

# 12<sup>th</sup> HACKERS KA JUGRAD

## d and f block Elements

### Introduction

d block

- last electron ji subshell m jaayega, element block ho jaayega

- d block starts from 4<sup>th</sup> period

- group no. - 9-12.

### Transition Metal

- There are four series in d block - 3d, 4d, 5d, 6d

#### Transition Series

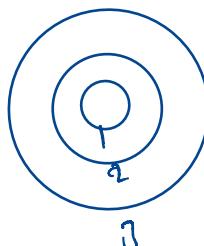
1 <sup>st</sup>	3d series	Sc <sub>21</sub> - Zn <sub>30</sub>	10 ✓
2 <sup>nd</sup>	4d series	Y <sub>39</sub> - Cd <sub>48</sub>	10 ✓
3 <sup>rd</sup>	5d series	La <sub>57</sub> - Hf <sub>72</sub> - Hg <sub>80</sub>	9 + 1 = 10 ✓
4 <sup>th</sup>	6d series	Ac <sub>89</sub> , Unq <sub>104</sub> - Uub <sub>112</sub>	9 + 1 = 10 ✓

Shell no.

1  
2  
3  
4

subshell

1s  
s<sub>1</sub> p  
2s 2p  
s<sub>1</sub> p<sub>3</sub> d  
s<sub>1</sub> p<sub>3</sub> d, f  
4s 4p 4d 4f



	1	2						(18)
1	3						He	8
2							Ne	8
3	11						N	18
4	19	3	4	5	6	7	8	18
	20	21	22	23	24	25	26	30
5	37	38	39	40	41	42	43	44
6	55	56	57	15 (1d + 5F)				54
7	87	88	15 (1d + 4F)					86
			5d (5.8 - 7.1) (7.2 - 8.0)	1d	14F	9d		Rn
								118
								4u0
								32
								32

d block → no group = 10

$8, 8, 18, 18, 32, 32$

- D Block elements / ions having incompletely filled d orbital either in ground state or in most stable oxidation state are called transition elements
- All d-Block elements are not transition elements. Ex- Zn, Cd, Hg are not transition elements  
→ All d block elements are transition Element → Except Zn, Cd, Hg
- The d-block occupies the large middle section of the periodic table between s- and p-blocks in the periodic table
- All are metal

d subshell

no. of orbitals

$$= 5$$

1L | 1L | 1L | 1L | 1L

\* no. of  $e^-$  in an orbital = 2

$$\therefore \text{no. of } e^- \text{ in } d = 5 \times 2 \\ = 10$$

$d^{10}$  → completely filled

Zn, Cd & Hg are Pseudo transition metals

Cu, Ag & Au are class coinage metals.

$d^1$   
 $d^2$   
 $d^3$   
 $d^4$   
 $d^5$   
 $d^6$   
 $d^7$   
 $d^8$   
 $d^9$

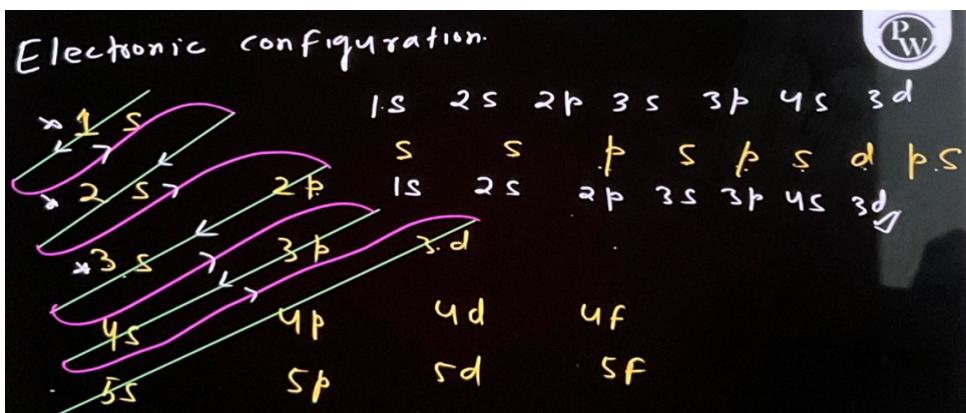
} incompletely filled

Electronic Configuration

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

exceptions -  $Cr = 4s^1 3d^5$   
 $Cu = 4s^1 3d^{10}$   
 $Pd = 5s^0 4d^{10}$

shell/orbit	Subshell	orbital
K 1	s	
L 2	s, p	
M 3	s, p, d	
N 4	s, p, d, f	



Sub shell  $\rightarrow$  shape  $\rightarrow$  spherical

no. of orbital = 1

no. of  $e^-$  in an orbital = 2

no. of  $e^-$  in s = 2

p sub shell  $\rightarrow$  shape - dumbbell

no. of orbital = 3

no. of p  $e^-$  = 6  $\Rightarrow p^6$

d sub shell  $\rightarrow$  shape - double dumbbell

no. of orbitals = 5

$$\text{no. of } e^- = 5 \times 2 \\ = 10 \Rightarrow d^1.$$

f sub-shell  $\rightarrow$  no. of orbitals = 7

$$\text{no. of } e^- \text{ in f} = 7 \times 2 \\ = 14$$

साईटिस्ट		वैकरमन			फेकोनी			कु जन		
	Sc	Tl	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Z	21	22	23	24	25	26	27	28	29	30
4s	2	2	2	1	2	2	2	2	1	2
3d	1	2	3	5	5	6	7	8	10	10

BKT  
 3d - 4, 9  
 4d - 3, 9 X  
 5d - 8 X  
 6d - 9 ✓ X

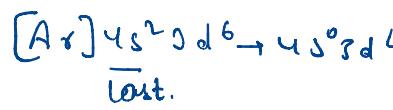
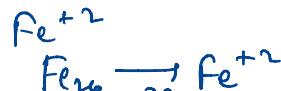
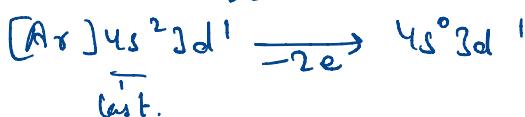
2 <sup>nd</sup> Series										
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Z	39	40	41	42	43	44	45	46	47	48
5s	2	2	1	1	1	1	1	0	1	2
4d	1	2	4	5	6	7	8	10	10	10
	1	2	3	4	5	6	7	8	9	10

3 <sup>rd</sup> Series										
	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Z	57	72	73	74	75	76	77	78	79	80
6s	✓2	✓2	✓2	✓2	✓2	✓2	✓2	✓1	✓1	✓2
5d	1	2	3	4	5	6	7	9	10	10
	1	2	3	4	5	6	7	8	9	10

#### 4<sup>th</sup> Series

	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn
Z	89	104	105	106	107	108	109	110	111	112
7s	2	2	2	2	2	2	2	2	1	2
6d	1	2	3	4	5	6	7	8	10	10

3d - 4, 9  
 4d - 3, 9  
 5d - 8 X  
 6d - 9

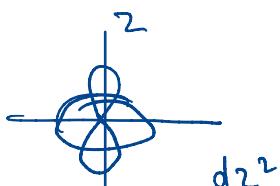
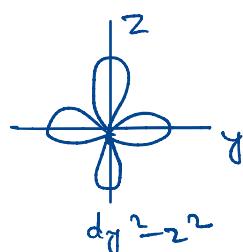
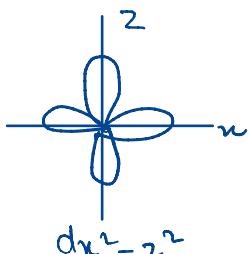
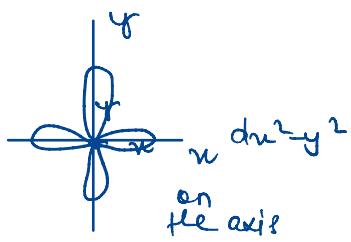
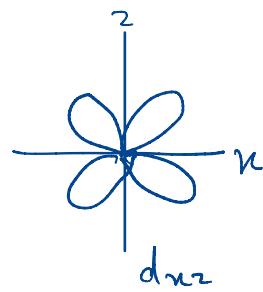
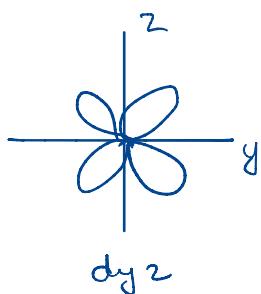
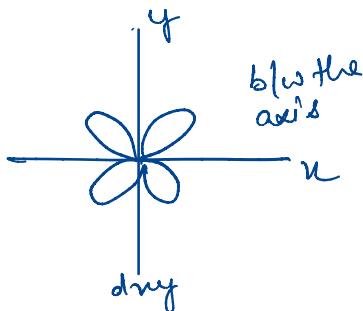
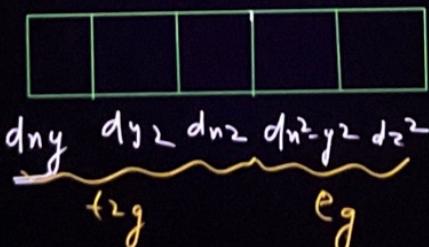


\* e<sup>-</sup> hamisha outer most (last shell) ke nikala jaata h.

## d-orbital

- There are five types of d orbitals, often labeled as  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$ ,  $d_{x^2-y^2}$ , and  $d_{z^2}$ . Each of these orbitals has a specific shape and orientation in space, contributing to the overall electron distribution around the nucleus

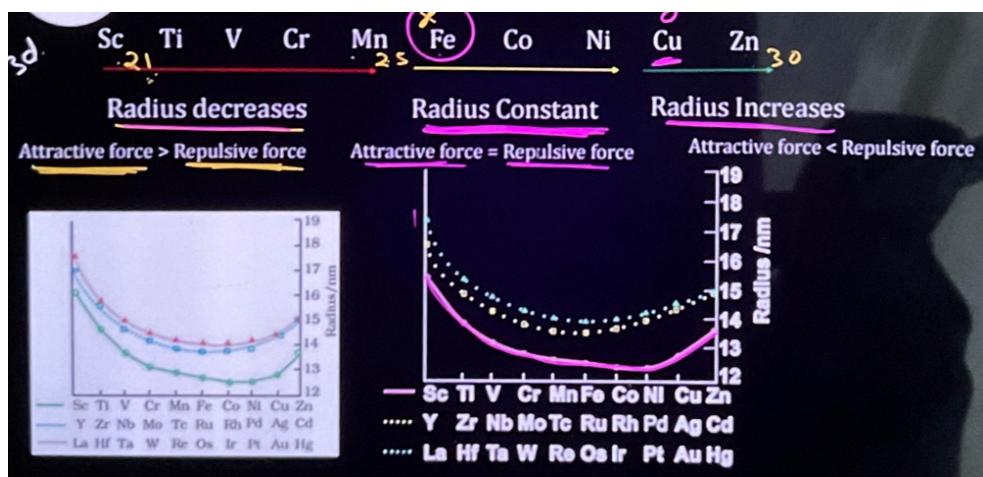
$n, g, \Sigma$



## Physical properties

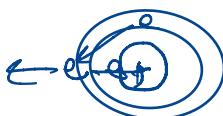
- ✓ All the transition elements display typical metallic properties such as high tensile strength, ductility, malleability, high thermal and electrical conductivity and metallic lustre
- ✓ The transition metals (with the exception of Zn, Cd and Hg) are very hard and have low volatility
- ✓ Hg is liquid
- ✓ Their melting and boiling points are high
- ✓ They have high enthalpies of atomisation

## Atomic size



distance from centre of nucleus  
to the outermost  $e^-$

- \* proton & electron  $\rightarrow$  attractive force
- \* electron & electron  $\rightarrow$  repulsive
- \*  $F_{\text{net}} = F_{\text{attr}} - F_{\text{rep.}}$



nucleus  $\rightarrow$  proton & neutron

$$R \propto 1/F_{\text{attr}}$$

$$R \propto F_{\text{rep.}}$$

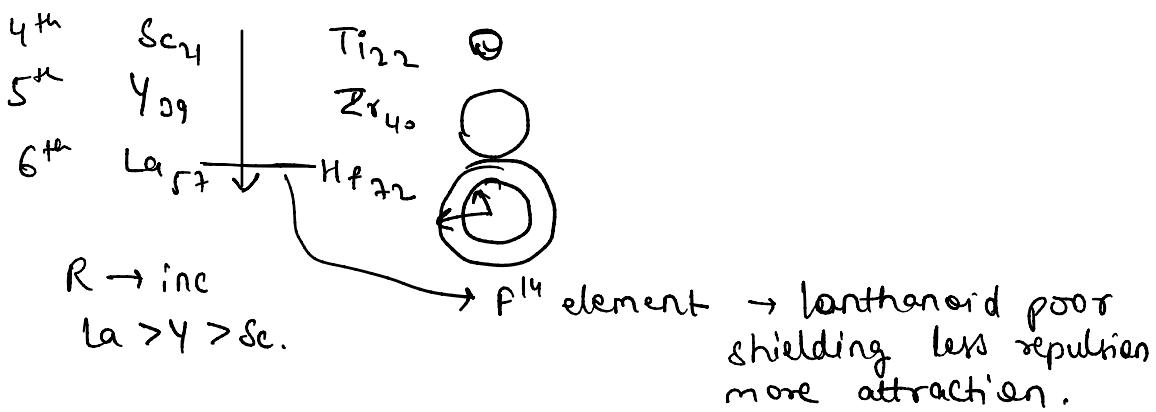
# Lanthanoid Contraction

$3d$	$Sc$	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	$\rightarrow 1st$
$ud$	$Y$	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	$\rightarrow 2nd$
$sd$	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	$\rightarrow 3rd$

$$(R)_{ud} = (R)_{sd}$$

$$La > Y > Sc$$

$$s > p > d > f$$



Shielding / screening  $\propto$  repulsive force  
(e-e)

Order of size

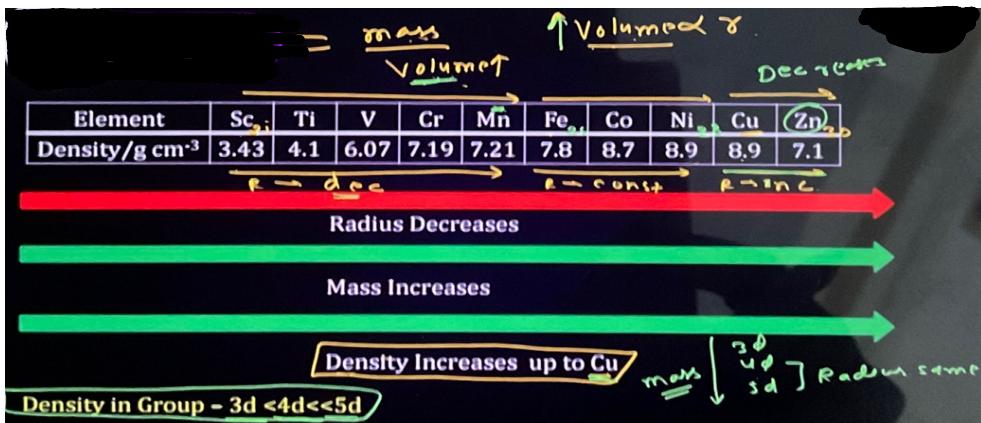
$s < p < d < f$

  $\rightarrow$

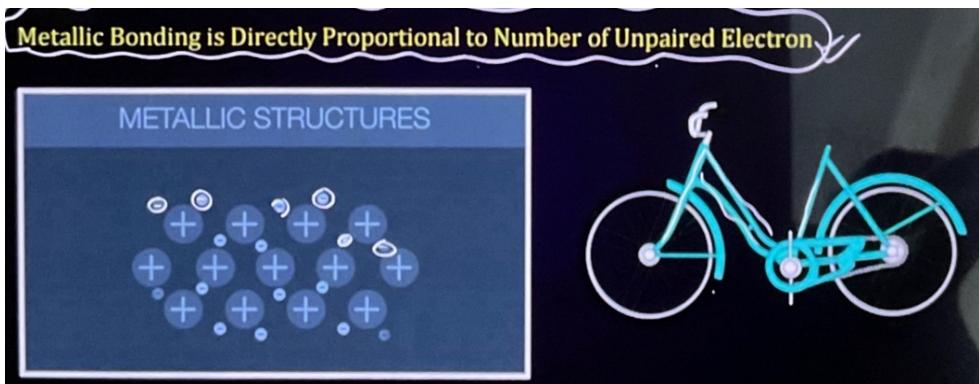
The net result of the Lanthanoid contraction is that the second and the third d series exhibit similar radii (e.g.,  $160\text{ pm}$ ,  $Hf$  159 pm) and have

very similar physical and chemical properties.

## Density

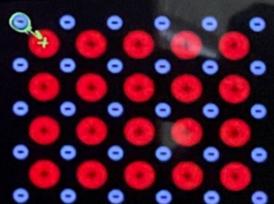


## Metallic Character-

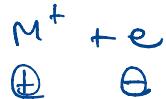
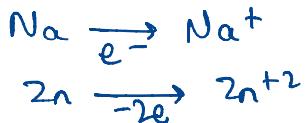


- Metallic bond, force that holds atoms together in a metallic substance
- Metallic bonding is a type of Chemical Bond that arises from the electrostatic attractive force between Conduction electrons and positively charged metal ions
- Metallic Bond Strength is directly proportional to charge on metal and Number of valence electron
- Metallic Bond strength is inversely proportional to size of metal

$$\text{Metallic bond} \rightarrow \text{metal cation} \\ f = \frac{k q_1 q_2}{r^2} \quad \text{Electron}$$

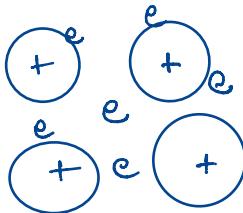


metal = e<sup>-</sup> donor



$$F = \frac{Kq_1 q_2}{r^2}$$

metallic bond



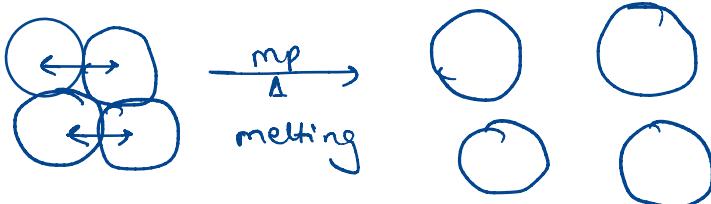
$q_1$  = charge on metal

$q_2$  = charge on electrons

$q_2 \propto$  no. of unpaired electrons

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$\xrightarrow{\text{no. of unpaired e}^- \uparrow \text{es}}$					$\xrightarrow{\text{no. of unpaired e}^- \uparrow \text{es}}$				
n	1	2	3	6	5	4	3	2	1
$\xrightarrow{\text{M.C. } \uparrow \text{es}}$					$\xrightarrow{\text{M.C. } \uparrow \text{es}}$				

## Melting & boiling point



$$mp \propto IMF$$

↳ intermolecular force

$$\frac{k_p}{mp} \propto \text{metallic bond strength}$$



## Melting and Boiling Point



Melting & Boiling Point  $\alpha$

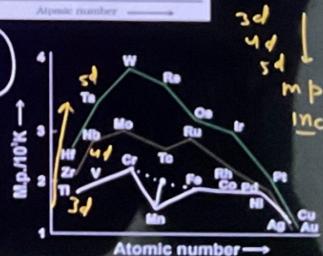
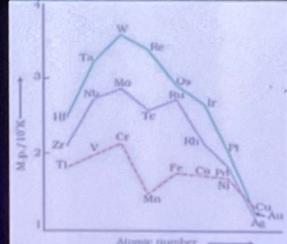
Melting & Boiling Point  $\alpha$

Metallic Bond Strength

Number of Unpaired Electron

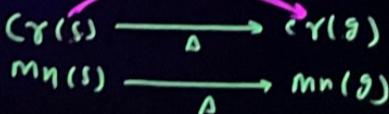
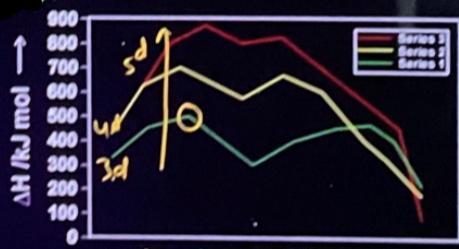
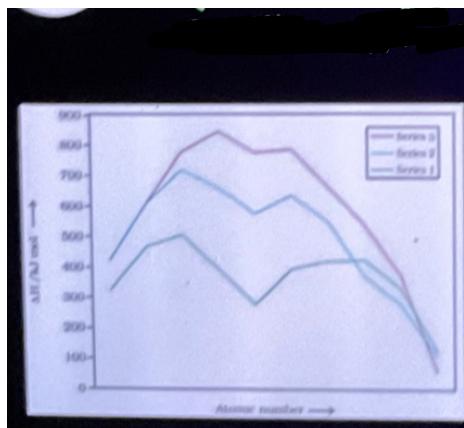
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
n 1	2	3	6	5	4	3	2	1

$Mn_{3s} \rightarrow 4s^2 3d^5$   
Half filled  
metallic bond  
Strength  $\rightarrow$  less.



## Enthalpy of Atomisation

$\propto$  no. of unpaired e<sup>-</sup>

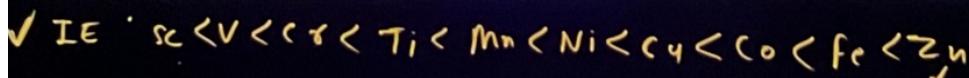


- They have high enthalpies of atomization.
- The maxima at about the middle of each series indicate that one unpaired electron per d orbital is particularly favourable for strong interatomic interaction.
- In general, greater the number of valence electrons, stronger is the resultant bonding.

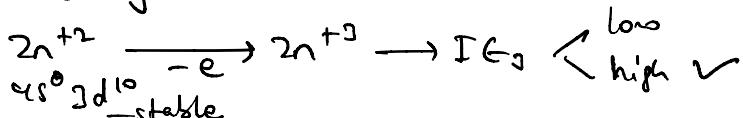
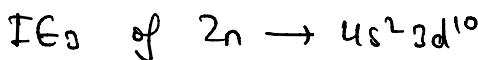
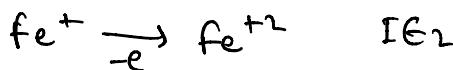
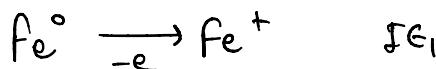
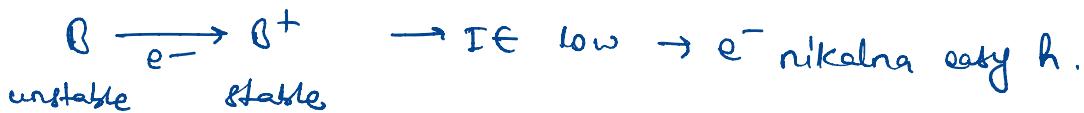
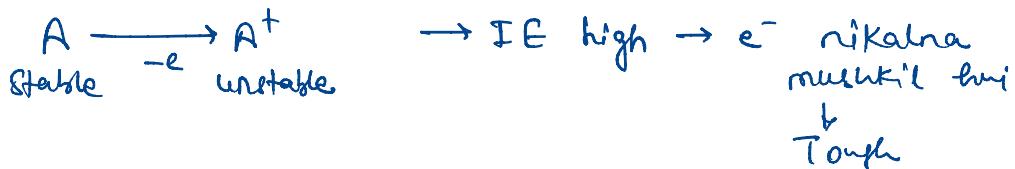
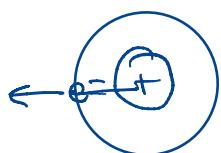
\* Enthalpy Atomization  $\propto$  no. of unpaired e<sup>-</sup>

## Ionisation Enthalpies

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic number	21	22	23	24	25	26	27	28	29	30
Enthalpy of atomization, $\Delta_h^{\circ}$ /kJ mol <sup>-1</sup>										
	326	473	515	397	281	416	425	430	339	126
Ionisation enthalpy / $\Delta_i^{\circ}$ /kJ mol <sup>-1</sup>										
$\Delta_i^{\circ}$	I	631	656	650	653	717	762	758	736	745
$\Delta_i^{\circ}$	II	1235	1309	1414	1592	1509	1561	1644	1752	1958
Density/g cm <sup>-3</sup>		3.43	4.1	6.07	7.19	7.21	7.8	8.7	8.9	7.1

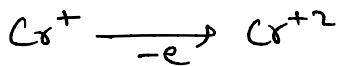


Energy req. to remove an  $e^-$  from its isolated gaseous state is called ionization energy



$\text{IE}_2$  of Cr

$4s^1 3d^5$



$4s^1 3d^5$   
stable

half filled

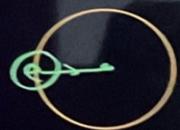
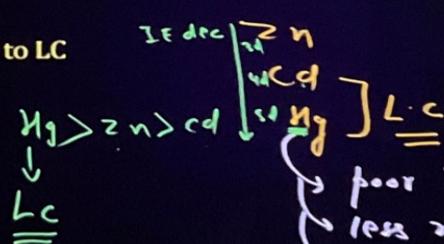
$\text{IE}_2 \rightarrow \text{high}$ .

There is an increase in ionisation enthalpy along each series of the transition elements from left to right

IE of 5d > 4d

Hg > Zn > Cd due to LC

2<sup>nd</sup> IE  
3<sup>rd</sup> IE of Zn



poor shielding  
less repulsion  
more attraction.

## Oxidation State

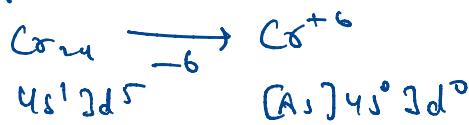
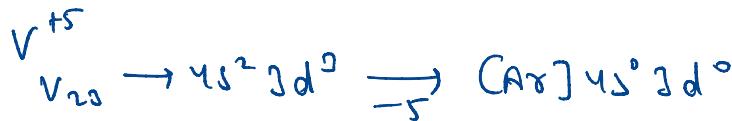
Due to less energy difference between 3d & 4s d block elements show variable oxidation state

3	4	5	6	7	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
(+3)	+2	+2	+2	+2	(+3)	+3	+3	+3	+3	+2	+2	+2	+1	+2
(+4)	+3	+3	+4	+3	(+4)	+4	+4	+4	+4	+3	+3	+3	+2	+2
max 0.5 = group up to no.	4s <sup>2</sup> 3d <sup>2</sup>	4s <sup>1</sup> 3d <sup>1</sup>												

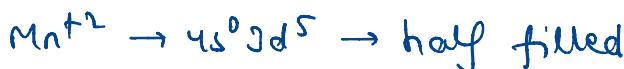
4s<sup>1</sup> 3d<sup>5</sup> 4s<sup>2</sup> 3d<sup>5</sup>

6 7

- \* La & Sc don't show variable oxidation state
- \* Stable oxidation
  - a) Inert gas
  - b) fully filled d<sup>10</sup>
  - c) half filled d<sup>5</sup>
  - d) trig half filled d<sup>3</sup>.

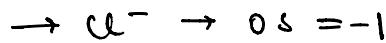
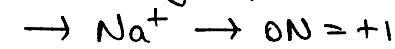


Unstable gas



### Oxidation state / number

- charge per atom

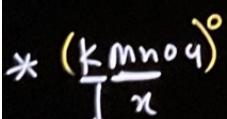


max<sup>n</sup> OS = group no.  
or  
group no. - 10

group no.	ON
1	1
2	2
3	3
4	4
5	5
6	6
7*	7*

Group 2	
H	Be
Li	Mg
Na	Ca
K	Sr
Rb	Ba
Cs	
Fr	
+1	+2


 $F_g \xrightarrow{+1} Ne$     $O \rightarrow -2$   
 $O \xrightarrow{-1} Ar$     $N \rightarrow -3$   
 $B \xrightarrow{-1} Kr$     $Z \rightarrow X_e$   
 $2+1 \rightarrow X_e$   
 $O_8 \xrightarrow{+2} [Ne]_{10}$   
 $N_7 \xrightarrow{-3} [Ne]_{10}$



$$+1 + n + 4 \times (-2) = 0$$

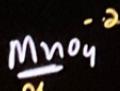
$$1 + n - 8 = 0$$

$$n = +7 \checkmark$$



$$2 + 2n - 14 = 0$$

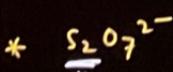
$$n = +6$$



$$n + 4(-2) = -2$$

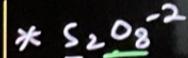
$$n - 8 = -2$$

$$n = +6 \checkmark$$



$$2n - 14 = -2$$

$$\underline{n = +6}$$



$$2n + 8(-2) = -2$$

$$2n - 16 = -2$$

$$2n = -2 + 16$$

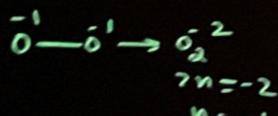
$$2n = 14$$

$$n = 7 \times$$



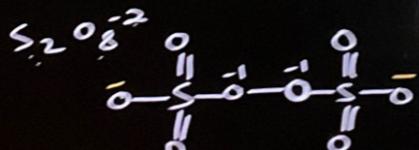
O → -2 → oxide

O → -1 → peroxide



\*  $2n - 12 - 2 = -2$   
 $n = +6$

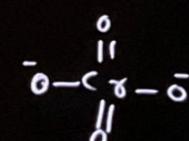
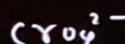
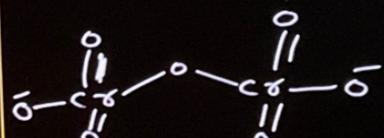
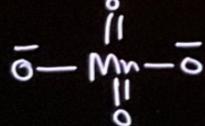
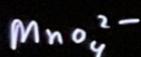
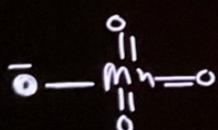
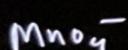
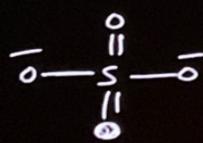
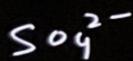
X



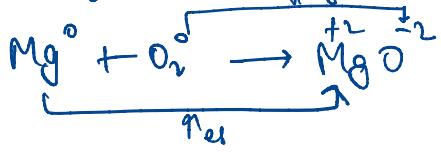
→ oxygen forms two bonds for stability →  $\text{O}_2 + 2e \rightarrow [\overset{+2}{\text{O}}_2]$

→ A=O |  $\overset{+2}{\text{O}}_2 \rightarrow \text{A}$  |  $\overset{+2}{\text{O}}_2 \rightarrow \text{A}$

→ O-A-O



Oxidising agent  $\rightarrow$  oxidises others



OA  $\rightarrow$  reduction      RA  $\rightarrow$  oxidation      Jukka



$$x - 2 = 0$$

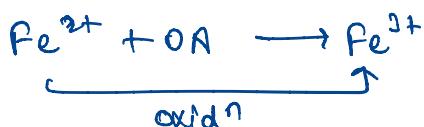
$$n = 2$$



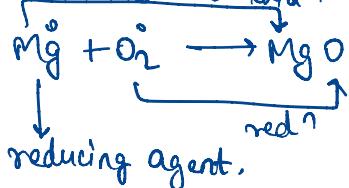
$$2n = 0$$

$$n = 0.$$

Oxidising agent



reducing agent



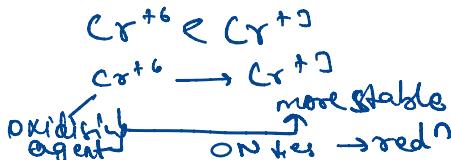
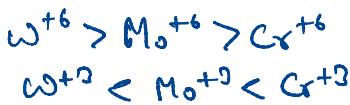
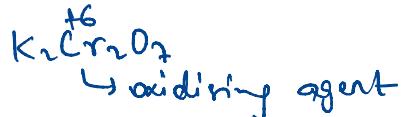
reducing agent.

## Oxidation state

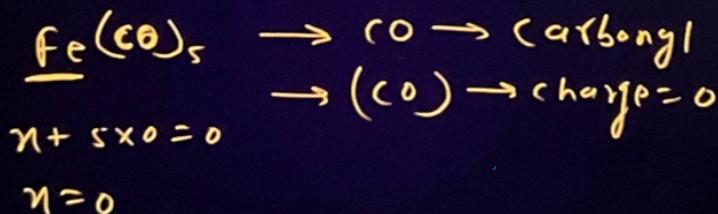
- Most common oxidation state of d-block elements is 2 except Sc, maximum oxidation is +8 shown by Ru & Os
- In the p-block the lower oxidation states are favoured by the heavier members (due to inert pair effect), the opposite is true in the groups of d-block
- For example, in group 6, Mo(VI) and W(VI) are found to be more stable than Cr(VI).
- Thus Cr(VI) in the form of dichromate in acidic medium is a strong oxidising agent, whereas  $\text{MoO}_3$  and  $\text{WO}_3$  are not.

Cr	+6	+2	stability ↓ <sub>ee</sub>
Mo	high	low	
W	HOS	LOS	

↑<sub>ee</sub> stability

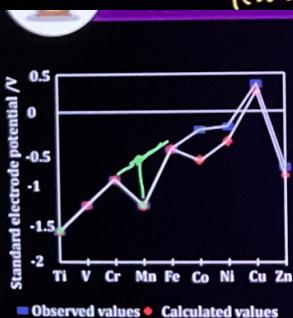
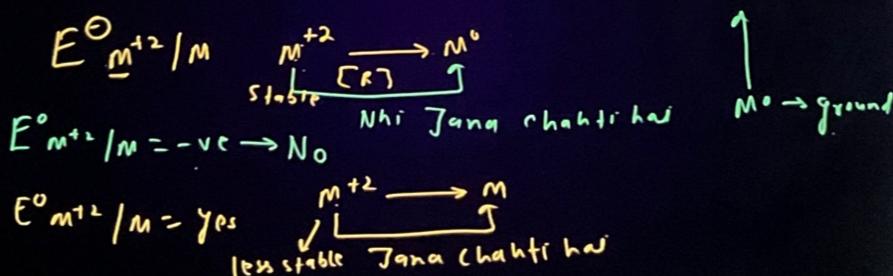


Low oxidation states are found when a complex compound has ligands capable of  $\pi$ -acceptor character in addition to the  $\sigma$ -bonding. For example, in  $\text{Ni}(\text{CO})_4$  and  $\text{Fe}(\text{CO})_5$ , the oxidation state of nickel and iron is zero



## M<sup>+</sup>/M Standard electrode Potential

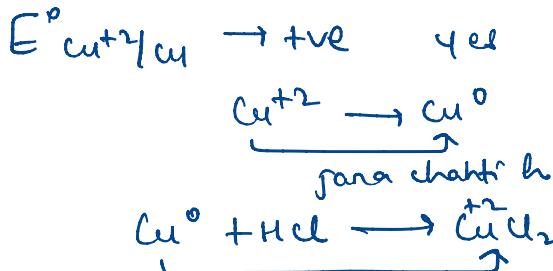
- E<sup>θ</sup>/V is negative this means that ion is not interested for reduction
- E<sup>θ</sup>/V is positive this means that ion is interested for reduction



Element (M)	$\Delta_a H^{\ominus}$ (M)	$\Delta_f H_1^{\ominus}$	$\Delta_f H_2^{\ominus}$	$\Delta_{hyd} H^{\ominus}$ ( $\text{M}^{2+}$ )	$E^{\theta}/V$
Ti	469	656	1309	-1866	-1.63
V	515	650	1414	-1895	-1.18
Cr	398	653	1592	-1925	-0.90
Mn	279	717	1509	-1862	-1.18
Fe	418	762	1561	-1998	-0.44
Co	427	758	1644	-2079	-0.28
Ni	431	736	1752	-2121	-0.25
Cu*	339	745	1958	-2121	0.34
Zn	130	906	1734	-2059	-0.76

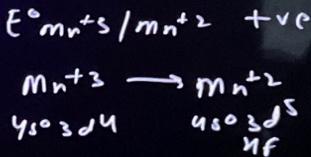
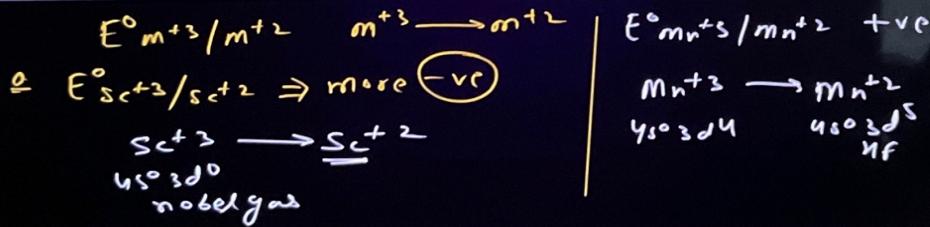
- The unique behaviour of Cu, having a positive  $E^{\theta}$ , accounts for its inability to liberate  $\text{H}_2$  from acids.

- $\text{Cu} + \text{HCl} \rightarrow \text{CuCl}_2 + \text{H}_2$  Not Possible
- Only oxidising acids (nitric and hot concentrated sulphuric) react with Cu, the acids being reduced.
- The high energy to transform  $\text{Cu(s)}$  to  $\text{Cu}^{2+}(\text{aq})$  is not balanced by its hydration enthalpy.



- The general trend towards less negative  $E^\ominus$  values across the series is related to the general increase in the sum of the first and second ionisation enthalpies.
- It is interesting to note that the value of  $E^\ominus$  for Mn, Ni and Zn are more negative than expected from the trend.
- The stability of the half-filled d sub-shell in  $\text{Mn}^{2+}$  and the completely filled  $\text{d}^{10}$  configuration in  $\text{Zn}^{2+}$  are related to their  $E^\ominus$  values, whereas  $E^\ominus$  for Ni is related to the highest negative  $\Delta_{\text{hyd}} H^\ominus$ .

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic number	21	22	23	24	25	26	27	28	29	30
electrode $\text{M}^{2+}/\text{M}$	-	-1.63	-1.18	-0.90	-1.18	-0.44	-0.28	-0.25	+0.34	-0.76
Potential $E^\ominus / \text{V} \text{ M}^{3+}/\text{M}^{2+}$	-vc	-0.37	-0.26	-0.41	+1.57	+0.77	+1.97	-	-	+vc



- The highest value for Zn is due to the removal of an electron from the stable  $\text{d}^{10}$  configuration of  $\text{Zn}^{2+}$ .
- The comparatively high value for Mn shows that  $\text{Mn}^{2+}(\text{d}^5)$  is particularly stable, whereas comparatively low value for Fe shows the extra stability of  $\text{Fe}^{3+}(\text{d}^5)$ .
- The comparatively low value for V is related to the stability of  $\text{V}^{2+}$  (half-filled  $t_{2g}$  level)

Stability of higher oxidation states

- d Block elements form bond in higher oxidation state only with oxygen and fluorine
- The ability of fluorine to stabilise the highest oxidation state is due to either higher lattice or higher Bond enthalpy
- Oxygen stabilises the higher oxidation state by forming multiple bond

**Stability of Higher Oxidation States**

**Formulas of Halides of 3d Metals**

Oxidation Number	+6	+5	+4	+3	+2	+1	
	$\text{CrF}_6$	$\text{VF}_5$	$\text{CrX}_4$	$\text{MnF}_4$			$\text{MnF}_7$ is not stable
		$\text{CrX}_3$	$\text{MnF}_3$	$\text{FeX}_3^{\text{l}}$	$\text{CoF}_3$		$\text{MnO}_3\text{F}$
		$\text{VX}_3$	$\text{MnX}_2$	$\text{FeX}_2$	$\text{CoX}_2$		$\text{Mn}^{+7}\text{F}$
		$\text{TiX}_2^{\text{III}}$	$\text{CrX}_2$				$\text{NiX}_2$
							$\text{CuX}_2^{\text{II}}$
							$\text{ZnX}_2$
							$\text{CuX}^{\text{III}}$

Key: X = F → I; X<sup>l</sup> = F → Br; X<sup>II</sup> = F, Cl; X<sup>III</sup> = Cl → I  
 The +7 state for Mn is not represented in simple halides but  $\text{MnO}_3\text{F}$  is known

$\text{CuF}_2 \checkmark \quad \text{CuCl}_2 \checkmark \quad \text{CuBr}_2 \checkmark \quad \underline{\text{CuI}_2 \times} \quad \text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2 \quad \text{OA}$

- All  $\text{Cu}^{\text{II}}$  halides are known except the iodide. In this case,  $\text{Cu}^{2+}$  oxidises  $\text{I}^-$  to  $\text{I}_2$

$$2\underline{\text{Cu}^{2+}} + 4\underline{\text{I}^-} \rightarrow \underline{\text{Cu}_2^{\text{I}_2}}(\text{s}) + \underline{\text{I}_2} \quad \text{Cu}^{+2} + \text{F}^- \rightarrow \underline{\text{Cu}^{\text{I}}\text{F}_2} + \text{F}_2 \quad \text{OA}$$

Many copper (i) compounds are unstable in aqueous solution and undergo disproportionation because of hydration energy

$$2\underline{\text{Cu}^+} \rightarrow \underline{\text{Cu}^{2+}} + \underline{\text{Cu}} \quad \text{Cu}^{+2} \quad \text{Cu}^{+1}$$

$$\text{DPP} \quad \text{Yt}^{\text{n}} \quad \text{Cu}^+ \rightarrow \text{Cu}^{+2} + \text{Cu}^{\circ} \quad \text{H}_2\text{O} \quad \text{H}_2\text{O} \quad \text{H}_2\text{O} \quad \text{H}_2\text{O} \quad \text{H}_2\text{O} \quad \text{H}_2\text{O} \quad \text{H}_2\text{O}$$

$$\Delta E \quad \underline{\text{Cu}^{+2} > \text{Cu}^+} \quad \text{E}$$

oxides of 3d metals

Oxidation Number	Groups									
	3	4	5	6	7	8	9	10	11	12
+7					Mn <sub>2</sub> O <sub>7</sub>					
+6					CrO <sub>3</sub>					
+5			V <sub>2</sub> O <sub>5</sub>							
+4		TiO <sub>2</sub>	V <sub>2</sub> O <sub>4</sub>	CrO <sub>2</sub>	MnO <sub>2</sub>					
+3	Sc <sub>2</sub> O <sub>3</sub>	Ti <sub>2</sub> O <sub>3</sub>	V <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	Mn <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>				
					Mn <sub>3</sub> O <sub>4</sub>	Fe <sub>3</sub> O <sub>4</sub>	Co <sub>3</sub> O <sub>4</sub>			
+2		TiO	VO	(CrO)	MnO	FeO	CoO	NiO	CuO	ZnO
+1									Cu <sub>2</sub> O	

## Magnetic Properties

- Diamagnetic substances are repelled by the applied field, while the paramagnetic substances are attracted
- Substances which are attracted very strongly are said to be ferromagnetic.
- In fact ferromagnetism is an extreme form of para Magnetism

Calculated and Observed Magnetic Moments (BM)

Ion	Configuration	Unpaired electron(s)	Magnetic moment	
			Calculated	Observed
Sc <sup>3+</sup>	3d <sup>0</sup>	0	0	0
Ti <sup>3+</sup>	3d <sup>1</sup>	1	1.73	1.75
Ti <sup>2+</sup>	3d <sup>2</sup>	2	2.84	2.76
V <sup>2+</sup>	3d <sup>3</sup>	3	3.87	3.86
Cr <sup>2+</sup>	3d <sup>4</sup>	4	4.90	4.80
Mn <sup>2+</sup>	3d <sup>5</sup>	5	5.92	5.96
Fe <sup>2+</sup>	3d <sup>6</sup>	4	4.90	5.3 – 5.5
Co <sup>2+</sup>	3d <sup>7</sup>	3	3.87	4.4 – 5.2
Ni <sup>2+</sup>	3d <sup>8</sup>	2	2.84	2.9 – 3.4
Cu <sup>2+</sup>	3d <sup>9</sup>	1	1.73	1.8 – 2.2
Zn <sup>2+</sup>	3d <sup>10</sup>	0	0	

If no. of unpaired e<sup>-</sup> = 0, diamagnetic

If no. of unpaired e<sup>-</sup> ≠ 0, paramagnetic

$$\text{magnetic moment } \mu = \sqrt{n(n+2)} \text{ BM}$$

$n = \text{no. of unpaired e}^-$ .

## Formation of colored ions

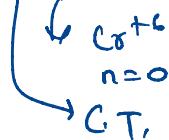
### Ions in $M^{+2}$ state

- V<sup>2+</sup> → Violet → V → Very ✓
  - Cr<sup>2+</sup> → Blue → B → Beautiful ✓
  - Mn<sup>2+</sup> → Pink → P → Pink ✓
  - Fe<sup>2+</sup> → Green → G → Girl ✓
  - Co<sup>2+</sup> → Pink → P → Pinky ✓
  - Ni<sup>2+</sup> → Green → G → G ✓
  - Cu<sup>2+</sup> → Blue → B → Bhut ✓
  - Zn<sup>2+</sup> → Colourless → C → Cute-hai ✓
- Ions in  $M^{3+}$  state**
- Sc<sup>3+</sup> → Colourless → C → Cute ✓
  - Ti<sup>3+</sup> → Purple → P → Purple ✓
  - V<sup>3+</sup> → Green → G → Girl ✓
  - Cr<sup>3+</sup> → Violet → V → Vinni ✓
  - Mn<sup>3+</sup> → Violet → V → Very ✓
  - Fe<sup>3+</sup> → Yellow → Y → Young ✓

Configuration	Example	Colour
3d <sup>0</sup>	Sc <sup>3+</sup>	colourless
3d <sup>0</sup>	Ti <sup>4+</sup>	colourless
3d <sup>1</sup>	Ti <sup>3+</sup>	purple
3d <sup>1</sup>	V <sup>4+</sup>	blue
3d <sup>2</sup>	V <sup>3+</sup>	green
3d <sup>3</sup>	V <sup>2+</sup>	violet
3d <sup>3</sup>	Cr <sup>3+</sup>	violet
3d <sup>4</sup>	Mn <sup>3+</sup>	violet
3d <sup>4</sup>	Cr <sup>2+</sup>	blue
3d <sup>5</sup>	Mn <sup>2+</sup>	pink
3d <sup>5</sup>	Fe <sup>3+</sup>	yellow
3d <sup>6</sup>	Fe <sup>2+</sup>	green
3d <sup>6</sup> 3d <sup>7</sup>	Co <sup>3+</sup> Co <sup>2+</sup>	bluepink
3d <sup>8</sup>	Ni <sup>2+</sup>	green
3d <sup>9</sup>	Cu <sup>2+</sup>	blue
3d <sup>10</sup>	Zn <sup>2+</sup>	colourless

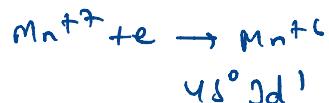
If unpaired e<sup>-</sup>  $n=0$ , colourless

If unpaired e<sup>-</sup>  $n \neq 0$ , colored.

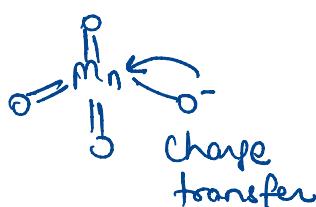


n=0

colorless



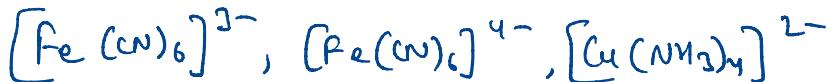
n=1



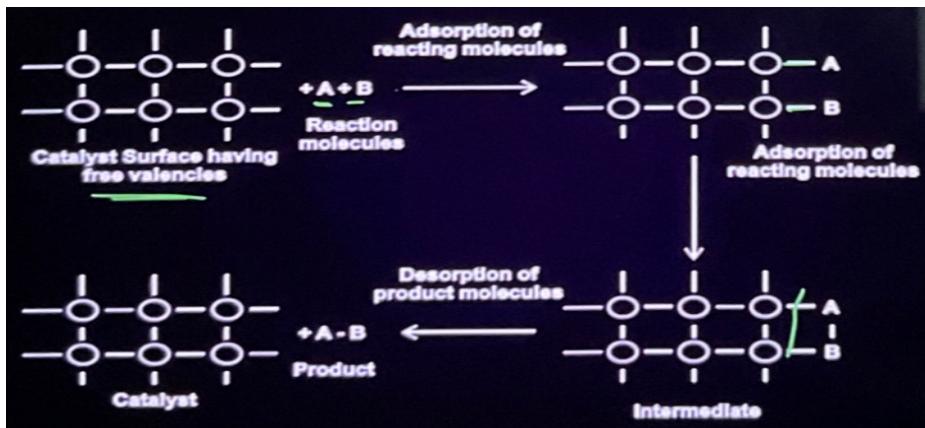
## Formation of Complex Compounds

Transition metals form a large number of complex compound. This is due to

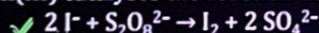
- Comparatively smaller sizes of the metal ions
- High, ionic charges
- The availability of d. orbital for bond formation



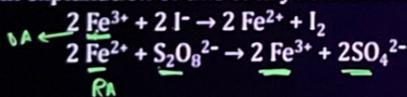
## Catalytic Properties



Iron(III) catalyses the reaction between iodide and persulphate ions.



An explanation of this catalytic action can be given as:



Some Important Catalyst -

Contact Process -  $\text{V}_2\text{O}_5$  ( $\text{SO}_2$  to  $\text{SO}_3$ )

Haber's Process -  $\text{Fe}_2\text{O}_3, \text{Al}_2\text{O}_3, \text{K}_2\text{O}$  ( $\text{NH}_3$ )

Ostwald's Process -  $\text{Pt/Rh}$  ( $\text{HNO}_3$ )

Zeigler Natta -  $\text{TiCl}_4 + (\text{C}_2\text{H}_5)_3\text{Al}$  (Polymerization of Alkene)

Hydrogenation of Alkene -  $\text{Ni/Pd}$

Wilkinson's Catalyst -  $\text{RhCl} + \text{PPh}_3$

## Formation of Interstitial Compounds

Interstitial compounds are those which are formed when small atoms like H C or N are trapped inside the crystal lattice of metals

They are usually non stoichiometric and are neither typically, ionic nor covalent, for example  $Ti:C$ ,  $Mn_4N$ ,  $Fe_3H$ ,  $VH_{0.56}$  &  $TiH_{1.7-1.8}$



The principal, physical and chemical characteristics of these compounds are as follows

1. They have high melting points higher than those of pure metals
2. They are very hard. Some borides approach diamond hardness.
3. They retain metallic conductivity
4. They are chemically inert

### Alloy formation

Alloys are formed by atoms with metallic radii that are within about 15% of each other

Because of similar radii and other characteristics of transition metals, alloys are readily formed by these metals

brass ( $Cu-Zn$ )  
bronze ( $Cu-Sn$ )

### Imp. Compounds of transition Elements

Oxides and oxoanions of metal

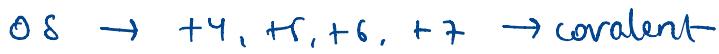
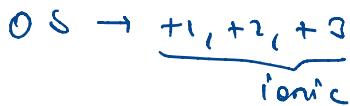
-These oxides are generally formed by the reaction of metals with oxygen at high temperatures

-All the metals except scandium form  $MO$  oxide which are ionic

-As the oxidation number of a metal increases, ionic character decreases in the case of Mn,  $Mn_2O_7$  is a covalent Green oil

-Even  $Cr_2O_3$  and  $V_2O_5$  have low melting points

# Metal oxide

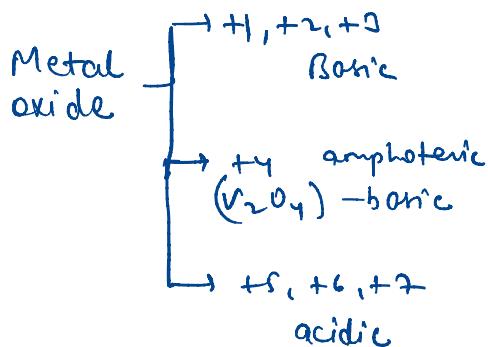


$$2n - l_4 = 0 \\ u = +7$$

acid =  $H^+$  donor  
 $= e^-$  acceptor

base  $\rightarrow OH^-$  donor  
 $\rightarrow e^-$  donor

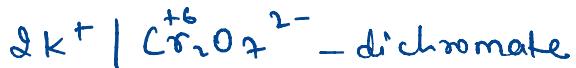
Amphoteric  $\rightarrow$  acid  
 as well as base



Amphoteric Trick					
ZnO	BeO	Al <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	Ca <sub>2</sub> O <sub>3</sub>	SnO <sub>2</sub> SnO <sub>2</sub>
<u>Zn</u>	<u>Be</u>	<u>Al</u>	<u>Pb</u>	<u>Ca</u>	<u>Sn</u>
Znate		Al <sub>3</sub>	Punjab	Gana	Sura.
+3	+3	+3	+5		
Cr	As	Si	V		
Kar	Ashwari	Savili	ko impress. frenge.		
Cr <sub>2</sub> O <sub>3</sub>	As <sub>2</sub> O <sub>3</sub>	Si <sub>2</sub> O <sub>3</sub>	V <sub>2</sub> O <sub>5</sub>		
Cr <sub>2</sub> O <sub>3</sub> Acidic	As <sub>2</sub> O <sub>3</sub>	Si <sub>2</sub> O <sub>3</sub>	V <sub>2</sub> O <sub>5</sub>		

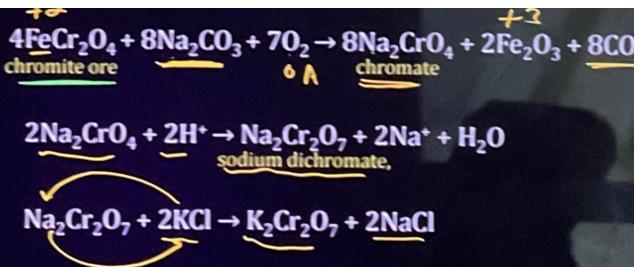
-3	+4	+5
$\Rightarrow V_2O_3$	$V_2O_4$	$V_2O_5$
<u>Basic</u>	<u>Basic</u>	<u>Amphoteric</u>
$\Rightarrow CrO$	$Cr_2O_3$	$CrO_3$
<u>Basic</u>	<u>Amphoteric</u>	<u>Acidic</u>
$\Rightarrow MnO$	$MnO_2$	$Mn_2O_7$
<u>Basic</u>	<u>Amphoteric</u>	<u>Acidic</u>

# Potassium dichromate $K_2Cr_2O_7$



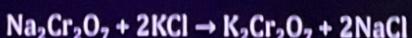
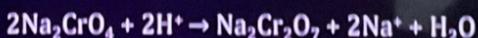
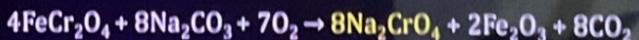
## Preparation

Dichromates are generally prepared from chromate, which in turn are obtained by the fusion of chromite ore ( $FeCr_2O_4$ ) with sodium or potassium carbonate in free access of air. The reaction with sodium carbonate occurs as follows:



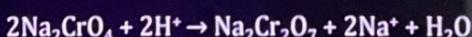
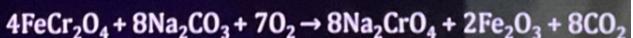
## Preparation

The yellow solution of sodium chromate is filtered and acidified with sulphuric acid to give a solution from which orange sodium dichromate,  $Na_2Cr_2O_7 \cdot 2H_2O$  can be crystallised

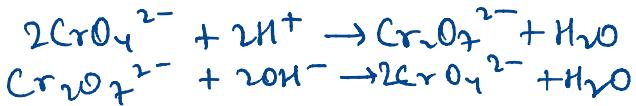


## Preparation

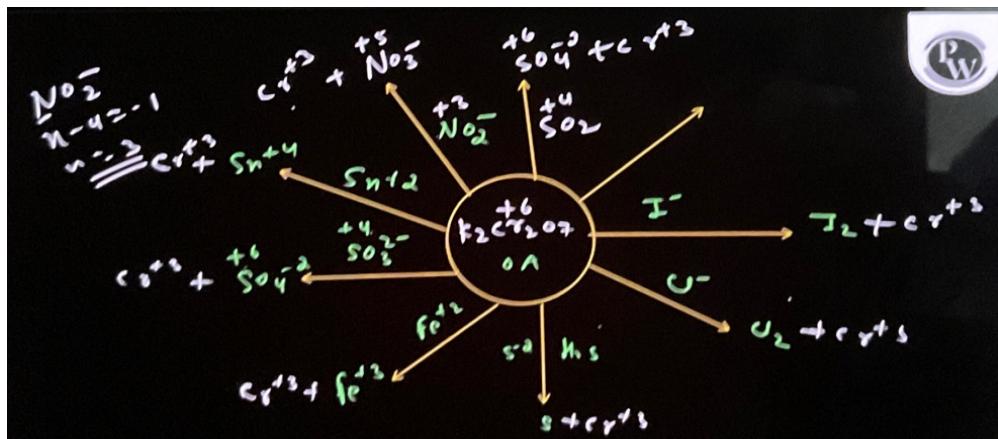
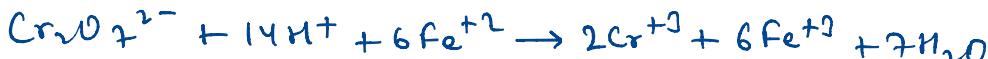
Sodium dichromate is more soluble than potassium dichromate. The latter is therefore, prepared by treating the solution of sodium dichromate with potassium chloride.



action of pH

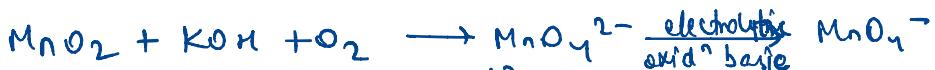


In acidic sol<sup>n</sup>, its oxidising action can be represented as follows.

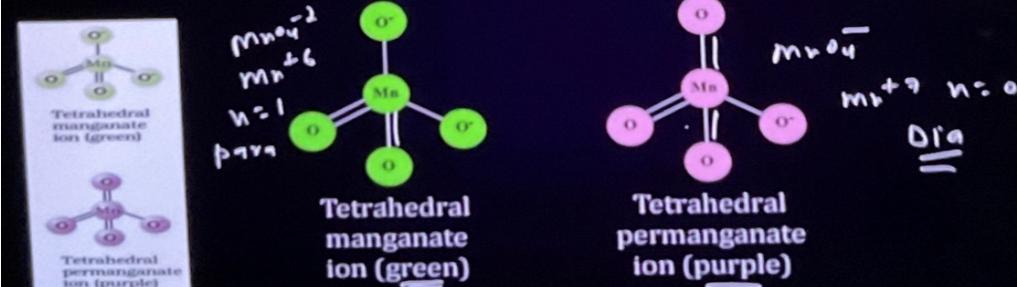


## Potassium Permanganate $\text{KMnO}_4$

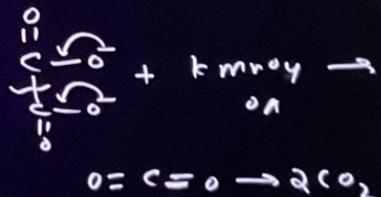
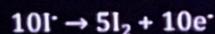
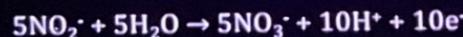
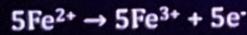
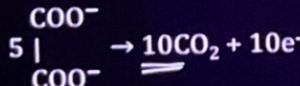
Preparation -



The green manganate is paramagnetic because of one unpaired electron but the permanganate is diamagnetic due to the absence of unpaired electron.



Acidified permanganate solution oxidises oxalates to carbon dioxide, iron(II) to iron(III), nitrites to nitrates and iodides to free iodine. The half-reactions of reductants are:



## In acid solutions :

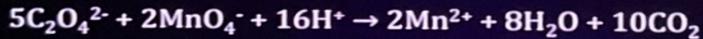
(a) Iodine is liberated from potassium iodide :



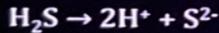
(b)  $Fe^{2+}$  ion (green) is converted to  $Fe^{3+}$  (yellow) :



(c) Oxalate ion or oxalic acid is oxidised at 333 K :



(d) Hydrogen sulphide is oxidised, sulphur being precipitated :



(e) Sulphurous acid or sulphate is oxidised to a sulphate or sulphuric acid :

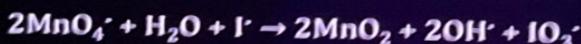


(f) Nitrite is oxidised to nitrate :

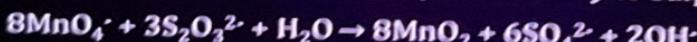


**In neutral or faintly alkaline solutions :**

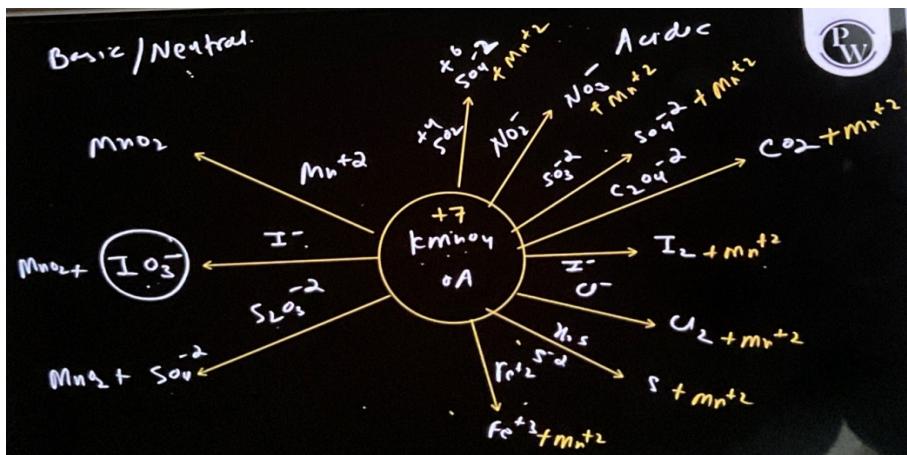
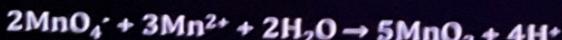
(a) A notable reaction is the oxidation of iodide to iodate :



(b) Thiosulphate is oxidised almost quantitatively to sulphate :



(c) Manganous salt is oxidised to MnO<sub>2</sub>; the presence of zinc sulphate or zinc oxide catalyses the oxidation :



## F-block elements

Electronic Configurations & Radii of Lanthanum & Lanthanoids

Atomic Number	Name	Symbol	Electronic Configurations			Radii/pm		
			Ln	Ln <sup>2+</sup>	Ln <sup>3+</sup>	Ln <sup>4+</sup>	Ln	Ln <sup>3+</sup>
57	Lanthanum	La	5d <sup>1</sup> 6s <sup>2</sup>	5d <sup>1</sup>	4f <sup>0</sup>	4f <sup>0</sup>	187	106
58	Cerium	Ce	4f <sup>1</sup> 5d <sup>1</sup> 6s <sup>2</sup>	4f <sup>1</sup>	4f <sup>1</sup>	4f <sup>0</sup>	183	103
59	Praseodymium	Pr	4f <sup>1</sup> 6s <sup>2</sup>	4f <sup>1</sup>	4f <sup>1</sup>	4f <sup>1</sup>	182	101
60	Neodymium	Nd	4f <sup>4</sup> 6s <sup>2</sup>	4f <sup>4</sup>	4f <sup>3</sup>	4f <sup>2</sup>	181	99
61	Promethium	Pm	4f <sup>6</sup> 6s <sup>2</sup>	4f <sup>6</sup>	4f <sup>5</sup>	4f <sup>4</sup>	181	98
62	Samarium	Sm	4f <sup>6</sup> 6s <sup>2</sup>	4f <sup>6</sup>	4f <sup>5</sup>	4f <sup>4</sup>	180	96
63	Europium	Eu	4f <sup>7</sup> 6s <sup>2</sup>	4f <sup>7</sup>	4f <sup>6</sup>	4f <sup>5</sup>	199	95
64	Gadolinium	Gd	4f <sup>7</sup> 5d <sup>1</sup> 6s <sup>2</sup>	4f <sup>7</sup> 5d <sup>1</sup>	4f <sup>7</sup>	4f <sup>6</sup>	180	94
65	Terbium	Tb	4f <sup>9</sup> 6s <sup>2</sup>	4f <sup>9</sup>	4f <sup>8</sup>	4f <sup>7</sup>	178	92
66	Dysprosium	Dy	4f <sup>10</sup> 6s <sup>2</sup>	4f <sup>10</sup>	4f <sup>9</sup>	4f <sup>8</sup>	177	91
67	Holmium	Ho	4f <sup>11</sup> 6s <sup>2</sup>	4f <sup>11</sup>	4f <sup>10</sup>	4f <sup>9</sup>	176	89
68	Erbium	Er	4f <sup>12</sup> 6s <sup>2</sup>	4f <sup>12</sup>	4f <sup>11</sup>	4f <sup>10</sup>	175	88
69	Thulium	Tm	4f <sup>13</sup> 6s <sup>2</sup>	4f <sup>13</sup>	4f <sup>12</sup>	4f <sup>11</sup>	174	87
70	Ytterbium	Yb	4f <sup>14</sup> 6s <sup>2</sup>	4f <sup>14</sup>	4f <sup>13</sup>	4f <sup>12</sup>	173	86
71	Lutetium	Lu	4f <sup>14</sup> 5d <sup>1</sup> 6s <sup>2</sup>	4f <sup>14</sup> 5d <sup>1</sup>	4f <sup>14</sup>	-	-	-

- f-block elements are called inner transition element
- There are 2 series in f-block
  - ① Lanthanoid  $\rightarrow$  (58 - 71)
  - ② Actinoid  $\rightarrow$  (90 - 103)

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
संक्ष पर	Nadu प्रेम	सार्व यू गद्दा तब	दिल	युा	एरे	तम युक्ति	लाइट	हो					
संक्ष पर	नेंदू प्पार	स्मार्ट यूरोप गधा			Dyanium	Hocker	ने यूरोप के	तमाम युवकों को लृप्ता					
Sadak पर	Nandy प्रभास	smart यूरोप	gadha, Tal	Dyanium	Hocker	Europe	Tamom	Yaloo Lu					
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
थापा ने ऊज्ज्वले नापा	Pure	American				कैमरा बेका गया	कैलिफोर्निया ने आईस्टीन के	फॉर्म को	मोदीनगर पर नंबर पर लगवाया				
Thalpa usma	ko	Nap, pgr				Camra Beta califor	Einsten form	modi Number					
						gg,	ura	ke	leo	nagar	lalitpur		

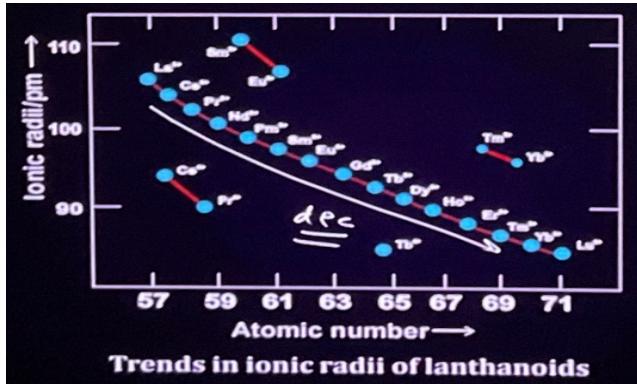
Some Properties of Actinium and Actinoids

Atomic Number	Name	Symbol	Electronic Configurations			Radii/pm	
			M	M <sup>2+</sup>	M <sup>3+</sup>	M <sup>3+</sup>	M <sup>2+</sup>
89	Actinium	Ac	6d <sup>1</sup> 7s <sup>2</sup>	5f <sup>0</sup>		111	
90	Thorium	Th	6d <sup>1</sup> 7s <sup>2</sup>	5f <sup>0</sup>	5f <sup>0</sup>	99	
91	Protactinium	Pa	5f <sup>6</sup> d <sup>1</sup> 7s <sup>2</sup>	5f <sup>2</sup>	5f <sup>2</sup>	96	
92	Uranium	U	5f <sup>6</sup> d <sup>1</sup> 7s <sup>2</sup>	5f <sup>2</sup>	5f <sup>2</sup>	103	93
93	Neptunium	Np	5f <sup>6</sup> d <sup>1</sup> 7s <sup>2</sup>	5f <sup>3</sup>	5f <sup>3</sup>	101	92
94	Plutonium	Pu	5f <sup>6</sup> 7s <sup>2</sup>	5f <sup>6</sup>	5f <sup>6</sup>	100	90
95	Americium	Am	5f <sup>7</sup> 7s <sup>2</sup>	5f <sup>6</sup>	5f <sup>5</sup>	99	89
96	Curium	Cm	5f <sup>7</sup> d <sup>1</sup> 7s <sup>2</sup>	5f <sup>7</sup>	5f <sup>6</sup>	99	88
97	Berkelium	Bk	5f <sup>7</sup> 7s <sup>2</sup>	5f <sup>6</sup>	5f <sup>7</sup>	98	87
98	Californium	Cf	5f <sup>8</sup> 7s <sup>2</sup>	5f <sup>8</sup>	5f <sup>8</sup>	98	86
99	Einsteinium	Es	5f <sup>9</sup> 7s <sup>2</sup>	5f <sup>10</sup>	5f <sup>9</sup>	-	-
100	Fermium	Fm	5f <sup>10</sup> 7s <sup>2</sup>	5f <sup>11</sup>	5f <sup>10</sup>	-	-
101	Mendelevium	Md	5f <sup>10</sup> 7s <sup>2</sup>	5f <sup>12</sup>	5f <sup>11</sup>	-	-
102	Nobelium	No	5f <sup>10</sup> 7s <sup>2</sup>	5f <sup>13</sup>	5f <sup>12</sup>	-	-
103	Lawrencium	Lr	5f <sup>14</sup> 6d <sup>1</sup> 7s <sup>2</sup>	5f <sup>14</sup>	5f <sup>13</sup>	-	-

## Atomic and ionic sizes

- The overall decrease in atomic and ionic radii from lanthanum to lutetium (the lanthanoid contraction) is a unique feature in the chemistry of the lanthanoids.

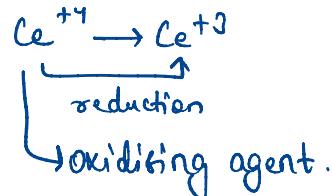
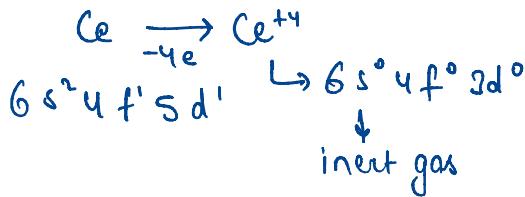
Ce pr Nd pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu  
 ↓  
 Lanthanoid contraction  
 radius ↓es  
 ↓  
 less repulsion ↓  
 more ← shielding  
 attraction  
 f<sup>14</sup>



## Oxidation state (Ln)

In the Lanthanoids, Ln(III) compounds are predominant species. However, they also exhibits +2 and +4.

Thus, the form of Ce<sup>IV</sup> is favoured by its noble gas configuration, but it is a strong oxidant reverting to the common +3 state.



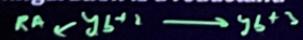
Oxidation state (Ln)

Pr, Nd, Tb and Dy also exhibit +4 state but only in oxides,  $\text{MO}_2$

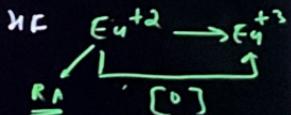
Eu<sup>2+</sup> (f7 configuration) is a strong reducing agent changing to the common +3 state



Yb<sup>2+</sup> which has f<sup>14</sup> configuration is a reductant.



Tb<sup>IV</sup> has half-filled f-orbitals and is an oxidant



The behaviour of samarium is very much like europium, exhibiting both +2 and +3 oxidation states.

## Oxidation state (Ac)

The actinoids show in general +3 oxidation state.

Oxidation States of Actinium and Actinoids

Ac	Th	Pb	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	NO	Lr
(3)		3	3	3	3	3	3	3	3	3	3	3	3	3
	(4)	4	4	4	4	4	4	4	4	4	3	3	3	3
		(5)	5	5	5	5	5							
			(6)	6	6	6	.6							
				(7)	(7)									

## General characteristics of Lanthanoids

All the lanthanoids are silvery white soft metals.

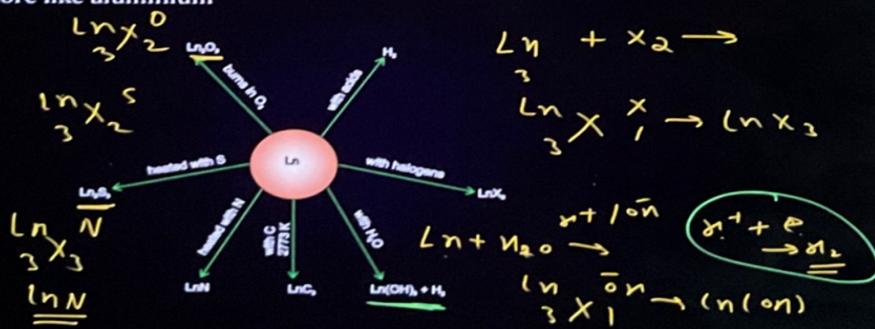
The hardness increases with increasing atomic number, samarium being steel hard.

Their melting points range between 1000 to 1200 K but samarium melts at 1623 K.

They have typical metallic structure and are good conductors of heat and electricity.

- Neither  $\text{La}^{3+}$  nor  $\text{Lu}^{3+}$  ion shows any colour but the rest do so  
 $4f^{14} 6s^2 5d^0$
- The lanthanoid ions other than the  $f^0$  type ( $\text{La}^{3+}$  and  $\text{Ce}^{4+}$ ) and the  $f^{14}$  type ( $\text{Yb}^{2+}$  and  $\text{Lu}^{3+}$ ) are all paramagnetic.
- A well known alloy is mischmetall which 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 and lighter flint

In their chemical behaviour, in general, the earlier members of the series are quite reactive similar to calcium but, with increasing atomic number, they behave more like aluminium



## General Characteristics of Actinoid

- The actinoids are radioactive elements and the earlier members have relatively long half-lives, the latter ones have half-life values ranging from a day to 3 minutes for lawrencium ( $Z=103$ ).
- Transuranic elements are members of the actinide series beyond uranium, beginning with neptunium (atomic number 93)
- There is a gradual decrease in the size of atoms or  $M^{3+}$  ions across the series.

THANK You !!