"Bringing Excellence to Students"

Handwritten Notes
on
D & F Block

d and f-block elements

d-Block elements

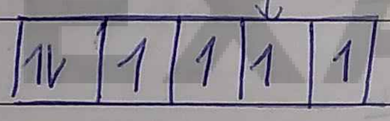
Those elements in which last electron enters into penultimate d-subshell.

$E.C = [noble\ gas]\ (n-1)d^{1-10}\ ns^2$

Transition elements: Those elements which contain partially filled d-subshell either in ground state or most common oxidation state.

Ex1 $Fe\ (Z=26)$

$E.C = [Ar]^{18}\ 3d^6\ 4s^2$



3d

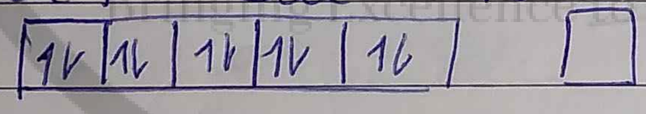
∴ d block element

∴ transition element

Ex-2 $Cu\ (Z=29)$

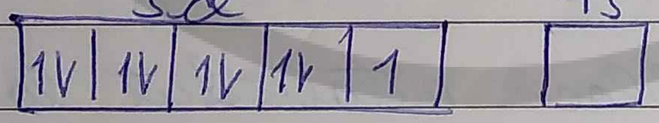
$E.C = [Ar]^{18}\ 3d^{10}\ 4s^1$ ∴ d block metal

Cu^+ :



3d 4s

Cu^{2+}



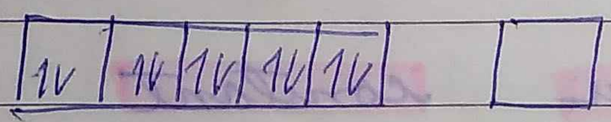
∴ Cu is a transition metal.

3d 4s

Ex3 $Zn\ (Z_n=30)$

$E.C = [Ar]^{18}\ 3d^{10}\ 4s^2$ ∴ d block metal.

Zn^{2+} : $[Ar]^{18}$



3d 4s.

∴ Zn is not a transition metal.

Zn, Cd, Hg are d block metal but not

Transition metals.

"All transition metals are d-block metals but all d-block metals can not be transition metal"

Position of d-block element in periodic table

3d series = 10 elements (Z = 21 — 30)
4d series = 10 elements (Z = 39 — 48)
5d series = 10 elements (Z = 57 — 72 — 80)
6d series = 10 elements (Ac : Z = 89 — 104 — 112)

$E.C = (n-1)d^{1-10} ns^{0-2}$

Exceptional configuration
Cr : $3d^5\ 4s^1$
Cu : $3d^{10}\ 4s^1$

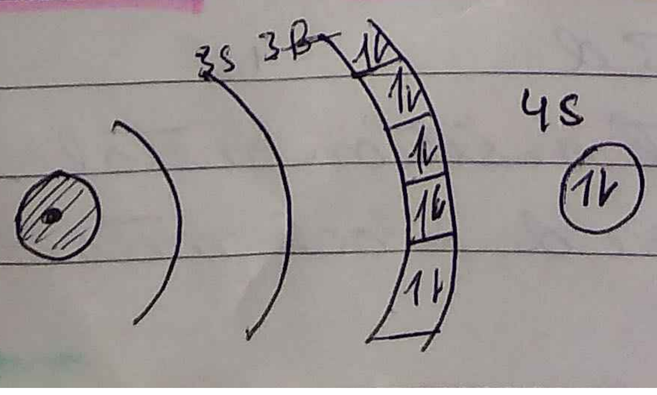
- Physical properties

I Atomic Radii :
Smaller than s-block metals but larger than p-block elements.

- In a series
3d : Sc Ti V Cr Mn Fe Co Ni Cu Zn

decreases constant increases.

Reason :



- unpaired d electron are involved in covalent bond formation.
- Covalent bond is stronger than metallic bond
- Due to weak metallic bonding Hg exists in liquid state.

- Sc – Cr : Due to increase in effective nuclear charge size decreases.

- Mn – Ni : Due to e^- pairing there is repulsion and Zeff is balanced by electronic repulsion. Hence size remains constant (atomic radii)

- Cu – Zn : Zeff < electronic repulsion
electronic repulsion dominate hence atomic radii increases.

- Groups : 3d : atomic radii increases from 3d to 4d.
4d : atomic radii decreases from 4d to 5d.

4f
5d

Ex (4d) Zr = 160 pm
(5d) Hf = 159 pm
Reason : Lanthanoid contraction

2 Metallic character
- All d block elements are metal.
- Hard, malleable, ductile metals (except Hg = liquid).
- Zn, Cd = soft metals.

E.C : $(n-1)d^{1-10}$ ns^{2-1}
↓ ↓
covalent bond metallic bond
(d – d)

Zn : $3d^{10}4s^2$
Cd : $4d^{10}4s^2$ } Mutallic bond only, no covalent
Hg : $5d^{10}4s^2$ } bond.

Fe : $3d^6 4s^2$ ---→ unpaired e^- : hard metal.

- Ductile metals have CCP lattice.
- B.P also called ΔH atomisation.
- M.P / B.P ∝ unpaired electron = metallic bonding.

- Type of lattice

CCP → Ag, Au, Pt, Cu.
HCP → Ru, Rh, Cd.

– High m.p and high Br.p.

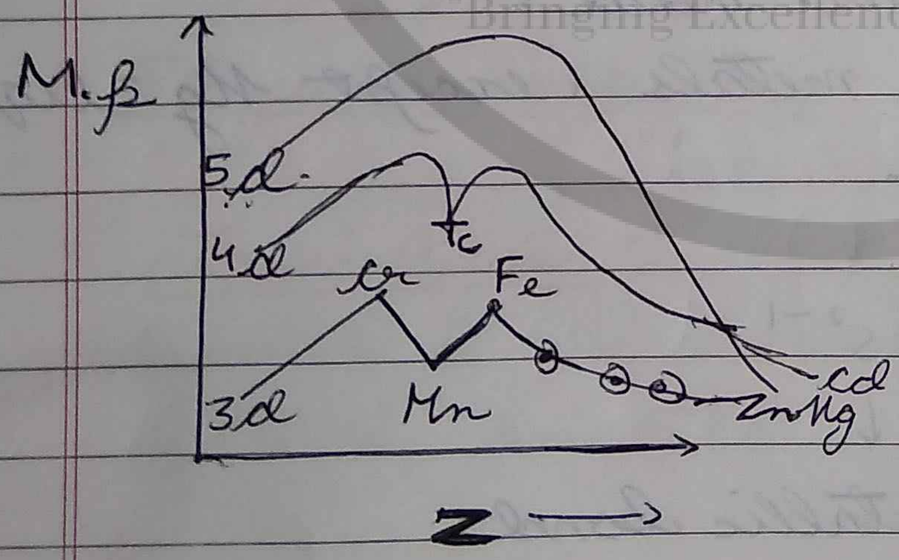
– These metals show high thermal and electrical conductivity.
Ag – (Best conductor)

3 Melting point and boiling point

– High melting and boiling point.

solid ⟶ liquid ⟶ Vapour.

- ΔH atomisation is very high due to strong metallic bonding.



Reason

Ti – $3d^2 4s^2$
V – $3d^3 4s^2$
Cr – $3d^5 4s^1$
Mn ——— $3d^5 4s^2$ ↓ d orbital exactly half filled
Fe $3d^6 4s^2$

✡ Abnormally low m.p of Mn and Tc is due to their stable configuration (i.e d orbital don't take part in metallic bonding).

4 High Density : $d = \frac{\text{mass}}{\text{volume}}$.

— They have high density :

— lowest density (Sc = 3.5 g/cc)
highest density (Ir = 22.6 g/cc)

- Series → with increasing atomic no density also increases (mid-way).

- Ionisation energy -

- Due to high Zeff and small size, d-block metals are having high I.E.

- In a series I.E gradually increases due to increase in Zeff.

- I.E$_1$ of Zn, Cd, Hg is very high (stable E.C)

- I.E$_1$ of Mn is very high ($3d^5 4s^2$)

- I.E$_2$ of Cr ($3d^5 4s^1$) and Cu is ($3d^{10} 4s^1$) very high.

- Ionisation energy helps us to predict the thermodynamic stability of oxidation state.

~~Ni~~	$I.E_1 + I.E_2$	$I.E_1 + I.E_2 + I.E_3 + I.E_4$
Ni	2.46×10^3 kj/mole	11.9×10^3 KJ/mole.
Pt	2.66×10^3 kj/mole	9.6×10^3 KJ/mole.

- down the group Zeff increases I.E increases.
- from left to right I.E. increases regularly

∴ Ni (II) is more stable than Pt (II).

∴ Pt (IV) is more stable than Ni (IV)

- **Oxidation state**

- Transition metals exhibits variable O.S exept first and last member of each series.

- These elements have electrons in valence s-subshell and penultimate d sub-shell, and they can use both due to small energy difference.

E.C ⑪ ① ① ① ① ⑪
(n-1)d ns

- They can show +ve, -ve and even 0 oxidation state.

- 3d series : Most common O.S is +2 except Sc (+3)
  - Max — (Mn : +7) in $K\overset{+7}{M}nO_4$

- In the periodic table: highest O.S is shown by Os, Ru : +8

- Higher O.S of metal is shown with either F or oxygen.

- Nature of metal

In Higher O.S = covalent nature
lower O.S = ionic nature.

Ex $\overset{+2}{Mn}Cl_2$ $\overset{+7}{Mn_2O_7}$
ionic covalent

- Magnetic Properties

- Most of the transition metal and their compounds are paramagnetic.

- Higher the number of unpaired electron higher will be paramagnetism.

- $\mu = \sqrt{n(n+2)}$ B.M
n = no. of unpaired electrons.

Q1 Compare the magnetic moment of Fe, Co, Ni

sol Fe : (Z = 26) : | ↑↓ | 1 | 1 | 1 | 1 | ↑↓ | 1 | 1 | 1 | = 4e⁻
Co : (Z = 27) : | ↑↓ | ↑↓ | 1 | 1 | 1 | ↑↓ | 1 | 1 | 1 | = 3e⁻
Ni : (Z = 28) : | ↑↓ | ↑↓ | ↑↓ | 1 | 1 | ↑↓ | 1 | 1 | 1 | = 2e⁻

Fe > Co > Ni

Q2 Which one is most magnetic?
(I) $CuSO_4$ (II) $ZnSO_4$ (III) $Cr_2(SO_4)_3$ ✓

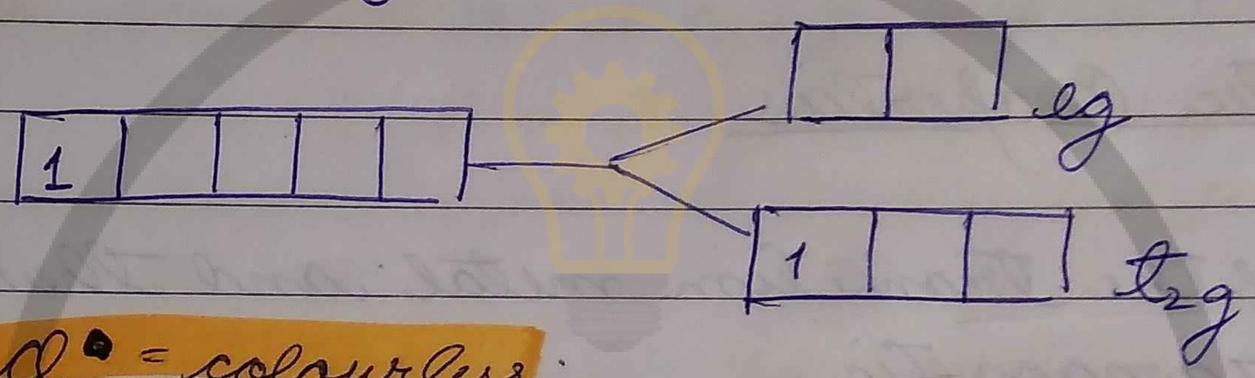
Cu^{2+} = $3d^9\ 4s^0$ = 1e⁻ $\mu = \sqrt{1(1+2)}$ B.M
Zn^{2+} = $3d^{10}\ 4s^0$ = 0e⁻
Cr^{3+} = $3d^3\ 4s^0$ = 3e⁻ $\mu = \sqrt{3(3+2)}$ B.M

Formation of coloured ions

- d-block compounds and their aqueous solution are coloured.

Reason :

- Colour mainly arises due to d-d Transition.



- d^0 = colourless
- d^{10} = colourless
- $d^{2-}d^9$ = coloured.

Q Which of the following are coloured.
I) $ScCl_3$ II) $ZnSO_4$ III) $FeCl_3$ ✓

sol
$Sc^{3+} = 3d^0$ $Zn^{2+} = 3d^{10}$ $Fe^{3+} = 3d^5$

☆ $K_2Cr_2O_7$ and $KMnO_4$ are coloured.

$Cr = +6 = 3d^0$ $Mn = +7 = 3d^0$
$3d^5 4s^1$ $Mn = 3d^5 4s^2$

☆ Reason : I.M.P due to charge transfer spectra.

due to repulsion between oxygen transfers

- Cu does not react with dil acid. and reacts with conc. HNO_3 and conc. H_2SO_4 but H_2 gas is not evolved. It is a poor reducing agent.

- **Electrode potential** (E^{2+}_{M}/M)

3d series

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

$M(s) \longrightarrow M_{(v)}$ $\Delta H_{sub} = +ve$

$M(v) \longrightarrow M^{+}(g)$ $\Delta H_{I.E_1} = +ve$

$M^{+}(g) \longrightarrow M^{2+}(g)$ $\Delta H\ I.E_2 = +ve$

$M^{2+}(g) + aq \longrightarrow M^{2+}_{aq}$ $\Delta H_{hyd} = -ve$

$M(s) \longrightarrow M^{2+}(aq)$ $\Delta H = \Delta_s + \Delta H_{I.E_1+I.E_2} + \Delta H_{hyd}$

- **3d series**

Except Cu ($E^\circ = +0.34\ V$) all metals have -ve E° reduction.

- Copper metal can not evolve H_2 gas when reacts with dil. acid

Reason :

Δ Hyd of Cu can not compensate large values of $\Delta H_s + \Delta H_{I.E}$

- E°_{Zn}, E°_{Mn} is more negative than expected (due to stable configuration)

★ $E^\circ\ M^{3+}/M^{2+}$

Ti V Cr — Mn Fe Co

-ve — +ve

strong R.A in Ti^{2+}, V^{2+}, Cr^{2+} in (+2 state). ⇓ +3 state more stable

strong O.A in +3 State ⇓ +2 state more stable

- **Complex formation**

Ex → $K_4[Fe(CN)_6]$

d-Block elements show high tendency to form complex due to →

(i) High Z_{eff}

↓

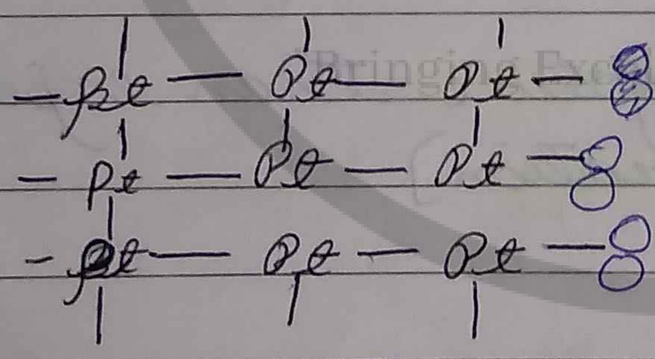
they can attract ligand around them.

(ii) They have vacant d orbital.

- **Catalytic activity**

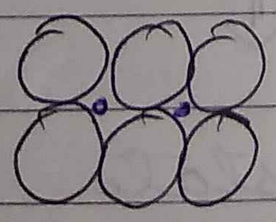
– Transition metal and their compounds show catalytic activity.

due to its ability of formation of transition state and variable O.S.



- **Formation of interstitial compounds**

– Transition metals form interstitial compounds with small size atoms such as C, H, N etc.



– Generally non-stochiometric.

Hard metals, melting point increases, chemically inert.

- Alloy formation
  - Easily forms alloy due to similar size.
  - Hg - amalgam
  - ☆ - (Fe), (Pt) do not form amalgam, hence can be used to store Hg.
  - Properties of alloy
    - Hardness ↑, m.p ↑, chemically inert.

- Chemical Properties
  - ☆ - low chemical reactivity due to:
    - High $\Delta H_{sublimation}$
    - High I.E
    - low ΔH_{hyd}.

- Oxides

M + air $\xrightarrow{\text{high temp}}$ metal oxide

Lower O.S	Higher O.S	Intermediate O.S
MnO	Mn_2O_7	MnO_2
Basic	Acidic	Amphoteric
Ionic	Covalent	Covalent

- $Na_2Cr_2O_7$ is more soluble in water as compared to $K_2Cr_2O_7$

Potassium dichromate ($K_2Cr_2O_7$)

→ Obtained from chromite ore $FeO.Cr_2O_3$

Preparation

I Conversion of chromite ore into sodium chromate

$$FeO.Cr_2O_3 + Na_2CO_3 + air \xrightarrow[\text{Roasting}]{} Na_2CrO_4 + Fe_2O_{3(s)} + CO_2\uparrow$$

II Conversion of sodium chromate into sodium dichromate.

$$Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7$$

yellow solution → orange

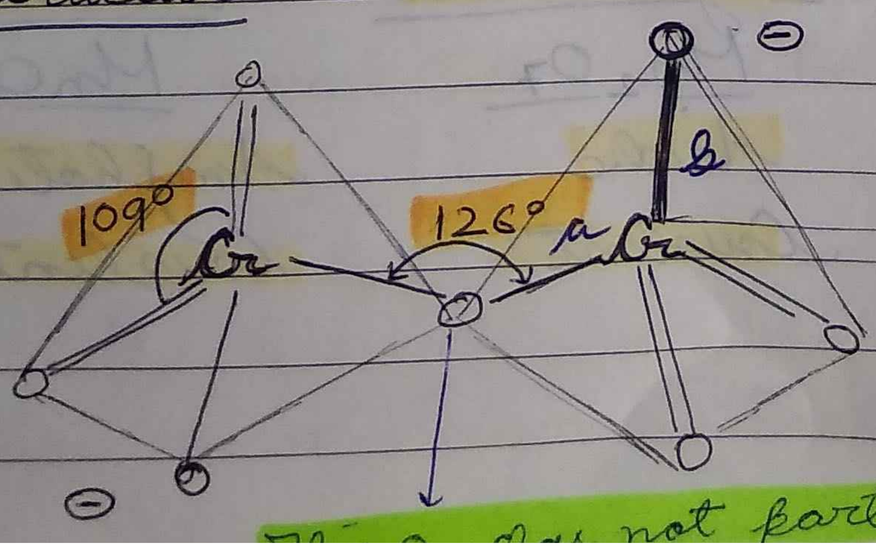
III Conversion of sodium dichromate into potassium dichromate.

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

↓

orang crystalline solid.

- Structure

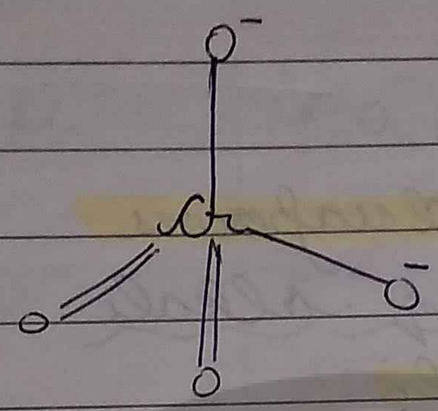


→ sp^3 $b \neq a$

do not participate in resonance.

- $K_2Cr_2O_7$ is strong O.A but weaker O.A than Cl_2.

- 6 Cr–O bond lengths are equal. (resonance) ☆
- $Cr = \overset{\delta^-}{O} \longrightarrow \sigma \quad \pi\ (p\pi - d\pi)$
- CrO_4^{2-}



all bond lengths are equal.

- Properties

- Potassium dichromate and chromate ions are interconvertible depending upon the pH of solution in aq medium.

☆ $Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-} + 2H^+$
orange yellow

Acidic $\rightarrow H^+ \rightarrow$ orange, Basic $\rightarrow OH^- \rightarrow$ yellow.

- As an oxidising agent

$\overset{+6}{K_2Cr_2O_7}$ $(E^\circ red = +1.33\ V)$

$\overset{+6}{Cr_2O_7} + 6e^- \longrightarrow 2Cr^{3+}$ $\quad E = \frac{M}{6}$

- $KI \longrightarrow I_2$
- $KCl \longrightarrow Cl_2$
- $CH_3COOH \longrightarrow CO_2$
- $H_2S \longrightarrow SO_2$
- $Fe^{2+} \longrightarrow Fe^{3+}$

} Powerful O.A.

★ Chromyl chloride test

$NaCl$ + $K_2Cr_2O_7$ + conc. H_2SO_4

Chloride salt

$\downarrow \Delta$

(CrO_2Cl_2) Orange red vapours

$\downarrow$ aq. alkali

yellow soln

(Na_2CrO_4) ⟶ (Na_2CrO_4)

★★★ IMP → This test is not given by chlorides of Ag, Hg, Pb, Zn, Sb → antimony

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• Potassium permanganate $KMnO_4$

Ore : MnO_2 (pyrolusite)

Preparation

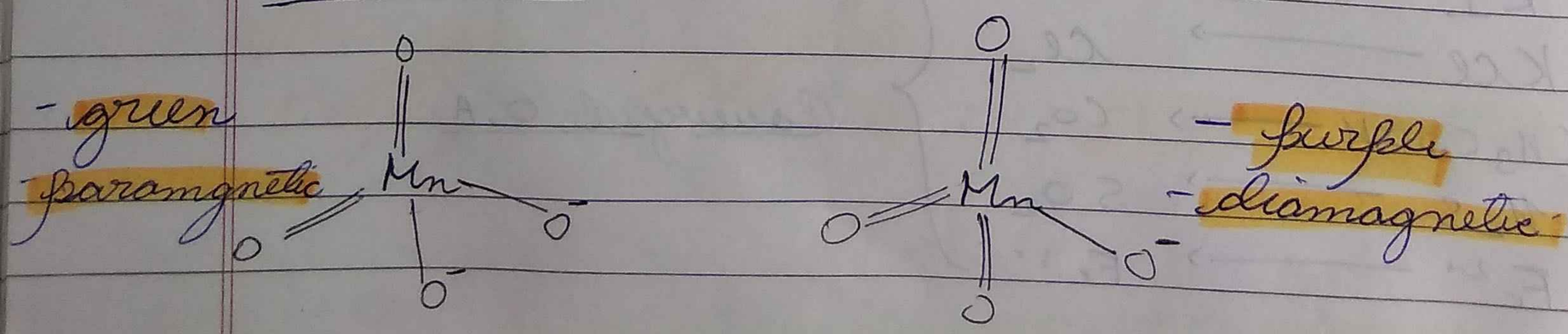
I $MnO_2 + KOH + KNO_3 \xrightarrow{\text{fusion}} K_2MnO_4$ (green solution)

II Oxidation of K_2MnO_4

$K_2\overset{+6}{Mn}O_4 \xrightarrow{\text{electricity}} \overset{+7}{KMn}O_4 \longrightarrow$ solid

(purple solution)

structure



☆ $KMnO_4$ behaves as weak O.A in basic medium as compared to when present in other medium.

Properties : strong O.A

Acidic	Neutral	Basic
$\overset{+7}{Mn}O_4^- \longrightarrow Mn^{2+}$	$\overset{+7}{Mn}O_4^- + 3e^- \rightarrow MnO_2$	$MnO_4^- + e^- \longrightarrow \overset{2-}{Mn}O_4$
$E^\circ = 1.52V$	$E^\circ = 1.69\ V$	$E^\circ = 0.53V$
	Strongest	
$E^\circ = \frac{M}{5}$	$E = \frac{M}{3}$	$E = \frac{M}{1}$
(i) ✓ $KI \longrightarrow I_2$	☆ CH_2 ‖ CH_2 → CH_2 \ / O / CH_2	✓ $KI \longrightarrow KIO_3^-$
$H_2S \longrightarrow S$		$Na_2S_2O_3 \longrightarrow Na_2SO_4$
COOH | COOH $\longrightarrow CO_2$	$KMnO_4 \rightarrow KMnSO_4$	
$NO_2^- \longrightarrow NO_3^-$		

☆ · It behaves as the strongest O.A in neutral medium, and also called Bayers reagent To convert alkenes to epoxide

✓. Also used volumetric titration of Fe^{2+} and iodide.

f-Block elements

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

4f ⇒ Lanthanoids

* Promethium (Pm) is radioactive.

☆ Lanthanum and Actinium are d-block elements.

5f ⇒ Actinoids
- → all are radioactive
- 3 elements (natural)
- 11 metal (synthetic)

- **Atomic radii**

Gradual decrease in atomic / ionic radii

→ Lanthanoid contraction
→ Actinoid contraction

Due to imperfect shielding of nucleus by f-orbitals.

- **Oxidation state**

Lanthanoids : +2, +3, +4

Actinoids : +2, +3, +4, +5, +6

Most stable O.S is +3

$M^{2+} \longrightarrow M^{3+} + e^-$ (R.A)
most stable

$M^{4+} + e^- \longrightarrow M^{3+}$ (O.A)

- Colour → f-f- transition

☆ :
- Ionisation Energy → low, hence highly reactive
- Magnetic nature → most paramagnetic