Very Short Answer Questions

Very Short Answer Questions (PYQ)

Q.1. Copper atom has completely filled *d*-orbitals in its ground state but it is a transition element. Why?

[*CBSE Chennai 2015*]

Ans. Copper exhibits +2 oxidation state wherein it has incompletely filled d orbitals ($3d^9\ 4s^0$) hence a transition element.

Q.2. Zn^{2+} salts are white while Cu^{2+} salts are coloured. Why?

[*CBSE Patna 2015*]

Ans. Cu^{2+} ($3d^9\ 4s^0$) has one unpaired electron in *d*-subshell which absorbs radiation in visible region resulting in *d*-*d* transition and hence Cu^{2+} salts are coloured.
Zn^{2+} ($3d^{10}\ 4s^0$) has completely filled *d*-orbitals. No radiation is absorbed for *d*-*d* transition and hence Zn^{2+} salts are colourless.

Q.3. Why is zinc not regarded as a transition element?

[*CBSE Guwahati 2015*]

Ans. As zinc atom has completely filled *d*-orbitals ($3d^{10}$) in its ground state as well as oxidised state, therefore, it is not regarded as transition element.

Q.4. Give reason:

Zn is soft whereas Cr is hard.

[*CBSE South 2016*]

Ans. Cr ($3d^5\ 4s^1$) has five unpaired electrons in its *d*-orbitals whereas Zn ($3d^{10}\ 4s^2$) has no unpaired electrons in its *d*-orbitals. As a result of this weak metallic bonds exist in Zn whereas strong metallic bonds exist in Cr. Hence, Zn is soft whereas Cr is hard.

Very Short Answer Questions (OIQ)

Q.1. Why are transition elements so named?

Ans. Transition elements are so named because their properties are in between those of *s*-block and *p*-block.

Q.2. How many elements are present in the *d*-block of the periodic table?

Ans. 40 elements.

Q.3. Why does a transition series contain 10 elements?

Ans. There are five *d*-orbitals in an energy level and each orbital can contain two electrons. As we move from one element to the next, an electron is added and for complete filling of the five *d*-orbitals, 10 electrons are required.

Q.4. Why are transition elements known as *d*-block elements?

Ans. The last electron enters ($n - 1$) *d*-orbital, *i.e.*, *d*-orbital of the penultimate shell. Hence, these are known as *d*-block elements.

Q.5. Why do transition elements show similarities along the horizontal period?

Ans. All transition elements contain incompletely filled *d*-subshell whereas the outer shell electronic configuration remains the same.

Q.6. What is the general formula by which the electronic configuration of the transition elements is represented?

Ans. $(n - 1)\, d^{1-10}\, ns^{1-2}$.

Q.7. Reactivity of transition elements decreases almost regularly from Sc to Cu. Explain.

[*NCERT Exemplar*]

Ans. It is due to regular increase in ionisation enthalpy.

Q.8. Why does copper not replace hydrogen from acids?

[*NCERT Exemplar*]

Ans. Cu shows E^o positive value.

Q.9. Name a transition element which does not exhibit variable oxidation state.

Ans. Scandium ($Z = 21$) does not exhibit variable oxidation states.

Q.10. What is the common oxidation state of Cu, Ag and Au?

Ans. The common oxidation state of Cu, Ag and Au is +1.

Q.11. Name a transition metal which does not exhibit variation in oxidation state in its compounds.

Ans. Zn.

Q.12. What are the two important oxidation states of Group 6 elements of the periodic table?

Ans. +3 and +6.

Q.13. Why do Zr and Hf exhibit almost similar properties?

Ans. Zr and Hf have similar ionic size.

Q.14. Which divalent metal ion has maximum paramagnetic character among the first transition metals? Why?

Ans. Mn^{2+} has the maximum paramagnetic character because of the maximum number of unpaired electrons, *viz.*, 5.

Q.15. **Write any one use of pyrophoric alloys.**

Ans. Pyrophoric alloys emit sparks when struck. Hence, they are used in making flints for lighters.

Q.16. Name one ore each of manganese and chromium.

Ans. MnO_2 (pyrolusite) is an ore of Mn whereas $FeCr_2O_4$ (chromite) is an ore of Cr.

Q.17. Why are lanthanoids called *f*-block elements?

Ans. Lanthanoids are called *f*-block elements because the last electron in them enters into *f*-orbital.

Q.18. Write the outer electronic configuration of lanthanoids.

Ans. $4f^{1-14}\ 5d^{0-1}\ 6s^2$.

Q.19. Which is the most common oxidation state of lanthanoids?

Ans. +3 is the most common oxidation state of lanthanoids.

Q.20. Name a member of the lanthanoid series which is known to exhibit +4 oxidation state.

Ans. Cerium ($Z = 58$) exhibits + 4 oxidation state.

Q.21. Name the lanthanoid element which exhibits +4 oxidation state besides +3 oxidation state.

Ans. Cerium exhibits both +3 and +4 oxidation states.

Q.22. Give the general electronic configuration of actinoids.

Ans. $5f^{1-14}\,6d^{0-1}\,7s^2$.

Q.23. What is the maximum oxidation state shown by actinoids?

Ans. +7.

Q.24. Out of Cu_2Cl_2 and $CuCl_2$, which is more stable and why?

[*NCERT Exemplar*] [*HOTS*]

Ans. $CuCl_2$ is more stable than Cu_2Cl_2. The stability of $Cu^{2+}(aq)$ is more than $Cu^{+}(aq)$ due to the much more negative $\Delta_{hyd.}H^o$ of $Cu^{2+}(aq)$ than $Cu^{+}(aq)$.

Q.25. Fe has higher melting point than Cu. Why?

[*HOTS*]

Ans. This is because Fe ($3d^6\,4s^1$) has four unpaired electrons in 3*d*-subshell. While Cu ($3d^{10}\,4s^1$) has only one electron in the 4*s*-subshell. Hence, metallic bonds in Fe are much stronger than those in Cu.

Q.26. Discuss the relative stability in aqueous solutions of +2 oxidation state among the elements: Cr, Mn, Fe and Co. How would you justify this situation?

(At. Nos. Cr = 24, Mn = 25, Fe = 26, Co = 27)

[*HOTS*]

Ans. On the basis of electrochemical series, the standard electrode potential shows the following order:

$E^o Mn^{2+}/Mn < E^o Cr^{2+}/Cr < E^o Fe^{2+}/Fe < E^o Co^{2+}/Co$

Therefore, Co^{2+} gets easily reduced to metallic cobalt while it is difficult to reduce Mn^{2+}. Hence, Mn^{2+} will be the most stable and the increasing stability order will be

$Co^{2+} < Fe^{2+} < Cr^{2+} < Mn^{2+}$

Q.27. How would you account for the increasing oxidising power in the series $VO_2^+ < Cr\,2O_7^{2-} < MnO_4^-$?

[*HOTS*]

Ans. This is due to the increasing stability of the lower species to which they are reduced.

Q.28. Arrange the following in increasing order of acidic character:

CrO_3, CrO, Cr_2O_3

[*HOTS*]

Ans. $CrO < Cr_2O_3 < CrO_3$. Higher the oxidation state, more will be acidic character.

Q.29. Although Cr^{3+} and Co^{2+} ions have same number of unpaired electrons but the magnetic moment of Cr^{3+} is 3.87 BM and that of Co^{2+} is 4.87 BM. Why?

[*NCERT Exemplar*] [*HOTS*]

Ans. Due to symmetrical electronic configuration there is no orbital contribution in Cr^{3+} ion. However, appreciable orbital contribution takes place in Co^{2+} ion.

Q.30. For the first row transition metals the values are:

E^o	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**CU**
(M^{2+}/M)	**–1.18**	**–0.91**	**–1.18**	**–0.44**	**–0.28**	**–0.25**	**+0.34**

Explain the irregularity in the above values.

Ans. The E^o (M^{2+}/M) values are not regular which can be explained from the irregular variation of ionisation enthalpies ($\Delta_i H_1 + \Delta_i H_2$) and also the sublimation enthalpies which are relatively much less for manganese and vanadium.

Short Answer Questions-I

Short Answer Questions-I (PYQ)

Q.1. How would you account for the following:

Q. Mn (III) undergoes disproportionation reaction easily.

Ans. Mn^{3+} is less stable and changes to Mn^{2+} which is more stable due to half filled *d*-orbital configuration. That is why, Mn^{3+} undergoes disproportionation reaction.

Q. Co (II) is easily oxidised in the presence of strong ligands.

[*CBSE (F) 2011*]

Ans. Co (II) has electronic configuration $3d^7\ 4s^0$, *i.e.*, it has three unpaired electrons. In the presence of strong ligands, two unpaired electrons in 3*d*-subshell pair-up and third unpaired electron shifts to higher energy subshell from where it can be easily lost and hence oxidised to Co(III).

Q.2. In the following ions:

Mn^{3+}, V^{3+}, Cr^{3+}, Ti^{4+}

(Atomic no. : Mn = 25, V = 23, Cr = 24, Ti = 22)

i. **Which ion is most stable in an aqueous solution?**
ii. **Which ion is the strongest oxidizing agent?**
iii. **Which ion is colourless?**
iv. **Which ion has the highest number of unpaired electrons?**

[*CBSE (F) 2017*]

Ans. (i) Cr^{3+} because of half filled t_{2g} level.

(ii) Mn^{3+}, as the change from Mn^{3+} to Mn^{2+} results in stable half filled (d^5) configuration.

(iii) Ti^{4+}, as Ti^{4+} has empty *d*-orbitals therefore *d*-*d* transition cannot occur in Ti^{4+}.

(iv) Mn^{3+} ($3d^4 4s^0$). It has 4 unpaired electrons.

Q.3. Complete the following chemical equations

Q.

$$8\,\mathrm{MnO_4^-} + 3S_2O_3^{2-} + H_2O \;\rightarrow$$

Ans.

$$\begin{array}{rcl}
8\,\mathrm{MnO}_4^- + 2H_2O + 3e^- & \rightarrow & \mathrm{MnO}_2 + 4\,\mathrm{OH}^- \,] \times 8 \\
S_2O_3^{2-} + 10\,\mathrm{OH}^- & \rightarrow & 2\,\mathrm{SO}_4^{2-} + 5H_2O + 8e^- \,] \times 3 \\
\hline
8\,\mathrm{MnO}_4^- + 3S_2O_3^{2-} + H_2O & \rightarrow & 8\,\mathrm{MnO}_2 + 6\,\mathrm{SO}_4^{2-} + 2\,\mathrm{OH}^- \\
\hline
\end{array}$$

Q.

$$\mathrm{Cr}_2\,O_7^{2-} + 3\,\mathrm{Sn}^{2+} + 14H^+ \rightarrow$$

Ans.

$$\begin{array}{rcl}
\mathrm{Cr}_2\,O_7^{2-} + 14H^+ + 6e^- & \rightarrow & 2\,\mathrm{Cr}^{3+} + 7H_2O \\
\mathrm{Sn}^{2+} & \rightarrow & \mathrm{Sn}^{4+} + 2e^- \,] \times 3 \\
\hline
\mathrm{Cr}\,2O_7^{2-} + 2\,\mathrm{Sn}^{2+} + 14H^+ & \rightarrow & 2\,\mathrm{Cr}^{3+} + 3\,\mathrm{Sn}^{4+} + 7H_2O \\
\hline
\end{array}$$

Q.4. Explain each of the following observations:

Q. Actinoids exhibit a much larger number of oxidation states than the lanthanoids.

Ans. This is due to small energy gap between 5*f*, 6*d* and 7*s* subshells in actinoids.

Q. There is hardly any increase in atomic size with increasing atomic numbers in a series of transition metals.

[*CBSE (F) 2012*]

Ans. This is because with increase in atomic number in a series, the increased nuclear charge is partly cancelled by the increased shielding effect of electrons in the *d*-orbitals of penultimate shell.

Q.5. Complete the following equations:

Q.

$$\mathrm{Cr}_2\,O_7^{2-} + 2\,\mathrm{OH}^- \rightarrow$$

Ans.

$$\mathrm{Cr}_2\,O_7^{2-} + 2\,\mathrm{OH}^- \rightarrow 2\,\mathrm{CrO}_4^{2-} + H_2O$$

Que.

$$\mathrm{MnO_4^-} + 4H^+ + 3e^- \rightarrow$$

Ans.

$$\mathrm{MnO_4^-} + 4H^+ + 3e^- \overset{\text{Heat}}{\rightarrow} \mathrm{MnO_2} + 2H_2O$$

Q.6. Write one similarity and one difference between the chemistry of lanthanoids and that of actinoids.

[*CBSE Allahabad 2015*]

Ans. Similarities between lanthanoids and actinoids

- **i.** Both lanthanoids and actinoids mainly show an oxidation state of +3.
- **ii.** Actinoids show actinoid contraction like lanthanoid contraction is exhibited by lanthanoids.
- **iii.** Both lanthanoids and actinoids are electropositive.

(*any one*)

Differences between lanthanoids and actinoids

- **i.** The members of lanthanoid exhibit less number of oxidation states than the corresponding members of actinoid series.
- **ii.** Lanthanoid contraction is smaller than the actinoid contraction.
- **iii.** Lanthanoids except promethium are non-radioactive metals while actinoids are radioactive metals.

(*any one*)

Q.7. Explain each of the following observations:

Q. Mn^{2+} is much more resistant than Fe^{2+} towards oxidation.

[*CBSE Delhi 2012*]

Ans. Mn^{3+}(d^4) is less stable than Mn^{2+} (d^5, half filled) while Fe^{3+} (d^5, half filled) is more stable than Fe^{2+} (d^4). That is why Mn^{2+} is more resistance than Fe^{2+} towards oxidation.

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

[*CBSE (AI) 2012*]

Ans. Lanthanoid metals show +2 and +4 oxidation states to attain extra stable f^0 and f^7 configurations.

Short Answer Questions-I (OIQ)

Q.1. On what basis can you say that scandium (Z = 21) is a transition element but zinc (Z = 30) is not?

Ans. On the basis of incompletely filled 3*d*-orbitals in case of scandium atom in its ground state ($3d^1$), it is regarded as a transition element. On the other hand, zinc atom has completely filled *d*-orbitals ($3d^{10}$) in its ground state as well as in its oxidised state, hence it is not regarded as a transition element.

Q.2. Account for the following:

Q. Silver atom has completely filled *d*-orbitals ($4d^{10}$) in its ground state yet silver is a transition element.

Ans. Silver (Z = 47) can exhibit +2 oxidation state wherein it will have incompletely filled *d*-orbitals (4*d*), hence a transition element.

Q. Highest oxidation state of a metal exhibited in its oxide or fluoride only.

Ans. Due to small size and high electronegativity, oxygen or fluorine can oxidise a metal to its highest oxidation state.

Q.3. Give reasons for the following:

Q. The halides of transition elements become more covalent with increasing oxidation state of the metal.

Ans. As the oxidation state increases, size of the ion of transition element decreases. As per Fajan’s rule, as the size of metal ion decreases, covalent character of the bond formed increases.

Q. Ionisation enthalpies of Ce, Pr and Nd are higher than Th, Pa and U.

Ans. It is because in the beginning, when 5f-orbitals begin to be occupied, they will penetrate less into the inner core of electrons. The 5*f*-electrons will therefore, be more effectively shielded from the nuclear charge than 4*f*-electrons of the corresponding lanthanoids. Therefore, outer electrons are less firmly held and they are available for bonding in the actinoids.

Q.4. Transition metals can act as catalysts because these can change their oxidation state. How does Fe(III) catalyse the reaction between iodide and persulphate ions?

[*NCERT Exemplar*]

Ans.

Reaction between iodide and persulphate ions is:

$$2I^- + S_2O_8^{2-} \xrightarrow{\text{Fe(III)}} I_2 + 2\,SO_4^{2-}$$

Role of Fe(III) ions:

$$2\,Fe^{3+} + 2I^- \rightarrow 2\,Fe^{2+} + I_2$$

$$2\,Fe^{2+} + S_2O_8^{2-} \rightarrow 2\,Fe^{3+} + 2\,SO_4^{2-}$$

Q.5. Answer the following questions:

Q. Calculate the magnetic moment of a divalent ion in aqueous solution if its atomic number is 25.

Ans. The divalent ion in aqueous solution will have d^5 configuration (five unpaired electrons) with atomic number 25. The magnetic moment, μ is

$$\mu = \sqrt{5(5+2)}\ \text{BM} = 5.92\ \text{BM}$$

Q. While filling up of electrons in the atomic orbitals, the 4*s* orbital is filled before the 3*d* orbital but reverse happens during the ionisation of the atom. Explain why.

[*NCERT Exemplar*]

Ans. $n + l$ rule: For $3d = n + l = 3 + 2 = 5$

$4s = n + l = 4 + 0 = 4$

So, electron will enter in 4*s* orbital.

Ionisation enthalpy is responsible for the ionisation of atom, 4*s* electrons are loosely held by the nucleus. So, electrons are removed from 4*s* orbital prior to 3*d*.

Q.6. How do the oxides of transition elements in lower oxidation states differ from those in higher oxidation state in the nature of metal-oxygen bonding and why?

Ans. In the lower oxidation state the transition metal oxides are basic and they are acidic if the metal is in higher oxidation state. The oxides are amphoteric when the metal is in intermediate oxidation state. For example,

+3	+4	+7
Mn_2O_3	MnO_2	Mn_2O_7
Basic	Amphoteric	Acidic

Q.7. Give reasons for the following:

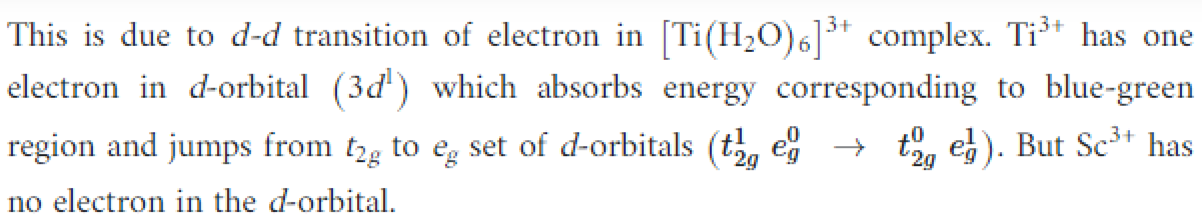
Q. E^o values of Mn, Ni and Zn are more negative than expected.

Ans. Negative E^o values for Mn^{2+} and Zn^{2+} are related to stabilities of half-filled and fully filled configurations, respectively. But for Ni^{2+}, E^o value is related to the highest negative enthalpy of hydration.

Q. $[Ti(H_2O)]^{3+}$ is coloured while $[Sc(H_2O)_6]^{3+}$ is colourless.

[*HOTS*]

Ans.



This is due to *d*-*d* transition of electron in $[Ti(H_2O)_6]^{3+}$ complex. Ti^{3+} has one electron in *d*-orbital $(3d^1)$ which absorbs energy corresponding to blue-green region and jumps from t_{2g} to e_g set of *d*-orbitals $(t_{2g}^1\ e_g^0 \rightarrow t_{2g}^0\ e_g^1)$. But Sc^{3+} has no electron in the *d*-orbital.

Q.8. Name the following:

Q. A transition metal which does not exhibit variation in oxidation state in its compounds.

Ans. Scandium (Sc)

Q. A compound where the transition metal is in the +7 oxidation state.

Ans. Potassium permanganate ($KMnO_4$) in which manganese shows +7 oxidation state.

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

Ans. Cerium (Ce)

Q. Ore used in the preparation of potassium dichromate.

[*CBSE Sample Paper 2016*]

Ans. Chromite ore ($FeCr_2O_4$)

Q.9. Explain the following observations:

Q. Colour of $KMnO_4$ disappears when oxalic acid is added to its solution in acidic medium.

Ans. $KMnO_4$ acts as oxidising agent. It oxidises oxalic acid to CO_2 and itself changes to Mn^{2+} ion which is colourless.

$$5C_2O_4^{2-} + \underset{(\text{ Coloured })}{2\,\mathrm{MnO}_4^-} + 16H^+ \to \underset{(\text{ Colourless })}{2\,\mathrm{Mn}^{2+}} + 8H_2O + 10\,\mathrm{CO}_2$$

Q. A green solution of potassium manganate turns purple when CO_2 gas is passed through the solution.

[*HOTS*]

Ans.

CO_2 reacts with water to form carbonic acid as given below:

$$\mathrm{CO}_2 + H_2O \rightleftharpoons H_2\,\mathrm{CO}_3 \rightleftharpoons H^+ + \mathrm{HCO}_4^-$$

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

$$\underset{\substack{(\text{ Green}\\ \text{solution })}}{3\,\overset{+6}{\mathrm{Mn}}\mathrm{O}_4^{2-}} + 4H^+ \to \underset{\substack{(\text{ Purple}\\ \text{solution })}}{2\,\overset{+7}{\mathrm{Mn}}\mathrm{O}_4^-} + \overset{+4}{\mathrm{Mn}}\mathrm{O}_2 + 2H_2O$$

Q.10. Complete the following chemical reaction equations:

Q.

$$\mathrm{MnO}_4^-\,(\mathrm{aq}) + C_2O_4^{2-}\,(\mathrm{aq}) + H^+\,(\mathrm{aq}) \rightarrow$$

Ans.

$$\begin{array}{rcl}
[\mathrm{MnO}_4^- + 8H^+ + 5e^- & \rightarrow & \mathrm{Mn}^{2+} + 4H_2O] \times 2 \\
[C_2O_4^{2-} & \rightarrow & 2\,\mathrm{CO}_2 + 2e^-] \times 5 \\
\hline
\mathrm{MnO}_4^- + 5C_2O_4^{2-} + 16H^+ & \rightarrow & 2\,\mathrm{Mn}^{2+} + 10\,\mathrm{CO}_2 + 8H_2O \\
\hline
\end{array}$$

Q.

$$\mathrm{Cr}\,2O_7^{2-}\,(\mathrm{aq}) + \mathrm{Fe}^{2+}\,(\mathrm{aq}) + H^+\,(\mathrm{aq}) \rightarrow$$

Ans.

$$\begin{array}{rcl}
\mathrm{Cr}_2\,O_7^{2-} + 14H^+ + 6e^- & \rightarrow & 2\,\mathrm{Cr}^{3+} + 7H_2O \\
\mathrm{Fe}^{2+} & \rightarrow & \mathrm{Fe}^{3+} + e^-] \times 6 \\
\hline
\mathrm{Cr}_2\,O_7^{2-} + 6\,\mathrm{Fe}^{2+} + 14H^+ & \rightarrow & 2\,\mathrm{Cr}^{3+} + 6\,\mathrm{Fe}^{3+} + 7H_2O \\
\hline
\end{array}$$

Short Answer Questions-II

Short Answer Questions-II (PYQ)

Q.1. Assign suitable reasons for the following:

Q. The Mn^{2+} compounds are more stable than Fe^{2+} towards oxidation to their +3 state.

Ans. The electronic configuration of Mn^{2+} is [Ar] $3d^5$ which is half filled and hence stable. So Mn^{2+} cannot lose third electron easily. On the other hand, Fe^{2+} has electronic configuration [Ar] $3d^6$. It tends to lose one electron to acquire stable [Ar] $3d^5$ electronic configuration. Hence Mn^{2+} is more stable than Fe^{2+} towards oxidation.

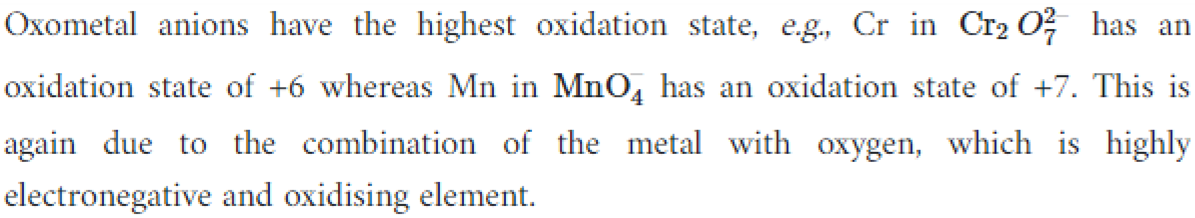
Q. Sc^{3+} is colourless in aqueous solution whereas Ti^{3+} is coloured.

Ans. Ti^{3+} has one unpaired electron in *d*-orbitals ($3d^1$) which can absorb light in visible region for *d*–*d*transition. Hence, it is coloured in aqueous solution. Sc^{3+} has no *d* electron ($3d^0$), therefore, no light is absorbed for *d*–*d* transition. Hence, it is colourless in aqueous solution.

Q. The highest oxidation state is exhibited in oxo-anions of a metal.

[*CBSE (F) 2014*]

Ans.



Oxometal anions have the highest oxidation state, *e.g.*, Cr in $Cr_2O_7^{2-}$ has an oxidation state of +6 whereas Mn in MnO_4^- has an oxidation state of +7. This is again due to the combination of the metal with oxygen, which is highly electronegative and oxidising element.

Q.2. The elements of 3*d* transition series are given as:

Sc Ti V Cr Mn Fe Co Ni Cu Zn

[*CBSE East 2016*]

Answer the following:

i. **Copper has exceptionally positive $E^\circ_{M^{2+}/M}$ value. Why?**

ii. **Which element is a strong reducing agent in +2 oxidation state and why?**

iii. **Zn^{2+} salts are colourless. Why?**

Ans. (i) Because the sum of sublimation enthalpy and hydration enthalpy to convert Cu(*s*) to Cu^{2+}(*aq*) is so high that it is not balanced by its hydration enthalpy.

(ii) Cr is strongest reducing agent in +2 oxidation state. Cr^{2+} has configuration $3d^4$. After losing one electron it forms Cr^{3+} which has stable half filled t_{2g} level.

(iii) $Zn^{2+}(3d^{10})$ has completely filled *d*-orbitals. As a result of this, *d*-*d* transition cannot occur and hence Zn^{2+} salts are colourless.

Q.3. Why do transition elements show variable oxidation states? How is the variability in oxidation states of *d*-block different from that of the *p*-block elements?

[*CBSE Ajmer 2015*]

Ans. In transition elements, the energies of (*n* –1)*d* orbitals and *ns* orbitals are nearly same. Therefore, electrons from both can participate in bond formation and hence show variable oxidation states.

In transition elements, the oxidation states differ from each other by unity, *e.g*., Fe^{2+} and Fe^{3+}, Cu^{+} and Cu^{2+}, etc. while in *p*-block elements the oxidation state differ by units of two, *e.g*., Sn^{2+} and Sn^{4+}, Pb^{2+} and Pb^{4+}, etc. In transition elements the higher oxidation states are more stable for heavier elements in a group, *e.g*., Mo(VI) and W(VI) are more stable than Cr(VI) in group 6 whereas in *p*-block elements the lower oxidation states are more stable for heavier elements due to the inert pair effect, *e.g*., Pb(II) is more stable than Pb (IV) in group 16.

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

Q. Many of the transition elements and their compounds can act as good catalysts.

Ans. The catalytic activity of transition metals is attributed to the following reasons:

- **a.** Because of their variable oxidation states transition metals form unstable intermediate compounds and provide a new path with lower activation energy for the reaction.
- **b.** In some cases, the transition metal provides a suitable large surface area with free vacancies on which reactants are adsorbed.

Q. The metallic radii of the third (5*d*) series of transition elements are virtually the same as those of the corresponding members of the second series.

Ans. This is due to filling of 4*f*-orbitals which have poor shielding effect or due to lanthanoid contraction.

Q. There is a greater range of oxidation states among the actinoids than among the lanthanoids.

[*CBSE (AI) 2009*]

Ans. This is due to more comparable energies of 5*f*, 6*d* and 7*s* orbitals in actinoids.

Q.5. Answer the following questions:

Q. How would you account for the following:

a. **Highest fluoride of Mn is MnF_4 whereas the highest oxide is Mn_2O_7.**
b. **Transition metals and their compounds show catalytic properties.**

Ans. (a) As oxygen stabilises manganese more than fluorine by forming multiple bonds.

(b) The catalytic activity of transition metals and their compounds is attributed to the following reasons:

- Due to their tendency to show variable oxidation states transition metals form unstable intermediate compounds and provide a new path for the reaction with lower activation energy.
- In some cases, the transition metals provide a suitable large surface area with free valencies on which reactants are adsorbed.

Q. Complete the following equation:

$$3\,\mathrm{MnO}_4^{2-} + 4H^+ \rightarrow$$

[*CBSE (F) 2015*]

Ans.

$$\underset{\text{Manganate ion}}{3\,\mathrm{MnO}_4^{2-}} + 4H^+ \rightarrow \underset{\text{Permanganate ion}}{2\,\mathrm{MnO}_4^{-}} + \mathrm{MnO}_2 + 4H_2O$$

Q.6.

E **°Mn^{2+}/Mn**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**

	– 0.91	**– 1.18**	**– 0.44**	**– 0.28**	**– 0.25**	**+ 0.34**

From the given data *E*º values, answer the following questions:

i. **Why is *E* º(Cu^{2+}/Cu) value exceptionally positive?**
ii. **Why is *E* º(Mn^{2+}/Mn) value highly negative as compared to other elements?**
iii. **Which is a stronger reducing agent Cr^{2+} or Fe^{2+} ? Give reason.**

[*CBSE Patna 2015*] [*HOTS*]

Ans. (i) Copper has high enthalpy of atomisation and low enthalpy of hydration. Since the high energy to transform Cu (*s*) to Cu^{2+} (*aq*) is not balanced by hydration enthalpy, therefore, *E* ºCu^{2+}/Cu value is exceptionally positive.

(ii) This is due to extra stability of half-filled 3*d*-orbitals of $Mn^{2+}(3d^5)$.

(iii) Cr^{2+}, $d^4 \rightarrow d^3$ occurs in case of Cr^{2+} to Cr^{3+} while $d^6 \rightarrow d^5$ occurs in case of Fe^{2+} to Fe^{3+}. As in a medium like water d^3 is more stable as compared to d^5, therefore, Cr^{2+} is stronger reducing agent than Fe^{2+}.

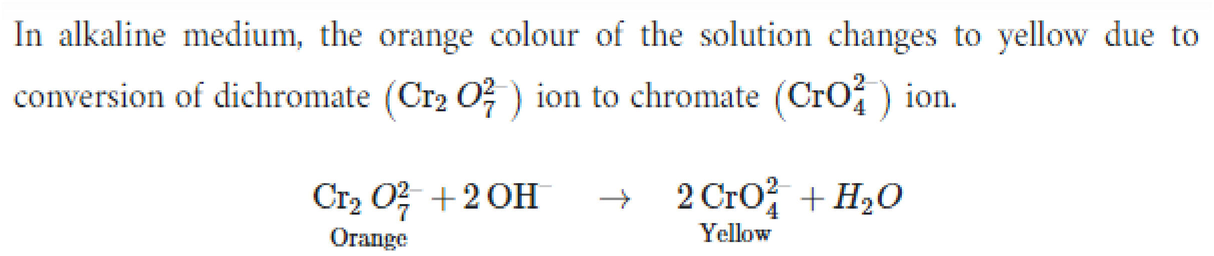
Q.7. Account for the following:

Q. Eu^{2+} is a strong reducing agent.

Ans. This is because Eu^{2+} tends to change to Eu^{3+} as +3 is the common oxidation state of lanthanoids.

Q. Orange colour of dichromate ion changes to yellow in alkaline medium.

Ans.



In alkaline medium, the orange colour of the solution changes to yellow due to conversion of dichromate $\left(\mathrm{Cr_2}\,O_7^{2-}\right)$ ion to chromate $\left(\mathrm{CrO_4^{2-}}\right)$ ion.

$$\underset{\text{Orange}}{\mathrm{Cr_2}\,O_7^{2-}} + 2\,\mathrm{OH^-} \quad \rightarrow \quad \underset{\text{Yellow}}{2\,\mathrm{CrO_4^{2-}}} + H_2O$$

Q.

$E^\circ_{(M^{2+}/M)}$ values for transition metals show irregular variation.

[CBSE (F) 2017]

Ans. The irregularity is due to the irregular variation of ionisation enthalpies ($\Delta_i H + \Delta_i H_2$) and also the sublimation enthalpies which are relatively much less for Mn (240 kJ mol^{-1}) and V (470 kJ mol^{-1}).

Q.8. When pyrolusite ore MnO_2 is fused with KOH in presence of air, a green coloured compound (*A*) is obtained which undergoes disproportionation reaction in acidic medium to give a purple coloured compound (*B*).

[*CBSE South 2016*] [*HOTS*]

i. **Write the formulae of the compounds (*A*) and (*B*).**
ii. **What happens when compound (*B*) is heated?**

Ans.

i. $A = K_2MnO_4$, $B = KMnO_4$

ii. $$\underset{\substack{\text{Potassium}\\ \text{premanganate}}}{2\,KMnO_4} \xrightarrow{513\ K} \underset{\substack{\text{Potassium}\\ \text{manganate}}}{K_2MnO_4} + MnO_2 + O_2$$

Short Answer Questions-II (OIQ)

Q.1. Describe the trends in the following properties of the first series of the transition elements:

i. **Oxidation states**
ii. **Atomic sizes**
iii. **Magnetic behaviour of dipositive gaseous ions (M^{2+}).**

Ans. (i) As there is very little energy difference between 4*s* and 3*d* orbitals, electrons from both energy levels can be used for chemical bond formation. Therefore, all elements except Sc and Zn of the first transition series show a number of oxidation states.

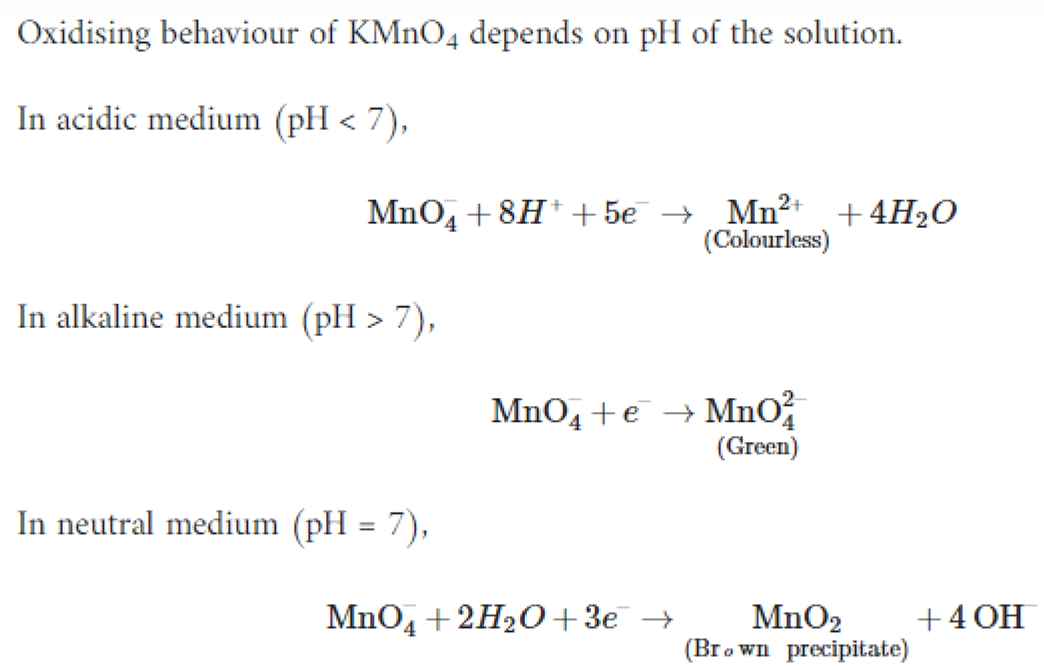
(ii) Atomic radii of the first transition series decrease from Sc to Cr, then remains almost constant till Ni and then increases from Cu to Zn. The reason of this variation in atomic radii has been attributed to the increase in nuclear charge in the beginning of the series. But as the electrons continue to be filled in *d*-orbitals, they screen the outer 4*s* electrons from the influence of nuclear charge. When the increased nuclear charge and the increased screening effect balance each other in the middle of transition series, the atomic radii become almost constant (Mn to Fe). Towards the end of the series, the repulsive interaction between electrons in orbitals become very dominant. As a result there is an expansion of the electron cloud; consequently, the atomic size increases.

(iii) Except Zn^{2+}, all other divalent gaseous ions of the first series of the transition elements contain unpaired electrons in their 3*d*-subshell and are therefore paramagnetic in nature.

Q.2. 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?

[*NCERT Exemplar*]

Ans.



Oxidising behaviour of $KMnO_4$ depends on pH of the solution.

In acidic medium (pH < 7),

$$MnO_4^- + 8H^+ + 5e^- \rightarrow \underset{\text{(Colourless)}}{Mn^{2+}} + 4H_2O$$

In alkaline medium (pH > 7),

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

In neutral medium (pH = 7),

$$MnO_4^- + 2H_2O + 3e^- \rightarrow \underset{\text{(Brown precipitate)}}{MnO_2} + 4\,OH^-$$

Q.3. Lanthanum, gadolinium and lutetium are extraordinarily stable in +3 oxidation state. Explain.

(Atomic number: La = 57, Gd = 64, Lu = 71)

Ans. ${}_{57}La \rightarrow {}_{54}La^{3+}$

[Xe] 5d1 6s2 [Xe] 5d 0 6s0

$$_{64}\mathrm{Gd} \rightarrow {}_{61}\mathrm{Gd}^{3+}$$

$$[\mathrm{Xe}]\ 4f^{7}\ 5d^{1}\ 6s^{2} \qquad [\mathrm{Xe}]\ 4f^{7}\ 5d^{0}\ 6s^{0}$$

$$_{71}\mathrm{Lu} \rightarrow {}_{68}\mathrm{Lu}^{3+}$$

$$[\mathrm{Xe}]\ 4f^{14}\ 5d^{1}\ 6s^{2} \qquad [\mathrm{Xe}]\ 4f^{14}\ 5d^{0}\ 6s^{0}$$

From their electronic configurations, we find that La^{3+}, Gd^{3+} and Lu^{3+} have empty, exactly half-filled and fully filled valency shells, respectively, which make them extra stable.

Q.4. Assign reasons for the following:

Q. The second and third rows of transition elements resemble each other much more than they resemble the first row.

Ans. Due to lanthanoid contraction, the atomic radii of the second and third row transition elements is almost same. So they resemble each other much more as compared to first row elements.

Q. $K_2[PtCl_6]$ is a well-known compound whereas the corresponding Ni compound is not known.

Ans. The oxidation state of Pt in $K_2[PtCl_6]$ is +4, which is a stable oxidation state for Pt. The +4 oxidation state for Ni is very difficult to achieve because the sum of the first four ionisation enthalpies is very high. Hence, the corresponding Ni (II) compound is not formed.

Q.5. Explain the following observations:

Q. The enthalpies of atomisation of transition metals are quite high.

Ans. This is because transition metals have strong metallic bonds as they have large number of unpaired electrons.

Q. There is a close similarity in physical and chemical properties of the 4*d* and 5*d* series of the transition elements, much more than expected on the basis of usual family relationship.

Ans. This is because 5*d* and 4*d*-series elements have virtually the same atomic and ionic radii due to lanthanide contraction. Due to equality in size of Zr and Hf, Nb and Ta, Mo and W, etc., the two elements of each pair have the same properties.

Q. The members in the actinoid series exhibit larger number of oxidation states than the corresponding members in the lanthanoid series.

[*NCERT Exemplar*]

Ans. The members in the actinoid series exhibit larger number of oxidation states than the corresponding members in the lanthanide series due to the fact that the 5*f*, 6*d* and 7*s* levels are of comparable energies.

Q.6. How would you account for the following:

Q. Transition metals sometimes exhibit very low oxidation state such as +1 and 0.

Ans. +1 oxidation state is shown by element like Cu because after loss of one electron, it acquires stable configuration of $3d^{10}$. Zero oxidation state is shown in forming metal carbonyl, because *p*-electrons donated by ligands are accepted into the empty *d*-orbitals.

Q. Cr^{2+} is reducing in nature while with the same *d*-orbital configuration (d^4) Mn^{3+} is an oxidising agent.

Ans. Cr^{2+} is reducing as its configuration changes from d^4 to d^3, a more stable half-filled t_{2g} configuration while Mn^{3+} is oxidising as Mn^{3+} to Mn^{2+} change results in a more stable half-filled d^5 configuration.

Q. E^o of Cu is +0.34 V while that of Zn is –0.76 V.

[*HOTS*]

Ans. High ionisation enthalpy to transform Cu(*s*) to $Cu^{2+}(aq)$ is not balanced by its hydration enthalpy. However, in case of Zn after removal of electrons from 4*s*-orbital, stable $3d^{10}$ configuration is acquired.

Q.7. Answer the following questions:

Q. For M^{2+}/M and M^{3+}/M^{2+} systems, Eo 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.**

Ans. (a) Higher the reduction potential of a species, greater is the ease with which it undergo reduction. Among these pairs, Mn^{3+}/Mn^{2+} has largest positive reduction potential. Hence Mn^{3+} can be easily reduced to Mn^{2+} *i.e.*, Mn^{3+} is least stable. Cr^{3+}/Cr^{2+} has a negative $E°$ value, therefore, Cr^{3+} is most stable. Fe^{3+}/Fe^{2+} has a positive value but small. Hence, Fe^{3+} is more stable than Mn^{3+} but less stable than Cr^{3+}.

(b) Lower the reduction potential or higher the oxidation potential of a species, greater is the ease with which it undergo oxidation. Among these pairs, Mn^{2+}/Mn has the most negative reduction potential or most positive oxidation potential. Therefore, it will be most easily oxidised. Thus, the decreasing order of their ease of oxidation is Mn > Cr > Fe.

Q. What can be inferred from the magnetic moment of the complex $K_4[Mn(CN)_6]$, Magnetic moment: 2.2 BM?

[*CBSE Sample Paper 2016*]

Ans. In the complex $K_4[Mn(CN)_6]$, Mn is in +2 oxidation state. Magnetic moment 2.2 BM indicates that it has only one unpaired electron and hence forms inner orbital or low spin octahedral complex. In presence of CN^-, a strong ligand the hybridisation involved is d^2sp^3.

Q.8. Account for the following:

Q. Mn_2O_7 is acidic whereas MnO is basic.

Ans. Mn has + 7 oxidation state in Mn_2O_7 and + 2 in MnO. In low oxidation state of the metal, some of the valence electrons of the metal atom are not involved in bonding. Hence, it can donate electrons and behave as a base. On the other hand, in higher oxidation state of the metal, valence electrons are involved in bonding and are not available. Instead effective nuclear charge is high and hence it can accept electrons and behave as an acid.

Q. Though copper has completely filled *d*-orbital (d^{10}) yet it is considered as a transition metal.

Ans. Copper exhibits +2 oxidation state wherein it will have incompletely filled *d*-orbitals ($3d^9$), hence a transition metal.

Q. Actinoids show wide range of oxidation states.

[*CBSE (F) 2016*]

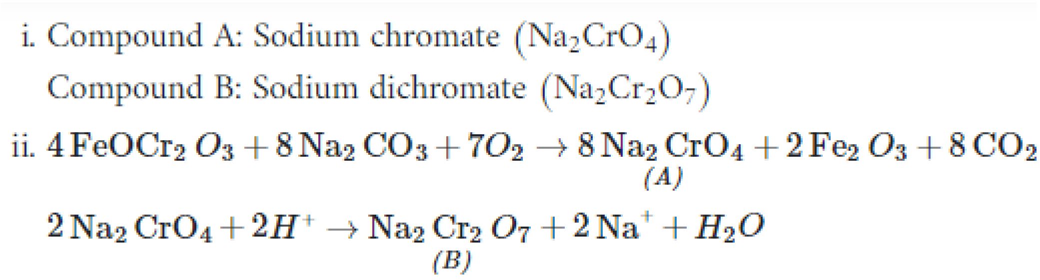
Ans. This is due to comparable energies of 5*f*, 6*d* and 7*s* orbitals.

Q.9. A mixed oxide of iron and chromium, $FeOCr_2O_3$ is fused with sodium carbonate in the presence of air to form a yellow coloured compound (A). On acidification the compound (A) forms an orange coloured compound (B), which is a strong oxidising agent.

- **i. Identify the compounds (A) and (B).**
- **ii. Write balanced chemical equation for each step.**

[*HOTS*]

Ans.



i. Compound A: Sodium chromate (Na_2CrO_4)

Compound B: Sodium dichromate $(Na_2Cr_2O_7)$

ii. $4\,FeOCr_2O_3 + 8\,Na_2CO_3 + 7O_2 \rightarrow 8\,\underset{(A)}{Na_2CrO_4} + 2\,Fe_2O_3 + 8\,CO_2$

$2\,Na_2CrO_4 + 2H^+ \rightarrow \underset{(B)}{Na_2Cr_2O_7} + 2\,Na^+ + H_2O$

Q.10. When a brown compound of manganese (A) is treated with HCl it gives a gas (B). The gas taken in excess, reacts with NH_3 to give an explosive compound (C). Identify compounds A and B.

[*NCERT Exemplar*] [*HOTS*]

Ans. A = MnO_2 , B = Cl_2 , C = NCl_3

$$\underset{(A)}{MnO_2} + 4HCl \rightarrow MnCl_2 + \underset{(B)}{Cl_2} + 2H_2O$$

$$NH_3 + \underset{(\text{excess})}{3\,Cl_2} \rightarrow \underset{(C)}{NCl_3} + 3\,HCl$$

Long Answer Questions

Long Answer Questions (PYQ)

Q.1. Answer the following questions:

Q.

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?

Ans. (a) In transition elements, the oxidation states differ from each other by unity, *e.g.*, and Fe^{2+}, Fe^{3+}, Cu^{2+} and Cu^{2+} etc. while in *p*-block elements the oxidation state differ by units of two, *e.g.*, Sn^{2+} and Sn^{4+}, Pb^{2+} and Pb^{4+}, etc. In transition elements the higher oxidation states are more stable for heavier elements in a group, *e.g.*, Mo(VI) and W(VI) are more stable than Cr(VI) in group 6 whereas in *p*-block elements the lower oxidation states are more stable for heavier elements due to the inert pair effect, *e.g.*, Pb(II) is more stable than Pb (IV) in group 14.

(b) Cu^+ is unstable in aqueous solutions. This is because in aqueous solution Cu^+ undergoes disproportionation to form a more stable Cu^{2+} ion.

$$2\,Cu^+(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$$

The higher stability of Cu^{2+} ion in aqueous solution may be attributed to its greater negative $\Delta_{Hyd}H^0$ than that of Cu^+. It compensates the second ionisation enthalpy of Cu involved in the formation of Cu^{2+} ions.

(c) This is due to formation of chromate ion which is yellow in colour.

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

Q. Chemistry of actinoids is complicated as compared to lanthanoids. Give two reasons.

[*CBSE Delhi 2017*]

Ans. This is because of the following reasons:

- **a.** Actinoids are radioactive.
- **b.** Actinoids show wide range of oxidation states as energy difference between 5*f*, 6*d* and 7*s* subshells of the actinoids is small.

Q.2. (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. Eo 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.

[*CBSE Delhi 2017*]

Ans. i. (a) The tendency to form complex compounds is due to:

—Small size and high charge on metal ion.

—The availability of *d* orbitals for accommodating electrons donated by the ligand.

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

(c) Much large third ionisation energy of Mn (where the required change is stable half filled d^5 to d^4) is mainly responsible for this.

ii. Similarities

— Both show mainly an oxidation state of +3.

— Actinoids show actinoid contraction like lanthanoid contraction is shown by lanthanoids.

— Both are electropositive and very reactive.

(*Any one*)

Differences

— Except promethium (Pm) lanthanoids are non-radioactive whereas actinoids are radioactive.

— Lanthanoids do not form oxocation whereas actinoids form oxocation, e.g., , etc.

— Lanthanoids have less tendency towards complex formation whereas actinoids have greater tendency towards complex formation.

(***Any one***)

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

a. **Transition metals show variable oxidation states.**
b. **Zn, Cd and Hg are soft metals.**
c. **E^o value for the Mn^{3+}/Mn^{2+} couple is highly positive (+ 1.57 V) as compared to Cr^{3+}/Cr^{2+}.**

Ans. i. (a) Transition elements show variable oxidation states because electrons in *ns* and (*n* – 1) *d*-orbitals are available for bond formation as they have nearly same energy.

(b) Zn, Cd and Hg have fully filled *d*-orbitals. Absence of unpaired electrons cause weak metallic bonding. Hence, they are soft.

(c) Much large third ionisation energy of Mn (where the required change is stable half filled d^5 to d^4) is mainly responsible for this.

Q.4. (i) Complete the balance the following chemical equations:

a. $Cr_2 O_7^{2-} + I^- + H^+ \rightarrow$
b. $MnO_4^- + SO_3^{2-} + H^+ \rightarrow$

(ii) Explain the following observations:

a. **Transition elements and their compounds are known to act as catalysts.**
b. **The higher oxidation states are usually exhibited by the members in the middle of a series of transition elements.**
c. **The metal-metal bonding is more frequently found with the second and third series of transition elements.**

[*CBSE (F) 2012*]

Ans.

$$(a)\ \mathrm{Cr_2}\,O_7^{2-} + 14H^{+} + 6e^{-} \rightarrow 2\,\mathrm{Cr}^{3+} + 7H_2O$$

$$2I^{-} \rightarrow I_2 + 2e^{-}\,] \times 3$$

$$\mathrm{Cr_2}\,O_7^{2-} + 6I^{-} + 14H^{+} \rightarrow 2\,\mathrm{Cr}^{3+} + 3I_2 + 7H_2O$$

$$(b)\ \mathrm{MnO_4^{-}} + 8H^{+} + 5e^{-} \rightarrow \mathrm{Mn}^{2+} + 4H_2O] \times 2$$

$$\mathrm{SO_3^{2-}} + H_2O \rightarrow \mathrm{SO_4^{2-}} + 2H^{+} + e^{-}\,] \times 5$$

$$2\,\mathrm{MnO_4^{-}} + 5\,\mathrm{SO_3^{2-}} + 6H^{+} \rightarrow 2\,\mathrm{Mn}^{2+} + 5\,\mathrm{SO_4^{2-}} + 3H_2O$$

ii. (*a*) The catalytic activity of transition metals and their compounds is attributed to the following reasons:

- Due to their tendency to show variable oxidation states transition metals form instable intermediate compounds and provide a new path for the reaction with lower activation energy.
- In some cases, the transition metals provide a suitable large surface area with free valencies on which reactants are adsorbed.

(*b*) It is due to greater number of unpaired electrons in (*n*–1)*d* and *ns* orbitals at the middle of the series.

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

Q.5. Answer the following questions:

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

Ans. Manganese ($3d^5 4s^2$) shows maximum number of oxidation states as its atoms have 5 unpaired electrons in 3*d* orbitals. It shows all the oxidation states from +2 to +7.

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

Ans. Copper has positive E^o (M^{2+}/M) value, as high energy ($\Delta_a H$ + ; $\Delta_i H$) to transform Cu(*s*) to Cu^{2+}(*aq*) is not balanced by hydration enthalpy.

Q. Out of Cr^{3+} and Mn^{3+}, which is a stronger oxidising agent and why?

Ans. Mn^{3+} is stronger oxidising agent as the change from Mn^{3+} to Mn^{2+} results in half filled, d^5 configuration which has extra stability.

Q.6. Answer the following questions:

Q. Why do transition elements show variable oxidation states?

a. Name the element showing maximum number of oxidation states among the first series of transition metals from Sc (Z = 21) to Zn (Z = 30).
b. Name the element which shows only +3 oxidation state.

Ans. Transition elements show variable oxidation states because electrons in *ns* and (*n* – 1) *d*-orbitals are available for bond formation as they have nearly same energy.

a. Manganese
b. Scandium

Q. What is lanthanoid contraction? Name an important alloy which contains some of the lanthanoid metals.

[*CBSE (AI) 2013*]

Ans. The steady decrease in the atomic and ionic radii (having the same charge) with increase in atomic number as we move across the series from lanthanum to lutetium is known as lanthanoid contraction.

Misch metal.

Q.7. Answer the following questions:

Q. How do you prepare:

a. K_2MnO_4 from MnO_2?
b. $Na_2Cr_2O_7$ from Na_2CrO_4?

Ans. (a) Pyrolusite is fused with KOH in the presence of atmospheric oxygen to give K_2MnO_4.

$$\underset{\text{Pyrolusite}}{2\,\mathrm{MnO_2}} + 4\mathrm{KOH} + O_2 \xrightarrow{\text{Heat}} \underset{\text{Potassium manganate}}{2K_2\,\mathrm{MnO_4}} + 2H_2O$$

(b) Na_2CrO_4 is extracted with water and acidified with H_2SO_4 to give $Na_2Cr_2O_7$.

$$\underset{\text{Sodium chromate}}{2\,\mathrm{Na_2\,CrO_4}} + H_2\,\mathrm{SO_4} \rightarrow \underset{\text{Sodium dichromate}}{\mathrm{Na_2\,Cr_2}\,O_7} + \mathrm{Na_2\,SO_4} + H_2O$$

Q. Account for the following:

- a. **Mn^{2+} is more stable than Fe^{2+} towards oxidation to +3 state.**
- b. **The enthalpy of atomisation is lowest for Zn in 3*d* series of the transition elements.**
- c. **Actinoid elements show wide range of oxidation states.**

[*CBSE Delhi 2014*]

Ans. (a) The electronic configuration of Mn^{2+} is [Ar] $3d^5$ which is half-filled and hence stable. So Mn^{2+}cannot lose third electron easily. On the other hand, Fe^{2+} has electronic configuration [Ar] $3d^6$. It tends to lose one electron to acquire stable [Ar] $3d^5$ electronic configuration. Hence Mn^{2+} is more stable than Fe^{2+} towards oxidation.

(b) In the formation of metallic bonds, no electrons from 3*d*-orbitals are involved in case of zinc, while in all other metals of the 3*d* series, electrons from the *d*-orbitals are always involved in the formation of metallic bonds. That is why, the enthalpy of atomisation of zinc is the lowest in the series.

(c) This is due to comparable energies of 5*f*, 6*d* and 7*s* orbitals.

Q.8. Answer the following questions:

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

Ans.

S.No.	**Lanthanoids**	**Actinoids**
(*i*)	Atomic or ionic radii does not show much variation.	Atomic or ionic radii shows much variation.
(*ii*)	Besides +3 oxidation state, they show +2 and +4 oxidation states in few cases.	Besides +3 oxidation states, they show higher oxidation states of +4, +5, +6, +7 also.

Q. Name a member of the lanthanoid series which is well known to exhibit +4 oxidation state.

Ans. Cerium, Ce ([Xe] $4f^2\ 5d^0\ 6s^2$). Formation of Ce^{4+} is favoured by its noble gas configuration

([Xe] $4f^0\ 5d^0\ 6s^0$).

Q. Complete the following equation:

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

Ans.

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

Q. Out of Mn^{3+} and Cr^{3+}, which is more paramagnetic and why?

(Atomic nos.: Mn = 25, Cr = 24)

[*CBSE (AI) 2014*]

Ans. $Mn^{3+}(3d^4\ 4s^0)$ has 4 unpaired electrons while $Cr^{3+}(3d^3\ 4s^0)$ has 3 unpaired electrons, therefore, Mn^{3+} is more paramagnetic than Cr^{3+}.

Q.9.(i) Account for the following:

- a. **Transition metals form coloured compounds.**
- b. **Cr^{2+} is a strong reducing agent.**
- c. **Actinoids show irregularities in their electronic configurations.**

(ii) Define lanthanoid contraction. Write the common oxidation state of lanthanoids.

[*CBSE Chennai 2015*]

Ans. i. **(*a*)** This is due to *d-d* transition. Under the influence of the ligand attached, the *d*-orbitals in a transition metal complex split in two sets of orbitals having slightly different energies. When white light falls on these complexes they absorb a particular colour from the white light for the promotion of electrons and remaining colours are emitted. The colour of the complex is due to this emitted radiations.

(*b*) Cr^{2+} is a strong reducing agent because after the loss of one electron Cr^{2+} becomes Cr^{3+} which has more stable t^3_{2g} (half-filled) configuration in a medium like water.

(*c*) The irregularities in the electronic configuration of the actinoids is due to stability of the f^0, f^7 and f^{14} occupancies of the 5*f*-orbitals.

ii. The overall decrease in atomic and ionic radii from lanthanum to lutetium, due to poor shielding effect of 4*f* electrons is called lanthanoid contraction. The common oxidation state of lanthanoids is +3.

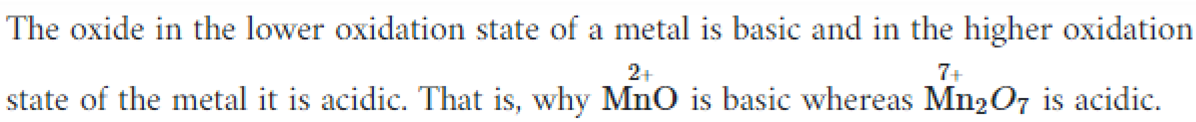
Q.10. Account for the following:

Q. Zr and Hf have almost similar atomic radii.

Ans. This is due to filling of 4*f* orbitals which have poor shielding effect (Lanthanoid contraction).

Q. MnO is basic whereas Mn_2O_7 is acidic in nature. Why?

Ans.



The oxide in the lower oxidation state of a metal is basic and in the higher oxidation state of the metal it is acidic. That is, why $\overset{2+}{\mathrm{Mn}}\mathrm{O}$ is basic whereas $\overset{7+}{\mathrm{Mn}}_2O_7$ is acidic.

Q. E^o value for the Mn^{3+}/Mn^{2+} couple is positive (+ 1.5 V) whereas that of Cr^{3+}/Cr^{2+} is negative (–0.4 V). Why?

Ans. The positive E^o value for the couple Mn^{3+}/Mn^{2+} is due to much higher third ionisation enthalpy of Mn, where the change is d^5 (extra stable) to d^4 . As Cr^{3+} (t^3_{2g}) is more stable than Cr^{2+}, therefore, E^o value for the couple Cr^{3+}/Cr^{2+} is negative.

Q. Zn has lowest enthalpy of atomisation in 3*d* series.

Ans. Because in the formation of metallic bonds no electron from 3*d* orbitals are involved in case of zinc as it has completely filled *d*-orbitals ($3d^{10}\ 4s^2$), while in all other metals of 3*d* series electrons from the *d*-orbitals are always involved in the formation of metallic bonds.

Q. The chemistry of actinoids is more complicated as compared to lanthanoids.

[*CBSE Chennai 2015*]

Ans. Because actinoids are radioactive and exhibit wide range of oxidation states.

Q.11. Answer the following questions:

Q. The elements of 3*d* transition series are given as:

Sc Ti V Cr Mn Fe Co Ni Cu Zn

Answer the following:

a. **Which element has the highest m.p. and why?**
b. **Which element is a strong oxidising agent in +3 oxidation state and why?**
c. **Which element is soft and why?**

Ans.

- **a.** Cr, the highest melting point of Cr is attributed to the involvement of greater number of electrons(5) from 3*d* in addition to 4*s* electrons in interatomic metallic bonding.
- **b.** Mn, because the change from Mn^{3+} (d^4) to Mn^{2+} (d^5) results in the half filled configuration which has extra stability.
- **c.** Zn, in Zn ($3d^{10}\ 4s^2$) all the electrons present in *d*-orbitals are paired and hence metallic bonds present in it are weak. That is why, it is soft.

Q. Write the equations involved in the preparation of potassium dichromate from sodium chromate (Na_2CrO_4).

[*CBSE (F) 2016*]

Ans. Sodium chromate is acidified with sulphuric acid to give a solution from which orange sodium dichromate, $Na_2Cr_2O_7.2H_2O$ can be crystallised.

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

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

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

Long Answer Questions (OIQ)

Q.1. Give reasons for the following:

Q. Transition metals have high enthalpies of atomisation.

Ans. Because of large number of unpaired electrons in their atoms, the transition metals have strong interatomic interactions and hence stronger bonding between atoms, resulting in higher enthalpies of atomisation.

Q. Among the lanthanoids, Ce(III) is easily oxidised to Ce(IV).

Ans. Because Ce (IV) has extra stability due to empty f^0 orbital.

$$Ce^{3+} \quad \rightarrow \quad Ce^{4+} \quad + \quad e^-$$

$$\text{Xe}]4f^1\ 5d^0\ 6s^0 \qquad [\text{Xe}]4f^0\ 5d^0\ 6s^0$$

Q. Fe^{3+} | Fe^{2+} redox couple has less positive electrode potential than Mn^{3+} | Mn^{2+} couple.

Ans. In Mn^{2+}, d^5 configuration leads to extra stability of half-filled configuration, so Mn^{3+} (d^4) tends to get converted to stable d^5, configuration of Mn^{2+}, by accepting an electron so Mn^{3+}/Mn^{2+} redox couple has more positive potential than $Fe^{3+}(d^5)/Fe^{2+}(d^4)$ couple.

Q. Copper (I) has d^{10} configuration, while copper (II) has d^9 configuration, still copper (II) is more stable in aqueous solution than copper (I).

Ans. Due to more negative enthalpy of hydration of $Cu^{2+}(aq)$ than $Cu^{+}(aq)$ which compensates for second ionisation enthalpy of copper.

Q. The second and third transition series elements have almost similar atomic radii.

Ans. In the third transition series after lanthanum there is lanthanoid contraction, due to ineffective shielding by intervening 4*f*-orbital electrons and hence second and third transition series elements have similar atomic radii.

Q.2. Answer the following questions:

Q. Assign reasons for the following:

- **a. In the series Sc (Z = 21) to Zn (Z = 30), the enthalpy of atomisation of Zn is the lowest.**
- **b. Zr and Hf have almost identical radii.**
- **c. Transition metals show variable oxidation states.**
- **d. The $E^{o}_{M2+/M}$ value for copper is positive (+ 0.34 V).**

Ans.

- **a.** In the formation of metallic bonds, no electrons from 3*d*-orbitals are involved in case of zinc, while in all other metals of the 3*d* series, electrons from the *d*-orbitals are always involved in the formation of metallic bonds. That is why, the enthalpy of atomisation of zinc is the lowest in the series.
- **b.** This is due to filling of 4*f* orbitals which have poor shielding effect (lanthanoid contraction).
- **c.** Transition elements show variable oxidation states because electrons in *ns* and (*n* – 1) *d*-orbitals are available for bond formation as they have nearly same energy.
- **d.** This is because the sum of enthalpies of sublimation and ionisation is not balanced by hydration enthalpy.

Q. Although +3 oxidation state is the characteristic oxidation state of lanthanoids but cerium shows +4 oxidation state also. Why?

[*NCERT Exemplar*]

Ans. It is because after losing one more electron Ce acquires stable 4*f* ^{0} electronic configuration.

Q.3. Answer the following questions:

Q. In the titration of $FeSO_4$ with $KMnO_4$ in the acidic medium, why is dil. H_2SO_4 used instead of dil. HCl?

Ans. Dil. H_2SO_4 is an oxidising agent and oxidises $FeSO_4$ to $Fe_2(SO_4)_3$. Dil. HCl is a reducing agent and liberates chlorine on reacting with $KMnO_4$ solution.

Hence, the part of the oxygen produced from $KMnO_4$ is used up by HCl.

Q. Give reasons:

- **a.** **Among transition metals, the highest oxidation state is exhibited in oxoanions of a metal.**
- **b.** **Ce^{4+} is used as an oxidising agent in volumetric analysis.**
- **c.** **Zn^{2+} salts are white while Cu^{2+} salts are blue.**

Ans.

- **a.** In these oxoanions the oxygen atoms are directly bonded to the transition metal. Since oxygen is highly electronegative, the oxoanions bring out the highest oxidation state of the metal.
- **b.** Ce^{4+} has the tendency to attain +3 oxidation state which is more stable and so it is used as an oxidising agent in volumetric analysis.
- **c.** Zn^{2+} ion has all its orbitals completely filled whereas in Cu^{2+} ion there is one half-filled 3*d*-orbital. Therefore, due to *d*-*d* transition Cu^{2+} has a tendency to form coloured salts whereas Zn^{2+} has no such tendency.

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

Q. There is a gradual decrease in the atomic sizes of transition elements in a series with increasing atomic numbers.

Ans. There is a gradual decrease in the atomic sizes of transition elements in a series with increasing atomic numbers due to poor shielding effect of *d*-electrons, the net electrostatic attraction between the nucleus and the outermost electrons increases.

Q. The atomic radii of the metals of the third (5*d*) series of transition elements are virtually the same as those of the corresponding members of the second (4*d*) series.

Ans. This is due to filling of 4*f*-orbitals which have poor shielding effect (lanthanide contraction).

Q. 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.

Ans. The *E*º value for the Mn^{3+}/Mn^{2+} couple is much more positive than Cr^{3+}/Cr^{2+} couple or Fe^{3+}/Fe^{2+} couple because Mn^{3+} ion receiving an electron gets *d*-subshell half-filled which is highly stable, while in case of Fe^{3+}, *d*-subshell is already half-filled, so it does not receive electron easily.

Q. The transition elements have great tendency for complex formation.

Ans. The transition elements have great tendency for complex formation due to presence of vacant *d*-orbitals of suitable energy, small size of cations and higher nuclear charge.

Q. Although Zr belongs to 4*d* and Hf belongs to 5*d* transition series but it is quite difficult to separate them.

Ans. Due to lanthanoid contraction, they have almost same size (Zr = 160 pm) and (Hf = 159 pm).

Q.5. On the basis of lanthanoid contraction, explain the following:

Q. Nature of bonding in La_2O_3 and Lu_2O_3.

Ans. As the size decreases covalent character increases. Therefore, La_2O_3 is more ionic and Lu_2O_3 is more covalent.

Q. Trends in the stability of oxo salts of lanthanoids from La to Lu.

Ans. As the size decreases from La to Lu, stability of oxosalts also decreases.

Q. Stability of the complexes of lanthanoids.

Ans. Stability of the complexes increases as the size of lanthanoids decreases.

Q. Radii of 4*d* and 5*d* block elements.

Ans. Radii of 4*d* and 5*d* block elements will be almost same.

Q. Trends in acidic character of lanthanoid oxides.

[*NCERT Exemplar*]

Ans. Acidic character of oxides increases from La to Lu.

Q.6. Assign reasons for the following:

Q. The enthalpies of atomisation of transition elements are high.

Ans. This is because transition metals have strong metallic bonds as they have a large number of unpaired electrons.

Q. The transition metals and many of their compounds act as good catalysts.

Ans. The catalytic activity of transition metals is attributed to the following reasons:

- **a.** Because of their variable oxidation states, transition metals form unstable intermediate compounds and provide a new path with lower activation energy for the reaction.
- **b.** In some cases, the transition metal provides a suitable large surface area with free valencies on which reactants are adsorbed.

Q. From element to element, the actinoid contraction is greater than the lanthanoid contraction.

Ans. This is due to poorer shielding by 5*f*-electrons in actinoids than that by 4*f*-electrons in the lanthanoids.

Q. The E^0 value for the Mn^{3+}/Mn^{2+} couple is much more positive than that of Cr^{3+}/Cr^{2+}.

Ans. This is due to much larger third ionisation energy of Mn as Mn^{2+} is very stable on account of stable d^5 configuration.

Q. Scandium ($Z = 21$) does not exhibit variable oxidation states and yet it is regarded as a transition element.

Ans. This is because scandium has partially filled *d*-orbitals in the ground state ($3d^1\ 4s^2$).

Q.7. Answer the following questions:

Q. Compare non transition and transition elements on the basis of their

- **a. Variability of oxidation states**
- **b. Stability of oxidation states.**

Ans.

- **a.** Oxidation states of transition elements differ from each other by unity. In non-transition elements oxidation states normally differ by a unit of two.

b. In transition elements higher oxidation states are favoured by heavier elements whereas in non-transition elements lower oxidation state is favoured by heavier elements.

Q. Give chemical reactions for the following observations:

a. Potassium permanganate is a good oxidising agent in basic medium.
b. Inter convertibility of chromate ion and dichromate ion in aqueous solution depends upon pH of the solution.
c. Potassium permanganate is thermally unstable at 513K.

[*CBSE Sample Paper 2013*]

Ans.

$$\begin{array}{lrcl}
\text{a.} & \mathrm{MnO_4^-} + 2H_2O + 3e^- & \rightarrow & \mathrm{MnO_2} + 4\,\mathrm{OH^-}\ ] \times 2 \\
 & I^- + 6\,\mathrm{OH^-} & \rightarrow & \mathrm{IO_3^-} + 3H_2O + 6e^- \\
\hline
 & 2\,\mathrm{MnO_4^-} + I^- + H_2O & \rightarrow & \mathrm{IO_3^-} + 2\,\mathrm{MnO_2} + 2\,\mathrm{OH^-} \\
\hline
\end{array}$$

$$\text{b. } 2\,\mathrm{CrO_4^{2-}} + 2H^+ \underset{\text{Alkali (pH more than 7)}}{\overset{\text{Acid (pH less than 7}}{\rightleftharpoons}} \mathrm{Cr_2}\,O_7^{2-} + H_2O$$

$$\text{c. } 2\,\mathrm{KMnO_4} \xrightarrow{513\ K} K_2\,\mathrm{MnO_4} + \mathrm{MnO_2} + O_2$$

Q.8. Answer the following questions:

Q. Write balanced equations to represent what happens when

a. Cu^{2+} is treated with KI.
b. Acidified potassium dichromate solution is reacted with iron (II) solution. (ionic equation)

Ans.

$$\text{a. } 2\,\mathrm{Cu^{2+}} + 4I^- \rightarrow \mathrm{Cu_2}\,I_2 + I_2$$

$$\begin{array}{lrcl}
 & \mathrm{Cr_2}\,O_7^{2-} + 14H^+ + 6e^- & \rightarrow & 2\,\mathrm{Cr^{3+}} + 7H_2O \\
\text{b.} & \mathrm{Fe^{2+}} & \rightarrow & \mathrm{Fe^{3+}} + e^-\ ] \times 6 \\
 & \mathrm{Cr_2}\,O_7^{2-} + 6\,\mathrm{Fe^{2+}} + 14H^+ & \rightarrow & 2\,\mathrm{Cr^{3+}} + 6\,\mathrm{Fe^{3+}} + 7H_2O
\end{array}$$

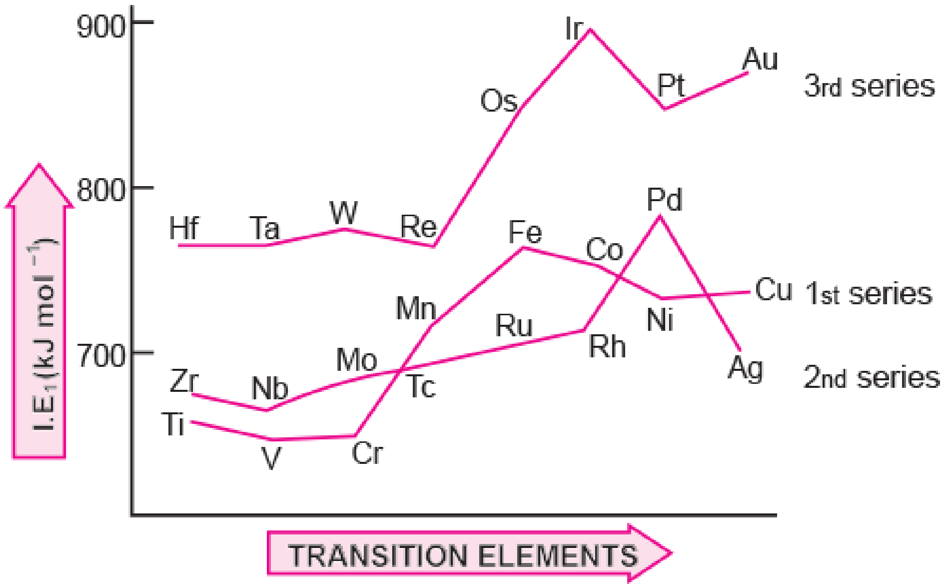
Q. (a) The figure given alongside illustrates the first ionization enthalpies of first, second and third series of transition elements. Answer the question that follows:

Which series amongst the first, second and third series of transition elements have the highest first ionization enthalpy and why?

(b) Separation of lanthanoid elements is difficult. Explain.

(c) Sm^{2+}, Eu^{2+} and Yb^{2+} ions in solutions are good reducing agents but an aqueous solution of Ce^{4+} is a good oxidising agent. Why?

[*CBSE Sample Paper 2015*]



Ans.

- **a.** Third series has the highest first ionization energy due to poorest shielding effect of the fully filled 4*f*subshell.
- **b.** This is due to lanthanoid contraction.
- **c.** Sm^{2+}, Eu^{2+} and Yb^{2+} ions are good reducing agents as they tend to acquire common oxidation state of + 3 shown by lanthanoids by the loss of one electron while Ce^{4+} gains one electron to attain + 3. Hence, Ce^{4+} is an oxidising agent.

Q.9. Answer the following questions:

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

Ans. Conversion of pyrolusite (MnO_2) into potassium manganate (K_2MnO_4).

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

Electrolytic oxidation:

$$K_2MnO_4 \rightleftharpoons 2K^+ + MnO_4^{2-}$$

At anode: $MnO_4^{2-} \rightarrow MnO_4^- + e^-$

At cathode: $H^+ + e^- \rightarrow H, \quad 2H \rightarrow H_2$

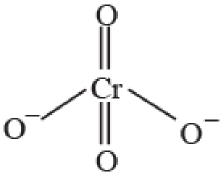
It oxidises oxalate $(C_2O_4^{\ 2-})$ to carbon dioxide (CO_2) in acidic medium.

$$\begin{array}{rcl} MnO_4^- + 8H^+ + 5e^- & \rightarrow & Mn^{2+} + 4H_2O] \times 2 \\ C_2O_4^{2-} & \rightarrow & 2\,CO_2 + 2e^-] \times 5 \\ \hline 2\,MnO_4^- + 5C_2O_4^{2-} + 16H^+ & \rightarrow & 2\,Mn^{2+} + 10\,CO_2 + 8H_2O \\ \hline \end{array}$$

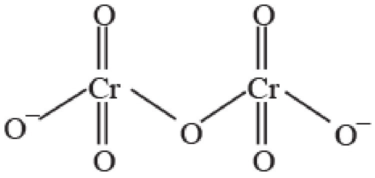
Q. Draw the structures of chromate and dichromate ions.

[*CBSE Sample Paper 2017*]

Ans.



Chromate ion



Dichromate ion

Q.10. Answer the following questions:

Q. Is the variability in oxidation number of transition elements different from that of non–transition elements? Illustrate with examples.

Ans. In transition elements, the oxidation states differ from each other by unity, *e.g.*, Fe^{3+} and Fe^{2+} etc., while in non-transition elements (*p*-block elements), the oxidation states differ by two, e.g., Pb^{4+} and Pb^{2+}, etc.

In transition elements the higher oxidation states are more stable for the heavier elements in a group, *e.g.*, Mo(VI) is more stable than Cr(VI) whereas in non-transition elements (*p*-block elements), the lower oxidation states are more stable for heavier elements due to inert pair effect, *e.g.*, Pb(II) is more stable than Pb(IV).

Q. Give reasons:

a. ***d*-block elements exhibit more oxidation states than *f*-block elements.**
b. **Orange solution of potassium dichromate turns yellow on adding sodium hydroxide to it.**
c. **Zirconium (Z = 40) and Hafnium (Z = 72) have almost similar atomic radii.**

[*CBSE Sample Paper 2017*]

Ans. (a) *d*–block elements exhibit more oxidation states because of less energy gap between *d* and *s* subshell whereas *f*-block elements have large energy gap between f and d subshell.

(b) On adding NaOH, pH of solution increases and the orange colour of the solution changes to yellow due to conversion of dichromate ion to chromate ion.

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

(c) This is due to filling of 4*f*-orbitals which have poor shielding effect (Lanthanoid contraction).

Q.11. A violet compound of manganese (A) decomposes on heating to liberate oxygen and compounds (B) and (C) of manganese are formed. Compound (C) reacts with KOH in the presence of potassium nitrate to give compound (B). On heating compound (C) with conc. H_2SO_4 and NaCl, chlorine gas is liberated and a compound (D) of manganese along with other products is formed. Identify compounds A to D and also explain the reactions involved.

[*NCERT Exemplar*] [*HOTS*]

Ans. A = $KMnO_4$, B = K_2MnO_4, C = MnO_2, D = $MnCl_2$

$$\underset{(A)}{2\,KMnO_4} \xrightarrow{\Delta} \underset{(B)}{K_2MnO_4} + \underset{(C)}{MnO_2} + O_2$$

$$2\,MnO_2 + 4KOH + O_2 \rightarrow \underset{(B)}{2K_2MnO_4} + 2H_2O$$

$$MnO_2 + 4NaCl + 4H_2SO_4 \rightarrow \underset{(D)}{MnCl_2} + 4\,NaHSO_4 + 2H_2O + Cl_2$$

Q.12. When an oxide of manganese (A) is fused with KOH in the presence of an oxidising agent and dissolved in water, it gives a dark solution of compound (B). Compound (B) disproportionates in neutral or acidic solution to give purple compound (C). An alkaline solution of compound (C) oxidises potassium iodide solution to a compound (D) and compound (A) is also formed. Identify compounds A to D and also explain the reactions involved.

[*NCERT Exemplar*] [*HOTS*]

Ans. A = MnO_2, B = K_2MnO_4, C = $KMnO_4$, D = KIO_3

$$2\underset{(A)}{\mathrm{MnO_2}} + 4\mathrm{KOH} + O_2 \rightarrow 2\underset{(B)}{K_2\,\mathrm{MnO_4}} + 2H_2O$$

$$3\,\mathrm{MnO_4^{2-}} + 4H^+ \rightarrow 2\underset{(C)}{\mathrm{MnO_4^-}} + \mathrm{MnO_2} + 2H_2O$$

$$2\,\mathrm{MnO_4^-} + H_2O + \mathrm{KI} \rightarrow 2\underset{(A)}{\mathrm{MnO_2}} + 2\,\mathrm{OH^-} + \underset{(D)}{\mathrm{KIO_3}}$$

Q.13. (i) A blackish brown coloured solid ‘A’ when fused with alkali metal hydroxides in presence of air, produces a dark green coloured compound ‘B’, which on electrolytic oxidation in alkaline medium gives a dark purple coloured compound C. Identify A, B and C and write the reactions involved.

(ii) What happens when an acidic solution of the green compound (B) is allowed to stand for some time? Give the equation involved. What is this type of reaction called?

[*HOTS*]

Ans.

i. $A = \underset{\text{Pyrolusite ore}}{\mathrm{MnO_2}}$, $B = \underset{\substack{\text{Potassium}\\ \text{manganate}}}{K_2\,\mathrm{MnO_4}}$, $C = \underset{\substack{\text{Potassium}\\ \text{permanganate}}}{\mathrm{KMnO_4}}$,

Reactions involved:

$$2\mathrm{MnO_2} + 4\mathrm{KOH} + \mathrm{O_2} \rightarrow 2\mathrm{K_2MnO_4} + 2\mathrm{H_2O}$$

$$\underset{\substack{\text{Manganate ion}\\ (\text{Green})}}{\mathrm{MnO_4^{2-}}} \xrightarrow[\text{in alkaline solution}]{\text{Electrolytic oxidation}} \underset{\substack{\text{Permanganate ion}\\ (\text{Purple})}}{2\,\mathrm{MnO_4^-}} + e^-$$

ii. In acidic medium, $\mathrm{K_2MnO_4}$ changes to give purple coloured compound along with black precipitate.

$$\underset{\substack{\text{Green}\\ \text{compound}}}{3\,\mathrm{MnO_4^{2-}}} + 4H^+ \rightarrow \underset{\substack{\text{Purple}\\ \text{compound}}}{2\,\mathrm{MnO_4^-}} + \underset{\text{Black}}{\mathrm{MnO_2}} + 2H_2O$$

This type of reaction is called disproportionation reaction.