

8



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

Facts that Matter

- Electronic configuration of transition elements is $(n - 1)d^{1-10}ns^{1-2}$. The name of transition metal refers to *d*-block. The inner transition metals refers to *f*-block elements *d*-block contain group 3-12 elements where *d* orbitals are progressively filled, whereas *f*-block contain elements in which the 4*f* and 5*f* orbitals are progressively filled. Three series of transition metals are present, 3*d* series (Sc-Zn), 4*d* series (Y-Cd), 5*d* series (La-Hg omitting Ce-Lu).

The name transition is given because of their position between *s* and *p* block elements. Zn, Cd and Hg are not regarded as transition elements because their *d*-orbitals are completely filled.

Properties of *d*-Block Elements

- Transition metals are quite hard, they have high melting point, high enthalpies of atomisation, high ionisation enthalpies because of strong metallic bond, covalent bond and unpaired electrons. Transition elements show variable oxidation states due to the participation of *ns* and $(n - 1)$ *d*-electrons in bonding. Highest oxidation state shown by transition element is eight.
- $\mu = \sqrt{n(n+2)}$, where, μ is the magnetic moment and *n* is the number of unpaired electrons. Transition elements and their compounds are paramagnetic in nature because they contain unpaired electrons. Transition metals form a large number of complex compounds due to small size of the metal ions, high ionic charges and availability of vacant *d*-orbitals.
- Transition metals form coloured compounds due to *d-d* transition.
- The transition metals and some of their compounds can act as catalyst due to variable oxidation states, and large surface area.
- Interstitial compounds are those which are formed when small atoms like H, C or N are trapped inside the crystal lattice of metals. Transition metal compounds form interstitial compounds because some voids are present inside the crystal lattice. The transition metals form a number of alloys because of similar atomic size. For Example; Brass (Copper, Zinc), Bronze (Copper-Tin).

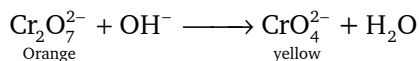
Oxides and Oxo-anions

As the oxidation number of a metal increases, its ionic character decreases. So Mn_2O_7 is acidic V_2O_3 is basic, V_2O_5 is amphoteric, CrO is basic, Cr_2O_3 is amphoteric while MnO_2 is amphoteric.

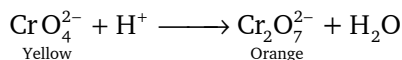
- Preparation of $K_2Cr_2O_7$ (Potassium dichromate)**



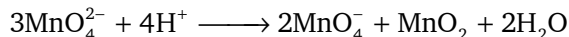
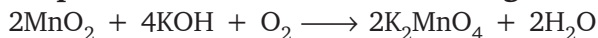
On increasing the pH of Chromate:



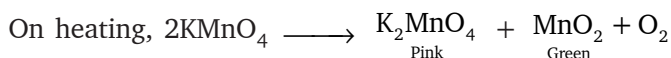
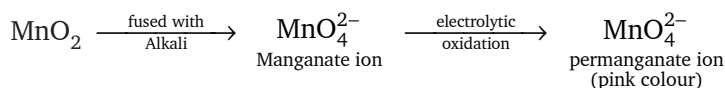
On decreasing the pH of Chromate:



• Preparation of Potassium Permanganate (KMnO₄)



• Commercial preparation



• Manganate and permanganate ions are tetrahedral, while chromate ion is tetrahedral.

Uses

- KMnO₄ — oxidation, bleaching of wool, cotton, silk, analytical chemistry, disinfectant for water.
- K₂Cr₂O₇ — oxidant, chrome tanning in leather industry.

f-block elements

It consists of two series—

1. Lanthanoids—14 elements: Cerium to Lutetium are similar to lanthanum.
 2. Actinoids—14 elements: Thorium to lawrencium are similar to actinium.
- Misch metal 95% lanthanoid metals and 5% iron plus traces of S, C, Ca, Al.
 - The different oxidation states exhibited by lanthanoids are +2, +3, +4.
 - Actinoids exhibits a large number of oxidation states than the corresponding lanthanoids because of larger size.
 - Electronic configuration of lanthanoid is $4f^{1-14} 5d^{0-1} 6s^2$.

Similarity between Lanthanoids and Actinoids

- Both shows +3 oxidation states.
- Same number of unpaired electrons.
- Contraction in atomic sizes.
- *f* orbitals are progressively filled.
- Electropositive and highly active.
- Compounds are less basic.

Differences between Lanthanoids and Actinoids

Lanthanoids	Actinoids
1. Binding energy of 4 <i>f</i> orbital is higher.	1. Binding energy of 5 <i>f</i> orbital is lower.
2. Most ions are colourless.	2. Ions are coloured.
3. Non-radioactive.	3. Radioactive.
4. Tendency to form complexes is less.	4. Tendency to form complexes is more.

Lanthanoid Contraction

The steady decrease in atomic size of lanthanoid elements with increase in atomic number is called lanthanoid contraction.

Cause

Nuclear charge increases from left to right, and compensated by shielding effect by 4f electrons. (f electrons orbitals have poor shielding effect.) So, there is a steady decrease in atomic size.

Consequence

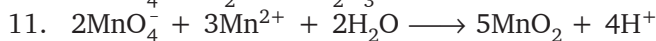
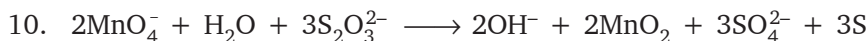
Separation of lanthanoids are difficult as they have similar properties.

- Similarity in the atomic size of the elements of second and third transition series in the same group. Example, Zr–Hf have similar atomic size.
- Variation in basic strength of hydroxide:
The basic strength decreases from $\text{La}(\text{OH})_3$ to $\text{Lu}(\text{OH})_3$. Because of size M^{+3} ion decreases.

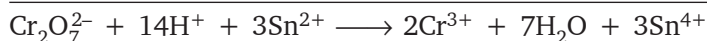
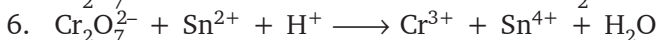
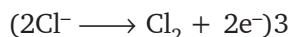
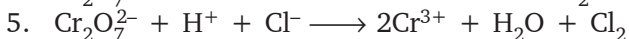
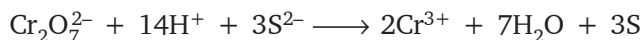
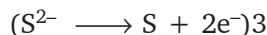
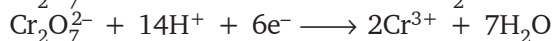
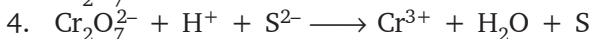
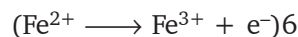
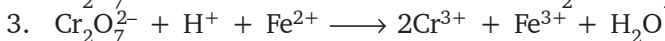
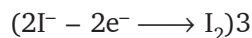
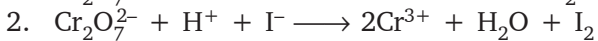
A Few Ionic Equations Related to the d-Block Elements

For Mn^{2+}

1. $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$
2. $\text{MnO}_4^- + 8\text{H}^+ + 5\text{Fe}^{2+} \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} + 5\text{Fe}^{3+}$
 $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$
 $(\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + \text{e}^-)5$
3. $\text{MnO}_4^- + 8\text{H}^+ + 5\text{Fe}^{2+} \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} + 5\text{Fe}^{3+}$
 $\text{MnO}_4^- + \text{H}^+ + \text{C}_2\text{O}_4^{2-} \longrightarrow \text{Mn}^{2+} + \text{H}_2\text{O} + \text{CO}_2$
 $(\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O})2$
 $(\text{C}_2\text{O}_4^{2-} \longrightarrow 2\text{CO}_2 + 2\text{e}^-)5$
4. $2\text{MnO}_4^- + 16\text{H}^+ + 5\text{C}_2\text{O}_4^{2-} \longrightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 10\text{CO}_2$
 $\text{MnO}_4^- + \text{H}^+ + \text{S}^{2-} \longrightarrow \text{Mn}^{2+} + \text{H}_2\text{O} + \text{S}$
 $(\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O})2$
 $(\text{S}^{2-} \longrightarrow \text{S} + 2\text{e}^-)5$
5. $2\text{MnO}_4^- + 16\text{H}^+ + 5\text{S}^{2-} \longrightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 5\text{S}$
 $\text{MnO}_4^- + \text{H}^+ + \text{I}^- \longrightarrow \text{Mn}^{2+} + \text{H}_2\text{O} + \text{I}_2$
 $(\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O})2$
 $(2\text{I}^- \longrightarrow \text{I}_2 + 2\text{e}^-)5$
6. $2\text{MnO}_4^- + 16\text{H}^+ + 10\text{I}^- \longrightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 5\text{I}_2$
 $\text{MnO}_4^- + \text{H}^+ + \text{NO}_2^- \longrightarrow \text{Mn}^{2+} + \text{H}_2\text{O} + \text{NO}_3^-$
 $(\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O})2$
 $(\text{NO}_2^- + \text{H}_2\text{O} \longrightarrow \text{NO}_3^- + 2\text{H}^+ + 2\text{e}^-)5$
7. $2\text{MnO}_4^- + 16\text{H}^+ + 5\text{NO}_2^- + 5\text{H}_2\text{O} \longrightarrow 5\text{NO}_3^- + 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 10\text{H}^+$
i.e. $2\text{MnO}_4^- + 6\text{H}^+ + 5\text{NO}_2^- \longrightarrow 2\text{Mn}^{2+} + 3\text{H}_2\text{O} + 5\text{NO}_3^-$
 $\text{SO}_3^{2-} + \text{MnO}_4^- + \text{H}^+ \longrightarrow \text{Mn}^{2+} + 8\text{H}_2\text{O} + \text{SO}_4^{2-}$
 $(\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O})2$
 $(\text{SO}_3^{2-} + \text{H}_2\text{O} \longrightarrow \text{SO}_4^{2-} + 2\text{H}^+ + 2\text{e}^-)5$
8. $2\text{MnO}_4^- + 16\text{H}^+ + 5\text{SO}_3^{2-} + 5\text{H}_2\text{O} \longrightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 5\text{SO}_4^{2-} + 10\text{H}^+$
i.e. $2\text{MnO}_4^- + 6\text{H}^+ + 5\text{SO}_3^{2-} \longrightarrow 2\text{Mn}^{2+} + 5\text{SO}_4^{2-} + 3\text{H}_2\text{O}$
9. In a neutral or alkaline solution:
 $2\text{MnO}_4^- + \text{H}_2\text{O} + \text{I}^- \longrightarrow 2\text{MnO}_2 + 2\text{OH}^- + \text{IO}_3^-$
9. $2\text{MnO}_4^- + 2\text{OH}^- \longrightarrow 2\text{MnO}_4^{2-} + \text{H}_2\text{O} + (\text{O})$



For Cr^{3+}



NCERT IN-TEXT QUESTIONS SOLVED

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

Ans. The outer electronic configuration of Ag ($Z = 47$) is $4d^{10} 5s^1$. In addition to +1, it shows an oxidation state of +2 (e.g., AgO and AgF₂). In +2 oxidation state, the configuration is d^9 , i.e. the d-subshell is incompletely filled. Hence, it is a transition element.

8.2. In the series Sc ($Z = 21$) to Zn ($Z = 30$) the enthalpy of atomisation of Zinc is the lowest, i.e. 126 kJ mol^{-1} . Why?

Ans. In the series Sc to Zn, all elements have one or more unpaired electrons, except zinc which has no unpaired electron as its outer electronic configuration is $3d^{10} 4s^2$. Hence, atomic intermetallic bonding is weakest in zinc. Therefore, enthalpy of atomisation is the lowest.

8.3. Which of the 3d series of the transition metal exhibits the largest number of oxidation states and why?

Ans. Mn exhibits the largest number of oxidation states because it has electrons in its valence shell which can take part in bond formation.

8.4. The $E^\ominus (M^{2+}/M)$ value for copper is positive (+0.34 V). What is possibly the reason for this? (Hint: Consider its high $\Delta_a H^\ominus$ and low $\Delta_{\text{hyd}} H^\ominus$)

Ans. It is because hydration energy and Lattice energy of Cu^{2+} is more than that of Cu^+ .

8.5. How would you account for the irregular variation of ionisation enthalpies (first and second) in the first series of the transition elements?

Ans. The irregular variation is due to different stabilities of their electronic configuration.

8.6. Why is the highest oxidation state of a metal exhibited in its oxide or fluoride only?

Ans. It is because F_2 and O_2 are considered as the strongest oxidising agents due to the high electronegativity of O and F atoms.

8.7. Which is a stronger reducing agent Cr^{2+} or Fe^{2+} and why?

Ans. Fe^{2+} is a stronger reducing agent because it will get oxidised to Fe^{3+} which has stable half filled d -orbital electronic configuration.

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

Ans. $M^{2+}(aq)$ ($Z = 27$);



$$\text{Magnetic moment } \mu = \sqrt{n(n+2)}$$

$$\begin{aligned} \text{B.M.} &= \sqrt{3 \times 5} = \sqrt{15} \\ &= 3.87 \text{ B.M.} \end{aligned}$$

8.9. Explain why Cu^+ ion is not stable in aqueous solutions? [AI 2014]

Ans. Hydration energy of Cu^{2+} ion is very high which can overcome the second ionisation energy, that is why Cu^{2+} is more stable than Cu^+ ion.

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

Ans. In actinoids there is a poor shielding effect of $4f$ and $5f$ orbitals electrons whereas in lanthanoids there is poor shielding effect of $4f$ electrons only, that is why effective nuclear charge increases more from element to element in actinoids than in case of lanthanoids.

NCERT TEXTBOOK QUESTIONS SOLVED

8.1. Write down the electronic configuration of:

(i) Cr^{3+} (ii) Pm^{3+} (iii) Cu^+

(iv) Ce^{4+} (v) Co^{2+} (vi) Lu^{2+}

(vii) Mn^{2+} (viii) Th^{4+}

Ans. (i) Cr^{3+} (24) $- 1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$
(ii) Pm^{3+} (61) $- 1s^2 2s^2 2p^6 3s^2 3d^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 4f^4$
(iii) Cu^+ (29) $- 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$
(iv) Ce^{4+} (58) $- 1s^2 2s^2 2p^6 3s^2 3d^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6$
(v) Co^{2+} (27) $- 1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$
(vi) Lu^{2+} (71) $- 1s^2 2s^2 2p^6 3s^2 3d^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 4f^{14} 5d^1$
(vii) Mn^{2+} (25) $- 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$
(viii) Th^{4+} (90) $- 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6$

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

Ans. Mn^{2+} is more stable than Mn^{3+} due to stable electronic configuration whereas Fe^{3+} is more stable than Fe^{2+} due to more stable half filled d -orbitals, electronic configuration.

8.3. Explain briefly how +2 state becomes more and more stable in the first half of the first row transition elements with increasing atomic number?

Ans. It is due to increase in the effective nuclear charge after losing 2 electrons from *s*-orbitals, resulting in decrease of ionic size and increase in stability.

8.4. 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 examples.

Ans. The elements in the first-half of the transition series exhibit many oxidation states, with Mn exhibiting the maximum number of oxidation states (+2 to +7). The stability of +2 oxidation state increases with the increase in atomic number. This happens as more electrons are getting filled in the *d*-orbital.

Sc³⁺ has a stable electronic configuration, therefore Sc³⁺ is more stable than Sc⁺. Fe³⁺ is more stable than Fe²⁺ due to stable half filled *d*-orbitals, Mn²⁺ is more stable than Mn³⁺ due to stable half filled *d*-orbitals, V⁵⁺ is more stable than V³⁺ due to more stable electronic configuration.

8.5. What may be the stable oxidation state of the transition element with the following *d*-electron configuration in the ground state of their atoms: 3*d*³, 3*d*⁵, 3*d*⁸ and 3*d*⁴?

Ans. (i) **3*d*³:** Stable oxidation state will be +5 due to outer electronic configuration — 3*d*³ 4*s*²
(ii) **3*d*⁵:** Stable oxidation state will be +7 due to outer electronic configuration—
3*d*⁵ 4*s*²
(iii) **3*d*⁸:** Stable oxidation state will be +2 due to outer electronic configuration—
3*d*⁸ 4*s*²
(iv) **3*d*⁴:** Stable oxidation state will be +6 due to outer electronic configuration—
3*d*⁴ 4*s*².

8.6. Name the oxometal anions of the first series of the transition metals in which the metal exhibits the oxidation state to its group number. [Delhi 2017]

Ans. In MnO₄⁻, oxidation state of Mn is +7 which is equal to its group number.
In CrO₄²⁻ oxidation state of Cr is +6 which is equal to its group number.

8.7. What is lanthanoid contraction? What are the consequences of lanthanoid contraction?

Ans. The decrease in atomic and ionic size with increase in atomic number in lanthanoids is called lanthanoid contraction.

8.8. What are the characteristics of transition elements and why are they called transition elements? Which of the *d*-block elements may not be regarded as the transition elements?

Ans. Characteristics of transition elements:

- Most of the transition elements form coloured compounds.
- Their compounds are generally paramagnetic in nature.
- They have great tendency to form complexes.
- They show variable oxidation states.

They are called transition elements because they are less electropositive than *s*-block elements and more electropositive than *p*-block elements. Zn, Cd, Hg are not regarded as transition elements, since their *d*-orbital is completely filled.

8.9. In what way is the electronic configuration of the transition elements different from that of the non-transition elements?

Ans. Transition elements contain incompletely filled *d*-subshell, *i.e.* their electronic configuration is $(n - 1) d^{1-10} ns^{0-2}$ whereas non-transition elements have no *d*-subshell or their *d*-subshell is completely filled and have ns^{1-2} or $ns^2 np^{1-6}$ as their outermost shell electronic configuration.

8.10. What are the different oxidation states exhibited by the lanthanoids?

Ans. The most common oxidation state of Lanthanoids is +3. However, some lanthanoids also shows oxidation states of +2 and +4. For example, Eu shows an oxidation state of +2 and Ce shows an oxidation state of +4.

8.11. Explain giving reasons:

- (i) Transition metals and many of their compounds show paramagnetic behaviour.
- (ii) The enthalpies of atomisation of transition metals are high.
- (iii) The transition metals generally form coloured compounds.
- (iv) Transition metals and their many compounds act as good catalyst.

Ans. (i) It is due to the presence of unpaired electrons, due to which they are attracted by the magnetic field and exhibits paramagnetism.
(ii) It is due to strong metallic bonding and additional covalent bonding due to the presence of unpaired electrons in *d*-orbitals due to which they have high lattice energy and consequently high enthalpy of atomisation.
(iii) It is due to the presence of unpaired electrons, by the virtue of which they undergo *d-d* transitions by absorbing light from the visible region and radiate the complementary colour.
(iv) It is due to their variable oxidation states. They have a large surface area and can form interstitial compounds with the reactants which readily changed into products.

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

Ans. Interstitial compounds are those which are formed when small atoms like H, C or N are trapped inside the crystal lattice of metals. Because of the nature of the composition of transition metal compounds, they are referred to as interstitial compounds.

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

Ans. They differ by one in transition metal, e.g., Fe²⁺, Fe³⁺, Cr²⁺ Cr³⁺, In non-transition metals they differ by two, e.g. Ti⁺ and Ti³⁺, Sn²⁺ and Sn⁴⁺, Bi³⁺ and B⁵⁺.

8.14. Describe the preparation of potassium dichromate from iron chromite ore. What is the effect of increasing pH on a solution of potassium dichromate.

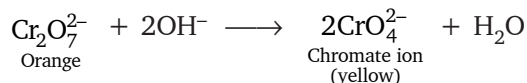
Ans. $4\text{FeCr}_2\text{O}_4 + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 \longrightarrow 8\text{Na}_2\text{CrO}_4 + 2\text{Fe}_2\text{O}_3 + 8\text{CO}_2$
The yellow solution of sodium chromate is filtered and acidified using sulphuric acid solution to form a solution from which orange sodium dichromate, Na₂Cr₂O₇ · 2H₂O is crystallised.



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

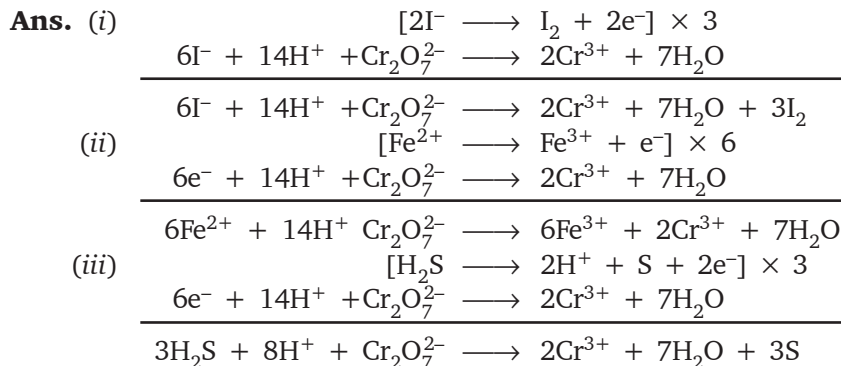


Orange crystals of potassium dichromate crystallises out. On increasing the pH of the solution, the H⁺ ions are used up and reaction proceeds in the forward direction producing yellow chromate solution.



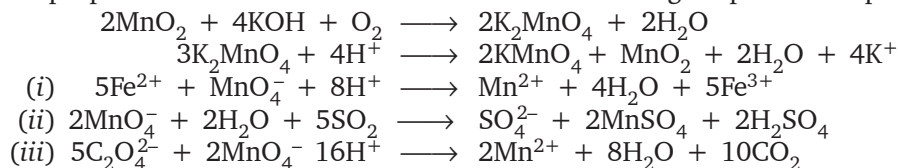
8.15. Describe the oxidising action of potassium dichromate and write the ionic equation for its reaction with:

- (i) iodide
 - (ii) iron(II) solution and
 - (iii) H₂S
- [AI 2014]

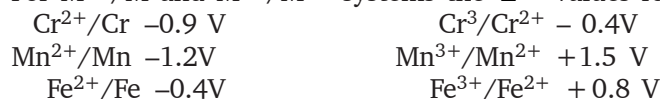


8.16. Describe the preparation of potassium permanganate. How does the acidified permanganate solution react with (i) iron(II) ions (ii) SO_2 and (iii) oxalic acid? Write the ionic equations for the reactions.

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



8.17. For M^{2+}/M and $\text{M}^{3+}/\text{M}^{2+}$ systems the E^\ominus values for some metals are as follows:



Use this data to comment upon:

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

Ans. (i) Fe^{3+} is more stable than Cr^{3+} or Mn^{3+} .

(ii) Iron can be easily oxidised as compared to Cr or Mn.

8.18. Predict which of the following will be coloured in aqueous solutions? Ti^{3+} , V^{3+} , Cu^+ , Sc^{3+} , Mn^{2+} , Fe^{3+} and Co^{2+} . Give reasons for each.

Ans. Ti^{3+} , V^{3+} , Mn^{2+} , Fe^{3+} and Co^{2+} are coloured due to the presence of unpaired electrons, they can undergo $d-d$ transitions. Cu^+ , Sc^{3+} are colourless due to the absence of unpaired electrons.

8.19. Compare the stability of +2 oxidation state for the elements of the first transition series.

Ans. In general, the stability of +2 oxidation state in first transition series decreases from left to right due to the increase in the sum of first and second ionisation energies. However Mn^{2+} is more stable due to half filled d -orbitals ($3d^5$) and Zn^{2+} is more stable due to completely filled d -orbitals ($3d^{10}$).

8.20. Compare the chemistry of actinoids with that of lanthanoids with special reference to:

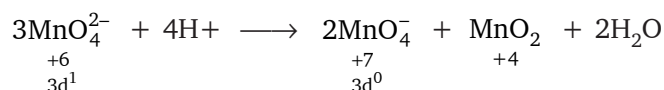
- | | |
|------------------------------|-----------------------------|
| (i) electronic configuration | (ii) atomic and ionic sizes |
| (iii) oxidation state | (iv) chemical reactivity. |

- Ans.** (i) **Electronic configuration:** In lanthanoids 4f-orbitals are progressively filled whereas in actinoids 5f-orbitals are progressively filled.
- (ii) **Atomic and ionic sizes:** Both show decrease in size of their atoms or ions in +3 oxidation state. In lanthanoids, the decrease is called lanthanoid contraction whereas in actinoids it is called actinoid contraction. However, the contraction is greater from element to element in actinoids due to poorer shielding by 5f electrons.
- (iii) **Oxidation state:** Lanthanoids show +3 oxidation state. Some elements show +2 and +4 oxidation states also. Actinoids show +3, +4, +5, +6, +7 oxidation states. Although +3 and +4 are most common.
- (iv) **Chemical reactivity:** Actinoids are more reactive than lanthanoids due to bigger atomic size and lower ionisation energy.

8.21. How would you account for the following:

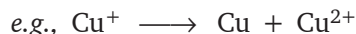
- (i) of the d^4 species, Cr^{2+} is strongly reducing while manganese (III) is strongly oxidising.
- (ii) Cobalt (II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidised.
- (iii) The d^1 configuration is very unstable in ions.

- Ans.** (i) Cr^{2+} is a strong reducing agent because it readily changes to Cr^{3+} ion which is more stable because Cr^{3+} has higher hydration energy whereas in case of Mn^{3+} is strongly oxidising because it readily changes to Mn^{2+} which is more stable due to half filled d -orbitals.
- (ii) Co(II) gets oxidised to Co(III) in the presence of a complexing agent because Co(III) is more stable than Co(II) . Most of the strong field ligands causes pairing of electrons, forming diamagnetic octahedral complexes which are very stable due to very large crystal field stabilisation energy.
- (iii) d^1 configuration is very unstable in ions because d^0 state achieved after losing one more electron will be more stable. All the elements with d^1 configuration are either reducing or undergo disproportionation reaction e.g.,



8.22. What is meant by 'disproportionation'. Give two examples of disproportionation reaction in aqueous solution.

Ans. The reaction in which the same substance is oxidised and reduced simultaneously is called disproportionation reaction.



Cr(V) undergoes disproportionation in acidic medium as follows:



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

Ans. Copper exhibits +1 oxidation state frequently due to stable electronic configuration.

8.24. Calculate the number of unpaired electrons in the following gaseous ions: Mn^{3+} , Cr^{3+} , V^{3+} and Ti^{3+} . Which one of these is most stable in aqueous solution?

- Ans.** $\text{Mn}^{3+} = [\text{Ar}] 4s^0 3d^4$ No of unpaired electrons = 4
 $\text{Cr}^{3+} = [\text{Ar}] 4s^0 3d^3$ No of unpaired electrons = 3
 $\text{V}^{3+} = [\text{Ar}] 4s^0 3d^2$ No of unpaired electrons = 2
 $\text{Ti}^{3+} = [\text{Ar}] 4s^0 3d^1$ No or unpaired electrons = 1

8.25. Give examples and suggest reasons for the following features of the transition metal chemistry:

- (i) The lowest oxide of transition metal is basic, the highest is amphoteric/acidic.
- (ii) A transition metal exhibits highest oxidation state in oxides and fluorides.
- (iii) The highest oxidation state is exhibited in oxoanions of a metal. [CBSE 2017]

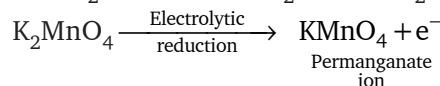
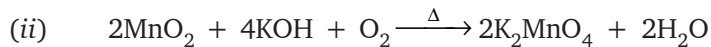
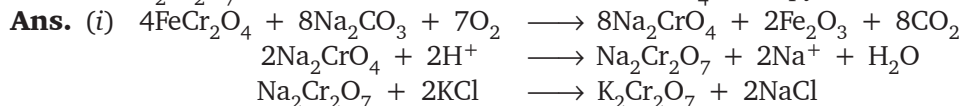
Ans. (i) The lower oxide of transition metal is basic because the metal atom has lower oxidation state whereas the highest oxide is acidic due to highest oxidation state of the metal. For example, MnO is basic whereas Mn_2O_7 is acidic.

In the lower oxidation state of the metal, some of the valence electrons of the metal atom are not involved in bonding. Hence, it can donate the electrons and behaves as a base. In the higher oxidation state valence electrons are involved in bonding and hence are not freely available. Instead effective nuclear charge is high. Hence, it can only accept electrons and behaves as an acid.

- (ii) A transition metal exhibits higher oxidation states in oxides and fluorides because oxygen and fluorine are highly electronegative elements, small in size (and strongest oxidising agents). For example, osmium shows an oxidation state of +6 in OsF_6 and vanadium the shows an oxidation state of +5 in V_2O_5 .
- (iii) Oxometal anions have the highest oxidation state, e.g. Cr in $\text{Cr}_2\text{O}_7^{2-}$ or CrO_4^{2-} has an oxidation state of +6 whereas Mn in MnO_4^- has an oxidation state of +7. This is again due to the combination of metal with oxygen, which is highly electronegative and the oxidising element.

8.26. Indicate the steps in the preparation of:

- (i) $\text{K}_2\text{Cr}_2\text{O}_7$ from chromite ore.
- (ii) KMnO_4 from pyrolusite ore.



8.27. What are alloys? Name an important alloy which contains some of the Lanthanoid metals. Mention its uses.

Ans. Alloys are homogeneous mixture of two or more metals. One of them can be a non metal also. Mischmetal is an alloy which contains some of the lanthanoid metals. It contains 45% lanthanoid metals, iron ~ 5% and traces of S, C, Ca and Al.

Mischmetal is used in Mg-based alloys to produce bullets, shells and lighter flint.

Addition of 3% mischmetal to magnesium increases its strength and is used in making jet engine parts.

8.28. What are inner transition elements? Decide which of the following atomic numbers are the atomic numbers of the inner transition elements: 29, 59, 74, 95, 102, 104.

Ans. Lanthanoids and Actinoids are called inner transition elements because inner *f*-orbitals are progressively filled. Elements with atomic numbers 59, 95, 102 are inner transition metals because they belong to lanthanoids and actinoids. *f*-orbitals are progressively filled up in these series of elements as shown below:

Pr (59) – $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^3$
 Am (95) – $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^7$
 No (102) – $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 5d^{10} 5f^{14} 6s^2 6p^6 7s^2$

8.29. The chemistry of the actinoid elements is not so smooth as that of the lanthanoids. Justify this statement by giving some examples from the oxidation state of these elements.

Ans. Lanthanoids shows a limited number of oxidation states, +2, +3 and +4 (out of which +3 is the most common). This is because of large energy gap between 4f, 5d and 6s subshells. The dominant oxidation state of actinoids is also +3 but they show a number of other oxidation state also. e.g., uranium (Z = 92) and plutonium (Z = 94) show +3, +4, +5 and +6 and neptunium (Z = 94) shows +3, +4, +5 and +7 oxidation states, etc. This is due to small energy difference between 5f, 6d and 7s subshells of the actinoids.

8.30. Which is the last element in the series of the actinoids? Write the electronic configuration of this element. Comment on the possible oxidation state of this element.

Ans. Last actinoid element is = Lawrencium (Z = 103)

Electronic configuration = $[\text{Rn}]^{86} 5f^{14} d^1 7s^2$

Possible oxidation state = +3

8.31. Use Hund's rule to derive the electronic configuration of Ce^{3+} ion, and calculate its magnetic moment on the basis of 'spin only' formula.

Ans. ${}_{58}\text{Ce} = [\text{Xe}]^{54} 4f^1 5d^1 6s^2$

$$\mu = \sqrt{n(n+2)} \text{ BM} = \sqrt{1(1+2)} \sqrt{3} \text{ BM} = 1.73 \text{ BM}$$

8.32. Name the members of the lanthanoid series which exhibit +4 oxidation states and those which exhibit +2 oxidation states. Try to correlate this type of behaviour with the electronic configuration of these elements?

Ans. +4 = ${}_{58}\text{Ce}$, ${}_{59}\text{Pr}$, ${}_{60}\text{Nd}$, ${}_{65}\text{Tb}$, ${}_{66}\text{Dy}$

+2 = ${}_{60}\text{Nd}$, ${}_{62}\text{Sm}$, ${}_{63}\text{Eu}$, ${}_{69}\text{Tm}$, ${}_{70}\text{Yb}$

+2 oxidation state is exhibited when the configuration is $5d^0 6s^2$ so that 2 electrons are easily lost.

+4 oxidation state is exhibited when the configuration is close to $4f^0$ (e.g., $4f^0$, $4f^1 4f^2$) or close to $4f^7$ (e.g., $4f^7$ or $4f^8$)

8.33. Compare the chemistry of actinoids with that of lanthanoids with reference to:

(i) Electronic configuration (ii) Oxidation states and

(iii) Chemical reactivity

Ans. (i) **Electronic configuration:** In lanthanoids 4f-orbitals are progressively filled whereas in actinoids 5f-orbitals are progressively filled.

(ii) **Oxidation state:** Lanthanoids show +3 as the common oxidation state. Some elements show +2 and +4 oxidation states also. Actinoids show a large no. of o.s., eg. +3, +4, +5, +6 +7 oxidation states. Although +3 and +4 are most common oxidation states in actinoids.

(iii) **Chemical reactivity:** Actinoids are more reactive than lanthanoids due to bigger atomic size and lower ionisation energy.

8.34. Write the electronic configuration of the elements with the atomic numbers 61, 91, 101 and 109.

Ans. Z = 61 (Pm)

E.C. = $[\text{Xe}]^{54} 4f^5 5d^0 6s^2$

Z = 91 (Pa)

E.C. = $[\text{Rn}]^{86} 5f^2 6d^1 7s^2$

Z = 101 (Md)

E.C. = $[\text{Rn}]^{86} 5f^{13} 6d^0 7s^2$

Z = 109 (Mt)

E.C. = $[\text{Rn}]^{86} 5f^{14} 6d^7 7s^2$

8.35. Compare the general characteristics of the first series of the transition metals with those of the second and third series metals in the respective vertical columns. Give special emphasis on the following points:

(i) Electronic configurations (ii) Oxidation states

(iii) Ionisation enthalpies and (iv) Atomic size

Ans. (i) **Electronic configuration:** In first transition series, $3d$ orbitals are progressively filled whereas in second transition series, $4d$ orbitals are progressively filled and in the 3rd transition series $5d$ -orbitals are progressively filled.

(ii) **Oxidation states:** Elements show variable oxidation states in both the series. The highest oxidation state is equal to total number of 's' as well as 'd' orbital. The number of oxidation states shown are less in $5d$ transition series than in $4d$ transition series.

In $3d$ series, +2, +3 oxidation states are common and they form stable complexes in these oxidation states. In the other series OsO_4 and PtF_6 are formed, which are quite stable in higher oxidation state.

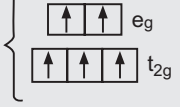
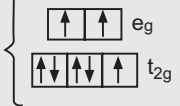
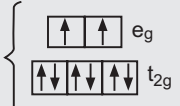
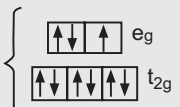
(iii) **Ionisation enthalpies:** The ionisation enthalpy of $5d$ series elements is higher than that of $3d$ and $4d$ series elements due to lanthanoid contraction and higher effective nuclear charge.

(iv) **Atomic sizes:** The atomic size of $4d$ and $5d$ series elements do not differ appreciably due to lanthanoid contraction. The atomic radii of second elements and third series are however larger than $3d$ series.

8.36. Write down the number of $3d$ electrons in each of the following ions: Ti^{2+} , V^{2+} , Cr^{3+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} and Cu^{2+} . Indicate how would you expect the five $3d$ orbitals to be occupied for these hydrated ions (octahedral).

Ans.

Ion	Configuration	No. of $3d$, electrons	No. of unpaired electrons	Occupancy of $3d$ orbitals
(i) Ti^{2+}	$3d^2$	2	2	t_{2g}^2
(ii) V^{2+}	$3d^3$	3	3	t_{2g}^3
(iii) Cr^{3+}	$3d^3$	3	3	t_{2g}^3
(iv) Mn^{2+}	$3d^5$	5	5	$t_{2g}^3 e_g^2$
(v) Fe^{2+}	$3d^6$	6	4	$t_{2g}^4 e_g^2$

(vi)	Fe ³⁺	3d ⁵	5	5	t _{2g} ³ e _g ²	
(vii)	Co ²⁺	3d ⁷	7	3	t _{2g} ⁵ e _g ²	
(viii)	Ni ²⁺	3d ⁸	8	2	t _{2g} ⁶ e _g ²	
(ix)	Cu ²⁺	3d ⁹	9	1	t _{2g} ⁶ e _g ³	

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

Ans. (i) In first transition series lower oxidation state is more stable whereas in heavier transition elements higher oxidation states are more stable.

(ii) The ionisation enthalpy of 5d transition series elements is higher than the 3d and 4d transition series element.

(iii) M-M bonding is most common in heavier transition metals but less common in first transition series.

(iv) The elements of first transition series do not form complexes with higher coordination number of 7 and 8 while heavier transition elements do so.

(v) The elements of first transition series can form high spin or low spin complexes depending upon the strength of the ligands but elements of second and third series form low spin complexes preferably, the irrespective of the strength of ligands.

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

Example	Magnetic Moment (BM)
K ₄ [Mn(CN) ₆]	2.2
[Fe(H ₂ O) ₆] ²⁺	5.3
K ₂ [MnCl ₄]	5.9

Ans. Magnetic moment $(\mu) = \sqrt{n(n+2)}$ BM

When $n = 1$ $\mu = \sqrt{1(1+2)} = \sqrt{3} = 1.73$

When $n = 2$ $\mu = \sqrt{2(2+2)} = \sqrt{8} = 2.83$

When $n = 3$ $\mu = \sqrt{3(3+2)} = \sqrt{15} = 3.87$

When $n = 4$ $\mu = \sqrt{4(4+2)} = \sqrt{24} = 5.66$

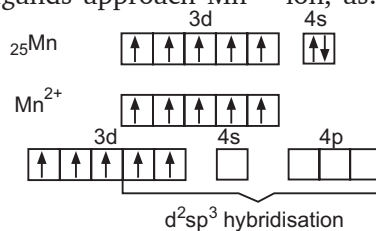
When $n = 5$ $\mu = \sqrt{5(5+2)} = \sqrt{35} = 5.92$

(i) $K_4[Mn(CN)_6]$: In this complex Mn is in +2 oxidation state, i.e. as Mn^{2+}

$$\mu = 2.2 \text{ BM}$$

It shows that it has only one unpaired electron.

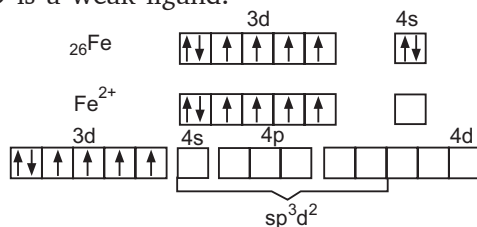
Thus, when CN^- ligands approach Mn^{2+} ion, as:



(ii) $[Fe(H_2O)_6]^{2+}$: In this complex, Fe is in +2 state, i.e. as Fe^{2+}

$$\mu = 5.3 \text{ BM}$$

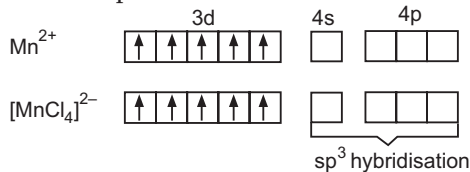
It shows that there are four unpaired electrons. This means that the electrons in 3d do not get paired up when the ligands, H_2O molecules approach the metal ion. Thus, H_2O is a weak ligand.



(iii) $K_2[MnCl_4]$: In this complex, Mn is in +2 state, i.e., as Mn^{2+}

$$\mu = 5.9 \text{ BM}$$

It shows that there are five unpaired electrons. Thus, the hybridisation involved will be sp^3 and the complex will be tetrahedral.



ADDITIONAL QUESTIONS SOLVED

I. Very Short Answer Type Questions

(1 Mark)

Q1. Write the electronic configuration of the element with atomic number 102.

[AI CBSE 2006]

Ans. $[Rn]^{88} 5f^{14} 4d^0 7s^2$

Q2. Write ionic equation for the reaction between $Cr_2O_7^{2-}$ ions and Fe^{2+} ions in acidic medium.

[CBSE 2005]

Ans. $Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

Q3. What are coinage metals?

Ans. Cu, Ag and Au, which have been used in making of coins in ancient times are called coinage metals.

Q4. Out of Al, Zn, Mg and Fe, which is the densest element?

Ans. Fe

Q5. Why do transition elements show similarities along the horizontal period?

Ans. This is because all of them contains completely filled d -subshell whereas the outer shell electronic configuration remains the same.

- Q6.** What is the effect of increasing pH on $K_2Cr_2O_7$ solution?
- Ans.** In aqueous solution, we have
 $Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-} + 2H^+$
 When $pH < 4$ (acidic medium) it exists as $Cr_2O_7^{2-}$ and colour is orange and when $pH > 7$ (basic medium) it exists as CrO_4^{2-} and the colour is yellow.
- Q7.** Give the general electronic configuration of actinoides?
- Ans.** $5f^{1-14} 6d^{0-1} 7s^2$
- Q8.** Why does vanadium pentoxide act as a catalyst?
- Ans.** Vanadium exists in multiple oxidation states.
- Q9.** Why Lanthanoids are called *f*-block elements?
- Ans.** This is because the last electron enters into the *f*-orbital.
- Q10.** Why is copper (At No. 29) considered as a transition metal?
- Ans.** This is because copper in oxidation state +2, i.e. Cu^{2+} has incompletely filled *d*-subshell ($3d^9$).
- Q11.** Which is the most common oxidation state of lanthanoides?
- Ans.** +3
- Q12.** Name the elements which are not really transition elements but are discussed with them.
- Ans.** Zinc, Cadmium, Mercury,
- Q13.** Write the general electronic configuration of transition elements or *d*-block elements?
- Ans.** $(n - 1) d^{1-10} ns^{0-2}$
- Q14.** Why are transition elements so named?
- Ans.** This is because their properties are in between those of *s*-block and *p*-block elements.
- Q15.** Write the outer electronic configuration of Cr atom ($z = 24$) [CBSE 2006]
- Ans.** Cr (24) : $[Ar] 3d^5 4s^1$
- Q16.** Which property of transition metals make them good catalysts. [CBSE 2004 F]
- Ans.** They show variable oxidation states and have vacant *d*-orbitals.
- Q17.** Why is the third ionisation energy of manganese (At. No. = 25) unexpectedly high? [CBSE 2003]
- Ans.** Mn (25) has E.C. = $[Ar] 4s^2 3d^5$
 Mn^{2+} has E.C. = $[Ar] 4s^0 3d^5$
 after losing 2 electrons, it has half-filled *d*-orbital, which is quite stable, that is why Mn^{2+} has exceptionally high third ionisation energy.
- Q18.** Why is Ce^{4+} in aqueous solution is a good oxidising agent? [CBSE 2003 C]
- Ans.** Ce^{4+} gains electron to form Ce^{3+} ion, therefore it is considered a good oxidising agent.
- Q19.** Name the Lanthanoid element which exhibits +4 oxidation state besides +3 oxidation state?
- Ans.** Cerium shows +3 as well as +4 oxidation states.
- Q20.** What is Lanthanoid contraction?
- Ans.** The steady decrease in the atomic and ionic size with the increase in atomic number is called Lanthanoid contraction.
- Q21.** What is the basic difference between the electronic configuration of lanthanoids and those of actinoids?
- Ans.** In lanthanoids *4f* orbital is progressively filled whereas in actinoids, *5f*-orbital is progressively filled.
- Q22.** Why do transition metals have high enthalpy of hydration?
- Ans.** Transition metal ions are smaller in case of size and have higher ionic charge, therefore they have high enthalpy of hydration.
- Q23.** Which trivalent cation is the largest in the lanthanoid series?
- Ans.** La^{3+} ion is the largest in lanthanoid series.
- Q24.** Why do most transition metal ions exhibit paramagnetism?
- Ans.** Most transition metal ions exhibits paramagnetism due to the presence of unpaired electrons.
- Q25.** Calculate the magnetic moment of Fe^{3+} ion (Atomic No. of Fe = 26)

Ans. Fe^{3+} has the electronic configuration: $[\text{Ar}] 4s^0 3d^5$

It is 5 unpaired electrons

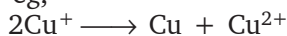
$$\begin{aligned}\therefore \mu &= \sqrt{n(n+2)} \\ &= \sqrt{5(5+2)} = \sqrt{35} \\ &= 5.9 \text{ BM}\end{aligned}$$

Q26. Why is KMnO_4 kept in dark coloured bottles?

Ans. KMnO_4 is kept in dark coloured bottles because KMnO_4 gets decomposed to form K_2MnO_4 in the presence of sunlight.

Q27. What is meant by disproportionation reactions? Give example.

Ans. The reactions in which the same substance is oxidised and reduced are called disproportionation reactions. For eg,



is a disproportionation reaction.

Q28. Which of the following ions is paramagnetic?

Sc^{3+} ($Z = 21$), Cu^+ ($Z = 29$)

Ans. None of them is paramagnetic.

Q29. What is the highest oxidation state shown by Cr ($Z = 24$)?

Ans. The highest oxidation state is shown by chromium, +6.

Q30. Why is Pt (IV) more stable than Ni (IV)?

Ans. Pt (IV) is more stable than Ni (IV) because energy required to remove four electrons is less in case of Pt than Ni.

Q31. Arrange the following in increasing order of acidic character?

CrO_3 , CrO , Cr_2O_3

Ans. $\text{CrO} < \text{Cr}_2\text{O}_3 < \text{CrO}_3$, \therefore Higher the oxidation state, more will be the acidic character.

Q32. What is the most stable oxidation state of Mn ($Z = 25$)?

Ans. The most stable oxidation state of Mn is +7.

Q33. Arrange the following in increasing order of basic character:

MnO , MnO_2 , Mn_2O_7

Ans. $\text{Mn}_2\text{O}_7 < \text{MnO}_2 < \text{MnO}$.

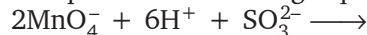
Q34. Name the d-block elements which are not considered as d-block elements.

Ans. Zn, Cd, Hg are not considered as d-block element.

Q35. Write the outer electronic configuration of Lanthanoids.

Ans. $4f^{1-14} 5d^{0-1} 6s^2$ is the outer electronic configuration of Lanthanoids.

Q36. Complete the following equation:



[CBSE 2014]

Ans. $2\text{MnO}_4^- + 6\text{H}^+ + 5\text{SO}_3^{2-} \longrightarrow 2\text{Mn}^{2+} + 3\text{H}_2\text{O} + 5\text{SO}_4^{2-}$

II. Short Answer Type Questions

(2 or 3 Marks)

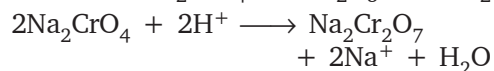
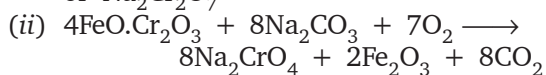
Q1. A metal oxide of iron and chromium $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ is fused with sodium carbonate in the presence of air to form a yellow coloured compound (A). On acidification the compound (A) forms an orange coloured compound (B). Which is a strong oxidising agent. Identify:

(i) the compound (A) and (B)

(ii) Write balanced chemical equation for each step. [CBSE 2009]

Ans. (i) Compound (A) is sodium chromate or Na_2CrO_4

Compound (B) is sodium dichromate or $\text{Na}_2\text{Cr}_2\text{O}_7$



Q2. Explain the following facts:

(a) Transition metals act as catalysts.

(b) Chromium group elements have the highest melting points in their respective series.

(c) Transition metals form coloured complexes. [CBSE 2009]

Ans. (a) Due to their ability to show multiple oxidation states, they form complexes.

(b) They have maximum number of unpaired electrons in d-orbitals because of which maximum d-d transitions occur.

(c) This is due to d-d transitions.

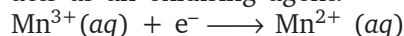
Q3. How would you account for the following situations?

- (i) The transition metal generally form coloured compounds
- (ii) With $3d^4$ configuration, Cr^{2+} acts as a reducing agent but Mn^{3+} acts as an oxidising agent.
(Atomic masses, Cr = 24, Mn = 25)
- (iii) The actinoids exhibit a larger number of oxidation states than the corresponding Lanthanoids. [CBSE 2008]

Ans. (i) Due to the presence of unpaired electrons, they undergo $d-d$ transitions by absorbing light from visible region and radiate the complementary colour.

- (ii) It can be explained on the basis of E^0 values of Cr^{3+}/Cr^{2+} (-0.4 V) and Mn^{3+}/Mn^{2+} ($+1.5$ V). On the basis of these values, it is clear that Cr^{2+} has a greater tendency to oxidise to Cr^{3+} , thus it acts as reducing agent.

While Mn^{3+} has a great tendency to get reduced into Mn^{2+} ions, thus it acts as an oxidising agent.



- (iii) Actinoids show a large number of oxidation states because of the small energy gap between $5f$, $6d$ and $7s$ subshells.

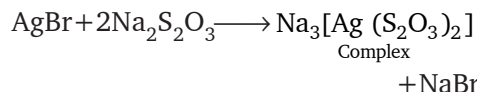
Q4. How would you account for the following observations:

- (i) The enthalpies of atomisation of transition metals are high.
- (ii) Of the lanthanoids only cerium ($Z = 58$) is known to exhibit quite stable +4 oxidation state in solutions.
- (iii) Sodium thiosulphate is used in fixing step of photography? [CBSE 2006 C]

Ans. (i) As transition metals have a large number of unpaired electron in the d -orbitals of their atoms, therefore they have strong interatomic attraction or metallic bonds. Hence, they have high enthalpies of atomisation.

- (ii) Ce (III) has electronic configuration $4f^1 5d^0 6s^0$. It easily loses an electron to acquire the configuration $4f^0$ and forms Ce (IV). Infact this is the only lanthanoid which exists with + (IV) oxidation state in solutions.

- (iii) Sodium thiosulphate (hypo) is used in the fixing step of photography to remove unchanged silver bromide as a soluble complex.



Q5. Assign reasons for the following observations:

- (i) Mn^{2+} compounds are more stable than Fe^{2+} compounds towards oxidation to their +3 state.
- (ii) Interstitial compounds are well known for transition elements.
- (iii) An aqueous solution of potassium chromate is yellow but changes its colour on decreasing the pH of solution. [CBSE 2006]

Ans. (i) Electronic configuration of ${}_{25}Mn^{2+}$ is $[Ar] 3d^5 4s^0$ whereas that of ${}_{25}Mn^{3+}$ is $[Ar] 3d^4 4s^0$.

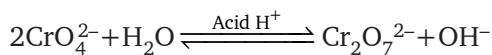
As half-filled orbitals are more stable, Mn^{2+} compounds are more stable than Mn^{3+} compounds.

The electronic configuration of ${}_{26}Fe^{2+}$ is $[Ar] 3d^6 4s^0$,



Thus, Fe^{3+} is more stable than Fe^{2+} due to more stable configuration.

- (ii) In the crystal lattice, of transition elements they have interstitial vacant spaces into which small size non-metal atoms (H, C, N, B) can fit, resulting in the formation of interstitial compounds.
- (iii) When the pH of the solution of potassium dichromate is decreased the colour of the solution changes from yellow to orange due to the conversion of CrO_4^{2-} ions into $Cr_2O_7^{2-}$ ions.



Q6. What is meant by 'lanthanoid contraction'. State one use each of lanthanoid metals and their oxides.

[CBSE 2006]

Ans. The steady decrease in the atomic/ionic radius from La^{3+} to Lu^{3+} is called lanthanoid contraction.

Uses of Lanthanoids and their oxides:

- (i) Mischmetal, an alloy of a Lanthanoid metal, is used in Mg-based alloy to produce bullets shells and lighter flints.
- (ii) Some Lutetium oxides are used as phosphorescence materials in television screens.

Q7. Explain the metallic character of transition elements. [CBSE 2006]

Ans. Metallic character:

- (i) Since the numbers of electrons in the outermost shell are two or one and they can be removed easily. Therefore, all the transition elements are metals.
- (ii) The electrons present in the outermost orbitals form metallic bond. Due to these metallic bonds, they have high melting point, high boiling point, high thermal and electrical conductivities.
- (iii) All transition metals except mercury (Hg) are highly malleable and ductile.

Q8. (a) How is the magnetic moment of a species related to the number of unpaired electrons?

- (b) Calculate the magnetic moment of a divalent ion in aqueous solution of its atomic number is 25. [CBSE 2005]

Ans. (a) **Magnetic moment:** Magnetic moment is determined by the number of unpaired electrons and is calculated by using the spin-only formula

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

Where n = No. of unpaired electrons.

μ = magnetic moment.

Its SI unit is μB (Bohr Magneton, BM).

- (b) $Z = (25) = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$
Its divalent ion has 5 unpaired electrons.

$$n = 5$$

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

$$= \sqrt{5(5+2)}$$

$$\mu = \sqrt{35} = 5.92 \text{ BM}$$

Q9. Explain any one of the following statements:

- (i) The transition metals are well known to form interstitial compounds.
- (ii) The largest number of oxidation states are exhibited by manganese in the first series of transition elements.

[Foreign 2007]

Ans. (i) In the crystal lattice, transition elements have interstitial vacant spaces into which small size non-metals atom (H, C, N, B) can fit, resulting in the formation of interstitial compounds.

- (ii) Mn (25): $4s^2 3d^5$ have five unpaired electrons in '3d' orbital and two electrons in 's' orbital i.e. it has maximum no. of electrons which can take part in bond formation, therefore it shows maximum number of oxidation states.

Q10. Answer the following questions:

- (i) Which element in the first series of transition elements does not exhibit variable oxidation state and why?
- (ii) Why do actinoids, in general, exhibit a greater range of oxidation states than lanthanoids? [Foreign 2007]

Ans. (i) Zinc does not show variable oxidation state because it has completely filled d -orbitals.

- (ii) They have lower ionisation energy and less effective nuclear charge. Therefore more number of valence electrons can take part in bond formation.

Q11. Write chemical equations for the reactions involved in the manufacture of potassium permanganate from pyrolusite ore. [CBSE 2006]

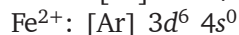
Ans. (i) $2\text{MnO}_2 + 4\text{KOH} + \text{O}_2 \xrightarrow{\Delta} 2\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O}$

(ii) $\text{MnO}_4^{2-} \xrightarrow{\text{Electrolysis}} \text{MnO}_4^- + e^-$
Purple

Q12. Why is +2 oxidation state of manganese quite stable, while the same is not true for iron?

[Mn = 25, Fe = 26] [AI 2006]

Ans. Mn^{2+} is more stable due to half-filled electronic configuration of d -orbitals but Fe^{2+} is not stable because it does not have half-filled stable d -orbital electronic configuration.



Q13. What is misch metal (mischmetal)?

Mention its two important uses.

[Foreign 2006]

Ans. Misch metal consists of Lanthanoids (95%), iron, (~5%) and traces of S, C, Ca and Al.

Uses:

- (i) It is used to make bullets.
- (ii) It is used in making shells and lighter flints.

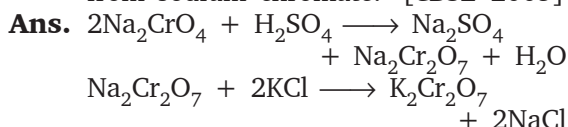
Q14. How is variability in oxidation states of the transition elements different from that of the non-transition elements? Illustrate with examples.

[AI 2006 C]

Ans. Transition metals show variable oxidation states because electrons from both 's' as well as 'd'-orbitals take part in bond formation. For eg., Mn (25) shows +2, +3, +4, +6, +7 oxidation states.

On the other hand, non-transition elements does not exhibit variable oxidation states. Infact they show a general fixed oxidation state of elements in their compounds.

Q15. Describe the steps involved in the preparation of potassium dichromate from sodium chromate. [CBSE 2005]



Q16. The outer electronic configuration of two transition metals are (i) $3d^5 4s^2$ and (ii) $3d^6 4s^2$, respectively. Based on this information predict the relative stability of +2 and +3 oxidation state of these metals. Which one of these two exhibits larger number of oxidation states? [Foreign 2004]

Ans. (i) +2 oxidation state will be more stable than +3 due to half-filled d -orbitals.

- (ii) The metal will be more stable in +3 oxidation state than +2, due to stable electronic configuration, *i.e.* half-filled d -orbitals.

The metal with configuration $3d^5 4s^2$ will exhibit larger number of oxidation states such as +2, +3, +4, +5, +6, +7.

Q17. (a) Name two properties of the central metal ion which enable it to form stable complex entities.

- (b) Account for the following:

Zinc salts are white while Cu^{2+} salts are coloured.

[At. Nos: Zn = 30, Cu = 29]

[CBSE 2003]

Ans. (a)(i) Smaller size of cation.

- (ii) High charge on the cation (metal ion)

- (b) In Zinc salts, Zn^{2+} does not have unpaired electrons, therefore it cannot undergo $d-d$ transitions. Whereas in Cu^{2+} ions there is an unpaired electron due to which it can undergo $d-d$ transitions.

Q18. How do you account for the following?

- (i) All scandium salts are white? (At. No. of Sc = 21)
- (ii) The first ionisation energies of the 5d transition elements are higher than those of the 3d and 4d transition elements in respective groups?

[CBSE 2003]

Ans. (i) Sc^{3+} ions does not have any unpaired electron and has empty d -orbitals, therefore cannot undergo $d-d$ transitions. Hence its salts are white.

- (ii) It is due to lanthanoid contraction, which is due to poor shielding effect of 5d and 4f electrons, effective nuclear charge increases. Hence ionisation energy of 5d transition elements is more than that of 3d and 4d transition elements in respective groups.

Q19. Explain the following observations:

- (a) The elements of the *d*-series exhibit a larger number of oxidation states than the elements of *f*-series.
(b) The Cu^+ salts are colourless while Cu^{2+} salts are coloured (At. No. of Cu = 29) [CBSE 2003]

Ans. (a) In *d*-series, there are large number of unpaired electrons which can take part in bond formation due to less effective nuclear charge, therefore number of oxidation states are more than *f*-block elements in which there is more elements effective nuclear charge due to poor shielding effect of *f*-orbitals, and lesser number of electrons take part in bond formation.
(b) Cu^+ ion does not have unpaired electron therefore it cannot undergo *d-d* transitions. That is why Cu^+ salts are colourless whereas Cu^{2+} salts are coloured due to the presence of one unpaired electron, it can undergo *d-d* transition by absorbing light from the visible region and radiate blue colour.

Q20. Write balanced equations to represent what happens when

- (i) Acidified KMnO_4 solution reacts with iron (II) ions
(ii) Pyrolusite is fused with KOH in the presence of air [Foreign 2003]

Ans. (i) $5\text{Fe}^{2+} + \text{MnO}_4^- + 8\text{H}^+ \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} + 5\text{Fe}^{3+}$
(ii) $2\text{MnO}_2 + 4\text{KOH} + \text{O}_2 \xrightarrow{\Delta} 2\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O}$

Q21. Mention the direct consequence of the following factors on the chemical behaviour of the transition elements:

- (i) They have incompletely filled *d*-orbitals in the ground state or in one of the oxidised state of their atoms.
(ii) They contribute more valence electrons per atom in the formation of metallic bonds.

Ans. (i) (a) They can form complex compounds.
(b) They show variable oxidation states.
(c) They are used as catalysts.
(ii) (a) They are hard.

- (b) They have high melting and boiling points.
(c) They have high enthalpy of atomisation.
(d) They are malleable and ductile.

Q22. Explain why

- (i) E^0 for $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple is more positive than that for $\text{Fe}^{3+}/\text{Fe}^{2+}$ (At. Nos. of Mn = 25, Fe = 26)
(ii) Ce^{3+} can be easily oxidised to Ce^{4+} (At. No. of Ce = 58).

Ans. (i) Mn^{2+} is more stable ($4s^0 3d^5$) because of its half-filled *d*-orbitals than Mn^{3+} ($4s^0 3d^4$) whereas Fe^{3+} ($4s^0 3d^6$) is more stable than Fe^{2+} ($4s^0 3d^6$), therefore Mn^{3+} can be easily reduced to Mn^{2+} whereas Fe^{3+} is not easily reduced to Fe^{2+} . Infact Fe^{2+} is more easily oxidised to Fe^{3+} .
(ii) Ce^{4+} is more stable than Ce^{3+} because of stable electronic configuration and higher hydration energy because *f*-orbitals are vacant, hence Ce^{3+} is easily oxidised to Ce^{4+} .

Q23. With the help of ionic equation describe what happens when:

- (i) pH of solution of dichromate ions is raised.
(ii) potassium manganate is electrochemically oxidised.

Ans. (i) $\text{Cr}_2\text{O}_7^{2-} + 2\text{OH}^- \xrightleftharpoons[\text{pH}]{\text{higher pH}} 2\text{CrO}_4^{2-} + \text{H}_2\text{O}$
(orange) (yellow)

when pH is increased, i.e. solution is more basic, orange coloured dichromate ion changes to yellow coloured chromate ion.

(ii) $\text{MnO}_4^{2-} \xrightarrow{\text{Electrolysis}} \text{MnO}_4^- + \text{e}^-$
Purple

Q24. Explain the following giving reasons:

- (i) It is difficult to separate Lanthanoid elements in pure state.
(ii) The transition elements form interstitial compounds.

Ans. (i) It is because lanthanoids have similar ionic sizes, therefore they occur together and their separation becomes difficult.

(ii) The transition metals have voids in their crystal lattice into which small atoms like H, C and N resulting in the formation of interstitial compounds.

Q25. (a) Write the electronic configuration of the element with atomic number 102.

(b) What is lanthanoid contraction? What is its effect on the chemistry of the elements which follow the lanthanoids? [AI 2006]

Ans. (a) E.C. = [Rn] $^{86}5f^{14}6d^07s^2$

(b) The decrease in atomic and ionic size with increase in atomic number among lanthanoids is called lanthanoid contraction. The elements after lanthanoids closely resemble with the elements exactly above them due to similar ionic size. Eg. Zr and Hf have similar atomic size.

Q26. Give reason for each of the following:

(i) Size of the trivalent lanthanoid cations decreases with increase in the atomic number.

(ii) Transition metal fluorides are ionic in nature, whereas bromides and chlorides are usually covalent in nature.

(iii) Chemistry of all the lanthanoids is quite similar. [AI 2005 C]

Ans. (i) It is due to poor shielding effect of *f*-electrons, increase in effective nuclear charge and decrease in ionic size.

(ii) F is more electronegative than Cl and Br. Therefore fluorides are ionic whereas chlorides and bromides are covalent.

(iii) Lanthanoids due to similar ionic size which is due to lanthanoid contraction resemble in their properties.

Q27. Explain why do transition elements show variable oxidation states. Write all the possible oxidation states of an element having atomic number 25.

[AI 2005 C]

Ans. They show variable oxidation state because electrons from 's' as well as *d*-orbitals take part in bond formation. Mn (25) can show +2, +3, +4, +6, and +7 oxidation states.

Q28. The outer electronic configuration of atoms of two members of lanthanoid series are given below:

(i) $4f^1 5d^1 6s^2$

(ii) $4f^7 5d^0 6s^2$

Find their atomic numbers. What oxidation states will possibly be exhibited by these elements?

[Foreign 2005]

Ans. (i) Ce (58). It shows +4 oxidation state.

(ii) Eu (63). It shows +2 oxidation state.

Q29. Identify the first row transition metal ions which have outer electronic configuration of $3d^4$ and $3d^6$ and describe their oxidation states.

[CBSE 2005 F]

Ans. Cr^{2+} ion has electronic configuration $3d^4$. Chromium also shows +3 and +6 oxidation states.

Fe^{2+} ion has electronic configuration of $3d^6$. Iron exhibits oxidation states of +2 and +3.

Q30. Discuss the general characteristics of the *3d* series of the transition elements with special reference to their

(i) atomic size

(ii) enthalpies of atomisation

(iii) tendency for complex formation

[Foreign 2003]

Ans. (i) **Atomic size:** The atomic size in *3d* transition series decreases from Sc to Mn and then Fe, Co, Ni have almost same atomic size while copper has bigger size. It is because number of unpaired electrons in *d*-orbitals increases in the beginning till Mn. Therefore effective nuclear charge increases hence atomic size decreases. Then pairing of electrons in *d*-orbitals take place, so the atomic size remains the same and finally it increases due to repulsion between paired electrons in *d*-orbitals which leads to decrease in effective nuclear charge.

- (ii) They have high enthalpy of atomisation due to strong metallic bonds and additional covalent bonding due to the presence of unpaired electrons in d -orbitals.
- (iii) The tendency single to form complex compounds increases due to decrease in atomic size and increase in positive charge.

Q31. Why is Cr^{2+} reducing and Mn^{3+} oxidising when both have d^4 configuration?

Ans. Cr^{2+} ion has d^4 configuration. When Cr^{2+} changes to Cr^{3+} , then the configuration changes from d^4 to d^3 , the later having a half filled $t_{2g}^3 e_g^0$ stable configuration.

On the other hand the change from Mn^{3+} to Mn^{2+} , it results in the half filled (d^5) configuration which has extra stability.

Q32. Answer the following questions:

- (i) Name the transition element which dose not exhibit variable oxidation states.
- (ii) Name a member of the lanthanoid series which is well known to exhibit +4 oxidation state.

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

(ii) Cerium ($Z = 58$)

Q33. Complete the following equations:



Ans. (i) $\text{Cr}_2\text{O}_7^{2-} + 2\text{OH}^- \longrightarrow 2\text{CrO}_4^{2-} + \text{H}_2\text{O}$



Q34. Account for the following: (3-mark)

- (i) Zn (Cd, Hg) is not considered as a transition element.
- (ii) Transition metals form a large number of complexes.
- (iii) The E^0 value for the $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple is much more positive than that for Cr^{3+} couple. [AI 2017]

Ans. (i) Zinc (Cd/Hg) is not considered a transition element because it does not have partially filled(or incomplete)

d -subshell. It has $3d$ -subshell fully filled.

(ii) The transition elements form complexes because of the following reasons:

- Comparitively smaller size of their metal ions.
- Their high ionic charges.
- Availability of vacant d -orbitals so that these orbitals can accept the lone pair of electrons donated by the ligands.

(iii) In case of Mn '+2' oxidation state is more stable than '+3' oxidation state and in case of Cr '+3' oxidation state is more stable than '+2' oxidation state.

Q35. (i) With reference to structural variability and chemical reactivity, write the differences between lanthanoids and actinoids.

(ii) Name a member of the lanthanoid series which is well known to exhibit +4 oxidation state. [CBSE 2014]

Ans. (i)

Lanthanoids	Actinoids
<ul style="list-style-type: none"> • Their magnetic properties can be explained easily. • Except promethium, they are non-radioactive. • Besides +3 oxidation state, they show +2 and +4 oxidation states only in few cases. • Lanthanoid compounds are less basic. 	<ul style="list-style-type: none"> • Their magnetic properties cannot be explained easily, as they are more complex. • They are all radioactive. • Besides +3 oxidation state, they show higher oxidation states, e.g. +4, +5, +6, +7 also. • Actinoid compounds are more basic.

(ii) Ce

Q36. Why do the transition elements have higher enthalpies of atomisation? In 3d series (Sc to Zn), which element has the lowest enthalpy of atomisation and why? [CBSE 2015]

Ans. Transition metals have high effective nuclear charge, greater number of valence electrons and some unpaired electrons. They thus have strong metal-metal bonding.

Hence, transition metals have high enthalpies of atomisation.

In the 3d series, from Sc to Zn, only zinc has filled valence shells. The valence shell electronic configuration of Zn is $3d^{10}4s^2$. Due to the absence of unpaired electrons in ns and $(n-1)d$ shells, the interatomic electronic bonding is the weakest in zinc.

Consequently, zinc has the least enthalpy of atomisation in the 3d series of transition elements.

Q37. How would you account for the following:

- (i) The chemistry of actinoids is more complicated as compared to lanthanoids.
- (ii) Transition metals form complex compounds.

Ans. (i) The energy difference between the 6d, 7s and 5f orbitals is very small in case of actinoids. In addition, the 5f orbitals of the actinoids are less shielded than the 4f orbitals of lanthanoids. Thus, in the lanthanoids, only 4f electrons of Ce participate in chemical bonding, whereas in the lighter actinoids, upto americium, the 5f electrons also take part. This makes the chemistry of actinoids more complicated than that of lanthanoids.

- (ii) The transition elements form complexes because they are able to accept pair of electrons from donor molecules or ions to form dative covalent bonds. This happens because they have vacant orbitals of suitable energy which can accept the non-bonding pair from the ligands.

Q38. The elements of 3d transition series are given as:

Sc Ti V Cr Mn Fe Co

Answer the following:

- (i) Write the element which shows maximum number of oxidation states. Give reason.
- (ii) Which element has the highest m.p?
- (iii) Which element shows only +3 oxidation state?

- (iv) Which element is a strong oxidising agent in +3 oxidation state and why?

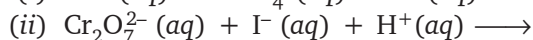
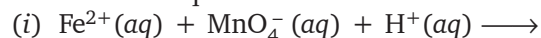
Ans. (i) Mn shows the maximum oxidation state of +7. Mn ($3d^5 4s^2$) has half-filled d orbitals and it can lose all the seven valence electrons.

- (ii) Cr has the highest melting point.
- (iii) Sc shows only +3 oxidation state.
- (iv) Mn is a strong oxidising agent in the +3 oxidation state because it achieves the stable $3d^5$ configuration in the +2 oxidation state.

III. Long Answer Type Questions

(5 Marks)

Q1. (a) Complete the following chemical reaction equations:

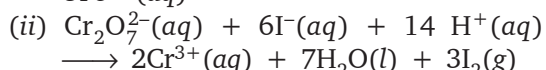


(b) Explain the following observations:

- (i) Transition elements are known to form many interstitial compounds.
- (ii) With the same d^4 configuration Cr^{2+} ion is reducing while Mn^{3+} ion is oxidising.
- (iii) The enthalpies of atomisation of transition elements are quite high.

[CBSE 2009, Delhi 2012]

Ans. (a) (i) $5\text{Fe}^{2+}(\text{aq}) + \text{MnO}_4^- (\text{aq}) + 8\text{H}^+(\text{aq}) \longrightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l}) + 5\text{Fe}^{3+}(\text{aq})$



- (b) (i) The transition metals have voids in their crystal lattice into which small atoms like H, C, N, are trapped inside, resulting in the formation of Interstitial compounds.
- (ii) Cr^{2+} ion is reducing as its configuration changes from d^4 to d^3 , the later having half-filled configuration. While the change from Mn^{2+} to Mn^{3+} results in half-filled (d^5) configuration which has extra stability.
- (iii) Because of large number of unpaired electrons in their atoms they have stronger interatomic interactions and

hence stronger bonding between atoms resulting in higher enthalpies of atomisation.

Q2. (a) Describe the general trends in the following properties of the first series of the transition elements.

- (i) Stability of +2 oxidation state.
- (ii) Formation of oxometal ions.
- (b) Assign reason for each of the following.
 - (i) Transition elements exhibits variable oxidation states.
 - (ii) Transition metal ions are usually coloured. [CBSE 2007]

Ans. (a) (i) Most of the transition metals show +2 oxidation state. Mn^{2+} is more stable due to half filled *d*-orbitals.

- (ii) They form oxometal ions because they show variable oxidation states and form stable oxoanions like MnO_4^- , CrO_4^{2-} and $Cr_2O_7^{2-}$.
- (b) (i) Transition metals show variable oxidation states because electrons from both 's' and 'd' orbitals take part in bond formation.
- (ii) Transition metal ions have unpaired electrons due to which they can undergo *d-d* transitions by absorbing light from the visible region and radiating complementary colour.

Q3. (a) Write the steps involved in the preparation of

- (i) $K_2Cr_2O_7$ from Na_2CrO_4
- (ii) $KMnO_4$ from K_2MnO_4
- (b) What is meant by lanthanoid contraction? What effect does it have on the chemistry of elements which follow lanthanoids? [CBSE 2007]

Ans. (a) (i) $2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$
 $Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$

(ii) $MnO_4^{2-} \xrightarrow{\text{Electrolysis}} MnO_4^- + e^-$

- (b) The decrease in atomic and ionic size with the increase in atomic number in lanthanoids is called lanthanoid contraction.

Effects.

- (i) The ionisation energy of 5*d* series is more than 3*d* and 4*d*-series.
- (ii) There is resemblance between properties of 4*d* and 5*d* series.

Q4. (a) Explain why do transition elements show variable oxidation states. Write all the possible oxidation states of an element having atomic number 25.

- (b) Compare the chemistry of actinoids with that of the lanthanoids in reference to

- (i) Atomic and ionic size
- (ii) Oxidation states. [AI 2006 C]

Ans. (a) Transition metals show variable oxidation states because electrons from both 's' as well as 'd'-orbitals take part in bond formation.

Mn (25) shows +2, +3, +4, +6, +7 oxidation states.

- (b) (i) Actinoids show actinoid contraction like lanthanoids but the contraction is greater from element to element in their series resulting from poor shielding by 5*f* electrons.
- (ii) Lanthanoids show +3 as most common oxidation state along with +2 and +4 shown by some of elements. Actinoids show +2, +3, +4, +5, +6 and +7 oxidation states due to lesser ionisation energy.

Q5. (a) The outer electronic configuration of two members of the lanthanoid series are as follows:

$4f^1 5d^1 6s^2$ and $4f^7 5d^0 6s^2$, what are their atomic numbers? Predict the oxidation states exhibited by these elements in their compounds.

- (b) Assign reason for the following statement:

The largest number of oxidation states are exhibited by the elements in the middle of the first row of the transition elements. [AI 2005]

Ans. (a) Ce (58) and Eu (63) are elements. Ce shows +3 and +4 oxidation states

whereas Eu shows +2 and +3 oxidation states.

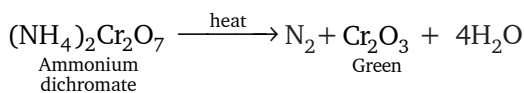
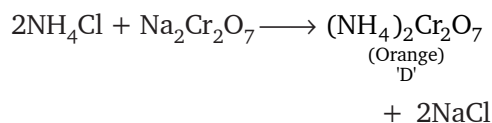
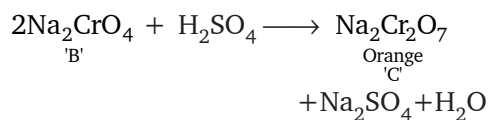
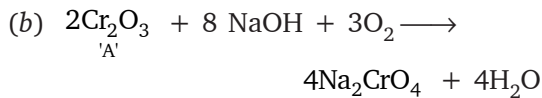
- (b) It is because they have maximum number of unpaired electrons in the middle of the first row of transition elements.

Q6. Explain the following:

- (i) Transition elements tend to be unreactive with increasing atomic number in the series.
 (ii) d-block elements exhibit more oxidation state than f-block elements.
 (iii) A green chromium compound (A), On fusion with alkali gives yellow compound (B) which on acidification gives an orange coloured compound (C). 'C' on treatment with NH_4Cl gives an orange coloured product (D) which on heating decomposes to give back compound (A). Identify A, B, C and D. Write equation for the reactions.

[CBSE 2004 C]

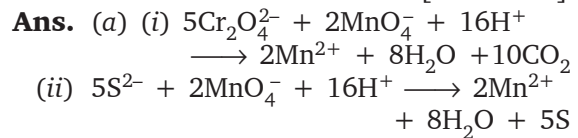
- Ans.** (i) Transition metals can form layer of oxides on their surface due to which they become unreactive. Secondly, reactivity decreases with increase in the atomic number due to decrease in size and increase in ionisation energy.
 (ii) In d-block elements, electrons of s-orbital and d-orbitals both take part in bond formation. In f-block elements due to poor shielding effect of f-electrons, effective nuclear charge increases. Therefore, lesser number of oxidation states are shown.



Q7. (a) Give balanced chemical equations of two reactions in which KMnO_4 acts as an oxidising agent in acidic medium.

(b) Give reason:

- (i) Cr^{2+} is a strong reducing agent whereas Mn^{2+} is not (Cr = 24, Mn = 25).
 (ii) The transition metal ions such as Cu^+ , Ag^+ and Sc^{3+} are colourless.
 (iii) Chemistry of the actinoids is much more complicated than that of the lanthanoids. [AI 2004 C]



- (b) (i) Cr^{2+} is less stable than Cr^{3+} therefore it is good reducing agent whereas Mn^{2+} is stable due to half-filled d-orbitals, therefore it is not a good reducing agent.
 (ii) Cu^+ , Ag^+ , Sc^{3+} are colourless because they do not have unpaired electrons.
 (iii) In actinoids energies of 5f, 6d and 7s orbitals are comparable and therefore they show large number of oxidation states, that is why their chemistry is more complicated. Secondly all of them are radioactive.

Q8. (a) Out of Ag_2SO_4 , CuF_2 , MgF_2 and CuCl , which compound will be coloured and why?

(b) Explain:

- (i) CrO_4^{2-} is a strong oxidising agent while MnO_4^{2-} is not
 (ii) Zr and Hf have identical atomic/ionic size.
 (iii) The lowest oxidation state of manganese is basic while the highest is acidic.
 (iv) Mn (II) shows maximum paramagnetic character amongst the divalent ions of the first transition series. [CBSE 2009]

Ans. (a) CuF_2
 In CuF_2 , Cu^{2+} ($3d^9$) has one unpaired electron.

- (b) (i) Oxidation state of Mn in MnO_4^{2-} is +6. Mn can further lose an electron

to raise its oxidation state to +7, which is the highest oxidation state of manganese.

Oxidation state of Cr in CrO_4^{2-} is +6. This is its maximum oxidation state and it can only further gain electrons.

- (ii) This is due to lanthanoid contraction.
- (iii) In its highest oxidation state manganese can only accept electrons and so is acidic in behaviour. Similarly in its lowest oxidation state it can donate electrons and hence is basic.
- (iv) Mn (II) ions has maximum number of unpaired electrons, *i.e.* $3d^5$.

Q9. (a) In the titration of FeSO_4 with KMnO_4 in the acidic medium, why is dil. H_2SO_4 used instead of dil. HCl ?

(b) Give reason:

- (i) Among transition metals, the highest oxidation states is exhibited on oxo-anions of a metal.
- (ii) Ce^+ is used as an oxidising agent in volumetric analysis.
- (iii) Transition metals form a number of interstitial compounds.
- (iv) Zn^{2+} salts are white while Cu^{2+} salts are blue. [CBSE 2009]

Ans. (a) Dil H_2SO_4 is an oxidising agent and oxidises FeSO_4 to $\text{Fe}_2(\text{SO}_4)_3$. On the other hand, dil. HCl is a reducing agent and liberates chlorine on reacting with KMnO_4 solution. Thus, a part of the oxygen produced from KMnO_4 is used up by HCl .

(b) (i) In these oxoanions the oxygen atoms are directly bonded to the transition metal atom/ion.

Since oxygen is highly electronegative, therefore, the oxoanions bring out the highest oxidation state of the metal.

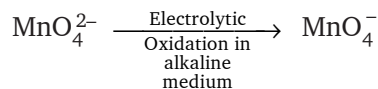
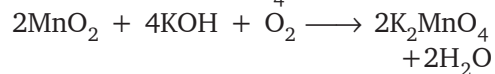
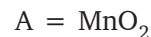
- (ii) Ce^{4+} has the tendency to attain +3 oxidation state and so it is used as an oxidising agent in volumetric analysis.
- (iii) This is due to the presence of voids of appropriate size in their crystal lattices.

(iv) Zn^{2+} ions has all its orbitals completely filled whereas in Cu^{2+} ion there is one half filled $3d$ -orbital. It therefore has a tendency to form coloured salts whereas Zn^{2+} has no such tendency.

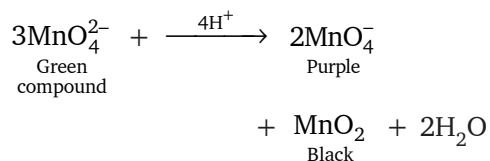
Q10. (a) A blackish brown coloured solid 'A' when fused with alkali metal hydroxides in presence of air produces a dark green coloured compound 'B' which on electrolytic oxidation in alkaline medium gives a dark purple coloured compound 'C'. Identify A, B and C and write the reactions involved.

(b) What happens when an acidic solution of the green compound (B) is allowed to stand for sometime? Give the equation involved. What is this type of reaction called. [CBSE 2009]

Ans.



(b) In acidic medium, K_2MnO_4 changes to give purple coloured solution along with a black precipitate.



It is called disproportionation reaction.

Q11. Give reasons for the following:

- (a) Transition metals have high enthalpies of atomisation.
- (b) Among the lanthanoids, Ce(III) is easily oxidised to Ce (IV).
- (c) $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple has less positive electrode potential than $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple.
- (d) Copper(I) has d^{10} configuration while copper(II) has d^9 configuration. Still

copper(II) is more stable in aqueous solution than copper(I).

- (e) The second and third transition series elements have almost similar atomic radii. [CBSE 2009, AI 2014]

Ans. (a) Due to strong interatomic interactions between the unpaired valence electrons.

- (b) Ce(IV) has extra stability due to empty f^0 orbital.

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

- (d) Due to more negative enthalpy of hydration of $\text{Cu}^{2+}(\text{aq})$ than $\text{Cu}^+(\text{aq})$, which compensates for second ionisation enthalpy of copper, Cu(II) is more stable than Cu(I).

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

Q12. (a) Account for the following:

- (i) Mn shows the highest oxidation state of +7 with oxygen but with fluorine, it shows the oxidation state of +4.
 (ii) Cr^{2+} is a strong reducing agent.
 (iii) Cu^{2+} salts are coloured, while Zn^{+2} salts are white.

(b) Complete the following equations:

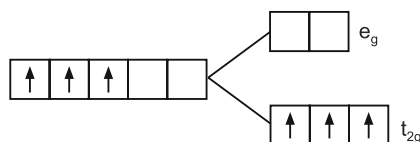


[CBSE 2016]

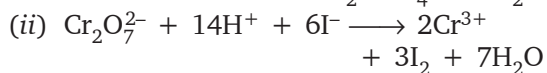
Ans. (i) In case of oxygen, Mn shows the highest oxidation state of +7. This is because Mn forms $p\pi-d\pi$ multiple

bonds using 2p orbitals of oxygen and 3d orbitals of Mn. With F, Mn displays an oxidation state of +4 because of the single bond formation caused by the unavailability of 2p orbitals of F for multiple bonding.

- (ii) Cr^{2+} is strongly reducing in nature. It has a d^4 configuration. While acting as a reducing agent, it gets oxidised to Cr^{3+} (with electronic configuration d^3). This d^3 configuration can be written as t_{2g}^3 configuration, which represents a more stable configuration.



- (iii) Zn^{2+} salts have a completely filled set of d-orbitals ($3d^{10}$), while Cu^{2+} has an incompletely filled set of d-orbitals ($3d^9$), and therefore, d-d transition is possible in Cu^{2+} , leading to its blue colour.



IV. Value-Based Questions

Q1. A poster suggests the following life style on the part of families/ individuals.

- (a) Use organic food products.
 (b) Use KMnO_4 for bleaching purpose instead of using chlorine based bleaching agents.
 (c) Use alloy steel to furnish home needs than wood.
 (d) Use bicycle for travelling short distances rather than petrol/diesel based vehicles.

Questions:

- (i) Which environmental values are promoted through these life style.
 (ii) Suggest one additional life style action for promotion of green chemistry.

(iii) Give reason for the bleaching action of KMnO_4

Ans. (i) Environmental conservation.

(ii) Use jute bags or cloth bags in place of polythene bags.

(iii) KMnO_4 acts a strong oxidising agent.

Q2. An NGO decided to supply KMnO_4 in villages in monsoon to be added to water bodies. Why? What is the value behind this decision.

Ans. It can be used as a disinfectant and germicide to clean the wounds and to purify water.

Social responsibility and awareness.

Q3. An element X has low melting point and high density. It is used in thermometers and barometers and its oxide is used in batteries.

(i) Name the element X.

(ii) Why is the use of the element X in skin lightening creams not recommended?

(iii) Should we advocate the use of metal free cosmetics? What value is reflected in this approach?

Ans. (i) Mercury (Hg)

(ii) Mercury is used in skin lightening creams but is not recommended because it is toxic in nature.

(iii) We should advocate the use of metal free cosmetics as most of them are carcinogenic in nature. Self awareness, critical thinking.

Q4. For automotive catalytic converters, transition metals like Pt, Pd, Rd, Fe, Cr, etc. used in industry are expensive while ceramic cores are inexpensive.

(i) Which property of transition metal makes them useful as catalyst?

(ii) Which value is promoted through the use of catalytic converters in industry?

(iii) As a student of chemistry would you suggest the use of expensive and rare metals like Pt, Pd and Rh. Give reasons.

Ans. (i) Transition metals can adopt multiple oxidation state and they can provide large surface area for the

formation of bond between the reactant molecules.

(ii) Social responsibility, Critical thinking.

(iii) Use of expensive metals like Pd, Pt and Rh is advisable as they can be used as catalytic convertors-like catalyst, in jewellery making, in synthesis of various organic compounds etc.

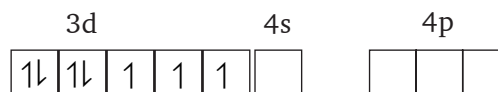
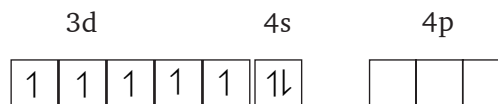
V. HOTS Questions

Q1. Give the electronic configuration of d -orbitals of $\text{K}_3[\text{Fe}(\text{CN})_6]$ and $\text{K}_3[\text{FeF}_6]$ and explain why these complexes give different colour with same solution.

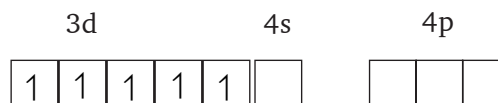
(At. No. of Fe = 26u)

Ans. Oxidation state of Fe in $\text{K}_3[\text{Fe}(\text{CN})_6]$ is +3

Configuration of Fe^{3+} is $[\text{Ar}]3d^5$



It has 5 unpaired electrons in 3d orbital which gets paired up leaving behind one unpaired electron only. In $\text{K}_3[\text{FeF}_6]$ oxidation state of Fe is +3 and 5 unpaired electrons are there in 3d orbitals.



Because of the presence of different no. of unpaired electrons these impart different colour to the same solution.

Q2. (a) Compare non-transition and transition elements on the basis of their:

(i) Variability of oxidation states.

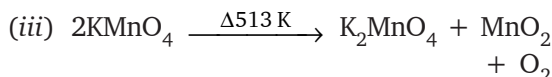
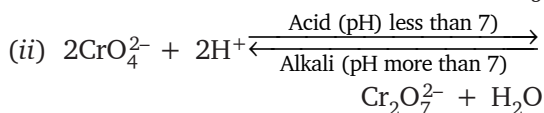
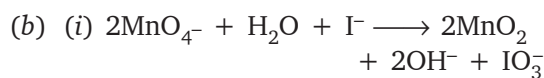
(ii) Stability of oxidation states.

(b) Give chemical reactions for the following observations:

- (i) Potassium permanganate is a good oxidising agent in basic medium.
- (ii) Interconvertibility of chromate ions and dichromate ions in aqueous solution depends upon the pH of the solution.
- (iii) Potassium permanganate is thermally unstable at 513K.

Ans. (a) (i) Oxidation state of transition elements differ from each other by unity. In case of non transition elements oxidation state normally differ by two units.

- (ii) In transition elements higher oxidation states are favoured by heavier elements whereas in non transition elements lower oxidation state are favoured by transition elements.



Q3. How would you account for the following?

- (i) Of the d^4 species, Cr^{2+} is strongly reducing while manganese(III) is strongly oxidising.
- (ii) Cobalt(II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidised.
- (iii) The d^1 configuration is very unstable in ions.

Ans. (i) Cr^{+2} is a strong reducing agent, it changes to Cr^{3+} by losing an electron, Cr^{3+} is more stable due to half filled electronic configuration. Mn^{3+} is oxidising agent and reduced to Mn^{2+} which has half filled (d^5) stable electronic configuration.

- (ii) Cobalt(II) is oxidised to Co(III) because Co(III) is more stable than Co(II).

- (iii) Transition metal ion with d^1 configuration loses its electron readily to form stable noble gas configuration of d^0 . Hence, ion with d^1 configuration is unstable.

Q4. Give examples and suggest reasons for the following features of the transition metal chemistry:

- (i) The lowest oxide of transition metal is basic; the highest is amphoteric/acidic.
- (ii) A transition metal exhibits highest oxidation state in oxides and fluorides.
- (iii) The highest oxidation state is exhibited in oxo-anions of a metal.

Ans. (i) In the lowest oxidation state, ionic bond is formed, less number of electrons are involved.

Oxides donate electrons and behave like a base.

In the highest oxidation state, covalent bond is formed. In higher oxidation state, more electrons are involved in bonding. Oxides can gain electron and behaves like a Lewis acid.

- (ii) Because oxygen and fluorine are strong oxidising and highly electronegative elements.
- (iii) Due to high electronegativity of oxygen.

Q5. Which is the last element in the series of the actinoids? Write the electronic configuration of this element. Comment on the possible oxidation state of this element.

Ans. Lr, $Z = 103$, is the last element of actinoid series. Its electronic configuration is $[\text{Rn}]^{86}5f^{14}6d^{17}s^2$. The possible oxidation state shown by it is +3.

□□□