CHEMISTRY STUDY MATERIALS FOR CLASS 12(NCERT BASED QUESTIONS WITH ANSWERS)GANESH KUMARDATE:- 18/08/2021

The d & f - Block Elements

Question 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.
- **Solution 11: (i)** Transition metals show paramagnetic behaviour. Paramagnetism arises due to the presence of unpaired electrons with each electron having a magnetic moment associated with its spin angular momentum and orbital angular momentum. However, in the first transition series, the orbital angular momentum is quenched. Therefore, the resulting Paramagnetism is only because of the unpaired electron.
 - (ii)Transition elements have high effective nuclear charge and a large number of valence electrons.
 Therefore, they form very strong metallic bonds. As a result, the enthalpy of atomization of transition metals is high.
 - (iii)Most of the complexes of transition metals are coloured. This is because of the absorption of radiation from visible light region to promote an electron from one of the *d*-orbitals to another. in the presence of ligands, the *d*-orbitals split up into two sets of orbitals having different energies. Therefore, the transition of electrons can take place from one set to another. The energy required for these transitions is quite small and falls in the visible region of radiation. The ions of transition metals absorb the radiation of a particular wavelength and the rest is reflected, imparting colour to the solution.
 - (iv) The catalytic activity of the transition elements can be explained by two basic facts.
 - (a)Owing to their ability to show variable oxidation states and form complexes, transition metals form unstable intermediate compounds. Thus, they provide a new path with lower activation energy, *E*a, for the reaction.
 - (b) Transition metals also provide a suitable surface for the reactions to occur.

Question 12: What are interstitial compounds? Why are such compounds well known for transition metals?

- **Solution 12:** Transition metals are large in size and contain lots of interstitial sites. Transition elements can trap atoms of other elements (that have small atomic size), such as H, C, N, in the interstitial sites of their crystal lattices. The resulting compounds are called interstitial compounds.
- Question 13: How is the variability in oxidation states of transition metals different from that of the non- transition metals? Illustrate with examples.
- **Solution 13:** In transition elements, the oxidation state can vary from +1 to the highest oxidation state by removing all its valence electrons. Also, in transition elements, the oxidation states differ by 1 (Fe^{2+} and Fe^{3+} Cu¹⁺ and Cu²⁺) in non-transition elements, the oxidation states differ by 2, for example, +2 and +4 or +3 and +5, etc.
- Question 14: Describe the preparation of potassium dichromate from iron chromite ore. What is the effect of increasing pH on a solution of potassium dichromate?

Solution 14: Potassium dichromate is prepared from chromite ore *FeCr₂O₄* lin the following steps.

Step (1): Preparation of sodium chromate

Step (2): Conversion of sodium chromate into sodium dichromate

$$2Na_2CrO_4 + conc.H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

Step(3): Conversion of sodium dichromate to potassium dichromate

Na2Cr2O7 + 2KCl → K2Cr2O7 + 2NaCl

Potassium chloride being less soluble than sodium chloride is obtained in the form of orange coloured crystals and can be removed by filtration. The dichromate ion CrO_4^{2-} exists in equilibrium with chromate CrO_4^{2-} ion at pH 4. However, by changing the pH, they can be interconverted.

CrO ₄ -2 <u>acid</u> alkali	2HCrO₄-1 ←a	cid Cr2O7 ⁻² Ikali
Chromate	Hydrogen	Dichromate
(Yellow)	Chromate	(Orange)

Question 15: Describe the oxidizing action of potassium dichromate and write the ionic equations for its reaction with: (i) iodide (ii) iron(II) solution and (iii) H2 S

Solution 15: *K*₂*Cr*₂*O*₇ acts as a very strong oxidizing agent in the acidic medium.

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

*(i)K*₂*Cr*₂*O*₇ takes up electrons to get reduced and acts as an oxidizing agent. The reaction with other iodide, iron (II) solution, and *H*₂*S* are given below. (i) *K*₂*Cr*₂*O*₇ oxidizes iodide to iodine.

 $Cr_{2}O_{7}^{2-} + 14H^{+} + 6e^{-} \longrightarrow 2Cr^{31} + 7H_{2}O$ $2I^{-} \longrightarrow I_{2} + 2e^{1}]x3$ $Cr_{2}O_{7}^{2-} + 6I^{-} + 14H^{+} \longrightarrow 2Cr^{3+} + 3I_{2} + 7H_{2}O$

(ii)K₂Cr₂O₇ oxidizes iron (II) solution to iron (III) Solution i.e., ferrous ions to ferric ions.

Cr ₂ O ₇ ²⁻ +14H ⁺ + 6e ⁻	→ 2Cr ³ +7H ₂ O
Fe ²⁺	<i>Fe</i> ³⁺ + <i>e</i> ⁻]x6
Cr ₂ O ₇ ²⁻ +14H ⁺ + 6Fe ²⁺	2Cr ³⁺ + 6Fe ³⁺ +7H₂O

(iii) K₂Cr₂O₇ Oxidizes H2S to sulphur

$$Cr_{2}O_{7}^{2-} + 14H^{+} + 6e^{-} \longrightarrow 2Cr^{31} + 7H_{2}O$$

$$H_{2}S \longrightarrow S + 2H^{+} + 2e^{-}] \times 3$$

$$Cr_{2}O_{7}^{2-} + 8H^{+} + 3H_{2}S \longrightarrow 2Cr^{3+} + 3S + 7H_{2}O$$

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.

$$2MnO_2 + 4KOH + O_2 \xrightarrow{Heat} 2K_2MnO_4 + 2H_2O$$
(Green)

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

 $2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$ $2MnO_4^{2-} + Cl_2 \longrightarrow 2MnO_4^{1-} + 2Cl^{-1}$

Oxidation by ozone

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

$$MnO_4^{1-} + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-] \times 5$$

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

(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.

$$MnO_{4^{1-}} + 8H^{+} + 5e^{-} \longrightarrow Mn^{2+} + 4H_2O] \times 2$$

$$C_2O_{4^{2-}} \longrightarrow 2CO_2 + 2e^{-}] \times 5$$

$$2MnO_{4^{1-}} + 5C_2O_{4^{2-}} + 16H^{+} \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

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} / Mn Cr^{2} / Cr Fe^{2} / Fe. So, the oxidation of Fe to Fe^{2+} is not as easy as the oxidation of Cr to Cr²⁺ and the oxidation of Mn to Mn²⁺. 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^{30} , V^{30} , Cu^{0} , Sc^{30} , Mn^{20} , Fe^{30} and CO^{20} . 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	V ³⁺	[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.

Question 19:	Compare the stabilit	y of +2 oxidation	state for the elements	s of the first transition ser	ies.
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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					
