Chapter -8 (d and f block elements)

LEVEL-1 QUESTIONS

Q.1-Explain briefly how +2 oxidation states becomes more and more stable in the first half of the first row transition elements with increasing atomic number.

Ans.1-In M^{2+} ions, 3d-orbitals get occupied gradually as the atomic number increases. Since, the number of empty d-orbitals decreases, the stability of cations increases from Sc^{2+} to Mn^{2+} . Mn^{2+} is most stable as all d-orbitals are singly occupied.

Q.2- Explain why transition elements have many irregularities in their electronic configurations?

Ans.2-In the transition elements, there is a little difference in the energy of (n-1) d-orbitals and nsorbitals. Thus, incoming electron can occupy either of shell. Hence, transition elements exhibit many irregularities in their electronic configurations.

Q.3-What are different oxidation states exhibited by Lanthanides?

Ans.3-The common stable oxidation state of lanthanides is +3.However some members also show oxidation states of +2 & +4.

Q.4-How is the variability in oxidation states of transition metals different from that of the non-transition metals? Illustrate with examples.

Ans.4-The transition elements use its (n-1)d, ns and np orbital and the successive oxidation states differ by unity. For example, Mn shows all the oxidation states from +2 to +7. On other hand non transition elements use its ns, np and nd orbitals and the successive oxidation states differ by two units e.g. Sn^{2+} , Sn^{4+} etc.

Q.5- Why do transition elements show variable oxidation states?

Ans.5- The transition elements show variable oxidation state due to small energy difference between (n-1) d &ns orbital as a result both (n-1)d &ns electrons take part in bond formation.

Q.6-Why are Mn^{2+} compounds more stable than Fe^{2+} compounds towards oxidation to +3 state?

Ans.6-The electronic configuration of Mn^{2+} is [Ar] $3d^5$, i.e. all five d-orbitals are singly occupied. Thus this is stable electronic configuration and further loss of electron requires high energy .on other hand side the electronic configuration of Fe²⁺is [Ar] $3d^6$, i.e. Loss of one electron requires low energy.

Q.7-To what extend do the electronic configuration decide the stability of oxidation state in the first series of the transition elements? Illustrate your answer with an example.

Ans.7-In a transition series, the oxidation state which lead to exactly half filled or completely filled orbitals are more stable.e.g. the electronic configuration of Feis [Ar] $3d^6$, $4s^2$. It shows various oxidation state but Fe(III) is more stable than Fe(II).

Q.8- Which metal in the first series of transition metals exhibits +1 oxidation state most frequently and why?

Ans.8- Copper with configuration [Ar] $3d^{10} 4s^1$ exhibits +1 oxidation state. Copper loses $4s^1$ electron easily and achieved a stable configuration $3d^{10}$ by forming Cu⁺.

Q.9- What are inner transition elements?

Ans.9- The f-block elements in which the last electron accommodated on (n-2) f-subshell are called inner transition elements. These include atomic numbers 58 to 71 and from 90 to 103.

Q.10- The paramagnetic character in 3d-transition series elements increases upto Mn and then decreases. Explain why?

Ans.10- In the 3d-transition series as we move from Sc (21) to Mn (25) the number of unpaired electrons increases and hence paramagnetic character increases. After Mn, the pairing of electrons in the d-orbital starts and the number of unpaired electrons decreases and hence, paramagnetic character decreases.

Q.11- Comment on the statement that elements of the first transition series possess many properties different from those of heavier transition metal

Ans.11-The following points justify that the given statement is true:-

(i) Ionization enthalpies of heavier transition elements are higher than the elements of 3d series. Consequently, heavier transition elements are less reactive in comparison to 3d-elements.

(ii) Melting points of heavier transition elements are higher than 3d-elements.

(iii) Higher oxidation states of heavier transition elements are stable whereas lower oxidation states are stable in 3d-elements.

Q.12-What are transition elements? Which d-block elements are not regarded as transition elements and why?

Ans.12- An element which has partially filled (n-1) d orbital is known as transition elements. Group 12 elements i.e. Zn, Cd, Hg have completely filled (n-1) d-orbital in atomic & ionic state & thus these elements are not considered as Transition Elements.

Q.13-What are interstitial compounds? Why are such compounds well known for transition metal?

Ans.13- Compounds of transition metal with relatively smaller non-metals are known as interstitial compounds. These compounds are well known for transition metals because size of C, N, O, and B is similar to size of interstitial voids of transition metal.

Q.14-(a) What is actinides contraction? What effect does it have on the chemistry of the elements, which follow actinides?

(b) Name an important alloy, which contains some of the lanthanide metals. Mention its uses. Ans.14- (a) The size of actinoid and its trivalent ion decreases from Ac to Lw. It is known as 1 actinides contraction.

Cause: - It is due to poor shielding of 5f electrons.

Consequences of actinides contraction: -

- (i) Basic strength of hydroxide decreases from Ac(OH)₃ To Lw(OH)₃.
- (ii) (ii) Because of similar chemical properties l actinides are difficult to separate.

(b) An important alloy containing lanthanoid metals is mischmetal, which contains 95% lanthanide metal and 5% Fe along with traces of S, C, Ca and Al. It is used in Mg-based alloy to produce bullets, shells and lighter flint.

LEVEL-2 QUESTIONS

- Q1. (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.
 - (v)Transition metals have a strong tendency to form complexes.

Ans.1- (i)Transition metals and many of their compounds show paramagnetic behaviour due to presence of unpaired electrons in (n-1) d orbital.

- (ii) The enthalpies of atomisation of the transition metals are high Because of large number of unpaired electrons in their atoms, they have stronger interatomic interaction and hence strong metallic bonding is present between atoms.
- (iii) The transition metals generally form coloured compounds due to presence of unpaired electrons in (n-1) d orbital & thus they can undergo d-d transition.
- (iv) Transition metals and their many compounds act as good catalyst It is due to (i) partially filled (n-1) d orbital (ii) Variable oxidation state (iii) Ability to change oxidation state frequently.

(v) Transition metals have a strong tendency to form complexes Most of transition elements form complex compounds due to (i) small size (ii) high charge (iii) presence of vacant d-orbital of suitable energy.

Q.2- Give reasons for the following:-

(i) Fe has higher melting point than Cu.

- (ii) [Ti (H₂O)₆]³⁺ is coloured while [Sc(H₂0)₆] is colourless.
- (iii)The 4d and 5d series of transition metals have more frequent metal-metal bonding in Their compound than do the 3d metals.

(iv)Transition metals some time exhibit very low oxidation state such as +1and 0.(v)Hg is not considered a transition metal.

Ans.2-(i) this is because Fe $(3d^6, 4s^1)$ has four unpaired electrons in 3d-subshell. While Cu $(3d^{10}, 4s^1)$ only one unpaired electron in 4s shell. Hence metallic bonding is stronger in Fe than those in Cu.

(ii) The oxidation state of Ti in [Ti $(H_2O)_6$]³⁺ is +3 and its configuration is [Ar] 3d¹ i.e one unpaired electron and hence it is coloured. Whereas the oxidation state of Sc in [Sc $(H_2O)_6$]³⁺ is +3 and its configuration is [Ar] 3d⁰ i.e no unpaired electron and hence it is colourless.

(iii)In the same group of d-block elements, the 4d and 5d transition elements are larger size than that of 3d elements. Hence, the valence electrons are less tightly held and form metal-metal bond more frequently.

(iv)+1 oxidation state is shown by elements like Cu because after loss of one electron, it acquire stable configuration. Zero oxidation state is shown in metal carbonyl, because \prod -electrons donated by CO are accepted into the empty orbital.

(v)The characteristic properties of transition metal are due to partially filled d-orbitals. Hg has completely filled d-orbital; as a result it doesn't show properties of transition metals and hence is not considered as transition metal.

Q.3-(a) write electronic configuration of element having atomic number 101.

(b) Which element show maximum oxidation state in 3d transition series?

- (c) What is mischmetal?
- (d) Explain why Cu⁺ ion is not stable in aqueous solution?
- (e) Name the transition metal which is well known to exhibit +4 oxidation state? Ans.3-(a) [Rn] 5f¹³,6d⁰, 7s².
- (b) Mn, Which shows +7 oxidation state in KMnO₄.

(c) It is an important alloy, which contains 95% lanthanide metal and 5% Fe along with traces of S, C,

Ca and Al. It is used in Mg-based alloy to produce bullets, shells and lighter flint.

(d) Water is a good complexing agent and thus Cu forms complex by losing one more electron from 3d

orbital.

(e)Cerium (Z=58)

Q.4-(a) Write the preparation of potassium dichromate from iron chromite. What happens when potassium dichromate reacts with (i) Hydrogen sulphide (ii) FeSO4?

(b) Why do Zr and Hf exhibit almost similar properties?

(c)Why is La(OH)3 stronger base than Lu(OH)3.

Ans.4- (a) Preparation:- It takes place in three steps-

- (i) Conversion of chromite ore to sodium chromate.
- (ii) Conversion of sodium chromate to sodium dichromate.
- (iii) Conversion of sodium dichromate to potassium dichromate

Following reaction takes place:--

4 FeCr₂O₄+ 4 Na₂CO₃ +7O₂- \rightarrow $2 \text{ Na}_2 \text{CrO}_4 + 2\text{Fe}_2 \text{O}_3 + 8 \text{ CO}_2$

 $\begin{array}{ccc} 2Na_2CrO_4+2\ H^+ & \longrightarrow Na_2Cr_2O_7+2\ Na^++H_2O \\ Na_2Cr_2O_7+2\ KCl & \longrightarrow & K_2Cr_2O_7+2\ NaCl \end{array}$

Reactions: - (i) $Cr_2O_7^{2-} + 8 H^+ + 3 H_2S \rightarrow 2Cr^{3+} + 7 H_2O + 3S$

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

(b) Because both have similar ionic size

(c)Due to lanthanoid contraction size of La^{3+} is smaller than Lu^{3+} as a result Lu-O bond will stronger than La-O bond.

Q.5- Give reasons for the following:-

(i) Transition metals have high enthalpy of hydration.

(ii) Zn, Cd and Hg are not regarded as transition metal.

(iii) d block elements exhibit a large number of oxidation state than f block elements.

(iv)The second and third members in each group of transition element have similar atomic radii.

(v) K₂ [PtCl₆] is well known compound whereas the corresponding Ni compound is not known.

Ans.5-(i) Transition metal ions are smaller and have higher charge, therefore have high enthalpy of hydration.

(ii) Group 12 elements i.e. Zn, Cd, Hg have completely filled (n-1) d-orbital in atomic & ionic state & thus these elements are not considered as transition elements.

(iii)The difference in the energy of (n-1) d orbital and ns orbital is very small and thus both sub-shells are used for bond formation. Whereas in f block elements (n-2)f orbitals lie underneath and hence are not available for bond formation.

(iv) The second and third members in each group of transition element have similar atomic radii due to lanthanoid contraction. It arises due to poor shielding of d and f electron.

(v)The oxidation state of Pt in is +4 which is stable for Pt. The +4 oxidation state for Ni is very difficult to achieve because the sum of first four ionization energies is very high. Hence, the corresponding Ni(II) compound is known.

Q.6-What is meant by disproportionation? Give two examples.

Ans.6-Those reactions in which same substance undergoes oxidation as well as reduction are called disproportionation reactions.e.g.

 $\begin{array}{ccc} 2Cu^+ & \rightarrow & Cu^{2+} + Cu \\ 3 \text{ MnO}_4^{2-} + 4 \text{ H}^+ & \rightarrow & 2 \text{ MnO}_4^{-} + \end{array}$ 2 MnO_4 + MnO_2 + 2 H_2O

Q.7- Complete following reactions:-

(i) MnO4 ⁻ + H ⁺ + Fe ²⁺	\rightarrow	+++
(ii) $MnO_4^- + C_2O_4^{2-} + H^+$	\rightarrow	+++
(iii) MnO_4 + OH^2 + I^2	\rightarrow	+++
Ans.7-(i) $MnO_4^- + 8H^+ + 5 Fe^{2+}$	\rightarrow	Mn^{2+} + 5 Fe ³⁺ + 4H ₂ O
(ii) $2 \text{ MnO}_4^- + 5 \text{ C}_2\text{O}_4^{2-} + 16 \text{ H}^+$	\rightarrow	2 Mn^{2+} + 10 CO_2 + $8\text{H}_2\text{O}$
(iii) $2 \text{ MnO}_4^- + \text{H}_2\text{O} + \text{I}^-$	\rightarrow	$2MnO_2$ + $2OH^-$ + IO_3^-

Q.8-For the first row of transition metals the E⁰ values are:-

E ⁰ values	V	Cr	Mn	Fe	Со	Ni	Cu
M ²⁺ /M	-1.18	-0.91	-1.18	-0.44	-0.28	-0.25	+0.34

Explain the irregularity in the above values.

Ans.8-The E^0 (M²⁺/M) values are not regular which can be explained from the irregular variation of ionization energy and sublimation energy of Mn due to half-filled orbitals.

Q.9- Decide giving reason which one of the following pairs exhibits the property indicated: (i)Sc³⁺ or Cr³⁺ exhibits paramagnetism

(ii)V or Mn exhibits more number of oxidation states

(iii)V⁴⁺ or V⁵⁺ exhibits colour

Ans.9- (i) $Sc=[Ar] 3d^{1}4s^{2}$; $Sc^{3+}=[Ar]$; it has no unpaired electron so diamagnetic

- Cr=[Ar] $3d^54s^1$; Cr³⁺=[Ar] $3d^3$; it has three unpaired electrons paramagnetic (ii) V=[Ar] $3d^34s^2$ Mn=[Ar] $3d^54s^2$ Thus V exhibit oxidation states of +2, +3, -
- (ii) $V=[Ar] 3d^34s^2$ Mn=[Ar] $3d^54s^2$ Thus V exhibit oxidation states of +2, +3, +4, +5 Whereas Mn exhibit oxidation states of +2 to +7.

(iii) $V^{4+}=[Ar] 3d^1 \rightarrow \text{coloured} \qquad V^{5+}=[Ar] \rightarrow \text{colourless}$

Q.10-(a) Describe the general trends in the following properties of the first series of the transition elements:-

(i) Stability of +2-oxidation state

(ii) Formation of oxometal ions

(b) Write steps involved in the preparation of KMnO4 from K2MnO4

Ans.11- (a) i-The elements of first transition series show decreasing tendency to form divalent cation as we move left to right in the series. This trend is due to general increase in the first and second ionization energy. The greater stability of Mn^{2+} is due to half filled d⁵ configuration and that of zinc is due to d¹⁰ configuration.

(ii) All metal except Sc from oxide of type MO which are basic. The highest oxidation number in all oxide, coincide with the group number and is attain in Sc_2O_3 to Mn_2O_7 . Formation of oxoanions is due to high electro negativity and small size of oxygen atom.

(b) It takes place in two steps:-

- (i) Conversion of pyrolusite ore into potassium mangnate.
- (ii) Conversion of potassium mangnate to potassium permanganate. Following reactions take place:- $2 MnO_2 + 4 KOH + O_2 \longrightarrow 2 K_2MnO_4 + 2H_2O$
 - $3 \text{ MnO}_4^{2-} + 4\text{H}^+ \longrightarrow 2 \text{ MnO}_4^- + \text{MnO}_2 + 2\text{H}_2\text{O}$

Q.12-(a) Write the steps involve in the preparation of K2Cr2O7 from chromite ore. (b) What is the effect of pH on dichromate ion solution?

Ans.12-(a):- It takes place in three steps-

- (i) Conversion of chromite ore to sodium chromate.
- (ii) Conversion of sodium chromate to sodium dichromate.
- (iii) Conversion of sodium dichromate to potassium dichromate

Following reactions take place:--

$4 \text{ FeCr}_2\text{O}_4 + 4 \text{ Na}_2\text{CO}_3 + 7\text{O}_2$		> 2	$Na_2CrO_4 + 2$	$2Fe_2O_3 + 8CO_2$
2Na2CrO4 + 2 H ⁺	→Na2Cr2	O7 + 2 l	$Na^+ + H2O$	
Na2Cr2O7 + 2 KCl	> K2Cr2	207 + 2	NaCl	

(b) Dichromate ion is orange in acidic solution (pH<7) and turns yellow in basic solution. It is due to interconversion of dichromate ion to chromate ion. Following reactions take place:-

 $2 \operatorname{Cr}0_4^{2-} (\text{yellow}) + 2 \operatorname{H}^+ \rightarrow \operatorname{Cr}_2 \operatorname{O7}^{2-} (\text{orange}) + \operatorname{H}_2 \operatorname{O}$ $\operatorname{Cr}_2 \operatorname{O7}^{2-} (\text{orange}) + 2 \operatorname{OH}^- \rightarrow 2 \operatorname{Cr}0_4^{2-} (\text{yellow}) + \operatorname{H}_2 \operatorname{O}.$

Q.13- (a) What is lanthanide contraction? What effect does it have on the chemistry of the elements, which follow lanthanoids?

(b) The chemistry of actinoid elements is not so much smooth as that of lanthanoids. Justify these statements by giving some examples from the oxidation state of these elements.

Ans.13- (a)The size of Lanthanoids and its trivalent ion decreases from La to Lu. It is known as lanthanoids contraction.

Cause: - It is due to poor shielding of 4f electrons.

Consequences of lanthanide contraction: - (i) Basic strength of hydroxide decreases from La(OH)₃ TO Lu(OH)₃. (ii) Because of similar chemical properties lanthanides are difficult to separate.

(b) Lanthanoids show limited number of oxidation states i.e. +2, +3, +4 (out of which +3 is most common). This is because of a large energy gap between 4f, 5d and 6s subshell. The dominant oxidation state of actinides is also +3 but they show a number of other oxidation state also e.g. +4, +5, and +7. This is due to small energy difference between 5f, 6d and 7s orbitals.

Q.14- Give examples 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 highest oxidation state in oxides and fluorides.

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

Ans.14-(i) the oxide of transition metals in lower oxidation states are generally basic while those in the higher oxidation states are acidic. Acidic character increases with increase in oxidation state is due to decrease in size of metal ion and increase in charge density.e.g. MnO (basic), Mn_3O_4 (amphoteric), Mn_2O_7 (acidic).

(ii) A transition metal exhibits higher oxidation states in oxides and fluorides because oxygen and fluorine are the most electronegative elements and thus easily can unpair electrons of metal atom.

(iii) Because oxidizing and reducing property depends on E^0 value. Since E^0 value of Cr^{3+}/Cr^{2+} is negative while that of Mn^{3+}/Mn^{2+} is positive, as a result Cr(II) act as reducing agent and Mn(III) is strong oxidizing.

Q.15-For M ²⁺ /M and M ³⁺ /M ²⁺ system	s ,the E ^o values for som	ne metals are as follows:
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Cr ²⁺ /Cr	-0.9V	Cr ³⁺ /Cr ²⁺	-0.4V
Mn ²⁺ /Mn	-1.2V	Mn ³⁺ /Mn ²⁺	+ 1.5V
Fe ²⁺ /Fe	-0.4V	Fe³⁺/Fe²⁺	+ 0.8V

Use this data to comment upon :-

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

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

Ans.15- (i)E^o for Cr^{3+}/Cr^{2+} is -0.4V i.e. negative, this means Cr^{3+} ions in the solution cannot be reduced to Cr^{2+} easily i.e. Cr^{3+} is stable. As Mn^{3+}/Mn^{2+} is +1.5V i.e positive means Mn^{3+} can easily reduced to Mn^{2+} ions in comparison to Fe³⁺ ions. Thus relatively stability of these ions is:-

$$4n^{3+} < Fe^{3+} < Cr^{3+}$$

(ii) The oxidation potentials for the given pairs will be +0.9V, +1.2V and 0.4V. Thus, the order of their getting oxidized will be in the order Mn>Cr>Fe.

Q.16-Account for the following statements:

(i)Cobalt (II) is stable in aqueous solution but in the presence of strong ligands and air, it can be oxidized to Co (III).

(ii)The d¹ configuration is very unstable in ions.

(iii)One among the lanthanides, Ce (III) can be easily oxidized to Ce (IV).

Ans.16- (i) Strong ligands force cobalt (II) to lose one more electron from 3d-subshell and thereby induced d^2sp^3 hybrisation.

(ii) The ion with d^1 configuration try to lose the only electron in order to acquire inert gas configuration.

(iii) The configuration of Ce is [Xe] $4f^1$, $5d^1$, $6s^2$. There is no much difference between the energy of 4f, 5d and 6s orbitals and thus, Ce can utilize electrons present in these orbitals and hence oxidation state of +4.

Q.17- Compare the chemistry of actinides with that of the lanthanoids with special reference to:

(i) electronic configuration

(ii) atomic and ionic sizes and

(iii) oxidation state(iv) chemical reactivity

Ans.17-

Comparison of Lanthanoids and Actinides

Properties	Lanthanoids	Actinides
Electronic	[Xe] $4f^{1-14}$, $5d^{0-1}$, $6s^2$	$[Rn] 5f^{1-14}, 6d^{0-1}, 7s^{2}$
configuration		
Atomic/ionic	Size decreases from La to Lu, and	Size decreases from Ac to Lw, and
sizes	size is more than actinides.	size is smaller than lanthanoids due to
		poorer shielding of 5f electrons
Oxidation	Common oxidation is +3 where	Common oxidation is +3 where other
states	other oxidation states are $+2$, $+4$.It	oxidation states are $+2$, $+4$, $+5$ and $+7$
	is due to a large energy gap	due to due to small energy difference
	between 4f, 5d and 6s sub shell	between 5f, 6d and 7s orbitals
Chemical	The earlier member quite reactive	The actinides highly reactive,
reactivity	but with increasing atomic number	especially in finely divided.
	they behave like aluminium.	
Complex	Less tendency to form complex	More tendencies to form complex due
formation	due to less charge density.	to high charge density.

LEVEL-3 QUESTIONS

1. When a brown compound of manganese (A) is treated with HCl it gives a gas (B). The gas taken in excess reacts with NH₃ to give an explosive compound (C). Identify compounds A and B.

Ans: $A=MnO_2$ $B=Cl_2$ $C=NCl_3$ $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$ $NH_3 + 3Cl_2 \longrightarrow NCl_3 + 3HCl$

2. A mixed oxide of iron and chromium FeOCr₂O₃ is fused with sodium carbonate in the presence of air to form a yellow colored compound (A). On acidification the compound (A) forms an orange colored compound (B), which is a strong oxidizing agent.

a. Identify compound (A) and (B)

b. Write a balanced chemical equation.

Ans: (i) A= Sodium chromate

B= Sodium dichromate

(ii) $4FeOCr_2O_3 + 8 Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$ $2Na_2CrO_4 + H^+ \longrightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$

3. A green solution of potassium manganate turns purple when CO₂ gas is passed through the solution. Explain why?

Ans: CO₂reacts with water to form carbonic acid as given below:

 $CO_2 + H_2O \longrightarrow H_2CO_3 \longrightarrow H^+ + HCO_3^-$

In acidic medium, MnO_4^2 undergoes disproportionation to form MnO_4^- ions which imparts purple colour to solution.

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

4. Draw structure of the following-

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

Ans-

