CHEMISTRY STUDY MATERIALS FOR CLASS 12(NCERT BASED QUESTIONS WITH ANSWERS)GANESH KUMARDATE:-22/07/2020

The d & f - Block Elements

Question 16: Describe the preparation of potassium permanganate. How does the acidified Permanganate solution react with (i) iron (II) ions (ii) SO2 and (iii) oxalic acid? Write the ionic equations for the reactions.

Solution 16: Potassium permanganate can be prepared from pyrolusite (MnO₂). The ore is fused with KOH in the presence of either atmospheric oxygen or an oxidizing agent, such as KNO₃ or *KClO*₄, to give K₂MnO₄.

The green mass can be extracted with water and then oxidized either electrolytically or by passing chlorine/ozone into the solution. Electrolytic oxidation.

 $2K_2MnO_4 \longrightarrow 2K^+ + MnO_4^{2-}$ $H_2O \longrightarrow H^+ + OH^-$

At anode, manganate ions are oxidized to permanganate ions.

$$MnO_4^{2-} \longrightarrow MnO_4^{1-} + e^-$$

Green Purple

Oxidation by chlorine

2K2MnO4 + Cl2 → 2KMnO4 + 2KCl

 $2MnO_4^{2-} + Cl_2 \longrightarrow 2MnO_4^{1-} + 2Cl^{-1}$

Oxidation by ozone

(i)Acidified KMnO₄ solution oxidizes Fe (II) ions to Fe (III) ions i.e.,

*MnO*₄¹⁻ +8*H*+ +5e⁻ → *Mn*²⁺ +4*H*₂O

 $Fe^{2+} \longrightarrow Fe^{3+} + e^{-}] \times 5$ $MnO_4^{1-} + 5Fe^{20} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

(ii)Acidified potassium permanganate oxidizes SO₂ to sulphuric acid.

$$MnO_{4}^{1-} + 8H^{+} + 5e^{-} \longrightarrow Mn^{2+} + 4H_{2}O] \times 2$$

$$2H_{2}O + 2SO_{2} + O_{2} \longrightarrow 4H^{+} + 2SO_{4}^{2-} + 2e^{-}] \times 5$$

$$2MnO_{4}^{1-} + 2H_{2}O + 10SO_{2} + 5O_{2} \longrightarrow 2Mn^{2+} + 10SO_{4}^{2-} + 4H^{+}$$

(iii)Acidified potassium permanganate oxidizes oxalic acid to carbon dioxide.

$$MnO_{4^{1-}} * 8H^{+} + 5e^{-} \longrightarrow Mn^{2+} + 4H_{2}O] \times 2$$

$$C_{2}O_{4^{2-}} \longrightarrow 2CO_{2} + 2e^{-}] \times 5$$

$$2MnO_{4^{1-}} + 5C_{2}O_{4^{2-}} + 16H^{+} \longrightarrow 2Mn^{2+} + 10CO_{2} + 8H_{2}O$$

Question 17: For M²⁺ / Mand M³⁺ / M² systems, the E¹ values for some metals are as follows

$$Cr^{2+} / Cr = 0.9V$$
 $Cr^{3+} / Cr^{2+} = 0.4V$ $Mn^{2+}/Mn = 1.2V$ $Mn^{3+}/Mn^{2+} = 1.5V$ $Fe^{2+}/Fe = 0.4V$ $Fe^{3+}/Fe^{2+} = 0.8V$

Use this data to comment upon:

- (i) The stability of Fe³⁺ in acid solution as compared to that of Cr³⁺or Mn³⁺ and
- (ii) The ease with which iron can be oxidized as compared to a similar process for either chromium or manganese metal.
- Solution 17: (i) The E^{II} value for Fe³⁺ / Fe²⁺ is higher than that for Cr³⁺ / Cr²⁺ and lower than that for Mn³⁺ / Mn²⁺. So, the reduction of Fe³⁺ to Fe²⁺ is easier than the reduction of Mn³⁺ to Mn²⁺, but not as easy as the reduction of Cr³⁺ to Cr²⁺ Hence, Fe³⁺ is more stable than Mn³⁺, but less stable than Cr³⁺. These metal ions can be arranged in the increasing order of their stability as: Mn³⁺ < Fe³⁺ < Cr³⁺

(ii)The reduction potentials for the given pairs increase in the following order.

 $Mn^{2_{II}} / Mn \square Cr^{2_{II}} / Cr \square Fe^{2_{II}} / Fe$. So, the oxidation of *Fe* to $Fe^{2_{+}}$ is not as easy as the oxidation of Cr to Cr^{2_+} and the oxidation of Mn to Mn^{2_+}. Thus, these metals can be arranged in the increasing order of their ability to get oxidized as: Fe < Cr < Mn

Question 18: Predict which of the following will be coloured in aqueous solution?

 $Ti^{3_{\parallel}}, V^{3_{\parallel}}, Cu^{\parallel}, Sc^{3_{\parallel}}, Mn^{2_{\parallel}}, Fe^{3_{\parallel}}$ and $CO^{2_{\parallel}}$. Give reasons for each.

Solution 18: Only the ions that have electrons in *d*-orbital will be coloured. The ions in which *d*-orbital is empty will be colourless.

Element	Atomic Number	Ionic State	Electronic configuration in ionic State		
Ti	22	TI ³⁺	[Ar]3d ¹		
V	23	V3+	[Ar]3d ²		
Cu	29	Cu⁺	[Ar]3d ¹⁰		
Sc	21	Sc ³⁺	[Ar]		
Mn	25	Mn ²⁺	[Ar]3d⁵		
Fe	26	Fe ³⁺	[Ar]3d⁵		
Со	27	Co ²⁺	[Ar]3d ⁷		

From the above table, it can be easily observed that only Sc³⁺ has an empty *d*-orbital. All other

ions, except , Sc³⁺, will be coloured in aqueous solution because of d-d transitions.

Sc			+3				
Ti	+1	+2	+3	+4			
V	+1	+2	+3	+4	+5		
Cr	+1	+2	+3	+4	+5	+6	
Mn	+1	+2	+3	+4	+5	+6	+7
Fe	+1	+2	+3	+4	+5	+6	
Co	+1	+2	+3	+4	+5		
Ni	+1	+2	+3	+4			
Cu	+1	+2	+3				
Zn		+2					