

Ankit Gupta Classes



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UNIT—8

THE d- AND f-BLOCK ELEMENTS

Some Important Terms :

Compounds / Minerals / Reagents or mixtures etc of d- and f- block elements.

1. Argentite — Ag_2S
2. Argenti ferrous galena — $\text{PbS} + \text{Ag}_2\text{S}$
3. Azurite — $\text{Cu}(\text{OH})_2 \cdot 2\text{CuCO}_3$
4. Benedict Solution — Alkaline Solution cupric ions complexed with citrate ions.
5. Blue Vitriol — $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
(Blue Stone)
6. Bayer's Reagent — Cold alkaline KMnO_4 Solution
7. Blister Copper — 99% Pure Copper
8. Corrosive Sublimate — HgCl_2
9. Calomel — Hg_2Cl_2
10. Calamine — ZnCO_3
11. Coinage metal — Cu, Ag and Au
12. Copper Pyrite — CuFeS_2 or $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$
13. Copper glance — Cu_2S
14. Cinnabar — HgS
15. Chromyl Chloride — CrO_2Cl_2
16. Chrome Yellow — PbCrO_4
(Lemon Chrome)

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17. Calaverite — AuTe_2
18. Chromic acid mixture — $\text{K}_2\text{CrO}_7 + \text{Con. H}_2\text{SO}_4$
19. Delomite — $\text{CaCO}_3 \cdot \text{MgCO}_3$
20. Delta Metal — Cu (55%), Zn (41%), Fe (4%)
21. Fischer's Salt — $\text{K}_3 [\text{CO} (\text{NO}_2)_4]$
22. Fehling Solution — $\text{CuSO}_4 + \text{Sod. Pot. Tartarate} + \text{NaOH}$
23. Green Vitriol — $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$
(Hara Kasis)
24. Ferro Chrome — $\text{Fe} + 2 \text{Cr} + 4 \text{CO}$
25. Guigret's green — $\text{Cr}_2\text{O}_3 \cdot 2 \text{H}_2\text{O}$
26. Haematite — Fe_2O_3
(Red Haematite)
27. Horn Silver — AgCl
(Chloragynite)
28. Lucas reagent — $\text{Conc. HCl} + \text{anhydrous ZnCl}_2$
29. Lunar Caustic — AgNO_3
30. Lithopone — $\text{ZnS} + \text{BaSO}_4$
31. Lindar Catalyst — Palladised Charcoal deactivated with Sulphur compounds.
32. Malachite — $\text{Cu} (\text{OH})_2 \cdot 2 \text{CuCO}_3$
33. Monel Metal — Cu, Ni and Mn
34. Nessler's reagent — K_2HgI_4
35. Prussian blue — $\text{Fe}_4 [\text{Fe} (\text{CN})_6]_3$
36. Pyrites (Fool's Gold) — FeS_2
37. Quick Silver — Hg
38. Schweitzer reagent — Tetramine Copper (II) Sulphate

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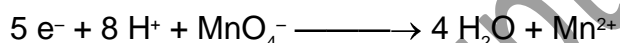
39. Sterling Silver — Solution of Cu in Hg
40. Scheelite — CaWO_4 (Calcium tungstate)
41. Tollen's reagent — $\text{AgNO}_3 + \text{NaOH}$
42. Tailing of mercury — Hg_2O
43. Vermilion — HgS
44. Willemite — Zn_2SiO_4
45. Zincite — ZnO
46. Zinc butter — $\text{ZnCl}_2 \cdot 3 \text{H}_2\text{O}$

1 MARK QUESTIONS

Q. 1. What is the equivalent wt. of KMnO_4 in :

(a) Acidic Medium (b) Neutral Medium (c) In alkaline Medium

Ans. (a) In Acidic Medium the reaction is :



$$\therefore \frac{M}{5} = \frac{158}{5} = 31.6 \text{ g}$$

(b) In Neutral Medium the reaction is :



$$\therefore \text{eq. wt.} = \frac{M}{3} = \frac{158}{3} = 52.67$$

(c) In Alkaline Medium the reaction is :

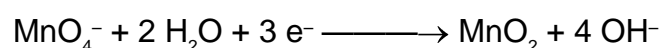
(i) Strongly Alkaline Medium



manganate ion

$$\therefore \frac{M}{1} = \frac{158}{1} = 158$$

(ii) In Weakly Alkaline Medium the reaction is :



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Same as in neutral medium

$$\therefore \frac{M}{3} = \frac{158}{3} = 52.67$$

Q. 2. $K_2Pt^{+4}Cl_6$ is well known compound and corresponding Ni^{+4} Salt it unknown ? Whereas Ni^{+2} is more stable than Pt^{+2} .

Ans. The stability of the compounds depend upon sum of ionization enthalpies :

$$IE_1 + IE_2 < IE_1 + IE_2$$

in Ni in Pt

$\therefore Ni^{2+}$ is stable than Pt^{+2} .

$$IE_1 + IE_2 + IE_3 + IE_4 < IE_1 + IE_2 + IE_3 + IE_4$$

in Pt^{4+}

in Ni^{4+}

$\therefore Pt^{4+}$ is stable, $\therefore K_2PtCl_6$ is well known compound.

Q. 3. Sc^{3+} is more stable than Sc^{2+} .

Ans. $Sc = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$

$$Sc^{3+} = 1s^2 2s^2 2p^6 3s^2 3p^6$$

Inert gas configuration \therefore more stable.

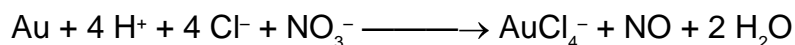
Q. 4. Why $KMnO_4$ is bright in colour ?

Ans. It is due to charge transfer. In MnO_4^- an electron is momentarily transferred from O to the metal, thus momentarily O^{2-} is changed to O^- and reducing the oxidation state of the metal from Mn (VII) to Mn (VI).

Q. 5. Why gold, Pt are dissolved in aqua Regia ?

Ans. $Au + 4 Cl^- \longrightarrow AuCl_4^- + 3 e^-$ (oxidation)

$3 e^- + 4 H^+ + NO_3^- \longrightarrow NO + 2 H_2O$ (reduction)



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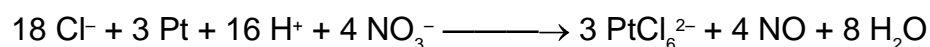
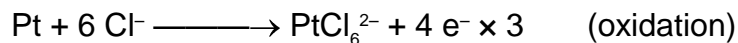
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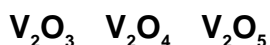
Q. 6. (a) CrO is basic but Cr₂O₃ is amphoteric ?



O. N. + 2 + 3

Ans. (a) Higher the oxidation state higher the acidity. In lower oxidation state some of valence e⁻ of the metal atom are not involved in bonding, ∴ can donate e⁻ and behave as base. In higher oxidation state e⁻ are involved in bonding and are not available, rather it can accept e⁻ and behave as an acid.

(b) Why the following is the order :



O. N. + 3 + 4 + 5



Basicity.

Ans. ∴ Basicity $\propto \frac{1}{\text{Oxidation No.}}$

refer (a) for reason.

Q. 7. (a) How is Lanthanoids magnetic moment is calculated ?

Ans. $b = \sqrt{4S(S+1) + L(L+1)}$ B. M.

Where S = Spin quantum no.

L = Orbital quantum no.

(b) In the titration of Fe²⁺ ions with KMnO₄ in acidic medium, why dil. H₂SO₄ is used and not dil. HCl.

Ans. KMnO₄ produce Cl₂ KMnO₄ in presence of dil. HCl acts as oxidising agent, Oxygen produced is used up partly for oxidation of HCl :

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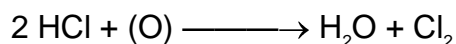
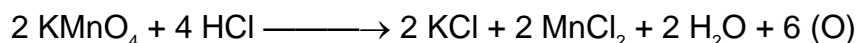
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Q. 8. (a) The E° value for $\text{Ce}^{4+}/\text{Ce}^{3+}$ is 1.74 Volt.

(b) $\text{K}_2\text{Cr}_2\text{O}_7$ is used as Primary Standard in volumetric analysis.

Ans. (a) Ce^{4+} is strong oxidant, being Lanthanoid it reverts to Ce^{3+} as + 3 is most stable.

(b) $\text{K}_2\text{Cr}_2\text{O}_7$ is not much soluble in cold water. However, it is obtained in pure state and is not Hygroscopic in nature.

Q. 9. (a) Although Cu^+ has configuration $3 \text{d}^{10} 4 \text{s}^0$ (stable) and Cu^{2+} has configuration 3d^9 (unstable configuration) still Cu^{2+} compounds are more stable than Cu^+ .

(b) Titanium (IV) is more stable than Ti (III) or Ti (II).

Ans. (a) It is due to much more $(-)\Delta \text{Hydration } H^-$ of $\text{Cu}^{2+}(\text{aq})$ than Cu^+ , which is more than compensates for the II ionization enthalpy of Cu.

(b) ${}_{22}\text{Ti} = 3 \text{d}^2 4 \text{s}^2$

$\text{Ti}^{\text{III}} = 3 \text{d}^1$

$\text{Ti}^{\text{II}} = 3 \text{d}^2$

$\text{Ti}^{\text{IV}} = 3 \text{d}^0$

most stable configuration.

$\therefore \text{Ti}^{\text{IV}}$ is more stable than Ti^{III} and Ti^{II} .

Q. 10. The actinoids exhibit more number of oxidation states and give their common oxidation states.

Ans. As the distance between the nucleus and 5 f orbitals (actinoides) is more than the distance between the nucleus and 4 f (lanthanoids) hence the hold of the nucleus on valence electrons decrease in actinoids. For this reason the actinoids exhibit more number of oxidation states in general.

Common O. N. exhibited are + 3 (similar to Lanthanoids) besides + 3 state, also show + 4, maximum oxidation state in middle of series i. e. Pu and Np. have oxidation state upto + 7.

Q. 11. (a) Give reason CrO_3 is an acid anhydride.

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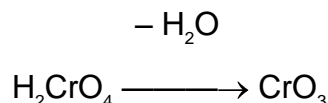


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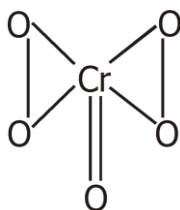
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(b) Give the structure of CrO_5 .

Ans. (a) $\text{CrO}_3 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{CrO}_4$ i. e. CrO_3 is formed by loss of one H_2O molecule from chromic acid :



(b)

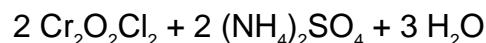


Q. 12. A wellknown orange crystalline compound (A) when burnt impart violet colour to flame. (A) on treating (B) and conc. H_2SO_4 gives red gas (C) which gives red yellow solution (D) with alkaline water. (D) on treating with acetic acid and lead acetate gives yellow p. pt. (E). (B) sublimes on heating. Also on heating (B) with NaOH gas (F) is formed which gives white fumes with HCl . What are (A) to (F) ?

Ans. (i) $\text{K}_2\text{Cr}_2\text{O}_7 + 4 \text{NH}_4\text{Cl} + 3 \text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 +$

(A)

(B) Sublime



Chromyl Chloride red gas (C)

(ii) $\text{CrO}_2\text{Cl}_2 + 4 \text{NaOH} \longrightarrow \text{Na}_2\text{CrO}_4 + 2 \text{NaCl} + 2 \text{H}_2\text{O}$

(D) Yellow Soln.

(iii) $\text{Na}_2\text{CrO}_4 + (\text{CH}_3\text{COO})_2\text{Pb} \longrightarrow \text{PbCrO}_4 + 2 \text{CH}_3\text{COONa}$

Yellow p. pt. (E)

Q. 13. Why is Cr^{2+} reducing and Mn^{3+} oxidising when both have d^4 configuration ?

Ans. Cr^{2+} is reducing as its configuration changes from d^4 to d^3 , the d^3 has half-filled t_{2g} level. On the other hand, the change from Mn^{2+} to Mn^{3+} results in the half filled (d^5) configuration which has extra stability.

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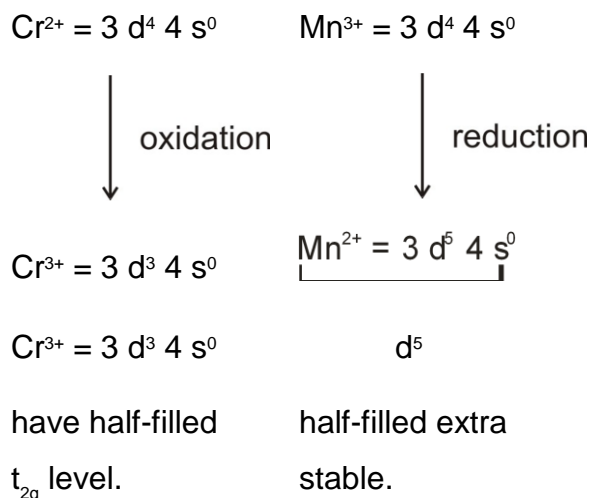
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Q. 14. (a) In MnO_4^- ion all the bonds formed between Mn and Oxygen are covalent. Give reason.

(b) Beside + 3 oxidation state Terbium Tb also shows + 4 oxidation state. (Atomic no. = 65)

Ans. (a) In MnO_4^- , O. N. is + 7, but it is not possible to lose 7 electrons because very high energy is required to remove 7 electrons. Therefore it forms covalent bonds.

(b) Tb = 65 E. C. is $4f^9 6s^2$
 $\text{Tb}^{4+} = 4f^7 6s^0$
 half-filled f-orbital ∴ stable.
 after losing 4 e⁻ it attains half-filled orbital.

Q. 15. (a) Highest manganese flouride is MnF_4 whereas the highest oxide is Mn_2O_7 .

(b) Copper can not librate H_2 from dil acids :

Note : Although only oxidising acids (HNO_3 and hot conc. H_2SO_4) react with Cu light.

Ans. (a) The ability of oxygen to form multiple bonds to metals, explain its superiority to show higher oxidation state with metal.

(b) Positive E° value (+ 0.34 Volt) accounts for its inability to liberate H_2 from acids. The high energy to transform Cu (s) to Cu^{2+} (aq) is not balanced by its Hydration enthalpy.

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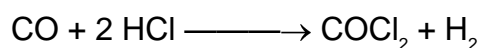
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Note : For (b) Consult Fig. 8.4 in NCERT

Q. 16. A metal which is strongly attracted by a magnet is attacked slowly by the HCl liberating a gas and producing a blue solution. The addition of water to this solution causes it to turn pink, the metal is

Ans. The metal is CO



blue solution

COCl_2 in solution is $[\text{CO}(\text{H}_2\text{O})_6]^{2+}$

blue

pink

□□□

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