CHAPTER 7

'd' AND 'f' BLOCK ELEMENTS

Syllabus

- *General introduction, electronic configuration, occurrence and characteristics of transition metals, general trends in properties of the first row transition metals – metallic character, ionization enthalpy, oxidation states, ionic radii, colour, catalytic property, magnetic properties, interstitial compounds, alloy formation, preparation and properties of $K_2Cr_2O_7$ and $KMnO_4$.*
- *Lanthanoids : Electronic configuration, oxidation states, chemical reactivity and lanthanoid contraction and its consequences.*
- *Actinoids : Electronic configuration, oxidation states and comparison with lanthanoids.*

Chapter Analysis

List of Topics	2016		2017		2018
	D	OD	D	OD	D/OD
Identification of compounds/elements/ions	1Q (2 marks)*	1Q (5 marks)#		1Q (5 marks)@	
Complete the equations	1Q (2 marks)*	1Q (5 marks)#		1Q (5 marks)@	1Q (2 marks)
Give reason	1Q (3 marks)	1Q (5 marks)#	1Q (5 marks)^	1Q (5 marks)@	1Q (3 marks)
Properties of d-block elements			1Q (1 mark) 1Q (5 marks)^		
Lanthanoids and actinoids			1Q (5 marks)^	1Q (5 marks)@	

- * One question of 2 marks with two choices was asked.
- # One question of 5 marks with two choices was asked. First choice has one question of 3 marks of give reason type and one question of 2 marks on complete the equations. Second choice was on identification of elements from the given properties.
- ^ One question of 5 marks with two choices was asked. First choice has one question of 3 marks on stating the reason for various characteristics of elements and one question of 2 marks on difference between lanthanoids and actinoids. Second choice was on characteristics of d-block elements, lanthanoids and actinoids.
- @One question of 5 marks with two choices was asked. First choice has one question of 3 marks on stating the reason for various characteristics of elements and one question of 2 marks on difference between lanthanoids and actinoids. Second choice had one question of 3 marks on identification of ions and one of 2 marks on complete the equations.

  On the basis of above analysis, it can be said that from exam point of view, Lanthanoids, Actinoids and Properties of d-block Elements are the most important topics of the chapter. Also, Identification of Compounds/Elements/Ions, Complete the Equations and Give Reason type of questions are frequently asked.

TOPIC-1
d-Block Elements, their Properties and Compounds

Revision Notes

- ***d*-block elements :** The elements in which last electron enters the *d* - sub-shell of penultimate shell and lies in the middle of the periodic table belonging to groups 3-12.
- **Transition elements :** The elements of *d*-block are known as transition elements as they possess properties that are transitional between the *s*-block and *p*-block elements. Transition elements are defined as elements which have incompletely filled *d*-orbitals in their ground states or in any of its oxidation state. Transition elements have four series :

(i) First transition series : These elements have incomplete 3*d*-orbitals and they are from Sc (21) to Zn (30).

(ii) Second transition series : These elements have incomplete 4*d*-orbitals and they are from Y (39) to Cd (48).

(iii) Third transition series : These elements have incomplete 5*d*-orbitals and they are La (57) and from Hf (72) to Hg (80).

(iv) Fourth transition series : This series is yet incomplete and these elements have incomplete 6*d*-orbitals. Known elements of this series are–actinium (89) and Rf (104) to and three other elements.

3. General electronic configuration of transition elements : Valence shell electronic configuration is $(n\text{–}1)d^{1\text{–}10}$, $ns^{1\text{–}2}$, where n is the outermost shell.

Electronic configuration of *d*-block elements

Series	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8	Group 9	Group 10	Group 11	Group 12
3*d* series	Sc (21) $4s^2\,3d^1$	Ti (22) $4s^2 3d^2$	V (23) $4s^2\,3d^3$	Cr (24) $4s^1\,3d^5$	Mn (25) $4s^2 3d^5$	Fe (26) $4s^2 3d^6$	Co (27) $4s^2 3d^7$	Ni (28) $4s^2\,3d^8$	Cu (29) $4s^1 3d^{10}$	Zn (30) $4s^2\,3d^{10}$
4*d* series	Y (39) $5s^2 4d^1$	Zr (40) $5s^2 4d^2$	Nb (41) $5s^1 4d^4$	Mo (42) $5s^1 4d^5$	Tc (43) $5s^2 4d^5$	Ru (44) $5s^1 4d^7$	Rh (45) $5s^1 4d^8$	Pd (46) $5s^0 4d^{10}$	Ag (47) $5s^1 4d^{10}$	Cd (48) $5s^2 4d^{10}$
5*d* series	La (57) $6s^2 5d'\,4f^0$	Hf (72) $6s^2 5d^2 4f^{14}$	Ta (73) $6s^2 5d^3 4f^{14}$	W (74) $6s^2 5d^4\,4f^{14}$	Re (75) $6s^2 5d^5 4f^{14}$	Os (76) $6s^2 5d^6 4f^{14}$	Ir (77) $6s^2 5d^7 4f^{14}$	Pt (78) $6s^1 5d^9 4f^{14}$	Au (79) $6s^1 5d^{10} 4f^{14}$	Hg (80) $6s^2 5d^{10} 4f^{14}$
6*d* series	Ac (89) $7s^2 5f^0 6d^1$	Rf (104) $7s^2 5f^{14} 6d^2$	Db (105) $7s^2 5df^{14} 6d^3$	Sg (106) $7s^2 5f^{14} 6d^4$	Bh (107) $7s^2 5f^{14} 6d^5$	Hs (108) $7s^2 5f^{14} 6d^6$	Mf (109) $7s^2 5f^{14} 6d^7$	Ds (110) $7s^2 5f^{14} 6d^8$	Rg (111) $7s^1 5f^{14} 6d^{10}$	uub (112) $7s^2 5f^{14} 6d^{10}$

- **General characteristics of Transition Elements :**
  Physical Properties :

(i) All are metals.

(ii) These are malleable and ductile except mercury which is liquid.

(iii) High thermal and electrical conductivity.

(iv) Metallic lustre and sonorous.

(v) Atomic radii : Smaller than those of *s*-block elements, 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 constant and then increases towards end of the period.
It usually increase down the group. The size of 4*d* elements is almost the same size of the 5*d* series elements. The filling of 4*d* before 5*d* orbitals results in regular decrease in atomic radii which is called as lanthanoid contraction.

(vi) Ionic radii : The ionic radii decrease, with increase in oxidation state.

(vii) Density : From left to right in a period, density increases.

(viii)Ionisation enthalpy : Along the series from left to right, there is an increase in ionisation enthalpy. Irregular trend in the Ist ionisation enthalpy of 3*d* metals is due to irregularity in electronic configuration of 4*s* and 3*d* orbitals. In a group, IE decreases from 3*d* to 4*d*-series but increases from 4*d* to 5*d* series due to lanthanoid contraction.

(ix) Metallic bonding : In metallic bonding, regular lattice of positive ions is held together by a cloud of free electrons, which can move freely through the lattice. Transition metal atoms are held together by strong metallic bonds.

(x) Enthalpy of atomisation : Enthalpy of atomisation is the heat required to convert 1 mole of crystal lattice into free atoms. Transition elements have high enthalpy of atomisation. It first increases, becomes maximum in the middle of the series and then decreases regularly.

(xi) Variable oxidation state : Since the energies of *ns* and $(n–1)$ *d* electrons are almost equal, therefore the electrons of both these orbitals take part in the reactions, due to which transition elements show variable oxidation states. Transition metal ions show variable oxidation states except the first and last member of the series.

(xii) Electrode potential : The electrode potential develops on a metal electrode when it is in equilibrium with a solution of its ions, leaving electrons from the electrode. Transition metals have lower value of reduction potential. Variation in E° value is irregular due to the regular variation in ionisation enthalpies $(I.E_1 + I.E_2)$, sublimation and hydration enthalpies.

(xiii) Catalytic properties : Many of the transition metals and their compounds, particularly oxides act as catalysts for a number of chemical reactions. Iron, cobalt, nickel, platinum, chromium, manganese and their compounds are commonly used catalysts.
All transitional metals show multiple oxidation states and have large surface area so, all metals work as a catalyst.

(xiv) Magnetic properties : On the basis of the behaviour of substances in magnetic field, they are of two types :
(i) Diamagnetic, (ii) Paramagnetic.
Diamagnetic substances have paired electrons only. *e.g.,* Zn has only paired electrons.
In paramagnetic substances, it is necessary to have at least one unpaired electron. Paramagnetism increases with the increase in number of unpaired electrons.
Paramagnetism may be measured by magnetic moment.
Magnetic moment. $(\mu) = \sqrt{n(n+2)}$ B.M.,
where n = number of unpaired electrons in atom or ion and B.M. = Bohr magneton (unit of magnetic moment). Diamagnetic and paramagnetic substances are repelled and attracted in the magnetic field respectively (Magnetic properties of transition elements).

(xv) Melting and boiling points : Except zinc, cadmium and mercury, all other transition elements have high melting and boiling points. This is due to strong metallic bonds and presence of partially filled *d*-orbitals in them.

(xvi) Complex formation : They have tendency to form complex ions due to high charge on the transition metal ions and the availability of *d*-orbitals for accommodating electrons donated by the ligand atoms.

(xvii) Formation of coloured compounds : Transition metals form coloured ions due to the presence of unpaired *d*-electrons. As a result, light is absorbed in the visible region to cause excitation of unpaired *d*-electrons ($d – d$ transition) and colour observed corresponds to the complementary colour of the light absorbed. Cu^+, Zn^{2+} and Cd^{2+} are colourless due to the absence of unpaired *d*-electron (d^{10}).

(xviii) Formation of alloys : Alloy formation is due to almost similar size of the metal ions, their high ionic charges and the availability of *d*-orbitals for bond formation. Therefore, these metals can mutually substitute their position in their crystal lattice to form alloys. eg. steel, brass.

(xix) Formation of interstitial compounds : Interstitial compounds are known for transition metals as small-sized atoms of H, B, C, N, etc. can easily occupy positions in the voids present in the crystal lattices of transition metals. Characteristics of interstitial compounds :
- High melting points.
- Hard.
- Chemically inert.
- Retain metallic conductivity.
- Non-stoichiometric.

➢ **Oxides of Transition metals :** They 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 while those in the higher oxidation states are amphoteric or acidic. For example,

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

➢ **Potassium Dichromate ($K_2Cr_2O_7$)**

Preparation : It is prepared from chromate ore in the following steps :

(i) Chromate ore is fused with sodium carbonate in the presence of air to give sodium chromate.

$$2\,FeCr_2O_4 + 4Na_2CO_3 + 7/2O_2 \rightarrow Fe_2O_3 + \underset{\text{Sodium chromate}}{4Na_2CrO_4} + 4CO_2$$

(ii) Na_2CrO_4 is filtered and acidified with conc. H_2SO_4 to give $Na_2Cr_2O_7$.

$$2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O.$$

(iii) Sodium dichromate solution is treated with KCl to give $K_2Cr_2O_7$.

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

Properties :

(a) It is an orange, crystalline solid.

(b) With alkali :

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

(c) With acid :

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

(d) It is a powerful oxidising agent. For example,

(i) It oxidises ferrous to ferric.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$
$$[Fe^{2+} \rightarrow Fe^{3+} + e^-] \times 6$$
$$\overline{Cr_2O_7^{2-} + 6Fe^{2+}\ 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O}$$

(ii) It oxidises stannous to stannic.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$
$$[Sn^{2+} \rightarrow Sn^{4+} + 2e^-] \times 3$$
$$\overline{Cr_2O_7^{2-} + 3Sn^{2+}\ 14H^+ \rightarrow 2Cr^{3+} + 7H_2O + 3Sn^{4+}}$$

(iii) It oxidises sulphur dioxide to sulphuric acid.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$
$$[SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-] \times 3$$
$$\overline{Cr_2O_7^{2-} + 3SO_2 + 2H^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O}$$

(iv) It oxidises hydrogen sulphide to sulphur.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$
$$[H_2S \rightarrow 2H^+ + S + 2e^-] \times 3$$
$$\overline{Cr_2O_7^{2-} + 3H_2S + 8H^+ \rightarrow 2Cr^{3+} + 3S + 7H_2O}$$

(v) It oxidises iodides to iodine.

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

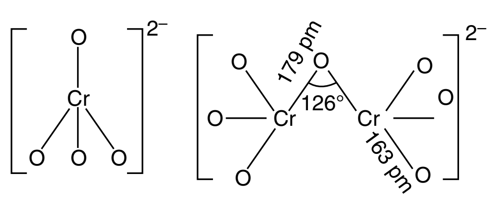
Uses :

(i) In leather industry for chrome tanning.

(ii) Preparation of azo compounds.

(iii) As a primary standard in volumetric analysis for the estimation of reducing agent.

Structure :



Chromate ion **Dichromate ion**

➢ **Potassium permanganate ($KMnO_4$)**

Preparation :

(i) It is prepared from pyrolusite ore with KOH in the presence of oxidising agent like KNO_3. The dark green potassium manganate undergoes electrolytic oxidation to produce potassium permanganate.

$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$
$$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

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

$$MnO_2 + 2e^- \xrightarrow[\text{Oxidised with air/}KNO_3]{\text{Fused with KOH}} \underset{\text{Manganate ion}}{MnO_4^{2-}}$$

$$MnO_4^{2-} \xrightarrow[\text{in alkaline solution}]{\text{Electrolytic oxidation}} \underset{\text{Permanganate ion}}{MnO_4^- + 1e^-}$$

(iii) In laboratory, by oxidation of manganese (II) ion salt by peroxodisulphate.

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

Properties :

(i) Dark purple crystalline solid.

(ii) Sparingly soluble in water.

(iii) Decomposes on heating at 513 K.

$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$$

(iv) Acts as a powerful oxidising agent in acidic, alkaline and neutral medium. For example :

1. **In acidic medium oxidises :**

(i) Iodide to iodine

$$[MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O] \times 2$$
$$[2I^- \rightarrow I_2 + 2e^-] \times 5$$
$$2MnO_4^- + 10I^- + 16H^+ \rightarrow 2Mn^{2+} + 5I_2 + 8H_2O$$

(ii) Ferrous to ferric

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$
$$[Fe^{2+} \rightarrow Fe^{3+} + e^-] \times 5$$
$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

(iii) Oxalate to carbon dioxide :

$$[MnO_4^- + 8H + 5e^- \rightarrow Mn^{2+} + 4H_2O] \times 2$$
$$[C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-] \times 5$$
$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

(iv) Hydrogen sulphide to sulphur

$$[MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O] \times 2$$
$$[S^{2-} \rightarrow S + 2e^-] \times 5$$
$$2MnO_4^- + 5S^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 5S + 8H_2O$$

(v) Sulphite to sulphate

$$[MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O] \times 2$$
$$[SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^-] \times 5$$
$$5SO_3^{2-} + 2MnO_4^- + 6H^+ \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$$

(vi) Nitrite to nitrate

$$[MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O] \times 2$$
$$[NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^-] \times 5$$
$$2MnO_4^- + 5NO_2^- + 6H^+ \rightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$$

2. **In neutral alkaline medium :**

(i) Iodide to iodate

$$[MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-] \times 2$$
$$I^- + 6OH^- \rightarrow IO_3^- + 3H_2O + 6e^-$$
$$2MnO_4^- + I^- + H_2O \rightarrow IO_3^- + 2MnO_2 + 2OH^-$$

(ii) Manganous to manganese dioxide

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

Uses :

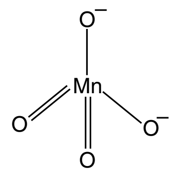
(i) Bleaching of wool, silk, cotton and other textile fibres etc.

(ii) Decolourisation of oils.

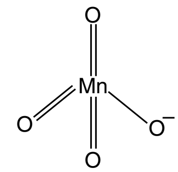
(iii) In analytical chemistry (titration).

(iv) In organic synthesis.

Structure :



Tetrahedral manganate ion (Green)



Tetrahedral permanganate ion (Purple)

Know the Terms

- **Oxidation state :** The measure of the electronic state of an atom in a particular compound, equal to the number of electron it has, more than or less than the number of electrons in free atom.
- **Ferromagnetic substances :** Substances which are attracted very strongly by the applied magnetic field. *e.g.,* Fe, Co, Ni etc.
- **Alloy :** A mixture of two elements, one of which is a metal. For example, brass (Cu + Zn), bronze (Cu + Sn).

Very Short Answer-Objective Type Questions (1 mark each)

A. Multiple choice Questions:

Q. 1. Electronic configuration of a transition element X in +3 oxidation state is [Ar]$3d^5$. What is its atomic number?

(a) 25 **(b) 26**
(c) 27 **(d) 24**

A **[NCERT Exemp. Q. 1, Page 105]**

Ans. Correct option : (b)

Explanation : It is formed by the loss of 3 electrons, the configuration of element X is [Ar] $3d^6$ $4s^2$.
Therefore, Atomic number = 26.

Q. 2. The electronic configuration of Cu(II) is $3d^9$ whereas that of Cu(I) is $3d^{10}$. Which of the following is correct?

(a) Cu(II) is more stable
(b) Cu(II) is less stable
(c) Cu(I) and Cu(II) are equally stable
(d) Stability of Cu(I) and Cu(II) depends on nature of copper salts U **[NCERT Exemp. Q. 2, Page 105]**

Ans. Correct option : (a)

Explanation : Cu(II) is more stable due to nuclear charge of Cu.

Q. 3. Metallic radii of some transition elements are given below. Which of these elements will have highest density?

Element	Fe	Co	Ni	Cu
Metallic radii/pm	126	125	125	128

(a) Fe **(b) Ni**
(c) Co **(d) Cu**

A **[NCERT Exemp. Q. 3, Page 105]**

Ans. Correct option : (d)

Explanation : In periodic table when moving from left to right along period, its metallic radius decreases and mass increases. Decrease in metallic radius coupled with increase in atomic mass which results in the increase in density of metal. Therefore, among above four options, copper belongs to right side of periodic table in transition metal and it has the highest density.

Q. 4. When $KMnO_4$ solution is added to oxalic acid solution, the decolourisation is slow in the beginning but becomes instantaneous after some time because

(a) CO_2 is formed as the product.
(b) Reaction is exothermic.
(c) MnO_4^- catalyses the reaction.
(d) Mn^{2+} acts as auto-catalyst.

A&E **[NCERT Exemp. Q. 9, Page 107]**

Ans. Correct option : (d)

Explanation : When $KMnO_4$ solution is added to oxalic acid solution, the decolourisation is slow in the beginning but becomes instantaneous after sometime because Mn^{2+} acts as an auto-catalyst.

Reduction half-reaction :

$$[MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O] \times 2$$

Oxidation half-reaction :

$$[C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-] \times 5$$

Overall equation :

$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

End point of this reaction : Colourless to light pink.

Q. 5. The magnetic moment is associated with its spin angular momentum and orbital angular momentum. Spin only magnetic moment value of Cr^{3+} ion is

(a) **2.87 BM** **(b) 3.87 BM**
(c) **3.47 BM** **(d) 3.57 BM**

A **[NCERT Exemp. Q. 15, Page 108]**

Ans. Correct option : (b)

Explanation : The magnetic moment is associated with its spin angular momentum and orbital angular momentum.

Spin only magnetic moment value of Cr^{3+} ion is $3d^3$.
Hence, magnetic moment

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

$= \sqrt{3(3+2)} = \sqrt{15}$

$= 3.87$ BM

Q. 6. Although Zirconium belongs to 4d transition series and Hafnium to 5d transition series even then they show similar physical and chemical properties because

(a) both belong to d-block.

(b) both have same number of electrons.

(c) both have similar atomic radius.

(d) both belong to the same group of the periodic table. A&E **[NCERT Exemp. Q. 20, Page 109]**

Ans. Correct option : (c)

Explanation : Zirconium (Zr) and hafnium (Hf) have similar atomic radius hence they show similar physical and chemical properties.

Q. 7. Highest oxidation state of manganese in fluoride is +4 (MnF_4) but highest oxidation state in oxides is +7 (Mn_2O_7) because

(a) fluorine is more electronegative than oxygen.

(b) fluorine does not possess d-orbitals.

(c) fluorine stabilises lower oxidation state.

(d) in covalent compounds fluorine can form single bond only while oxygen forms double bond. A&E **[NCERT Exemp. Q. 19, Page 108]**

Ans. Correct option : (d)

B. Match the following :

Q. 1. Match the species given in Column I with those mentioned in Column II.

	Column I (Catalyst)		Column II (Process)
(i)	Ni in the presence of hydrogen	(a)	Ziegler-Natta catalyst
(ii)	Cu_2Cl_2	(b)	Contact process
(iii)	V_2O_5	(c)	Vegetable oil to ghee
(iv)	Finely divided iron	(d)	Sandmeyer reaction
(v)	$TlCl_4+Al(CH_3)_3$	(e)	Haber's Process
		(f)	Decomposition of $KClO_3$

[NCERT Ex. Q. 52, Page 112]

Ans.

Column I	Column II	Explanation
(i)	(c)	Nickel in the presence of hydrogen is used for the process of vegetable oil to ghee.
(ii)	(d)	In Sandmeyer reaction Cu_2Cl_2 is used as catalyst.
(iii)	(b)	In contact process V_2O_5 is used as catalyst in the reaction.
(iv)	(e)	In Haber's process finely divided iron powder is used as catalyst.
(v)	(a)	Zieglar-Natta catalyst is $[TiCl_4 + Al(CH_3)_3]$.

C. Answer the following:

Q. 1. Write the formula of an oxo-anion of Manganese (Mn) in which it shows the oxidation state equal to its group number.

A **[CBSE Delhi Set-1, 3 2017]**

Ans. $MnO_4^-/KMnO_4$ 1

[CBSE Marking Scheme 2017]

Q. 2. Write the formula of an oxo-anion of Chromium (Cr) in which it shows the oxidation state equal to its group number. A **[CBSE Delhi Set-2 2017]**

Ans. $Cr_2O_7^{2-}/CrO_4^{2-}/K_2Cr_2O_7/K_2CrO_4$ 1

[CBSE Marking Scheme 2017]

Q. 3. Assign the reason for the following :

Copper (I) ion is not known in aqueous solution.

A&E**[CBSE OD 2012]**

Ans. Copper (I) compounds are unstable in aqueous solution and undergo disproportionation.

$$2Cu^+ \rightarrow Cu^{2+} + Cu$$

The higher stability of Cu^{2+} is due to high heat of hydration of Cu^{+2} than Cu^+. 1

Q. 4. Explain the following :

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

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

A&E**[CBSE Comptt. Delhi 2012]**

Ans. (i) The transition elements exhibit high enthalpies of atomization because they have large number of unpaired electrons in their atoms. Due to which they have stronger interatomic interaction and hence stronger bonding between atoms. ½

(ii) Transition elements and their compounds shows good catalytic properties because :

(a) They have variable valencies, show multiple oxidation states, forms unstable intermediate compounds and provides a new path with lower activation energy for the reaction.

(b) In some cases, transition elements provide a suitable surface for the reaction to take place. ½

Q. 5. Explain the following observation :

Most of the transition metal ions exhibit characteristic colour in aqueous solution.

A&E**[CBSE Delhi 2012]**

Ans. Most of complexes of transition elements are coloured due to d-d transition. This is because of the absorption of radiation from visible light region to promote an electron from one of the *d*-orbitals to another. The ions of transition elements absorb the radiation of a particular wavelength and the rest is reflected, imparting colour to the solution. **1**

AI **Q. 6. How would you account for the following ?**
Many of the transition elements are known to form interstitial compounds. A&E **[CBSE Delhi 2012]**

Ans. In the crystal lattice, transition elements have interstitial vacant space into which small sized non-metal atoms such as H, B, C, or N are trapped. These compounds are non-stoichiometric, neither typically ionic nor covalent. *e.g.*, TiC, MH, Fe_3H etc. **1**

Q. 7. When Cu^{2+} ion is treated with KI, a white precipitate is formed. Explain the reaction with the help of chemical equation.
A&E **[NCERT Exemp. Q. 36, Page 111]**

Ans. $2Cu^{2+} + 4I^- \rightarrow \underset{\text{White ppt.}}{Cu_2I_2} + I_2$

Cu^{2+} gets reduced to Cu^+ while I^- oxidizes to I_2. **1**

Short Answer Type Questions **(2 marks each)**

Q. 1. What are the transition elements ? Write two characteristics of the transition elements.
R **[CBSE Delhi 2015]**

Ans. These atoms or ions whose *d*-orbital are incomplete in ground state or in one of the most common oxidation state are called transition elements or d-block elements. The valence shell electronic configuration of transition elements is $(n-1)d^{1-10}ns^{1-2}$. **1**

Two characteristics of transition elements :
(i) Transition metals show variable oxidation states. **1**
(ii) All transition metals act as catalyst.

Answering Tip
- Use the precise definition and mention the main characteristics.

AI **Q. 2. What is meant by 'disproportionation' ? Give an example of a disproportionation reaction in aqueous solution.** R

OR

Suggest reasons for the following features of transition metal chemistry :
(i) The transition metals and their compounds are usually paramagnetic.
(ii) The transition metals exhibit variable oxidation states. A&E **[CBSE Comptt. Delhi 2015]**

Ans. Disproportionation is the reaction in which an element undergoes self-oxidation and self-reduction simultaneously. For example – **1**
$2Cu^+ (aq) \rightarrow Cu^{2+} (aq) + Cu(s)$ **1**
(Or any other correct equation)

OR

(i) Due to presence of unpaired electrons in *d*-orbitals. **1**
(ii) Due to incomplete filling of d-orbitals. Due to very small energy difference in between $(n-1)\ d$ and $n\ s$-orbitals. **1**

[CBSE Marking Scheme 2015]

Q. 3. Complete the following chemical equations :
(i) $MnO_4^-(aq) + S_2O_3^{2-}(aq) + H_2O(l) \rightarrow$
(ii) $Cr_2O_7^-(aq) + Fe^{2+}(aq) + H^+(aq) \rightarrow$
R **[CBSE Delhi 2012]**

Ans. (i) $8MnO_4^-(aq) + 3S_2O_3^{2-}(aq) + H_2O(l) \rightarrow 8MnO_2(s)$ $6SO_4^{2-}(aq) + 2OH^-(aq)$

(ii) $Cr_2O_7^- + 14H^+(aq) + 6Fe^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 6Fe^{3+}(aq) + 7H_2O(aq)$. **1+1**

Commonly Made Error
- Many students write unbalanced equations. Some students fail to write the correct products.

Q. 4. Complete and balance the following chemical equations:
(a) $Fe^{2+} + MnO_4^- + H^+ \rightarrow$
(b) $MnO_4^- + H_2O + I^- \rightarrow$
R **[CBSE Delhi/OD 2018]**

Ans. (a) $5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$ **1**
(b) $2MnO_4^- + H_2O + I^- \rightarrow 2MnO_2 + 2OH^- + IO_3^-$ **1**
(Half mark to be deducted in each equation for not balancing)
[CBSE Marking Scheme 2018]

Commonly Made Error
- Many students write unbalanced equations. Some students fail to write the correct products.

Q. 5. In the following ions:
Mn^{3+}, V^{3+}, Cr^{3+}, Ti^{4+}
(Atomic no: Mn = 25, V = 23, Cr = 24, Ti = 22)
(a) Which ion is most stable in an aqueous solution?
(b) Which ion is the strongest oxidizing agent?
(c) Which ion is colourless?
(d) Which ion has the highest number of unpaired electrons? U **[CBSE Foreign Set-1, 2, 3 2017]**

Ans. (a) Cr^{3+} ½ **(b)** Mn^{3+} ½
(c) Ti^{4+} ½ **(d)** Mn^{3+} ½
[CBSE Marking Scheme 2017]

Q. 6. Explain the following observations:
(i) Copper atom has completely filled *d* orbitals ($3d^{10}$) in its ground state, yet it is regarded as a transition element.
(ii) Cr^{2+} is a stronger reducing agent than Fe^{2+} in aqueous solution.
A&E **[CBSE Comptt. OD Set-1 2017]**

Ans. (i) Because it has incompletely filled d orbitals in one of its oxidation state (Cu^{2+}). **1**

(ii) $Cr^{2+}(d^4)$ changes to $Cr^{3+}(d^3)$ while $Fe^{2+}(d^6)$ changes to Fe^{3+} (d^5). In aqueous medium d^3 is more stable than d^5. **1**

[CBSE Marking Scheme 2017]

Q. 7. Name the following :

(i) A transition metal which does not exhibit variation in oxidation state in its compounds.

(ii) A compound where the transition metal is in the +7 oxidation state.

(iii) A member of the lanthanoid series which is well known to exhibit +4 oxidation state.

(iv) Ore used in the preparation of Potassium dichromate. R **[CBSE SQP 2016]**

Ans. (i) Scandium (Sc). ½

(ii) $KMnO_4$ or any other suitable example. ½

(iii) Cerium (Ce) or any other example. ½

(iv) Chromite ore. ½

AI **Q. 8. Explain why :**

(i) E° for Mn^{3+}/Mn^{2+} couple is more positive than that for Fe^{3+}/Fe^{2+}. (At. Nos. Mn = 25, Fe = 26).

(ii) Ce^{3+} can be easily oxidised to Ce^{4+}. (At. No. Ce = 58). A&E **[CBSE OD 2012]**

Ans. (i) Stable half-filled $3d^3$ configuration of Mn^{2+} results in high 3rd ionisation enthalpy of Mn. While in case of Fe^{2+}, configuration is $3d^6$. Hence, it can easily loose one electron to give stable configuration $3d^5$. **1**

(ii) Ce^{3+}, ions having the configuration $4f^1 5d^0 6d^0$ can easily lose electron to acquire the configuration $4f^0$ $5d^0 6s^0$ and form Ce^{4+} ion. **1**

Q. 9. Explain the following observation

(i) Zn^{2+} salt are colourless.

(ii) Copper has exceptionally positive $E^o_{M^{2+}/M}$ value.

A&E **[CBSE Comptt. OD Set-3 2017]**

Ans. (i) Due to absence of unpaired electrons. **1**

(ii) Due to high $\Delta_a H°$ and low $\Delta_{hyd} H°$. **1**

[CBSE Marking Scheme 2017]

Detailed Answer:

(i) Zinc has no unpaired electrons in its d orbital and has a stable fully filled d orbital state. Thus, due to absence of unpaired electrons, Zn^{2+} salts are colourless. **1**

(ii) As copper has high energy of atomisation $\Delta_a H°$ and low hydration energy $\Delta_{hyd} H°$, due to which E° value is positive. **1**

Answering Tip

- Write the cause and consequence of the condition.

Q. 10. Give reasons :

(i) Zn is not regarded as a transition element.

(ii) Cr^{2+} is a strong reducing agent.

A&E **[CBSE Comptt. Delhi 2016]**

Ans. (i) Due to both Zn and Zn^{2+} ion absence of incompletely filled d-orbital, Zn is not regarded as a transition element. **1**

(ii) Cr^{2+} has d^4 configuration while Cr^{3+} has more stable d^3 (t_{2g}^3) configuration. Thus, Cr has a tendency to acquire Cr^{3+} due to greater stability of +3 oxidation state. Cr^{2+} acts as strong a reducing agent. **1**

Q. 11. Explain the following observation :

(i) Silver atom has completely filled d-orbitals ($4d^{10}$) in its ground state, yet it is regarded as a transition element.

(ii) E° value for Mn^{3+}/Mn^{2+} couple is much more positive than Cr^{3+}/Cr^{2+}.

A&E **[CBSE Comptt. OD Set-2 2017]**

Ans. (i) Silver can exhibit +2 oxidation state wherein it will have incompletely filled d-orbital. **1**

(ii) Much higher third ionisation energy of Mn where the required change is from d^5 to d^4. **1**

[CBSE Marking Scheme 2017]

Q. 12. When chromite ore $FeCr_2O_4$ is fused with NaOH in presence of air, a yellow coloured compound (A) is obtained which on acidification with dilute sulphuric acid gives a compound (B). Compound (B) on reaction with KCl forms a orange coloured crystalline compound (C).

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

(ii) Write one use of compound (C). U

OR

Complete the following chemical equations :

(i) $KMnO_4^- + 3S_2O_3^{2-} + H_2O \rightarrow ?$

(ii) $Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \rightarrow ?$

R **[CBSE Delhi 2016]**

Ans. (i) $4FeCr_2O_4 + 16NaOH + 7O_2 \rightarrow 8Na_2CrO_4\,[A] + 2Fe_2O_3 + 8H_2O$

$2Na_2CrO_4\,[A] + H_2SO_4 \rightarrow Na_2Cr_2O_7\,[B] + Na_2SO_4 + H_2O$

$Na_2Cr_2O_7\,[B] + 2KCl \rightarrow K_2Cr_2O_7\,[C] + 2NaCl$

A : Na_2CrO_4 B : $Na_2Cr_2O_7$

C : $K_2Cr_2O_7$ **1**

(ii) Use of $K_2Cr_2O_7$ (C) : It is used as a strong oxidizing agent in industries. **1**

OR

(i) $2MnO_4^- + 5S_2O_3^{2-} + 6H^+ \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$ **1**

(ii) $Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O + 3Sn^{4+}$ **1**

Answering Tip

- Write the balanced chemical equations.

Q. 13. Describe the preparation of potassium permanganate. How does the acidified permanganate solution react with oxalic acid ? Write the ionic equations for the reactions.

OR

Describe the oxidising action of potassium dichromate and write the ionic equations for its reaction with (i) an iodide (ii) H_2S.

R [CBSE Comptt. OD 2015]

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

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

$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4 + MnO_2 + 2H_2O$ **1**

Oxalate ion or oxalic acid is oxidised at 333 K :

$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2$ **1**

[CBSE Marking Scheme 2015]

Answering Tip

- Write the balanced chemical equations involved in the preparation.

OR

(i) $Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$ **1**

(ii) $Cr_2O_7^{2-} + 3H_2S + 8H^+ \rightarrow 2Cr^{3+} + 3S + 7H_2O$ **1**

[CBSE Marking Scheme 2015]

Answering Tip

- Write the balanced chemical equations.

Q. 14. A solution of $KMnO_4$ on reduction yields either a colourless solution or a brown precipitate or a green solution depending on pH of the solution. What different stages of the reduction do these represent and how are they carried out?

C [NCERT Exemp. Q. 46, Page 111]

Ans. The oxidising behaviour of $KMnO_4$ depends upon pH of solution. Different compounds with different colours are formed at different pH.

$$MnO_4^- + 8H^+ + 5e^- \rightarrow \underset{\text{Colourless}}{Mn^{2+}} + \underset{\text{(in acidic medicum, pH<7)}}{4H_2O}$$

$$MnO_4^- + e^- \rightarrow \underset{\text{Green}}{MnO_4^{2-}}$$

In neutral medium :

$$MnO_4^- + H_2O + 3e^- \rightarrow \underset{\text{(Brown ppt)}}{MnO_2} + \left(\underset{\text{In neutral medium pH=7}}{4OH^-}\right)$$ **2**

Q. 15. Silver atom has completely filled d orbitals ($4d^{10}$) in its ground state. How can you say that it is a transition element? C [NCERT]

Ans. Those elements which have partially filled d or f subshell in any oxidation state are called transition elements. Silver (Ag) has a completely filled 4d orbital ($4d^{10}\ 5s^1$) in its ground state. Now, silver displays two oxidation states (+1 and +2). In the +1 oxidation state, an electron is removed from the s-orbital. However, in the +2 oxidation state, an electron is removed from the d-orbital. Thus, the *d*-orbital now becomes incomplete ($4d^9$). Hence, it is a transition element. **2**

Long Answer Type Questions-I (3 marks each)

Q. 1. Complete the following reactions—

(i) $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow$

(ii) $2CrO_4^{2-} + 2H^+ \rightarrow$

(iii) $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow$ **R [CBSE Delhi 2013]**

Ans. (i) $Cr_2O_7^{2-}(aq) + 6Fe^{2+}(aq) + 14H^+(aq) \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$ **1**

(ii) $2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$ **1**

(iii) $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$ **1**

[CBSE Marking Scheme 2013]

Answering Tip

- Ensure all the products are mentioned and the equation is balanced.

Q. 2. The magnetic moment of few transition metal ions are given below:

Metal ion	**Magnetic moment (BM)**
Sc^{3+}	0.00
Cr^{2+}	4.90
Ni^{2+}	2.84
Ti^{3+}	1.73

(at no. Sc = 21, Ti = 22, Cr = 24, Ni = 28)

Which of the given metal ions:

(i) has the maximum number of unpaired electrons?

(ii) force colourless aqueous solution?

(iii) exhibits the most stable +3 oxidation state?

OR

Consider the standard electrode potential values (M^{2+}/M) of the elements of the first transition series.

Ti	**V**	**Cr**	**Mn**	**Fe**
−1.63	−1.18	−0.90	−1.18	−0.44
Co	**Ni**	**Cu**	**Zn**	
−0.28	−0.25	+0.34	−0.76	

Explain :

(i) E° value for copper is positive.

(ii) E° value of Mn is more negative as expected from the trend.

(iii) Cr^{3+} is a stronger reducing agent than Fe^{2+}.

A **[CBSE SQP 2017]**

Ans. (i) Cr^{2+} 1

(ii) Sc^{3+} 1

(iii) Sc^{3+} 1

OR

(i)) The high energy to transform Cu(s) to Cu^{2+}(aq) is not balanced by its hydration enthalpy. 1

(ii) Mn^{2+} has d^5 configuration (stable half-filled configuration) 1

(ii) d^5 to d^3 occurs in case of Cr^{2+} to Cr^{3+}.(More stable t^32g) while it changes from d^6 to d^5 in case of Fe^{2+} to Fe^{3+}. 1

[CBSE Marking Scheme 2017]

Q. 3. (i) Complete the following equations :

(a) $2MnO_4^- + 5SO_3^{2-} + 6H^+ \rightarrow$

(b) $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow$

(ii) Based on the data, arrange Fe^{2+}, Mn^{2+} and Cr^{2+} in the increasing order of stability of +2 oxidation state.

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

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

$E^\circ_{Fe^{3+}/Fe^{2+}} = +0.8$ V R + U

OR

Write the preparation of following :

(i) $KMnO_4$ **from** K_2MnO_4

(ii) Na_2CrO_4 **from** $FeCr_2O_4$

(iii) $Cr_2O_7^{2-}$ **from** CrO_4^{2-}

R **[CBSE Comptt. Delhi/OD 2018]**

Ans. (i) (a) $2MnO_4^- + 5SO_3^{2-} + 6H^+ \rightarrow 2Mn^{2+} + 3H_2O + 5SO_4^{2-}$ 1

(b) $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$ 1

(ii) $Cr^{2+} < Fe^{2+} < Mn^{2+}$ 1

OR

(i) $3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$ 1

(or any other correct equation)

(ii) $2FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$ 1

(iii) $2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$ 1

[CBSE Marking Scheme 2018]

Answering Tip

- Write the balanced chemical equations.

Q. 4. Account for the following :

(i) $CuCl_2$ **is more stable than** Cu_2Cl_2.

(ii) Atomic radii of 4*d* and 5*d* series elements are nearly same.

(iii) Hydrochloric acid is not used in permanganate titration. A&E **[CBSE Foreign Set-1, 2 2017]**

Ans. (i) In $CuCl_2$, Cu is in +2 oxidation state which is more stable due to high hydration enthalpy as compared to Cu_2Cl_2 in which Cu is in +1 oxidation state. 1

(ii) Due to lanthanoid contraction. 1

(ii) Because HCl is oxidised to chlorine. 1

[CBSE Marking Scheme 2017]

Q. 5. (i) Give reasons for the following :

(a) Compounds of transition elements are generally coloured.

(b) MnO is basic while Mn_2O_7 is acidic.

(ii) Calculate the magnetic moment of a divalent ion in aqueous medium if its atomic number is 26.

A&E + A **[CBSE Comptt. OD Set-1, 2, 3 2017]**

Ans. (i) (a) Due to d-d transition. 1

(b) Due to higher oxidation state of Mn_2O_7 / Due to high polarizing power of Mn(VII). 1

(ii) $\mu = \sqrt{4(4+2)} = 4.90$ B.M. 1

[CBSE Marking Scheme 2017]

Q. 6. Give reasons :

(i) Mn shows the highest oxidation state of +7 with oxygen but with fluorine it shows the highest oxidation state of +4.

(ii) Transition metals show variable oxidation states.

(iii) Actinoids show irregularities in their electronic configurations. A&E **[CBSE Delhi 2016]**

Ans. (i) Mn can form $p\pi$ -$d\pi$ bond with oxygen by using 2*p* orbital of oxygen and 3*d*-orbital of Mn because of which it shows highest oxidation state of +7. With fluorine, Mn cannot form $p\pi - d\pi$ bond thus shows the highest oxidation state of +4. 1

(ii) Transition metal show variable oxidation state due to comparable energies of *ns* and (*n*-1)*d* orbitals and partially filled *d* orbitals. So, both these orbitals take part in the reactions. 1

(iii) Due to comparable energies of 5*f*, 6*d* and 7*s* orbitals and the relative stabilities of f^0, f^7 and f^{14} occupancies of the 5*f* orbitals. 1

Answering Tip

- Be specific while writing reason. Avoid unnecessary explanations.

Q. 7. (i) Account for the following :

(a) Cu^+ is unstable in an aqueous solution.

(b) Transition metals form complex compounds.

(ii) Complete the following equation :

$$Cr_2O_7^{2-} + 8H^+ + 3NO_2^- \rightarrow$$

A&E + R **[CBSE OD 2015]**

Ans. (i) (a) Because Cu^+ undergoes disproportionation as $2Cu^+ \rightarrow Cu + Cu^{2+}$ Hydration enthalpy of Cu^{2+} is higher than that of Cu^+ which compensates the I.E.$_2$ of Cu involved in the formation of Cu^{2+} ions. 1

(b) Because of small size of metal, high ionic charge and availability of vacant *d*-orbital. 1

(ii) $Cr_2O_7^{2-} + 8H^+ + 3NO_2^- \rightarrow 2Cr^{3+} + 3NO_3^- + 4H_2O$ (Balanced equation only) 1

[CBSE Marking Scheme 2015]

Q. 8. Explain the following observations giving an appropriate reason for each :

(i) The enthalpies of atomization of transition elements are quite high.

(ii) There occurs much more frequent metal-metal bonding in compounds of heavy transition metals (i.e., 3rd series).

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

Ans. (i) The transition elements exhibit high enthalpies of atomization because they have large number of unpaired electron in their atoms. Due to which they have stronger interatomic interaction and hence stronger bonding between atoms. **1**

(ii) 4d and 5d transition elements (2nd and 3rd series) are larger in size than the corresponding 3d elements. Hence, the valence electrons are less tightly held and form metal-metal bond more frequently. **1**

(iii) Mn^{2+} is much more resistant than Fe^{2+} towards oxidation.

$Mn^{2+} \rightarrow 3d^5$

$Fe^{2+} \rightarrow 3d^6$

As Mn^{2+} has stable configuration hence it is resistant towards oxidation. While in Fe^{2+}, electronic configuration is $3d^6$, so it can lose one electron to give stable configuration $3d^5$. **1**

Q. 9. Give reasons :

(a) E° value for Mn^{3+}/Mn^{2+} couple is much more positive than that for Fe^{3+}/Fe^{2+}.

(b) Iron has higher enthalpy of atomization than that of copper.

(c) Sc^{3+} is colourless in aqueous solution whereas Ti^{3+} is coloured. A&E **[CBSE Delhi/OD 2018]**

Ans. (a) The comparatively high value for Mn shows that $Mn^{2+}(d^5)$ is particularly stable / Much larger third ionisation energy of Mn (where the required change is from d^5 to d^4) **1**

(b) Due to higher number of unpaired electrons. **1**

(c) Absence of unpaired d-electron in Sc^{3+} whereas in Ti^{3+} there is one unpaired electron or Ti^{3+} shows d-d transition. **1**

[CBSE Marking Scheme 2018]

Detailed Answer:

(a) Because Mn^{2+} is more stable than Mn^{3+} due to half-filled d^5 configuration whereas Fe^{2+} becomes unstable after loosing an electron from half-filled orbital. **1**

(b) Due to presence of higher number of unpaired electrons in iron, they have stronger metallic bonding. Hence, the enthalpy of atomization is more of iron than that of copper. **1**

(c) Sc^{3+} is colourless as it does not contain unpaired electrons to undergo d-d transition while Ti^{3+} is coloured as it contains unpaired electrons to undergo d-d transition by absorbing light from visible region and radiate complementary colour. **1**

Q. 10. (i) For M^{2+}/M and M^{3+}/M^{2+} systems, E° values for some metals are as follows :

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

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

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

Use this data to comment upon

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

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

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

Ans. (i) (a) Cr^{3+}/Cr^{2+} has a negative reduction potential. Hence, Cr^{3+} cannot be reduced to Cr^{2+}. Cr^{3+} is most stable. Mn^{3+}/Mn^{2+} have large positive E° values. Hence, Mn^{3+} can be easily reduced to Mn^{2+}. Thus Mn^{3+} is least stable. Fe^{3+}/Fe^{2+} couple has a positive E° value but is small. Thus, the stability of Fe^{3+} is more than Mn^{3+} but less stable than Cr^{3+}. **1**

(b) If we compare the reduction potential values, Mn^{2+}/Mn has the most negative value *i.e.,* its oxidation potential value is most positive. Thus, it is most easily oxidised. Therefore, the decreasing order for their ease of oxidation is Mn > Cr > Fe. **1**

(ii) $K_4[Mn(CN)_6]$

Mn is in +2 oxidation state. Magnetic moment 2.2 indicates that it has one unpaired electron and hence forms inner orbital or low spin complex. In presence of CN^- which is a strong ligand, hybridisation involved is d^2sp^3 (octahedral complex). **1**

Answering Tip

- Comprehend what is being asked before answering by reading the question carefully. Write all events in sequence.

Q. 11. A mixed oxide of iron and chromium is fused with sodium carbonate in free access of air to form a yellow coloured compound (A). On acidification the compound (A) forms an orange coloured compound (B), which is a strong oxidizing agent. Identify compound (A) and (B). Write chemical reactions involved.

A **[CBSE Comptt. OD Set-1, 2, 3 2017]**

Ans. A : Na_2CrO_4 B : $Na_2Cr_2O_7$ ½+½

$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$ **1**

$2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$ **1**

[CBSE Marking Scheme 2017]

Commonly Made Error

- Most of the students write either incorrect or incomplete equations. In many cases, the equations are unbalanced.

Answering Tip

- Write complete and balanced chemical equations.

Long Answer Type Questions-II (5 marks each)

AI Q. 1. (i) Following are the transition metal ions of 3d series:
Ti^{4+}, V^{2+}, Mn^{3+}, Cr^{3+}
(Atomic number : Ti = 22, V = 23, Mn = 25, Cr = 24)
Answer the following :
(a) Which ion is most stable in an aqueous solution and why?
(b) Which ion is a strong oxidizing agent and why?
(c) Which ion is colourless and why?
(ii) Complete the following equations:
(a) $2MnO_4^- + 16H^+ + 5S^{2-} \rightarrow$
(b) $KMnO_4 \xrightarrow{\text{heat}}$

A + R **[CBSE OD Set-1, 2, 3 2017]**

Ans. (i) (a) Cr^{3+}, half filled t^3_{2g} ½+½
(b) Mn^{3+}, due to stable d^5 configuration in Mn^{2+} ½+½
(c) Ti^{4+}, No unpaired electrons ½+½
(ii) (a) $2MnO_4^- + 16H^+ + 5S^{2-} \rightarrow 5S + 2Mn^{2+} + 8H_2O$ **1**
(b) $2KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2$ **1**
[CBSE Marking Scheme 2017]

Answering Tips
- Read the question carefully. Do not forget to answer the sub-parts.
- Write complete and balanced chemical equation.

26. (a) (i) Transition metals show variable oxidation states, because of presence of incompletely filled d orbitals, their oxidation states differ from each other by unity.
Example → $V^{2+}, V^{3+}, V^{4+}, V^{5+}$

(ii) Zn, Cd and Hg have fully filled d-orbitals, so, their d electrons do not contribute in metallic bonding. Hence, due to weak interatomic interactions, contributed only by ns electrons, Zn, Cd and Hg are soft metals.

(iii) E° value of Mn^{3+}/Mn^{2+} couple is highly positive (+1.57 V), as, on gaining 1 electron, Mn attains very stable $3d^5$ electronic configuration (exactly half-filled). But for $Cr^{3+} + e^- \longrightarrow Cr^{2+}$, the chromium ion becomes unstable as, the $3d^3$ electronic configuration (exactly half filled t_{2g} level), which is quite stable, is converted to $3d^4$ configuration. Hence, E° value of Cr^{3+}/Cr^{2+} is less than that of Mn^{3+}/Mn^{2+} couple.

(b) Similarity between chemistry of Lanthanoid and Actinoid Elements :—
both Lanthanoid and actinoid elements are reactive and show +3 as the most common oxidation state in their respective series.

Difference between chemistry of Lanthanoid and Actinoid Elements :—

Lanthanoids	Actinoids
Lanthanoids have less tendency for complex formation and do not form oxocations	Actinoids have more tendency for complex formation and form oxocations like UO_2^{2+}, PuO_2^{2+}, etc.
Magnetic properties of Lanthanoids can be easily interpreted.	Magnetic properties of Actinoids are very difficult to explain.

[Topper's Answer 2017] 5

Q. 2. (i) Complete the following equations :

(a) $Cr_2O_7^{2-} + 2OH^- \rightarrow$

(b) $MnO_4^- + 4H^+ + 3e^- \rightarrow$

(ii) Account for the following :

(a) Zn is not considered as a transition element.

(b) Transition metals form a large number of complexes.

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

R + A&E **[CBSE OD 2014]**

Ans. (i) (a) $Cr_2O_7^{2-} + 2OH^- \rightarrow 2\,CrO_4^{2-} + H_2O$ **1**

(b) $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$ **1**

(ii) (a) Because Zn/Zn^{2+} has fully filled *d*-orbitals. **1**

(b) This is due to smaller ionic sizes, higher ionic charge and availability of *d*-orbitals. **1**

(c) Because Mn^{2+} is more stable ($3d^5$) than Mn^{3+}($3d^4$). Cr^{+3} is more stable due to t_2g^3/d^3 configuration. **1**

[CBSE Marking Scheme 2014]

Answering Tips

- Write complete and balanced chemical equation.
- Read the question carefully. Do not forget to answer the sub-parts.

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

R **[CBSE Comptt. OD 2013]**

Ans. Potassium permanganate is prepared from pyrolusite ore with KOH in the presence of oxidising agent like KNO_3. The dark green potassium manganate undergoes electrolytic oxidation to produce potassium permanganate.

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

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

Oxidising nature of potassium permanganate can be shown as :

Ferrous to ferric

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

$$[Fe^{2+} \rightarrow Fe^{3+} + e^-] \times 5$$

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

2

Commonly Made Error

- Most of the students are not able to write balanced equations correctly. Equations are either unbalanced or incomplete. Many students just described the preparation of potassium permanganate missing balanced equations.

Answering Tip

- Describe the method for preparation of potassium permanganate with balanced chemical equations.

Q. 4. (i)Describe the following characteristics of the first series (Sc to Zn) :

(a) Atomic radii, (b) Oxidation states, (c) Ionisation enthalpies.

(ii) Name an important alloy which contains some of the lanthanoid metals. Mention its two uses.

R **[CBSE OD 2012]**

Ans. (i) (a) Atomic radii : From scandium to chromium atomic size decreases, increases in manganese and remains constant in Fe, Co, Ni, then increases in Cu and Zn.

The atomic radius decreases in a period in the beginning because with increase in atomic number, the nuclear charge goes on increasing progressively. The shielding effect of *d*-electrons is so small so that the net electrostatic attraction between the nuclear charge and the outermost electron increases consequently the atomic radius decreases, as the number of *d*-electrons increases. This neutralizes the effect of increased nuclear charge due to increase in atomic number. Consequently, atomic radius remain almost unchanged after chromium towards the end of the series there are increased electron-electron repulsion between the added electrons in the same orbital which exceed the attractive forces due to increased nuclear charge and their size increases. **1**

(b) Oxidation states : The transition elements exhibit a variety of oxidation states in their compounds. This is due to the fact that (n–1)d-orbitals are of comparable energy to ns orbitals and therefore some or all of the (n – 1)d

electrons can be used along with ns electrons in compound formation. Some common oxidation states exhibited by elements of first transition series are listed below :

Elements	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Configuration	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$
Oxidation States	(+ 2)	+ 2	+ 2	+ 2	+ 2	+ 2	+ 2	+ 2	+ 1	+ 2
	+ 3	+ 3	+ 3	+ 3	+ 3	+ 3	+ 3	(+ 3)	+ 2	
		+ 4	+ 4	(+ 4)	(+ 4)	(+ 4)	(+ 4)			
			+ 5	(+ 6)	(+ 6)	(+ 6)				
					+ 7					

(The values in parentheses are less common oxidation states) **1**

(c) Ionisation enthalpy : The ionisation enthalpy of transition elements lie between those of *s*-block and *p*-block element. They are higher than those of *s*-block elements and lower than those of *p*-block elements. **1**

(ii) Lanthanoids find special use for the production of alloy called mischmetall.
Mischmetall contains lanthanoid metal (95%) + iron (5%) and traces of S, C, Ca, Al. It is used to produce bullets, shells and lighter flint. **2**

Answering Tip

- Comprehend what is being asked before answering by reading the question carefully.

Q. 5. When chromite ore is fused with sodium carbonate in free excess of air and the product is dissolved in water, a yellow solution of compound (A) is obtained. On acidifying the yellow solution with sulphuric acid, compound (B) is crystallized out. When compound (B) is treated with KCl, orange crystals of compound (C) crystallize out. Identify (A), (B) and (C) and write the reactions involved.

A [CBSE Comptt. OD Set-1, 2, 3 2017]

Ans. A : Na_2CrO_4 B : $Na_2Cr_2O_7$ C : $K_2Cr_2O_7$ **½+½+1**

$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$ **1**

$2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$ **1**

$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$ **1**

[CBSE Marking Scheme 2017]

Commonly Made Error

- Most of the students write either incorrect or incomplete equations. In many cases, the equations are unbalanced.

Answering Tip

- Write complete and balanced chemical equations.

Q. 6. Comment on the statement that elements of the first transition series possess many properties different from those of heavier transition elements.

C [NCERT]

Ans. The properties of the elements of the first transition series differ from those of the heavier transition elements in many ways.

(i) The atomic sizes of the elements of the first transition series are smaller than those of the heavier elements (elements of 2nd and 3rd transition series).
However, the atomic sizes of the elements in the third transition series are virtually the same as those of the corresponding members in the second transition series. This is due to lanthanoid contraction. **1**

(ii) +2 and +3 oxidation states are more common for elements in the first transition series, while higher oxidation states are more common for the heavier elements. **1**

(iii) The enthalpies of atomisation of the elements in the first transition series are lower than those of the corresponding elements in the second and third transition series. **1**

(iv) The melting and boiling points of the first transition series are lower than those of the heavier transition elements. This is because of the occurrence of stronger metallic bonding (M−M bonding). **1**

(v) The elements of the first transition series form low-spin or high-spin complexes depending upon the strength of the ligand field. However, the heavier transition elements form only low-spin complexes, irrespective of the strength of the ligand field. **1**

TOPIC-2
f-Block Elements: Lanthanoids and Actinoids

Revision Notes

- ***f*-block elements :** The elements in which filling of electrons takes place in (n–2) f-subshell which belongs to anti-penultimate (third to the outermost) energy shell. This block consists of two series of elements known as **Lanthanoids and Actinoids**. These elements are also known as inner transition elements. The general electronic configuration of the f - block elements is

$$(n-2)f^{1-14}\ (n-1)d^{0-1}\ ns^2$$

For Lanthanoids, n is 6 while its value is 7 for Actinoids. There are many exceptions in the electronic configuration.

- **Lanthanoids :** The series involving the filling of 4f-orbitals following lanthanum La (Z = 57) is called the lanthanoid series. There are 14 elements in this series starting with Ce (Z = 58) to Lu (Z = 71).
  - **Electronic configuration :** [Xe] $4f^{1-14}\ 5d^{0-1}\ 6s^2$
  - **Physical properties :**

(i) Highly dense metals, soft, malleable and ductile.

(ii) High melting point.

(iii) Forms alloys easily with other metals.

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

(v) **Atomic and ionic sizes :** With increasing atomic number, the atomic and ionic radii decreases from one element to the other but the decrease is very small.

A steady decrease in the size of lanthanoids with increase in atomic number is known as **lanthanoid contraction.**

Consequences of Lanthanoid contraction :

(a) It leads to similar physical and chemical properties among lanthanoids.

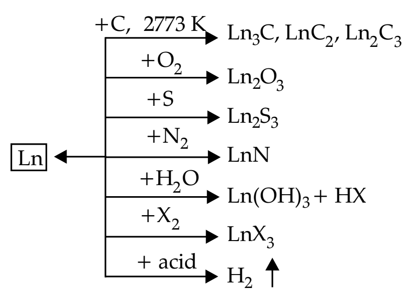
(b) Zr and Hf have same properties, due to similar atomic radii.

(c) Chemical separation of lanthanoids become difficult.

(vi) **Oxidation state :** They mainly give +3 oxidation state. Some elements show +2 and +4 oxidation states.

(vii) **Colour :** Some of the trivalent ions are coloured. This happens due to the absorption in visible region of the spectrum resulting in f-f transitions.

Chemical properties : All lanthanoids are highly electropositive metals and have almost similar chemical reactivity.



Uses :

(i) Mischmetall is the alloy of cerium (about 55%) and various other Lanthanoid elements (40-43%). It also contains iron upto 5% and traces of sulphur, carbon, silicon calcium and aluminium. It is a pyrophoric material, hence it is used in lighter flints.

(ii) Lanthanoid oxides are used for polishing glass.

(iii) Cerium salts are used in dyeing cotton and also as catalysts.

(iv) Lanthanoid compounds are used as catalyst for hydrogenated dehydrogenation and petroleum cracking.

(v) Pyrophoric alloys are used for making tracer bullets and shells.

- **Actinoids :** The series involving the filling of 5f orbitals from actinium, Ac (Z = 89) upto lawrencium, Lr (Z = 103) comprises of actinoids.
  - **Electronic configuration :** [Rn] $5f^{1-14}\ 6d^{0-1}\ 7s^2$
  - **Physical properties :**

(i) Highly dense metals and form alloys with other metals.

(ii) Silvery white metals.
(iii) Highly electropositive.
(iv) High melting point.
(v) **Ionic and atomic radii :** The atomic and ionic size decreases with an increase in atomic number due to actinoid contraction. The electrons are added to 5*f* shell resulting in an increase in the nuclear charge causing the shell to shrink inwards. This is known as actinoid contraction.
(vi) **Colour :** Many actinoid ions are coloured.
(vii) **Magnetic properties :** Many actinoid ions are paramagnetic.
(viii) **Oxidation State :** The common oxidation state exhibited is +3. They also exhibit oxidation state of +4, +5, +6 and +7.
(ix) Many elements are radioactive.

- **Chemical reactivity :** Less reactive towards acids.
- **Uses :**

(i) Thorium is used in the treatment of cancer and in incandescent gas mantles.
(ii) Uranium is used in the glass industry, in medicines and as nuclear fuel.
(iii) Plutonium is used in atomic reactors and in atomic bombs.

➢ **Difference between Lanthanoids and Actinoids :**

S. No.	Lanthanoids	Actinoids
(i)	4*f* orbital is progressively filled.	5*f* orbital is progressively filled.
(ii)	+3 oxidation state is most common along with +2 and +4.	+3 oxidation state is most common, but exhibit higher oxidation state of +4, +5, +6, +7.
(iii)	Except promethium, all are non-radioactive.	All are radioactive.
(iv)	Less tendency of complex formation.	Strong tendency of complex formation.
(v)	Chemically less reactive than actinoids.	More reactive than lanthanoids.

Know the Terms

➢ **Coinage metals or currency metals :** Copper (Cu), silver (Ag) and gold (Au) present in group-11 are known as coinage metals or currency metals.

➢ **Transuranic elements :** All the elements beyond uranium are known as transuranic or man-made elements. These elements do not occur in nature because their half-life periods are so short.

➢ **Occlusion :** It is the adsorption of H_2 by transitions metals such as Pt, Pd, Ni etc.

➢ **Platinum black :** It is the finely reduced form of platinum in the form of velvety black powder.

Very Short Answer-Objective Type Questions (1 mark each)

A. Multiple choice Questions:

Q. 1. Which of the following oxidation state is common for all lanthanoids?

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

R **[NCERT Exemp. Q. 7, Page 106]**

Ans. Correct option : (b)

Q. 2. There are 14 elements in actinoid series. Which of the following element does not belong to this series?

(a) U **(b)** Np
(c) Tm **(d)** Fm

R **[NCERT Exemp. Q. 10, Page 107]**

Ans. Correct option : (c)

Explanation : Tm (Thulium) is a lanthanoid.

Q. 3. $KMnO_4$ acts as an oxidizing agent in acidic medium. The number of moles of $KMnO_4$ that will be needed to react with one mole of sulphide ions in acidic solution is

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

U **[NCERT Exemp. Q. 11, Page 107]**

Ans. Correct option : (a)

Explanation :

$$2MnO_4^- + 5S^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 5S + 8H_2O$$

For 5 moles of S the number of moles of $KMnO_4$ = 2

For 1 mole of S the number of moles of $KMnO_4$ = 2/5

Q. 4. When acidified $K_2Cr_2O_7$ solution is added to Sn salts then Sn^{2+} changes to

(a) **Sn** **(b)** **Sn^{3+}**
(c) **Sn^{4+}** **(d)** **Sn^+**

A **[NCERT Exemp. Q. 18, Page 108]**

Ans. Correct option : (c)

Explanation : **When acidified $K_2Cr_2O_7$ solution is added to Sn^{2+} salt, Sn^{2+} changes to Sn^{4+}. The reaction is given here :**

Oxidation

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

Reduction

B. Match the following :

Q. 1. Match the species given in Column I with those mentioned in Column II.

Column I (Property)		Column II (Element)	
(a)	**Lanthanoid which shows +4 oxidation state**	**(i)**	**Pm**
(b)	**Lanthanoid which can show +2 oxidation state**	**(ii)**	**Ce**
(c)	**Radioactive lanthanoid**	**(iii)**	**Lu**
(d)	**Lanthanoid which has $4f^7$ electronic configuration in +3 oxidation state**	**(iv)**	**Eu**
(e)	**Lanthanoid which has $4f^{14}$ electronic configuration in +3 oxidation state**	**(v)**	**Gd**
		(vi)	**Dy**

[NCERT Exemp. Q. 57, Page 113]

Ans. (a) → (ii), (b) → (iv), (c) → (i), (d) → (v), (e) → (iii)

Column I	Column II	Explanation
(a)	**(ii)**	Lanthanoids which shows +4 oxidation state is Ce. $_{58}Ce = [Xe]4f^2\ 5d^0\ 6s^2$; Oxidation state = +3, +4
(b)	**(iv)**	Lanthanoids which can show +2 oxidation state is Eu. $_{63}Eu = [Xe]4f^7 5d^0 6s^2$; Oxidation state = +2, +3
(c)	**(i)**	Radioactive lanthanoids is Pm.
(d)	**(v)**	Lanthanoids which has $4f^7$ electronic configuration in +3 oxidation state is Gd. $_{64}Gd = [Xe]4f^7 5d^1 6s^2$; Oxidation state = +3
(e)	**(iii)**	Lanthanoid which has $4f^{14}$ electronic configuration in +3 oxidation state is Lu.

C. Answer the following:

Q. 1. How would you account for the following? Zr (Z = 40) and Hf (Z = 72) have almost identical radii.

A&E **[CBSE Delhi 2013]**

Ans. Due to lanthanoid contraction, the atomic radii of 4*d* and 5*d* transition series elements are almost same. **1**

AI **Q. 2. Explain the following observation: The members of the actinoid series exhibit a large number of oxidation states than the corresponding members of the lanthanoid series.**

A&E **[CBSE OD 2012]**

Ans. Due to the comparable energies of 5*f*, 6*d* and 7*s* levels members of actinoid series exhibit a large number of oxidation states. **1**

Q. 3. What are the different oxidation states exhibited by the lanthanoids? R **[NCERT]**

Ans. In the lanthanide series, +3 oxidation state is most common that is Ln (III) compounds are predominant. However, +2 and +4 oxidation states can also be found in the solution or in solid compounds. **1**

Short Answer Type Questions (2 marks each)

Q. 1. Write one similarity and one difference between the chemistry of lanthanoids and actinoids ?

U **[CBSE OD 2015]**

Ans. Similarity : (i) Both show contraction in size. **(ii)** Both show irregularity in their electronic configuration. **(iii)** Both are stable in +3 oxidation state. **1**

Difference : (i) Actinoids are mainly radioactive but lanthanoids are not. **(ii)** Actinoids show wide range of oxidation states but lanthanoids do not. **(iii)** Actinoid contraction is greater than lanthanoid contraction. **1**

(Write any one of these or any other one similarity and one difference)

Answering Tip

- Students write irrelevant content. Be specific. Read question carefully and write only what is asked.

Q. 2. Identify the following:

(i) Oxoanion of chromium which is stable in acidic medium.

(ii) The lanthanoid element that exhibits +4 oxidation state. U **[CBSE SQP 2017]**

Ans. (i) $Cr_2O_7^{2-}$ **1**

(ii) Cerium **1**

Q. 3. Identify the following :

(i) Transition metal of 3d series that exhibits the maximum number of oxidation states.

(ii) An alloy consisting of approximately 95% lanthanoid metal used to produce bullet, shell and lighter flint. U **[CBSE Comptt. Delhi/OD 2018]**

Ans. (i) Mn **1**

(ii) Mischmetall **1**

[CBSE Marking Scheme 2018]

Q. 4. In what way is the electronic configuration of the transition elements different from that of the non-transition elements? C **[NCERT]**

Ans. Electronic configuration of transition elements = $(n-1)d^{1-10}\ ns^{0-2}$. ½

Electronic configuration of non-transition elements = ns^{1-2} or $ns^2\ np^{1-6}$. ½

Transition metals have a partially filled d-orbitals whereas the non-transition elements do not have *d*-orbitals. **1**

Long Answer Type Questions-I (3 marks each)

AI **Q. 1. What is lanthanoid contraction ? What are its two consequences ?** R **[CBSE Comptt. Delhi 2013]**

Ans. The steady decrease in the size of lanthanoid ions (M^{3+}) with the increase in atomic number is called **lanthanoid contraction.** **1**

Consequences of lanthanoid contraction :

(i) Separation of lanthanoids is difficult due to lanthanoid contraction because due to this contraction their ionic radii is very small.

(ii) The basic strength of hydroxides decreases from $La(OH)_3$ to $Lu(OH)_3$. Due to lanthanoid contraction, the size of M^{3+} ions decreases and there is increase in the covalent character in M – OH bond. **2**

Commonly Made Error

- At times correct definition of lanthanoid contraction is not given. The consequences is not written correctly in many cases.

Q. 2. Account for the following:

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

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

(iii) E°(M^{2+}/M) values for transition metals show irregular variation.

A&E **[CBSE Foreign Set-2 2017]**

Ans. (i) Eu^{2+} is a strong reducing agent because Eu^{3+} is more stable than Eu^{2+}. **1**

(ii) Dichromate ion changes to chromate ion/OH^- **1**

$Cr_2O_7^{2-}$ (orange) → CrO_4^{2-} (yellow)

(iii) Due to the irregular variation in ionisation enthalpies (sum of 1st and 2nd ionisation enthalpies), heat of sublimation and enthalpy of hydration/due to irregular electronic configurations from left to right in a period which changes the ionisation potential.

[CBSE Marking Scheme 2017] 1

OR

Detailed Answer:

(i) Electronic configuration of Eu^{2+} = $4f^7 6s^2$. On oxidation, the evolution of the electrons takes place. Hence, after the removal of 2 electrons it achieves stable half filled electronic configuration acting as a strong reducing agent. **1**

(ii) $$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2Cr_2O_4^{2-} + 2H^+$$

(Orange) (yellow)

When an alkali is added to an orange solution of dichromate, a yellow solution is obtained due to the formation of chromate ions. **1**

Answering Tip

- Be specific. Read question carefully and write only what is asked.

Q. 3. (i) How would you account for the following :

(a) Actinoid contraction is greater than lanthanoid contraction.

(b) Transition metals form coloured compounds.

(ii) Complete the following equation : $2MnO_4^- + 6H^+ + 5NO_2^- \rightarrow$ A&E **[CBSE Delhi 2015]**

Ans. (i) (a) Actinoid contraction is greater than lanthanoid contraction due to ineffective shielding by intervening 5*f*-electrons. **1**

(b) Transition elements generally forms coloured compounds on account of *d-d* transition. When the visible light falls on the compounds, they absorb certain radiations and reflect others. The colour observed corresponds to absorbed light. **1**

(ii) $2MnO_4^- + 6H^+ + 5NO_2^- \rightarrow 5NO_3^- + 2Mn^{2+} + 3H_2O$. **1**

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

(i) Among lanthanoids, Ln (III) compounds are predominant. However, occasionally in solutions or in solid compounds, +2 and +4 ions are also obtained.

(ii) The $E°_{M^{2+}/M}$ for copper is positive (0.34 V). Copper is the only metal in the first series of transition elements showing this behaviour.

(iii) The metallic radii of the third (5*d*) series of transition metals are nearly the same as those of the corresponding members of the second series.

A&E **[CBSE OD 2012]**

Ans. (i) Lanthanoids exhibit occasionally +2, +4 ions because of extra stability of empty, half-filled and completely filled 4*f*-subshell respectively *i.e.*, $4f^0$, $4f^7$, $4f^{14}$ configuration. **1**

(ii) The E° (M^{2+}/M) for copper is positive. This is because high energy is required to transform Cu to Cu^{2+} which is not balanced by its hydration enthalpy. **1**

(iii) In moving down a group, there is increase in number of shells leading to increase in size. So, size of elements of 4*d* series is larger than those of 3*d* series. The similar atomic radii of second and third transition series is due to phenomenon called lanthanoid contraction, associated with intervention of 4*f*-orbitals which must be filled before the 5*d* series of elements begin. **1**

Answering Tip

- Comprehend what is being asked before answering by reading the question carefully.

Q. 5. How would you account for the following :

(i) With the same *d*-orbital configuration (d^4) Cr^{2+} is a reducing agent while Mn^{3+} is an oxidizing agent ?

(ii) The actinoids exhibit a larger number of oxidation states than the corresponding members in the lanthanoids series ?

(iii) Most of the transition metal ions exhibit characteristic colours in aqueous solutions ?

A&E **[CBSE Delhi 2012]**

Ans. (i) Cr (24) = $3d^5 4s^1$

Configuration. of $Cr^{+3} = 3d^4$

As Cr^{+3} has stable t^3_{2g} configuration so, Cr^{+2} has a tendency to change to Cr^{+3}. Hence, it is a reducing agent.

Mn (25) = $3d^5 4s^2$

$Mn^{+3} = 3d^4$

Mn^{+3} changes to Mn^{+3} $(3d)^5$ which is half filled state configuration. Hence, Mn^{+3} acts as oxidising agent. 1

(ii) Actinoids exhibit a large number of oxidation states because 5*f*, 6*d* and 7*s* levels have almost comparable energies (very small energy difference between sub shells) than the energy difference between 4*f* and 5*d* orbitals in case of lanthanoid. **1**

(iii) Most of the transition metal ions exhibit characteristic colours in aqueous solutions because of *d-d* transitions, as they have maximum number of unpaired electrons. **1**

Answering Tip

- Write the electronic configuration in such questions to score better.

Q. 6. Explain the following observations :

(i) Many of the transition elements are known to form interstitial compounds.

(ii) There is a general increase in density from titanium (Z = 22) to copper (Z = 29).

(iii) The numbers of the actinoid series exhibit a larger number of oxidation states than the corresponding members of the lanthanoid series.

A&E **[CBSE Delhi 2012]**

Ans. (i) Many of the transition elements are known to form interstitial compounds because of unpaired electrons in the *d*-orbital. Transition elements have vacant interstitial sites and are able to trap small atoms like H, C or N to form such compounds. **1**

(ii) As the atomic radii decreases moving across from titanium to Cu, its volume will decrease and density is expected to increase. **1**

(iii) Actinoids exhibit a large number of oxidation states because 5*f*, 6*d* and 7*s* levels have almost comparable energies (very small energy difference between sub-shells than the energy difference between 4*f* and 5*d* orbitals) in case of lanthanoids. **1**

Answering Tip

- Comprehend what is being asked before answering by reading the question carefully.

Q. 7. Explain the following:

(a) Out of Sc^{3+}, Co^{2+} and Cr^{3+} ions, only Sc^{3+} is colourless in aqueous solutions. (Atomic no.: Co = 27; Sc = 21 and Cr = 24)

(b) The $E^{\circ}{}^{Cu^{2+}/Cu}$ for copper metal is positive (+0.34), unlike the remaining members of the first transition series.

(c) $La(OH)_3$ is more basic than $Lu(OH)_3$.

A&E **[CBSE SQP 2018-2019]**

Ans. (a) Co^{2+} : $[Ar]3d^7$ Sc^{3+} : $[Ar]3d^0$ Cr^{3+} : $[Ar]3d^3$

Co^{2+} and Cr^{3+} have unpaired electrons. Thus, they are coloured in aqueous solution. Sc^{3+} has no unpaired electron. Thus it is colourless. **1**

(b) Metal copper has high enthalpy of atomisation and enthalpy of ionisation. Therefore the high energy required to convert Cu(s) to Cu^{2+}(aq) is not balanced by its hydration enthalpy. 1

(c) Due to lanthanoid contraction the size of lanthanoid ion decreases regularly with increase in atomic size. Thus covalent character between lanthanoid ion and OH^- increases from La^{3+} to Lu^{3+}. Thus the basic character of hydroxides decreases from $La(OH)_3$ to $Lu(OH)_3$. 1

[CBSE Marking Scheme 2018]

Answering Tip

- Comprehend what is being asked before answering by reading the question carefully.

Long Answer Type Questions-II (5 marks each)

Q. 1. (i) Compare the chemistry of the actinoids with that of lanthanoids with reference to the following :

(a) electronic configurations,

(b) oxidation states,

(c) chemical reactivity.

(ii) Write balanced chemical equations of two reactions in which $KMnO_4$ acts as an oxidising agent in the acid medium. U + A **[CBSE Comptt. Delhi 2011]**

Ans. (i) Comparison between chemistry of Actinoids Lanthanoids

S. No.	Character-istics	Actinoids	Lanthanoids
(a)	**Electronic configuration**	[Rn] $5f^{1-14}$ $6d^{0-1}$ $7s^2$	[Xe] $4f^{1-14}5d^{0-1}$ $6s^2$
(b)	**Chemical reactivity**	These are highly reactive metals.	These are less reactive metals.

(c)	**Oxidation states**	Besides +3 oxidation state, actinoids show higher oxidation state of +4, +5, +6, +7 also because of smaller energy gap between 5*f*, 6*d* and 7*s* subshell.	Besides +3 oxidation state, lanthanoids show +2 and +3 oxidation state, only in a few cases + 4.

3

(ii) $KMnO_4$ as oxidising agent in acidic medium :

(a) Ferrous salts to ferric salts :

$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

(b) H_2S to sulphur :

$2MnO_4^- + 5S^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5S$ **2**

Q. 2. (i) With reference to structural variability and chemical reactivity, write the differences between lanthanoids and actinoids.

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

(iii) Complete the following equation : $MnO_4^- + 8H^+ + 5e^- \rightarrow$

(iv) Out of Mn^{3+} and Cr^{3+}, which is more paramagnetic and why ?

(Atomic nos. : Mn = 25, Cr = 24) $\boxed{\text{U + A\&E}}$ **[CBSE OD 2014]**

Ans. (i)

S. No.	Lanthanoids	Actinoids
(a)	4*f* orbital is progressively filled.	5*f* orbitals is progressively filled.
(b)	+3 oxidation state is most common along-with +2 and +4.	+3 oxidation state is most common, but exhibit higher oxidation state of +4, +5, +6 and +7.
(c)	Except promethium, all are non-radioactive.	All are radioactive.
(d)	Less tendency of complex formation.	Strong tendency of complex formation.
(e)	Chemically less reactive than actinoids.	More reactive than lanthanoids.

2

(ii) Cerium (Ce^{4+}) **1**

(iii) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ **1**

(iv) Mn^{3+} is more paramagnetic.

Because Mn^{3+} has 4 unpaired electrons ($3d^4$) therefore more paramagnetic whereas Cr^{3+} has 3 unpaired electrons ($3d^3$). **[CBSE Marking Scheme 2014] 1**

Commonly Made Error

- (iv) Relationship between paired/unpaired electrons and magnetic behavior is unclear to students.

Answering Tip

- (iv) Learn the concept of electronic configuration of elements and reason for paramagnetism clearly.

Q. 3. (i) Account for the following:

(a) Mn shows the highest oxidation state of +7 with oxygen but with fluorine it shows the highest oxidation state of +4.

(b) Zirconium and Hafnium exhibit similar properties.

(c) Transition metals act as a catalysts. **(Atomic nos. : Mn = 25, Cr = 24)**

(ii) Complete the following equations:

(a) $2MnO_2 + 4KOH + O_2 \xrightarrow{\Delta}$

(b) $Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow$ $\boxed{\text{A\&E + R}}$

OR

The elements of 3d transition series are given as:

Sc Ti V Cr Mn Fe Co Ni Cu Zn

Answer the following:

(i) Write the element which is not regarded as a transition element. Give reason.

(ii) Which element has the highest m.p?

(iii) Write the element which can show an oxidation state of +1.

(iv) Which element is a strong oxidizing agent in +3 oxidation state and why? $\boxed{\text{A}}$ **[CBSE OD Set-2 2016]**

Ans.

24. (a) i) Mn shows its highest oxidation state in Mn_2O_7 and its highest oxidation state with fluorine in MnF_4. Highest oxidation states are seen with oxygen because oxygen has the ability to form multiple bonds with the metal atom while fluorine does not form multiple bonds.

ii) Zirconium and Hafnium have similar properties and similar radii because of Lanthanoid Contraction. Zr is an element of 4d series and Hf is an element of 5d series. Before 5d series, there is the 4f series. The screening due to 4f electrons is poor, hence the effective attraction on 5d electrons by the nucleus is more. The increase in size due to addition of new shell is compensated by the poor screening of 4f electrons when we move from 4d to 5d. Hence Zr and Hf have similar size and properties.

iii) Transition metals act as good catalyst because of their ability to adopt multiple oxidation states and form complexes.

They form complexes because of their small size, high charge (i.e. large surface charge density) and the d-orbitals.

b)

i) $2MnO_2 + 4KOH + O_2 \xrightarrow{\Delta} 2K_2MnO_4 + 2H_2O$

ii) $Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 3I_2 + 2Cr^{3+} + 7H_2O$

[Topper's Answer 2016] 5

Detailed Answer:

(i) Zn , because it does not have partially filled d-orbital in its ground state or ionic state. **1½**

(ii) Cr has the highest melting point. As the number of unpaired electrons increases upto d^5 configuration, it results in the increase in the strength of metallic bonds. To break the metallic bond, significant energy is required thus Cr with highest number of unpaired electrons *i.e.*, 6 has the highest melting point. **1**

(iii) Cu can show +1 oxidation state as it can loose one electron present in 4s orbital. **1**

(iv) Mn is a strong oxidising agent in +3 oxidation state because change of Mn^{3+} to Mn^{2+} give stable half filled (d^5) configuration. **1½**

Answering Tips

- Comprehend what is being asked before answering by reading the question carefully.
- Don't forget to answer further sub-parts of the questions.

Q. 4. (i) Account for the following:

(a) Transition metals form large number of complex compounds.

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

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

(ii) Write one similarity and one difference between the chemistry of lanthanoid and actinoid elements.
U + A&E

OR

(i) (a) How is the variability in oxidation states of transition metals different from that of the *p*-block elements?

(b) Out of Cu^+ and Cu^{2+}, which ion is unstable in aqueous solution and why?

(c) Orange colour of $Cr_2O_7^{2-}$ ion changes to yellow when treated with an alkali. Why?

(ii) Chemistry of actinoids is complicated as compared to lanthanoids. Give two reasons.
A&E **[CBSE Delhi Set-1, 2, 3 2017]**

Ans. (i) (a) Due to small size and high ionic charge/availability of *d* orbitals. **1**

(b) Higher is the oxidation state higher is the acidic character/as the oxidation state of a metal increases, ionic character decreases **1**

(c) Because Mn^{2+} has d^5 as a stable configuration whereas Cr^{3+} is more stable due to stable t^3_{2g} **1**

(ii) Similarity-both are stable in +3 oxidation state/both show contradiction/irregular electronic configuration (or any other suitable similarity) **1**

Difference– actinoids are radioactive and lanthanoids are not/actinoids show wide range of oxidation states but lanthanoids don't (or any other correct difference) **1**

OR

(i) (a) In *p*-block elements the difference in oxidation state is 2 and in transition metals the difference is 1. **1**

(b) Cu^+, due to disproportionation reaction/low hydration enthalpy **½+½**

(c) Due to formation of chromate ion/CrO_4^{2-} ion, which is yellow in colour **1**

(ii) Actinoids are radioactive, actinoids show wide range of oxidation states **1+1**

[CBSE Marking Scheme 2017]

Detailed Answer :

(i) (a) This is due to the comparatively smaller sizes of the metal ions, their high ionic charges and the availability of d orbitals for bond formation. **1**

(b) Transition metal oxides are basic in lower oxidation states as in lower oxidation states, transition metals behave like metals. With an increase in oxidation state, its metallic character decreases due to decrease in size resulting in lesser metallic or more non-metallic. Oxides of a non-metal may be acidic or neutral. Therefore, in higher oxidation states, transition metal oxides are amphoteric or acidic. **1**

OR

(b) In aqueous solution, Cu^{2+} is more stable due to higher hydration energy which compensates to the ionization energy of $Cu^{2+} \rightarrow Cu^+$.

In aqueous solution, Cu^+ undergoes disproportionation reaction

$2Cu^+ \rightarrow Cu + Cu^{2+}$ **1**

(c) $Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-} + 2H^+$
(Orange) (yellow)

When an alkali is added to an orange solution of dichromate, a yellow solution is obtained due to the formation of chromate ions. **1**

Answering Tips

- Comprehend what is being asked before answering by reading the question carefully.
- Don't forget to answer further sub-parts of the questions.

AI **Q. 5. (i) Account for the following:**

(a) Transition metals show variable oxidation states.

(b) Zn, Cd and Hg are soft metals.

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

(ii) Write one similarity and one difference between the chemistry of lanthanoid and actinoid elements.
A + E&U **[CBSE OD Set-1, 2, 3 2017]**

Ans. (i) (a) Availability of partially filled *d*-orbitals/comparable energies of ns and $(n-1)d$ orbitals **1**

(b) Completely filled d-orbitals/absence of unpaired *d* electrons cause weak metallic bonding **1**

(c) Because Mn^{2+} has d^5 as a stable configuration whereas Cr^{3+} is more stable due to stable t^3_{2g}: **1**

(ii) Similarity-Both are stable in +3 oxidation state/both show contraction/irregular electronic configuration (or any other suitable similarity) **1**

Difference-actinoids are radioactive and lanthanoids are not/actinoids show wide range of oxidation states but lanthanoids don't (or any other correct difference) **1**

[CBSE Marking Scheme 2017]

Detailed Answer:

(i) (a) The valence electrons of transition metals are in $(n-1)d$ and ns orbitals. As there is almost little energy difference between orbitals, both the energy levels can be used for bond formation. Thus, they exhibit variable oxidation states. **1**

(b) Because they contain fully filled d-orbitals, no unpaired d electrons are present resulting in weak metallic bonding. **1**

Q. 6. (i) (a) Which transition element in 3d series has positive $E^0_{M^{2+}/M}$ value and why?

(b) Name a member of lanthanoid series which is well known to exhibit +4 oxidation state and why?

(ii) Account for the following

(a) The highest oxidation state is exhibited in oxoanions of transition metals.

(b) HCl is not used to acidify $KMnO_4$ solution.

(c) Transition metals have high enthalpy of atomisation.

A&E **[CBSE Comptt. Delhi Set-1, 2, 3 2017]**

Ans. (i) (a) Copper; Due to high $\Delta_g H^-$ and low $\Delta_{hyd}H^-$ ½,+½

(b) Cerium; Due to stable $4f^0$ configuration/Tb; Due to stable $4f^7$ configuration ½,+½

(ii) (a) Due to ability of oxygen to form multiple bonds to metal **1**

(b) HCl is oxidized to chlorine **1**

(c) Due to strong interatomic bonding **1**

[CBSE Marking Scheme 2017]

Detailed Answer:

(ii) (a) Due to high electronegativity and small size oxygen acts as a strong oxidising agent. This results in oxygen's ability to oxidise the metal to attain highest oxidation state. **1**

(b) As $KMnO_4$ is a very strong oxidising agent, it oxidizes HCl resulting in evolution of chlorine gas. Therefore, HCl is not used to acidify $KMnO_4$ solution. **1**

AI **Q. 7. (i) Name the element of 3*d* transition series which shows maximum number of oxidation states. Why does it show so ?**

(ii) Which transition metal of 3*d* series has positive E°(M^{2+}/M) value and why ?

(iii) Out of Cr^{3+} and Mn^{3+}, which is a stronger oxidizing agent and why ?

(iv) Name a member of the lanthanoid series which is well known to exhibit + 2 oxidation state.

(v) Complete the following equation :

$$MnO_4^- + 8H^+ + 5e^- \rightarrow$$

A&E + R **[CBSE Delhi 2014]**

Ans. (i) Mn, because of presence of 5 unpaired electrons in 3*d* subshell. ½+½

(ii) Cu, because enthalpy of atomization and ionisation enthalpy is not compensated by enthalpy. ½+½

(iii) Mn^{3+} because Mn^{2+} is more stable due to its half filled ($3d^5$) configuration. ½+½

(iv) Eu^{+2}(Eu). **1**

(v) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ **1**

[CBSE Marking Scheme 2014]

Q. 8. On the basis of Lanthanoid contraction, explain the following :

(a) Nature of bonding in La_2O_3 and Lu_2O_3.

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

(c) Stability of the complexes of lanthanoids.

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

(e) Trends in acidic character of lanthanoid oxides.

C **[NCERT Exemp. Q. 67, Page 115]**

Ans. (a) La_2O_3 is ionic because La has largest atomic size and lowest ionization enthalpy, whereas Lu_2O_3 is covalent because Lu has smallest atomic size and has highest ionization enthalpy. **1**

(b) As the size decreases from La to Lu, therefore, the stability of oxo cations also decreases. **1**

(c) The stability of complexes increases as the size of lanthanoid decreases. **1**

(d) Radii of 4d and 5d elements are almost same due to lanthanoid contraction. **1**

(e) Acidic character of oxides of lanthanoid increases because metallic character decreases due to decrease in atomic size and increase in ionization enthalpy.**1**