# d and f- Block Elements

**d- block elements:** Those elements in which the last $e^-$ enters $(n-1)d$ orbital or penultimate d- orbital.

General E.C. of d- block elements: $ns^{1-2}(n-1)d^{1-10}$

$n = 4, 5, 6, 7$

- 4 Transition series

MCQ. 1st Transition series : Sc (21) to Zn (30)

$4s^{1-2}\,3d^{1-10}$

2nd Transition series : Y (39) to Cd (48)

$5s^{1-2}\,4d^{1-10}$

3rd transition series : La (57), Hf (72) to Hg (80)

4th transition series : Rf (104) to –

d-block elements are called transition elements.

↓

There is transition in properties of elements from s-block to p-block via d-block elements

# Not all d-block elements are considered as transition elements.

**Criteria for transition elements:** V-imp-

d-block Element must have incomplete d-orbital either in its ground state or in any of its oxidation state.

Zn, Hg & Cd ⇒ d-block elements but are not considered as transition elements.

E.C : ① Zn (30) :- $4s^2 3d^{10}$ ; $Zn^{2+}$ : $3d^{10}$ → completely filled d-orbital.

$Cu(29)$ : $4s^1 3d^{10}$ filled d-orbital.

$Cu^+$ : $3d^{10}$ filled d-orbital.

$Cu^{2+}$ : $3d^9$ → incomplete d-orbital.

∴ Cu is a d-block element as well as transition element

**Q. Write outer electronic configuration of the following:**

(i) $Fe^{2+}$ — $Fe \rightarrow 4s^2 3d^6$ ; $Fe^{2+}$ :- $3d^6$

(ii) $Cr^{3+}$ — $Cr$ :- $4s^1 3d^5$ ; $Cr^{3+}$ :→ $3d^3$.

(iii) $Ni^{2+}$ — $Ni$ : $4s^2 3d^8$ ; $Ni^{2+}$ : $3d^8$

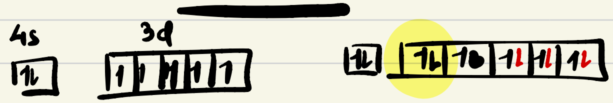
1 Q in CBSE is must →

## General Properties of d-block elements:

- Atomic size
- I.E
- M.P & B.P
- Hard & soft
- Enthalpy of atomisation
- Oxidation state
- Catalyst
- Form complex
- Coloured complex
- Magnetic property
- Alloy formation
- Interstitial compounds

## (I) Atomic size :

1st series: Sc Ti V Cr Mn Fe Co Ni Cu Zn




s > d > p - block elements.

Within transition series :

- Atomic size decreases : 1st atomic size decreases due to increase in effective nuclear charge

- Atomic size remains almost same : In the middle of T.S because effective nuclear charge & $e^- - e^-$ repulsion becomes equal & they cancel out each others effect.

- Atomic size increases : At the end of the series. no. of $e^-$ which are paired increases which increases the $e^- - e^-$ repulsion and due to which at. size increases.

## (I) Ionisation Enthalpy : → show irregularity in a transition series.

$$I.E \propto \frac{1}{\text{atomic size}}$$

- At. size ↓es ⇒ I.E ↑es
- At size remain same ⇒ I.E is also comparable
- At size ↑es ⇒ I.E ↓es.

## (II) M.P & B.P and Enthalpy of atomisation ($\Delta_a H$)

$M(s) \longrightarrow M(g)$ atoms. $\Delta_a H = +ve$

↑ in case of metals depends on metallic bond or inter atomic interaction.

$\Delta_a H$ Higher = High M.P or B.P

Metallic bond depends on no. of unpaired $e^-$.

strength of metallic bond $\propto$ no. of unpaired $e^-$

Sc  Ti  V  Cr  Mn  Fe  Co  Ni  Cu  Zn

$3d^1$  $3d^2$  $3d^3$ $4s^1 3d^5$ = $3d^5$  $3d^6$  $3d^7$  $3d^8$ $4s^1 3d^{10}$  $3d^{10}$

| | | | | |
|---|---|---|---|---|
| 4 | 3 | 2 | 1 | 0 |

no. of unpaired $e^-$ ↑es

strength of metallic bond ↑es.

$\Delta_a H$ increases.

no. of unpaired $e^-$ ↓es to zero

Strength of metallic bond ↓es.

$\Delta_a H$ ↓es.

* Zn, Hg, Cd have lowest M.P | B.P / $\Delta_a H$ in their respective transition series.

**Hard and softness:** Generally, d-block elements are hard except Zn, Hg and Cd.

↓

No unpaired $e^-$

↓

Metallic bond or interatomic interaction is weak.

# Oxidation Number

- d-block elements except the first & last element of transition series **show variable oxidation state.**

↓

Energy difference b/w ns & (n-1)d orbital is very less

⇐ both ns & (n-1)d orbital of transition element can participate in bond formation

$Mn \rightarrow +2$ to $+7$

$Fe^{2+}$ , $Fe^{3+}$ , $Cu^{+}$ , $Cu^{2+}$

| Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|---|---|---|---|---|---|---|---|---|---|
| $3d^1 4s^2$ | $3d^2 4s^2$ | $3d^3 4s^2$ | $3d^5 4s^1$ | $3d^5 4s^2$ | $3d^6 4s^2$ | $3d^7 4s^2$ | $3d^8 4s^2$ | $3d^{10} 4s^1$ | $3d^{10} 4s^2$ |
| +3 | +2 | +2 | +2 | **+2** | **+2** | **+2** | **+2** | +1 | +2 |
| | +3 | +3 | **+3** | +3 | **+3** | **+3** | +3 | **+2** | |
| | **+4** | +4 | +4 | +4 | +4 | +4 | +4 | | |
| | | **+5** | +5 | +5 | | | | | |
| | | | **+6** | +6 | +6 | | | | |
| | | | | **+7** | | | | | |

Common oxidation state (highlighted) →

Sc, Cu, Zn does not show variable O.S ?

Sc after losing $3e^-$ → $3d^0$ (fully filled orbital)

Zn after losing $2e^-$ ⇒ $3d^{10}$ (fully-filled orbital)
↓
Stable electronic configuration

Ex: * $Mn^{3+}$ is a good oxidising agent : undergoing redn

$Mn (3d^5 4s^2) \Rightarrow Mn^{3+} (3d^4) + 1e^- \rightarrow Mn^{2+} (3d^5)$ Half-filled
↓
Stable E.C

Ex: Acidic character ∝ Oxidation State

$\overset{+7}{Mn_2O_7} > \overset{+2}{MnO}$ acidic nature

(a) basic in nature.

Ex: Redn potential related Qs / O.S related Qs.

$E^\circ_{red} (M^+/M)$ ⇒ Tendency of Metal to undergo redn.

$$E^0_{red} = I.E + \Delta_a H + \Delta_{Hyd.} H$$

($I.E$ → +ve, $\Delta_a H$ → +ve, $\Delta_{Hyd.} H$ → −ve)

$E^0_{red}$ = +ve (if $|I.E + \Delta_a H| > |\Delta_{Hyd} H|$)

$E^0_{red}$ = −ve (if $[I.E + \Delta_a H] < |\Delta_{Hyd.} H|$)

$Cu^{+1}(aq)$ state is not stable or $Cu^{+}(aq)$ undergoes disproportionation process

$$Cu^{+}(aq) \longrightarrow Cu(s) + Cu^{2+}(aq)$$

Hydration enthalpy is large. It compensates the I.E reqd. to release 1e⁻ from $Cu^{+1}$ to becomes $Cu^{2+}$.

Ex: $Fe^{2+}$ & $Mn^{3+}$ → oxidising in nature

↳ reducing in nature.

$Mn^{3+}$ ($3d^4$) + $1e^-$ $\longrightarrow$ $Mn^{2+}$ ($3d^5$) . Half-filled orbital
. stable E.C

$Fe^{2+}$ ($3d^6$) $\longrightarrow$ $Fe^{3+}$ ($3d^5$) + $1e^-$

Q. $Mn^{2+}$ is more stable towards oxidation to +3 state whereas $Fe^{2+}$ can be easily oxidised to +3 state. Explain

Q. Oxo anion $\Rightarrow$ $F^-$ (anion)

$MnO_4^-$ (oxo anion)

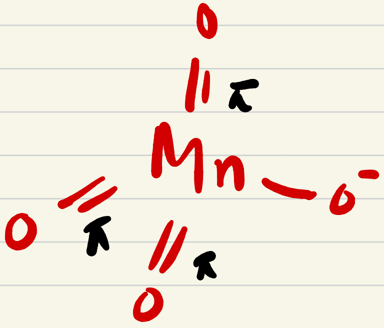
* Give one example of oxoanion of d-block element in which O.S of transition metal is same as that of its group no.

Ex: $MnO_4^-$ $Mn^{+7}$ group no = 7

$Cr_2O_7^{2-}$ Cr(+6) group no = 6.

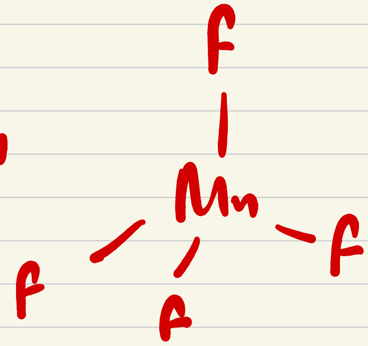
# Mn shows highest O.S of +7 with oxygen & +4 as highest oxidation state with fluorine. Why?

$MnO_4^-$



$p\pi - d\pi$ multiple bond is possible

$MnF_4$



$p\pi - d\pi$ multiple bond not possible in F as it has only 1 unpaired $e^-$.

* 2nd pd. elements ⇒ $p\pi - p\pi$ multiple bond

**They are used as catalyst**

accumulation of gas particles over the surface of solid.

- They have variable oxidation state
- They have larger surface area. Adsorption of gaseous reactant takes place effectively.

Ex: Habers process [ synthesis of $NH_3$ ) → Fe-Mo

Ex: Hydrogenation of unsaturated Hydrocarbon → Ni, or Pd or Pt

Ex: Oxidation of $SO_2$ to $SO_3$ → $V_2O_5$ [manufacture of $H_2SO_4$]

Ex: decomposition of $H_2O_2$ solⁿ → $MnO_2$

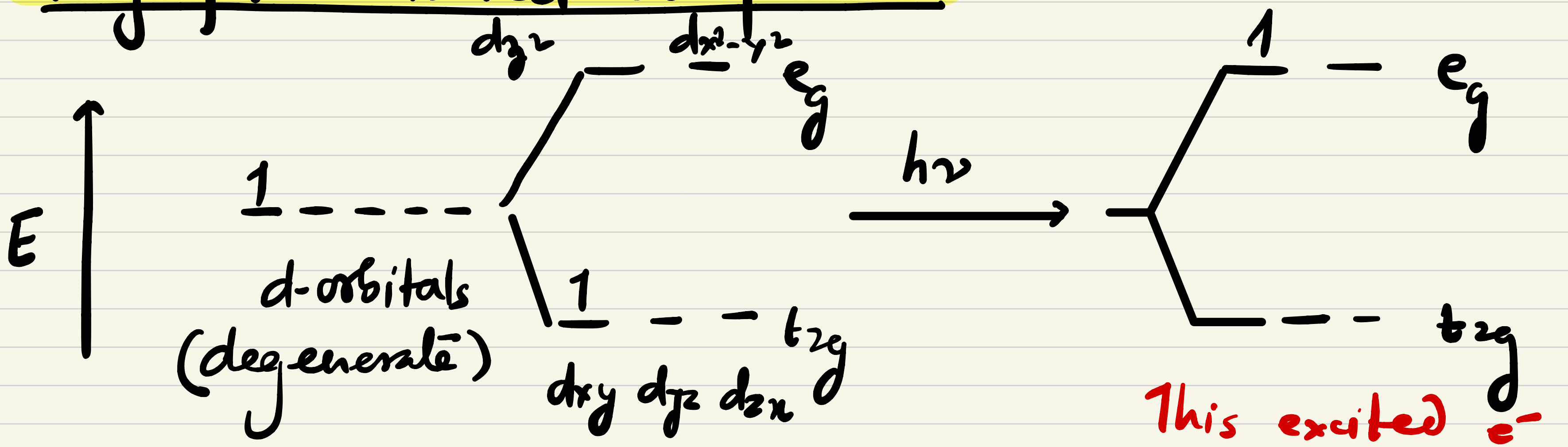
**They form complex compounds (or coordination compounds)**

With central metal atom or ion, $e^-$ rich species form coordinate bond. → coordination compounds

**Reason:** 1. Availability of d-orbitals to accept l.p e⁻ from ligands

2. high nuclear charge & small size.

**They form coloured compounds :**



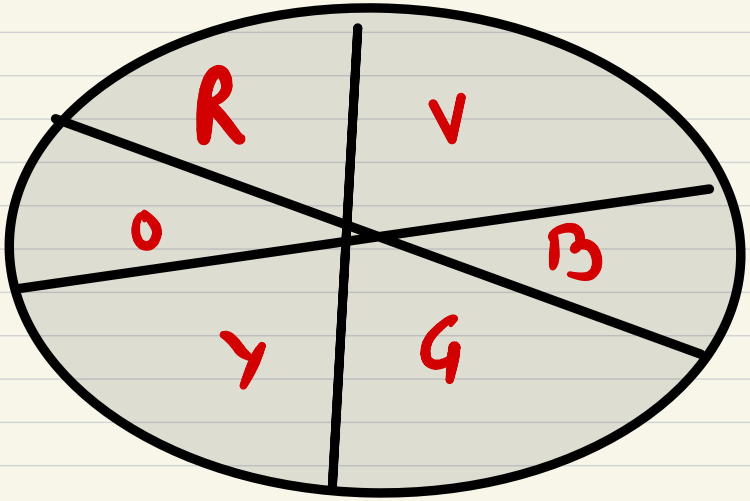

This excited e⁻ loses energy & comes back to the ground state by emitting radiation of visible region.

* They form coloured compounds due to d- d electronic transition.

\# Which type of d- block element compounds donot show colour → $d^0, d^{10}$

* Colour of the compound is complementary to absorbed colour.

Ex: If violet colour is generated by coordination compound then which colour is absorbed during d-d transition?




Q. $[Ti(H_2O)_6]^{3+}$ is violet in colour. Which region of visible spectrum is absorbed during d-d $e^-$ transition.

Q. Why $[Ti(H_2O)_6]^{3+}$ becomes colourless on heating?

On heating, removal of water takes place. In absence of water, splitting of d-orbitals in $t_{2g}$ & $e_g$ does not take place. So no d-d electronic takes place.

Q. Why are $ZnSO_4$, Sc(III) salts, $TiO_2$ white in colour?

$ZnSO_4$, $Zn^{2+}$ : $3d^{10} 4s^0$

$Sc^{3+}$ : $4s^0 3d^0$

$Ti^{4+}$ : $4s^0 3d^0$

$d^0$ & $d^{10}$ ⇒ No d-d electronic transition

∴ white in colour.

Q. $MnO_4^-$ (or $K\overset{+7}{Mn}O_4$) ⇒ purple.

$Mn^{+7}$ : $[Ar] 4s^0 3d^0$ ⇒ No d-d electronic transition.

⇒ Charge transfer

# Compounds of d-block elements & their magnetic properties

(a) Diamagnetic ⇒ All the $e^-$ are paired.

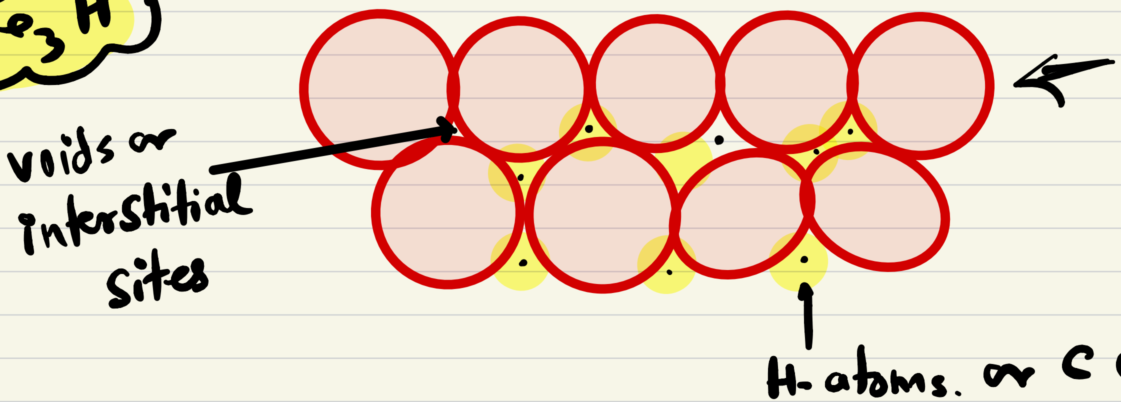
(b) Paramagnetic ⇒ Atleast one unpaired $e^-$.

magnetic moment (spin only), $\mu = \sqrt{n(n+2)}$ B.M

$n$ = no. of unpaired $e^-$.

## Formation of interstitial Compounds: → Can be non-stoichiometric

$Fe_3H$




$TiH_{1.7}$ ; $ZrH_{1.9}$

$H_2O$ (2:1)

$CO_2$ (1:2)

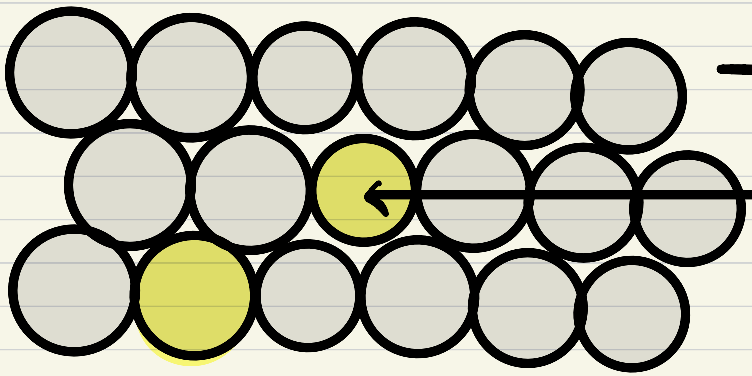
$Fe_2O_3$ (2:3)

Metallic compounds that consist of crystal latice of atoms in which smaller atoms occupy interstitial sites.

**Alloy formation:** Homogeneous mixture of metal with metal or metal & non-metal.

# d-block elements readily form alloys.
↓
Similar atomic radii & other properties.

Ex: **Steel alloy**
Fe + Cr + V + Mo + W + Mn.



→ Fe metal crystal lattice

← Cr atom.

**Oxides of d-block elements:**

$MO$, $M_2O_3$, $MO_2$, $M_2O_4$, $M_2O_5$, $MO_3$, $M_2O_7$

| S.No | General Formula of Metal oxide | Examples |
| --- | --- | --- |
| 1. | $MO$ | Any 3d series metals except Sc<br>M = Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn |
| 2. | $M_2O_3$ | M = Sc, Ti, V, Cr, Mn, Fe |
| 3. | $MO_2$ | M = Ti, Cr, Mn |
| 4. | $M_2O_4$ | M = V |
| 5. | $M_2O_5$ | M = V |
| 6. | $MO_3$ | M = Cr |
| 7. | $M_2O_7$ | M = Mn. |

* Acidic character :-

Higher is O.S of Metal, higher is the acidic character.

$V_2O_3 < V_2O_4 < V_2O_5$

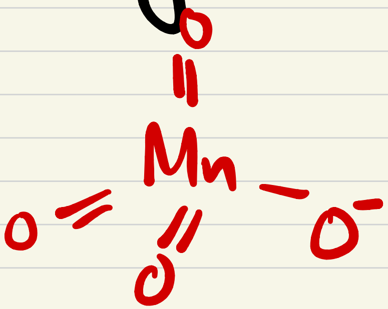
**$Mn_2O_7$ acidic**

# Some Imp. Compounds of d- block elements

1. Potassium permanganate  2. potassium dichromate.

## I. Potassium Permanganate ($KMnO_4$)

$MnO_4^-$



**Preparation:**

From potassium manganate

$$MnO_2 + KOH + O_2 \longrightarrow K_2MnO_4 + H_2O$$

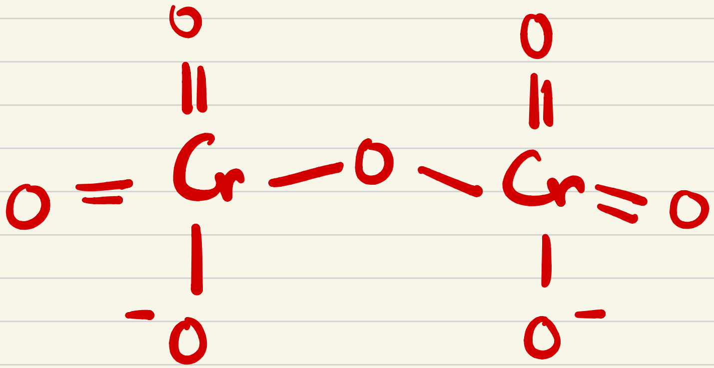
$$K_2MnO_4 + Cl_2 \longrightarrow KMnO_4 + KCl$$

$MnO_4^-$ permanganate

$MnO_4^{2-}$ manganate

## II) Potassium dichromate $K_2Cr_2O_7$

$Cr_2O_7^{2-}$




$CrO_4^{2-}$ chromate

$Cr_2O_7^{2-}$ dichromate

**Preparation:-** From iron chromite ore

$$FeCr_2O_4 + O_2 + Na_2CO_3 \longrightarrow Na_2CrO_4 + Fe_2O_3 + CO_2$$

Chromate

$$Na_2CrO_4 + H^+ \longrightarrow Na_2Cr_2O_7 + H_2O$$

(dichromate)

$$Na_2Cr_2O_7 + KCl \longrightarrow K_2Cr_2O_7 + NaCl$$

(pot. dichromate)

# Balancing of Redox reactions

→ add$^n$ of $e^-$.

$\overset{+6}{Cr_2O_7^{2-}}$ ⟶ $Cr^{3+}$ (red$^n$) (acidic)

$\overset{+7}{MnO_4^-}$ ⟶ $Mn^{2+}$ (red$^n$) (acidic medium)

⟶ $\overset{+4}{MnO_2}$ (red$^n$) (alkaline medium)

**Oxid$^n$** → loss of $e^-$.

$I^- \rightarrow I_2$

$H_2S \rightarrow S$

$Sn^{2+} \rightarrow Sn^{4+}$

$Fe^{2+} \rightarrow Fe^{3+}$

$C_2O_4^{2-} \rightarrow CO_2$

$S^{2-} \rightarrow S$

$SO_3^{2-} \rightarrow SO_4^{2-}$

$NO_2^- \rightarrow NO_3^-$

$I^- \rightarrow IO_3^-$ (basic medium) or neutral

$S_2O_3^{2-} \rightarrow SO_4^{2-}$ (basic medium) or neutral.

**Q.** $MnO_4^- + Fe^{2+} + H^+ \longrightarrow$ ⇝ indicates that rxn is in acidic medium.

Complete & balance it.

$MnO_4^- + Fe^{2+} \longrightarrow Mn^{2+} + Fe^{3+}$ (acidic medium)

Half-cell rxns:-

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

$-1 + 8 = +7$ $\qquad\qquad$ $+2 + 0 = +2$

atoms ✓

Oxygen → $H_2O$ ✓

Hydrogen → $H^+$

charge → $e^-$

(II) $Fe^{2+} \longrightarrow Fe^{3+} + 1e^-$ ] × 5

$+2$ $\qquad\qquad$ $+3$

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

Q. Complete and balance the following eq$^n$:-

$$MnO_4^- + Fe^{2+} + H_2O \longrightarrow$$

* whenever $H_2O$ is given
↳ basic medium

OR

$$MnO_4^- + Fe^{2+} \longrightarrow \quad \text{in basic medium}$$

Ans:- $MnO_4^- + Fe^{2+} \longrightarrow MnO_2 + Fe^{3+}$

atom ✓
O ⇒ $H_2O$ ✓
H ⇒ $H^+$ ✓
Charge ⇒ $e^-$

Half-cell rxn:

(I) $MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_2 + 2H_2O$

$-1 + 4 = +3$ $\qquad$ $0 + 0 = 0$

(II) $Fe^{2+} \longrightarrow Fe^{3+} + 1e^-$ ] × 3

$(+2) \qquad (+3)$

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

$4OH^-$ $\qquad$ $4OH^-$

$$MnO_4^- + 4H_2O + 3Fe^{2+} \longrightarrow MnO_2 + 2H_2O + 3Fe^{3+} + 4OH^-$$

$$\Rightarrow MnO_4^- + 2H_2O + 3Fe^{2+} \longrightarrow MnO_2 + 3Fe^{3+} + 4OH^-$$

Q Complete and balance the following eqn: 3 marks.

(i) $Cr_2O_7^{2-} + Sn^{2+} + H^+ \longrightarrow$ — acidic medium.

$$Cr_2O_7^{2-} + Sn^{2+} \longrightarrow Cr^{3+} + Sn^{4+}$$

(I) $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$

$-2 + 14 = +12$ $\qquad$ $+6 + 0 = +6$

(II) $Sn^{2+} \longrightarrow Sn^{4+} + 2e^-$ ] × 3

$$Cr_2O_7^{2-} + 14H^+ + 3Sn^{2+} \longrightarrow 2Cr^{3+} + 7H_2O + 3Sn^{4+}$$

atom ✓
O – $H_2O$ ✓
H – $H^+$ ✓
Charge – $e^-$

Same Q. for 1 mark :

$$Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 3Sn^{4+} + 7H_2O$$

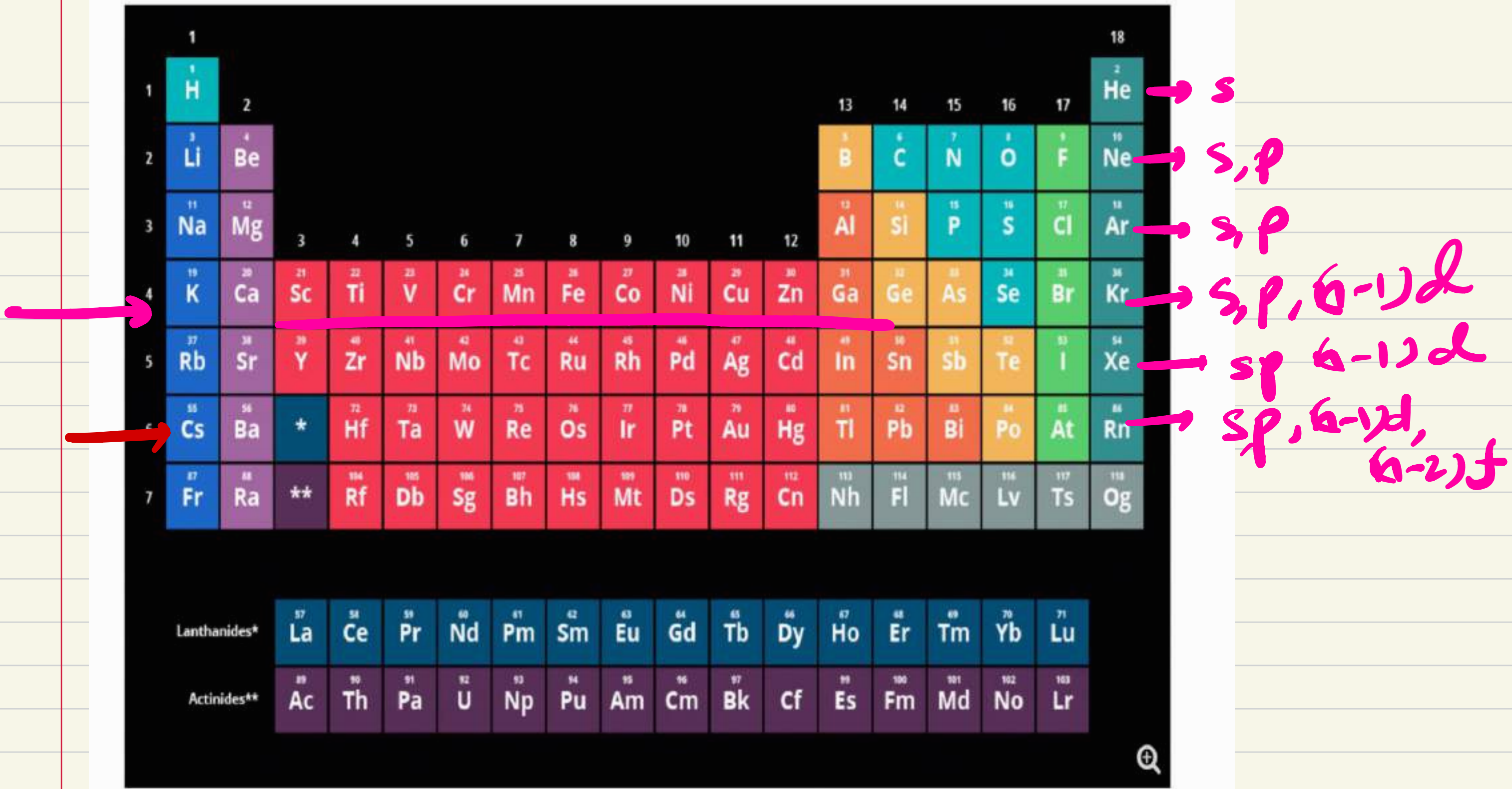
Complete & balance the following eqn: 1 mark

(i) $2MnO_4^- + 5S^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 5S + 8H_2O$

(ii) $Cr_2O_7^{2-} + 3H_2S + 8H^+ \longrightarrow 2Cr^{3+} + 3S + 7H_2O$

(iii) $2MnO_4^- + 5SO_2 + 2H_2O \longrightarrow$ Try yourself.

Next page




The Periodic Table of Elements

## Lanthanoid Contraction: (V. V. V. V. imp).

In lanthanoid series, with increase in atomic no. there is progressive decrease in atomic radii from $La^{3+}$ to $Lu^{3+}$.

**Reason:-** Due to addition of new $e^-$ in f-subshell & poor shielding of one $e^-$ by another in f-orbitals, nuclear charge increases & hence size decreases.

## Consequences:

(1) Atomic size of 4d & 5d transition metals are same. Zr & Hf have similar size.

(ii) Basic strength of oxides & hydroxides of Lanthanoids decreases with increase in at. no

## f-block Elements ⇒ inner transition elements

**Lanthanoids** (Ln) (58-71)

$[Xe]\ 4f^{1-14}\ 5d^{0-1}\ 6s^2$

**Actinoids** (at. no 90 - 103)

$5f^{1-14}\ 6d^{0-1}\ 7s^2$

$(n-2)f^{1-14}\ (n-1)d^{0-1}\ ns^2$

antepenultimate shell or prepenultimate shell.

## General Characteristics of Lanthanoids -

1. Atomic size ⇒ decreases due to Lanthanoid Contraction.

2. Oxidation state ⇒ Most common O.S = +3

But +2, +4 are also possible.

3. Coloured ions → due to f-f electronic transition.

4. Magnetic properties → Most of +3 O.S = paramagnetic

**Lanthanoid Contraction:** The atomic and ionic radii of lanthanoids show gradual decrease with increase in atomic no. It is known as Lanthanoid contraction.

# Extra Q/A

$3d^{10}4s^0$ no d-d transition

$3d^9$ d-d electronic transition.

1. $Zn^{+2}$ salt are white while $Cu^{+2}$ salts are coloured. Why

2. Transition metals & their compounds exhibit a paramagnetic behaviour. Why? T.M = incompletely filled d. orbitals. → same unpaired e⁻ ⇒ paramagnetic

3. Zn, Cd, Hg are soft metals. Why?
completely filled d-orbitals. So they do not have unpaired e⁻ ⇒ Metallic bond is weaker

4. Transition metals & their compounds show catalytic property. Why? ⇒ large surface area & variable Oxidation state.

5. Assign a reason for each of the following:
(i) T.M are hard, have high M.P & B.P ⇒ T.M have incompletely filled d-orbitals. They have unpaired e⁻ So metallic bond is stronger
(ii) I.E of 1st Transition series are found to vary irregularly.

6. Which metal in the first transition series (3d) exhibit +1 O·state most frequently & why?

→ Cu $3d^{10} 4s^{1}$

↓

$Cu^{+1}$ $3d^{10}$ (more stable)

7. Which of the following cations are coloured in aq. soln & why?

$d^{1} \leftrightarrow d^{9}$

$Sc^{3+}$, $V^{3+}$, $Ti^{4+}$, $Mn^{+2}$

Ans: $Sc^{3+} \rightarrow 3d^{0}$, $V^{3+} \rightarrow 3d^{2}$, $Mn^{+2} \rightarrow 3d^{5}$

$V^{3+}$ and $Mn^{+2}$: d-d electronic transition

$Ti^{4+} \rightarrow 3d^{0}$

↑ no d-d transition.

8. What is Misch metal ? Give its one use.

Misch metal is an alloy of lanthanum metal and iron and traces of S, Ca, C or Al.

It is used in making bullets and lighter flint.

## Actinoids

Thorium (90) to Lawrencium (103)

- trans-uranic elements → Man-made elements, with at.no higher than 92, which are prepared by nuclear reactions involving transformation of naturally occuring elements.
- Atomic size decreases in series due to actinoid contraction
- oxidation state → +3 (most common), +4, +5, +6.
- Form coloured complexes

Thorium (Th), Proactinium (Pa) and Uranium (U) ⇒ Natural elements.

Q. Differentiate between Lanthanoids and Actinoids

| Lanthanoids | Actinoids |
|---|---|
| • Last differentiating e⁻ occupies 4f orbital. | Last differentiating e⁻ occupies 5f orbital. |
| They are the elements of first inner transition series. | Elements of 2nd inner transition series |
| Most of lanthanoids are non-radio-active. Except (Promethium) | All are radioactive |
| • do not form oxo cation | form oxo-cations $UO_2^{2+}$, $UO^+$ |
| • Contraction in atomic radii is relatively less | Contraction in atomic radii is relatively greater in actinoids |
| Lanthanoids show +2, +3, +4 ox. state | Actinoids show +3, +4, +5, +6, +7 O.S |
| Less tendency to form complexes | Actinoids have greater tendency to form complex. |
| • Hydroxides are less basic in nature | • More basic in nature. |

1. Why do the transition elements exhibit higher enthalpies of atomisation?
Because of large number of unpaired electrons in their atoms they have stronger interatomic interaction and hence stronger bonding between atoms resulting in higher enthalpies of atomisation.

2. Name a transition element which does not exhibit variable oxidation state. Scandium (Sc)

3. The $E^\circ(M^{2+}|M)$ value for copper is positive (+0.34 V). What is the possible for this?
Cu has a high atomisation energy ($\Delta_a H^\circ$) and low hydration enthalpy ($\Delta_{hyd} H^\circ$).

4. How would you account for the increasing oxidising power in the series $VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$ ?
This is due to increasing stability of lower species to which they are reduced

**Example 8.6** For the first row transition metals the $E^\ominus$ values are:

| $E^\ominus$ | V | Cr | Mn | Fe | Co | Ni | Cu |
|---|---|---|---|---|---|---|---|
| $(M^{2+}/M)$ | −1.18 | − 0.91 | −1.18 | − 0.44 | − 0.28 | − 0.25 | +0.34 |

Explain the irregularity in the above values.

**Solution** The $E^\ominus$ $(M^{2+}/M)$ values are not regular which can be explained from the irregular variation of ionisation enthalpies $(\Delta_i H_1 + \Delta_i H_2)$ and also the sublimation enthalpies which are relatively much less for manganese and vanadium.

**Example 8.7** Why is the $E^\ominus$ value for the $Mn^{3+}/Mn^{2+}$ couple much more positive than that for $Cr^{3+}/Cr^{2+}$ or $Fe^{3+}/Fe^{2+}$? Explain.

**Solution** Much larger third ionisation energy of Mn (where the required change is $d^5$ to $d^4$) is mainly responsible for this. This also explains why the +3 state of Mn is of little importance.

Q Calculate the magnetic moment of a divalent ion in aqueous solution if its atomic no. is 25.

Q. Name a member of the lanthanoid series which is well known to exhibit +4 O.S. Cerium (Z = 58)

Q. Actinoid contraction is greater from element to element than lanthanoid contraction. Why?

due to poor shielding by 5f $e^-$ in actinoids than that by 4f $e^-$ in the lanthanoids.

## Compounds of d-Block Elements

### Potassium Permanganate ($KMnO_4$):

Preparation:-

$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$

or

$$2MnO_2 + 2K_2CO_3 + O_2 \longrightarrow 2K_2MnO_4 + CO_2$$

$$2K_2MnO_4 + Cl_2 \longrightarrow KMnO_4 + 2KCl$$

In Lab: $2Mn^{2+} + S_2O_8^{2-} + 8H_2O \longrightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$

($S_2O_8^{2-}$: peroxodisulphate)

## Chemical property :

**Redox rxn :**

| acidified $KMnO_4$ | | Neutral or alkaline $KMnO_4$ |
|---|---|---|
| $H_2S \longrightarrow S$ | | $Br^- \longrightarrow BrO_3^-$ |
| $SO_2 \longrightarrow SO_4^{2-}$ | | $I^- \longrightarrow IO_3^-$ |
| $NO_2^- \longrightarrow NO_3^-$ | | $S_2O_3^{2-} \longrightarrow SO_4^{2-}$ |
| $Fe^{2+} \longrightarrow Fe^{3+}$ | | $Mn^{2+} \longrightarrow MnO_2$ |
| $Cl^- \longrightarrow Cl_2$ | | |
| $HCOOH \longrightarrow CO_2 + H_2O$ | | $MnO_4^- \longrightarrow MnO_2$ |
| $H_2C_2O_4 \longrightarrow CO_2 + H_2O$ | | |
| $S_2O_3^{2-} \longrightarrow S_4O_6^{2-}$ | | |
| $MnO_4^- \longrightarrow Mn^{2+}$ | | |

# Potassium Dichromate ($K_2Cr_2O_7$):

**Preparation:**

$$\underset{\text{(Chromite ore)}}{FeO.Cr_2O_3} + Na_2CO_3 + O_2 \longrightarrow Na_2CrO_4 + Fe_2O_3 + CO_2$$

$$Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

$$Na_2Cr_2O_7 + KCl \longrightarrow K_2Cr_2O_7 + NaCl$$

## Practice Qs:-

1. Give reason: Zirconium ($Z=40$) & Hafnium ($Z=72$) have almost similar atomic radii.

Ans: Due to lanthanoid contraction.

2. Is the variability of oxidation number of transition elements different from that of non-transition elements? Illustrate with examples.

Ans. Yes. In transition elements, oxidation state differ by unity whereas in non-transition elements the oxidation state differ by 2.

3. Why is the E° value for $Mn^{3+}/Mn^{2+}$ couple much more positive than that for $Cr^{3+}/Cr^{2+}$ or $Fe^{3+}/Fe^{2+}$? Explain. (Try yourself)

4. Give reason: d-block elements exhibit more oxidation states than f-block elements.

Ans: d-block elements exhibit more oxidation states because of comparable energy gap between $(n-1)d$ & $ns$ subshell. whereas f-block elements have large energy gap b/w $(n-2)f$ & $(n-1)d$ subshell.

5. $E^\circ$ of Cu is $+0.34$ V while that of Zn is $-0.76$ V. Explain.

Ans: $E^\circ$ value for copper is positive because the high energy to transform $Cu(s)$ to $Cu^{2+}(aq)$ is not balanced by its hydration enthalpy. whereas $E^\circ$ value for zinc is negative due to greater stability of $Zn^{2+}$.

Q.6 Following are the transition metal ions of 3d series: $Ti^{4+}$, $V^{2+}$, $Mn^{3+}$, $Cr^{3+}$.

Answer the following:-

i) Which ion is most stable in an aqueous $sol^n$ & why?

ii) Which ion is a strong oxidising agent & why?

iii) Which ion is colourless & why?

Ans i) $Cr^{3+}$ is most stable in an aqueous $sol^n$ due to stable $t_{2g}^3$ configuration.

ii) $Mn^{3+}$ is a strong oxidising agent because of its high tendency to get reduced to more stable $Mn^{2+}$ ($3d^5$ configuration)

Q7. Which is a stronger reducing agent $Cr^{2+}$ or $Fe^{2+}$ & why? (Try yourself)

Q8. Of the $d^4$ species, $Cr^{2+}$ is strongly reducing while manganese (III) is strongly oxidising. Explain.

Ans: $Cr^{2+}$ is strongly reducing in nature. It has a $d^4$ configuration. While acting as reducing agent, it gets oxidised to more stable $Cr^{3+}$ $t_{2g}^3 e_g^0$. In the case of $Mn^{3+}$, $d^4$, it act as oxidising agent & gets reduced to $Mn^{2+}$ ($3d^5$)

Q9. Name the following: A member of the lanthanoid series which is well known to exhibit +4 oxidation state.

**Ans:** Cerium [ Ce ]

Q10. Name an important alloy which contains some of the lanthanoid metals. Mention its two uses.

**Ans:** Mischmetals is well known alloy which consist of lanthanoid metals (about 95%), iron (about 5%) and traces of S, C, Ca, Al etc.

**Uses:** Used in Mg based alloy to produce bullets shells & lighter flint.

Q11. Write one similarity and one difference between the chemistry of lanthanoid & actinoid elements.

Ans: Similarity: The elements of both the series are electropositive in nature. They are reactive metals & act as strong reducing agents.

Difference: Lanthanoids except promethium are non-radioactive elements, while all the actinoids are radioactive elements.

Q12 Chemistry of actinoids is complicated as compared to lanthanoids. Give two reasons.

Ans i) Most of the actinoids are radioactive & the study of their chemistry in the laboratory is difficult.

ii) Actinoids show greater no of oxidation state due to the comparable energies of 5f, 6d & 7s orbitals.

Q13. Assign reason for the following:
From element to element actinoid contraction is greater than lanthanoid contraction.

Ans: The actinoid contraction is more than lanthanoid contraction because of poor shielding by $5f-e^-$.

Q14. With reference to structural variability and chemical reactivity, write the differences between lanthanoids & actinoids.

Ans: Structure: All the lanthanoids are silvery white soft metals.
The actinoids display a variety of structures.
↳ also silvery in appearence

<u>Chemical reactivity</u> : Earlier members of lanthanoid series are quite reactive similar to Ca but with increasing atomic no. they behave more like aluminium.

The actinoids are highly reactive in finely divided state.

Q15. Compare the chemistry of the actinoids with that of lanthanoids with reference to

i) electronic configuration

ii) Oxidation states

iii) chemical reactivity.

—x—