Important Questions for Class 12

Chemistry

Chapter 8 – d & f Block Elements

Very Short Answer Questions 1 Mark

1. Write the electronic configuration of Cr^{3+} ion (atomic number of Cr = 24)

Ans: The atomic number of chromium is 24, hence the electronic configuration of Cr^{3+} will be $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^3$.

2. Explain $CuSO_4.5H_2O$ is blue while $ZnSO_4$ and $CuSO_4$ are colourless?

Ans: Water acts as a ligand in $CuSO_4.5H_2O$, causing crystal field splitting. As a result, in $CuSO_4.5H_2O$, a d-d transition is possible and visible. Due to the lack of water in anhydrous $CuSO_4$ and $ZnSO_4$, ligand crystal field splitting is not feasible, and hence no colour is produced.

3. Why is the third ionisation energy of Manganese (Z = 25) is unexpectedly high?

Ans: Manganese has an atomic number of 25 and an electronic configuration of $[Ar]4s^2,3d^5$. The loss of two electrons transforms Mn^{2+} into $[Ar]3d^5$, a structure with a half-filled d-orbital that is exceedingly stable. As the third electron must be removed from the stable configuration of Mn^{2+}, the third ionisation energy is extremely large.

4. Which elements among 3d - transition elements, exhibit the highest oxidation state?

Ans: The electronic configuration of manganese is $[Ar]4s^2,3d^5$.

In the d-subshell of manganese, there are the most unpaired electrons (5 electrons). As a result, manganese has the most oxidation states, spanning from $+2$ to $+7$.

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

Ans: In its ground state, silver possesses a totally filled $4d$-orbital $\left(4d^{10}, 5s^{1}\right)$.The oxidation states of silver are now $+1$ and $+2$. An electron is removed from the s-orbital in the $+1$ oxidation state. The d-orbital, on the other hand, loses one electron in the $+2$ oxidation state. As a result, the d-orbital is now incomplete $(4d^{9})$. As a result, it's a transitional element.

6. In 3d series $(Sc \rightarrow Zn)$, the enthalpy of atomisation of Zn is low. Why?

Ans: The enthalpy of atomization is determined by the amount of metallic bonding that an element has. An element's enthalpy of atomization increases as its metallic bonding becomes more extensive. There are some unpaired electrons in all transition metals (except zinc, electronic configuration: $3d^{10}, 4s^{2}$), which explain for their stronger metallic bonding. The inter-atomic electrical bonding in zinc is the weakest due to the absence of these unpaired electrons, and as a result, it has the lowest enthalpy of atomization.

7. Out of the following elements, identify the element which does not exhibit variable oxidation state?

Chromium(Cr), Cobalt(Co), Zinc(Zn)

Ans: The only element which does not exhibit variable oxidation states, among the above given elements is zinc.

8. The +3 oxidation state of lanthanum $(Z = 57)$, gadolinium $(Z = 64)$ and lutetium $(Z = 71)$ are especially stable. Why?

Ans: Lanthanum (57) $5d^1,6s^2,4f^0$, Lutetium (71) $4f^{14},5d^1,6s^2$, and Gadolinium (64) $4f^7,5d^1,6s^2$ have the same electrical configuration. As a result, they have an empty, fully filled, and half-filled $4f$ -subshell, and their $+3$ oxidation state is stable.

9. Mention one consequence of Lanthanoid Contraction?

Ans: In the lanthanoids, from $La(OH)_3$ to $Lu(OH)_3$, the basic strength of hydroxides drops. The size of M^{3+} ions reduces as a result of lanthanoid contraction, and the covalent character of the $M-OH$ bond increases.

10. The first ionization enthalpies of $5d$ – series elements is higher than those of 3d and 4d series elements why?

Ans: Because of weak shielding by $4f$ electrons, the first ionisation energy of $5d$ elements is higher than that of $3d$ elements. This is owing to the greater effective nuclear charge acting on outer valence electrons.

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

Ans: The electronic configuration of Mn^{2+} is $[18Ar]3d^5$ and the electronic configuration of Fe^{2+} is $[18Ar]3d^6$.

As Mn^{2+} has a stable half-filled electronic structure, Mn^{2+} compounds are more resistant to oxidation to their $+3$ state than Fe^{2+} compounds. Fe^{2+} $(3d^6)$ can easily lose one electron to become Fe^{3+} ($3d^5$, stable configuration).

12. Calculate the magnetic moment of Cu^{2+} (Z =29) on the basis of “spin-only” formula.

Ans: The formula for calculating the magnetic moment is: $\mu = \sqrt{n(n+2)}$ B.M, where n is the number of unpaired electrons.

The electronic configuration of Cu^{2+} is $[Ar]^{18}3d^{10}$. Hence, it has only one unpaired electron.

So, its magnetic moment will be:

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

$$\mu = \sqrt{1(1 + 2)} = 1.73 \text{ B.M}$$

13. What is the shape of chromate ions?

Ans: The shape of chromate ions is tetrahedral.

14. Why does vanadium pentoxide act as a catalyst?

Ans: Vanadium is a transition metal that quickly switches between oxidation states. It can create unstable intermediates in one oxidation state and then quickly convert to products by gaining a new stable oxidation state, opening up a new reaction pathway.

15. What are interstitial compounds?

Ans: Interstitial compounds are formed when very small atoms, such as hydrogen, nitrogen, and carbon, become trapped inside the crystal lattices of metals. These chemicals are usually non-stoichiometric and not ionic or covalent.

16. The transition metals and their compounds are known for their catalytic activity. Give two specific reasons to justify the statement.

Ans: Transition metals have a wide range of oxidation states and are capable of forming complexes. They produce unstable intermediates. They open up a novel pathway with lower reaction activation energy. They also provide an appropriate surface for the reaction to take place on.

17. Write the chemical equation for the reaction of thiosulphate ions and alkaline potassium permanganate.

Ans: The chemical equation is as follows:

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

18. Mention the name and formula of the ore from which potassium dichromate is prepared.

Ans: Potassium dichromate is prepared from an ore named chromite, and its formula is $FeCr_2O_4$.

19. Write the electronic configuration of Lu^{3+} (At. No. =71).

Ans: The electronic configuration of Lu^{3+} is $[Xe]4f^{14}\ 5d^1\ 6s^2$

20. What is the most common oxidation state of actinoids?

Ans: $+3$ is the most common oxidation state achieved by actinoids.

21. Write the names of the catalyst used in the:

(a) Manufacture of sulphuric acid by contact process.

Ans: Vanadium oxide is the catalyst used in the manufacture of sulphuric acid by contact process.

(b) Manufacture of polythene.

Ans: Ziegler Nata catalyst which is the combination of titanium tetrachloride and trimethyl aluminium is used in the manufacture of polythene.

22. Mention the name of the element among lanthanoids known to exhibit $+4$ oxidation state.

Ans: Cerium is the element in the lanthanoid series which is known to exhibit $+4$ oxidation state

23. Name one ore each of manganese and chromium.

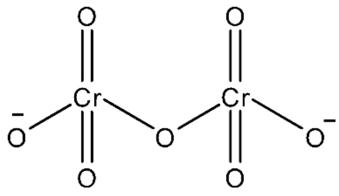
Ans: The ore of manganese is pyrolusite and chromite is known as the ore of chromium.

24. Why is Cd^{2+} ion white?

Ans: Cd^{2+} has $5d^{10}$ electrical structure. It signifies it has a full packed d-subshell. As a result, there will be no d-d transition, and hence, Cd^{2+} will remain white.

25. Draw the structure of dichromate anion.

Ans: The structure of dichromate anion is:



26. Arrange the following monoxides of transition metals on the basis of decreasing basic character TiO, VO, CrO, FeO.

Ans: Moving over a period, the basic character of transition metal oxides often declines. As a result, the proper sequence is: $TiO > VO > CrO > FeO$

Short Answer Type Questions **2 Marks**

1. Write the chemical equation, when the yellow colour of aqueous solution of Na_2CrO_4 changes to orange on passing CO_2 gas?

Ans: The chemical equation is as follows:

$$Na_2CrO_4 \xrightarrow[H_2O]{CO_2} Na_2Cr_2O_7$$

Sodium chromate is yellow in colour but when carbon dioxide gas is passed through it, it changes to sodium dichromate, which is orange in colour.

2. The stability of Cu^{2+} (aq) is more than that of Cu^{+} (aq) . Why?

Ans: The hydration energy (enthalpy) of the ions when they connect to the water molecules determines their stability. Cu^{2+} ions have a higher charge density than Cu^{+} ions, forming much stronger interactions and releasing more energy as a result.

3. Indicate the steps in the preparation of $K_2Cr_2O_7$

(a) From Chromite ore $KMnO_4$

Ans: The steps of preparations are: $K_2Cr_2O_7$ from Chromite ore: Potassium dichromate is prepared in three steps:

i. Synthesis of sodium chromate from chromite ore:
$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

ii. Sodium chromate to sodium dichromate conversion
$2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$

iii. Sodium dichromate to potassium dichromate conversion:
$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$

(b) From Pyrolusite ore.

Ans: From Pyrolusite ore: Potassium permanganate is prepared by:

$$2MnO_2 + 4KOH + O_2 \xrightarrow[\Delta]{} 2K_2MnO_4 + 2H_2O$$

4. Give reason for:

(a) In permanganate ions, all bonds formed between manganese and oxygen are covalent.

Ans: MnO_4^- in the highest oxidation state, $+7$. Transition metals produce covalent bonds in high oxidation states (according to Fajan's rules, as oxidation state increases, ionic character decreases).

(b) Permanganate titrations in presence of hydrochloric acid are unsatisfactory.

Ans: Because hydrochloric acid is oxidised to chlorine, permanganate titrations in the presence of the acid are unreliable. In preparative organic chemistry, this is a preferred oxidant.

5. Write complete chemical equations for:

(a) Oxidation of Fe_2^+ by $Cr_2O_7^{2-}$ in acidic medium

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

(b) Oxidation of Mn^{2+} by MnO_4^- in neutral or faintly alkaline medium.

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

6. Answer the following:

(a) Why do transition metals show high melting points?

Ans: Transition metals have a high density, as well as high melting and boiling temperatures. Metallic bonding via delocalized d electrons causes these characteristics, which leads to increased cohesion as the number of shared electrons grows.

(b) Out of Fe and Cu, which one would exhibit higher melting point?

Ans: The melting point of Fe is greater than that of Cu. This is due to the fact that iron contains four unpaired electrons in the $3d$ -subshell, but copper only has one electron in the $4s$ -subshell. As a result, iron's metallic connections are significantly stronger than that of copper's.

7. Describe giving reason which one of the following pairs has the property indicated:

(a) Cr^{2+} or Fe^{2+} (stronger reducing agent).

Ans: Cr^{2+} is a more powerful reducer than Fe^{2+} . The conventional electrode potential values $E^\circ\left(Cr^{3+}/Cr^{2+} = --0.41\ V\right)$ and $E^\circ\left(Fe^{3+}/Fe^{2+} = +\ 0.77\ V\right)$ can be used to explain this. As a result, Cr^{2+} is quickly oxidised to Cr^{3+} , but Fe^{2+} is not as easily oxidised to Fe^{3+} .

(b) Co^{2+} or Ni^{2+} (lower magnetic moments).

Ans: The electronic configuration of Co^{2+} is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7$ and the electronic configuration of Ni^{2+} is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8$. Hence, the magnetic moment of Ni^{2+} lower than Co^{2+} , because unpaired electrons are less in the valence shell of Ni^{2+} than Co^{2+} .

8. Of the ions $Co^{2+}, Sc^{3+}, Cr^{3+}$ which one will give colourless aqueous solution and how will each of them respond to magnetic field and why?

Ans: The electronic configurations of $Co^{2+}:[Ar]3d^7$; $Sc^{3+}:[Ar]3d^0$; $Cr^{3+}:[Ar]3d^3$. Unpaired electrons exist in Co^{2+} and Cr^{3+} . They are so coloured in an aqueous solution. Sc^{3+} does not have any unpaired electrons. As a result, it is colourless.

9. Complete the following equations:

(a) $MnO_2 + KOH + O_2 \rightarrow$

Ans: The complete equation is as followed:

$$MnO_2 + KOH + O_2 \rightarrow KMnO_4 + H_2O$$

(b) $Na_2Cr_2O_7 + KCl \rightarrow$

Ans: The complete equation is as followed:

$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_2 + 2NaCl$

10. Transition metals show low oxidation states with carbon monoxide.

Ans: Synergic bonds enable the formation of complexes by transition elements in zero oxidation states. In metal carbonyl, the metal-carbon bond has both s and p character. The M-C sigma bond is created when a lone pair of electrons from the carbonyl carbon are donated to a metal's empty orbital. The M-C bond is created when a pair of electrons from a metal's full d orbital are donated to carbon monoxide's unoccupied anti bonding pi* orbital. The synergic action of metal to ligand bonding enhances the connection between carbon monoxide and the metal.

11. For the first row transition metals the enthalpy of atomisation value are:

	Sc	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
$\Delta_a H^o$ / kJ mol^{-1}	**326**	**473**	**515**	**397**	**281**	**416**	**425**	**430**	**339**	**26**

Assign reason for the following:

(a) Transition elements have higher values of enthalpies of atomisation.

Ans: The reasons for the above statements are:

Transition elements contain a large number of valence electrons and a high effective nuclear charge. As a result of the existence of an unpaired electron in the $(n-1)d$ -sub-shell, they form extremely strong metallic bonds with a high enthalpy of atomisation.

(b) The enthalpy of atomisation of zinc is the lowest in 3d – series.

Ans: Due to the lack of unpaired electrons and weak metallic connections, zinc has the lowest enthalpy of atomisation.

12. Account for the following:

(a) Copper shows its inability to liberate hydrogen gas from the dilute acids.

Ans: The reason behind it is that the Copper has a positive electrode potential, it cannot release hydrogen from acids. Hydrogen gas is liberated by metals with a negative electrode potential. So, Copper shows its inability to liberate hydrogen gas from the dilute acids.

(b) Scandium (Z =21) does not exhibit variable oxidation states.

Ans: In the ground state, Scandium (Z=21) possesses partially filled $3d$ -orbitals $(3d^1)$. As a result, it's classified as a transitional element.

13. Copper (I) compounds undergo disproportionation. Write the chemical equation for the reaction involved and give reason.

Ans: The chemistry of copper(I) is restricted by a reaction that happens in solution involving simple copper(I) ions. This is an excellent illustration of disproportionation, which occurs when something oxidises and then reduces itself. Copper(I) ions in solution are disproportionately converted to copper(II) ions and a copper precipitate.

The reaction is: $2Cu^{+}(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$

14. Iron (III) catalyses the reaction: $\mathbf{2I^{-} + S_2O_8^{2-} \xrightarrow{Fe^{3+}} I_2 + 2SO_4^{2-}}$

Ans: The catalytic action of iron (III) is determined as:

$2Fe^{3+} + 2I^{-} \rightarrow 2Fe^{2+} + I_2$

$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$

15. Complete the equations:

(a) $\mathbf{MnO_4^{-} + NO_2^{-} + H^{+} \rightarrow}$

Ans: The complete reaction is: $2MnO_4^- + 3NO_2^- + H^+ \rightarrow 3NO_3^- + 2MnO_2 + OH^-$

(b) $\mathbf{KMnO_4 \xrightarrow{513K}}$

Ans: The complete reaction is: $2KMnO_4 \xrightarrow{513K} K_2MnO_2 + O_2$

16. The following two reactions of HNO_3 with Zn are given:

(a) $\mathbf{Zn + conc. HNO_3 \rightarrow Zn(NO_3)_2 + X + H_2O}$

Ans: The complete and balanced equation is:
$4Zn + 4HNO_3(conc.) \rightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$

(b) $\mathbf{Zn + dil. HNO_3 \rightarrow Zn(NO_3)_2 + Y + H_2O}$

Ans: The complete and balanced equation is:
$4Zn + 10HNO_3(dil.) \rightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$

17. Titanium shows magnetic moment of 1.73 BM in its compound. What is the oxidation number of Ti in the compound?

Ans: The formula for finding the magnetic moment is: $\mu = \sqrt{n(n+2)}$ BM. The value of magnetic moment (μ) is 1.73 BM. So, it will have one unpaired electron.

The electronic configuration of titanium is $[Ar]^{18}3d^2, 4s^2$. So, titanium will lose three electrons, so that it will have one unpaired electron left. Thus, the oxidation number will be $+3$.

18. Account for the following:

(a) Transition metals and majority of their compounds act as good catalysts.

Ans: Transition metals and their compounds are effective catalysts because of their ability to exhibit changing oxidation states and form complexes, as well as the fact that they give a suitable surface for reaction to occur. For example, in the contact process, vanadium oxide is used, while in Haber's Process, finely split iron is used.

(b) From element to element, actinoid contraction is greater than lanthanoid contraction.

Ans: Due to inadequate shielding by $5f$ -electrons in actinoids compared to $4f$ -electrons in lanthanoids, actinoid contraction is higher than lanthanoid contraction from element to element.

19. Calculate the number of electrons transferred in each case when $KMnO_4$ acts as an oxidising agent to give

(i) MnO_2

Ans: The oxidation state of manganese in $KMnO_4$ is $+7$. The oxidation state of manganese in MnO_2 is $+4$. Hence, three electrons transfer will take place.

(ii) Mn^{2+}

Ans: The oxidation state of manganese in $KMnO_4$ is $+7$. The oxidation state of manganese in Mn^{2+} is $+2$. Hence, a transfer of five electrons will take place.

(iii) $Mn(OH)_3$

Ans: The oxidation state of manganese in $KMnO_4$ is $+7$. The oxidation state of manganese in $Mn(OH)_3$ is $+3$. Hence, a transfer of four electrons will take place.

(iv) MnO_4^{2-}

Ans: The oxidation state of manganese in $KMnO_4$ is $+7$. The oxidation state of manganese in MnO_4^{2-} is $+6$. Hence, a transfer of one electron will take place.

20. Calculate the number of moles of $KMnO_4$ that is needed to react completely with one mole of sulphite ion in acidic medium.

Ans: In acidic solution, the balanced chemical equation is as followed:

$$2MnO_4^- + 5SO_3^{2-} + 6H^+ \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$$

According to the above reaction:

5 moles of SO_4^{2-} ions required 2 moles of MnO_4^- ions to change.

1 mole of SO_4^{2-} ion will require $\frac{2}{5}$ moles of MnO_4^- ions to change.

Short Answer Type Questions **3 Marks**

1. Account for the following:

(a) $La(OH)_3$ is more basic than $Lu(OH)_3$

Ans: The most basic is $La(OH)_3$ while the least basic is $Lu(OH)_3$. The covalent nature of the hydroxides rises as the size of lanthanide ions falls from La^{3+} to Lu^{3+} , and therefore the basic strength lowers.

(b) Zn^{2+} salts are white.

Ans: There are no unpaired electrons in the electronic arrangement of Zn^{2+} $(3d^{10})$ salts. The presence of an unpaired electron in metal ions allows for electron transition in the visible range. This is why Zn^{2+} ion salts are white in colour.

(c) $Cu\,(I)$ compounds are unstable in aqueous solution and undergo disproportionation.

Ans: Cu^+ is more unstable in aqueous solution than Cu^{2+} because, while copper's 2nd I.E. is considerable, Cu^{2+} hydrations enthalpy is significantly lower than Cu^+ , and so it more than compensates for copper's 2nd I.E. As a result, many Cu^+ complexes in aqueous solution are unstable and disproportionate.

2. Describe the oxidising action of potassium dichromate with following. Write ionic equations for its reaction with.

(a) Iodide ion

Ans: The ionic equation is: $Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$

(b) Iron (II)

Ans: The ionic equation is: $Cr_2O_7{}^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

(c) H_2S

Ans: The ionic equation is: $Cr_2O_7{}^{2+} + 3H_2S + 8H^+ \rightarrow 2Cr^{3+} + 3S + 7H_2O$

3. Answer the following questions:

(a) Deduce the number of $3d$ electrons in the following ions: Fe^{3+} , Cu^{2+} and Sc^{3+} .

Ans: The electronic configuration of Fe^{3+} is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$. So, Fe^{3+} has 5 electrons in $3d$-orbital. The electron configuration of Cu^{2+} is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$. So, Cu^{2+} has 9 electrons in $3d$-orbital. The electronic configuration of Sc^{3+} is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^0$. So, Sc^{3+} has no electrons in $3d$-orbitals.

(b) Why do transition metals form alloys?

Ans: Transition metals have atomic sizes that are extremely close to one another. Due to their comparable atomic sizes, one metal may easily replace the other in its lattice and create a solid solution, which is the alloy. This is why, in the molten state, transition metals create homogenous mixes with one another.

(c) Write any two characteristics of interstitial compounds.

Ans: The melting temperature of interstitial compounds is higher than that of pure metals, and they are tougher and more corrosion resistant.

4. In the following reaction, Mn(VI) changes to Mn(VII) and Mn(IV) in acidic solution.

$3Mn^{VI}O_4{}^{2-} + 4H^+ \rightarrow 2Mn^{VII}O_4{}^- + Mn^{IV}O_2 + 2H_2O$

(a) Explain why Mn(VI) changes to Mn(VII) and Mn(IV).

Ans: Mn(VI) is oxidized to Mn(VII), therefore oxidation process occurs and it also gets reduced to Mn(IV) and hence reduction process also happens in this reaction.

(b) What special name is given to such type of reactions?

Ans: The reaction given is a disproportionation reaction. As MnO_4^{2-} gets reduced to MnO_2 and it gets oxidized to MnO_4^-.

5. What happens when: Write the chemical equations for the reactions involved?

(a) thiosulphate ions react with alkaline $KMnO_4$.

Ans: $8MnO_4^- + 3S_2O_3^{2-} + H_2 \rightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$

(b) Ferrous oxalate reacts with acidified $KMnO_4$.

Ans: $5Fe_2C_2O_4 + 3KMnO_4 + 24H^+ \rightarrow 5Fe^{3+} + 10CO_2 + 3Mn^{2+} + 3K^+ + 12H_2$

(c) Sulphurous acid reacts with acidified $KMnO_4$.

Ans: $2MnO_4^- + 5SO_3^{2-} + 6H^+ \rightarrow 5SO_4^{2-} + 2Mn^{2+} + 3H_2O$

6. Name the catalysts used in the:

(a) Manufacture of ammonia by Haber's Process.

Ans: Iron is used as a catalyst in the Haber's Process.

(b) Oxidation of ethyne to ethanol.

Ans: Palladium (II) chloride is used in the oxidation of ethyne to ethanol.

(c) Photographic industry.

Ans: Silver metal is used as a catalyst in photographic industry.

7. Among $TiCl_4$, VCl_3 and $FeCl_2$, which one will be drawn more strongly into a magnetic field and why?

Ans: The transition metal ion with the most unpaired electrons will be significantly pulled into the magnetic field among the above given halides.

The electronic configuration of Ti^{4+} will be $1s^2\ 2s^2\ 2p^4\ 3s^2\ 3p^6\ 3d^0$. It has non paired electrons in its outermost shell and hence its magnetic moment will be zero. The electronic configuration of V^{3+} will be $1s^2\ 2s^2\ 2p^4\ 3s^2\ 3p^6\ 3d^2$. It has two unpaired electronic in its d-orbital and hence its magnetic moment will be $2.76\ B.M$. The electronic configuration of Fe^{2+} will be $1s^2\ 2s^2\ 2p^4\ 3s^2\ 3p^6\ 3d^6$. It has four unpaired electrons and hence its magnetic moment will be $4.9\ B.M$. As the number of unpaired electrons in Fe^{2+} are higher, its magnetic moment will also be greater. Hence, $FeCl_2$ will be drawn more strongly into a magnetic field.

8. Complete the following equations

(a) $\mathbf{MnO_4^{2-} + H^+ \rightarrow}$

Ans: The complete and balanced equation is:

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

(b) $\mathbf{KMnO_4 \xrightarrow{Heat}}$

Ans: The complete and balanced equation is:

$$2KMnO_4 \xrightarrow{Heat} K_2MnO_4 + MnO_2 + O_2$$

(c) $\mathbf{K^+ + MnO_4^- + Fe^{2+} + C_2O_4^{2-}}$

Ans: The complete and balanced equation is:

$$2MnO_4^- + Fe^{2+} + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + Fe^{+3} + 10CO_2 + 8H_2O$$

9. How do you account for the following?

(a) With the same d-orbital configuration (d^4) , Cr^{2+} is a reducing agent while Mn^{3+} is an oxidising agent.

Ans: The configuration of Cr^{2+} is $3d^4$. Cr^{3+} , which has a stable $3d^3$ structure, can lose one electron (as it has half -filled t_2g level). As a result, it has a reducing property. Mn^{3+} , on the other hand, has a $3d^4$ structure but can acquire an electron to become Mn^{2+} , which has a stable $3d^5$ shape (as it is exactly half - filled). As a result, it is oxidising.

(b) The actinoids exhibit a larger number of oxidation states than the corresponding members in the lanthanoid series.

Ans: Because of the narrow energy gap between the $5f$, $6d$, and $7s$ subshells, actinides have greater oxidation states than lanthanides. As a result, the outermost electrons are easily stimulated to higher energy levels, resulting in oxidation states that are changeable.

(c) Most of transition metal ions exhibit characteristic colours in aqueous solutions.

Ans: The presence of unpaired d-electrons in transition metal ions in aqueous solution gives them their colour. These unpaired d-electrons are stimulated to a higher energy d-orbital of the same n value from a lower energy level of a metal ion in a complex. The frequency of light absorbed corresponds to the energy of excitation, and this frequency is visible. The colour seen is the complementary colour of the light that has been absorbed. The type of the ligand determines the frequency of light absorbed. Water molecules are ligands in aqueous solutions, and the colours of the ions detected are mentioned in the table below.

Long Answer Type Questions 5 Marks

1. A green compound 'A' on fusion with $NaOH$ in presence of air forms yellow compound 'B' which on acidification with dilute acid, gives orange solution of compound 'C'. The orange solution when reacted with equi-molar ammonuim salt gives compound 'D' which when heated liberates nitrogen gas and compound 'A'. Identify compounds A to D and write the chemical equation of the reactions involved.

Ans: The overall reaction from A to D is:

$$Cr_2O_3 \xrightarrow[\text{NaOH}]{\text{Fusion with}} Na_2CO_4 \xrightarrow[\text{Acidification}]{H_2SO_4} Na_2Cr_2O_7 \xrightarrow{NH_4Cl} (NH_4)_2Cr_2O_4 \xrightarrow[\Delta]{} Cr_2O_3$$

The chemical equations involved in the above conversions are:

$$2Cr_2O_3 + 8NaOH + 3O_2 \rightarrow 4Na_2CrO_4 + 4H_2O$$

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

$$Na_2Cr_2O_7 + 2NH_4Cl \rightarrow (NH_4)_2Cr_2O_7 + 2NaCl$$

$$(NH_4)_2Cr_2O_7 \xrightarrow[\Delta]{} Cr_2O_3 + N_2 + 4H_2O$$

2. Assign reasons for the following:

(a) There is no regular trends in E° values of M^{2+}/M systems in 3d series.

Ans: Due to uneven electronic configurations from left to right, irregular change in ionisation enthalpies (sum of 1st and 2nd ionisation enthalpies), heat of sublimation, and enthalpy of hydration from left to right in the period. As a result, irregular variations in $E^{\circ}\left(M^{2+}/M\right)$ values for ionisation metals are caused by irregular variations in ionisation enthalpies, and heat of sublimation and hydration enthalpy.

(b) There is gradual decrease in the ionic radii of M^{2+} ion in 3d series.

Ans: The ionic radii get smaller as the nuclear charge gets higher. Because incoming electrons enter the inner $(n-1)d$ orbitals as nuclear charge rises, this reduction occurs. When the oxidation state goes from $+2$ to $+3$, the ionic radii gradually decrease.

(c) Majority of transition metals form complexes.

Ans: Transition metals are the d-block elements having the outer shell electronic configuration as $ns^2(n-1)d^{1-10}$. These metal ions can easily form complexes with a group of negative ions or neutral molecules that have lone pairs of electrons. This is due to: the metals' small size and strong nuclear charge. Availability of empty d-orbitals with sufficient energy to accept ligand-donated lone pairs of electrons.

(d) Ce^{3+} can be easily oxidised to Ce^{4+}

Ans: The outer shell electronic configuration of Ce^{3+} is $4f^1\ 5d^0\ 6s^0$. Ce^{3+} can easily lose one electron from the $4f$ -orbital and forms Ce^{4+} with an outer shell electronic configuration of $4f^0\ 5d^0\ 6s^0$. Thus, Ce^{3+} gets easily oxidized to Ce^{4+}.

(e) Tantalum and palladium metals are used to electroplate coinage metals.

Ans: At a bare minimum, the coinage metals are those metallic chemical elements that have historically been utilised as components in coin alloys. Tantalum and palladium are valuable materials for electroplating coinage because of their chemical inertness.

3. Account for the following:

(a) Actinoids display a variety of oxidation states.

Ans: Actinides have a wide range of oxidation states, ranging from $+3$ to $+6$. This is owing to the small energy gap between the subshells $5f$, $6d$, and $7s$. The two main oxidation states are $+3$ and $+4$, with $+3$ being the most stable. In Thorium and Plutonium, the $+4$ oxidation state is the most stable.

(b) Yb^{2+} behaves as a good reductant.

Ans: Ytterbium (Yb) has the electrical configuration $4f^{14}\ 6s^{2}$. Although Yb in the $+2$ oxidation state acquires a fully filled $4f^{14}$ structure, it nevertheless oxidises to its $+3$ states, making it a powerful reducing agent or reductant.

(c) Cerium (IV) is a good analytical reagent.

Ans: Cerium (IV), often known as Ce^{4+} , is a useful analytical reagent. Because the electronics configuration of Ce^{4+} is $[Xe]4f^{0}$, a good analytical reagent is a chemical compound with a high standard of purity. Ce^{4+} ions in solution are good oxidising agents because they tend to return to the more stable oxidation state of $+3$ when an electron is lost or gained. $[Ce^{4+}/Ce^{3+}]$ has an E^{o} value of $1.74\ V$, indicating that it can oxidise water. Cerium (IV) has considerable kinetic stability, resulting in a very slow reaction rate, making it a useful analytical reagent.

(d) Transition metal fluorides are ionic in nature while chlorides and bromides are covalent in nature.

Ans: Fluorides of transition metals are ionic in nature, whereas bromides and chlorides are frequently covalent. According to Fajan's rule, the bigger the anion, the more polarizable it is, and thus the more covalent it is. The size of an atom grows as it moves along a group. Fluorides are hence smaller than chlorides and bromides.

(e) Hydrochloric acid attacks all the actinoids.

Ans: Actinoids are more reactive than lanthanides; these metals are attacked by hydrochloric acid because no protective oxide layer forms on their surface, but only a little amount of nitric acid is added because a protective oxide layer forms on their surface.

4. Explain by giving suitable reason:

(a) Co(II) is stable in aqueous solution but in the presence of complexing agent it is readily oxidised.

Ans: Although $\mathrm{Co(II)}$ is stable in aqueous solutions, it is oxidised to $\mathrm{Co(III)}$ in the presence of strong field complexing agents. Despite the fact that Cobalt's third ionisation energy is large, the higher number of crystal field stability field ligands overcomes it. In addition, Co^{3+} ions are more likely than Co^{2+} ions to form coordination complexes.

(b) Eu^{2+}, Yb^{2+} are good reductants whereas Tb^{4+} is an oxidant.

Ans: Europium's (Eu) electrical configuration is $4f^7\,6s^2$ while Ytterbium's (Yb) is $4f^{14}\,6s^2$. In the $+2$ oxidation state, Europium and Ytterbium form half-filled $(4f^7)$ and fully-filled $(4f^{14})$ configurations, although they nevertheless oxidise to their typical $+3$ states, acting as powerful reducing agents or reductants. Terbium possesses a $4f^7$ half-filled stable structure in the $+4$ state, but it quickly reduces to the common $+3$ state, and so it acts as an oxidant.

(c) AgCl dissolves in ammonia solution.

Ans: Because it forms $[\mathrm{Ag(NH_3)_2}]\mathrm{Cl}$ complexes, AgCl is soluble in ammonia. Because the complex $[\mathrm{Ag(NH_3)_2}]^+$ ion is formed, it behaves as an ionic ion, making it soluble.

(d) Out of Cr^{2+} or Fe^{2+}, which one is a stronger reducing agent?

Ans: Cr^{2+} is a stronger reducing agent than Fe^{2+}, due to the conventional electrode potential values $E^o\left(\mathrm{Cr}^{3+}/\mathrm{Cr}^{2+} = -0.41\ \mathrm{V}\right)$ and $E^o\left(\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+} = 0.77\ \mathrm{V}\right)$ which is higher for iron than chromium. As a result, Cr^{2+} is quickly oxidised to Cr^{3+}, whereas Fe^{2+} is difficult to oxidise to Fe^{3+}.

(e) The highest oxidation state is exhibited in oxoanions of a transition metal

Ans: Metal oxoanions are covalent in nature, with oxygen participating in multiple bonding with the metal atom. The elevated oxidation state of the metal in oxoanions is due to this reason. For example, the element Mn has a $+7$ oxidation state in permanganate ion.

5. When a white crystalline compound A is heated with $K_2Cr_2O_7$ and conc. H_2SO_4 , a reddish brown gas B is evolved, which gives a yellow coloured solution C when passed through $NaOH$. On adding CH_3COOH and $(CH_3COO)Pb$ to solution C, a yellow coloured ppt. D is obtained. Also on heating A with $NaOH$ and passing the evolved gas through K_2HgI_4 solution, a reddish brown precipitate E is formed. Identify A, B, C, D and E and write the chemical equations for the reactions involved.

Ans: The following reactions are:

$$4NH_4Cl + K_2Cr_2O_2 + 6H_2SO_4 \rightarrow 2CrO_2Cl_2 + 4NH_4HSO_4 + 2KHSO_4 + 3H_2O$$

$$CrOCl_2 + 2NaOH \rightarrow Na_2CrO_4 + 2HCl$$

$$Na_2CrO_4 + (CH_3COO)_2Pb \rightarrow PbCrO_4 \downarrow + 2CH_3COONa$$

$$NH_4Cl + NaOH \rightarrow NaCl + H_2O + NH_3$$

$$2K_2HgI_2 + NH_3 + 3KOH \rightarrow NH_2(HgO)HgI + 7KI + 2H_2O$$

According to the above reaction, the compound A is NH_4Cl, compound B is CrO_2Cl_2, compound C is Na_2CrO_4, compound D is $PbCrO_4$ and compound E is $NH_2(HgO)HgI$ which is also known as Millon's base.

6. Answer the following:

(a) Describe the preparation of potassium dichromate $(K_2Cr_2O_7)$. Write the chemical equations of the reactions involved.

Ans: Potassium dichromate is manufactured from chromite ore $(FeO.Cr_2O_3)$ in the following steps:

Step 1: Chromite ore is roasted into sodium chromate:

$$4FeO.Cr_2O_3 + 8Na_2CO_3 + 7O_2 \rightarrow 2Fe_2O_3 + 8Na_2CrO_4 + 8CO_2$$

Step 2: Sodium chromate is converted into sodium dichromate:

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

Step 3: Sodium dichromate converted to potassium dichromate:

$$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$$

(b) “The chromates and dichromates are interconvertible by the change in pH of medium.” Why? Give chemical equations in favour of your answer.

Ans: The equilibrium reaction of dichromate and chromate ions is given as:

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-} + 2H^+$$

In the above reaction, dichromate ions $(Cr_2O_7^{2-})$ give orange colour and chromate ions (CrO_4^{2-}) give yellow colour.

So, when the concentration of H^+ ions is increased in the solution, the pH decreases, that means that pH of the solution is acidic and the equilibrium of the reaction shifts towards left side and it gives orange coloured dichromate ions. When the concentration of OH^- ions is increased in the solution, the pH of the solution increases and the equilibrium of the reaction shifts towards right side and it gives yellow coloured chromate ions.

7. Explain giving reasons:

(a) Transition metals are less reactive than the alkali metals and alkaline earth metals.

Ans: Because of their high ionisation potential and melting temperature, transition metals are less reactive than alkali metals. Electrons occupy the same shell or orbital as they move from left to right on the periodic table, with the alkali metals having the least full outermost shells, one electron, implying that they have fewer protons. As a result, they have lower nucleus attraction, whereas comparable transition metals of the same period have more protons interacting with electrons at the same distance from the nucleus as alkali metals.

(b) $E^o(Cu^{2+}/Cu)$ has positive value

Ans: In comparison to H^+/H_2 , a positive result for Cu^{2+}/Cu shows that this reduction occurs quickly. As a result, it is a more powerful oxidising agent, with the redox couple Cu^{2+}/Cu being more powerful than H^+/H_2. It also means that Cu is unable to convert H^+ ions in an acid to H_2.

(c) Elements in the middle of transition series have higher melting points.

Ans: The higher melting point of transition metals is due to the interatomic metallic bonding involving a bigger number of $(n-1)d$ electrons in addition to the ns electrons. Except for anomalous values of manganese and technetium, the melting points of these metals climb to a maximum at d^5 as the atomic number increases during a period of $3d$ series.

(d) The decrease in atomic size of transition elements in a series is very small.

Ans: The outer electrons have a higher nuclear charge due to the weak shielding effect of d-electrons. Because they have a higher effective nuclear charge, their size reduces somewhat, resulting in less fluctuation in transition element size.

8. Answer the following:

(a) Compare the chemistry of the actinoids with that of lanthanoids with reference to:

1. **Electronic configuration**

   Ans: Electronic configuration: The electrical configuration of lanthanoids is $[Xe]4f^{1-14}\ 5d^{0-1}\ 6s^2$. The electronic configuration of actinoids is $[Rn]5f^{1-14}\ 6d^{0-1}\ 7s^2$.

2. **Oxidation states**

Ans: Oxidation states: Due to the wide energy difference between the $4f$ and $5d$ subshells, lanthanoids have $+2$ and $+4$ oxidation states in addition to the $+3$ oxidation state. Due of the narrow energy difference between the $5f$ and $6d$ subshells, actinoids have a high variety of oxidation states.

3. **Chemical reactivity.**

Ans: Chemical reactivity: Lanthanoids with high electropositivity exhibit chemical reactivity that is almost identical. Actinoids (electropositive and highly reactive) are more reactive than lanthanides (especially in finely split form).

(b) How would you account for the following:

1. **Of the d^4 species, Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidising.**

Ans: The usual electrode potential for Cr^{3+}/Cr^{2+} is $(-0.41V)$, while Mn^{3+}/Mn^{2+} is $(+1.57V)$. Cr^{2+} is a reducing agent that can undergo oxidation. Mn^{3+} is an oxidising agent that can undergo reduction.

2. **The lowest oxide of a transition metal is basic whereas highest is amphoteric or acidic.**

Ans: Some of the valence electrons of the metal atom are not engaged in bonding in the low oxidation state of the metal. As a result, it has the ability to transfer electrons and act as a base. Valence electrons, on the other hand, are engaged in bonding and are not available in higher oxidation states of the metal. Instead, because the effective nuclear charge is large, it may take electrons and act like an acid.

9. Answer the following:

(a) What is meant by disproportionation of an oxidation state. Give one example.

Ans: Disproportionation occurs when a state becomes less stable in comparison to two different oxidation states, one lower and one higher.

The example for the disproportionation of oxidation state is:

$3Mn^{VI}O_4^{2-} + 4H^+ \rightarrow 2Mn^{VII}O_4^- + Mn^{IV}O_2 + 2H_2O$

(b) Explain why europium (II) is more stable than Ce(II)?

Ans: The effective nuclear charge increases as we travel from left to right, causing lanthanide contraction. The dominance of the inert pair effect increases. $Eu\,(II)$ is more stable than $Ce\,(II)$ due to its lower oxidation property.

10. Answer the following:

(a) For M^{2+}/M and M^{3+}/M^{2+} systems, the E^o values for some metals are as follows:

**$Cr^{2+}/Cr = -0.9V$ and $Cr^{3+}/Cr^{2+} = -0.4V$ **

$Mn^{2+}/Mn = -1.2\,V$ and $Mn^{3+}/Mn^{2+} = +1.5V$,

$Fe^{2+}/Fe = -0.4V$ and $Fe^{3+}/Fe^{2+} = +0.8V$

Use this data to comment upon:

(i) The stability of Fe^{3+} in acid solution as compared to that of Cr^{3+} and Mn^{3+}

Ans: The stability of Fe^{3+} in acid solution as compared to that of Cr^{3+} and Mn^{3+} Because the reduction potential of Cr^{3+}/Cr^{2+} is negative, $Cr\,(III)$ is the most stable compound because it cannot be reduced to $Cr\,(II)$. Mn^{3+}/Mn^{2+} has a significant positive value, and $Mn\,(III)$ is the least stable since it may be converted to $Mn\,(II)$ quickly. Fe^{3+}/Fe^{2+} has a modest positive value, and $Fe\,(III)$ is more stable than $Mn\,(III)$, but not as much as $Cr\,(III)$.

(ii) The ease with which iron can be oxidised as compared to a similar process for either chromium or manganese.

Ans: Mn^{2+}/Mn has the highest negative reduction potential and is the easiest to oxidise. $Mn > Cr > Fe$ is the order of oxidation easiness.

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

Ans: The involvement of $(n-1)d$ orbitals and ns orbitals in transition elements causes oxidation state fluctuation. By a factor of one, the oxidation states vary. As a result, vanadium has oxidation states of $+2, +3, +4, +5, +6, \text{and } +7$, whereas manganese has oxidation states of $+2, +3, +4, +5, +6, \text{and } +7$. The varied oxidation states indicated by some p-block elements, on the other hand, differ by two units. Tin has oxidation states of $+2$ and $+4$, while indium has oxidation levels of $+1$ and $+3$.