



LESSON AT A GLANCE

- **d-block elements:** The elements are classified into four blocks namely: s, p, d and f, after the type of the atomic orbital which receives the last electron. These blocks of elements consist of scandium, yttrium and lanthanum together with the three periods of transition elements. These elements contain the elements of the group 3–12 in which the *d*-orbitals are progressively filled.

- **f-block Elements**

- Placed outside at the bottom of the periodic table.
- In the elements of this block *4f* and *5f* orbitals are progressively filled.

- **Lanthanoid Contraction:** The filling of *4f*- before *5d*-orbital results in a regular decrease (contraction) in the atomic and ionic radii of Lanthanoids with increasing atomic number is known as Lanthanoid contraction.

The net result of the lanthanoid contraction is that the second and the third *d* series exhibit similar radii (*e.g.*, Zr 160 pm. Hf 159 pm) and have very similar physical and chemical properties.

- **Chemical reactivity:** The metals of first series with the exception of copper are relatively more reactive. The E^\ominus values for M^{2+}/M indicate a decreasing tendency to form divalent cations across the series, general trend towards less negative E^\ominus values is related to the increase in the sum of the first and second ionisation enthalpies.
- **Diamagnetism:** It is the property due to which certain substances are repelled by an applied magnetic field. Those substances which do not have unpaired electrons are diamagnetic in nature. *e.g.* Zn, Cd, Hg are diamagnetic.

- **Paramagnetism:** It is the property due to which a substance is attracted by magnetic field. Those substances, which have unpaired electrons are paramagnetic in nature, e.g. Co, Ni, Cr, Mn etc.
- **Alloy formation:** They form alloys due to similar ionic sizes. The alloys formed are hard and have high melting points.
The best known are ferrous alloys: Chromium, vanadium, tungsten, molybdenum. Alloys of transition metals with non-transition metals such as brass (copper-zinc), bronze (copper-tin) are also of considerable industrial importance.
- **Physical properties**
 - It is orange coloured solid.
 - It is highly soluble in water.

TEXTBOOK QUESTIONS SOLVED

8.1 Write down the electronic configuration of :

- | | |
|-----------------|------------------|
| (i) Cr^{3+} | (ii) Pm^{3+} |
| (iii) Cu^+ | (iv) Ce^{4+} |
| (v) Co^{2+} | (vi) Lu^{2+} |
| (vii) Mn^{2+} | (viii) Th^{4+} |

- Ans.**
- | | | |
|----------------------|---|--|
| (i) Cr^{3+} (24) | – | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$ |
| (ii) Cu^+ (29) | – | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ |
| (iii) CO^{2+} (27) | – | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$ |
| (iv) Mn^{2+} (25) | – | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$ |
| (v) Pm^{3+} (61) | – | $1s^2 2s^2 2p^6 3s^2 3d^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 4f^4$ |
| (vi) Lu^{2+} (71) | – | $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3p^{10} 4p^6 5s^2 4d^{10} 5p^6 4f^{14} 5d^1$ |
| (vii) Th^{4+} (90) | – | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6$ |

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

- Ans.** Outer electronic configuration of Mn^{2+} and Fe^{2+} are $3d^5$ and $3d^6$, respectively. $3d^5$ is half-filled hence more stable than $3d^6$. Therefore, it becomes difficult to have Mn^{3+} ions, but it is easier to have Fe^{3+} ions.

8.3 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. It is due to increase in effective nuclear charge after losing 2 electrons from s-orbitals, ionic size decreases, stability increases.

8.4 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 examples.

Ans. 3d-transition elements show oxidation states from +1 (only Cu) to +7. Only those oxidation states are stable which have stable electronic configurations such as with half-filled or completely filled d orbitals.

Mn forms stable oxidation state M^{2+} with d^5 configuration while Zn^{2+} is highly stable with d^{10} configuration.

8.5 What may be the stable oxidation state of the transition element with the following d electron configurations in the ground state of their atoms: $3d^3$, $3d^5$, $3d^8$ and $3d^4$?

Ans. General electronic configuration of the transition elements in the ground state is $(n-1)d^{1-10}ns^{1-2}$. The ground state electronic configuration for the given atoms would be

Atom with EC	Ground state EC	Stable oxidation state
$3d^3$	$3d^3 4s^2$	+5
$3d^5$	$3d^5 4s^1$ and $3d^5 4s^2$	+6, +2 and +7
$3d^8$	$3d^8 4s^2$	+2
$3d^4$	$(3d^4 4s^2) \rightarrow 3d^5 4s^1$	+6 (also +3)

The maximum oxidation state is given by the sum of 3d and 4s electrons upto Mn.

8.6 Name the oxometal anions of the first series of the transition metals in which the metal exhibits the oxidation state equal to its group number.

Ans. CrO_4^{2-} and $Cr_2O_7^{2-}$ (Group number of Cr = 6, oxidation state = +6).

MnO_4^- (Group number of Mn = 7, oxidation state = +7)

8.7 What is lanthanoid contraction? What are the consequences of lanthanoid contraction?

Ans. The decrease in atomic and ionic size with increase in atomic number in lanthanoids is called lanthanoid contraction.

8.8 *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 transition elements:**

- (i) Most of the transition elements form coloured compounds.
- (ii) Their compounds are generally paramagnetic in nature.
- (iii) They have great tendency to form complexes.
- (iv) They show variable oxidation states.

They are called transition elements because they are less electropositive than *s*-block elements and more electropositive than *p*-block elements. Zn, Cd, Hg are not regarded as transition elements.

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

Ans. Electronic configuration of transition elements is $(n-1)d^{1-10} ns^{1-2}$ while that of non-transition elements is ns^{1-2} for *s*-block element and $ns^2 np^{1-6}$ for *p*-block elements. Non-transition elements do not have *d* orbitals in their valence shells.

8.10 *What are the different oxidation states exhibited by the lanthanoids?*

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

8.11 *Explain giving reasons:*

- (a) *Transition metals and many of their compounds show paramagnetic behaviour.*
- (b) *The enthalpies of atomisation of the transition metals are high.*
- (c) *The transition metals generally form coloured compounds.*
- (d) *Transition metals and their many compounds act as good catalyst.*

Ans. (i) It is due to the presence of unpaired electrons due to which they are attracted by magnetic field and show paramagnetism.

- (ii) It is due to strong metallic bonding and additional covalent bonding due to the presence of unpaired electrons in *d*-orbitals due to which they have high lattice energy and consequently high enthalpy of atomisation.

(iii) It is due to the presence of unpaired electrons, they undergo *d-d* transitions by absorbing light from visible region and radiate complementary colour.

(iv) It is due to variable oxidation states. They have large surface area and can form intermediate with reactants which readily changed into products.

8.12 *What are interstitial compounds? Why are such compounds well known for transition metals?*

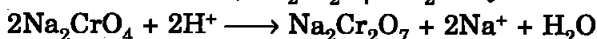
Ans. Interstitial compounds are those which are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals. Because of the nature of the composition of transition metal compounds are referred to as interstitial compounds.

8.13 *How is the variability in oxidation states of transition metals different from that of the non-transition metals? Illustrate with examples.*

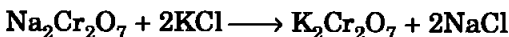
Ans. They differ by one in transition metal, e.g., Fe^{2+} , Fe^{3+} , Cr^{2+} , Cr^{3+} . In non-transition metals they differ by two, e.g. Ti^{+} , Ti^{3+} , Sn^{2+} and Sn^{4+} , B^{3+} , and B_1^{5+} .

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

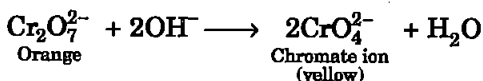
Ans. $4\text{FeCr}_2\text{O}_4 + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 \longrightarrow 8\text{Na}_2\text{CrO}_4 + 2\text{Fe}_2\text{O}_3 + 8\text{CO}_2$
The yellow solution of sodium chromate is filtered and acidified with sulphuric acid to give a solution from which orange sodium dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ crystallised.



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

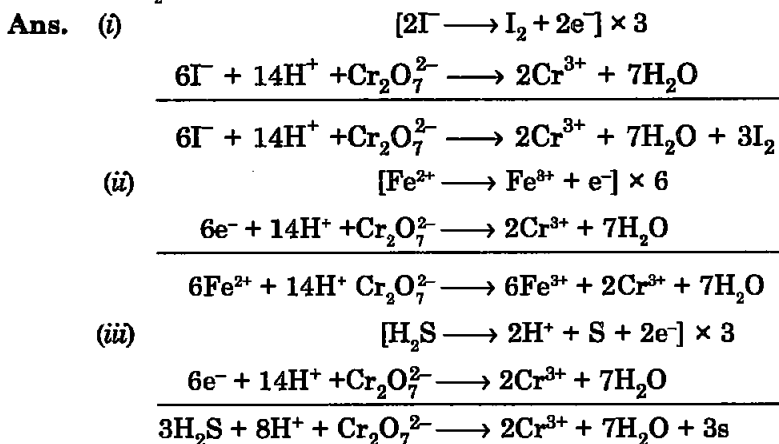


Orange crystals of potassium dichromate crystallise out. On increasing the pH of solution, the H^+ ions are used up and reaction proceed in forward direction producing yellow chromate solution.



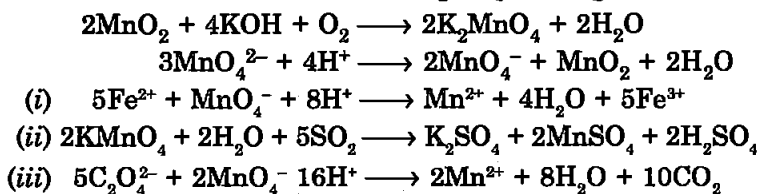
8.15 Describe the oxidising action of potassium dichromate and write the ionic equations for its reaction with:

- (i) iodide, (ii) iron(II) solution, and
(iii) H_2S



8.16 Describe the preparation of potassium permanganate. How does the acidified permanganate solution react with (i) iron(II) ions, (ii) SO_2 , and (iii) oxalic acid? Write the ionic equations for the reactions.

Ans. Potassium permanganate is prepared by fusion of MnO_2 with an alkali metal hydroxide and an oxidising agent like KNO_3 . This produces dark green K_2MnO_4 which disproportionates in a neutral or acidic solution to give permanganate.



8.17 For M^{2+}/M and M^{3+}/M^{2+} systems the E^\ominus values for some metals are as follows:

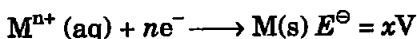
Cr^{3+}/Cr	- 0.9V	Cr^3+/Cr^{2+}	- 0.4 V
Mn^{2+}/Mn	- 1.2V	Mn^{3+}/Mn^{2+}	+ 1.5 V
Fe^{2+}/Fe	- 0.4V	Fe^{3+}/Fe^{2+}	+ 0.8 V

Use this data to comment upon:

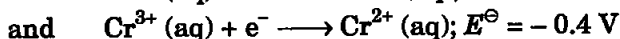
- (i) the stability of Fe^{3+} in acid solution as compared to that of Cr^{3+} or Mn^{3+} , and

(ii) *the ease with which iron can be oxidised as compared to a similar process for either chromium or manganese metal.*

Ans. Consider the half-reaction



If E^{\ominus} value is negative then the metal M has the tendency to go into solution (acidic) and form M^{n+} ions. This tendency is reversed for positive E^{\ominus} values in acidic medium. Now, for



These values suggest that relative stabilities of the ions would be in the order

$Fe^{2+} (aq) > Fe^{3+} (aq)$; $Cr^{3+} (aq) > Cr^{2+}$; and $Mn^{2+} (aq) > Mn^{3+} (aq)$
Further $Fe^{3+} (aq) > Mn^{3+} (aq)$ and $Fe^{3+} (aq) < Cr^{3+} (aq)$.

8.18 *Predict which of the following will be coloured in aqueous solution?*

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

Ans. Ti^{3+} , V^{3+} , Mn^{2+} , Fe^{3+} and Co^{2+} are coloured due to the presence of unpaired electrons, they can undergo *d-d* transitions. Cu^{+} , Sc^{3+} are colourless due to the absence of unpaired electrons.

8.19 *Compare the stability of +2 oxidation state for the elements of the first transition series.*

Ans. In general, the stability of +2 oxidation state in first transition series decreases from left to right due to increase in the sum of first and second ionisation energies. However Mn^{2+} is more stable due to half filled *d*-orbitals ($3d^5$) and Z^{2+} is more stable due to completely filled *d*-orbitals ($3d^{10}$).

8.20 *Compare the chemistry of actinoids with that of the lanthanoids with special reference to:*

- (i) *electronic configuration*
- (ii) *atomic and ionic sizes and*
- (iii) *oxidation state, and*
- (iv) *chemical reactivity.*

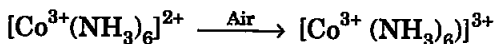
- Ans.** (i) **Electronic Configuration:** In lanthanoids $4f$ -orbitals are progressively filled whereas in actinoids $5f$ -orbitals are progressively filled.
- (ii) **Oxidation States:** Lanthanoids show +3 oxidation state. Some elements show +2 and +4 oxidation states also. Actinoids show +3, +4, +5, +6, +7 oxidation states. Although +3 and +4 are most common.
- (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:** Actinoids are more reactive than lanthanoids due to bigger atomic size and lower ionisation energy.

8.21 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^\ominus values for the Cr^{3+}/Cr^{2+} and Mn^{3+}/Mn^{2+} couples are
 $Cr^{3+}(aq) + e^- \longrightarrow Cr^{2+}(aq); E^\ominus = -0.41 V$
 $Mn^{3+}(aq) + e^- \longrightarrow Mn^{2+}(aq); E^\ominus = +1.551 V$
 These E^\ominus values indicate that Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidising.

- (ii) The tendency to form complexes is high for Co(III) oxidation state as compared to Co(II) oxidation state. Co^{2+} ions are very stable and are difficult to oxidise. Co^{3+} ions are less stable and are reduced by water. In contrast, many Co(II) complexes are readily oxidised to Co(III) complexes, and Co(III) complexes are very stable, e.g.,

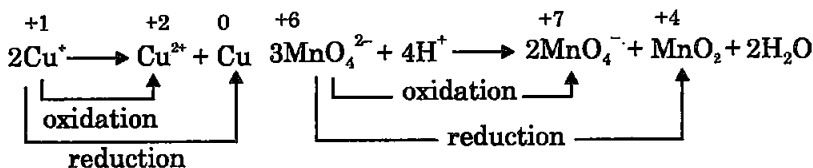


This happens because the crystal field stabilising energy of Co(III) with a d^6 ($t_{2g}^6 e_g^0$) configuration is higher than for Co(II) with a d^7 ($t_{2g}^6 e_g^1$) arrangement.

- (iii) Transition metal ions with d^1 configuration have a tendency to lose this single electron and give ion with a noble gas configuration.

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

Ans. Disproportionation reactions are those in which the same ion undergoes oxidation as well as reduction. Examples are:



8.23 Which metal in the first series of transition metals exhibits +1 oxidation state most frequently and why?

Ans. Copper exhibits +1 oxidation state in its compounds such as Cu_2I_2 .

Electronic configuration of Cu in the ground state is $3d^{10}4s^1$. So, Cu can easily lose $4s^1$ electron to give a stable $3d^{10}$ configuration. Thus, it shows +1 oxidation state.

8.24 Calculate the number of unpaired electrons in the following gaseous ions: Mn^{3+} , Cr^{3+} , V^{3+} and Ti^{3+} . Which one of these is the most stable in aqueous solution?

Ans.

Ion	Electronic configuration	No. of unpaired electrons
Mn^{3+}	$3d^4$	4
Cr^{3+}	$3d^3$	3
V^{3+}	$3d^2$	2
Ti^{3+}	$3d^1$	1

8.25 Give examples and suggest reasons for the following features of the transition metal chemistry:

- The lowest oxide of transition metal is basic, the highest is amphoteric/acidic.
- A transition metal exhibits highest oxidation state in oxides and fluorides.
- The highest oxidation state is exhibited in oxoanions of a metal.

Ans. (i) The lower oxide of transition metal is basic because the metal atom has low oxidation state whereas highest is acidic due to highest oxidation state. For example, $\text{M}_n^{\text{II}}\text{O}$ is basic whereas $\text{Mn}_2^{\text{VII}}\text{O}_7$ is acidic.

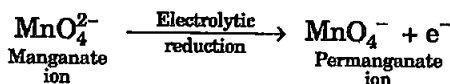
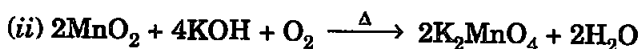
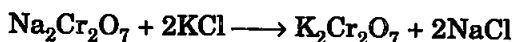
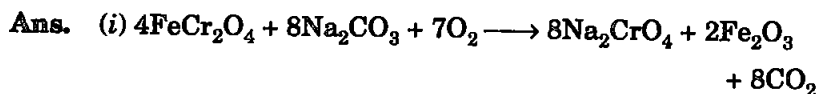
In the low oxidation state of the metal, some of the valence electrons of the metal atom are not involved in bonding. Hence, it can donate electrons and behave as a base. In the higher oxidation state valence electrons are involved in the bonding and are not available. Instead effective nuclear charge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

- (ii) Being small in size and high in electronegativity, fluorine and oxygen can bring about higher oxidation states in the compounds of transition elements. Examples are Mn_2O_7 , CrO_3 , OsF_6 .
- (iii) Transition metals showing higher oxidation states in the oxoanions are Cr and Mn, e.g., CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, MnO_4^{2-} , MnO_4^- . This is due to the small size and high electronegativity of oxygen besides its ability to form multiple π -bonds with the metal (See structures of CrO_4^{2-} , MnO_4^-).

8.26 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.



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

Ans. Alloys are homogeneous mixture of two or more metals. One of them can be non metal also. Mischmetal is an alloy which contains some of the Lanthanoid metals. It contains 45% Lanthanoid metals and iron ~ 5% and traces of S, C, Ca and Al.

Mischmetal is used in Mg-based alloy to produce bullets, shell and lighter flint.

Addition of 3% mischmetal to magnesium increases its strength and used in making jet engine parts.

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

Ans. The f-block elements are called inner-transition elements. They comprise 4f (lanthanoids from atomic number 58-71), and 5f elements (actinoids from atomic number 90-103). Thus, elements with atomic numbers, 59, 95, and 102 are inner-transition elements.

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

8.30 *Which is the last element in the series of the actinoids? Write the electronic configuration of this element. Comment on the possible oxidation state of this element.*

Ans. Lawrencium (Lr) with $Z = 103$ is the last actinoid.

Its electronic configuration is $[\text{Rn}] 5f^{14} 6d^1 7s^2$. The possible oxidation is +3 obtained by losing $6d^1$ and $7s^2$ electrons.

8.31 *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. ${}_{58}\text{Ce} = [\text{Xe}] 4f^1 5d^1 6s^2$, and ${}_{58}\text{Ce}^{3+} = [\text{Xe}] 4f^1$ with one unpaired electron magnetic moment, μ for one unpaired electron ($n-1$) is

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

8.32 *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 configurations of these elements.*

Ans. Lanthanoids showing +4 oxidation state are, ${}_{58}\text{Ce}$, ${}_{59}\text{Pr}$, ${}_{65}\text{Tb}$ and ${}_{66}\text{Dy}$.

Lanthanoids showing +2 oxidation state are

${}_{60}\text{Nb}$, ${}_{61}\text{Pm}$, ${}_{62}\text{Sm}$, ${}_{63}\text{Eu}$, ${}_{69}\text{Tm}$ and ${}_{70}\text{Yb}$.

+4 and +2 oxidation states occur, particularly when they lead to :

- (i) a noble gas configuration, *i.e.*, Ce^{4+} (f^0), (+4 oxidation state).
- (ii) A half-filled f -orbital (f^7), *e.g.*, Eu^{2+} (for + 2 oxidation state) and Tb^{4+} (for + 4 oxidation state).
- (iii) a completely filled f -orbital (f^{14}), *e.g.*, Yb^{2+} (for +2 oxidation state).

8.33 Compare the chemistry of the actinoids with that of lanthanoids with reference to:

- (i) electronic configuration, (ii) oxidation states, and
- (iii) chemical reactivity.

Ans. (i) **Electronic configuration:** In lanthanoids $4f$ -orbitals are progressively filled whereas in actinoids $5f$ -orbitals are progressively filled.

(ii) **Oxidation states:** Lanthanoid shows +3 oxidation state. Some elements show +2 and +4 oxidation states also. Actinoids show +3, +4, +5, +6 +7 oxidation states. Although +3 and +4 are most common.

(iii) **Chemical reactivity:** Actinoids are more reactive than lanthanoids due to bigger atomic size and lower ionisation energy.

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

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

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

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

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

8.35 Compare the general characteristics of the first series of the transition metals with those of the second and third series metals in the respective vertical columns. Give special emphasis on the following points:

- (i) electronic configurations
- (ii) oxidation states
- (iii) ionisation enthalpies and
- (iv) atomic sizes.

Ans. (i) *Electronic configurations:*

Electronic configuration of Group 3 elements (Sc, Y, La) is [noble gas] $(n-1)d^1 ns^2$.

Elements of Group 6 (Cr, Mo and W) show exception in electronic configuration, [Noble gas] $(n-1)d^5$ and for W it is [Noble gas] $4f^{14}5d^4 6s^2$.

Group 11 elements (Cu, Ag and Au) also show exceptional electronic configuration:

$\text{Cu} = [\text{Ar}] 3d^{10}4s^1$, $\text{Ag} = [\text{Kr}]4d^{10}5s^1$, $\text{Au} = [\text{Xe}]4f^{14} 5d^{10} 6s^1$

In Group 10 (Ni, Pd and Pt), Pd and Pt show exceptional electronic configuration:

$\text{Pd} = [\text{Kr}] 4d^{10}$; $\text{Pt} [\text{Xe}] 4f^{14} 5d^9 6s^1$.

(ii) *Oxidation states:* Elements within the same group show similar oxidation states. Highest number of oxidation states are shown by the elements lying in the middle of the transition series. Minimum oxidation states are shown by the elements lying near to left and far right side of the series.

(iii) *Ionisation enthalpies:* Ionisation enthalpies generally decrease down a group. This trend is followed from 3d to 4d elements but the ionisation enthalpies either remain same or increase in going from 4d to 5d series with the same group. This reverse trend is due to the poor shielding of the nuclear charge by the inner 4f-electrons. This increases the Z_{eff} and in turn increases the ionisation enthalpy.

(iv) *Atomic Size:* Reason same as in (iii). Increase in Z_{eff} also decreases the size. So the atomic sizes increase from 3d to 4d but decrease or remain almost the same from 4d to 5d.

8.36 Write down the number of 3d 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. (With H_2O as ligand the orbitals t_{2g} and e_g have higher energy gap).

Ion	Electronic configuration	No. of 3d electrons	Octahedral d-orbitals splitting configurations
Ti ²⁺	3d ²	2	t_{2g}^2
V ²⁺	3d ³	3	t_{2g}^3
Cr ³⁺	3d ³	3	t_{2g}^3
Mn ²⁺	3d ⁵	5	t_{2g}^5
Fe ²⁺	3d ⁶	6	t_{2g}^6
Fe ³⁺	3d ⁵	5	t_{2g}^5
Co ²⁺	3d ⁷	7	$t_{2g}^5 e_g^2$
Ni ²⁺	3d ⁸	8	$t_{2g}^6 e_g^2$
Cu ²⁺	3d ⁹	9	$t_{2g}^6 e_g^3$

(The electrons in t_{2g} and e_g orbitals are filled in accordance to Hund's rule).

8.37 Comment on the statement that elements of the first transition series possess many properties different from those of heavier transition elements.

Ans. Following comments justify the statement:

- Atomic sizes of 3d series are smaller than those of corresponding elements of 4d and 5d series. However, sizes of 4d and 5d are very near to the same.
- Ionisation enthalpies of 3d elements are smaller than those of corresponding elements of 4d and 5d elements. Because of 14 4f electrons in 5d elements, their sizes are similar to 4d elements, and consequently ionisation enthalpies are higher.
- Melting point, boiling point and enthalpies of atomisation of heavier transition elements (4d and 5d) are higher than the corresponding elements of the first series (3d).

8.38 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

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

When $n = 1$ $\mu = \sqrt{1(1+2)} = \sqrt{3} = 1.73$

When $n = 2$ $\mu = \sqrt{2(2+2)} = \sqrt{8} = 2.83$

When $n = 3$ $\mu = \sqrt{3(3+2)} = \sqrt{15} = 3.87$

When $n = 4$ $\mu = \sqrt{4(4+2)} = \sqrt{24} = 5.66$

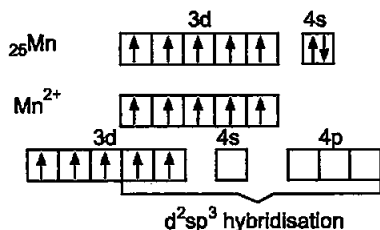
When $n = 5$ $\mu = \sqrt{5(5+2)} = \sqrt{35} = 5.92$

(i) $K_4[Mn(CN)_6]$ In this complex Mn is in +2 oxidation state, i.e. as Mn^{2+}

$$\mu = 2.2 \text{ BM}$$

shows that it has only one unpaired electron.

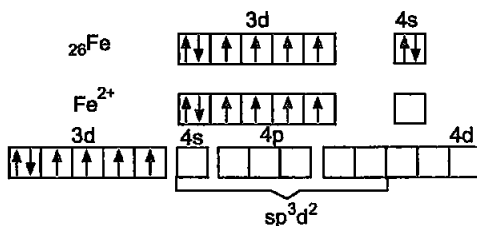
Thus, when CN^- ligands approach Mn^{2+} ion,



(ii) $[Fe(H_2O)_6]^{2+}$ In this complex, Fe is in +2 state. i.e. Fe^{2+}

$$\mu = 5.3 \text{ BM}$$

shows that there are four unpaired electrons. This means that the electrons in 3d do not pair up when the ligands, H_2O molecules approach. Thus, H_2O is a weak ligand.



(iii) $K_2[MnCl_4]$ In this complex, Mn is in +2 state, i.e., as Mn^{2+}
 $\mu = 5.92 \text{ BM}$

shows that there are five unpaired electrons. Thus, the hybridisation involved will be sp^3 and the complex will be tetrahedral.

