[Mn(H_2O)_6]^{2+}$　**(iv)** $[Ti(H_2O)_6]^{3+}$

7. In the transition series, starting from lanthanum ($_{57}La$), the next element hafnium ($_{72}Hf$) has an atomic number of 72. Why do we observe this jump in atomic number?

8. Discuss the nature of bonding in metal carbonyls.

9. What is actinoid contraction? How is it different from lanthanoid contraction.

10. Explain the structure of $[NiCl_4]^{2-}$ on the basis of V.B.T.

11. The mercurous ion exists as Hg_2^{2+} ion while the cuprous ion exists as Cu^+. Explain.

12. The hexaaquamanganese (II) ion contains five unpaired electrons while the hexacyanomanganate ion contains only one unpaired electron. Explain using crystal field theory.

13. Assign reasons for the following :

(i) Actinoids exhibit greater range of oxidation states than lanthanoids.

(ii) Unlike Cr^{3+}, Mn^{2+}, Fe^{3+} and the subsequent other M^{2+} ions of the 3*d* series of element, the 4*d* and the 5*d* series metals generally do not form stable cationic species.

(iii) Transition metals generally form coloured compounds.

14. Explain :

(i) What will be the correct order for the wavelength of absorption in the visible region for the following :

$[Ni(NO_2)_6]^{4-}$, $[Ni(NH_3)_6]^{2+}$, $[Ni(H_2O)_6]^{2+}$?

(ii) $[Ni(H_2O)_6]^{2+}$ is green and becomes violet when ethane 1, 2-diamine is added to it.

15. **(i)** Why is Cr^{2+} reducing and Mn^{3+} oxidising in nature when both have d^4 configuration?

(ii) Explain how $[Ti(H_2O)_6]^{3+}$ becomes purple coloured ?

OR

(i) Explain the following observations.

(a) The metal-metal bonding is more frequent for the second and third series of transition elements than that for the first series.

(b) The higher oxidation states are usually exhibited by members in the middle of a series of transition elements.

(ii) Compare the nature of oxides of 3*d*-series of transition elements.

16. **(i)** A solution containing 0.319 g of $CrCl_3.6H_2O$ was passed through a cation exchange resin and the acid coming out of the resin required 28.5 mL of 0.125 M NaOH. Determine the correct structural formula of the complex. (Mol. wt. of the complex = 266.5 g mol^{-1})

(ii) Write the chemical formula of Sodium (ethylenediaminetetraacetate) chromate(II).

17. Explain :

(i) Why does melting point of transition elements generally increase towards the middle in each series?

(ii) The enthalpies of atomisation of transition metals are quite high.

(iii) Why is third ionisation energy of Mn exceptionally high ?

18. **(i)** What do you mean by labile and non-labile complexes? Give examples.

(ii) Why is geometrical isomerism not possible in tetrahedral complexes having two different types of unidentate ligands coordinated with the central metal ion?

19. Explain :

(i) Chemistry of the actinoid elements is not so smooth as that of lanthanoids. Justify the statement by giving some examples from the oxidation state of these elements.

(ii) Use Hund's rule to derive the electronic configuration of Ce^{3+} ion and calculate its magnetic moment on the basis of 'spin only' formula.

20. **(i)** Dilute equimolar solutions of each of the following compounds were prepared. Arrange these compounds in increasing order of molar conductivity of their solutions.

(a) $Na_3[Co(NO_2)_6]$ (b) K[Co(EDTA)]

(c) $[Co(py)_3(CN)_3]$ (d) $[Cr(NH_3)_5Cl]Cl_2$

(e) $[Pt(NH_3)_6]Br_4$

(ii) Out of the following two coordination entities, which is chiral (optically active) ?

(a) *cis* - $[CrCl_2(ox)_2]^{3-}$

(b) *trans* - $[CrCl_2(ox)_2]^{3-}$

21. Explain :

(i) A yellow translucent solution is obtained on passing H_2S gas through an acidified solution of $KMnO_4$. Identify the solution and write the balanced chemical equation.

(ii) Describe the oxidising action of potassium dichromate and write the ionic equations for its reactions with

(a) iodide ion (b) iron(II) solution and

(c) H_2S.

22. Explain :

(i) Among $[Ag(NH_3)_2]Cl$, $[Ni(Cl)_4]^{2-}$ and $[CuCl_4]^{2-}$ which

(a) has square planar geometry?

(b) remains colourless in aqueous solution and why?

[Atomic number of Ag = 47, Ni = 28, Cu = 29]

(ii) $FeSO_4$ solution mixed with $(NH_4)_2SO_4$ solution in 1:1 molar ratio gives the test of Fe^{2+} ion but $CuSO_4$ solution mixed with aqueous ammonia in 1:4 molar ratio does not give the test of Cu^{2+} ion. Explain why?

23. Dr. S.P. Rahman, a professor of Medical Science, organised a seminar on cancer. The following paragraph highlights the important message given by him :

" Cancer is not a communicable disease and it occurs due to unlimited growth of body cells leading to tumours. We should shake hands, eat together with the people suffering from cancer. These activities will boost up the confidence in them for living."

(i) Mention the values reflected by the message given by Dr. Rahman.

(ii) Write the name of coordination compound used for the treatment of cancer and give its structure.

(iii) Give the uses of two other coordination compounds in medicinal chemistry.

24. **(i)** What happens when : (give only ionic equations)

(a) potassium manganate is treated with ozone.

(b) sodium thiosulphate is treated with acidified $K_2Cr_2O_7$.

(c) potassium iodide is treated with alkaline $KMnO_4$.

(ii) Give reasons for the following :

(a) The transition metals form interstitial compounds.

(b) Silver halides find use in photography.

OR

(i) What happens when : (give only ionic equations)

(a) hydrogen peroxide is treated with acidified potassium dichromate solution.

(b) hydrogen peroxide is treated with acidified potassium permanganate solution.

(ii) Mention the direct consequence of the following factors on the chemical behaviour of the transition elements.

(a) They have incompletely filled *d*-orbitals in the ground state or in one of the oxidised states of their atoms.

(b) They contribute more valence electrons per atom in the formation of metallic bonds.

25. For the complex $[Fe(en)_2Cl_2]Cl$, identify :

(i) oxidation number of iron and name of complex (At. no. of Fe = 26)

(ii) the hybrid orbitals and shape of the complex

(iii) the magnetic behaviour of the complex

(iv) the number of geometrical isomers and

(v) whether there is any optical isomer also.

OR

(i) Describe the application of complex formation in qualitative identification of cations. Give specific examples.

(ii) (a) Draw the structure of the $[Pt(trien)]^{2+}$ chelate.

(b) How many bonding sites are present in this ligand?

(c) What is the chemical name of this ligand?

26. The gas liberated, on heating a mixture of two salts with NaOH, gives a reddish-brown precipitate with an alkaline solution of K_2HgI_4.The aqueous solution of the mixture on treatment with $BaCl_2$ gives a white precipitate, which is sparingly soluble in conc. HCl. On heating the mixture with $K_2Cr_2O_7$ and conc. H_2SO_4, red vapours (*A*) are produced. The aqueous solution of the mixture gives a deep blue colouration (*B*) with potassium ferricyanide solution. Identify the radicals in the given mixture and write the balanced equations for the formation of (*A*) and (*B*).

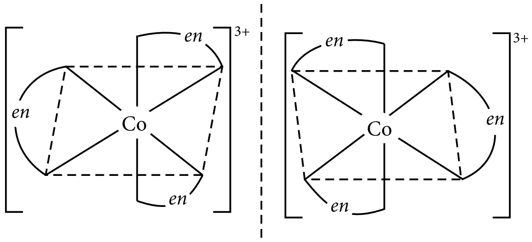
OR

A green chromium compound (*A*) on fusion with alkali gives a yellow compound (*B*) which on acidification gives an orange coloured compound (*C*). (*C*) on treatment with NH_4Cl gives an orange coloured product (*D*) which on heating decomposes to give back compound (*A*). Identify (*A*), (*B*), (*C*) and (*D*) and write down the structure of (*C*).

SOLUTIONS

1. Hydration enthalpy of Cu^{2+} ion is more negative which more than compensates for the high second ionisation enthalpy of Cu.

2. $[Co(en)_3]Cl_3$ shows optical isomerism.



3. Transition metals show very low oxidation states in compounds having ligands which act as π acceptors *e.g.*, CO, NO etc.

4. No pairing occurs in outer octahedral complexes, hence, they have many unpaired electrons and show large values of magnetic moments.

5. The $E°$ value for Ce^{4+}/Ce^{3+} is 1.74 V which suggests that it can oxidise water however, the reaction rate is very slow and hence Ce (IV) is a good analytical reagent.

6. **(i)** Tetraamminechloridonitrito-N-cobalt (III) chloride.

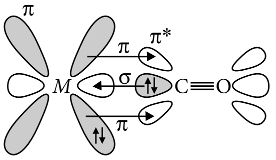
(ii) Diamminechlorido(methylamine)platinum (II) chloride

(iii) Hexaaquamanganese (II) ion

(iv) Hexaaquatitanium (III) ion

7. This is because after $_{57}La$, filling of 4*f*-orbital starts which is complete at atomic number 71. These 14 elements therefore, belong to *f*-block and are placed separately at the bottom of the periodic table.

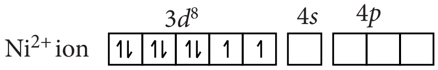
8. The metal-carbon bond in metal carbonyls possess both σ and π character. The *M*-C σ bond is formed by the donation of lone pair of electrons on the carbonyl carbon into a vacant orbital of the metal. The *M*-C π-bond is formed by the donation of a pair of electrons from a filled *d*-orbital of metal into the vacant antibonding π^* -orbital of carbon monoxide. The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal.



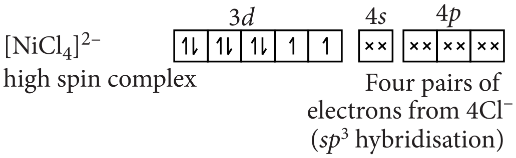
Synergic bonding

9. The gradual decrease in the atomic as well as ionic sizes (M^{3+} ions) of actinoids along the series is called actinoid contraction.
It is different from the lanthanoid contraction by the fact that the decrease in size or contraction between two successive elements is higher in actinoids due to poor screening by 5*f*-electrons.

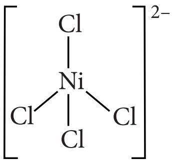
10. In $[NiCl_4]^{2-}$, Ni is in +2 oxidation state and has $3d^8$ outer electronic configuration.



Under the influence of weak field ligand :



It is sp^3 hybridised hence, structure is tetrahedral.



11. Hg_{80} : $[Xe]_{54}\ 4f^{14}\ 5d^{10}\ 6s^2$

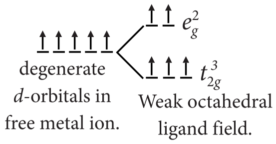
Hg^+ : $[Xe]_{54}\ 4f^{14}\ 5d^{10}\ 6s^1$

In Hg(I), there is one unpaired electron and we expect Hg(I) (mercurous) salts to be paramagnetic. But mercurous salts are found to be diamagnetic which is only possible when 6*s* orbitals of the two Hg^+ ions overlap to form a Hg – Hg covalent bond. Hence, mercurous ion exists as Hg_2^{2+}.

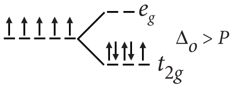
$$Cu_{29} : [Ar]3d^{10}\ 4s^1$$
$$Cu^+ : [Ar]3d^{10}$$

Cu(I) has no unpaired electron to form dimeric species and also its salts are diamagnetic hence, it exists as Cu^+.

12. $[Mn(H_2O)_6]^{2+}$ contains Mn^{2+}- $3d^5$ configuration C.N. = 6, octahedral structure, H_2O is a weak field ligand, hence $\Delta_o < P$



Electrons enter into e_g orbital before pairing. It has five unpaired electrons.
$[Mn(CN)_6]^{4-}$ contains Mn^{2+} ion-$3d^5$ configuration. C.N. = 6, octahedral geometry, CN^- is strong field ligand, $\Delta_o > P$



Hence pairing of electrons in t_{2g} orbitals takes place. It has only one unpaired electron.

13. **(i)** This is because there is less energy difference between 5*f* and 6*d* orbitals in actinoids than the energy difference between 4*f* and 5*d* orbitals in case of lanthanoids.

(ii) This is because due to lanthanoid contraction the expected increase in size does not occur hence, they have very high value of ionisation enthalpy.

(iii) This is due to *d*-*d* transition. When visible (white) light falls on transition metal compounds, they absorb certain radiation of visible light for transition of electrons from lower *d* level to higher *d* level and transmit the remaining ones. The colour observed corresponds to complementary colour of the light absorbed.

14. **(i)** The strength of the ligands in the spectrochemical series follows the order (increasing Δ_o value) $H_2O < NH_3 < NO_2^-$

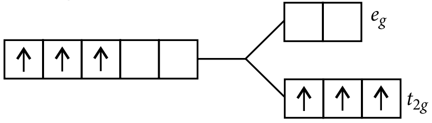
As $\Delta_o = \frac{hc}{\lambda}$, the order of wavelength absorbed is

$[Ni(NO_2)_6]^{4-} < [Ni(NH_3)_6]^{2+} < [Ni(H_2O)_6]^{2+}$

(ii) Ethane-1,2-diamine is stronger ligand than H_2O. When H_2O molecule is replaced by ethane-1,2-diamine (*en*), the crystal field splitting energy (Δ_o) increases. Complex absorbs light of higher frequency for *d*-*d* transition and hence colour of the complex changes from green to violet.

$\underset{\Delta_o \text{ small}}{[Ni(H_2O)_6]^{2+}}$ – Green, $\underset{\Delta_o \text{ large}}{[Ni(en)_3]^{2+}}$ – violet

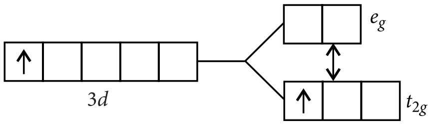
15. (i) Cr^{2+} is reducing as its configuration changes from d^4 to d^3, a more stable half filled t_{2g} configuration.



Mn^{3+} is oxidising because its configuration also changes from d^4 to d^5 (which is half-filled) and has extra-stability.

(ii) In $[Ti(H_2O)_6]^{3+}$, titanium has $3d^1\ 4s^0$ configuration. In Ti^{3+} ion, the *d*-orbitals split up into two parts t_{2g} and e_g. The t_{2g} part has three out of five *d*-orbitals (d_{xy}, d_{yz}, d_{zx}) with energy lower than the atomic orbitals whereas e_g have two orbitals ($d_{x^2-y^2}$ and d_{z^2}) having energy more than the atomic orbitals.

Due to less energy difference between t_{2g} and e_g orbitals, the electrons transit between these two orbital groups (called *d*-*d* transition). The energy required for this purpose is sufficiently available in the visible region. The *d*-*d* transition absorbs yellow region light and therefore colour observed is purple (complementary colour).



OR

(i) (a) Nearly all the transition metals have the simple *hcp*, *ccp* or *bcc* lattice characteristics of true metals in which atoms are held together by strong metal-metal bonding. As we go down the group, electrons of elements of second and third series are available more easily as compared to first series hence, metal-metal bonding is more frequent in 4*d* and 5*d*-series of elements.

(b) The lesser number of oxidation states on the extreme ends of the series can be due to the presence of too few electrons or due to the presence of too many electrons and thus, fewer empty orbitals to share electrons with the ligands. In the middle of the series, *ns* and (*n* – 1)*d* electrons are involved hence, higher oxidation states are exhibited by them.

(ii) While moving along a period from Sc to Zn, basic nature decreases and acidic nature increases.

Also, with increase in the oxidation state of a given transition metal, the covalent character of its compound increases and thus acidic character also increases.

16. (i) Let the number of Cl^- ion outside the coordination sphere, *i.e.*, the number of ionisable Cl^- ions be *n*.

When the solution of the complex is passed through cation exchanger, nCl^- ions will combine with nH^+ ions to form *n*HCl.

$nCl^- + nH^+ \longrightarrow nHCl$

$\therefore$ 1 mole of complex = *n* moles of HCl

$\equiv$ *n* moles of NaOH.

$$\text{Moles of the complex} = \frac{0.319}{266.5} = 0.0012 \text{ mol}$$

$$\text{Moles of NaOH used} = \frac{28.5 \times 0.125}{1000} = 0.0036 \text{ mol}$$

Thus, 0.0012 mol of complex $\equiv$ 0.0036 mol of NaOH $\equiv$ 0.0036 mol of HCl

$$\therefore\ 1 \text{ mole of complex} = \frac{0.0036}{0.0012} = 3 \text{ mol of HCl}$$

$\therefore\ n = 3$

Thus, all the Cl^- ions are outside the coordination sphere and formula of the complex is $[Cr(H_2O)_6]Cl_3$.

(ii) $Na_2[Cr(EDTA)]$

17. (i) The transition elements are characterised by high melting points. It is attributed to the involvement of greater number of electrons from (*n* – 1)*d* orbital in addition to *ns* electrons in the interatomic metallic bonding. In general, greater the number of valence electrons, stronger is the resultant metallic bonding. In any series, the melting point rises to a maximum at about the middle of each series which indicates that one unpaired electron per *d*-orbital is particularly favourable for strong interatomic bonding.

(ii) The enthalpy of atomisation is the amount of energy (heat) required to break the metal lattice to get free atoms. As transition metals contain a large number of unpaired electrons, they have strong interatomic attractive forces, *i.e.*, metallic bonds. As a large amount of energy is required to break these metallic bonds, transition metals have high enthalpies of atomisation.

(iii) Mn^{2+} has the outer electronic configuration $[Ar]3d^5$. Due to highly symmetrical, half-filled *d*-subshell, the removal of third electron is very difficult. Therefore, third ionisation energy of Mn is very high.

18. (i) Complex ions in which ligands can be interchanged rapidly are said to be labile. $[Cu(H_2O)_4]^{2+}$ and $[Cu(NH_3)_4]^{2+}$ are labile complexes.

A complex ion that exchanges ligands slowly is said to be non-labile or inert. In general, complex ions of the first transition series, except for those of Cr(III) and Co(III) are kinetically labile. Those of the second and third transition series are generally kinetically inert.

(ii) Tetrahedral complexes do not show geometrical isomerism because the relative positions of the unidentate ligands attached to the central metal atom are same with respect to each other.

19. (i) Lanthanoids show only few oxidation states such as +2, +3 and +4 (+3 oxidation state is the most stable one). Actinoids show more oxidation states (from +3 to +6), +3 being the most stable. Lesser number of oxidation states for lanthanoids is due to large energy gap between 4*f*, 5*d* and 6*s* orbitals whereas the energy gap between 5*f*, 6*d* and 7*s* orbitals is comparatively small. Hence actinoids show more oxidation states.

(ii) Ce(58) : $[Xe]\ 4f^1\ 5d^1 6s^2$ (1)

$Ce^{3+} : [Xe]4f^1$

$\Rightarrow \quad n = 1$ (only one unpaired electron)

By 'spin-only' formula,

$$\text{Magnetic moment of } Ce^{3+}(\mu) = \sqrt{n(n+2)}$$
$$= \sqrt{1(1+2)} = \sqrt{3}$$
$$= 1.73 \text{ BM}$$

20. (i) These compounds will ionise as follows in their solutions :

(a) $Na_3[Co(NO_2)_6] \rightleftharpoons 3Na^+ + [Co(NO_2)_6]^{3-}$
= 4 ions

(b) $K[Co(EDTA)] \rightleftharpoons K^+ + [Co(EDTA)]^-$
= 2 ions

(c) $[Co(py)_3(CN)_3]$
No ionisation (molecular complex)

(d) $[Cr(NH_3)_5Cl]Cl_2 \rightleftharpoons [Cr(NH_3)_5Cl]^{2+} + 2Cl^-$
= 3 ions

(e) $[Pt(NH_3)_6]Br_4 \rightleftharpoons [Pt(NH_3)_6]^{4+} + 4Br^-$
= 5 ions

As molar conductivity is proportional to the number of ions produced in the solution, therefore, the order is as follows :

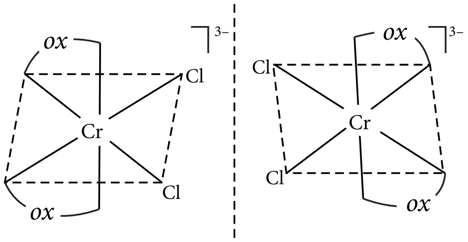
$[Co(py)_3(CN)_3] < K[Co(EDTA)] < [Cr(NH_3)_5Cl]Cl_2 < Na_3[Co(NO_2)_6] < [Pt(NH_3)_6]Br_4$

(ii) (a) *cis*-$[CrCl_2(ox)_2]^{3-}$

(b) *trans*-$[CrCl_2(ox)_2]^{3-}$

Out of the two, (a) *cis*-$[CrCl_2(ox)_2]^{3-}$ is chiral (optically active).

The two entities are represented as



21. (i) When H_2S gas is passed through an acidified solution of $KMnO_4$, a translucent solution is obtained due to the oxidation of H_2S into colloidal sulphur by $KMnO_4$.

$5S^{2-} + 2MnO_4^- + 16\ H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5S$

The yellow translucent solution is of colloidal sulphur in water.

(ii) $K_2Cr_2O_7$ acts as a powerful oxidising agent in acidic medium (dilute H_2SO_4). the $Cr_2O_7^{2-}$ ion takes up electrons and hence acts as oxidising agent. In this reaction, Cr (+6) is reduced to Cr (+3). The potential equation for reduction is

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O (E^\circ = 1.33\text{ V})$$

(a) Iodine is liberated from iodide solution.

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

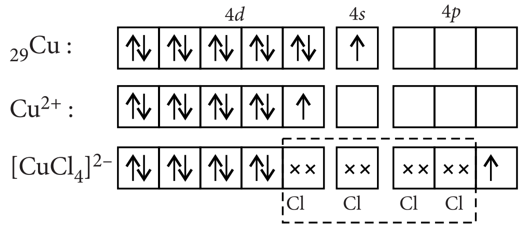
(b) Ferrous ion is oxidised to ferric ion.

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

(c) H_2S is oxidised to sulphur.

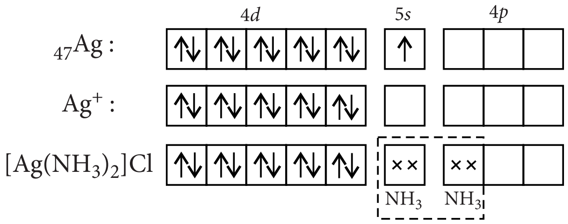
$$Cr_2O_7^{2-} + 8H^+ + 3H_2S \longrightarrow 2Cr^{3+} + 3S + 7H_2O$$

22. (i) (a) $[CuCl_4]^{2-}$ has the square planar geometry.



*dsp*² hybridisation

(b) $[Ag(NH_3)_2]Cl$ is colourless because there are no unpaired electrons in its *d*-orbitals hence, no *d*—*d* transition is possible.



sp hybridisation

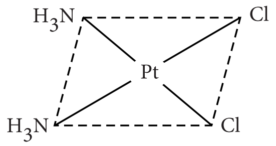
(ii) On mixing $FeSO_4$ and $(NH_4)_2SO_4$ in 1:1 molar ratio, a double salt, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ (Mohr's salt) is formed which on ionisation gives all constituent ions. Thus, it gives the test of Fe^{2+} ions.

When $CuSO_4$ solution and aqueous ammonia are mixed in 1 : 4 molar ratio, a complex salt, $[Cu(NH_3)_4]SO_4$ is formed. This complex compound on ionisation gives $[Cu(NH_3)_4]^{2+}$ and SO_4^{2-} ions and not Cu^{2+} ions. Due to absence of free Cu^{2+} ions, it does not give the test of Cu^{2+} ions.

23. (i) We should show compassion and empathy towards cancer patients and they should be encouraged to live a normal life.

(ii) *cis*-platin, *cis* $[Pt(NH_3)_2Cl_2]$ is used for the treatment of cancer.

It has a square planar structure.



(iii) (a) Copper and iron when present in toxic proportions in plants and animals are removed by chelating agent *D*–penicillamine and desferrioxime –*B*.

(b) EDTA is used for the treatment of lead poisoning.

24. (i) (a) Potassium permanganate is formed.

$$2MnO_4^{2-} + O_3 + H_2O \longrightarrow 2MnO_4^- + 2OH^- + O_2$$

(b) Sodium sulphate is formed

$$Cr_2O_7^{2-} + 8H^+ + \underset{\text{Thiosulphate}}{3S_2O_3^{2-}} \longrightarrow 2Cr^{3+} + \underset{\text{Sulphate}}{3SO_4^{2-}} + 3S + 4H_2O$$

(c) Potassium iodate is formed

$$2MnO_4^- + \underset{\text{Iodide}}{I^-} + H_2O \longrightarrow 2MnO_2 + \underset{\text{Iodate}}{IO_3^-} + 2OH^-$$

(ii) (a) Transition metals form a large number of interstitial compounds because small atoms of certain non metallic elements (H, B, C, N, etc.) get trapped in voids or vacant spaces of lattice of the transition metals.

As a result of filling up of the interstitial spaces such interstitial compounds are hard and rigid.

(b) Under the action of light, decomposition of silver bromide takes place in traces where it is illuminated. The number of silver atoms formed is proportional to the quantity of light falling on the surface.

OR

(i) (a) A deep blue colour, due to the formation of perchromic acid $[CrO(O_2)_2]$, is obtained.

$$Cr_2O_7^{2-} + 2H^+ + 4H_2O_2 \longrightarrow \underset{\substack{\text{Perchromic acid}\\ \text{(Blue colour)}}}{2CrO_5} + 5H_2O$$

(b) Oxygen is evolved.

$$2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2 \uparrow$$

(ii) (a) Vacant *d*-orbitals can accept lone pair of electrons donated by other groups (ligands), consequently transition elements form a large number of complex compounds. Paramagnetism and colour of compound is also due to incompletely filled *d*-orbital.

(b) Due to presence of large number of valence electrons per atom, the metallic bonds in transition elements are quite strong. Due to the presence of strong metallic bonds the transition metals are hard, possess high densities and high enthalpies of atomisation.

25. (i) $[Fe(en)_2Cl_2]Cl$

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

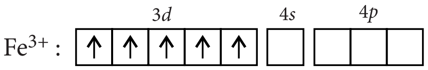
$\therefore \quad x = +3$

$\therefore$ Fe is present as Fe (III).

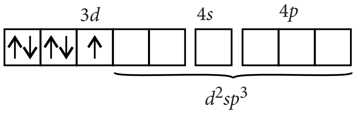
Name of the complex is :

dichloridobis(ethane-1, 2-diamine)iron (III) chloride

(ii) Coordination number of Fe is 6 therefore, hybridisation is as follows :



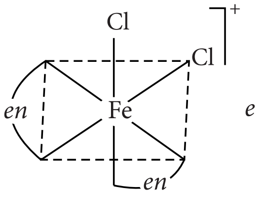
en ligand is a strong field ligand and therefore, electrons get paired up giving d^2sp^3 hybridisation.



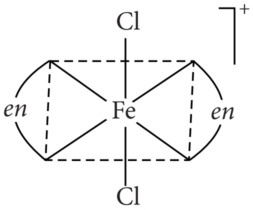
Shape of the complex : Octahedral

(iii) As it has one unpaired electron, it is paramagnetic.

(iv) It shows two geometrical isomers.

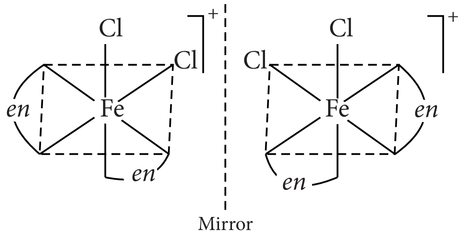


cis-isomer



trans-isomer

(v) The *cis*-isomer will show optical isomerism.



OR

(i) Complex formation is frequently encountered in qualitative identification of cations. For example,

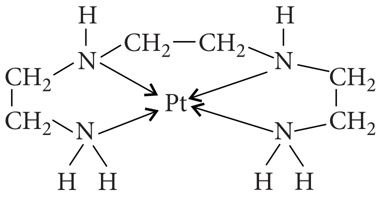
(a) Identification of Cu^{2+} ion is based on the formation of blue coloured tetraamminecopper (II) ion in solution.

$$Cu^{2+} + 4NH_3 \longrightarrow \underset{\substack{\text{Blue colour} \\ \text{Tetraamminecopper (II) ion}}}{[Cu(NH_3)_4]^{2+}}$$

(b) Fe^{3+} ion can be identified by the blood red coloured complex, potassium hexathiocyanoferrate (III), it forms with KCNS.

$$FeCl_3 + 6KCNS \rightarrow \underset{\substack{\text{Red coloured complex} \\ \text{potassiumhexathiocyanatoferrate (III)}}}{K_3[Fe(SCN)_6]} + 3KCl$$

(ii) (a)



(b) The ligand present in above chelate is tetradentate *i.e.*, it has four bonding sites.

(c) The chemical name of the ligand is

N, N-bis(2-aminoethyl)-1,2-ethanediamine.

26. Liberation of gas (might be NH_3) with NaOH and reddish brown precipitate (which are due to liberated NH_3 and K_2HgI_4) with Nessler's reagent (K_2HgI_4) confirms the presence of ammonium radical (NH_4^+).

$$NH_4^+ + NaOH \longrightarrow NH_3 \uparrow + H_2O + Na^+$$

$$NH_3 + K_2HgI_4 \longrightarrow Hg(NH_2I)$$

Formation of white precipitate with $BaCl_2$, which is sparingly soluble in conc. HCl, indicates the presence of sulphate radical (SO_4^{2-}).

$$SO_4^{2-} + BaCl_2 \longrightarrow \underset{\substack{\text{White ppt.}\\ \text{(sparingly soluble in conc. HCl)}}}{BaSO_4 \downarrow} + 2Cl^-$$

Evolution of red vapours (CrO_2Cl_2)with $K_2Cr_2O_7$ and H_2SO_4 confirms the presence of chloride radical (Cl^-).

$$4Cl^- + K_2Cr_2O_7 + 3H_2SO_4 \xrightarrow{\text{heat}} K_2SO_4 + \underset{\substack{(A)\\ \text{Chromyl chloride}\\ \text{(Red vapours)}}}{2CrO_2Cl_2} + 2SO_4^{2-} + 3H_2O$$

Formation of deep blue colouration (*B*) with potassium ferricyanide solution confirms the presence of ferrous radical (Fe^{2+}).

$$2K_3[Fe(CN)_6] + 3Fe^{2+} \longrightarrow \underset{\substack{(B)\\ \text{Ferroferricyanide}\\ \text{(deep blue colour)}}}{Fe_3[Fe(CN)_6]_2} + 6K^+$$

Hence in the mixture, NH_4^+, Fe^{2+}, Cl^- and SO_4^{2-} radicals are present and (*A*) is chromyl chloride (CrO_2Cl_2) and (*B*) is ferroferricyanide, $Fe_3[Fe(CN)_6]_2$.

OR

The yellow coloured compound (*B*) is sodium chromate which is formed on fusion of chromium (III) oxide (*A*) and NaOH. Compound (*B*) on acidification gives sodium dichromate (*C*), which on treatment with NH_4Cl gives ammonium dichromate (*D*), which on heating gives chromium (III) oxide.

(i) $$\underset{\substack{\text{Chromium(III)}\\ \text{oxide}(A)}}{2Cr_2O_3} + 3O_2 + 8NaOH \xrightarrow{\to} \underset{\text{Sodium chromate}}{4Na_2CrO_4} + 4H_2O$$

(ii) $$\underset{(B)}{2Na_2CrO_4} + H_2SO_4 \longrightarrow \underset{\substack{\text{Sodium dichromate}\\ \text{(orange)}(C)}}{Na_2Cr_2O_7} + Na_2SO_4 + H_2O$$

(iii) $$Na_2Cr_2O_7 + 2NH_4Cl \rightarrow \underset{\substack{\text{Ammonium dichromate}\\ \text{(orange)}(D)}}{(NH_4)_2Cr_2O_7} + 2NaCl$$

(iv) $$(NH_4)_2Cr_2O_7 \xrightarrow{\text{heat}} Cr_2O_3 + 4H_2O + N_2 \uparrow$$

Structure of (C) :