d & f BLOCK ELEMENTS

BASIC CONCEPTS

- 'd' Block Elements : The d-block elements are those elements is which the last electron enters the d-subshell of penultimate shell. The general electronic configuration of these element is (n-1) d¹⁻¹⁰ ns¹⁻², where n is outermost shell. The d-block consisting of groups 3-12 occupies the large middle section of the periodic table.
- 2. Transition Elements : The elements of d-block are known as transition element as they process properties that are transitional between the s and p block element. 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 3d-series : Scandium ($_{21}$ Sc) to zinc ($_{30}$ Zn)

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

Third transition series or 5d-series : Lanthanum ($_{57}$ La) to Mercury ($_{80}$ Hg)

Fourth transition series or 6d-series :

Begins with actinium (₈₉Ac) is still incomplete.

Zinc cadmium and mercury of group 12 have full d¹⁰ 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 element 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 counterbalances the effect of increased nuclear charge, therefore, the atomic radii remain almost constant in the middle of the series. Increase in atomic radii toward 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 increases down the group. But the atomic radii of the element 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 element follow the same order as their atomic radii. In general, the ionic radii decrease with increase in oxidation state.

(c) Ionization enthalpies : The first ionization enthalpies of transition elements are higher than those of s-block elements but lower than p-block elements. In a particular transition series ionization enthalpy increases gradually with increase in atomic number, though some irregularities are observed.

(*d*) **Meltallic 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.

(e) Oxidation states : All transition element except first and last member of the series exhibit variable oxidation states as (n - 1) d and ns have comparable energies so that both can enter into chemical bond formation.

(g) Standard electrode potential : The E^o 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-orbital in case of Mn^{2+} and Zn^{2+} and the highest negative enthalpy of hydration, Ni²⁺.



(*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 d⁰ (Sc⁺³, Ti⁺⁴) and d¹⁰ (Cu⁺, Zn⁺²) configurations, all other simple ions of transition elements contain unpaired electrons in their

(n - 1) d subshell and are, therefore, paramagnetic.

(*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-orbital for accommodating electrons donated by the ligand atoms.

(*j*) **Catalytic property :** Most of the transition metals and their compounds possess catalytic properties.

(*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.

(*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 position in the voids present in the crystal lattices of transition metals.

4. Some Important Compounds of Transition Elements :

(i) their high enthalpies of sublimation, and(ii) their high ionization 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 MnO Basic Amphoteric Amphoteric Amphoteric Amphoteric Amphoteric Amphoteric Amphoteric Acidic

(a) Potassium Dichromate, $K_2Cr_2O_7$: It is prepared from the chromite ore. Different reactions involves in the preparation of potassium dichromate from chromite ore are : $4FeO.Cr_2O_3 + 8Na_2CO_3 + 7O_2 \xrightarrow{Roasted} Chromite ore \\ 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2 \\ 2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$ $Na_2Cr_2O_7 + 2KCI \longrightarrow K_2Cr_2O_7 + 2NaCI$

 $K_2Cr_2O_7$ is separated by fractional crystallization.

Properties : Potassium dichromate is a powerful oxidizing agent. In acidic medium, its oxidizing action can be represented as follows $K_2Cr_2O_7 + 4H_2SO_7 \rightarrow 3$

$$K_{2}^{+}SO_{4} + Cr_{2}(SO_{4})_{3} + 4H_{2}O + 3[O]$$

 $Cr_{2}O_{7}^{2^{-}} + 14H^{+} + 6e^{-} \longrightarrow 2Cr^{3^{+}} + 7H_{2}O$

(i) It oxidizes ferrous to ferric. $Cr_2O_7^{2^-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3^+} + 7H_2O$ $Fe^{2^+} \longrightarrow Fe^{3^+} + e^- \times 6$

 $\operatorname{Cr}_{2}\operatorname{O}_{7}^{2-}$ + 6Fe²⁺ + 14H⁺ \longrightarrow 2Cr³ + 6Fe³⁺ + 7H₂O

Structures of chromate and dichromate ions :



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

$$2\operatorname{CrO}_{4}^{2-} + 2\operatorname{H}^{+} \longrightarrow \operatorname{Cr}_{2}\operatorname{O}_{7}^{2-}$$

Dichromate ion (orange red)
$$\operatorname{Cr}_{2}\operatorname{O}_{7}^{2-} + \overline{\operatorname{OH}} \longrightarrow 2\operatorname{CrO}_{4}^{2-} + \operatorname{H}_{2}\operatorname{O}$$

Chromate ion (orange red)

Potassium dichromate is used as primary statndard in volumetric analysis.

(b) Potassium permaganate, $KMnO_4$: It is prepared by fusion of pyrolusite, MnO_2 , with KOH in the presence of an Oxidizing agent like KNO_3 . This produces the dark green potassium magnate, $K2MnO_4$ which disproportionates in a neutral or acidic solution to give purple permanganate.

 $\begin{array}{l} 2MnO_2 + 4KOH + O_2 \longrightarrow K_2MnO_4 + 2H_2O\\ 3MnO_4^{2^-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O\\ \text{Commercially it is prepared by alkaline oxidative}\\ \text{fusion of } MnO_2 \text{ followed by the electrolytic} \end{array}$

oxidation of manganate(VI).

Properties :

Potassium permanganate is a dark purple crystalline solid.

On heating it decomposes at 513 K and $\rm O_2$ is evolved.

 $2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$

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

1. In acidic medium potassium permanganate oxidizes :

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.



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Tetrahedral manganate ion (green)

Tetrahedral permanganate ion (purple)

INNER TRANSITION ELEMENTS (f-BLOCK ELEMENTS)

The inner transition elements consist of lanthanoids and actionoids. They are characterized by filling of the 'f' orbitals.

- 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 on the state of lanthanoid element is +3. Some of the element 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 they have partily filled orbitals.

(iii) Magnetic properties : Among lanthanoids La³⁺ and Lu³⁺, which have 4f⁰ or 4f¹⁴ electronic configurations are diamagnetic and all the other trivalent lantanoid ions are paramagnetic because of the presence of unpaired electrons.

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

(v) Lanthanoid contraction : In lanthanoid, 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 localized inner shell. Hence, the attraction of the nucleus for the outermost electrons increases steadily with the atomic number

7. Differences between Lanthanoids and Actinoids

Lanthanoids	Actinoids	
(i) 4f-orbital is progressively filled.	(i) 5f-orbital is progressively filled.	
(ii) +3 oxidation state is most common along with	(ii) They show +2, +3,+4, +5, +6, +7 oxidation	
+2 and +4.	states.	
(iii) Only promethium (Pm) is radioactive.	(iii) All are radioactive.	
(iv) They are less reactive than actinoids.	(iv) They are more reactive.	
(v) Magnetic properties are less complex.	(v) Magnetic properties are more complex.	

	SOLVED PROBLEMS					
Q.1	Write down the electronic configurat(a) Cr ³⁺ (b) Cu ⁺ (c)(d) Mn ²⁺ (e) Pm ³⁺ (f)(a) Lu ²⁺ (h) Th ⁴⁺	ion of: A) Co ²⁺ Ce ⁺⁴	ins.	The first row of transition elements include elements from Sc ($z = 21$) to Zn ($Z = 30$). In its first half i.e. from Sc ($z = 21$) to Mn ($z = 25$), the stability of $+ 2$ oxidation		
Ans.	(a) $_{24}Cr^{3+}$; [Ar] 3d ³ or 1s ² 2s ² 2p ⁶ 3s ² (b) $_{29}Cu^+$; [Ar] 3d ¹⁰ or 1s ² 2s ² 2p ⁶ 3s ² (c) $_{27}Co^{2+}$; [Ar] 3d ⁷ or 1s ² 2s ² 2p ⁶ 3s ² (d) $_{25}Mn^{2+}$; [Ar] 3d ⁵ or 1s ² 2s ² 2p ⁶ 3s ² (e) $_{61}Pm^{3+}$; [Xe] 4f ⁴ or 1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ² 3d ¹⁰ 4p ⁶ 5s ² 4d ¹	² 3p ⁶ 3d ³ 3p ⁶ 3d ¹⁰ ² 3p ⁶ 3d ⁷ ² 3p ⁶ 3d ⁵ ⁰ 5p ⁶ 4 <i>f</i> ⁴).4	increases from Sc to Mn because of increase in effective nuclear charge. To what extent do the electronic configurations decide the stability of oxidation states in the first series of the transition elements? Illustrate your answer		
	(f) $_{58}Ce^{+4}$; [Xe] or $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24$ (g) $_{71}Lu^{2+}$; [Xe] $4f^{14}5d^1$ or $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^64$ (h) $_{90}Th^{4+}$; [Rn] or $1s^22s^22p^63s^23p^64s^24p^64d^{10}4f^{414}5s^25p^65d^{10}$	¹ d ¹⁰ 5p ⁶ A f ⁴¹⁴ 5d ¹ ⁰ 6s ² 6p ⁶	ins.	with example. To a large extent, the electronic configurations decide the stability of oxidation state in the first series of transition elements. Elements with larger number of oxidation states are found in or near the middle of the series		
Q.2	Why are Mn ²⁺ compounds more stabl Fe ²⁺ towards oxidation to their + 3 s	e than		e.g. Mn ($Z = 25$) exhibits all the states from + 2 to + 7. The elements with lesser number of exidation states are present at the extreme		
Ans.	The electron configuration of Mn^{2+} in [/ and in it 3d – orbitals are half – filled (ea orbital has one electron) which is a configuration as compared to that of F	Ar] $3d^5$ ach d – stable e^{2+} i.e.		ends stems and they have a few electrons to lose or share e.g. Sc $(3d^{1}4s^{2})$, Ti $(3d^{2}s^{2})$ or too many electrons hence fewer orbitals are available e.g. Cu $(3d^{10}4s^{1})$ Zn $(3d^{10}4s^{2})$ etc.		
	lose an electron to form Fe^{3+} having a stable configuration [Ar] $3d^{5}$ (stable due to half filled orbitals).	a more Q	2.5	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 ?		
Q.3	Explain briefly how +2 state becomes and more stable in the first half of th row transition elements with incre atomic number?	s more A le first easing	ins.	3d ⁵ would be most stable because in this state the 3d – orbitals are half – filled (each d – orbitals has one electron)		
	Ground state configuration	Eleme	ent	Stable oxidation state		
	$3d^{3}4s^{2}$ $3d^{5}4s^{1}$ $3d^{5}4s^{2}$	V Cr Mn		+5, V^{+5} more stable than V^{3+} +3, $Cr^{3+} > Cr^{2+}$ +2 $Mn^{2+} > Mn^{3+}$		

Q.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.

 $3d^84s^2$

Ans. MnO₄⁻, permanganate. In it the oxidation state of Mn is +7 which is equal to group number of

Mn (i.e. group, 7) or \mathbf{CrO}_{4}^{2-} , In it the oxidation state of Cr is + 6 which is equal to group number of Cr (i.e. group 6).

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

 $+2, Ni^{+2}$

Ni

Ans.	Lanthanoid contraction. On moving from lanthanum (La) to Lutetium (Lu), a gradual decrease in size of lanthanoids is observed with increase in atomic number. This is known as lanthanoid contraction.	Q.10 Ans.	What are the different oxidation states exhibited by the lanthanoids? Various oxidation states shown by lanthanoids are +2, +3 and +4. The +3 state is common to all the lanthanoids.
	 Consequences (i) The properties of 4d – and 5d – elements closely resemble because of lanthanoid contraction. (ii) There is only a little variation in chemical properties among lanthanoids. 	Q.11	Explain giving reason: (a) Transition metals and many of their compounds show paramagnetic behavior. (b) The enthalpies of atomization of the transition metals are high. (c) The transition metals generally form
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.	 coloured compounds. (d) Transition metals and their many compounds act as good catalyst. (a) The paramagnetic behaviour is due to presence of unpaired electron in the atom or ion of transition metals.
Ans.	 (i) They belong to d - block of the periodic table. (ii) They show variable oxidation states. (iii) They are coloured. (iv) They are generally paramagnetic in nature. (v) They have a tendency to form complexes. They are called transition elements because their properties lie in between those of s - block elements (metals) and p - block elements (non - metals). They are more electropositive than s - block elements but less electropositive than s - block elements but less electropositive than s - block elements 		 (b) The high enthalpies of atomization of transition metals can be attributed to strong metallic bond and additional covalent bond because of the presence of unpaired d – electrons in such metals. (c) The colour of transition metal compounds is due to d – d transition in them. The unpaired electron present in them undergo d – d transition by absorbing light from the u.v. region and thereby radiate complementary colour. (d) The transition metals and their compounds act as good catalysts because they can show variable oxidation states.
	The elements Zn, Cd and Hg are not regarded as transition elements because neither the atoms of these elements nor their ions (Cd ²⁺ , Zn ²⁺ or Hg ²⁺) have partially filled d – orbitals.	Q.12 Ans.	What are interstitial compound? Why are such compounds well known for transition metals? Crystal lattices of transition metals have interstitial voids in between the adjacent
Q.9 Ans.	In what way is the electronic configuration of the transition elements different from that of the non – transition elements? In case of transition elements the incoming		atoms, consequently, the small sized atoms like H, B, C, N etc. can be taken up by these voids to form socalled intersitial compounds. The chemical properties of interstitial
	electron enters $(n - 1) d$ – orbitals whereas is case of non – transition elements (i.e. s – block and p – block elements) the incoming electron enters the <i>ns</i> – or <i>np</i> – orbitals. In case of transition elements the last two shells are incomplete whereas in case of non – transition elements only the last shell is incomplete and is being progressively filled up.		compounds are quite similar to those of parent metal, however in physical properties such as hardness, rigidity and electrical conductance these compounds differ from parent metal. There is a decrease in malleability and ductility but an increase in tenacity. e.g. steel and cast iron are harder than pure iron. It is due to formation of interstitials of iron with carbon in case of steel and cast iron.

- Q.13 How is the variability in oxidation states of transition metals different from that of the non transition metals? Illustrate with examples.
- **Ans.** In transition metals the oxidation states differ by 1 (e.g. Fe^{2+} and Fe^{3+} , Cr^{2+} and Cr^{3+} etc.) whereas in non – transition elements they differ by two (e.g. Tl^+ and Tl^{3+} , Sn^{2+} and Sn^{4+} etc.). The variable oxidation states of transition metals are due to availability of both (n – 1) d and ns orbitals which have nearly same energy where as the variable oxidation state in non – transition metals are due to the availability of ns²np1⁻⁶ electrons for bond formation.
- 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. It is prepared as under:

(i) Preparation of sodium chromite. The chromite ore is heated with molten alkali in presence of air in a reverbatory furnace $4\text{FeCrO}_4 + 16 \text{ NaOH} + \text{O}_2 \rightarrow 8\text{Na}_2\text{CrO}_4 + 2\text{Fe}_2\text{O}_3 + 8\text{CO}_2$

(ii) Conversion of Sodium chromate into sodium dichromate. Sodium chromate is extracted with water and acidified.

 $3Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$ On cooling Na_2SO_4 separates out as $Na_2SO_4.10H_2O$ and $Na_2Cr_2O_7$ remains in solution. (iii) Conversion of $Na_2Cr_2O_7$ into $K_2Cr_2O_7$.

The solution containing $Na_2Cr_2O_7$ is treated with KCl

 $Na_{2}Cr_{2}O_{7} + 2KCI \rightarrow K_{2}Cr_{2}O_{7} + 2NaCI$

Sodium chloride being less soluble separates out.

Effect of pH

The chromate ion, CrO_4^{2-} and dichromate ion $Cr_2O_7^{2-}$ exist in equilibrium and interconvertible by alternating pH of the solution.

In alkaline solution (*increasing the pH*), the dichromate ions get converted to chromate ions whereas in acidic solution (decreasing the pH), the chromate ions changes to dichromate ions $2\text{CrO}_4^{2-} + 2\text{H}^+ \leftrightarrows 2\text{HCrO}_4^{-} \leftrightarrows \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$ (yellow) (Basic solution) (orange) (Acidic solution)

- Q.15 Describe the oxidizing action of potassium dichromatic and write the ionic equations for its reaction with:
 (a) Iodide
 (b) Iron
 - (II) solution (c) H_2S
- **Ans.** Potassium dichromate acts as a strong oxidizing agent in acidic medium.

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)$$

+ $4H_2O + 3[O]$.

The reactions are

(i) $2I^- \rightarrow I_2 + 2e^-] \times 3$ $Cr_2O_7^{2-} + 14 H^+ + 6e^- \rightarrow 2Cr^{3+} + 7 H_2O$ $Cr_2O_7^{2-} + 14 H^+ + 6I^- \rightarrow 2Cr^{3+} + 7 H_2O$

(ii)
$$Fe^{2+} \rightarrow Fe^{3+} + e^{-}] \times 6$$

 $Cr_2O_7^{2-} + 14 H^+ + 6e^{-} \rightarrow 2Cr^{3+} + 7 H_2O$
 $Cr_2O_7^{2-} + 14 H^+ + 6Fe^{2+} \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$
(iii) $H_2S \rightarrow 2H^+ + S + 2e^{-}] \times 3$
 $Cr_2O_7^{2-} + 14 H^+ + 6e^{-} \rightarrow 2Cr^{3+} + 7 H_2O$
 $Cr_2O_7^{2-} + 8 H^+ + 3H_2S \rightarrow 2Cr^{3+} + 7 H_2O$
 $+ 3S$

Q.16 Describe the preparation of potassium permanganate. How does the acidified permanganate solution reaction with (a) iron (II) ions (b) SO₂ (c) oxalic acid?

Write the ionic equations for the reactions.

Ans. KMnO₄ is prepared from *Pyrolusite* as follows. Pyrolusite is fused with potassium hydroxide and the molten liquid is stirred in presence of air when the following reactions occurs and K_2MnO_4 (potassium manganate) is formed:

> $2MnO_2$ (Pyrolusite) + 4KOH + O_2 (air) \rightarrow $2K_2MnO_4 + 2H_2O$

 K_2MnO_4 is then electrolysed electrochemically. The MnO_4^{2-} ions get oxidized to MnO_4^{-} ions at anode and hydrogen gas in evolved at cathode $K_2MnO_4 \leftrightarrows 2K^+ + MnO_4^{2-}$

 $H_2O \leftrightarrows H^+ + OH^-$

 $MnO_4^{2-} \rightarrow MnO_4^{-} + e^{-}$ (at anode)

 $2H_2O + e^- \rightarrow H_2 + 2OH^-$ (at cathode)

Reactions of Acidified $\mathsf{KMnO}_{\scriptscriptstyle 4}$ (It is a oxidizing agent)

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

/

(ii) $2KMnO_4 + 2H_2O + 5SO_2 \rightarrow K_2SO_4 + MnSO_4 + 2H_2SO_4$

(iii)
$$\begin{pmatrix} \text{COO}^- \\ | \\ \text{COO}^- \end{pmatrix} \rightarrow 2\text{CO}_2 + 2e^-] \times 5$$

 $\begin{array}{l} {\rm MnO_4^{-} + 8 \ H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O] \times 2} \\ {\rm 2MnO_4^{-} + 16 \ H^+ + 5C_2O_4^{-2-} \rightarrow} \\ {\rm 5CO_2 + 2Mn^{2+} + 8H_2O} \end{array}$

Q.17 For M²⁺ / M and M³⁺ / M²⁺ system the E⁻ values for some metals are as follows:

Cr²+ / Cr	– 0.9 V
Cr ³⁺ / Cr ²⁺	– 0.4 V
Mn²+ / Mn	– 1.2 V
Mn ³⁺ / Mn ²⁺	+ 1.5 V
Fe ²⁺ / Fe	– 0.4 V
Fe ³⁺ / Fe ²⁺	+ 0.8 V

Use this data to comment upon:

(a) The stability of Fe³⁺ in acid solution as compared to that of Cr³⁺ or Mn³⁺

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

Ans. (a) In acidic medium the stability of Fe³⁺ is more than the stability of Mn³⁺ but less than that of Cr³⁺.

(b) Iron can be easily oxidized as compared to Cr and Mn.

Q.18 Predict which of the following will be coloured in aqueous solution? Ti³⁺, V³⁺, Cu⁺, Sc³⁺, Mn²⁺, Fe³⁺, Co²⁺

and MnO_4^- . Give reason for each.

Ans. The coloured ions are Ti^{3+} , V^{3+} , Mn^{2+} , Fe^{3+} , Co^{2+} and MnO_4^{-} . Their colour is due to presence of unpaired electrons in them. The unpaired electrons in them can undergo d – d transitions by absorbing light from visible region and the complementary colour in radiated.

- Q.19 Compare the stability of + 2 oxidation state for the elements of the firs transition series.
- **Ans.** The stability of +2 oxidation state increase from Sc (z = 21) to Mn (z = 25) which is attributed to the increase in effective nuclear charge. After that in case of Iron, Fe²⁺ is less stable than Fe²⁺ as also Mn²⁺; Co²⁺ is less stable than Co³⁺ but Ni²⁺ is more stable than Ni³⁺ and Cu²⁺ is more stable than Cu⁺, Zn²⁺ is most stable because of its stable electronic configuration. Thus we have

 $Cu^{2+} > Ni^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+} > V^{2+} >$

$$Ti^{2+} > Sc^{2+}$$

- Q.20 Name chief ore of iron. How is the pig iron converted into steel? Describe any one method of steel making in detail.
- Ans. Chief ore of iron is *haematite*

Any one of the following processes can be used to convert pig iron into steel.

- (i) Bessemer process
- (ii) Open hearth process
- (iii) The oxygen top blowing process
- (iv) The electric arc process
- (v) The high frequency induction process.

Open – hearth Process

In this process, a mixture of molten pig iron, scrap steel and lime stone in heated on a shallow hearth furnace by producer gas. The furnace is adapted for different types of pig iron feed by using *acidic* or *basic* lining. The impurities get oxidized by iron oxide and form slag with the lining. e.g.

 $3C + Fe_2O_3 \rightarrow 2Fe + 3CO$

(impurity) (iron oxide)

Oxides of P and Si + lining (CaO + MgO) \rightarrow Phosphate and silicate (slag).

Towards the end (after 10 hours), an alloy of Mn, Fe and C (Spiegleisen) is added along with alloying metal.

Q.21 Name the chief ore of copper and zinc. Describe the principle of extraction of these metals from the respective ore.

Ans. Chief ores

Copper – Copper pyrites (CuFeS₂) Zinc – Zinc blende (ZnS) Principle of extraction of copper from copper pyrites

The extraction involves the following steps:

(i) **Concentration.** It is concentrated by froth floatation process.

(ii) **Roasting.** The concentrated ore is roasted in a current of air in a reverberatory furnace, below the fusion point, to remove arsenic and sulphur as their volatile oxides.

2CuFeS₂ (ore) + O₂ (air) -heat \rightarrow Cu₂S + 2FeS + SO₂ 2FeS + O \rightarrow 2FeO + SO

$$FeS + O_2 \rightarrow 2FeO + SO_2$$

(iii) The temperature is then allowed to rise above the fusion point and silica (SiO_2) is added as flux. Iron (II) oxide (FeO) reacts with silica to form iron silicate (FeSiO₃) which is removed as slag.

 $FeO + SiO_2 \rightarrow FeSiO_3$

(iv) Bessemerisation. The matte consists of Cu_2S and FeS. The mate is charged into silicalined converted through which hot compressed air is passed. The remaining sulphide is converted into FeO which reacts with silica to form slag. Copper (I) sulphide is reduced to copper by Cu₂O.

 $2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$

 $2Cu_{2}O + Cu_{2}S \rightarrow 6Cu + SO_{2}$

The copper thus obtained is known as **blister** copper.

(v) Electrolytic Refining. Impure copper is made the anode, pure copper is taken as cathode and acidified CuSO₄ solution is taken as electrolyte. When electrolyzed pure copper gets deposited at cathode and impure copper from anode goes in solution.

Anode Cu (impure) \rightarrow Cu²⁺ + 2e⁻

Cathode $Cu^{2+} + 2e^{-} \rightarrow Cu$ pure

Extraction of zinc from zinc blende (ZnS)

It involves the following steps:

(i) **Concentration.** The ore is concentrated by *froth* floatation process.

(ii) **Roasting.** It is heated in presence of air when ZnS changes to ZnO and SO₂ goes out 2ZnS (ore) + $3O_2$ (air) $\rightarrow 2ZnO + SO_2^{\uparrow}$

(iii) Bessemerization. During this remaining ZnS converts ZnO to Zn.

 $2ZnO + ZnS \rightarrow 2Zn$ (Impure) + SO_2

(iv) Electrorefining. The impure zinc is made anode and pure zinc made cathode. An acidified solution of $ZnSO_4$ is used as electrolye when pure zinc gets deposited at cathode and impure zinc from anode gets dissolved.

At Anode Zn (Impure) \rightarrow Zn²⁺ + 2e⁻ At Cathode Zn²⁺ + 2e⁻ \rightarrow Zn(S) (pure)

Q.22 Describe the chemistry of the three stages of photography, i.e., exposure, developing and fixing.

Ans. Exposure. The film is loaded in a camera and the light from the object is allowed to fall on the film by opening the shutter of the camera for a moment. The image of the object is formed on the film. In this AgBr changes to Ag particles. Developing. It is the process in which exposed photographic film is treated with a reducing agent (generally an alkaline of hydroquinone). This agent is called developer (AgBr is reduced to Ag). The rate of reduction depends upon intensity of illumination through the exposure period. Thus parts of film which were most illuminated become darkest.

Fixing. Removal of unreduced AgBr from the surface of developed film is called *fixing*. For this the developed film is dipped in a solution of sodum thiosulphate $(Na_2S_2O_3, hypo)$ in a dark room. AgBr forms a soluble complex

 $AgBr + 2Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2]$

(soluble) + NaBr

- Q.23 Compare the chemistry of actinoids with that of the lanthanids with special reference to:
 - (a) electronic configuration
 - (b) oxidation state
 - (c) atomic and ionic sizes and
 - (d) chemical reactivity
- **Ans.** (a) Electronic configuration. In case of lanthanoids the 4 *f* orbitals are progressively filled whereas is case of actinoids 5 *f* orbitals are filled up.

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	 (b) Oxidation states. The most common oxidation state shown by lanthanoids is + 3 though some of them also show + 2 and + 4 states. The oxidation states shown by actinoids are + 3, + 4, + 5, + 6 and + 7. (c) Atomic and ionic sizes. The size is larger in case of actinoids than that of lanthanoids. (d) Chemical reactivity. Actinoids are more reactive than lanthanodis because of their 	Q.27 Ans.	Calculate the number of unpaired electrons in following gaseous ions: Mn^{3+} , Cr^{3+} , V^{3+} and Ti^{3+} . Which one of these is the most stable in aqueous solution? ₂₅ Mn; $Mn^{3+} - [Ar] 3d^4$ i.e. It has four unpaired electrons. ₂₄ Cr; $Cr^{3+} - [Ar] 3d^3$ i.e. It has three unpaired electrons. ₂₃ V; $V^{3+} - [Ar] 3d^2$ i.e. It has two unpaired
Q.24	 larger size and low I. E. How would you account for the following: (a) Of the d⁴ species, Cr²⁺ is strongly reducing while manganese (III) is strongly oxidizing. (b) Cobalt (III) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidized. (c) The d¹ configuration is very unstable 	Q.28	electrons. ₂₂ Ti; Ti ³⁺ - [Ar] 3d ¹ i.e. It has one unpaired electrons. of these Cr ³⁺ is most stable in aqueous solution. Give example and suggest reason for the following features of the transition metal chemistry: (a) The lowest oxide of transition metal is basic the highest is acidic
Ans.	 (a) Cr²⁺ is strongly reducing because it changes to Cr³⁺ which is more stable but Mn³⁺ is strongly oxidizing because it changes to Mn²⁺ which is more stable. (b) Co²⁺ gets oxidized to Co³⁺ in presence of a complexing agent because Co³⁺ is more stable than Co²⁺. (c) In ions d¹ configuration is quite unstable because after losing one electron it will become stable. All elements in d¹ configuration are either reducing agents or they undergo disproportionation. 	Ans.	 (b) A transition metal exhibits higher oxidation states in oxides and fluorides. (c) The highest oxidation state is exhibited in oxoanions of a metal. (a) In lowest oxidation state, ionic bonds are formed. Metals are electropositive and so they form basicoxides. (b) Since both oxygen and fluorine are strong oxidizing agents so they can provide energy for excitation of electrons. (c) In oxoanions, the highest oxidation state is exhibited because oxygen is a strong oxidizing
Q.25	What is meant by 'dispropotionation'? Give two examples of disproportionation reaction in aqueous solution.	Q.29	Indicate the steps in the preparation of: (a) $K_2Cr_2O_7$ from chromite ore (b) KMnO from pyrolusite ore
ANS.	substance is oxidised as well as reduced. <i>e.g.</i> Examples $2Cu^+ \rightarrow Cu^{2+} + Cu$ $3CrO_4^{3-} + 8H^+ \rightarrow 2CrO_4^{2-} + Cr^{3+} + 4H_2O$	Ans.	 (c) Copper sulphate from metallic copper (d) Calomel from corrosive sublimate. (a) Preparation of sodium chromite. The chromite ore is heated with molten alkali in presence of air in a reverbatory furnace
Q.26 Ans.	Which metal in the first series of transition metals exhibits + 1 oxidation state most frequently and why? Copper Reason. With formation of Cu ⁺ from Cu, a stable electronic configuration is attained. 29Cu: 1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ¹⁰ 4s ¹ Cu ⁺ : 1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ¹⁰ (completely filled d – orbitals)		4FeCrO ₄ + 16 NaOH + O ₂ \rightarrow 8Na ₂ CrO ₄ + 2Fe ₂ O ₃ + 8CO ₂ (b) Refer to Q. 16. (c) Cu + 2H ₂ SO ₄ -heat \rightarrow CuSO ₄ + 2H ₂ O + SO ₂ (copper) (Conc.) (copper sulphate) (d) HgCl ₂ + Hg -heat \rightarrow Hg ₂ Cl ₂ Corrosive sublimate (Mercury) Calomel

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Q.30	What happens when aqueous ammonia	Q.33	What are inner transition elements? Decide
	reacts with:		which of the following atomic numbers are
	(a) silver chloride		the atomic numbers of the inner transition
	(b) mercury (I) chloride		elements: 29, 59, 74, 95, 102, 104.
	(c) mercury (II) chloride?	Ans.	Lanthanoids and actinoids are known as inner
Ans.	(a) A soluble complex is formed.		transition elements.
	$AgCl + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]Cl$		Lanthanoids are 14 elements following Ln
	(soluble) Diammine silver (I) chloride.		(z = 57). They include atomic number 58 to
	(b) Disproportionation occurs		71.
	$Hg_{2}CI_{3} + 2NH_{2}(aq) \rightarrow Hg + [Hg(NH_{3})]CI + NH_{2}CI_{3}$		Actinoids are 14 elements following Ac
	(c) An infusible white precipitate is formed		(z = 89).
	Hq (I + 2NH (aq) \rightarrow [Hq (NH)] (I + NH (I		They include atomic number 90 to 103.
	$\operatorname{Hig}_2\operatorname{Ci}_2 + 2\operatorname{Hig}_3(\operatorname{Ci}_4) + \operatorname{Hig}_4\operatorname{Ci}_3$ white pot		Of the given atomic number the inner transition
	white ppt.		elements are the elements with atomic numbers
Q.31	Describe the two uses of each of the		59 (a lanthanoids) and 95, 102 (both actinoids).
	following:	Q.34	The chemistry of the actinoid elements is
	(a) Copper sulphate (b) Silver nitrate		not so smooth as that of the lanthanoids.
	(c) Silver bromide		Justify this statement by giving some
Ans.	(a) Copper sulphate is used		examples from the oxidation state of these
	(i) in copper plating		elements.
	(ii) as germicide and fungicide under the trade	Ans.	All actinoids are radioactive and due to this
	name Bordeaux mixture which is a mixture of		their study is difficult However naturally
	Cu_sO_4 and $Ca(OH)_2$.		occurring actinoids and the earlier members of
	(iii) as a timber preservative.		the series have relatively long hair - lives as
	(b) AgNO ₃ is used		compared to synthetic elements.
	(i) in producing light sensitive films		Inere is a greater range of oxidation states as
	(II) as a medicine in nervous diseases		compared to that of lanthanolds. Lanthanolds
	(III) as a laboratory reagent.		show oxidation states of +2 and +4 in addition
	(c) AGBP is used		The actingide show evidation state of +5.
	(i) in princing out papers (P. O. P.)		The actinoids show oxidation states of $\pm 3 \pm 4 \pm 5 \pm 6$ and ± 7
		0 35	Which is the last element in the series of
Q.32	What are alloys? Name an important alloy	Q.55	the actinoids? Write the electronic
	which contains some of the lanthanoid		configuration of these elements. Comment
4	metals. Mention its uses.		on the possible oxidation state of this
AIIS.	metals or a metal and non – metal.		element.
	Misch metal is an alloy. It contains some of	Ans.	The last member of actinoid series is
	the lanthanoid metals (upto 45%), iron (5%)		Lr(z = 103).
	and traces of C, S, Ca and Al.		,,,₂Lr : [Rn] 5 <i>f</i> ¹⁴6d¹7s²
	misch metal is used in tracer bullets and flints		Its possible oxidation state is + 3.
	ion lighteron		

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- Q.36 Use Hund's rule to derive the electronic configuration of Ce³⁺ ion, and calculate its magnetic moment on the basis of 'spin only' formula.
- **Ans.** Ce^{3+} ; [Xe] $4f^1$ i.e. It has one unpaired electron

 $\upsilon = \sqrt{4s(s+1)}$

 $\therefore \qquad = \sqrt{4 \times \frac{1}{2} \left(\frac{1}{2} + 1 \right)}$

- Q.37 Name the members of the lanthnoid 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.** Actinoids showing + 2 state and + 4 state are $_{58}$ Ce; [Xe] $4f^{1}5d^{1}6s^{2}$ – It shows + 4 oxidation state

 $_{63}$ Eu; [Xe] 4f⁷5d⁰6s² - It shows + 2 oxidation state $_{70}$ Yb; [Xe] 4f¹⁴5d⁰6s² - It shows + 2

oxidation state

After losing electrons they acquires stable configuration.

- **Q.38** 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 case of lanthanoids the 4 f – orbitals are progressively filled whereas is case of actinoids 5 f – orbitals are filled up.

(ii) Oxidation states. The most common oxidation state shown by lanthanoids is + 3 though some of them also show + 2 and + 4 states. The oxidation states shown by actinoids are + 3, + 4, + 5, + 6 and + 7.

(iii) Chemical reactivity. Actinoids are more reactive than lanthanodis because of their larger size and low I. E.

- Q.39 What is lanthanoid contraction? What is its effect on the chemistry of the elements which follow the lanthanoids?
- Ans. Lanthanoid contraction. On moving from lanthanum (La) to Lutetium (Lu), a gradual decrease in size of lanthanoids is observed with increase in atomic number. This is known as lanthanoid contraction.

Consequences

(i) The properties of 4d – and 5d – elements closely resemble because of lanthanoid contraction.

(ii) There is only a little variation in chemical properties among lanthanoids.

Q.40 Write the electronic configurations of the elements with the atomic numbers 61, 91, 101 and 109.

Ans. $_{61}$ Pm; [Xe] $6s^{2}4f^{5}$ $_{91}$ Pa; [Rn] $7s^{2}5f^{2}6d^{1}$ $_{101}$ Md; [Rn] $7s^{2}5f^{13}$ $_{109}$ Mt; [Rn] $7s^{2}5f^{14}6d^{7}$.

Ξ

E	XERCISE-I	UI	NSOL	VED PROBLEMS
Q.1	A silver atom has (4d ¹⁰) in its goun that it is a transit	s completely filled d-orbitals nd state. How can you say ion element ?	Q.15	What may be the stable oxidation state of the transition element with the following d-electron configureation in the gorund state of their atoms ?
Q.2	In the series Sc(2 enthalpy of atom	Z = 21) to Zn (Z = 30), the ization of zinc is the lowest,	0.16	3d ³ , 3d ⁵ , 3d and 3d ⁴
Q.3	Which of the 3d se exhibits the larges and why ?	eries of the transition metals st number of oxidation states	Q.10	of the transition metals in which the metal exhibits the oxidation state equal to its group number.
Q.4	The E ^o (M ²⁺ /M) positive (+0.34 V)	value value for copper is). What is possibly the reason	Q.17	What is lanthanoid contraction ? What are the consequences of lanthanoid contraction ?
Q.5	for this ? How would you variation of ioniz second) in first ser	account for the irregular zation enthalpies (first and ries of the transition elements	Q.18	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?
Q.6	Why is the higher exhibited in its ox	st oxidation state of a metal ide or fluoride only ?	Q.19	In what way is the electronic configuration of transition elements different from that of the non-transition elements ?
Q.7	Which is a strong $-$ Cr ²⁺ or Fe ²⁺ an	er reducing agent d why ?	Q.20	What are the different oxidation states exhibited by lanthanoids ?
Q.8	Calculate the spin M^{2+} (aq) ion (Z =	n only magnetic moment of 27).	Q.21	Give reasons for the following : (i) Transition metals and many of their compounds show paramagnetic behaviour
Q.10	Actinoid contracti to element than l	ion is greater from element anthanoid contraction. Why		 (ii) The enthalpies of atomization of the transition metals are high (iii) The transition metals generally form coloured compounds (iv) Transition metals and their many
Q.11	Write down the e (i) Cr ³⁺	lectronic configuration of (ii) Cu+		compounds act as good catalyst.
	(iii) Co ²⁺ (v) Pm ³⁺ (vii) Lu ²⁺	(iv) Mn ²⁺ (vi) Ce ⁴⁺ (viii) Th ⁴⁺	Q.22	What are interstitial compounds ? Why are such compounds well known for transition metals ?
Q.12	Why are Mn ²⁺ cc Fe ²⁺ compounds t state ?	ompounds more stable than owards oxidation to their +3	Q.23	How is the variability in oxidation states of transition metals different from that of the non-transition metals ?
Q.13	Explain briefly how more stable in the transition eleme number.	v +2 state becomes more and ne first half of the first row nts with increasing atomic	Q.24	Describe the preparation of potassium dichromate from iron chromite ore and write the effect of increasing pH on a solution of potassium dichromate.
Q.14	To what extent do decide the stabili first series of the t your answer with	the electronic configurations ty of oxidation states in the ransition elements? Illustrate example.	Q.25	Predict which of the following will be coloured in aqueous solution ? Ti^{3+} , V^{3+} , Sc^{3+} , Mn^{2+} , Fe^{3+} , Co^{2+} and MnO_4^{-}

E	XERCISE-II	ВС	DARC	PROBLEMS
Q.1 Q.2	Why do Zr and properties ? In transition serie number, the ator very much. Why	Hf exhibit almost similar s, with an increase in atomic nic radius does not change is it so ?	Q.7	Assign a reason for each of the following : (i) The third ionization energy of Mn ($Z = 25$) is higher than that of either Cr ($Z = 24$) or Fe ($Z = 26$). (ii) Simple copper (I) salts are not stable in
Q.3	Why do the d-blo number of oxid elements ?	ock elements exhibit a large ation states than f-block	Q.8	aqueous solutions. Describe the trends in the following properties
Q.4	Assign reasons for (i) The enthalpie elements are high (ii) The transition compounds act a (iii) From element contraction is gre contraction. (iv) The E ^o value much more position (v) Scandium (Z so oxidation states and transition element	r the following : es of atomization of transition n metals and many of their s good catalysts. In to element, the actinoid reater than the lanthanoid for the Mn ³⁺ /Mn ²⁺ couple is ve than that of Cr ³⁺ /Cr ²⁺ . = 21) does not exhibit variable and yet it is regareded as a t.	Q.9	 of the first series of the transition elements : (i) Oxidation states (ii) Atomic sizes (iii) Magnetic behaviour of dipositive gaseous ions (M²⁺). How would you account for the following : (i) Many of the transition elements and their compounds can act as good catalystis. (ii) The metallic radii of the third (5d) series of transition elements are virtually the same as those of the corresponding members of the second series. (iii) There is a greater range of oxidation states
Q.5	Discuss the relativ	e stability in aqueous solution rate among the elements :		among the actinoids than among the lanthanoids.
	Cr, Mn, Fe and Co situation ? (At. Nos. Cr = 24,	Mn = 25, Fe = 26, Co = 27)	Q.10	How would you account for the following :(i) The atomic radii of the metals of the third(5d) series of transition elements are virtuallythe same as those of the corresponding
Q.6	Compare actino reference to their (i) electronic con (ii) oxidation sta (iii) general chem	ids and lanthanoids with figuration of atoms tes of elements hical reactivity of elements.		members of the second (4d) series. (ii) The E ^o value for the Mn^{3+} / Mn^{2+} couple is much more positive than that for Cr^{3+} / Cr^{2+} couple or Fe ³⁺ /Fe ²⁺ couple.

	(iii) The highest oxidation state of a metal is exhibited in its oxide or fluoride.	Q.15	(a) Give reasons for the following :(i) Mn3+ is a good oxidising agent.
Q.11	How would you account for the following :(i) Mn (III) undergoes disproportionation reaction easily.(ii) Co (II) is easily oxidized in the presence of strong ligands.		 (ii) E⁰_{M²⁺/M} values are not regular for first row transition metals (3d series) (iii) Although 'F' is more electronegative tha 'O', the highest Mn fluoride is MnF₄, wherea the highest oxides is Mn₂O₇. (b) Complete the following equations
Q.12	 Explain giving a suitable reason for each of the following (i) Transition metals and their compounds are generally found to be good catalysts. (ii) Metal –metal bonding is more frequent for the 4d and the 5d series of transition metals than that for the 3d series. 		 (i) 2CrO²⁻₄ + 2 H⁺ (ii) KMnO₄ heat OR (a) Why do transition elements show variable oxidation states ? (i) Name the element showing maximum number of oxidation states among the first series of transition metals from Sc(Z = 21) to 2n(Z = 30)
Q.13	 State reasons for the following ; (i) Cu (I) ion is not stable in an aqueous solution. (ii) Unlike Cr³⁺, Mn²⁺, Fe³⁺ and the subsequent other M²⁺ ions of the 3d series of elements, the 4d and the 5d series metals generally do not form stable cationic species. 		(ii) Name the eelement which shs only +3 oxidation state.(b) What is lanthanoid contraction ? Name an important alloy which contains some fo the langthoid metals.
Q.14	Complete the following chemical equaitons : (i) $MnO_{4}^{-}(aq) + S_{2}O_{3}^{2-}(aq) + H_{2}O(I) \longrightarrow$ (ii) $Cr_{2}O_{7}^{2-}(aq) + Fe^{2+}(aq) + H^{+}(aq) \longrightarrow$		