

DAY TWENTY THREE

The *d*- and *f*-Block Elements

Learning & Revision for the Day

- Transition Elements
- Some Important Compounds of Transition Elements

- Inner Transition Elements (*f*-Block Elements)

The *d*-block elements of the periodic table contains the elements of the group 3-12 in which the *d*-orbitals are progressively filled in each of the four long periods.

The elements constituting the *f*-block are those in which the *4f* and *5f*-orbitals are progressively filled in the latter two long periods. These elements are formal members of 3rd group from which they have been taken out to develop a separate *f*-block of the periodic table.

Transition Elements

- *d*-block elements are known as transition elements because their position in the periodic table is between the *s*-block and *p*-block elements.
- Transition elements have incomplete filled *d*-orbital in their ground state or in any of its oxidation state.
- There are mainly three series of the transition metals, (i) 3*d*-series (Sc to Zn), (ii) 4*d*-series (Y to Cd) and (iii) 5*d*-series (La to Hg), omitting (Ce to Lu).

Electronic Configuration

- Electronic configuration of the transition elements is $(n-1)d^{1-10}ns^{1-2}$.
- Zn, Cd, Hg have electronic configuration $[(n-1)d^{10}ns^2]$, are *d*-block elements, but not transition metals because they have completely filled *d*-orbitals.

Transition Metals or *d*-Block Elements

3 rd group	4 th group	5 th group	6 th group	7 th group
$ns^2(n-1)d^1$	$ns^2(n-1)d^2$	$ns^2(n-1)d^3$	$ns^1(n-1)d^4$	$ns^2(n-1)d^5$
Sc	Ti	V	Cr	Mn
Y	Zr	Nb	Mo	Tc
La	Hf	Ta	W	Re
8 th group	9 th group	10 th group	11 th group	12 th group
$ns^2(n-1)d^6$	$ns^2(n-1)d^7$	$ns^2(n-1)d^8$	$ns^2(n-1)d^9$	$ns^2(n-1)d^{10}$
Fe	Co	Ni	Cu	Zn
Ru	Rh	Pd	Ag	Cd
Os	Ir	Pt	Au	Hg

- Some of the exceptions are observed in electronic configuration. e.g., Cr : $3d^5 4s^1$ instead of $3d^4 4s^2$, Cr : $3d^{10} 4s^1$ instead of $3d^9 4s^2$

General Trends in Properties of the Transition Elements

The general properties of d -block elements and their trends are discussed below:

Physical Properties

- All the transition elements exhibit typical metallic properties such as high tensile strength, ductility etc.
- Their melting and boiling points are high which are due to the involvement of $(n-1)d$ electrons resulting into strong interatomic bonding.

1. Atomic and Ionic Radii

- In transition metals, on moving from left to right net nuclear charge increases due to poor shielding effect. Due to this, the atomic and ionic radii for transition elements for a given series shows a decreasing trend for first five elements and then becomes almost constant for next five elements of the series. At the end of the period, there is a slight increase in the atomic radii.
- The atomic and ionic radii of the elements of $4d$ -series are higher than corresponding element of $3d$ -series due to increase in number of shells.
- However, the elements of $4d$ and $5d$ -series have almost similar radii and very similar physical and chemical properties.

2. Enthalpy of Atomisation

Transition elements exhibit higher enthalpy of atomisation because of large number of unpaired electrons in their atoms. They have stronger interatomic interaction and hence form stronger bond. Thus, transition elements have very high melting and boiling points.

3. Ionisation Enthalpies

- The first ionisation enthalpy of transition elements lies in between s -block and p -block elements. In a series from left to right, ionisation enthalpy increases due to increase in nuclear charge.
- The irregular trend in the first ionisation enthalpy of the $3d$ -orbitals, can be accounted by considering that the removal of one electron alters the relative energies of $4s$ and $3d$ -orbitals.
- Ionisation enthalpy values for $5d$ -series are higher than that of $3d$ and $4d$ -series due to weak shielding effect of $4f$ -electrons present in $5d$ -series transition elements.

- Ionisation enthalpy values of Zn, Cd and Hg are abnormally higher on account of greater stability of completely filled d -orbital (d^{10}).

4. Oxidation States

Transition metals show variable oxidation states due to the fact that the difference in the energy of $(n-1)d$ electron and ns electrons is low which implies that electrons from both energy level can take part in bonding.

Stable oxidation states of the first row transition metals are :

Sc (+3), Ti (+4), V (+5), Cr (+3, +6), Mn (+2, +7),

Fe (+2, +3), Co (+2, +3), Ni (+2), Cu (+2), Zn (+2)

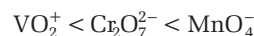
- In each period, the highest oxidation state increases with increase in atomic number, attains a maximum value in the middle and then decreases, for example, Mn ($3d$ -series), Ru ($4d$ -series) and Os ($5d$ -series) has maximum value for oxidation state as +7, +8, +8 respectively.
- The transition elements in their lower oxidation states (+2 and +3) usually forms ionic compounds. In higher oxidation state compounds are normally covalent. Ni and Fe in Ni(CO)_4 and Fe(CO)_5 show zero oxidation state.

5. Trends in the Standard Electrode Potentials

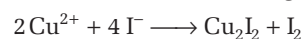
- The potential difference in transformation of the solid metal atoms to M^{2+} ions in solution is their standard electrode potentials. If sum of the first and second ionisation enthalpies is greater than hydration enthalpy, standard potential ($E_{M^{2+}/M}^\circ$) will be positive and reactivity will be lower and *vice-versa*.
- In general along a period, there is a decrease in electropositive character.

6. Trends in Stability of Higher Oxidation States

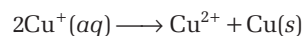
- The highest oxidation numbers are achieved in TiX_4 , VF_5 and CrF_6 . The +7 oxidation state for Mn is not represented in simple halides but MnO_3F is known and beyond Mn, no metal has a trihalide except FeX_3 and CoF_3 . The increasing order of oxidising power in the series is



- The highest oxidation states of transition metals are found in their compounds with fluorine and oxygen only because of their higher electronegativity and small atomic size.
- In low oxidation states, fluorine is unstable. However, Cu(II) halides are known including CuF_2 except iodide.



Most of the Cu(I) compounds are unstable in aqueous solution and undergo disproportionation.



7. Magnetic Properties

- The magnetic properties of a *d*-block elements are due to spin of unpaired electrons.
- The magnetic moment is determined by the number of unpaired electrons (*n*) which is given by
$$\mu = \sqrt{n(n+2)} \text{ B.M (Bohr Magneton)}.$$
- Paramagnetism is due to the presence of unpaired electrons, each such electron having a magnetic moment associated with its spin angular momentum. If all electrons are paired, substance will be diamagnetic and magnetic moment will be zero.
- Substances which are attracted very strongly by applied field and their domains are aligned in one direction are known as ferromagnetic, e.g. Fe, Co, Ni.

8. Formation of Coloured Ions

- The *d*-orbitals are non-degenerated in presence of ligands. When an electron from a lower energy *d*-orbital is excited to a higher energy *d*-orbital, the energy of required wavelength is absorbed and rest light is transmitted out. Therefore, the colour observed corresponds to the complementary colour of the light absorbed.
- In V_2O_5 , V is in +5 oxidation state. Inspite of d^0 , it is coloured compound. This colour arises due to defects in the crystal lattice.
- Some transition elements are coloured due to charge transfer spectra.

9. Formation of Complex Compounds

Transition metals have small size and high nuclear charge which facilitate the acceptance of lone pair of electrons from ligands. They have vacant *d*-orbitals of appropriate energy in order to accommodate the lone pair of electrons and thus form large number of complex compounds.

10. Catalytic Properties

- Transition metals have the ability to adopt multiple oxidation states and to form complexes, therefore used as a catalyst.
- Transition metals also provide larger surface area for the reactant to be adsorbed.

11. Formation of Interstitial Compounds

Small atoms of non-metals (H, C, N) fit into the voids of crystalline solid of transition metals and form interstitial compounds.

The physical and chemical characteristics of these compounds are as follows:

- They have high melting points, higher than those of pure metals.
- They are very hard, some borides approach diamond in hardness.
- They retain metallic conductivity.
- They are chemically inert.

12. Alloy Formation

Alloy is the homogeneous solid solution of two or more metals. Transition metals have approximate same size, therefore in molten form they can fit to each other's crystalline structure and form alloy. e.g. brass (copper-zinc) and bronze (copper-tin) etc.

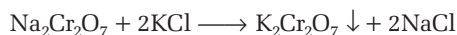
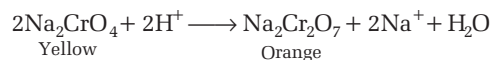
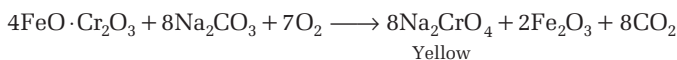
Some Important Compounds of Transition Elements

Some important compounds of transition metals are potassium dichromate and potassium permanganate which are discussed below :

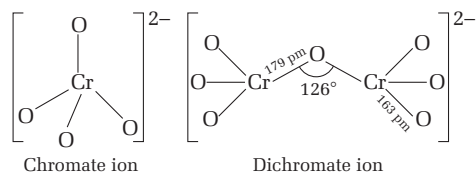
1. Potassium Dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$)

Ore : Ferrochrome or chromite ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$) or (FeCr_2O_4)

Preparation

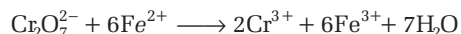
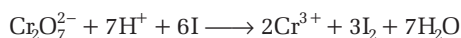
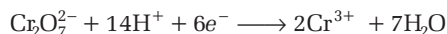


Sodium dichromate is more soluble than potassium dichromate. Chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solutions.



Properties

Sodium and potassium dichromates are strong oxidising agents, thus, acidified $\text{K}_2\text{Cr}_2\text{O}_7$ will oxidise iodides to iodine, sulphides to sulphur, tin (II) to tin (IV) and iron (II) salts to iron (III).



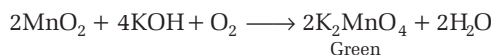
Uses of $\text{K}_2\text{Cr}_2\text{O}_7$

- $\text{K}_2\text{Cr}_2\text{O}_7$ is used as oxidising agent in volumetric analysis.
- It is used in mordant dyes, leather industry, photography (for hardening of film).
- It is used in chromyl chloride test.
- It is used in cleaning glassware.
- It is used in the preparation of chrome alum
 $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$.

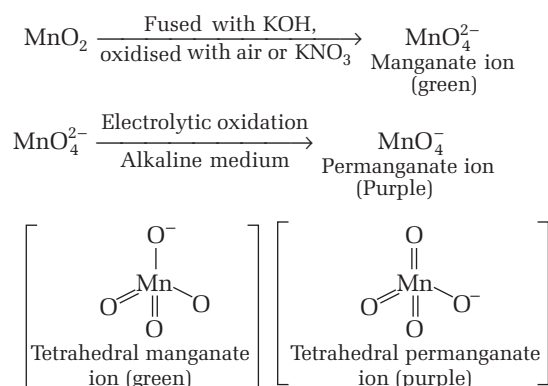
2. Potassium Permanganate (KMnO₄)

Ore : Pyrolusite (MnO₂)

Preparation



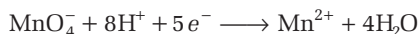
Commercial Preparation



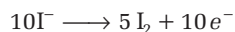
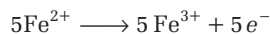
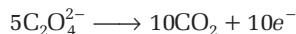
Properties

It acts as strong oxidising agent. The actual oxidising action of KMnO₄ depends upon its use in neutral, alkaline or acidic medium.

- (i) In presence of dilute H₂SO₄, KMnO₄ is reduced to manganous salt (Mn²⁺)

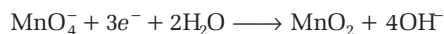


Acidified KMnO₄ solution oxidises oxalates to CO₂, iron (II) to iron (III), nitrites to nitrates and iodides to iodine. The half-reactions of reductants are



To acidify KMnO₄, only H₂SO₄ is used and not HCl or HNO₃ because HCl reacts with KMnO₄ and produce Cl₂, while HNO₃, itself acts as oxidising agent.

- (ii) In alkaline medium, KMnO₄ is reduced to MnO₂.



Alkaline or neutral KMnO₄ solution oxidises I⁻ to IO₃⁻, S₂O₃²⁻ to SO₄²⁻, Mn²⁺ to MnO₂ etc.

Uses of KMnO₄

- (i) In laboratory preparation of Cl₂.
- (ii) As an oxidising agent, disinfectant.
- (iii) In making Baeyer's reagent.

Inner Transition Elements (f-Block Elements)

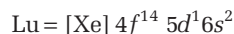
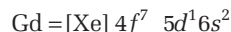
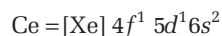
The f-block elements also known as inner transition elements consist of the two series, lanthanoids and actinoids.

Lanthanoids are known as rare earth metals (Ce to Lu) and actinoids are known as radioactive elements (Th to Lr).

1. Lanthanoids

- Fourteen elements of first row (4f-series) from Ce to Lu which follow La in the periodic table are called lanthanoids.
- General configuration of lanthanoids are [Xe] 4f¹⁻¹⁴, 5d⁰⁻¹, 6s².

Only Ce, Gd, Lu have electron in 5d-orbitals as well



Properties of Lanthanoids

Some of the properties of lanthanoids are as follows :

- (i) Atomic and ionic size of lanthanoids decreases from left to right, due to increase in nuclear charge. This is known as **lanthanoid contraction**.

The consequences of lanthanoid contraction is as follows :

- (a) The basic character of hydroxides decreases from La(OH)₃ to Lu(OH)₃.
- (b) The normal increase in size from Sc → Y → La disappear after the lanthanides and pair of elements such as Zr and Hf, Nb and Ta, Mo and W have nearly same size and properties.

- (ii) All the lanthanoids are silvery white soft metals and tarnish rapidly in air.

- (iii) Many trivalent lanthanoid ions are coloured both in the solid state and in aqueous solutions. Neither La³⁺ nor Lu³⁺ ion shows any colour. Lanthanoid ions with *xf*-electrons have similar colour to those with (14 - x) *f*-electrons.

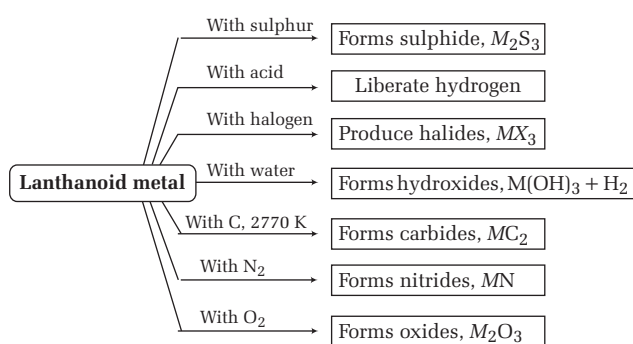
- (iv) The lanthanoid ions other than the *f*⁰ type (La³⁺ and Ce⁴⁺) and the *f*¹⁴ type (Yb²⁺ and Lu³⁺) are all paramagnetic. Neodymium shows maximum paramagnetism.

- (v) **Oxidation States** The most stable oxidation states of lanthanoids is + 3 but some of them also show +2 and +4 oxidation states. Ce⁴⁺ (in some elements) is favoured by its noble gas configuration, but it is a strong oxidant reverting to the common +3 state.

- The *E*_{value} for Ce⁴⁺ / Ce³⁺ is +1.74 V, the reaction rate is very slow and hence, Ce(IV) is a good analytical reagent.

- Pr, Nd, Tb and Dy also exhibit +4 state but only in oxides. Eu^{2+} is formed by losing the two s -electrons and its f^7 configuration accounts for the formation of this ion.
- However, Eu^{2+} is a strong reducing agent changing to the common +3 state. Similarly, Yb^{2+} which has f^{14} configuration is a reductant, Tb^{4+} has half-filled f -orbitals and is an oxidant.

(vi) **Reactivity** Lanthanoid are very reactive metals like alkaline earth metals. The generalised reactions of lanthanoids are summarised below:



NOTE Misch metals, contain lanthanoids about 90–95%; Ce = 40.5%, lanthanum and neodymium = 44%, iron = 4.5%, calcium, carbon and silicon about 10.5%, are used in cigarette and gas lighters, toys, tank and tracer bullets. It is a pyrophoric alloy, i.e. takes up fire easily.

2. Actinoids

- Fourteen elements of 5*f*-series from Th to Lr which follows actinium in the 7th period of periodic table is known as **actinoids**.
- **General configuration of actinoids** are $[\text{Rn}] 5f^{1-14}, 6d^{0-2}, 7s^2$.

Properties of Actinoids

- Actinoids exhibit a range of **oxidation states** due to comparable energies of 5*f*, 6*d* and 7*s*-orbitals. The general oxidation state of actinoids is +3.
- All the actinoids are strong reducing agents and very reactive.
- Actinoids also react with oxygen, halogen, hydrogen and sulphur, etc., like lanthanoids.
- Actinoids are radioactive in nature and therefore, it is difficult to study their chemical nature.
- The atomic and ionic radii of actinoids decreases regularly across the series due to poor shielding effect of 5*f*-electrons. This is known as **actinoid contraction**.
- The allocation of electrons to the 5*f* or 6*d*-orbitals in the actinoid atoms is more uncertain than the allocation to the 4*f* or 5*d*-orbitals in the lanthanoid atoms, because the external shielding of the 5*f*-electrons is less than that of the 4*f*-electrons.

- NOTE**
- The magnetic properties of *f*-block elements are due to both the orbital motion as well as spin magnetic moment for *d*-block elements.
 - Magnetic moment for *f*-block elements, $\mu = \sqrt{4s(s+1) + l(l+1)}$ where, s is the sum of spin quantum numbers and l is the angular momentum quantum numbers.
 - Thorium is used in the atomic reactors and in the treatment of cancer, uranium is used as nuclear fuel.

DAY PRACTICE SESSION 1

GRADED QUESTIONS EXERCISE

- Electronic configuration of a transition element X in +3 oxidation state is $[\text{Ar}]3d^5$. What is its atomic number?
(a) 25 (b) 26 (c) 27 (d) 24
- Metallic radii of some transition elements are given below. Which of these elements will have highest density?

Element	Fe	Co	Ni	Cu
Metallic radii/pm	126	125	125	128

(a) Fe (b) Ni (c) Co (d) Cu
- The atomic numbers of V, Cr, Mn and Fe respectively are 23, 24, 25 and 26. Which one of these may be expected to have the highest second ionisation enthalpy?
(a) Cr (b) Mn (c) Fe (d) V
- Highest oxidation state of manganese in fluoride is +4 (MnF_4) but highest oxidation state in oxides is +7 (Mn_2O_7) because
(a) fluorine is more electronegative than oxygen
(b) fluorine does not possess *d*-orbitals
(c) fluorine stabilises lower oxidation state
(d) in covalent compounds, fluorine can form single bond only while oxygen forms double bond
- The element with which of the following outer electron configuration may exhibit the largest number of oxidation states in its compounds. → JEE Main (Online) 2013
(a) $3d^5 4s^2$
(b) $3d^8 4s^2$
(c) $3d^7 4s^2$
(d) $3d^6 4s^2$

- 6** Iron exhibits + 2 and +3 oxidation states. Which of the following statements about iron is incorrect? → AIEEE 2012
- Ferrous oxide is more basic in nature than the ferric oxide
 - Ferrous compounds are relatively more ionic than the corresponding ferric compounds
 - Ferrous compounds are less volatile than the corresponding ferric compounds
 - Ferrous compounds are more easily hydrolysed than the corresponding ferric compounds
- 7** In context with the transition elements, which of the following statements is incorrect? → JEE Main 2009
- In addition to the normal oxidation state, the zero oxidation state is also shown by these elements in complexes
 - In the highest oxidation states, the transition metal shows basic character and form cationic complexes
 - In the highest oxidation states of the first five transition elements (Sc to Mn), all the 4s and 3d-electrons are used for bonding
 - Once the d^5 configuration is exceeded, the tendency to involve all the 3d-electrons in bonding decreases
- 8** Four successive members of the first row transition elements are listed below with atomic numbers. Which one of them is expected to have the highest $E_{M^{3+}/M^{2+}}^\circ$ value? → JEE Main (Online) 2013
- Mn (Z = 25)
 - Fe (Z = 26)
 - Co (Z = 27)
 - Cr (Z = 24)
- 9** The correct order of $E_{M^{2+}/M}^\circ$ values with negative sign for the four successive elements Cr, Mn, Fe and Co is → AIEEE 2010
- Mn > Cr > Fe > Co
 - Cr > Fe > Mn > Co
 - Fe > Mn > Cr > Co
 - Cr > Mn > Fe > Co
- 10** Atomic number of an element is 26. The element shows
- ferromagnetism
 - diamagnetism
 - paramagnetism
 - None of these
- 11** The magnetic moment of a transition metal of 3d-series is 6.92 BM. Its electronic configuration would be
- $3d^4 4s^2$
 - $3d^5 4s^1$
 - $3d^8 4s^1$
 - $3d^5 4s^0$
- 12** The magnetic moment is associated with its spin angular momentum and orbital angular momentum. Spin only magnetic moment value of Cr^{3+} ion is
- 2.87 BM
 - 3.87 BM
 - 3.47 BM
 - 3.57 BM
- 13** The pair having the same magnetic moment is [at. no. Cr = 24, Mn = 25, Fe = 26 and Co = 27] → JEE Main 2016
- $[Cr(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{2+}$
 - $[Mn(H_2O)_6]^{2+}$ and $[Cr(H_2O)_6]^{2+}$
 - $[CoCl_4]^{2-}$ and $[Fe(H_2O)_6]^{2+}$
 - $[Cr(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$
- 14** Which of the following compounds is not coloured?
- Na_2CuCl_4
 - Na_2CdCl_4
 - $FeSO_4$
 - VI_3
- 15** Among the following, the coloured compound is
- CuCl
 - $K_3[Cu(CN)_4]$
 - CuF_2
 - $[Cu(CH_3CN)_4]BF_4$
- 16** Which pair of compounds is expected to show similar colour in aqueous medium?
- $FeCl_3$ and $CuCl_2$
 - $VOCl_2$ and $CuCl_2$
 - $VOCl_2$ and $FeCl_2$
 - $FeCl_2$ and $MnCl_2$
- 17** Identify the incorrect statement. → JEE Main (Online) 2013
- Cu_2O is colourless
 - Copper (I) compounds are colourless except where colour results from charge transfer.
 - Copper (I) compounds are diamagnetic
 - Cu_2S is black
- 18** The ability of d-block elements to form complexes is due to
- small and highly charged ions
 - vacant low energy orbitals to accept lone pair of electrons from ligands
 - Both (a) and (b) are correct
 - None of the above is correct
- 19** Which one of the following characteristics of the transition metals is associated with their catalytic activity?
- Colour of hydrated ions
 - Variable oxidation states
 - High enthalpy of atomisation
 - Paramagnetic behaviour
- 20** Which of the following arrangements does not represent the correct order of the property stated against it? → JEE Main (Online) 2013
- $V^{2+} < Cr^{2+} < Mn^{2+} < Fe^{2+}$: paramagnetic behaviour
 - $Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+}$: ionic size
 - $Co^{3+} < Fe^{3+} < Cr^{3+} < Sc^{3+}$: stability in aqueous solution
 - $Sc < Ti < Cr < Mn$: number of oxidation states
- 21** Which of the following ions will finally give a black precipitate with Ag^+ ion?
- SO_3^{2-}
 - Br^-
 - CrO_4^{2-}
 - $S_2O_3^{2-}$
- 22** Compound A on strong heating gives two oxides of sulphur. If aqueous NaOH solution is added to the aqueous solution of A, a dirty green precipitate is formed which starts turning brown on exposure to air. Compound A is
- ferrous hydroxide
 - ferric sulphate
 - ferrous sulphate
 - ferric oxide
- 23** For the given aqueous reaction which of the statement is not true?
- $$KI + K_3[Fe(CN)_6] \xrightarrow{\text{Dilute } H_2SO_4} \text{Brownish yellow solution}$$
- $$\downarrow ZnSO_4$$
- White precipitate + Brownish yellow filtrate
- $$\downarrow Na_2S_2O_3$$
- Colourless solution. → AIEEE 2012
- The first reaction is a redox reaction
 - White ppt. is $Zn_3[Fe(CN)_6]_2$
 - Addition of filtrate to starch solution gives blue colour
 - White ppt. is soluble in NaOH solution

- 24** $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ on heating gives a gas which is also given by
 (a) heating NH_4NO_2 (b) heating NH_4NO_3
 (c) $\text{Mg}_3\text{N}_2 + \text{H}_2\text{O}$ (d) $\text{Na} + \text{H}_2\text{O}_2$

- 25** In alkaline H_2O_2 , $\text{Cr}_2\text{O}_7^{2-}$ changes to tetraperoxo species ... having oxidation number of Cr as ...
 (a) CrO_4^{2-} , 6 (b) CrO_5 , 6
 (c) CrO_8^{3-} , 5 (d) CrO_8^{3-} , 11

- 26** Potassium dichromate when heated with concentrated sulphuric acid and a soluble chloride, gives brown-red vapours of
 → JEE Main (Online) 2013
 (a) CrO_3 (b) CrCl_3
 (c) CrO_2Cl_2 (d) Cr_2O_3

- 27** An explosion takes place when conc. H_2SO_4 is added to KMnO_4 . Which of the following is formed?
 (a) Mn_2O_7 (b) MnO_2
 (c) MnSO_4 (d) Mn_2O_3

- 28** One of the products formed due to the reaction between KMnO_4 and HCl is
 (a) red liquid (b) MnO_2
 (c) greenish yellow gas (d) HClO_4

- 29** Which one of the following compounds does not decolourise an acidified aqueous solution of KMnO_4 ?
 (a) Sulphur dioxide (b) Ferric chloride
 (c) Hydrogen peroxide (d) Ferrous sulphate

- 30** MnO_4^- on reduction in acidic medium forms
 (a) MnO_2 (b) Mn^{2+} (c) MnO_4^{2-} (d) Mn

- 31** When MnO_2 is fused with KOH , a coloured compound is formed, the product and its colour is
 (a) K_2MnO_4 , purple colour (b) KMnO_4 , purple
 (c) Mn_2O_3 , brown (d) Mn_3O_4 , black

- 32** The colour of KMnO_4 is due to
 → JEE Main 2015
 (a) $M \rightarrow L$ charge transfer transition
 (b) $d-d$ transition
 (c) $L \rightarrow M$ charge transfer transition
 (d) $\sigma-\sigma$ transition

- 33** When a small amount of KMnO_4 is added to concentrated H_2SO_4 , a green oily compound is obtained which is highly explosive in nature. Compound may be
 → JEE Main (Online) 2013
 (a) MnSO_4 (b) Mn_2O_7
 (c) MnO_2 (d) Mn_2O_3

- 34** The electronic configuration of Eu (at. no. 63) and Tb (at. no. 65) are
 (a) $[\text{Xe}]4f^6 5d^1 6s^2$ and $[\text{Xe}]4f^9 6s^2$
 (b) $[\text{Xe}]4f^6 5d^1 6s^2$ and $[\text{Xe}]4f^8 5d^1 6s^2$
 (c) $[\text{Xe}]4f^7 6s^2$ and $[\text{Xe}]4f^9 6s^2$
 (d) $[\text{Xe}]4f^7 5s^2$ and $[\text{Xe}]4f^8 5d^1 6s^2$

- 35** The outer electron configuration of Gd (atomic number 64) is
 → AIEEE 2011
 (a) $4f^3 5d^5 6s^2$ (b) $4f^8 5d^0 6s^2$
 (c) $4f^4 5d^4 6s^2$ (d) $4f^7 5d^1 6s^2$

- 36** Arrange Ce^{3+} , La^{3+} , Pm^{3+} and Yb^{3+} in the increasing order of their ionic radii.

- (a) $\text{Yb}^{3+} < \text{Pm}^{3+} < \text{Ce}^{3+} < \text{La}^{3+}$
 (b) $\text{Ce}^{3+} < \text{Yb}^{3+} < \text{Pm}^{3+} < \text{La}^{3+}$
 (c) $\text{Yb}^{3+} < \text{Pm}^{3+} < \text{La}^{3+} < \text{Ce}^{3+}$
 (d) $\text{Pm}^{3+} < \text{La}^{3+} < \text{Ce}^{3+} < \text{Yb}^{3+}$

- 37** Cerium ($Z = 58$) is an important member of the lanthanides. Which of the following statements about cerium is incorrect?

- (a) The common oxidation states of cerium are +3 and +4
 (b) The +3 oxidation state of cerium is more stable than +4 oxidation state
 (c) The +4 oxidation state of cerium is not known in solutions
 (d) Cerium (IV) acts as an oxidising agent

- 38** In context of the lanthanoids, which of the following statements is not correct?
 → AIEEE 2011

- (a) There is a gradual decrease in the radii of the members with increasing atomic number in the series
 (b) All the members exhibit +3 oxidation state
 (c) Because of similar properties the separation of lanthanoids is not easy
 (d) Availability of 4f-electrons results in the formation of compounds in +4 state for all the members of the series

- 39** Knowing that the chemistry of lanthanoids (Ln) is dominated by its +3 oxidation state, which of the following statements is incorrect?
 → JEE Main 2009

- (a) Because of the large size of the Ln (III) ions the bonding in its compounds is predominantly ionic in character
 (b) The ionic sizes of Ln (III) decrease in general with increasing atomic number
 (c) Ln (III) compounds are generally colourless
 (d) Ln (III) hydroxide are mainly basic in character

- 40** Identify the incorrect statement among the following.

- (a) d-block elements show irregular and erratic chemical properties among themselves
 (b) La and Lu have partially filled d-orbitals and no other partially filled orbitals
 (c) The chemistry of various lanthanoids is similar
 (d) 4f and 5f-orbitals are equally shielded

- 41** Match the properties in Column I with the metals given in Column II.

	Column I	Column II
A.	A element which can show +8 oxidation state	1. Mn
B.	3d-block element that can show upto +7 oxidation state	2. Cr
C.	3d-block element with highest melting point	3. Os
D.	Radioactive lanthanoid	4. Pm

Codes

	A	B	C	D		A	B	C	D
(a)	3	1	2	4	(b)	1	2	4	3
(c)	2	4	3	1	(d)	2	3	4	1

Direction (Q. No 42-45) In the following question, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct answer out of the following choices.

- (a) Both A and R are true and R is correct explanation of A
- (b) Both A and R are true but R is not correct explanation of A
- (c) A is true but R is false
- (d) Both A and R are false

42 Assertion (A) Separation of Zr and Hf is difficult.

Reason (R) Because Zr and Hf lie in the same group of the periodic table.

43 Assertion (A) Actinoids form relatively more stable complexes as compared to lanthanoids.

Reason (R) Actinoids can utilise their 5f-orbitals along with 6d-orbitals in bonding but lanthanoids do not use their 4f-orbital for bonding.

44 Assertion (A) To a solution of potassium chromate, if a strong acid is added, it changes its colour from yellow to orange.

Reason (R) The colour change is due to the change in oxidation state of potassium chromate.

45. Assertion (A) Out of Mn^{2+} , Fe^{2+} and Cr^{2+} , Mn^{2+} is readily oxidised.

Reason (R) Mn^{2+} is more stable than Fe^{2+} and Cr^{2+} due to completely filled d-orbitals.

DAY PRACTICE SESSION 2

PROGRESSIVE QUESTIONS EXERCISE

1 Among $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (A), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (B), $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (C), $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ (D) isomorphous salts are

- (a) A and C
- (b) A and D
- (c) C and B
- (d) A and B

2 Choose the correctly paired gaseous cation and its magnetic (spin only) moment in (B.M).

- (a) Ti^{2+} , 3.87 BM
- (b) Cr^{2+} , 4.90 BM
- (c) Co^{3+} , 3.87 BM
- (d) Mn^{2+} , 4.90 BM

3 Among the following compounds, the one which is both paramagnetic and coloured is

- (a) $\text{K}_2\text{Cr}_2\text{O}_7$
- (b) $(\text{NH}_4)_2[\text{TiCl}_2]$
- (c) VOSO_4
- (d) $\text{K}_3[\text{Cu}(\text{CN})_4]$

4 MnO_4^- is of intense pink colour, though Mn is in (+7) oxidation state. It is due to

- (a) oxygen gives colour to it
- (b) charge transfer where oxygen gives its electron to Mn making it Mn (VI) hence, coloured
- (c) charge transfer when Mn gives its electron to oxygen
- (d) None of the above

5 Which one of the following does not correctly represent the correct order of the property indicated against it?

- (a) $\text{Ti} < \text{V} < \text{Cr} < \text{Mn}$ increasing number of oxidation states
- (b) $\text{Ti}^{3+} < \text{V}^{3+} < \text{Cr}^{3+} < \text{Mn}^{3+}$ increasing magnetic moment
- (c) $\text{Ti} < \text{V} < \text{Cr} < \text{Mn}$ increasing melting point
- (d) $\text{Ti} < \text{V} < \text{Mn} < \text{Cr}$ increasing 2nd ionisation enthalpy

6 When a certain compound X (used in laboratory for analysis) is added to copper sulphate solution a yellow-brown precipitate is obtained which turns white on addition of excess of $\text{Na}_2\text{S}_2\text{O}_3$ solution.

On addition to Ag^+ ion solution, a yellow curdy precipitate is obtained which is insoluble in NH_4OH . The X is

- (a) H_2S
- (b) HCl
- (c) KI
- (d) NaCN

7 Amongst the following the lowest degree of paramagnetism per mole of the compound at 298 K will be shown by

- (a) $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$
- (b) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
- (c) $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$
- (d) $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$

8 Lanthanoid contraction is caused due to

- (a) the appreciable shielding on outer electrons by 4f-electrons from the nucleus
- (b) the appreciable shielding on outer electrons by 5d-electrons from the nucleus
- (c) the same effective nuclear charge from Ce to Lu
- (d) the imperfect shielding on outer electrons by 4f-electrons from the nucleus

9 Larger number of oxidation states are exhibited by the actinoids than those by the lanthanoids, the main reason being

- (a) 4f-orbitals are more diffused than the 5f-orbitals
- (b) lesser energy difference between 5f and 6d than between 4f and 5d-orbitals
- (c) more energy difference between 5f and 6d than between 4f and 5d-orbitals
- (d) more reactive nature of the actinoids than the lanthanoids

10 A red solid is insoluble in water however, it becomes soluble, if some KI is added to water. Heating the red solid in a test tube results in liberation of some violet coloured fumes and droplets of a metal appear on the cooler parts of the test tube. The red solid is

- (a) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$
- (b) HgI_2
- (c) Hg
- (d) Pb_3O_4

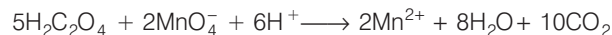
11 Copper exhibits only +2 oxidation state in its stable compounds. Why?

- (a) Copper is transition metal in +2 state
 (b) +2 state compounds of copper are formed by exothermic reactions
 (c) Electron configuration of copper in +2 state is [Ar] 3d⁹, 4s⁰
 (d) Copper gives coloured compounds in +2 state

12 KMnO₄ can be prepared from K₂MnO₄ as per the reaction, 3MnO₄²⁻ + 2H₂O → 2MnO₄⁻ + MnO₂ + 4OH⁻. The reaction can go completion by removing OH⁻ ions by adding

- (a) HCl (b) KOH (c) CO₂ (d) SO₂

13 A 0.081 g sample of pyrolusite ore (impure MnO₂) is treated with 1.651 g of oxalic acid (H₂C₂O₄ · H₂O) in an acidic medium. Following this reaction the excess oxalic acid is titrated with 30.6 mL of 0.1 M KMnO₄, the percentage of MnO₂ in the ore will be (Mn = 55)



- (a) 25% (b) 50%
 (c) 70% (d) 82%

14 Which of the following statements is not true?

- (a) On passing H₂S through acidified K₂Cr₂O₇ solution, a milky colour is observed
 (b) Na₂Cr₂O₇ is preferred over K₂Cr₂O₇ in volumetric analysis
 (c) K₂Cr₂O₇ solution in acidic medium is orange
 (d) K₂Cr₂O₇ solution becomes yellow on increasing the pH beyond 7

15 Cuprous ion is colourless while cupric ion is coloured because

- (a) both have half-filled *p* and *d*-orbitals
 (b) cuprous ion has incomplete *d*-orbital and cupric ion has a complete *d*-orbital
 (c) both have unpaired electrons in the *d*-orbitals
 (d) cuprous ion has a completely filled *d*-orbital and cupric ion has an incompletely filled *d*-orbital

ANSWERS

SESSION 1

1 (b)	2 (d)	3 (a)	4 (d)	5 (a)	6 (d)	7 (b)	8 (c)	9 (a)	10 (a)
11 (b)	12 (b)	13 (a)	14 (b)	15 (c)	16 (b)	17 (a)	18 (c)	19 (b)	20 (a)
21 (d)	22 (c)	23 (b)	24 (a)	25 (c)	26 (c)	27 (a)	28 (c)	29 (b)	30 (b)
31 (a)	32 (c)	33 (b)	34 (c)	35 (d)	36 (a)	37 (a)	38 (d)	39 (c)	40 (d)
41 (a)	42 (b)	43 (a)	44 (c)	45 (d)					

SESSION 2

1 (a)	2 (b)	3 (c)	4 (b)	5 (c)	6 (c)	7 (b)	8 (d)	9 (b)	10 (b)
11 (b)	12 (c)	13 (d)	14 (b)	15 (d)					

Hints and Explanations

SESSION 1

1 Electronic configuration of transition element X in +3 oxidation state = [Ar]3d⁵

⇒ It means, it loses 3e⁻ to attain +3 oxidation state.

∴ Electronic configuration of element X in ground state, = [Ar]3d⁶4s²

This configuration is of iron which has atomic number = 26

2 Density = mass/volume. As we move from Fe to Cu, mass increases and volume decreases. Hence, density increases [Fe(7.87), Co(8.90), Ni(8.91), Cu(8.95)]. Increase in mass in case of Cu dominates over small increases in volume.

3 The electronic configuration of Cr = 3d⁵4s¹; After removing 4s¹-electron, the next electron is to be removed from relatively more stable half-filled 3d⁵-subshell, which will require more energy for its ionisation.

4 Highest oxidation state of manganese in fluoride is +4 (MnF₄) but highest oxidation state in oxides is +7 (Mn₂O₇). The reason is that in covalent compounds fluorine can form single bond while oxygen forms double bond.

5 Due to the presence of maximum number of unpaired electrons, element having 3d⁵, 4s² (Mn), configuration may exhibit the largest number of oxidation states in its compounds.

6 (a) FeO > Fe₂O₃ (basic character). Thus, the statement is correct.

(b) FeCl₂ > FeCl₃ (ionic nature), larger the charge greater the polarising power thus, greater the covalent nature. Thus, the statement is correct.

(c) Fe²⁺ salts are more ionic thus, less volatile than Fe³⁺ salts. Thus, the statement is correct.

(d) Greater the covalent nature, more easily they are hydrolysed. Thus, FeCl₃ is more hydrolysed than FeCl₂. Thus, the statement is incorrect.

7 As oxidation state increases, electronegativity increases thus, acidic character increases and not the basic character.

8 $E_{M^{3+}/M^{2+}}$ value is highest for $\text{Co}^{3+} / \text{Co}^{2+}$ ion, because of the extra stability of $\text{Co}^{2+} (d^6)$ ion than $\text{Co}^{3+} (d^7)$.

9 Usually across the first transition series, the negative values for $E_{M^{2+}/M}$ decrease except for Mn due to stable d^5 configuration. So, the correct order is $\text{Mn} > \text{Cr} > \text{Fe} > \text{Co}$.

10 Ferromagnetic substances are those substances which are strongly attracted towards magnetic field and their domain aligned in the same direction. Iron with atomic number = 26 shows ferromagnetism.

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

or $6.92 = \sqrt{n(n+2)}$
[Here, n = number of unpaired electrons]
 $n = 6$

Hence, metal = Cr = $3d^5 4s^1$

12 The electronic configuration of Cr^{3+} ion is $3d^3$. Hence, spin only magnetic moment (μ) = $\sqrt{n(n+2)}\text{BM}$ where, n = number of unpaired electrons.
 $= \sqrt{3(3+2)} = \sqrt{15} = 3.87 \text{ BM}$

13 The pair that have same number of unpaired electron will have same magnetic moment.

Complex ion	Electronic configuration of metal ion	Number of unpaired electrons (n)
$[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$	$\text{Cr}^{2+}; [\text{Ar}] 3d^4$	$\boxed{1} \boxed{1} \boxed{1} \boxed{1} \boxed{} \boxed{}; 4$
$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	$\text{Fe}^{2+}; [\text{Ar}] 3d^6$	$\boxed{1} \boxed{1} \boxed{1} \boxed{1} \boxed{1} \boxed{1}; 4$
$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$	$\text{Mn}^{2+}; [\text{Ar}] 3d^5$	$\boxed{1} \boxed{1} \boxed{1} \boxed{1} \boxed{1}; 5$
$[\text{CoCl}_4]^{2-}$	$\text{Co}^{2+}; [\text{Ar}] 3d^7$	$\boxed{1} \boxed{1} \boxed{1} \boxed{1} \boxed{1} \boxed{1}; 3$

14 Those compounds which have unpaired electrons will be coloured. Na_2CdCl_4 does not have unpaired electrons. Hence, it will be colourless.

15 In the crystalline form, CuF_2 is blue coloured as in CuF_2 , Cu^{2+} ions exist, having d^9 configuration. The unpaired electron causes colour ($d-d$) transition.

16 In VOCl_2 , V is in +4 state ($3d^1$) and in CuCl_2 , Cu is in +2 state ($3d^9$). Both have one unpaired electron hence, show similar colour.

17 Cu_2O is coloured because of the presence of one unpaired electron, which makes $d-d$ transition possible.
 $\text{Cu}^{2+} = [\text{Ar}] 3d^9$



18 Transition metals have small size and high nuclear charge. They also have vacant d -orbitals of appropriate energy which facilitate the acceptance of lone pair of electron from ligands. Thus, they have ability to form complexes.

19 Transition metals have ability to adopt variable oxidation state and to form complexes, therefore they are used as a catalyst.

20 (a) $\text{V}^{2+} = 3d^3 4s^0$ – 3 unpaired electrons
 $\text{Cr}^{2+} = 3d^4 4s^0$ – 4 unpaired electrons
 $\text{Mn}^{2+} = 3d^5 4s^0$ – 5 unpaired electrons
 $\text{Fe}^{2+} = 3d^6 4s^0$ – 4 unpaired electrons
Hence, the order of paramagnetic behaviour should be
 $\text{V}^{2+} < \text{Cr}^{2+} = \text{Fe}^{2+} < \text{Mn}^{2+}$

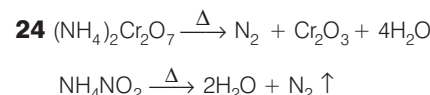
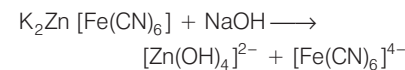
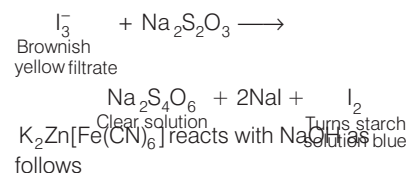
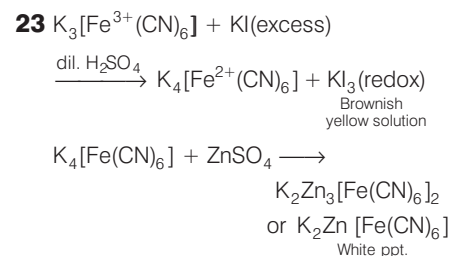
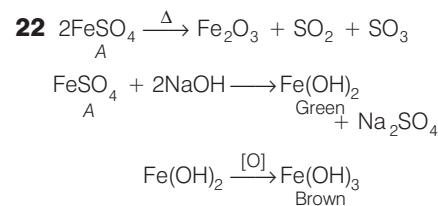
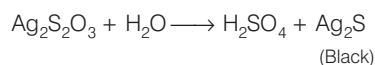
(b) Ionic size decreases from left to right in the same period.

(c) $\text{Co}^{3+} / \text{Co}^{2+} = 1.97$;
 $\text{Fe}^{3+} / \text{Fe}^{2+} = 0.77$;
 $\text{Cr}^{3+} / \text{Cr}^{2+} = -0.41$

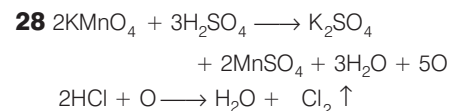
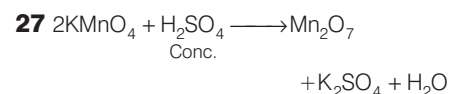
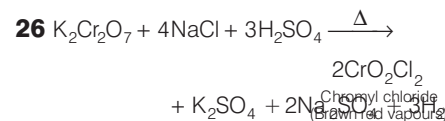
Sc^{3+} is highly stable as it has $3d^0 4s^0$ electronic configuration (it does not show +2).

(d) The oxidation states increases as we go Sc to Mn in $3d$ transition series.

21 $2\text{Ag} + \text{S}_2\text{O}_3^{2-} \longrightarrow \text{Ag}_2\text{S}_2\text{O}_3$, white ppt which readily changes to yellow, orange, brown and finally black due to formation of silver sulphide.

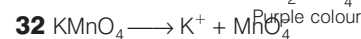
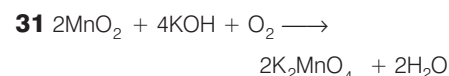


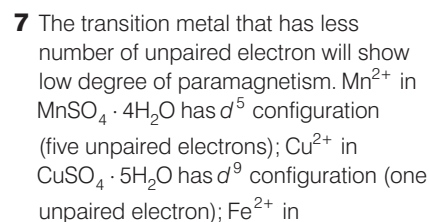
25 Tetra peroxo species $[\text{Cr}(\text{O}_2)_4]^{3-}$
Oxidation number of Cr = $x - 8 = -3$
 $x = +5$



29 FeCl_3 is not a reducing agent. KMnO_4 will not react with oxidising agent KMnO_4 and hence, no colour is discharged.

30 MnO_4^- on reduction in acidic medium forms Mn^{2+} ion.
 $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$





$\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ has d^6 configuration (four unpaired electrons); Ni^{2+} in $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ has d^2 configuration (two unpaired electrons).

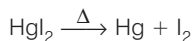
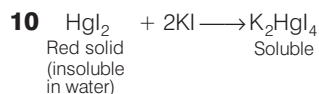
Thus, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ has lowest degree of paramagnetism.

- 8** Lanthanoid contraction is due to imperfect shielding of outer electrons by $4f$ -electrons from the nucleus.

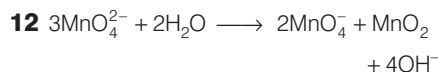
- 9** Lanthanoids $[\text{Xe}]4f^{1-14} 5d^{0-1} 6s^2$

Actinoids $[\text{Rn}] 5f^{1-14} 6d^{0-1} 7s^2$

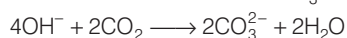
Lanthanoids and actinoids use core d and f -orbitals to show higher oxidation state. As actinoids have comparatively low energy difference between $5f$ and $6d$ -orbitals because external shielding of $5f$ electrons is less than that of the $4f$ electrons they show more oxidation states.



- 11** Copper exhibits only +2 oxidation state in its stable compounds because +2 state compounds of copper are formed by exothermic reaction.



The reaction can go completion by removing OH^- ions by adding CO_2 as it reacts with OH^- ions to form CO_3^{2-} ions.



- 13** MnO_4^- used = 30.6×0.1 millimol
 = 3.06×10^{-3} mol

2 mole of MnO_4^-

= 5 mole of $\text{H}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$

Thus, 3.06×10^{-3} mole of MnO_4^-

= 7.65×10^{-3} mol unreacted

$(\text{H}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O})$ taken

$$\frac{1.651}{108} = 1.53 \times 10^{-2} \text{ mol}$$

Used $\text{H}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ by MnO_2

$$= (1.53 \times 10^{-2} - 7.65 \times 10^{-3})$$

$$= 7.650 \times 10^{-3} \text{ mol}$$

1 mole of $\text{H}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O} \equiv$ 1 mole of MnO_2

$\therefore 7.65 \times 10^{-3}$ mole of $\text{H}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$

= 7.65×10^{-3} mole of MnO_2

= $7.65 \times 10^{-3} \times 87$ g pure MnO_2

= 0.6655 g in 0.81 g impure MnO_2

\therefore Percentage of pure

$$\text{MnO}_2 = \frac{0.6655}{0.81} \times 100 = 82.16\% \approx 82\%$$

- 14** Being hygroscopic or deliquescent sodium dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7$ cannot be used in volumetric analysis. The rest of the statements are true.

- 15** Cuprous ion is colourless while cupric ion is coloured because cuprous ion has a completely filled d -orbital, i.e. $3d^{10}, 4s^0$ configuration and cupric ion has an incompletely d -orbitals due to $3d^9, 4s^0$ configuration. So, this one unpaired electron make $d-d$ transition possible and impart colour.