#### **UNIT – 4 – TRANSITION AND INNER TRANSITION ELEMENTS II. Answer the following questions:**

#### 1. What are transition metals? Give four examples.

The metallic elements that have incompletely filled d or f subshell in the neutral or cationic state are called transition metals.

Examples: Copper, Iron, Cobalt, Nickel.

- 2. Explain the oxidation states of 4d series elements.
- 4 The oxidation states of 4d metals vary from +3 for Y and La to +8 for Ru and Os.
- The highest oxidation state of 4d and elements are found in their compounds with the higher electronegative elements like O, F and Cl.

#### Example:

- $\downarrow$  RuO<sub>4</sub>, OsO<sub>4</sub> and WCl<sub>6</sub>.
- Generally in going down a group, a stability of the higher oxidation state increases while that of lower oxidation state decreases.
- 4 It is evident from the Frost diagram ( $\Delta G_0$  vs oxidation number) as shown below,For titanium,vanadium and chromium, the most thermodynamically stable oxidation state is +3.

#### 3. What are inner transition elements?

- 4 The elements in which the extra electron enters (n-2)f orbitals are called f-block elements.
- These elements are also called as inner transition elements because they form a transition series within the transition elements.
- As the f orbitals lie inner to the penultimate shell, therefore these elements having partially filled f orbitals, are also called inner transition elements.
- 4 In the inner transition elements there are two series of elements.
  - Lanthanoids (Previously called lanthanides)
  - Actinoids (Previously called actinides)
- 4. Justify the position of lanthanides and actinides in the periodic table. (or) Describe the position of f-block elements in the periodic table. [PTA–1, SRT-22]

#### Lanthanides:

- ↓ The actual position of lanthanides in the periodic table is at group number 3 and period number 6. In the sixth period, the electrons are perferentially filled in inner 4f-sub shell.
- The 14 elements following lanthanum (Ce to Lu) show similar chemical properties. Hence they are grouped together and placed at the bottom of the periodic table.
- This position is justified as follows: Lanthanoids have general electronic configuration [Xe] 4f<sup>1-14</sup> 5d<sup>0-1</sup> 6s<sup>2</sup>. The common oxidation state of lanthanoids is +3. All these elements have similar physical and chemical properties.

#### Actinides:

- Similarly the 14 elements following actinium (Th to Lr) resemble in their physical and chemical properties.
- **4** If we place these elements after Lanthanum in the periodic table below 4d series and actinides below 5d series, the properties of the elements belongs to a group would be different and it would affect the proper structure of the periodic table. Hence a separate position is provided to the inner transition elements at the bottom of the periodic table.
  - Actinoids have general electronic configuration [Rn]  $5f^{0-14} 6d^{0-2} 7s^2$
  - The common oxidation state of actinoids is +3
  - In addition to that actinoids show variable oxidation states such as +2, +3, +4, +5, +6 and +7.

#### 5. What are actinoids? Give three examples.

- 4 Similarly the 14 elements following actinium (Th to Lr) are called actinoids.
- 4 Similer to lanthanoids, hence a separate position is provided to the inner transition elements at the bottom of the periodic table.
- 4 Actinoids have general electronic configuration [Rn] 5f<sup>0-14</sup> 6d<sup>0-2</sup> 7s<sup>2</sup>

**Example:** Actinium (Ac), Thorium (Th), Protactinium (Pa), Uranium (U), Neptunium (Np), Plutonium (Pu), Americium (Am), Curium (Cm), Berkelium (Bk), Californium (Cf), Einstenium (Es), Fermium (Fm), Mendelevium (Md), Nobelium (No) and Lawrentium (Lr)

- 6. Describe the preparation of potassium dichromate. [PTA-2, SRT.OY-23]
- **4** Important Ore:  $K_2Cr_2O_7$  is prepared from chromite–Iron ore, or Chromite ore.
- **Concentration method:** The ore is converted by gravity separation
- 4 Conversion of chromite iron ore into sodium chromate.

$$4 \operatorname{FeCr}_{2}O_{4} + 8 \operatorname{Na}_{2}CO_{3} + 7 \operatorname{O}_{2} \xrightarrow{900 - 1000^{0}C} 8 \operatorname{Na}_{2}CrO_{4} + 2 \operatorname{Fe}_{2}O_{3} + 8 \operatorname{CO}_{2} \uparrow$$

Conversion of sodium chromate into sodium dichromate: 2

$$Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$
  
sodium chromate  
(verllow)

4 Conversion of sodium dichromate into potassium dichromate :

Na, Cr, O, + 2KCl  $\longrightarrow$ K,Cr,O, + 2NaCl potassium dichromate sodium

7. What is lanthanide construction and what are the effects of lanthanide contraction? [PTA-3, SEP-20, JUN-23, OY-23, MAR-24]

(orange red)

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

#### **Consequences of lanthanoid contraction:**

(orange

#### **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<sup>3+</sup> 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.

The elements of the second and third transition series resemble each other more closely than the elements of the first and second transition series.

#### 8. Complete the following

a. 
$$\operatorname{MnO_4^{2-}} + \operatorname{H^+} \longrightarrow ?$$
  
 $3\operatorname{MnO_4^{2-}} + 4\operatorname{H^+} \longrightarrow 2\operatorname{MnO_4^{-}} + \operatorname{MnO_2} + 2\operatorname{H_2O}$   
Manganate Acid Permanganate Manganese  
ion dioxide  
b.  $C_6H_5CH_3 \xrightarrow{\operatorname{acidified}}_{KMnO_4} ?$   
 $C_6H_5CH_3 \xrightarrow{\operatorname{acidified}}_{KMnO_4} C_6H_5COOH$   
Toluene (Oxidation) Benzoic acid  
c.  $\operatorname{MnO_4^{-}} + \operatorname{Fe^{2+}} \longrightarrow ?$ 

**UNIT – IV – TRANSITION AND INNER TRANSITION ELEMENTS** Mr. S.JOHNSON., M.Sc., M.Sc., B.Ed.,  $2MnO_4^-$  + 10 Fe<sup>2+</sup> + 16 H<sup>+</sup>  $\longrightarrow 2Mn^{2+}$  + 10 Fe<sup>3+</sup> + 8H<sub>2</sub>O Permanganate (Oxidation) Ferric Ferrous ion ion ion d. KMnO<sub>4</sub>  $\xrightarrow{\Delta}$  ?  $\begin{array}{ccc} 2KMnO_4 & & \underline{\Delta} \\ Potassium & & Red hot \\ Potassium & & Potassium \\ \end{array} \xrightarrow{} \begin{array}{c} K_2MnO_4 & + & MnO_2 + O_2 \\ Potassium & & Manganese \\ \end{array}$ Permanganate Manganate dioxidee.  $Cr_2O_7^{2-} + I^- + H^+ \longrightarrow ?$  $\operatorname{Cr_2O_7^{2-}} + 6 \operatorname{I^-} + 14\operatorname{H^+} \longrightarrow 2\operatorname{Cr^{3+}} + 3\operatorname{I_2} + 7\operatorname{H_2O}$ Iodide ion (Oxidation) f.  $Na_2Cr_2O_7 + KCl \longrightarrow ?$  $Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$ Sodium dichromate Potassium dichromate 9. What are interstitial compounds? [PTA-1, SEP-20, AUG-21, OY, MAY-22, JUN, SUT-23, QY-23, SRT-24] + 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. 4 They are usually non-stoichiometric compounds. Transition metals form a number of interstitial compounds such as TiC, ZrH<sub>1.92</sub>, Mn<sub>4</sub>N etc.  $\downarrow$  The elements that occupy the metal lattice provide them new properties. 10.Calculate the number of unpaired electrons in Ti<sup>3+</sup>, Mn<sup>2+</sup> and calculate the spin only magnetic moment. [PTA-6, AUG-21] Ti (Z = 22). Electronic configuration [Ar]  $3d^2 4s^2$  $Ti^{3+}$  – Electronic configuration [Ar]  $3d^1$ So, the number of unpaired electrons in  $Ti^{3+}$  is equal to 1. Spin only magnetic moment  $\mu_s = \sqrt{n(n+2)}$  $\mu_s = \sqrt{1(1+2)} = \sqrt{3} = 1.732 BM$ Mn (Z = 25). Electronic configuration [Ar]  $3d^5 4s^2$  $Mn^{2+}$  – Electronic configuration [Ar]  $3d^5$ So, the number of unpaired electrons in  $Mn^{2+}$  is 5. Spin only magnetic moment  $\mu_s = \sqrt{n(n+2)}$   $\mu_s = \sqrt{5(5+2)} = \sqrt{35} = 5.92 BM$ **11.Write the electronic configuration of Ce<sup>4+</sup> and CO<sup>2+</sup>.**  $Ce (Z = 58) \rightarrow Ce^{4+} + 4e^{-1}$  $Ce^{4+} - Is^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6$  $C_0^{2+} - Is^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5.$ 12.Explain briefly how +2 states becomes more and more stable in the first half of the first row transition elements with increasing atomic number. 4 It can be easily observed that except Sc all other metals possess +2 oxidation state. Also, on moving from Sc to Mn, the atomic number increases from 21 to 25. 4 This means the number of electrons in the 3d – orbital also increases from 1 to 5.  $Sc^{2+} = d^1$  $Ti^{2+} = d^2$  $V^{2+} = d^3$  $Cr^{2+} = d^4$  $Mn^{2+} = d^5$ 4 +2 oxidation state is attained by the loss of the two 4s electrons by these metals. 4 Since the number of d electrons in (+2) state also increases from Ti2+ to Mn2+ the stability of +2 state increases. 4 As a result d- orbital is becoming more and more half-filled which is highly stable.

#### 13. Which is more stable? Fe<sup>3+</sup> or Fe<sup>2+</sup> – explain. [QY19, MAY, QY22, SUT, QY23, MAR24] $Fe \rightarrow Fe^{2+} + 2e^{-}$

Fe (Z = 26)

- $Fe \rightarrow Fe^{3+} + 3e^{-}$
- 4 Fe<sup>2+</sup> [Number of electrons 24] Electronic configuration = [Ar]3d<sup>6</sup>
- Partially filled d-subshell is less stable.
- 4 Fe<sup>3+</sup> [Number of electrons 23] Electronic configuration = [Ar]3d<sup>5</sup>
- 4 Among Fe<sup>3+</sup> and Fe<sup>2+</sup>, Fe<sup>3+</sup> is more stable due to half filled d-orbital. This can be explained by Aufbau principle. Half filled and completely filled d-orbitals are more stable than partially filled d-orbitals. So  $Fe^{3+}$  is more stable than  $Fe^{2+}$ .

#### **14.Explain the variation in E^{0}\_{M2+/M3+} 3d series.**

- 4 In transition series, as we move down from Ti to Zn, the standard reduction potential  $E_{M}^{0}^{2+}/M^{3}$  value is approaching towards less negative value and copper has a positive reduction potential, i.e. elemental copper is more stable than  $Cu^{2+}$ .
- $4 E_{M}^{0}^{2+}/M$  value for manganese and zinc are more negative than regular trend. It is due to extra stability arises due to the half filled d<sup>5</sup> configuration in Mn<sup>2+</sup> and completely filled  $d^{10}$  configuration in  $Zn^{2+}$ .
- $\downarrow$  The standard electrode potential for the M<sup>3+</sup>/M<sup>2+</sup> half cell gives the relative stability between  $M^{3+}$  and  $M^{2+}$ .
- + The high reduction potential of  $Mn^{3+} / Mn^{2+}$  indicates  $Mn^{2+}$  is more stable than  $Mn^{3+}$ .
- $\downarrow$  For Fe<sup>3+</sup> / Fe<sup>2+</sup> the reduction potential is 0.77 V, and this low value indicates that both Fe<sup>3+</sup> and Fe<sup>2+</sup> can exist under normal condition.
- 4 Mn<sup>3+</sup> has a 3d<sup>2</sup> configuration while that of Mn<sup>2+</sup> is 3d<sup>5</sup>. The extra stability associated with a half filled d sub-shell makes the reduction of  $Mn^{3+}$  very feasible [E° = +1.51 V]

#### 15.Compare lanthanides and actinides. [PTA-4, OY, HY-19, JUL-22, OY, HY22, MAR-23, SUT, QY-23]

S. NO.	LANTHANOIDS	ACTINOIDS					
1	Differentiating electron enters in 4f orbital	Differentiating electron eneters in 5f orbital					
2	Binding energy of 4f orbitals are higher	Binding energy of 5f orbitals are lower					
3	They show less tendency to form	They show greater tendency to form					
	complexes	complexes					
4	Most of the lanthanoids are colourless	Most of the actinoids are coloured. For					
		example.					
		$U^{3+}$ (red), $U^{4+}$ (green) , $UO_2^{2+}$ (yellow)					
5	They do not form oxo cations	They do form oxo cations such as $UO_2^{2+}$ ,					
		$NpO_2^{2+}$ etc					
6	Besides +3 oxidation states lanthanoids	Besides +3 oxidation states actinoids					
	show +2 and +4 oxidation states in few	show higher oxidation states such as +4,					
	cases.	+5, +6 and +7.					

**16.**Explain why Cr<sup>2+</sup> is strongly reducing while Mn<sup>3+</sup> is strongly oxidizing. [PTA-5]

4 Cr<sup>2+</sup> is strong reducing while Mn<sup>3+</sup> is strongly oxidising.

- $\downarrow$  E° value for Cr<sup>3+</sup>/Cr<sup>2+</sup> is negative (-0.41 V). If the standard electrode potential E° of a metal is large and negative, the metal is a powerful reducing agent because it loses electrons easily. 4 E° value for Mn<sup>3+</sup>/Mn<sup>2+</sup> is positive (+ 1.51 V)
- $\downarrow$  If the standard electrode potential E° of a metal is large and positive, the metal is a powerful oxidising agent because it gains electrons easily.

#### **17.**Compare the ionization enthalpies of first series of the transition elements.

- Ionization energy of transition element is intermediate between those of s and p block elements.
- As we move from left to right in a transition metal series, the ionization enthalpy increases as expected. This is due to increase in nuclear charge corresponding to the filling of d electrons.

**4** The following figure show the trends in ionisation enthalpy of transition elements.



Transition metals have smaller atomic radii and higher nuclear charger which increase the ionisation energy when compound to alkali metals.

- The first ionisation energy of 5d series of element are much higher than those of 3d and 4d series of elements.
- The increase in first ionisation enthalpy with increase in atomic number along a particular series is not regular.
- 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.
- **4** Therefore, it leads to variation in the ionization energy values.
- The ionisation enthalpy values can be used to predict the thermodynamic stability of their compounds. Let us compare the ionisation energy required to form Ni<sup>2+</sup> and Pt<sup>2+</sup> ions.
- ♣ For Nickel, IE + IE = 737 + 1753 = 2490 kJmol<sup>-1</sup>
- ↓ For Platinum, IE + IE = 864 + 1791 = 2655 kJmol<sup>-1</sup>
- Since, the energy required to form Ni<sup>2+</sup> is less than that of Pt<sup>2+</sup>, Ni(II) compounds are thermodynamically more stable than Pt(II) compounds.
- **18.Actinoid** contraction is greater from element to element than the lanthanoid contraction, why?
- Actinoid contraction is greater from element to element than lanthanoid contraction. The 5f orbitals in Actinoids have a very poorer shielding effect than 4f orbitals in lanthanoids.
- Thus, the effective nuclear charge experienced by electron in valence shells in case of actinoids is much more than that experienced by lanthanoids.
- In actinoids, electrons are shielded by 5d, 4f, 4d and 3d whereas in lanthanoids, electrons are shielded by 4d, 4f only.
- **4** Hence, the size contraction in actinoids is greater as compared to that in lanthanoids.

#### **19.Out of LU(OH)**<sub>3</sub> and La(OH)<sub>3</sub> which is more basic and why? [PTA-2]

- 4 La(OH)<sub>3</sub> is more basic than Lu(OH)<sub>3</sub>
- 4 As we move from Ce<sup>3+</sup> to Lu<sup>3+</sup>, the basic character of Lu<sup>3+</sup> ions decreases.
- Due to lanthanoid contraction the size of lanthanoid ions decreases regularly with increase in atomic size.
- Due to the decrease in the size of Lu<sup>3+</sup> ions, the ionic character of Lu OH bond decreases, covalent character increases which results in the decrease in the basicity.
- **4** So actinoid show greater contraction.

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

- 4 Eu<sup>2+</sup> Electronic configuration [Xe] 4f<sup>7</sup> 5d<sup>0</sup> 6s<sup>0</sup>
- 4 Ce<sup>2+</sup> Electronic configuration [Xe] 4f<sup>1</sup> 5d<sup>1</sup> 6s<sup>0</sup>
- **4** In Eu(II), 4f subshell a half filled and 5d subshell is empty.
- According to Aufbau principle, half filled and completely filled d (or) f orbitals are more stable than partially filled f orbitals.
- 4 Hence  $Eu^{2+}$  [Xe]  $4f^7 5d^0 6s^0$  is more stable than  $Ce^{2+}$  [Xe]  $4f^1 5d^0 6s^0$
- 21. Why do zirconium and Hafnium exhibit similar properties?
- Zr and Hf exhibit similar properties due to lanthanoid contraction.
- Electrons present in f subshell have poor shielding due to which with the increasing atomic number or increasing effective nuclear charge, size gets constricted.
- Thus size of hafnium and zirconium becomes almost equal, and hence both have similar properties.
- 22. Which is stronger reducing agent Cr<sup>2+</sup> or Fe<sup>2+</sup>? [SRT-22]

 $[E^{0}_{Cr2+/Cr} = -0.91V, E^{0}_{Fe2+/Fe} = -0.44V]$ 

**Reason:**  $Cr^{2+}$  is a stronger reducing agent than  $Fe^{2+}$ .

**4** This can be explained on the basis of the standard electrode potential values.

$$(E^{0}_{Cr2+/Cr} = -0.91V)$$
 and  $(E^{0}_{Fe2+/Fe} = -0.44V)$ 

- 4 Thus  $Cr^{2+}$  is easily oxidised to  $Cr^{3+}$  but  $Fe^{2+}$  cannot oxidised to  $Fe^{3+}$ .
- 4 Cr<sup>2+</sup> standard electrode potential values is more negative value.

23. The  $E^{0}_{M2+/M}$  value for copper is positive. Suggest a possible reason for this.

 $E^{0}_{(M2+/M)}$  value for copper metal is the sum of enthalpy changes taking place in the steps given below.

$$\begin{split} M_{(s)} + \Delta_a \ H^0 &\rightarrow M^+_{(g)} \\ (\Delta_a H^0 = \text{Standard enthalpy of atomisation}) \\ M^+_{(g)} + \Delta_i \ H^0 &\rightarrow M^{2+}_{(g)} \\ (\Delta_i H^0 = \text{Standard ionisation enthalpy}) \\ M^{2+}_{(g)} + \Delta_{hyd} \ H^0_{aq} &\rightarrow M^{2+}_{(aq)} \\ (\Delta_{hyd} H^0 = \text{Standard hydration enthalpy}) \end{split}$$

Copper has a high enthalpy of atomisation (energy absorbed), but low enthalpy of hydration (energy released)

Thus  $E^{0}_{(Cu2+/Cu)}$  is positive.

### 24.Describe the variable oxidation state of 3d series elements. [AUG-21]

- The first transition metal Scandium exhibits only +3 oxidation state, but all other transition elements exhibit variable oxidation states by loosing electrons from (n-l)d orbital and ns orbital as the energy difference between them is very small.
- ↓ At the beginning of the 3d series, +3 oxidation state is stable but towards the end +2 oxidation state becomes stable.

- The number of oxidation states increases with the number of electrons available, and it decreases as the number of paired electrons increases. For example, in the 3d series, 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.
   Mn<sup>2+</sup> (3d<sup>5</sup>) is more stable than Mn<sup>4+</sup> (3d<sup>3</sup>) is due to half filled stable configuration.
- 25. Which metal in the 3d series exhibits +1 oxidation state most frequently and why? [SEP-20]
- Cu is the only metal in the first transition series (2d series) which exhibits only +1 oxidation state most frequently.
- 4 It is unique in 3d series having a stable +1 oxidation state. This is because the Electronic configuration of Cu (Z = 29) is [Ar]  $3d^{10} 4s^1$  and after losing one electron it acquires a stable  $3d^{10}$  configuration.
- 4 So copper element only can have +1 oxidation state.
- 26. Why first ionization enthalpy of chromium is lower than that of zinc? [SRT-22]
- + The first ionization enthalpy of chromium is lower than that of zinc. Cr (Z = 24) Electronic configuration [Ar]  $3d^5 4s^1$ .
- In the case of Cr, first electron has to be removed easily from 4s orbital to attain the more stable half filled configuration. So Cr has lower ionization enthalpy.
- **4** But in the case of Zinc (Z = 30), electronic configuration [Ar]  $3d^{10} 4s^2$ .
- The first electron has to be removed from the most stable fully filled electronic configuration becomes difficult and it requires more energy.
- 27. Transition metals show high melting points why? [PTA-6]
- The melting points of the transition metals are high due to the 3d electrons being available for metallic bonding.
- As we move from left to right along the transition metal series, melting point first increases as the number of unpaired d electrons available for metallic bonding inceases, reach a maximum value and then decreases, as the d electrons pair up and become less available for bonding.
- For example, in the first series the melting point inceases from Scandium (m.pt 1814K) to a maximum of 2183K for vanadium, which is close to 2180K for chromium. However, manganese in 3d series and Tc in 4d series have low melting point. The maximum melting point at about the middle of transition metal series indicates that d5 configuration is favourable for strong interatomic attraction.

### ELEMENTS EVALUATE YOURSELF

1. Compare the stability of Ni<sup>4+</sup> and Pt<sup>4+</sup> from their ionisation enthalpy values

IE	Ni	Pt
Ι	737	864
II	1753	1791
III	3395	2800
IV	5297	4150

- The value of the ionisation enthalpies can be used in estimating the relative stability of various transition metal compounds (or ions).
- 4 Formation of Pt<sup>4+</sup> requires lesser energy as compared to the formation of Ni<sup>4+</sup>
- Pt<sup>4+</sup> compounds are stable than Ni<sup>4+</sup> compounds because the energy needed to remove 4 electrons in Pt is less than that of Ni.

- 2. Why iron is more stable in +3 oxidation state than in +2 and the reverse is true for **Manganese?**
- Fe (Z = 26). Electronic configuration [Ar]  $3d^6 4s^2$
- $\downarrow$  Fe  $\rightarrow$  Fe<sup>3+</sup> + 3e<sup>-</sup> Fe<sup>3+</sup> Electronic configuration [Ar] 3d<sup>5</sup>. If d' orbital is half filled, it is more stable than . Fe<sup>2+</sup> where it is [Ar] 3d<sup>6</sup>.
- Mn (Z = 25). Electronic configuration [Ar]  $3d^5 4s^2$
- 4 Mn  $\rightarrow$  Mn<sup>2+</sup> + 2e<sup>-</sup>By the loss of 2e<sup>-</sup>, Mn<sup>2+</sup> is more stable due to half filled configuration.  $Mn \rightarrow Mn^{3+} + 3e^{-}$ .  $Mn^{3+}$  Electronic configuration [Ar]  $3d^4 4s^{\circ}$ .
- 4 Among this Fe<sup>3+</sup> is more stable than Fe<sup>2+</sup> and the Mn<sup>2+</sup> is more stable than Mn<sup>3+</sup>. **GOVERNMENT EXAM QUESTION PAPER**
- 1. Classify the following elements into d-block and f-block elements: [MAR-20]
  - b) Ruthenium c) Promethium a) Tungstan d) Einsteinium - d block
- a) Tungstan
- b) Ruthenium - d block
- c) Promethium - f block
- d) Einsteinium - f block
- 2. Why do transition metals form Coordination Compound? (or) Do transition elements form complex co-ordinate compounds? (or) Why do d-block elements readily form coordination compounds? [QY-19, SRT-22]
- **u** 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.
- **W** 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.

**Ex:**  $[Fe(CN)_6]^{4-}$ ,  $[Co(NH_3)_6]^{3+}$ , etc..

3. What is Zeigler – Natta catalyst? Give its use. [JUL-22]

A mixture of  $TiCl_4$  and trialkyl aluminium is used for polymerization.



**Uses:** It is used for polymerisation.

- 4. What is chromyl chloride test? Give equations. (or) Write the Chromyl chloride test. [GMQ-19, MAR-20, SUT, QY-23]
- $\downarrow$  When potassium dichromate is heated with any chloride salt in the presence of Conc.H<sub>2</sub>SO<sub>4</sub>, orange red vapours of chromyl chloride  $(CrO_2Cl_2)$  is evolved.
- $\downarrow$  This reaction is used to confirm the presence of chloride ion in inorganic qualitative analysis.  $K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \longrightarrow 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2 \uparrow + 3H_2O_4$
- Chromyl chloride The chromyl chloride vapours are dissolved in sodium hydroxide solution and then acidified with acetic acid and treated with lead acetate. A vellow precipitate of lead chromate is obtained.

$$CrO_{2}Cl_{2} + 4NaOH \longrightarrow Na_{2}CrO_{4} + 2NaCl + 2H_{2}O$$

$$Na_{2}CrO_{4} + (CH_{3}COO)_{2}Pb \longrightarrow PbCrO_{4} \qquad \downarrow + 2CH_{3}COONa$$

$$\underset{(Yellowprecipitate)}{\overset{Leadchromate}{(Yellowprecipitate)}} \downarrow + 2CH_{3}COONa$$

5. Explain the preparation of potassium permanganate from pyrolusite. (or) Explain the preparation of KMnO<sub>4</sub>. [GMQ-19]

Potassium permanganate is prepared from pyrolusite  $(MnO_2)$  ore. The preparation involves the following steps.

**Conversion of MnO\_2 to potassium manganate**: Powdered ore is fused with KOH in the presence of air or oxidising agents like KNO<sub>3</sub> or KClO<sub>3</sub>. 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  $(O_3)$  or chlorine to get potassium permanganate.

$$2MnO_{4}^{2-} + O_{3} + H_{2}O \longrightarrow 2MnO_{4}^{-} + 2OH^{-} + O$$

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

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

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

Manganate ions are converted into permanganate ions at anode.

 $2 \operatorname{MnO}_4^{2-} \rightleftharpoons 2 \operatorname{MnO}_4^{-} + 2 e^{-}$ 

Green purple

H<sub>2</sub>is liberated at the cathode.

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

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

- 6. Give brief account on the Oxidation State of Lanthanoids. [SRT-22]
- The common oxidation state of lanthanoids is +3. In addition to that some of the lanthanoids also show either +2 or +4 oxidation states.
- Gd<sup>3+</sup> and Lu<sup>3+</sup> ions have extra stability, it is due to the fact that they have exactly half filled and completely filled f-orbitals respectively.their electronic c onfigurations are

$$Gd^{3+}$$
: [Xe]4f<sup>7</sup>

 $Lu^{3+}$ : [Xe]4f<sup>14</sup>

- Similarly Cerium and terbium attain 4f<sup>0</sup> and 4f<sup>7</sup> configurations respectively in the +4 oxidation states. Eu<sup>2+</sup> and Yb<sup>2+</sup> ions have exactly half filled and completely filled f orbitals respectively.
- The stability of different oxidation states has an impact on the properties of these elements. The following table shows the different oxidation states of lanthanoids.

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
		+2		+2	+2						+2	+2	
+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3
+4	+4	+4					+4	+4					

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#### UNIT – IV – TRANSITION AND INNER TRANSITION ELEMENTS Mr. S.JOHNSON., M.Sc., M.Sc., B.Ed.,

- 7. Write the properties of interstitial compound. [MAY-22]
- + They are hard and show electrical and thermal conductivity
- They have high melting points higher than those of pure metals
- Transition metal hydrides are used as powerful reducing agents
- 4 Metallic carbides are chemically inert.
- 8. Calculate the equivalent weight of KMnO<sub>4</sub> in the following reactions. [QY-19]
  a) MnO<sub>4</sub><sup>-</sup> + 2H<sub>2</sub>O + 3e<sup>-</sup> → MnO<sub>2</sub> + 4OH<sup>-</sup>
  - b)  $2MnO_4^- + 10Fe^{2+} + 16H^+ \rightarrow 2Mn^{2+} + 10Fe^{3+} + 8H_2O_1^-$

a) Equivalent weight of KMnO<sub>4</sub> in neutral medium =  $\frac{Molecular weight of KMnO_4}{no.of moles of electrons transferred}$ 

$$=\frac{158}{2}=52.67$$

b) Equivalent weight of KMnO<sub>4</sub> in neutral medium =  $\frac{Molecular weight of KMnO_4}{no.of moles of electrons transferred}$ 

$$=\frac{158}{5}=31.6$$

# 9. (i) The first ionisation energy of Chromium is less than that of Zinc. Why? [SRT-22] (ii) Why do 3d series transition elements possess variable oxidation states?

(i)  $Cr - [Ar]3d^54s^2$ 

 $Zn - [Ar]3d^{10}4s^2$ 

Ionisation energy Cr is lower than that of zinc first electron has to be remove from full filled orbital and full filled electronic configuration is more stable than half filled so it require high energy to remove electron from it.

(ii) 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. At the beginning of the series, +3 oxidation state is stable but towards the end +2 oxidation state becomes stable.

The number of oxidation states increases with the number of electrons available, and it decreases as the number of paired electrons increases. Hence, the first and last elements show less number of oxidation states and the middle elements with more number of oxidation states. 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.

# **10.Explain the structure of permanganate ion. [HY-22]** Permanganate ion has tetrahedral geometry in which the central Mn<sup>7+</sup> is sp<sup>3</sup> hybridised.



- 11. Give the conditions for the formation of alloys by Hume-Rothery rule. [SUT-23]
- According to Hume-Rothery rule to form a substitute alloy the difference between the atomic radii of solvent and solute is less than 15%.
- **Both** the solvent and solute must have the same crystal structure and valence and their electro negativity difference must be close to zero.
- Transition metals satisfying these mentioned conditions form a number of alloys among themselves, since their atomic sizes are similar and one metal atom can be easily replaced by another metal atom from its crystal lattice to form an alloy.

## 12. What are the causes of lanthanide contraction? [SRT-24]

In f-block elements, the positive charge on the nucleus rises by one unit, and one additional electron enters the same 4f subshell, as the atomic number increases.

- Electrons in the 4f subshell poorly shield each another. Shielding is less in a 4f subshell than in a d subshell.
- ♣ As the nuclear charge increases, the valence shell is drawn closer to the nucleus. Hence, as a result contraction takes place.
- 13.Which metal in the 3d series exhibits + 1 oxidation State most frequently and why? [SEP-20]
- 4 The first transition metal copper exhibits only only +1 oxidation state
- **4** It is unique in 3d series having a stable +1 oxidation state
- 4 Cu (Z = 29) Electronic configuration is [Ar]  $3d^{10} 4S^{1}$
- **4** So cupper elements only can have +1 oxidation state