



8.11. Explain giving reasons:

- (i) Transition metals and many of their compounds show paramagnetic behaviour.
- (ii) The enthalpies of atomisation of the transition metals are high.
- (iii) The transition metals generally form coloured compounds.
- (iv) Transition metals and their many compounds act as good catalyst

Sol:

(i) Magnetic properties: Transition elements and many of their compounds are paramagnetic, i.e., they are weakly attracted by a magnetic field. This is due to the presence of unpaired electrons in atoms, ions or molecules. The paramagnetic character increases as the number of unpaired electrons increases. The paramagnetic character is measured in terms of magnetic moment and is given by

$$\mu = \sqrt{n(n+2)}$$

where n = number of unpaired electrons.

(ii) Because of large number of unpaired electrons in d-orbitals of their atoms they have stronger interatomic interactions and hence stronger metallic bonding between atoms resulting in higher enthalpies of atomisation.

(iii) Formation of coloured compounds (both in solid state as well as in aqueous solution) is another very common characteristics of transition metals. This is due to absorption of some radiation from visible light to cause d-d transition of electrons in transition metal atom. The d-orbitals do not have same energy and under the influence of ligands, the d-orbitals split into two sets of orbitals having different energies; transition of electrons can take place from one set of d-orbitals to another set within the same sub-shell. Such transitions are called d-d transitions. The energy difference for these d-d transitions fall in the visible region. When white light is incident on compounds of transition metals, they absorb a particular frequency and remaining colours are emitted imparting a characteristic colour to the complex. Zn^{2+} and Ti^{4+} salts are white because they do not absorb any radiation in visible region.

(iv) Catalytic properties: Many of transition metals and their compounds act as catalyst in variety of reactions, e.g., finely divided iron in manufacture of NH_3 by Haber's process, V_2O_5 or Pt in manufacture of H_2SO_4 by Contact process, etc.). The catalytic activity is due to following two reasons.

(a) The ability of transition metal ion to pass "easily" from one oxidation state to another and thus providing a new path to reaction with lower activation energy.

(b) The surface of transition metal acts as very good adsorbent and thus provides increased concentration of reactants on their surface causing the reaction to occur.

8.12. What are interstitial compounds? Why are such compounds well known for transition metals?

Sol: Transition metals form large number of interstitial compounds. They are able to entrap small atoms of elements like H, C, N, B, etc., in their crystal lattice and even can make weak bonds with them. Due to formation of interstitial compounds, their malleability and ductility decreases and tensile strength increases. Steel and cast iron are hard in comparison to wrought iron due to the presence of

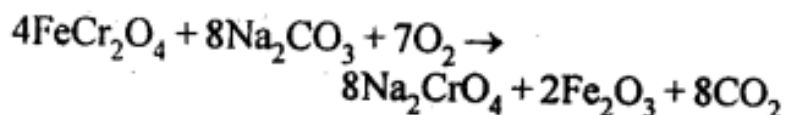
trapped carbon atoms in interstitial spaces.

8.13. How is the variability in oxidation states of transition metals different from that of the non transition metals? Illustrate with examples.

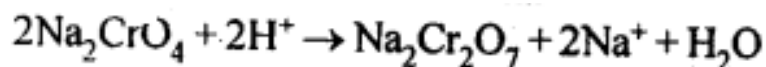
Sol: The variability of oxidation states, a characteristic of transition elements, arises due to incomplete filling of d-orbitals in such a way that their oxidation states differ from each other by unity, e.g., Fe^{2+} , Fe^{3+} , Cr^{2+} , Cr^{3+} . This is in contrast with the variability of oxidation states of non-transition elements where oxidation states normally differ by a unit of two. i.e., Sn^{2+} , Sn^{4+} , P^{3+} and P^{5+} , etc. in the p-block the lower oxidation states are favoured by the heavier members (due to inert pair effect), the opposite is true in the groups of d-block. For example, in group 6, Mo (VI) and W (VI) are found to be more stable than Cr (VI). Thus Cr (VI) in the form of dichromate in acidic medium is a strong oxidising agent, whereas MOO_3 and WO_3 are not.

8.14. Describe the preparation of potassium dichromate from iron chromite ore. What is the effect of increasing pH on a solution of potassium dichromate?

Sol: Potassium dichromate is prepared from chromate, which in turn is obtained by the fusion of chromite ore (FeCr_2O_3) with sodium or potassium carbonate in free excess of air. The reaction with sodium carbonate occurs as follows:



The yellow solution of sodium chromate is filtered and acidified with sulphuric acid to give a solution from which orange sodium dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ can be crystallised.



Sodium dichromate is more soluble than potassium dichromate. The latter is therefore, prepared by treating the solution of sodium dichromate with potassium chloride.



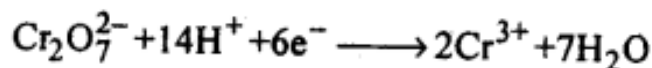
Orange crystals of potassium dichromate crystallise out. The chromates and dichromates depending upon p^{H} of the solution. If p^{H} of potassium dichromate is increased it is converted to yellow potassium chromate.



8.15. Describe the oxidising action of potassium dichromate and write the ionic equations for its reaction with:

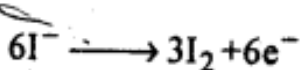
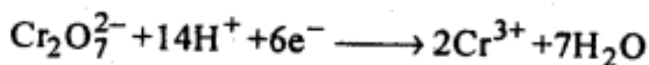
- (i) iodide
- (ii) iron (II) solution and
- (iii) H_2S

Sol: $\text{K}_2\text{Cr}_2\text{O}_7$ is a powerful oxidising agent. In dilute sulphuric acid medium the oxidation state of Cr changes from +6 to +3. The oxidising action can be represented as follows:



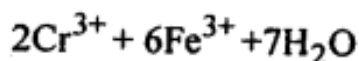
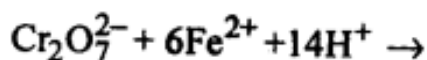
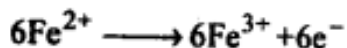
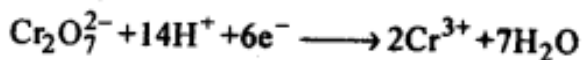
- (i) **Iodide:** Iodide ion (I^-) is oxidised to I_2 by the acidified solution of $\text{K}_2\text{Cr}_2\text{O}_7$.

Reaction:

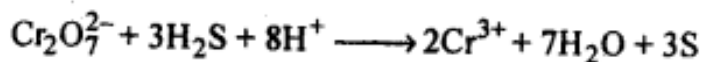


- (ii) **Iron (II) solution:** Ferrous salts (Fe^{2+}) are oxidised to ferric (Fe^{3+}) salts when they are treated with acidified $\text{K}_2\text{Cr}_2\text{O}_7$.

Reaction:



- (iii) **H_2S :** H_2S is oxidised to sulphur.



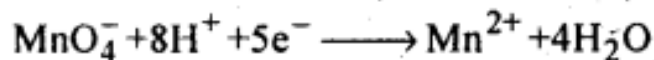
8.16. Describe the preparation of potassium permanganate. How does the acidified permanganate solution react with (i) iron (II) ions (ii) SO_2 and (iii) oxalic acid? Write the ionic, equations for the reactions.

Sol: Potassium permanganate (KMnO_4) is prepared by the fusion of a mixture of pyrolusite (MnO_2), potassium hydroxide and oxygen, first green coloured potassium manganate is formed. $2\text{MnO}_2 + 4\text{KOH} + \text{O}_2 \rightarrow 2\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O}$ The potassium manganate is extracted by water, which then undergoes disproportionation in neutral or acidic solution to give potassium permanganate.

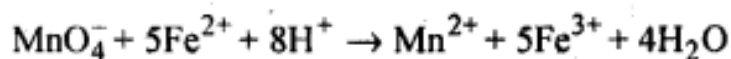
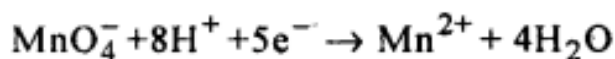
Electrolytically:



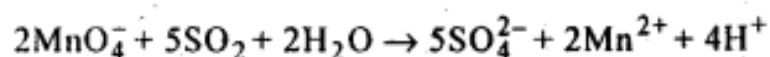
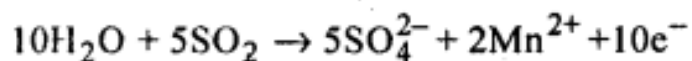
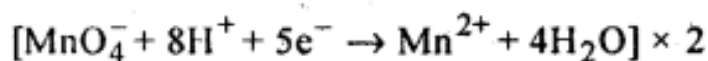
In acidic medium of dilute sulphuric acid, KMnO_4 acts as strong oxidising agent and it reacts as:



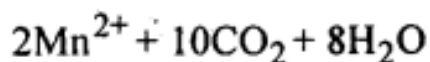
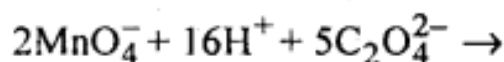
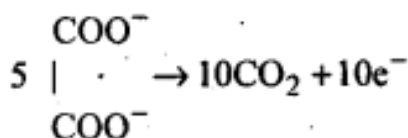
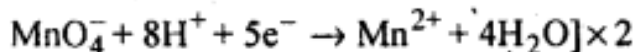
(i) **Iron (II) solution** : Ferrous (Fe^{2+}) ion solution to ferric (Fe^{3+}) ion solution



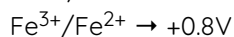
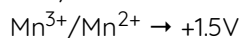
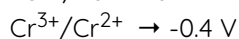
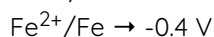
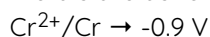
(ii) **Sulphur dioxide (SO_2)**



(iii) **Oxalic acid**



8.17. For M^{2+}/M and $\text{M}^{3+}/\text{M}^{2+}$ systems the E° values for some metals are as follows:



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

Sol:

(i) $\text{Cr}^{3+}/\text{Cr}^{2+}$ has negative reduction potential. Hence, Cr^{3+} cannot be reduced to Cr^{2+} . $\text{Mn}^{3+}/\text{Mn}^{2+}$ has a large positive reduction potential. Hence, Mn^{3+} can be easily reduced to Mn^{2+} .

$\text{Fe}^{3+}/\text{Fe}^{2+}$ has small positive reduction potential. Hence, Fe^{3+} is more stable than Mn^{3+} but less stable than Cr^{3+} .

(ii) From the E° values, the order of oxidation of the metal to the divalent cation is: $\text{Mn} > \text{Cr} > \text{Fe}$.

8.18. Predict which of the following will be coloured in aqueous solution? Ti^{3+} , V^{3+} , Cu^+ , Sc^{3+} , Mn^{2+} , Fe^{3+} and Co^{2+} . Give reasons for each.

Sol: Among the above mentioned ions, Ti^{3+} , V^{3+} , Mn^{2+} , Fe^{3+} and Co^{2+} are coloured. These ions are coloured due to presence of unpaired electrons, they can undergo d-d transitions

8.19. Compare the stability of +2 oxidation state for the elements of the first transition series.

Sol: In general, the stability of +2 oxidation state in first transition series decreases from left to right due to increase in the sum of first and second ionisation energies. However Mn^{2+} is more stable due to half filled d-orbitals ($3d^5$) and Zn^{2+} is more stable due to completely filled d-orbitals ($3d^{10}$).

8.20. Compare the chemistry of actinoids with that of the lanthanoids with special reference to

- (i) electronic configuration,
- (ii) atomic and ionic sizes and
- (iii) oxidation state
- (iv) chemical reactivity.

Sol:

(i) Electronic configuration: The general electronic configuration of lanthanoids is $[\text{Xe}]^{54} 4f^{1-14} 5d^{0-1} 6s^2$ and that of actinoids is $[\text{Rn}]^{86} 5f^{0-14} 6d^{0-1} 7s^2$, lanthanoids belong to 4 f series whereas actinoids belong to 5f-series.

(ii) Atomic and ionic sizes: Both lanthanoids and actinoids show decrease in size of their atoms or ions in + 3 oxidation state as we go from left to right. In lanthanoids, the decrease is called lanthanoid contraction whereas in actinoids, it is called actinoid contraction. The contraction is greater from element to element in actinoids due to poorer shielding by 5f electrons.

(iii) Oxidation state: Lanthanoids show limited oxidation states (+ 2, + 3, + 4) out of which + 3 is most common whereas actinoids show +3, +4, +5, +6, +7 oxidation states. This is because of large energy gap between 4f 5d and 6s orbitals. However, actinoids show a large number of oxidation states because of small energy gap between 5f 6d and 7s orbitals.

(iv) Chemical reactivity: The earlier members of the lanthanoids series are quite reactive similar to calcium but, with increase in atomic number, they behave more like aluminium. The metals combine with hydrogen when gently heated in the gas. Carbides, Ln_3C , Ln_2C_3 and LnC_2 are formed when the metals are heated with carbon. They liberate hydrogen from dilute acid and burn in halogens to form halides. They form oxides M_2O_3 and hydroxides $\text{M}(\text{OH})_3$.

Actinoids are highly reactive metals, especially when finely divided. The action of boiling water on them gives a mixture of oxide and hydride and combination with most non-metals take place at moderate temperatures. HCl attacks all metals but most are slightly affected by nitric acid owing to the formation of protective oxide layers, alkalis have no action. Actinoids are more reactive than lanthanoids due to bigger atomic size and lower ionisation energy.

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