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<u>Unit – 4 Transition and inner transition elements</u> **Book back**

Answer the following questions

1. What are transition metals?. Give four examples

- ❖ IUPAC defines transition metal as an element whose atom has an **incomplete d sub shell** or which can give rise to **cations** with an incomplete d sub shell.
- ❖ Their properties are transitional between highly reactive metals of s block and elements of p block which are mostly non metals.

Example: Fe, Cu, Ni, CO

2. Explain the oxidation state of 4d series elements

- 1) The oxidation states of 4d metals vary from +3 for Y and La to +8 for Ru and Os.
- 2) The highest oxidation state of 4d elements are found in their compounds with the higher electronegative elements like O, F and Cl. for example: RuO₄, OsO₄ and WCl₆.
- 3) First element of 4d series Yttrium has only one oxidation state +3.
- 4) Last element of 4d series has only one oxidation state +2.
- 5) Middle element Ru has seven different oxidation states from +2 to +8.
- 6) +2 & +3 are their common oxidation states.

3. What are inner transition elements?

- \clubsuit The elements in which the extra electron enters (n-2)f orbitals are called f block elements.
- **❖** They are called as **inner transition elements** they form a **transition series within the transition elements**.

4. Justify the position of lanthanoids and actinoids in periodic table

- 1) The actual position of Lanthanoids in the periodic table is at group number 3 and period
- 2) number 6.
- 3) However, in the sixth period after lanthanum, the electrons are preferentially filled in inner 4f sub shell and these fourteen elements following lanthanum show similar chemical properties.
- 4) Therefore these elements are grouped together and placed at the bottom of the periodic table.
- 5) If we place these elements after Lanthanum in the periodic table below 4d series, the properties of the elements belongs to a group would be different and it would affect the proper structure of the periodic table.
- 6) Hence a separate position is provided to the inner transition elements.

Lanthanoids have general electronic configuration $[Xe]4f^{1-14}5d^{0-1}6s^2$.

Actinoids have general electronic configuration [Rn]5f²⁻¹⁴6d⁰⁻²7s²

The **common oxidation state** of lanthanoids and actinoids are +3

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All these elements have similar physical and chemical properties.

5. What are actinides?. Give three examples

- The fourteen elements following actinium, i.e., from Thorium (Th) to Lawrentium (Lr) are called actinoids.
- ❖ Similar to lanthanoids, they are placed at the bottom of the periodic table.
- ❖ Actinoids have general electronic configuration [Rn]5f²⁻¹⁴6d⁰⁻²7s²

Ex: Actnium, Thorium, Uranium

6.Why Gd³⁺ is colourless?

 $Gd - [Xe]4f^75d^16s^2$

 $Gd^{3+} - [Xe]4f^{7}5d^{0}6s^{0}$

d-d transition is **not possible** because it has **no paired electrons** in their outer d orbital. So they are colourless.

7.Explain why compounds of Cu⁺² are coloured but those Zn⁺² are colourless.

i)
$$Cu^{+2} - 3d^9$$
 ii) $Zn^{+2} - 3d^{10}$

- ightharpoonup In Zn^{+2} **d-d transition** is **not possible** because it has completely filled d orbital . So they are colourless
- ❖ In Cu⁺² **d-d transition is possible** because it has **paired electrons** in their outer d orbital. So they are coloured (**blue**)

8.Describe the preparation of potassium dichromate

- ❖ It is prepared from chromate ore.
- ❖ The ore is concentrated by gravity separation.
- ❖ It is then mixed with excess sodium carbonate and lime and roasted in a reverberatory furnace.

$$4FeCr2O + 8 Na2CO3 + 7 O2$$

900 – 1000°C

 $8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2 \uparrow$

- ❖ The roasted mass is treated with water to separate soluble sodium chromate from insoluble iron oxide.
- ❖ The yellow solution of sodium chromate is treated with concentrated sulphuric acid which converts sodium chromate into sodium dichromate.

$$2Na_2CrO_4 + H_2SO_4$$

 \longrightarrow Na₂CrO₇ + Na₂SO₄ + H₂O

- ❖ The above solution is concentrated to remove less soluble sodium sulphate. The resulting solution is filtered and further concentrated.
- ❖ It is cooled to get the crystals of Na₂SO₄.2H₂O.
- ❖ The saturated solution of sodium dichromate in water is mixed with KCl and then concentrated to get crystals of NaCl.
- \clubsuit It is filtered while hot and the filtrate is cooled to obtain $K_2Cr_2O_7$ crystals.

9. What is lanthanide contraction and what are the effects of lanthanide contraction? Lanthanide contraction

As we move across 4f series, the atomic and ionic radii of lanthanoids show gradual decrease with increase in atomic number. This decrease in ionic size is called lanthanoid contraction.

Effects of lanthanide contraction

1. Basicity differences

As we from Ce^{3+} to Lu^{3+} , the basic character of Ln^{3+} ions decrease. Due to the decrease in the size of Ln^{3+} ions, the ionic character of Ln OH $^-$ bond decreases (covalent character increases) which results in the decrease in the basicity.

2. Similarities among lanthanoids:

In the complete f - series only 10 pm decrease in atomic radii and 20 pm decrease in ionic radii is observed because of this very small change in radii of lanthanoids, their chemical properties are quite similar.

10.Complete the reaction

a.
$$3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^{-} + MnO_2 + 2H_2O$$

b. $C_6H_5CH_3 + 2KMnO_4 \xrightarrow{\text{acidified} \atop KMnO_4} C_6H_5COOH + 2MnO_2 + 2KOH$
c. $MnO_4^{-} + 5Fe^{2+} \xrightarrow{8H^+} 5Fe^{3+} + Mn^{2+} + 4H_2O$
d. $2KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2$
e. $Cr_2O_7^{2-} + 6I^- + 14H^+ \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$
f. $Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$

11. What are interstitial compounds?

An interstitial compound or alloy is a compound that is formed **when small atoms like hydrogen, boron, carbon or nitrogen are trapped in the interstitial holes** in a metal lattice. They are usually non-stoichiometric compounds

Example: TiC, ZrH_{1.92}

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12. Calculate the number of unpaired electrons in Ti^{3+} , Mn^{2+} and calculate the spin only magnetic moment

 Ti^{3+} - $1s^22s^22p^63s^23p^63d^1$ No of unpaired electron = 1

$$\mu = \sqrt{n(n+2)} = \sqrt{1(3)} = \sqrt{3} = 1.732B.M$$

 Mn^{2+} - $1s^22s^22p^63s^23p^63d^5$ No of unpaired electron = 5

$$\mu = \sqrt{n(n+2)} = \sqrt{5(7)} = \sqrt{35} = 5.92 \text{ B.M}$$

similarly

Ion	Configuration	n	$\mu = \sqrt{n(n+2)} \mu_B$	μ _(observed)
Sc3+ ,Ti4+ ,V5+	dº	0	$\mu = \sqrt{0(0+2)} = 0 \mu_{\rm B}$	diamagnetic
Ti3+, V4+	ď	1	$\mu = \sqrt{1(1+2)} = \sqrt{3} = 1.73 \mu_{\rm B}$	1.75
Ti^{2+}, V^{3+}	ď²	2	$\mu = \sqrt{2(2+2)} = \sqrt{8} = 2.83 \mu_{\rm B}$	2.76
Cr3+, Mn4+, V2+	d^3	3	$\mu = \sqrt{3(3+2)} = \sqrt{15} = 3.87 \mu_{\rm B}$	3.86
Cr ²⁺ , Mn ³⁺	ď4	4	$\mu = \sqrt{4(4+2)} = \sqrt{24} = 4.89 \mu_{\rm B}$	4.80
Mn ²⁺ , Fe ³⁺	d ⁵	5	$\mu = \sqrt{5(5+2)} = \sqrt{35} = 5.91 \mu_{\rm B}$	5.96
Co ³⁺ , Fe ²⁺	\mathbf{d}^6	4	$\mu = \sqrt{4(4+2)} = \sqrt{24} = 4.89 \mu_{\rm B}$	5.3-5.5
Co ²⁺	\mathbf{d}^7	3	$\mu = \sqrt{3(3+2)} = \sqrt{15} = 3.87 \mu_{\rm B}$	4.4-5.2
Ni ²⁺	d ⁸	2	$\mu = \sqrt{2(2+2)} = \sqrt{8} = 2.83 \mu_{\rm B}$	2.9-3.4
Cu ²⁺	ď°	1	$\mu = \sqrt{1(1+2)} = \sqrt{3} = 1.732 \ \mu_{\rm B}$	1.8-2.2
Cu^+ , Zn^{2+}	d ¹⁰	0	$\mu = \sqrt{0(0+2)} = 0 \mu_{\rm B}$	diamagnetic

13. Write the electronic configuration of Ce^{4+} and Co^{2+}

 Ce^{4+} - [Xe]4f⁰ or $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^6$ 4f⁰

 Co^{2+} - [Ar]3d⁷ or $1\text{s}^22\text{s}^22\text{p}^63\text{s}^23\text{p}^63\text{d}^7$

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

- ❖ It is observed that except Sc all other metals possess +2 oxidation state
- ❖ In the first half of the first row transition elements from Sc to Mn atomic number increases from 21 − 25 so that number of electrons in 3d − orbital also increases from 1 to 5.

 $Sc^{+2} - d^1$

 $Ti^{+2} - d^2$

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 V^{+2} - d^3

 $Cr^{+2} - d^4$

 $Mn^{+2} - d^5$

- ❖ +2 oxidation state is attained by the loss of two electrons by these metals
- ❖ Number of d electrons in +2 oxidation state increases from Ti⁺² to Mn⁺² the stability of +2 state increases
- ❖ As a result d orbital is becoming more and more half filled which is more stable

15. Which is more stable? Fe^{3+} or Fe^{2+} - explain.

Fe³⁺ has 3d⁵ configuration in its outermost shell

Fe²⁺ has 3d⁶ configuration in its outermost shell

Fe³⁺ ion is more stable due to its half filled configuration

16. Explain the variation in $E_{M^{2+}/_{M}}^{0}$ 3d series.

- ❖ In 3d series as we move from Ti to Zn, the standard reduction potential $(E_{M^{2+}/M}^{0})$ value is approaching towards less negative value and copper has a positive reduction potential. i.e., elemental copper is more stable than Cu²⁺
- ❖ There are two deviations., In the general trend, value for manganese and zinc are more negative than the regular trend.
- ❖ It is due to extra stability which arises due to the half filled d⁵ configuration in Mn²⁺ and completely filled d¹⁰ configuration in Zn²⁺

17. Compare lanthanides and actinides

Lanthanoids	Actinoids
Differentiating electron enters in 4f orbital	Differentiating electron enters in 5f orbital
Binding energy of 4f orbitals are higher	Binding energy of 5f orbitals are lower
They show less tendency to form complexes	They show greater tendency to form complexes
Besides +3 oxidation states lanthanoids show +2 and +4 oxidation states in few cases.	Besides +3 oxidation states actinoids show higher oxidation states such as +4, +5, +6 and +7

+2 CHEMISTRY SAIV	EERA ACADEMY	STUDY MATERIAL
They do not form oxo cations	They do form ox	o cations such as UO2 ²⁺
Most of the lanthanoids are colourles	Most of the actine example. U ³⁺ (re	oids are coloured . For d),

18. Explain why Cr²⁺ is strongly reducing while Mn³⁺ is strongly oxidizing.

- ❖ Cr²⁺ is strongly reducing in nature .It has d⁴ configuration. While acting as reducing agent, it get oxidized to Cr³⁺ which has d³ configuration.
- \clubsuit This d³ configuration can be written as $3t_{2g}$ configuration which is most stable configuration.
- ❖ For Mn²⁺ which has d⁴ configuration acts as an oxidizing agent and get reduced to Mn²⁺ which has d⁵ configuration
- ❖ It has half filled configuration, so it is more stable.

19. Compare the ionization enthalpies of first series of the transition elements.

- 1) Ionization energy of transition element is **intermediate between those of s and p block elements.**
- 2) As we move **from left to right** in a transition metal series, the **ionization enthalpy increases** as expected.
- 3) This is due to **increase in nuclear charge** corresponding to the filling of d electrons.
- 4) The increase in first ionisation enthalpy with increase in atomic number along a particular series is not regular.
- 5) The added electron **enters** (**n-1**)**d orbital** and the inner electrons act as a shield and decrease the effect of nuclear charge on valence ns electrons. Therefore, it leads to variation in the ionization energy values.
- 6) In 3d series ionisation enthalpy of **first four members** (**Sc**, **Ti**, **V**, **Cr**) show **little differences** in values
- 7) Because, effective nuclear charge is more than that of repulsive force of d electron on electrons on its outer most shell. Last four (Fe, Co, Ni, Cu) are also fairly close
- 8) **Zn** shows **high values** due to extra stability of **completely filled d orbitals**.

20.Actinoid contraction is greater from element to element than the lanthanoid contraction, why?

- ❖ These 5f orbital have **poor shielding effect** than 4f orbital which leads to decrease in atomic or ionic radii.
- ❖ Therefore in actinoids effective nuclear charge experienced by outermost electrons is more than experienced by lanthanoids.
- ❖ So actinoid shows greater contraction.

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21.Out of Lu(OH)₃ and La(OH)₃ which is more basic and why?

- \clubsuit La(OH)₃ is more basic than Lu(OH)₃.
- \clubsuit As we move from Ce^{3+} to Lu^{3+} , the basic character of Ln^{3+} decrease .
- \clubsuit Due to decrease in size of Ln³⁺ on account of lanthanoid contraction, the ionic character of Ln OH bond decreases (Covalent character increases) which result in the decrease in the basicity.

22. Why Europium (II) is more stable than Cerium (II)?

Eu (II) $- [Xe] 4f^7$

 $Ce(II) - [Xe] 4f^2$

Eu (II) has half filled subshell which provide more stability due to exchange of energy.

23. Why do zirconium and Hafnium exhibit similar properties?

- ❖ In the complete f series only 10 pm decrease in atomic radii and 20 pm decrease in ionic radii is observed, because of this very small change in radii of lanthanoids, their chemical properties are quite similar.
- \clubsuit Due to lanthanoid contraction, second and third rows of d block transition elements are quite close in properties

24. Which is stronger reducing agent Cr^{2+} or Fe^{2+} ?

When Cr²⁺ acts as reducing agent

$$Cr_{(aq)}^{3+} + e^{-} \rightarrow Cr_{(aq)}^{2+} E^{0} = -0.41 V$$

When Fe²⁺ acts as reducing agent

$$Fe_{(aq)}^{3+} + e^{-} \rightarrow Fe_{(aq)}^{2+} E^{0} = +0.77 V$$

- ❖ If the standard electrode potential (E⁰), of a metal is large and negative, the metal is a powerful reducing agent, because it loses electrons easily.
- * Thus Cr²⁺ is easily oxidized to Cr³⁺ but Fe²⁺ cannot be easily oxidized to Fe³⁺
- **❖** Hence Cr²⁺ is powerful reducing agent

25. The $E_{M^{2+}/M}^{0}$ value for copper is positive. Suggest a possible reason for this.

- Copper has high atomisation energy (Energy observed), but low hydration enthalpy (energy released).
- ❖ Hence the E^0 value for copper is positive (+0.34 v) .i.e elemental copper is more stable than Cu^{2+}

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26. Predict which of the following will be coloured in aqueous solution Ti^{2+} , V^{3+} , Sc^{4+} , Cu^+ , Sc^{3+} , Fe^{3+} , Ni^{2+} and Co^{3+}

Only the ions having unpaired electrons in d-orbital will have d-d transition which makes ion coloured

Ions	Outer configuration	Colour
Ti ²⁺	$3d^2$	coloured
V ³⁺	$3d^2$	coloured
Sc ⁴⁺	$3d^0$	colourless
Cu ⁺	3d ¹⁰	coloured
Sc ³⁺	$3d^0$	colourless
Fe ³⁺	3d ⁵	coloured
Ni ²⁺	3d ⁸	coloured
Co ³⁺	$3d^6$	coloured

27. Describe the variable oxidation state of 3d series elements.

- 1) The first transition metal Scandium exhibits **only** +3 **oxidation state**, but all other transition elements exhibit variable oxidation states by loosing electrons from (n-1)d orbital and ns orbital as the energy difference between them is very small.
- 2) At the beginning of the series, +3 oxidation state is stable but towards the end +2 oxidation state becomes stable.
- 3) The number of oxidation states increases with the number of electrons available, and it decreases as the number of paired electrons increases.
- 4) Hence, the first and last elements show less number of oxidation states and the middle elements with more number of oxidation states.
- 5) For example, the first element **Sc has only one oxidation state +3**; the middle element **Mn has six different oxidation states from +2 to +7**. The last element **Cu shows +1 and +2 oxidation states** only.

28. Which metal in the 3d series exhibits +1 oxidation state most frequently and why?

- 1) Cu is only metal in the 3d series exhibits +1 oxidation state
- 2) Cu has electronic configuration [Ar] $3d^{10}4s^1$ and after losing one electron it acquires a stable $3d^{10}$ configuration which is more stable.

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29. Why first ionization enthalpy of chromium is lower than that of zinc?

 $Zn: 3d^{10} 4s^2$ $Cr: 3d^{10} 4s^1$

In Cr first electron has to be remove from $4s^1$ (half filled) orbital with less amount of energy.

In Zn first electron has to be remove from $4s^2$ (completely filled)orbital, so it requires high energy to remove electron from it.

So first ionization enthalpy of chromium is lower than that of zinc.

30. Transition metals show high melting points why?

The melting point of the transition metals are high due to **greater number of unpaired delectrons for metallic** bonding.

Book inside short answer questions

1. What are the applications of transition metals?

Tungsten in light bulb filaments

Titanium in manufacturing artificial joints

Molybdenum in boiler plants

Platinum in catalysis.

They also play vital role in living system, for example iron in haemoglobin, cobalt in vitamin B_{12} etc.

2.Write the the electronic configurations of Cr and Cu

Cr - [Ar] 3d⁵ 4s¹

Cu - [Ar] 3d10 4s1

3. Write the general electronic configuration of d- block elements

[Noble gas $](n-1)d^{1-10}ns^{1-2}$ n = 4 to 7

In periods 6 and 7, [Noble gas]f¹⁻¹⁴(n-1)d¹⁻¹⁰ns¹⁻²

4. Why there is maximum melting point in the middle of transition metal

The maximum melting point at about the middle of transition metal series indicates that d⁵ configuration is favorable for strong interatomic attraction.

5. What is Bayer's reagent and write down its use

Cold dilute alkaline KMnO₄ is known as Bayer's reagent. It is used to oxidise alkenes into diols. For example, ethylene can be converted into ethylene glycol and this reaction is used as a test for unsaturation.

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6. What is standard electrode potential?

Standard electrode potential is the value of the standard emf of a cell in which molecular hydrogen under standard pressure (1atm) and temperature (273K) is oxidised to solvated protons at the electrode.

7. Why many industrial processes use transition metals or their compounds as catalysts?

Transition metal has energetically available d orbitals that can accept electrons from reactant molecule or metal can form bond with reactant molecule using its d electrons.

8. Explain about Hume-Rothery rule to form a substitute alloy

- 1) The difference between the atomic radii of solvent and solute is less than 15%.
- 2) Both the solvent and solute must have the **same crystal structure and valence** and their **electro negativity difference must be close to zero.**

8. What are the properties of interstitial compounds

- (i) They are hard and show electrical land thermal conductivity
- (ii) They have high melting points higher than those of pure metals
- (iii) Transition metal hydrides are used as powerful reducing agents
- (iv) Metallic carbides are chemically inert.

9. Why transition metals form complexes?

- Transition elements have a tendency to form coordination compounds with a species that has an ability to donate an electron pair to form a coordinate covalent bond.
- Transition metal ions are small and highly charged and they have vacant low energy orbitals to accept an electron pair donated by other groups.
- ❖ Due to these properties, transition metals form large number of complexes.

Examples: [Fe(CN)₆]⁴⁻

10. What is Chromyl chloride test

When potassium dichromate is heated with any chloride salt in the presence of Conc H₂SO₄, orange red vapours of chromyl chloride (CrO₂Cl₂) is evolved. This reaction is used to confirm the presence of chloride ion in inorganic qualitative analysis.

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \longrightarrow 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2 \uparrow + 3H_2O_4 + 4NaHSO_4 + 2CrO_2Cl_2 \uparrow + 3H_2O_4 +$$

11. How will you prepare lead chromate?

The chromyl chloride vapours are dissolved in sodium hydroxide solution and then acidified with acetic acid and treated with lead acetate. A yellow precipitate of lead chromate is obtained.

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12. What are the uses of potassium dichromate

- 1.It is used as a **strong oxidizing agent**.
- 2. It is used in dyeing and printing.
- 3. It used in **leather tanneries** for chrome tanning.
- 4. It is used in quantitative analysis for the estimation of iron compounds and iodides

13. What are general electronic configuration of lanthanide and actinides Lanthanide - $[Xe]4f^{2-14}5d^{0-1}6s^2$

Actinide $-[Rn]5f^{2-14}6d^{0-2}7s^2$

14.A substance is found to have magnetic moment of 3.9 $\mu_B\,$.How many unpaired electrons it have

$$\mu = 3.9$$
 $\mu = \sqrt{n(n+2)} = 3.9$
 $n(n+2) - (3.9)^2 = 0$
 $n = 3$

14. What is advantage of catalyst?

- 1) They require low energy
- 2) Minimize waste production
- 3) Enhance the conversion of reactants to products

15. What is Zeigler Natta catalyst?

A mixture of TiCl₄ and trialkyl aluminium

16. Why HCl and HNO₃ cannot be used to make KMnO₄ acidic

HCl cannot be used for making the medium acidic since it reacts with KMnO₄ as follows.

$$2MnO_4^- + 10 Cl^- + 16H^+ \longrightarrow 2Mn^{2+} + 5Cl_2 + 8H_2O$$

HNO₃ cannot be used since it is good oxidizing agent reacts with reducing agent in the reaction .

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Book inside long answers

- 1.Explain about preparation of potassium permanganate
 - ❖ Potassium permanganate is prepared from pyrolusite (MnO₂) ore
 - ❖ Conversion of MnO₂ to potassium manganate:
 - ❖ Powdered ore is fused with KOH in the presence of air or oxidising agents like KNO₃ or KClO₃. A green coloured potassium manganate is formed.
 - Oxidation of potassium manganate to potassium permanganate:
 - Potassium manganate thus obtained can be oxidised in two ways, either by chemical oxidation
 - ❖ or electrolytic oxidation.

Chemical oxidation:

In this method potassium manganate is treated with ozone (O₃) or chlorine to get potassium permanganate.

$$2MnO_4^{2-} + O_3 + H_2O \longrightarrow 2MnO_4^{-} + 2OH^{-} + O_2$$

 $2MnO_4^{2-} + Cl_2 \longrightarrow 2MnO_4^{-} + 2Cl^{-}$

Electrolytic oxidation

In this method aqueous solution of potassium manganate is electrolyzed in the presence of little alkali.

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

 $H_1O \rightleftharpoons H^+ + OH^-$

Manganate ions are converted into permanganate ions at anode.

$$MnO_4^{2-} \rightleftharpoons MnO_4^{-} + e^{-}$$

Green purple

H,is liberated at the cathode.

$$2H^+ + 2e^- \longrightarrow H_1^{\uparrow}$$

The purple coloured solution is concentrated by evaporation and forms crystals of potassium permanganate on cooling.

- 2. Potassium permanganate is a strong oxidising agent. Explain
- a) In neutral medium:

In neutral medium, it is reduced to MnO,

$$MnO_4^- + 2H_1O_+ 3e^- \longrightarrow MnO_2 + 4OH^-$$

(i) It oxidises H2S to sulphur

$$2MnO_4^- + 3H_2S \longrightarrow 2MnO_2 + 3S + 2OH^- + 2H_2O$$

(ii) It oxidises thiosulphate into sulphate

$$8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 6SO_4^{2-} + 8MnO_2 + 2OH^-$$

b) In alkaline medium:

In the presence of alkali metal hydroxides, the permanganate ion is converted into manganate.

$$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$$

This manganate is further reduced to MnO, by some reducing agents.

$$MnO_4^{2-} + H_2O \longrightarrow MnO_2 + 2OH^- + [O]$$

So the overall reaction can be written as follows.

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$$

This reaction is similar as that for neutral medium.

c) In acid medium:

In the presence of dilute sulphuric acid, potassium permanganate acts as a very strong oxidising agent. Permanganate ions is converted into Mn^{2+} ion.

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

The oxidising nature of potassium permanganate (permanganate ion) in acid medium is illustrated in the following examples.

(i) It oxidises ferrous salts to ferric salts.

$$2MnO_4^- + 10Fe^{2+} + 16H^+ \longrightarrow 2Mn^{2+} + 10Fe^{3+} + 8H_2O$$

(ii) It oxidises iodide ions to iodine

$$2MnO_4^- + 10 I^- + 16H^+ \longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O$$

(iii) It oxidises sulphide oxalic acid to CO,

$$2MnO_4^- + 5(COO)^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

(iv) It oxidises sulphide ion to sulphur

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

(v) It oxidises nitrites to nitrates

$$2MnO_4^- + 5NO_2^- + 6H^+ \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$$

(vi) It oxidises alcohols to aldehydes.

$$2KMnO_4 + 3H_2SO_4 + 5CH_3CH_2OH \longrightarrow 2K_2SO_4 + 2MnSO_4 + 5CH_3CHO + 8H_2O$$

(vii) It oxidises sulphite to sulphate

$$2MnO_4^- + 5SO_3^{2-} + 6H^+ \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O_4^{2-}$$

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3. What are Uses of potassium permanganate:

- 1. It is used as a strong oxidizing agent.
- 2. It is used for the treatment of various skin infections and fungal infections of the foot.
- 3. It used in water treatment industries to remove iron and hydrogen sulphide from well water.
- 4. It is used as a Bayer's reagent for detecting unsaturation in an organic compound.
- 5. It is used in **quantitative analysis** for the estimation of ferrous salts, oxalates, hydrogen peroxide and iodides.

4. What are Cause of lanthanoid contraction

As we move from one element to another in 4f series (Ce to Lu) the nuclear charge increases by one unit and an additional electron is added into the same inner 4f sub shell. We know that 4f sub shell have a diffused shapes and therefore the shielding effect of 4f elelctrons relatively poor, hence, with increase of nuclear charge, the valence shell is pulled slightly towards nucleus. As a result, the effective nuclear charge experienced by the 4f electrons increases and the size of Ln³⁺ ions decreases.

5. Write about Variation of atomic and ionic size:

It is generally expected a steady decrease in atomic radius along a period as the nuclear charge increases and the extra electrons are added to the same sub shell. But for the 3d transition elements, the expected decrease in atomic radius is observed from Sc to V , thereafter up to Cu the atomic radius nearly remains the same.

As we move from Sc toZn in 3d series the extra electrons are added to the 3d orbitals, the added 3d electrons only partially shield the increased nuclear charge and hence the effective nuclear charge increases slightly. However, the extra electrons added to the 3d sub shell strongly repel the 4s electrons and these two forces are operated in opposite direction and as they tend to balance each other, it leads to constancy in atomic radii.

At the end of the series, d – orbitals of Zinc contain 10 electrons in which the repulsive interaction between the electrons is more than the effective nuclear charge and hence, the orbitals slightly expand and atomic radius slightly increases.

Generally as we move down a group atomic radius increases, the same trend is expected in d block elements also. As the electrons are added to the 4d sub shell, the atomic radii of the 4d elements are higher than the corresponding elements of the 3d series. However there is an unexpected observation in the atomic radius of 5d elements which have nearly same atomic radius as that of corresponding 4d elements.

6.Potassium dichromate is powerful reducing agent .Explain

Potassium dichromate is a powerful oxidising agent in acidic medium.

(i) It oxidises ferrous salts to ferric salts.

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

(ii) It oxidises iodide ions to iodine

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

(iii) It oxidises sulphide ion to sulphur

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

(iv) It oxidises sulphur dioxide to sulphate ion

$$Cr_2O_7^{2-} + 3SO_7 + 2H^+ \longrightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O_7^{3-}$$

(v) It oxidises stannous salts to stannic salt

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

(vi) It oxidises alcohols to acids.

$$2K_{2}Cr_{2}O_{7} + 8H_{3}SO_{4} + 3CH_{3}CH_{2}OH \longrightarrow 2K_{2}SO_{4} + 2Cr_{2}(SO_{4})_{3} + 3CH_{3}COOH + 11H_{2}O$$

7. Write about examples of transition metals which acts as catalyst

(i) Hydroformylation of olefins

Propene + CO +
$$H_2$$
 $Co_2(CO)_8$ CHO + CH

(ii) Preparation acetic acid from acetaldehyde.

(iii) Zeigler - Natta catalyst

A mixture of TiCl4 and trialkyl aluminium is used for polymerization.

$$\begin{array}{c|c} H_3C & \hline & TiCl_4 + Al(C_2H_5)_3 \\ \hline & Propylene & \hline & poly propylene \\ \end{array}$$