

4 The *d* and *f*-Block Elements

Fastrack Revision

► The *d*-Block Elements

- The elements are lying in the middle of periodic table belonging to groups 3 to 12 are known as *d*-block elements.
- Their general electronic configuration is $(n-1) d^{1-10} ns^{1-2}$, where, $(n-1)$ stands for penultimate shell.

► Transition Elements

- A transition element is defined as the one which has incompletely filled *d*-orbitals in its ground state or in any one of its oxidation states.
- Zinc, cadmium and mercury are not regarded as transition metals due to completely filled *d*-orbital.

► Four Transition Series

- **3*d*-transition Series:** It consists of elements with atomic number 21(Sc) to 30(Zn) and having incomplete 3*d*-orbitals. It is called the First Transition Series.
- **4*d*-transition Series:** It consists of elements with atomic number 39(Y) to 48(Cd) and having incomplete 4*d*-orbitals. It is called Second Transition Series.
- **5*d*-transition Series:** It consists of elements with atomic number 57(La), 72(Hf) to 80(Hg) having incomplete 5*d*-orbitals. It is called Third Transition Series.
- **6*d*-transition Series:** It consists of elements with atomic number 89(Ac), 104(Rf) to 112(Cn) having incomplete 6*d*-orbitals. It is called Fourth Transition Series.

► General Characteristics of Transition Elements

- **Metallic Character:** All transition elements are metallic in nature, *i.e.* they have strong metallic bonds. This is because of presence of unpaired electrons. This gives rise to properties like high density, high enthalpies of atomisation and high melting and boiling points.
- **Atomic Radii:** The atomic radii decreases from Sc to Cr because the effective nuclear charge increases. The atomic size of Fe, Co and Ni are almost same because the attraction due to increase in nuclear charge is cancelled by the repulsion because of increase in shielding effect. Cu and Zn have bigger size because the shielding effect increases and electron-electron repulsion increases.
- **Ionisation Enthalpy:** The ionisation enthalpy of 5*d*-transition series is much higher than 3*d* and 4*d*-transition series because of Lanthanoid contraction.

- **Oxidation State:** Transition metals show variable oxidation states due to tendency of $(n-1)d$ as well as *ns* electrons to take part in bond formation.

- **Magnetic Properties:** Most of transition metals are paramagnetic in nature as a result of which they give coloured compounds and it is all due to presence of unpaired electrons. It increases from Sc to Cr and then decreases because number of unpaired electrons increases from Sc to Cr and then decreases. They are rarely diamagnetic.

- **Catalytic Properties:** Most of transition metals are used as catalyst because of (i) presence of incomplete or empty *d*-orbitals, (ii) large surface area, (iii) variable oxidation state, (iv) ability to form complexes, *e.g.*, Fe, Ni, V_2O_5 , Pt, Mo, Co are used as catalyst.

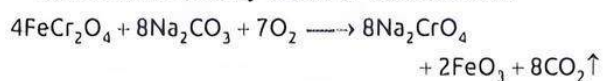
- **Formation of Coloured Compounds:** They form coloured ions. Due to the presence of incompletely filled *d*-orbitals and unpaired electrons, they can undergo *d-d* transition by absorbing colour from visible region and radiating complementary colour.

- **Interstitial Compounds:** Transition metals have voids or interstitials in which C, H, N, B, etc., can fit into resulting in formation of interstitial compounds. They are non-stoichiometric, *i.e.*, their composition is not fixed, *e.g.*, steel. They are harder and less malleable and ductile.

- **Alloy Formation:** They form alloys due to similar ionic size. Metals can replace each other in crystal lattice, *e.g.*, brass, bronze, steel, etc.

► Potassium Dichromate, $K_2Cr_2O_7$

- Potassium dichromate is an acidic compound in which Cr is present in +6 oxidation state.
- **Preparation:** It is prepared from sodium chromate, which is obtained by fusion of chromite ore.



► Properties of Potassium Dichromate

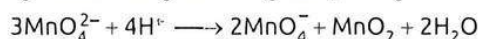
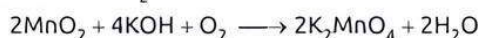
- Its colour depends upon the pH of the solution.
- It is used as primary standard solution in volumetric analysis in acidic medium.
- It acts as a strong oxidising agent.

► Potassium Permanganate, $KMnO_4$

- $KMnO_4$ is an acidic compound in which Mn has (+7) oxidation state.

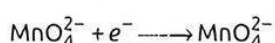
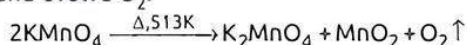


- **Preparation:** It is prepared by fusion of pyrolusite ore (MnO_2) with alkali metal hydroxide in the presence of O_2 .



► Properties of Potassium Permanganate

- KMnO_4 is a dark purple coloured crystalline solid.
- KMnO_4 decomposes to give K_2MnO_4 and MnO_2 on heating and evolve O_2 .



- KMnO_4 acts as an oxidising agent in all the three mediums *i.e.*, acidic, basic and neutral.

► The f-Block Elements

- The elements constituting the f-block are those in which 4f and 5f-orbitals are progressively filled in the latter two long periods.

- These elements are called inner transition elements and their general electronic configuration is $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$.

- **Lanthanoids:** The 14 elements immediately following Lanthanum, *i.e.*, Cerium (58) to Lutetium (71) are called Lanthanoids. They belong to first inner transition series.

- Their electronic configuration is $[\text{Xe}] 4f^{1-14} 5d^{0-1} 6s^2$.
- They mainly give +3 oxidation state while some elements give +2 and +4 oxidation states.
- The radii of members of 5d-series are similar to those of corresponding members of the 4d-series due to lanthanoid contraction.

- **Actinoids:** The 14 elements immediately following actinium *i.e.*, Thorium (90) to Lawrencium (103) are called actinoids in which 5f-orbitals are progressively filled.

- Their general electronic configuration is $5f^{1-14} 6d^{0-1} 7s^2$.
- In general, actinoids show +3 oxidation state. These resemble the Lanthanoids in having more compounds in +3 state than in the +4 state. However, +3 and +4 ions tend to hydrolyse.



Practice Exercise



Multiple Choice Questions

- Q 1. In transition elements, the element belongs to 4d series is:

a. $_{37}\text{A}$ b. $_{47}\text{B}$ c. $_{57}\text{C}$ d. $_{30}\text{D}$

- Q 2. Which electron(s) is/are released to achieve the maximum oxidation state of a transition metal?

a. ns electron b. $(n+1)d$ electron
c. $(n-1)d$ electron d. $ns + (n-1)d$ electron

- Q 3. Which one among the following metals of 3d series has the lowest melting point? (CBSE 2023)

a. Fe b. Mn c. Zn d. Cu

- Q 4. Which of the transition element does not exhibit variable oxidation state?

a. Ti b. V c. Fe d. Sc

- Q 5. Which of the following transition metals shows +1 and +2 oxidation states? (CBSE 2023)

a. Mn b. Zn c. Sc d. Cu

- Q 6. Match the properties with the elements of 3d series: (CBSE 2023-24)

(i) Lowest enthalpy of atomisation	(p) Sc
(ii) Shows maximum number of oxidation states	(q) Mn
(iii) Transition metal that does not form coloured compounds	(r) Zn
	(s) Ti

a. (i)-(r), (ii)-(q), (iii)-(p) b. (i)-(r), (ii)-(s), (iii)-(p)
c. (i)-(p), (ii)-(q), (iii)-(r) d. (i)-(s), (ii)-(r), (iii)-(p)

- Q 7. Which of the following ions has the maximum number of unpaired d-electrons? (CBSE 2023)

a. Fe^{3+} b. V^{3+} c. Ti^{3+} d. Sc^{3+}

[Atomic number: Fe = 26, V = 23, Ti = 22, Sc = 21]

- Q 8. The most common and stable oxidation state of a Lanthanoid is: (CBSE 2023)

a. +2 b. +3
c. +4 d. +6

- Q 9. Formation of coloured ions is possible, when the compound contains:

a. paired electron
b. unpaired electron
c. non-bonding electron
d. None of these

- Q 10. 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

(NCERT EXEMPLAR)

a. Fe b. Ni
c. Co d. Cu

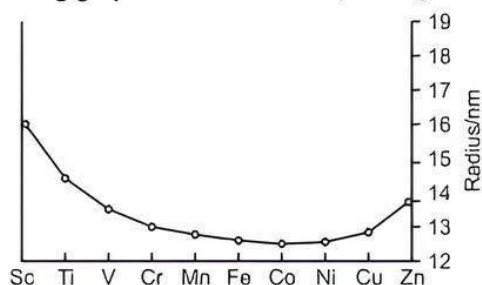
- Q 11. The ions of metals of Group 12 (Zn, Cd and Hg) have completely filled d orbitals and so they: (CBSE 2023)

a. behave like semiconductors
b. are very high melting solids
c. do not behave like transition metals
d. behave like superconductors

- Q 12. Which of the following characteristics of transition metals is associated with their catalytic activity? (CBSE 2023)

a. Paramagnetic nature
b. Colour of hydrated ions
c. High enthalpy of atomisation
d. Variable oxidation states

- Q 13. The trend of which property is represented by the following graph? (CBSE SQP 2023-24)



- a. Ionization enthalpy
b. Atomic radii
c. Enthalpy of atomization
d. Melting point
- Q 14. Match the Column I with Column II and mark the appropriate choice.

	Column I (Property)	Column II (Metal)
A.	Element with highest second ionisation enthalpy	(i) Cr
B.	Element with highest third ionisation enthalpy	(ii) Cu
C.	M in $M(\text{CO})_6$ is	(iii) Zn
D.	Element with highest heat of atomisation	(iv) V

	A	B	C	D
a.	(ii)	(iii)	(i)	(iv)
b.	(iv)	(iii)	(i)	(ii)
c.	(iii)	(i)	(ii)	(iv)
d.	(i)	(ii)	(iii)	(iv)

- Q 15. KMnO_4 acts as an oxidising agent in alkaline medium. When alkaline KMnO_4 is treated with KI, iodide ion is oxidised to: (NCERT EXEMPLAR)
- a. I_2 b. IO^- c. IO_3^- d. IO_4^-
- Q 16. KMnO_4 is coloured due to: (CBSE SQP 2022-23)
- a. $d-d$ transitions
b. charge transfer from ligand to metal
c. unpaired electrons in d -orbital of Mn
d. charge transfer from metal to ligand
- Q 17. Lanthanoid element among the following elements is:
a. Rh b. Ce c. Ac d. Zr
- Q 18. Gadolinium belongs to $4f$ series. Its atomic number is 64. Which of the following is the correct electronic configuration of gadolinium? (NCERT EXEMPLAR)
- a. $(\text{Xe}) 4f^7 5d^1 6s^2$ b. $(\text{Xe}) 4f^6 5d^2 6s^2$
c. $(\text{Xe}) 4f^8 6d^2$ d. $(\text{Xe}) 4f^9 5s^1$
- Q 19. There are 14 elements in actinoid series. Which of the following elements does not belong to this series? (NCERT EXEMPLAR)
- a. U b. Np c. Tm d. Fm

- Q 20. Which of the following is/are amphoteric oxide?

$\text{Mn}_2\text{O}_7, \text{CrO}_3, \text{Cr}_2\text{O}_3, \text{CrO}, \text{V}_2\text{O}_5, \text{V}_2\text{O}_4$

a. $\text{V}_2\text{O}_5, \text{Cr}_2\text{O}_3$ b. $\text{Mn}_2\text{O}_7, \text{CrO}_3$
c. $\text{CrO}, \text{V}_2\text{O}_5$ d. $\text{V}_2\text{O}_5, \text{V}_2\text{O}_4$

- Q 21. 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

- Q 22. Interstitial compounds are formed when small atoms are trapped inside the crystal lattice of metals. Which of the following is not the characteristic property of interstitial compounds?
- a. They have high melting points in comparison to pure metals.
b. They are very hard.
c. They retain metallic conductivity.
d. They are chemically very reactive.

- Q 23. Out of the following transition elements, the maximum number of oxidation states are shown by: (CBSE 2020)
- a. Sc ($Z = 21$) b. Cr ($Z = 24$)
c. Mn ($Z = 25$) d. Fe ($Z = 26$)



Assertion & Reason Type Questions

Directions (Q. Nos. 24-35): Each of the following questions consists of two statements, one is Assertion (A) and the other is Reason (R). Give answer:

- a. Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of Assertion (A).
b. Both Assertion (A) and Reason (R) are true but Reason (R) is not the correct explanation of Assertion (A).
c. Assertion (A) is true but Reason (R) is false.
d. Assertion (A) is false but Reason (R) is true.
- Q 24. Assertion (A): Cu^{2+} iodide is not known.
Reason (R): Cu^{2+} oxidises I^- to iodine. (NCERT EXEMPLAR)
- Q 25. Assertion (A): Copper is a non-transition element.
Reason (R): Copper has completely filled d -orbitals in its ground state. (CBSE 2023)
- Q 26. Assertion (A): Transition metals show their highest oxidation state with oxygen.
Reason (R): The ability of oxygen to form multiple bonds to metals. (CBSE 2023)
- Q 27. Assertion (A): Transition metals have high enthalpy of atomisation.
Reason (R): Greater number of unpaired electrons in transition metals results in weak metallic bonding. (CBSE 2023)
- Q 28. Assertion (A): Zr and Hf have almost identical radii.
Reason (R): Both Zr and Hf exhibit similar properties. (CBSE 2023)

Q 29. Assertion (A): Separation of Zr and Hf is difficult.
Reason (R): Because Zr and Hf lie in the same group of the periodic table. (NCERT EXEMPLAR)

Q 30. Assertion (A): Actinoids form relatively less stable complexes as compared to lanthanoids.
Reason (R): Actinoids can utilise their 5f orbitals along with 6d orbitals in bonding, but lanthanoids do not use their 4f orbital for bonding. (NCERT EXEMPLAR)

Q 31. Assertion (A): Magnetic moment values of actinides are lesser than the theoretically predicted values.
Reason (R): Actinide elements are strongly paramagnetic. (CBSE SQP 2022-23)

Answers

- (b) $_{47}\text{B}$
4d-series consists of ten elements from atomic number 39 to atomic number 48.
- (c) $(n-1)d$ electron
The +1 and +2 oxidation states involve the participation of ns-electrons, but higher oxidation states such as +3, +4, +5, +6 etc. involve the use of $(n-1)d$ electrons in addition to ns-electrons for bond formation.
- (c) Zn
Due to the absence of d-electrons, zinc has the lowest melting point in 3d series.
- (d) Sc
- (d) Cu
- (a) (i)-(r), (ii)-(q), (iii)-(p)
Zinc has no unpaired electrons in 3d or 4s orbitals, so enthalpy of atomization is low Mn = $3d^5 4s^2$ shows +2, +3, +4, +5, +6 and +7 oxidation state, maximum number in 3d series.
- (a) Fe^{3+}
 Fe^{3+} has the maximum number of unpaired electrons i.e., 5.
- (b) +3
- (b) unpaired electron
- (b) Ni
- (c) do not behave like transition metals
Transition metals have partially filled d-orbital either in their elemental state or in most common oxidation state but ions of metals of Group 12 (Zn, Cd and Hg) have completely filled d-orbitals and so they do not behave like transition metals.
- (d) variable oxidation states
The transition elements on account of their variable valency are able to form unstable intermediate compounds very readily and hence show catalytic behaviour.
- (b) atomic radii
- (b) A-(iv), B-(iii), C-(i), D-(ii)
- (c) IO_3^-
 $2\text{MnO}_4^- + \text{H}_2\text{O} + \text{I}^- \longrightarrow 2\text{MnO}_2 + 2\text{OH}^- + \text{IO}_3^-$

Q 32. Assertion (A): Zinc is not regarded as a transition element.

Reason (R): In zinc, 3d-orbitals are completely filled in its ground state as well as in its oxidised state. (CBSE 2023)

Q 33. Assertion (A): Fe^{2+} acts as a reducing agent.
Reason (R): Fe^{3+} state is stable due to 3d⁵ configuration. (CBSE 2023)

Q 34. Assertion (A): Cu cannot liberate hydrogen from acids.
Reason (R): Because it has positive electrode potential. (NCERT EXEMPLAR)

Q 35. Assertion (A): The highest oxidation state of osmium is +8.
Reason (R): Osmium is a 5d-block element. (NCERT EXEMPLAR)

16. (b) charge transfer from ligand to metal
 The Mn atom in KMnO_4 has +7 oxidation state with electron configuration $(\text{Ar})3d^0 4s^0$. Since no unpaired electrons are present in it, d-d transitions are not possible. The molecule should, therefore, be colourless. Its intense purple colour is due to $\text{L} \rightarrow \text{M}$ (ligand to metal) charge transfer i.e. $2p(\text{L})$ of O to $3d(\text{M})$ of Mn.

17. (b) Ce **18.** (a) $(\text{Xe}) 4f^7 5d^1 6s^2$

19. (c) Tm **20.** (a) V_2O_5 , Cr_2O_3

21. (b) 3.87 BM

Number of unpaired electrons in Cr^{3+} ions = 3

Spin only magnetic moment of $\text{Cr}^{3+} = \sqrt{3(3+2)} = \sqrt{15} = 3.87 \text{ BM}$

22. (d) They are chemically very reactive
 Interstitial compounds are chemically inert.

23. (c) Mn ($Z = 25$)

Transition Element	Oxidate States
Sc	+3
Cr	+2, +3, +4, +5, +6
Mn	+2, +3, +4, +5, +6, +7
Fe	+2, +3, +4, +6

24. (a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of Assertion (A).

25. (d) Copper is a transition element but it has completely filled d-orbitals in its ground state. Hence, assertion is false but reason is true.

26. (a) The ability of oxygen to form multiple bonds with metals results in the formation of stable compounds in which metals can exist in their highest oxidation states.

27. (c) Transition metals have high enthalpy of atomisation because they have high effective nuclear charge, greater number of valence electrons and some unpaired electrons which result in strong metallic bonding.
 Hence, assertion is true but reason is false.

28. (b) Zr and Hf have almost identical radii due to lanthanoid contraction. Also, both Zr and Hf exhibit similar properties. Hence, assertion and reason both are true but reason is not the correct explanation of assertion.
29. (b) Both Assertion (A) and Reason (R) are true but Reason (R) is not the correct explanation of Assertion (A).
30. (d) Assertion (A) is false but Reason (R) is true.
Assertion is false because actinoids form more stable complexes as compared to lanthanoids.
31. (b) The magnetic moment is less as the 5f electrons of actinides are less effectively shielded which results in quenching of orbital contributions. Also, they are strongly paramagnetic due to the presence of unpaired electrons.
32. (a) Zinc is not regarded as a transition element because it forms only Zn^{2+} ions with all the 3d electrons present. Zn has 3d-orbital completely filled by 10 electrons that are paired. Hence, they can't release these electrons and can only lose electrons.
33. (a) Fe^{2+} acts as a reducing agent due to the increasing stability of the lower species to which they are reduced. Hence, assertion is true.
Also, Fe^{3+} state is stable due to 3d⁵ configuration i.e. half filled electronic configuration. So, reason is also true and it is also the correct explanation of assertion.
34. (a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of Assertion (A).
35. (b) Both Assertion (A) and Reason (R) are true but Reason (R) is not the correct explanation of Assertion (A).



Case Study Based Questions

Case Study 1

When an orange coloured crystalline compound [A] was heated with common salt and concentrated sulphuric acid, an orange red coloured gas [B] was evolved. The gas [B] on passing through NaOH solution gave a yellow solution [C]. The solution on reacting with an aqueous solution of lead acetate gave a yellow precipitate.

Read the given passage carefully and give the answer of the following questions:

Q 1. The crystalline compound [A] is:

- cobalt nitrate
- manganese sulphate
- potassium dichromate
- ammonium dichromate

Q 2. The gas [B] is:

- chlorine
- bromine
- chromyl chloride
- nitrogen peroxide

Q 3. What happens when potassium iodide reacts with acidic solution of potassium dichromate?

- It liberates iodine
- Potassium sulphate is formed
- Chromium sulphate is formed
- All the above products are formed

Q 4. One mole of acidified $K_2Cr_2O_7$, on reaction with excess KI will liberate mole (s) of I_2 .

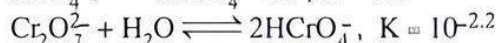
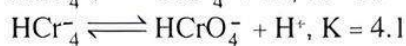
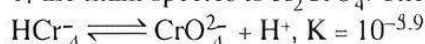
- 3
- 1
- 7
- 2

Answers

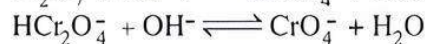
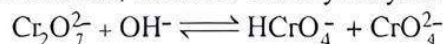
- (c) potassium dichromate
- (c) chromyl chloride
- (d) All the above products are formed
- (a) 3

Case Study 2

In basic solution with pH 6, CrO_3 forms the tetrahedral yellow chromate ion, CrO_4^{2-} . Between pH 2 and 6, $HCrO_4^-$ and the orange red dichromate ion, $Cr_2O_7^{2-}$, are in equilibrium. At pH values below 1, the main species is H_2CrO_4 . The equilibria are:



In addition, these are base-hydrolysis equilibria



The pH dependent equilibria are quite labile and on addition of cations that form insoluble chromates (e.g., Ba^{2+} , Pb^{2+} and Ag^+), the chromates and not the dichromates are precipitated.

Read the given passage carefully and give the answer of the following questions:

Q 1. Which of the following statement is correct?

- Acid solutions of dichromate are strong oxidants
- In alkaline solution, the chromate ion is strong oxidant
- Acid solutions of dichromate are poor oxidants
- Both a. and b.

Q 2. In the redox reaction involving $Cr_2O_7^{2-}$ and Fe^{2+} ions, the number of electrons absorbed per chromium atoms is:

- 1
- 3
- 4
- 6

Q 3. What happens when a solution of potassium chromate is treated with an excess of dilute nitric acid?

- Cr^{3+} and $Cr_2O_7^{2-}$ are formed
- $Cr_2O_7^{2-}$ and H_2O are formed
- CrO_4^{2-} is reduced to +3 state of Cr
- CrO_4^{2-} is oxidised to +7 state of Cr

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

- a. Sn b. Sn^{3+}
c. Sn^{4+} d. Sn^+

Answers

- (a) Acid solutions of dichromate are strong oxidants
- (b) 3
- (b) $Cr_2O_7^{2-}$ and H_2O are formed
- (c) Sn^{4+}

Case Study 3

The d -block occupies the large middle section flanked between s - and p -blocks in the periodic table. The name 'transition' given to the elements of d -block is only because of their position between s and p -block elements.

The d -orbitals of the penultimate energy level in their atoms receive electrons giving rise to the three rows of the transition metals, i.e., $3d$, $4d$, and $5d$. The fourth row of $6d$ is still incomplete. First transition series or $3d$ -series: Scandium (Sc) to Zinc (Zn).

Second transition series or d -series: Yttrium (Y) to Cadmium (Cd).

Third transition series or $5d$ -series: Lanthanum (La) to Mercury (Hg) excluding Ce to Lu.

Fourth transition series or $6d$ -series: Actinium (Ac) to Copernicium (Cn) excluding Th to Lr.

Read the given passage carefully and give the answer of the following questions:

- Q 1. Silver atom has completely filled d -orbitals ($4d^{10}$) in its ground state. How can you say that it is a transition element?
- Q 2. In the series Sc ($Z = 21$) to Zn ($Z = 30$), the enthalpy of atomisation of zinc is lowest, i.e., 126 kJ mol^{-1} . Why?
- Q 3. Why is the highest oxidation state of a metal exhibited in its oxide or fluoride only?

OR

The $E^\circ_{M^{2+}/M}$ value of copper is positive (+0.34V). What is the possible reason for this?

Answers

1. Silver in its +1 oxidation state, exhibits $4d^{10}5s^0$ configuration. But in some compounds, it also shows +2 oxidation state, so the configuration becomes $4d^9 5s^0$. Here, d -orbital is not completely filled. Therefore, silver is a transition element.
2. Zinc has stable ground state due to its completely filled d -orbitals. It therefore, has least tendency to form metallic bonds, in the series and thus requires least enthalpy of atomisation to get atomised.

3. Oxygen and fluorine both have small size and high value of electronegativity. So, they can oxidise the metal to their highest oxidation states.

OR

$E^\circ_{M^{2+}/M}$ value of copper is positive as value of hydration enthalpy is less than the sum of values of ionisation enthalpy and enthalpy of ionisation.



Very Short Answer Type Questions

Q 1. Transition elements exhibit variable valency. Why?

Ans. Transition elements exhibit variable valency because of the presence of electrons in $(n-1)d$ and ns -subshells and very closeness of shells of d and s -subshells. Thus, transition elements readily lose electrons from the inner shell and hence, the oxidation state increases.

Q 2. In $3d$ series of transition elements, which element exhibit maximum number of oxidation states and why?

Ans. Manganese ($Z = 25$, electronic configuration = $(Ar) 3d^5 4s^2$) contains five unpaired electrons in $3d$ orbital and 2 electrons in $4s$ orbital. So, it exhibits oxidation states from +2 to +7, which is the largest number of oxidation state exhibited in $3d$ series.

Q 3. Why are +3 and +4 oxidation states of cerium (atomic number = 58) more stable?

Ans. ${}_{58}Ce = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10} 4f^2, 5s^2 5p^6, 6s^2$.

In cerium, the energy order of subshells is $4f < 4d$. Thus, $4f$ subshell contains 2 electrons which are removed one by one with the two electrons of $6s$ to exhibit +3 and +4 oxidation states, which are stable.

Q 4. Most of the transition metals exhibit paramagnetic behaviour. Why?

Ans. In transition metals, d -subshell of $(n-1)$ shell contains unpaired electrons (with the exception of Zn, Cd and Hg). Because of the presence of unpaired electrons, transition metals usually exhibit paramagnetic behaviour.

Q 5. Write the chemical equation for obtaining chlorine from potassium permanganate.

Ans. $2KMnO_4 + 3H_2SO_4 + 10HCl \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5Cl_2 \uparrow$

Q 6. Why is the highest oxidation state of a metal exhibited by its fluoride and oxide only?

(NCERT INTExT)

Ans. Both fluorine and oxygen have very high electronegativity values. They can oxidise the metals to the highest oxidation state. As a result, the highest oxidation states are shown by the fluorides and oxides of the metals; transition metals in particular.

Q 7. What is the effect of increasing pH on the colour of $K_2Cr_2O_7$ solution?

Ans. When pH is less than 7 (acidic medium), $K_2Cr_2O_7$ ($Cr_2O_7^{2-}$) has orange colour. In the basic medium with pH more than 7, the colour of the solution changes to yellow due to the formation of K_2CrO_4 (CrO_4^{2-} ion).

Q 8. Why is third ionisation enthalpy of manganese exceptionally high?

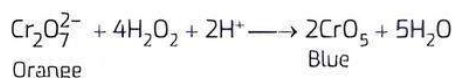
Ans. Mn^{2+} has the configuration $[\text{Ar}]3d^5$. With highly symmetrical configuration, the removal of third electron is very difficult. Therefore, third ionisation enthalpy of the metal is exceptionally high ($\Delta_i H_3 \approx 3200 \text{ kJ mol}^{-1}$).

Q 9. Why are all salts of scandium white?

Ans. In these salts, scandium exists as Sc^{3+} ion which is iso-electronic with $(\text{Ar})^{18}$. With completely filled orbitals, the salts of Sc^{3+} are white.

Q 10. What happens when H_2O_2 is shaken with acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution?

Ans. The colour of the solution changes from orange to blue.



Q 11. When H_2S is passed through dilute solution of $\text{K}_2\text{Cr}_2\text{O}_7$, milkiness appears. Why?

Ans. This is due to oxidation of H_2S to sulphur which is of colloidal nature. Therefore, the solution appears to be milky white or pale yellow.

Q 12. Transition metals tend to be unreactive with increasing atomic numbers in a series. Why?

Ans. This is because of gradual increase in the values of ionisation enthalpies which make the participation of electrons rather difficult.

Q 13. There is a greater range of variable oxidation states among the actinoids than among the lanthanoids. Why?

Ans. In actinoids, there is less energy difference in the 5f, 6d and 7s orbitals as compared to 4f, 5d and 6s orbitals in case of lanthanoids. This means that more electrons are available for bonding in actinoids as compared to the members of lanthanoid family.

Q 14. Why is there a general increase in density of elements from titanium ($Z = 22$) to copper ($Z = 29$)?

Ans. In general, the atomic radii and the atomic volumes of the elements gradually decrease along 3d series. However, their atomic masses increase. This means that the densities (Mass/Volume) of the elements are likely to increase from left to the right in the series.

Q 15. There occurs much more frequently metal-metal bonding in the compounds of heavy transition elements (3d series). Assign reason.

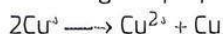
Ans. In transition elements, a number of ns and $(n-1)d$ electrons are available for bonding since these are unpaired. As a result, metal-metal bonding is quite frequent in these. These are supported by the fact that metals are lustrous, hard and have high melting and boiling points.

Q 16. Why is Cu^+ ion not stable in aqueous solution?

OR

Why is Cu^+ not known in aqueous solution?

Ans. Cu(I) compounds involving Cu^+ ions are unstable in aqueous solution and undergo disproportionation.



The stability of Cu^{2+} ions as compared to Cu^+ ion is due to more negative $\Delta_{hyd}H^\circ$ of $\text{Cu}^{2+}(\text{aq})$ than $\text{Cu}^+(\text{aq})$ which compensates the second ionisation enthalpy of Cu involved in the formation of Cu^{2+} ion.

Q 17. Among the divalent cations in the first transition series, manganese exhibits maximum paramagnetic character. Explain.

Ans. Mn^{2+} ion has $3d^5$ configuration and has a maximum of five unpaired electrons. Therefore, it exhibits maximum paramagnetic character among the divalent cations of first transition series.

Q 18. La^{3+} ($Z = 57$) and Lu^{3+} ($Z = 71$) do not show any colour in solution. Assign reason.

Ans. La^{3+} ion has the configuration of Xe while Lu^{3+} ion $(\text{Xe}) 4f^{14}$ has completely filled orbitals and there is no transition. Therefore, both these ions do not show any colour.

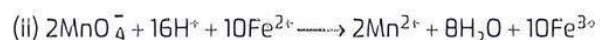
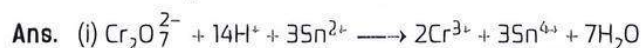
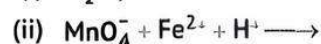
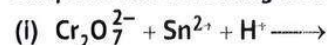
Q 19. Write the formula of an oxo-anion of manganese (Mn) in which it shows the oxidation state to its group number. (CBSE 2017)

Ans. MnO_4^- is an oxo-anion of manganese (Mn) in which it shows the oxidation state equal to its group number. Here, oxidation state of Mn is +7 which is same as its group number (7).

Q 20. Write the formula of an oxo-anion of chromium (Cr) in which it shows the oxidation state equal to its group number. (CBSE 2017)

Ans. The formula is $\text{Cr}_2\text{O}_7^{2-}$ (dichromate ion) in which oxidation state of Cr is +6 which is equal to its group number (6).

Q 21. Complete the following reactions:

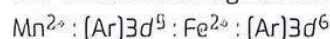


Q 22. Explain why Zn^{2+} salts are colourless while Ni^{2+} salts are coloured.

Ans. Zn^{2+} with configuration $(\text{Ar})^{18}3d^{10}$ has all filled orbitals. Therefore, its salts are colourless. Ni^{2+} with configuration $(\text{Ar})^{18}3d^8$ has some half-filled orbitals. Therefore, its salts are coloured.

Q 23. Why is +2 oxidation state of manganese quite stable while the same not true for iron?

Ans. The electronic configurations of both the ions are:



The Mn^{2+} ion has more symmetrical configuration than Fe^{2+} ion and is therefore, more stable. Thus, +2 oxidation state of manganese is quite stable while that of iron is not.

Q 24. Write the electronic configuration of an element with atomic number 102.

Ans. The configuration of the element ($Z = 102$) is $(\text{Rn})5f^{14}7s^2$. It is Nobelium (No).

Q 25. Why is $\text{La}(\text{OH})_3$ more basic than $\text{Lu}(\text{OH})_3$?

Ans. $\text{La}(\text{OH})_3$ is more basic than $\text{Lu}(\text{OH})_3$ because the latter has greater covalent character as compared to the former on account of lanthanoid contraction. The release of OH^- ion from $\text{Lu}(\text{OH})_3$ is more difficult and is less basic than $\text{La}(\text{OH})_3$.

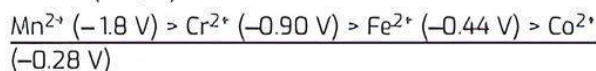
Q 26. Why are Zn, Cd and Hg quite soft and have low melting points?

Ans. These metal atoms have completely filled d-orbitals (d^{10} configuration). This means that d-electrons are not readily available for metallic bond formation. Quite obviously, the metallic bonds are weak and as a result, these metals are quite soft and also have low melting points.

Q 27. Discuss the relative stability in aqueous solutions of +2 oxidation states among the elements:

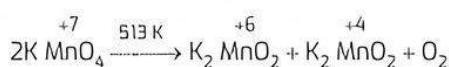
Cr, Mn, Fe and Co.

Ans. The relative stability of the +2 oxidation states (decreasing order) can be compared in terms of E° values. (M^{2+}/M)



Q 28. Why is potassium permanganate thermally unstable at 513 K?

Ans. At 513 K, potassium permanganate undergoes disproportionation reaction. The products are more stable than the reactants.



Q 29. Name the transition metal which shows maximum number of oxidation states in the first transition series.

Ans. The element manganese (Mn) shows maximum number of oxidation states (+2, +3, +4, +5, +6 and +7).

Q 30. Which metal of the first transition series exhibits +1 oxidation state most frequently and why?

Ans. The element copper (Cu) shows +1 oxidation state most frequently. Its configuration is $(\text{Ar}) 3d^{10} 4s^1$. By losing one electron, it acquires a stable electronic configuration.

Q 31. Explain the following:

(i) Cu^+ is colourless and Cu^{2+} is coloured.

(ii) Zn shows only +2 oxidation state in its compounds.

Ans. (i) Cu^+ has $3d^{10}$ configuration (no d-d transition of electrons) while Cu^{2+} ion has $3d^9$ configuration (d-d transition is possible). As a result, Cu^+ is colourless and Cu^{2+} is coloured.

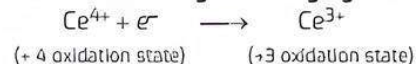
(ii) The configuration of Zn is $(\text{Ar}) 3d^{10} 4s^2$. By losing two electrons, Zn^{2+} ion has $(\text{Ar}) 3d^{10}$ configuration which is symmetrical. Zn^{2+} ion has no tendency to lose any more electrons. Therefore, Zn shows only +2 oxidation state in its compounds.

Q 32. Explain why is zinc not regarded as a transition element?

Ans. Zinc (Zn) is the last element of first transition series ($3d^{10}$ configuration). It does not fulfill the criteria of a transition element which must have incompletely filled d-orbitals in its ground state. Therefore, it is not a transition element.

Q 33. Explain why is Ce^{4+} ion a strong oxidising agent.

Ans.



Ce^{4+} ion is a strong oxidising agent because +3 oxidation state is more stable than +4 oxidation state.

Q 34. In the transition series of metals, the metal which exhibits the greatest number of oxidation states occurs in the middle of the series. Explain.

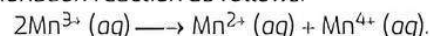
Ans. In the middle of the series (d^5 configuration), there is a participation of two ns electrons and five $(n-1)d$ electrons in the bond formation. Therefore, the elements in the middle of the transition series exhibit maximum oxidation state. (e.g., Mn present in 3d series).

Q 35. Metal-metal bonding is more extensive in the 4d and 5d series of transition elements than the 3d series. Explain.

Ans. Down the group in the transition metals, the atomic size increases. Therefore, electrons in element belonging to 4d and 5d series are less loosely held by the nucleus as compared to the elements present in the 3d series, but in the same group. The metal-metal bonding is more extensive or stronger. In other words, the metallic character increases down the group.

Q 36. Why does Mn(III) undergo disproportionation reaction easily?

Ans. Mn (III) is highly unstable as it is clear from its very $E^\circ_{\text{Mn}^{3+}/\text{Mn}^{2+}}$ value (+1.57 V). As such, it undergoes disproportionation reaction as follows:

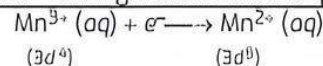


Q 37. Why is enthalpy of atomisation the lowest for Zn in 3d series of transition elements?

Ans. Zinc ($Z = 30$) has symmetrical electronic configuration $(\text{Ar})^{18} 4s^2 3d^{10}$. As a result d-d interactions are negligible and the metallic bonds are quite weak. The element has, therefore, lowest enthalpy of atomisation (126 kJ mol^{-1}) in the 3d transition series of elements.

Q 38. Out of Cr^{3+} and Mn^{3+} , which is a stronger oxidising agent and why?

Ans. Mn^{3+} is a strongest oxidising agent because after accepting an electron from the reducing agent, it acquires Mn^{2+} configuration which is quite stable.



Q 39. Name a member of the lanthanoid series which is well known to exhibit +2 oxidation state.

Ans. The element Europium ($Z = 63$) has a stable configuration: $(\text{Xe}) 4f^7 5d^0 6s^2$. By losing two electrons, it achieves a noble gas electronic configuration. The element, therefore, exhibits +2 oxidation state in its compounds.

Q 40. Silver atom has completely filled d -orbitals ($4d^{10}$) in its ground state, but it is still regarded as a transition metal. Explain.

Ans. The configuration of silver is $[\text{Kr}] 4d^{10} 5s^1$. It acquires $4d^{10}$ configuration by losing $5s^1$ electron. Moreover, the last electron is filled in the $4d$ subshell. Therefore, the element is regarded as a transition metal.



Short Answer Type-I Questions

Q 1. What do you mean by variable oxidation states? Explain it in context of transition elements.

Ans. **Variable Oxidation States:** When an element exhibits two or more than two oxidation states then the oxidation states are called Variable Oxidation States. With the exception of Zn and Cd of zinc group, all other transition elements exhibit variable oxidation states. This is because the energy difference between the energy of s -subshell of the outermost shell and d -subshell of penultimate shell is very less in case of these elements, so electrons of both the subshells can be used for bond formation.

For example, iron (Fe) exhibits + 2 and + 3 oxidation states and copper (Cu) exhibits + 1 and +2 oxidation states.

Q 2. Which elements are called actinoids? Write their main uses.

Ans. In the periodic table, actinium ($_{89}\text{Ac}$) and the 14 elements placed after it (from $_{90}\text{Th}$ to $_{103}\text{Lw}$) are called actinoids. This series is formed by the successive filling of electrons in f -subshell.

Uses: Important uses of these elements are as follows:

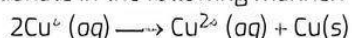
- These elements are highly reactive metals. Thus, they can be used as strong reductant.
- These are used for the formation of complex compounds.

Q 3. What are interstitial compounds? Why are such compounds well known for transition metals?

Ans. The compounds in which interstitial spaces in the crystal lattice are trapped by small atoms (like H, C or N), are called interstitial compounds. These are well known for transition metals because the small atoms like H, N or C get easily trapped in the voids present in crystal lattice of transition metals.

Q 4. Explain why Cu^+ ion is not stable aqueous solutions. (NCERT TEXT)

Ans. Cu^+ (aq) is more stable than Cu^{2+} (aq). This is because second ionisation enthalpy of copper is more, but for Cu^{2+} (aq), $\Delta_{\text{hyd}} H$ is more negative as compared to Cu^+ (aq). So it compensates more for the second ionisation enthalpy of copper. Thus, mostly copper (I) compounds are unstable in aqueous solution and disproportionate in the following manner:

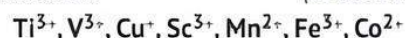


Q 5. Actinoid contraction is greater from element to element than lanthanoid contraction. Why?

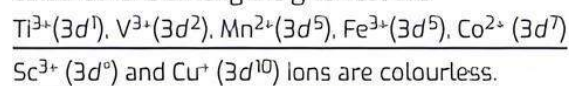
(NCERT TEXT)

Ans. The decrease or contraction in atomic radii as well as ionic radii in actinoid elements (actinoid contraction) is more as compared to lanthanoid contraction because $5f$ electrons have more poor shielding effect as compared to $4f$ electrons. Therefore, the effect of increased nuclear charge leading to contraction in size is more in case of actinoid elements.

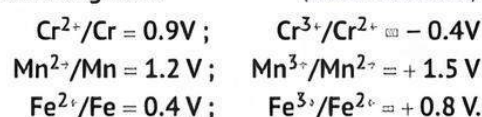
Q 6. Predict which of the following will be coloured in aqueous solution? (NCERT EXERCISE)



Ans. Only those ions will be coloured which have incomplete d -orbitals. The ions with either empty or filled d -orbitals are colourless. Keeping this in view, the coloured ions among the given list are:



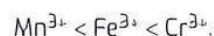
Q 7. For M^{2+}/M and $\text{M}^{3+}/\text{M}^{2+}$ systems, the E° values of some metals are given: (NCERT EXERCISE)



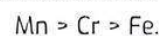
Use this data to comment upon:

- The stability of Fe^{3+} in acid solution as compared to that of Cr^{3+} or Mn^{3+} .
- The ease with which iron can be oxidised as compared to the similar process for either chromium or manganese metal. (NCERT EXERCISE)

Ans. (i) As $E^\circ_{\text{Cr}^{3+}/\text{Cr}^{2+}}$ is negative (-0.4V), this means that Cr^{3+} ions in solution cannot be reduced to Cr^{2+} ions or Cr^{3+} ions are very stable. As further comparison of E° values shows that Mn^{3+} ions can be reduced to Mn^{2+} ion more readily than Fe^{3+} ions. Thus, in the light of this, the order of relative stabilities of different ions is:

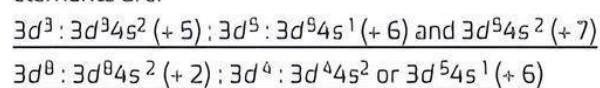


- From the E° values, the order of oxidation of the metal to the divalent cation is :



Q 8. What must be the stable oxidation state of the transition elements with the following electronic configuration in the ground states of their atoms: $3d^3, 3d^5, 3d^8, 3d^4$? (NCERT EXERCISE)

Ans. The maximum oxidation states of reasonable stability in the transition metals of $3d$ series correspond to the sum of s and d -electrons up to Mn. However, after Mn there is an abrupt decrease in oxidation states. In the light of this, most stable oxidation states of the elements are:



Q 9. To what extent do the electronic configurations decide the stability of oxidation states in the first series of the transition elements? Illustrate your answer with an example. (NCERT EXERCISE)

Ans. The presence of half filled or completely filled orbitals imparts stability to a particular element/ion. Greater the number of such orbitals, more will be the relative stability. For example, let us write the different oxidation states of Mn ($Z = 25$) along with the electronic configurations:

Mn ($Z = 25$) along with the electronic configurations.

Mn : $(\text{Ar}) 3d^5 4s^2$; Mn^{2+} : $(\text{Ar}) 3d^5$; Mn^{3+} : $(\text{Ar}) 3d^4$; Mn^{4+} : $(\text{Ar}) 3d^3$.

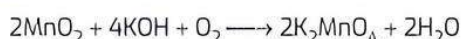
+2 oxidation state of the element is likely to be the most stable because the corresponding electronic configuration of Mn^{2+} is highly symmetrical (all the five 3d-orbitals are half filled).

Q 10. Silver has completely filled d-orbitals ($4d^{10}$) in its ground state. How can you say that it is a transition metal? (NCERT INTEXT)

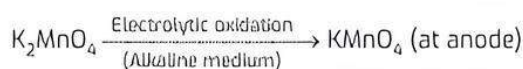
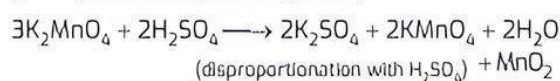
Ans. Silver ($Z = 47$) belongs to group 11 of d-block (Cu, Ag, Au) and its outer electronic configuration is $4d^{10} 5s^1$. It shows +1 oxidation state ($4d^{10}$ configuration) in silver halides (e.g. AgCl). However, it can also exhibit +2 oxidation state ($4d^9$ configuration) in compounds like AgF_2 and AgO. Due to the presence of half-filled d-orbital, silver is a transition metal.

Q 11. How is KMnO_4 prepared from pyrolusite? Give steps involved with equations. (CBSE 2019)

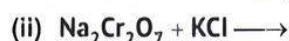
Ans. (i) When pyrolusite is fused with KOH in presence of air or oxidising agent, potassium manganate is produced.



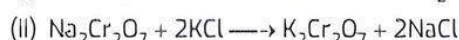
(ii) Potassium manganate upon further oxidation or disproportionation in a neutral or acidic medium gives potassium permanganate.



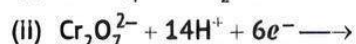
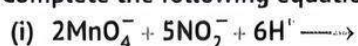
Q 12. Complete and balance the following equations: (CBSE 2019)



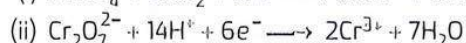
Ans. (i) $2\text{MnO}_4^- + 10\text{I}^- + 16\text{H}^+ \longrightarrow 2\text{Mn}^{2+} + 5\text{I}_2 + 8\text{H}_2\text{O}$



Q 13. Complete the following equations: (CBSE 2023)

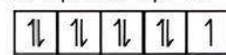
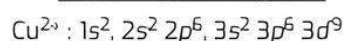


Ans. (i) $2\text{MnO}_4^- + 5\text{NO}_2^- + 6\text{H}^+ \longrightarrow 2\text{Mn}^{2+} + 5\text{NO}_3^- + 3\text{H}_2\text{O}$



Q 14. Explain paramagnetic and diamagnetic characteristics in transition elements with one example.

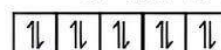
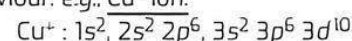
Ans. If d-subshell of the transition metal atom/ion contains unpaired electrons then they are paramagnetic. e.g. Cu^{2+} ion is paramagnetic.



One unpaired e^-

This ion contains one unpaired electron, so it is paramagnetic.

On the other hand, the transition metal atom/ion having no unpaired electron in d-subshell exhibits diamagnetic behaviour. e.g., Cu^+ ion.

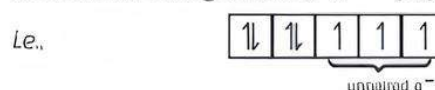


It contains no unpaired electrons, so it is diamagnetic.

Q 15. Calculate the 'spin only' magnetic moment of M^{2+} (aq) ion ($Z = 27$). (NCERT INTEXT)

Ans. Electronic configuration of atom $\text{M}(Z = 27) = (\text{Ar}) 3d^7 4s^2$.

\therefore Electronic configuration of $\text{M}^{2+} = (\text{Ar}) 3d^7$



Thus, it contains three unpaired electrons.

Spin only magnetic moment (μ) = $\sqrt{n(n+2)}$ B.M.

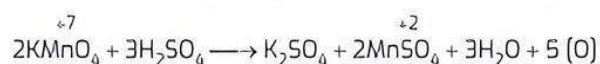
where, n = number of unpaired electrons.

$$= \sqrt{3(3+2)} = \sqrt{15} \text{ B.M.}$$

$$= 3.87 \text{ B.M.}$$

Q 16. Equivalent weight of KMnO_4 is different in acidic and basic medium. Why?

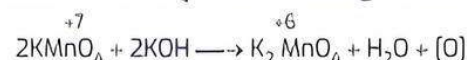
Ans. In acidic medium, KMnO_4 shows following reaction:



Thus, equivalent weight of KMnO_4

$$= \frac{\text{Molecular wt. of } \text{KMnO}_4}{\text{Oxidation change}} = \frac{39 + 55 + 64}{7 - 2} = \frac{158}{5} = 31.6$$

In alkaline medium, KMnO_4 shows following reaction:



Thus, equivalent weight of KMnO_4

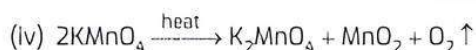
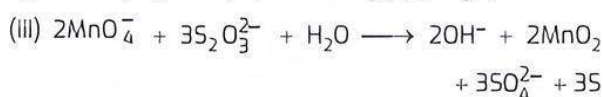
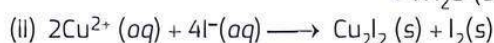
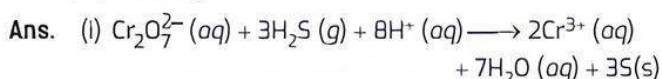
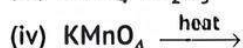
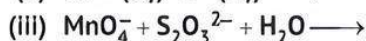
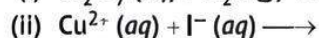
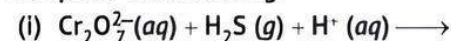
$$= \frac{39 + 55 + 64}{7 - 6} = \frac{158}{1} = 158$$

Q 17. What are alloys? Name an important alloy which contains some of the lanthanoid metals. Mention its use. (NCERT EXERCISE)

Ans. Alloys are the homogeneous mixtures of different metals which are obtained by mixing different metals. These are in fact, homogeneous solid solutions in which atoms of one metal are irregularly dispersed

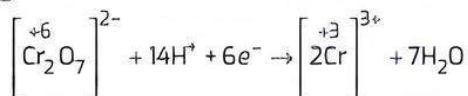
in between the atoms of another metal. This type of alloys are formed by the atoms, metallic radii of which have a difference of 15%. One such famous alloy is misch metal which contains 50% cerium, 25% lanthanum and traces of neodymium, praseodymium and other elements. Most of the misch metal is used in alloys based on magnesium which are used for making bullet for guns, armour or guard and light flint.

Q 18. Complete the following:



Q 19. $\text{K}_2\text{Cr}_2\text{O}_7$ is a good oxidising agent in acidic medium. Explain.

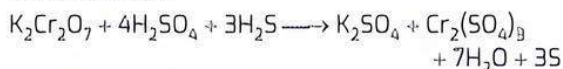
Ans. In acidic medium, Cr undergoes a decrease in oxidation state from +6 in $\text{Cr}_2\text{O}_7^{2-}$ ion to +3 in Cr^{3+} ion. Since +3 oxidation state is more stable than +6 oxidation state therefore, $\text{K}_2\text{Cr}_2\text{O}_7$ is a good oxidising agent in the acidic medium.



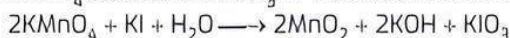
Q 20. (i) Write an oxidising reaction of $\text{K}_2\text{Cr}_2\text{O}_7$ in the acidic medium.

(ii) Write one oxidising reaction of KMnO_4 in the basic medium.

Ans. (i) $\text{K}_2\text{Cr}_2\text{O}_7$ oxidise H_2S to a sulphur (yellow ppt.) in the acidic medium.



(ii) KMnO_4 oxidise KI to KIO_3 in the basic medium.



Short Answer Type-II Questions

Q 1. Define transition metals. Why Zn, Cd and Hg are not called transition metals? How is the variability in oxidation states of transition metals different from that of p-block elements? (CBSE 2022 Term-2)

Ans. Transition metals are defined as metals which have incomplete d-subshell either in neutral atom or in their ions.

Zn, Cd and Hg have full d^{10} configuration in their ground state as well as in their common oxidation states and hence, are not regarded as transition metals.

In p-block, the lower oxidation states are favoured by the heavier members due to the inert pair effect whereas higher oxidation states are most stable for heavier elements in transition elements.

Q 2. Give reasons for the following statements:

(i) Transition elements and their compounds act as good catalysts.

(ii) $E^\circ(\text{Mn}^{2+}/\text{Mn})$ value is highly negative as compared to other elements.

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

(CBSE 2022 Term-2)

Ans. (i) Transition elements have the ability to adopt multiple oxidation states and to form complexes which makes them a good catalyst.

(ii) $E^\circ_{(\text{Mn}^{2+}/\text{Mn})}$ value is highly negative as compared to other elements due to stability of half-filled d subshell (d^5).

(iii) 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. Therefore, Cr^{2+} acts as a strong reducing agent.

Q 3.

$E^\circ_{\text{M}^{2+}/\text{M}}$	Cr	Mn	Fe	Co	Ni	Cu	Zn
	-0.91	-1.18	-0.44	-0.28	-0.25	-0.34	-0.76

From the given E° values of the first row transition elements, answer the following questions:

(i) Why is $E^\circ_{\text{Mn}^{2+}/\text{Mn}}$ value highly negative as compared to other elements?

(ii) What is the reason for the irregularity in the above E° values?

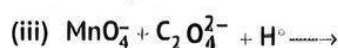
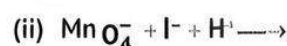
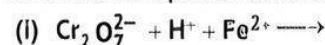
(iii) Why is $E^\circ_{\text{Cu}^{2+}/\text{Cu}}$ value exceptionally positive? (CBSE 2022 Term-2)

Ans. (i) E° value of $(\text{Mn}^{2+}/\text{Mn})$ is highly negative as compared to other elements due to the greater stability of half-filled d-subshell of $\text{Mn}^{2+}(3d^5)$.

(ii) The $E^\circ_{\text{M}^{2+}/\text{M}}$ values are not regular which can be explained from the irregular variation of ionisation enthalpies ($\Delta_1H_1 + \Delta_2H_2$) and also the sublimation enthalpies which are relatively much less for manganese and vanadium.

(iii) Copper has high enthalpy of atomisation (Δ_aH°) and low enthalpy of hydration ($\Delta_{\text{hyd}}H^\circ$). Since the high energy to transform $\text{Cu}(\text{s})$ to $\text{Cu}^{2+}(\text{aq})$ is not balanced by hydration enthalpy, therefore, $E^\circ_{\text{Cu}^{2+}/\text{Cu}}$ value is exceptionally positive.

Q 4. Complete the following chemical equation for reactions in aqueous solution.

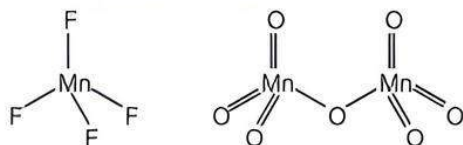


- Ans. (i) $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{Fe}^{2+} \longrightarrow 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 7\text{H}_2\text{O}$
 (ii) $2\text{MnO}_4^- + 16\text{H}^+ + 10\text{I}^- \longrightarrow 2\text{Mn}^{2+} + 5\text{I}_2 + 8\text{H}_2\text{O}$
 (iii) $2\text{MnO}_4^- + 5\text{C}_2\text{O}_4^{2-} + 16\text{H}^+ \longrightarrow 2\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O}$

Q 5. Give reasons for the following:

- Mn^{3+} is a good oxidising agent.
- $E^\circ_{\text{M}^{2+}/\text{M}}$ values are not regular for first row transition metals (3d series).
- Although 'F' is more electronegative than 'O', the highest fluoride of Mn is MnF_4 while the highest oxide is Mn_2O_7 . (CBSE 2015)

- Ans. (i) Mn^{3+} is a good oxidising agent because $E^\circ_{\text{Mn}^{3+}/\text{Mn}^{2+}}$ is very high (+1.57 V). As a result, Mn^{3+} ion can be easily reduced to Mn^{2+} ion by accepting an electron. Therefore, it is a good oxidising agent.
 (ii) It is due to the reason that, the variation in the value of enthalpy of atomisation and enthalpy of hydration for M^{2+} ions are not quite regular.
 (iii) It is probably due to the reason that the element oxygen can form multiple bonds with the transition metals, but fluorine cannot do so. As a result, the element Mn exhibits +4 oxidation state in MnF_4 and +7 oxidation state in Mn_2O_7 .



Q 6. Give reasons for the following statements:

- Copper does not displace hydrogen from acids.
- Transition metals and most of their compounds show paramagnetic behaviour.
- Zn, Cd and Hg are soft metals. (CBSE 2022 Term-2)

- Ans. (i) Copper does not displace hydrogen from acids because Cu has positive E° value, i.e., it is less reactive than hydrogen whose E° value is 0.0V.
 (ii) Transition metals and most of their compounds show paramagnetic behaviour due to the presence of one or more unpaired electrons in d subshell.
 (iii) Zn, Cd and Hg have completely filled d-orbitals in the ground state as well as in their common oxidation states. Thus, due to absence of any unpaired electrons and weak metal-metal bonding, they are soft in nature.

Q 7. Give reasons for the following:

- The only oxidation state shown by scandium is +3.
- $[\text{Ti}(\text{H}_2\text{O})_6]^{4+}$ is colourless.
- MnO is basic while Mn_2O_7 is acidic. (CBSE 2019)

- Ans. (i) Sc (21) has electronic configuration: $[\text{Ar}]3d^14s^2$

It has 3 electrons in its outer orbitals. So, to gain d^0 electronic configuration, it has the tendency to lose these 3 electrons. At +3 oxidation state, stable d^0 is obtained.

- $[\text{Ti}(\text{H}_2\text{O})_6]^{4+}$ is colourless and it cannot undergo d-d transition as it does not have unpaired electrons. So, it is colourless.
- 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, MnO (oxidation state +2) is basic whereas Mn_2O_7 (oxidation state +7) is acidic.

Q 8. Answer the following:

- What is the general electronic configuration of lanthanoids?
- What are the common oxidation states of cerium (At. no. 58)?
- Why do actinoids show a wide range of oxidation states?

- Ans. (i) The general electronic configuration of lanthanoids is $[\text{Xe}] 4f^{1-14} 5d^{0-1} 6s^2$.
 (ii) The common oxidation states of cerium (At. no. 58) are +3 and +4.
 (iii) There is a greater range of oxidation states in actinoids. It is due to the fact that 5f, 6d and 7s levels are of comparable energies.

Q 9. Give reasons for the following statements:

- Scandium ($Z = 21$) is a transition element, but Zn ($Z = 30$) is not.
- $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is coloured while $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$ is colourless.
- Physical and chemical properties of the 4d and 5d series of the transition elements are quite similar than expected. (CBSE 2022 Term-2)

- Ans. (i) Scandium has incompletely filled d orbitals ($3d^1$) in its ground state, so it is regarded as a transition element. On the other hand, zinc 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.
 (ii) Ti in $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is in +3 oxidation state and Sc in $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$ is in +3 oxidation state. Ti^{3+} has one unpaired electron in 3d orbital to undergo d-d transition by absorbing light from visible region and radiating complementary colour. Therefore, $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is coloured. Sc^{3+} does not contain unpaired electrons to undergo d-d transition. Therefore, $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$ is colourless.
 (iii) This is because 4d and 5d series elements have virtually the same atomic and ionic radii due to lanthanide contraction.



Q 10. Account for the following:

- CuCl_2 is more stable than Cu_2Cl_2 .
- Atomic radii of 4d and 5d series elements are nearly same.
- Hydrochloric acid is not used in permanganate titrations. (CBSE 2017)

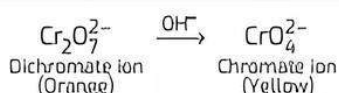
- Ans. (i) In CuCl_2 , Cu is in +2 oxidation state which is more stable due to high hydration enthalpy as compared to Cu_2Cl_2 in which Cu is in +1 oxidation state.
- (ii) Atomic radii of 4d and 5d series elements are nearly same due to lanthanoid contraction.
- (iii) Hydrochloric acid (HCl) is not used in permanganate titrations because HCl is oxidised to chlorine.

Note: The lanthanide contraction is greater than expected decrease in ionic radii of the elements in the lanthanide series.

Q 11. Account for the following:

- Eu^{2+} is a strong reducing agent.
- Orange colour of dichromate ion changes to yellow in alkaline medium.
- $E^\circ_{(M^{2+}/M)}$ values for transition metals show irregular variation. (CBSE 2017)

- Ans. (i) Eu^{2+} having electronic configuration $(\text{Xe})4f^7$ is a strong reducing agent because in the aqueous solution, it reverts back to the most stable +3 oxidation state, i.e. Eu^{3+} .
- (ii) When orange solution containing $\text{Cr}_2\text{O}_7^{2-}$ (dichromate ion) is treated with an alkali, a yellow solution of CrO_4^{2-} (chromate ion) is obtained.



- (iii) ns and $(n-1)d$ electrons of transition metal have very little difference in the energies and hence both can participate in bonding, which results in variable oxidation states. When ns electrons take part in bonding, they exhibit lower oxidation states whereas $(n-1)d$ electrons along with ns electrons participate in bonding, they exhibit variable oxidation states.

- Q 12. (i) Write any two consequences of lanthanoid contraction.
- (ii) Name the element of 3d series which exhibits the largest number of oxidation states. Give reason. (CBSE 2022 Term-2)

- Ans. (i) **Consequences of Lanthanoid Contraction:**
- Due to lanthanoid contraction, the third transition series atom has roughly the same size (atomic and ionic radii) as the second transition series atom.
 - Due to lanthanoid contraction, the basic strength of oxides and hydroxides of lanthanoids decrease with increase in atomic number.

- (ii) Manganese ($3d^5 4s^2$) has maximum number of electrons to lose or share (all the 3d electrons are unpaired). Hence, it exhibits the largest number of oxidation states (from +2 to +7).

Q 13. (i) Which ion amongst the following is colourless and why?



(Atomic number of Ti = 22, Cr = 24, V = 23)

- Why is Mn^{2+} much more resistant than Fe^{2+} towards oxidation?
- Highest oxidation state of a metal is shown in its oxide or fluoride only. Justify the statement. (CBSE 2022 Term-2)

- Ans. (i) Electronic configuration of given ions is:
 $\text{Ti}^{4+} = [\text{Ar}] 3d^0 4s^0$; $\text{Cr}^{3+} = [\text{Ar}] 3d^3 4s^0$ and $\text{V}^{3+} = [\text{Ar}] 3d^2 4s^0$
 Since, Ti^{4+} does not contain unpaired electrons to undergo $d-d$ transition, it is colourless.
- (ii) Electronic configuration of $\text{Mn}^{2+} = [\text{Ar}] 3d^5$
 Electronic configuration of $\text{Fe}^{2+} = [\text{Ar}] 3d^6$
 Mn^{2+} has stable d^5 (half-filled) configuration while Fe^{2+} has $3d^6$ configuration and by losing one e^- , its configuration change to more stable $3d^5$ configuration.
 Therefore, Mn^{2+} is much more resistant than Fe^{2+} towards oxidation.
- (iii) Oxygen and fluorine act as strong oxidising agents because of their small size and high electronegativity. Hence, a transition metal exhibits highest oxidation state in its oxide or fluoride.



Long Answer Type Questions

Q 1. Explain the following observation:

- d-block elements exhibit more oxidation states as compared to elements of f-block.
- Cu^+ salts are colourless, whereas Cu^{2+} salts are coloured. (Atomic number of Cu = 29).
- Mn^{2+} ion is more stable than Mn^{3+} ion.
- Transition elements form several complex compounds.
- Zn^{2+} salts are white whereas Cu^{2+} salts are blue.

- Ans. (i) d-block elements contain a large number of unpaired electrons which take part in bond formation. Because of this, effective nuclear charge is less. So, they exhibit more number of oxidation states as compared to f-block elements. In f-block, effective nuclear charge becomes more effective due to weak shielding effect of f-orbitals and hence, less electrons take part in bond formation.
- (ii) Cu^+ ion does not have unpaired electron, so it can not exhibit $d-d$ transition. Thus, Cu^+ salts are colourless. Cu^{2+} salts are coloured because they have an unpaired electron, so they can show $d-d$ transition. They scatter blue colour by absorbing light from visible region.

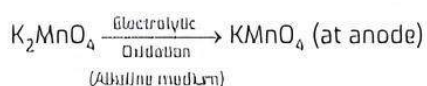
- (iii) $\text{Mn}^{2+} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5$ (half-filled) whereas in Mn^{3+} , d-subshell of third shell is incomplete.
 $\text{Mn}^{3+} = 1s^2, 2s^2, 2p^6, 3s^2 3p^6 3d^4$ (incomplete)
 Half filled subshell ($3d^5$) is more stable than partially filled subshell ($3d^4$). So, Mn^{2+} ion is more stable than Mn^{3+} ion.
- (iv) Transition elements form a large number of complex compounds. This is because of:
 (a) Their small size and high charge density.
 (b) The availability of vacant subshells.
 (c) Their different oxidation states.
- (v) $\text{Zn}^{2+} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}$
 In this configuration, d-subshell is completely filled due to which the salt is colourless or white whereas,
 $\text{Cu}^{2+} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^9$
 In this configuration, d-subshell is partially filled due to which the salt is coloured or blue.

Q 2. (i) Account for the following:

- (a) Transition metals form complex compounds.
 (b) The $E^\circ_{\text{Mn}^{2+}/\text{Mn}}$ values for manganese is highly negative whereas $E^\circ_{\text{Mn}^{3+}/\text{Mn}^{2+}}$ is highly positive.
 (c) Cu^+ ion is unstable in aqueous solution.
- (ii) Write the equations involved in the preparation of KMnO_4 from pyrolusite ore (MnO_2).

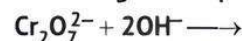
(CBSE 2023)

- Ans. (i) (a) Due to the comparatively smaller size of the metal ions, high ionic charges and the availability of vacant d-orbitals for bond formation, transition metals form a large number of complex compounds.
- (b) $E^\circ_{\text{Mn}^{2+}/\text{Mn}}$ value is highly negative for manganese due to the greater stability of half-filled d-subshell of $\text{Mn}^{2+}(3d^5)$ whereas, $E^\circ_{\text{Mn}^{3+}/\text{Mn}^{2+}}$ is highly positive due to the fact that $\text{Mn}^{2+}(d^5)$ is quite stable.
- (c) Cu^+ (aq) is more stable than Cu^{2+} (aq). This is because second ionisation enthalpy of copper is more, but for Cu^{2+} (aq), $\Delta_{\text{hyd}} H$ is more negative as compared to Cu^+ (aq). So it compensates more for the second ionisation enthalpy of copper. Thus, mostly copper (I) compounds are unstable in aqueous solution and disproportionate in the following manner:
 $2\text{Cu}^+ (\text{aq}) \longrightarrow \text{Cu}^{2+} (\text{aq}) + \text{Cu}(\text{s})$
- (ii) The equations involved in the preparation of KMnO_4 from pyrolusite ore (MnO_2) are as under:
 $2\text{MnO}_2 + 4\text{KOH} + \text{O}_2 \longrightarrow 2\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O}$
 $3\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{SO}_4 \longrightarrow 2\text{K}_2\text{SO}_4 + 2\text{KMnO}_4 + 2\text{H}_2\text{O}$
Disproportionation+ MnO_2



Q 3. (i) Account for the following:

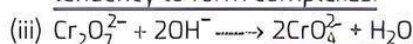
- (a) Transition metals form alloys.
 (b) Ce^{4+} is a strong oxidising agent.
 (ii) Write one similarity and one difference between chemistry of Lanthanoids and Actinoids.
 (iii) Complete the following ionic equation:



- Ans. (i) (a) Transition metals have similar atomic sizes due to which one metal can easily replace the other metal from its lattice to form alloy. Also transition metals are miscible with one another in the molten state which on cooling forms an alloy.
- (b) $\text{Ce}^{4+} + e^- \longrightarrow \text{Ce}^{3+}$
 (≈ 4 oxidation state) (≈ 3 oxidation state)
 Ce^{4+} ion is a strong oxidising agent because +3 oxidation state is more stable than +4 oxidation state.

- (ii) **Similarity:** Both lanthanoid and actinoid elements show a common oxidation state +3 and both are electropositive and very reactive.

Difference: Lanthanoid have less tendency to form complexes whereas actinoids have greater tendency to form complexes.



Q 4. (i) Identify the following:

- (a) Transition metal of 3d series that exhibits only one oxidation state.
 (b) Transition metal of 3d series that acts as a strong reducing agent in +2 oxidation state in aqueous solution.
- (ii) Complete and balance the following equations:
 (a) $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{Fe}^{2+} \longrightarrow$
 (b) $\text{KMnO}_4 \xrightarrow{\text{heat}}$ (CBSE 2023)
- (iii) What is Misch metal? Write its one use.

- Ans. (i) (a) Cu is a transition metal of 3d series that exhibits only one oxidation state.
 (b) Cr is the strongest reducing agent in +2 oxidation state.
- (ii) (a) $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{Fe}^{2+} \longrightarrow 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 7\text{H}_2\text{O}$
 (b) $2\text{KMnO}_4 \xrightarrow{\text{heat}} \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2 \uparrow$
- (iii) Misch metal is an alloy that consists of a lanthanoid metal (-95%) and iron (-5%) and traces of S, C, Ca and Al
It is used in Mg-based alloy to produce bullets, shell and lighter flint.

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 $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple is highly positive (+ 1.57 V) as compared to $\text{Cr}^{3+}/\text{Cr}^{2+}$.

(CBSE 2017)

(ii) Write one similarity and one difference between the chemistry of lanthanoid and actinoid elements.

- Ans. (i) (a) Transition metals have very little difference between ns and $(n-1)d$ electrons and hence both can participate in bonding, which results in variable oxidation states. When ns electrons take part in bonding, they exhibit lower oxidation states whereas when $(n-1)d$ electrons along with ns electrons participate in bonding, they exhibit variable oxidation states.
- (b) In Zn, Cd and Hg, all the electrons in d -subshell are paired. Hence, weak metallic bonds are present in them. This is the reason, they are soft metals with low melting and boiling points.
- (c) The comparatively high E° value for Mn^{3+}/Mn^{2+} is due to the fact that Mn^{2+} (d^5) is quite stable whereas comparatively low value for Cr^{3+}/Cr^{2+} is because of the extra stability of Cr^{3+} . Therefore, Cr^{3+} cannot be reduced to Cr^{2+} .
- (ii) **Similarity:** Both lanthanoid and actinoid elements show a common oxidation state +3 and both are electropositive and very reactive.
- Difference:** Lanthanoids have less tendency to form complexes whereas actinoids have greater tendency to form complexes.

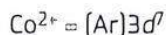
Q 6. (i) Account for the following:

- (a) Copper (I) compounds are white whereas Copper (II) compounds are coloured.
- (b) Chromates change their colour when kept in an acidic solution.
- (c) Zn, Cd, Hg are considered as d -block elements, but not as transition elements.

(ii) Calculate the spin-only moment of Co^{2+} ($Z = 27$) by writing the electronic configuration of Co and Co^{2+} . (CBSE 2020)

- Ans. (i) (a) Cu^+ ($3d^{10}$) compounds are white because of absence of unpaired electrons while Cu^{2+} ($3d^9$) compounds are coloured due to unpaired electrons and they show $d-d$ transition.
- (b) Chromates change their colour when kept in an acidic solution; because they change to dichromates (Cr_2).
- (c) Zn, Cd and Hg are considered as d -block elements, but not as transition elements due to completely filled d -orbitals in their ground state as well as in excited state.

(ii) Electronic configuration of Co ($Z = 27$) = $[Ar] 3d^7 4s^2$



By the electronic configuration of Co^{2+} ion, it is clear that it has 3 unpaired electrons. Hence,

Spin-only moment of Co^{2+} , $\mu = \sqrt{n(n+2)}$

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

$$= 3.92 \text{ B.M.}$$

Q 7. Answer the following:

- (i) Why are all copper halides known except that copper iodide?
- (ii) Why is the $E^\circ_{(V^{3+}/V^{2+})}$ value for vanadium comparatively low?
- (iii) Why HCl should not be used for potassium permanganate titrations?
- (iv) Explain the observation, at the end of each period, there is a slight increase in the atomic radius of d block elements.
- (v) What is the effect of pH on dichromate ion solution?

- Ans. (i) All copper halides are known except that copper iodide because Cu^{2+} oxidizes iodide ion to form iodine but copper iodide is not formed whereas other halogens combine to form copper halides.
- (ii) The comparatively low E° value for Vanadium is due to the stability of V^{2+} (half-filled t^2g level).
- (iii) Potassium permanganate titrations in presence of hydrochloric acid are unsatisfactory since hydrochloric acid is oxidised to chlorine. Hence, HCl should not be used for potassium permanganate titrations.
- (iv) The d orbital is complete when it gets filled with ten electrons and then it shields the electrons present in the higher s -orbital to a greater extent resulting in increase in size. So, there is a slight increase in the atomic radius of d block elements at the end of each period.
- (v) The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution. On increasing the pH (in basic solution) of dichromate ions, a colour change from orange to yellow is observed as dichromate ions change to chromate ions.

Q 8. (i) Give three points of difference between lanthanoids and actinoids.

- (ii) Give reason and select one atom/ion which will exhibit asked property:
- (a) Sc^{3+} or Cr^{3+} (Exhibit diamagnetic behaviour)
- (b) Cr or Cu (High melting and boiling point)

(CBSE 2020)

Ans. (i) Difference between Lanthanoids and Actinoids

S. No.	Lanthanoids	Actinoids
1.	Most of the lanthanoids are <u>non-radioactive</u> .	All actinoids are <u>radioactive elements</u> .
2.	They <u>do not show a wide range of oxidation states</u> .	They show a <u>wide range of oxidation states</u> .
3.	Most of their ions are <u>colourless</u> .	Most of their ions are <u>coloured</u> .

(ii) (a) Sc^{3+} ; because of absence of unpaired electrons.

(b) Cr; because of presence of strong intermetallic bonding than Cu.



Q 9. (i) Following are the transition metal ions of 3d series:



(Atomic numbers: Ti = 22, V = 23, Mn = 25, Cr = 24)

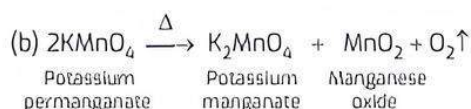
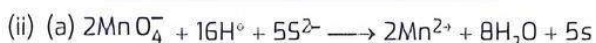
Answer the following:

- Which ion is most stable in an aqueous solution and why?
- Which ion is a strong oxidising agent and why?
- Which ion is colourless and why?

(ii) Complete the following equations:



- Ans. (i) (a) Out of the given four ions, Cr^{3+} is most stable due to crystal field splitting theory. In Cr^{3+} , t_{2g} is half-filled. Hence, it is most stable among the given other ions.
- (b) Out of the given four ions, Mn^{3+} is strongest oxidising agent because Mn^{3+} can easily be changed into Mn^{2+} which has d^5 configuration. It is a stable half-filled configuration.
- (c) Out of the given four ions, Ti^{4+} is colourless because it has no unpaired electrons for excitation to the higher energy level.



Q 10. (i) Account for the following:

- Transition metals form large number of complex compounds.
- The lowest oxide of transition metal is basic whereas the highest oxide is amphoteric or acidic.
- E° value for the $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple is highly positive (+ 1.57 V) as compared to $\text{Cr}^{3+}/\text{Cr}^{2+}$.

(ii) Write one similarity and one difference between the chemistry of lanthanoid and actinoid elements. (CBSE 2017)

- Ans. (i) (a) Due to the comparatively smaller size of the metal ions, high ionic charges and the availability of vacant d-orbitals for bond formation, transition metals form a large number of complex compounds.
- (b) In lower oxidation states, transition metals behave like metals and metal oxides are basic in nature. Thus, in lower oxidation states, transition metal oxides are basic. As the oxidation state increases, its metallic character decreases due to decrease in size, thus, it becomes less metallic or more non-metallic. Oxides of a non-metal may be acidic or neutral. Thus, in higher oxidation states transition metal oxides are amphoteric or acidic.

(c) The comparatively high E° value for $\text{Mn}^{3+}/\text{Mn}^{2+}$ is due to the fact that Mn^{2+} (d^5) is quite stable where, as comparatively low value for $\text{Cr}^{3+}/\text{Cr}^{2+}$ is because of the extra stability of Cr^{3+} . Therefore, Cr^{3+} cannot be reduced to Cr^{2+} .

(ii) **Similarity:** Both lanthanoid and actinoid elements show a common oxidation state + 3 and both are electropositive and very reactive.

Difference: Lanthanoid have less tendency to form complexes whereas actinoids have greater tendency to form complexes.

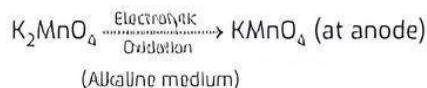
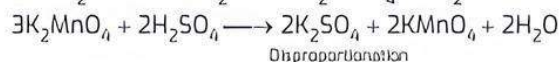
Q 11. (i) Account for the following:

- E° value for $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple is much more positive than that for $\text{Cr}^{3+}/\text{Cr}^{2+}$.
- Sc^{3+} is colourless whereas Ti^{3+} is coloured in an aqueous solution.
- Actinoids show wide range of oxidation states.

(ii) Write the chemical equations for the preparation of KMnO_4 from MnO_2 .

- Ans. (i) (a) The comparatively high E° value for $\text{Mn}^{3+}/\text{Mn}^{2+}$ is due to the fact that Mn^{2+} (d^5) is quite stable whereas comparatively low value for $\text{Cr}^{3+}/\text{Cr}^{2+}$ is because of the extra stability of Cr^{3+} . Therefore, Cr^{3+} cannot be reduced to Cr^{2+} .
- (b) Sc^{3+} does not contain unpaired electrons to undergo $d-d$ transition. So, it is colourless. Ti^{3+} has one unpaired electron in 3d orbital to undergo $d-d$ transition by absorbing light from visible region and radiating complementary colour. So, Ti^{3+} is coloured in an aqueous solution.
- (c) There is a greater range of oxidation states in actinoids. It is due to the fact that 5f, 6d and 7s levels are of comparable energies.

(ii) The chemical equations for the preparation of KMnO_4 from MnO_2 are:



Q 12. (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?

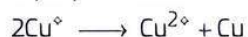
(c) Orange colour of $\text{Cr}_2\text{O}_7^{2-}$ ion changes to yellow colour when treated with an alkali. Why?

(ii) Chemistry of actinoids is complicated as compared to lanthanoids. Give two reasons.

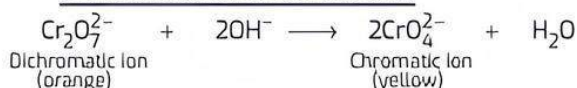
(CBSE 2017)

Ans. (i) (a) The variability in oxidation states of transition metal is due to the incomplete filling of d -orbitals in such a way, that their oxidation states differ from each other by unity, for example, Fe^{2+} and Fe^{3+} etc. In case of p -block elements, the oxidation state differ by units by two, for example, $+3$ and $+5$. Moreover, in transition elements, the higher oxidation states are more stable for heavier elements in a group. For example, Mo^{6+} is more stable than Cr^{4+} . In p -block elements, the lower oxidation states are more stable for heavier members due to inert pair effect, for example, Pb^{2+} is more stable than Pb^{4+} .

(b) Cu^+ ion is unstable in aqueous solution than Cu^{2+} . This is because, although second ionisation enthalpy of copper is large, but hydration enthalpy for Cu^{2+} is much more negative than that for Cu^+ and hence, it is more than compensates for the second ionisation enthalpy of copper. Therefore, many Cu^+ compounds are unstable in aqueous solution and undergo disproportionation.



(c) Orange colour of $\text{Cr}_2\text{O}_7^{2-}$ ion changes to yellow colour when treated with an alkali because of the formation of chromate ions.



(ii) Chemistry of actinoids is complicated as compared to lanthanoids because:

(a) Actinoids show a wide range of oxidation states i.e., $+3$, $+4$, $+5$, and $+6$ due to small energy difference between $5f$, $6d$ and $7s$ subshells of actinoids.

(b) Actinoids are radioactive due to which, their chemistry is complicated.

Q 13. (i) Account for the following:

(a) Zn^{2+} salts are colourless while Ni^{2+} salts are coloured.

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

(c) Transition metals and their compounds show catalytic activities.

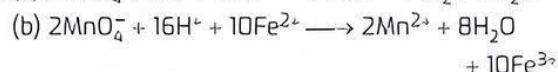
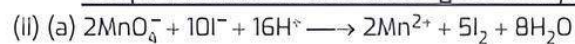
(ii) Write the ionic equations for the oxidizing action of MnO_4^- in acidic medium with (CBSE 2023)

(a) I^- ion, and (b) Fe^{2+} ion.

Ans. (i) (a) Zn^{2+} with configuration $(\text{Ar})^{18} 3d^{10}$ has all filled orbitals. Therefore, its salts are colourless. Ni^{2+} with configuration $(\text{Ar})^{18} 3d^8$ has some half-filled orbitals. Therefore, its salts are coloured.

(b) 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. Therefore, Cr^{2+} acts as a strong reducing agent.

(c) Transition elements have the ability to adopt multiple oxidation states and to form complexes which makes them a good catalyst.



Q 14. Assign reason for each of the following:

(i) Manganese exhibits the highest oxidation state of $+7$ among the $3d$ series of transition elements.

(ii) Transition metals and their compounds are generally found to be good catalysts in chemical reactions.

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

(iv) Zn has lowest enthalpy of atomisation.

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

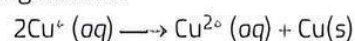
Ans. (i) Manganese ($Z = 25$, electronic configuration = $(\text{Ar}) 3d^5 4s^2$) contains five unpaired electrons in $3d$ orbital and 2 electrons in $4s$ orbital. So, it exhibits oxidation states from $+2$ to $+7$, which is the largest number of oxidation state exhibited in $3d$ series.

(ii) This is due to their variable valency and complex forming tendency. Bonds are formed between the reactant molecules and surface atoms of the catalyst at its solid surface. For the bond formation, metals of first transition series use $3d$ and $4s$ electrons. So, the reactant concentration at the catalyst surface increases and the bonds present between reactant molecules become weak leading to decrease in the value of activation energy. Thus, transition metals are found to be good catalysts in chemical reactions.

(iii) Cr^{2+} is reducing as its configuration changes from d^4 to d^3 which is a more stable configuration. Mn^{3+} is oxidising as it changes to Mn^{2+} resulting in the half filled d^5 configuration which has extra stability.

(iv) Zinc ($Z = 30$) has symmetrical electronic configuration $(\text{Ar})^{18} 4s^2 3d^{10}$. As a result $d-d$ interactions are negligible and the metallic bonds are quite weak. The element has, therefore, lowest enthalpy of atomisation (126 kJ mol^{-1}) in the $3d$ transition series of elements.

(v) Cu^+ (aq) is more stable than Cu^{2+} (aq). This is because second ionisation enthalpy of copper is more, but for Cu^{2+} (aq), $\Delta_{\text{hyd}} H$ is more negative as compared to Cu^+ (aq). So it compensate more for the second ionisation enthalpy of copper. Thus, mostly copper (I) compounds are unstable in aqueous solution and disproportionate in the following manner:



- Q 15. (i) Name two oxometal anions of the 3d series of the transition metals in which the metal exhibits the oxidation state equal to its group number.
 (ii) What is the effect of increasing pH on a solution of $K_2Cr_2O_7$?
 (iii) Why is Cu^+ not stable in aqueous solution?
 (iv) Name a member of Lanthanoid series which is well-known to exhibit +4 oxidation state.
 (v) Name two elements of 3d series which show anomalous electronic configuration.

Ans. (i) The two oxometal anions are MnO_4^- and CrO_4^{2-} . Mn has +7 oxidation number and group number is 7. Cr has +6 oxidation state and group number is 6.
 (ii) On increasing the pH, $K_2Cr_2O_7$ changes into K_2CrO_4 i.e. orange colour changes to yellow in alkaline medium.
 (iii) $Cu(I)$ compounds involving Cu^+ ions are unstable in aqueous solution and undergo disproportionation.

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

 The stability of Cu^{2+} ions as compared to Cu^+ ion is due to more negative $\Delta_{hyd}H^\circ$ of Cu^{2+} (aq) than Cu^+ (aq) which compensates the second ionisation enthalpy of Cu involved in the formation of Cu^{2+} ion.
 (iv) Cerium – $Ce(Xe) 4f^0 5d^0 6s^2$
 Formation of Ce^{4+} is favoured by its noble gas configuration i.e. $Ce(Xe) 4f^0 5d^0 6s^0$.
 (v) Cr and Cu are the elements of 3d series which show anomalous electronic configuration.

Q 16. Attempt any five of the following:

- (i) Which of the following ions will have a magnetic moment value of 1.73 BM?
 Sc^{3+} , Ti^{3+} , Ti^{2+} , Cu^{2+} , Zn^{2+}
 (ii) In order to protect iron from corrosion, which one will you prefer as a sacrificial electrode, Ni or Zn? Why? (Given standard electrode potentials of Ni, Fe and Zn are -0.25 V, -0.44 V and -0.76 V respectively.)
 (iii) The second ionization enthalpies of chromium and manganese are 1592 and 1509 kJ/mol respectively. Explain the lower value of Mn.
 (iv) Give two similarities in the properties of Sc and Zn.
 (v) What is actinoid contraction? What causes actinoid contraction?
 (vi) What is the oxidation state of chromium in chromate ion and dichromate ion?
 (vii) Write the ionic equation for reaction of KI with acidified $KMnO_4$. (CBSE SQP 2023-24)

Ans. (i) Both Ti^{3+} and Cu^{2+} have 1 unpaired electron, so the magnetic moment for both will be 1.73 BM.
 (ii) Zn, it has a more negative electrode potential so will corrode itself in place of iron.
 (iii) Mn^+ has $3d^5 4s^1$ configuration and configuration of Cr^+ is $3d^5$, therefore, ionisation enthalpy of Mn^+ is lower than Cr^+ .

- (iv) Sc and Zn both form colourless compounds and they are diamagnetic.
 (v) The decrease in the atomic and ionic radii with increase in atomic number of actinoids is actinoid contraction. It is caused due to poor shielding effect of 5f electron.
 (vi) In both chromate and dichromate ion, the oxidation state of Cr is +6.
 (vii) $10I^- + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5I_2$
 (Any five)

Q 17. What can be inferred from the magnetic moment values of the following complex species?

Example	Magnetic moment (BM)
(i) $K_4[Mn(CN)_6]$	2.2
(ii) $[Fe(H_2O)_6]^{2+}$	5.3
(iii) $K_2[MnCl_4]$	5.9 (NCERT EXERCISE)

Ans. The magnetic moment of a compound is given by the relation $\mu = \sqrt{n(n+2)}$ B.M., where n is the number of unpaired electrons.

For one unpaired electron ($n = 1$):

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

For two unpaired electrons ($n = 2$):

$$\mu = \sqrt{2(2+2)} = \sqrt{8} = 2.83 \text{ B.M.}$$

For three unpaired electrons ($n = 3$):

$$\mu = \sqrt{3(3+2)} = \sqrt{15} = 3.87 \text{ B.M.}$$

For four unpaired electrons ($n = 4$):

$$\mu = \sqrt{4(4+2)} = \sqrt{24} = 4.9 \text{ B.M.}$$

For five unpaired electrons ($n = 5$):

$$\mu = \sqrt{5(5+2)} = \sqrt{35} = 5.92 \text{ B.M.}$$

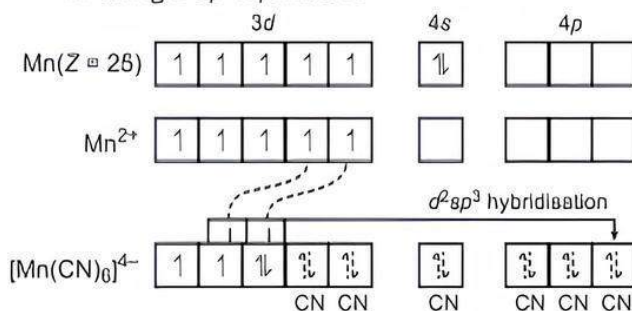
In the light of the above value, let us gather the desired information about the complex species that are mentioned.

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

Oxidation state of Mn: $[Mn(CN)_6]^{4-}$,

$$x + 6(-1) = -4 \text{ or } x = -4 + 6 = +2$$

The magnetic value of 1.73 B.M., indicates the presence of one unpaired electron in the complex. When six CN^- ions (or ligands) approach Mn^{2+} ion, electrons in 3d orbitals pair up to make available six vacant orbitals involving d^2sp^3 hybridisation.

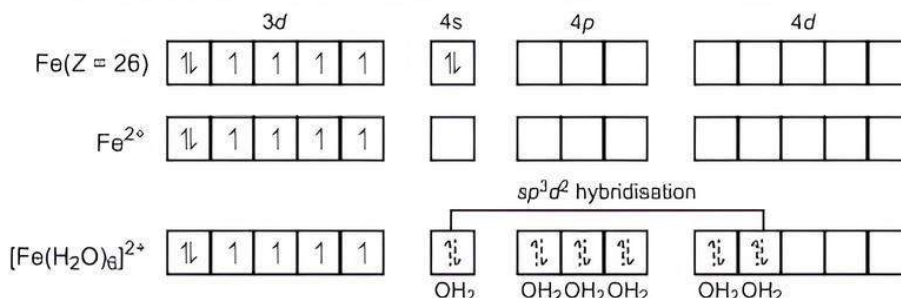


The complex is octahedral and is paramagnetic due to one unpaired electron.

(ii) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$

Oxidation state of Fe : $[\text{Fe}(\text{H}_2\text{O})_6]^{2+} : x + 6(0) = +2$

The magnetic moment value of 5.3 B.M. indicates that there are four unpaired electrons in the complex.



The complex is octahedral and is paramagnetic due to four unpaired electrons. It is also called outer orbital complex because $4d$ ($n = 4$) orbitals are involved.

This means that the electrons in Fe^{2+} ion do not pair up when six H_2O molecules (or ligands) approach it. Since the desired number of vacant orbitals (six) are available, the complex formed is sp^3d^2 hybridised.

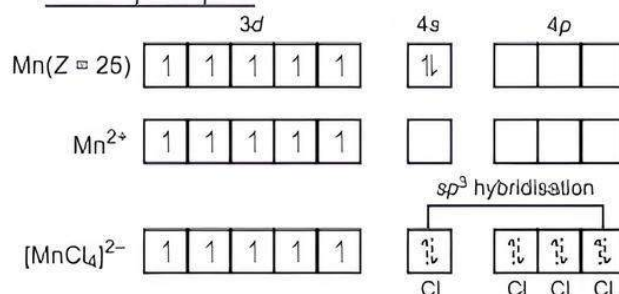
(iii) $\text{K}_2[\text{MnCl}_4]$

Oxidation State of Mn:

$$[\text{MnCl}_4]^{2-}, x + 4(-1) = -2 \text{ or } x = -2 + 4 = +2$$

The magnetic moment value of 5.3 B.M. indicates that there are five unpaired electrons in the complex. This means that all the five $3d$ orbitals in Mn^{2+} ion are involved in the bond formation. The complex is sp^3

hybridised in which one vacant $4s$ and three vacant $4p$ orbitals participate.



The complex is therefore, tetrahedral in nature.



Chapter Test

Multiple Choice Questions

- Q 1. In which of the following compounds manganese has oxidation number equal to that of iodine in KIO_4 ?
- Potassium manganate
 - Potassium permanganate
 - Dimanganese decacarbonyl
 - Manganese chloride
- Q 2. CuSO_4 is paramagnetic while ZnSO_4 is diamagnetic because:
- Cu^{2+} ion has $3d^9$ configuration while Zn^{2+} ion has $3d^{10}$ configuration.
 - Cu^{2+} ion has $3d^5$ configuration while Zn^{2+} ion has $3d^6$ configuration.
 - Cu^{2+} half filled orbitals while Zn^{2+} has fully-filled orbitals.
 - CuSO_4 is blue in colour while ZnSO_4 is white.
- Q 3. Zr and Hf have almost equal atomic and ionic radii because of:
- diagonal relationship
 - lanthanide contraction
 - actinoid contraction
 - belonging to the same group

- Q 4. The magnetic moment of a divalent ion in aqueous solution with atomic number 25 is:

- 5.9 B.M.
- 2.9 B.M.
- 6.9 B.M.
- 9.9 B.M.

Assertion and Reason Type Questions

Directions (Q. Nos. 5-6): Each of the following questions consists of two statements, one is Assertion (A) and the other is Reason (R). Give answer:

- Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of Assertion (A).
 - Both Assertion (A) and Reason (R) are true but Reason (R) is not the correct explanation of Assertion (A).
 - Assertion (A) is true but Reason (R) is false.
 - Assertion (A) is false but Reason (R) is true.
- Q 5. Assertion (A): Cr^{2+} is reducing and Mn^{3+} is oxidising. Reason (R): Cr^{2+} and Mn^{3+} have d^4 configuration.
- Q 6. Assertion (A): The ability of oxygen to stabilise high oxidation states exceeds that of fluorine. Reason (R): The highest oxidation number in the oxides coincides with the group number.

Case Study Based Question

Q 7. The transition metals when exposed to oxygen at low and intermediate temperatures form thin, protective oxide films of up to some thousands of Angstroms in thickness. Transition metal oxides lie between the extremes of ionic and covalent binary compounds formed by elements from the left or right side of the periodic table. They range from metallic to semiconducting and deviate by both large and small degrees from stoichiometry. Since d -electron bonding levels are involved, the cations exist in various valence states and hence give rise to a large number of oxides. The crystal structures are often classified by considering a cubic hexagonal close-packed lattice of one set of ions with the other set of ions filling the octahedral or tetrahedral interstices. The actual oxide structures, however, generally show departures from such regular arrays due in part to distortions caused by packing of ions of different size and to ligand field effects. These distortions depend not only on the number of d -electrons, but also on the valence and the position of the transition metal in a period or group.

Read the given passage carefully and answer the following questions:

- Why do cations of transition metals exist in various valence states?
- How are oxides and oxoanions of metals formed?
- Mention the trend in ionic character when oxidation number of a metal increases. Discuss with an example.

OR

Write two factors on which the distortions in oxides of transition metals depend.

Very Short Answer Type Questions

- Explain the following observations. The members of the actinoid series exhibit a large number of oxidation states than the corresponding members of the lanthanoid series.
- How would you account for the following? Many of the transition elements are known to form interstitial compounds.

Short Answer Type-I Questions

- When MnO_2 is fused with KOH in the presence of KNO_3 as an oxidising agent, it gives a dark green compound (A). Compound (A) disproportionates in acidic solution to give purple compound (B). An alkaline solution of compound (B) oxidises KI to compound (C) whereas an acidified solution of compound (B) oxidises KI to (D). Identify (A), (B), (C) and (D).
- Write one similarity and one difference between the chemistry of lanthanoids and that of actinoids.

Q 12. When chromite ore, FeCr_2O_4 is fused with NaOH in the 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 an orange coloured crystalline compound (C).

- Write the formulae of the compounds (A), (B) and (C).
- Write one use of compound (C).

Short Answer Type-II Questions

Q 13. Account for the following:

- Transition metals and their compounds show catalytic activities.
- Zn , Cd and Hg are non-transition elements.
- Zr and Hf are of almost identical atomic radii.

Q 14. (i) Silver atoms has completely filled d -orbitals in its ground state, it is still considered to be a transition element. Justify the statement.

(ii) Why are $E^\circ_{\text{M}^{2+}/\text{M}}$ values of Mn and Zn more negative than expected?

(iii) Why do transition metals form alloys?

Q 15. (i) Why are melting points of transition metals high?

(ii) Why the transition metals generally form coloured compounds?

(iii) Why E° value for $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple is highly positive?

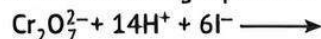
Long Answer Type Questions

Q 16. (i) With reference to structural variability and chemical reactivity, write differences between lanthanoids and actinoids.

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

(iii) Out of Mn^{3+} and Cr^{3+} , which is more paramagnetic and why? (Atomic no's: $\text{Mn} = 25$, $\text{Cr} = 24$).

(iv) Complete the following equation:



Q 17. Give reasons:

(i) Actinoids show irregularities in their electronic configurations.

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

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

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

(v) Transition metals have high enthalpy of atomisation.

