Exercise-1

Marked Questions may have for Revision Questions.

OBJECTIVE QUESTIONS

- Section (A) : Electronic configuration, atomic and ionic size, density, melting and boiling points
- A-1. Sol. General electronic configuration of transition elements is [Noble gas] $(n 1) d^{1-10} ns^{1-2}$.
- A-2. Sol. In these groups the d-orbitals are progressively filled in each of the four long periods (4 to 7).
- A-3. Sol. (1) Configuration of d-block element is (inert gas) ns²(n 1)d¹⁻¹⁰.
 (2) These element have properties b/w s and p-block.
 - (3) d-block element starts with $Sc_{21} [Ar]_{18} 4s^2 3d^1$.
- **A-4.** Sol. ${}_{46}Pd = [Kr]^{36}4d^{10}5s^0$; ${}_{47}Ag = [Kr]^{36}4d^{10}5s^1$; ${}_{48}Cd = [Kr]^{36}4d^{10}5s^2$.
- **A-5.** Sol. All transition element have partially filled (n 1) d orbital.
- **A-6.** Sol. Strong metallic bonds between the atoms of transition elements attribute to their high melting and boiling points. Zinc has all electrons paired ([Ar] 3d¹⁰ 4s²) and thus do not participate in metallic bonding. So accordingly its melting point is least.
- **A-7.** Sol. ${}_{22}\text{Ti} = 3d^2 4s^2$, $\text{Ti}^{2+} = 3d^2$; ${}_{23}\text{V} = 3d^3 4s^2$, $\text{V}^{3+} = 3d^2$. ${}_{24}\text{Cr} = 3d^5 4s^1$, $\text{Cr}^{4+} = 3d^2$; ${}_{25}\text{Mn} = 3d^5 4s^2$, $\text{Mn}^{5+} = 3d^2$.

Section (B) : Ionization enthalpy, oxidation state, Electrode potential and chemical reactivity

B-1. Sol. (1) There is irregular trend in the first ionisation enthalpy of the 3d metals.

	Se	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
In kJ/mol :	631	656	650	653	717	762	758	736	745	906

- B-2. Sol. Os shows + 8 oxidation state in its compound with oxygen i.e., in OsO₄.
- **B-3.** Sol. (3) it show maximum oxidation state equal to + 7 because the energy of (n 1) d and ns orbitals are nearly same and thus seven electrons can participate in bonding.
- B-4. Sol. The lesser number of oxidation states in the begining of series can be due to the presence of smaller number of electrons to lose or share (Sc, Ti). On the other hand, at the extreme right hand side end (Cu, Zn), lesser number of oxidation state is due to large number of d electrons so that only a fewer orbitals are available in which the electron can share with other for higher valence.
- **B-5.** Sol. As stability of compounds in aqueous solution depends on the electrode potential which in turns depends on all these enthalpies.
- B-6. Sol. (1) Cr²⁺ is reducing as it involves change from d⁴ to d³, the latter is more stable configuration (t³_{2g}) Mn(III) to Mn(II) is from 3d⁴ to 3d⁵ again 3d⁵ is an extra stable configuration.
 (2) Due to higher CFSE of d⁶ configuration in presence of ligands which more than compensates the 3rd IE.

(3) The hydration or lattice energy more than compensates the ionisation enthalpy involved in removing electron from d^1 .

d & f-block Elements

B-7. Sol. The order of shielding effect of various orbital electrons is s > p > d > f. Due to the poor shielding effect of 4f- electrons in 5d-series elements, there is enhanced increase in effective nuclear charge. As a result of this the valence electrons are tightly bound with the nucleus and thus their removal require higher energy.

Section (C) : Magnetic properties, formation of coloured ions.

- **C-1.** Sol. ${}_{30}$ Zn [Ar]¹⁸ 3d¹⁰, so n = 0, Fe²⁺ [Ar]¹⁸ 3d⁶, so n = 4; Ni²⁺ [Ar]¹⁸ 3d⁸, so n = 2; Cu²⁺ [Ar]¹⁸ 3d⁹, so n = 1.
- **C-2.** Sol. n; Cr^{2+} [Ar]¹⁸ 3d⁴; so n = 4; Mn^{2+} [Ar]¹⁸ 3d⁵ so n = 5; Fe^{2+} [Ar]¹⁸ 3d⁶ so n = = 4 n = Number of unpaired electron(s).
- **C-3. Sol.** Ni²⁺, Fe²⁺ and Cu²⁺ has 2, 4 and 1 unpaired electrons respectively. So in presence of ligands dd transition takes place and these hydrated ions produce colour in aqueous solutions. Cu⁺ is diamagnetic with 3d¹⁰ configuration; so no d-d transition is possible and thus colourless.
- **C-4.** Sol. $\sqrt{15} = \sqrt{n(n+2)}$; n = 3, and three unpaired electrons are found when Mn is in Mn⁴⁺ i.e., 3d³ 4s⁰ configuration as its metal electron configuration is [Ar]¹⁸ 3d⁵ 4s².
- C-5. Sol. The colour of the compounds of transition metals may be attributed to the presence of incomplete (n 1) d-sub-shell. Under the influence of approaching ions towards the central metal ion, the d-orbitals of the central metal split into different energy levels. This phenomenon is called crystal field splitting. In the case of the transition metal ions, the electron can be easily promoted from one energy level to another in the same d-sub-shell. These are called d-d transitions. The amount of energy required to excite some of the electrons to higher energy states within the same d-sub-shell corresponds to energy of certain colours of visible light. Therefore, when white light falls on a transition metal compound, some of its energy corresponding to a certain colour, is absorbed and the electron gets raised from lower energy set of orbitals.

Section (D) : Catalytic properties, formation of interstitial compounds, alloy formation.

D-1. Sol. The catalytic property of transition metals is due to their tendency to form reaction intermediates with suitable reactants. These intermediates give reaction paths of lower activation energy and, therefore, increase the rate of the reaction.

These reaction intermediates readily decompose yielding the products and regenerating the original substance. The transition metals form these reaction intermediates due to the presence of vacant orbitals or their tendency to form variable oxidation states.

- **D-2.** Sol. Transition metals like Fe, Co, Ni, Cu etc. form interstitial compounds with elements such as hydrogen, boron, carbon and nitrogen. The small atoms of these non-metallic elements (H, B, C, N, etc.) get trapped in vacant spaces of the lattices of the transition metal atoms.
- D-3. Ans. (1) This activity is ascribed to their ability to adopt multiple oxidation state and to form complexes.
 (2) Because of having larger number of unpaired electrons in their atoms, they have stronger inter atomic interaction and hence stronger bonding between the atoms.

(3) Transition metals like Fe, Co, Ni, Cu etc. form interstitial compounds with elements such as hydrogen, boron, carbon and nitrogen. The small atoms of these non-metallic elements (H, B, C, N, etc.) get trapped in vacant spaces of the lattices of the transition metal atoms.

Section (E) : Important d-block metal compounds

E-1. Sol. $2CrO_{4^{2-}}$ (yellow) + $2H^+ \longrightarrow Cr_2O_{7^{2-}}$ (organge) + H_2O .

- **E-2.** Sol. $6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$.
- **E-3.** Sol. 4FeO. Cr_2O_3 (chromite ore) + $8Na_2CO_3 + 7O_2 \xrightarrow{Roasting in air} 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$ $2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$

 $Na_2Cr_2O_7 + 2KCI \longrightarrow K_2Cr_2O_7 + 2 NaCI$

E-4. Sol. $2MnO_{4^{-}} + 3Mn^{2+} + 2H_2O \rightarrow 5MnO_2 + 4H^+$

E-5. Sol. Mn_2O_7 is an acid anhydride of $HMnO_4$ and thus MnO_4^- is oxo-salt of Mn_2O_7 . $Mn_2O_7 + H_2O \longrightarrow 2HMnO_4$; $2HMnO_4 + KOH \longrightarrow 2KMnO_4 + H_2O$.

E-6. Sol. $2KMnO_4 \xrightarrow{513 \text{ K}} K_2MnO_4 + MnO_2 + O_2$

E-7. Sol. $K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$ [SO₂ + [O] + H₂O \longrightarrow H₂SO₄ × 3.

> $K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3$ (Green coloured) + 3H₂O Acidified $K_2Cr_2O_7$ is oxidising agent and undergoes reduction to form green coloured solution of Cr₂ (SO₄)₃.

- **E-8.** Sol. (1) It is simply a double salt called hydrated ferrous ammonium sulphate.
 - (2) MgSO₄. 7H₂O is Epsom salt.
 - (3) FeSO₄. $(NH_4)_2$ SO₄. $6H_2O$ is Mohr's salt.
 - (4) FeSO₄. 7H₂O is Green vitriol.

Section (F) : Lanthanoids and actinoids

- **F-1.** Sol. Electronic configuration of f-block element $(n 2) f^{1-14}$, $(n 1)d^{10}$, ns² f-block starts with 6th period (n = 6).
- F-2. Sol. Pm is a artificial or synthesis element.
- **F-3.** Sol. Lanthanum = d-block element. Cerium = lanthanoide element & samarium, plutonium = actinoide element.
- **F-4.** Sol. Across lanthanoide series basicity of lanthanoide hydroxide decreases.
- F-5. Sol. Actinides element shows variable valency.
- **F-6.** Sol. Electronic configuration lanthanoid 4f¹⁻¹⁴ 5d¹ 6s² and electronic configuration of actinoide 5f¹⁻¹⁴ 6d¹, 7s².
- F-7. Sol. In ion exchange method, lanthanoids are separated on the basis of their size.

Exercise-2

Marked Questions may have for Revision Questions.

PART - I : OBJECTIVE QUESTIONS

- **1. Sol.** ${}_{24}Cr^{6+} [Ar]^{18} 3d^0$; ${}_{22}Ti^{4+} {Ar]^{18} 3d^0}$; ${}_{25}Mn^{7+} [Ar]^{18}3d^0$
- 2. Sol. After mid way i.e. after Cr as the electrons enters the last but one shell, the added d-electron shields the outer most electrons. Hence with the increase in the d-electrons screening effect increases. This counter balances the increased nuclear charge. As a result, the atomic radii remain practically same after chromium.
- **3. Sol.** All statements are true.
- **5. Sol.** (1) Have higher enthalpy of atomization because of the involvement of greater number of valence electrons in the bonding. So their melting points are higher.

(2) They show catalytic activity due to their variable oxidation states.

(3) Energy of ns and (n - 1) d orbitals are nearly same and thus electrons of ns and (n-1)d orbitals can take part in bonding.

(4) Only heavier p-block elements show inert pair effect, not d-block elements.

6. Sol. ${}_{24}Cr = [Ar]^{18} 3d^54s^1; {}_{25}Mn = [Ar]^{18} 3d^54s^2$ ${}^{25}Cu = [Ar]^{18} 3d^{10} 4s^1; {}_{30}Zn = [Ar]^{18} 3d^{10} 4s^2.$

SECTION-B

- 7. Sol. ${}_{28}Ni(I) = 3d^84s^1$; ${}_{30}Zn(I) = 3d^{10}4s^1$; ${}_{29}Cu(I) = 3d^{10}$ 1752 1734 1950 kJ mol⁻¹
- 8. Sol. $Cr^{3+} + e^{-} \longrightarrow Cr^{2+}$, $E^{\circ} = -0.41$ volts and $Mn^{3+} + e^{-} \longrightarrow Mn^{2+}$, $E^{\circ} = +1.51$ volts This shows that Cr^{2+} is unstable and has a tendency to acquire more stable Cr^{3+} state by acting as a reducing agent. On the other hand Mn^{3+} is unstable and is reduced to more stable Mn^{2+} state.
- **9. Sol.** $VOSO_4 = VO^{2+} + SO_{4^{2-}}$; ax(-2) = +2 = +4.
- **10. Sol.** It is because the unpairing of electrons in d-orbitals require a very high ionisation energy which is not available under bond forming condition. Therefore, transition metal form covalent compounds by simple sharing of electrons with more electronegative O and F.

11.

Sol. $\Delta_a H^{\circ}$ (M) = 339 kJ mol⁻¹ $\Delta_{hyd} H^{\circ} (M^{2+}) = -221 \text{ kJ mol}^{-1}$ E/V = +0.34

12.

Sol.
$$_{25}Mn^{2+} - 3d^5$$
 configuration, n = 5, so $\mu = \sqrt{5(5+2)} = 5.93$
 $_{26}Fe^{3+} - 3d^5$ configuration, n = 5, so $\mu = \sqrt{5(5+2)} = 5.93$

13.

Sol. (1) MnSO₄.4H₂O ; valence shell electron configuration of Mn²⁺ is [Ar]¹⁸ 3d⁵ ; so n = 5
(2) CuSO₄.5H₂O ; valence shell electron configuration of Cu²⁺ is [Ar]¹⁸ 3d⁹ ; so n = 1
(3) FeSO₄.6H₂O ; valence shell electron configuration of Fe²⁺ is [Ar]¹⁸ 3d⁶ ; so n = 4
(4) NiSO₄.6H₂O ; valence shell electron configuration of Ni²⁺ is [Ar]¹⁸ 3d⁸ ; so n = 2
Paramagnetism increases with increasing number of unpaired electrons. Thus Cu²⁺ has lowest degree of paramagnetism.

14.

Sol. (1) In Cr₂O₇²⁻, the valence shell electron configuration of Cr(VI) is 3d⁰. Thus Cr(VI) is diamagnetic but coloured due to the charge transfer spectrum.

(2) In $(NH_4)_2$ [TiCl₆], the valence shell electron configuration of Ti(IV) is 3d⁰. Thus Ti(IV) is diamagnetic and colourless.

(3) In VOSO₄, the valence shell electron configuration of V(IV) is $3d^{1}$. Thus V(IV) is paramagnetic and blue coloured due to d-d transition.

(4) In $K_3[Cu(CN)_4]$, the valence shell electron configuration of Cu(I) is $3d^{10}$. Thus Cu(I) is diamagnetic and colourless.

15.

- **Sol.** (1) $Cu^{+}[Ar]^{18} 3d^{10}$, so n = 0; $Zn^{2+} [Ar]^{18} 3d^{10}$, so n = 0; $Sc^{3+} [Ar]^{18} 3d^{0}$, so n = 0
 - (2) $Mn^{2+} [Ar]^{18} 3d^5$, so n = 5; $Fe^{3+} [Ar]^{18} 3d^5$, so n = 5; $Ni^{2+} [Ar]^{18} 3d^8$, so n = 2
 - (3) $Cr^{2+}[Ar]^{18} 3d^4$, so n = 4; $Mn^{3+} [Ar]^{18} 3d^4$, so n = 4; $Sc^{3+}[Ar]^{18} 3d^0$, so n = 0
 - (4) $Cu^{2+} [Ar]^{18} 3d^9$, so n = 1; Ni²⁺ [Ar]¹⁸ 3d⁸, so n = 2; Ti⁴⁺ [Ar]¹⁸ 3d⁰, so n = 0

16.

Sol. Valence shell electron configuration of ₃₀Zn²⁺ is 3d¹⁰ 4s⁰. As there is no unpaired electrons for d–d transition, the solution of ions will be colourless.

Valence shell electron configuration of ${}_{28}Ni^{2+}$ is $3d^8 4s^0$. As there are 2 unpaired electrons, there is d–d transition of electron, so the solution of ions will be coloured.

Valence shell electron configuration of ${}_{24}Cr^{3+}$ is $3d^3 4s^0$. As there are 3 unpaired electrons, there is d–d transition of electron, so the solution of ions will be coloured.

17.

- **Sol.** Paramagnetic substance has unpaired electrons. More the number of unpaired electrons, more will be paramagnetic character.
 - (1) $Fe^{2+} 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^0, 3d^6$
 - 3d⁶ means :. 4 unpaired electrons (2) Fe³⁺ 1s², 2s², 2p⁶, 3s², 3p⁶, 4s⁰, 3d⁵ 3d⁵ means 5 unpaired electrons *.*.. Cr³⁺ 1s², 2s², 2p⁶, 3s², 3p⁶, 4s⁰, 3d³ (3) 1 3d³ means 3 unpaired electrons *.*.. Mn³⁺ 1s², 2s², 2p⁶, 3s², 3p⁶, 4s⁰, 3d⁴, (4) 3d⁴ means 4 unpaired electrons *:*.. Fe³⁺ has highest number of unpaired electrons *:*..
 - : It is most paramagnetic.

18.

- **Sol.** (1) Valence shell electron configuration of $_{26}$ Fe is $3d^6 4s^2$.
 - (2) Valence shell electron configuration of ${}_{26}Fe^{2+}$ is $3d^6 4s^0$.

d & f-block Elements

(3) Valence shell electron configuration of ${}_{26}Fe^{3+}$ is $3d^5 4s^0$. or therefore, Fe³⁺ contains maximum number of unpaired electrons equal to 5.

19. Sol. Elingham diagram shows a number of oxide plots with slopes defined by $\Delta G / T = -\Delta \Sigma$. When the temperature is raised a point will be reached where the graph crossed the $\Delta G = 0$ line. Below this temperature the free energy of formation of oxide is negative, so the oxide is stable. Above this temperature the free energy of formation of the oxide is positive, and the oxide becomes unstable and should decompose into metal and oxygen. This explains why Ag₂O, for instance, decomposes

spontaneously into its elements when heated.

$$Ag_2O \rightarrow 2Ag + \frac{1}{2}O_2$$

1

SECTION-D

20. Sol. (1) Associated with d-d transition of electron.

(2) The transition metals form the reaction intermediates due to the presence of vacant orbitals or their tendency to form variable oxidation states.

(3) Associated with the number of unpaired electrons participating in metallic bonding.

(4) As
$$\mu = \sqrt{n(n+2)}$$
, so it is associated with number of unpaired electron.

- **21. Sol.** German silver is an alloy of copper, zinc and nickel, It is also known as nickel silver. It does not contain silver.
- 22. Sol. Brass contains only Cu and Zn.
- 23.
- Sol. Stainless steel is an alloy of iron with 8% Cr and 5% Mn.

SECTION-E

(2)

- **24.** Sol. $2MnO_4^- + 5 + 6H^+ \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$.
 - \therefore ⁵ mole of MnO₄⁻ for one mole SO₃²⁻.
- **25.** Sol. $2KMnO_4 + KBr + H_2O \longrightarrow KBrO_3 + 2KOH + 2MnO_2$.

26. Sol. (1)
$$3MnO_{4^{2-}} + 4H^{+} \longrightarrow 2MnO_{4^{-}} + MnO_{2} + 2H_{2}O$$
.

$$O = Cr = O C Cr = O C$$

(3) $2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$

- (4) $2MnO_4^- + H_2O + I^- \longrightarrow 2MnO_2 + 2OH^- + IO_3^-$
- 27. Sol. Option (2) is incorrect as alkaline oxidative fusion of MnO₂ gives K₂MnO₄.
- **28.** Sol. $K_2Cr_2O_7$ acts as oxidising agent and Cl_2 is evolved. $K_2Cr_2O_7 + 14HCI \rightarrow 2KCI + 2CrCl_3 + 3Cl_2 + 7H_2O.$
- **29.** Sol. Iodometric estimation. O.A. + I^- +H⁺ \rightarrow I₂ ; I₂+R.A. \rightarrow I⁻

 $Cr_2O_7^{2-} + H^+ + I^- \longrightarrow 2Cr^{3+} + I_2$; $I_2 + S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + I^-$

30.

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Sol. 4Cl^- + Cr_2O_7^{2-} + 6H^+ (conc.) \longrightarrow 2CrO_2Cl_2 (deep red vapours) + 3H_2O
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31. Sol. Cr_2O_7^{-2} + 2OH^- \rightarrow 2CrO_4^{-2} + H_2O_{yallow}
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32. Sol. Cr_2O_7^{2-} + 2H^+ + 4H_2O_2 \longrightarrow 2CrO_5 + 5H_2O
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SECTION-F

- **33. Sol.** Np and Pu shows maximum oxidation number + 7.
- **34.** Sol. ₂₁La(OH)₃ is more basic than Lu(OH)₃.
- **35. Sol.** Lanthanide contraction is due to increase in effective nuclear charge.
- 36. Sol. Curium, Californium, uranium are actionide elements
- **37.** Sol. S_1 : Lanthanide contraction.

 S_3 : Across a period from left to right ionisation energies gradually increase with increase in atomic number. This is because the nuclear charge increases and the atomic size decreases with increase in atomic number along the period. Consequently making the removal of outer electron difficult.

 S_4 : La³⁺ (f⁰) and Lu³⁺ (f¹⁴) have no unpaired electron. The colour of the ions in f-block elements may be attributed to the presence of unpaired f-electrons.

PART - II : ASSERTION / REASONING

1. Ans. (1)

Sol. The atomic radii of the second (4d series) and third, (5d series) transition series are almost the same. This phenomenon is associated with the intervention of the 4f orbitals which must be filled before the 5d series of elements begin. The filling of 4f before 5d orbital results in a regular decrease in atomic radii called

Lanthanoid contraction which essentially compensates for the expected increase in atomic size with increasing atomic number. The net result of the lanthanoid contraction is that the second and the third d series exhibit similar radii (e.g., Zr 160 pm, Hf 159 pm).

- **2. Ans.** (1)
- **Sol.** Greater the number of valence electrons, stronger is the resultant bonding and higher the enthalpy of atomisation.
- **3. Ans.** (3)
- Sol. Assertion : Electron configuration of Cr(g) is [Ar]¹⁸ 3d⁵ 4s¹ and, therefore, it has six unpaired electrons.
 Reason : Fully filled orbital is more stable than half filled orbital on account of more number of exchange of electrons resulting into the greater release of exchange energy.
- 4. Ans. (1)
- Sol. ${}_{23}V^{2+}$ (aq) [Ar]¹⁸ 3d³ \rightarrow Violet colour. ${}_{24}Cr^{3+}$ (aq) – [Ar]¹⁸ 3d³ – \rightarrow Violet colour. cSaxuh jaxA
- 5. Ans. (1)

- Sol. In 3d series element the SRP values of aqueous Mn³⁺ and CO³⁺ are very low. So these ions are strongest oxidising agents. Statment second is right explanation for statement first, according to their E⁰ (Mn³⁺/Mn²⁺) and E⁰ (Co³⁺/Co²⁺) values.
 6. Ans. (1)
 Sol. Assertion is incorrect statements but Reason is correct statements. 2Cu⁺ → Cu²⁺ + Cu⁺ so copper (I) compound are unsatable in aqueous solution and undergo disproportional.
- **7. Ans.** (1)
- **Sol.** It is an acid anhydride of H_2CrO_4 . CrO₃ + 2NaOH \rightarrow Na₂CrO₄ + H₂O.

Exercise-3

- 8. Ans. (1)
- **Sol.** Assertion : Correct statement and Reason is correct explanation of Assertion.

Green $\rightarrow \frac{MnO_4^{2-}}{MnO_4^{2-}}$ - [Ar]¹⁸ 3d¹ 4S^o; there is one unpaired electron, so paramagnetic.

Purple $\rightarrow \frac{MnO_4^{2-}}{18}$ - [Ar]¹⁸ 3d^o 4s^o; here all electrons are paired, so diamagnetic.

PART - I : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

OFFLINE JEE-MAIN

Sol.

1.

2.



Sol. (1) Valence shell electron configuration of Mn^{2+} is $3d^5$, therefore, has the maximum number of

unpaired electrons equal to 5 and, therefore, has maximum magnetic moment. (2) Valence shell electron configuration of Fe²⁺ is 3d⁶, therefore, has the maximum number of unpaired

electrons equal to 4. (3) Valence shell electron configuration of Ti²⁺ is 3d², therefore, has the maximum number of unpaired electrons equal to 2.

(4) Valence shell electron configuration of Cr^{2+} is $3d^4$, therefore, has the maximum number of unpaired electrons equal to 4.

3. Sol. Cerium Ce₅₈[Xe]4f¹5d¹6s²

Its most stable oxidation state is +3 but +4 is also existing.

- 4. Sol. $2CrO_{4^{2-}} + 2H^+ \longrightarrow Cr_2O_{7^{2-}} + H_2O$.
- 5. Sol. $AgNO_3 \longrightarrow Ag + NO_2 + 1/2O_2$.

- **6. Sol.** Cr⁺ has stable half filled electronic configuration, [Ar]¹⁸ 3d⁵ 4s⁰. the removal of one more electron from this stable half filled configuration will require higher energy.
- 7. Sol. Cu, Ag, Au group of elements are called coinage metals as these are used in minting coins.
- 8. Sol. Fe_{26} -[Ar]3d⁶4s² $Fe^{2+}(24 \text{ electrons}) - [Ar] 3d^{6}4s^{0}$
- 9. Sol. It is a reason for given fact.

 $NH_3 + H^+ \longrightarrow NH_4^+$; NH_4^+ does not act as ligand because it does not have a lone pair of electron to donate to Cu^{2+} ions to form $[Cu(NH_3)_4]^{2+}$.

- **10.** Sol. Due to lanthanide contraction there occurs net decrease in size. Only one 0.85Å is smaller one. So radius of Lu_{71}^{3+} will be closest to 0.85Å.
- **11. Sol.** (3) Cerium can also show the oxidation state of +4 in solution as it leads to a noble gas configuration, from [Xe]⁵⁴ 4f¹ 5d¹ 6s² to [Xe]⁵⁴, after losing four electrons. It is only Ce⁴⁺ which exist in solution among the lanthanides.
- 12. Sol. The atomic radii of the second and third transition series are almost the same. This phenomenon is associated with the intervention of the 4f orbitals which must be filled before the 5d series of elements begin. The filling of 4f before 5d orbital results in a regular decrease in atomic radii called Lanthanoid contraction which essentially compensates for the expected increase in atomic size with increasing atomic number. The net result of the lanthanoid contraction is that the second and the third d series exhibit similar radii (e.g., Zr 160 pm, Hf 159 pm).
- **13. Sol.** Lanthanide contraction is due to poor shielding of one of 4*f* electron by another in the sub-shell.
- **14.** (4) 1.73

..

number of unpaired electrons (n) = 2

$$\mu = \sqrt{n(n+2)} = \sqrt{2(2+2)} = \sqrt{8} \approx 2.84$$



- **15. Sol.** Lanthanoid contraction is due to ineffective shielding produced by larger f-subshell.
- **16. Sol.** The decrease in the force of attraction exerted by the nucleus on the valency electrons due to presence of electrons in the inner shells is called shielding effect. An 4f orbital is nearer to the nucleus than 5f orbitals. In addition, the 20 electrons of 3d and 4d orbitals contribute the shielding to 4f electron while 44 electrons of 3d, 4d, 5d and 4f contribute the shielding to 5f. Hence shielding of 5f is more than 4f.
- **17. Sol.** The distance between the nucleus and 5f orbitals (actinides) is more than the distance between the nucleus and 4f orbitals (lanthanides). Hence the hold of nucleus on valence electron decreases in actinides. For this Statement-2 the actinoids exhibit more number of oxidation states in general.
- **18. Sol.** There is very small energy difference between 5f and 6d orbitals in actinoids than those of between 4f and 5d orbitals. Hence, electrons present in 5f and 6d orbitals can take part in bonding.
- **19. Sol.** The basic character of any element changes with the oxidation state, low oxidation states are more basic and high oxidation state are more acidic. For example, MnO and Mn₂O₃ are basic while Mn₂O₇ is acidic in nature.

- **20.** Sol. Most of the trivalent lanthanoid compounds except that of La³⁺ and Lu³⁺ are coloured both in the solid state and in the aqueous solution. The colour of these ions can be attributed due to the presence of unpaired f-electrons.
- **21. Sol.** Generally across the first transition series, the negative values for standard electrode potential decrease (exception Mn- due to stable d⁵ configuration)

- **22. Sol.** Availability of 4f electrons donot results in the formation of compounds in +4 state for all the members of the series.
- **23.** Sol. Lutetium (71Lu) = $[Xe]^{54} 4f^{14}5d^{1}6s^{2}$
- **24.** Sol. Fe^{3+} is easily hydrolysed than Fe^{2+} due to more positive charge.

25.

- **Sol.** (1) $V^{2+} = 3$ unpaired electrons
 - Cr²⁺ = 4 unpaired electrons
 - $Mn^{2+} = 5$ unpaired electrons
 - $Fe^{2+} = 4$ unpaired electrons

Hence the order of paramagnetic behaviour should be

 V^{2+} < Cr^{2+} = Fe²⁺ < Mn²⁺

- (2) ionic size decrease from left to right in same period
- (3) As per data from NCERT.
 - $Co^{3+}/Co^{2+}= 1.97$; $Fe^{3+}/Fe^{2+}=0.77$; $Cr^{3+}/Cr^{2+}= -0.41$
- (4) The oxidation states increases as we go from group 3 to group 7 in same period.
- 26. Sol. E^o_{Cr3+/Cr2+} = 0.41 V ; E^o_{Mn3+/Mn2+} = + 1.57 V ; E^o_{Fe3+/Fe2+} = + 0.77 V ; E^o_{Co3+/Co2+} = + 1.97 V SRP value normaly increases from left to right in the period of d-block elements. Some SRP value are exceptionally higher due to stability of product ion. For e.g. E^o_{Mn3+/Mn2+} = + 1.57 V ; E^o_{Co3+/Co2+} = + 1.97 V.
- 27. Sol. The correct reaction are as follows :
 - $(1) Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2, H_2SO_4 + 2FeSO_4 + \frac{1}{2}O_2 \longrightarrow Fe_2(SO_4)_3 + H_2O$ $Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3 (s) + 3SO_3 \uparrow (This is given Wrongly)$ $(2) Fe \xrightarrow{O_2} \\ A \longrightarrow FeO (it could also be Fe_2O_3 or Fe_3O_4)$ $FeO + H_2SO_4 \longrightarrow FeSO_4 + H_2O$ $2FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_2 + SO_3$ $(3) Fe \xrightarrow{A} \\ Cl_2 \longrightarrow FeCl_3 \xrightarrow{\Delta} Fe_3O_4 \xrightarrow{CO} \\ FeO \xrightarrow{CO} \\ FeO$

28.	Sol.	(1) $Li_2O + KCI \longrightarrow 2LiCI + K_2O$					
	wrong e	equation, since a stronger base (K ₂ O) cannot be generated by a weaker base Li ₂ O					
	(2) [CoCl(NH ₃)₅] + 5H [⊕] —→ Co ²⁺ (aq) + 5NH₄ [⊕] + Cl [−]						
	This is correct. All ammine complexes can be destroyed by adding H^\oplus						
	(3) $[Mg(H_2O)_6]^{2+} + edta^{4-} \xrightarrow{OH^-} [Mg(edta]^{2+} + 6H_2O]$						
	[M] = [M]						
	$(4) 2 \cup U \cup U_4 + 1 \cup K \cup N \longrightarrow 2 K_3 [\cup U (\cup N)_4] + 2 K_2 \cup U_4 + (\cup N)_2 \uparrow^{\times}$						
	it is a w	wrong option, as given in paper.					
29.							
Sol.	TiCl ₃ –	Ziegler-Natta polymerisation					
	$PdCl_2 \rightarrow Wacker process$						
	$CuCl_2 \rightarrow Deacon's process$						
	$V_2O_5 \rightarrow Contact \ process$						
30.	Sol.	Colour of KMnO ₄ is due to charge transfer from O^{2-} (ligand) to Mn(VII) (Central metal ion).					

ONLINE JEE-MAIN

5. Sol. Na₂C₂O₇ is more soluble than $K_2Cr_2O_7$.

6.

Sol. (1) MnO_4^{2-} disproportionates in naatural or acidic solution

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

(3) Many Cu⁺ compounds a are unstable in aqueous solution and undergo disproportionation as follows $2Cu^+ \rightarrow Cu^{2+} Cu$

- 7. Sol. Fact.
- 8. Sol. $6Li + N_2 \rightarrow 2Li_3N$

2Li₃N $\xrightarrow{\Delta}$ 6Li + N₂ Li₃N + 3H₂O \rightarrow 3Li(OH)+ NH₃

 $CuSO_4 + 4NH_3 \rightarrow [Cu(NH_3)_4]SO_4$

deep blue

PART - II : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

1. Sol. (A) MnO_{4^-} ; x + 4(-2) = -1. So, x = +7 ; (B) $[Cr(CN)_6]^{3-}$; x + 6(-1) = -3. So, x = +3. (C) $[NiF_6]^{2^-}$; x + 6(-1) = -2. So, x = +4 ; (D) CrO_2Cl_2 ; x + 2(-2) + 2(-1) = 0. So, x = +6.

2. Sol. $C_6H_4(OH)_2 + 2AgBr \longrightarrow 2Ag + C_6H_4O_2 + 2HBr.$

 $AgBr + 2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr.$

3.

Sol. $Cr_2O_7^{2-} + 14 H^+ + 6e^- \rightarrow 2Cr^{3+} + 7 H_2O.$ $2 I^- \rightarrow I_2 + 2e^- \times 3$

 $Cr_2O_7^{2-}$ + 14 H⁺ + 6I⁻ \rightarrow 2Cr³⁺ + 3I₂ + 7H₂O

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Molecular weight 6 So eq. wt. =

- 4. Sol. With (A), (C) and (D) reactions only hydrated ferric chloride is obtained (as reactions take place in aqueous medium) but with metallic iron on heating in a stream of Cl₂ the anhydrous FeCl₃ is obtained $2Fe + 3Cl_2 \rightarrow 2FeCl_3$ (anhydrous).
- 5. Sol. Pyrolusite on fusion with KOH in air gives green coloured manganate. $2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_2$ (green) + $2H_2O$
- $MnO_{4^{-}}$; x + 4(-2) = -1 7. Sol. x = +7;or CrO_2Cl_2 ; x + 2(-2) + 2(-1) = + 6 or x = +6.
- 8. Sol. The colour of the transition metal ions is mainly attributed to d-d transition. d-d transition takes place because of the presence of unpaired electrons.

The metal ions having same number of unpaired electrons may give same colour in their aqueous solution.

In VOCl₂, V^{IV} ion having 3d¹ configuration has one unpaired electron. Similarly in CuCl₂, the Cu²⁺ ion having 3d⁹ configuration also has one unpaired electron. So VOCl₂ and CuCl₂ are expected to exhibit same colour i.e. blue colour.

Mn²⁺ has five unpaired and Fe²⁺ has four unpaired electrons.

9. Sol. Developer is usually a weak reducing agent like potassium ferrous oxalate, an alkaline solution of pyrogallol or an alkaline solution of quinol.

In the process of development of the photographic film, the exposed/activated AgBr grains are preferentially reduced by one of the reducing agent described above.



Hydroquinone

 $AgBr + e^- \rightarrow Ag(s) + Br^-$

The photographic film is then fixed by washing with hypo solution to remove the unreduced AgBr grains from the film.

AgBr + $2Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2] + NaBr$. $S_2O_3^{2-} + H_2O \rightarrow 2SO_2 + 2H^+ + 4e^-$. $S_2O_3^{2-} + 6H^+ \rightarrow 2S \downarrow$ (white milky) + $3H_2O$.

- 10. CuF2 contains Cu+2, having d⁹ configuration, therefore, there is one unpaired electron which Sol. undergoes d–d transition in visible region. CuF₂ in crystalline form is blue in colour.
- 11. Sol. CuSO₄ will be absorbing orange-red colour & hence will be of blue colour.
- 12. Sol. Fe + conc. HNO₃ \rightarrow Passivity Cu + conc. HNO₃ \rightarrow NO₂ Au + NaCN + $O_2 \rightarrow [Au(CN)_2]^ Zn + NaOH \rightarrow Na_2ZnO_2 + H_2$

APSP Solutions

PART-I

(1) Electron configuration of V is [Ar] 3d³ 4s² and thus maximum 5 electrons participate in bonding.
 (2) Electron configuration of Cr is [Ar] 3d⁵ 4s¹ and thus maximum 6 electrons participate in bonding.

(3) Electron configuration of Co is [Ar] $3d^7 4s^2$. In octahedral splitting in presence of ligands, half filled t_{2g}^{v} has higher CFSE and thus +3 oxidation state is most stable.

(4) Electron configuration of Sc is [Ar] 3d¹ 4s² and thus maximum 3 electrons participate in bonding.

2. Transition metal oxide with highest oxidation states is most acidic in character because of the very less difference in the values of electronegativity between Mn⁷⁺ and O²⁻, and the decreasing order of acidic

character is $\dot{Mn}_{2}^{+7}O_{7} > \dot{Mn}_{2}^{+4}O_{2} > \dot{Mn}_{2}^{+3}O_{3} > > \dot{Mn}_{0}^{+2}O_{3}$.

- **3.** First ionisation energies of 3d-series (first transition series) increase with increase in atomic number due to (1) increase in nuclear charge (2) decrease in atomic size.
- **4.** (i) Valence shell electron configuration of Ti⁴⁺ is 3d¹⁰ 4s⁰. As there is no unpaired electrons for d–d transition, the solution of ions will be colourless.

(ii) Valence shell electron configuration of Cu^+ is $3d^{10} 4s^0$. As all electrons are paired, there is no d–d transition, so the solution of ions will be colourless.

(iii) Valence shell electron configuration of Co^{3+} is $3d^6 4s^0$. As there are 4 unpaired electrons, there is dd transition of electron, so the solution of ions will be coloured.

(iv) Valence shell electron configuration of Fe²⁺ is 3d⁶ 4s⁰. As there are 4 unpaired electrons, there is d– d transition of electron, so the solution of ions will be coloured.

- (1) Valence shell electron configuration of Co^{3+} is $3d^6 4s^0$. So has 4 unpaired electrons.
 - (2) Valence shell electron configuration of Fe^{3+} is $3d^54s^0$. So has 5 unpaired electrons.
 - (3) Valence shell electron configuration of Cr^{2+} is $3d^4 4s^0$. So has 4 unpaired electrons.

(4) Valence shell electron configuration of V^{3+} is $3d^2 4s^0$. So has 2 unpaired electrons.

It has least number of unpaired electrons, so it has least magnetic moment.

- **6.** If a non-metal occupies interstitial sites of a metal, the metal becomes less malleable. This is because the non-metal atom forms covalent bonds with metal atoms and covalent bond is rigid and directional.
- 7. (1) Oxidation state of iron is +3 but it can exceed to a maximum of +6. Oxidation state of cobalt is +3 but it can exceed to a maximum of +4.

(2) Highest oxidation state of Cr in CrO_2Cl_2 is + 6 and highest oxidation state of Mn in MnO_4^- is + 7.

(3) Oxidation state of titanium is +2 but it can exceed to a maximum of +4. Oxidation state of Mn is +4 but it can exceed to a maximum of +7.

(4) Oxidation state of cobalt is +3 but it can exceed to a maximum of +4. Oxidation state of Mn is +7 which is its highest oxidation state.

8. CuCl absorbs CO, SO₂, C₂H₂

CuCl + 2CO \longrightarrow 2CuCl.CO.

9. (3) FeCl₃ exists as Fe₂Cl₆ (a dimer) in vapour state. The solution is acidic due to the formation of HCl and brown due to the formation of Fe(OH)₃.

 $FeCI_3 + 3H_2O \rightarrow Fe(OH)_3 (Brown) + 3HCI$

- **10.** (1) Cu_2O is red white CuO is black.
 - (2) Obtained on heating malchite ore not heamatite

 $CuCO_3.Cu(OH)_2 \xrightarrow{\Delta} 2 CuO + CO_2 + H_2O$

- (3) 3 CuCl₂.2H₂O $\xrightarrow{\Delta}$ CuO + 2CuCl + 2HCl + Cl₂ + 5H₂O
- (4) $2CuFeS_2 + 4O_2 \longrightarrow Cu_2S + 2FeO + 3SO_2$
- 11. All are facts.
- 12. $2CuSO_4 + 2NaCl + SO_2 + 2H_2O \longrightarrow Cu_2Cl_2 + Na_2SO_4 + 2H_2SO_4$

 $Cu_2Cl_2 + H_2S \longrightarrow Cu_2S + 2HCl$

5.

(Black ppt.)

 Cu_2Cl_2 + aq. $NH_3 \longrightarrow [Cu(NH_3)_2]Cl$ Soluble complex

 $Cu_2Cl_2 + 4 HCl \longrightarrow 2 H_2CuCl_3$

 $2FeCl_3.6H_2O \xrightarrow{Heat} Fe_2O_3 + 6HCI + 9H_2O$ 13. True, (1)

- False, FeSO₄ is oxidised to Fe³⁺ early, so it is not used as primary standard. But Mohr's salt (2) [FeSO₄.(NH₄)₂SO₄.6H₂O] can be used. (3)
 - False, $ZnCl_2 + H_2S \rightarrow ZnS + 2HCl$
- white precipitate (4) False, $CuSO_4 + 4NH_4OH \rightarrow [Cu(NH_3)_4]SO_4 + 4H_2O$ Deep blue solution $FeSO_4 + 2NH_4OH \rightarrow Fe(OH)_2 + (NH_4)_2SO_4$ Insoluble
- 14. $S_2O_3^{2-}$, CN^- , SCN^- and I^- act as reducing agent $Cu^{2+} + S_2O_3^{2-} \longrightarrow Cu^+ + S_4O_6^{2-}$ $Cu^{2+} + CN^{-} \longrightarrow Cu^{+} + (CN)_{2}$ $Cu^{2+} + SCN^{-} \longrightarrow Cu^{+} + (SCN)_{2}$
- 15. SO₂ and SO₃ $FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_2 \uparrow + SO_3 \uparrow + O_2 \uparrow$ The acidic gases produced are SO₂ and SO₃
- $X : [K_3 Fe(CN)_6)$ Y : Fe [Fe(CN)₆] 16.
- $2KMnO_4 \xrightarrow{750K} K_2MnO_4 + MnO_2 + O_2$. 17.
- 18. $MnO_4^- + 3e^- + 2H_2O \longrightarrow MnO_2 + 4OH^-$ (neutral / weak alkaline medium)
- $2KMnO_4 + 3H_2SO_4 \rightarrow 2KHSO_4 + (MnO_3)_2SO_4 + 2H_2O$ 19. $(MnO_3)_2SO_4 + H_2O \rightarrow Mn_2O_7 + H_2SO_4$ $Mn_2O_7 \xrightarrow{\Delta} 2MnO_2 + \overline{2}O_2$
- (1) $Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$. 20. (2) In acidic solution, actually chromate is converted to dichromate. $2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O_1$
 - (3) $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + 4H_2O + Cr_2O_3$.
 - (4) $6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O.$
- 21. Quinol developer (a reducing agent) reduces AgBr to Ag. $2AgBr^{*}(s) + 2OH^{-}(aq) + C_{6}H_{5}(OH)_{2}(aq) \longrightarrow 2Ag(s) + 2H_{2}O + C_{6}H_{4}O_{2}(aq) + 2Br^{-}(aq)$ Where AgBr* represents a molecules of AgBr exposed to light.
- $CO_2 + H_2O \rightarrow H_2CO_3 \implies 2H^+ + CO_3^{2-}$; $CrO_4^{2-} + 2H^+ \implies Cr_2O_7^{2-}$ (orange red) + H₂O 22.
- In FeO₄²⁻, Fe is in very high oxidation state (+6) and hence unstable, so it gets reduced to Fe³⁺ liberating 23. O_2 , CrO_4^{2-} in acidic medium converted to $Cr_2O_7^{2-}$.
- AqCI \xrightarrow{hv} Aq \downarrow + 1/2 Cl₂ 24. (black) If souce of light is removed, we get back Agce and blacknem due to Ag removed.

- **25.** Ag +dilute $HNO_3 \rightarrow AgNO_3 + NO(g)$ Ag + conc. $HNO_3 \rightarrow AgNO_3 + NO_2(g)$ Ag + conc. $H_2SO_4 \rightarrow Ag_2SO_4 + SO_2(g)$
- 27. Aqueous solution of $CuSO_4$ is acidic in nature, it converts some $CuCrO_4$ to $CuCr_2O_7$.
- **28.** In Co⁺³ ion, electronic configuration $|Ar|_{18} 3d^64s^0$. For octahedral complex 4 unpaired electron get paired and in configuration become $t_{2g^6} eg^0$ and hybridization d^2sp^3 . Os has maximam VIII oxidation state.
- **29.** After uranium all elements are transuranic element.

PART - II

- **1.** The general electronic configuration of Zn, Cd and Hg is $(n 1)d^{10} ns^{2}$.
- **2.** V = 135 pm ; Mn = 137 pm ; Ti = 147 pm ; Co = 125 pm.
- **3.** High melting point of Cr is attributed to the involvement of greater number of electrons from (n 1) d i.e. 5 in addition to the ns i.e. 1 electrons in the interatomic metallic bonding.
- **4.** $[Ni(CO)_4]$; Ni is in zero oxidation state. CO acts as σ doner as well as π acceptor.
- **5.** Cr^{2+} is reducing as its configuration changes from d⁴ to d³, the latter having a half-filled t_{2g} level. On the other hand, the change from Mn³⁺ to Mn²⁺ results in the half-filled (d⁵) configuration which has extra stability.
- 6. Mn exhibits all the oxidation states from +2 to +7.
- 8. $3.87 = \sqrt{n (n+2)}$; n = number of unpaired electrons. So n = 3.
- 9. 4FeCr₂O₄ + 8Na₂CO₃ + 7O₂ $\xrightarrow{\text{Fusion}}$ Na₂^{+VI}O₄ $\xrightarrow{\text{H}^+}$ Na₂^{+VI}O₇ $\xrightarrow{\text{H}^+/\text{H}_2\text{O}_2}$ $\stackrel{\text{H}^+/\text{H}_2\text{O}_2}{\xrightarrow{\text{H}^+/\text{H}_2\text{O}_2}}$ $\stackrel{\text{H}^-/\text{H}_2\text{O}_2}{\xrightarrow{\text{H}^+/\text{H}_2\text{O}_2}}$ $\stackrel{\text{H}^-/\text{H}_2\text{O}_2}{\xrightarrow{\text{H}^+/\text{H}_2\text{O}_2}}$ $\stackrel{\text{H}^-/\text{H}_2\text{O}_2}{\xrightarrow{\text{H}^+/\text{H}_2\text{O}_2}}$ $\stackrel{\text{H}^-/\text{H}_2\text{O}_2}{\xrightarrow{\text{H}^-/\text{H}_2\text{O}_2}}$ $\stackrel{\text{H}^-/\text{H}_2\text{O}_2}{\xrightarrow{\text{H}^-/\text{H}_2\text{O}_2}}$ $\stackrel{\text{H}^-/\text{H}_2\text{O}_2}{\xrightarrow{\text{H}^-/\text{H}_2\text{O}_2}}$ $\stackrel{\text{H}^-/\text{H}_2\text{O}_2}{\xrightarrow{\text{H}^-/\text{H}_2\text{O}_2}}$ $\stackrel{\text{H}^-/\text{H}_2\text{O}_2}{\xrightarrow{\text{H}^-/\text{H}_2\text{O}_2}}$ $\stackrel{\text{H}^-/\text{H}_2\text{O}_2}{\xrightarrow{\text{H}^-/\text{H}_2\text{O}_2}}$ $\stackrel{\text{H}^-/\text{H}_2\text{O}_2}{\xrightarrow{\text{H}^-/\text{H}_2\text{O}_2}}$ $\stackrel{\text{H}^-/\text{H}_2\text{O}_2}{\xrightarrow{\text{H}^-/\text{H}_2\text{O}_2}}$ $\stackrel{\text{H}^-/\text{H}_2\text{O}_2}{\xrightarrow{\text{H}^-/\text{H}_2\text{O}_2}}$ $\stackrel{\text{H}^-/\text{H}_2\text{O}_2}{\xrightarrow{\text{H}^-/\text{H}_2}}$ $\stackrel{\text{H}^-/\text{H}_2\text{O}_2}{\xrightarrow{\text{H}^-/\text{H}_2}}$ $\stackrel{\text{H}^-/\text{H}_2}{\xrightarrow{\text{H}^-/\text{H}_2}}$ $\stackrel{\text{H}^-/\text$
- 11. (1) Cu = 8.95 (2) Ni = 8.91 (3) Sc = 3.0 (4) Zn = 7.14. Acorss the period atomic volumes decreases upto copper due poor shielding of d-orbital electrons and addition of extra electrons in inner orbitals and then increases in zinc due to interelectronic repulsions in completely filled d- and s-orbitals. Consequently densities increase from Sc to Cu and then decreases in Zn.
- **12.** In electron configuration of d-block element last electron filled in (n 1) d subshell & these element placed between s-block & p-block element in periodic table. In f-block element, last electron filled in (n 2) f-subshell and these elements are placed in IIIrd B group in transition element. These element knwon as inner transition metal elements.
- **13.** Valence shell electronic configuration of palladium is 4d¹⁰ 5s⁰. As last electron enters in the 4d sub-shell, it belongs to 4d-series not 3d-series.
- $14. V_2O_5 + NaOH \rightarrow 2Na_3VO_4 + 3H_2O$
- **15.** ${}_{22}\text{Ti} = |\text{Ar}|_{18} \ 3\text{d}^2 \ 4\text{s}^2$ magnetic moment of Ti⁺ⁿ ion is 1.73 BM it means this ion contents one unpaied electron so after removing 3 electron Ti⁺³ ion formed. Ti⁺³ = $|\text{Ar}|_{18} \ 3\text{d}^1 \ 4\text{s}^{0}$.

- **16.** $6KMnO_4 + 10FeC_2O_4 + 24H_2SO_4 \longrightarrow 3K_2SO_4 + 6MnSO_4 + 5Fe_2(SO_4)_3 + 20CO_2 + 24H_2O.$ <u>3</u>
 - $\div~^5$ mole of KMnO4 for one mole ferrous oxalate.
- **17.** Increase in atomic mass results in a general increase in the density of these elements from Cr to Ni. i.e. 8.9 > 8.7 > 7.8 > 7.21 > 7.19 g cm⁻³.
- **18.** Cr³⁺ is most stable because in aqueous solution it has higher CFSE on account of half filled t³_{2g} energy level of 3d orbitals in octahedral spliting.
- **20.** All f and d-block element contains only metal.
- All bivalent metal cations form oxide of type MO.
 Copper forms two types of oxides Cu₂O₂, CuO
 Barium forms BaO
 Silver forms Ag₂O
 Lead forms PbO, PbO₂
 Silver cannot form MO type of oxide because it forms monovalent cation (Ag⁺).
- **22.** (1) Valence shell electron configuration of ${}_{50}Sn^{3+}$ is $5s^1 5p^0$.
 - (2) Valence shell electron configuration of Fe^{3+} is $3d^5 4s^0$.
 - Fe³⁺ will be most stable because it has extra stability due to exactly half filled 3d orbitals.
 - (3) Valence shell electron configuration of ${}_{82}\text{Pb}^{3+}\text{is}~4d^{10}~5s^1$.
 - (4) Valence shell electron configuration of Ag^{3+} is $4d^8 5s^0$.
- 23. German silver is alloy of Cu, Zn and Ni. It has no silver in it but it shines like silver.

Alloy	Components
Bronze	Cu (80 – 90%) and Sn (20 – 10%)
Brass	Cu and Zn
Gun metal	Cu (72 – 80%) and Sn (28 – 20%)
Bell metal	Cu + Sn + Zn

- 24. Copper, silver and gold (Cu, Ag, Au) are called coinage metals becuse they are used in making coins because they are inert. But Ni is not coinage metal.
- **25.** The metal with higher oxidation state have the tendency to oxidise the substance and itself gets reduced.
- 27. V^{+3} (3d²)get oxide ise into V^{+5} ($|Ar|_{18}$ 3d⁰) so it behave as strong reducing agent

28. The element having unpaired electron is paramagnetic, More the number of unpaired electrons, more will be paramagnetic character.
Write the valence shell configuration of the given element to find which one of than will have maximum

Write the valence shell configuration of the given element to find which one of than will have maximum paramagnetic character.

$Mn (25) = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^5,$:.	5 unpaired electrons
Fe (26) = 1s ² , 2s ² , 2p ⁶ , 3s ² , 3p ⁶ , 4s ² , 3d ⁶ ,	:.	4 unpaired electrons
Ni (28) = 1s ² , 2s ² , 2p ⁶ , 3s ² , 3p ⁶ , 4s ² , 3d ⁸	÷.	2 unpaired electrons
Cu (29) = 1s ² , 2s ² , 2p ⁶ , 3s ² , 3p ⁶ , 4s ¹ , 3d ¹⁰	:.	1 unpaired electrosn
• Mn bas maximum and Cu bas least para i	magnetic pro	portv

Mn has maximum and Cu has least para magnetic property.



30.		lon	E.C.	Number of unpaired electron	$\mu = \sqrt{n(n+2)}$ B.M.
	(i)	$_{23}V^{+4} =$	Ar ₁₈ 3d ¹ 4s ⁰	1	$\sqrt{3}$
	(ii)	25 Mn +4=	= Ar ₁₈ 3d ³ 4s ⁰	3	√15
	(iii)	26 Fe +3 =	= Ar ₁₈ 3d ⁵ 4s ⁰	5	$\sqrt{35}$
	(iv)	₂₈ Ni ⁺² =	= Ar ₁8 3d ⁸ 4s ⁰	2	$\sqrt{8}$
	So ca	rrect orde	er of megnetic m	oment is : (iii) > (ii) > (iv) > (i)	

- 29Cu = |Ar|₁₈ 3d¹⁰4s¹
 29Cu⁺ |Ar|₁₈ 3d¹⁰ 4s⁰
 in Cu⁺¹ ion, electronic configuration is 3d¹⁰ (Complete d orbital) so removal of electron recquired higher energy.
- **32.** (ii) According to electronic configuration, it is a f-block element.
- **33.** $Cr_2O_7^{-2} + 14H^+ + 6I^- \rightarrow 2Cr^{+3} 3I_2 + 7H_2O$

Number of unpaired electron $\mu = \sqrt{n(n+2)}$ B.M. lon E.C. $\sqrt{15}$ 24Cr+3 |Ar|18 3d3 450 3 (A) $\sqrt{24}$ (B) 26Fe⁺² |Ar|18 3d⁶ 45⁰ 4 $\sqrt{8}$ (C) ₂₈Ni+2 |Ar|18 3d⁸ 45⁰ 2 $\sqrt{35}$ 5 (D) 25Mn+2 |Ar|18 3d⁵ 45⁰

35. Because these type of metal get only reduce in chemical reaction. So it act as oxidizing agent.

36. $\mu = \sqrt{n (n+2)}$; 3d⁵ has maximum, 5 unpaired electrons so it will have highest magnetic moment.

- **37.** ${}_{25}Mn^{+2} = |Ar|_{18} 3d^54s^0$ No. of unpaired electron = 5 magnetic moment = $\sqrt{n(n+2)} = \sqrt{35} = 5.93$ BM
- **38.** $2MnO_4^- + 10Cl^- + 16H^+ \longrightarrow 2Mn^{2+} + 5Cl_2 + 8H_2O$
- **39.** Mn⁺² contains half filled (d⁵) d orbital, it gives stability to ion.
- **40.** $Cr_2O_7^{-2} + 3SO_2 + 2H^+ \rightarrow 2Cr^{+3} 3SO_4^{-2} + H_2O$ change in O.N. of SO₂ from 4 to 6.
- **41.** Mercury (Hg) contains filled d-orbital that prevents d-d overlapping of orbital and it has less strong metellic bond.

42. (1)
$$2Ag_2O(s) \xrightarrow{\Delta} 4Ag(s) + O_2(g)$$
; (2) $2H_2O_2 \xrightarrow{\text{or finely divided}} 2H_2O(I) + O_2(g)$
(3) $2KCIO_3 \xrightarrow{\Delta} 2KCI + 3O_2$; $NaNO_3 \longrightarrow NaNO_2 + 1/2 O_2$
 $2KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2$

43. Fe becomes passive on treatment with concentrated HNO₃. Pt at all does not react with HNO₃.

34.

44. S₁ : Increased nuclear charge is poorly screened by d-orbital electrons so attraction between nucleus and electron increases. Hence size decreases and density increases.

 $\textbf{S}_{2}: {}_{24}Cr^{2+} \ [Ar]^{18} \ \ 3d^{4} \ ; \ \mu_{BM} = \ \sqrt{n(n+2)} = \sqrt{4(4+2)} = 4.90 \ \ BM.$

 S_3 : Interstitial compounds they have high melting points which are higher than those of pure metals because of strong interatomic bonding.

S₄ : In alkaline medium it also acts as oxidising agent according to the following reaction ; $e^- + MnO_4^- \rightarrow MnO_4^{2-}$.