Chapter 4 Transition and Inner Transition Elements

I. Choose the correct answer.

Questions 1.

Sc (Z=21) is a transition element but Zinc (z=30) is not because

(a) both Sc^{3+} and Zn^{2+} ions are colourless and form white compounds.

(b) in case of Sc, 3d orbital are partially filled but in Zn these are completely filled

(c) last electron as assumed to be added to 4s level in case of zinc

(d) both Sc and Zn do not exhibit variable oxidation states

Answer:

(c) in case of Sc, 3d orbital are partially filled but in Zn these are completely filled

Question 2.

Which of the following d block element has half filled penultimate d sub shell as well as half filled valence sub shell?

(a) Cr

(b) Pd

(c) Pt

(d) none of these

Answer:

(a) Cr Hint: $Cr \Rightarrow [Ar]3d^5 4s^1$

Question 3.

Among the transition metals of 3d series, the one that has highest negative (M^{2+}/M) standard electrode potential is

(a) Ti (b) Cu

(c) Mn (d) Zn Answer:

(a) Ti

Question 4.

Which one of the following ions has the same number of unpaired electrons as present in V^{3+} ?

- (a) Ti³⁺
- (b) Fe³⁺
- (c) Ni^{2+}
- (d) Cr³⁺

(c) Ni²⁺

Question 5.

The magnetic moment of Mn^{2+} ion is (a) 5.92BM (b) 2.80BM (c) 8.95BM (d) 3.90BM **Answer:** (a) 5.92BM Hint: $Mn^{2+} \Rightarrow 3d$ contains 5 unpaired electrons n = 5

$$= \sqrt{n(n+2)BM} = \sqrt{5(5+2)} = \sqrt{35} = 5.92 \text{ BM}$$

Question 6.

Which of the following compounds is colourless?

(a) Fe³⁺

(6) Ti⁴⁺

(c) CO²⁺

(d) Ni^2

Answer:

(b) Ti⁴⁺

Hint: Ti⁴⁺ contains no unpaired electrons in d orbital, hence no d-d transition.

Question 7.

The catalytic behaviour of transition metals and their compounds is ascribed mainly due to

.....

(a) their magnetic behaviour

(b) their unfilled d orbitals

(c) their ability to adopt variable oxidation states

(d) their chemical reactivity

Answer:

(c) their ability to adopt variable oxidation states

Question 8.

The correct order of increasing oxidizing power in the series

(a) V0+2 < Cr202-7 < Mn0-4(b) Cr202-7 < V0+2 < Mn0-4(c) Cr202-7 < Mn0-4 < V0+2(d) Mn0.4 < Cr202-7 < V0+2

(d) Mn0-4 < Cr202-7 < V0+2

Answer:

(a) VO+2 < Cr2O2-7 < MnO-4+5 +6 +7 $VO_2^+ < Cr_2O_7^{2-} < MnO_4^{-1}$

Hint:

greater the oxidation state, higher is the oxidising power.

Question 9.

The alloy of copper that contain Zinc is

- (a) Monel metal
- (b) Bronze
- (c) bell metal
- (d) brass

Answer:

(d) brass

Question 10.

Which of the following does not give oxygen on heating?

- (a) K₂Cr₂O₇
- (b) (NH₄)₂Cr₂O₇
- (c) KClO₃
- (d) $Zn(ClO_3)_2$

Answer:

(b) (NH₄)₂Cr₂O₇ Hint:

$$2K_{2}Cr_{2}O_{7} \xrightarrow{\Delta} 2K_{2}CrO_{4} + Cr_{2}O_{3} + \left(\frac{3}{2}\right)O_{2}$$

$$(NH_{4})_{2}Cr_{2}O_{7} \xrightarrow{\Delta} Cr_{2}O_{3} + 4H_{2}O + N_{2}$$

$$KClO_{3} \xrightarrow{\Delta} KCl + \left(\frac{3}{2}\right)O_{2}$$

$$Zn(ClO_{3}) \xrightarrow{\Delta} ZnCl_{2} + 3O_{2}$$

Question 11.

In acid medium, potassium permanganate oxidizes oxalic acid to

- (a) Oxalate
- (b) Carbon dioxide
- (c) acetate
- (d) acetic acid

Answer:

(b) Carbon dioxide

Hint:
$$5(COO)_2^{2-} + 2MnO_4^{-} + 16H^+ \bigtriangleup 2Mn^{2+} + 10CO^{2+} \uparrow + 8H^{2}O$$

Question 12.

Which of the following statements is not true?

(a) on passing H₂S, through acidified K₂Cr₂O₇ solution, a milky colour is observed.

(b) Na₂Cr₂O₇ is preferred over K₂Cr₂O₇ in volumetric analysis

(c) K₂Cr₂O₇ solution in acidic medium is orange in colour

(d) K₂Cr₂O₇ solution becomes yellow on increasing the pH beyond 7

Answer:

(b) Na₂Cr₂O₇ is preferred over K₂Cr₂O₇ in volumetric analysis

Question 13.

Permanganate ion changes to in acidic medium

(a) MnO_4^{2-} (b) Mn^{2+} (c) Mn^{3+} (d) MnO_2 **Answer:** (b) Mn^{2+}

Hint: MnO_4^- + 8H⁺ + 5e⁻ \rightarrow Mn²⁺ + 4H₂O

Question 14.

A white crystalline salt (A) react with dilute HCl to liberate a suffocating gas (B) and also forms a yellow precipitate . The gas (B) turns potassium dichromate acidified with dil H_2SO_4 to a green coloured solution(C). A,B and C are respectively

(a) Na₂SO₃, SO₂, Cr₂(SO₄)₃ (b) Na₂S₂O₃, SO₂, Cr₂(SO₄)₃ (c) Na₂S, SO₂, Cr₂(SO₄)₃ (d) Na₂SO₄, SO₂, Cr₂(SO₄)₃ Answer: (a) Na₂SO₃, SO₂, Cr₂(SO₄)₃ *Hint* : Na₂S₂O₃ + 2HCl \rightarrow 2NaCl + SO₂↑ + S↓ + H₂O (A) (B) yellow ppt K₂Cr₂O₇ + H₂SO₄ + 3SO₂ \rightarrow K₂SO₄ + Cr₂(SO₄)₃ + H₂O (C)

Question 15.

MnO-4 react with Br in alkaline P^{H} to give MnO_{4}^{-} react with Br in alkaline P^{H} to give

- (a) BrO_3^- , MnO₂
- (b) Br_{3} , MnO_{4}^{2-}
- (c) Br₃, MnO₃
- (d) BrO⁻, MnO_4^{2-}

(a) BrO_3^- , MnO₂

Hint: $2MnO_4^-$ + Br- + H₂O \rightarrow 2OH- + 2MnO₂ + BrO_3^-

Question 16.

How many moles of I_2 are liberated when 1 mole of potassium dichromate react with potassium iodide?

(a) 1 (b) 2 (c) 3 (d) 4 Answer (c) 3 Hint: K₂Cr₂O₇ + 6KI + 7H₂SO₄ \rightarrow 4K₂SO₄ + Cr₂ (SO₄)₃ + 7H₂O + 3I₂

Question 17.

The number of moles of acidified $KMnO_4$ required to oxidize 1 mole of ferrous oxalate(FeC_2O_4) is

oxalate(FeC₂O₄) is (a) 5 (b) 3 (c) 0.6 (d) 1.5 Answer: (c) 0.6 *Hint*: MnO₄⁻ + FeC₂O₄ \rightarrow Mn²⁺ + Fe³⁺ + 2CO₂ 5e⁻ acception 3e⁻ release 5 moles of FeC₂O₄ \equiv 3 moles of KMnO₄ 5 moles of FeC₂O₄ \equiv $\left(\frac{3}{5}\right)$ moles of KMnO₄ 5 moles of FeC₂O₄ \equiv 0.6 moles of KMnO₄

Question 18.

When a brown compound of Mn (A) ids treated with HCl, it gives a gas (B). The gas (B) taken in excess reacts with NH_3 to give an explosive compound (C). The compound A, B and C are

(a) MnO₂, Cl₂, NCl₃
(b) MnO, Cl₂, NH₄Cl
(c) Mn₃O₄, Cl₂, NCl₃
(d) MnO₃, Cl₂, NCl₂
Answer:

(a) MnO₂, Cl₂, NCl₃
MnO₂ + 4HCl
$$\rightarrow$$
 MnCl₂ + Cl₂↑ + H₂O
(A) (B)
NH₃ + 3Cl₂ \rightarrow NCl₃ + 3HCl
(C)

Question 19.

Which one of the following statements related to lanthanons is incorrect?

(a) Europium shows +2 oxidation state.

(b) The basicity decreases as the ionic radius decreases from Pr to Lu.

(c) All the lanthanons are much more reactive than aluminium.

(d) Ce⁴⁺ solutions are widely used as oxidising agents in volumetric analysis.

Answer:

(c) All the lanthanons are much more reactive than aluminium.

Hint: As we move from La to Lu , their metallic behaviour because almost similar to that of aluminium.

Question 20.

Which of the following lanthanoid ions is diamagnetic?

(a) Eu²⁺

(b) Yb²⁺

(c) Ce^{2+}

(d) Sm²⁺

Answer:

(6) Yb²⁺

Hint: $Yb^{2+} - 4f^{14} - no$ unpaired electrons – diamagnetic

Question 21.

Which of the following oxidation states is most common among the lanthanoids? (a) 4

(a) 4

(b) 2

(c) 5

(d) 3

Answer:

(d) 3

Question 22.

Assertion: Ce⁴⁺ is used as an oxidizing agent in volumetric analysis.

Reason: Ce^{4+} has the tendency of attaining +3 oxidation state.

(a) Both assertion and reason are true and reason is the correct explanation of assertion.

(b) Both assertion and reason are true but reason is not the correct explanation of assertion.

(c) Assertion is true but reason is false. .

(d) Both assertion and reason are false.

(a) Both assertion and reason are true and reason is the correct explanation of assertion.

Question 23.

The most common oxidation state of actinoids is

(a) +2 (b) +3 (c) +4

(d) +6 **Answer:**

(c) + 4

Question 24.

The actinoid elements which show the highest oxidation state of +7 are (a) Np, Pu, Am (b) U, Fm, Th

(c) U, Th, Md (d) Es, No, Lr

Answer:

(a) Np, Pu, Am

Question 25.

Which one of the following is not correct?

(a) La(OH)₂ is less basic than Lu(OH)₃

(b) In lanthanoid series ionic radius of Ln³⁺ ions decreases

(c) La is actually an element of transition metal series rather than lanthanide series

(d) Atomic radii of Zr and Hf are same because of lanthanide contraction

Answer:

(a) $La(OH)_2$ is less basic than $Lu(OH)_3$

II. Answer the Following Questions:

Question 1.

What are transition metals? Give four examples.

Answer:

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.

Question 2.

Explain the oxidation states of 3d series elements.

Answer:

1. The first transition metal Scandium exhibits only +3 oxidation state, but all other

transition elements exhibit variable oxidation states by losing electrons from (n-l)d orbital and ns orbital as the energy difference between them is very small.

2. At the beginning of the 3d 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. For example, in 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.

4. Mn^{2+} (3d⁵) is more stable than Mn^{4+} (3d³) is due to half-filled stable configuration.

Question 3.

What are inner transition elements? **Answer:**

The elements which in their elemental or ionic form have partly filled f orbitals are called f block 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.

Question 4.

Justify the position of lanthanides and actinides in the periodic table. (PTA – 1) **Answer:**

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 fourteen 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: (1) General electronic configuration:

Question 4.

Justify the position of lanthanides and actinides in the periodic table.

Answer:

1. In sixth period after lanthanum, the electrons are preferentially filled in inner 4f sub shell and these 14 elements following lanthanum show similar chemical properties.

Therefore these elements are grouped together and placed at the bottom of the periodic table. This position can be justified as follows.

- Lanthanoids have general electronic configuration [Xe] 4f²⁻¹⁴ 5d⁰⁻¹ 6s²
- The common oxidation state of lanthanoids is +3
- All these elements have similar physical and chemical properties.

2. Similarly the fourteen elements following actinium resemble in their physical and chemical properties.

3. 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.

4. Hence a separate position is provided to the inner transition elements at the bottom of the periodic table.

Question 5.

What are actinoids? Give three examples.

Answer:

Potassium dichromate is prepared from chromite – Iron ore, or Chromite ore.

Concentration method: gravity separation

i) Conversion of chromite iron ore into sodium chromate.

4 $\operatorname{FeCr}_2O_4 + 8 \operatorname{Na}_2CO_3 + 7 \operatorname{O}_2 \xrightarrow{900 - 1000^0C} 8 \operatorname{Na}_2\operatorname{CrO}_4 + 2 \operatorname{Fe}_2O_3 + 8 \operatorname{CO}_2 \uparrow$

ii) Conversion of sodium chromate into sodium dichromate: $2 \operatorname{Na}_{2}\operatorname{CrO}_{4} + \operatorname{H}_{2}\operatorname{SO}_{4} \longrightarrow \operatorname{Na}_{2}\operatorname{Cr}_{2}\operatorname{O}_{7} + \operatorname{Na}_{2}\operatorname{SO}_{4} + \operatorname{H}_{2}\operatorname{O}_{8}$

(vellow)

(orange red)

iii) Conversion of sodium dichromate into potassium dichromate :

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Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl
                                    potassium dichromate
sodium dichromate
(orange red)
                                    (orange red)
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Question 6.

Why Gd³⁺ is colourless?

Answer:

Gd – Electronic Configuration: [Xe] 4f⁷ 5d¹ 6s²

Gd³⁺ – Electronic Configuration: [Xe] 4f⁷

In Gd³⁺, no electrons are there in outer d-orbitals. d-d transition is not possible. So it is colourless.

Question 7.

Explain why compounds of Cu^{2+} are coloured but those of Zn^{2+} are colourless.

Cu (Z = 29) Electronic configuration is [Ar] $3d^{10} 4s^1$

Cu²⁺: Electronic configuration is [Ar] 3d⁹.

In Cu²⁺, promotion of electrons take place in outer d-orbital by the absorption of light form visible region involves d-d transition. Due to this Cu²⁺ compounds are coloured. Where in Zn²⁺ electronic configuration is [Ar]3d¹⁰. It has completely filled d-orbital. So there is no chance of d – d transition. So Zn²⁺ compounds are colourless.

Question 8.

Describe the preparation of potassium dichromate.

Answer:

Preparation of potassium dichromate:

1. Potassium dichromate is prepared from chromite ore. The ore FeO. Cr₂O₃ is concentrated by gravity separation process.

2. The concentrated ore is mixed with excess sodium carbonate and lime and roasted in a reverbratory furnace.

$$4\mathsf{FeCr}_2\mathsf{O}_4 + 8\mathsf{Na}_2\mathsf{CO}_3 + 7\mathsf{O}_2 \underbrace{900 - 1000^0C}_{} 8 \mathsf{Na}_2\mathsf{CrO}_4 + 2\mathsf{Fe}_2\mathsf{O}_3 + 8\mathsf{CO}_2\uparrow$$

3. 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.

 $\begin{array}{cccc} 2Na_2CrO_4 &+& H_2SO_4 &\longrightarrow& Na_2Cr_2O_7 &+& Na_2SO_4 &+ H_2O\\ sodium chromate & sodium dichromate & (orange red) \end{array}$

4. The above solution is concentrated to remove less soluble sodium sulphate. The resulting solution is filtered and concentrated. It is cooled to get the crystals of Na₂SO₂.2H₂O. 5. The saturated solution of sodium dichromate in water is mixed with KCl and then concentrated to get crystals of NaCl. It is filtered while hot and the filtrate is cooled to obtain $K_2Cr_2O_7$ crystals.

 $\begin{array}{rcl} Na_2Cr_2O_7 &+& 2KCl &\longrightarrow & K_2Cr_2O_7 &+& 2NaCl \\ \text{sodium dichromate} & & & \text{potassium dichromate} \\ (\text{orange red}) & & & (\text{orange red}) \end{array}$

Question 9.

What is lanthanide contraction and what are the effects of lanthanide contraction? **Answer:**

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 (or) Consequences of lanthanoid contraction:

1. Basicity differences: As we move 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.

The elements of second and third transition series resemble each other more closely than the elements of first and second transition series due to lanthanoid contraction. For example,

- 4d series Zr Atomic radius 145 pm
- 5d series Hf Atomic radius 144 pm

Question 10. Complete the following Answer: a. MnO₄²⁻ + H⁺ ---- ? $3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^{-} + MnO_2 + 2H_2O_4^{-}$ Manganate Acid Permanganate Manganese ion medium ion dioxide b. $C_6H_5CH_3 \xrightarrow{acidified}{KMnO_4}$? $C_6H_5CH_3 \xrightarrow{acidified}{KMnO_4} C_6H_5COOH$ Toluene (Oxidation) Benzoic acid c. $MnO_4^- + Fe^{2+} \longrightarrow ?$ $2MnO_4^-$ + 10 Fe²⁺ + 16 H⁺ $\longrightarrow 2Mn^{2+}$ + 10 Fe³⁺ + 8H₂O Permanganate Ferrous (Oxidation) Ferric ion ion ion d. KMnO₄ $\xrightarrow{\Delta}$? $\begin{array}{ccc} 2KMnO_4 & & & \Delta \\ \hline \text{Red hot} & & K_2MnO_4 & + & MnO_2 + O_2 \\ Potassium & Potassium & Manganese \end{array}$ Permanganate Manganate dioxide e. $\operatorname{Cr}_{2}O_{7}^{2-} + I^{-} + H^{+} \longrightarrow ?$ $\operatorname{Cr}_2\operatorname{O_7}^{2-} + 6 \operatorname{I}^- + 14\operatorname{H}^+ \longrightarrow 2\operatorname{Cr}^{3+} + 3\operatorname{I}_2 + 7\operatorname{H}_2\operatorname{O}$ Iodide ion (Oxidation) Iodine f. $Na_2Cr_2O_7 + KCl \longrightarrow ?$

 $\begin{array}{rcl} Na_2Cr_2O_7 &+& 2KCl &\longrightarrow & K_2Cr_2O_7 &+& 2NaCl \\ Sodium dichromate & & Potassium dichromate \end{array}$

Question 11. What are interstitial compounds? **Answer:**

- 1. 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.
- 2. They are usually non-stoichiometric compounds.
- 3. Transition metals form a number of interstitial compounds such as TiC, ZrH_{1.92}, Mn₄N etc.
- 4. The elements that occupy the metal lattice provide them new properties.
 - 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
 - Metallic carbides are chemically inert.

Question 12.

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

Answer:

Ti³⁺:

Ti (Z = 22). Electronic configuration [Ar] $3d^2 4s^2$

Ti³⁺ – Electronic configuration [Ar] 3d¹

So, the number of unpaired electrons in Ti^{3+} is equal to 1.

Spin only magnetic moment of Ti³⁺ = $\sqrt{1(1+2)}$ = $\sqrt{3}$ = 1.73 μ_B

Mn²⁺:

Mn (Z = 25). Electronic configuration [Ar] $3d^5 4s^2$

Mn²⁺ – Electronic configuration [Ar] 3d⁵

Mn²⁺ has 5 unpaired electrons.

Spin only magnetic moment of $Mn^{2+} = \sqrt{5(5+2)} = \sqrt{35} = 5.91 \mu_B$

Question 13.

Write the electronic configuration of Ce⁴⁺ and CO²⁺. **Answer:** Ce (Z = 58) \rightarrow Ce⁴+4e⁻ Ce⁴⁺ - Is² - 2s²2p⁶3s²3p⁶4s²3d¹⁰4p⁶ 5s²4d¹⁰ 5p⁶ CO²⁺ - Is²2s²2p⁶3s²3p⁶4s²3d⁵.

Question 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.

First transition series.

Answer:

Question 15.

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

Answer:

Fe (Z = 26) Fe \rightarrow Fe²⁺ + 2e⁻ Fe \rightarrow Fe³⁺ + 3e⁻ Fe²⁺ [Number of electrons 24] Electronic configuration = [Ar]3d⁶ Fe³⁺ [Number of electrons 23]

Electronic configuration = $[Ar]3d^5$

Among Fe³⁺ and Fe²⁺, Fe³⁺ 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 Fe³⁺ is more stable than Fe²⁺.

Question 16.

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

Answer:

1. In transition series, as we move down from Ti to Zn, the standard reduction potential $E^{0}M^{2+}/M^{3}$ value is approaching towards less negative value and copper has a positive reduction potential, i.e. elemental copper is more stable than Cu^{2+} .

2. $E^{0}M^{2+}/M$ value for manganese and zinc are more negative than regular trend. It is due to extra stability arises due to the half filled d⁵ configuration in Mn²⁺ and completely filled d¹⁰ configuration in Zn²⁺.

3. The standard electrode potential for the M^{3+} / M^{2+} half cell gives the relative stability between M^{3+} and M^{2+} .

4. The high reduction potential of Mn^{3+} / Mn^{2+} indicates Mn^{2+} is more stable than Mn^{3+} . 5. For Fe³⁺ / Fe²⁺ the reduction potential is 0.77 V, and this low value indicates that both Fe³⁺ and Fe²⁺ can exist under normal condition.

6. Mn^{3+} has a $3d^2$ configuration while that of Mn^{2+} is $3d^5$. The extra stability associated with a half filled d sub-shell makes the reduction of Mn^{3+} very feasible [E° = +1.51 V]

Question 17.

Compare lanthanides and actinides.

Lanthanoids:

- 1. Differentiating electron enters in 4f orbital
- 2. Binding energy of 4f orbitals are higher
- 3. They show less tendency to form complexes
- 4. Most of the lanthanoids are colourless
- 5. They do not form oxo cations
- 6. Besides +3 oxidation states lanthanoids show +2 and +4 oxidation states in few cases.

Actinoids:

- 1. Differentiating electron enters in 5f orbital
- 2. Binding energy of 5f orbitals are lower
- 3. They show greater tendency to form complexes
- 4. ost of the actinoids are coloured.

E.g : U³⁺ (red), U⁴⁺ (green), UO_2^{2+} (yellow)

- 5. They do form oxo cations such as $UO_2^{2+}\;NpO_2^{2+}$ etc.
- 6. Besides +3 oxidation states actinoids show higher oxidation states such as +4, +5, +6 and +7.

Question 18.

Explain why Cr²⁺ is strongly reducing while Mn³⁺ is strongly oxidizing. **Answer:** Cr²⁺ is strong reducing while Mn³⁺ is strongly oxidising. $E^{0}_{Cr}^{3+}/Cr^{2+}$ is -0.41 V Cr²⁺ + 2e⁻ \rightarrow Cr E° = -0.91V. 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. Mn \rightarrow Mn³⁺ + 3e⁻ Mn³⁺ + e⁻ \rightarrow Mn²⁺ Mn³⁺ [Ar]3d⁴ E° = + 1.51 V 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.

Question 19.

Compare the ionization enthalpies of first series of the transition elements. Ionization enthalpies of first transition series: Answer:

- 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. This is due to increase in nuclear charge corresponding to the filling of d electrons.
- 3. The increase in first ionisation enthalpy with increase in atomic number along a particular series is not regular. The added electron enters (n-l)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.

Question 20.

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

Answer:

- 1. 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.
- 2. Thus, the effective nuclear charge experienced by electron in valence shells in case of actinoids is much more than that experienced by lanthanoids.
- 3. 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.

Question 21.

Out of $LU(OH)_3$ and $La(OH)_3$ which is more basic and why? **Answer:**

- 1. As we move from Ce^{3+} to Lu^{3+} , the basic character of Lu^{3+} ions decreases.
- Due to the decrease in the size of Lu³⁺ ions, the ionic character of Lu OH bond decreases, covalent character increases which results in the decrease in the basicity.
- 3. Hence, $La(OH)^3$ is more basic than $Lu(OH)^3$.

Question 22.

Why europium (II) is more stable than Cerium (II)?

Answer:

Eu (Z = 63) – Electronic configuration – [Xe] $4f^7 5d^\circ 6s^2$

Eu²⁺ – Electronic configuration Electronic 6s¹

Ce (Z = 58) – configuration – [Xe] $4f^{2+} 5d^{\circ} 6s^{2+}$

Ce²⁺ – Electronic confluration – [Xe] 4f² 5d°

According to Aufbau principle, half filled and completely filled d (or) f orbitals are more

stable than partially filled f orbitals. Hence Eu²⁺ [Xe] $4f^7 5d^\circ$ is more stable than Ce²⁺ [Xe] $4f^2 5d^\circ$

Question 23.

Why do zirconium and Hafnium exhibit similar properties? **Answer:**

- 1. The element of second and third transition series resemble each other more closely than the elements of first and second transition series due to lanthanoid contraction.
- 2. e.g., Zr 4d series -Atomic radius 145 pm Hf 5d series Atomic radius 144 pm
- 3. The radii are very similar even though the number of electrons increases.
- 4. Zr and Hf have very similar chemical behaviour, having closely similar radii and electronic configuration.
- 5. Radius dependent properties such as lattice energy, solvation energy are similar.
- 6. Thus lanthanides contraction leads to formation of pair of elements and those known as chemical twins, e.g., Zr Hf

Question 24.

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Which is stronger reducing agent Cr<sup>2+</sup> or Fe<sup>2+</sup>?
Answer:
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Cr<sup>2+</sup> and Fe<sup>2+</sup>
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Cr (Z = 24) – Electronic configuration – [Ar] 3d^5 4s^1
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Cr^{2+} Electronic configuration – [Ar] 3d^4 4s^0
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Fe (Z = 26) – Electronic configuration – [Ar] 3d^6 4s^2
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 Fe^{2+} Electronic confimiration – [Ar] $3d^6 4s^0$

If standard electrode potential (E°) of a metal is large and negative, the metal is a powerful reducing agent

 $Cr^{2+} + 2e^- \rightarrow Cr$ $Fe^{2+}+2e^- \rightarrow Fe$ $E^\circ = -0.91V$ $E^\circ = -0.44V$ By comparing the above equation, Cr^{2+} is a powerful reducing agent.

Question 25.

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

Answer:

1. Copper has a positive reduction potential. Elemental copper is more stable than Cu^{2+} .

- 2. Copper having positive sign for electrode potential merely means that copper can undergo reduction at faster rate than reduction of hydrogen.
- 3. The electron giving reaction (oxidation) of copper is slower than that of hydrogen. It is determined from the result of S.H.E (Standard Hydrogen Electrode) potential value experiment.

Question 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+}

Answer:

Among Ti²⁺, V³⁺, Sc⁴⁺, Cu⁺, Sc³⁺, Fe³⁺, Ni²⁺ and CO³⁺ in aqueous solution state. Ti (Z = 22) – Ti²⁺ – Electronic configuration is [Ar] 3d² V (Z = 23) – V³⁺ – Electronic configuration is [Ar] 3d² Sc (Z = 21) – SC⁴⁺ – Electronic configuration is [Ar] 1s² 2s² 2p⁶ 3s² 3p⁵ Cu (Z = 29) – Cu⁺ – Electronic configuration is [Ar] 3d¹⁰ Sc (Z = 21) – SC³⁺ – Electronic configuration is [Ar] 3d°4s°

Fe (Z = 26) – Fe³⁺ – Electronic configuration is [Ar] $3d^5$

Ni (Z = 28) – Ni²⁺ – Electronic configuration is [Ar] $3d^5$

 $CO(Z = 27) - CO^{3+}$ – Electronic configuration is [Ar] 3d⁶

A transition metal ion is coloured if it has one or more unpaired electrons in (n-l)d orbital, i.e. 3d orbitals in the case of first transition series, when such species are exposed to visible radiation, d – d transition take place and the species are coloured.

$Ti^{2+}(3d^2)$	All are coloured due to the presence of unpaired 'd' electrons where $d - d$ transition is possible by the absorption of visible light.
$V^{3+}(3d^2)$	
Fe ³⁺ (3d ⁵)	
Ni ²⁺ (3d ⁶)	
Co ³⁺ (3d ⁵)	
Sc4+ 3d orbital	All are colourless due to the absence of d electrons (or) completely filled d electrons where there is no $d - d$ transition take place.
(No electrons)	
Cu ⁺ (3d ¹⁰)	
Sc ³⁺ 3d orbital	
(No electrons)	

Question 27.

Describe the variable oxidation state of 3d series elements.

Answer:

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-l)d orbital and ns orbital as the energy difference between them is very small.

2. At the beginning of the 3d 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. 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.

4. Mn^{2+} (3d⁵) is more stable than Mn^{4+} (3d³) is due to half filled stable configuration.

Question 28.

Which metal in the 3d series exhibits +1 oxidation state most frequently and why? **Answer:**

1. The first transition metal copper exhibits only +1 oxidation state.

2. It is unique in 3d series having a stable +1 oxidation state.

Cu (Z = 29) Electronic configuration is [Ar] $3d^{10} 4s^2$

3. So copper element only can have +1 oxidation state.

Question 29.

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

Answer:

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. 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.

Question 30.

Transition metals show high melting points why? **Answer:**

- 1. All the transition metals are hard.
- 2. Most of them are hexagonal close packed, cubic close packed (or) body centered cubic which are characteristics of true metals.
- 3. The maximum melting point at about the middle of transition metal series indicates that d⁵ configuration of favourable for strong inter atomic attraction.
- 4. Due to the strong metallic bonds, atoms of the transition elements are closely packed and held together. This leads to high melting point and boiling point.