Unit-4- TRANSITION AND INNER TRANSITION ELEMENTS

Choose the best answer:

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

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

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

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

a) Ti^{3+} b) Fe^{3+} c) Ni^{2+} d) Cr^{3+}

5. The magnetic moment of Mn^{2+} ion is

a) 5.92BM b) 2.80BM c) 8.95BM d) 3.90BM

6. Which of the following compounds is colourless?

a) Fe^{3+} ***b) Ti^{4+}*** c) Co^{2+} d) Ni^{2+}

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

8. The correct order of increasing oxidizing power in the series

a) $VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$ b) $Cr_2O_7^{2-} < VO_2^+ < MnO_4^-$

c) $Cr_2O_7^{2-} < MnO_4^- < VO_2^+$ d) $MnO_4^- Cr_2O_7^{2-} < VO_2^+$

9. The alloy of copper that contain Zinc is

a) Monel metal b) Bronze c) bell metal ***d) brass***

10. Which of the following does not give oxygen on heating?

a) $K_2Cr_2O_7$ ***b) $(NH_4)_2Cr_2O_7$*** c) $KClO_3$ d) $Zn(ClO_3)_2$

11. In acid medium, potassium permanganate oxidizes oxalic acid to

a) oxalate ***b) Carbon dioxide*** c) acetate d) acetic acid

12. **Which of the following statements is not true?**

a) on passing H_2S, through acidified $K_2Cr_2O_7$ solution, a milky colour is observed.

b) $Na_2Cr_2O_7$ is preferred over $K_2Cr_2O_7$ in volumetric analysis

c) $K_2Cr_2O_7$ solution in acidic medium is orange in colour

d) $K_2Cr_2O_7$ solution becomes yellow on increasing the P_H beyond 7

13. Permanganate ion changes to _____ in acidic medium

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

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 H2SO4 to a green coloured solution(C). A,B and C are respectively**

a) Na_2SO_3 , SO_2 , $Cr_2(SO_4)_3$ b) $Na_2S_2O_3$, SO_2 , $Cr_2(SO_4)_3$

c) Na_2 S , SO_2 , $Cr_2(SO_4)_3$ d) Na_2 SO_4 , SO_2 $Cr_2(SO_4)_3$

15. MnO_4^- react with Br^- in alkaline P_H to give

a) BrO_3^- , MnO_2 , b) Br_2 , MnO_4^{2-} c) Br_2 , MnO_2 d) BrO^- , MnO_4^{2-}

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

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

a) 5 b) 3 ***c) 0.6*** d) 1.5

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 NH3 to give an explosive compound (C). The compound A, B and C are**

a) MnO_2 , Cl_2 , NCl_3 b) MnO, Cl_2 , NH_4Cl

c) Mn_3O_4 , Cl_2 , NCl_3 d) MnO_3 , Cl_2 , NCl_3

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) Ce^{4+} solutions are widely used as oxidising agents in volumetric analysis.

20. Which of the following lanthanoid ions is diamagnetic?

a) Eu^{2+} ***b) Yb^{2+}*** c) Ce^{2+} d) Sm^{2+}

21. Which of the following oxidation states is most common among the lanthanoids?

a) 4 b) 2 c) 5 ***d) 3***

22. **Assertion : Ce^{4+} 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.

23. The most common oxidation state of actinoids is

a) +2 b) +3 ***c) +4*** d) +6

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

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 Ln^{3+} 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 the following questions:

1.What are transition metals? Give four examples.

The metallic elements that have incompletely filled d or f sub shell in the neutral or cationic state are called transition metals.(E.g) Cu,Zn ,Ni,Co

2. Explain the oxidation states of 3d series elements.

(i)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 nsorbital as the energy difference between them is very small.

(ii) 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 +2oxidation states only

(iii)The relative stability of different oxidation states of 3d metals is correlated with theextra stability of half filled and fully filled electronic configurations. Example: (Mn^{2+}) $3d^5$ is more stable than (Mn^{4+}) $3d^3$

3. What are inner transition elements?

The f-block elements are only called the inner transition elements. The elements of the 6th and that of the 7th periods of Group 3 fall under this category. The series of elements that exhibit similar properties are lanthanides (4f) and actinides(5f).

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

The actual position of Lanthanoids in the periodic table is at group number 3 and period number 6.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.

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

1. Lanthanoids have general electronic configuration
2. The common oxidation state of lanthanoides is +3
3. All these elements have similar physical and chemical properties.

Similarly the fourteen elements following actinium resemble in their physical and chemical properties. If we place these elements after Lanthanum in the periodic tablebelow4d series, the properties of the elements belongs to a group would be different and it would affect the proper structure of the periodic table

5. What are actinides? Give three examples.

The fourteen elements following actinium ,i.e., from thorium (Th) to lawrentium (Lr)are called actinoids. Unlike the lanthanoids, all the actinoids are radioactive and most of them have short half lives. Only thorium and uranium (U) occur in significant amount in nature and a trace amounts of Plutonium(Pu) is also found in Uranium ores.Neptunium(Np)and successive heavier elements are produced synthetically by the artificial transformation of naturally occuring elements by nuclear reactions.

6. Why Gd^{3+} is colourless?

Gd - $[Xe]4f^7 5d^1 6s^2$
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 of Zn^{2+} are colourless?

. Zn^{2+} has completely filled *d* –orbitals ($3d^{10}$) so it is colorless,while **Cu^{2+}** has incompletely filled *d* –orbitals ($3d^9$).So **Cu^{2+}** has blue coloured

8. Describe the preparation of potassium dichromate.

$K_2Cr_2O_7$ Preparation:

Potassium dichromate 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 reverbratory furnace.

$$4\,FeCr_2O_4 + 8\,Na_2CO_3 + 7\,O_2 \xrightarrow{900^0C - 1000^0C} 8\,Na_2CrO_4 + 2\,Fe_2O_3 + 8\,CO_2\uparrow$$

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.

$$2\,Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

sodium chromate (yellow) → sodium dichromate (orange red)

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 $Na_2SO_4.2H_2O$.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.

$Na_2Cr_2O_7$ + 2KCl → $K_2Cr_2O_7$ + 2NaCl
sodium dichromate (orange red) — potassium dichromate (orange red)

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 increse in atomic number. This decrese in ionic size is called lanthanoid contraction.

Effects of lanthanide contraction:

From Ce^{3+} to Lu^{3+} , the basic character of Ln^{3+} ions decrease. Due to the decrease in the size of Ln3+ ions, the ionic character of Ln −OH bond decreases (covalent character increases) which results in the decrease in the basicity.

10. complete the following

a) $MnO_4^{2-} + H^+$ -→?

$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4 + MnO_2 + 2H_2O$

b) $C_6H_5CH_3$ —acidified $KmnO_4$→

$C_6H_5CH_3 \xrightarrow{acidified\ KmnO_4} C_6H_5COOH$ (Benzoic acid)

c) $MnO_4^- + Fe^{2+}$ →

$MnO_4^- + 5Fe^{2+} \xrightarrow{8H^+} 5Fe^{3+} + Mn^{2+} + 4H_2O$

d) KmnO4 —Red hot→

$KmnO4 \xrightarrow{Red\ hot} K_2MnO_4 + MnO_2 + O_2$

e) $Cr_2O_7^{2-} + I^- + H^+$ →

$Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$

f) Na2Cr2O7 +KCl →

$Na2Cr2O7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$

11. What are interstitial compounds?

An interstitial compound or alloy is a compound that is formed when small atoms are trapped in the interstitial holes in a metal lattice

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

Atomic number of Ti= 22
Electronic configuration of Ti is = $1s^2\ 2s^2\ 2p^6\ 3S^2\ 3p^6\ 3d^2 4s^2$
Electronic configuration of Ti^{3+} = $1s^2\ 2s^2\ 2p^6\ 3S^2\ 3p^6\ 3d^1$
The number of unpaired electrons =1
spin only magnetic moment = $\sqrt{n(n+2)}$
Atomic number of Mn = 25
Electronic configuration of Mn is = $1s^2\ 2s^2\ 2p^6\ 3S^2\ 3p^6\ 3d^5 4s^2$
Electronic configuration of Mn^{2+} = $1s^2\ 2s^2\ 2p^6\ 3S^2\ 3p^6\ 3d^5$
The number of unpaired electrons =5
spin only magnetic moment = $\sqrt{n(n+2)}$
= $\sqrt{5(5+2)}$ =5.92BM

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

Ce $^{4+}$ =$1s^2$ $2s^2$ $2p^6$ $3S^2$ $3p^6$ $3d^{10}4s^2$$4p^6$ $4d^{10}5s^2$$5p^6$

Co^{2+} = $1s^2$ $2s^2$ $2p^6$ $3S^2$ $3p^6$ $3d^7$

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.

All the metals display +2 oxidation states except Sc.
On moving from the Sc to the Mn, the atomic numbers increase from 21 to the 25.
It 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 and Mn (+2) = d^5.
The +2 oxidation state is achieved by loss of the 2 4s electrons by the metals.

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

Fe^{3+} ion is more stable due to its half-filled $3d^5$ electronic configuration.
As half filled and completely filled shells are more stable Fe $^{3+}$ ion is more stable.
While Fe^{2+} is not stable.

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

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

Reaction	Standard reduction potential (V)
$Ti^{3+} + e^- \longrightarrow Ti^{2+}$	−0.37
$V^{3+} + e^- \longrightarrow V^{2+}$	−0.26
$Cr^{3+} + e^- \longrightarrow Cr^{2+}$	−0.41
$Mn^{3+} + e^- \longrightarrow Mn^{2+}$	+1.51
$Fe^{3+} + 2e^- \longrightarrow Fe^{2+}$	+0.77
$Co^{3+} + 2e^- \longrightarrow Co^{2+}$	+1.81

The negative values for titanium, vanadium and chromium indicate that the higher oxidation state is preferred.
The high reduction potential of Mn^{3+} / Mn^{2+} indicates Mn $^{2+}$ is more stable than Mn $^{3+}$.

17. Compare lanthanides and actinides.

S.Nm	Lanthanides	Actinides
1	Electrons enter in the 4f orbitals	Electrons enter in the 5f orbitals
2	Binding energy of the 4f orbitals is high	Binding energy of the 5f orbitals is low
3	They do not form complex	They form complex
4	They do not form Oxocation	They form Oxocation. Ex. UO_2^{+2}
5	They are colourless	They are coloured. Ex. U^{+3} is red and U^{+5} is green
6	They show +2, +3 and +4 oxidation states	They show +3, +4, +5, +6 and +7 oxidation states

18. Explain why Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidizing.

Cr^{2+} is strongly reducing in nature. It has a d^4 configuration. While acting as a reducing agent, it gets oxidized to Cr^{3+} (electronic configuration, d^3). This d^3 configuration can be written as configuration, which is a more stable configuration. In the case of Mn^{3+} (d^4), it acts as an oxidizing agent and gets reduced to Mn^{2+} (d^5). This has an exactly half-filled d-orbital and is highly stable.

19. 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.
- The increase in first ionisation enthalpy with increase in atomic number along a particularseries is not regular. The added electron enters (n-1)d orbital and the inner electrons act as ashield and decrease the effect of nuclear charge on valence ns electrons. Therefore, it leads to variation in the ionization energy values.

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

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

21. Out of $Lu(OH)_3$ and $La(OH)_3$ which is more basic and why?

La(OH)3 isis more basic than Lu(OH)3. Due to lanthanoid contraction the size of lanthanoid ions decreases regularly with increase in atomic size .As a result of decrease in size,their covalent character between lanthanoid ion and OH ion increases from La3+to Lu3+. Therefore the basic character f hydroxides decreases from La(Oh)3 to Lu(OH)3

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

Europium(II) is **more stable** trhan **Cerium (II)** As we from left to right, effective nuclear charge increases due to which lanthanide contraction takes place. The inert pair effect becomes **more** dominative. The higher oxidation property tendency decreases which makes Eu(**II**) **more stable than** Ce(**II**).

23. Why do zirconium and Hafnium exhibit similar properties?

Zr and Hf exhibit similar properties due to lanthanoid contraction. Electrons present in f subshell didn't **do** good shielding due to which with the increasing atomic number or increasing effective nuclear charge size gets constricted and size of Halfenium and Zirconium becomes almost equal.

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

The following reactions are involved when Cr^{2+} and Fe^{2+} act as reducing agents.

$Cr^{2+} \longrightarrow Cr^{3+}$ $Fe^{2+} \longrightarrow Fe^{3+}$

The $E^{\circ}_{Cr^{3+}/Cr^{2+}}$ value is - 0.41 V and $E^{\circ}_{Fe^{3+}/Fe^{2+}}$ is +0.77 V. This means that Cr^{2+} can be easily oxidized to Cr^{3+}, but Fe^{2+} does not get oxidized to Fe^{3+} easily. Therefore, Cr^{2+} is a better reducing agent that Fe^{3+}.

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

The $E^0(M^{2+}/M)$ value of a metal depends on the energy changes involved in the following reactions:

1.Sublimation energy: The energy needed to convert one mole of atoms from a solid state to gaseous state.

2. Ionization energy: The energy supplied to remove electrons from one mole of atoms, which are in the gaseous state.

3. Hydration energy: The energy emitted to hydrate one mole of ions.Now, copper has a high ionisation energy and low hydration energy. Hence, the $E^0(M^{2+}/M)$ value for copper is positive.

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.

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-points** of the **transition metals** are **high** due to the 3d electrons being available for metallic bonding. The densities of the **transition metals** are **high** for the same reason as the **high boiling points**. **Transition metals** are all dense **metals**with **high melting** and **boiling points**.

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