

CHAPTER - 16

THE d- AND f-BLOCK ELEMENTS

SYNOPSIS

- 1. d Block Elements :** Elements which receive the last electron in $(n-1)$ d subshell are called d-block elements. They have a general outer electronic configuration $ns^{0-2}, (n-2)f^0 \text{ OR } 14 (n-1)d^{1-10}$.
There are 4 series of d-block elements namely 3d, 4d, 5d and 6d series out of which 3d series are discussed mainly in this chapter.
- 2. Transition Elements (TE's) :** Originally, d-block elements were called T.E's because of their position in between highly electropositive s-block and electronegative p-block of elements.
In modern terminology they are defined as d-block elements with incomplete d-subshell in any one of their oxidation states, including the elementary state.
According to this definition, Zn, Cd and Hg (having a maximum oxidation state of +2 only) are not typical T.E's as they do not have incompletely filled d-subshell in any oxidation state.
- 3. Characteristics of T.E's**
 - 3.1 They are metals with typical metallic properties. (By metallic property we do not mean electropositive nature)
 - 3.2 They have bright metallic lustre, high melting point, boiling point, density and heat of atomisation. The high metallic properties are attributed to strong metallic bond resulting from inter atomic bonding through d - d overlap. As the number of unpaired electrons increases in the d-orbitals, the bond - strength increases and so m.p., b.p, heat of atomisation and hardness increase.
(However, Mn with $3d^5$ configuration has a lower melting point than Ti, V, Cr or Fe)
 - 3.3 They show variable oxidation state
 - 3.4 They trap smaller atoms in the interstitial voids of metallic crystals and form **non-stoichiometric compounds**
 - 3.5 They readily form alloys due to comparable atomic size and similarity in general characteristics
 - 3.6 They react with O_2 or halogens, only at higher temperature due to high activation energy of reaction as a consequence of the higher heat of atomisation and $\Delta_i H$
 - 3.7 They have higher values of $\Delta_i H$'s and the successive $\Delta_i H$'s are influenced by the electronic configuration. eg. $\Delta_i H_2$ of Cr and Cu are exceptionally high.
 - 3.8 They have irregular trend in the value of standard reduction potential due to varying stability of the cations under going reduction / oxidation. The stability of a cation in a particular oxidation state depends not only on the electronic configuration, but also on the algebraic sum of (1) Heat of atomisation (2) IE's and (3) enthalpy of hydration. The enthalpy of hydration is usually contributed by CFSE of the cation in the ligand field of H_2O .

3.9 Unlike p-block elements, the stability of higher O.S increases as one moves down in the group. eg. (a) CrO_3 is an oxidiser but WO_3 is not an oxidiser. (b) Pt^{+4} is thermodynamically more stable than Ni^{+2} .

For 3d series, +2 oxidation state is apparently more stable in aqueous solution but among the trivalent cations Cr^{3+} is most stable, excepting Sc^{3+} .

3.10. They show paramagnetism due to the presence of unpaired electrons. The magnetic moment of transitional elements is mainly due to the spin of unpaired electrons and hence called spin only magnetic moment (μ_s).

μ_s is related to the number of unpaired electrons (n) by the expression.

$$\mu_s = \sqrt{n(n+2)} \mu_B \text{ where } \mu_B \text{ is called Bohr Magnetron equal to } \frac{eh}{4\pi mc}$$

The spin only magnetic moment calculated by this formula is nearly equal to the experimentally determined magnetic moment in the case of many transition elements and their cations. But the observed magnetic moments of ferromagnetic elements (Fe, Co and Ni) are much higher.

3.11. They readily form co-ordination complexes, helped by (a) higher oxidation state, (b) smaller cationic size and (c) availability of vacant d-orbitals. Only in carbonyls, the metal makes complexes in the zero oxidation state.

3.12 : They act as good catalysts.

3.13 : They form interstitial compounds.

3.13. They form coloured compounds and complexes. The colour may be due to (a) d - d* transition (b) charge transfer transition or (b) polarisation of the anion.

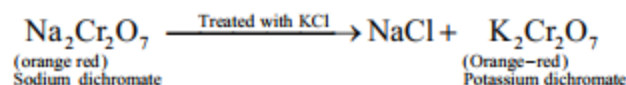
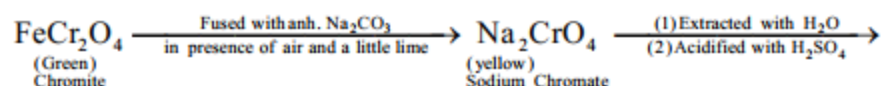
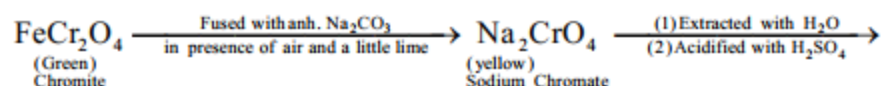
Cations with unpaired electrons in the d-orbitals exhibit colour due to d - d* transition.

Oxo-anions (CrO_4^{2-} , MnO_4^- , $\text{Cr}_2\text{O}_7^{2-}$ etc.) in which the metal has an apparently vacant d-subshell, show colour due to charge - transfer transition.

AgI , AgBr , HgI_2 , CdS etc are coloured even though the cations in these compounds have $(n-1)d^{10}$ configuration. They are coloured due to polarisation of the larger anions.

4. Potassium dichromate $\text{K}_2\text{Cr}_2\text{O}_7$

It is manufactured from chromite ore FeCr_2O_4 by the following procedure.



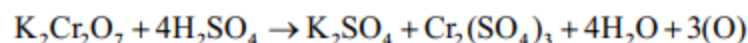
4.1. Conversion of chromate to dichromate is not a redox reaction

4.2. Properties of $\text{K}_2\text{Cr}_2\text{O}_7$. It is an orange -red crystalline solid, fairly soluble in water.

4.3. Chemical properties:-

4.3a. Action of heat : Decomposes into K_2CrO_4 , Cr_2O_3 and O_2 .

4.3b. Oxidising property : $\text{K}_2\text{Cr}_2\text{O}_7$ has the potential to generate nascent oxygen in acid - medium and acts as an oxidiser.



4.3c. in acid medium it oxidises

(i) FeSO_4 to $\text{Fe}_2(\text{SO}_4)_3$

(ii) SO_2 to H_2SO_4

(iii) SO_3^{2-} to SO_4^{2-}

(iv) H_2S to H_2O & S

(v) I^- to I_2

(vi) Sn^{2+} to Sn^{4+}

(Equivalent mass of $\text{K}_2\text{Cr}_2\text{O}_7$ in the redox reaction is Mol. Mass/6)

4.3d. Uses of $\text{K}_2\text{Cr}_2\text{O}_7$

$\text{K}_2\text{Cr}_2\text{O}_7$ is used :-

(i) as a **primary standard** in volumetric analysis

(ii) as an oxidiser in organic synthesis

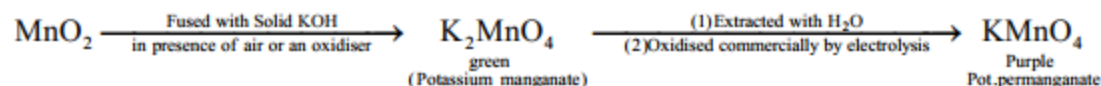
(iii) in the manufacture of chrome alum and processing of leather

(iv) as an analytical reagent in the detection of H_2S , SO_2 , Cl^- , peroxide etc.

Acidified $\text{K}_2\text{Cr}_2\text{O}_7$ can oxidise oxalic acid but it is not used to estimate oxalic acid.

5. Potassium permanganate KMnO_4

KMnO_4 is manufactured from pyrolusite (MnO_2) by the following procedure.



5.a. In the laboratory KMnO_4 is produced by oxidation of Mn^{2+} by persulphate.

5.1. K_2MnO_4 may be oxidised by ozone, CO_2 or Cl_2 but commercial production employs electrolytic oxidation

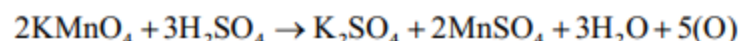
5.2. Properties of KMnO_4 : It is a dark purple coloured crystalline solid, less soluble in water

5.3. Chemical properties

5.3a. Action of heat - KMnO_4 decomposes into K_2MnO_4 , MnO_2 and O_2

5.3b. Oxidising property in acid medium :-

KMnO_4 has the potential to generate nascent oxygen in acid medium and so acts as an oxidiser



Note : Eq. mass of KMnO_4 in the redox reaction in acid medium is Mol. Mass /5

5.3c. It Oxidises :

i) FeSO_4 to $\text{Fe}_2(\text{SO}_4)_3$ in acid medium

ii) Oxalic acid to H_2O and CO_2 in acid medium

iii) I^- to I_2 in acid medium

iv) H_2S to H_2O and S in acid medium

v) SO_2 to H_2SO_4 in acid medium

vi) SO_3^{2-} to SO_4^{2-} in acid medium

vii) NO_2^- to NO_3^- in acid medium

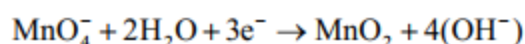
viii) HCl to H_2O and Cl_2 in acid medium

ix) H_2O_2 to H_2O and O_2 in acid medium

5.4. Oxidising property in neutral and alkaline media :

KMnO_4 has the potential to generate nascent oxygen in neutral as well as in alkaline medium. So it acts as oxidising agent in these media.





Note :- Eq. mass of KMnO_4 = Mol. mass/3

5.4a. It oxidises :

- i) I^- to IO_3^-
- ii) $\text{S}_2\text{O}_3^{2-}$ to SO_4^{2-}
- iii) MnCl_2 to MnO_2

Note :- In neutral or faintly alkaline medium.

5.4b. Uses : KMnO_4 is used :

- i) as an external antiseptic and disinfectant
- ii) in volumetric analysis
- iii) as an oxidiser in organic synthesis
- iv) as an analytical reagent to detect unsaturation in organic chemistry.

Note :- KMnO_4 is not used as a primary standard

5.5. f-block elements

Elements which receive the last electron in (n-2) f subshell are f-block elements. They have a general outer electronic configuration $ns^2 (n-1)d^{0-2} (n-2)f^{0-14}$. Owing to difference in effective nuclear charge in a few elements the electron enters into (n-1)d subshell which can not be explained by (n + l) rule but it could be interpreted on the basis of Z_{eff} penetration effect and inter-electronic repulsion.

5.6 Lanthanoids (Rare Earths Elements) (Ln's)

There are 14 lanthanoids from (Ce to Lu) and often La is included in the study of Ln's. Out of the 14 elements only promethium is an artificially prepared element.

5.6a. General characteristics :-

5.6a(i). They are silvery white soft metals and Sm is the hardest lanthanoid having the highest M.P.

5.6a(ii). They are strongly electropositive with $\Delta_i H_1$ and $\Delta_i H_2$ in the range of 600KJ and 1200 KJ/mol respectively

5.6a(iii). They have a highly -ve SRP. ($E^\circ \text{Ln}^{3+} / \text{Ln}$) in the range of -2.0Volt to -2.4 volt and they can liberate H_2 from water and acids.

5.6a(iv). They have larger atomic size but atomic size decreases from La to Lu due to increase in Z_{eff} resulting from poor shielding effect of 4f orbitals. Terminal seven elements have smaller atomic size than Yttrium of the 5th period and terminal 4 Ln^{3+} ions have shorter ionic radius than Y^{3+}

5.6a(v). They form ionic compounds and basic oxides. The basic nature of oxides decreases from La_2O_3 to Lu_2O_3 .

5.6a(vi). They are highly reactive as calcium. The reactivity decreases gradually across the series due to Lanthanoid - contraction.

5.6a(vii). They directly combine with H_2 , O_2 , N_2 , carbon, sulphur, halogens etc. They act as strong reducing agents and occur as mixed phosphates.

5.6a(viii). They have high density and low melting point. (1000 K to 1200 K except Sm for which MP is 1623K)

5.6a(ix). They show paramagnetism when unpaired electrons are present. The magnetic moment is not only due to spin but also due to orientation. Therefore the magnetic moment can not be calculated using the spin only formula.

5.6a(x). They show stable O.S of +3. Ce, Pr, Nd, Tb and Dy show +4 O.S whereas Sm, Eu and Yb show +2. O.S. Ln^{+4} cations are oxidisers and Ln^{2+} cations are reducers. Only Ce shows +4 O.S in aq. solution.

5.7. Colour of Ln^{3+} ions :-

Ln^{3+} ions containing 0, 1 and 7 electrons in 4f subshells are colourless. Ln^{3+} ion with $4f^n$ ($n \neq 0, 1 \text{ or } 7$) has the same colour as Ln^{3+} ion with $4f^{14-n}$

5.8. Lanthanoid contraction : Atomic and ionic radii of Ln's decrease from La to Lu due to an increased nuclear attraction on the outer shell resulting from poor shielding effect of f-orbitals. The difference in the atomic or ionic radii of two adjacent members is negligible but the cumulative difference is about 22 pm.

5.9. Consequences of Lanthanoid - Contraction

- i) Tb, Dy, Ho, Er, Tm, Yb and Lu have shorter atomic radius than Yttrium of 5th period
- ii) Er^{3+} , Tm^{3+} , Yb^{3+} and Lu^{3+} have shorter ionic radius than Y^{3+}
- iii) Reactivity decreases from Ce to Lu
- iv) Basic character of oxides and hydroxides decreases across the series.
- v) Post - lanthanoid d-block element have nearly the same atomic radius as their pre lanthanoid group members.
- vi) Chemical twins are formed because adjacent members do not differ much in their ionic radii
- vii) Separation of Ln's by ion exchange method is facilitated.

5.10. Uses of Lanthanoids

- i) Ce is used as a scavenger of O_2
- ii) $\text{Ce}(\text{SO}_4)_2$ is an oxidiser in cerimetry
- iii) CeO_2 and ThO_2 are used to make gas - mantles
- iv) Misch Metal alloys containing 95% Ln's, 4 -5% Fe and traces of C, S, Ca & Al, are used as pyrophoric alloys for making lighter flints.
- v) Sm_2O_3 is used for making phosphor screens
- vi) Mixed oxides of Ln's are used as catalysts in petroleum cracking

5.11 Actinoids.

There are 14 Actinoids out of which only 4 are naturally occurring. The **heaviest primordial** element is Plutonium which has a half life of several million years and existed before the formation of earth. Actinoids resemble lanthanoids in having a stable oxidation state of +3 (except Th). They show higher oxidation states upto +7. The higher oxidation state is relevant in the first half of the series only. Only Np and Pu have +7 o.s. U, Np, Pu and Am have +6 o.s. None of them is found to have +2 o.s. Similar to Lanthanoid - contraction, there is Actinoid contraction but the difference between adjacent members in the ionic radii is much significant and hence no chemical twins are formed. Their compounds in +3 and +4 o.s are easily hydrolysed. The multiplicity of o.s makes the chemistry of Actinoids much complex and the radio activity causes radiolysis in several reactions.

PART-I (JEE MAIN)**SECTION-I- Straight objective type questions**

- The correct order of the first ionization enthalpies is:
 - 1) $Mn < Ti < Zn < Ni$
 - 2) $Ti < Mn < Ni < Zn$
 - 3) $Zn < Ni < Mn < Ti$
 - 4) $Ti < Mn < Zn < Ni$
- The third ionization enthalpy is minimum for:
 - 1) Fe
 - 2) Ni
 - 3) Co
 - 4) Mn
- The transition element among the following with the lowest enthalpy of atomization is:
 - 1) Zn
 - 2) Cu
 - 3) V
 - 4) Fe
- The following statements are related to standard reduction potentials of the elements of first transition series. Which is incorrect?
 - 1) $E_{M^{2+}/M}^0$ for copper is positive (0.34 V) which accounts for inability of Cu to liberate H_2 from acids
 - 2) The value of $E_{M^{2+}/M}^0$ for Mn, Ni and Zn are more negative than expected from the trend
 - 3) $E_{M^{3+}/M^{2+}}^0$ for Mn, Fe and Co are negative
 - 4) The decreasing oxidising power is $Co^{3+} > Mn^{3+} > Fe^{3+}$
- Which of the following ions does not liberate hydrogen gas on reaction with dilute acids?
 - 1) Ti^{2+}
 - 2) V^{2+}
 - 3) Cr^{2+}
 - 4) Mn^{2+}
- A compound containing the metal ion M^{x+} ($Z = 25$) has a spin-only magnetic moment of $\sqrt{24}$ B.M. The number of unpaired electrons in the compound and the oxidation state of the metal ion are respectively
 - 1) 4, 2
 - 2) 5, 3
 - 3) 3, 2
 - 4) 4, 3
- The nature of Mn_2O_7 , V_2O_5 and CrO are respectively
 - 1) Acidic, acidic and basic
 - 2) Basic, amphoteric and amphoteric
 - 3) Acidic, amphoteric and basic
 - 4) Acidic, basic and amphoteric

8. Given below are two statements:

Statement-I : Potassium permanganate on heating at 513 K decomposes to form potassium manganate, manganese dioxide and oxygen gas.

Statement-II : Both potassium permanganate and potassium manganate are tetrahedral and paramagnetic in nature.

In the light of the above statements, choose the most appropriate answer from the options given below

- 1) Statement-I is true but Statement-II is false
 - 2) Both statement I and statement-II are true
 - 3) Statement-I is false but Statement-II is true
 - 4) Both statement-I and statement-II are false
9. The correct electronic configuration and spin-only magnetic moment of Gd^{3+} ($Z = 64$), respectively, are
- 1) $[Xe]4f^7$ and 8.9 BM
 - 2) $[Xe]4f^7$ and 7.9 BM
 - 3) $[Xe]5f^7$ and 8.9 BM
 - 4) $[Xe]5f^7$ and 7.9 BM
10. The highest possible oxidation state of uranium and plutonium, respectively, are:
- 1) 6 and 6
 - 2) 7 and 6
 - 3) 7 and 7
 - 4) 6 and 7
11. The lanthanide ion that would show colour is:
- 1) Sm^{3+}
 - 2) La^{3+}
 - 3) Lu^{3+}
 - 4) Yb^{2+}
12. The pair of elements that has similar atomic radii is:
- 1) Sc and Ni
 - 2) Ti and Hf
 - 3) Mo and W
 - 4) Mn and Re

SECTION-II - Numerical Type Questions

13. The total number of pi bonds between chromium and oxygen atoms in chromate ion and dichromate ion is _____
14. How many of the following has/have atomic radius greater than that of Cr?
Sc, Ti, V, Mn, Fe, Co, Ni
15. The oxidation state of chromium in the final product formed in the reaction between KI and acidified potassium dichromate solution is x. The oxidation state of iodine in the final product formed in the reaction between KI and acidified potassium permanganate solution is y. The value of $x + y$ is
16. Eu^{y+} is a strong reductant whereas Ce^{x+} is a strong oxidant. Total number of unpaired electrons in Eu^{y+} and Ce^{x+} is.....

PART-II (JEE ADVANCED)**Section-III - Only one option correct type****Passage-I (1-3)**

The $E_{M^{x+}/M}^0$ values for certain d-block elements are listed below

M^{x+} / M	E^0
Zn^{2+}/Zn	-0.76 V
Fe^{2+}/Fe	-0.44 V
Ni^{2+}/Ni	-0.25 V
Cu^{2+}/Cu	+0.34 V
Ag^+/Ag	+0.80 V
Mn^{2+}/Mn	-1.21 V
Pt^{2+}/Pt	+1.20 V

17. The most unreactive metal among the following is
 A) Ag B) Fe C) Mn D) Pt
18. The metal that does not displace hydrogen from dilute acids among the following is
 A) Zn B) Mn C) Ag D) Fe
19. The $E_{M^{2+}/M}^0$ value for copper is positive because copper has
 A) Low atomisation enthalpy and low hydration enthalpy
 B) High atomisation enthalpy and high hydration enthalpy
 C) High atomisation enthalpy and low hydration enthalpy
 D) Low atomisation enthalpy and high hydration enthalpy

Passage-II (4-9)

A chrome iron ore (X) was heated with dry Na_2CO_3 in the presence of quick lime and air in a furnace. The mixture was extracted with water and filtered. The filtrate was yellow (A) which on adding conc. H_2SO_4 turned to orange red. The solution was evaporated and cooled when crystals of B were obtained. To the crystals of B in aqueous solution, NH_4Cl was added. On fractional crystallization, orange red crystals (C) were formed.

20. 'C' on heating will give
 A) NH_3 B) N_2 C) NO_2 D) CO_2
21. Compound 'B' is
 A) NaCl B) $Na_2Cr_2O_7$ C) $(NH_4)_2Cr_2O_7$ D) NH_4Cl
22. The correct statement among the following is
 A) Chromate ion disproportionates in the acidic medium
 B) Dichromate ion is stable in the acidic medium
 C) Chromate ion is stable in the acidic medium
 D) Dichromate ion disproportionates in the acidic medium
23. 'B' was obtained by fractional crystallization. The compound crystallized first was
 A) $Na_2Cr_2O_7 \cdot 2H_2O$ B) NaCl C) Na_2CO_3 D) $Na_2SO_4 \cdot 10H_2O$
24. The bond angle in 'A' is
 A) 126° B) 107° C) 111° D) 109.5°

Section IV - One or more option correct type

25. Which of the following lanthanoids show(s) +2 oxidation state besides the characteristic oxidation state of +3?
 A) Ce B) Eu C) Yb D) Ho
26. Which of the following statement(s) is/are correct?
 A) At low pH, yellow chromate ion is converted to orange dichromate ion in aqueous solution
 B) Manganate ion disproportionates to yield permanganate ion and manganese dioxide in presence of H^+ ions
 C) In dichromate ion, each chromium atom is linked to four oxygen atoms
 D) $Ti_{(aq)}^{3+}$ is purple while $Ti_{(aq)}^{4+}$ is colourless
27. The tetrahedral $[MO_4]^{n-}$ ions are known for the metal ion(s)
 A) Mn^{5+} B) Mn^{7+} C) Mn^{6+} D) V^{5+}
28. Select the correct statement(s) from the following
 A) V_2O_4 dissolves in acids to form VO^{2+} salts
 B) V_2O_5 dissolves in acids to form VO_4^{3-} salts
 C) V_2O_4 dissolves in acids to form VO_4^{3-} salts
 D) V_2O_5 dissolves in acids to form VO_2^+ salts

29. Select the compound(s) in which d-d transition of electrons is possible

- A) $[\text{Cu}(\text{NH}_3)_4]^{2+}$ B) KMnO_4 C) $\text{K}_2\text{Cr}_2\text{O}_7$ D) $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$

Section V - Numerical type questions

30. The total number of triangular faces in the molecular structure of permanganate ion is
31. The number of species among Ti^{2+} , Cr^{2+} , Mn^{2+} , Fe^{2+} and Co^{2+} that is/are more reducing than V^{2+} is
32. How many statements among the following is/are correct?
 i) Pyrolusite ore on fusion with KNO_3 and KOH gives K_2MnO_4
 ii) K_2MnO_4 on electrolytic oxidation in the alkaline medium gives KMnO_4
 iii) $\text{K}_2\text{Cr}_2\text{O}_7$ is less soluble than $\text{Na}_2\text{Cr}_2\text{O}_7$ in water
 iv) The $\text{Cr}-\text{O}-\text{Cr}$ bond angle in $\text{K}_2\text{Cr}_2\text{O}_7$ is greater than 109.5°
33. The number of moles of precipitate formed when 5 moles of hydrogen sulphide is oxidised with acidified potassium dichromate is
34. The number of moles of KMnO_4 reduced by one mole of KI in the alkaline medium is

Section-VI - Matrix match type

35. Match the following

Column-I (Elements)

- I) Cd
 II) Rh
 III) Fm
 IV) Gd

Column-II (Classification)

- P) d-block metal
 Q) Transition metal
 R) Inner transition metal
 S) Lanthanoid
 T) Actinoid
- A) $\text{I} \rightarrow \text{PQ}$; $\text{II} \rightarrow \text{PQ}$; $\text{III} \rightarrow \text{RS}$; $\text{IV} \rightarrow \text{RS}$
 B) $\text{I} \rightarrow \text{P}$; $\text{II} \rightarrow \text{PQ}$; $\text{III} \rightarrow \text{RT}$; $\text{IV} \rightarrow \text{RS}$
 C) $\text{I} \rightarrow \text{PQ}$; $\text{II} \rightarrow \text{P}$; $\text{III} \rightarrow \text{PQ}$; $\text{IV} \rightarrow \text{RS}$
 D) $\text{I} \rightarrow \text{P}$; $\text{II} \rightarrow \text{PQ}$; $\text{III} \rightarrow \text{PQ}$; $\text{IV} \rightarrow \text{RS}$

36. Match the following:

Column-I (Pair of compounds)

- I) $\text{NiSO}_{4(\text{aq})}$ and $\text{VO}^{+}_{(\text{aq})}$
 II) $\text{TiCl}_{4(\text{aq})}$ and $\text{ZnSO}_{4(\text{aq})}$
 III) $\text{MnCl}_{2(\text{aq})}$ and $\text{CoCl}_{2(\text{aq})}$
 IV) $\text{FeCl}_{3(\text{aq})}$ and $\text{MnSO}_{4(\text{aq})}$

Column-II (Characteristics)

- P) Same magnetic moment
 Q) Same/similar colour
 R) Same oxidation state of metal
 S) Same outer electronic configuration of metal
- A) $\text{I} \rightarrow \text{Q}$; $\text{II} \rightarrow \text{P}$; $\text{III} \rightarrow \text{R}$; $\text{IV} \rightarrow \text{PQS}$
 B) $\text{I} \rightarrow \text{Q}$; $\text{II} \rightarrow \text{P}$; $\text{III} \rightarrow \text{QR}$; $\text{IV} \rightarrow \text{PQS}$
 C) $\text{I} \rightarrow \text{Q}$; $\text{II} \rightarrow \text{P}$; $\text{III} \rightarrow \text{QR}$; $\text{IV} \rightarrow \text{PQ}$
 D) $\text{I} \rightarrow \text{PQ}$; $\text{II} \rightarrow \text{PQ}$; $\text{III} \rightarrow \text{QR}$; $\text{IV} \rightarrow \text{PS}$