TOPIC : d & f BLOCK ELEMENTS
EXERCISE # 1

SECTION (A)

1. General electronic configuration of transition elements is [Noble gas] $(n-1)\,d^{1-10}\,ns^{1-2}$.

2.✍ The general electronic configuration of Zn, Cd and Hg is $(n-1)d^{10}\,ns^{2}$.

3. In these groups the d-orbitals are progressively filled in each of the four long periods (4 to 7).

4. (1) Configuration of d-block element is [inert gas] $ns^2(n-1)d^{1-10}$.
(2) These element have properties b/w s and p-block.
(3) d-block element starts with Sc_{21} – $[Ar]_{18}\,4s^2\,3d^1$.

5.✍ $_{46}Pd = [Kr]^{36}4d^{10}5s^0$; $_{47}Ag = [Kr]^{36}\,4d^{10}5s^1$; $_{48}Cd = [Kr]^{36}\,4d^{10}5s^2$.

6.✍ V = 135 pm ; Mn = 137 pm ; Ti = 147 pm ; Co = 125 pm.

7. 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.

8.✍ Strong metallic bonds between the atoms of transition elements attribute to their high melting and boiling points. Zinc has all electrons paired ($[Ar]\,3d^{10}\,4s^2$) and thus do not participate in metallic bonding. So accordingly its melting point is least.

9. $_{22}Ti = 3d^2\,4s^2$, $Ti^{2+} = 3d^2$; $_{23}V = 3d^3\,4s^2$, $V^{3+} = 3d^2$.
$_{24}Cr = 3d^5\,4s^1$, $Cr^{4+} = 3d^2$; $_{25}Mn = 3d^5\,4s^2$, $Mn^{5+} = 3d^2$.

SECTION (B)

1. (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

2. Os shows + 8 oxidation state in its compound with oxygen i.e., in OsO_4 .

3.✍ (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.

4.✍ $[Ni(CO)_4]$; Ni is in zero oxidation state. CO acts as σ doner as well as π acceptor.

5. 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.

6. As stability of compounds in aqueous solution depends on the electrode potential which in turns depends on all these enthalpies.

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

8.✍ 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.

9. Mn exhibits all the oxidation states from +2 to +7.

SECTION (C)

1. ${}_{30}Zn\ [Ar]^{18}\ 3d^{10}$, so n = 0, $Fe^{2+}\ [Ar]^{18}\ 3d^6$, so n = 4 ; $Ni^{2+}\ [Ar]^{18}\ 3d^8$, so n = 2 ; $Cu^{2+}\ [Ar]^{18}\ 3d^9$, so n = 1.

2. n ; $Cr^{2+}\ [Ar]^{18}\ 3d^4$; so n = 4 ; $Mn^{2+}\ [Ar]^{18}\ 3d^5$ so n = 5 ; $Fe^{2+}\ [Ar]^{18}\ 3d^6$ so n = = 4
n = Number of unpaired electron(s).

4. Ni^{2+} , Fe^{2+} and Cu^{2+} has 2, 4 and 1 unpaired electrons respectively. So in presence of ligands d-d transition takes place and these hydrated ions produce colour in aqueous solutions. Cu^+ is diamagnetic with $3d^{10}$ configuration; so no d-d transition is possible and thus colourless.

5. $3.87 = \sqrt{n\ (n+2)}$; n = number of unpaired electrons.
So n = 3.

6.✍ $\sqrt{15} = \sqrt{n(n+2)}$; n = 3, and three unpaired electrons are found when Mn is in Mn^{4+} i.e., $3d^3\ 4s^0$ configuration as its metal electron configuration is $[Ar]^{18}\ 3d^5\ 4s^2$.

7.✍ 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 to higher energy set of orbitals.

SECTION (D)

1. 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.

2. 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.

3.✍ (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)

1. $2CrO_4^{2-}$ (yellow) + $2H^+ \longrightarrow Cr_2O_7^{2-}$ (organge) + H_2O.

2. $6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$.

3. $4FeO.\ Cr_2O_3$ (chromite ore) + $8Na_2CO_3 + 7O_2 \xrightarrow{\text{Roasting in air}} 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$
$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$
$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2\ NaCl$

4. $2MnO_4^- + 3Mn^{2+} + 2H_2O \longrightarrow 5MnO_2 + 4H^+$

5.✍ Mn_2O_7 is an acid anhydride of $HMnO_4$ and thus MnO_4^- is oxo-salt of Mn_2O_7.

$Mn_2O_7 + H_2O \longrightarrow 2HMnO_4$;

$2HMnO_4 + KOH \longrightarrow 2KMnO_4 + H_2O$.

7.✍ $2KMnO_4 \xrightarrow{513\ K} K_2MnO_4 + MnO_2 + O_2$

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

$[SO_2 + [O] + H_2O \longrightarrow H_2SO_4 \times 3$.

$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3$ (Green coloured) $+ 3H_2O$

Acidified $K_2Cr_2O_7$ is oxidising agent and undergoes reduction to form green coloured solution of $Cr_2(SO_4)_3$.

9.✍ (1) It is simply a double salt called hydrated ferrous ammonium sulphate.

(2) $MgSO_4 . 7H_2O$ is Epsom salt.

(3) $FeSO_4 . (NH_4)_2 SO_4 . 6H_2O$ is Mohr's salt.

(4) $FeSO_4 . 7H_2O$ is Green vitriol.

SECTION (F)

1. Electronic configuration of f-block element $(n – 2) f^{1–14}, (n – 1)d^{10}, ns^2$ f-block starts with 6th period (n = 6).

2. Pm is a artificial or synthesis element.

3.✍ Lanthanum = d-block element.
Cerium = lanthanoide element & samarium, plutonium = actinoide element.

4. Across lanthanoide series basicity of lanthanoide hydroxide decreases.

5. **Gd^{3+} :** [Xe] $4f^7$

6. Actinides element shows variable valency.

7.✍ Due to poor shielding of (n – 2)f-electrons, size of Zr and Hf remain same.

8. Electronic configuration lanthanoid $4f^{1–14}\ 5d^1\ 6s^2$ and electronic configuration of actinoide $5f^{1–14}\ 6d^1, 7s^2$.

9.✍ In ion exchange method, lanthanoids are separated on the basis of their size.

EXERCISE # 2

1. $_{24}Cr^{6+}$ – $[Ar]^{18}\ 3d^0$; $_{22}Ti^{4+}$ – $\{Ar\}^{18}\ 3d^0$; $_{25}Mn^{7+}$ – $[Ar]^{18}3d^0$

2. 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. All statements are true.

4. (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.

5. 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.

6. Valence shell electronic configuration of palladium is $4d^{10}\ 5s^0$. As last electron enters in the 4d sub-shell, it belongs to 4d-series not 3d-series.

7. (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.

8. ${}_{24}Cr = [Ar]^{18}\ 3d^5 4s^1$; ${}_{25}Mn = [Ar]^{18}\ 3d^5 4s^2$
${}^{25}Cu = [Ar]^{18}\ 3d^{10}\ 4s^1$; ${}_{30}Zn = [Ar]^{18} 3d^{10}\ 4s^2$.

9.✍ 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. This is because of poor shielding of one of the 4 f-electrons by another in the sub-shell.

10. ${}_{28}Ni(I) = 3d^8 4s^1$; ${}_{30}Zn(I) = 3d^{10} 4s^1$; ${}_{29}Cu(I) = 3d^{10}$
1752 1734 1950 kJ mol^{-1}

11.✍ $Cr^{3+} + e^- \longrightarrow Cr^{2+}$, $E^\ominus = -0.41$ volts and $Mn^{3+} + e^- \longrightarrow Mn^{2+}$, $E^\ominus = +1.51$ 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.

12. Transition metal oxide with highest oxidation states is most acidic in character because of the very less difference in the values of electronegativity between Mn^{7+} and O^{2-} , and the decreasing order of acidic character is $\overset{+7}{Mn}_2O_7 > \overset{+6}{Mn}_2O_3 > \overset{+4}{Mn}O_2 > \overset{+2}{Mn}O$.

13. (1) Electron configuration of V is [Ar] $3d^3\ 4s^2$ and thus maximum 5 electrons participate in bonding.
(2) Electron configuration of Cr is [Ar] $3d^5\ 4s^1$ 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^3_{2g} has higher CFSE and thus +3 oxidation state is most stable.
(4) Electron configuration of Sc is [Ar] $3d^1\ 4s^2$ and thus maximum 3 electrons participate in bonding.

14. $VOSO_4 = VO^{2+} + SO_4^{2-}$; ax(– 2) = + 2 = + 4.

15.✍ 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.

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

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

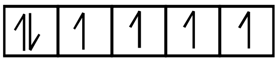
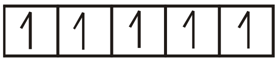
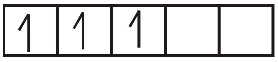
18. (1) $MnSO_4.4H_2O$; valence shell electron configuration of Mn^{2+} is $[Ar]^{18}\ 3d^5$; so n = 5
(2) $CuSO_4.5H_2O$; valence shell electron configuration of Cu^{2+} is $[Ar]^{18}\ 3d^9$; so n = 1
(3) $FeSO_4.6H_2O$; valence shell electron configuraiton of Fe^{2+} is $[Ar]^{18}\ 3d^6$; so n = 4
(4) $NiSO_4.6H_2O$; valence shell electron configuration of Ni^{2+} is $[Ar]^{18}\ 3d^8$; so n = 2
Paramagnetism increases with increasing number of unpaired electrons. Thus Cu^{2+} has lowest degree of paramagnetism.

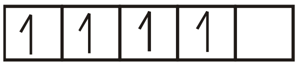
19. (1) In $Cr_2O_7^{2-}$, the valence shell electron configuration of Cr(VI) is $3d^0$. Thus Cr(VI) is diamagnetic but coloured due to the charge transfer spectrum.
(2) In $(NH_4)_2\ [TiCl_6]$, the valence shell electron configuration of Ti(IV) is $3d^0$. Thus Ti(IV) is diamagnetic and colourless.
(3) In $VOSO_4$, 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.

20.✍ (i) Valence shell electron configuration of Ti^{4+} is $3d^o\ 4s^o$. 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 $3d^{10}\ 4s^o$. 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 $3d^6\ 4s^o$. As there are 4 unpaired electrons, there is d–d transition of electron, so the solution of ions will be coloured.
(iv) Valence shell electron configuration of Fe^{2+} is $3d^6\ 4s^o$. As there are 4 unpaired electrons, there is d–d transition of electron, so the solution of ions will be coloured.

21. (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 ; $Ni^{2+}\ [Ar]^{18}\ 3d^8$, so n = 2; $Ti^{4+}\ [Ar]^{18}\ 3d^0$, so n = 0

22. Valence shell electron configuration of ${}_{30}Zn^{2+}$ is $3d^{10}\ 4s^o$. 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 $3d^8\ 4s^o$. 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 $3d^3\ 4s^o$. As there are 3 unpaired electrons, there is d–d transition of electron, so the solution of ions will be coloured.

23. Paramagnetic substance has unpaired electrons. More the number of unpaired electrons, more will be paramagnetic character.
(1) $Fe^{2+}\ 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^0, 3d^6$
$3d^6$ means 
∴ 4 unpaired electrons
(2) $Fe^{3+}\ 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^0, 3d^5$
$3d^5$ means 
∴ 5 unpaired electrons
(3) $Cr^{3+}\ 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^0, 3d^3$
$3d^3$ means 
∴ 3 unpaired electrons
(4) $Mn^{3+}\ 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^0, 3d^4$,

$3d^4$ means 

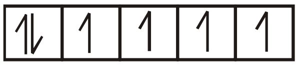
$\therefore$ 4 unpaired electrons

$\therefore$ Fe^{3+} has highest number of unpaired electrons

$\therefore$ It is most paramagnetic.

24. (1) Valence shell electron configuration of $_{26}Fe$ is $3d^6\ 4s^2$.

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

(3) Valence shell electron configuration of $_{26}Fe^{3+}$ is $3d^5\ 4s^0$. or 

Therefore, Fe^{3+} contains maximum number of unpaired electrons equal to 5.

25.✍ 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 Ag_2O, for instance, decomposes spontaneously into its elements when heated. $Ag_2O \rightarrow 2Ag + \frac{1}{2}O_2$.

26. $_{22}Ti = |Ar|_{18}\ 3d^2\ 4s^2$ 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. $Ti^{+3} = |Ar|_{18}\ 3d^1\ 4s^0$.

27. (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.

28. German silver is an alloy of copper, zinc and nickel, It is also known as nickel silver. It does not contain silver.

29. Brass contains only Cu and Zn.

30.✍ $2K_2MnO_4 + Cl_2 \rightarrow 2KMnO_4 + 2KCl$; $2K_2MnO_4 + H_2O + O_3 \rightarrow 2KMnO_4 + 2KOH + O_2$.

$3K_2MnO_4 + 2CO_2 \rightarrow 2KMnO_4 + MnO_2 + 2K_2CO_3$.

31. $2MnO_4^{-} + 5SO_3^{2-} + 6H^+ \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$.

$\therefore \frac{2}{5}$ mole of MnO_4^{-} for one mole SO_3^{2-}.

32. Iodometric estimation.

O.A. + $I^- + H^+ \rightarrow I_2$; I_2 + R.A. $\rightarrow I^-$

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

$I_2 + S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + I^-$

33. $4Cl^- + Cr_2O_7^{2-} + 6H^+$ (conc.) $\longrightarrow 2CrO_2Cl_2$ (deep red vapours) + $3H_2O$

34. $\underset{\text{Orange}}{Cr_2O_7^{-2}} + 2OH^- \rightarrow \underset{\text{yallow}}{2CrO_4^{-2}} + H_2O$

35. $Cr_2O_7^{2-} + 2H^+ + 4H_2O_2 \longrightarrow 2CrO_5 + 5H_2O$

36. $_{21}La(OH)_3$ is more basic than $Lu(OH)_3$.

37.✍ After uranium all elements are transuranic element.

38. Lanthanide contraction is due to increase in effective nuclear charge.

39. Curium, Californium, uranium are actionide elements

40. Pyrolusite on fusion with KOH in air gives green coloured manganate.

$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_2 \text{ (green)} + 2H_2O$$

41. CuF_2 contains Cu^{+2}, having d^9 configuration, therefore, there is one unpaired electron which undergoes d–d transition in visible region. CuF_2 in crystalline form is blue in colour.

EXERCISE # 3

PART - I

1. $La(OH)_3$ is more basic than $Li(OH)_3$. In lanthaniodes the basic character of hydroxides decreaes as the ionic radius decreases.

2. Most of trasition metals have unpaired electron in their elotronic configuration so they are paramagnetic in nature.

3. In lanthanides (At no of elements 58 to 71) the electronic configuration of three outermost shells are $(n-2)f^{1-14}$, $(n-1)s^2\,p^6d^{0\text{ to }1}\,ns^2$.

4. The correct order of ionic radii of Y^{3+}, La^{3+}, Eu^{3+} and Lu^{3+}, is $Y^{3+} < Lu^{3+} < Eu^{3+} < La^{3+}$ becuase Eu and Lu are the members of lanthanide series (so they show lanthanide contraction) and La is the representative element of all elements of such series and Y^{3+} ion has lower radii as comparison to La^{3+} because it lies immerdiately above it in the periodic table.

5. The order of basic character of the transition metal monoxide is TiO > VO > CrO > FeO because basic character of oxides decreases with increase in atomic number. Hence, oxides of transitional metals in low oxidation state ie, + 2 and +3 are generaly basic except Cr_2O_3.

6. Lanthanides are the 14 elements of IIIB groups and sixth period (At no = 58 to 71) that are filling 4f sub-shell of antipenultimates shell from 1 to 14.. Actually, they are placed below the periodic table in horizontal row as lanthanide series.

8. The electronic configuration of Mn is $3d^54s^2$, after removing two electron. it has electronic configuration $= 3d^5$ which get more stability due to half filled, orbitals, so it has higher IIIrd I. E. among the ions

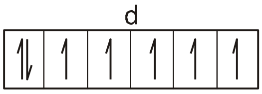
9. $_{21}Sc = 1s^2, 2s^2\,2p^6, 3s^2\,3p^63d^1,4s^2$

So, $Sc^{3+} = 1s^2, 2s^22p^6,3s^23p^6$

It is colourless due to absence of unpaired electron in d-subshell

$_{26}Fe = 1s^2, 2s^2\,2p^6, 3s^2\,3p^63d^6,4s^2$

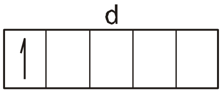
So, $Fe^{2+} = 1s^2, 2s^22p^6,3s^23p^6\,3d^6$



(It is coloured due to presence of four unpaired electrons in d-subshell)

$_{22}Ti = 1s^2, 2s^22p^6, 3s^2\,3p^63d^2, 4s^2$

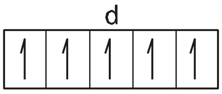
$Ti^{3+} = 1s^2, 2s^22p^6, 3s^23p^63d^1$



(It is coloured due to presence of an unpaired electron in d-subshell)

$_{25}Mn = 1s^2, 2s^22p^6, 3s^23p^63d^5, 4s^2$

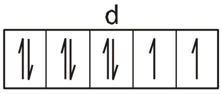
$Mn^{2+} = 1s^2, 2s^2\,2p^6, 3s^23p^63d^5$



(It is coloured due to presence of five unpaired electrons in d-subshell)

10. $_{28}Ni = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^8, 4s^2$

$Ni^{2+} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^8$

$3d^8$  [2 unpaired electrons]

$_{22}Ti = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^2, 4s^2$

Ti^{3+} $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^1$

[1 unpaired electron]

$_{21}Sc = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^1, 4s^2$

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

[no unpaired electron]

$_{29}Cu = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^1$

$Cu^+ = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}$

[no unpaired electron]

Hence in the above ions, Ni^{2+} and Ti^{3+} are coloured in aqueous solution due to presence of unpaired electrons in d sub-shell.

11. The regular decrease in the radii of lanthanide ions from La^{3+} to Lu^{3+} is known as lathanides contraction. It is due to the greater effect of the increased nuclear charge than that of screening effect (sheilding effect).

As a result of lathanide contraction, the atomic radii of element of 4d and 5d comes closer, so the properties of 4d and 5d transition element shows the similarities.

12. Ti^{3+} (Z = 22)

Ions which have unpaired electrons exhibit colour in solution. Ti^{3+} has an outer electronic configuration of $4s^0\ 3d^1$, i.e., 1 unpaired electron. Thus its solution will be coloured.

$Sc^{3+} \rightarrow d^0$

In case of La^{3+}, $4f^0$ configuration is present and in Lu^{3+}, $4f^{14}$ is present. So, there is no possibility of f-f transition, hence these ions do not appear coloured.

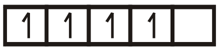
13. The electronic configuration of the given ions is :

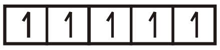
(1) Ni^{3+} : $[Ar]3d^7 4s^0$
(2) Mn^{3+} : $[Ar]3d^4 4s^0$
(3) Fe^{3+} : $[Ar]3d^5 4s^0$
(4) Co^{3+} : $[Ar]3d^6 4s^0$

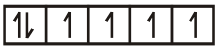
Thus, Co^{3+} is the ion with the desired configuration.

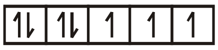
14. Zr^{4+} and Hf^{4+} belong to group IVB. But, Hf^{4+} has same size as Zr^{4+} due to the addition of 14 lanthanide elements before in which electrons are added into the f-subshell which poorly shield the outer electrons and contraction in size occurs.

15. The d-electron configurations of Cr^{2+}, Mn^{2+}, Fe^{2+} and Co^{2+} are d^4, d^5, d^6 and d^7 respectively. So stability order is Mn > Fe > Cr > Co

16. Cr^{2+} d^4  4

Mn^{2+} d^5  5

Fe^{2+} d^6  4

Co^{2+} d^7  3

Minimum Paramagnetic behaviour = $[Co(H_2O)_6]^{2+}$

17. Melting point of Mn and Zn has low M.P. than their adjacent element due to stable configuration.

18. $E^0_{Cu^{+2}/Cu} = 0.34$ volt, other has –ve $E^0_{R.P.}$

19. Has variable oxidation state
e.g. V_2O_5 catalyst in contact process.

20. Only Ac form Ac^{+3}

21. Sm^{+2} (Z = 62) [Xe] $4f^6$
Eu^{+2} (Z = 63) [Xe] $4f^7$
Yb^{+2} (Z = 70) [Xe] $4f^{14}$
Ce^{+2} (Z = 58) [Xe] $4f^1$, 5d'
Only Yb^{+2} is diamagnetic.

22. Interstitial compounds are generally chemically inert.

23. $\mu = 2.83$, n = 2
so Ni^{2+} $(3d^8 4s^0)$

24. There is no change in O.N. of Iron in $Fe + 5CO \longrightarrow Fe(CO)_5$

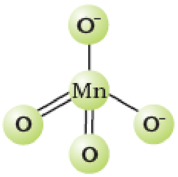
26. Ce^{+4} is strong oxidising agent and easily convert into Ce^{+3}
Eu^{+2} exist and behave as reducing agent lanthanons are much more reactive than aluminum.
Lanthanoids are basic in nature and their acidity is three.

27. Actinoids show greater number of oxidation sates because 5f, 6d and 7s levels having comparable energies (NCERT Page 231)

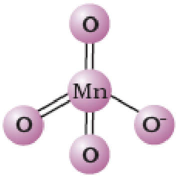
28. $KMnO_4$ is an oxidising so it can oxidise SO_2 readily.
$KMnO_4 + SO_2$? $Mn^{2+} + SO_3$
NO_2 is strong oxidising agent, CO_2 is neither oxidising agent nor reducing agent,

29. $Co^{3+} = 3d^6$ n = 4 $\mu = \sqrt{24}$ B.M.
$Cr^{3+} = 3d^3$ n = 3 $\mu = \sqrt{15}$ B.M.
$Fe^{3+} = 3d^5$ n = 5 $\mu = \sqrt{35}$ B.M.
$Ni^{2+} = 3d^8$ n = 2 $\mu = \sqrt{8}$ B.M.

30.



Tetrahedral
manganate
(green) ion

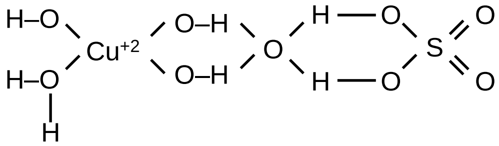


Tetrahedral
permanganate
(purple) ion

NCERT Page No. 233

……… The mangate and permanganate ions are tetrahedral ; the π–bonding takes place by overlap of p orbitals of oxygen with d orbitals of manganese.

31.



32. $2KMnO_4 + H_2O + KI \xrightarrow[\text{Medium}]{\text{Alkaline}} 2MnO_2 + 2OH^- + IO_3^-$ (Iodate)

X is IO_3^- (iodate)

PART - II

1. $3MnO_4^{2-} + 2H_2O \quad 2MnO_4^- + MnO_2 + 4OH^-$.

2. Species which have incompletely filled d-orbitals form coloured compounds whereas species with completely filled or vacant d orbitals are colourless.

$V^{+3}Cl_3$ **(coloured)**

$V^{3+} = 1s^2\ 2s^2 2p^6\ 3s^2 3p^6 3d^2$

VSO_4**(coloured)**

$V^{2+} = 1s^2\ 2s^2 2p^6 3s^2 3p^6 3d^3$

$Na_3\overset{+5}{V}O_4$ **(colourless)**

$V^{+5} = 1s2\ 2s^2 2p^6 3s^2 3p^6$

$[\overset{+2}{V}(H_2O)_6]SO_4 . H_2O$ = coloured.

$V^{2+} = 1s^2\ 2s^2 2p^6 3s^2 3p^6 3d^3$

3. H_2O_2 reduces acidified $KMnO_4$ to colourless $MnSO_4$.

$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O_4 + 3H_2O + 5[O]$

$[H_2O_2 + O \longrightarrow H_2O + O_2] \times 5$

$\underset{\text{Pink}}{2KMnO_4} + 5H_2O_2 + 3H_2SO_4 \longrightarrow K_2SO_4 + \underset{\text{colourless}}{2MnSO_4} + 8H_2O + 5O_2$

2 mol of $KMnO_4$ oxidise 5 mol of H_2O_2

$\therefore$ 1 mole of $KMnO_4$ will oxidise $\frac{5}{2}$ mole of H_2O_2.

4. As we move down in 13, 14 and 15 groups the interness of s^2 electrons of valence shell increases and therefore, metals in the lower portion of the group show lower oxidation state e.g. lead show + 2 inspite of +4. Similarly + 3 oxidation state of bismuth is more stable than + 5 oxidation state. Thus, due to inert pair effect , titanium shows + 1 oxidation state rather than + 3.

5. Cu^+ has $3d^{10}$ outer electronic configuration (completely filled d-orbital) with zero unpaired electrons, as a result d-d- transitions (responsible for absorption of light radiation and hence imparting colour) are not possible. Thus compounds of Cu^+ are colourless.

6. $MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$

Equivalent mass = $\frac{\text{molecular mass}}{3} = \frac{158}{3}$ = 52.66.

7. (1) Cr_2O_3 is an amphoteric oxide. ; (2) CrO_3 is an acidic oxide.

(3) V_2O_3 is basic oxide. ; (4) TiO is basic oxide.

8. Magnetic moment $\mu = \sqrt{n(n+2)}$ where n = number of unpaired electrons $\sqrt{15} = \sqrt{n(n+2)}$ n =3

9. The magnetic moments are lesser than the theoetically predicted value. This is due to the fact that 5f electrons of actinides are the less effectively shielded which result in quenching of orbital contribution.

10. 4f-orbital is nearer to nucleus as compared to 5f-orbital.

14. Cr^{3+} gives violet colour

15. Fe^{2+} quickly oxidizes to Fe^{3+} in aqueous medium.

16. MnO_4^- stable in acidic medium

MnO_4^{2-} disproportionate

CrO_4^{2-} Convert into $Cr_2O_7^{2-}$ and FeO_4^{2-} decompose

17. $AgNO_3 \longrightarrow Ag$ not decompose by H_2O at room temp. but reduce to silver in presence of light and reducing agent like glucose

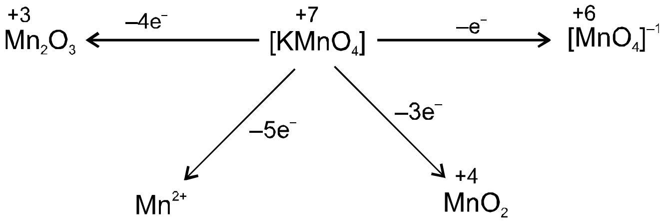
18. In basic medium

$KMnO_4^- \xrightarrow{OH^-} MnO_4^{2-}$

purple green

PART - III

1.



2. (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 Fe^{2+} is $3d^6$, therefore, has the maximum number of unpaired electrons equal to 4.

(3) Valence shell electron configuration of Ti^{2+} is $3d^2$, 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. Cerium $Ce_{58}[Xe]4f^15d^16s^2$

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

4. Cr^+ has stable half filled electronic configuration, $[Ar]^{18}\ 3d^5\ 4s^0$. the removal of one more electron from this stable half filled configuration will require higher energy.

5. Cu, Ag, Au group of elements are called coinage metals as these are used in minting coins.

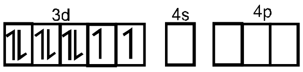
6. Due to lanthanide contraction there occurs net decrease in size. Only one 0.85Å is smaller one. So radius of Lu_{71}^{3+} will be closest to 0.85Å.

7. (3) Cerium can also show the oxidation state of +4 in solution as it leads to a noble gas configuration, from $[Xe]^{54}\ 4f^1\ 5d^1\ 6s^2$ to $[Xe]^{54}$, after losing four electrons. It is only Ce^{4+} which exist in solution among the lanthanides.

8. 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).

9. Lanthanide contraction is due to poor shielding of one of $4f$ electron by another in the sub-shell.

10. Valence shell electron configuration of $_{28}Ni^{2+}$ is $3d^8\ 4s^0$. or



So, number of unpaired electrons (n) = 2

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

11. Lanthanoid contraction is due to ineffective shielding produced by larger f-subshell.

12. 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.

13. 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.

14. 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.

15. 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 Mn_2O_3 are basic while Mn_2O_7 is acidic in nature.

16. Most of the trivalent lanthanoid compounds except that of La^{3+} and Lu^{3+} 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.

17. Generally across the first transition series, the negative values for standard electrode potential decrease (exception Mn- due to stable d^5 configuration)

Standard electrode potential –

	Mn	Cr	Fe	Co	
M^{2+}/M	–1.18	–0.90	–0.44	–0.28	eV

So, correct order is Mn > Cr > Fe > Co.

18. Availability of 4f electrons donot results in the formation of compounds in +4 state for all the members of the series.

19. Lutetium ($_{71}Lu$) = $[Xe]^{54}\ 4f^{14}5d^16s^2$

20. (1) V^{2+} = 3 unpaired electrons
Cr^{2+} = 4 unpaired electrons
Mn^{2+} = 5 unpaired electrons
Fe^{2+} = 4 unpaired electrons

Hence the order of paramagnetic behaviour should be

$V^{2+} < Cr^{2+} = Fe^{2+} < Mn^{2+}$

(2) ionic size decrease from left to right in same period

(3) As per data from NCERT.
$Co^{3+}/Co^{2+} = 1.97$; $Fe^{3+}/Fe^{2+} = 0.77$; $Cr^{3+}/Cr^{2+} = -0.41$
Sc^{3+} is highly stable
(It does not show +2)

(4) The oxidation states increases as we go from group 3 to group 7 in same period.

Ans is (1)

21. $E^o_{Cr3+/Cr2+} = -0.41$ 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.

22. Colour of $KMnO_4$ is due to charge transfer from O^{2-} (ligand) to Mn(VII) (Central metal ion).

11. Maximum number of unpaired electrons possible = 5

Spin only magnetic moment = $\sqrt{n(n+2)}\ \text{BM} = \sqrt{5(5+2)} = 5.92\text{B.M.}$

12. Due to weak metallic bonding.

13. $_{71}$Lu : [Xe] $4f^{14}\ 6s^2\ 5d^1$ (Last electron enters 5d orbital)

14. Sc shows only +3 oxidation state.

15. $2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$
(A) (Green) (B)
$3K_2MnO_4 + 4HCl \longrightarrow 2KMnO_4 + MnO_2 + 4KCl + 2H_2O$
(B) (Purple) (C)
$2KMnO_4 + KI + H_2O \longrightarrow 2MnO_2 + KIO_3 + 2KOH$
(C) (A) (C)

16. According to CFT, H_2O is weak field ligand
$Fe^{2+} = t_{2g}^{211} e_g^{11}$
$Co^{2+} = t_{2g}^{221}\ e_g^{11}$
$V^{2+} = t_{2g}^{111}\ e_g^{00}$
$\therefore M^{2+}$ is V^{2+}, Co^{2+}

17.

Element	Eu	Ce	Ho	N
Atomic radius (in pm)	199	183	176	70