

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

basic concepts

- 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.
- 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 ($_{21}\text{Sc}$) to Zinc ($_{30}\text{Zn}$)

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

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

Fourth transition series or 6*d*-series: Begins with Actinium ($_{89}\text{Ac}$) 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 *3d*-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 *4s*-orbital of the stable $3d^{10}4s^2$ configuration.

The first ionisation enthalpies of *5d*-transition elements are higher than those of *3d* and *4d* 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 *4f*-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.

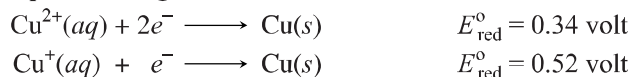
In moving along series from left to right, the melting and boiling points of transition elements first increase to a maximum and then decrease towards the end of the period. As the number of unpaired electrons increases, the tendency to form metallic and covalent bonds also increases. In first transition 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 $3d^54s^2$ 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:



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



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 $3d$ -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.

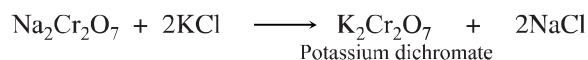
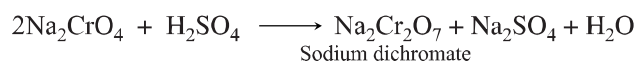
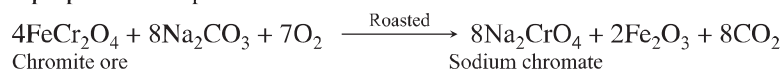
4. **Some Important Compounds of Transition Elements:** Though the transition elements are sufficiently electropositive, yet they are not very reactive because of

- (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,

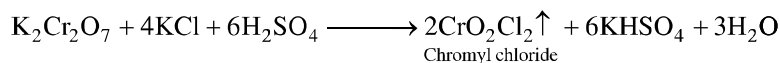
+2	+3	+8/3	+4	+7
MnO	Mn ₂ O ₃	Mn ₃ O ₄	MnO ₂	Mn ₂ O ₇
Basic	Amphoteric	Amphoteric	Amphoteric	Acidic

(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:

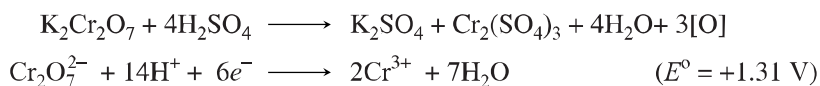


$K_2Cr_2O_7$ is separated by fractional crystallisation.

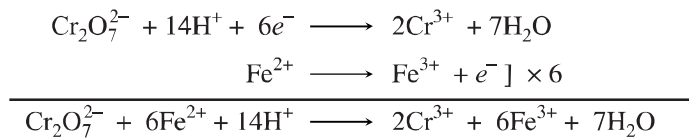
Properties: When potassium dichromate is heated with any ionic chloride (e.g., NaCl, BaCl₂, etc.) and concentrated H_2SO_4 , red vapours of chromyl chloride are obtained.



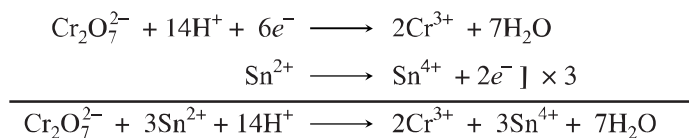
Potassium dichromate is a powerful oxidising agent. In acidic medium, its oxidation action can be represented as follows:



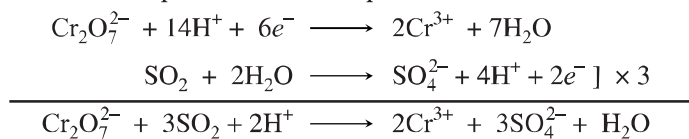
(i) It oxidises ferrous to ferric.



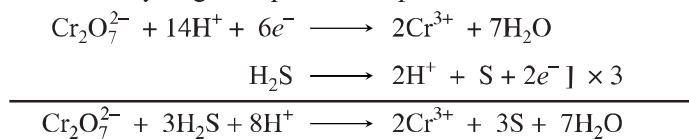
(ii) It oxidises stannous to stannic.



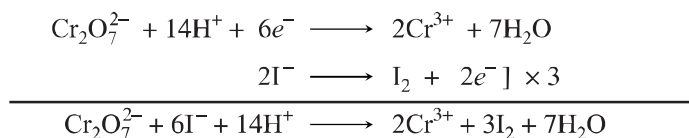
(iii) It oxidises sulphur dioxide to sulphuric acid.



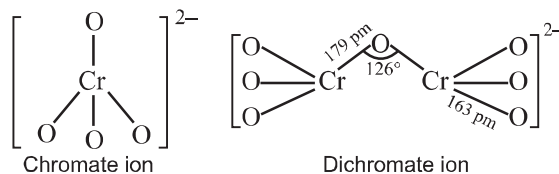
(iv) It oxidises hydrogen sulphide to sulphur.



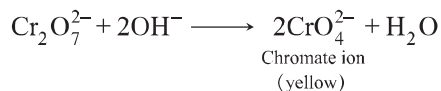
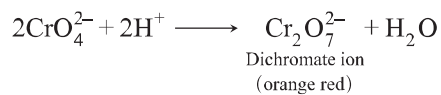
(v) It oxidises iodides to iodine.



Structures of chromate and dichromate ions:

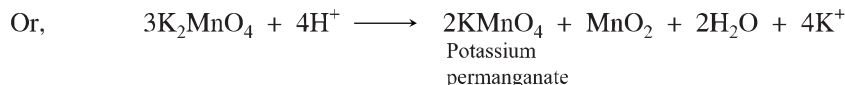
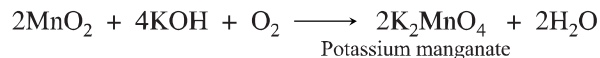


The chromate and dichromate ions are interconvertible in aqueous solution depending upon the pH of the solution.

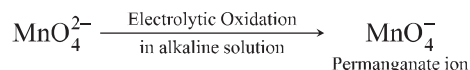
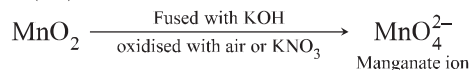


Potassium dichromate is used as primary standard in volumetric analysis.

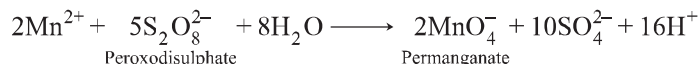
(b) **Potassium permanganate, KMnO_4 :** It is prepared by fusion of pyrolusite, MnO_2 , with KOH in the presence of an oxidising agent like KNO_3 . This produces the dark green potassium manganate, K_2MnO_4 which disproportionates in a neutral or acidic solution to give purple permanganate.



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



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



Properties:

Potassium permanganate is a dark purple crystalline solid.

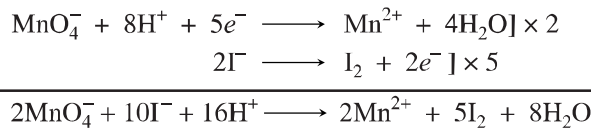
On heating, it decomposes at 513 K and O_2 is evolved.



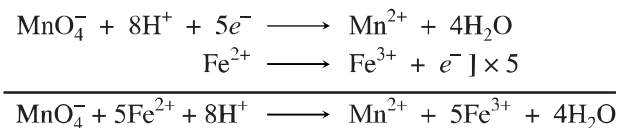
Potassium permanganate acts as a powerful oxidising agent in acidic, alkaline and neutral media. Few important oxidation reactions of KMnO_4 are given below:

1. In acidic medium potassium permanganate oxidises:

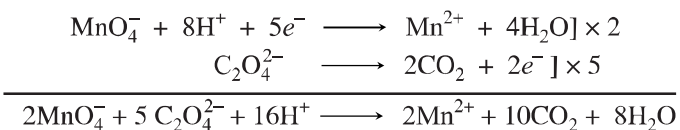
(i) Iodide to iodine



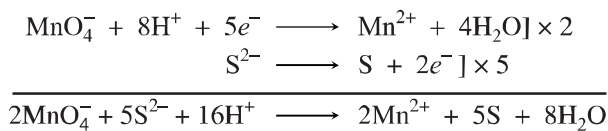
(ii) Ferrous to ferric



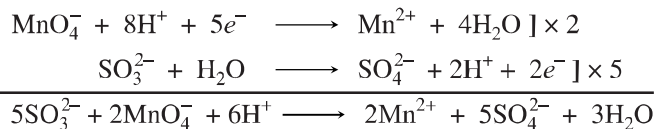
(iii) Oxalate to carbon dioxide



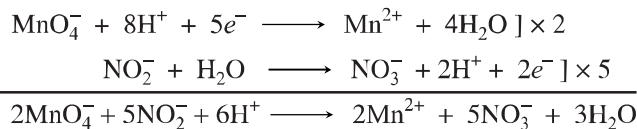
(iv) Hydrogen sulphide to sulphur



(v) Sulphite to sulphate

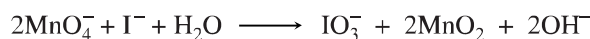


(vi) Nitrite to nitrate

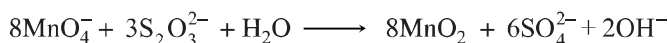


2. In neutral or faintly alkaline solutions potassium permanganate oxidises:

(i) Iodide to iodate



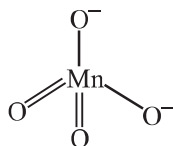
(ii) Thiosulphate to sulphate



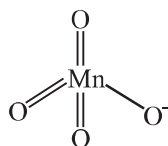
(iii) Manganous salt to MnO_2 in presence of zinc sulphate or zinc oxide



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 4f-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 $4f$ -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 $5f$ -subshell, as a result the nuclear charge increases causing the shells to shrink inwards.
- (ii) **Electronic configuration:** The actinoids involve the filling of $5f$ -subshells. Actinium has the electronic configuration $6d^1 7s^2$. From thorium ($Z = 90$) onwards, $5f$ -orbitals get progressively filled up. Because of equal energy of $5f$ and $6d$ subshells, there are some uncertainties regarding the filling of $5f$ and $6d$ 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)	$4f$ -orbital is progressively filled.	$5f$ -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 ($4d$), 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 $3d$ -orbitals are involved in case of zinc, while in all other metals of the $3d$ 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 $3d$ 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 $E^\circ (M^{2+}/M)$ value for copper is positive (+0.34 V). What is possible reason for this?

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

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



Copper has high enthalpy of ionisation and relatively low enthalpy of hydration. So, $E^\circ_{(Cu^{2+}/Cu)}$ 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 $3d$ 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., $\boxed{\uparrow\downarrow} \boxed{\uparrow\downarrow} \boxed{\uparrow} \boxed{\uparrow} \boxed{\uparrow}$

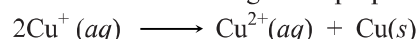
Hence, it has three unpaired electrons.

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

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.



The higher stability of Cu^{2+} in aqueous solution may be attributed to its greater negative $\Delta_{hyd} H^\circ$ 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 $5f$ 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) $\text{Cr}^{3+} = [\text{Ar}] 3d^3$ (ii) $\text{Cu}^+ = [\text{Ar}] 3d^{10}$
(iii) $\text{Co}^{2+} = [\text{Ar}] 3d^7$ (iv) $\text{Mn}^{2+} = [\text{Ar}] 3d^5$
(v) $\text{Pm}^{3+} = [\text{Xe}] 4f^4$ (vi) $\text{Ce}^{4+} = [\text{Xe}]$
(vii) $\text{Lu}^{2+} = [\text{Xe}] 4f^{14} 5d^1$ (viii) $\text{Th}^{4+} = [\text{Rn}]$

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 $3d$ -orbital also increases from 1 to 5. +2 oxidation state is attained by the loss of the two $4s$ 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). $\text{Mn}(+2)$ 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 $3d$ -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 $4s$ 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. $\text{Cr}_2\text{O}_7^{2-}$ 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 $\text{La}(\text{OH})_3$ to $\text{Lu}(\text{OH})_3$.
- (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).

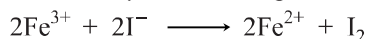
(ii) The transition elements exhibit high enthalpy of atomisation because they have large number of unpaired electrons in their atoms. Due to this they have stronger interatomic interaction.

(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.



An explanation of this catalytic action is given as under:



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.

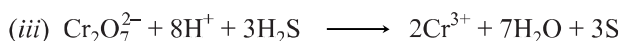
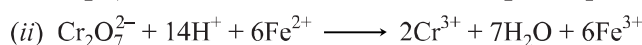
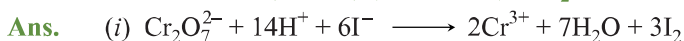
Ans. The oxidation states of transition elements differ from each other by unity *e.g.*, Fe^{2+} and Fe^{3+} , Cu^+ and Cu^{2+} (due to incomplete filling of *d*-orbitals) whereas oxidation states of non-transition elements normally differ by two units *e.g.*, Pb^{2+} and Pb^{4+} , Sn^{2+} and Sn^{4+}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

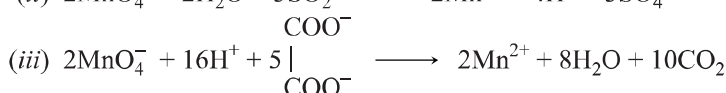
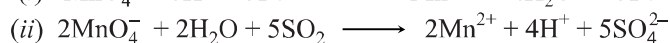
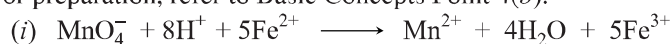
In aqueous solution, dichromate and chromate ions exist in equilibrium. On increasing the pH, *i.e.*, on making the solution alkaline, dichromate ions (orange coloured) are converted into chromate ions and thus, the solution turns yellow.

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) H₂S.



Q. 16. Describe the preparation of potassium permanganate. How does the acidified permanganate react with (i) iron (II) ions (ii) SO₂ (iii) oxalic acid? Write the ionic equations for the reaction.

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



Q. 17. For M²⁺/M and M³⁺/M²⁺ systems, E⁰ values for some metals are as follows:

$\text{Cr}^{2+}/\text{Cr} = -0.9 \text{ V}$

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

$\text{Mn}^{2+}/\text{Mn} = -1.2 \text{ V}$

$\text{Mn}^{3+}/\text{Mn}^{2+} = +1.5 \text{ V}$

$\text{Fe}^{2+}/\text{Fe} = -0.4 \text{ V}$

$\text{Fe}^{3+}/\text{Fe}^{2+} = +0.8 \text{ V}$

[CBSE Sample Paper 2016]

Use this data to comment upon

(i) the stability of Fe³⁺ in acid solution as compared to that of Cr³⁺ and Mn³⁺.

(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, Mn³⁺/Mn²⁺ has largest positive reduction potential. Hence Mn³⁺ can be easily reduced to Mn²⁺ *i.e.*, Mn³⁺ is least stable. Cr³⁺/Cr²⁺ has a negative E⁰ value, therefore, Cr³⁺ is most stable. Fe³⁺/Fe²⁺ has a positive value but small. Hence, Fe³⁺ is more stable than Mn³⁺ but less stable than Cr³⁺.

(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, Mn²⁺/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?

Ti³⁺, V³⁺, Cu⁺, Sc³⁺, Mn²⁺, Fe³⁺, Co²⁺. Give reasons for each.

Ans. An ion is coloured when it has one or more unpaired electrons. Thus, Ti³⁺, V³⁺, Mn²⁺, Fe³⁺ and Co²⁺ are coloured, due to the presence of unpaired electrons and *d-d* transitions. Cu⁺ and Sc³⁺ 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.

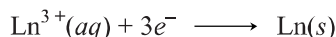
[CBSE 2020 (56/1/1)]

Ans. (i) **Electronic configuration:** The general electronic configuration of lanthanoids is [Xe]⁵⁴ 4f¹⁻¹⁴ 5d⁰⁻¹ 6s² whereas that of actinoids is [Rn]⁸⁶ 5f¹⁻¹⁴ 6d⁰⁻¹ 7s². Thus, lanthanoids belong to 4f-series whereas actinoids belong to 5f-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 $4f$, $5d$ and $6s$ subshells. On the other hand, actinoids show a large number of oxidation states because of small energy gap between $5f$, $6d$ and $7s$ 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 $5f$ -electrons.
- (iv) **Chemical reactivity:**

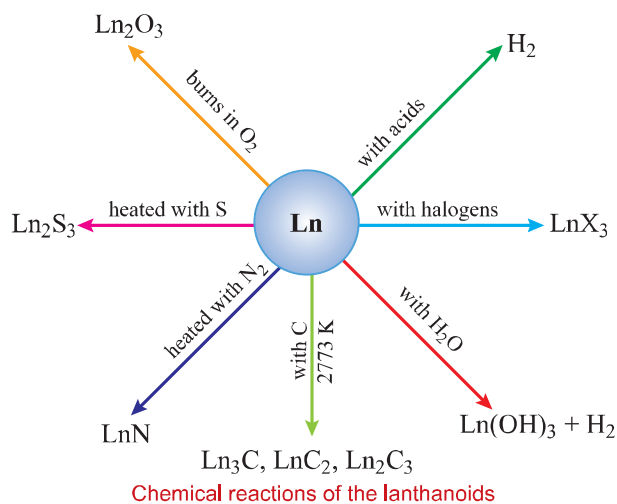
Lanthanoids: In general, the earlier members of the series are quite reactive (similar to calcium) but with increasing atomic number, they behave more like aluminium.

Values for E° for the half-reaction:



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 $\text{M}(\text{OH})_3$. The hydroxides are definite compounds, not just hydrated oxides, basic like alkaline earth metal oxides and hydroxides.



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.

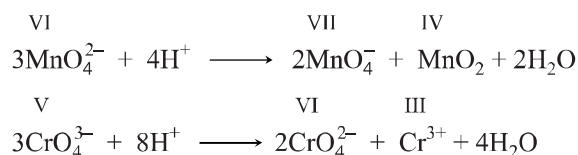
Q. 21. How would you account for the following:

- (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 $\text{Cr}^{3+}/\text{Cr}^{2+}$ is negative (-0.41 V) whereas E° value for $\text{Mn}^{3+}/\text{Mn}^{2+}$ 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,



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) $\text{Mn}^{3+} = 3d^4 = 4$ unpaired electrons (ii) $\text{Cr}^{3+} = 3d^3 = 3$ electrons

(iii) $\text{V}^{3+} = 3d^2 = 2$ electrons (iv) $\text{Ti}^{3+} = 3d^1 = 1$ electron.

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

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 $\text{Cr}_2\text{O}_7^{2-}$ 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) $\text{K}_2\text{Cr}_2\text{O}_7$ 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 along with 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 $4f$, $5d$ and $6s$ 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 $5f$, $6d$ and $7s$ 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 = $[\text{Rn}]^{86} 5f^{14} 6d^1 7s^2$

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

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

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

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 = ${}_{58}\text{Ce}$, ${}_{59}\text{Pr}$, ${}_{60}\text{Nd}$, ${}_{65}\text{Tb}$, ${}_{66}\text{Dy}$

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

+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 lanthanoids with reference to:

(i) electronic configuration

(ii) oxidation states and

(iii) chemical reactivity

Ans.

S.No.	Characteristics	Lanthanoids	Actinoids
(i)	Electronic configuration	$[\text{Xe}] 4f^{1-14} 5d^{0-1} 6s^2$	$[\text{Rn}] 5f^{1-14} 6d^{0-1} 7s^2$
(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 5f, 6d and 7s 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. = $[\text{Xe}] 4f^5 5d^0 6s^2$

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

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

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

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,

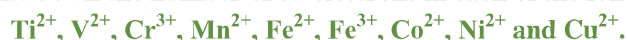
(iii) ionisation enthalpies, and

(iv) atomic sizes.

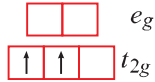
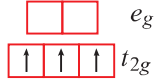
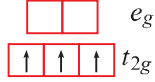
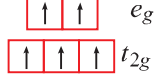
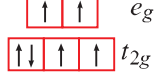
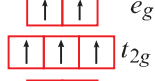
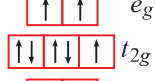
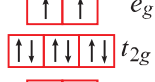
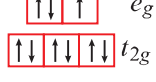
Ans. (i) **Electronic configurations:** The elements in the same vertical column generally have similar electronic configurations. Although, the first series shows only two exceptions, i.e., $\text{Cr} = [\text{Ar}] 3d^5 4s^1$ and $\text{Cu} = [\text{Ar}] 3d^{10} 4s^1$ but the second series shows more exceptions, e.g., $\text{Mo}(42) = [\text{Kr}] 4d^5 5s^1$, $\text{Ru}(44) = [\text{Kr}] 4d^7 5s^1$, $\text{Rh}(45) = [\text{Kr}] 4d^8 5s^1$, $\text{Pd}(46) = [\text{Kr}] 4d^{10} 5s^0$, $\text{Ag}(47) = [\text{Kr}] 4d^{10} 5s^1$. Similarly, in the third series, $\text{W}(74) = [\text{Xe}] 4f^{14} 5d^4 6s^2$, $\text{Pt}(78) = [\text{Xe}] 4f^{14} 5d^9 6s^1$ and $\text{Au}(79) = [\text{Xe}] 4f^{14} 5d^{10} 6s^1$. 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 ($4d$) series are higher while some of them have lower value than the elements of $3d$ - series in the same vertical column. However, the first ionisation enthalpies of third ($5d$) series are higher than those of $3d$ and $4d$ - series. This is because of weak shielding of nucleus of $4f$ -electrons in the $5d$ -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 $4d$ -series is larger than the corresponding elements of the $3d$ -series whereas those of corresponding elements of the $5d$ -series are nearly the same as those of $4d$ -series due to lanthanoid contraction.

Q. 36. Write down the number of $3d$ electrons in each of the following ions:



Indicate how would you expect the five $3d$ -orbitals to be occupied for these hydrated ions (octahedral).

Ans.	Ions	Electronic Configurations	No. of $3d$ electrons	$3d$ -orbitals occupied
(i)	Ti^{2+}	$[\text{Ar}]3d^2$	2	$t_{2g}^2 e_g^0$ 
(ii)	V^{2+}	$[\text{Ar}]3d^3$	3	$t_{2g}^3 e_g^0$ 
(iii)	Cr^{3+}	$[\text{Ar}]3d^3$	3	$t_{2g}^3 e_g^0$ 
(iv)	Mn^{2+}	$[\text{Ar}]3d^5$	5	$t_{2g}^3 e_g^2$ 
(v)	Fe^{2+}	$[\text{Ar}]3d^6$	6	$t_{2g}^4 e_g^2$ 
(vi)	Fe^{3+}	$[\text{Ar}]3d^5$	5	$t_{2g}^3 e_g^2$ 
(vii)	Co^{2+}	$[\text{Ar}]3d^7$	7	$t_{2g}^5 e_g^2$ 
(viii)	Ni^{2+}	$[\text{Ar}]3d^8$	8	$t_{2g}^6 e_g^2$ 
(ix)	Cu^{2+}	$[\text{Ar}]3d^9$	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 ($4d$ and $5d$ - series) are larger than those of the corresponding elements of the first transition series though those of $4d$ and $5d$ - series are very close to each other.
- (ii) Ionisation enthalpies of $5d$ - series are higher than the corresponding elements of $3d$ and $4d$ - series.
- (iii) Enthalpies of atomisation of $4d$ and $5d$ - 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)

2.2



5.3



5.9

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

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

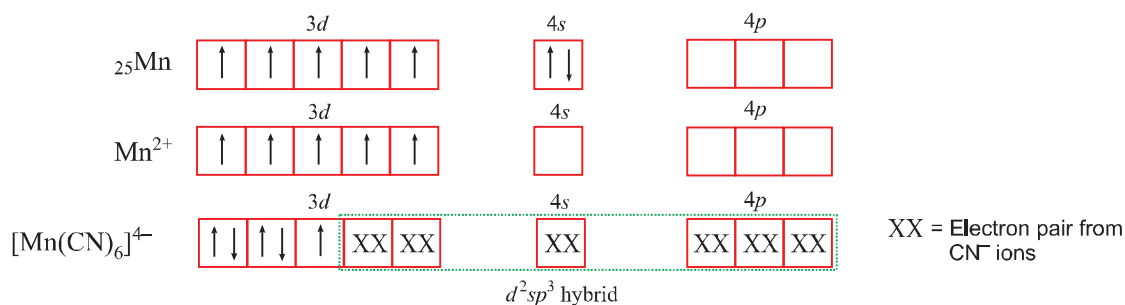
For $n=3$, $\mu = \sqrt{3(3+2)} = \sqrt{15} = 3.87$; For $n=4$, $\mu = \sqrt{4(4+2)} = \sqrt{24} = 4.90$

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

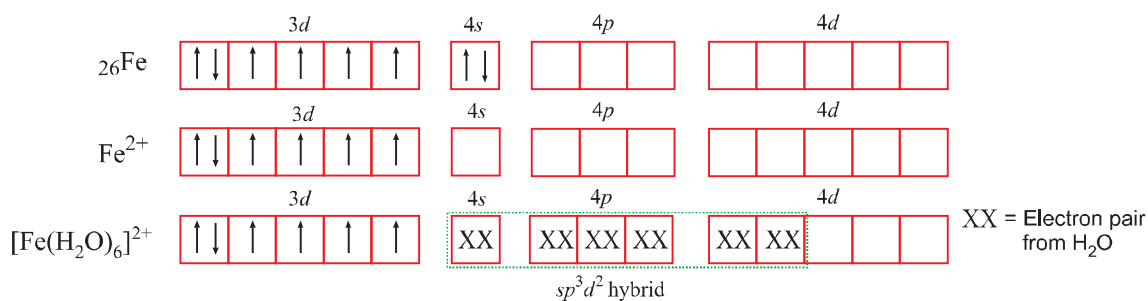


Here, Mn is in +2 oxidation state, *i.e.*, as Mn^{2+} , $\mu = 2.2$ BM shows that it has only one unpaired electron. Hence, when CN^- ligands approach Mn^{2+} ion, the electrons in $3d$ -subshell pair up.

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



Here, Fe is in +2 oxidation state, *i.e.*, as Fe^{2+} , $\mu = 5.3$ BM shows that there are four unpaired electrons. This means that the electrons in $3d$ -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.



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

