Chapter–8

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

basic concepts

1. **d-Block Elements:** The d-block elements are those elements in which the last electron enters the d–subshell of penultimate shell. The general electronic configuration of these elements is $(n-1)\,d^{1-10}\,ns^{1-2}$, where n is outermost shell. The d-block consisting of groups 3–12 occupies the large middle section of the periodic table.
2. **Transition Elements:** The elements of d-block are known as transition elements as they possess properties that are transitional between the s and p block elements. A transition element is defined as an element which has incompletely filled d-orbitals in its ground state or any one of its oxidation states. There are four series of transition elements spread between group 3 and 12.

   First transition series or 3*d*-series: Scandium ($_{21}$Sc) to Zinc ($_{30}$Zn)

   Second transition series or 4*d*-series: Yttrium ($_{39}$Y) to Cadmium ($_{48}$Cd)

   Third transition series or 5*d*-series: Lanthanum ($_{57}$La) and Hafnium ($_{72}$Hf) to Mercury ($_{80}$Hg) (Omitting $_{58}$Ce to $_{71}$Lu)

   Fourth transition series or 6*d*-series: Begins with Actinium ($_{89}$Ac) is still incomplete.

   Zinc, cadmium and mercury of group 12 have full d^{10} configuration in their ground state as well as in their common oxidation states and hence, are not regarded as transition metals. However, being the end elements of the three transition series, their chemistry is studied along with the chemistry of the transition elements.
3. **General Characteristics of Transition Elements**
   - (*a*) **Atomic radii:** The atomic radii of transition elements are smaller than those of s-block elements and larger than those of p-block elements in a period. In a transition series, as the atomic number increases, the atomic radii first decreases till the middle, becomes almost constant and then increases towards the end of the period. The decrease in atomic radii in the beginning is due to the increase in the effective nuclear charge with the increase in atomic number. However, with the increase in the number of electrons in $(n-1)$ d–subshell, the screening effect of these d-electrons on the outermost ns-electrons also increases. This increased screening effect counterbalances the effect of increased nuclear charge, therefore, the atomic radii remain almost constant in the middle of the series. Increase in atomic radii towards the end may be attributed to the electron–electron repulsion. The pairing of electrons in the d-orbitals of the penultimate shell occurs only after the d–subshell is half filled. The repulsive interactions between the paired electrons in d-orbitals (of the penultimate shell) become very dominant towards the end of the series and causes the expansion of the electron cloud and thus, resulting in increased atomic size.

     The atomic radii usually increase down the group. But the atomic radii of the elements of second and third transition series belonging to a particular group are almost equal. This is due to lanthanoid contraction.
   - (*b*) **Ionic radii:** The ionic radii of the transitional elements follow the same order as their atomic radii. In general, the ionic radii decrease with increase in oxidation state.
   - (*c*) **Ionisation enthalpies:** The first ionisation enthalpies of transition elements are higher than those of s-block elements but lower than p-block elements. In a particular transition series, ionisation enthalpy increases gradually with increase in atomic number, though some irregularities are observed.

Reason: The increase in ionisation enthalpy is due to increase in nuclear charge with increase in atomic number which tends to attract the electron cloud with greater force.

The addition of *d*-electron in penultimate shell with increase in atomic number provides a screening effect and shield the outer *s*-electrons from inward nuclear pull. Thus, the effect of increased nuclear charge and increased magnitude of screening effect tend to oppose each other. Consequently, the increase in ionisation enthalpy along the series of transition element is very small. The irregular variations of first and second ionisation enthalpies in the first transition series is mainly due to varying degree of stability of different 3*d*-configuration. For example, Cr has low first ionisation enthalpy because loss of one electron gives stable $3d^5$ configuration and Zn has very high first ionisation enthalpy because the electron has to be removed from 4*s*-orbital of the stable $3d^{10}4s^2$ configuration.

The first ionisation enthalpies of 5*d*-transition elements are higher than those of 3*d* and 4*d* elements. This is due to greater effective nuclear charge acting on the outer valence electrons in these elements because of the ineffective shielding of the nucleus by 4*f*-electrons.

(*d*) **Metallic character:** All the transition elements are metallic in nature. They show gradual decrease in electropositive character in moving from left to right in a series. The metallic bond in transition metals are very strong. This is due to greater effective nuclear charge, low ionisation energies and large number of vacant orbitals in their outermost shell. Nearly, all the transition metals are hard, possess high density and high enthalpy of atomisation. This is due to presence of strong metallic bonds.

(*e*) **Melting and boiling points:** Except zinc, cadmium and mercury all the other transition elements generally have high melting and boiling points. This is due to strong metallic bonds and presence of partially filled *d*-orbitals in them. Because of these half-filled orbitals some covalent bonds also exist between atoms of transition elements. As zinc, mercury and cadmium have fully filled *d*-orbitals, therefore, there is no covalent bonding amongst the atoms of these elements. This accounts for their low melting and boiling points.

In moving along series from left to right, the melting and boiling points of transition elements first increase to a maximum and then decrease towards the end of the period. As the number of unpaired electrons increases, the tendency to form metallic and covalent bonds also increases. In first transition series after chromium, the number of unpaired electrons decreases, hence the melting point also decreases. Manganese possesses anomalous melting and boiling points because it has stable $3d^5 4s^2$ configuration, *i.e.*, electrons are held tightly by nucleus so that the delocalisation is less and the metallic bond is much weaker than that of preceding element.

(*f*) **Oxidation states:** All transition elements except first and last member of the series exhibit variable oxidation states as $(n-1)d$ and *ns* orbitals have comparable energies so that both can enter into chemical bond formation. The maximum oxidation state shown by first series increases from Sc to Mn and then decreases. The common oxidation state of first series is +3 (except Sc). The highest oxidation state of transition elements is 8 (Os and Ru).

The compounds of transition elements in lower states +2 and +3 are mostly ionic and of higher oxidation states are covalent, *e.g.*, $ZnCl_2$ and $CdCl_2$ are ionic whereas $Cr_2O_7^{2-}$ and MnO_4^- are covalent in nature, higher oxidation state of transition elements are shown in oxides and oxoacids (*e.g.*, MnO_4^-). Transition metals with fluorine and oxygen exhibit higher oxidation state due to higher electronegative nature of fluorine and oxygen. Transition metals also exhibit +1 and 0 oxidation states. For example:

Cu_2Cl_2, AgCl, Hg_2Cl_2 (OS of metal is +1)
$Ni(CO)_4$, $Fe(CO)_5$ (OS of metal is 0)

When the metal exhibit more than one OS, their relative stabilities can be known from their standard electrode potential, *e.g.*,

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s) \qquad E^o_{red} = 0.34 \text{ volt}$$

$$Cu^{+}(aq) + e^- \longrightarrow Cu(s) \qquad E^o_{red} = 0.52 \text{ volt}$$

Lower standard reduction potential indicates Cu^{2+} is more stable than Cu^+ in aqueous medium.

(*g*) **Standard electrode potential:** Electrode potential is the electric potential developed on a metal electrode when it is in equilibrium with a solution of its own ions, taking electrons from the electrode. There is irregular variation in electrode potential due to irregular variation in ionisation enthalpy, sublimation energy and energy of hydration. The $E°$ value decreases from left to right across the series; Mn, Ni and Zn have higher values than expected because of their half-filled or completely filled 3*d*-orbitals in case of Mn^{2+} and Zn^{2+} respectively and the highest negative enthalpy of hydration, Ni^{2+}.

(*h*) **Magnetic properties:** Substances containing unpaired electrons are said to be paramagnetic. A diamagnetic substance is one in which all the electrons are paired. Except the ions of d^0 (Sc^{3+}, Ti^{4+}) and d^{10} (Cu^+, Zn^{2+}) configurations, all other simple ions of transition elements contain unpaired electrons in their $(n-1)$ *d* subshell and are, therefore, paramagnetic. The magnetic moments (μ) of the elements of first transition series can be calculated with the unpaired electrons (*n*) by the spin only formula.

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

(*i*) **Complex formation:** The tendency to form complex ions is due to

(*i*) the high charge on the transition metal ions,

(*ii*) the availability of *d*-orbitals for accommodating electrons donated by the ligand atoms.

(*j*) **Catalytic property:** Most of the transition metals and their compounds possess catalytic properties. The catalytic activity of transition metal ions is attributed to the following two reasons:

(*i*) Variable oxidation states due to which they can form a variety of unstable intermediate products.

(*ii*) Large surface area so that the reactants are adsorbed on the surface and come close to each other facilitating the reaction process.

(*k*) **Colour:** Most of the transition metal ions in solution as well as in solid states are coloured. This is due to the partial absorption of visible light. The absorbed light promotes the electron from one orbital to another orbital of the same *d*-subshell. Since the electronic transition occurs within the *d*-orbitals of the transition metal ions, they are called *d–d* transitions. It is because of these *d–d* transitions occurring in a transition metal ion by absorption of visible light that they appear coloured.

(*l*) **Alloy formation:** The transition metals have similar radii and other characteristics. Therefore, these metals can mutually substitute their position in their crystal lattices and form alloys. The alloys so formed are hard and often have high melting point. Various types of steel, brass, bronze are examples of this type of alloy.

(*m*) **Interstitial compounds:** Interstitial compounds are those in which small atoms occupy the interstitial sites in the crystal lattice. Interstitial compounds are well known for transition metals because small-sized atoms of H, B, C, N, etc., can easily occupy positions in the voids present in the crystal lattices of transition metals.

4. **Some Important Compounds of Transition Elements:** Though the transition elements are sufficiently electropositive, yet they are not very reactive because of

(*i*) their high enthalpies of sublimation, and

(*ii*) their high ionisation enthalpies.

Oxides: Transition metals form oxides of the general composition MO, M_2O_3, MO_2, M_2O_5 and MO_6. Oxides in the lower oxidation states are generally basic in nature and those in the higher oxidation states are amphoteric or acidic in nature. For example,

+2	+3	+8/3	+4	+7
MnO	Mn_2O_3	Mn_3O_4	MnO_2	Mn_2O_7
Basic	Amphoteric	Amphoteric	Amphoteric	Acidic

(*a*) **Potassium Dichromate, $K_2Cr_2O_7$:** It is prepared from the chromite ore. Different reactions involved in the preparation of potassium dichromate from chromite ore are:

$$\underset{\text{Chromite ore}}{4FeCr_2O_4} + 8Na_2CO_3 + 7O_2 \xrightarrow{\text{Roasted}} \underset{\text{Sodium chromate}}{8Na_2CrO_4} + 2Fe_2O_3 + 8CO_2$$

$$2Na_2CrO_4 + H_2SO_4 \longrightarrow \underset{\text{Sodium dichromate}}{Na_2Cr_2O_7} + Na_2SO_4 + H_2O$$

$$Na_2Cr_2O_7 + 2KCl \longrightarrow \underset{\text{Potassium dichromate}}{K_2Cr_2O_7} + 2NaCl$$

$K_2Cr_2O_7$ is separated by fractional crystallisation.

Properties: When potassium dichromate is heated with any ionic chloride (*e.g.*, NaCl, $BaCl_2$, etc.) and concentrated H_2SO_4, red vapours of chromyl chloride are obtained.

$$K_2Cr_2O_7 + 4KCl + 6H_2SO_4 \longrightarrow \underset{\text{Chromyl chloride}}{2CrO_2Cl_2\uparrow} + 6KHSO_4 + 3H_2O$$

Potassium dichromate is a powerful oxidising agent. In acidic medium, its oxidation action can be represented as follows:

$$\begin{array}{rcl} K_2Cr_2O_7 + 4H_2SO_4 & \longrightarrow & K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O] \\ Cr_2O_7^{2-} + 14H^+ + 6e^- & \longrightarrow & 2Cr^{3+} + 7H_2O \qquad (E^o = +1.31\text{ V}) \end{array}$$

(*i*) It oxidises ferrous to ferric.

$$\begin{array}{rcl} Cr_2O_7^{2-} + 14H^+ + 6e^- & \longrightarrow & 2Cr^{3+} + 7H_2O \\ Fe^{2+} & \longrightarrow & Fe^{3+} + e^-\,] \times 6 \\ \hline Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ & \longrightarrow & 2Cr^{3+} + 6Fe^{3+} + 7H_2O \\ \hline \end{array}$$

(*ii*) It oxidises stannous to stannic.

$$\begin{array}{rcl} Cr_2O_7^{2-} + 14H^+ + 6e^- & \longrightarrow & 2Cr^{3+} + 7H_2O \\ Sn^{2+} & \longrightarrow & Sn^{4+} + 2e^-\,] \times 3 \\ \hline Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ & \longrightarrow & 2Cr^{3+} + 3Sn^{4+} + 7H_2O \\ \hline \end{array}$$

(*iii*) It oxidises sulphur dioxide to sulphuric acid.

$$\begin{array}{rcl} Cr_2O_7^{2-} + 14H^+ + 6e^- & \longrightarrow & 2Cr^{3+} + 7H_2O \\ SO_2 + 2H_2O & \longrightarrow & SO_4^{2-} + 4H^+ + 2e^-\,] \times 3 \\ \hline Cr_2O_7^{2-} + 3SO_2 + 2H^+ & \longrightarrow & 2Cr^{3+} + 3SO_4^{2-} + H_2O \\ \hline \end{array}$$

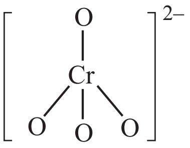
(*iv*) It oxidises hydrogen sulphide to sulphur.

$$\begin{array}{rcl} Cr_2O_7^{2-} + 14H^+ + 6e^- & \longrightarrow & 2Cr^{3+} + 7H_2O \\ H_2S & \longrightarrow & 2H^+ + S + 2e^-\,] \times 3 \\ \hline Cr_2O_7^{2-} + 3H_2S + 8H^+ & \longrightarrow & 2Cr^{3+} + 3S + 7H_2O \\ \hline \end{array}$$

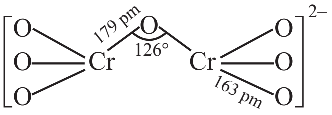
(*v*) It oxidises iodides to iodine.

$$\begin{array}{rcl} Cr_2O_7^{2-} + 14H^+ + 6e^- & \longrightarrow & 2Cr^{3+} + 7H_2O \\ 2I^- & \longrightarrow & I_2 + 2e^-\,] \times 3 \\ \hline Cr_2O_7^{2-} + 6I^- + 14H^+ & \longrightarrow & 2Cr^{3+} + 3I_2 + 7H_2O \\ \hline \end{array}$$

Structures of chromate and dichromate ions:



Chromate ion



Dichromate ion

The chromate and dichromate ions are interconvertible in aqueous solution depending upon the pH of the solution.

$$2CrO_4^{2-} + 2H^+ \longrightarrow \underset{\substack{\text{Dichromate ion} \\ \text{(orange red)}}}{Cr_2O_7^{2-}} + H_2O$$

$$Cr_2O_7^{2-} + 2OH^- \longrightarrow \underset{\substack{\text{Chromate ion} \\ \text{(yellow)}}}{2CrO_4^{2-}} + H_2O$$

Potassium dichromate is used as primary standard in volumetric analysis.

(*b*) **Potassium permanganate, $KMnO_4$:** It is prepared by fusion of pyrolusite, MnO_2, with KOH in the presence of an oxidising agent like KNO_3. This produces the dark green potassium manganate, K_2MnO_4 which disproportionates in a neutral or acidic solution to give purple permanganate.

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

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

Or, $$3K_2MnO_4 + 4H^+ \longrightarrow \underset{\substack{\text{Potassium}\\ \text{permanganate}}}{2KMnO_4} + MnO_2 + 2H_2O + 4K^+$$

Commercially, it is prepared by alkaline oxidative fusion of MnO_2 followed by the electrolytic oxidation of manganate (VI).

$$MnO_2 \xrightarrow[\text{oxidised with air or } KNO_3]{\text{Fused with KOH}} \underset{\text{Manganate ion}}{MnO_4^{2-}}$$

$$MnO_4^{2-} \xrightarrow[\text{in alkaline solution}]{\text{Electrolytic Oxidation}} \underset{\text{Permanganate ion}}{MnO_4^-}$$

In the laboratory, $KMnO_4$ is prepared by oxidation of manganese (II) ion salt by peroxodisulphate.

$$2Mn^{2+} + \underset{\text{Peroxodisulphate}}{5S_2O_8^{2-}} + 8H_2O \longrightarrow \underset{\text{Permanganate}}{2MnO_4^-} + 10SO_4^{2-} + 16H^+$$

Properties:

Potassium permanganate is a dark purple crystalline solid.

On heating, it decomposes at 513 K and O_2 is evolved.

$$2KMnO_4 \xrightarrow{\text{Heat}} \underset{\text{Potassium manganate}}{K_2MnO_4} + MnO_2 + O_2$$

Potassium permanganate acts as a powerful oxidising agent in acidic, alkaline and neutral media. Few important oxidation reactions of $KMnO_4$ are given below:

1. In acidic medium potassium permanganate oxidises:

(*i*) **Iodide to iodine**

$$\begin{array}{rcl} MnO_4^- + 8H^+ + 5e^- & \longrightarrow & Mn^{2+} + 4H_2O] \times 2 \\ 2I^- & \longrightarrow & I_2 + 2e^-] \times 5 \\ \hline 2MnO_4^- + 10I^- + 16H^+ & \longrightarrow & 2Mn^{2+} + 5I_2 + 8H_2O \\ \hline \end{array}$$

(*ii*) **Ferrous to ferric**

$$\begin{array}{rcl} MnO_4^- + 8H^+ + 5e^- & \longrightarrow & Mn^{2+} + 4H_2O \\ Fe^{2+} & \longrightarrow & Fe^{3+} + e^-] \times 5 \\ \hline MnO_4^- + 5Fe^{2+} + 8H^+ & \longrightarrow & Mn^{2+} + 5Fe^{3+} + 4H_2O \\ \hline \end{array}$$

(*iii*) **Oxalate to carbon dioxide**

$$\begin{array}{rcl} MnO_4^- + 8H^+ + 5e^- & \longrightarrow & Mn^{2+} + 4H_2O] \times 2 \\ C_2O_4^{2-} & \longrightarrow & 2CO_2 + 2e^-] \times 5 \\ \hline 2MnO_4^- + 5\,C_2O_4^{2-} + 16H^+ & \longrightarrow & 2Mn^{2+} + 10CO_2 + 8H_2O \\ \hline \end{array}$$

(*iv*) **Hydrogen sulphide to sulphur**

$$\begin{array}{rcl} MnO_4^- + 8H^+ + 5e^- & \longrightarrow & Mn^{2+} + 4H_2O] \times 2 \\ S^{2-} & \longrightarrow & S + 2e^-] \times 5 \\ \hline 2MnO_4^- + 5S^{2-} + 16H^+ & \longrightarrow & 2Mn^{2+} + 5S + 8H_2O \\ \hline \end{array}$$

(*v*) **Sulphite to sulphate**

$$\begin{array}{l} MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O\ ] \times 2 \\ SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2e^-\ ] \times 5 \\ \hline 5SO_3^{2-} + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O \\ \hline \end{array}$$

(*vi*) **Nitrite to nitrate**

$$\begin{array}{l} MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O\ ] \times 2 \\ NO_2^- + H_2O \longrightarrow NO_3^- + 2H^+ + 2e^-\ ] \times 5 \\ \hline 2MnO_4^- + 5NO_2^- + 6H^+ \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O \\ \hline \end{array}$$

2. In neutral or faintly alkaline solutions potassium permanganate oxidises:

(*i*) **Iodide to iodate**

$$2MnO_4^- + I^- + H_2O \longrightarrow IO_3^- + 2MnO_2 + 2OH^-$$

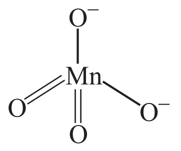
(*ii*) **Thiosulphate to sulphate**

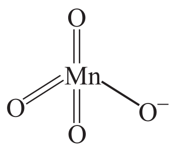
$$8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$$

(*iii*) **Manganous salt to MnO_2 in presence of zinc sulphate or zinc oxide**

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \longrightarrow 5MnO_2 + 4H^+$$

The MnO_4^{2-} and MnO_4^- are tetrahedral; the green MnO_4^{2-} is paramagnetic with one unpaired electron but the purple MnO_4^- is diamagnetic.


Tetrahedral manganate ion (green)


Tetrahedral permanganate ion (purple)

Inner Transition Elements (f-Block Elements)

The inner transition elements consist of lanthanoids and actinoids. They are characterised by filling of the '*f*' orbitals.

5. Lanthanoids

The series involving the filling of 4*f*-orbitals following lanthanum La (Z = 57) is called the lanthanoid series. There are 14 elements in this series, starting with cerium Ce (Z =58) to lutetium Lu (Z = 71). The lanthanoids

- are highly dense metals.
- have high melting points.
- form alloys easily with other metals.
- are soft, malleable and ductile with low tensile strength.

(*i*) **Oxidation state:** The most characteristic oxidation state of lanthanoid elements is +3. Some of the elements also exhibit +2 and +4 oxidation states.

(*ii*) **Colour:** Some of the trivalent ions of lanthanoids are coloured. This is due to the absorption in visible region of the spectrum, resulting in *f-f* transitions because they have partly filled orbitals.

(*iii*) **Magnetic properties:** Among lanthanoids, La^{3+} and Lu^{3+}, which have $4f^0$ or $4f^{14}$ electronic configurations are diamagnetic and all the other trivalent lanthanoid ions are paramagnetic because of the presence of unpaired electrons.

(*iv*) **Reactivity:** All lanthanoids are highly electropositive metals and have an almost similar chemical reactivity.

(*v*) **Lanthanoid contraction:** In lanthanoids, with increasing atomic number, the atomic and ionic radii decreases from one element to the other, but the decrease is very small. It is because, for every additional proton in the nucleus, the corresponding electron goes into a 4*f*-subshell, which is too diffused to screen the nucleus as effectively as the more localised inner shell. Hence, the attraction of the nucleus for the outermost electrons increases steadily with the atomic number.

(*vi*) **Uses of lanthanoids:** The pure metals have no specific use. So they are used as alloys or compounds.

➡ As alloys lanthanoids are used in making a misch metal which consists of lanthanoid metals (~95%) and iron (~5%) and traces of sulphur, carbon, calcium and aluminium. Magnesium mixed with 3% misch metal is used for making jet engine parts.

➡ Steel mixed with La, Ce, Pr and Nd is used in the manufacture of flame throwing tanks.

➡ Lanthanoid oxides are used for polishing glass. Neodymium and praseodymium oxides are used for making coloured glasses for goggles.

➡ Cerium salts are used in dyeing cotton and also as catalysts.

➡ Lanthanoid compounds are used as a catalyst for hydrogenation, dehydrogenation and petroleum cracking.

➡ Pyrophoric alloys are used for making tracer bullets and shells.

6. **Actinoids:** The elements following actinium, Ac (Z = 89), up to lawrencium (Z = 103), are called actinoids. The actinoids

➡ are highly dense metals with a high melting point and form alloys with other metals, specially iron.

➡ are silvery white metals, which are highly reactive.

➡ get tarnished when exposed to alkalis and are less reactive towards acids.

(*i*) **Actinoid contraction:** The atomic and ionic size decreases with an increase in atomic number. Electrons are added to the 5*f*-subshell, as a result the nuclear charge increases causing the shells to shrink inwards.

(*ii*) **Electronic configuration:** The actinoids involve the filling of 5*f*-subshells. Actinium has the electronic configuration $6d^1\ 7s^2$. From thorium ($Z = 90$) onwards, 5*f*-orbitals get progressively filled up. Because of equal energy of 5*f* and 6*d* subshells, there are some uncertainities regarding the filling of 5*f* and 6*d* subshells. Most of their properties are comparable to that of lanthanoids.

(*iii*) **Oxidation state:** Generally +3 oxidation state is preferred in actinoids. The elements in the first of actinoid series frequently exhibit higher states. For example, the maximum oxidation increases from +4 in Th to +5, +6 and +7 in Pa, U and Np, respectively, but decreases in succeeding elements.

(*iv*) **Colour:** The actinoid ions are coloured.

(*v*) **Magnetic properties:** Many of the actinoid ions are paramagnetic.

(*vi*) **Reactivity:** They are also highly electropositive and form salts as well as complexes. Many of these elements are radioactive.

(*vii*) **Uses of actinoids:**

- Thorium is used in the treatment of cancer and in incandescent gas mantles.
- Uranium is used in the glass industry, textile industry, in medicines and as nuclear fuel.
- Plutonium is used in atomic reactors and in atomic bombs.

7. Differences between Lanthanoids and Actinoids

S.No.	Lanthanoids	Actinoids
(*i*)	4*f*-orbital is progressively filled.	5*f*-orbital is progressively filled.
(*ii*)	+3 oxidation state is most common along with +2 and +4.	They show +3, +4, +5, +6, +7 oxidation states.
(*iii*)	Only promethium (Pm) is radioactive.	All are radioactive.
(iv)	They are less reactive than actinoids.	They are more reactive.
(*v*)	Magnetic properties are less complex.	Magnetic properties are more complex.

NCERT Textbook Questions

NCERT Intext Questions

Q. 1. Silver atom has completely filled *d*-orbitals ($4d^{10}$) in its ground state. How can you say that it is a transition element?

Ans. Silver ($Z = 47$) can exhibit +2 oxidation state wherein it will have incompletely filled *d*-orbitals (4*d*), hence a transition element.

Q. 2. In the series Sc (Z = 21) to Zn (Z = 30), the enthalpy of atomisation of zinc is the lowest, *i.e.*, 126 kJ mol^{-1}. Why?

Ans. In the formation of metallic bonds, no electrons from 3*d*-orbitals are involved in case of zinc, while in all other metals of the 3*d* series, electrons from the *d*-orbitals are always involved in the formation of metallic bonds. That is why, the enthalpy of atomisation of zinc is the lowest in the series.

Q. 3. Which of the 3*d* series of the transition metals exhibits the largest number of oxidation states and why?

Ans. Manganese (Z = 25), as it has the maximum number of unpaired electrons in *d*-subshell. Thus, it shows oxidation states from +2 to +7 (+2, +3, +4, +5, +6 and +7) which is the maximum number.

Q. 4. The E^o (M^{2+}/M) value for copper is positive (+0.34 V). What is possible reason for this?

(Hint: Consider its high $\Delta_a H^{\ominus}$ and low $\Delta_{hyd} H^{\ominus}$)

Ans. E^o (M^{2+}/M) for any metal is related to the sum of the enthalpy change taking place in the following steps:

$$M(s) + \Delta_a H \longrightarrow M(g), \qquad (\Delta_a H = \text{Enthalpy of atomisation})$$
$$M(g) + \Delta_i H \longrightarrow M^{2+}(g), \qquad (\Delta_i H = \text{Ionisation enthalpy})$$
$$M^{2+}(g) + aq \longrightarrow M^{2+}(aq) + \Delta_{hyd}H, \quad (\Delta_{hyd} H = \text{Hydration enthalpy})$$

Copper has high enthalpy of ionisation and relatively low enthalpy of hydration. So, $E^o_{(Cu^{2+}/Cu)}$ is positive. The high energy to transform Cu(*s*) to $Cu^{2+}(aq)$ is not balanced by its hydration enthalpy.

Q. 5. How would you account for the irregular variation of ionisation enthalpies (first and second) in first series of the transition elements?

Ans. Irregular variation of ionisation enthalpies is mainly attributed to varying degree of stability of different 3*d* configuration (*e.g.*, d^0, d^5, d^{10} are exceptionally stable).

Q. 6. Why is the highest oxidation state of a metal exhibited in its oxide or fluoride only?

Ans. Due to small size and high electronegativity, oxygen or fluorine can oxidise a metal to its highest oxidation state. As a result of this they can oxidise a metal to its highest oxidation state.

Q. 7. Which is a stronger reducing agent— Cr^{2+} or Fe^{2+} and why? ***[HOTS]***

Ans. Cr^{2+} is a stronger reducing agent than Fe^{2+} because after the loss of one electron Cr^{2+} becomes Cr^{3+} which has more stable t_{2g}^3 (half-filled) configuration in a medium like water.

Q. 8. Calculate the 'spin only' magnetic moment of $M^{2+}(aq)$ ion ($Z = 27$).

OR

Calculate the spin-only magnetic moment of Co^{2+}(Z=27) by writing the electronic configuration of Co and Co^{2+}. ***[CBSE 2020 (56/1/1)]***

Ans. Electronic configuration of M atom with Z = 27 is [Ar] $3d^7 4s^2$.

$\therefore$ Electronic configuration of M^{2+} = [Ar] $3d^7$, *i.e.*, $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$

Hence, it has three unpaired electrons.

$$\therefore \text{ Spin only magnetic moment } (\mu) = \sqrt{n(n+2)} \text{ BM}$$
$$= \sqrt{3(3+2)} \text{ BM} = \sqrt{15}\text{BM} = \mathbf{3.87\ BM}$$

Q. 9. Explain why Cu^+ ion is not stable in aqueous solutions? ***[HOTS]***

Ans. In aqueous solution Cu^+ undergoes disproportionation to form a more stable Cu^{2+} ion.

$$2Cu^+(aq) \longrightarrow Cu^{2+}(aq) + Cu(s)$$

The higher stability of Cu^{2+} in aqueous solution may be attributed to its greater negative $\Delta_{hyd.}H^o$ than that of Cu^+. It compensates the second ionisation enthalpy of Cu involved in the formation of Cu^{2+} ions.

Q. 10. Actinoid contraction is greater from element to element than lanthanoid contraction. Why?

Ans. This is because the 5*f* electrons themselves provide poor shielding from element to element in the series.

NCERT Textbook Exercises

Q. 1. Write down the electronic configuration of

(*i*) Cr^{3+} (*ii*) Cu^{+} (*iii*) Co^{2+} (*iv*) Mn^{2+} (*v*) Pm^{3+}

(*vi*) Ce^{4+} (*vii*) Lu^{2+} (*viii*) Th^{4+}

Ans. (*i*) $Cr^{3+} = [Ar]\ 3d^3$ (*ii*) $Cu^{+} = [Ar]\ 3d^{10}$

(*iii*) $Co^{2+} = [Ar]\ 3d^7$ (*iv*) $Mn^{2+} = [Ar]\ 3d^5$

(*v*) $Pm^{3+} = [Xe]\ 4f^4$ (*vi*) $Ce^{4+} = [Xe]$

(*vii*) $Lu^{2+} = [Xe]\ 4f^{14}\ 5d^1$ (*viii*) $Th^{4+} = [Rn]$

Q. 2. Why are Mn^{2+} compounds more stable than Fe^{2+} compounds towards oxidation to their +3 state?

Ans. Electronic configuration of Mn^{2+} is $3d^5$ which is half-filled and hence stable. So, 3rd ionisation enthalpy is very high, *i.e.*, 3rd electron cannot be easily lost. In case of Fe^{2+}, electronic configuration is $3d^6$. Thus, it can lose one electron easily to give the stable configuration $3d^5$.

Q. 3. Explain briefly how +2 state becomes more and more stable in the first half of the first row transition elements with increasing atomic number.

Ans. As the atomic number increases from 21 to 25, the number of electrons in the 3*d*-orbital also increases from 1 to 5. +2 oxidation state is attained by the loss of the two 4*s* electrons by these metals. Sc does not exhibit +2 oxidation state. As the number of *d*- electrons in +2 state increases from Ti to Mn, the stability of +2 state increases (*d*-orbital gradually becoming half filled). Mn(+2) has d^5 electrons which is highly stable.

Q. 4. To what extent do the electronic configurations decide the stability of oxidation states in the first series of the transition elements? Illustrate your answer with example.

Ans. The stability of oxidation states in the first series of the transition elements are related to their electronic configurations.

The first five elements of the first transition series up to Mn in which the 3*d*-subshell is not more than half-filled, the minimum oxidation state is given by the number of electrons in the outer *s*-subshell and the maximum oxidation state is given by the sum of the outer *s* and *d*-electrons. For example, Sc does not show +2 oxidation state. Its electronic configuration is $3d^1\ 4s^2$. It loses all the three electrons to form Sc^{3+}. +3 oxidation state is very stable as by losing all three electrons, it attains the stable configuration of Argon. For Mn, +2 oxidation state is very stable, as after losing two 4*s* electrons, the *d*-orbitals become half-filled.

Q. 5. What may be the stable oxidation state of the transition element with the following *d*-electron configuration in the ground state of their atoms?

$3d^3$, $3d^5$, $3d^8$ and $3d^4$

Ans. Stable oxidation states:

$3d^3$ (vanadium): +2, +3, +4, +5 $3d^5$ (chromium): +3, +4, +6

$3d^5$ (manganese): +2, +4, +6, +7 $3d^8$ (nickel): +2, +4

$3d^4$: There is no d^4 configuration in the ground state.

Q. 6. Name the oxo-metal anions of the first series of the transition metals in which the metal exhibits the oxidation state equal to its group number.

Ans. $Cr_2O_7^{2-}$ and CrO_4^{2-} (group no. = oxidation state of Cr = 6)

MnO_4^- (group no. = oxidation state of Mn = 7)

Vanadate: VO_3^- (group no. = oxidation state of V = 5)

Q. 7. What is lanthanoid contraction? What are the consequences of lanthanoid contraction?

Ans. Refer to Basic Concepts Point 5 (*v*).

The consequences of lanthanoid contraction are as follows:

(*i*) The properties of second and third transition series are similar.

(*ii*) Basic strength decreases from La$(OH)_3$ to Lu$(OH)_3$.

(*iii*) Lanthanide contraction makes separation of lanthanoids possible.

Q. 8. What are the characteristics of the transition elements and why are they called transition elements? Which of the *d*-block elements may not be regarded as the transition elements?

Ans. Characteristics of the transition elements: Refer to Basic Concepts Point 3.

The *d*-block elements are called transition elements because these elements represent change (or transition) in properties from the most electropositive *s*-block elements to the least electropositive *p*-block elements.

The electronic configuration of Zn, Cd and Hg are represented by the general formula $(n-1)\,d^{10}\,ns^2$. The orbitals in these elements are completely filled in the ground state as well as in their common oxidation states. Therefore, they are not regarded as transition elements.

Q. 9. In what way is the electronic configuration of transition elements different from that of the non-transition elements?

Ans. Transition elements contain incompletely filled *d*-subshell, *i.e.*, their electronic configuration is $(n-1)\,d^{1-10}\,ns^{1-2}$ whereas non-transition elements have no *d*-subshell or their subshell is completely filled and have ns^{1-2} or $ns^2\,np^{1-6}$ in their outermost shell.

Q. 10. What are the different oxidation states exhibited by lanthanoids?

Ans. +2, +3 and +4 (+3 being most common).

Q. 11. Explain giving reasons:

(*i*) Transition metals and many of their compounds show paramagnetic behaviour.

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

(*iii*) The transition metals generally form coloured compounds.

(*iv*) Transition metals and their many compounds act as good catalyst.

Ans. (*i*) Refer to Basic Concepts Point 3(*h*).

(*ii*) The transition elements exhibit high enthalpy of atomisation because they have large number of unpaired electrons in their atoms. Due to this they have stronger interatomic interaction.

(*iii*) Refer to Basic Concepts Point 3(*k*).

(*iv*) The transition metals and their compounds are known for their catalytic activity. This activity is due to their ability to adopt multiple oxidation states and to form complexes. Vanadium oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in catalytic hydrogenation) are some examples to mention. Catalysts at a solid surface involve the formation of bonds between reactant molecules and atoms of the surface of the catalyst (first row transition metals utilise 3*d* and 4*s* electrons for bonding). This has the effect of increasing the concentration of the reactants at the catalyst surface and also weakening of the bonds in the reacting molecules (the activation energy is lowering). Also, since the transition metal ions can change their oxidation states, they become more effective as catalysts. For example, iron(III) catalyses the reaction between iodide and persulphate ions.

$$2I^- + S_2O_8^{2-} \longrightarrow I_2 + 2SO_4^{2-}$$

An explanation of this catalytic action is given as under:

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

$$2Fe^{2+} + S_2O_8^{2-} \longrightarrow 2Fe^{3+} + 2SO_4^{2-}$$

Q. 12. What are interstitial compounds? Why are such compounds well known for transition metals?

Ans. Interstitial compounds are those in which small atoms occupy the interstitial sites in the crystal lattice. Interstitial compounds are well known for transition metals because small-sized atoms of H, B, C, N, etc., can easily occupy positions in the voids present in the crystal lattices of transition metals.

Q. 13. How is the variability in oxidation states of transition metals different from that of the non transition metals? Illustrate with examples.

Ans. The oxidation states of transition elements differ from each other by unity *e.g.*, Fe^{2+} and Fe^{3+}, Cu^+ and Cu^{2+} (due to incomplete filling of *d*-orbitals) whereas oxidation states of non-transition elements normally differ by two units *e.g.*, Pb^{2+} and Pb^{4+}, Sn^{2+} and Sn^{4+}, etc.

Q. 14. Describe the preparation of potassium dichromate from iron chromite ore. What is the effect of increasing pH on a solution of potassium dichromate?

Ans. For preparation of potassium dichromate from iron chromite ore refer to Basic Concepts Point 4(*a*).

In aqueous solution, dichromate and chromate ions exist in equilibrium. On increasing the pH, *i.e.*, on making the solution alkaline, dichromate ions (orange coloured) are converted into chromate ions and thus, the solution turns yellow.

Q. 15. Describe the oxidising action of potassium dichromate and write the ionic equations for its reaction with (*i*) iodide (*ii*) iron (II) solution (*iii*) H_2S.

Ans. (*i*) $Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 7H_2O + 3I_2$

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

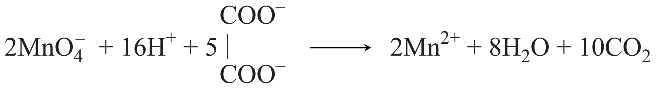
(*iii*) $Cr_2O_7^{2-} + 8H^+ + 3H_2S \longrightarrow 2Cr^{3+} + 7H_2O + 3S$

Q. 16. Describe the preparation of potassium permanganate. How does the acidified permanganate react with (*i*) iron (II) ions (*ii*) SO_2 (*iii*) oxalic acid? Write the ionic equations for the reaction.

Ans. For preparation, refer to Basic Concepts Point 4(*b*).

(*i*) $MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$

(*ii*) $2MnO_4^- + 2H_2O + 5SO_2 \longrightarrow 2Mn^{2+} + 4H^+ + 5SO_4^{2-}$

(*iii*)

$$2MnO_4^- + 16H^+ + 5\begin{array}{c}COO^-\\ |\\ COO^-\end{array} \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$$

Q. 17. For M^{2+}/M and M^{3+}/M^{2+} systems, E^o values for some metals are as follows:

$Cr^{2+}/Cr = -0.9$ V **$Cr^{3+}/Cr^{2+} = -0.4$ V**

$Mn^{2+}/Mn = -1.2$ V **$Mn^{3+}/Mn^{2+} = +1.5$ V**

$Fe^{2+}/Fe = -0.4$ V **$Fe^{3+}/Fe^{2+} = +0.8$ V** **[*CBSE Sample Paper 2016*]**

Use this data to comment upon

(*i*) the stability of Fe^{3+} in acid solution as compared to that of Cr^{3+} and Mn^{3+}.

(*ii*) the ease with which iron can be oxidised as compared to the similar process for either Cr or Mn metals.

Ans. (*i*) Higher the reduction potential of a species, greater is the ease with which it undergo reduction. Among these pairs, Mn^{3+}/Mn^{2+} has largest positive reduction potential. Hence Mn^{3+} can be easily reduced to Mn^{2+} *i.e.*, Mn^{3+} is least stable. Cr^{3+}/Cr^{2+} has a negative E^o value, therefore, Cr^{3+} is most stable. Fe^{3+}/Fe^{2+} has a positive value but small. Hence, Fe^{3+} is more stable than Mn^{3+} but less stable than Cr^{3+}.

(*ii*) Lower the reduction potential or higher the oxidation potential of a species, greater is the ease with which it undergo oxidation. Among these pairs, Mn^{2+}/Mn has the most negative reduction potential or most positive oxidation potential. Therefore, it will be most easily oxidised. Thus, the decreasing order of their ease of oxidation is Mn > Cr > Fe.

Q. 18. Predict which of the following will be coloured in aqueous solution?

$Ti^{3+}, V^{3+}, Cu^+, Sc^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}$. Give reasons for each.

Ans. An ion is coloured when it has one or more unpaired electrons. Thus, Ti^{3+}, V^{3+}, Mn^{2+}, Fe^{3+} and Co^{2+} are coloured, due to the presence of unpaired electrons and *d*-*d* transitions. Cu^+ and Sc^{3+} are colourless.

Q. 19. Compare the stability of +2 oxidation state for the elements of the first transition series.

Ans. Refer to Ans. 3. of NCERT Textbook Exercises.

Q. 20. Compare the chemistry of actinoids with that of lanthanoids with special reference to

(*i*) electronic configuration **(*ii*) oxidation states**

(*iii*) atomic and ionic sizes **(*iv*) chemical reactivity.**

OR

Give three points of difference between lanthanoids and actinoids. **[*CBSE 2020 (56/1/1)*]**

Ans. (*i*) **Electronic configuration:** The general electronic configuration of lanthanoids is $[Xe]^{54}\,4f^{1-14}\,5d^{0-1}\,6s^2$ whereas that of actinoids is $[Rn]^{86}\,5f^{1-14}\,6d^{0-1}\,7s^2$. Thus, lanthanoids belong to 4*f*-series whereas actinoids belong to 5*f*-series.

(*ii*) **Oxidation states:** Lanthanoids show limited oxidation states (+2, +3, +4), out of which, +3 is most common. This is because of a large energy gap between 4*f*, 5*d* and 6*s* subshells. On the other hand, actinoids show a large number of oxidation states because of small energy gap between 5*f*, 6*d* and 7*s* subshells.

(*iii*) **Atomic and ionic sizes:** Both show decrease in size of their atoms or ions in +3 oxidation state. In lanthanoids, the decrease is called lanthanoid contraction whereas in actinoids, it is called actinoid contraction. However, the contraction is greater from element to element in actinoids due to poorer shielding by 5*f*-electrons.

(*iv*) **Chemical reactivity:**

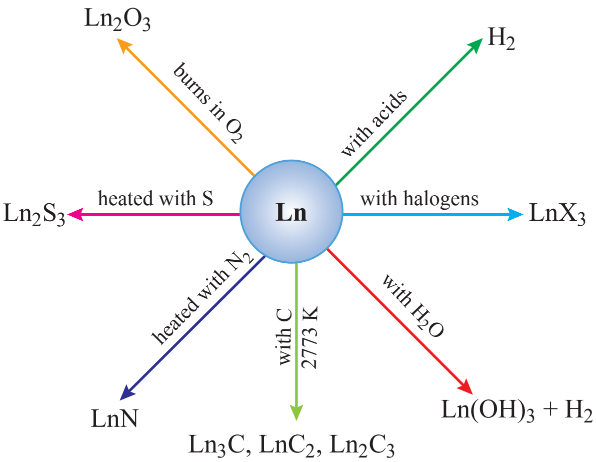
Lanthanoids: In general, the earlier members of the series are quite reactive (similar to calcium) but with increasing atomic number, they behave more like aluminium.

Values for E^o for the half-reaction:

$$Ln^{3+}(aq) + 3e^- \longrightarrow Ln(s)$$

are in the range of –2.2 to –2.4 V except for Eu for which the value is –2.0 V. This is ofcourse, a small variation.

The metals combine with hydrogen when gently heated in the gas. The carbides, Ln_3C, Ln_2C_3 and LnC_2 are formed when the metals are heated with carbon. They liberate hydrogen from dilute acids and burn in halogens to form halides. They form oxides and hydroxides—M_2O_3 and $M(OH)_3$. The hydroxides are definite compounds, not just hydrated oxides, basic like alkaline earth metal oxides and hydroxides.



Chemical reactions of the lanthanoids

Actinoids: The actinoids are highly reactive metals, especially when finely divided. The action of boiling water on them, for example, gives a mixture of oxide and hydride and combination with most non-metals takes place at moderate temperatures. Hydrochloric acid attacks all metals but most are slightly affected by nitric acid owing to the formation of protective oxide layers; alkalis have no action.

Actinoids are more reactive than lanthanoids due to bigger atomic size and lower ionisation energy.

Q. 21. How would you account for the following:

(*i*) Of the d^4 species, Cr^{2+} is strongly reducing while manganese (III) is strongly oxidising.

(*ii*) Cobalt (II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidised.

(*iii*) The d^1 configuration is very unstable in ions.

Ans. (*i*) $E°$ value for Cr^{3+}/Cr^{2+} is negative (–0.41 V) whereas $E°$ value for Mn^{3+}/Mn^{2+} is positive (+1.57 V). Thus, Cr^{2+} ions can easily undergo oxidation to give Cr^{3+} ions and, therefore, act as strong reducing agent. On the other hand, Mn^{3+} can easily undergo reduction to give Mn^{2+} and hence act as oxidising agent.

(*ii*) This is because in presence of complexing reagents the CFSE value compensates more than the third ionisation energy of cobalt.

(*iii*) The ions with d^1 configuration have the tendency to lose the only electron present in *d*-subshell to acquire stable d^0 configuration. Therefore, they are unstable and undergo oxidation or disproportionation.

Q. 22. What is meant by 'disproportionation'? Give two examples of disproportionation reaction in aqueous solution.

Ans. Disproportionation reactions are those reactions in which the same substance undergoes oxidation as well as reduction. In disproportionation reaction, oxidation number of an element increases as well as decreases to form two different products. For example,

$$\overset{\text{VI}}{3\text{MnO}_4^{2-}} + 4\text{H}^+ \longrightarrow \overset{\text{VII}}{2\text{MnO}_4^-} + \overset{\text{IV}}{\text{MnO}_2} + 2\text{H}_2\text{O}$$

$$\overset{\text{V}}{3\text{CrO}_4^{3-}} + 8\text{H}^+ \longrightarrow \overset{\text{VI}}{2\text{CrO}_4^{2-}} + \overset{\text{III}}{\text{Cr}^{3+}} + 4\text{H}_2\text{O}$$

Q. 23. Which metal in the first transition series exhibits +1 oxidation state most frequently and why?

Ans. Cu has the electronic configuration $3d^{10}\ 4s^1$. It can easily lose $4s^1$ electron to give the stable $3d^{10}$ configuration. Hence, it shows +1 oxidation state.

Q. 24. Calculate the number of unpaired electrons in the following gaseous ions:
(*i*) Mn^{3+}, (*ii*) Cr^{3+}, (*iii*) V^{3+} and (*iv*) Ti^{3+}.

Which one of these is the most stable in aqueous solution?

Ans. (*i*) $Mn^{3+} = 3d^4$ = 4 unpaired electrons (*ii*) $Cr^{3+} = 3d^3$ = 3 electrons
(*iii*) $V^{3+} = 3d^2$ = 2 electrons (*iv*) $Ti^{3+} = 3d^1$ = 1 electron.

Cr^{3+} is the most stable in aqueous solution because it has half-filled t_{2g} level (*i.e.*, t^3_{2g}).

Q. 25. Give example and suggest reasons for the following features of the transition metal chemistry:
(*i*) The lowest oxide of transition metal is basic, the highest is amphoteric/acidic.
(*ii*) A transition metal exhibits higher oxidation states in oxides and fluorides.
(*iii*) The highest oxidation state is exhibited in oxo-anions of a metal.

Ans. (*i*) The lowest oxide of transition metal is basic because the metal atom has low oxidation state. This means that it can donate valence electrons which are not involved in bonding to act like a base. Whereas the highest oxide is acidic due to the highest oxidation state as the valence electrons are involved in bonding and are unavailable. For example, MnO is basic whereas Mn_2O_7 is acidic.

(*ii*) A transition metal exhibits higher oxidation states in oxides and fluorides because oxygen and fluorine are highly electronegative elements, small in size (and strongest oxidising agents). For example, osmium shows an oxidation states of +6 in OsF_6 and vanadium shows an oxidation state of +5 in V_2O_5.

(*iii*) Oxometal anions have the highest oxidation state, *e.g.*, Cr in $Cr_2O_7^{2-}$ has an oxidation state of +6 whereas Mn in MnO_4^- has an oxidation state of +7. This is again due to the combination of the metal with oxygen, which is highly electronegative and oxidising element.

Q. 26. Indicate the steps in the preparation of
(*i*) $K_2Cr_2O_7$ from chromite ore.
(*ii*) $KMnO_4$ from pyrolusite ore.

Ans. (*i*) Refer to Basic Concepts Point 4(*a*).
(*ii*) Refer to Basic Concepts Point 4(*b*).

Q. 27. What are alloys? Name an important alloy which contains some of the lanthanoid metals. Mention its uses.

Ans. An alloy is a homogeneous mixture of two or more metals, or metals and non-metals. An important alloy containing lanthanoid metals is misch metal which contains 95% lanthanoid metals and 5% iron alongwith traces of S, C, Ca and Al. It is used in Mg-based alloy to produce bullets, shells and lighter flints.

Q. 28. What are inner-transition elements? Decide which of the following atomic numbers are the numbers of the inner-transition elements: 29, 59, 74, 95, 102, 104.

Ans. The *f*-block elements, *i.e.*, in which the last electron enters into *f*-subshell are called inner-transition elements. These include lanthanoids (58–71) and actinoids (90–103). Thus, elements with atomic numbers 59, 95 and 102 are inner-transition elements.

Q. 29. The chemistry of the actinoid elements is not so smooth as that of the lanthanoids. Justify this statement by giving some examples from the oxidation state of these elements.

Ans. Lanthanoids show a limited number of oxidation state, *viz.*, +2, +3 and +4 (out of which +3 is the most common). This is because of a large energy gap between 4*f*, 5*d* and 6*s* subshells. The dominant oxidation state of actinoids is also +3 but they show a number of other oxidation states also, *e.g.*, uranium ($Z = 92$) and plutonium ($Z = 94$) show +3, +4, +5 and +6, neptunium ($Z = 94$) shows +3, +4, +5 and +7, etc. This is due to small energy difference between 5*f*, 6*d* and 7*s* subshells of the actinoids.

Q. 30. Which is the last element of the series of the actinoids? Write the electronic configuration of this element. Comment on the possible oxidation state of this element.

Ans. Last actinoid = Lawrencium ($Z = 103$)

Electronic configuration = $[Rn]^{86}\ 5f^{14}\ 6d^{1}\ 7s^{2}$

Possible oxidation state = +3

Q. 31. Use Hund's rule to derive the electronic configuration of Ce^{3+} ion and calculate its magnetic moment on the basis of spin only formula.

Ans. $_{58}Ce = [Xe]^{54}\ 4f^{1}\ 5d^{1}\ 6s^{2}$

$Ce^{3+} = [Xe]^{54}\ 4f^{1}$, *i.e.*, there is only one unpaired electron, *i.e.*, $n = 1$.

Hence, $\mu = \sqrt{n\,(n+2)} = \sqrt{1(1+2)} = \sqrt{3} = \mathbf{1.73\ BM}$

Q. 32. Name the members of the lanthanoid series which exhibit +4 oxidation states and those which exhibit +2 oxidation states. Try to correlate this type of behaviour with the electronic configuration of these elements.

Ans. $+4 = {}_{58}Ce,\ {}_{59}Pr,\ {}_{60}Nd,\ {}_{65}Tb,\ {}_{66}Dy$

$+2 = {}_{60}Nd,\ {}_{62}Sm,\ {}_{63}Eu,\ {}_{69}Tm,\ {}_{70}Yb$

+2 oxidation state is exhibited when the lanthanoid has the configuration $5d^{0}\ 6s^{2}$ so that 2 electrons are easily lost. +4 oxidation state is exhibited when the configuration left is close to $4f^{0}$ (*e.g.*, $4f^{0}$, $4f^{1}$, $4f^{2}$) or close to $4f^{7}$ (*e.g.*, $4f^{7}$ or $4f^{8}$)

Q. 33. Compare the chemistry of the actinoids with that of landthanoids with reference to:

(*i*) electronic configuration **(*ii*) oxidation states and**

(*iii*) chemical reactivity

Ans.

S.No.	Characteristics	Lanthanoids	Actinoids
(*i*)	Electronic configuration	$[Xe]\ 4f^{1-14}\ 5d^{0-1}\ 6s^{2}$	$[Rn]\ 5f^{1-14}\ 6d^{0-1}\ 7s^{2}$
(*ii*)	Oxidation states	Besides +3 O.S lanthanoids show +2 and +4 O.S only in a few cases.	Besides +3 O.S actinoids show higher O.S of +4, +5, +6, +7 also because of smaller energy gap between 5*f*, 6*d* and 7*s* subshell.
(*iii*)	General chemical reactivity of elements	These are less reactive metals.	These are highly reactive metals.
		Lesser tendency towards complex formation.	Greater tendency towards complex formation.
		Do not form oxocation.	Form oxocation.
		Compounds are less basic.	Compounds are more basic.

Q. 34. Write the electronic configurations of the elements with atomic numbers 61, 91, 101 and 109.

Ans. Z = 61 (Promethium, Pm), E.C. = $[Xe]\ 4f^{5}\ 5d^{0}\ 6s^{2}$

Z = 91 (Protactium, Pa), E.C. = $[Rn]\ 5f^{2}\ 6d^{1}\ 7s^{2}$

Z = 101 (Mendelevium, Md), E.C. = $[Rn]\ 5f^{13}\ 6d^{0}\ 7s^{2}$

Z = 109 (Meitnerium, Mt), E.C. = $[Rn]\ 5f^{14}\ 6d^{7}\ 7s^{2}$

Q. 35. Compare the general characteristics of the first series of transition metals with those of the second and third series metals in the respective vertical columns on the basis of following points:

(*i*) electronic configurations, **(*ii*) oxidation states,**

(*iii*) ionisation enthalpies, and **(*iv*) atomic sizes.**

Ans. **(*i*) Electronic configurations:** The elements in the same vertical column generally have similar electronic configurations. Although, the first series shows only two exceptions, *i.e.*, Cr = $[Ar]\ 3d^{5}\ 4s^{1}$ and Cu = $[Ar]\ 3d^{10}\ 4s^{1}$ but the second series shows more exceptions, *e.g.*, Mo(42) = $[Kr]\ 4d^{5}\ 5s^{1}$, Ru(44) = $[Kr]\ 4d^{7}\ 5s^{1}$, Rh(45) = $[Kr]\ 4d^{8}\ 5s^{1}$, Pd(46) = $[Kr]\ 4d^{10}\ 5s^{0}$, Ag(47) = $[Kr]\ 4d^{10}\ 5s^{1}$. Similarly, in the third series, W(74) = $[Xe]\ 4f^{14}\ 5d^{4}\ 6s^{2}$, Pt(78) = $[Xe]\ 4f^{14}\ 5d^{9}\ 6s^{1}$ and Au(79) = $[Xe]\ 4f^{14}\ 5d^{10}\ 6s^{1}$. Hence, in the same vertical column, in a number of cases, the electronic configuration of the three series are not similar.

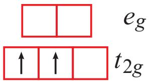
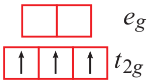
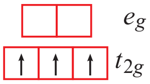
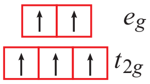
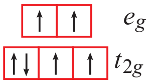
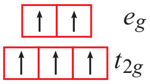
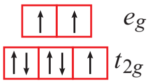
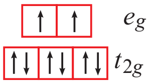
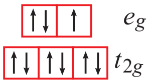
(*ii*) **Oxidation states:** The elements in the same vertical column generally show similar oxidation states. The number of oxidation states shown by the elements in the middle of each series is maximum and minimum at the extreme ends.

(*iii*) **Ionisation enthalpies:** The first ionisation enthalpies in each series generally increase gradually as we move from left to right though some exceptions are observed in each series. The first ionisation enthalpies of some elements in the second (4*d*) series are higher while some of them have lower value than the elements of 3*d*- series in the same vertical column. However, the first ionisation enthalpies of third (5*d*) series are higher than those of 3*d* and 4*d*- series. This is because of weak shielding of nucleus of 4*f*-electrons in the 5*d*-series.

(*iv*) **Atomic sizes:** Generally, ions of the same charge or atoms in a given series show progressively decrease in radius with increasing atomic number though the decrease is quite small. But the size of the atoms of the 4*d*-series is larger than the corresponding elements of the 3*d*-series whereas those of corresponding elements of the 5*d*-series are nearly the same as those of 4*d*-series due to lanthanoid contraction.

Q. 36. Write down the number of 3*d* electrons in each of the following ions:
Ti^{2+}, V^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+}.
Indicate how would you expect the five 3d-orbitals to be occupied for these hydrated ions (octahedral).

Ans.

	Ions	**Electronic Configurations**	**No. of 3*d* electrons**	**3*d*-orbitals occupied**	
(*i*)	Ti^{2+}	$[Ar]3d^2$	2	t_{2g}^2	
(*ii*)	V^{2+}	$[Ar]3d^3$	3	t_{2g}^3	
(*iii*)	Cr^{3+}	$[Ar]3d^3$	3	t_{2g}^3	
(*iv*)	Mn^{2+}	$[Ar]3d^5$	5	$t_{2g}^3 e_g^2$	
(*v*)	Fe^{2+}	$[Ar]3d^6$	6	$t_{2g}^4 e_g^2$	
(*vi*)	Fe^{3+}	$[Ar]3d^5$	5	$t_{2g}^3 e_g^2$	
(*vii*)	Co^{2+}	$[Ar]3d^7$	7	$t_{2g}^5 e_g^2$	
(*viii*)	Ni^{2+}	$[Ar]3d^8$	8	$t_{2g}^6 e_g^2$	
(*ix*)	Cu^{2+}	$[Ar]3d^9$	9	$t_{2g}^6 e_g^3$	

Q. 37. Comment on the statement that elements of the first transition series possess many properties different from those of heavier transition elements. **[*HOTS*]**

Ans. The given statement is true. Some evidences in support of this statement are:

(*i*) Atomic radii of the heavier transition elements (4*d* and 5*d*- series) are larger than those of the corresponding elements of the first transition series though those of 4*d* and 5*d*- series are very close to each other.

(*ii*) Ionisation enthalpies of 5*d*- series are higher than the corresponding elements of 3*d* and 4*d*- series.

(*iii*) Enthalpies of atomisation of 4*d* and 5*d*- series are higher than the corresponding elements of the first series.

(*iv*) Melting and boiling points of heavier transition elements are greater than those of the first transition series due to stronger intermetallic bonding.

Q. 38. What can be inferred from the magnetic moment values of the following complex species?

Example	**Magnetic Moment (BM)**
$K_4[Mn(CN)_6]$	2.2
$[Fe(H_2O)_6]^{2+}$	5.3
$K_2[MnCl_4]$	5.9

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

$$\text{For } n=1,\ \mu=\sqrt{1(1+2)}=\sqrt{3}=1.73; \quad \text{For } n=2,\ \mu=\sqrt{2(2+2)}=\sqrt{8}=2.83$$

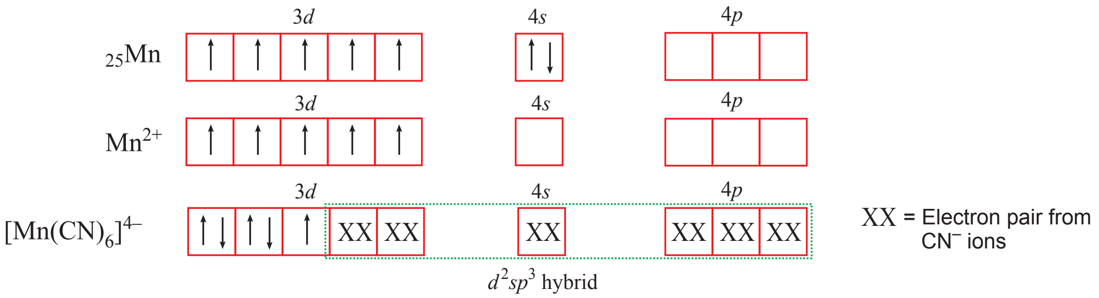
$$\text{For } n=3,\ \mu=\sqrt{3(3+2)}=\sqrt{15}=3.87; \quad \text{For } n=4,\ \mu=\sqrt{4(4+2)}=\sqrt{24}=4.90$$

$$\text{For } n=5,\ \mu=\sqrt{5(5+2)}=\sqrt{35}=5.92$$

$K_4[Mn(CN)_6]$

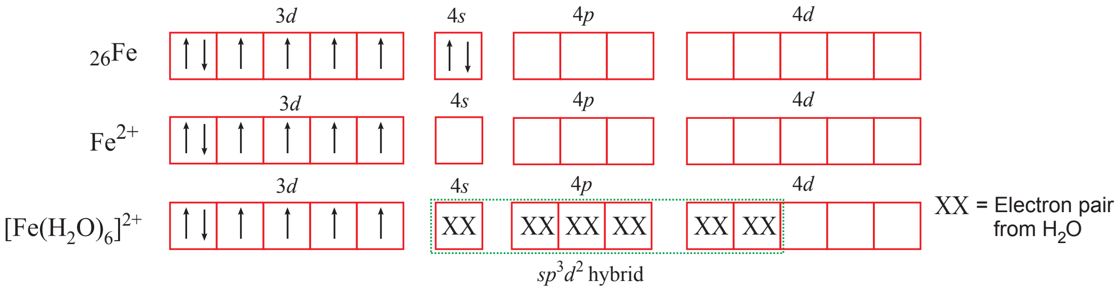
Here, Mn is in +2 oxidation state, *i.e.*, as Mn^{2+}, μ = 2.2 BM shows that it has only one unpaired electron. Hence, when CN^- ligands approach Mn^{2+} ion, the electrons in 3*d*-subshell pair up.

Hence, CN^- is a strong ligand. The hybridisation involved is d^2sp^3 forming inner orbital octahedral complex.



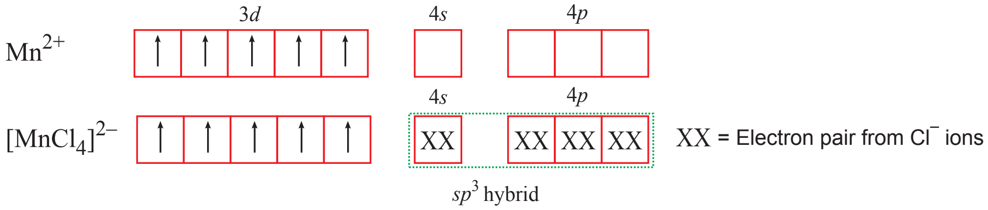
$[Fe(H_2O)_6]^{2+}$

Here, Fe is in +2 oxidation state, *i.e.*, as Fe^{2+}. μ = 5.3 BM shows that there are four unpaired electrons. This means that the electrons in 3*d*-subshell do not pair up when the ligand H_2O molecules approach. Hence, H_2O is a weak ligand. To accommodate the electrons donated by six H_2O molecules, the hybridisation will be sp^3d^2. Hence, it will be an outer orbital octahedral complex.



$K_2[MnCl_4]$

Here, Mn is in +2 state, *i.e.*, as Mn^{2+}. μ = 5.9 BM shows that there are five unpaired electrons. Hence, the hybridisation involved will be sp^3 and the complex will be tetrahedral.



Multiple Choice Questions [1 mark]

Choose and write the correct option(s) in the following questions.

1. **Electronic configuration of a transition element X in +3 oxidation state is $[Ar]3d^5$. What is its atomic number?** [*NCERT Exemplar*]
   (*a*) 25 (*b*) 26 (*c*) 27 (*d*) 24

2. **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**

[*NCERT Exemplar*]
   (*a*) Fe (*b*) Ni (*c*) Co (*d*) Cu

3. **Which of the following statements is not correct?** [*NCERT Exemplar*]
   (*a*) Copper liberates hydrogen from acids.
   (*b*) In its higher oxidation states, manganese forms stable compounds with oxygen and fluorine.
   (*c*) Mn^{3+} and Co^{3+} are oxidising agents in aqueous solution.
   (*d*) Ti^{2+} and Cr^{2+} are reducing agents in aqueous solution.

4. **Which of the following is amphoteric oxide?**
   Mn_2O_7, CrO_3, Cr_2O_3, CrO, V_2O_5, V_2O_4 [*NCERT Exemplar*]
   (*a*) V_2O_5, Cr_2O_3 (*b*) Mn_2O_7, CrO_3
   (*c*) CrO, V_2O_5 (*d*) V_2O_5, V_2O_4

5. **Which one of the following does not correctly represent the correct order of the property indicated against it ?**
   (*a*) $Ti < V < Cr < Mn$, increasing number of oxidation states
   (*b*) $Ti < V < Mn < Cr$, increasing second ionisation enthalpy
   (*c*) $Ti < V < Cr < Mn$, increasing melting point
   (*d*) $Ti^{3+} < V^{3+} < Cr^{3+} < Mn^{3+}$, increasing magnetic moment

6. **The magnetic moment is associated with its spin angular momentum and orbital angular momentum. Spin only magnetic moment value of Cr^{3+} ion is ____________.** [*NCERT Exemplar*]
   (*a*) 2.87 B.M. (*b*) 3.87 B.M. (*c*) 3.47 B.M. (*d*) 3.57 B.M.

7. **Transition elements show magnetic moment due to spin and orbital motion of electrons. Which of the following metallic ions have almost same spin only magnetic moment?** [*NCERT Exemplar*]
   (*a*) Co^{2+} (*b*) Cr^{2+} (*c*) Mn^{2+} (*d*) Cr^{3+}

8. **The electronic configuration of Cu(II) is $3d^9$ whereas that of Cu(I) is $3d^{10}$. Which of he following is correct?** [*NCERT Exemplar*]
   (*a*) Cu(II) is more stable
   (*b*) Cu(II) is less stable
   (*c*) Cu(I) and Cu(II) are equally stable
   (*d*) Stability of Cu(I) and Cu(II) depends on nature of copper salts

9. **Generally transition elements form coloured salts due to the presence of unpaired electrons. Which of the following compounds will be coloured in solid state?** [*NCERT Exemplar*]
   (*a*) Ag_2SO_4 (*b*) CuF_2 (*c*) ZnF_2 (*d*) Cu_2Cl_2

10. **Which of the following statement about transition element is not correct?**
   (*a*) They show variable oxidation states.
   (*b*) They exhibit diamagnetic and paramagnetic properties.
   (*c*) All ions are coloured.
   (*d*) They exhibit catalytic property.

11. On addition of small amount of $KMnO_4$ to concentrated H_2SO_4, a green oily compound is obtained which is highly explosive in nature. Identify the compound from the following. [*NCERT Exemplar*]

(*a*) Mn_2O_7 (*b*) MnO_2 (*c*) $MnSO_4$ (*d*) Mn_2O_3

12. Generally transition elements and their salts are coloured due to the presence of unpaired electrons in metal ions. Which of the following compounds are coloured? [*NCERT Exemplar*]

(*a*) $KMnO_4$ (*b*) $Ce(SO_4)_2$ (*c*) $TiCl_4$ (*d*) Cu_2Cl_2

13. When $KMnO_4$ solution is added to oxalic acid solution, the decolourisation is slow in the beginning but becomes instantaneous after some time because [*NCERT Exemplar*]

(*a*) CO_2 is formed as the product. (*b*) Reaction is exothermic.

(*c*) MnO_4^- catalyses the reaction. (*d*) Mn^{2+} acts as autocatalyst.

14. Which of the following reactions are disproportionation reactions? [*NCERT Exemplar*]

(*i*) $Cu^+ \longrightarrow Cu^{2+} + Cu$

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

(*iii*) $2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$

(*iv*) $2MnO_4^- + 3Mn^{2+} + 2H_2O \longrightarrow 5MnO_2 + 4H^+$

(*a*) (*i*), (*ii*) (*b*) (*i*), (*ii*), (*iii*) (*c*) (*ii*), (*iii*), (*iv*) (*d*) (*i*), (*iv*)

15. $KMnO_4$ acts an oxidising agent in acidic medium. The number of moles of $KMnO_4$ that will be needed to react with one mole of sulphide ions in acidic solution is [*NCERT Exemplar*]

(*a*) $\frac{2}{5}$ (*b*) $\frac{3}{5}$ (*c*) $\frac{4}{5}$ (*d*) $\frac{1}{5}$

16. $KMnO_4$ acts as an oxidising agent in alkaline medium. When alkaline $KMnO_4$ is treated with KI, iodide ion is oxidised to ____________. [*NCERT Exemplar*]

(*a*) I_2 (*b*) IO^- (*c*) IO_3^- (*d*) IO_4^-

17. Which of the following oxidation state is common for all lanthanoids? [*NCERT Exemplar*]

(*a*) +2 (*b*) +3 (*c*) +4 (*d*) +5

18. Gadolinium belongs to 4*f* series. It's atomic number is 64. Which of the following is the correct electronic configuration of gadolinium? [*NCERT Exemplar*]

(*a*) $[Xe]\,4f^7 5d^1 6s^2$ (*b*) $[Xe]\,4f^6 5d^2 6s^2$

(*c*) $[Xe]\,4f^8 6d^2$ (*d*) $[Xe]\,4f^9 5s^1$

19. Identify the incorrect statement among the following:

(*a*) Lanthanoid contraction is the accumulation of successive shrinkages.

(*b*) There is a decrease in the radii of the atoms or ions as one proceeds from La to Lu.

(*c*) As a result of lanthanoid contraction, the properties of 4*d* series of the transition elements have no similarities with the 5*d* series of elements.

(*d*) Shielding power of 4*f* electrons is quite weak.

20. Actinoids exhibit greater number of oxidation states than lanthanoids. The main reason being

(*a*) more energy difference between 5*f* and 6*d* than between 4*f* and 5*f* orbitals

(*b*) 4*f* orbitals are more diffused than the 5*f* orbitals

(*c*) lesser energy difference between 5*f* and 6*d* than between 4*f* and 5*d* orbitals

(*d*) more reactive nature of the actinoids than the lanthanoids.

Answers

1. (*b*) **2.** (*d*) **3.** (*a*) **4.** (*a*) **5.** (*c*) **6.** (*b*) **7.** (*a, d*) **8.** (*a*) **9.** (*b*) **10.** (*c*)

11. (*a*) **12.** (*a, b*) **13.** (*d*) **14.** (*a*) **15.** (*a*) **16.** (*c*) **17.** (*b*) **18.** (*a*) **19.** (*c*) **20.** (*c*)

Assertion-Reason Questions

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

- *(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).*
- *(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).*
- *(c) Assertion (A) is correct, but Reason (R) is incorrect statement.*
- *(d) Assertion (A) is incorrect, but Reason (R) is correct statement.*

1. **Assertion (*A*) :** In transition elements *ns* orbital is filled up first and $(n-1)d$ afterwards, during ionization *ns* electrons are lost prior to $(n-1)d$ electrons.
   Reason (*R*) : The effective nuclear charge felt by $(n-1)d$ electrons is higher as compared to that by *ns* electrons.
2. **Assertion (*A*) :** Zn, Cd and Hg cannot be regarded as transition elements.
   Reason (*R*) : These elements do not belong to the *d*-block of the periodic table.
3. **Assertion (*A*) :** Transition metals are strong reducing agents.
   Reason (*R*) : Transition metals form numerous alloys with other metals.
4. **Assertion (*A*) :** Amongst Cu^{2+} and Cu^{+} ions, the more stable ions is Cu^{2+}.
   Reason (*R*) : For determination of stability of an ion its electrode potential is more important factor than its electronic configuration.
5. **Assertion (*A*) :** Transition metals form complexes.
   Reason (*R*) : Transition metals have unpaired electrons.
6. **Assertion (*A*) :** A solution of ferric chloride on standing gives a brown precipitate.
   Reason (*R*) : $FeCl_3$ possesses covalent bonds and chlorine bridge structure.
7. **Assertion (*A*) :** Members of 4*d* and 5*d* series of transition elements have nearly same atomic radii.
   Reason (*R*) : Atomic and ionic radii for transition elements are smaller than their corresponding *s*-block elements.
8. **Assertion (*A*) :** The most common oxidation state exhibited by actinoids is +2.
   Reason (*R*) : All actinoids possess two electrons in 7*s* subshell.
9. **Assertion (*A*) :** Ce^{4+} is used as an oxidising agent in volumetric analysis.
   Reason (*R*) : Ce^{4+} has the tendency of attaining +3 oxidation state.
10. **Assertion (*A*) :** The degree of complex formation in actinides decreases in the order
    $M^{4+} > MO_2^{2+} > M^{3+} > MO_2^{+}$
    Reason (*R*) : Actinides form complexes with π-bonding ligands such as alkyl phosphines and thioethers.

Answers

1. (*a*) **2.** (*c*) **3.** (*d*) **4.** (*b*) **5.** (*b*) **6.** (*b*) **7.** (*b*) **8.** (*d*) **9.** (*a*) **10.** (*b*)

Passage-based/Case-based Questions

Read the given passages and answer the questions that follow.

PASSAGE–1

The *d*-block elements are those elements in which the last electron enters the *d*-subshell of the penultimate shell. The general electronic configuration of these elements is $(n-1)\,d^{1-10}\,ns^{1-2}$, where *n* is outermost shell. The *d*-block consisting of groups 3–12 occupies the large middle section of the periodic table. The elements of *d*-block are also known as transition elements as they possess properties that are transitional between the *s* and *p* block elements. A transition element is defined as an element which has incompletely filled *d*-orbitals in its ground state or any one of its oxidation states. There are four series of transition elements spread between group 3 and 12. First transition series or 3*d*-series: Scandium ($_{21}$Sc) to Zinc ($_{30}$Zn), Second transition series or 4*d*-series: Yttrium ($_{39}$Y) to Cadmium ($_{48}$Cd), Third transition series or 5*d*-series: Lanthanum ($_{57}$La) and Hafnium ($_{72}$Hf) to Mercury ($_{80}$Hg) (Omitting $_{58}$Ce to $_{71}$Lu), Fourth transition series or 6*d*-series: Begins with Actinium ($_{89}$Ac) is still incomplete.

1. In what way is the electronic configuration of transition elements different from that of the non-transition elements?

Ans. Transition elements contain incompletely filled *d*-subshell, *i.e.*, their electronic configuration is $(n-1)\,d^{1-10}\,ns^{1-2}$ whereas non-transition elements have no *d*-subshell or their subshell is completely filled and have ns^{1-2} or $ns^2\,np^{1-6}$ in their outermost shell.

2. Why is zinc not regarded as a transition clement? [*CBSE Guwahati 2015*]

Ans. As zinc atom has completely filled *d*-orbitals ($3d^{10}$) in its ground state as well as in oxidised state, therefore, it is not regarded as a transition element.

3. Why does a transition series contain 10 elements?

Ans. There are five *d*-orbitals in an energy level and each orbital can contain two electrons. As we move from one element to the next, an electron is added and for complete filling of the five *d*-orbitals, 10 electrons are required.

4. Name the element which shows outer electronic configuration $3d^3\,4s^2$.

Ans. Vanadium

5. What are interstitial compounds?

Ans. Interstitial compounds are those in which small atoms occupy the interstitial sites in the crystal lattice.

PASSAGE–2

Potassium permanganate, ($KMnO_4$) is prepared by fusion of pyrolusite, MnO_2 with KOH in the presence of an oxidising agent like KNO_3. This produces the dark green potassium manganate, K_2MnO_4 which disproportionates in a neutral or acidic solution to give purple permanganate ion. Potassium permanganate is an important oxidising agent in acidic, alkaline as well as neutral medium.

1. What is the state of hybridisation of Mn in MnO_4^-?

Ans. sp^3

2. Write an application of potassium permanganate.

Ans. It is used for the estimation of hydrogen peroxide.

3. What are the products formed after heating potassium permanganate?

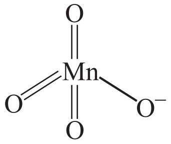
Ans. K_2MnO_4, O_2 and MnO_2 will be formed after heating of potassium permanganate.

4. How many electrons are involved in oxidation by $KMnO_4$ in an acidic medium?

Ans. Five electrons are involved in oxidation by $KMnO_4$ in an acidic medium.

5. Draw the structure of permanganate ion. Is it paramagnetic or diamagnetic?

Ans.



Tetrahedral permanganate ion
(purple)

It is diamagnetic.

Very Short Answer Questions [1 mark]

Q. 1. Copper atom has completely filled *d*-orbitals in its ground state but it is a transition element. Why? [*CBSE Chennai 2015*]

Ans. Copper exhibits +2 oxidation state wherein it has incompletely filled *d* orbitals ($3d^9\,4s^0$) hence, a transition element.

Q. 2. Give reason:

Zn is soft whereas Cr is hard. **[*CBSE South 2016*]**

Ans. Cr ($3d^5\ 4s^1$) has five unpaired electrons in its *d*-orbitals whereas Zn ($3d^{10}\ 4s^2$) has no unpaired electrons in its *d*-orbitals. As a result of this weak metallic bonds exist in Zn whereas strong metallic bonds exist in Cr. Hence, Zn is soft whereas Cr is hard.

Q. 3. Reactivity of transition elements decreases almost regularly from Sc to Cu. Explain. **[*NCERT Exemplar*]**

Ans. It is due to regular increase in ionisation enthalpy.

Q. 4. Arrange the following in increasing order of acidic character: **[*HOTS*]**

CrO_3, CrO, Cr_2O_3

Ans. CrO < Cr_2O_3 < CrO_3. Higher the oxidation state, more will be acidic character.

Q. 5. Why does copper not replace hydrogen from acids? **[*NCERT Exemplar*]**

Ans. Cu shows E^o positive value.

Q. 6. Which divalent metal ion has maximum paramagnetic character among the first transition metals? Why?

Ans. Mn^{2+} has the maximum paramagnetic character because of the maximum number of unpaired electrons, *viz*., 5.

Q. 7. Although Cr^{3+} and Co^{2+} ions have same number of unpaired electrons but the magnetic moment of Cr^{3+} is 3.87 BM and that of Co^{2+} is 4.87 BM. Why? **[*NCERT Exemplar*] [*HOTS*]**

Ans. Due to symmetrical electronic configuration there is no orbital contribution in Cr^{3+} ion. However, appreciable orbital contribution takes place in Co^{2+} ion.

Q. 8. Out of Cu_2Cl_2 and $CuCl_2$, which is more stable and why? **[*NCERT Exemplar*] [*HOTS*]**

Ans. $CuCl_2$ is more stable than Cu_2Cl_2. The stability of $Cu^{2+}(aq)$ is more than $Cu^{+}(aq)$ due to the much more negative $\Delta_{hyd.}H^o$ of $Cu^{2+}(aq)$ than $Cu^{+}(aq)$.

Q. 9. Zn^{2+} salts are white while Cu^{2+} salts are coloured. Why? **[*CBSE Patna 2015*]**

Ans. Cu^{2+} ($3d^9\ 4s^0$) has one unpaired electron in *d*-subshell which absorbs radiation in visible region resulting in *d-d* transition and hence Cu^{2+} salts are coloured. Zn^{2+} ($3d^{10}\ 4s^0$) has completely filled *d*-orbitals. No radiation is absorbed for *d-d* transition and hence Zn^{2+} salts are colourless.

Q. 10. Write any one use of pyrophoric alloys.

Ans. Pyrophoric alloys emit sparks when struck. Hence, they are used in making flints for lighters.

Short Answer Questions–I [2 marks]

Q. 1. Use the data to answer the following and also justify giving reason: **[*CBSE 2019 (56/4/1)*]**

	Cr	Mn	Fe	Co
$E^o_{M^{2+}/M}$	–0.91	–1.18	–0.44	–0.28
$E^o_{M^{3+}/M^{2+}}$	–0.41	–1.57	–0.77	+1.97

(*i*) Which is a stronger reducing agent in aqueous medium, Cr^{2+} or Fe^{2+} and why?

(*ii*) Which is the most stable ion in +2 oxidation and why?

Ans. (*i*) Cr^{2+}, due to lower standard reduction potential (E^o)/Higher standard oxidation potential.

(*ii*) Mn^{2+}, due to highest negative standard reduction potential.

Q. 2. In the following ions:

Mn^{3+}, V^{3+}, Cr^{3+}, Ti^{4+}

(Atomic no. : Mn = 25, V = 23, Cr = 24, Ti = 22)

(*i*) Which ion is most stable in an aqueous solution?

(*ii*) Which ion is the strongest oxidizing agent?

(*iii*) Which ion is colourless?

(*iv*) Which ion has the highest number of unpaired electrons? **[*CBSE (F) 2017*]**

Ans. (*i*) Cr^{3+} because of half filled t_{2g} level.

(*ii*) Mn^{3+}, as the change from Mn^{3+} to Mn^{2+} results in stable half filled (d^5) configuration.

(*iii*) Ti^{4+}, as Ti^{4+} has empty *d*-orbitals therefore *d*-*d* transition cannot occur in Ti^{4+}.

(*iv*) Mn^{3+} ($3d^4 4s^0$). It has 4 unpaired electrons.

Q. 3. Give reasons for the following:

(*i*) E^o values of Mn, Ni and Zn are more negative than expected.

(*ii*) $[Ti(H_2O)]^{3+}$ is coloured while $[Sc(H_2O)_6]^{3+}$ is colourless. **[*HOTS*]**

OR

Ti^{3+} is coloured whereas Sc^{3+} is colourless in aqueous solution. **[*CBSE 2020 (56/5/1)*]**

Ans. (*i*) Negative E^o values for Mn^{2+} and Zn^{2+} are related to stabilities of half-filled and fully filled configurations, respectively. But for Ni^{2+}, E^o value is related to the highest negative enthalpy of hydration.

(*ii*) This is due to *d*-*d* transition of electron in $[Ti(H_2O)_6]^{3+}$ complex. Ti^{3+} has one electron in *d*-orbital ($3d^1$) which absorbs energy corresponding to blue-green region and jumps from t_{2g} to e_g set of *d*-orbitals ($t_{2g}^1 e_g^0 \longrightarrow t_{2g}^0 e_g^1$). But Sc^{3+} has no electron in the *d*-orbital.

Q. 4. How would you account for the following:

(*i*) Mn (III) undergoes disproportionation reaction easily.

(*ii*) Co (II) is easily oxidised in the presence of strong ligands. **[*CBSE (F) 2011*]**

Ans. (*i*) Mn^{3+} is less stable and changes to Mn^{2+} which is more stable due to half filled *d*-orbital configuration. That is why, Mn^{3+} undergoes disproportionation reaction.

(*ii*) Co (II) has electronic configuration $3d^7 4s^0$, *i.e.*, it has three unpaired electrons. In the presence of strong ligands, two unpaired electrons in 3*d*-subshell pair-up and third unpaired electron shifts to higher energy subshell from where it can be easily lost and hence oxidised to Co(III).

Q. 5. When $FeCr_2O_4$ is fused with Na_2CO_3 in the presence of air it gives a yellow solution of compound (A). Compound (A) on acidification gives compound (B). Compound (B) on reaction with KCl forms an orange coloured (C). An acidified solution of compound (C) oxidises Na_2SO_3 to (D). Identify (A), (B), and (D.) **[*CBSE 2019 (56/2/1)*]**

Ans. $A = \underset{\text{Sodium chromate}}{Na_2CrO_4}$, $B = \underset{\text{Sodium dichromate}}{Na_2Cr_2O_7}$, $C = \underset{\text{Potassium dichromate}}{K_2Cr_2O_7}$, $D = \underset{\text{Sodium sulphate}}{Na_2SO_4}$

Q. 6. Complete the following chemical reaction equations:

(*i*) $MnO_4^-(aq) + C_2O_4^{2-}(aq) + H^+(aq) \longrightarrow$

(*ii*) $Cr_2O_7^{2-}(aq) + Fe^{2+}(aq) + H^+(aq) \longrightarrow$

Ans. (*i*)

$$\begin{array}{rcl}
[MnO_4^- + 8H^+ + 5e^- & \longrightarrow & Mn^{2+} + 4H_2O] \times 2 \\
[C_2O_4^{2-} & \longrightarrow & 2CO_2 + 2e^-] \times 5 \\
\hline
MnO_4^- + 5C_2O_4^{2-} + 16H^+ & \longrightarrow & 2Mn^{2+} + 10CO_2 + 8H_2O \\
\hline
\end{array}$$

(*ii*)

$$\begin{array}{rcl}
Cr_2O_7^{2-} + 14H^+ + 6e^- & \longrightarrow & 2Cr^{3+} + 7H_2O \\
Fe^{2+} & \longrightarrow & Fe^{3+} + e^-] \times 6 \\
\hline
Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ & \longrightarrow & 2Cr^{3+} + 6Fe^{3+} + 7H_2O \\
\hline
\end{array}$$

Q. 7. Complete the following chemical equations:

(*i*) $8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow$

(*ii*) $Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \longrightarrow$ **[*CBSE Delhi 2016*]**

Ans. (*i*)

$$\begin{array}{rcl}
8MnO_4^- + 2H_2O + 3e^- & \longrightarrow & MnO_2 + 4OH^-] \times 8 \\
S_2O_3^{2-} + 10OH^- & \longrightarrow & 2SO_4^{2-} + 5H_2O + 8e^-] \times 3 \\
\hline
8MnO_4^- + 3S_2O_3^{2-} + H_2O & \longrightarrow & 8MnO_2 + 6SO_4^{2-} + 2OH^- \\
\hline
\end{array}$$

(*ii*)

$$\begin{array}{rcl}
Cr_2O_7^{2-} + 14H^+ + 6e^- & \longrightarrow & 2Cr^{3+} + 7H_2O \\
Sn^{2+} & \longrightarrow & Sn^{4+} + 2e^-] \times 3 \\
\hline
Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ & \longrightarrow & 2Cr^{3+} + 3Sn^{4+} + 7H_2O \\
\hline
\end{array}$$

Q. 8. **Complete and balance the following equations:** **[*CBSE 2019 (56/5/2)*]**

(*i*) $MnO_4^- + I^- + H^+ \longrightarrow$

(*ii*) $Na_2Cr_2O_7 + KCl \longrightarrow$

Ans. (*i*) $2MnO_4^- + 10I^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5I_2$

(*ii*) $Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$

Q. 9. **Transition metals can act as catalysts because these can change their oxidation state. How does Fe(III) catalyse the reaction between iodide and persulphate ions?** **[*NCERT Exemplar*]**

Ans. Reaction between iodide and persulphate ions is:

$$2I^- + S_2O_8^{2-} \xrightarrow{Fe(III)} I_2 + 2SO_4^{2-}$$

Role of Fe(III) ions:

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

$$2Fe^{2+} + S_2O_8^{2-} \longrightarrow 2Fe^{3+} + 2SO_4^{2-}$$

Q. 10. **Explain each of the following observations:**

(*i*) **Mn^{2+} is much more resistant than Fe^{2+} towards oxidation.** **[*CBSE Delhi 2012*]**

(*ii*) **Among lanthanoids, Ln(III) compounds are predominant. However, occasionally in solutions or in solid compounds, +2 and +4 ions are also obtained.** **[*CBSE (AI) 2012*]**

Ans. (*i*) $Mn^{3+}(d^4)$ is less stable than Mn^{2+} (d^5, half filled) while Fe^{3+} (d^5, half filled) is more stable than Fe^{2+} (d^4). That is why Mn^{2+} is more resistance than Fe^{2+} towards oxidation.

(*ii*) Lanthanoid metals show +2 and +4 oxidation states to attain extra stable f^0 and f^7 configurations.

Q. 11. **Explain each of the following observations:**

(*i*) **Actinoids exhibit a much larger number of oxidation states than the lanthanoids.** **[*CBSE 2019 (56/2/1)*]**

(*ii*) **There is hardly any increase in atomic size with increasing atomic numbers in a series of transition metals.** **[*CBSE (F) 2012*]**

Ans. (*i*) This is due to small energy gap between 5*f*, 6*d* and 7*s* subshells in actinoids.

(*ii*) This is because with increase in atomic number in a series, the increased nuclear charge is partly cancelled by the increased shielding effect of electrons in the *d*-orbitals of penultimate shell.

Short Answer Questions–II [3 marks]

Q. 1.

$E^o_{Mn^{2+}/Mn}$	Cr	Mn	Fe	Co	Ni	Cu
	– 0.91	– 1.18	– 0.44	– 0.28	– 0.25	+0.34

From the given data of E^o values, answer the following questions:

(*i*) **Why is $E^o_{(Cu^{2+}/Cu)}$ value exceptionally positive?**

(*ii*) **Why is $E^o_{(Mn^{2+}/Mn)}$ value highly negative as compared to other elements?**

(*iii*) **Which is a stronger reducing agent Cr^{2+} or Fe^{2+} ? Give reason.** **[*CBSE Patna 2015*] [*HOTS*]**

Ans. (*i*) Copper has high enthalpy of atomisation and low enthalpy of hydration. Since the high energy to transform Cu(*s*) to Cu^{2+}(*aq*) is not balanced by hydration enthalpy, therefore, $E^o_{Cu^{2+}/Cu}$ value is exceptionally positive.

(*ii*) This is due to extra stability of half-filled 3*d*-orbitals of $Mn^{2+}(3d^5)$.

(*iii*) Refer to NCERT Intext Questions, Q. 7.

Q. 2. The elements of 3*d* transition series are given as:

Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn ***[CBSE East 2016]***

Answer the following:

(*i*) Copper has exceptionally positive $E^o_{M^{2+}/M}$ value. Why?

(*ii*) Which element is a strong reducing agent in +2 oxidation state and why?

(*iii*) Zn^{2+} salts are colourless. Why?

Ans. (*i*) Because the sum of sublimation enthalpy and hydration enthalpy to convert Cu(*s*) to Cu^{2+}(*aq*) is so high that it is not balanced by its hydration enthalpy.

(*ii*) Cr is strongest reducing agent in +2 oxidation state. Cr^{2+} has configuration $3d^4$. After losing one electron it forms Cr^{3+} which has stable half filled t_{2g} level.

(*iii*) $Zn^{2+}(3d^{10})$ has completely filled *d*-orbitals. As a result of this, *d*-*d* transition cannot occur and hence, Zn^{2+} salts are colourless.

Q. 3. (*i*) For M^{2+}/M and M^{3+}/M^{2+} systems, E^o values for some metals are as follows:

$Cr^{2+}/Cr = -0.9$ V $Cr^{3+}/Cr^{2+} = -0.4$ V

$Mn^{2+}/Mn = -1.2$ V $Mn^{3+}/Mn^{2+} = +1.5$ V

$Fe^{2+}/Fe = -0.4$ V $Fe^{3+}/Fe^{2+} = +0.8$ V

Use this data to comment upon

(*a*) the stability of Fe^{3+} in acid solution as compared to that of Cr^{3+} and Mn^{3+}.

(*b*) the ease with which iron can be oxidised as compared to the similar process for either Cr or Mn metals.

(*ii*) What can be inferred from the magnetic moment of the complex $K_4[Mn(CN)_6]$, Magnetic moment: 2.2 BM? ***[CBSE Sample Paper 2016]***

Ans. (*i*) (*a*) Higher the reduction potential of a species, greater is the ease with which it undergo reduction. Among these pairs, Mn^{3+}/Mn^{2+} has largest positive reduction potential. Hence Mn^{3+} can be easily reduced to Mn^{2+} *i.e.*, Mn^{3+} is least stable. Cr^{3+}/Cr^{2+} has a negative $E°$ value, therefore, Cr^{3+} is most stable. Fe^{3+}/Fe^{2+} has a positive value but small. Hence, Fe^{3+} is more stable than Mn^{3+} but less stable than Cr^{3+}.

(*b*) Lower the reduction potential or higher the oxidation potential of a species, greater is the ease with which it undergo oxidation. Among these pairs, Mn^{2+}/Mn has the most negative reduction potential or most positive oxidation potential. Therefore, it will be most easily oxidised. Thus, the decreasing order of their ease of oxidation is Mn > Cr > Fe.

(*ii*) In the complex $K_4[Mn(CN)_6]$, Mn is in +2 oxidation state. Magnetic moment 2.2 BM indicates that it has only one unpaired electron and hence forms inner orbital or low spin octahedral complex. In presence of CN^-, a strong ligand the hybridisation involved is d^2sp^3.

Q. 4. Account for the following:

(*i*) Eu^{2+} is a strong reducing agent.

(*ii*) Orange colour of dichromate ion changes to yellow in alkaline medium.

(*iii*) $E^o_{M^{2+}/M}$ values for transition metals show irregular variation. ***[CBSE (F) 2017]***

Ans. (*i*) This is because Eu^{2+} tends to change to Eu^{3+} as +3 is the common oxidation state of lanthanoids.

(*ii*) In alkaline medium, the orange colour of the solution changes to yellow due to conversion of dichromate ($Cr_2O_7^{2-}$) ion to chromate (CrO_4^{2-}) ion.

$$\underset{\text{Orange}}{Cr_2O_7^{2-}} + 2OH^- \rightleftharpoons \underset{\text{Yellow}}{2CrO_4^{2-}} + H_2O$$

(*iii*) The irregularity is due to the irregular variation of ionisation enthalpies ($\Delta_i H + \Delta_i H_2$) and also the sublimation enthalpies which are relatively much less for Mn (240 kJ mol^{-1}) and V (470 kJ mol^{-1}).

Q. 5. Complete the following reactions: **[CBSE 2019 (56/4/1)]**

(*i*) $MnO_2 + KOH + O_2 \longrightarrow$

(*ii*) $I^- + MnO_4^- + H^+ \longrightarrow$

(*iii*) $Cr_2O_7^{2-} + Sn^{2+} + H^+ \longrightarrow$

Ans. (*i*) $2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$

(*ii*) $10I^- + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5I_2$

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

Q. 6. When a brown compound of manganese (A) is treated with HCl it gives a gas (B). The gas taken in excess, reacts with NH_3 to give an explosive compound (C). Identify compounds A and B. **[*NCERT Exemplar*] [*HOTS*]**

Ans. A = MnO_2 [Manganese (IV) oxide]
B = Cl_2 (Chlorine)
C = NCl_3 (Nitrogen trichloride)

$$\underset{(A)}{MnO_2} + 4HCl \longrightarrow MnCl_2 + \underset{(B)}{Cl_2}\uparrow + 2H_2O$$

$$NH_3 + \underset{(excess)}{3Cl_2} \longrightarrow \underset{(C)}{NCl_3} + 3HCl$$

Q. 7. A solution of $KMnO_4$ on reduction yields either a colourless solution or a brown precipitate or a green solution depending on pH of the solution. What different stages of the reduction do these represent and how are they carried out? **[*NCERT Exemplar*]**

Ans. Oxidising behaviour of $KMnO_4$ depends on pH of the solution.

In acidic medium (pH < 7),

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

In alkaline medium (pH > 7),

$$MnO_4^- + e^- \longrightarrow \underset{(Green)}{MnO_4^{2-}}$$

In neutral medium (pH = 7),

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow \underset{(Brown\ precipitate)}{MnO_2} + 2OH^-$$

Q. 8. (*i*) How would you account for the following:

(*a*) Highest fluoride of Mn is MnF_4 whereas the highest oxide is Mn_2O_7.

(*b*) Transition metals and their compounds show catalytic properties. **[CBSE 2020 (56/5/1)]**

(*ii*) Complete the following equation:

$3MnO_4^{2-} + 4H^+ \longrightarrow$ **[CBSE (F) 2015]**

Ans. (*i*) (*a*) As oxygen stabilises manganese more than fluorine by forming multiple bonds.

(*b*) The catalytic activity of transition metals and their compounds is attributed to the following reasons:

- Due to their tendency to show variable oxidation states transition metals form unstable intermediate compounds and provide a new path for the reaction with lower activation energy.
- In some cases, the transition metals provide a suitable large surface area with free valencies on which reactants are adsorbed.

(*ii*)
$$\underset{Manganate\ ion}{3MnO_4^{2-}} + 4H^+ \longrightarrow \underset{Permanganate\ ion}{2MnO_4^-} + MnO_2 + 4H_2O$$

Q. 9. Explain the following observations:

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

(*ii*) There is a close similarity in physical and chemical properties of the 4*d* and 5*d* series of the transition elements, much more than expected on the basis of usual family relationship.

(*iii*) The members in the actinoid series exhibit larger number of oxidation states than the corresponding members in the lanthanoid series. **[*NCERT Exemplar*]**

Ans. (*i*) This is because transition metals have strong metallic bonds as they have large number of unpaired electrons.

(*ii*) This is because 5*d* and 4*d*-series elements have virtually the same atomic and ionic radii due to lanthanoid contraction. Due to equality in size of Zr and Hf, Nb and Ta, Mo and W, etc., the two elements of each pair have the same properties.

(*iii*) The members in the actinoid series exhibit larger number of oxidation states than the corresponding members in the lanthanoid series due to the fact that the 5*f*, 6*d* and 7*s* levels are of comparable energies.

Q. 10. Account for the following:

(*i*) Mn_2O_7 is acidic whereas MnO is basic.

(*ii*) Though copper has completely filled *d*-orbital (d^{10}) yet it is considered as a transition metal.

(*iii*) Actinoids show wide range of oxidation states. **[*CBSE (F) 2016*]**

Ans. (*i*) Mn has + 7 oxidation state in Mn_2O_7 and + 2 in MnO. In low oxidation state of the metal, some of the valence electrons of the metal atom are not involved in bonding. Hence, it can donate electrons and behave as a base. On the other hand, in higher oxidation state of the metal, valence electrons are involved in bonding and are not available. Instead effective nuclear charge is high and hence it can accept electrons and behave as an acid.

(*ii*) Copper exhibits +2 oxidation state wherein it will have incompletely filled *d*-orbitals ($3d^9$), hence a transition metal.

(*iii*) This is due to comparable energies of 5*f*, 6*d* and 7*s* orbitals.

Long Answer Questions [5 marks]

Q. 1. (*i*) The elements of 3*d* transition series are given as:

Sc Ti V Cr Mn Fe Co Ni Cu Zn

Answer the following:

(*a*) Which element has the highest m.p. and why?

(*b*) Which element is a strong oxidising agent in +3 oxidation state and why?

(*c*) Which element is soft and why?

(*ii*) Write the equations involved in the preparation of potassium dichromate from sodium chromate (Na_2CrO_4). **[*CBSE (F) 2016*]**

Ans. (*i*) (*a*) Cr, the highest melting point of Cr is attributed to the involvement of greater number of electrons(5) from 3*d* in addition to 4*s* electrons in interatomic metallic bonding.

(*b*) Mn, because the change from Mn^{3+} (d^4) to Mn^{2+} (d^5) results in the half filled configuration which has extra stability.

(*c*) Zn, in Zn ($3d^{10}\ 4s^2$) all the electrons present in *d*-orbitals are paired and hence metallic bonds present in it are weak. That is why, it is soft.

(*ii*) Sodium chromate is acidified with sulphuric acid to give a solution from which orange sodium dichromate, $Na_2Cr_2O_7.2H_2O$ can be crystallised.

$$2Na_2CrO_4 + 2H^+ \longrightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$$

Sodium dichromate is more soluble than potassium dichromate. The latter is therefore, prepared by treating the solution of sodium dichromate with potassium chloride.

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

Q. 2. ***(i)*** **Is the variability in oxidation number of transition elements different from that of non-transition elements? Illustrate with examples.**

(ii) **Give reasons:**

(a) ***d*-block elements exhibit more oxidation states than *f*-block elements.**

(b) **Orange solution of potassium dichromate turns yellow on adding sodium hydroxide to it.**

(c) **Zirconium (Z = 40) and Hafnium (Z = 72) have almost similar atomic radii.**

[CBSE Sample Paper 2017]

Ans. (*i*) In transition elements, the oxidation states differ from each other by unity, *e.g.*, Fe^{3+} and Fe^{2+} etc., while in non-transition elements (*p*-block elements), the oxidation states differ by two, *e.g.*, Pb^{4+} and Pb^{2+}, etc.

In transition elements the higher oxidation states are more stable for the heavier elements in a group, *e.g.*, Mo(VI) is more stable than Cr(VI) whereas in non-transition elements (*p*-block elements), the lower oxidation states are more stable for heavier elements due to inert pair effect, *e.g.*, Pb(II) is more stable than Pb(IV).

(*ii*) (*a*) *d*–block elements exhibit more oxidation states because of less energy gap between *d* and *s* subshell whereas *f*-block elements have large energy gap between *f* and *d* subshell.

(*b*) On adding NaOH, pH of solution increases and the orange colour of the solution changes to yellow due to conversion of dichromate ion to chromate ion.

$$\underset{\substack{\text{Dichromate ion}\\ \text{(Orange)}}}{Cr_2O_7^{2-}} + 2OH^- \rightleftharpoons \underset{\substack{\text{Chromate ion}\\ \text{(Yellow)}}}{2CrO_4^{2-}} + H_2O$$

(*c*) This is due to filling of 4*f*-orbitals which have poor shielding effect (Lanthanoid contraction).

Q. 3. ***(i)*** **Describe the preparation of potassium permanganate from pyrolusite ore. Write balanced chemical equation for one reaction to show the oxidizing nature of potassium permanganate.**

(ii) **Draw the structures of chromate and dichromate ions.** *[CBSE Sample Paper 2017]*

Ans. (*i*) Conversion of pyrolusite (MnO_2) into potassium manganate (K_2MnO_4).

$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$

Electrolytic oxidation:

$$K_2MnO_4 \rightleftharpoons 2K^+ + MnO_4^{2-}$$

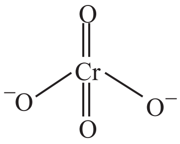
At anode: $MnO_4^{2-} \longrightarrow MnO_4^- + e^-$

At cathode: $H^+ + e^- \longrightarrow H,\quad 2H \longrightarrow H_2$

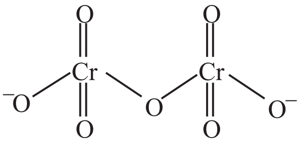
It oxidises oxalate ($C_2O_4^{2-}$) to carbon dioxide (CO_2) in acidic medium.

$$\begin{array}{rcl} MnO_4^- + 8H^+ + 5e^- & \longrightarrow & Mn^{2+} + 4H_2O] \times 2 \\ C_2O_4^{2-} & \longrightarrow & 2CO_2 + 2e^-] \times 5 \\ \hline 2MnO_4^- + 5C_2O_4^{2-} + 16H^+ & \longrightarrow & 2Mn^{2+} + 10CO_2 + 8H_2O \\ \hline \end{array}$$

(*ii*)



Chromate ion



Dichromate ion

Q. 4. **(*i*) Compare non transition and transition elements on the basis of their**

(*a*) Variability of oxidation states

(*b*) Stability of oxidation states.

(*ii*) Give chemical reactions for the following observations:

(*a*) Potassium permanganate is a good oxidising agent in basic medium.

(*b*) Inter convertibility of chromate ion and dichromate ion in aqueous solution depends upon pH of the solution.

(*c*) Potassium permanganate is thermally unstable at 513K. ***[CBSE Sample Paper 2013]***

Ans. (*i*) (*a*) Oxidation states of transition elements differ from each other by unity. In non-transition elements oxidation states normally differ by a unit of two.

(*b*) In transition elements higher oxidation states are favoured by heavier elements whereas in non-transition elements lower oxidation state is favoured by heavier elements.

(*ii*) (*a*)

$$\begin{array}{l} MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-] \times 2 \\ I^- + 6OH^- \longrightarrow IO_3^- + 3H_2O + 6e^- \\ \hline 2MnO_4^- + I^- + H_2O \longrightarrow IO_3^- + 2MnO_2 + 2OH^- \\ \hline \end{array}$$

(*b*) $2CrO_4^{2-} + 2H^+ \underset{\text{Alkali (pH more than 7)}}{\overset{\text{Acid (pH less than 7}}{\rightleftharpoons}} Cr_2O_7^{2-} + H_2O$

(*c*) $2KMnO_4 \xrightarrow{513\ K} K_2MnO_4 + MnO_2 + O_2$

Q. 5. **(*i*) In the titration of $FeSO_4$ with $KMnO_4$ in the acidic medium, why is dil. H_2SO_4 used instead of dil. HCl?**

(*ii*) Give reasons:

(*a*) Among transition metals, the highest oxidation state is exhibited in oxoanions of a metal.

(*b*) Ce^{4+} is used as an oxidising agent in volumetric analysis. ***[CBSE 2019(56/2/3)]***

(*c*) Zn^{2+} salts are white while Cu^{2+} salts are blue.

OR

Why is Cu^{2+} ion coloured while Zn^{2+} ion is colourless in aqueous solution?*[CBSE 2020 (56/3/1)]*

Ans. (*i*) Dil. H_2SO_4 is an oxidising agent and oxidises $FeSO_4$ to $Fe_2(SO_4)_3$. Dil. HCl is a reducing agent and liberates chlorine on reacting with $KMnO_4$ solution.

Hence, the part of the oxygen produced from $KMnO_4$ is used up by HCl.

(*ii*) (*a*) In these oxoanions the oxygen atoms are directly bonded to the transition metal.

Since oxygen is highly electronegative, the oxoanions bring out the highest oxidation state of the metal.

(*b*) Ce^{4+} has the tendency to attain +3 oxidation state which is more stable and so it is used as an oxidising agent in volumetric analysis.

(*c*) Zn^{2+} ion has all its orbitals completely filled whereas in Cu^{2+} ion there is one half-filled 3*d*-orbital. Therefore, due to *d-d* transition Cu^{2+} has a tendency to form coloured salts whereas Zn^{2+} has no such tendency.

Q. 6. **A violet compound of manganese (A) decomposes on heating to liberate oxygen and compounds (B) and (C) of manganese are formed. Compound (C) reacts with KOH in the presence of potassium nitrate to give compound (B). On heating compound (C) with conc. H_2SO_4 and NaCl, chlorine gas is liberated and a compound (D) of manganese along with other products is formed. Identify compounds A to D and also explain the reactions involved.** ***[NCERT Exemplar] [HOTS]***

Ans. A = $KMnO_4$ (Potassium permanganate), B = K_2MnO_4 (Potassium manganate),

C = MnO_2 (Manganese (IV) oxide), D = $MnCl_2$ (Manganese (II) chloride)

$$\underset{\text{(A)}}{2KMnO_4} \xrightarrow{\Delta} \underset{\text{(B)}}{K_2MnO_4} + \underset{\text{(C)}}{MnO_2} + O_2$$

$$\underset{(C)}{MnO_2} + 2KOH + KNO_3 \longrightarrow \underset{(B)}{K_2MnO_4} + H_2O + KNO_2$$

$$MnO_2 + 4NaCl + 4H_2SO_4 \longrightarrow \underset{(D)}{MnCl_2} + 4NaHSO_4 + 2H_2O + Cl_2$$

Q. 7. When an oxide of manganese (A) is fused with KOH in the presence of an oxidising agent and dissolved in water, it gives a dark solution of compound (B). Compound (B) disproportionates in neutral or acidic solution to give purple compound (C). An alkaline solution of compound (C) oxidises potassium iodide solution to a compound (D) and compound (A) is also formed. Identify compounds A to D and also explain the reactions involved. **[*NCERT Exemplar*] [*HOTS*]**

Ans. A = MnO_2 (Manganese (IV) oxide), B = K_2MnO_4 (Potassium manganate),
C = $KMnO_4$ (Potassium permanganate), D = KIO_3 (Potassium iodate)

$$\underset{(A)}{2MnO_2} + 4KOH + O_2 \longrightarrow \underset{(B)}{2K_2MnO_4} + 2H_2O$$

$$3K_2MnO_4 + 4H^+ \longrightarrow \underset{(C)}{2KMnO_4} + MnO_2 + 2H_2O + 4K^+$$

$$2MnO_4^- + H_2O + KI \longrightarrow \underset{(A)}{2MnO_2} + 2OH^- + \underset{(D)}{KIO_3}$$

Q. 8. ***(i)* Write balanced equations to represent what happens when**

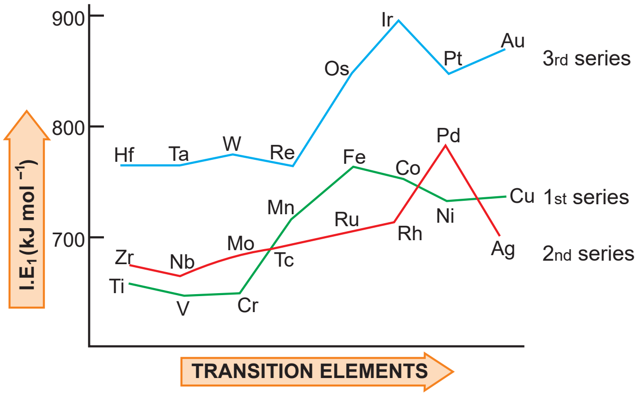
- **(*a*) Cu^{2+} is treated with KI.**
- **(*b*) Acidified potassium dichromate solution is reacted with iron (II) solution. (ionic equation)**

***(ii)* (*a*) The figure given illustrates the first ionization enthalpies of first, second and third series of transition elements. Answer the question that follows:**

Which series amongst the first, second and third series of transition elements have the highest first ionization enthalpy and why?

(*b*) Separation of lanthanoid elements is difficult. Explain. **[*CBSE 2020 (56/5/1)*]**

(*c*) Sm^{2+}, Eu^{2+} and Yb^{2+} ions in solutions are good reducing agents but an aqueous solution of Ce^{4+} is a good oxidising agent. Why? **[*CBSE Sample Paper 2015*]**



Ans. (*i*) (*a*) $2Cu^{2+} + 4I^- \longrightarrow Cu_2I_2 + I_2$

(*b*) $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-] \times 6$$

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

(*ii*) (*a*) Third series has the highest first ionization energy due to poorest shielding effect of the fully filled 4*f* subshell.

(*b*) Due to lanthanoid contraction, some pair of elements have almost similar size and as a result, such pairs have very similar properties which makes their separation difficult.

(*c*) Sm^{2+}, Eu^{2+} and Yb^{2+} ions are good reducing agents as they tend to acquire common oxidation state of + 3 shown by lanthanoids by the loss of one electron while Ce^{4+} gains one electron to attain + 3. Hence, Ce^{4+} is an oxidising agent.

Q. 9. (*i*) Account for the following:

(*a*) Transition metals form large number of complex compounds. [*CBSE 2019 (56/2/1)*]

(*b*) The lowest oxide of transition metal is basic whereas the highest oxide is amphoteric or acidic.

(*c*) E^o value for the Mn^{3+}/Mn^{2+} couple is highly positive (+ 1.57 V) as compare to Cr^{3+}/Cr^{2+}.

(*ii*) Write one similarity and one difference between the chemistry of lanthanoid and actinoid elements. [*CBSE Delhi 2017*]

Ans. (*i*) (*a*) The tendency to form complex compounds is due to:

—Small size and high charge on metal ion.

—The availability of *d* orbitals for accommodating electrons donated by the ligand.

(*b*) In low oxidation state of the metal, some of the valence electrons of the metal atom are not involved in bonding. Hence, it can donate electrons and behave as a base. On the other hand, in higher oxidation state of the metal, valence electrons are involved in bonding and are not available. Instead effective nuclear charge is high and hence it can accept electrons and behave as an acid.

(*c*) Much large third ionisation energy of Mn (where the required change is stable half filled d^5 to d^4) is mainly responsible for this.

(*ii*) **Similarities**

— Both show mainly an oxidation state of +3.

— Actinoids show actinoid contraction like lanthanoid contraction is shown by lanthanoids.

— Both are electropositive and very reactive. (*Any one*)

Differences

— Except promethium (Pm) lanthanoids are non-radioactive whereas actinoids are radioactive.

— Lanthanoids do not form oxocation whereas actinoids form oxocation.

— Lanthanoids have less tendency towards complex formation whereas actinoids have greater tendency towards complex formation. (*Any one*)

Q. 10. Assign reasons for the following:

(*i*) The enthalpies of atomisation of transition elements are high.

(*ii*) The transition metals and many of their compounds act as good catalysts.

(*iii*) From element to element, the actinoid contraction is greater than the lanthanoid contraction.

(*iv*) The E^0 value for the Mn^{3+}/Mn^{2+} couple is much more positive than that of Cr^{3+}/Cr^{2+}.

(*v*) Scandium ($Z = 21$) does not exhibit variable oxidation states and yet it is regarded as a transition element. [*CBSE 2019 (56/2/3)*]

Ans. (*i*) This is because transition metals have strong metallic bonds as they have a large number of unpaired electrons.

(*ii*) The catalytic activity of transition metals is attributed to the following reasons:

(*a*) Because of their variable oxidation states, transition metals form unstable intermediate compounds and provide a new path with lower activation energy for the reaction.

(*b*) In some cases, the transition metal provides a suitable large surface area with free valencies on which reactants are adsorbed.

(*iii*) This is due to poorer shielding by 5*f*-electrons in actinoids than that by 4*f*-electrons in the lanthanoids.

(*iv*) This is due to much larger third ionisation energy of Mn as Mn^{2+} is very stable on account of stable d^5 configuration.

(*v*) This is because scandium has partially filled *d*-orbitals in the ground state ($3d^1\ 4s^2$).

Self-Assessment Test

Time allowed: 1 hour **Max. marks: 30**

Choose and write the correct answer for each of the following. (3 × 1 = 3)

1. **Why is HCl not used to make the medium acidic in oxidation reactions of $KMnO_4$ in acidic medium?**
   (*a*) Both HCl and $KMnO_4$ act as oxidising agents.
   (*b*) $KMnO_4$ oxidises HCl into Cl_2 which is also an oxidising agent.
   (*c*) $KMnO_4$ is a weaker oxidising agent than HCl.
   (*d*) $KMnO_4$ acts as a reducing agent in the presence of HCl.

2. **Which element among the lanthanides has the smallest atomic radius?**
   (*a*) Cerium (*b*) Lutetium
   (*c*) Europium (*d*) Gadolinium

3. **In acidic medium, one mole of MnO_4^- ion accepts how many moles of electrons in a redox process?**
   (*a*) 1 (*b*) 2
   (*c*) 5 (*d*) 6

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

(*a*) *Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).*
(*b*) *Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).*
(*c*) *Assertion (A) is correct, but Reason (R) is incorrect statement.*
(*d*) *Assertion (A) is incorrect, but Reason (R) is correct statement.* (3 × 1 = 3)

4. **Assertion (*A*) :** Separation of Zr and Hf is difficult.
   Reason (*R*) : Because Zr and Hf lie in the same group of the periodic table.
5. **Assertion (*A*) :** Actinoids form relatively less stable complexes as compared to lanthanoids.
   Reason (*R*) : Actinoids can utilise their 5*f* orbitals along with 6*d* orbitals in bonding but lanthanoids do not use their 4*f* orbital for bonding.
6. **Assertion (*A*) :** Cu cannot liberate hydrogen from acids.
   Reason (*R*) : Because it has positive electrode potential.

Answer the following questions:

7. Why lanthanoids are called as *f*-block elements? (1)
8. Name a member of the lanthanoid series which is known to exhibit +4 oxidation state. (1)
9. Account for the following:.
   (*i*) Cobalt (III) is stable in aqueous solution but in the presence of complexing reagents, it is easily oxidised.
   (*ii*) The d^1 configuration is very unstable in ions. (2)
10. Complete the following equations:
    (*i*) $MnO_4^- + 4H^+ + 3e^- \longrightarrow$
    (*ii*) $Cr_2O_7^{2-} + 2OH^- \longrightarrow$ (2)

11. (*i*) Calculate the magnetic moment of a divalent ion in aqueous solution if its atomic number is 25.

(*ii*) While filling up of electrons in the atomic orbitals, the 4*s* orbital is filled before the 3*d* orbital but reverse happens during the ionisation of the atom. Explain why.

[*NCERT Exemplar*] (2)

12. Explain the following observations:

(*i*) Colour of $KMnO_4$ disappears when oxalic acid is added to its solution in acidic medium.

(*ii*) A green solution of potassium manganate turns purple when CO_2 gas is passed through the solution. **(2)**

13. Assign suitable reasons for the following:

(*i*) The Mn^{2+} compounds are more stable than Fe^{2+} towards oxidation to their +3 state.

(*ii*) Sc^{3+} is colourless in aqueous solution whereas Ti^{3+} is coloured.

(*iii*) The highest oxidation state is exhibited in oxo-anions of a metal. **[*CBSE (F) 2014*] (3)**

14. When pyrolusite ore MnO_2 is fused with KOH in presence of air, a green coloured compound (*A*) is obtained which undergoes disproportionation reaction in acidic medium to give a purple coloured compound (*B*).

(*i*) Write the formulae of the compounds (A) and (B).

(*ii*) What happens when compound (B) is heated? **[*CBSE (South) 2016*] (3)**

15. (*i*) With reference to structural variability and chemical reactivity, write the differences between lanthanoids and actinoids.

(*ii*) Name a member of the lanthanoid series which is well known to exhibit +4 oxidation state.

(*iii*) Out of Mn^{3+} and Cr^{3+}, which is more paramagnetic and why?
(Atomic nos.: Mn = 25, Cr = 24) **(3)**

16. On the basis of lanthanoid contraction, explain the following:

(*i*) Nature of bonding in La_2O_3 and Lu_2O_3.

(*ii*) Trends in the stability of oxo salts of lanthanoids from La to Lu.

(*iii*) Stability of the complexes of lanthanoids.

(*iv*) Radii of 4*d* and 5*d* block elements.

(*v*) Trends in acidic character of lanthanoid oxides. **(5)**

Answers

1. (*b*) **2.** (*b*) **3.** (*c*) **4.** (*b*) **5.** (*d*) **6.** (*a*)