

①

### d and f-block Elements.

Position in Periodic Table:-

d-block elements - Group-3 to Group-12.

f-block elements:-

Lanthanides (57-71)  
 4f  
 5f  
 → actinides (89-103)

laste fill in ↓  
 3d series - Iup  
 " 4d series - ✓  
 " 5d series - ✓  
 " 6d series - ✗

→ Scandium Titanium Vanadium Chromium Manganese Iron  
 Sc Ti V Cr Mn Fe

Cobalt Nickel Copper Zinc  
 Co Ni Cu Zn

→ Yttrium Zirconium Niobium Molybdenum Ruthenium Palladium Cadmium  
 4 2s Nb Mo Tc Ru Rh Pd Ag Cd  
 Technetium Rhodium Silver

→ Lanthanum Tantalum Rhenium Iridium Gold  
 La Hf Ta W Re Os Ir Pt Au Ag  
 Hafnium Tungsten Osmium Platinum Mercury

Actinium Dubnium Beryllium Neitrogenium Roentgenium  
 Ac Rf Db Sg Bh Hs Mt Ds Kg Cf.  
 Rutherfordium Seaborgium Hassium Darmstadtium Copernicium  
 Ac Rutherford Seaborg Hassium Darmstadtium Copernicium Country

Electronic Configuration:-

General  $\rightarrow$   $(n-1)d^{10} ns^2$

E.C.

or  $(n-1)d^{10} ns^1$  except Palladium (Pd)  $Z=46$

$(Z=21-30)$

$3d \rightarrow Sc\ Ti\ V\ Mn\ Fe\ Co\ Ni$

$(Z=39-48)$

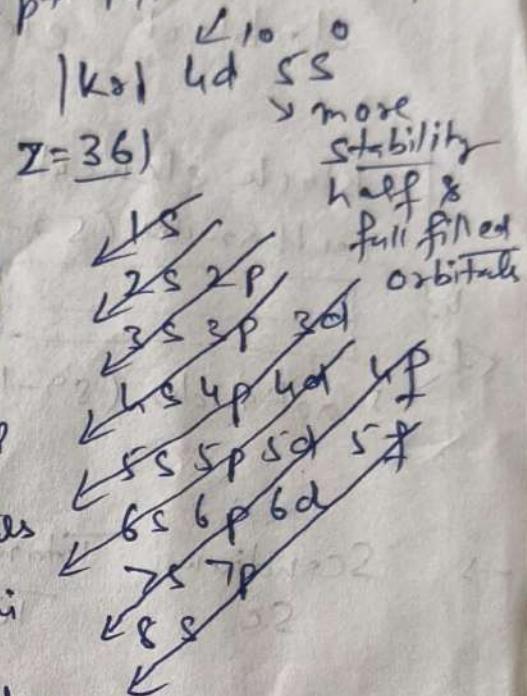
$4d \rightarrow Y\ Zr\ Nb\ Mo\ Tc\ Ru\ Rh$

$5d \rightarrow La\ Hf\ Ta\ W\ Re\ Os\ Ir\ Pt$

$(Z=57, 72-80)$

Cu	Zn
Ag	Cd
Au	Hg

Coinage metals  
M.P.R.P.  
Low solvability  
metals



Trick  $3d \rightarrow$  Science Teacher Vinits Crimani  
man fe Co Ni Cu  $2n]$   
Kyun 2aa 2alati ho

$4d \rightarrow$  Yari 2aa Nibha Maat Tak Rukavat Rahi Pade Aggi  
 $(ca) 254] 5t$

$5d \rightarrow$  La Hafsa Warha Re uholas Idhar Pitai Aas Hogi.

Exceptional  $\rightarrow$  (46) Pd  $\rightarrow [Ar] 4d^5 5s^0$  — full filled d-orbital (stability)

$\bar{e}$  configuration  $C_8 \rightarrow [Ar] 4s^1 3d^5 \rightarrow$  half filled d-orbital (stability)

$C_u \rightarrow [Ar] 4s^1 3d^{10} \rightarrow$  full filled d-orbital (stability)

Exceptional :  $\rightarrow$  Nb Cu Cr Mo Tc Ru Rh Pd Ag  $\boxed{Xet 54}$   
 $\bar{e}$  configuration Nawabi Kyun kare maat tak Ruka Rah Padgi Age Pt Au  
Trick: -  $[Ar] 4s^2 3d^4$   $\rightarrow$  one e difference extra in (d)

$[Ar] 4s^1 3d^5$   $\rightarrow$  one e difference extra in (d)

\* Transition elements:-

→ Which has incompletely filled d-orbitals in its ground state or in any one of its oxidation states.

e.g. SC :-  $[Ar] 4s^2 3d^1$  incompletely filled d-orbital

but Cu :-  $[\text{Ar}] 4s^1 3d^9$ ; in  $\text{Cu}^{2+} \rightarrow [\text{Ar}] 3d^9$   
 $2u^{2+} \rightarrow [\text{Ar}] 3d^10$   
 $2u \rightarrow [\text{Ar}] 4s^2 3d^10 \rightarrow \text{Non-Transition}$

$\rightarrow$   $Zn$ ,  $Cd$  &  $Hg$  of group  $\frac{10}{12}$  have full  $3d^{10}$  configuration in their ground state as well as in their common oxidation states and hence, are not regarded as transition metals.

$$\text{e.g. } \begin{array}{l} 2^{\text{h}} \rightarrow [Ar] 4s^2 3d^{10}, \\ 2^{\text{e}} = 30 \end{array}$$

$$Z=48 \rightarrow [Ar] 4s^2 3d^{10}, Cd^{2+} \rightarrow [Ar] 3d^{10}$$

$$\text{Hg} \rightarrow 1s^2 2p^6 3s^2 3p^6 3d^10 4s^2 \quad , \quad \text{Hg}^{2+} \rightarrow 1s^2 2p^6 3s^2 3p^6 3d^10$$

all d-block

Note: All the transition elements are d-block elements, but are not transition.

Ques: The value of magnetic quantum no. of the outermost  $e^-$  of  $Zn^+$  ion

~~transition elements~~  $\frac{1}{2} \uparrow \frac{1}{2} \downarrow L-1/2$

$$\text{Ans: } - \quad \underline{2} = 30(24) \\ \text{atomic} \\ \text{No.}$$

$$76^+ = 29$$

$$= \text{Ar} \text{ } 4s^1 3d^0$$

18 Azimuthal quantum no.  
 $\Sigma \pi \quad \varphi = 0$

Number	Symbol	Values
1. Principal Quantum No.	$m$	$1, 2, 3, 4 \dots n$
2. Angular Momentum Quantum No.	$\ell$	$0, 1, 2, 3 \dots (n-1)$
3. Magnetic //	$m_\ell$	$-\ell, -\ell+1, 0, 1, \dots \ell$
4. Spin //	$m_s$	$+1/2, -1/2$

So  $m=0$   
Magnetic quantum No:

	for $n=1$ S-subshell $\ell=0$	$n=2$ , P, $\ell=1$	$n=3$ , d, $\ell=2$	$n=4$ , f, $\ell=3$
No. of orbital ( $2\ell+1$ )	1	3	5	7
$m_l =$	0	-1, 0, +1	-2, -1, 0, +1, +2	-3, -2, -1, 0, +1, +2
				+3

### \* - Physical Properties:-

→ All the transition elements display typical metallic properties such as tensile strength, ductility, malleability, high thermal & electrical conductivity, metallic lustre.

→ With the exceptions of  $Zn, Cd, Hg, Mn$ , they have one or more typical metallic structures at normal temperatures like monoclinic, cubic, hexagonal, orthorhombic etc.

→ Transition metals ( $Zn, Cd, Hg$ ) are <sup>exception</sup> very much hard & have low volatility.

→ Their M.P & B.P. points are high.

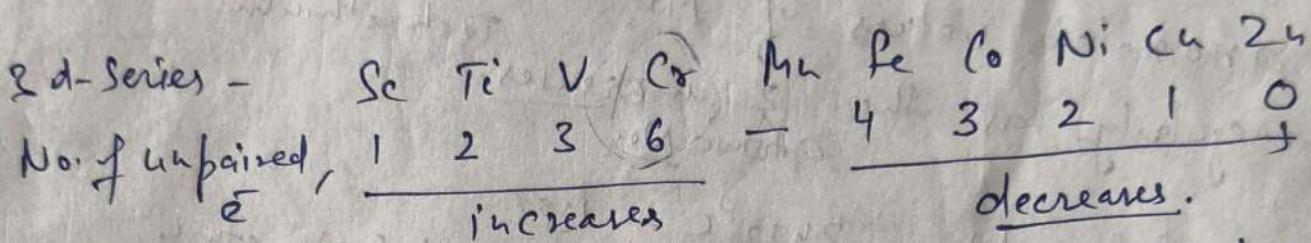
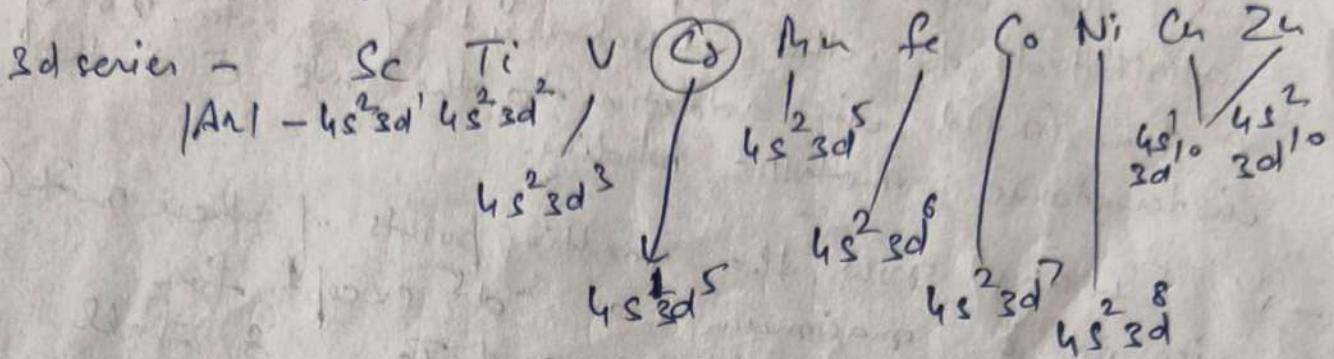
### \* Melting Point:- depends on metallic bonding, Strong ↑ , M.P. ↑

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

ii)  $Z_{eff}$  - effective nuclear charge.

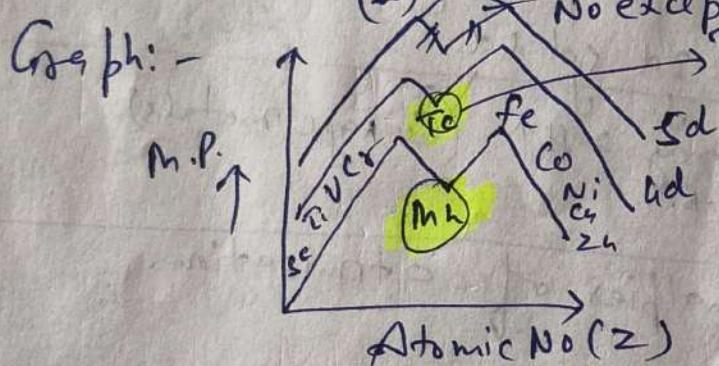
d-block -  $(n-1)d^{10} n_s^2 n_p^6 \rightarrow$  S. & d both participate in metallic bonding.  
 $\Delta E \downarrow +$  Energy gap So max no. of  $e^-$  participation

for No. of Unpaired  $e^-$



left to right - Strong metallic bond  $\rightarrow$  So. M.P.  $\rightarrow$  increases

Weak metallic bond  $\rightarrow$  So. M.P.  $\rightarrow$  decreases



Exception - Mn  $\rightarrow$  low M.P.

Reason  $\rightarrow$  It has no own crystal structure.

Ques:  $3d < 4d < 5d$  ( $Z_{eff.}$ )

In d-block, increase. (down the group)

( $\delta^0$ , M.P.)  $3d < 4d < 5d$  ( $Z_{eff.} \uparrow$ )

$Z_{eff.}$  - Net positive charge experienced by  $e^-$  in a multi- $e^-$  atom.

$$Z_{eff.} = \frac{Z - S}{A}$$

inner  $e^-$  shield the  
 outer  $e^-$  from  
 nucleus  
 Constant

### Melting Point:-

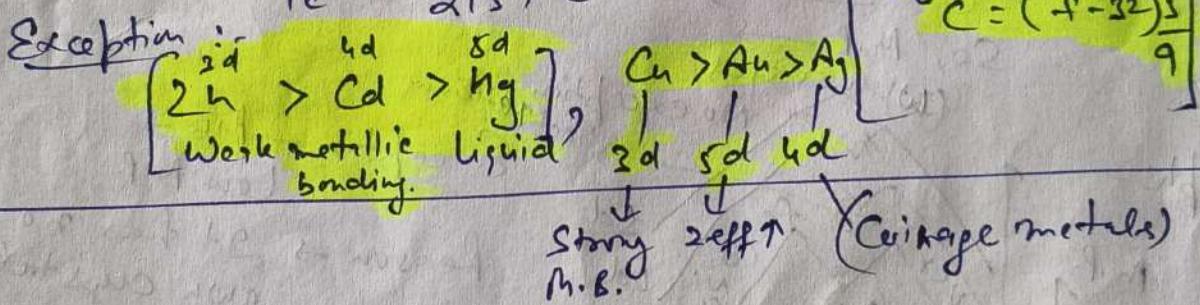
\* → The high melting points of these metals are attributed to the involvement of greater no. of  $e^-$  from (n-1)d in addition to the no.  $e^-$  in the interatomic metallic bonding.

→ In any row the melting points of these metals rise to a maximum at d<sup>5</sup> except for anomalous values of Mn and Tc. Technetium & fall regularly as the atomic No. increases.

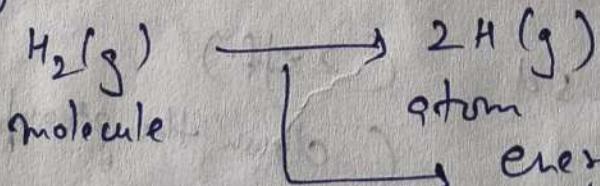
$$\text{M.P.} \rightarrow W - 3422^\circ\text{C} - \text{Max.}$$

$$\text{Mn} - 650^\circ\text{C} - \text{no crystal structure}$$

$$\text{Tc} - 2157^\circ\text{C} -$$



→ They have high enthalpies of atomisation.



every requirement  $\rightarrow$  enthalpy of atomisation.  
atom should in gaseous state  
 $\Delta_a H.$  or  
sublimation enthalpy.

Relation of enthalpy of atomisation with melting point.

So, M.P.  $\uparrow$   $\xrightarrow{\text{Solid} \rightarrow \text{Melt} \rightarrow \text{Gas}}$  then  $\Delta_a H \uparrow$ .

$$Sc > Ti > Ni > Co = Ni, \text{ atomisation.}$$

Aptm Ratns  $\rightarrow V > Ti > Ni > Co > Fe > Cr > Cu > Sc$  (7) (9)

General trend of  $\Delta_a H$  (enthalpy of atomisation)

$$3d < 4d < 5d$$

Ques:- Min  $\Delta_a H$  in 3d series.

Ans: Zn - ~~Va~~ (no unpaired  $e^-$ )  
Mn - ~~H~~ (6  $e^-$ )  
Fe - ~~C~~ (unpaired)

& More Questions are in  
of this concept.

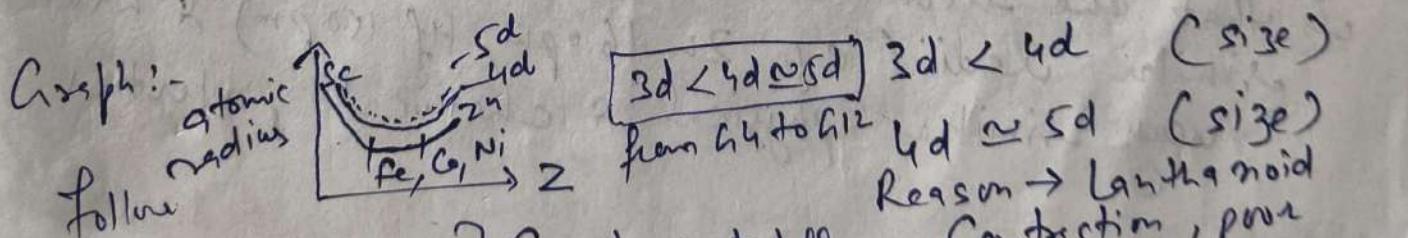
Ques - In the series Sc ( $Z=21$ ) to Zn ( $Z=30$ ),  
the enthalpy of atomisation of zinc is the lowest.

Ans.  $\rightarrow$  no unpaired  $e^-$ .  
So, Metal-Metal Bonding ↓ Statement + Questions, True false, Values,  
M.P. ↓ Assertion & Reasoning from this Concept.  $D = \frac{m}{V}$

Also,  $\Delta_a H \downarrow$ .

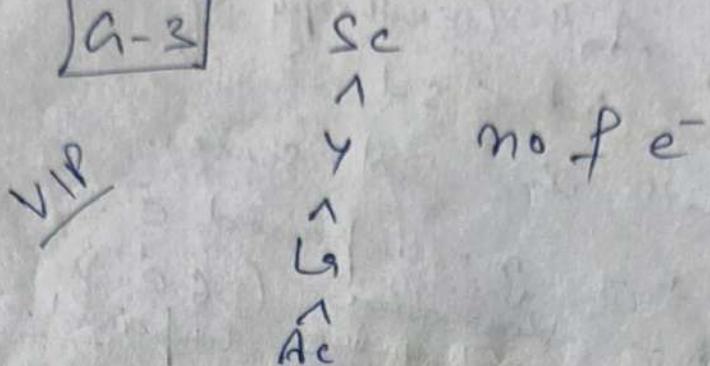
Ques The transition element that has lowest enthalpy of  
atomisation is Zn. (Zn is not transition) (many more)  
As  $\Delta_a H$ ,  $3d < 4d < 5d$  of this concept

\* Variation in atomic and ionic sizes:-  
 $\rightarrow$  In general, ions of the same charge in a given  
series show progressive decrease in radius with  
increasing atomic no.  $Sc > Ti > V > Cr > Mn > Fe > Co > Ni > Cu > Zn$



$[Sc > Ti > Mn = Zn > V > Cr > Cu] \quad$  (outermost shell)  $> Fe = Co = Ni$ , attraction ↑

But in A-3



Ques.  $\text{Zr} \approx \text{Hf}$ .

$$\begin{array}{ll} \text{Nb} \approx \text{Ta} & \text{Rh} \approx \text{Ir} \\ \text{Mo} \approx \text{W} & \text{Pd} \approx \text{Pt} \\ \text{Tc} \approx \text{Re} & \text{Ag} \approx \text{Au} \\ \text{Ru} \approx \text{Os} & \text{Cd} \approx \text{Hg} \end{array}$$

- The same trend is observed in the atomic radii of a given series.
- The radii of the third (5d) are virtually the same as those of the corresponding members of the second series.
- 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 no.
- The net result of the lanthanoid contraction is that the second and the third d-series exhibit similar radii (e.g. Zn 160 pm, Hf 150 pm) & have very similar physical & chemical properties.

Ques: The atomic radii of Ag is closest to  $\frac{\text{Au}}{(\text{s}^{\text{d}})}$ . (9)  
 Ans: (40)

\* Density:- The decrease in metallics coupled with increase in atomic mass results in a <sup>sradii</sup> general increase in the density of these elements. Thus, from titanium ( $Z=22$ ) to Cu ( $Z=29$ ) the significant increase in density.

$$\uparrow D = \frac{\text{mass}}{\text{Volume}} \quad \begin{array}{l} \text{General trend} \\ \xrightarrow{\text{Size decrease}} \\ \text{Vol. "} \end{array}$$

$\text{Sc} < \text{Ti} < \text{V} < \text{Zn} < \text{Cr} < \text{Mn} < \text{Fe} < \text{Co} < \text{Ni} < \text{Cu}$   
 So density increases ( $D = \frac{m}{v}$ )

In 3d series:-

min density : Sc  
 max density :  $D_{\text{Cu}} < (D)_{\text{Zn}}$  size  
 Ans:  $\boxed{\text{Cu}}$       Atomic No ( $2n > \text{Cu}$ )  
 $\xrightarrow{\text{Zadisize}}$

Ques: What is the correct order of the following elements w.r.t. their density?

- a)  $2n < Cr < Fe < Co < Cu$  ( $\checkmark \xrightarrow{\text{Zadisize}}$ )  
 b)  $Cr < Fe < Co < Cu < Zn$   
 c)  $Cr < Fe < Co < Cu < 2n$   
 d)  $Cr < 2n < Co < Cu < Fe$

Ans:- (A) Cu has highest density.

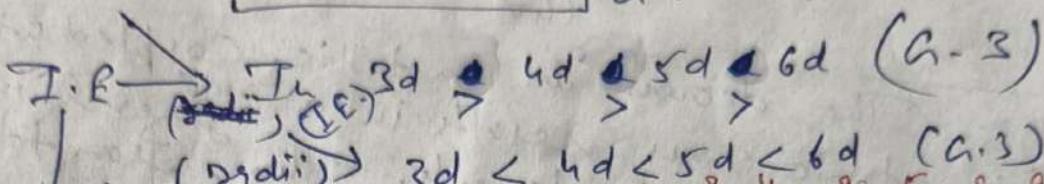
\* Tonisation Enthalpies:- Relation b/w radii

Generally radii  $\uparrow$  Tonisation Enthalpy  $\downarrow$

If ↓ radii  
 more attraction on outer  $e^-$ , then Tonisation Enthalpy ↑  
 (to remove  $e^-$  more energy)

Order of  
Radii

$$3d < 4d \approx 5d \quad \text{from } A_4 \text{ to } A_{12}$$



$$IE_1 \rightarrow 13425897610$$

$$IE_2 \rightarrow 12356471089$$

$$IE_3 \rightarrow 12364758910$$

from  $A_4$  to  $A_{12}$

$$3d > 4d \quad (\text{I.E.})$$

$$Sc < V < Cr < Ti < Mn < Ni < Cu < Co < Fe < Zn$$

$$Zr > Sc < V < Cr < Ti < Mn < Fe < Cr < Co < Zn < Ni < Cu$$

$$I.E_2 \rightarrow Sc < Ti < V < Mn < Fe < Cr < Co < Ni < Cu$$

$$I.E_3 \rightarrow Sc < Ti < V < Fe < Cr < Co < Ni < Cu < Zn$$

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$$4d < 5d \quad (\text{I.E.}) \quad \text{then } (Z_{\text{eff}})$$

$(4d) Z_{\text{eff}} < (5d) Z_{\text{eff}}$  Reason - Poor shielding of  $4f^6 e^-$ .  
 Canthoroid Contraction

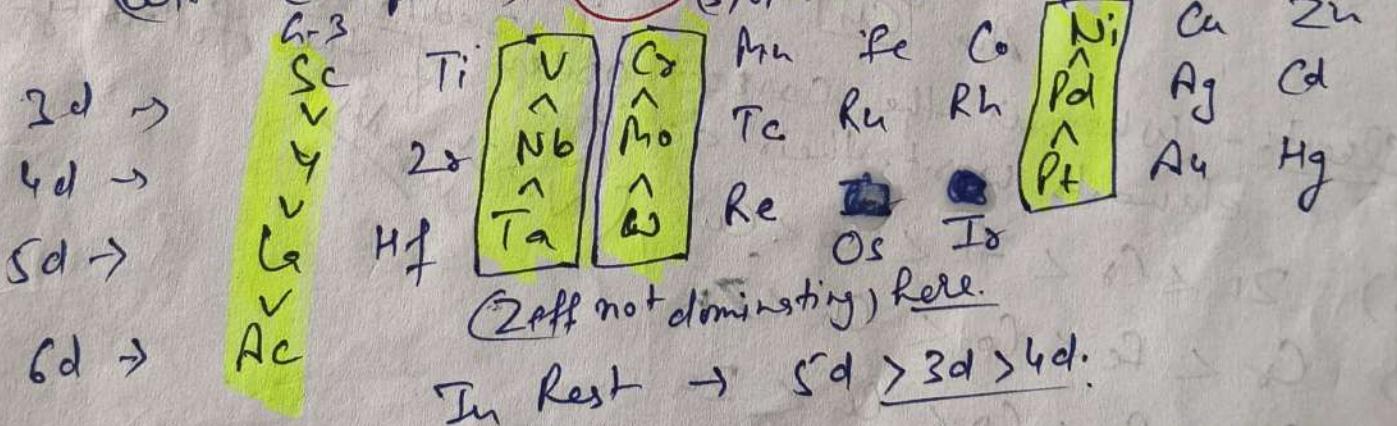
due to  $Z_{\text{eff}}$ .

(for  $A_4$  to  $A_{12}$ )

General trend.

$$5d > 3d > 4d$$

(with Exceptions)  $\rightarrow (VCN)$  (frick)  
 $(5, 6, 10)$ -groups.

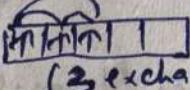


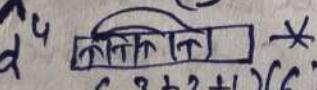
$\rightarrow$  In  $3d$  series, order of I.E.

Learn it :-  $Sc < Ti > V < Cr < Mn < Fe > Co > Ni < Cu < Zn$ .  
 203 exchange E so I.E. ↓

General Trend:

$\xrightarrow{\text{SOJ}}$  Reason for Vanadium:

$d^3$   - I.E. ↑  $e^-$  configuration:  $1A_1 | 4s^2 3d^3$   
 Similar spin energy release  $V \rightarrow V^+$ ,  $[Ar] 4s^1 3d^3$

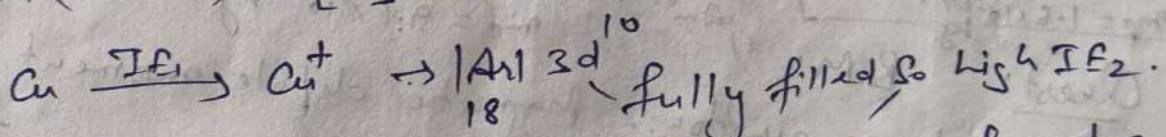
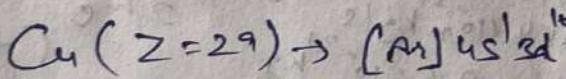
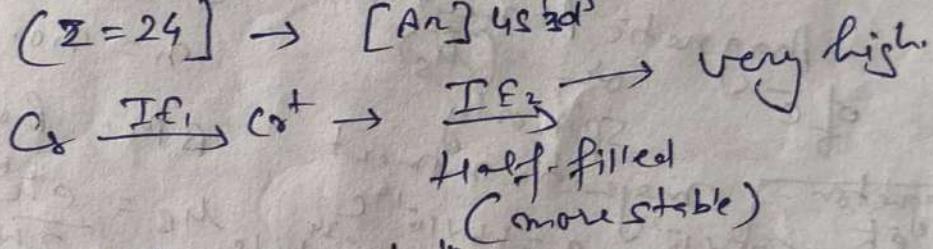
$d^4$   \* (exchange energy) ↑  $\rightarrow$  (stable)  $1A_1 | 3d^4$ .

### Ques. (I.E) points

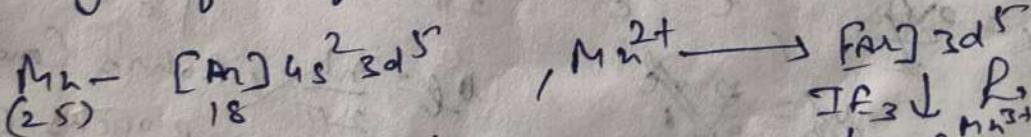
→ Element of 3d series have high value of ionisation enthalpy than 4d series elements but ionisation enthalpy of 4d series elements is lower than the 5d series elements.  $5d > 3d > 4d$  (Li to Zn) due to poor shielding of  $e^-$ . (11)

True false statement, Assertion - Reasoning question.

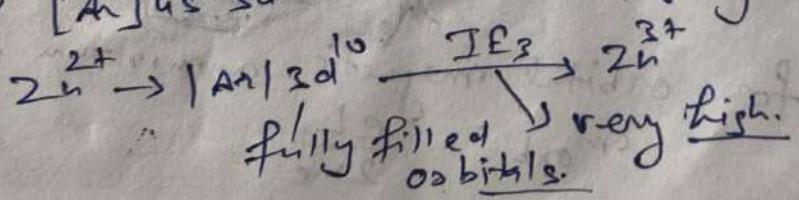
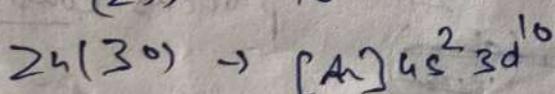
→ Cr and Cu have high value of  $I.E_2$  because of the extra stability of half filled and completely filled orbitals.



→ Mn and Zn have high value of  $I.E_3$  because of extra stability of half filled and completely filled orbitals.

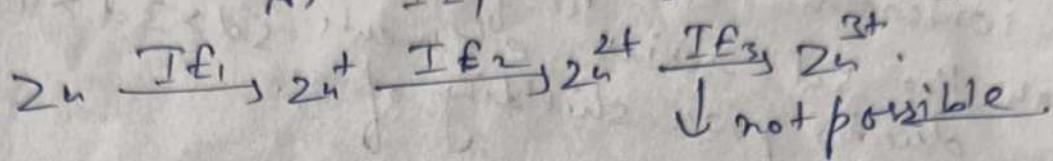


$I.E_3 \downarrow$  half filled  
very high.



$\rightarrow 2n^{+3}$  &  $Cu^{+3}$  not showed because of high value of  $IE_3$ .

As  $IE_1 < IE_2 < IE_3$  (Energy High)



### \* Magnetic Properties:-

↓                    ↓

Paramagnetic      Diamagnetic  
[At least one unpaired e<sup>-</sup>]      [No unpaired e<sup>-</sup>]

Magnetic Moment =  
of e<sup>-</sup> or ( $4s$ )  
spin only

$$\sqrt{n(n+2)} BM$$

n = no. of unpaired e<sup>-</sup>

BM = Bohr magneton

$$BM = \frac{e\hbar}{2me}$$

$$= 9.27 \times 10^{-24} A m^2$$

( $\hbar = \text{Planck's constant}$ )

Nuclear magneton -  
Monucleon =  $\frac{e\hbar}{2m_p} = 5.05 \times 10^{-27}$   
 $m_p = 1.6 \times 10^{-27} \text{ kg}$

Magnetic moment

$$I/T = e = 1.6 \times 10^{-19} C$$

$$Am^2$$

$$\hbar = 1.054 \times 10^{-34} \text{ m kg/s}$$

$$me = 9.1 \times 10^{-31} \text{ kg}$$

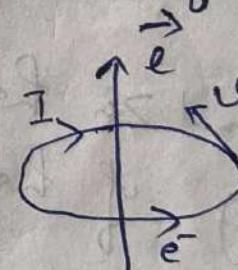
Ques: BM: ?

Bohr magneton:- magnetic dipole moment of a

revolving electron:-

Angular momentum

$$M_e = \frac{e \times \hbar}{2}, \quad l = m_e v r = \frac{nh}{2\pi} \times i)$$



$$M_e = \frac{e \times \hbar}{2}$$

$$l = \frac{nh}{2\pi} \quad \text{Bohr's Condition}$$

Planck's Const.

$$M_e = \frac{e(h)}{4\pi}$$

for orbital magnetic momentum of an e<sup>-</sup>

$$m_{orb} = \frac{eL}{2me}$$

(13)

$$\text{Now } m_{\text{orb}} = n \left( \frac{e h}{4 \pi m e} \right) \checkmark$$

for 1st orbit  $n=1$

$$m_{\text{orb}} = \frac{e h}{4 \pi m e} \text{ in R.M.}$$

$$= \frac{1.6 \times 10^{19} \times 6.67 \times 10^{-34}}{4 \pi \times 9.1 \times 10^{-31}} = 9.27 \times 10^{-24} \text{ J/T}$$

$\text{or } A_m^2$

Ques:- The spin only magnetic moments (in BM) for free  $\text{Ti}^{3+}$ ,  $\text{V}^{2+}$  and  $\text{Sc}^{3+}$  ions are  
 At. No - Sc-21, Ti=22, V=23.

Ans:-  $m_s = \sqrt{n(n+1)} \text{ R.M.}$

$$\text{Sc} - 1A_1 | 4s^2 3d^1 \quad m_s = 0 \quad \therefore n=0 \text{ here}$$

$$\text{Sc}^{3+} = 1A_1 | 0 \quad m_s = 0 \quad \text{unpaired } e^-$$

(18)  $\quad \quad \quad 18$

$$\text{V}^{2+} = 1A_1 | 6s^2 3d^3 / m_s = \sqrt{3(3+2)} \text{ R.M.} \quad n=3$$

$$= 3\sqrt{15} \text{ R.M.}$$

(21)  $= 3.87 \times 9.27 \times 10^{-24} \text{ J/T, } A_m^2$

$$\text{Ti}^{3+} = 1A_1 | 3d^1 \quad m_s = \sqrt{1(1+2)} \text{ R.M.}$$

(19)  $m_s = 1.732 \text{ R.M.}$

$$\text{So, } 1.73, 3.87, 0 \text{ Am.}$$

(R.M.)

Ques:- Which of the following is not correctly matched with the example given?

- A) An element of first transition series which has highest second ionisation enthalpy - Cu.  $\text{Cu}^{2+} \rightarrow [\text{Ar}] 3s^2 3d^10$  - Yes.
- B) An element of first transition series with third highest I.F. - Zn
- C) An element of first transition series with lowest enthalpy of atomisation - Zn
- D) Last element of third transition series - Cd.

Ans: (d)

Ques: The e<sup>-</sup> present in the penultimate orbit of coinage metal atoms are:-

Ans:-  $\text{Cu}, 29 = [\text{Ar}] 4s^1 3d^10$  Penultimate orbit.  
 $1s^2 2s^2 2p^6 3s^2 3p^6$  outermost shell.

$[3s^2 3p^6 2d^{10}]$  penultimate shell

Ques: Calculate the magnetic moment of a divalent ion in aqueous solution if its atomic no. is 25  
Sc Ti V Cr Mn

Ans: Mn(2S)  
 $\text{Mn}^{2+} \rightarrow [\text{Ar}] 3s^2 3d^5$

$$(23) \qquad n=5$$

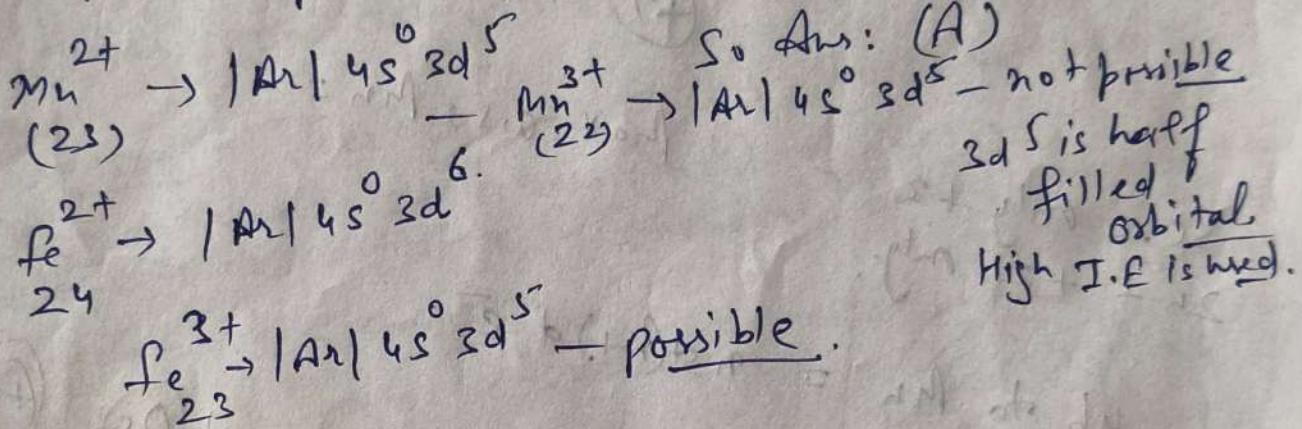
$$\text{so } M_s = \sqrt{s(s+1)} \frac{\text{R.M.}}{\text{R.M.}}$$

$$= \sqrt{25} \text{ Am.}$$

Ques:  $Mn^{2+}$  compounds are more stable than  $Fe^{2+}$  compounds towards oxidation in their +3 state because: (15)

- 3d<sup>5</sup> configuration is more stable than 3d<sup>6</sup> configuration
- 3d<sup>6</sup> " " " = " " 3d<sup>5</sup> "
- 3p<sup>5</sup> " " less " than 3p<sup>6</sup> "
- 3p<sup>6</sup> " " less " " 3p<sup>5</sup> "

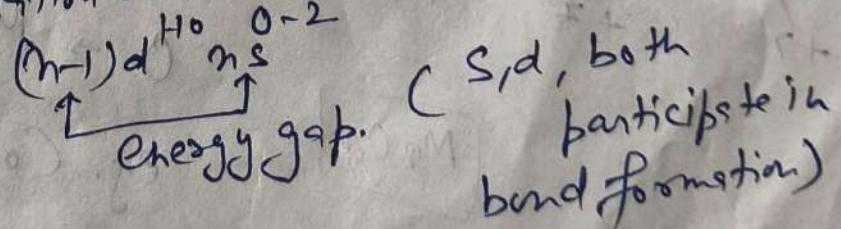
Ans:-  $Mn^{2+}$  compounds are



\* Oxidation States:-

These elements show variable oxidation states because energy levels of 3d, 4d & 5d orbitals are fairly closed to that of 4s, 5s, 6s respectively. Therefore in addition to ns electrons, variable number of (n-1)d are also lost in getting various oxidation states..

\* Variable oxidation states:-



As in p-block elements:

Oxidation States:-

2d - Scandium  $\text{Sc}^{+3}$   $\text{Ti}^{+4}$   $\text{V}^{+5}$   $\text{Cr}^{+6}$   $\text{Mn}^{+7}$   $\text{Fe}^{+2}$   $\text{Co}^{+2}$   $\text{Ni}^{+2}$   $\text{Cu}^{+1}$   $\text{Zn}^{+2}$

$\text{Sc}^{+2}$   $\text{Ti}^{+2}$   $\text{V}^{+2}$   $\text{Cr}^{+2}$   $\text{Mn}^{+3}$   $\text{Fe}^{+3}$   $\text{Co}^{+3}$   $\text{Ni}^{+2}$   $\text{Cu}^{+2}$   $\text{Zn}^{+2}$

$+3$   $+2$   $+3$   $+3$   $+4$   $+4$   $+4$   $+4$   $+4$   $+4$

$+4$

$+5$   $+5$

$+6$   $+6$

$+7$

Max. O.S.

$\text{Sc}^{+3}$   
 $2\text{n} - +_2 \text{n}^1$

$n_p + n_n = n_{st}(n-1) + e^-$ .

Max. O.S. =

(no.)  
Highest O.S. in periodic table  $\text{Ru}^{+8}$  and  $\text{Os}^{+8}$

$\text{O}_2^{+8-8}$  and  $\text{O}^{+8}$  and  $\text{O}^{-8}$ .

O.S. with oxygen. Max. O.S. is satisfied by

Generally Max. O.S. is satisfied by

Reason  $\rightarrow$   $\text{f}^-$  - small size  $\rightarrow$  strong bond formation

high electron density

$\text{Ti}^{+4}$ ,  $\text{Cr}^{+6}$ ,  $\text{Fe}^{+6}$   
 $+6$   $+6$

$\text{O} \rightarrow$  Multiple bond  
when single bond.

$\boxed{\text{MnO}_2}$

e.g.  $\text{Co}_2$ ,  $\text{O}_2\text{C}_2\text{O}_4$

$\text{O}$  is more oxygen for O.S. than  $\text{f}^-$  or  $\text{O}^{+8}$ .  
 $\text{No}_2 \rightarrow \text{N}^{+6}$

As in p-block elements:

Oxidation No. difference  $\rightarrow +2$  units

(17)

$$G-13 \rightarrow +1, +3.$$

$$G-14 \rightarrow +2, +4$$

$$G-15 \rightarrow +3, +5$$

$$G-16 \rightarrow +1, +3, +5, +7$$

But in d-block difference of 1 unit.

In p-block elements:- Higher Oxidation No. n-state

$\rightarrow$  Stability of down the group.

$\downarrow$  decreases

Reason:- Thresh pain effect  $\rightarrow$  The reluctance of heavy p-block electrons ( $n^2$ ) of heavy making them elements to participate in chemical bonding inert bonding

But in d-block elements:-

$\rightarrow$  Stability of O.x. state  $\uparrow$  increases

on down the group.

eg

$2d \quad \left\{ \begin{array}{l} \text{Reason} \\ 2e_{\text{eff.}} \end{array} \right. \rightarrow 3d < 4d < 5d$

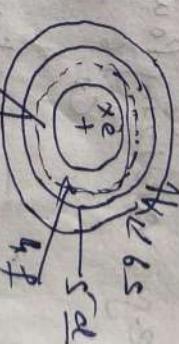
$4d \quad \left\{ \begin{array}{l} (Z-S) \rightarrow \text{Crystal field splitting} \\ \text{shielding} \end{array} \right. \rightarrow \text{Stability} \uparrow$

$5d \quad \left\{ \begin{array}{l} \text{splitting energy, } 2e_{\text{eff.}} \\ \text{constant} \end{array} \right. \rightarrow \Delta \uparrow$

(stability)  $\downarrow$  Stability of Complex  $\uparrow$

and so on

Cfse. The net energy decrease a closed shell formation metal d-orbitals when transition metal d-orbitals split into different energy levels remaining at a single due to ligand interactions rather than energy due to ligand (by different molecules)



Incomplete screening

e.g.  $Tin, Pb.$

$(50) (52)$

$10e^{-}$

$2e_{\text{eff.}}$

$10e^{-} - 2e_{\text{eff.}}$

$8e^{-}$

$5e^{-}$

$5e^{-}$

$5e^{-}$

$5e^{-}$

$5e^{-}$

$5e^{-}$

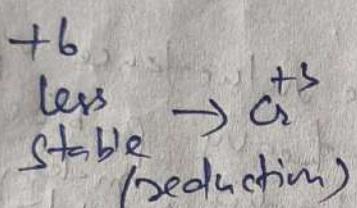
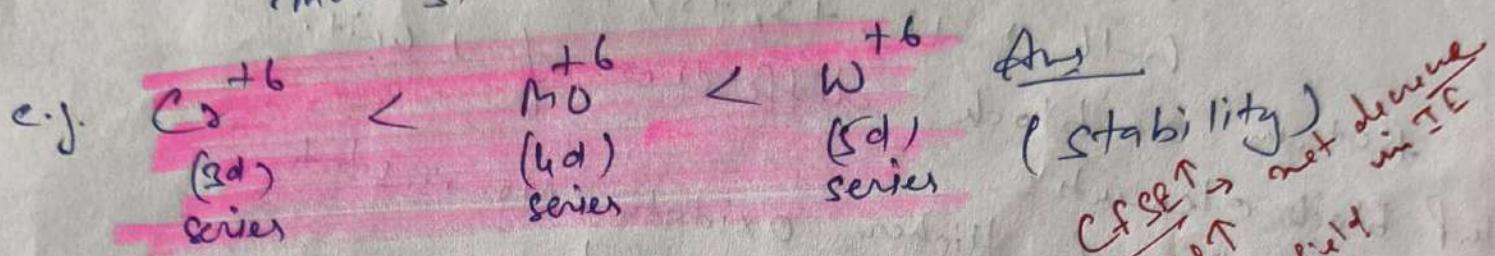
$5e^{-}$

$5e^{-}$

$5e^{-}$

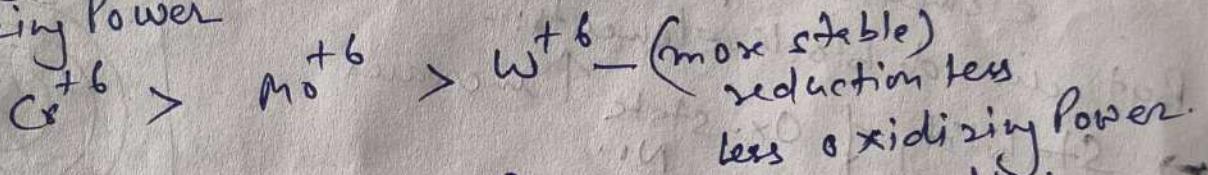
→ The higher oxidation state of 4d, and 5d series elements are generally more stable than those of the elements of 3d series.

→ e.g. Mo(VI) and W(VI) are found to be more stable than Cr(VI).



oxidising agent

e.g. Oxidizing Power



→ low oxidation states are found when a complex compound has ligands capable of pi acceptor character in addition to sigma bonding.  
 $\text{O} \rightarrow \text{O}^{\cdot}\text{State}$

→ e.g.  $\text{Ni}(\text{CO})_4$  and  $\text{Fe}(\text{CO})_5^-$

$\text{Co} \rightarrow \pi \text{ acceptor}$   
 $\sigma \text{ donor}$

Ques:- The element that usually does not show variable oxidation states is.

- a) Cu      b) Ti      c) Sc      d) V

Ans: Sc.

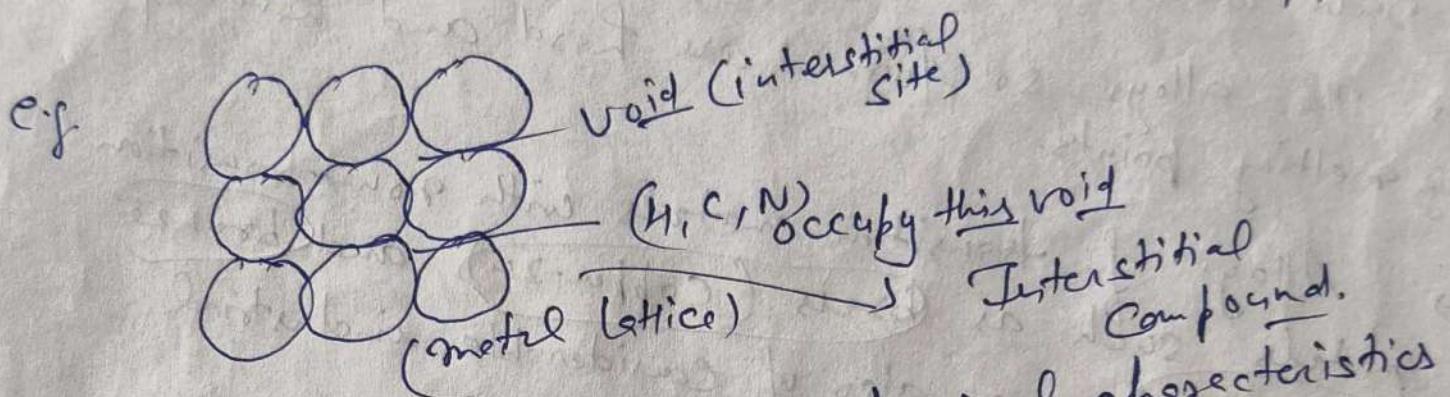
## \* Alloy formation:-

- Alloys may be homogeneous solid solutions in which the atoms of one metal are distributed randomly along the atoms of the other.
- Such alloys are formed by atoms with metallic radii within about 15 percent of each other.
- The alloys so formed are hard and have often high melting points.
- Alloys of transition metals with non-transition metals such as brass (Copper-Zn) and bronze (Copper-Sn) are also of considerable industrial importance.

## E.g. of Alloys:-

- Brass (Copper + Zn)
- Bronze (Cu + Sn)
- Cum metal (Cu 87% + Sn 10% + Zn 3%)
- German Silver [Cu 50% + Zn 28% + Ni 25%]
- Bell Metal (Cu 80% + Sn 20%)
- Stainless steel (Fe + Cr + Ni)      C Atom ligand  
    e.g.  $K_4[Fe(CN)_6]$   
    Containing  $\text{CN}^-$
- \* Formation of Complex Compounds:-
- The Transition metals form a large number of Complex Compounds.
- This is due to the comparatively smaller sizes of the metal ions, their high ionic charges ( $2^{+}, 3^{+}$ )? availability of d-orbitals for bond formation ligand free to vacant d-orbitals.

- Interstitial Compounds are those which are formed when small atoms like H, C or N trapped inside the crystal lattice of metals. (not a whole No.)
- They are usually non stoichiometric and are neither typically ionic nor covalent, e.g. TiC,  $\text{Mn}_2\text{N}$ ,  $\text{Fe}_2\text{H}$ ,  $\text{VH}_{0.56}$  etc.



- The principal physical and chemical characteristics of these compounds are:
- i) High M.P., higher than those of pure metals.
- ii) very Hard, some borides approach diamond in hardness.
- iii) They retain metallic conductivity.
- iv) They are chemically inert (don't react)

Ques:- The statement that is incorrect about the

Interstitial Compounds is:

- A) They have metallic conductivity.
- B) They have high melting points.
- C) They are chemically reactive ✓
- D) They are very hard.

(21)

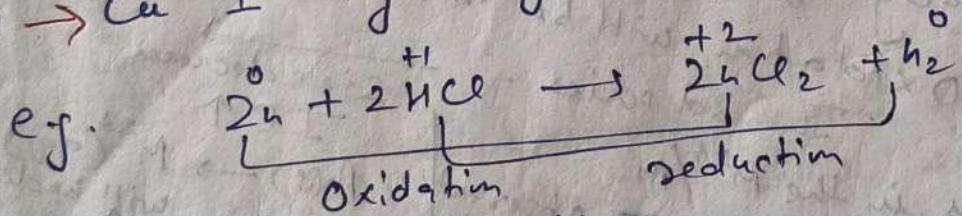
- \* Trends in the  $M^{2+}/M$  standard electrode potentials:
  - $E^\circ M^{2+}/M \rightarrow$  electrochemistry
  - No. of charges  $\downarrow \rightarrow$  reduction
- \* SRP  $\downarrow$  R.A  $\uparrow$  Reducing Agent.

So,  $f - Li$  (in electrochemical series)  $M \rightarrow M^{2+} + 2e^-$   
 best Oxidizing Agent  $\rightarrow$  best RA Reducing Agent No. of charg.  $\uparrow$ .  
 (in Redox Rxn)

Trick - Lazy kabir brought so cold mango mutation and

✓ Li K Ba Ca Na Mg Al Fe Zn Cr Fe Co Ni Sn Pb mango.

Hello zebra crossing. fast car can not stop properly while  
 hybrid car is always hot before police arrive.  
 $H \rightarrow Cu I Ag Hg Pt Au.$  five



(Reducing agent)

$$(SHE) E^\circ H^+/H_2 = 0 \text{ (SRP)}$$

Standard Hydrogen Electrode

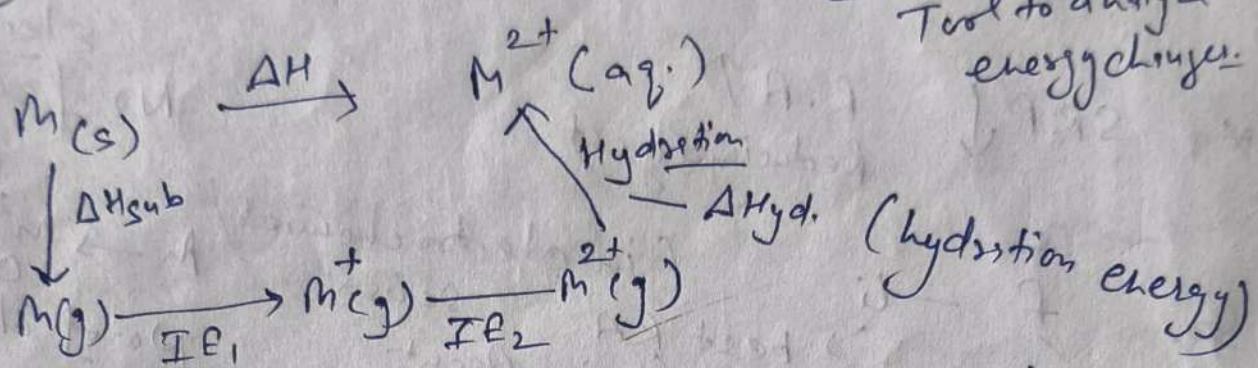
So here SRP  $\downarrow$  of  $Zn$  less than 0. (-ve)

$\rightarrow$  If metal's SRP is -ve that it liberates  $H_2$  from acid.

Here,  
 $Zn$  displaces  $H$  from  $HCl$ .

So, A metal with -ve SRP can displace  $H_2$  from dilute acids.

Born-Haber Cycle: -  
Tool to analyze energy changes.



Kess's law: - ,  $\Delta H = \Delta H_{\text{sub}} + IE_1 + IE_2 + \Delta H_{\text{hyd.}}$

(i) If  $\Delta H \downarrow$  then process will be easy  
 $\delta \Delta H_{\text{sub}} \downarrow + IE_1 \downarrow + IE_2 \downarrow + IE_3^+ (3^+) \downarrow$   
 $+ \Delta H_{\text{hyd.}} \uparrow$  (Released energy.)

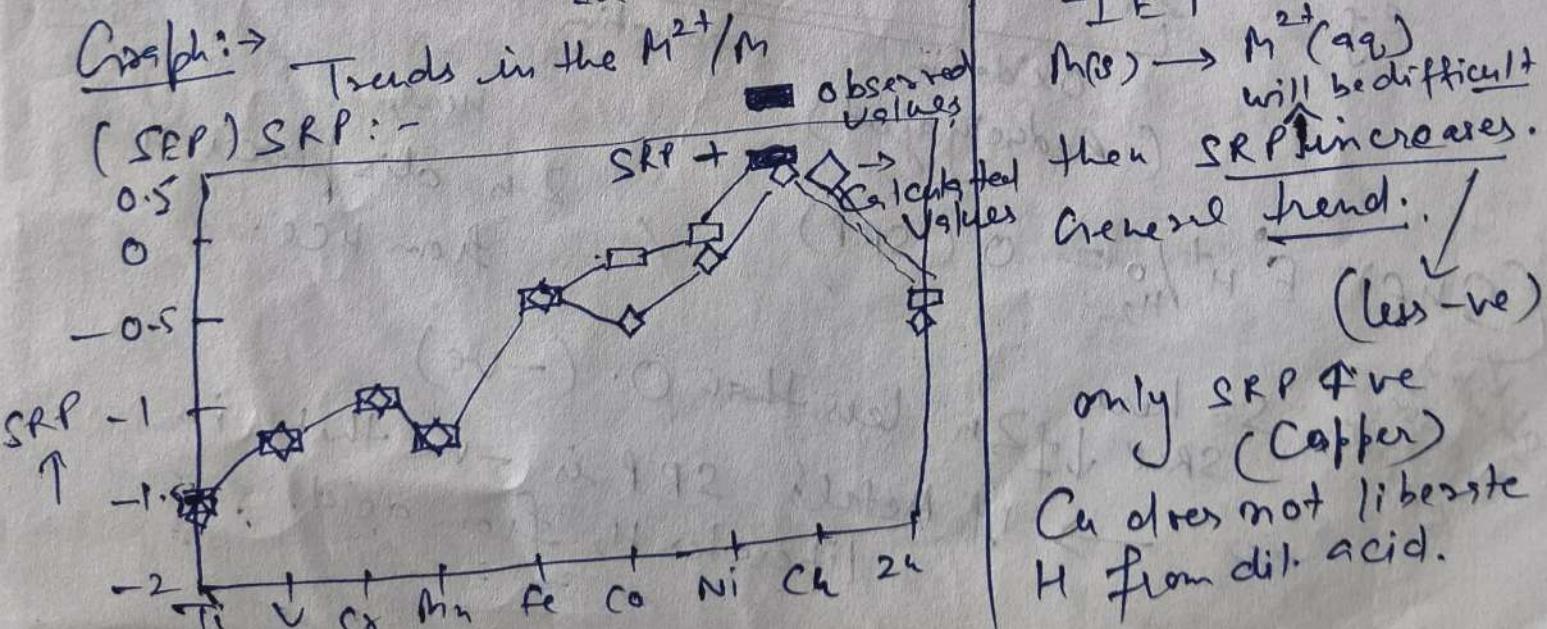
Ex (ii) SRP  $\downarrow$  (Process will be easy)

Reducing Agent  $\uparrow$  (good)

Oxidation will be more easy

In 3d series:

Graph: - Trends in the  $M^{2+}/M$



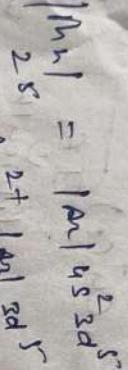
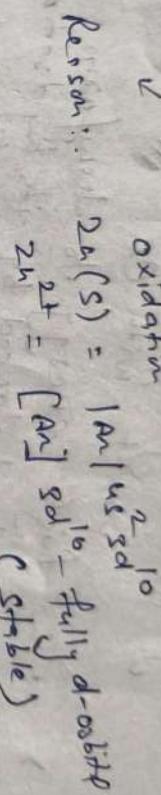
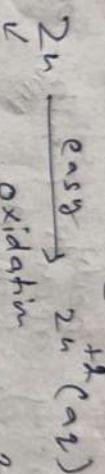
size decrease  
 $IE \uparrow$   
 $M(s) \rightarrow M^{2+}(aq)$   
 will be difficult  
 then SRP  $\uparrow$  increases.  
 General trend:  
 (less -ve)

only SRP  $\neq$  ve  
 (Copper)  
 Cu does not liberate  
 $H$  from dil. acid.

After Cu

2<sub>n</sub> S.P.R decreases in the graph so,

2<sub>n</sub> oxidation will be easy.



So  $\mu_{\text{H}}^{\text{2+}}$   $\xrightarrow[\text{oxidation}]{\text{easy}}$  value decreases from trend.

(G.P.)

The value of  $E^\circ$  for Mn Ni and 2<sub>n</sub> are more

negative than expected from the trend.

→ The stability of the half-filled d sub-shell in  $\text{Mn}^{\text{2+}}$  and completely filled  $d^{10}$  configuration in 2<sub>n</sub> are related to their  $E^\circ$  values, whereas  $E^\circ$  for Ni are related to the highest -ve Hydration energy.

is related to the higher  $-E^\circ$  (  $\Delta H_{\text{Hyd}} \rightarrow \uparrow$  )

for Ni  $\xrightarrow[\text{easy}]{\text{size small}}$  formula.

Ques:- Why S.P.R ↑ left to right

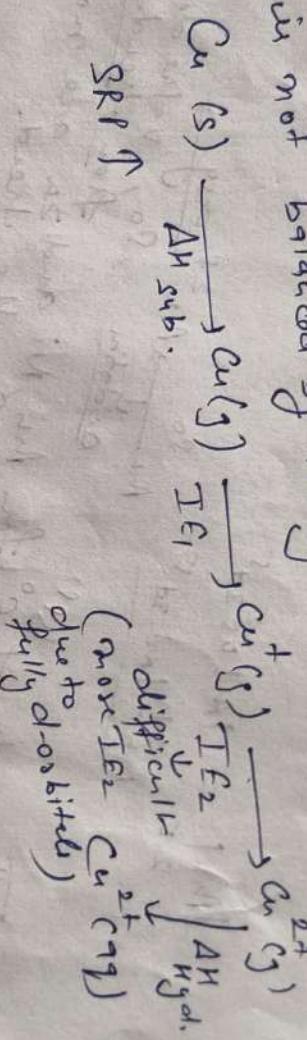
in 3d - I.E↑ (Concent Trend)

( $E^\circ$  cell =  $E^\circ_{\text{Cathode}} - E^\circ_{\text{Anode}}$ )

Ans:- → The general trend towards less negative ( $\uparrow$ )  $E^\circ$  values across the series is related to the general increase in the sum of the first and second ionisation energies.

→ The unique behavior of Cu, having a low  $E^\circ$ , account for its inability to liberate  $H_2$  from acids. Only oxidizing agents (nitric and hot conc.  $H_2SO_4$ ) react with Cu.

→ The high energy to transform  $Cu(s)$  to  $Cu^{2+}$  is not balanced by its hydronation enthalpy.



Quest: In the series the metal having the highest  $M^{2+}/M$  standard electrode potential is :-

- a) a      b) fe      c) Cu      d) 2n.

Ans: Cu  $\xrightarrow{\Delta H_{\text{SRP}}}$

Quest: The standard electrode potential ( $M^{2+}/M^{2+}$ ) for  $V, Cr, Mn \& Co$  are -0.26V, -0.16V, +1.52V & 1.92V respectively. The metal ions which can liberate  $H_2$  from a dilute acid are:-

- a)  $V^{2+} \& Mn^{2+}$     b)  $Cr^{2+} \& Co^{2+}$     c)  $V^{2+} \& Cr^{2+}$     d)  $Mn^{2+} \& Co^{2+}$ .

Ans:

$V^{2+}$

$Mn^{2+}$

$Co^{2+}$

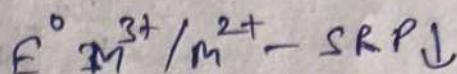
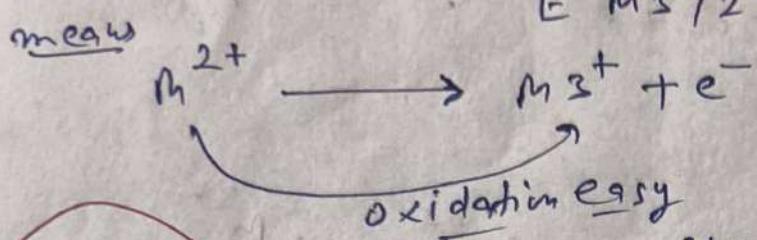
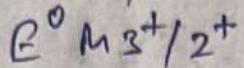
$Cr^{2+}$

$V^{2+}$

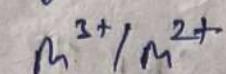
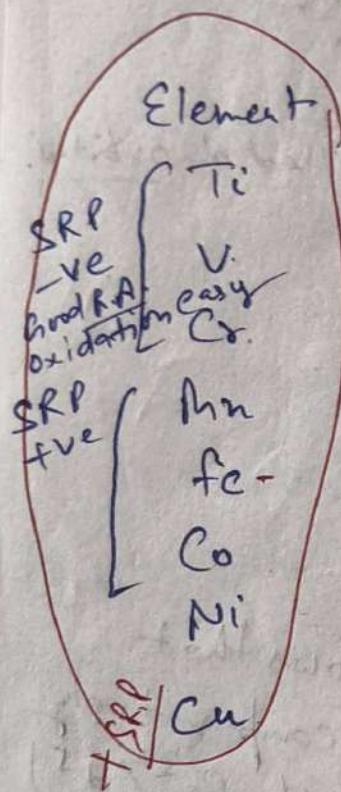
$Mn^{2+}$

\* Trends in the  $M^{3+}/M^{2+}$  SRP:-

(25)



good Reducing Agent  $\uparrow$



$$-0.37V$$

$$-0.26V$$

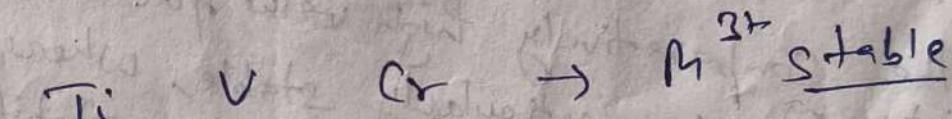
$$-0.41V - \text{exception}$$

$$1.57V$$

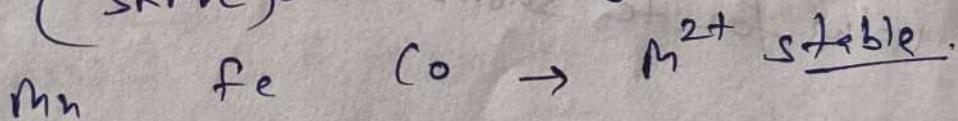
$$0.77V - \text{exception}$$

$$1.97V$$

increases  $\downarrow$  as you go down  $\swarrow$   
2d- Left to Right increases



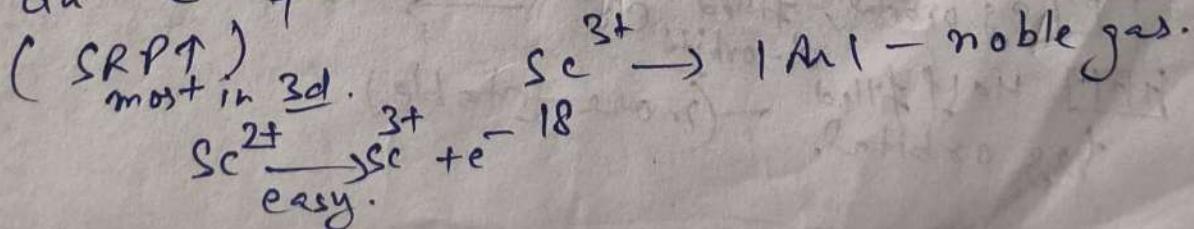
(SRP-ve) Oxidation easy

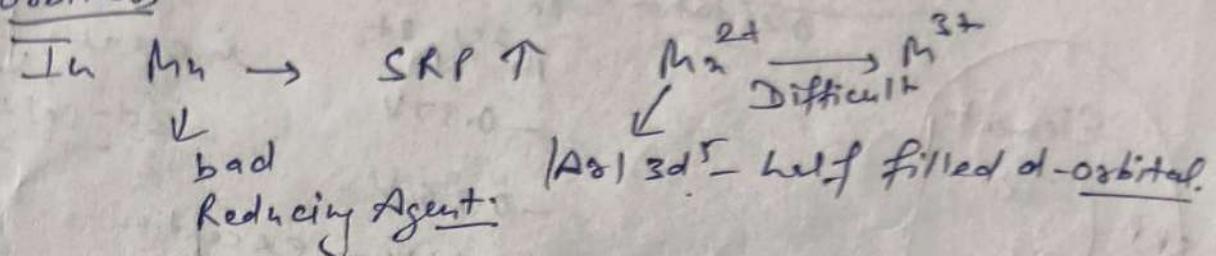
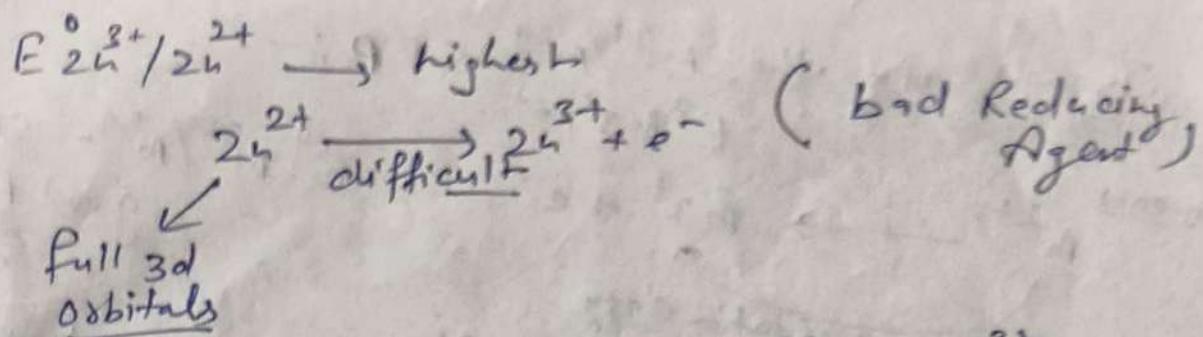


(SRP +ve)

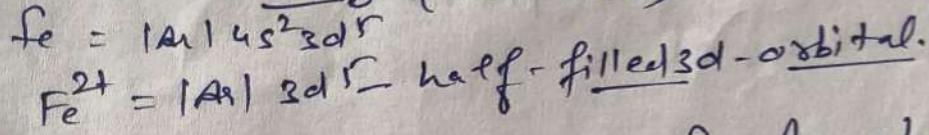
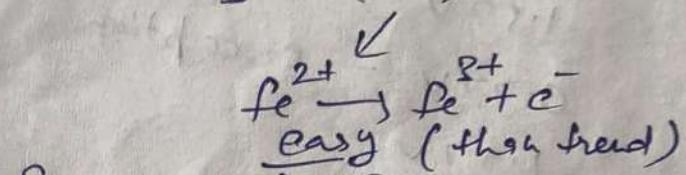
→ The low value for Sc reflects the stability of  $Sc^{3+}$  which has a noble gas configuration.

→ The highest value for  $Zn$  is due to the removal of an  $e^-$  from the stable  $d^{10}$  configuration of  $Zn^{2+}$ .



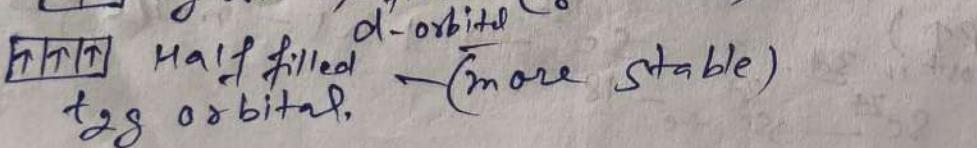
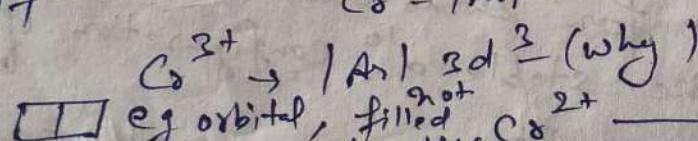
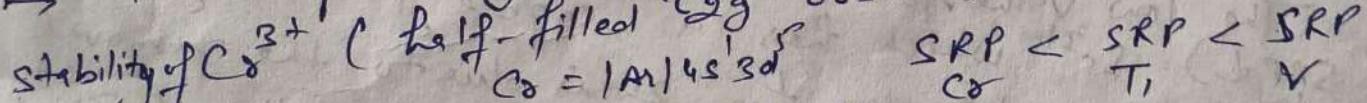


$$\text{SRP(Fe)} < \text{SRP(Mn)}$$

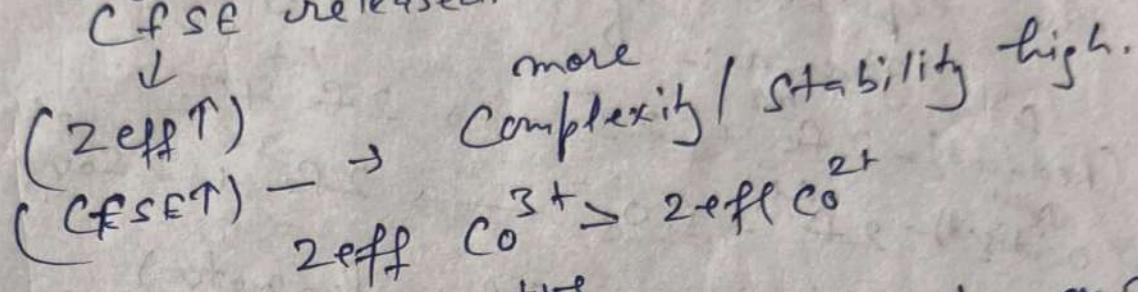


→ The comparatively high value for Mn shows that  $Mn^{2+}$  ( $d^5$ ) is particularly stable, whereas comparatively low value for Fe shows the extra stability of  $Fe^{2+}$  ( $d^5$ )

→ The comparatively low value for Co is related to the stability of  $Co^{3+}$  (half-filled  $t_{2g}$  orbital)

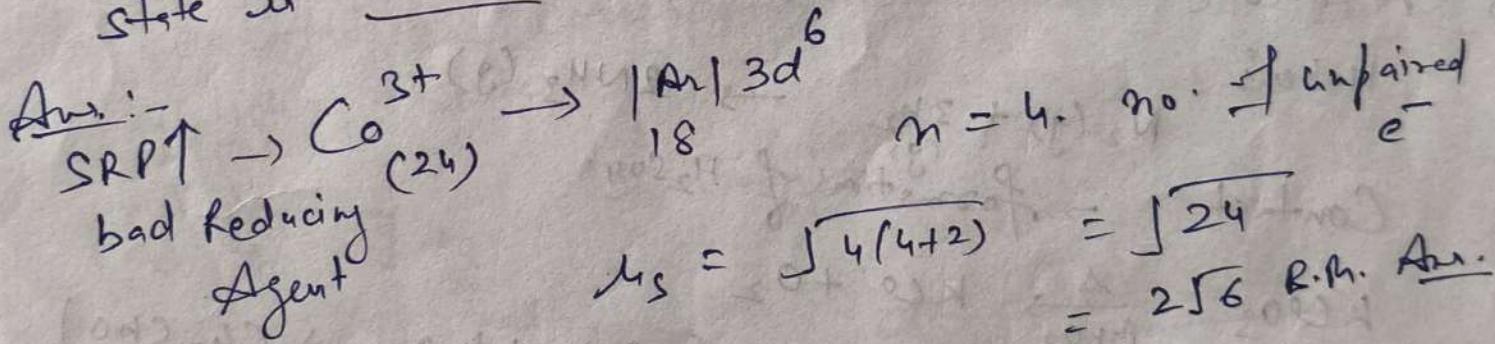


→ In aqueous solution,  $\text{Co}^{2+}$  is more stable and  $\text{Co}^{3+}$  is highly unstable (SRP↑) but  $\text{Co}^{3+}$  is highly stable in complex compounds due to high CFSE released.



→  $\text{Co}^{2+}$ ,  $\text{V}^{2+}$ ,  $\text{Ti}^{2+}$  are good reducing Agents and liberate  $\text{H}_2$  from dilute acids.

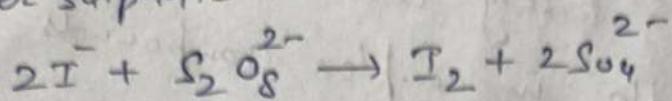
Ques. Among  $\text{Co}^{3+}$ ,  $\text{Ti}^{2+}$ ,  $\text{V}^{2+}$  &  $\text{Cr}^{2+}$  ions, one if used as a reagent cannot liberate  $\text{H}_2$  from dilute mineral acid in solution, its spin-only magnetic moment in gaseous state is \_\_\_\_\_ B.M.



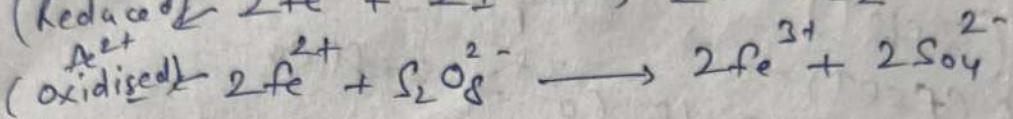
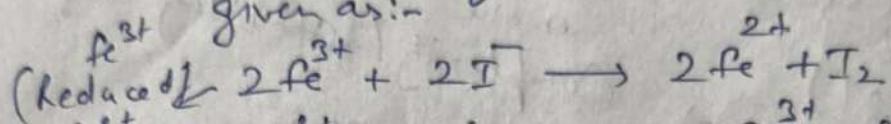
\* Catalytic Properties:-

→ The transition metals and their compounds are known for their catalytic properties. This activity is ascribed to their ability to adopt multiple oxidation states & to form complexer.

Ques: → e.g. iron (III) Catalyses the Rxn b/w iodide & per sulphate ion.



1. 2 An explanation of this catalytic action can be  
2. 6 given as:-



→ Fe - Haber's process (Mo - Promoter)

Ans → V<sub>2</sub>O<sub>5</sub> - Contact Process ( $S_0_2 + O_2 \rightarrow S_0_3$ )

→ MnO<sub>2</sub> - Thermal decomposition of KClO<sub>3</sub>

→ TiCl<sub>4</sub> + (C<sub>2</sub>H<sub>5</sub>)Al (Ziegler-Natta Catalyst) : Production of Polythene

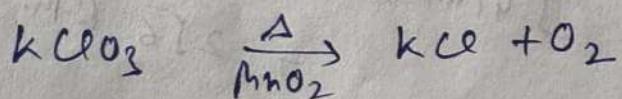
\* → Ni/Pd : Hydrogenation

→ Pt/Rh (Adam's Catalyst) : Used in reduction.

Haber's



Contact → formation of H<sub>2</sub>SO<sub>4</sub>.



→ PdCl<sub>2</sub> : Wacker's process ( $C_2H_4 + H_2O \rightarrow C_2H_3CHO$ )

→ Pt/Rh : Ostwald's process ( $NH_3 + O_2 \rightarrow NO + H_2O$ )

→ CuCl<sub>2</sub> → Deacon's process ( $HCl + O_2 \rightarrow H_2O + Cl_2$ )

Why used as catalyst → Reason - i) multiple oxidation states  
ii) less size & formation of complex compounds

Ques: Match list I with list II!

(29)

List - I  
Processes/Reactions

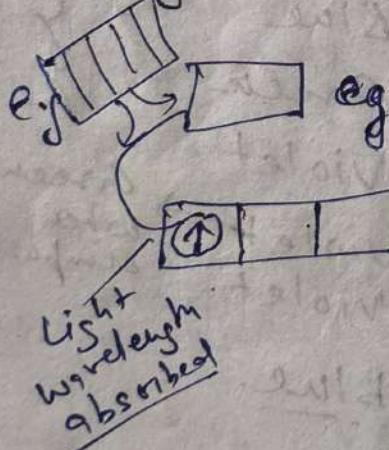
1.  $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3(g)$
2.  $4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O}$
3.  $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3(g)$
4. Veg. oil(l) +  $\text{H}_2 \rightarrow$  Vegetable ghee(s)

List - II  
Catalysts

1. Fe
2. Pt(s) - Rh(s)
3.  $\text{V}_2\text{O}_5$
4. Ni(s).

Ans: 1 - 3 -  $\text{V}_2\text{O}_5$  - Contact process.  
 2 - 2 Pt/Rh - Ostwald's process.  
 3 - 1 Fe - Haber's process  
 4 - 4 Ni/Pd (s) hydrogenation

\* formation of Coloured Ions:-  
 → When an electron from a lower energy d orbital excited to a higher energy d orbital, the energy of excitation corresponds to the frequency of light absorbed.



In Complex

d-d transition

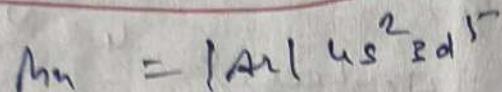
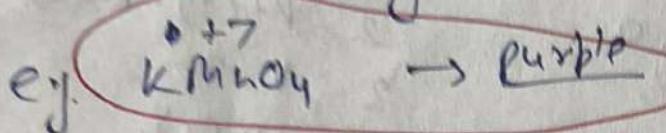
(i)  $d^0, d^{10} \rightarrow$  No d-d transition  
 So, generally there are colourless.

\* Reason of Colour  
 (iii) Charge transfer

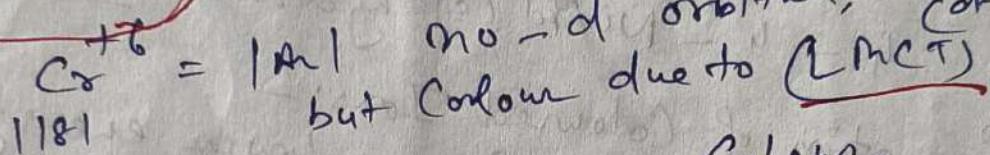
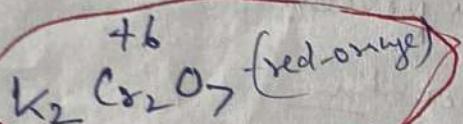
L M C T , M L C T , M M C T  
 Ligand metal (iii) Polarisation:  $\text{Ag}^+$ ,  $\text{Ag}^{\text{II}}$ .

b7  
7

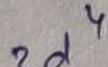
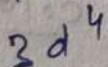
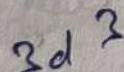
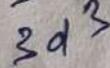
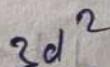
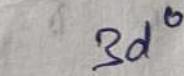
→ → This frequency generally lies in the visible region. The colour observed corresponds to the complementary colour of the light absorbed.



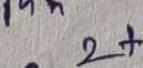
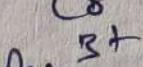
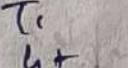
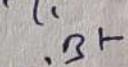
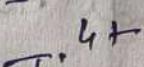
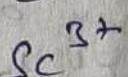
$\text{Mn}^{7+} = [\text{Ar}] - \text{No } (\text{d} - \text{e})$   
but purple colour due to  
(LMCT)  
Ligand metal charge Transfer.



### \* Configuration



### Example



Colour  
Colourless  
Colourless

Purple

Blue

Green

Violet

Violet

Green  
when  
impure.

(purple)  $\xrightarrow{\text{Violet}}$

Violet

blue.

## Configuration

$3d^5$

$3d^5$

$3d^6$

$3d^6, 3d^7$

$3d^8$

$3d^9$

$3d^{10}$

## Example

$Mn^{2+}$

$Fe^{3+}$

$Fe^{2+}$

$Co^{3+}, Co^{2+}$

$Ni^{2+}$

$Cu^{2+}$

$Zn^{2+}$

## Colour

Pink

Yellow

Green

Blue, Pink

Green

Blue

Colourless

(31)

But in complex, colour depends on its ligands

Imp  $\rightarrow$   $Cu^{2+}, Co^{3+}, Mn^{2+}, Fe^{3+}, Fe^{2+}$  pink, yellow green

e.g. green  $[Co(H_2O)_6]^{3+}$ , blue  $[Co(NH_3)_6]^{3+}$ ,  $[CoF_6]^{3-}$  pure (green)  
yellow orange (violet) impure (green)

Ques:- In following pairs, the one in which both transition metals ions are colourless:

- a)  $Sc^{3+}, Zn^{2+}$  b)  $Ti^{4+}, Cu^{2+}$  c)  $V^{2+}, Ti^{3+}$  d)  $Zn^{2+}, Mn^{2+}$

Ans:- (a)  $Sc^{3+}, Zn^{2+}$ .

\* Trends in stability of Higher oxidation state:-

→ The ability of fluorine to stabilise the highest oxidation state is due to either higher lattice energy as in case of  $CoF_3$  or higher bond enthalpy terms for the higher covalent compounds e.g.  $Vf_5$  &  $CoF_6$ .

## Oxidation No.

6

$CoF_6$

5

$CoF_5$

4

$Vf_4$

3

$CoX_4$

2

$CoX_3$

1

$CoX_2$

$MnF_4$

$MnF_3$

$MnX_2$

$FeX_3$

$FeX_2$

$FeX_2$

$CoF_3$

$CoX_2$

$NiX_2$

$CuX_2$

$CuX_2$

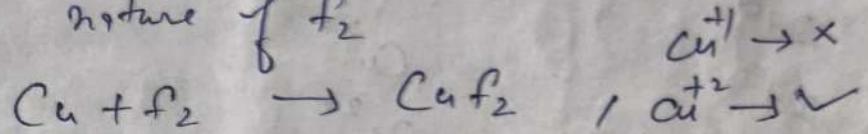
$CuX_2$

Key  $X = F \rightarrow I, X \frac{1}{2} F \rightarrow Br, X'' = F, Cl: X''' = Cl \rightarrow I$ .

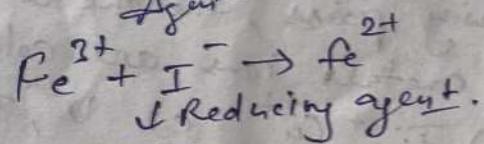
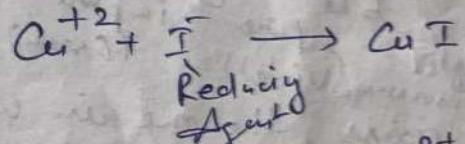
1  
\* → w  
→ g

air oxygen and fluorine (maximum <sup>Satisfy</sup> oxidation state.)  
 ↓  
 Superior less size & strong bond formation  
 multiple bond formation  
 (=) formation

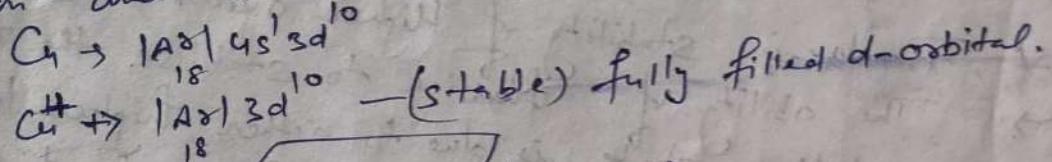
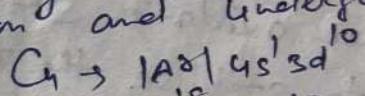
→ CuF does not exist because of the powerful oxidizing nature of F<sub>2</sub>



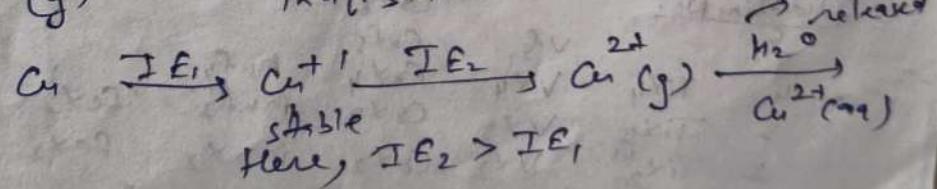
→ CuI<sub>2</sub> and FeI<sub>3</sub> do not exist (I<sup>-</sup> is a good reducing agent)



(Ex) → Many Copper (1) compounds are unstable in aqueous solution and undergo disproportionation.



→ Disproportionation rxn  
 Redox  
 Cu → 2 Cu<sup>+</sup> → Cu<sup>2+</sup> + Cu  
 (g) Reason (Hydrolysis)  
 in aq. state



(35) (33)

→ The stability of  $\text{Cu}^{2+}(\text{aq})$  is higher than  $\text{Cr}^{3+}(\text{aq})$   
 is due to the much more negative hydration enthalpy of  $\text{Cu}^{2+}$  than  $\text{Cr}^{3+}$ , which more than compensates for the second ionisation enthalpy of Copper.

Ques: The set of correct statement is:

1. Manganese exhibits +7 oxidation state in its oxide
  2. Ruthenium and Osmium exhibit +8 oxidation state in their oxides.
  3. Sc shows +4 oxidation state which is oxidising in nature
  4. Cr shows oxidising nature in +6 oxidation state.
- a) 2 & 3      b) 1, 2 & 4      c) 1 & 3      d) 2, 3 & 4.

Ans: —  $\text{Mn}_2\text{O}_7$ ,  $\text{Mn} \rightarrow +7 \checkmark$  (MnO<sub>3</sub>f) In (N.C.E.R.T)  
 $\text{Ru} \& \text{Os} \rightarrow +8 \checkmark$

Sc only shows +3

Cr — +6 ✓

So, (b) 1, 2 & 4.

\* Some Important Compounds of Transition Elements:-

\*  $\text{KMnO}_4 \rightarrow$  Potassium permanganate.

\*  $\text{K}_2\text{Cr}_2\text{O}_7 \rightarrow$  Potassium dichromate

Preparation: — & Properties :— Titration - Redox Rxn.

- \* Oxides & Oxyanions of Metals:-
  - All the metals except scandium form MO oxides which are ionic. (5)
  - $\text{Mn}_2\text{O}_7$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{V}_2\text{O}_5$  → Acidic in nature. lic
  - Thus,  $\text{Mn}_2\text{O}_7$  gives  $\text{HMnO}_4$  (permanganic acid) &  $\text{Cr}_2\text{O}_3$  gives  $\text{H}_2\text{CrO}_4$  (chromic acid) &  $\text{K}_2\text{Cr}_2\text{O}_7$  (Dichromic oxides) (3)
  - Nature of oxides:
    - $+1, +2, +3$  — Basic (metal oxides)
    - $\text{Cr}_2\text{O}_3$  is basic. exception  $\text{Cr}_2\text{O}_7$  — Amphoteric.  $\text{Cr}_2\text{O}_7$  is amphoteric
    - $+4$  — Amphoteric
    - $+5, +6, +7$  — Acidic
  - \* Preparation of  $\text{KMnO}_4$  → Purple colour ( $\text{MnO}_4^-$ )
    - It is prepared from pyrolusite ( $\text{MnO}_2$ ) involving the following steps:-
    - (i) Conversion of  $\text{MnO}_2$  into potassium manganeseate:
 

Powdered pyrolusite (black brown) is fused with an alkali metal hydroxide and an oxidising agent like  $\text{KNO}_3$  water soluble to give green coloured potassium manganeseate.

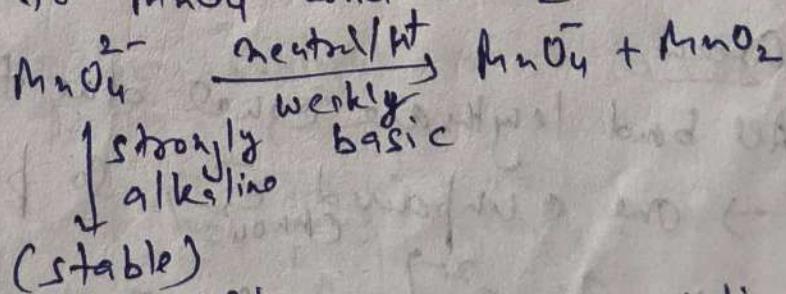
$$2\text{MnO}_2 + 4\text{KOH}/\text{K}_2\text{CO}_3 + \text{O}_2/\text{KNO}_3 \rightarrow 2\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O}$$

$\text{Potassium manganeseate}$   
 $(\text{green})$
- $(\text{MnO}_4^{2-})$       Then  $\text{KMnO}_4$       Oxidising done.

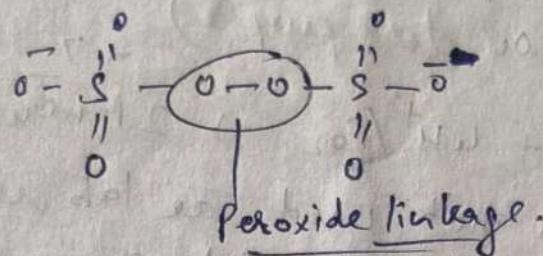
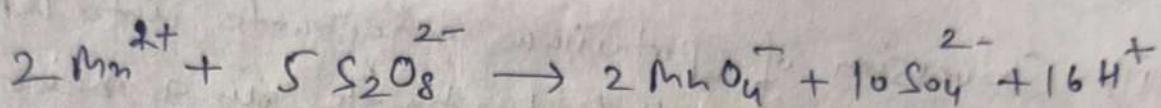
- (ii) Conversion of potassium manganate into  $\text{KMnO}_4$  :-
- $\text{K}_2\text{MnO}_4$  disproportionate in a neutral or acidic solution to give  $\text{KMnO}_4$  (dark purple)
- disproportionation  
Rxn. [  $3\text{MnO}_4^{2-} + 4\text{H}^+/\text{Co}_2 \rightarrow 2\text{MnO}_4^- + \text{MnO}_2 + 2\text{H}_2\text{O}$  ]  
 $\rightarrow$  This  $\text{KMnO}_4$  is not used as lab reagent because of the presence of traces of  $\text{MnO}_2$
- Electrolytic Oxidation of  $\text{MnO}_4^{2-}$  (Commercial method)  
 $\text{MnO}_4^{2-} \xrightarrow[\text{alkaline Solution}]{\text{Electrolytic oxidation}} \text{MnO}_4^- + \text{H}_2$  (Cathode)  
 Manganate (Electrolysis) permanganate ion.

- (ii) Potassium Permanganate ( $\text{KMnO}_4$ ) :-
- Conversion of  $\text{K}_2\text{MnO}_4$  into  $\text{KMnO}_4$
- (C)  $\text{MnO}_4^{2-} + \text{Cl}_2/\text{O}_3 \xrightarrow{\text{Oxidation}} \text{MnO}_4^- + \text{KCl}/\text{O}_2$

$\rightarrow \text{MnO}_2$  is stable only in strongly alkaline solution. In acidic or neutral or weakly basic medium, it disproportionates to  $\text{MnO}_4^-$  and  $\text{MnO}_2$ .

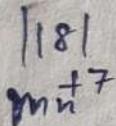
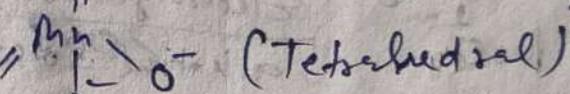
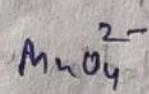
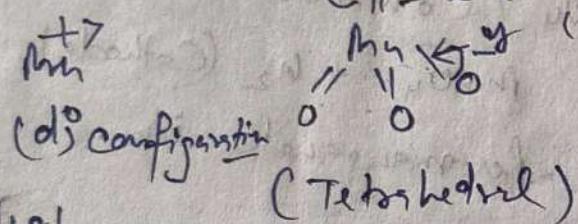
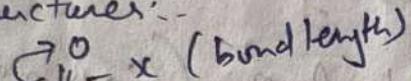


$\rightarrow$  In laboratory, a  $\text{Mn}^{2+}$  ion salt is oxidised by peroxodisulphate to permanganate



Type of hybridisation  
→

Structure:-



a)  $x > y$

b)  $x < y$

c)  $x = y$

d) Can not say

(by Steric No.)

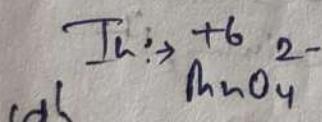
Steric No  $\rightarrow \frac{1}{2}$  (valence e<sup>-</sup> of C.A + Ni. of monovalent attached + cation charge - anion "])

Generally, single bond  $>$  double bond.

→ negative charge of Oxygen in resonance with = bond.

So,  $x = y$ .

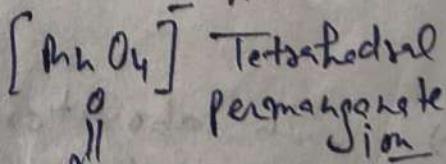
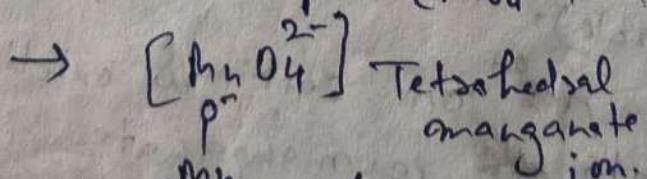
Colour is due to LMCT - Transfer  
Ligand Metal Charge



(d) Configuration  $\downarrow$  Green

All bond lengths are equal due to resonance.

$\text{Mn}^{2+} : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$  → one unpaired electron ( $\text{MnO}_4^-$ ), so paramagnetic in nature.



$\rightarrow$  So,  $\text{MnO}_4^-$  is paramagnetic with one unpaired electron (purple)

(41)

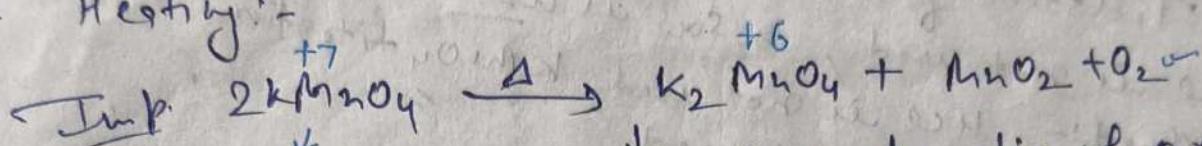
but  $MnO_4^-$  is diamagnetic.

(37)

\* Properties of  $KMnO_4$ :-

- It forms dark colour needle like crystals with a metallic lustre. Its melting point is 533K.
- It is moderately soluble in water giving a purple solution.

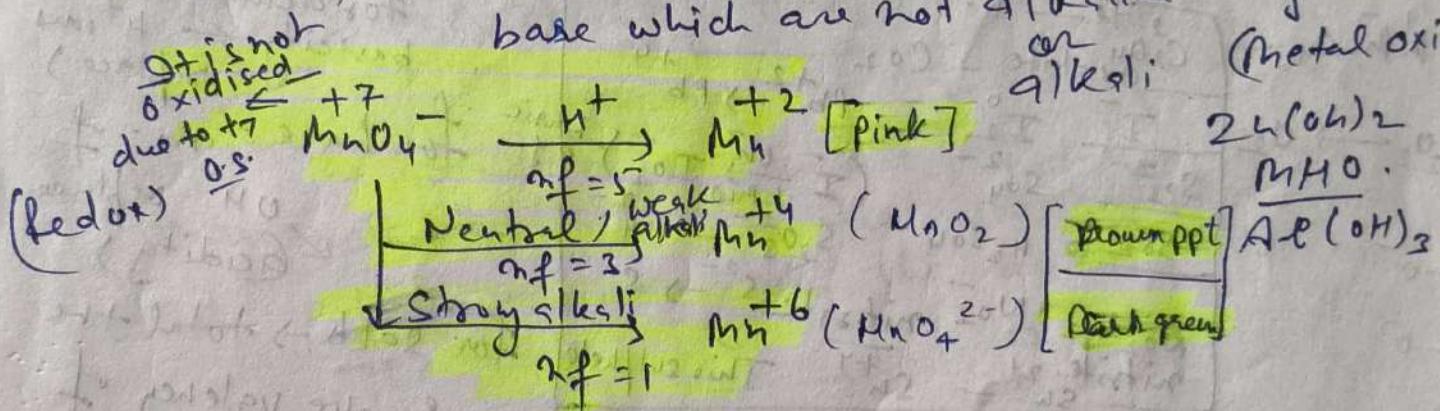
\* Heating:-



O.A. ↓ Method of preparation of oxygen.

- $KMnO_4$  is a powerful oxidising agent in acidic, neutral & alkaline medium.

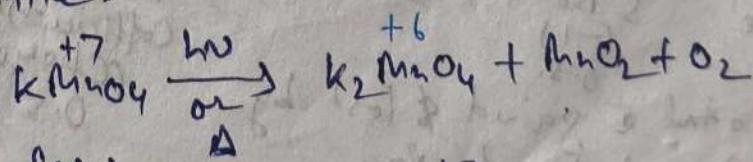
base which are not alkaline:- e.g.  $CuO$  or metal oxide



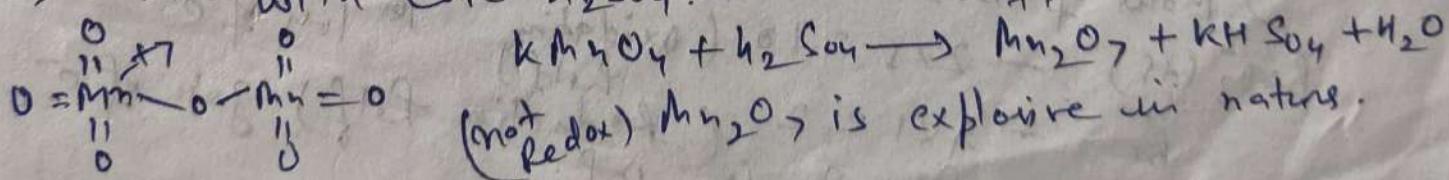
Oxidising nature of  $KMnO_4$ :-

In acidic > In neutral > In Basic

- It is unstable in sunlight so it is kept in dark coloured bottles



→ Rxn with conc.  $H_2SO_4$ :-



→ Rxn with conc. HCl →

$$KMnO_4 + \text{conc. HCl} \rightarrow MnCl_2 + Cl_2 + H_2O$$

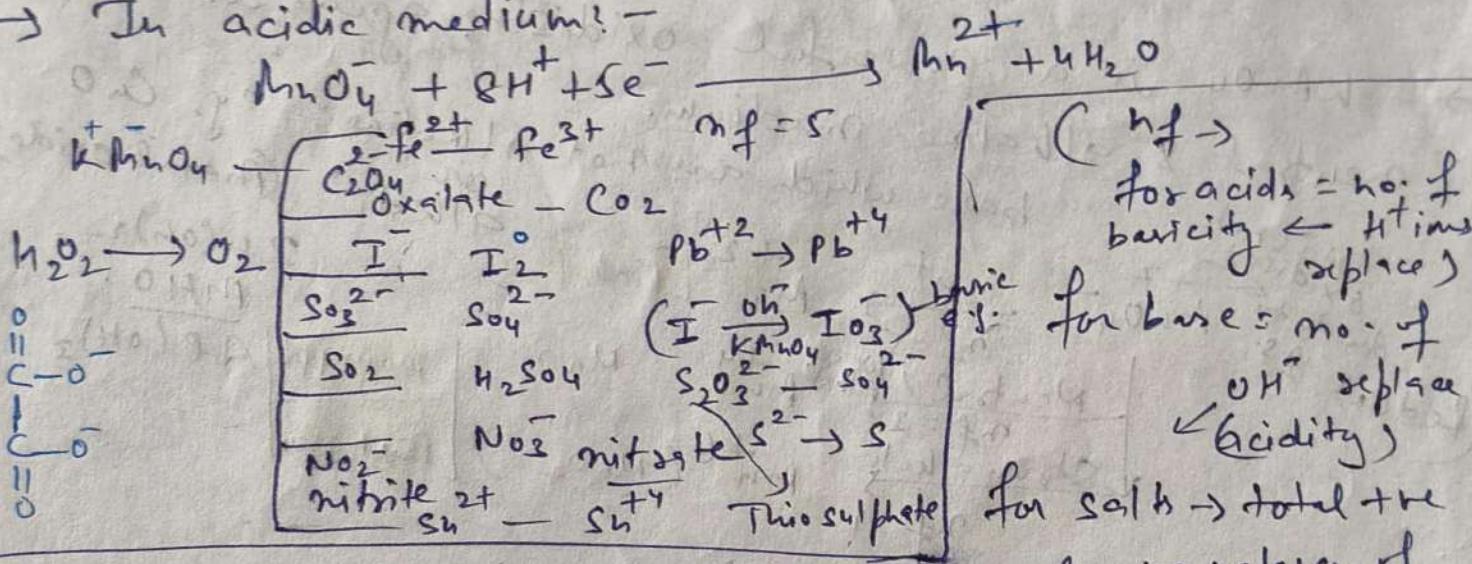
While using  $KMnO_4$  as oxidising agent in volumetric analysis, conc. HCl is not used to make solution acidic as it is oxidised to  $Cl_2$ . Conc.  $H_2SO_4$  is used instead.

In Titration of  $KMnO_4$  acidic medium is used.

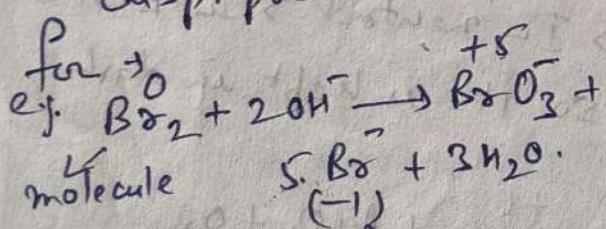
HCl is not used,  $H_2SO_4$  is used.

Imp. Quest: - HCl is not used,  $KMnO_4$  titration  $H_2SO_4$  is used,

→ In acidic medium:-



disproportionation Rxn:-



→ Total e<sup>-</sup> gained & lost by  
 2 moles of  $Ba_2$

$$BaO_3^{(+5)} - 2 \times 5 = 1.0 \quad (\text{oxidation half}) \quad 10 \text{ mol of } e^-$$

$$Ba^{(-1)} - 2 \times 1 = 2 \quad (\text{Reduction half}) \quad \text{gain of } e^-$$

so 8 in  $n_f$ .

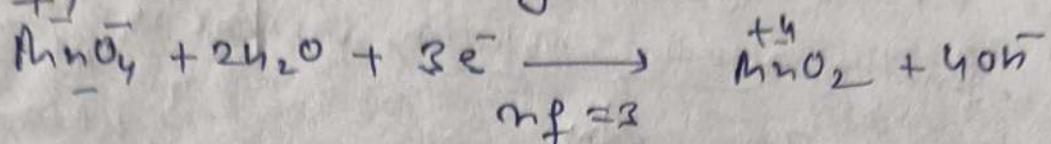
for redox →

Change in oxidation state  
 (Stoichiometric coefficient)  $\rightarrow$  per molecule or total  
 (Charge in O.S.) moles of e<sup>-</sup> gained or  
 $\frac{\text{mole mass}}{\text{Eq. mass}} = n_f$  lost.

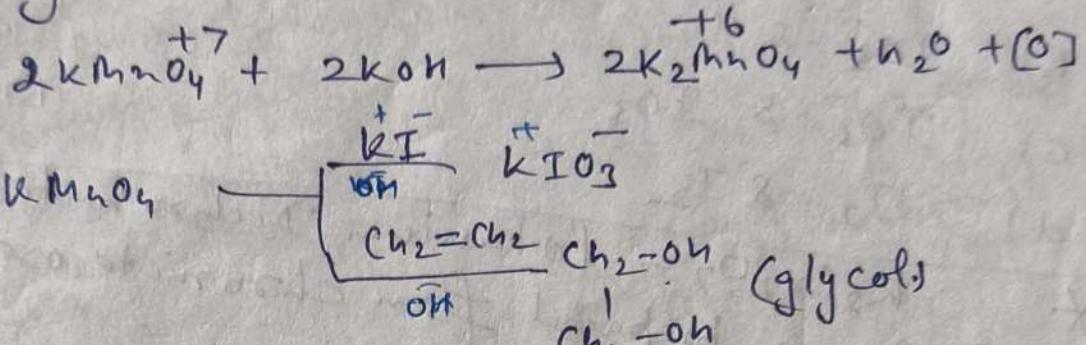
(11)

(39)

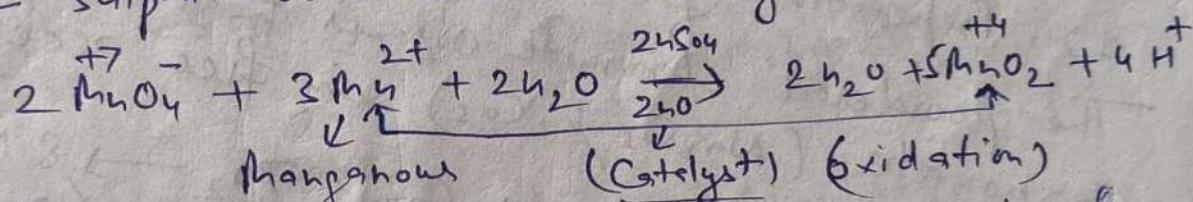
→ In neutral medium/ weakly alkaline medium:-



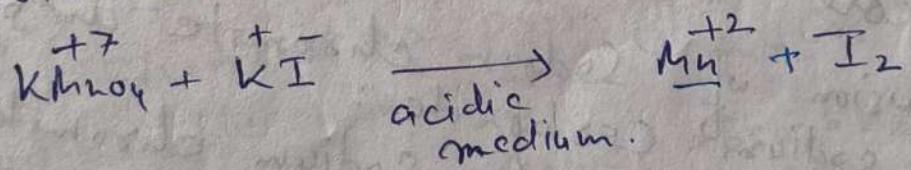
A → In strong alkaline medium:-



→ Manganese salt is oxidised to  $\text{MnO}_2$ : the presence of zinc sulphate or zinc oxide catalysts the oxidation.

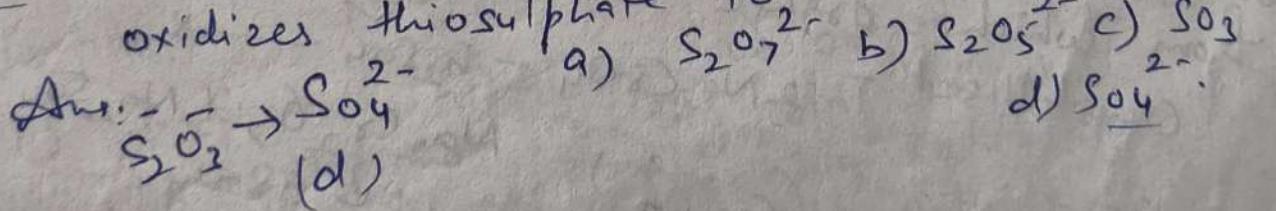


Ques:- The total change in the oxidation state of manganese involved in the reaction of  $\text{KMnO}_4$  and potassium iodide in the acidic medium is:

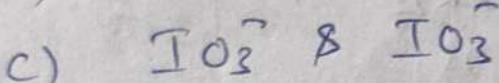
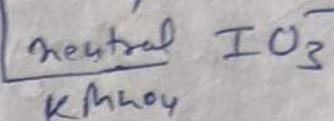
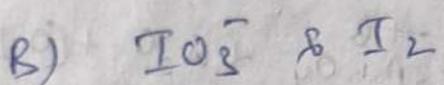
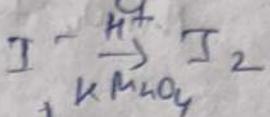
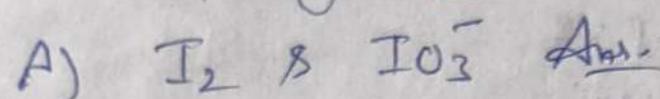


Ans: 5.

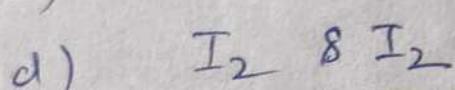
Ques:- In neutral or alkaline solution,  $\text{MnO}_4^-$  oxidizes thiosulphate to:



Ques: KMnO<sub>4</sub> oxidises I<sup>-</sup> in acidic & neutral/faintly alkaline solution, respectively to



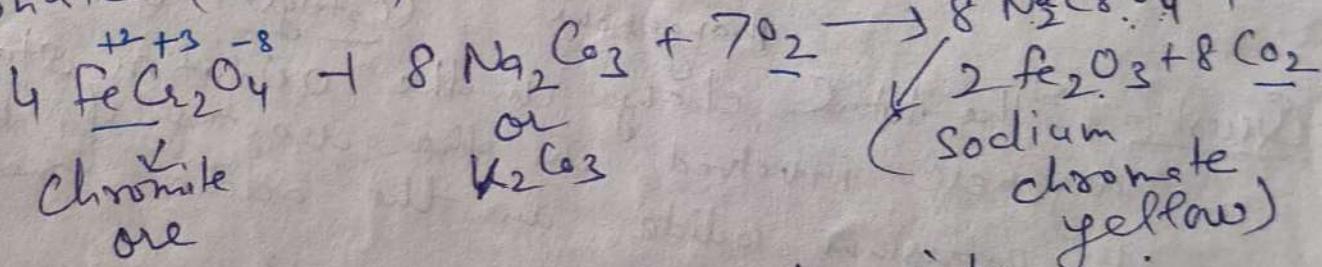
Both - neutral / basic



\* K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> - Potassium Dichromate  
K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is prepared from chromite ore. The steps involved are

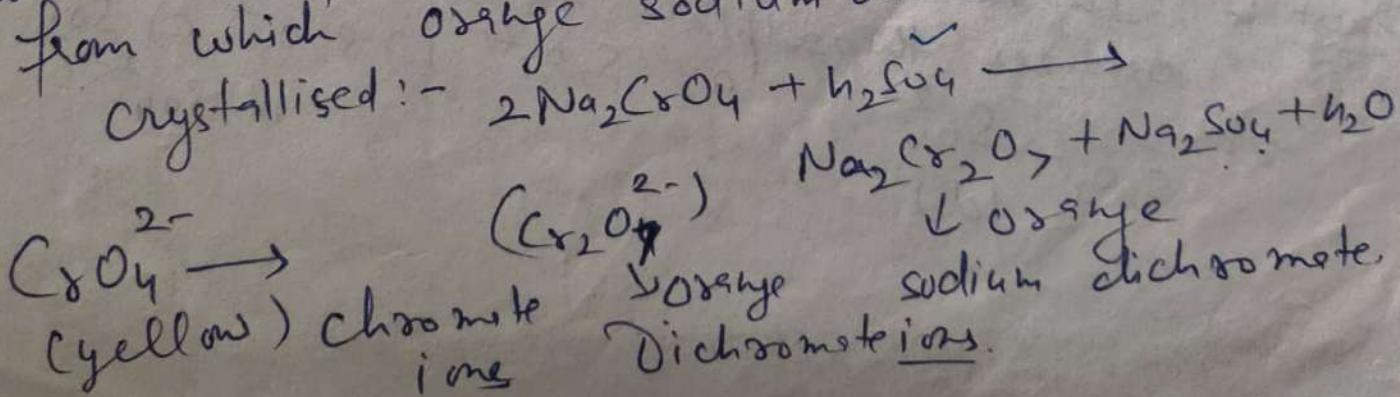
1) Preparation of sodium chromate:-

The powdered chromite ore is heated with Na or K carbonate (Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>) in free access of air.



2) Conversion of sodium chromate into sodium carbonate:

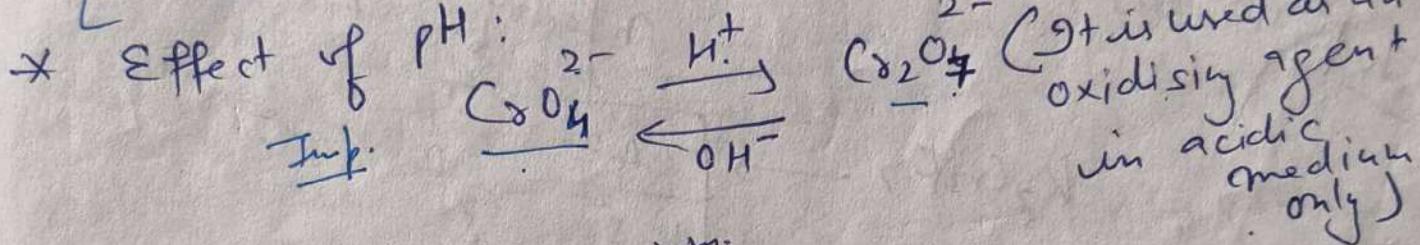
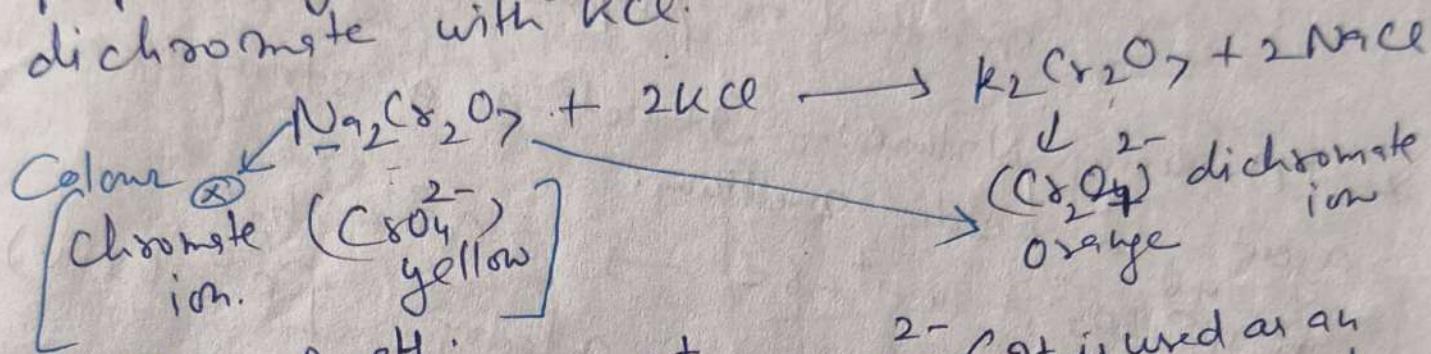
The solution of sodium chromate is filtered and acidified with H<sub>2</sub>SO<sub>4</sub> to give a solution from which orange sodium dichromate can be crystallised:-



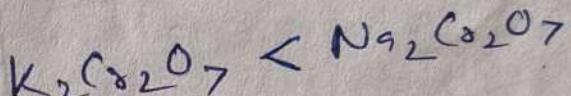
(41)

III) Conversion of sodium dichromate into potassium dichromate with  $\text{KCl}$  -

A) Sodium dichromate is more soluble than potassium dichromate. The latter is therefore, prepared by treating the solution of sodium dichromate with  $\text{KCl}$ .



\*  $K_{SP}$  Values:- Ionic equilibrium.



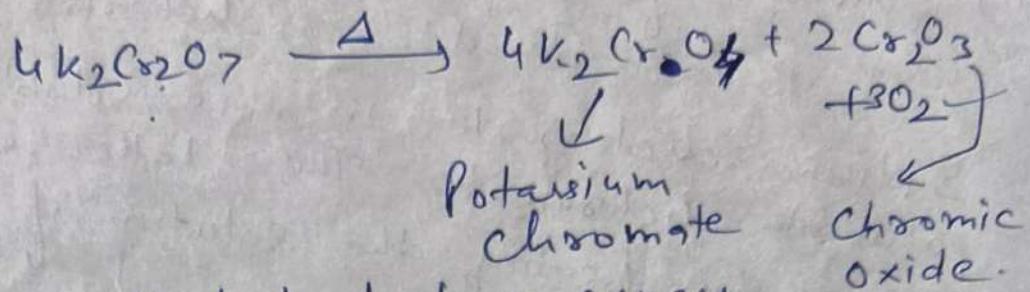
Solubility Product

$\rightarrow \text{Na}_2\text{Cr}_2\text{O}_7$  is used in organic reactions but not in redox titrations as primary standard because it is hygroscopic in nature.  $\text{K}_2\text{Cr}_2\text{O}_7$  is used as it is not hygroscopic (absorb  $\text{H}_2\text{O}$ ) change in conc.

In titration,  $(\text{N})_{\text{V}_1} = \text{N}_2\text{V}_2$  so it affects.

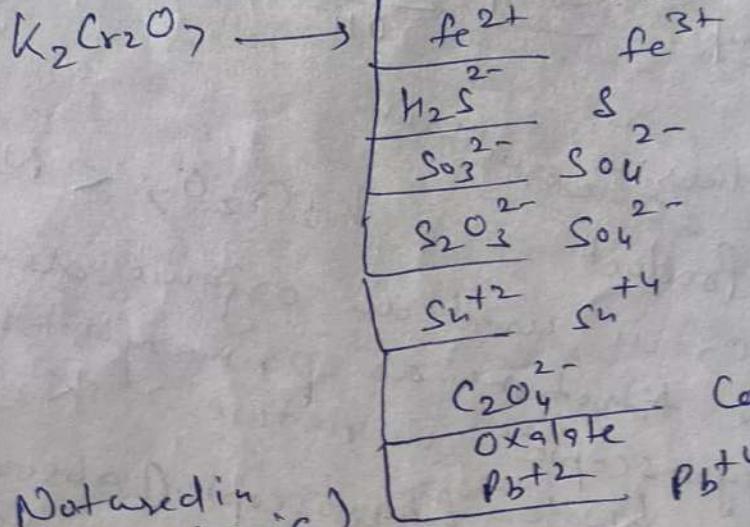
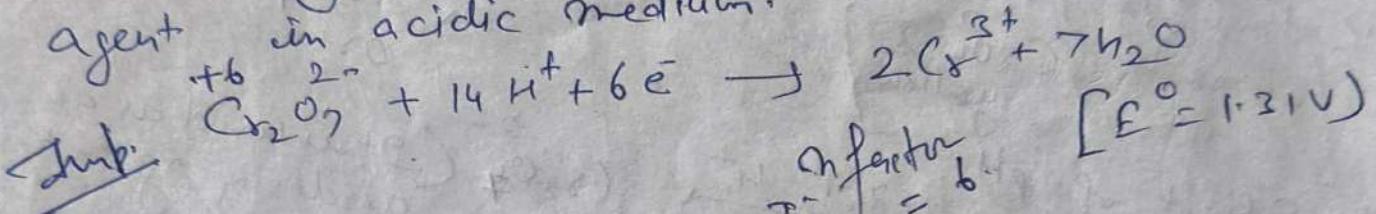
- i)  $\text{K}_2\text{Cr}_2\text{O}_7$  :- i) It is an orange crystalline solid with melting point 670K.  
 ii) It is appreciably soluble in hot water but moderately soluble in cold water.

\* (\*\*) Heating:-



method to prepare oxygen

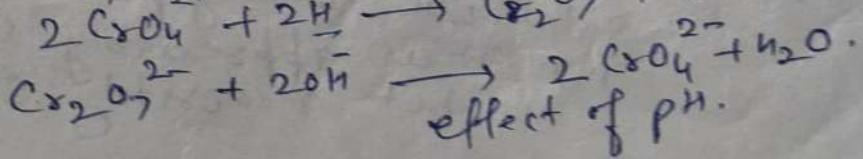
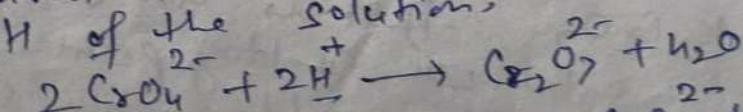
\* Oxidising Nature:- It acts as a strong oxidising agent in acidic medium.



Reason (Nature in basic medium)

Potassium tetroxido chromate (V) upon  $K_3(CrO_8)$  upon  $\frac{1}{2} H_2O_2$  present

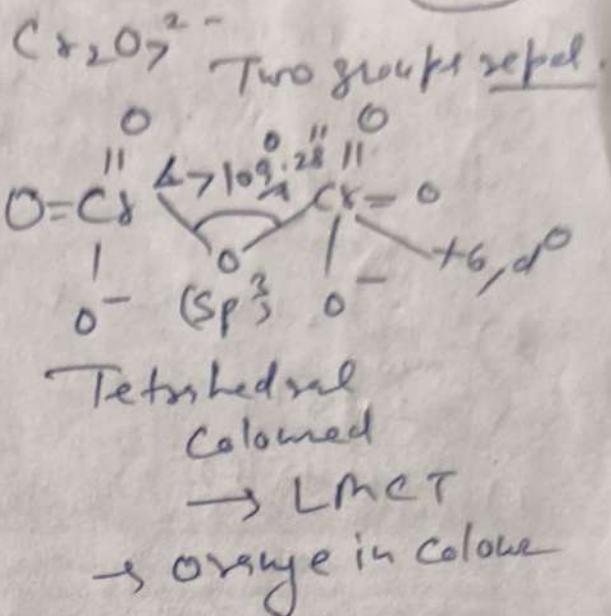
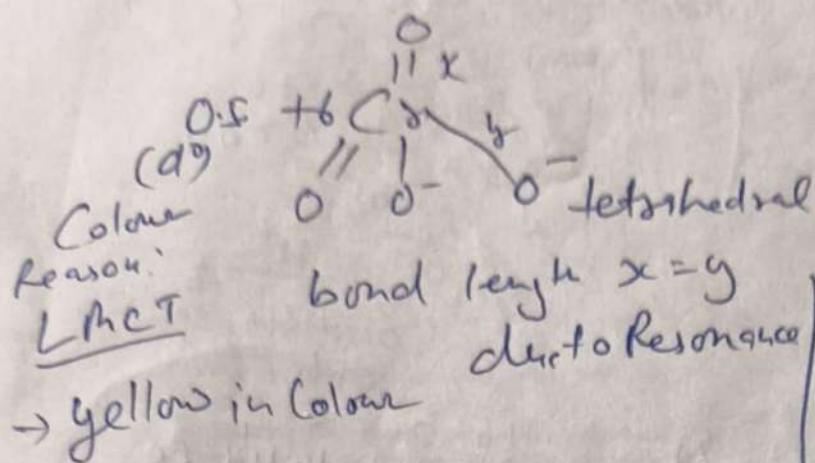
The chromates and dichromates are interconvertible in aqueous solution depending pH of the solution.



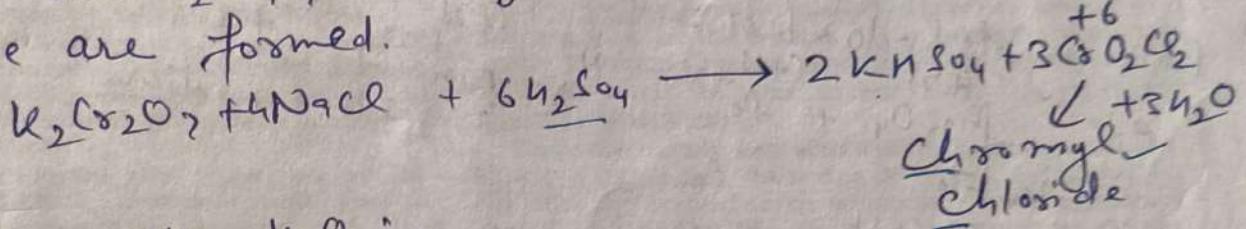
effect of pH.

(43)

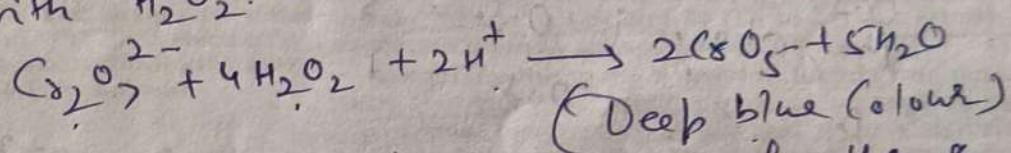
\* Structures of  $\text{CrO}_4^{2-}$



NEET  
\* When a mixture of metal  $\text{Cr}_2\text{O}_7^{2-}$  chloride and conc.  $\text{H}_2\text{SO}_4$ , orange red flames of chromyl chloride are formed.

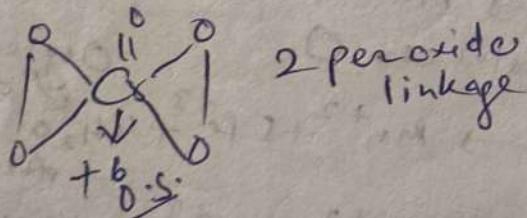


\* Reaction with  $\text{H}_2\text{O}_2^{2-}$



$\text{CrO}_5$  is stable only in presence of ether & pyridine.

Str. of  $\text{CrO}_5$ :



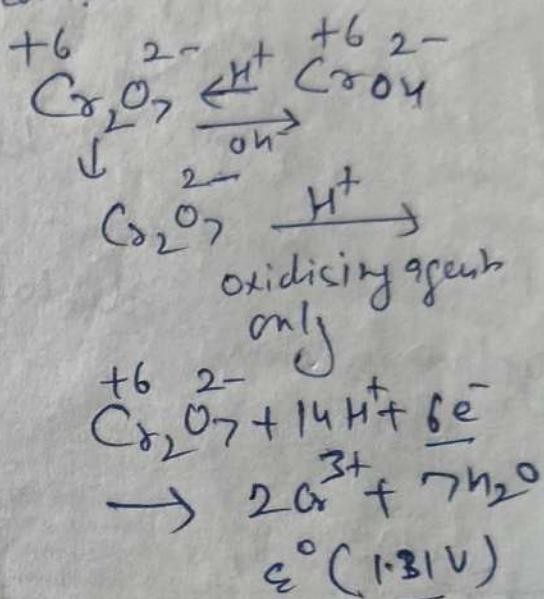
Ques:- Potassium dichromate acts as a strong oxidizing agent in acidic solution. During this process, the oxidation state changes from: -

- A) +3 to +1

B) +6 to +3 — ✓ Ans.

C) +2 to +1

D) +6 to +2



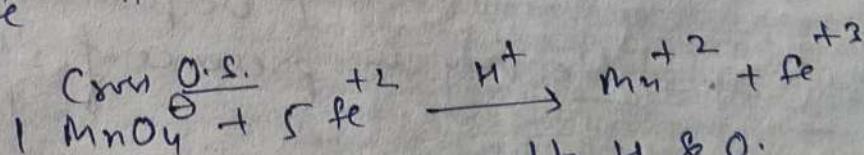
Balancing of Redox rxn:-

e.g.  $\text{MnO}_4^- + \text{Fe} \xrightarrow{\text{H}^+} \text{Mn}^{+2} + \text{Fe}^{+3}$   
in acidic medium

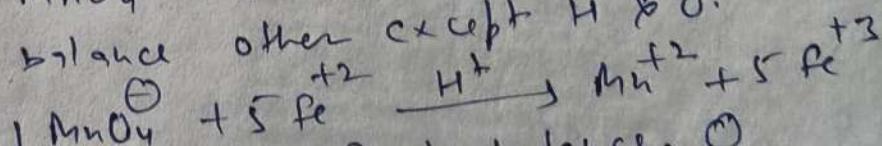
Gaulake

$$\text{O.S.}_{\text{Mn}} \xrightarrow{\text{ISL}} \text{change in O.S.} = 5$$

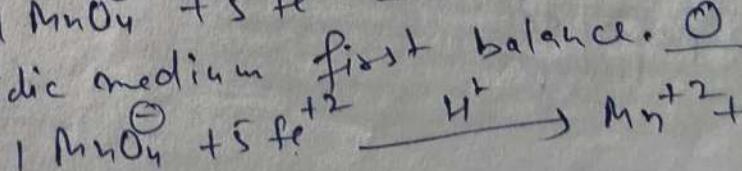
$$\text{Fe} \quad 1 \quad " \quad \text{O.S.} = 1$$



$\text{MnO}_4^- + 5 \text{Fe}^{2+} + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$



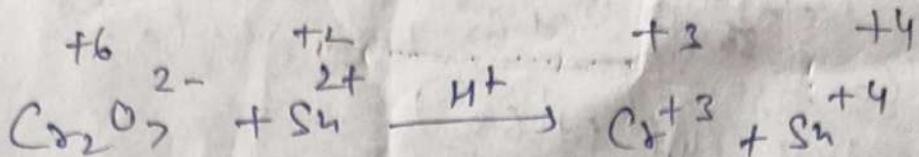
In acidic medium first balance.  $\text{O}^-$



$$8H^+ + 1MnO_4^- + 5Fe^{+2} \xrightarrow{\text{then } H_2} Mn^{+2} + 5Fe^{+3} + 4H_2O \text{ Water}$$

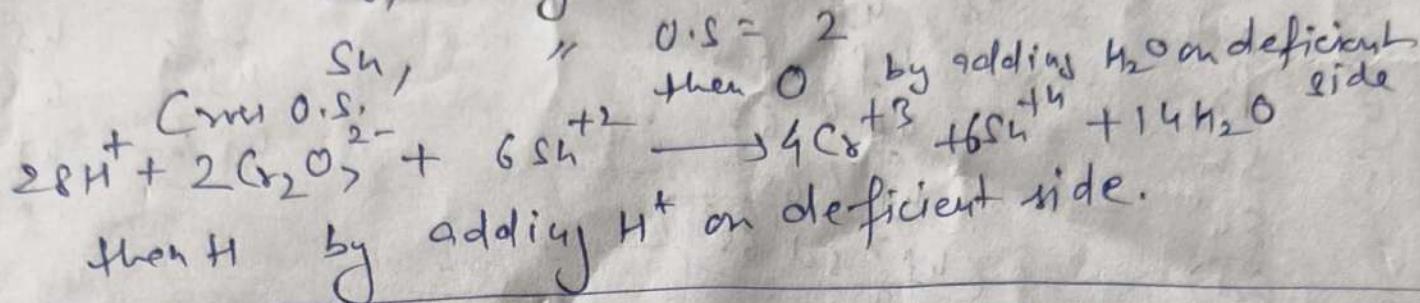
Ans.

r.f



(45)

$$\text{Cr}_2 \text{ charge in O.S.} = 3 \times 2 = 6 \quad (\text{G}_2)$$



### \* f-block Elements:-

hf series - Lanthanides  $Z = 58$  to  $71$

$\uparrow$  14 elements

sf series - Actinides  $Z = 90$  to  $103$

$\uparrow$  14 "

Electronic Configuration: -  $\text{Nel}(n-2)f^{1-14} (n-1)d^1 n s^2$ . General

Inner transition elements.

Here  $\rightarrow e^-$  fill in outermost shell  $n s^2$   
 $(n-2)f^{1-14}$   
in d-block -  $e^-$  add in  $(n-1)d^{1-10}$ .

\* The Lanthanoids:-  
Lanthanum  $\rightarrow$  Properties similar to f block, but it is a d block element.

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
Lanthanum	Cerium	Praseo-	Neo-	Eu-	Dy-	Samarium	Eu	Gado.	Dyspro-	Terbium	Holmium	Thulium	Ytterbium	
		dymium	dymium	methium	Eu	Sm	Eu	Plum.	Eu	Tb	Dy	Ho	Er	Tm Yb Lu
58	Ce	Rb	Nd	Pm	Sm	Eu	Eu	Eu	Eu	Ad	Ad	Ad	Ad	
Ticks	Gene for Nadiya Prerna	Samai	Samai	Samai	Samai	Samai	Samai	Samai	Samai	Samai	Samai	Samai	Samai	Samai

Gad-fab dil hue aur  
Gad

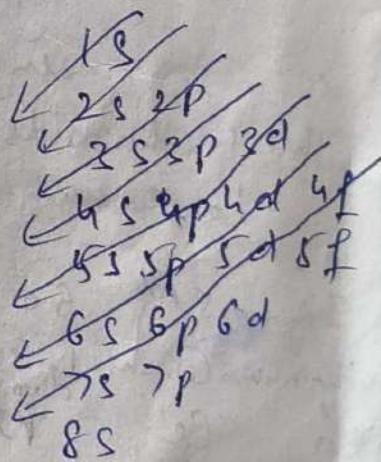
Lecto.

	$\text{Ce}$	$\text{Pr}$	$\text{Nd}$	$\text{Pm}$	$\text{Sm}$	$\text{Eu}$	$\text{Gd}$	$\text{Tb}$	$\text{Dy}$	$\text{Ho}$	$\text{Er}$	$\text{Tm}$	$\text{Yb}$	$\text{Lu}$
①	$\text{Ce}$	$\text{Pr}$	$\text{Nd}$	$\text{Pm}$	$\text{Sm}$	$\text{Eu}$	$\text{Gd}$	$\text{Tb}$	$\text{Dy}$	$\text{Ho}$	$\text{Er}$	$\text{Tm}$	$\text{Yb}$	$\text{Lu}$
②	$\text{La}^{+}$	$\text{Pr}^{+}$	$\text{Nd}^{+}$	$\text{Pm}^{+}$	$\text{Sm}^{+}$	$\text{Eu}^{+}$	$\text{Gd}^{+}$	$\text{Tb}^{+}$	$\text{Dy}^{+}$	$\text{Ho}^{+}$	$\text{Er}^{+}$	$\text{Tm}^{+}$	$\text{Yb}^{+}$	$\text{Lu}^{+}$
③	$\text{Ce}^{2+}$	$\text{Pr}^{2+}$	$\text{Nd}^{2+}$	$\text{Pm}^{2+}$	$\text{Sm}^{2+}$	$\text{Eu}^{2+}$	$\text{Gd}^{2+}$	$\text{Tb}^{2+}$	$\text{Dy}^{2+}$	$\text{Ho}^{2+}$	$\text{Er}^{2+}$	$\text{Tm}^{2+}$	$\text{Yb}^{2+}$	$\text{Lu}^{2+}$
④	$\text{Ce}^{3+}$	$\text{Pr}^{3+}$	$\text{Nd}^{3+}$	$\text{Pm}^{3+}$	$\text{Sm}^{3+}$	$\text{Eu}^{3+}$	$\text{Gd}^{3+}$	$\text{Tb}^{3+}$	$\text{Dy}^{3+}$	$\text{Ho}^{3+}$	$\text{Er}^{3+}$	$\text{Tm}^{3+}$	$\text{Yb}^{3+}$	$\text{Lu}^{3+}$

### Oxidation states:-

$\text{La}$	57	—	+3	—
$\text{Ce}$	58	—	+3	+4
$\text{Pr}$	59	—	+3	+4
$\text{Nd}$	60	+2	+3	+4
$\text{Pm}$	61	—	+3	—
$\text{Sm}$	62	+2	+3	—
$\text{Eu}$	63	+2	+3	—
$\text{Gd}$	64	—	+3	+4
$\text{Tb}$	65	—	+3	+4
$\text{Dy}$	66	—	+3	—
$\text{Ho}$	67	—	+3	—
$\text{Er}$	68	—	+3	—
$\text{Tm}$	69	+2	+3	—
$\text{Yb}$	70	+2	+3	—
$\text{Lu}$	71	—	+3	—

Generally first  $4f$  fill half  
then  $5d$  but  
in 2 cases  $5d$   
orbital. filled.

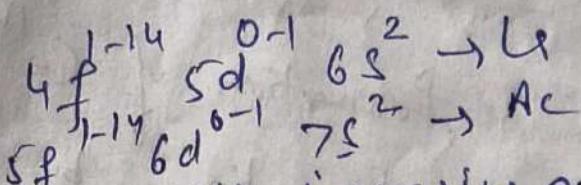


(47)

→ Because Lanthanum closely resembles the Lanthanoids. It is usually included in any discussion of the Lanthanoids for which the general symbol  $Ln$  is often used.

→ Similarly, a discussion of the actinoids includes actinium besides the fourteen elements constituting (Ac) the series.

General  $e^-$  configuration:-

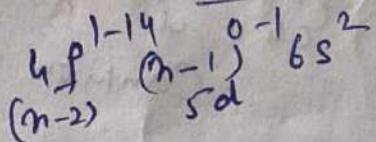


\* Atomic radius:-

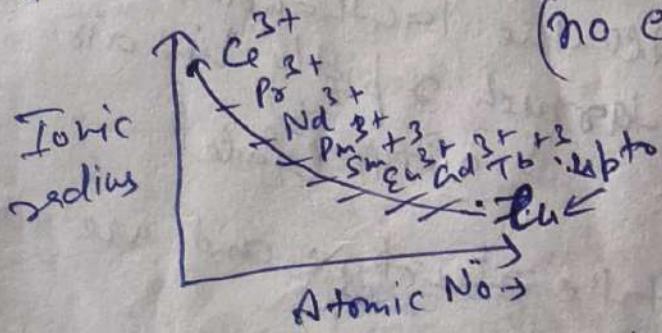
→ Atomic radius decreases with increasing atomic number because of the poor shielding of  $4f\ e^-$ .  
(Lanthanoid Contraction)

→ Exception -  $E_h$  - ~~max. size~~ increases.  
left to right

$z_{eff} \uparrow \rightarrow$   
size decreases



\* Ionic radius: ( $R^+$ )

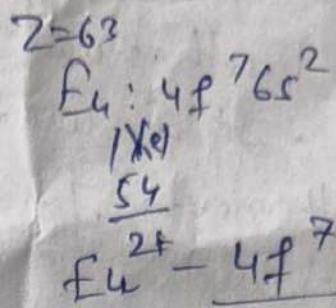
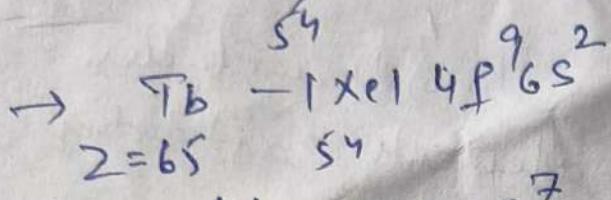
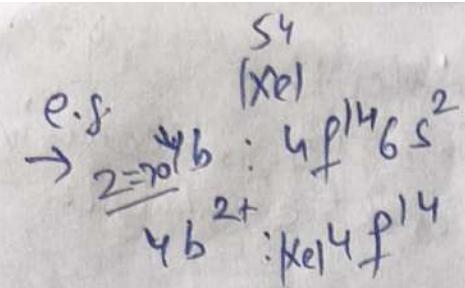


(no exception)

\* Oxidation states: → In the Lanthanoids,  $La(II)$  &  $Ln(III)$  Compounds are predominant species.

→ However, occasionally  $+2$  and  $+4$  ions in solution or in solid compounds are also obtained.

→ This irregularity arises mainly from the extra stability of empty, half-filled or filled f sub-shell.



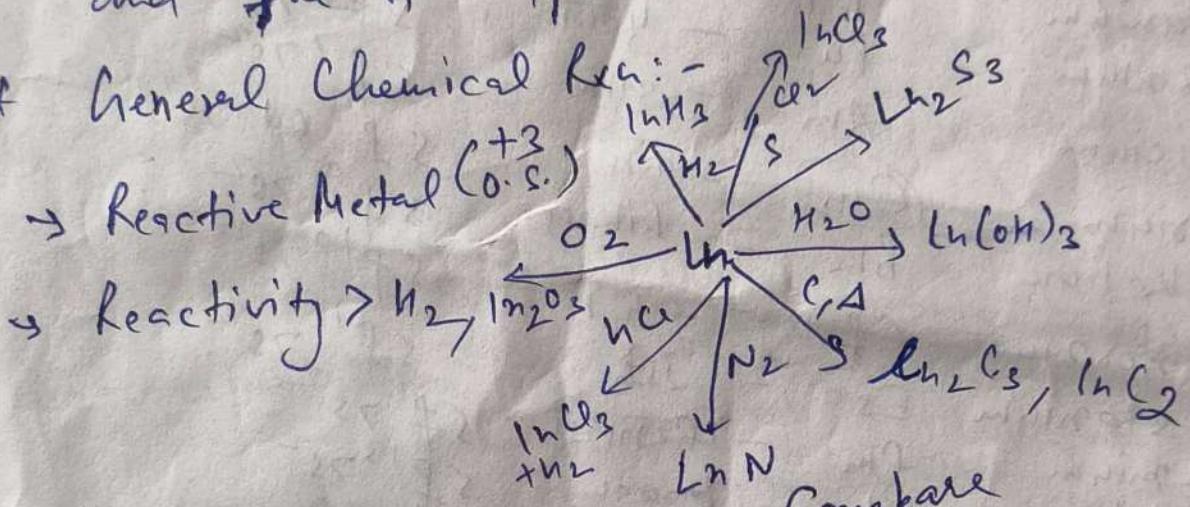
- $\rightarrow$  The formation of  $\text{Ce}^{IV(4+)} - \text{Ce} = \text{Xe}^{\underline{1}} \text{f}^7 \text{g}^1 \text{s}^2 \rightarrow \text{Xe}^{\underline{1}}$  is favoured by its noble gas configuration, but it is a strong oxidant reverting to the common +3 state.
- $\rightarrow$   $\text{Pr}$ ,  $\text{Nd}$ ,  $\text{Tb}$  and  $\text{Dy}$  also exhibit +4 state but only in oxides,  $\text{MO}_2$  ↓ metal.
- $\rightarrow$   $\text{Eu}^{2+}$  is a strong reducing agent changing to the common +3 state.

\* General characteristics: i) All the lanthanoids are silvery white soft metals and tarnish rapidly in air.  $\rightarrow$   $\text{CeO}_2$  (fade)

- ii) The hardness increases with increase in Z.
- iii) They have typically metallic structure and are good conductor of heat & electricity.
- iv) Their melting points range b/w 1000 to 1200 K but  $(\text{Sm})$  Samarium melts at 1623 K.
- v) Density & other properties change smoothly except for  $\text{Ce} \& \text{Yb}$ .  
 $\xrightarrow{\text{left to right}}$  ↓ max. size

- Many trivalent lanthanoid ions are coloured but in the solid state and in aqueous solution
- Colour of these ions may be attributed to the presence of f-electrons.
- Neither  $\text{La}^{3+}$  nor  $\text{Lu}^{3+}$  ion shows any colour but the rest do so.
- The lanthanoid ions other than the  $f^0$  type ( $\text{La}^{3+}$  &  $\text{Ce}^{4+}$ ) and the  $f^{14}$  type ( $\text{Yb}^{2+}$  and  $\text{Lu}^{3+}$ ) are all paramagnetic.

\* General Chemical Reactions:-



Oxidation. Basic strength:- Compare

$\text{Ln(OH)}_3$   
Size ↑  
bond length ↑  
basic character ↑

$\text{Ln(OH)}_3$   
Size ↓  
bond length ↓  
basic character ↓

- Uses:-
- The best single use of the lanthanoids is for the production of alloy steels for plates & pipes.
  - A well known alloy is mischmetall consists of a lanthanoid metal (~95%) and iron (~5%) and traces of S, C, Ca and Al. A good deal of mischmetall is used in Mg-based alloy to produce bullets, shell & lighter flint.
  - Mixed oxides of lanthanoids are employed as catalyst in petroleum cracking.
  - Some individual Ln oxides are used as phosphors

\* in television screens and similar fluorescing surfaces.

\* Actinoids — Z = 90 to 103. — 14 elements

or  
Actinides

- \* 89 — Actinium
- 90 Thorium
- 91 Protactinium
- 92 Uranium
- 93 Neptunium
- 94 Plutonium
- 95 Americium
- 96 Curium
- 97 Berkelium
- 98 Californium
- 99 Einsteinium
- 100 Fermium
- 101 Mendelevium
- 102 Nobelium
- 103 Lawrencium

	Ac	Rd	$5p^0$
	Th	—	$6d^1 7s^2$
	(Pa)	—	$6d^2 7s^2$
	U	—	$5f^2 6d^1 7s^2$
	Np	—	$5f^3 6d^1 7s^2$
	Pu	—	$5f^4 7s^2$
	Am	—	$5f^5 7s^2$
	(Cm)	—	$5f^6 7s^2$
	Bk	—	$5f^7 6d^1 7s^2$
	Cf	—	$5f^8 7s^2$
	Es	—	$5f^9 7s^2$
	Fm	—	$5f^{10} 7s^2$
	Md	—	$5f^{11} 7s^2$
	No	—	$5f^{12} 7s^2$
	(Ls)	—	$5f^{13} 7s^2$
			$5f^{14} 6d^1 7s^2$

After Uranium → Transuranium or Transactinide

General e<sup>-</sup> configuration: -  $(n-2)f^{1-4} (n-1)d^{0-1} ns^2$   
 $5f^{1-14} 6d^{0-1} 7s^2$

Ionic Radius: -

$r_{eff} \uparrow$   
 Left to right →  
 Size ↓, actinoid contraction, poor  
 shield of Sf along with 4f C.

\* Lanthanoid Contraction

< Actinoid contraction  
 more poor shielding effect.

(51)

## Oxidation states:-

→ There is a greater range of oxidation states which is attributed to the fact that the  $5f$ ,  $6d$  &  $7s$  levels are of comparable energies.

Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Fs	Fm	Md	No	Lu
+4	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3
+4	+4	+4	+4	+4	+4	+4	+4	+4	+4	+4	+4	+4	+4
+5	+5	+5	+5	+5	+5	+5	+5	+5	+5	+5	+5	+5	+5
+6	+6	+6	+6	+6	+6	+6	+6	+6	+6	+6	+6	+6	+6
		+7	+7										

+3 is dominating

(5d, 6d, 7s)

low energy gap.

- Characteristics:-
- i) Silvery in appearance
  - ii) Reactive metals
  - iii) The action of boiling water on them gives a mixture of oxide & hydride and combination with most non-metals takes place at moderate temp.
  - iv) HCl attacks all metals but most are slightly affected by nitric acid owing to the formation of protective oxide layer.
  - v) Alkalies have no actions
  - vi) Radioactive in nature

Imp:  $e^-$  configuration, atomic radius, ionic radius, Oxidation states.

Thank You (Answered )  
Questions - (3-4) IIT-JEE  
NEET-(5-6)