DAY TWENTY SEVEN

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

Learning & Revision for the Day

- *d*-Block Elements
- Some Important Compounds of Transition Elements
- *f*-Block Elements (Inner Transition Elements)

In *d*-block elements last electron enters in penultimate $(n-1)$ *d*-orbital while in *f*-block elements last electron enters in $(n-2)$ *f*-orbital.

d-Block Elements

d-block elements are present from fourth period onwards. There are mainly three series of the transition metals, (a) 3*d*-series (Sc to Zn), (b) 4*d*-series (Y to Cd) and (c) 5*d*-series (La to Hg, omitting Ce to Lu).

d-block elements are known as **transition elements** because of their position in the periodic table is between the *s*-block and p-block elements.

Electronic Configuration

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

Transition Metals or *d*-block Elements

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

Characteristics of Transition Metals

Following one the important characteristics of transition metals:

(i) The differentiating electron, enters in d-sub-shell.

(ii) These have incomplete d-sub-shell orbitals either in ground state or in most common oxidation state.

(iii) All the transition metals are electropositive in nature.

(iv) The electronegativity and ionisation energy of transition metals are more than of s-block elements but less, than of p-block elements, thus are called transition elements.

(v) These show variable oxidation states due to involvement of ns and $(n-1)d$-electrons.

General Trends in Properties of Transition Elements

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

1. Metallic Character

Metallic character of transition elements in each series are almost similar, all are metals due to less number of electrons in outermost subshell.

2. Enthalpies of Atomisation

Transition elements exhibit higher enthalpies of atomisation because of large number of unpaired electrons in their atoms. Transition elements have very high melting and boiling points.

3. Ionisation Enthalpy

The values of ionisation enthalpy 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 an account of greater stability of s-subshell.

4. Oxidation States

Transition metals show variable oxidation states due to two incomplete outermost shells. Only stable oxidation states of the first row transition metals are given below:

$$\text{Sc } (+3),\ \text{Ti } (+4),\ \text{V } (+5),\ \text{Cr } (+3, +6),\ \text{Mn} (+2, +7),$$
$$\text{Fe } (+2, +3)\ \text{Co } (+2, +3),\ \text{Ni } (+2), \text{Cu } (+2),\ \text{Zn } (+2)$$

- 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 Stability of Higher Oxidation States

- The highest oxidation numbers are achieved in $\text{Ti}X_4$, VF_5 and CrF_6. The +7 state for Mn is not represented in simple halides but MnO_3F is known and beyond Mn no metal has a trihalide except $\text{Fe}X_3$ and CoF_3. The increasing order of oxidising power in the series is
$$\text{VO}_2^+ < \text{Cr}_2\text{O}_7^{2-} < \text{MnO}_4^-.$$
- The highest oxidation states of transition metals are found in their compounds with fluorine and oxygen only because of their higher electronegativity and smaller atomic size.

6. Standard Electrode Potentials

The 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 $(E^\circ_{M^{2+}/M})$ will be positive and reactivity will be lower and vice-versa.

7. Atomic and Ionic Radii

- In transition metals radii decreases on moving left to right in a period, because of net nuclear charge increases due to poor shielding effect. Due to this, the atomic and ionic radii for transition elements for a given series show a decreasing trend for first five elements and then becomes almost constant for next four 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 corresponding elements of $4d$-and $5d$-series have almost similar values, e.g. Zr radii - 160 pm, Hf radii-159 pm. It is due to lanthanoid contraction. Nb and Ta, Mo and W also have nearly same size due to lanthanoid contraction.

Coloured Ions

- The d-orbitals are non-degenerated in the presence of ligands. When an electron from a lower energy d-orbital is excited to a higher energy d-orbital (d-d^* transition) 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. In spite of d° it is coloured compound. This colour arises due to defects in the crystal lattice and charge transfer.

8. 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.

9. Catalytic Properties

The transition metals have incomplete outermost orbitals and ability to adopt multiple oxidation states as well as forming complexes, therefore used as a catalyst. They also provide larger surface area for the reactant to be adsorbed.

10. 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 $\mu = \sqrt{n(n+2)}$ BM.

- When a magnetic field is applied to substances, mainly two types of magnetic behaviour are observed : **diamagnetism** and **paramagnetism**. Paramagnetism is due to the presence of unpaired electrons. Each such electron has a magnetic moment associated with its spin angular momentum. If all electrons are paired, substance will be diamagnetic and magnetic moment will be zero.

11. Interstitial Compounds

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

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

(i) They have high melting points, higher than those of pure metals.
(ii) They are very hard. Some borides approach diamond in hardness.
(iii) They retain metallic conductivity.
(iv) They are chemically inert.

12. Alloy Formation

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

Some Important Compounds of Transition Elements

Some important compounds of transition elements are as follows :

1. Potassium Dichromate ($K_2Cr_2O_7$)

Preparation

$K_2Cr_2O_7$ is prepared as follows :

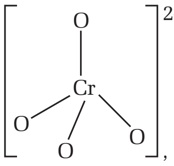
Ore Ferrochrome or chromite ($FeO\cdot Cr_2O_3$) or ($FeCr_2O_4$) is used to prepare $K_2Cr_2O_7$.

$$4FeO\cdot Cr_2O_3 + 8Na_2CO_3 + 7O_2 \longrightarrow \underset{\text{Yellow}}{8Na_2CrO_4} + 2Fe_2O_3 + 8CO_2$$

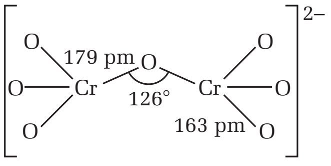
$$2Na_2CrO_4 + 2H^+ \longrightarrow \underset{\text{Orange}}{Na_2Cr_2O_7} + 2Na^+ + H_2O$$

$$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$$

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



Chromate ion
*sp*3



Dichromate ion
*sp*3

Properties

Sodium and potassium dichromates are strong oxidising agents, thus, acidified $K_2Cr_2O_7$ will oxidise iodides to iodine, sulphides to sulphur, tin (II) to tin (IV) and iron (II) salts to iron (III).

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

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

$$Cr_2O_7^{2-} + 14H^+ + 3Sn^{2+} \longrightarrow 3Sn^{4+} + 2Cr^{3+} + 7H_2O$$

Uses

$K_2Cr_2O_7$ 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 $K_2SO_4\cdot Cr_2(SO_4)_3\cdot 24H_2O$.

2. Potassium Permanganate ($KMnO_4$)

It is a salt of permanganic acid ($HMnO_4$). It can be prepared as follows :

Preparation

$KMnO_4$ can be prepared by pyrolusite ore (MnO_2) as follows :

$$2MnO_2 + 4KOH + O_2 \longrightarrow \underset{\text{Green}}{2K_2MnO_4} + 2H_2O$$

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

Commercial preparation of $KMnO_4$ takes place as follows :

$$MnO_2 \xrightarrow[\text{oxidised with air or KNO}_3]{\text{Fused with KOH,}} \underset{\text{Manganate ion}}{MnO_4^{2-}}$$

$$MnO_4^{2-} \xrightarrow[\text{(alkaline medium)}]{\text{Electrolytic oxidation}} \underset{\substack{\text{Permanganate ion}\\\text{(purple)}}}{MnO_4^-}$$

Properties

It acts as strong oxidising agent.

- In the presence of dilute H_2SO_4, $KMnO_4$ is reduced to manganous salt.

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

Acidic $KMnO_4$ solution oxidises oxalate to CO_2, iron (II) to iron (III), nitrites to nitrates and iodides to iodine. The half-reactions of reductants are

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

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

$$NO_2^- \longrightarrow NO_3^- + 2e^-$$

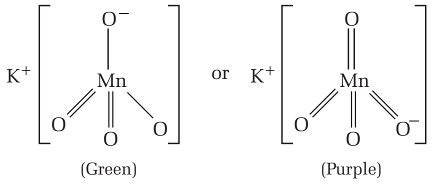
$$2I^- \longrightarrow I_2 + 2e^-$$

To acidify $KMnO_4$, only H_2SO_4 is used and not HCl or HNO_3 because HCl reacts with $KMnO_4$ and produces Cl_2 while HNO_3, itself acts as an oxidising agent.

- In alkaline medium, $KMnO_4$ is reduced to insoluble MnO_2.

$MnO_4^- + 3e^- + 2H_2O \longrightarrow MnO_2 + 4OH^-$

Alkaline or neutral $KMnO_4$ solution oxidises I^- to IO_3^-, $S_2O_3^{2-}$ to SO_4^{2-}, Mn^{2+} to MnO_2 etc.



(Green) (Purple)

Uses

(i) In laboratory preparation of Cl_2.
(ii) As an oxidising agent, disinfectant.
(iii) In making Baeyer's reagent.
(iv) Mn in MnO_4^- undergoes sp^3-hybridisation and hence, four O-atoms are arranged tetrahedrally around Mn.

Important Points about Transition Elements

- ScC_2 contains Sc^{3+} and C_2^{2-}. The extra electron lies in conduction band and makes it conductor.
- Silvering of mirror is based on reduction of ammoniacal silver nitrate solution by neutral solution of tartarate or glucose in cold.
- The transition metals except iron are resistant to corrosion. Chromium is highly corrosion resisting metal.
- $HgCl_2$ is corrosive sublimate. It is poisonous and best antidote for it is white of an egg.
- Hg_2Cl_2 is calomel. It is used for making calomel electrode, used as a reference electrode.

f-Block Elements (Inner Transition Elements)

The *f*-block consists of the two series, lanthanoids and actinoids. Lanthanoids are known as rare earth metals and actinoids are known as radioactive elements (Th to Lr).

Lanthanoids

The general configuration of lanthanoids as follows :

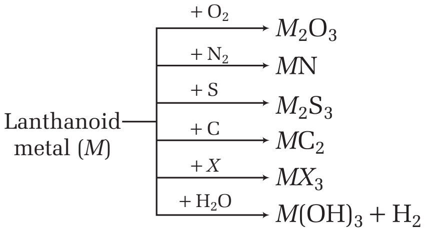
- **Electronic Configuration** : [Xe] $4f^{1-14}, 5d^{0-1}, 6s^2$.

Lanthanide Series

La	$5d^1 6s^2$	**Tb**	$4f^9 6s^2$
Ce	$4f^1 5d^1 6s^2$	**Dy**	$4f^{10} 6s^2$
Pr	$4f^3 6s^2$	**Ho**	$4f^{11} 6s^2$
Nd	$4f^4 6s^2$	**Er**	$4f^{12} 6s^2$
Pm	$4f^5 6s^2$	**Tm**	$4f^{13} 6s^2$
Sm	$4f^6 6s^2$	**Yb**	$6f^{14} 6s^2$
Eu	$4f^7 6s^2$	**Lu**	$4f^{14} 5d^1 6s^2$
Gd	$4f^7 5d^1 6s^2$		

Lanthanoid Contraction

- Atomic and ionic size, decreases from left to right, due to increase in nuclear charge. This is known as **lanthanoid contraction**. All the lanthanoids are silvery white soft metals and tarnish rapidly in air.
- Many trivalent lanthanoid ions are coloured both in the solid state and in aqueous solutions. Neither La^{3+} nor Lu^{3+} ion shows no colour but the rest do so. Lanthanoid ions with xf electrons have similar colour to those with $(14-x)$ f electrons.
- The lanthanoid ions other than the f^0 type ($La^{3+}$and Ce^{4+}) and the f^{14} type (Yb^{2+} and Lu^{3+}) are all **paramagnetic.** The paramagnetism arises to maximum in **neodymium**.
- **Oxidation states of lanthanoids** Ce^{4+} or some elements are favoured by its noble gas configuration, but it is a strong oxidant reverting to the common +3 state. The E°_{value} for Ce^{4+}/Ce^{3+} 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.
- **Chemical reactivity** are very similar with metals like alkaline earth metals.



The hydroxides are ionic and basic. The base strength decreases from $Ce(OH)_3$ to $Lu(OH)_3$.

- **Alloy of lanthanoids** are important, e.g. 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.

Actinoids

General electronic configuration of actinoids can be expressed as follows :

Electronic configuration [Rn] $5f^{0-14}, 6d^{0-2}, 7s^2$.

Actinide Series

Ac	$6d^1 7s^2$	**Bk**	$5f^9, 7s^2$
Th	$6d^2 7s^2$	**Cf**	$5f^{10} 7s^2$
Pa	$5f^2 6d^1 7s^2$	**Es**	$5f^{11} 7s^2$

U	$5f^3 6d^1 7s^2$	**Fm**	$5f^{12} 7s^2$
Np	$5f^4 6d^1 7s^2$	**Md**	$5f^{13} 7s^2$
Pu	$5f^6 7s^2$	**No**	$5f^{14} 7s^2$
Am	$5f^7 7s^2$	**Lr**	$5f^{14} 6d^1 7s^2$
Cm	$5f^7 6d^1 7s^2$		

- **Oxidation states of actinoids** are due to comparable energies of $5f$, $6d$ and $7s$ 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., unlike 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 $5f$-electrons. This is known as **actinoid contraction**.
- The allocation of electrons to the $5f$- or $6d$-orbitals in the actinoid atoms is more uncertain than the allocation to the $4f$- or $5d$-orbitals in the lanthanoid atoms, because the external shielding of the $5f$ electrons is less than that of the $4f$-electrons.
- 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,

  $$\mu_{\text{eff}} = \sqrt{4S(S+1) + L(L+1)} \text{ BM}$$

  where, S is the sum of spin quantum numbers and L is the angular momentum quantum numbers.

DAY PRACTICE SESSION 1

FOUNDATION QUESTIONS EXERCISE

1 Among the following series of transition metal ions, the one in which all metal ions have $3d^2$- electronic configuration is
(Atomic number: Ti = 22, V = 23, Cr = 24, Mn = 25)

(a) $Ti^{3+}, V^{2+}, Cr^{3+}, Mn^{4+}$
(b) $Ti^{+}, V^{4+}, Cr^{6+}, Mn^{7+}$
(c) $Ti^{4+}, V^{3+}, Cr^{2+}, Mn^{3+}$
(d) $Ti^{2+}, V^{3+}, Cr^{4+}, Mn^{5+}$

2 Which of the following elements has maximum first ionisation potential?

(a) V (b) Ti (c) Mn (d) Cr

3 For the four successive transition elements (Cr, Mn, Fe and Co), the stability of +2 oxidation state will be there in which of the following order? **→ CBSE-AIPMT 2011**
(Atomic number: Cr = 24, Mn = 25, Fe = 26, Co = 27)

(a) Fe > Mn > Co > Cr
(b) Co > Mn > Fe > Cr
(c) Cr > Mn > Co > Fe
(d) Mn > Fe > Cr > Co

4 Of the following outer electronic configurations of atoms, the highest oxidation state is achieved by which one of them?

(a) $(n-1)d^8 ns^2$
(b) $(n-1)d^5 ns^1$
(c) $(n-1)d^3 ns^2$
(d) $(n-1)d^5 ns^2$

5 Among the following pair of ions, the lower oxidation state in aqueous solution is more stable than the order is

(a) V^{2+}, VO^{2+} (b) Cr^{2+}, Cr^{3+} (c) Ti^{+}, Ti^{3+} (d) Cu^{+}, Cu^{2+}

6 The element with which of the following outer electronic configuration may exhibit the largest number of oxidation states in its compounds

(a) $3d^5 4s^2$
(b) $3d^8 4s^2$
(c) $3d^7 4s^2$
(d) $3d^6 4s^2$

7 Which of the following pair has the same size? **→ CBSE-AIPMT 2010**

(a) Fe^{2+}, Ni^{2+}
(b) Zr^{4+}, Ti^{4+}
(c) Zr^{4+}, Hf^{4+}
(d) Zn^{2+}, Hf^{4+}

8 Amongst TiF_6^{2-}, CoF_6^{3-}, Cu_2Cl_2 and $NiCl_4^{2-}$, the colourless species are (atomic number Ti = 22, Co = 27, Cu = 29, Ni = 28)

(a) CoF_6^{3-} and $NiCl_4^{2-}$
(b) TiF_6^{2-} and CoF_6^{3-}
(c) Cu_2Cl_2 and $NiCl_4^{2-}$
(d) TiF_6^{2-} and Cu_2Cl_2

9 Cuprous ion is colourless, while cupric ion is coloured because

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

10 Which of the following compounds, on reaction with NaOH and Na_2O_2, gives yellow colour?

(a) $Zn(OH)_2$ (b) $Al(OH)_3$ (c) $Cr(OH)_3$ (d) $CaCO_3$

11 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 when Mn gives its electron to oxygen
(c) charge transfer when oxygen gives its electron to Mn making it Mn (+ VI)
(d) presence of unpaired electrons

12 Which of the following compounds is not coloured?

(a) Na_2CuCl_4 (b) Na_2CdCl_4 (c) $FeSo_4$ (d) VI_3

13 The colour of the solution obtained by adding excess of KI in the solution of $HgCl_2$ is

(a) orange (b) brown (c) red (d) colourless

14 The colour of light absorbed by an aqueous solution of $CuSO_4$ is

(a) orange-red (b) blue-green
(c) yellow (d) violet

15 The formula of green vitriol is

(a) $FeSO_4 \cdot 7H_2O$ (b) $MgSO_4 \cdot 7H_2O$
(c) $ZnSO_4 \cdot 7H_2O$ (d) $CuSO_4 \cdot 5H_2O$

16 The aqueous solution containing which one of the following ions will be colourless? (Atomic number of Sc = 21, Fe = 26, Ti = 22, Mn = 25)

(a) Sc^{3+} (b) Fe^{2+} (c) Ti^{3+} (d) Mn^{2+}

17 Which of the following ions will finally give a black precipitate with Ag^+ ion?

(a) SO_3^{2-} (b) Br^- (c) CrO_4^{2-} (d) $S_2O_3^{2-}$

18 The catalytic activity of the transition metals and their compounds is ascribed to their

(a) magnetic behaviour
(b) chemical reactivity
(c) unfilled d-orbitals
(d) ability to adopt multiple oxidation states and their complexing ability

19 Among the following, compound that is both paramagnetic and coloured is

(a) $K_2Cr_2O_7$ (b) $(NH_4)_2[TiCl_6]$ (c) $VOSO_4$ (d) $K_3[Cu(CN)_4]$

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

(a) $MnSO_4 \cdot 4H_2O$ (b) $NiSO_4 \cdot 6H_2O$
(c) $FeSO_4 \cdot 6H_2O$ (d) $CuSO_4 \cdot 5H_2O$

21 Which of the following has highest magnetic moment?

(a) Ti^{3+} (b) Sc^{3+} (c) Mn^{2+} (d) Zn^{2+}

22 The spin only magnetic moment of Mn^{4+} ion is nearly

(a) 3 BM (b) 6 BM (c) 4 BM (d) 5 BM

23 Which shows maximum magnetic moment among the bivalent ions of the first transition series?

(a) Fe^{2+} (b) Co^{2+} (c) Ni^{2+} (d) Mn^{2+}

24 Which one of the following ions exhibits *d-d* transition and paramagnetism as well? → **NEET 2018**

(a) MnO_4^- (b) $Cr_2O_7^{2-}$ (c) CrO_4^{2-} (d) MnO_4^{2-}

25 Paramagnetism is given by the relation $\mu = 2\sqrt{S(S+1)}$ magnetons where '*S*' is the total spin. On this basis, the paramagnetism of Cu^+ ion is

(a) 3.88 magnetons (b) 2.83 magnetons
(c) 1.41 magnetons (d) zero

26 The magnetic moment of a transition metal of 3*d* series is 6.92 BM. Its electronic configuration would be

(a) $3d^4 4s^2$ (b) $3d^5 4s^1$ (c) $3d^6 4s^1$ (d) $3d^5 4s^0$

27 The *d*-electron configuration of Cr^{2+}, Mn^{2+}, Fe^{2+} and Co^{2+} are d^4, d^5, d^6 and d^7 respectively. Which one of the following will exhibit minimum paramagnetic behaviour?
(Atomic number of Cr = 24, Mn = 25, Fe = 26, Co = 27)

→ **CBSE-AIPMT 2011**

(a) $[Fe(H_2O)_6]^{2+}$ (b) $[Co(H_2O)_6]^{2+}$
(c) $[Cr(H_2O)_6]^{2+}$ (d) $[Mn(H_2O)_6]^{2+}$

28 Which of the following statements about the interstitial compounds is incorrect? → **NEET 2013**

(a) They are chemically reactive
(b) They are much harder than the pure metal
(c) They have higher melting points that the pure metal
(d) They retain metallic conductivity

29 Identify the alloy containing a non-metal as a constituent in it. → **CBSE-AIPMT 2012**

(a) Invar (b) Steel (c) Bell metal (d) Bronze

30 Acidified solution of potassium dichromate on treatment with H_2O_2 yields

(a) $CrO_5 + H_2O$ (b) $H_2Cr_2O_7 + H_2O + O_2$
(c) $Cr_2O_3 + H_2O + O_2$ (d) $CrO_3 + H_2O + O_2$

31 Which one of the following statements is correct when SO_2 is passed through acidified $K_2Cr_2O_7$ solution?

→ **NEET 2016, Phase I**

(a) The solution is decolourised
(b) SO_2 is reduced
(c) Green $Cr_2(SO_4)_3$ is formed
(d) The solution turns blue

32 Which of the statements is not true? → **CBSE-AIPMT 2012**

(a) On passing H_2S through acidified $K_2Cr_2O_7$ solution, a milky colour is observed
(b) $Na_2Cr_2O_7$ is preferred over $K_2Cr_2O_7$ in volumetric analysis
(c) $K_2Cr_2O_7$ solution in acidic medium is orange
(d) $K_2Cr_2O_7$ solution becomes yellow on increasing the pH beyond 7

33 $4K_2Cr_2O_7 \xrightarrow{\Delta} 4K_2CrO_4 + 3O_2 + X$

In the above reaction, *X* is

(a) CrO_3 (b) Cr_2O_7 (c) Cr_2O_3 (d) CrO_5

34 Acidified potassium permanganate solution is decolourised by

(a) bleaching power (b) white vitriol
(c) Mohr's salt (d) microcosmic salt

35 Name the gas that can readily decolourise acidified $KMnO_4$ solution. → **NEET 2017**

(a) CO_2 (b) SO_2 (c) NO_2 (d) P_2O_5

36 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

37 Which of the following lanthanoid ions is diamagnetic?
(Atomic numbers : Ce = 58, Sm = 62, Eu = 63, Yb = 70)

(a) Sm^{2+} (b) Eu^{2+} → **NEET 2013**

(c) Yb^{2+} (d) Ce^{2+}

38 The electronic configurations of Eu (Atomic no. 63), Gd (Atomic no. 64) and Tb (Atomic no. 65) are → **NEET 2016, Phase I**

(a) [Xe] $4f^6 5d^1 6s^2$, [Xe] $4f^7 5d^1 6s^2$ and [Xe] $4f^9 6s^2$
(b) [Xe] $4f^6 5d^1 6s^2$, [Xe] $4f^7 5d^1 6s^2$ and [Xe] $4f^8 5d^1 6s^2$
(c) [Xe] $4f^7 6s^2$, [Xe] $4f^7 5d^1 6s^2$ and [Xe] $4f^9 6s^2$
(d) [Xe] $4f^7 6s^2$, [Xe] $4f^8 6s^2$ and [Xe] $4f^8 5d^1 6s^2$

39 Which of the following ions will exhibit colour in aqueous solutions? → **CBSE-AIPMT 2010**

(a) La^{3+} ($Z = 57$) (b) Ti^{3+} ($Z = 22$)
(c) Lu^{3+} ($Z = 71$) (d) Sc^{3+} ($Z = 21$)

40 The electronic configuration of actinides cannot be assigned with degree of certainty because of

(a) small energy difference between $5f$- and $6d$- levels
(b) overlapping of inner orbitals
(c) free movement of electrons overall the orbitals
(d) All of the above

41 The reason for greater range of oxidation states in actinoids is attributed to → **NEET 2017**

(a) the radioactive nature of actinoids
(b) actinoid contraction
(c) $5f$, $6d$ and $7s$ levels having comparable energies
(d) $4f$ and $5d$ levels being close in energies

42. Which among the following show more number of oxidation states?

(a) Lanthanoids (b) Actinoids
(c) Alkali metals (d) Alkaline earth metals

DAY PRACTICE SESSION 2

PROGRESSIVE QUESTIONS EXERCISE

1 What is the general outer configuration of the coinage metal?

(a) ns^2, np^6 (b) $(n-1)d^{10}, ns^1$
(c) $(n-1)d^{10}, ns^2$ (d) $(n-)d^1, ns^2$

2 Iron exhibits + 2 and+3 oxidation states. Which of the following statements about iron is incorrect?

(a) Ferrous oxide is more basic in nature than the ferric oxide
(b) Ferrous compounds are relatively more ionic than the corresponding ferric compounds
(c) Ferrous compounds are less volatile than the corresponding ferric compounds
(d) Ferrous compounds are more easily hydrolysed than the corresponding ferric compounds

3 Second ionisation energies of chromium and copper are larger than those of their neighbouring elements (V, Mn, Ni, Zn). It is due to the fact that

(a) second electron in each case is removed from $4s$-orbital
(b) second electron is removed from stable half-filled $3d$-sub-orbit in case of chromium and from stable completely filled $3d$ sub-orbit in case of copper
(c) electrode potential of these elements (Cr and Cu) are higher than those of their neighbouring elements
(d) their atomic radii are different due to screening effect

4 Oxidation state of the final product of chromiun in the reaction between $K_2Cr_2O_7$ and KI in acidic medium is

(a) + 4 (b) + 6
(c) + 2 (d) + 3

5 Which of the following transition metal ions shows highest (largest) ionic radii in its most common oxidation state?

(a) Sc (b) V
(c) Cr (d) Mn

6 Ti^{2+} is purple, while Ti^{4+} is colourless, because

(a) there is no crystal field effect in Ti^{4+}
(b) Ti^{2+} has $3d^2$ configuration
(c) Ti^{4+} has $3d^2$ configuration
(d) Ti^{4+} is a very small cation when compared to Ti^{2+} and hence, does not absorb any radiation

7 Of the ions Zn^{2+}, Ni^{2+} and Cu^{3+} (At. nos Zn = 30, Ni = 28, Cr = 24)

(a) Only Zn^{2+} is colourless and Ni^{2+} and Cr^{3+} are coloured
(b) All there are colourless
(c) All three are coloured
(d) Only Ni^{2+} is coloured and Zn^{2+} and Cr^{3+} are colourless

8 Select the incorrect statement(s).

(a) Ionisation energies of $5d$-elements are greater than those of $3d$ and $4d$ elements
(b) Cu(I) is diamagnetic while Cu(II) is paramagnetic
(c) $[Ti(H_2O)_6]^{3+}$ is coloured while $[Sc(H_2O)_6]^{3+}$ is colourless
(d) Transition elements cannot form complexes

9 For the given aqueous reaction which of the statement is not true?

$$\mathrm{KI} + \mathrm{K_3\,[Fe(CN)_6]} \xrightarrow{\mathrm{Dil\cdot H_2SO_4}} \text{Brownish yellow solution}$$

$$\downarrow \mathrm{ZnSO_4}$$

$$\text{White precipitate} + \text{Brownish yellow filtrate}$$

$$\downarrow \mathrm{Na_2S_2O_3}$$

$$\text{Colourless solution.}$$

(a) The first reaction is a redox reaction.
(b) White ppt. is $Zn_3[Fe(CN)_6]_2$
(c) Addition of filtrate to starch solution gives blue colour.
(d) White ppt. is soluble in NaOH solution

10 In context of the lanthanoids, which of the following statements is not correct?

(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 4*f* electrons results in the formation of compounds in + 4 state for all the members of the series.

(a) Zn, Cu, Cd
(b) Fe, Co, Ni
(c) Zn, Hg, Se
(d) All of these

11 Select the coloured and paramagnetic ions

(a) Cu^+, Zn^{2+}, Cd^{2+}
(b) Sc^{3+}, Ti^{4+}, V^{5+}
(c) Cu^{2+}, Cr^+, Mn^2
(d) Ni^{2+}, Cu^+, Hg^{2+}

12 Magnetic moment of Cr $(Z = 24)$, Mn^+ $(Z = 25)$ and Fe^{2+} $(Z = 26)$ are x, y, z. They are in order

(a) $x < y < z$
(b) $x = y < z$
(c) $z < x = y$
(d) $x = y = z$

13 Which of the following statements is not correct?

(a) $La(OH)_3$ is less basic than $Lu(OH)_3$
(b) In lanthanide series ionic radius of Ln^{3+} ion decreases
(c) La is actually an element of transition series rather lanthanide
(d) Atomic radius of Zr and Hf are same because of lanthanide contraction

14 Magnetic moment 2.84 BM is given by:
(Atomic number of Ni = 28, Ti = 22, Cr = 24, Co = 27)

→ CBSE-AIPMT 2015, 2014

(a) Ni^{2+}
(b) Ti^{3+}
(c) Cr^{2+}
(d) Co^{2+}

15 A magnetic moment of 1.73 BM will be shown by one among the following.

(a) $[Ni(CN)_4]^{2-}$
(b) $TiCl_4$
(c) $[CoCl_6]^{4-}$
(d) $[Cu(NH_3)_4]^{2+}$

16 Match the metal ions given in Column I with the spin magnetic moments of the ions given in Column II and assign the correct code : **→ NEET 2018**

	Column I		Column II
1.	Co^{3+}	i.	$\sqrt{8}$ BM
2.	Cr^{3+}	ii.	$\sqrt{35}$ BM
3.	Fe^{3+}	iii.	$\sqrt{3}$ BM
4.	Ni^{2+}	iv.	$\sqrt{24}$ BM
		v.	$\sqrt{15}$ BM

	1	2	3	4
(a)	iv	i	ii	iii
(b)	i	ii	iii	iv
(c)	iv	v	ii	i
(d)	iii	v	i	ii

ANSWERS

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

SESSION 2	**1** (b)	**2** (d)	**3** (b)	**4** (d)	**5** (a)	**6** (b)	**7** (a)	**8** (d)	**9** (b)	**10** (d)
	11 (c)	**12** (c)	**13** (a)	**14** (a)	**15** (d)	**16** (c)				

Hints and Explanations

SESSION 1

1 Ti^{2+}, V^{3+}, Cr^{4+} and Mn^{5+} all have same configuration,
i.e. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^0$.

2 The first ionisation energies of V, Cr and Mn are 656, 650 and 717 kJ/mol respectively. Ionisation energies increase in a period from left to right. Hence, Mn has maximum first ionisation potential.

3 This can be understood on the basis of $E°$ values for M^{2+} / M.

$E°$/ V	Cr	Mn	Fe	Co
M^{2+}/M	–0.90	–1.18	–0.44	–0.28

$E°$ value for Mn is more negative than expected from general trend due to extra stability of half-filled Mn^{2+} ion.

Thus, the correct order should be

$$Mn > Cr > Fe > Co$$

An examination of $E°$ values for redox couple M^{3+}/M^{2+} shows that Cr^{2+} is strong reducing agent ($E°_{M^{3+}/M^{2+}} = 0.41$ V) and liberates H_2 from dilute acids.

$$2Cr^{2+}(aq) + 2H^+(aq) \longrightarrow 2Cr^{3+}(aq) + H_2\uparrow(g)$$

$\therefore$ The correct order is Mn > Fe > Cr > Co.

4 $(n-1)d^8ns^2$ $\underset{(n-1)d^8}{\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}}$ $\underset{ns^2}{\boxed{\uparrow\downarrow}}$ OS = 4(as in Ni)

$(n-1)d^5ns^1$ $\underset{(n-1)d^5}{\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}$ $\underset{ns^1}{\boxed{\uparrow}}$ OS = 6(as in Cr)

$(n-1)d^3ns^2$ $\underset{(n-1)d^3}{\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{}\boxed{}}$ $\underset{ns^2}{\boxed{\uparrow\downarrow}}$ OS = 5(as in V)

$(n-1)d^5ns^2$ $\underset{(n-1)d^5}{\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}$ $\underset{ns^2}{\boxed{\uparrow\downarrow}}$ OS = 7(as in Mn)

5 Ti^+ ions are more stable than Ti^{3+} and thus, Ti^{3+} ions change to Ti^+ ions there by acting as an oxidising agent.

$$\underset{\substack{\text{Less stable}\\\text{oxidising agent}}}{Ti^{3+}\text{ compounds}} + 2e^- \longrightarrow \underset{\substack{\text{More stable}\\\text{oxidising agent}}}{Ti^+\text{compounds}}$$

6 Due to the presence of maximum number of unpaired electrons, element having $3d^5 4s^2$, configuration may exhibit the largest number of oxidation states in its compounds.

7 In general, the atomic and ionic radii increases on moving down the group. But the elements of second transition series (e.g. Zr, Nb, Mo, etc) have the almost same radii as the elements of third transition series (e.g. Hf, Ta, W *etc*).

This is because of lanthanide contraction, i.e. poor shielding by one 4*f*-electron.

8 Transitional metal ions having unpaired electrons are coloured, while those which have no unpaired electron are colourless.

(i) In TiF_6^{2-}; Ti^{4+}; [Ar] $3d^0$; 0 unpaired electron; colourless

(ii) In Cu_2Cl_2; Cu^+; $[Ar]3d^{10}$; 0 unpaired electron; colourless

(iii) In CoF_6^{3-}; Co^{3+}; $[Ar]3d^6$; 4 unpaired electrons; coloured

(iv) In $NiCl_4^{2-}$; Ni^{2+}; $[Ar]3d^8$; 2 unpaired electrons; coloured

9 Cuprous ion (Cu^+) has completely filled *d*-subshell $3d^{10}$. Therefore, it is colourless. While cupric ion (Cu^{2+}) has one unpaired electron in *d*-subshell (d^9) due to which it is coloured.

10 Chromium hydroxide, $Cr(OH)_3$, when reacts with NaOH and Na_2O_2, gives sodium chromate, which is yellow in colour.

$$3Na_2O_2 + 2Cr(OH)_3 \longrightarrow \underset{\text{Yellow}}{2Na_2CrO_4} + 2H_2O + 2NaOH$$

11 Although in MnO_4^-, the oxidation state of Mn is + 7, i.e. it contains no unpaired electrons, yet it is coloured. This is because oxygen gives its one electron to Mn and converts it into Mn(VI), which is coloured. Thus, the colour of MnO_4^- is due to charge transfer.

12 Na_2CdCl_4 does not have unpaired electrons.

13 $HgCl_2 + 2KI \longrightarrow \underset{\text{(Red ppt.)}}{HgI_2}\downarrow + 2KCl$

$\underset{\text{(Red ppt.)}}{HgI_2} + 2KI \longrightarrow \underset{\text{Soluble, colourless}}{K_2[HgI_4]}$

14 The aqueous solution of $CuSO_4$ consists of the complex $[Cu(H_2O)_4]^{2+}$ ion which absorbs in orange red region impart deep blue colouration to the solution.

15 $FeSO_4 \cdot 7H_2O$ is green vitriol.

16 (a) $_{21}Sc^{3+} = 1s^2, 2s^2 2p^6, 3s^2 3p^6$.

It is colourless due to the absence of unpaired electrons in *d*-subshell.

(b) $_{26}Fe^{2+} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^6$.

It is coloured due to the presence of four unpaired electrons in *d*-subshell.

(c) $_{22}Ti^{3+} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^1$.

It is coloured due to the presence of one unpaired electron in *d*-subshell.

(d) $_{25}Mn^{2+} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5$.

It is coloured due to 5 unpaired electrons in *d*-subshell.

17 $2Ag + S_2O_3^{2-} \longrightarrow Ag_2S_2O_3$, white ppt. which readily changes to yellow, orange brown and finally black due to formation of silver sulphide.

$$Ag_2S_2O_3 + H_2O \longrightarrow H_2SO_4 + Ag_2S \text{ (black)}$$

18 Catalytic activity of transition metals is due to their ability to adopt multiple oxidation states and their complexing ability.

19 $VOSO_4$ is paramagnetic as well as coloured compound.

The oxidation state of vanadium in $VOSO_4$ is +4.

$$V[Z = 23] = [Ar]3d^3 4s^2 \text{ and } V^{4+}[Z = 23] = [Ar]3d^1 4s^0$$

It has one unpaired electron hence, it is paramagnetic and coloured in nature.

20 In $MnSO_4 \cdot 4H_2O$, Mn is present as Mn^{2+}.

$\mathbf{Mn^{2+}} = \overset{3d^5}{\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}$ $\overset{4s^0}{\boxed{}}$ (Unpaired electrons = 5)

In $CuSO_4 \cdot 5H_2O$, Cu is present as Cu^{2+}.

$\mathbf{Cu^{2+}} = \overset{3d^9}{\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}}$ $\overset{4s^0}{\boxed{}}$ (Unpaired electron = 1)

In $FeSO_4 \cdot 6H_2O$, Fe is present as Fe^{2+}.

$\mathbf{Fe^{2+}} = \overset{3d^6}{\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}$ $\overset{4s^0}{\boxed{}}$ (Unpaired electrons = 4)

In $NiSO_4 \cdot 6H_2O$, Ni is present as Ni^{2+}.

$\mathbf{Ni^{2+}} = \overset{3d^8}{\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}}$ $\overset{4s^0}{\boxed{}}$ (Unpaired electrons = 2)

Since, paramagnetic character $\propto$ unpaired electrons.

Thus, $CuSO_4 \cdot 5H_2O$ has the lowest degree of paramagnetism among the given at 298 K.

21 Outermost electronic configuration of given ions.

$$Ti^{3+} \longrightarrow 3d^1, 4s^0 \quad\text{and}\quad Sc^{3+} \longrightarrow 3d^0$$

$$Mn^{2+} \longrightarrow 3d^5, 4s^0 \quad\text{and}\quad Zn^{2+} \longrightarrow 3d^{10}4s^0$$

In Mn^{2+}, number of unpaired electrons = 5, so it has maximum magnetic moment. ($\because \mu = \sqrt{n(n+2)}$ BM)

i.e. 5.72 BM

22 The electronic configuration of Mn is ${}_{25}\text{Mn} = [\text{Ar}]3d^5 4s^2$

$\therefore \quad M_n^{+4} = [\text{Ar}]3d^3$

Thus, three unpaired electrons are present.

$\therefore$ Spin only magnetic moment, $\mu = \sqrt{n(n+2)}$ BM

$\because \quad n = 3$

$\therefore \quad \mu = \sqrt{3(3+2)} = \sqrt{15} = 3.87 \approx 4$ BM

23 Mn^{2+} (d^5) $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$

Magnetic moment $\propto$ number of unpaired electrons

Hence, M_2^{+2} will show maximum magnetic moment.

24 In *d-d* transition, an electron in a *d*-orbital of the metal is excited by a photon to another d-orbital of higher energy.

Paramagnetism The complex compound which contains unpaired electrons shows paramagnetism, while which contains paired electrons shows diamagnetism.

The complex which contains unpaired electrons exhibit *d-d* transition and paramagnetism.

(i) **In MnO_4^-**,

The electronic configuration of Mn^{7+} is [Ar] $3d^0$.

Number of unpaired electrons = 0

Therefore, it will be diamagnetic and will not show *d-d* transition.

(ii) **In $\text{Cr}_2\text{O}_7^{2-}$**,

The electronic configuration of Cr^{6+} is [Ar] $3d^0$.

Number of unpaired electrons = 0

So, it will be diamagnetic and will not show *d-d* transition.

(iii) **In CrO_4^{2-}**,

The electronic configuration of Cr^{6+} is [Ar] $3d^0$.

Number of unpaired electrons = 0

Therefore, it is also diamagnetic and will not show *d-d* transition.

(iv) **In MnO_4^{2-}**,

The electronic configuration of Mn^{6+} is [Ar] $3d^1$.

Number of unpaired electrons = 1

Since, it contains one unpaired electron so it will exhibit both *d-d* transition and paramagnetism.

25 $\text{Cu}^+ = [\text{Ar}]3d^{10}$

No unpaired electron, thus, $S = 0$. Paramagnetism of ion is also zero.

26 Magnetic moment = $\sqrt{n(n+2)}$ or $6.92 = \sqrt{n(n+2)}$

[Here, n = number of unpaired electrons.]

$n = 6$

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

27 $\text{Cr}^{2+} : d^4$ $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{}$

$\text{Mn}^{2+} : d^5$ $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$

$\text{Fe}^{2+} : d^6$ $\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$

$\text{Co}^{2+} : d^7$ $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$

$\therefore [\text{Co(H}_2\text{O)}_6]^{2+}$ has minimum number of unpaired electrons and thus, will show minimum paramagnetic behaviour.

28 Interstitial compounds are generally chemically inert.

29

S.No.	Alloy	Constituents
(i)	Invar	Fe + Ni
(ii)	Steel	Fe + C
(iii)	Bell metal	Cu(80%) + Sn(20%)
(iv)	Bronze	Cu(75.90%) + Sn(10.25)%

Among these alloys, only steel contains carbon, which is a non-metal.

30 $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 + 4\text{H}_2\text{O}_2 \longrightarrow \text{K}_2\text{SO}_4 + 2\text{CrO}_5 + 5\text{H}_2\text{O}$

31 When SO_2 is passed through acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution, green chromium sulphate is formed. In this reaction, oxidation state of Cr changes from +6 to +3.

$$\underset{\text{OS of Cr}=+6}{\text{K}_2\text{Cr}_2\text{O}_7} + \text{H}_2\text{SO}_4 + 3\text{SO}_2 \longrightarrow \text{K}_2\text{SO}_4 + \underset{\substack{\text{OS of Cr}=+3\\ \text{Green}}}{\text{Cr}_2(\text{SO}_4)_3} + \text{H}_2\text{O}$$

The appearance of green colour is due to the reduction of chromium metal.

32 Being hygroscopic, sodium dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7$ cannot be used in volumetric analysis.

All other given statements are true.

33 $4\text{K}_2\text{Cr}_2\text{O}_7 \xrightarrow{\Delta} 4\text{K}_2\text{CrO}_4 + 3\text{O}_2 + 2\text{Cr}_2\text{O}_3$

34 $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ is Mohr's salt.

$$2\text{KMnO}_4 + 8\text{H}_2\text{SO}_4 + 10\text{FeSO}_4 \longrightarrow \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 5\text{Fe}_2(\text{SO}_4)_3 + 8\text{H}_2\text{O}$$

35 SO_2 gas can readily oxidise acidified KMnO_4 solution because KMnO_4 is an oxidising agent and SO_2 act as reducing agent.

$2\text{MnO}_4^- + 5\text{SO}_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{Mn}^{2+} + 5\text{SO}_4^{2-} + 4\text{H}^+$.

While other options such as NO_2 (strong oxidising agent), CO_2 (neither oxidising agent nor reducing agent) cannot decolourise acidified KMnO_4 solution.

36 FeCl_3 is not a reducing agent it will not react with oxidising agent KMnO_4 and no colour is discharged.

37 Sm^{2+} $(Z = 62)$ $[\text{Xe}]4f^6$

and Eu^{2+} $(Z = 63)$ $[\text{Xe}]4f^7$

Yb^{2+} $(Z = 70)$ $[\text{Xe}]4f^{14}$

and Ce^{2+} $(Z = 58)$ $[\text{Xe}]4f^1 5d^1$

38 Electronic configuration of ${}_{63}\text{Eu} = [\text{Xe}]_{54}\ 4f^7 6s^2$ Electronic configuration of ${}_{64}\text{Gd} = [\text{Xe}]_{54}\ 4f^7 5d^1 6s^2$

Electronic configuration of ${}_{65}\text{Tb} = [\text{Xe}]_{54}\ 4f^9 6s^2$

39 Colour is obtained as a consequence of *d-d* (or *f-f*) transition, and for *d-d* (or *f-f*) transition, presence of unpaired electrons is the necessary condition.

La^{3+} $(Z = 57) = [\text{Xe}]\ 4f^0 5d^0 6s^0$ (no unpaired electron)

$Ti^{3+} (Z = 22) = [Ar]\ 3d^1 4s^0$ (one unpaired electron)

$Lu^{3+} (Z = 71) = [Xe] 4f^{14} 5d^0 6s^0$ (no unpaired electron)

$Sc^{3+} (Z = 21) = [Ar]\ 3d^0 4s^0$ (no unpaired electron)

Hence, only Ti^{3+} will exhibit colour in aqueous solution.

40 Since, there is a very small difference between the energies of 5*f*- and 6*d*- levels, thus the electron can go to 6*d* level or can remain in 5*f*-level. Hence, the electronic configuration of actinides cannot be assigned with degree of certainty.

41 The reason for greater range of oxidation states in actinoid is attributed to the 5*f*, 6*d* and 7*s* levels having comparable energies. The 5*f*-orbitals extend into space beyond the 7*s* and 6*p*-orbitals and participate in bonding. This is in direct contrast to the lanthanides where the 4*f*-orbitals are buried deep inside the atom, totally shielded by outer orbitals and thus unable to take part in bonding.

42 Due to very small energy difference between the 4*f*, 5*d* and 5*f* orbitals, actinoids show more number of oxidation states.

SESSION 2

1 Cu, Ag and Au are known as coinage metals having electronic configuration

$$(n-1)d^{10}, ns^1$$

Hence, (b) is the correct option.

2 (a) $FeO > Fe_2O_3$ (basic character)

(b) $FeCl_2 > FeCl_3$ (ionic nature), larger the charge greater the polarizing power thus greater the covalent nature. thus correct.

(c) Fe^{2+} salts are more ionic thus less volatile than Fe^{3+} salts. Thus, correct.

(d) Greater the covalent nature, more easily they are hydrolysed. Thus, $FeCl_3$ is more hydrolysed than $FeCl_2$ Thus, incorrect

3 When electron is removed from M^{+1} ion, the ionisation energy is called second ionisation energy. The second ionisation energy is higher for the elements having small size and half or fully-filled 3*d*-subshell (for first row of transition metals).

As chromium has half-filled 3*d*-electronic configuration and fully-filled for copper (Cu). Thus, these have higher second ionisation energy

∴ Option (b) is the correct answer.

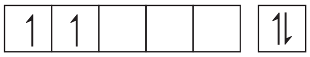
4 When $K_2Cr_2O_7$ reacts with KI in acidic medium, its oxidation state changes from (+) 6 to (+) 3. The reaction occurs as follows: (+) 6

$$K_2Cr_2O_7 + 7H_2SO_4 + 6KI \longrightarrow 4K_2SO_4 + \overset{+3}{Cr_2}(SO_4)_3 + 3I_2 + 7H_2O$$

Hence, oxidation state of the final product of the chromium is (+) 3.

5 As common oxidation state of transition metals is (+) 2 and ionic size decreases, as we move from left to right in a period. Scandium (Sc) has largest ionic radii among the given species.

6 $Ti(22) :\ [Ar]\ 4s^2\ 3d^2$



$Ti^{2+} :\ [Ar]\ 3d^2$

$Ti^{4+} :\ [Ar]\ 3d^0$

Ti^{2+} has two unpaired electrons in 3*d* and thus *d*-*d* * transition is possible due to absorption of light in visible region.

7 Among the given options, Zn^{2+} has no unpaired electron, thus is colourless, while Ni^{2+} and Cr^{3+} ions contain unpaired electrons, thus are coloured.

∴ Option (a) is the correct answer.

8 (a) It is expected that, as size of 5*d*-elements are more than of 3*d* and 4*d* elements (due to addition of new main shells) ionisation energy of 5*d* elements is less than of 3*d* and 4*d* elements but due poor screeing effect, the ionisation energy of 5*d* is elements are greater than of 3*d* and 4*d* elements.

(b) Cu(I) has no unpaired electron, thus is diamagnetic, while Cu (II) has one unpaired electron, thus is paramagnetic in nature.

(c) Ti^{3+} ion is coloured due to presence of unpaired electron, while Sc^{3+} ion is colourless due to empty *d*-subshell orbitals.

(d) Transition elements can form the complexes due to presence of vacant orbitals.

∴ Hence, (d) is the incorrect statement.

9 $$K_3[\overset{+3}{Fe}(CN)_6(CN)_6] + KI(\text{excess}) \longrightarrow K_4[Fe^{2+}(CN)_6] + \underset{\text{Brownish yellow solution}}{[KI_3(\text{redox})]}$$

$$K_4[Fe(CN)_6] + ZnSO_4 \longrightarrow K_2Zn_3[Fe(CN)_6]_2$$

or $$\underset{\text{white ppt.}}{K_3Zn\ [Fe(CN)_6]}$$

$$\underset{\substack{\text{Brownish yellow}\\\text{filtrate}}}{I_3^-} + Na_2S_2O_3 \longrightarrow \underset{\text{Clear solution}}{Na_2S_4O_6} + 2NaI + \underset{\substack{\text{Turns starch}\\\text{solution blue}}}{I_2}$$

$K_2Zn[Fe(CN)_6]$ reacts with NaOH as follows

$$K_2Zn\ [Fe(CN)_6] + NaOH \longrightarrow [Zn(OH)_4]^{2-} + [Fe(CN)_6]^{4-}$$

10 (a) There is a gradual decrease in the radii of the lanthanoids with increasing atomic number – a case of lanthanide contraction, thus true.

(b) Ionization potential for the formation of Lu^{3+} is comparatively low, hence, + 3 state is favourable, thus true.

(c) Due to lanthanide contraction – Zr and Hf; Nb and Ta, Mo and W have the same size and thus similar properties and thus separation is not easy, thus true.

(d) Formation of + 4 state requires very high energy, thus incorrect.

11 Ion is coloured, if there are unpaired electrons in *d*-suborbit. Paramagnetic nature is also due to unpaired electrons. Thus, every coloured ion is also paramagnetic.

$Cu^{2+} = [Ar]\ 3d^9$, one unpaired electron in 3*d*.

$Cr^{+} = [Ar]\ 3d^5$; five unpaired

$Mn^{2+} = [Ar]\ 3d^5$, electrons in 3*d*

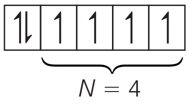
12 Magnetic moment, $\mu = \sqrt{N(N+2)}$ BM.

where, N = unpaired electrons

Cr(24) [Ar] $3d^5 4s^1$ $N = 6$, $\mu = \sqrt{48}$ BM $= x$

Mn^+ [Ar] $3d^5 4s^1$ $N = 6$, $\mu = \sqrt{48}$ BM $= y$

Fe^{2+} [Ar] $3d^6$ $N = 4$, $\mu = \sqrt{24}$ BM $= z$



Thus, $z < x = y$

13 The basic nature of lanthanoid hydroxides decreases with the decrease in ionic nature of hydroxides. As, La(OH)_3 is most ionic hydroxide among the lanthanoid hydroxides. It is more basic than other, i.e Lu(OH)_3 hydroxide.

14 Magnetic moment, $\mu = \sqrt{n(n+2)}$ BM where,

n = number of unpaired electrons, $\mu = 2.84$ (given)

$$\therefore \quad 2.84 = \sqrt{n(n+2)} \text{ B.M}$$

$$(2.84)^2 = n(n+2), \quad 8 = n^2 + 2n$$

$$n^2 + 2n - 8 = 0$$

$$n^2 + 4n - 2n - 8 = 0$$

$$n(n+4) - 2(n+4) = 0, \quad n = 2$$

$\text{Ni}^{2+} = [\text{Ar}]3d^8 4s^0$ (two unpaired electrons)

$\text{Ti}^{3+} = [\text{Ar}]3d^1 4s^0$ (one unpaired electron)

$\text{Cr}^{3+} = [\text{Ar}]3d^3 4s^0$ (three unpaired electrons)

$\text{Co}^{2+} = [\text{Ar}]3d^7 4s^0$ (three unpaired electrons)

So, only Ni^{2+} has 2 unpaired electrons.

15 $[\text{Cu (NH)}_3]_4^{2+}$ hybridisation dsp^2

$\text{Cu}^{2+} \ldots 3d^9$ has one unpaired electron.

So, magnetic moment $\mu = \sqrt{n(n+2)}$

$= \sqrt{1(1+2)}$

$= \sqrt{3} = 1.73$ BM

16 Spin magnetic moment can be calculated as

$$\mu = \sqrt{n(n+2)} \text{ BM}$$

where, μ = magnetic moment

BM = Bohr Magneton (unit of μ)

n = number of unpaired electrons in d-orbital.

The electronic configuration of Co^{3+} is [Ar] $3d^6$.

Here, $n = 4$

$$\mu = \sqrt{4(4+2)} = \sqrt{24} \text{BM}$$

The electronic configuration of Cr^{3+} is [Ar] $3d^3$.

Here, $n = 3$

$$\mu = \sqrt{3(3+2)}$$

$$= \sqrt{15} \text{ BM}$$

The electronic configuration of Fe^{3+} is [Ar] $3d^5$.

Here, $n = 5$

$$\mu = \sqrt{5(5+2)}$$

$$= \sqrt{35} \text{ BM}$$

The electronic configuration of Ni^{2+} is [Ar] $3d^8$.

Here, $n = 2$

$$\mu = \sqrt{2(2+2)} = \sqrt{8} \text{ BM}$$

So, the correct option is (c).