

Welcome to



# Aakash

+ BYJU'S LIVE

## The d and f-Block Elements



## Coinage Metals (Cu, Ag, Au)



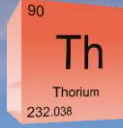
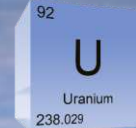
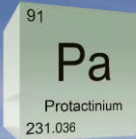
## Some ancient metal artifacts

Copper,  
iron used  
to make  
weapons.

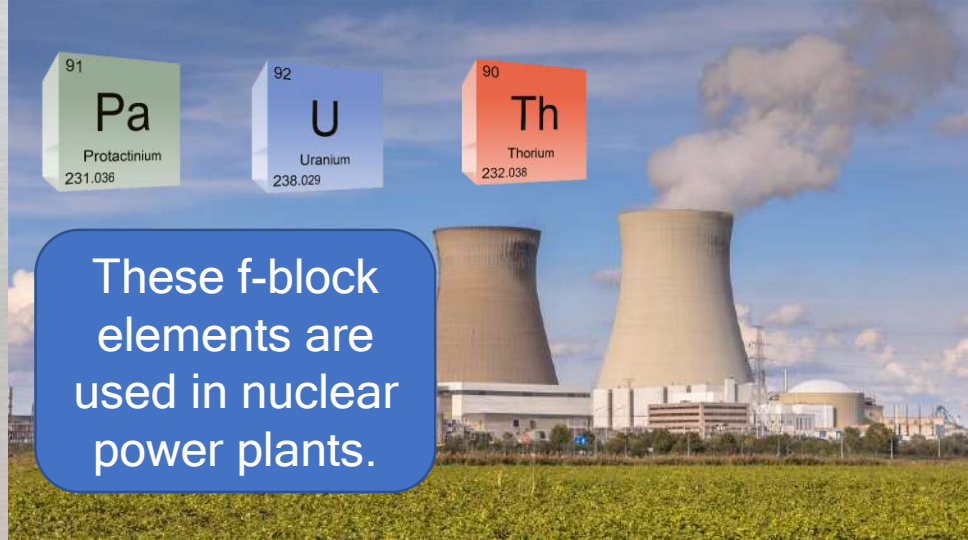


## “Dancing Girl”

Made up of  
bronze metal  
used in Harappan  
civilization.



These f-block  
elements are  
used in nuclear  
power plants.







# Pneumonic for d-Series

Sc Sachin

Ti Tendulkar

V Very

Cr Crazy

Mn Man

Fe Free

Co Coaching to

Ni Nitin's

Cu Cou

Zn Zin

Y Yes

Zr Zebras

Nb Never but

Mo Most

Tc Technicians

Ru Run

Rh Rhymes

Pd Purely sweet

Ag And

Cd Cute

La Larry

Hf Have fun

Ta Travelling

W World and

Re Reach

Os Out

Ir Ireland and

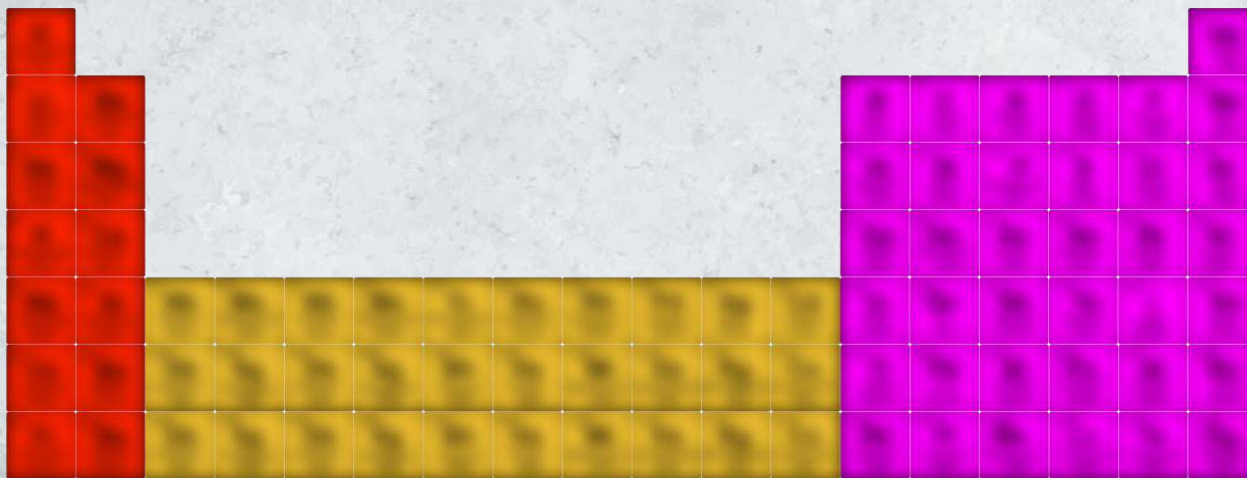
Pt Please

Au Ask

Hg Her



# f-Block elements



57 La Lanthanum	58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium
89 Ac Actinium	90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium

Lanthanoids

Actinoids



# d-Block Elements

**d-Block** & **f-block** elements are known as **transition** and **inner transition** elements, respectively

Generally, d-block elements are called **transition elements**

Because their chemical properties are **transitional** between those of **s- & p-block** elements

Known as transition metals

Metals that have **incomplete d subshell** either in neutral atom or in their ions.

# Transition Elements

**EXAMPLE**



Incomplete d subshell

Incomplete d subshell



# Inner Transition Elements

f-Block elements are called  
**inner transition** elements



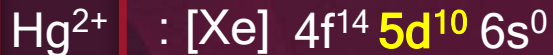
Because their valence shell  
electrons lie in **anti-penultimate  
energy level**

Example: Cerium (58)  
 $[\text{Xe}] 4f^1 5d^1 6s^2$





# Non-transition d-Block Elements



**Zn, Cd, Hg** of group 12 have **full  $d^{10}$**  configuration in their **ground state** as well as in their **common oxidation states**.

Known as **non-transition metals**

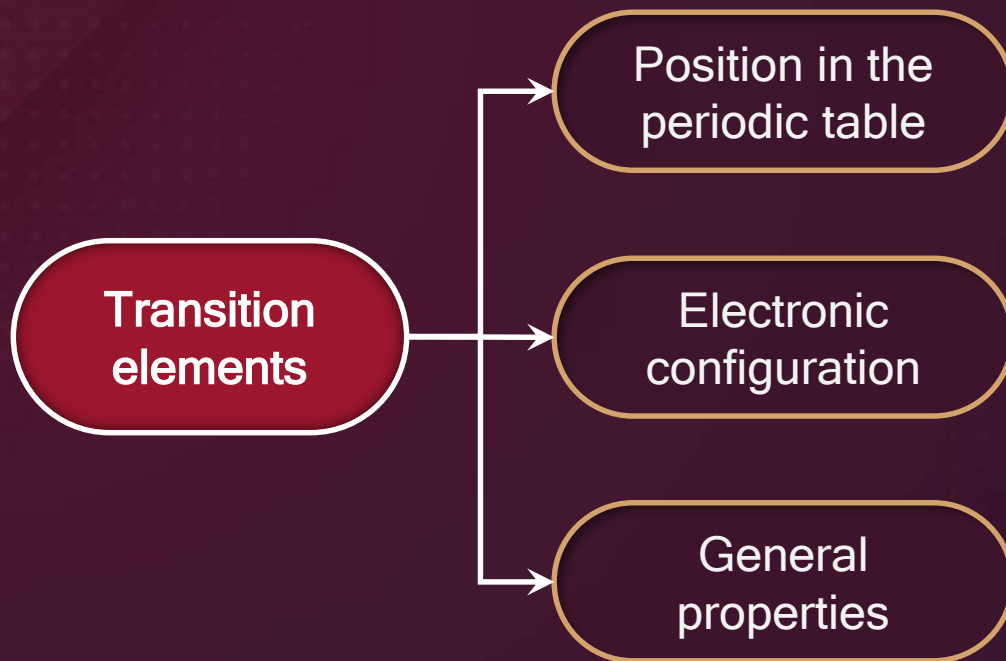


# Transition d-Block Elements

**Silver** is a **transition element** as it has incomplete d-orbital in its +2 oxidation state.



Incomplete in ionic state





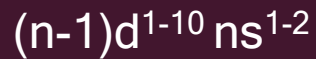
# Position of d-Block elements

		21	22	23	24	25	26	27	28	29	30						
		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn						
		scandium	Titanium	Vanadium	Chromium	Manganese	Iron	Cobalt	Nickel	Copper	Mercury						
		39	40	41	42	43	44	45	46	47	48						
		Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd						
		Yttrium	Zirconium	Niobium	Molybdenum	Technetium	Ruthenium	Rhodium	Palladium	Silver	Cadmium						
		57	72	73	74	75	76	77	78	79	80						
		La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg						
		89	104	105	106	107	108	109	110	111	112						
		Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn						

# Electronic Configuration of d-Block Elements



General configuration



Inner d-orbital

Last electron enters in the d-orbital

**Example**

Sc(21)



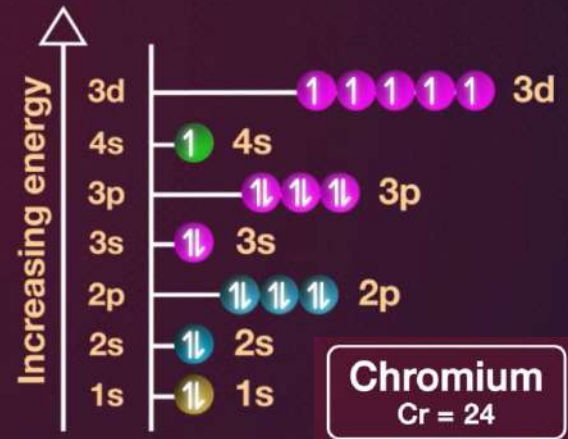
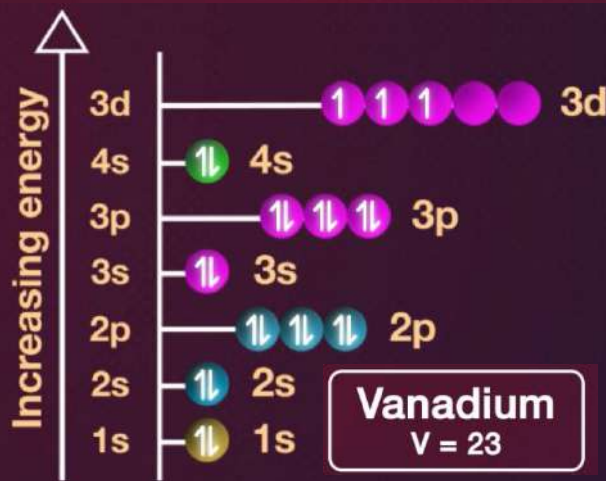
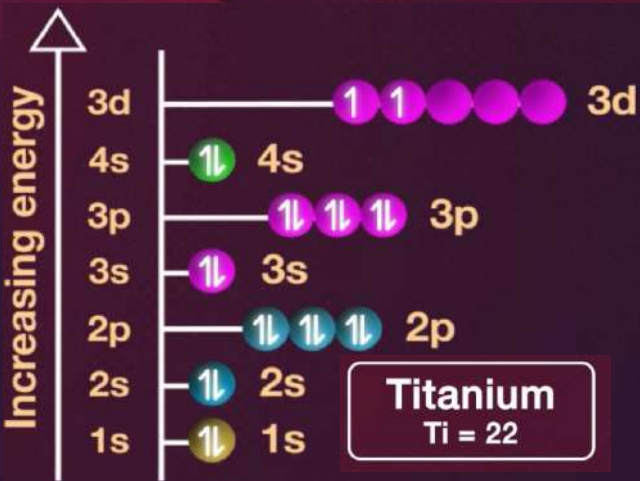
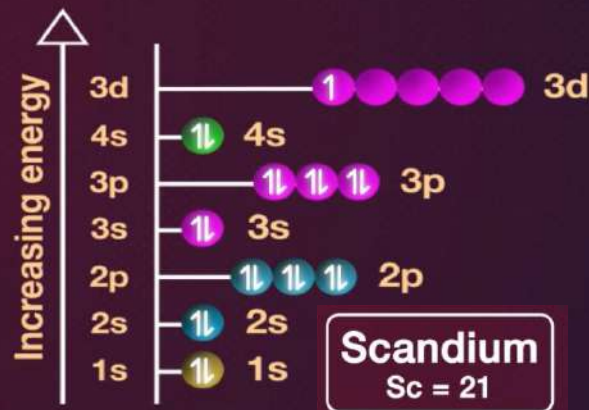
Co(27)

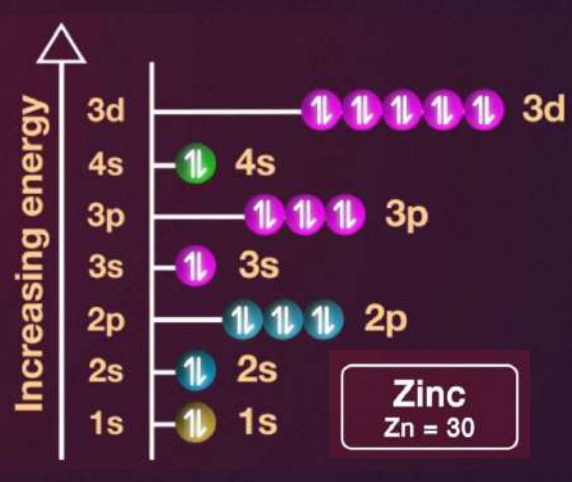
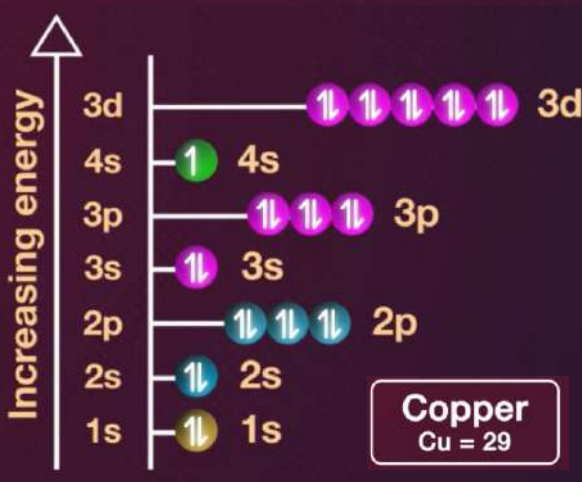
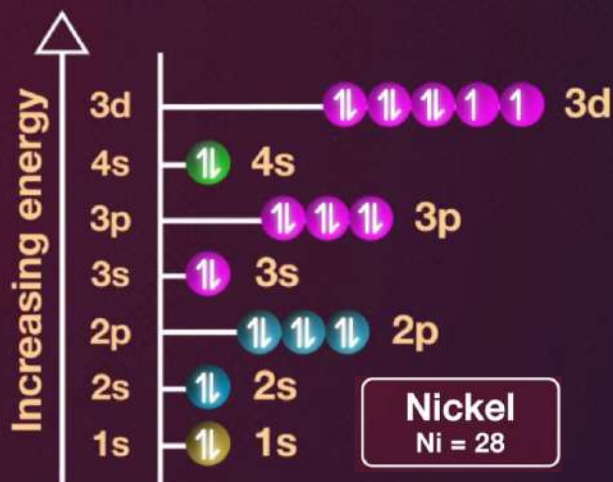
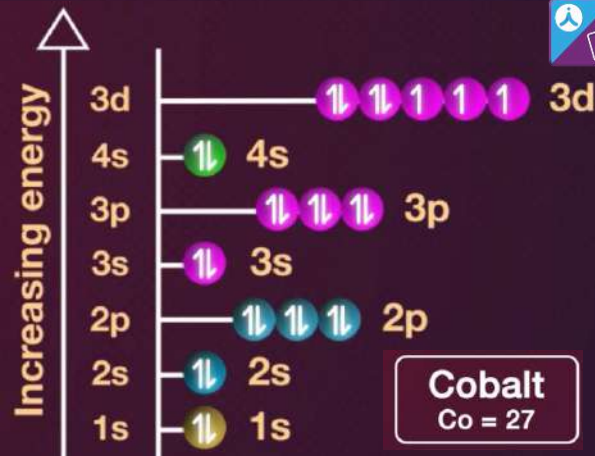
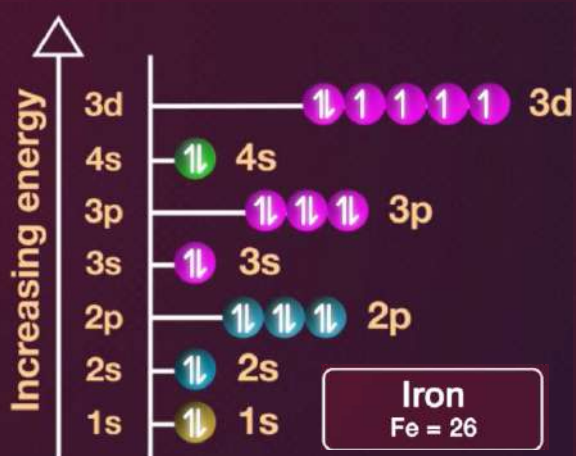


# Electrons filling in 3d elements



For 3d-series elements, electrons enter in 3d orbitals which is occupied generally after 4s orbital.







# Examples

The electronic configuration has several exceptions because of very little difference in energy of (n-1)d and ns electrons. This can be reflected in electronic configuration of Cr (half filled) and Cu (fully filled) in 3d series.

Cr(24)



[Ar] 3d<sup>4</sup> 4s<sup>2</sup>



Ag(47)



[Kr] 4d<sup>9</sup> 5s<sup>2</sup>



Cr(24)



[Ar] 3d<sup>5</sup> 4s<sup>1</sup>



Ag(47)



[Kr] 4d<sup>10</sup> 5s<sup>1</sup>



Mo(42)



[Kr] 4d<sup>4</sup> 5s<sup>2</sup>



Cu(29)



[Ar] 3d<sup>9</sup> 4s<sup>2</sup>



Mo(42)



[Kr] 4d<sup>5</sup> 5s<sup>1</sup>



Cu(29)



[Ar] 3d<sup>10</sup> 4s<sup>1</sup>



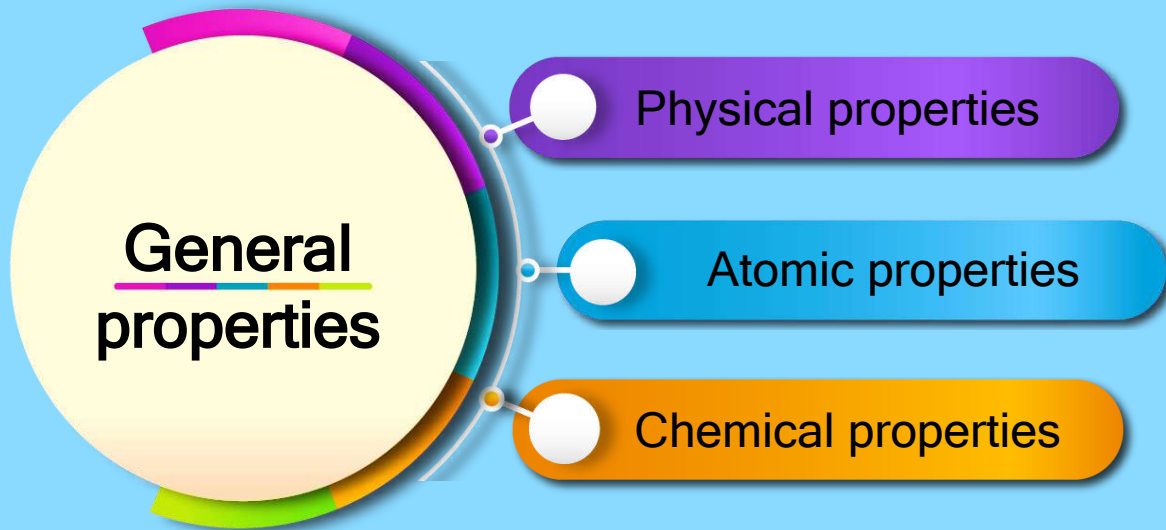


# Examples

Au(79)	→	[Xe] 4f <sup>14</sup> 5d <sup>9</sup> 6s <sup>2</sup>	✗
<b>Au(79)</b>	→	<b>[Xe] 4f<sup>14</sup> 5d<sup>10</sup> 6s<sup>1</sup></b>	✓
Pd(46)	→	[Kr] 4d <sup>8</sup> 5s <sup>2</sup>	✗
<b>Pd(46)</b>	→	<b>[Kr] 4d<sup>10</sup> 5s<sup>0</sup></b>	✓
Pt(78)	→	[Xe] 4f <sup>14</sup> 5d <sup>8</sup> 6s <sup>2</sup>	✗
<b>Pt(78)</b>	→	<b>[Xe] 4f<sup>14</sup> 5d<sup>9</sup> 6s<sup>1</sup></b>	✓



Transition elements exhibit certain **characteristic properties** due to **partially filled** d-orbitals.





# Physical Properties

All the transition elements display typical metallic properties

High tensile strength

High thermal and electrical conductivity

Malleability

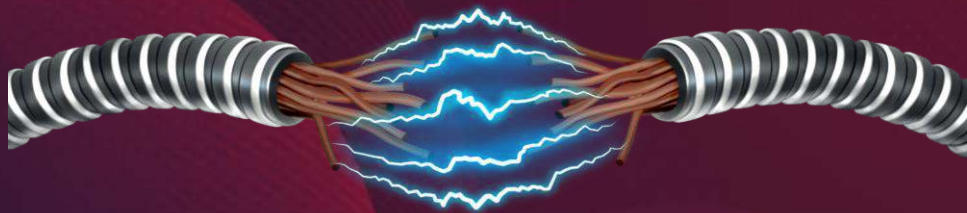
Ductility

Metallic lustre

Hard and less volatile

High melting and boiling points

High tensile strength

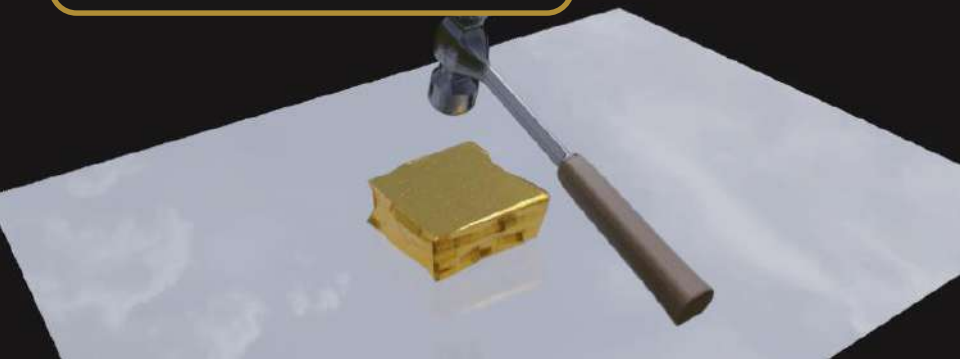


High electrical conductivity



High thermal conductivity

**Malleability:** Metals are highly malleable



**Ductility:** They are ductile and can be drawn into very thin wire



**Metallic lustre:** Metals are lustrous in nature



**Volatility:** Metals are non-volatile in nature





High boiling point

High melting point

Metals generally have  
high melting point

Metals generally have  
high boiling point



# Melting Point of Transition Elements

Melting point of transition metal is high because of the involvement of greater number of electrons from  $(n-1)d$  in addition to the  $ns$  electrons in the **interatomic metallic bonding**.

# Melting Point of Transition Elements



General rule

**Greater** the number of unpaired electrons



**Higher** will be the melting point

In any row,

3d metals rise to a maximum at  $d^5$



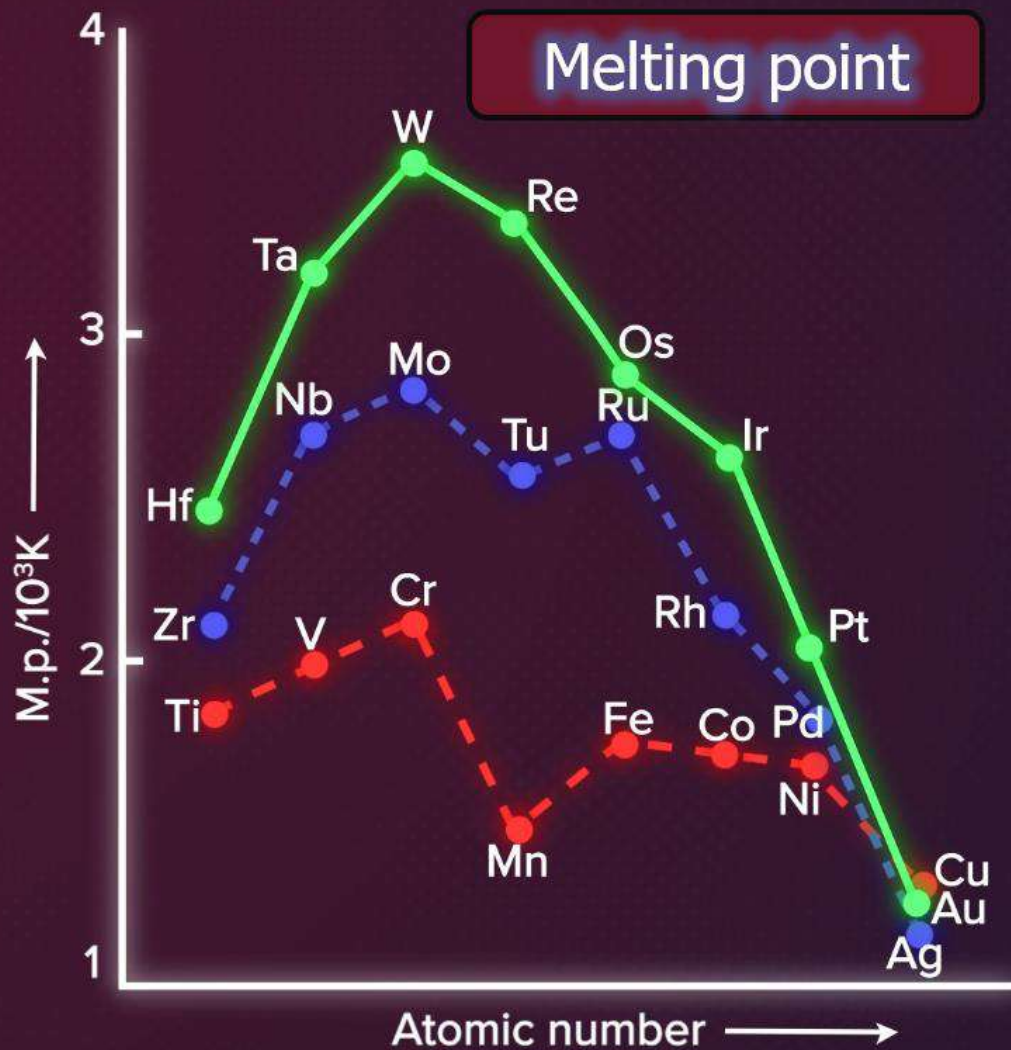
Then, fall regularly as the atomic number increases

Except for anomalous values of Mn and Tc



# Melting point

- 5d Series
- 4d Series
- 3d Series



# Boiling Point of Transition Elements



Transition elements  
have high boiling point  
due to high enthalpy  
of atomisation



# Enthalpy of Atomisation

It is the enthalpy change on **breaking one mole** of bonds completely to obtain atoms in the **gaseous phase**.



Transition elements exhibit higher enthalpies of atomization due to high effective nuclear charge and large number of valence electrons.



Form very strong metallic bonds.



Arise due to unpaired electrons in the  $(n-1)d$  subshell.



# Boiling Point of Transition Elements

General rule

Greater the number of  
valence electrons



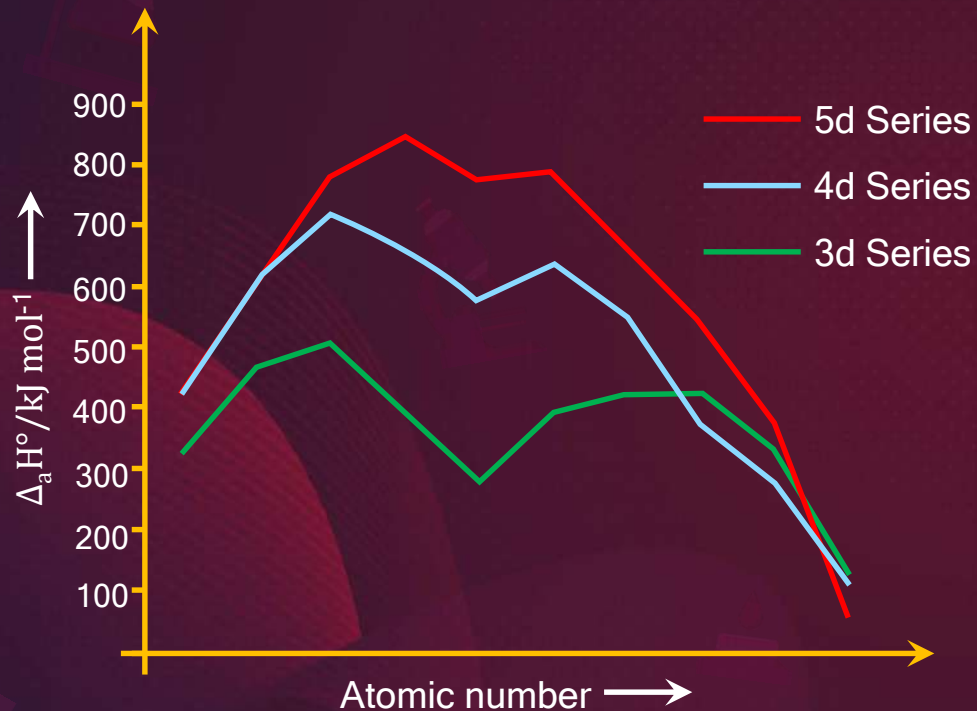
Stronger is the  
resultant bonding



Higher will be the  
boiling point.

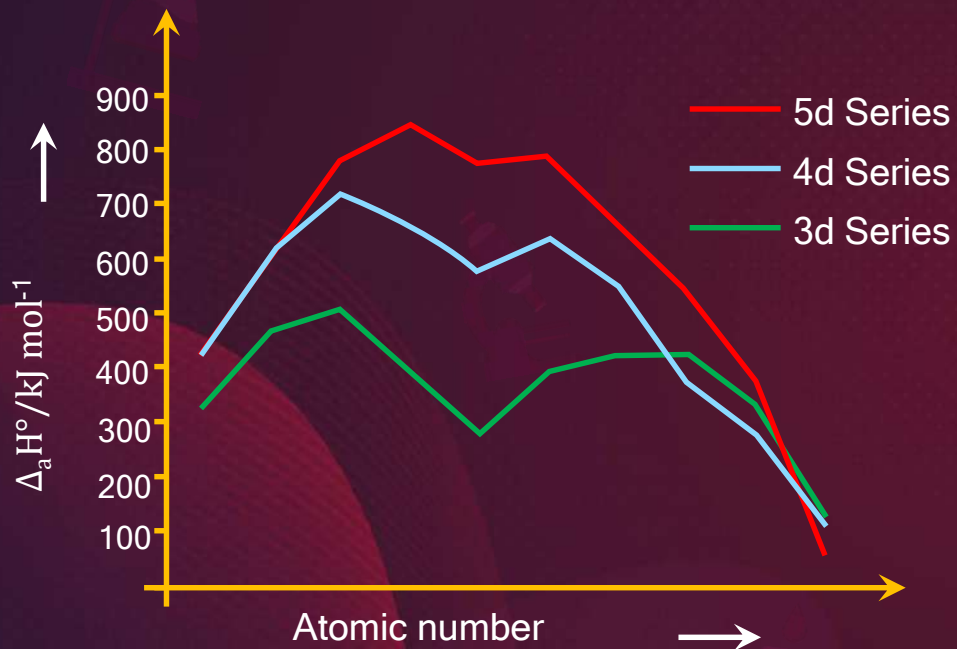


# Enthalpy of Atomisation



The maxima at about the middle of each series indicate that one unpaired electron per d orbital is particularly favourable for strong interatomic interaction.

# Enthalpy of Atomisation



Boiling point of transition elements **increases** down the group.



# Boiling Point of Transition Elements

Zn, Cd and Hg have low boiling point

Zn

Cd

Hg

Zero unpaired electrons



Weak metallic bonding



Lowest boiling and melting point



**Atomic  
properties**

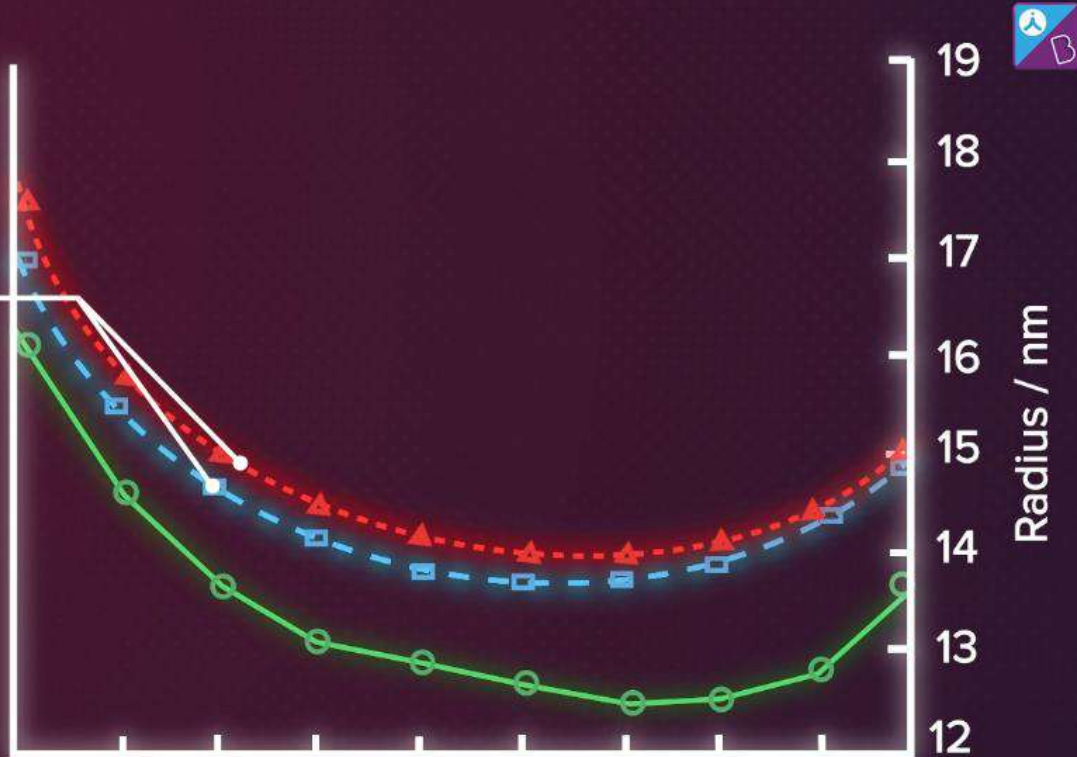
Atomic radii and  
ionic radii

Ionisation enthalpy



- 3d Series
- 4d Series
- 5d Series

Lanthanoid contraction



	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg





# Atomic Radii - 3d Series

Decreases gradually

Due to poor shielding by d electrons, attraction increases more than repulsion

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

Nearly constant

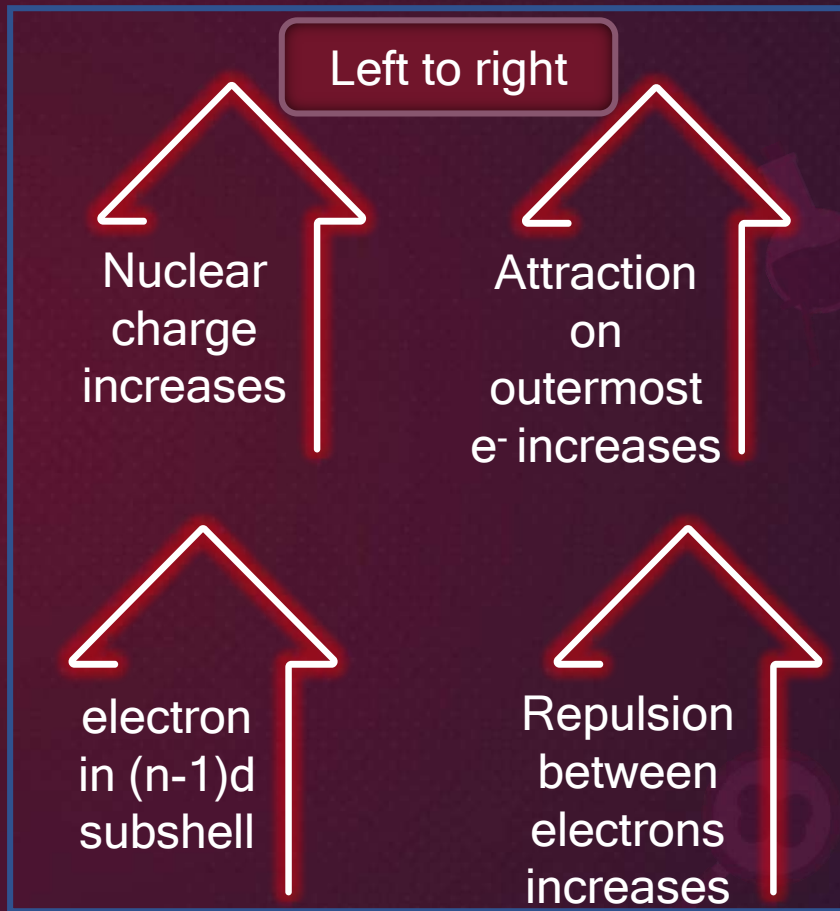
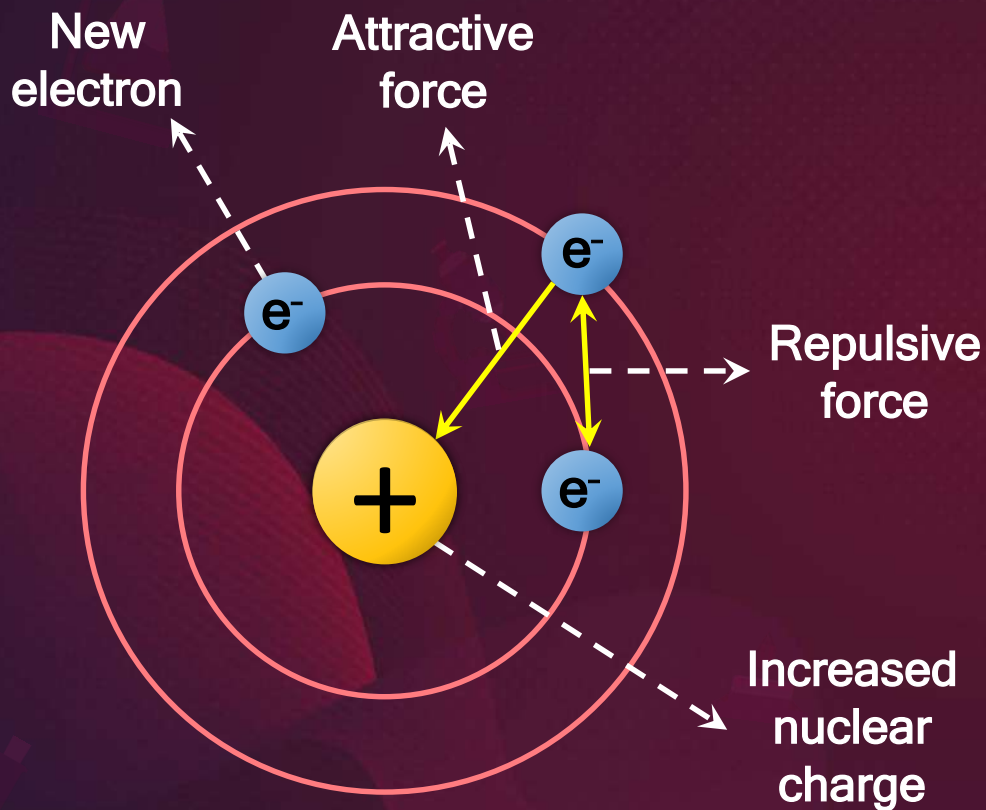
Increases

Repulsion almost balances out attraction

Repulsion dominates attraction

No. of (n-1)d electrons are very high

# Atomic Radii of Transition Elements





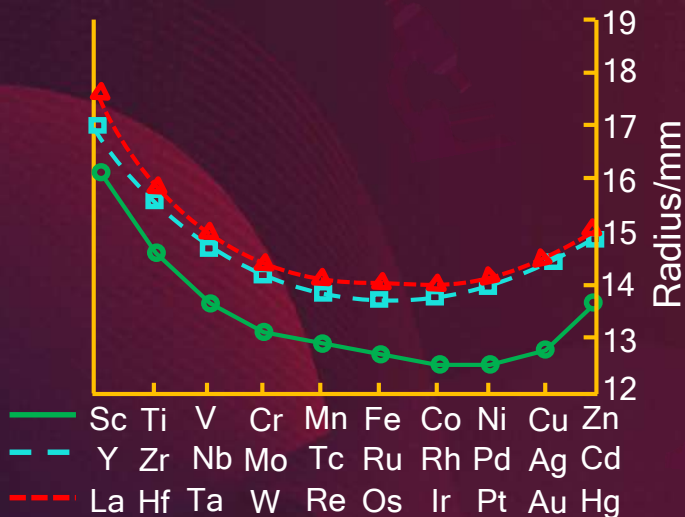
# Atomic Radii of 3d, 4d and 5d Series

Due to lanthanoid contraction

Radius of 4d series is similar to radius of 5d series

The filling of 4f before 5d orbital results in a regular decrease in atomic radii.

The **imperfect shielding** of one electron by another in the same set of orbitals.





# Lanthanoid Contraction

The filling of 4f before 5d orbital results in a **regular decrease** in atomic radii.

# Lanthanoid Contraction (Effect on Radii)



Down  
the  
group

Titanium (Ti)	→	$4s^2 3d^2$	147 pm
Zirconium (Zr)	→	$5s^2 4d^2$	160 pm
Hafnium (Hf)	→	$4f^{14} 6s^2 5d^2$	159 pm

↓

$Ti < Zr \approx Hf$

# Lanthanoid Contraction



Reason 1

Shielding power  
of orbitals

$s > p > d > f$

Size  
decreases

Nuclear attraction on  
outermost  $e^-$  increases





# Lanthanoid Contraction

## Reason 2

Titanium (Ti, 22)

Zirconium (Zr, 40)

Hafnium (Hf, 72)

+18 increase in positive charge

+32 increase in positive charge

Drastic increment in charge

Increase in attraction

Decrease in radii







# Lanthanoid Contraction

Lanthanoid contraction essentially compensates for the expected increase in atomic size with increasing atomic number.



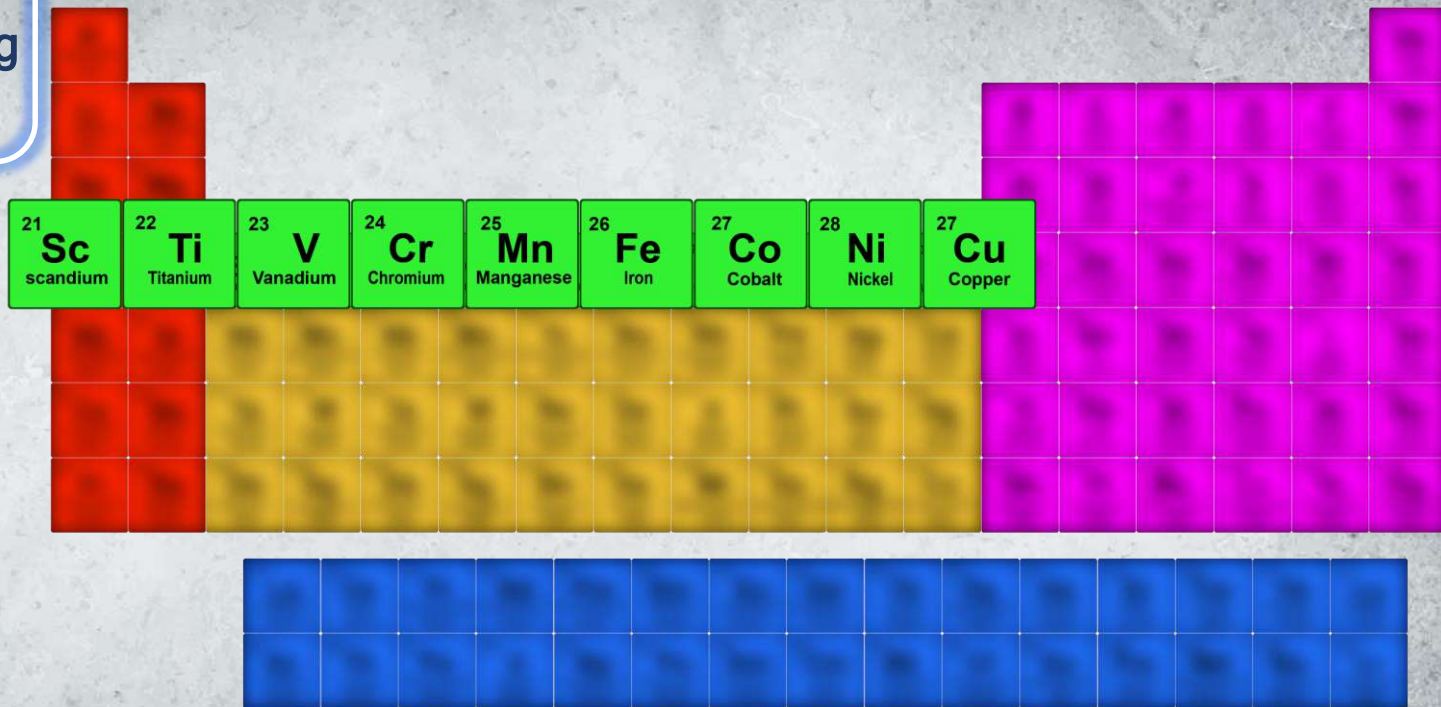
Due to lanthanoid contraction, 4d and 5d elements have very similar physical and chemical properties.

Due to decrease in radii and increase in atomic mass, density of transition elements is generally high.

Density increases down the group



Density increases  
from Sc to Cu along  
the period





# Trends in Ionisation Enthalpy

Reason

In general, from left to right ionization enthalpy **increases** Gradually.

Due to an increase in nuclear charge



Accompanied by the filling of the inner d-orbitals



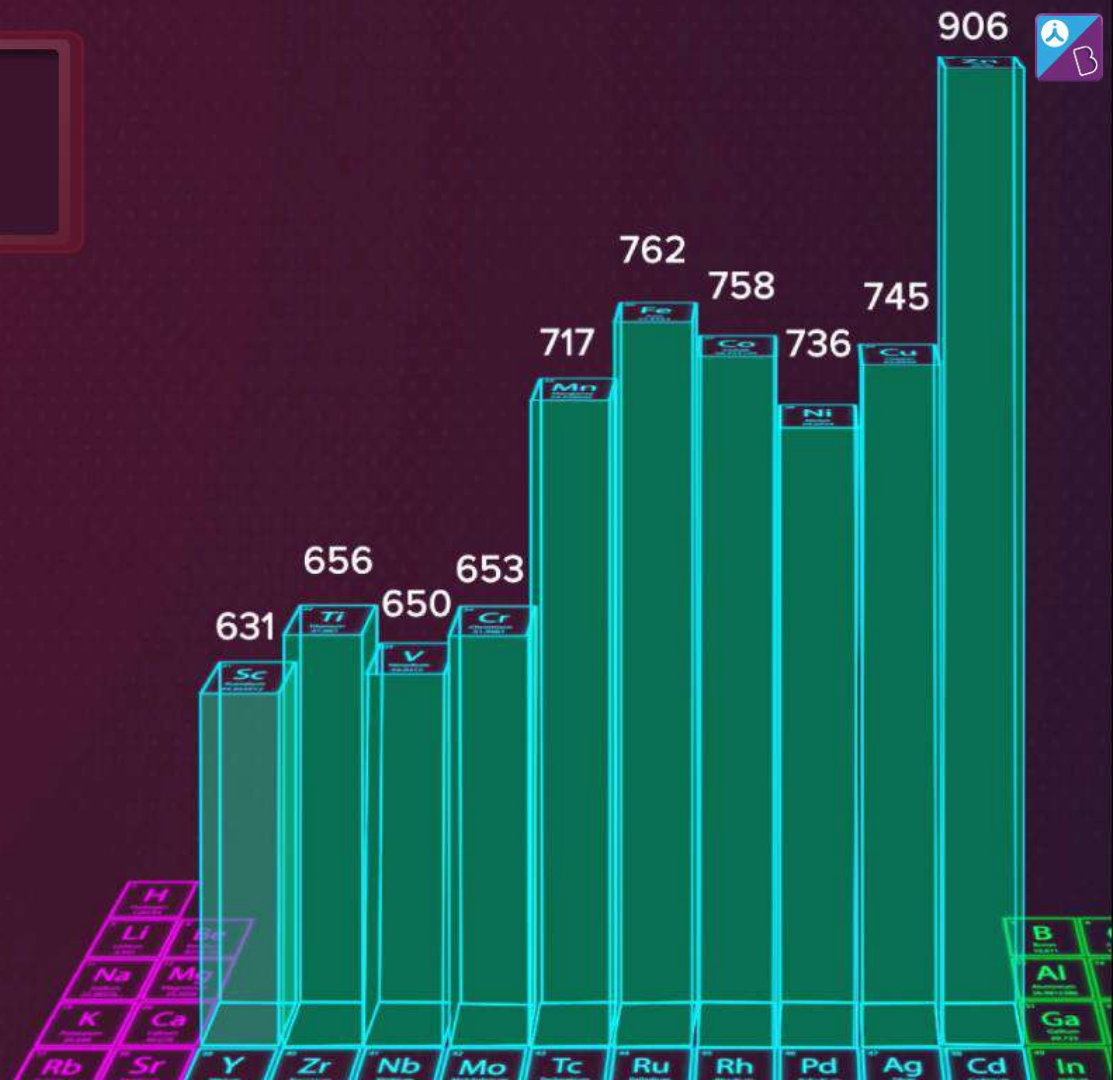
Ionisation enthalpy increases



# Ionisation Enthalpy Values For 3d Series

3d series	I.E <sub>1</sub> (kJmol <sup>-1</sup> )	I.E <sub>2</sub> (kJmol <sup>-1</sup> )	I.E <sub>3</sub> (kJmol <sup>-1</sup> )
Sc	631	1235	2393
Ti	656	1309	2657
V	650	1414	2833
Cr	653	1592	2990
Mn	717	1509	3260
Fe	762	1561	2962
Co	758	1644	3243
Ni	736	1752	3402
Cu	745	1958	3556
Zn	906	1734	3837

# Ionisation enthalpy (kJ/mol)



# Ionisation Enthalpy Values For 3d Series



3d series	I.E <sub>1</sub> (kJmol <sup>-1</sup> )	I.E <sub>2</sub> (kJmol <sup>-1</sup> )	I.E <sub>3</sub> (kJmol <sup>-1</sup> )
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Zn	<b>906</b>	1734	3837



# Ionisation Enthalpy

Zinc have significantly **higher ionisation enthalpy** than copper

Due to completely filled d and s electrons in Zn, its first ionisation energy is more than Cu.

$r_{\text{Zn}}$

>

$r_{\text{Cu}}$

$\text{I.E.}_{\text{Zn}}$

>

$\text{I.E.}_{\text{Cu}}$

First ionisation enthalpy

$3d^{10} 4s^2$

$3d^{10} 4s^1$

Fully filled



More stable

High I.E.

# Ionisation Enthalpy Values For 3d Series



3d series	I.E <sub>1</sub> (kJmol <sup>-1</sup> )	I.E <sub>2</sub> (kJmol <sup>-1</sup> )	I.E <sub>3</sub> (kJmol <sup>-1</sup> )
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# Ionisation Enthalpy

Manganese have abnormally **high ionisation enthalpy** compared to chromium

 $r_{\text{Cr}}$  $>$  $r_{\text{Mn}}$  $\text{I.E.}_{\text{Cr}}$  $<$  $\text{I.E.}_{\text{Mn}}$ 

First  
ionisation  
enthalpy

 $3d^5 4s^1$  $3d^5 4s^2$ 

High I.E.

More stable

Fully filled



# Trends in Ionisation Enthalpy

Down the  
group



Lanthanoid contraction

Poor shielding  
of f-orbitals

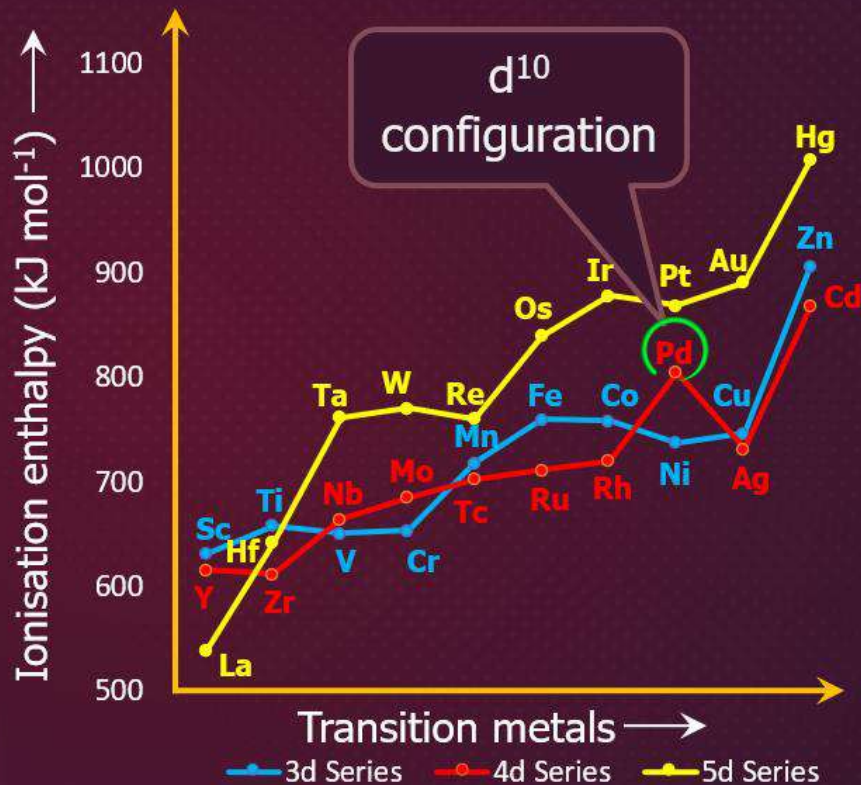
Radius increases

But, nuclear charge  
also increases

Irregular trend in ionisation  
energy is observed for  
3d & 4d series

# Trends in Ionisation Enthalpy

Down the group  
↓





# Chemical Properties

Oxidation state

Standard electrode potential and reactivity

Magnetic properties

Colour

Formation of complex compounds

Catalytic properties

Formation of interstitial compounds

Alloy formation

# Oxidation State of Transition Elements



Due to incomplete filling of d-orbitals

Transition elements show a great variety of oxidation states

$Mn^{2+}$



$Mn^{6+}$



$Mn^{7+}$



Manganese in different oxidation states

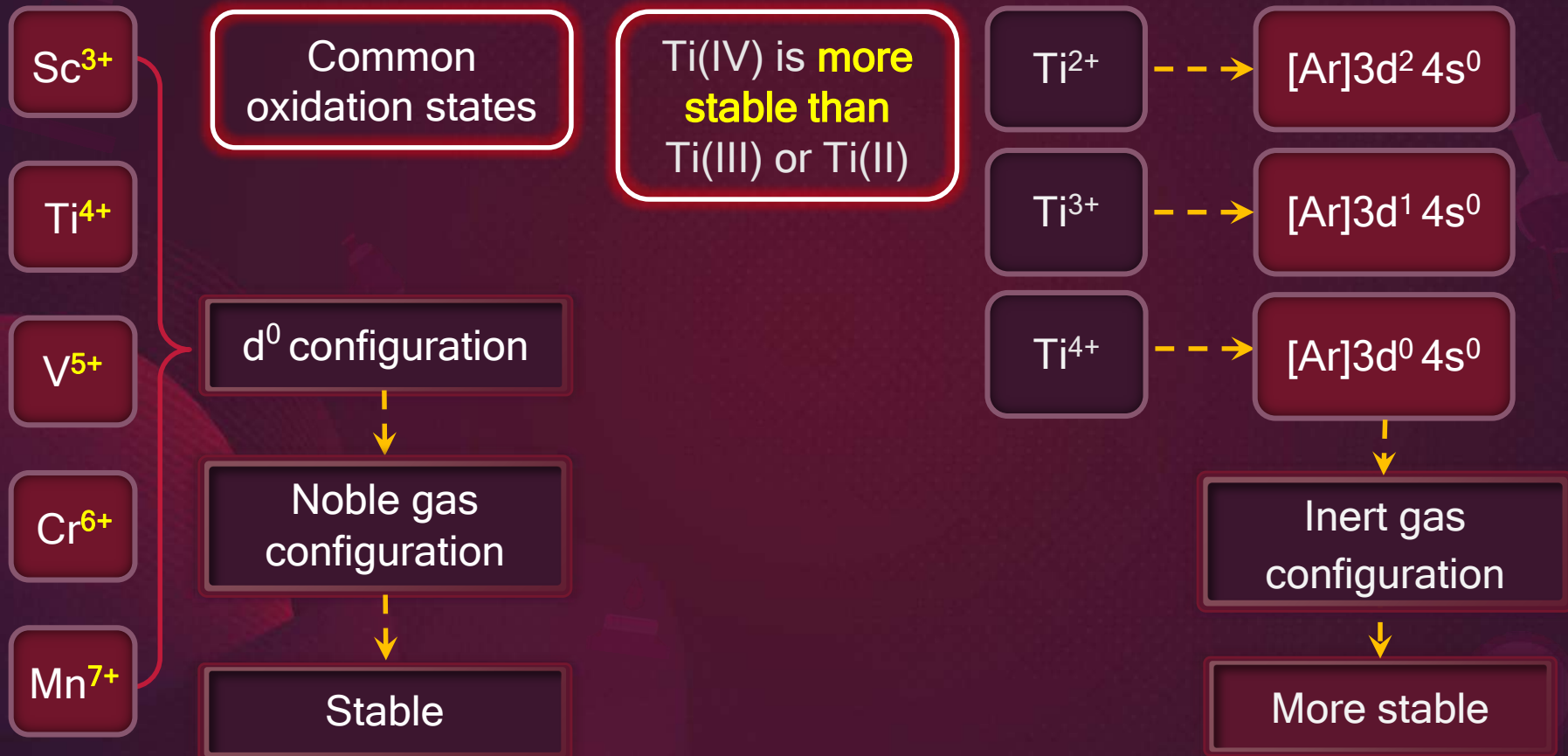
# Oxidation States of 3d Series Elements



Oxidation states form regular pyramid

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
								+1	
	+2	+2	+2	+2	+2	+2	+2	+2	+2
+3	+3	+3	+3	+3	+3	+3	+3		
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5					
			+6	+6	+6				
				+7					

# Oxidation State of 3d Transition Elements



# Oxidation State of 3d Transition Elements



Common oxidation states

$\text{Mn}^{2+}(25)$

$3d^5 4s^0$

$\text{Fe}^{3+}(26)$

Half-filled orbital

Stable

$\text{Zn}^{2+}$

$3d^{10} 4s^0$

Fully filled

More stable



# Oxidation State of 3d Transition Elements



Requires high energy for removing electron



# Oxidation State Stability - Down the Group



Inert pair effect



**p-block**

Lower oxidation states are favoured by heavier elements

Higher oxidation states are favoured by the heavier elements

**d-block**

Easier to remove valence electrons

# Oxidation State Stability - Down the Group



Example

Stability order

Mo (VI) & W (VI)

>

Cr (VI)

MoO<sub>3</sub> and WO<sub>3</sub>  
are not oxidising  
agents

Dichromate ion  
(Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>) in acidic  
medium is a  
strong oxidising  
agent

Inert pair effect

**p-block**

Oxidation state normally differ by unit of 2.



Oxidation state normally differ by unity

**d-block**

Successive removal of electrons from d-orbital

# Oxidation State in d-block Elements



Fe and Ni in  $\text{Fe}(\text{CO})_5$  and  $\text{Ni}(\text{CO})_4$  have **zero oxidation states** despite the d block elements favouring higher oxidation states



Low oxidation state is favoured by metals when a complex compound has ligands



Which are not just strong  **$\sigma$ -donors** but also  **$\pi$ -acceptors** like in  $\text{Ni}(\text{CO})_4$  and  $\text{Fe}(\text{CO})_5$ , etc.





# Stability of Higher Oxidation States

Fluorine stabilizes the highest oxidation state

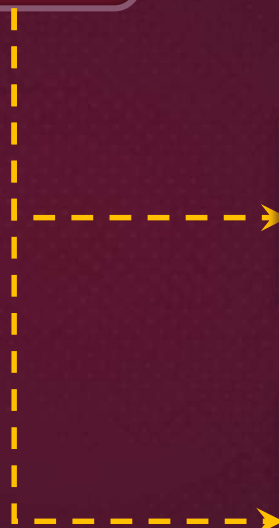
Stability through

Example:  $\text{CoF}_3$

Higher lattice energy

Higher bond enthalpy  
(higher covalent compound)

Example:  
 $\text{VF}_5$ ,  $\text{CrF}_6$



# Halides of 3d metals

$X$  : F  $\rightarrow$  I  
 $X^I$  : F  $\rightarrow$  Br  
 $X^{II}$  : F, Cl  
 $X^{III}$  : Cl  $\rightarrow$  I

Oxidation Number ↓	Group 3 →	4	5	6	7	8	9	10	11	12
+6										CrF <sub>6</sub>
+5				VF <sub>5</sub>	CrF <sub>5</sub>					
+4		TiX <sub>4</sub>	VX <sub>4</sub> <sup>I</sup>	CrX <sub>4</sub>	MnF <sub>4</sub>					
+3		TiX <sub>3</sub>	VX <sub>3</sub>	CrX <sub>3</sub>	MnF <sub>3</sub>	FeX <sub>3</sub> <sup>I</sup>	CoF <sub>3</sub>			
+2		TiX <sub>2</sub> <sup>III</sup>	VX <sub>2</sub>	CrX <sub>2</sub>	MnX <sub>2</sub>	FeX <sub>2</sub>	CoX <sub>2</sub>	NiX <sub>2</sub>	CuX <sub>2</sub> <sup>II</sup>	ZnX <sub>2</sub>
+1										CuX <sup>III</sup>

X: Cl, Br or I

All halides are known except iodide



## Note



1

**V(+5)** is represented only by  $\text{VF}_5$ .

The other halides, however, undergo hydrolysis to give **oxohalides**,  $\text{VOX}_3$ .



2

In lower oxidation states, fluorides are **unstable**.  
Example:  $\text{VX}_2$  (X = Cl, Br or I)

↓

On the other hand, all Cu(II) halides are known including  $\text{CuF}_2$  except the iodide.

↓

In this case,  $\text{Cu}^{2+}$  oxidises  $\text{I}^-$  to  $\text{I}_2$ .



# Instability of $\text{Cu}^{\text{II}}$ Iodides

$\text{Cu}^{2+}$  oxidises  $\text{I}^-$  to  $\text{I}_2$







# Oxides of 3d Metals

The ability of oxygen to stabilise these high oxidation states exceeds that of fluorine.

Oxides are more stable than halides due to ability of oxygen to form **multiple bonds** with metals.



Highest Mn fluoride



Highest Mn oxide



# Reactivity of Transition Metals

Transition metals vary widely in their chemical reactivity.



The study of **standard electrode potential** is important to understand the



Reactivity of transition elements

Stability of various oxidation states

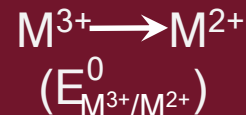
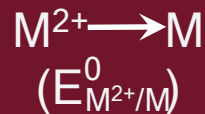


Standard electrode potentials are measurements of the equilibrium potentials.



Standard reduction potential

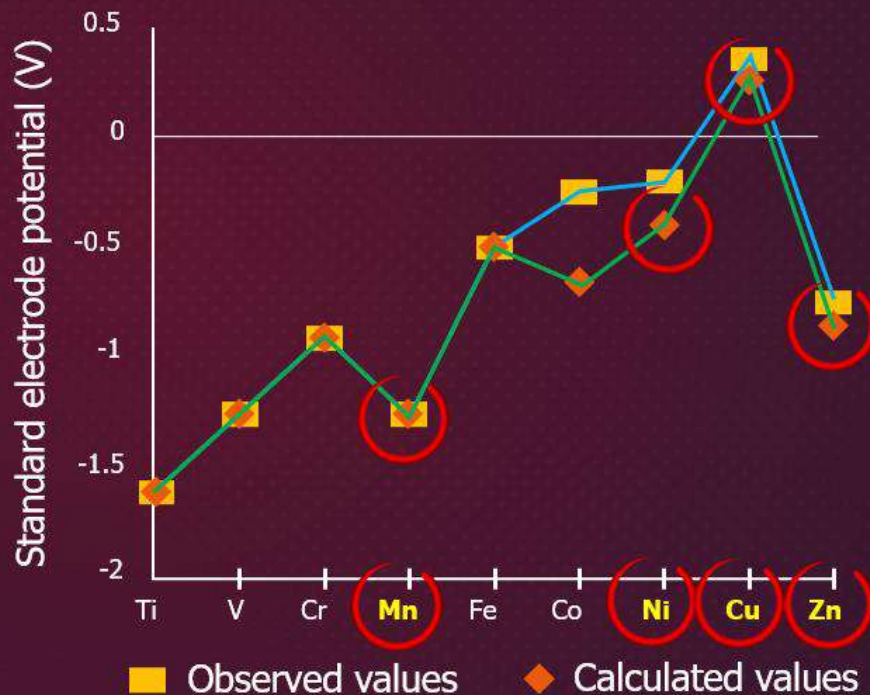
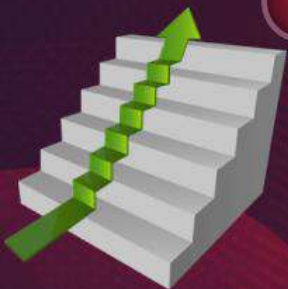
## Trends in standard electrode potentials



# Trends of Standard Electrode Potential

Generally,

The value of  $E_{M^{2+}/M}^0$   
**increases** from left  
 to right





Cu shows positive standard electrode potential

Sublimation enthalpy(+ve)

Enthalpy of atomisation & ionisation energies



+



High

Ionisation enthalpy (I.E.<sub>1</sub> + I.E.<sub>2</sub>), +ve



Low

Hydration enthalpy(-ve)

The high energy required to transform Cu (s) to Cu<sup>2+</sup> (g)

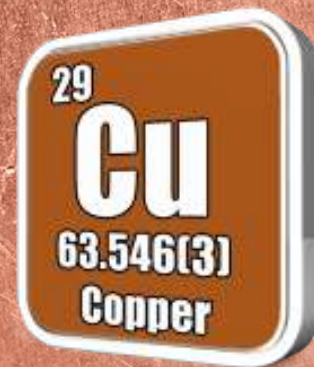


Not balanced by its hydration energy





Inability to liberate  
 $\text{H}_2$  from acid



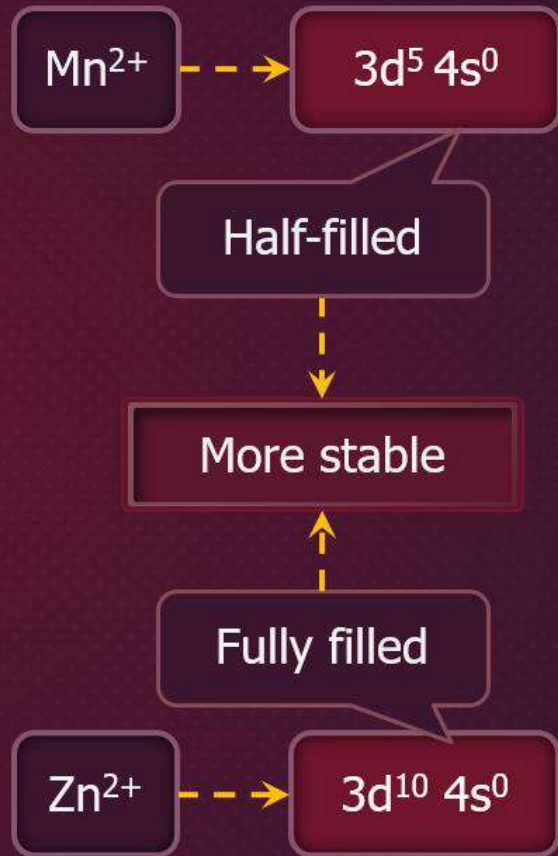
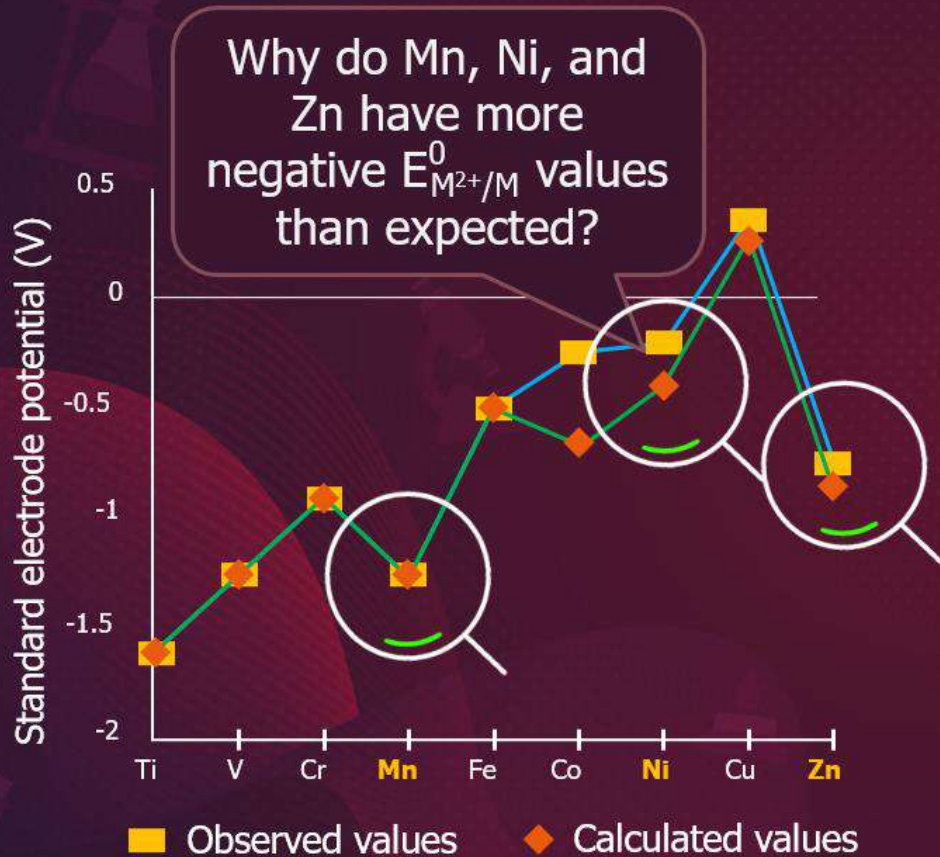
Only oxidising acids ( $\text{HNO}_3$ ,  
hot conc.  $\text{H}_2\text{SO}_4$ ) react with  
Cu to liberate  $\text{NO}_2$  and  $\text{SO}_2$   
and oxidise Cu to  $\text{Cu}^{2+}$



Whereas,



# Trends in the $E_{M^{2+}/M}^0$ Standard Electrode Potential

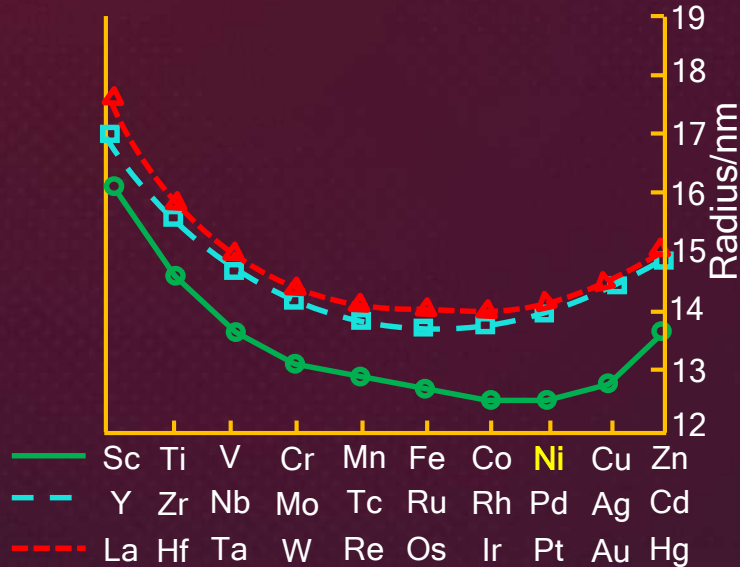




## Trends in the $E_{M^{2+}/M}^0$

In +2 state, Mn shows  $d^5$ , Ni with  $d^8$  has completely filled  $t_{2g}$  and Zn has completely filled  $d^{10}$ . So, they show more negative  $E^0$  values than expected

# Hydration Energy



Due to high charge density

$\text{Ni}^{2+}$  ion has the **highest negative enthalpy** of hydration among the elements of 3d series.

# Standard Electrode Potential $E^0_{M^{3+}/M^{2+}}$ of 3d Elements



Metal	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$E^0_{M^{3+}/M^{2+}}$	-2.10	-0.37	-0.26	-0.41	+1.57	+0.77	+1.97	-	-	-

Lower value for  $Sc^{3+}$  due to stable  $d^0$  configuration

Lower value for  $Fe^{3+}$  due to stable  $d^5$  configuration

# Standard Electrode Potential $E^0_{M^{3+}/M^{2+}}$ of 3d Elements



Metal	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$E^0_{M^{3+}/M^{2+}}$	-2.10	-0.37	-0.26	-0.41	+1.57	+0.77	+1.97	-	-	-

Higher value for  $Mn^{2+}$  due to stable  $d^5$  configuration

Highest value for  $Zn^{2+}$  due to stable  $d^{10}$  configuration

# Chemical Reactivity



Transition metals vary widely in their chemical reactivity.



Many are electropositive and dissolve in mineral acids.

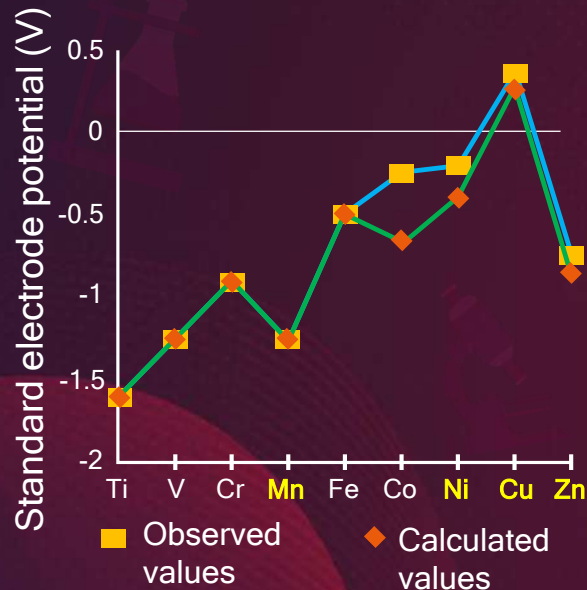


A few metals are **noble** or remain unreactive towards single acids.

Metals	Reactivity
Potassium	Reacts with water
Sodium	
Lithium	
Barium	
Strontium	
Calcium	
Magnesium	Reacts with acids
Aluminium	
Manganese	
Zinc	
Chromium	
Iron	
Cadmium	
Cobalt	
Nickel	
Tin	
Lead	Included for comparison
Hydrogen	
Antimony	
Bismuth	
Copper	
Mercury	
Silver	
Gold	
Platinum	



# Chemical Reactivity



Less negative  $E^0$  values

The  $E^0_{M^{2+}/M}$  values indicate decreasing tendency to form divalent cation

Due to **increase** in the sum of **first two ionisation enthalpies**



# Standard Electrode Potential $E^0_{M^{3+}/M^{2+}}$ of 3d Elements



Metal	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$E^0_{M^{3+}/M^{2+}}$	-2.10	-0.37	-0.26	-0.41	+1.57	+0.77	+1.97	-	-	-

**Mn<sup>3+</sup>** and **Co<sup>3+</sup>**  
ions are **strong  
oxidising agents**



# Standard Electrode Potential $E^0_{M^{3+}/M^{2+}}$ of 3d Elements



Metal	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$E^0_{M^{3+}/M^{2+}}$	-2.10	-0.37	-0.26	-0.41	+1.57	+0.77	+1.97	-	-	-

**Strong reducing agents**

Liberate **H<sub>2</sub>** from dil. acid





When a magnetic field is applied to substances, mainly two types of magnetic behaviours are observed.

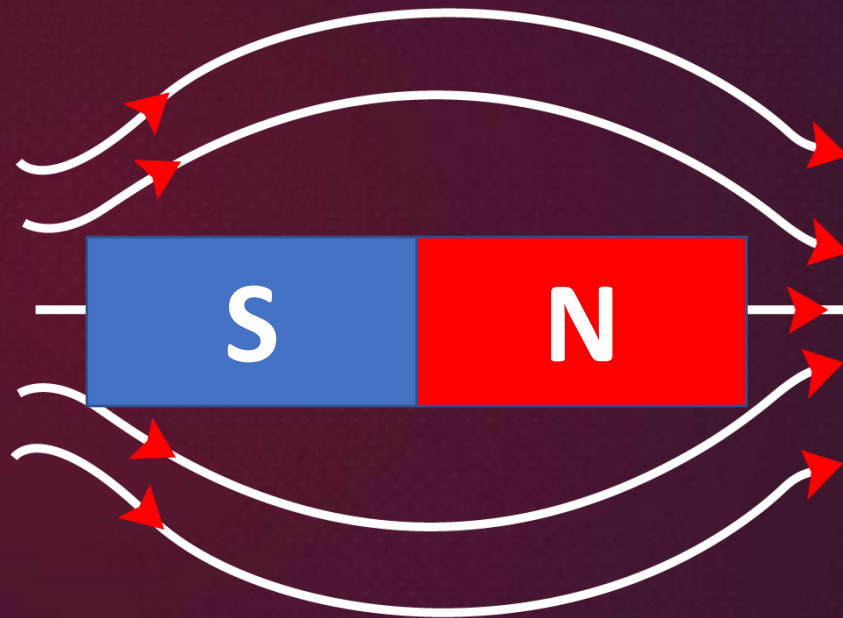
Diamagnetism

Paramagnetism



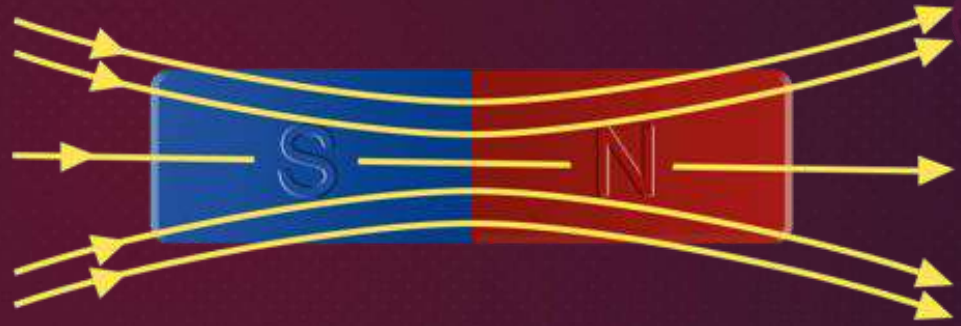
# Diamagnetic Nature

Diamagnetic substances are **repelled** by the applied field.



# Paramagnetic Nature

Paramagnetic substances are **attracted** by the applied field.





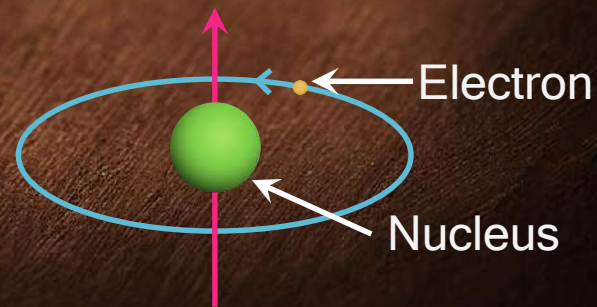
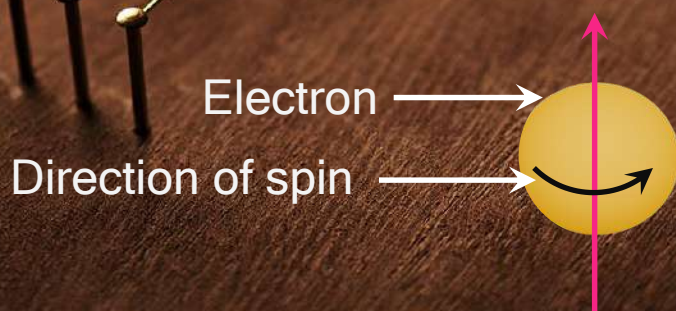
# Magnetic Properties

Transition elements are paramagnetic in nature.

Each electron has an associated magnetic moment, due to

Spin angular momentum

Orbital angular momentum





Magnetic  
moment

**Spin-only**  
magnetic  
moment (in  
BM)

$\mu$

=

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

Where,

$n$

=

No. of unpaired  
electron(s)

# Magnetic Moments of $\text{Mn}^{2+}$ Ion



**EXAMPLE**

$\text{Mn}^{2+}$

$[\text{Ar}] 3d^5 4s^0$

5 unpaired  
electrons

$\mu$

$= \sqrt{5(5 + 2)}$

$= 5.92 \text{ BM}$



# Calculated and Observed Magnetic Moments (BM)



Magnetic moment increases with number of unpaired electrons.

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	



# Formation of Coloured Ions: 3d Metal Ions

$Ti^{3+}$



$Cr^{3+}$



$Mn^{2+}$



$Fe^{3+}$



$Ti^{3+}$  : Purple

$Cr^{3+}$  : Green

$Mn^{2+}$  : Light pink

$Fe^{3+}$  : yellow

$Co^{2+}$  : pink

$Ni^{2+}$  : green

$Cu^{2+}$  : blue

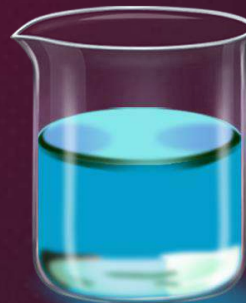
$Co^{2+}$



$Ni^{2+}$



$Cu^{2+}$

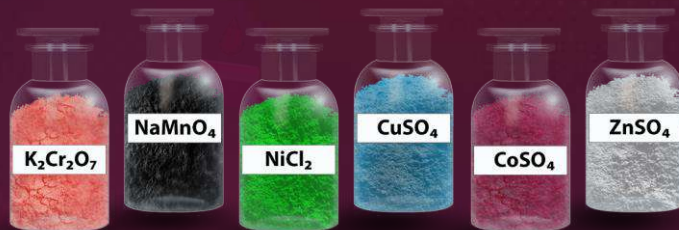




# Formation of Coloured Ions

When an electron from a lower energy d orbital is excited to a higher energy d-orbital

Due to this excitation, the compounds shows a **color**.





# Color of Transition Elements

This frequency generally lies in the **visible** region.

The colour observed corresponds to the **complementary colour** of the light absorbed.

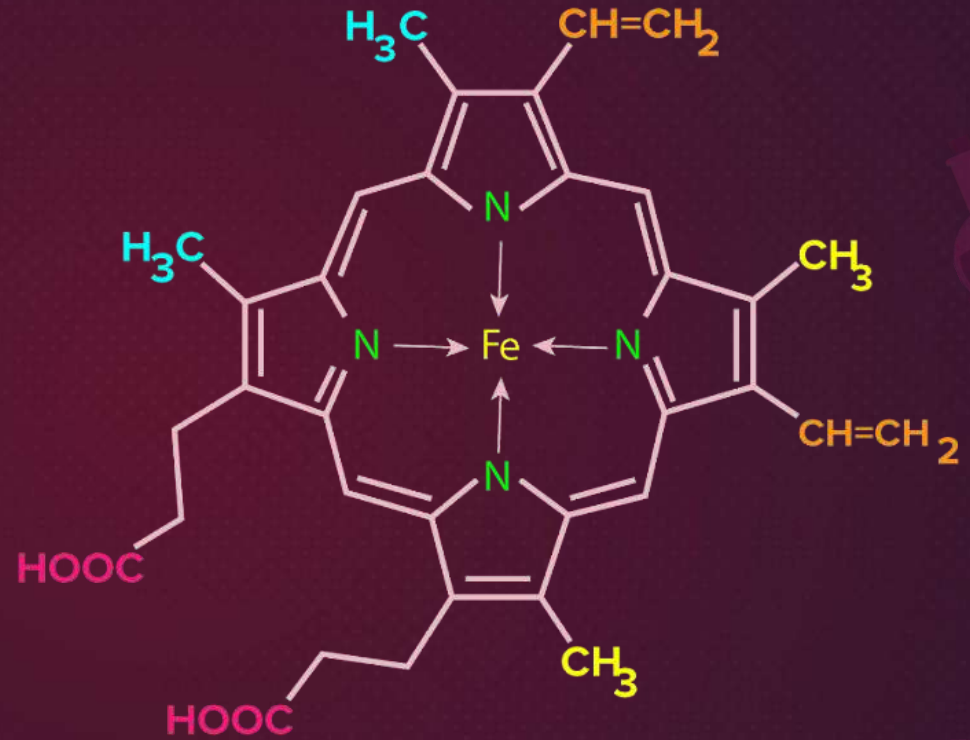


# Complex Compounds

Compounds in which the metal atoms/ions bind to a number of anions/neutral molecules, by sharing of electrons and forming complex species with characteristic properties.

Example:  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $[\text{PtCl}_4]^{2-}$ , etc.

# Haemoglobin



# Formation of Complex Compounds



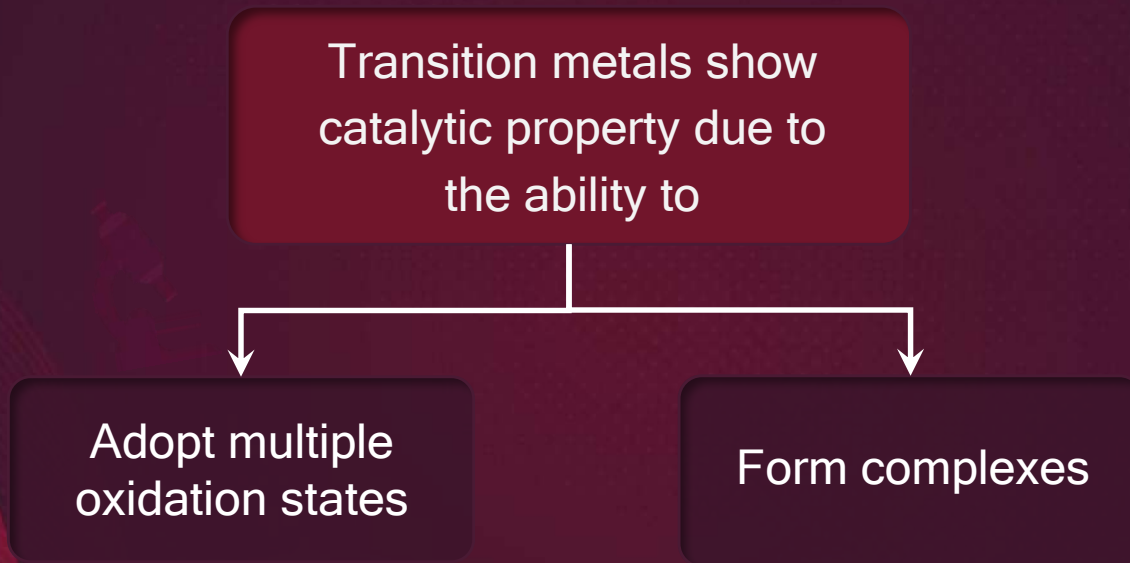
Reasons for  
complex  
formation

Comparatively  
smaller sizes

High ionic charges

Availability of d-orbitals  
for bond formation

# Catalytic Property of Transition Metals





# Catalytic Property of Transition Metals



**EXAMPLE**

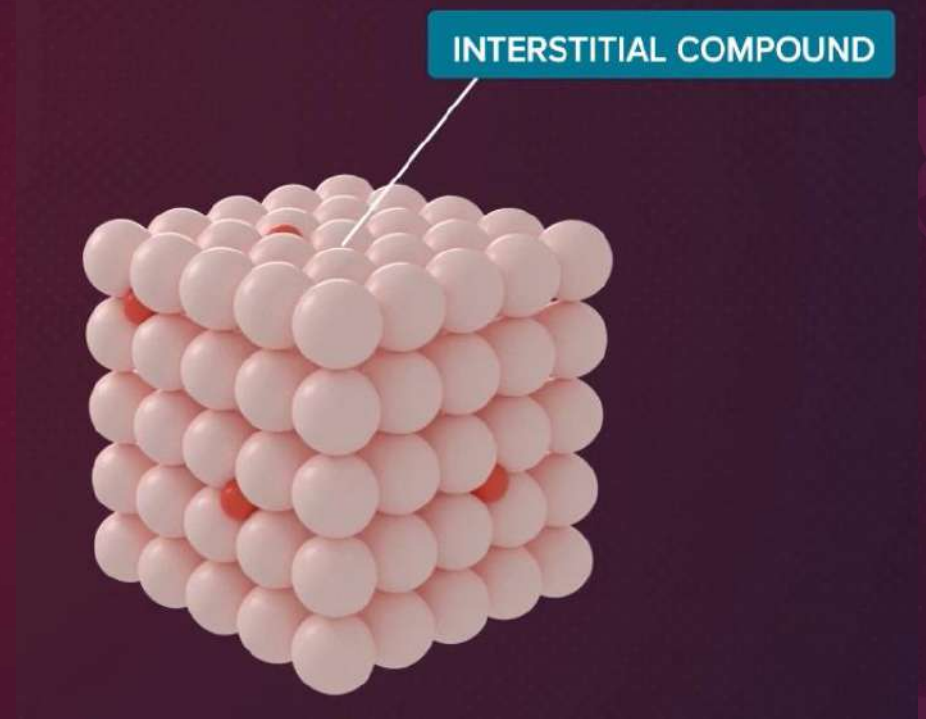
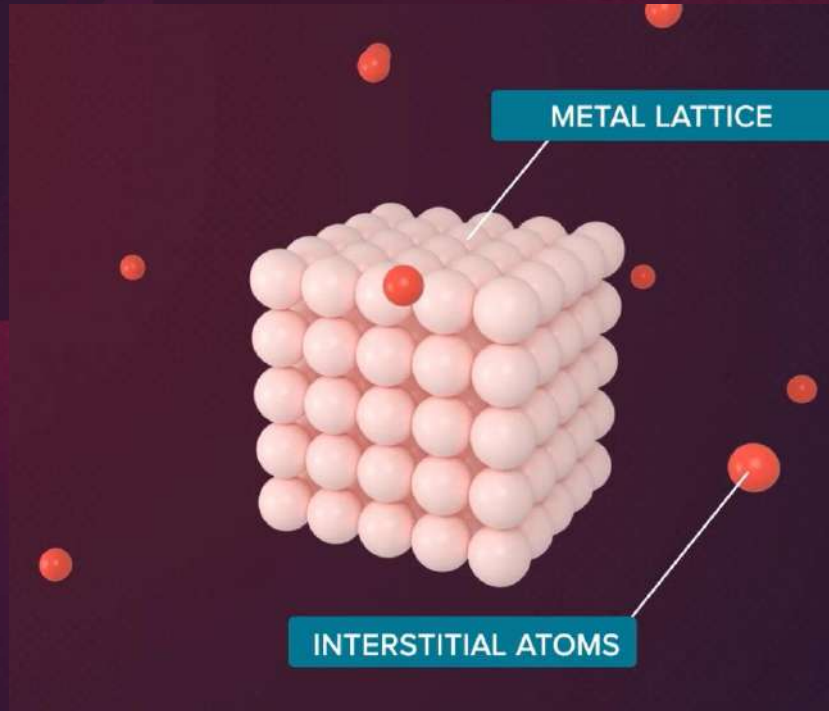
Iron(III) catalyses the reaction between iodide and persulphate ions.



Catalytic action,



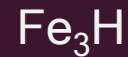
# Formation of Interstitial Compounds



# Formation of Interstitial Compounds



Interstitial compounds are formed when small atoms like H, C, or N are trapped inside the crystal lattices of metals.



Usually, non-stoichiometric compounds are neither typically ionic nor covalent.

# Characteristics of Interstitial Compounds



Higher than those of pure metals

i

High melting points.

Some borides approach diamond in hardness.

ii

Very hard.

iii

Retain metallic conductivity.

iv

Chemically inert.



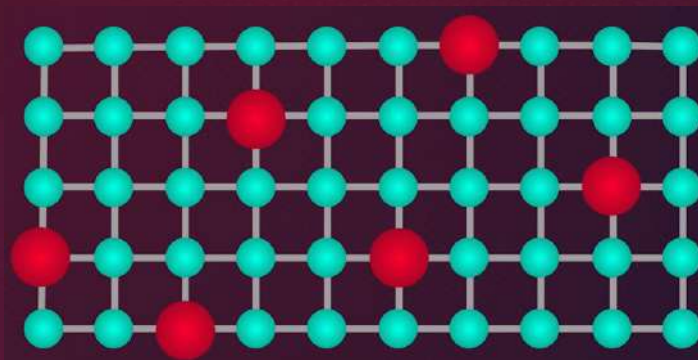
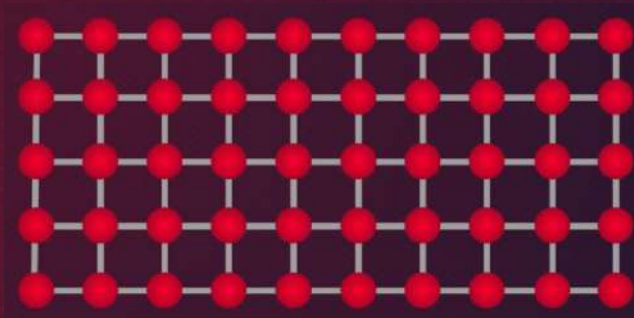
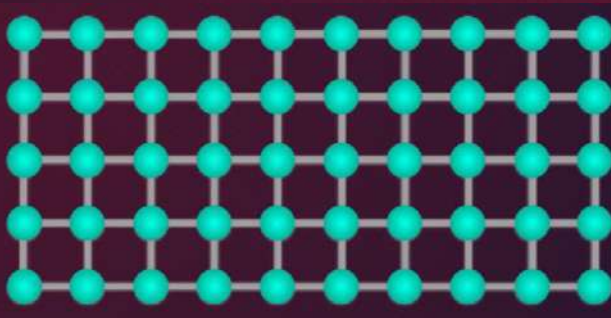
# Alloy

An alloy is a blend of metals prepared by mixing the components.

Alloys may be homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other.



# Alloy Formation



# Alloy Formation

Properties  
of alloys:

a

Are hard

b

Often have high  
melting points

c

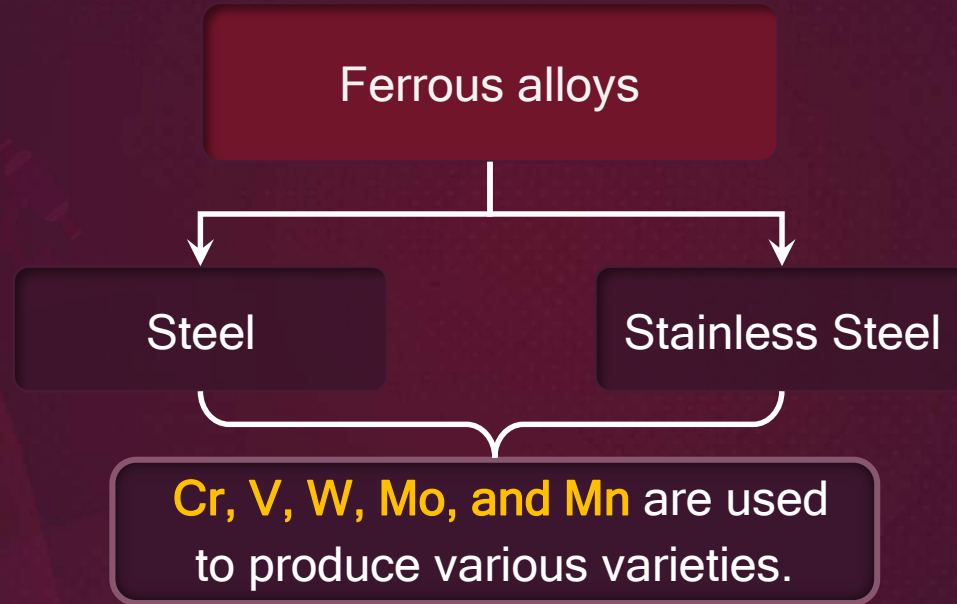
Show better  
conductivity

Transition metals form alloys  
due to **similar radii** along with  
the other characteristics

Within about 15% of  
each other

# Alloy Formation

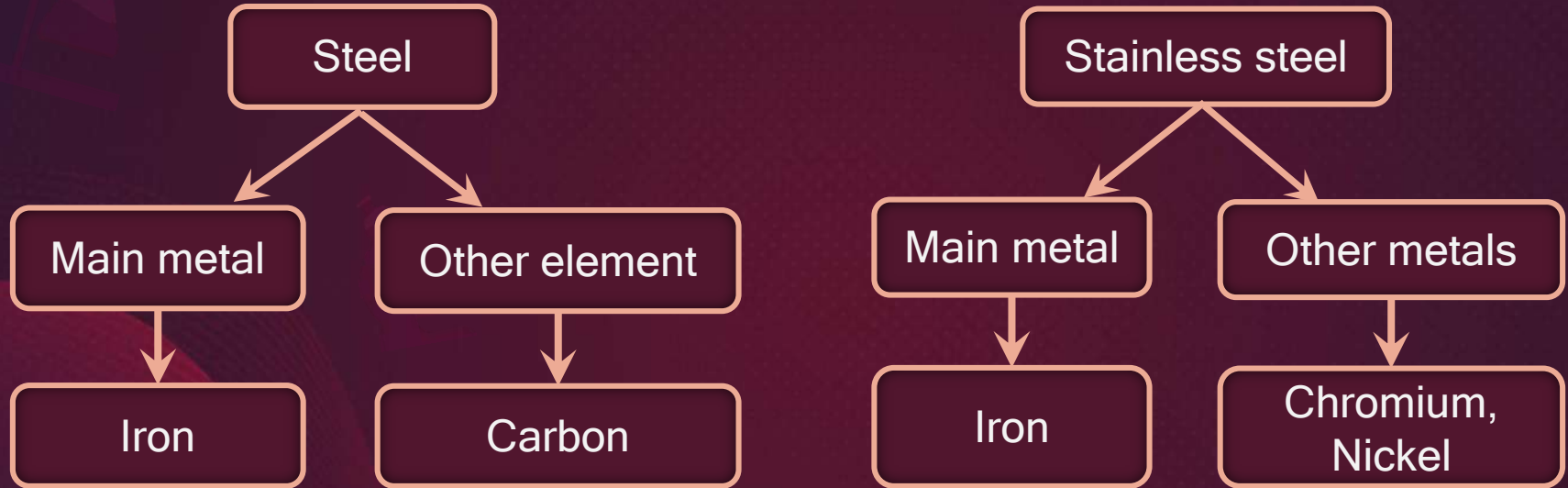
**EXAMPLE**



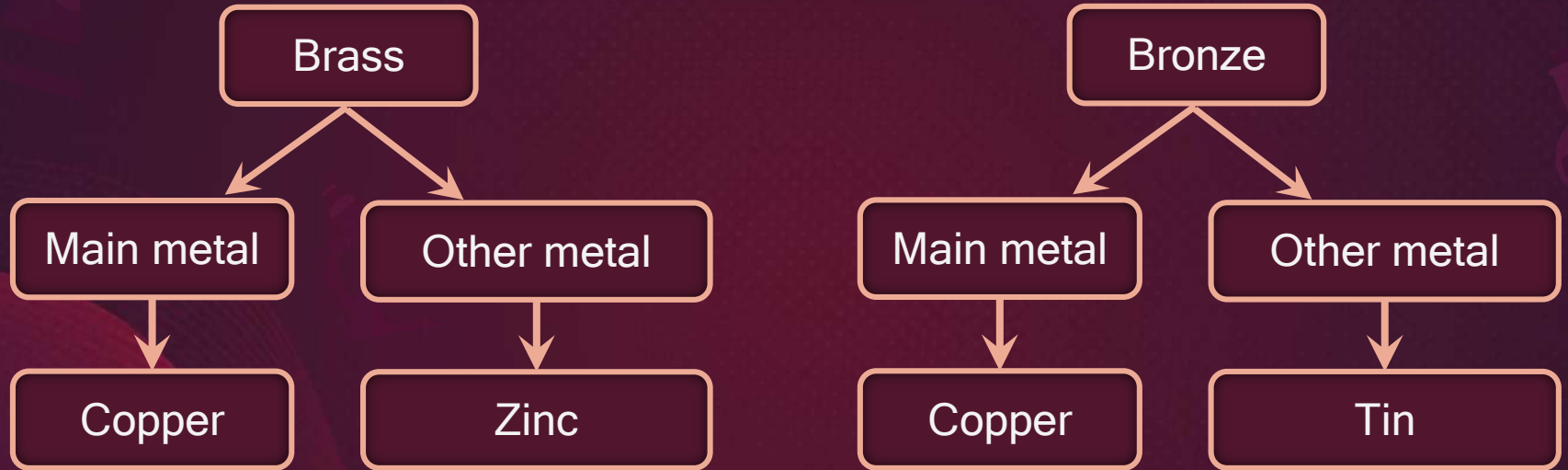


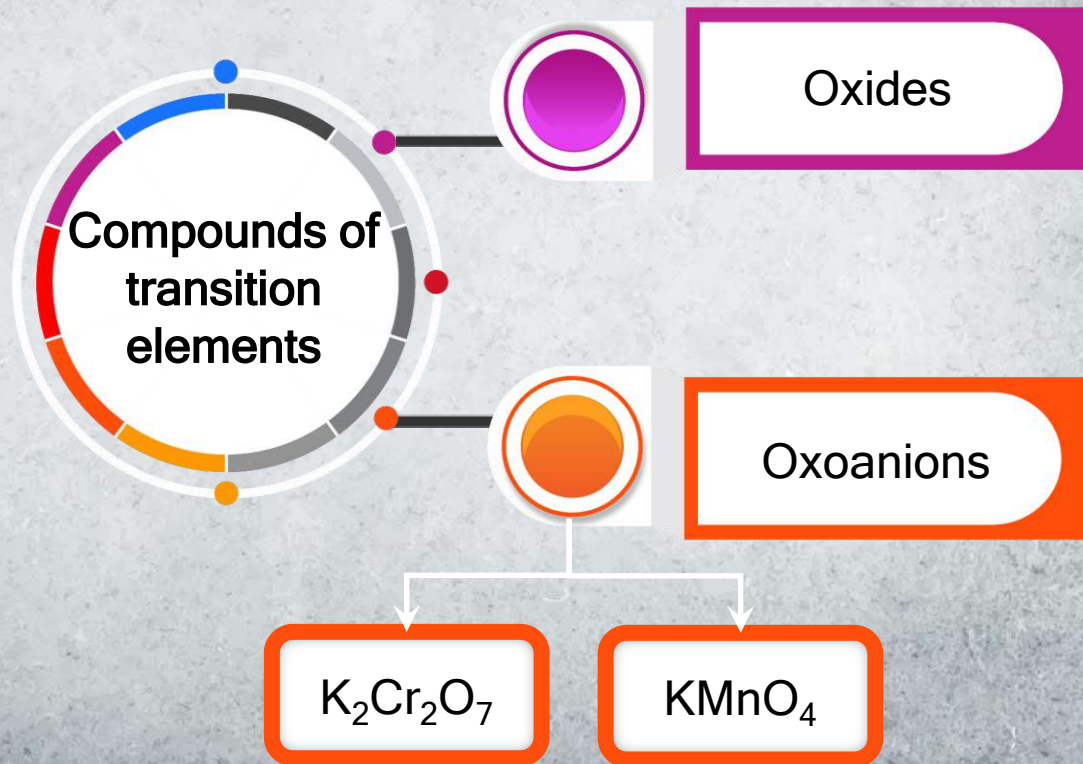


# Alloy Formation



# Alloy Formation







# Metal Oxides

Metal oxides are formed by reaction of metals with oxygen at high temperature.

Oxidation Number	↓ Group →	3	4	5	6	7	8	9	10	11	12
+7											$\text{Mn}_2\text{O}_7$
+6							$\text{CrO}_3$				
+5						$\text{V}_2\text{O}_5$					
+4			$\text{TiO}_2$	$\text{V}_2\text{O}_4$	$\text{CrO}_2$	$\text{MnO}_2$					
+3		$\text{Sc}_2\text{O}_3$	$\text{Ti}_2\text{O}_3$	$\text{V}_2\text{O}_3$	$\text{Cr}_2\text{O}_3$	$\text{Mn}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$				
								$\text{Mn}_3\text{O}_4$	$\text{Fe}_3\text{O}_4$	$\text{Co}_3\text{O}_4$	
+2			$\text{TiO}$	$\text{VO}$	$(\text{CrO})$	$\text{MnO}$	$\text{FeO}$	$\text{CoO}$	$\text{NiO}$	$\text{CuO}$	$\text{ZnO}$
+1											$\text{Cu}_2\text{O}$

# Properties of Transition Metal Oxides



## Properties of metal oxides

Ionic character

Melting point

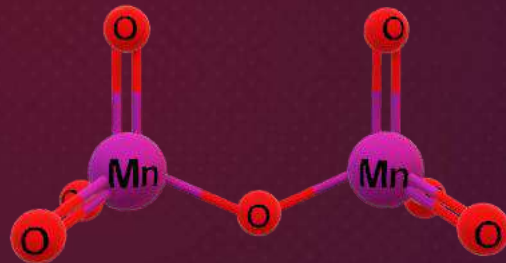
Acidic or basic nature



# Ionic Character of Transition Metal Oxides

Oxidation number of a metal in metal oxide increases

Ionic character of the oxide decreases.





# Transition Metal Oxides: Melting Points

$$\text{Oxidation number} \propto \frac{1}{\text{Ionic character}}$$

Ionic character  $\propto$  Melting point

Hence,  $\text{CrO}_3$  and  $\text{V}_2\text{O}_5$  have low melting points

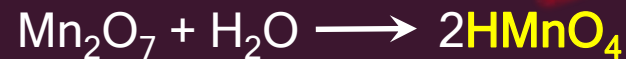
Oxidation number of a metal in metal oxide increases

Acidic character of the oxide increases.

# Important Oxides of Transition Metals



**EXAMPLE**



Strong acid



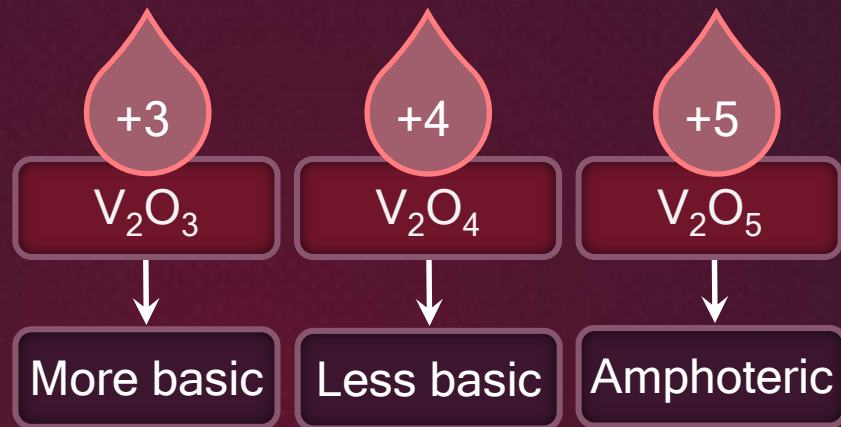
Strong acid



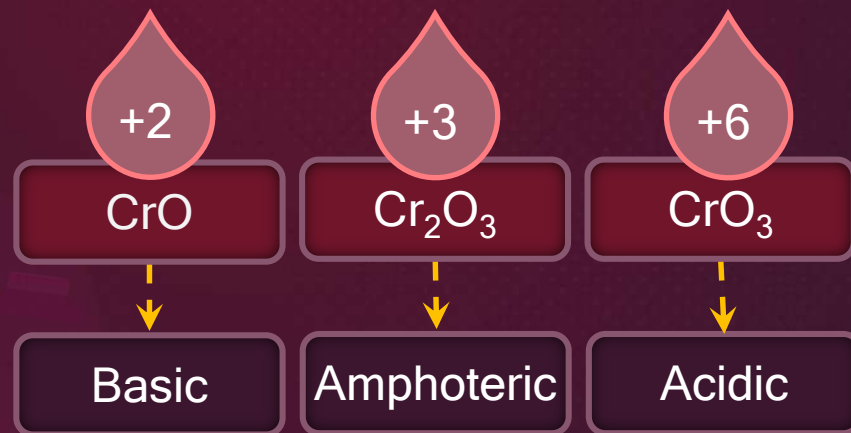


# Important Oxides of Transition Metals

Oxides of Vanadium



Oxides of Chromium

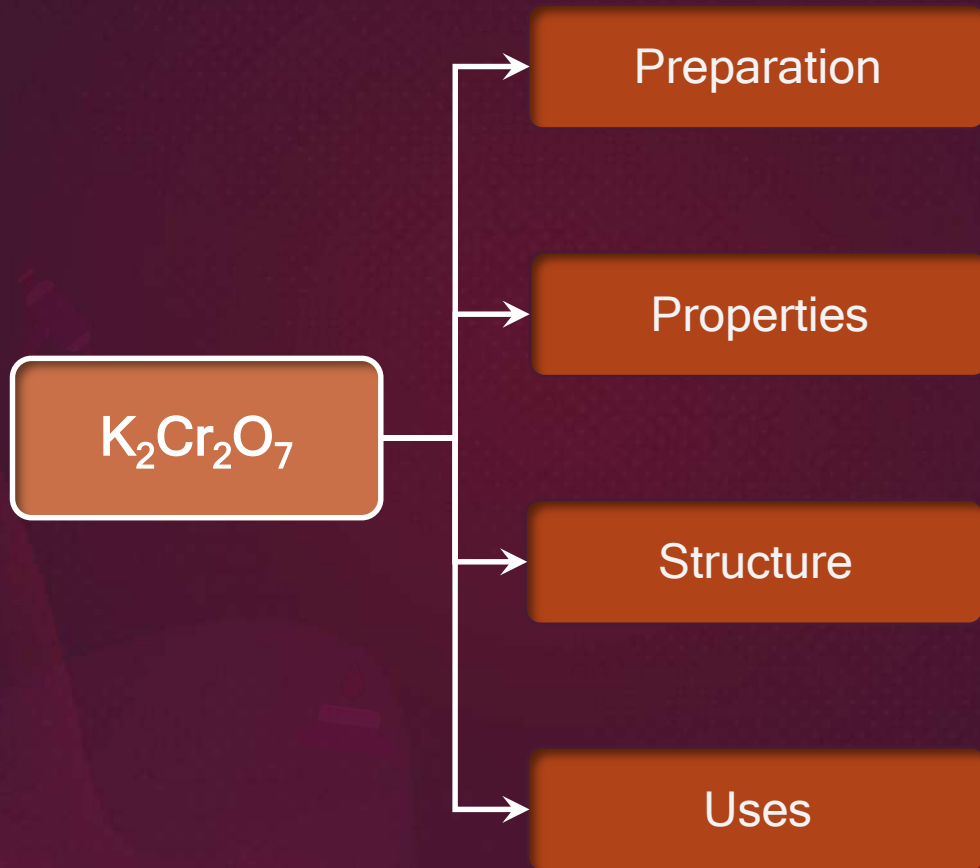


# Potassium Dichromate ( $K_2Cr_2O_7$ )





# Potassium Dichromate





# Preparation of $K_2Cr_2O_7$

i

Fusion of chromite ore with  $Na_2CO_3$



Filtered

**Yellow solution**

ii

Reaction with  $H_2SO_4$



**Orange solution**

# Preparation of $K_2Cr_2O_7$

iii

Reaction with KCl

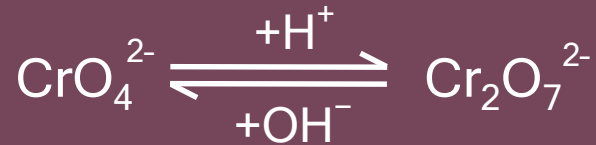
More soluble  
than  $K_2Cr_2O_7$

Crystallised



Orange  
Crystals

# Properties of $\text{K}_2\text{Cr}_2\text{O}_7$



Chromate



Dichromate



Weak acid



Alkaline  
solution



# Properties of $K_2Cr_2O_7$

Oxidising nature

Strong oxidising agent

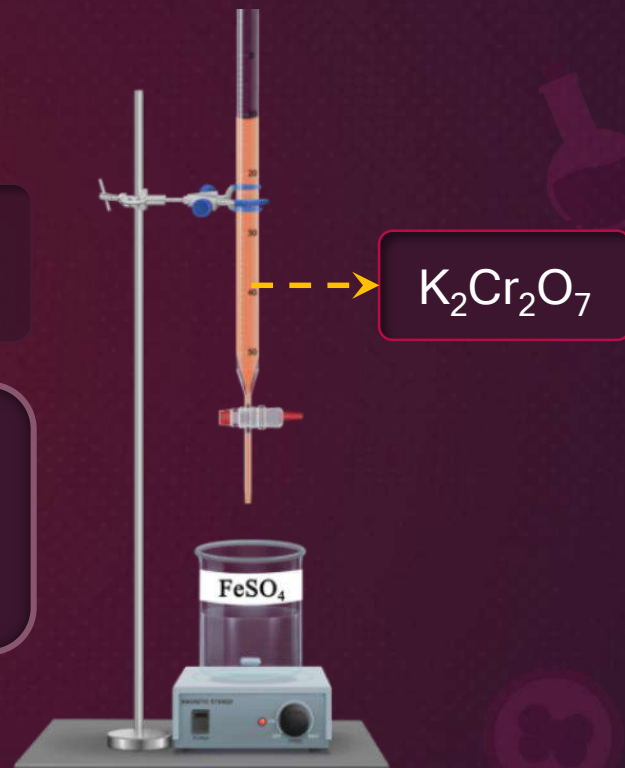


In organic chemistry

Also **greater solubility** in the polar solvent like  **$CH_3COOH$**



As a primary standard in **volumetric analysis**





# Properties of $\text{K}_2\text{Cr}_2\text{O}_7$



In acidic  
medium

Oxidising action



Standard electrode potential

$$E^0 = 1.33 \text{ V}$$





# Properties of $\text{K}_2\text{Cr}_2\text{O}_7$

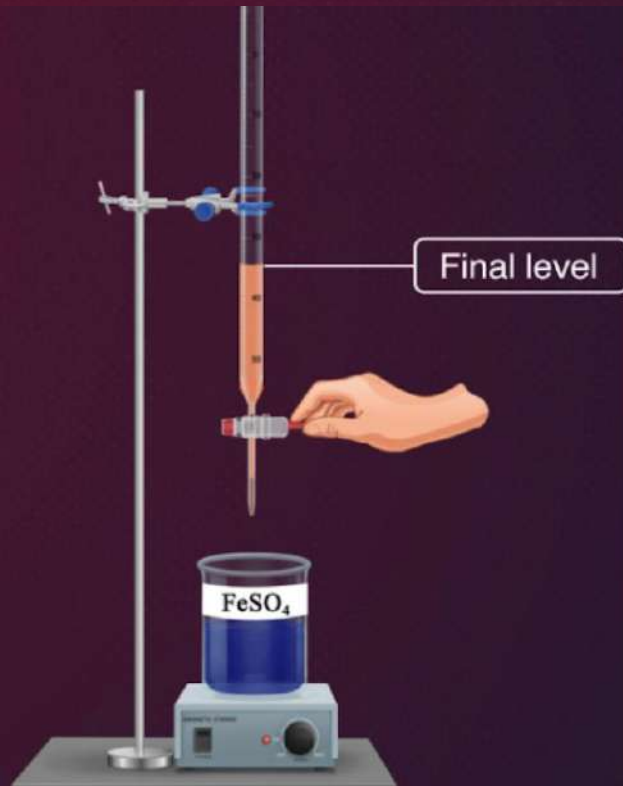
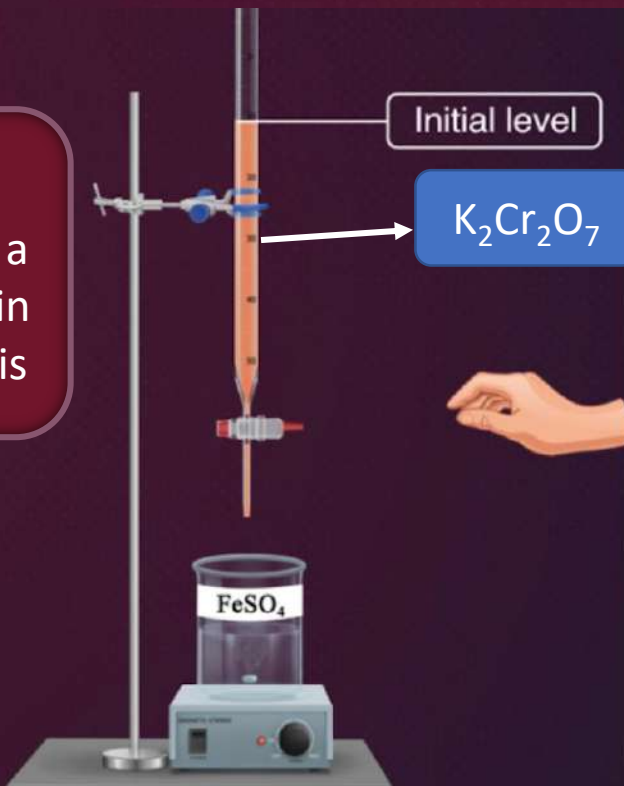
## EXAMPLE

Oxidation by acidified $\text{K}_2\text{Cr}_2\text{O}_7$	Half reactions
Iodides to Iodine	$6\text{I}^- \rightarrow 3\text{I}_2 + 6\text{e}^-$
Sulphides to Sulphur	$3\text{H}_2\text{S} \rightarrow 6\text{H}^+ + 3\text{S} + 6\text{e}^-$
Tin (II) to Tin (IV)	$3\text{Sn}^{2+} \rightarrow 3\text{Sn}^{4+} + 6\text{e}^-$
Fe (II) to Fe (III)	$6\text{Fe}^{2+} \rightarrow 6\text{Fe}^{3+} + 6\text{e}^-$



### Uses:

$\text{K}_2\text{Cr}_2\text{O}_7$  is used as a primary standard in Volumetric analysis

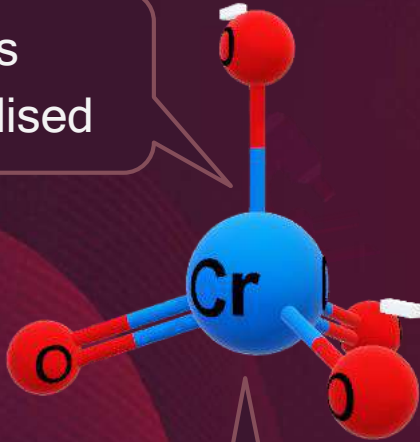


# Chromate: Structure



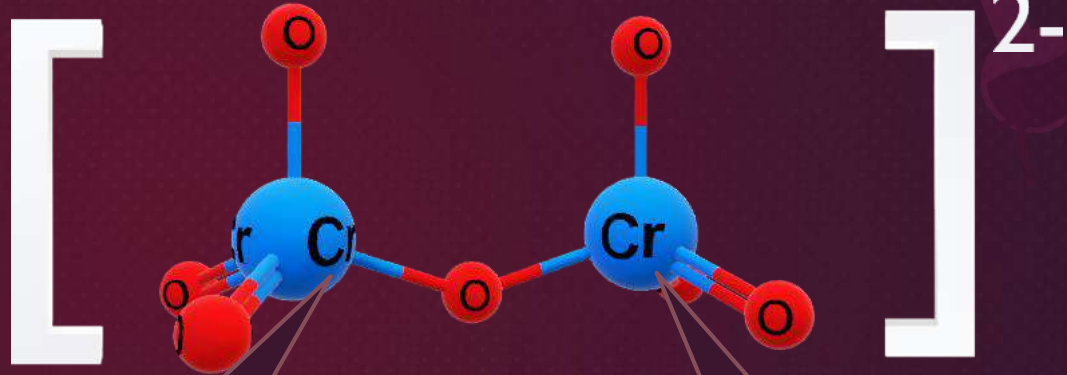
Chromate ion

$d^3s$   
hybridised



Tetrahedral

Dichromate ion



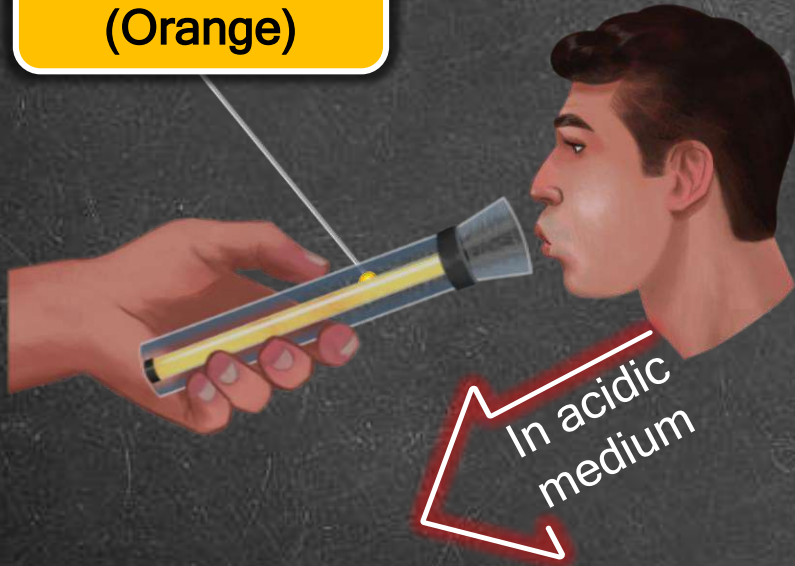
Tetrahedral

Tetrahedral

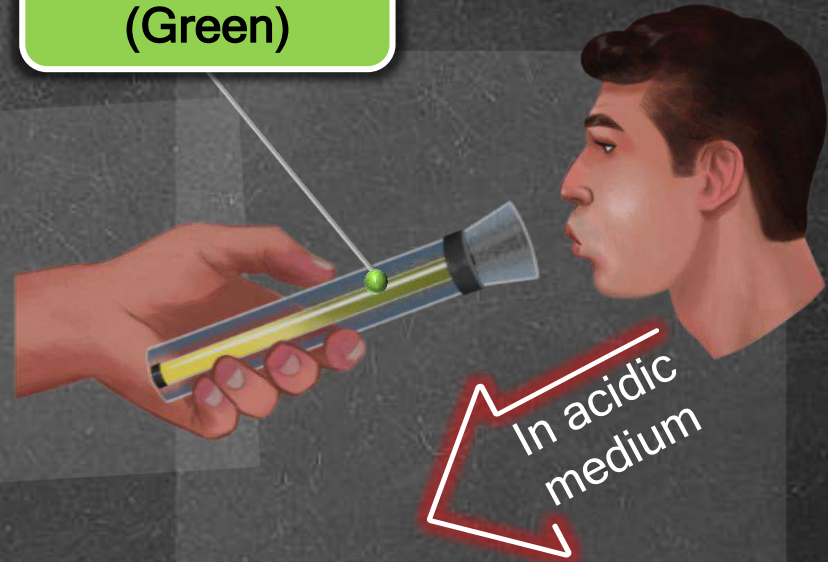
# BREATH ANALYSER

When orange  $\text{K}_2\text{Cr}_2\text{O}_7$  reacts with alcohol, it converts into green solution containing chromium sulfate.

$\text{Cr}^{6+}$  ion  
(Orange)

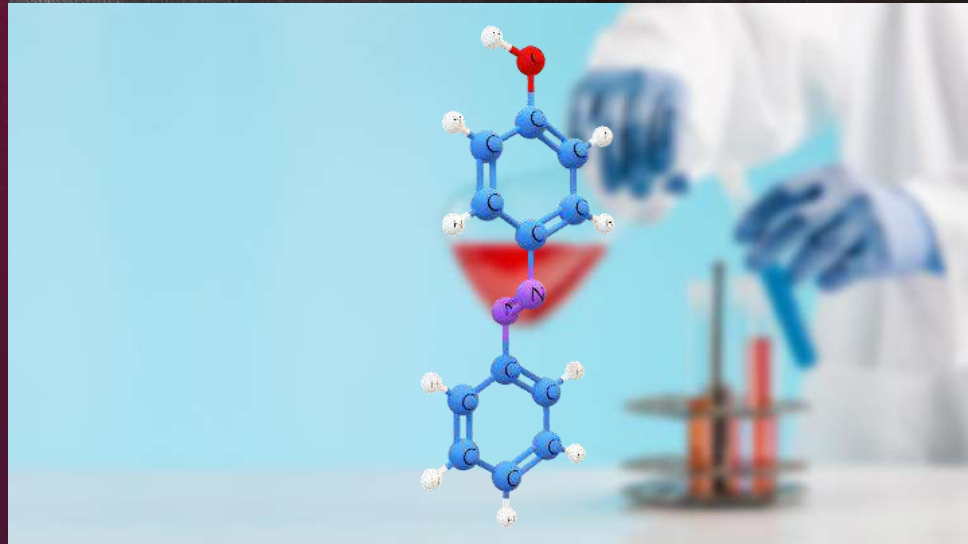


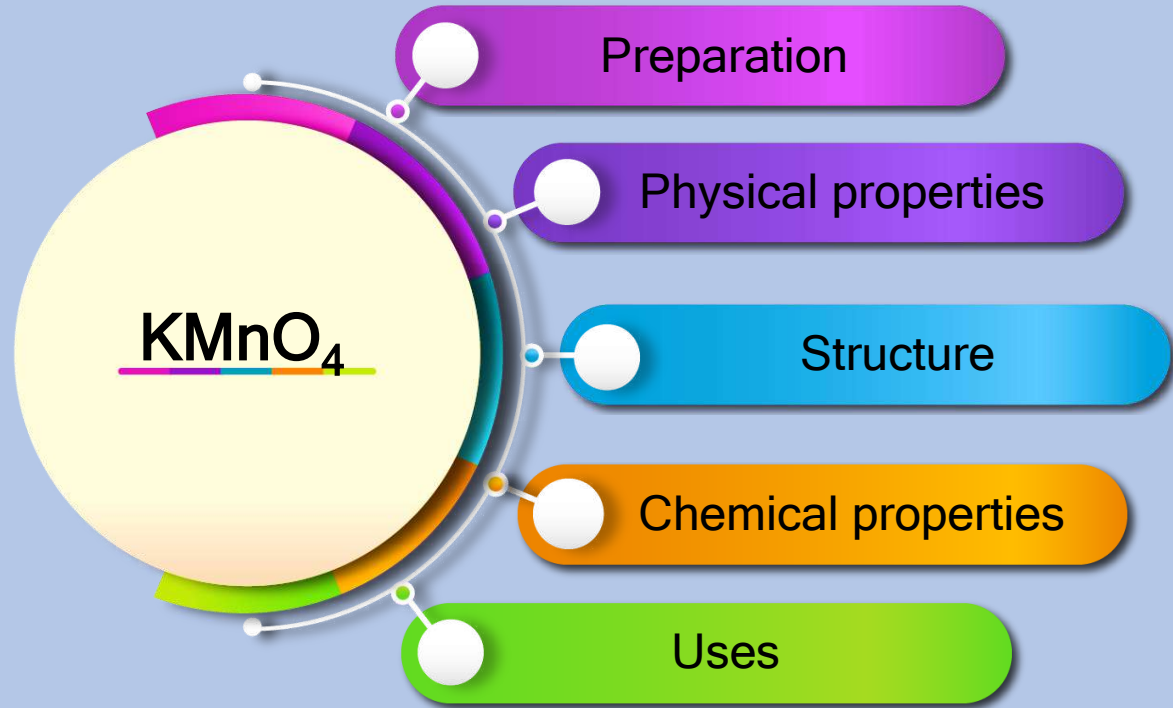
$\text{Cr}^{3+}$  ion  
(Green)



**USED IN LEATHER  
INDUSTRY**

**TO PREPARE  
AZO COMPOUNDS**





# Potassium Permanganate: Preparation



i

Fusion of pyrolusite  
( $\text{MnO}_2$ )



Black solid

Dark green

Disproportionation reaction  
in presence of an oxidising  
agent ( $\text{KNO}_3$  or  $\text{KClO}_3$ )

ii

Disproportionation of  
manganate ( $\text{MnO}_4^{2-}$ )



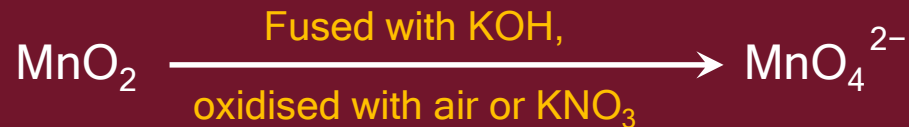
Dark purple

# Potassium Permanganate: Preparation

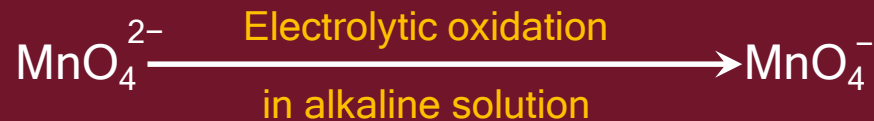


Commercial  
method

Step-1



Step-2



Laboratory  
method

Oxidation of manganese(II) ion





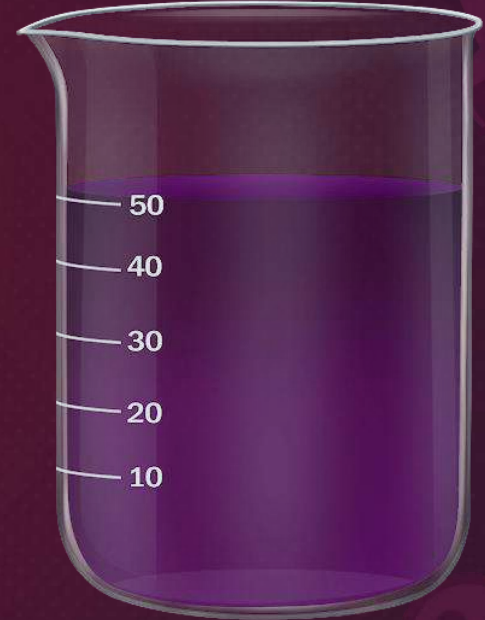
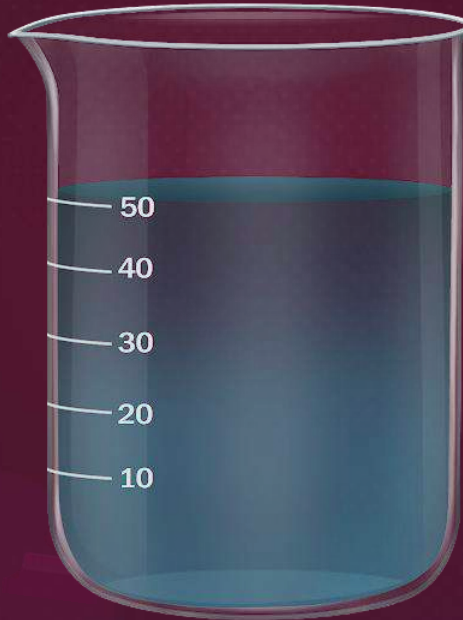
# Colour of $\text{MnO}_4^{2-}$ and $\text{MnO}_4^-$ Ions



Intense color  
(dark purple)

Manganate ion

Permanganate ion



Green

Purple



# Magnetic Property of $\text{KMnO}_4$



Heating  
effect

Diamagnetic  
(no unpaired  
electron)

Paramagnetic  
(one unpaired  
electron)



Dark  
purple

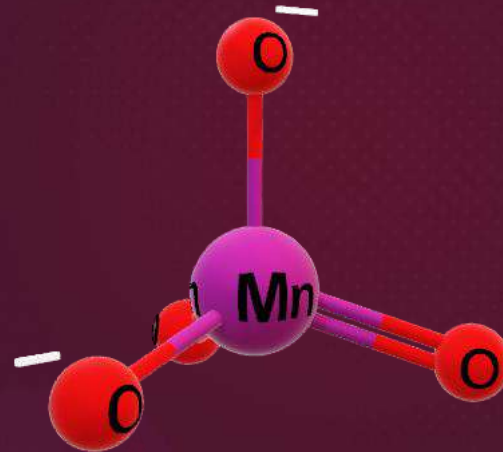
Green

Black

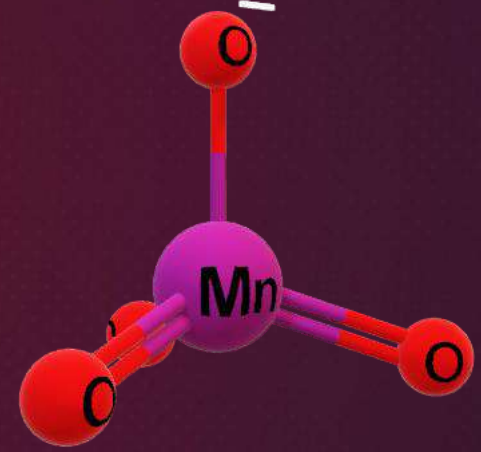
# Potassium Permanganate: Structure



Tetrahedral



Manganate ion



Permanganate ion

# Potassium Permanganate: Chemical Properties



Oxidising nature



Oxidising properties  
of  $\text{KMnO}_4$  in

Acidic  
medium

Neutral or  
faintly alkaline  
medium

Alkaline  
medium

In acidic  
medium



$$E^0 = 1.52 \text{ V}$$

## Oxidising nature of $\text{KMnO}_4$ in acidic medium



# Potassium Permanganate: Chemical Properties



**EXAMPLE**

Oxidising nature of  $\text{KMnO}_4$  in acidic medium

Liberation of  $\text{I}_2$  from  $\text{I}^-$  solution:



Conversion of Fe(II) to Fe(III):



Green

Yellow

# Potassium Permanganate: Chemical Properties



**EXAMPLE**

Oxidation of oxalate ion:



Oxidation of Nitrite ion:



# NOTE



Endpoint



Permanganate titration is not carried out in the presence of **hydrochloric acid** because some of the hydrochloric acid gets oxidised to **chlorine gas**. Hence, we do not get the correct endpoint for the given titration.



# Potassium Permanganate: Chemical Properties



In neutral  
medium



$$E^0 = 1.69 \text{ V}$$

# Potassium Permanganate: Chemical Properties



Oxidising nature of  $\text{KMnO}_4$   
in neutral medium

Thiosulphate is oxidised to sulphate:



Oxidation of iodide to iodate:



# Potassium Permanganate: Chemical Properties



The oxidation of  
manganous salt to  $\text{MnO}_2$



**$\text{ZnSO}_4$  or  $\text{ZnO}$**   
catalyst

# Potassium Permanganate: Chemical Properties



In alkaline  
medium



$$E^0 = 0.56 \text{ V}$$



# Uses of $\text{KMnO}_4$

As an oxidant



For bleaching of  
wool and textiles



Decolourising  
of oils



Decolourising  
of oils





# Periodic Table

d-Block  
elements

f-Block  
elements

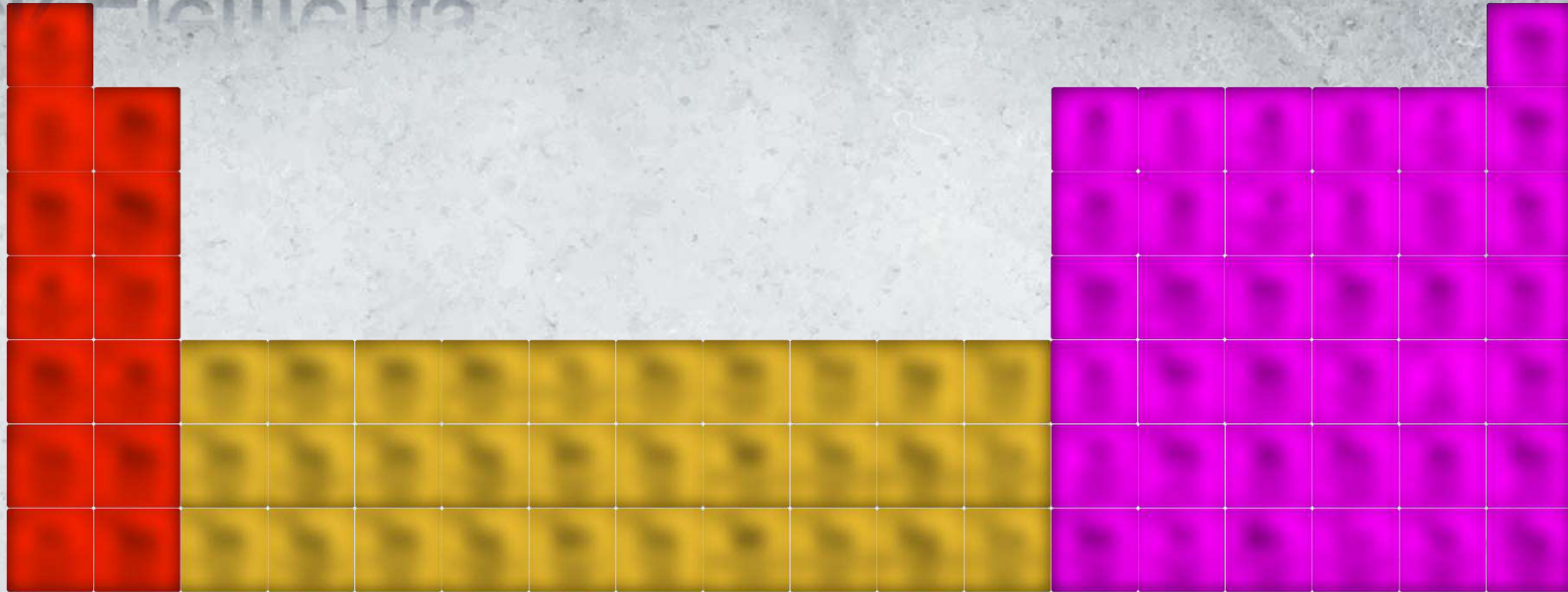
# Pokhran-I Operation Smiling Buddha (1974)



# Pokhran-II Operation Shakti (1998)



# f-Block Elements



57 <b>La</b> Lanthanum	58 <b>Ce</b> Cerium	59 <b>Pr</b> Praseodymium	60 <b>Nd</b> Neodymium	61 <b>Pm</b> Promethium	62 <b>Sm</b> Samarium	63 <b>Eu</b> Europium	64 <b>Gd</b> Gadolinium	65 <b>Tb</b> Terbium	66 <b>Dy</b> Dysprosium	67 <b>Ho</b> Holmium	68 <b>Er</b> Erbium	69 <b>Tm</b> Thulium	70 <b>Yb</b> Ytterbium	71 <b>Lu</b> Lutetium
89 <b>Ac</b> Actinium	90 <b>Th</b> Thorium	91 <b>Pa</b> Protactinium	92 <b>U</b> Uranium	93 <b>Np</b> Neptunium	94 <b>Pu</b> Plutonium	95 <b>Am</b> Americium	96 <b>Cm</b> Curium	97 <b>Bk</b> Berkelium	98 <b>Cf</b> Californium	99 <b>Es</b> Einsteinium	100 <b>Fm</b> Fermium	101 <b>Md</b> Mendelevium	102 <b>No</b> Nobelium	103 <b>Lr</b> Lawrencium





## Point to Remember

REMEMBER  
!

La and Ac closely resemble the lanthanoids and actinoids, respectively.



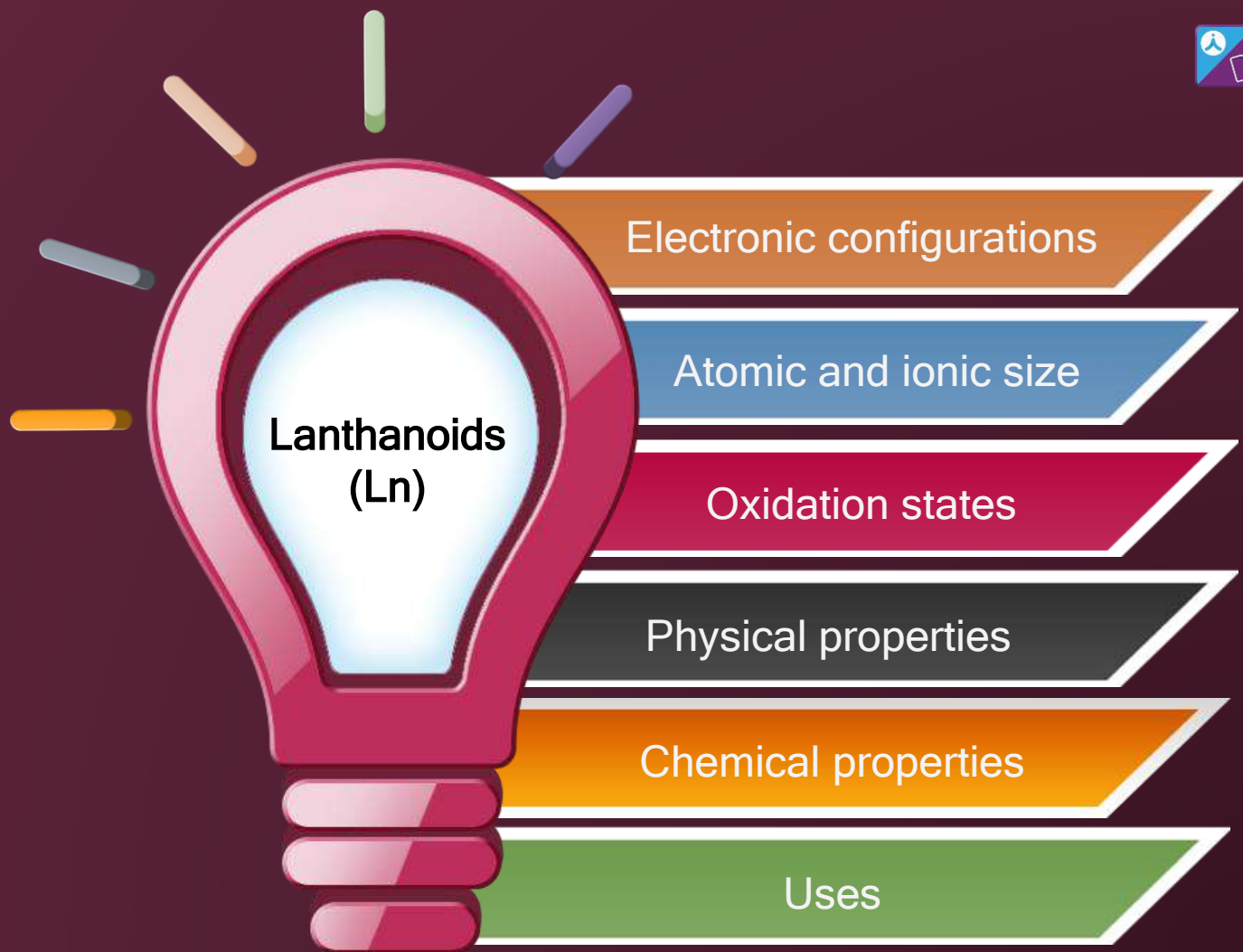
Included in discussion of the respective series besides the 14 elements.

# Lanthanoids



57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Lanthanum	Cerium	Praseodymium	Neodymium	Promethium	Samarium	Europium	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutetium

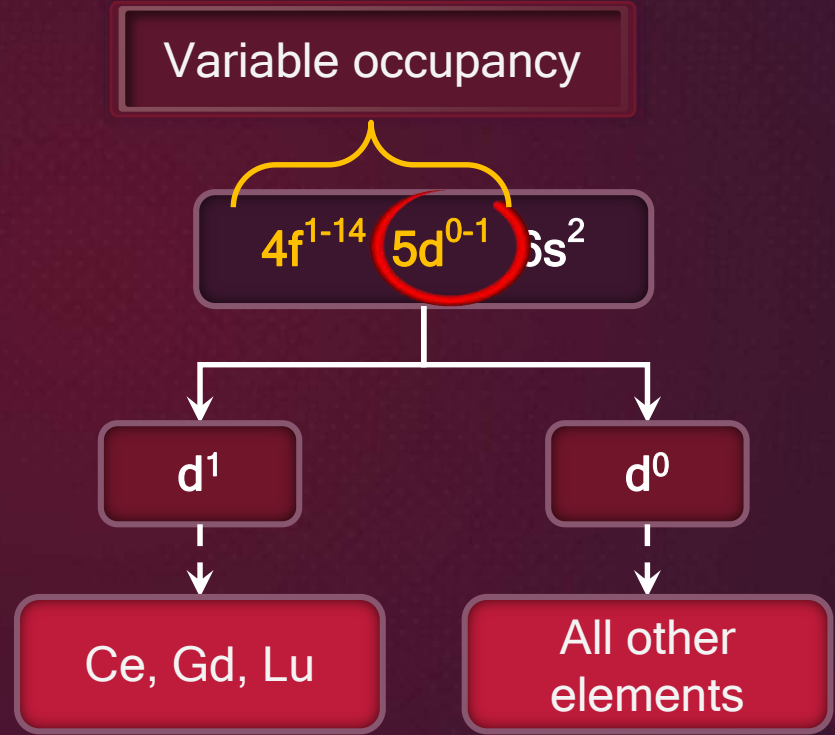
The periodic table shows the Lanthanoid series (La-Lu) highlighted in red, the Actinoid series (Ac-Lr) highlighted in yellow, and other elements highlighted in purple. The Lanthanoid series is shown in a separate row below the main table.



# Lanthanoids: Electronic Configuration



General configuration



# Lanthanoids: Electronic Configuration



Electronic configurations of lanthanum and lanthanoids

Atomic number	Name	Symbol	Electronic configuration
			Ln
57	Lanthanum	La	$5d^1 6s^2$
58	Cerium	Ce	$4f^1 5d^1 6s^2$
59	Praseodymium	Pr	$4f^3 6s^2$
60	Neodymium	Nd	$4f^4 6s^2$
61	Promethium	Pm	$4f^5 6s^2$
62	Samarium	Sm	$4f^6 6s^2$
63	Europium	Eu	$4f^7 6s^2$
64	Gadolinium	Gd	$4f^7 5d^1 6s^2$

# Lanthanoids: Electronic Configuration



Electronic configurations of lanthanum and lanthanoids

Atomic number	Name	Symbol	Electronic configuration
			Ln
65	Terbium	Tb	$4f^9 6s^2$
66	Dysprosium	Dy	$4f^{10} 6s^2$
67	Holmium	Ho	$4f^{11} 6s^2$
68	Erbium	Er	$4f^{12} 6s^2$
69	Thulium	Tm	$4f^{13} 6s^2$
70	Ytterbium	Yb	$4f^{14} 6s^2$
71	Lutetium	Lu	$4f^{14} 5d^1 6s^2$



# Lanthanoids: Atomic and Ionic Size

Lanthanoids  
(left to right)

57 <b>La</b> Lanthanum	58 <b>Ce</b> Cerium	59 <b>Pr</b> Praseodymium	60 <b>Nd</b> Neodymium	61 <b>Pm</b> Promethium	62 <b>Sm</b> Samarium	63 <b>Eu</b> Europium	64 <b>Gd</b> Gadolinium	65 <b>Tb</b> Terbium	66 <b>Dy</b> Dysprosium	67 <b>Ho</b> Holmium	68 <b>Er</b> Erbium	69 <b>Tm</b> Thulium	70 <b>Yb</b> Ytterbium	71 <b>Lu</b> Lutetium
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La → Lu

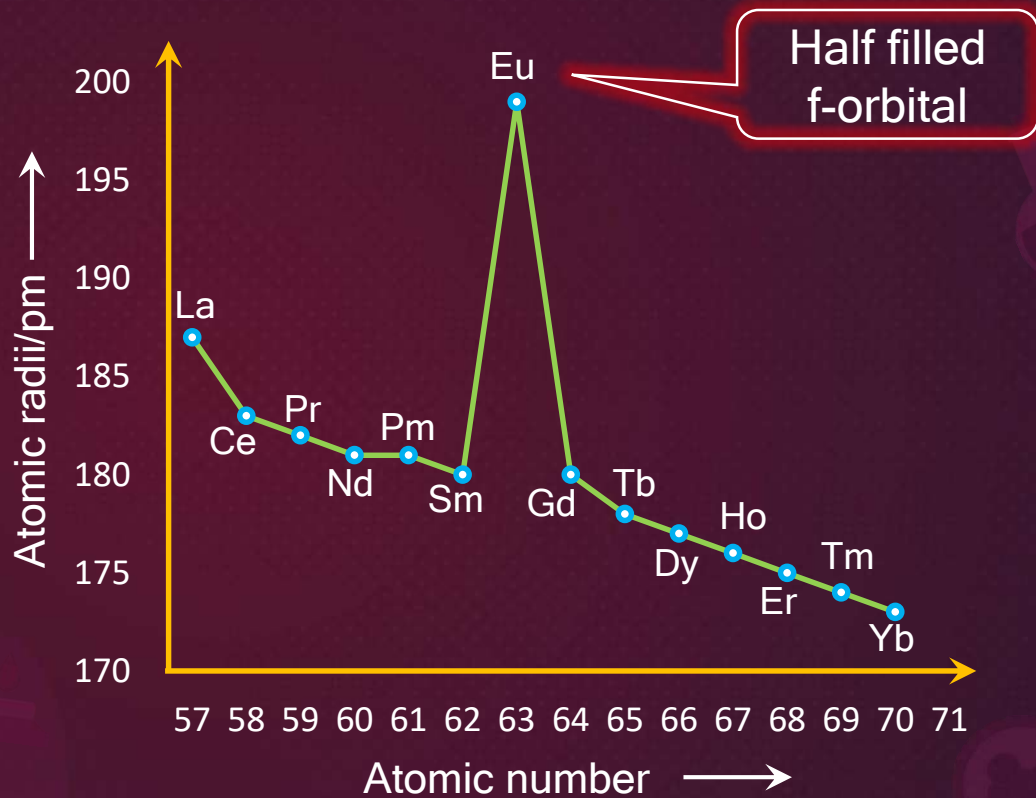
Due to **lanthanoid contraction**

Overall decrease in  
atomic and ionic radii

# Lanthanoids: Atomic Sizes



Overall decrease  
in atomic size

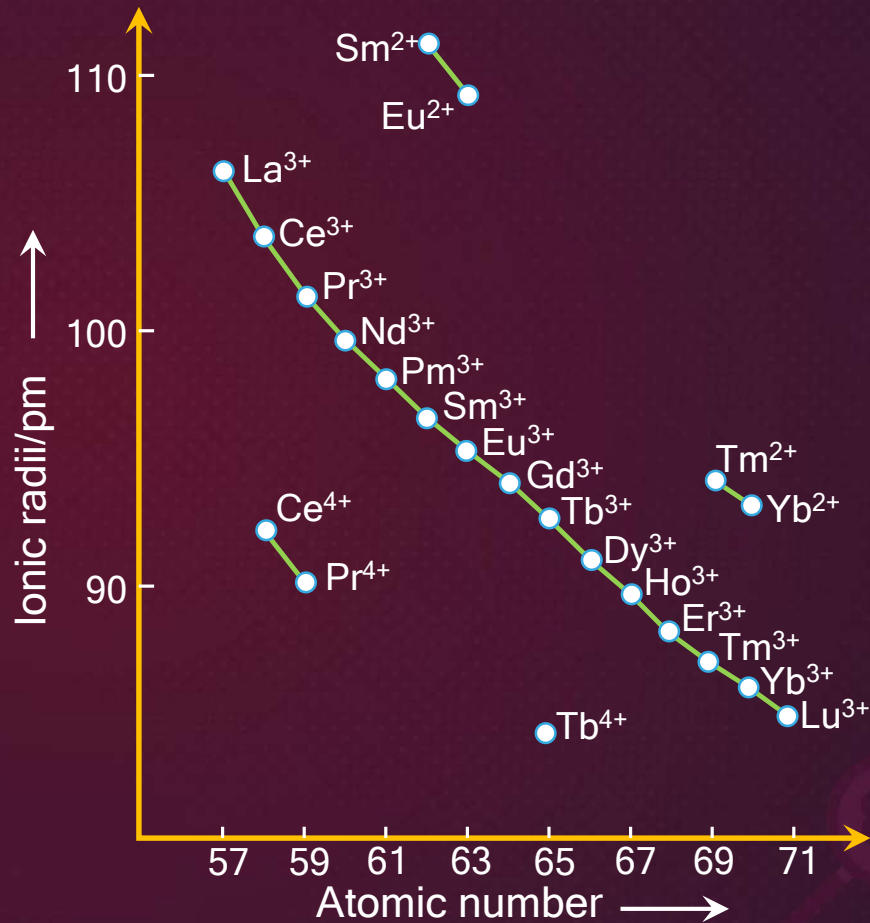
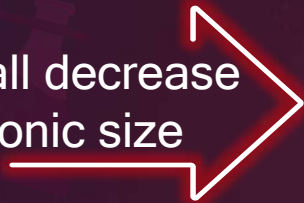




# Lanthanoids: Ionic Sizes



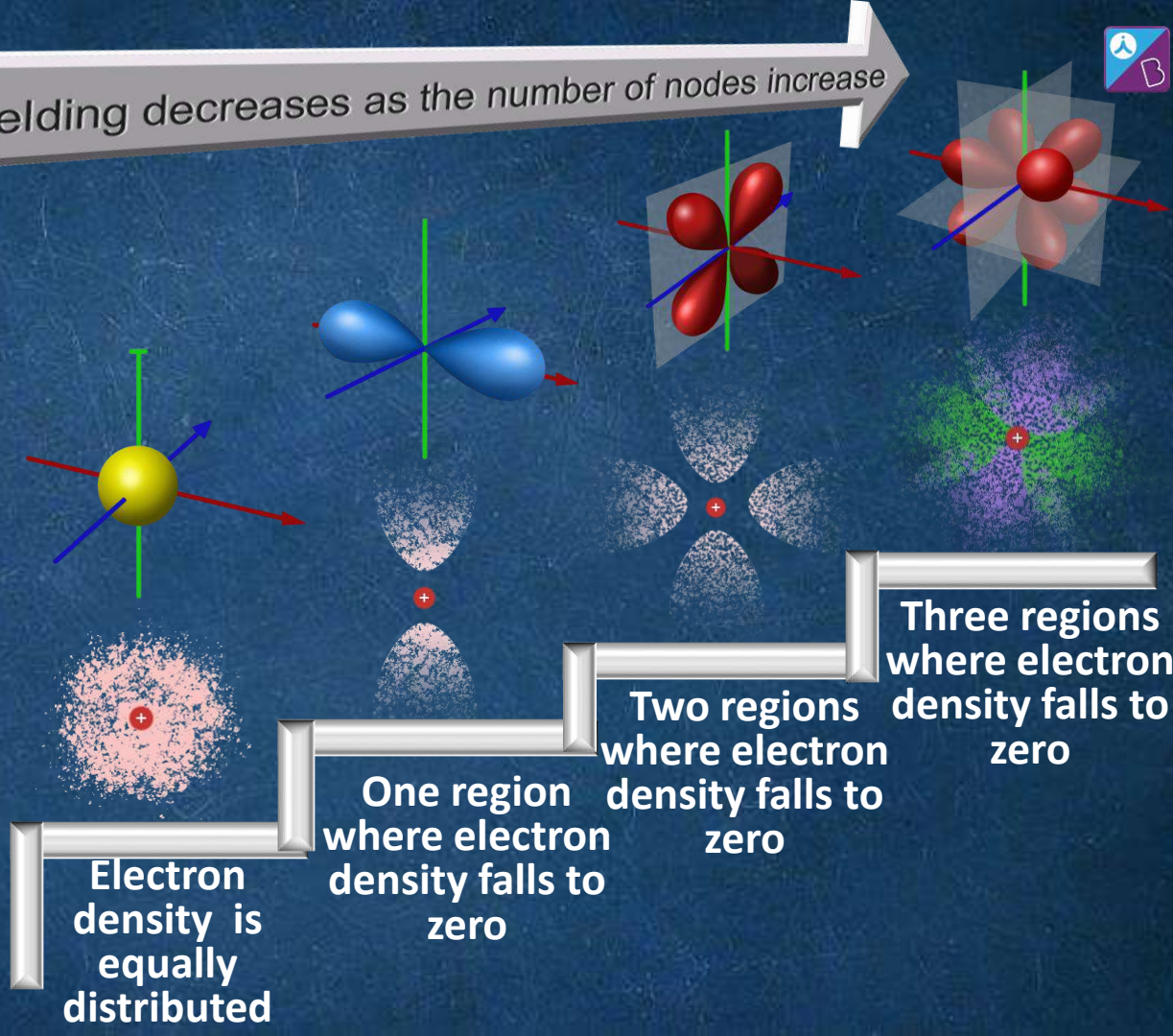
Overall decrease  
in ionic size



# Lanthanoid Contraction

Decrease in sizes fairly regular for Ln as compared to transition elements

Shielding decreases as the number of nodes increase



Electron density is equally distributed

One region where electron density falls to zero

Two regions where electron density falls to zero

Three regions where electron density falls to zero

# Lanthanoids: Oxidation States



Common  
oxidation state



Common oxidation  
state is Ln(III)

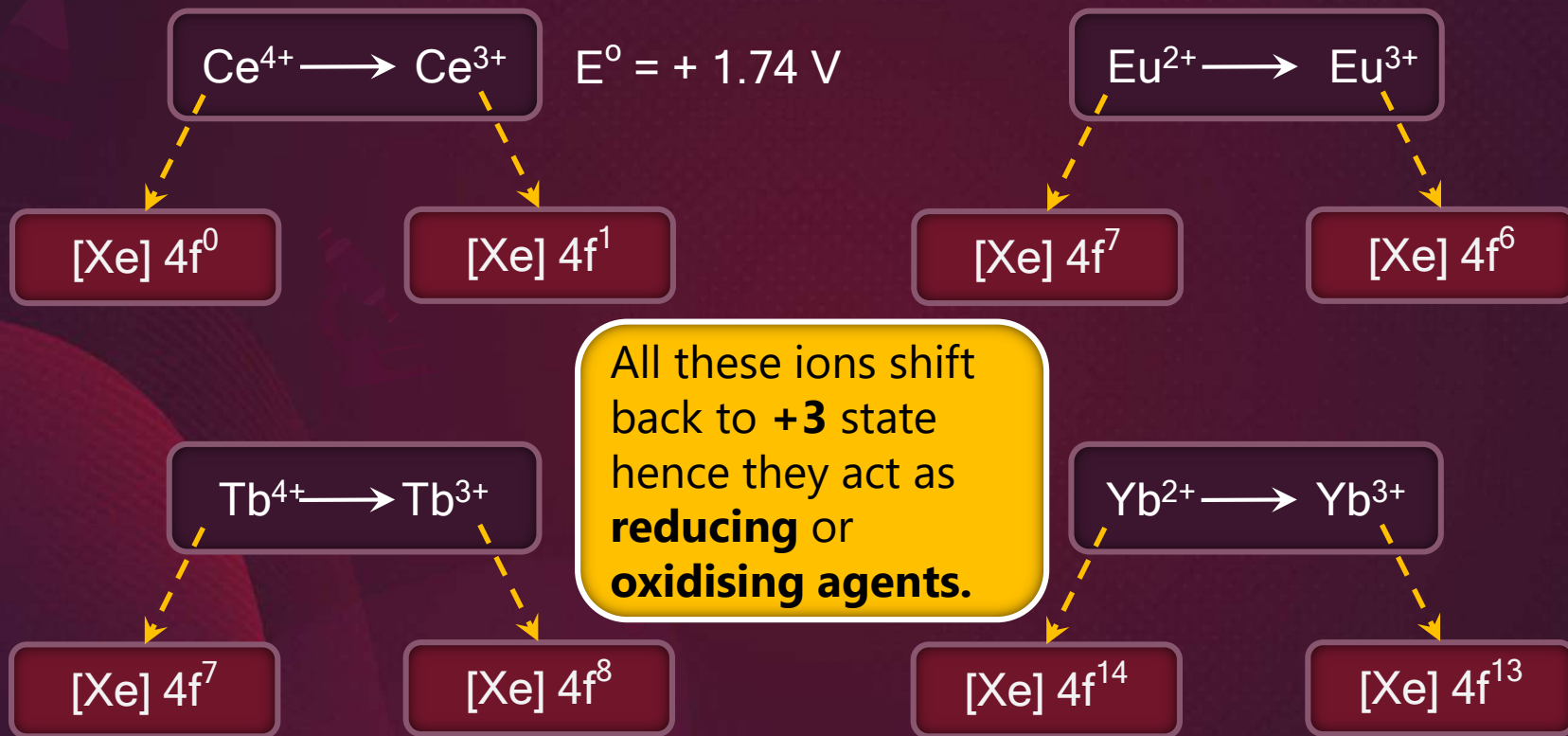
Easy removal of  
two 6s and one 5d  
(or 4f) electrons  
except Eu and Yb

Occasionally +2 and +4  
oxidation states are also  
obtained

Extra stability of  
empty, half-filled  
and fully filled f  
subshell



# Lanthanoids: Oxidation States



## Samarium(Sm) Metal



Lanthanoids are silvery white soft metals and tarnish rapidly in air.



## Gadolinium(Gd) Metal



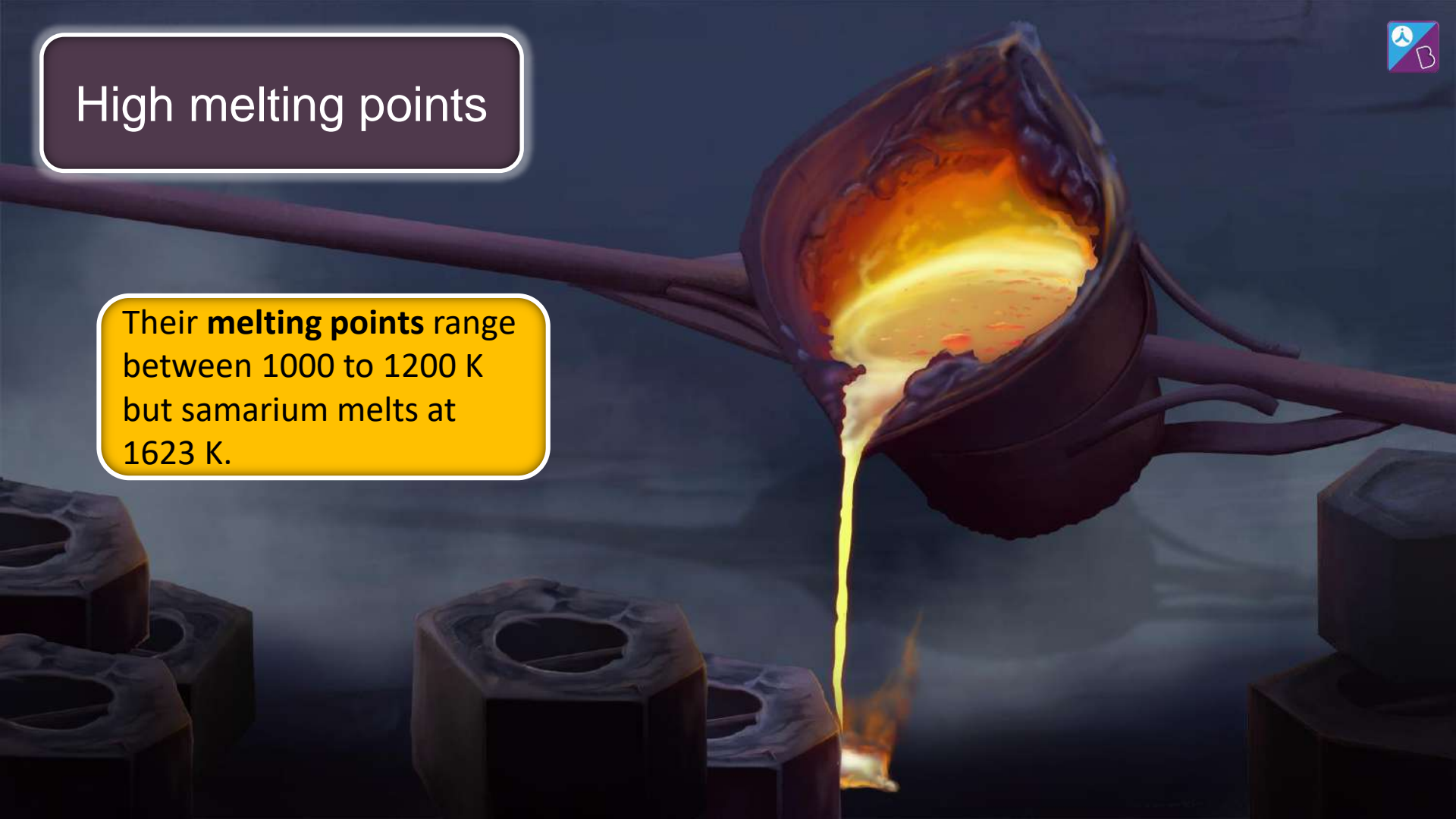
# Samarium (Steel Hard)

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



## High melting points

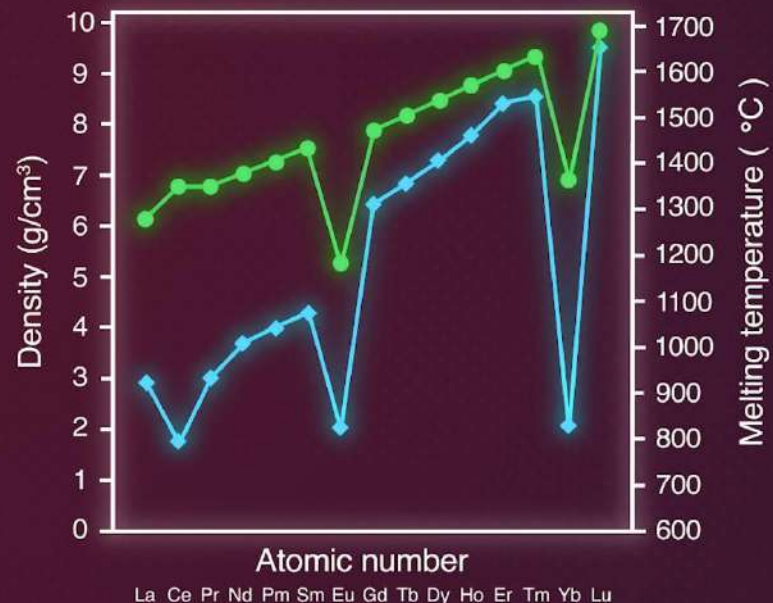
Their **melting points** range between 1000 to 1200 K but samarium melts at 1623 K.



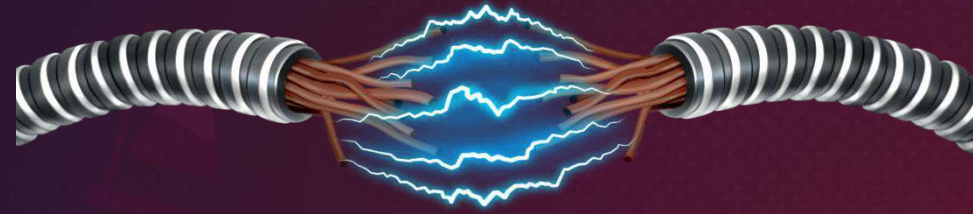
# Density

Density and other properties change smoothly except for Eu and Yb and occasionally for Sm and Tm.

—●— Density  
- - -◆- - - Melting temp.







High electrical conductivity



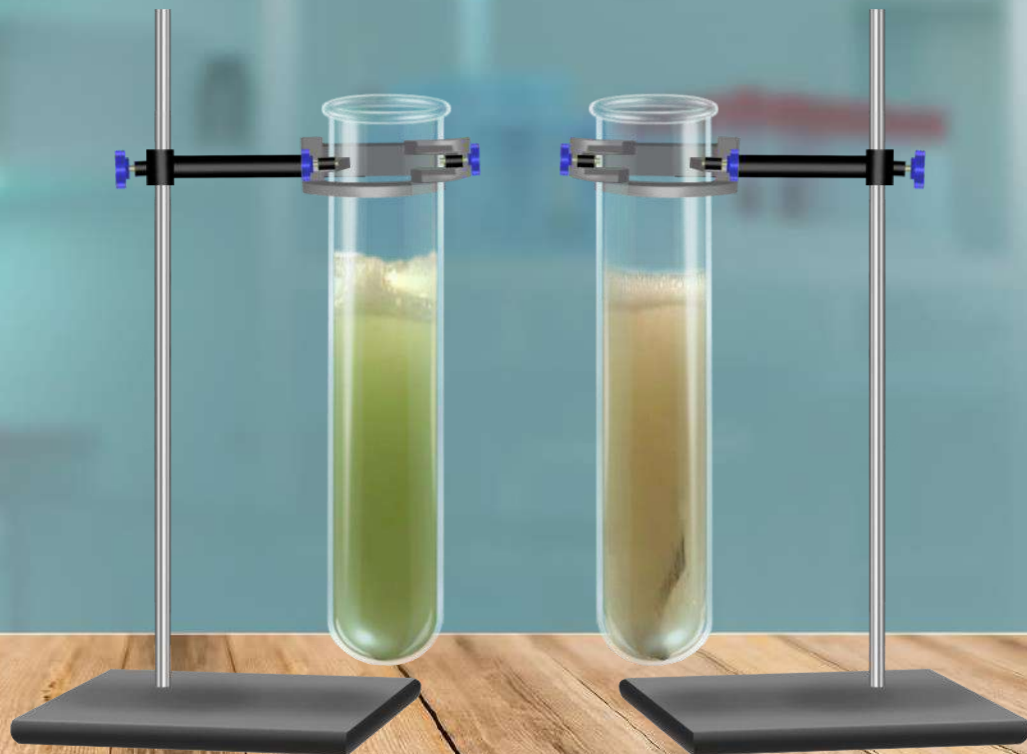
High thermal conductivity

They are good conductors  
of heat and electricity.



## Trivalent lanthanoid ions

Many trivalent lanthanoid ions are coloured both in the solid state and in aqueous solutions due to incomplete filling of f-orbitals except  $\text{La}^{3+}$  and  $\text{Lu}^{3+}$



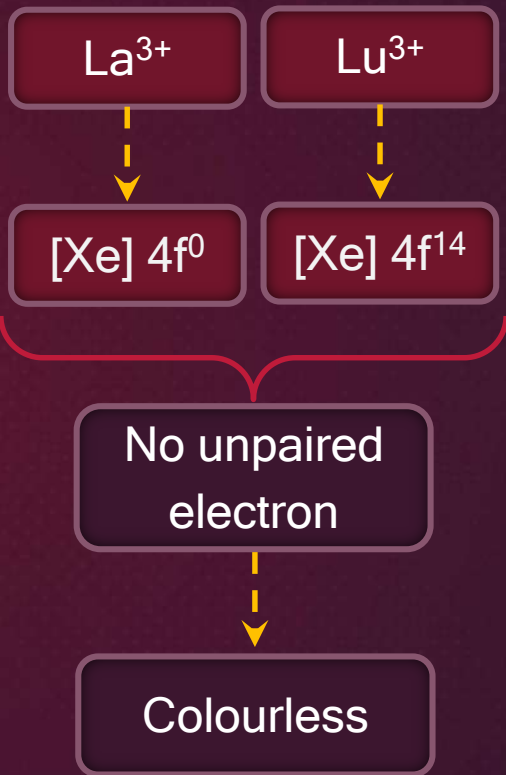
$\text{Pr}^{3+}$   
(aq. solution)

$\text{Sm}^{3+}$   
(aq. solution)



# Colour of Lanthanoid Ions

# NOTE





# Magnetic Properties

$f^0$  type

$f^{14}$  type

$\text{La}^{3+}$  &  $\text{Ce}^{4+}$

$\text{Yb}^{2+}$  &  $\text{Lu}^{3+}$

Other than these,  
all other ions are  
**paramagnetic.**



## Point to Remember

Ionisation enthalpies are **fairly low** and comparable to alkaline earth metals.

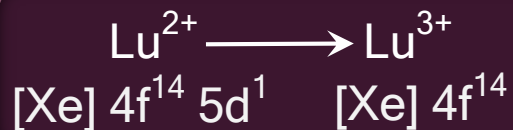
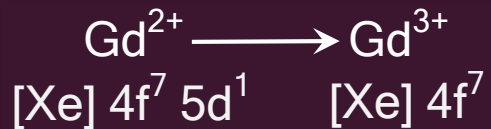
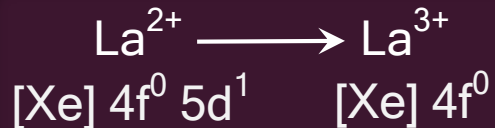


Hence, they are **good reducing agents**.

$\text{La}^{3+}$ ,  $\text{Gd}^{3+}$  and  $\text{Lu}^{3+}$  have abnormally low third ionisation enthalpy values.

Extra stability of  $f^0$ ,  $f^7$  and  $f^{14}$  orbitals

# Lanthanoids: Ionisation Enthalpy



Low values of  
ionization  
enthalpy (III)

Good reducing  
agents due to  
low IE values

$E^\circ$  values



$E^\circ$

$\approx$

-2.2 to -2.4 v

Except  
 $\text{Eu} = -2.0 \text{ V}$

# Lanthanoids : Chemical Properties



The earlier members of the series are **quite reactive**



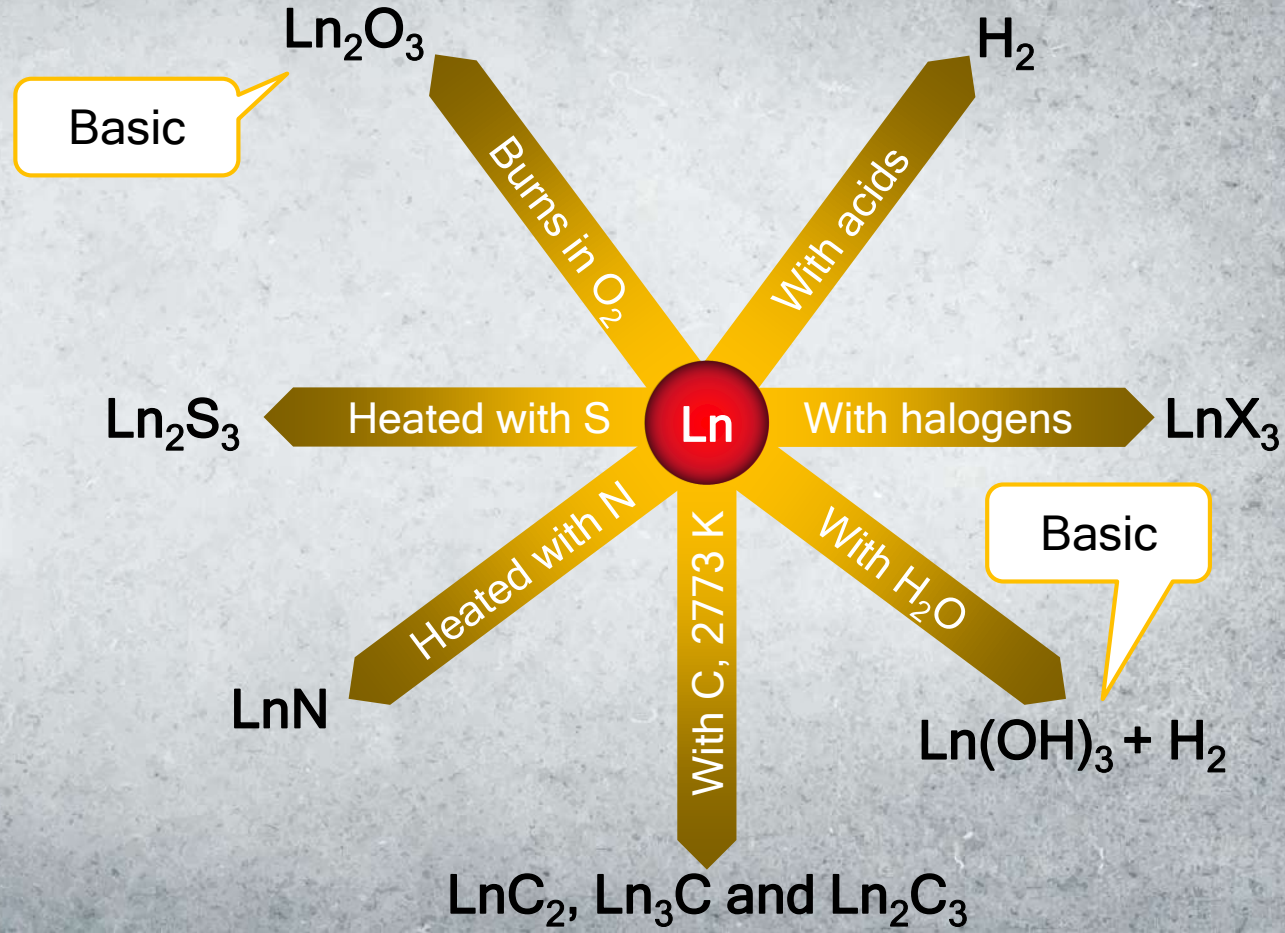
However, with **increasing atomic number**, they behave more like **aluminium**.



Typically form compounds which are ionic and trivalent( $\text{Ln}^{3+}$ )

Like **calcium**

# Chemical Reaction of Lanthanoids





# Uses of Inner Transition Metals



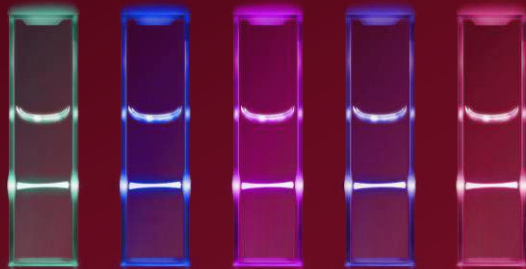
Alloy steels



Catalysts in petroleum cracking



Phosphors



Phosphors in television screen



Mischmetall

It consists of a lanthanoid metal (~ 95%), iron (~ 5%) and traces of S, C, Ca and Al.



Mischmetal bullets and shells



Mischmetal in lighter flint



Radioactive and used  
in nuclear reactors



Hiroshima and  
Nagasaki bomb attack



Chernobyl  
disaster



Radiotherapy

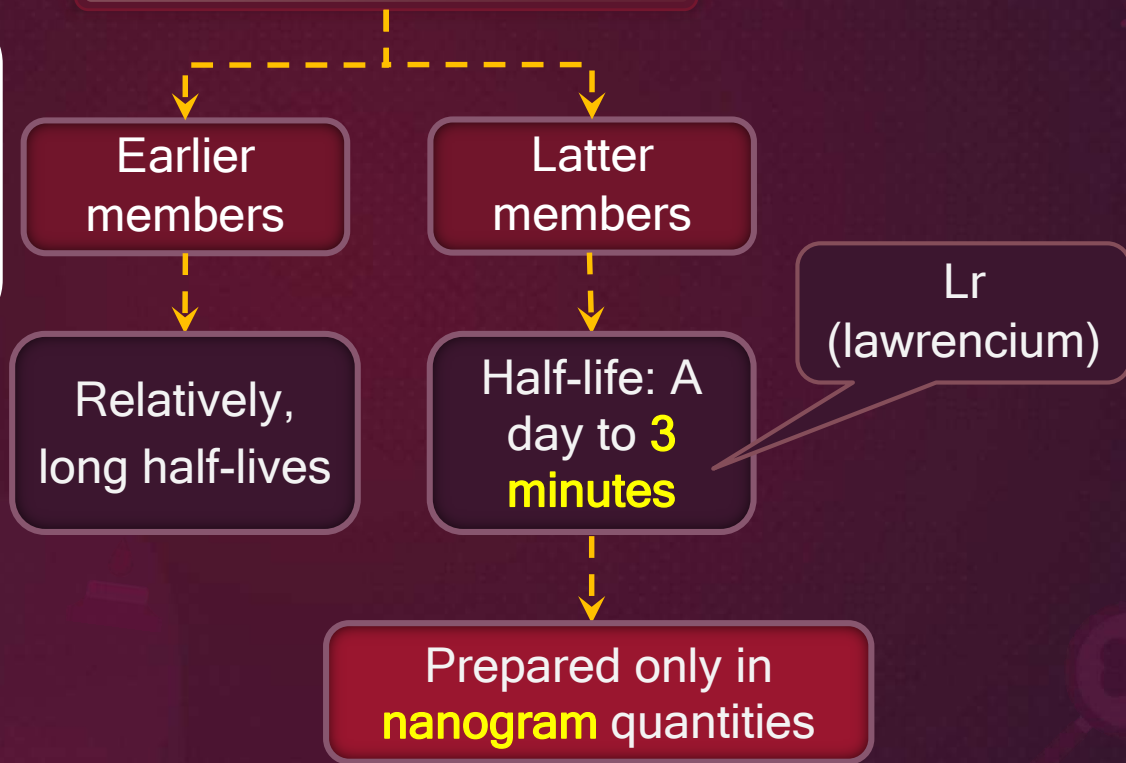


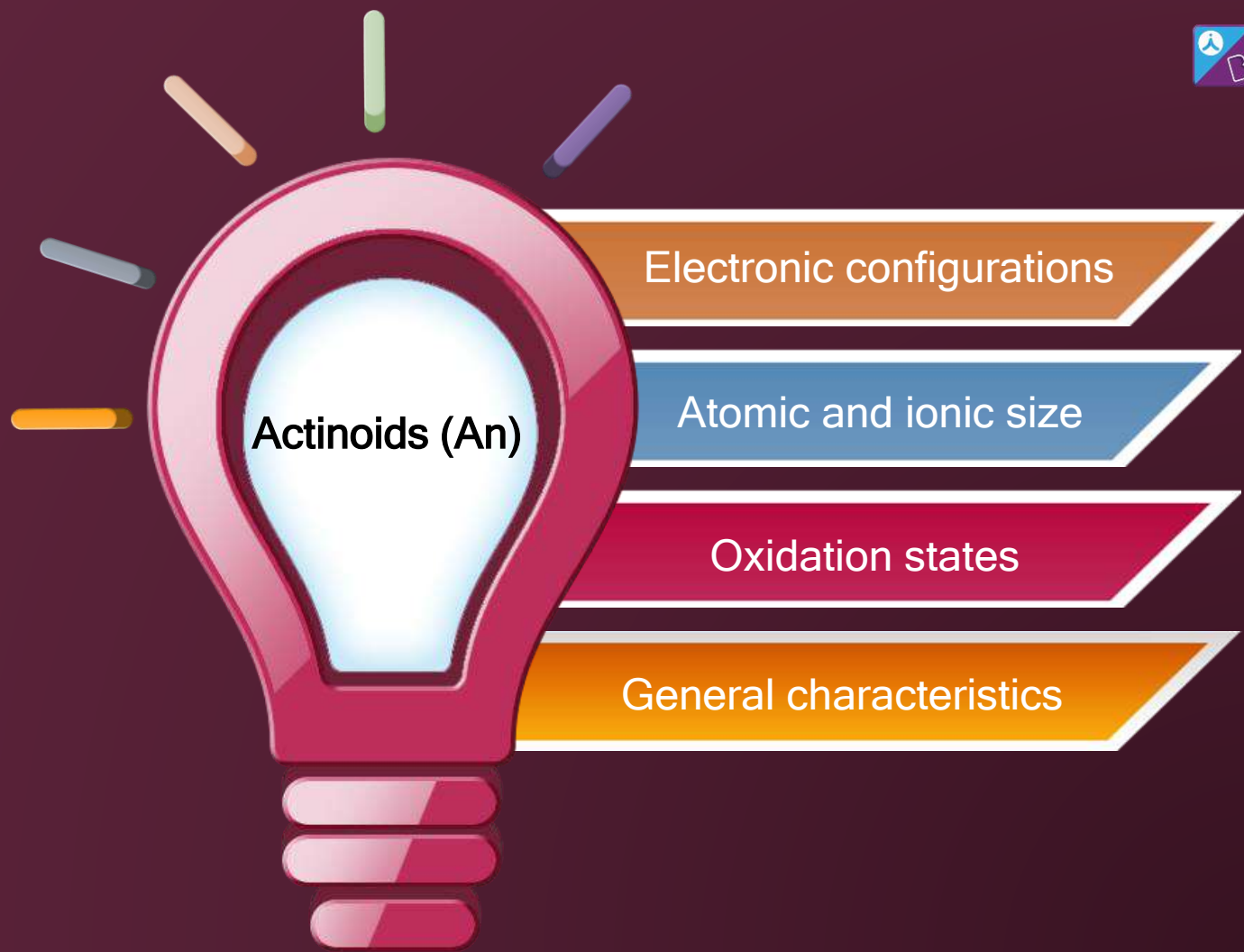


Uranium is the heaviest naturally occurring element.

After uranium, 12 more elements has been artificial synthesized (atomic number more than 92) and are called the **transuranium elements**

## Actinoids are radioactive elements





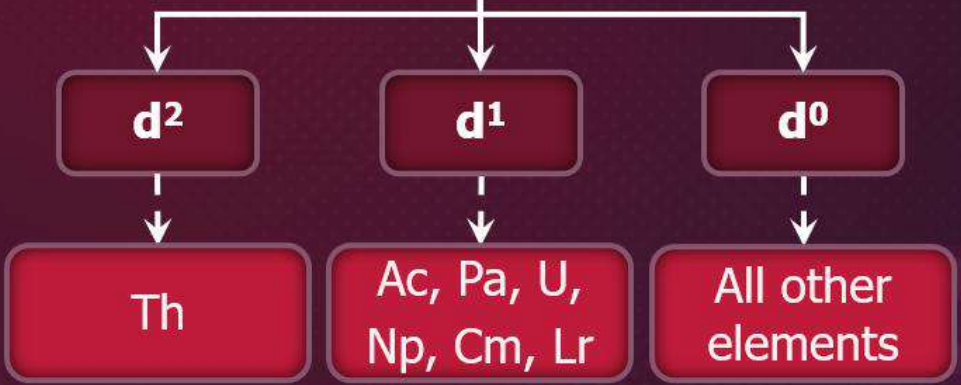


# Actinoids: Electronic Configuration

General configuration

89 Ac Actinium	90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium
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Variable occupancy



# NOTE



The difference between the energy levels of 5f and 6d orbitals are small



Thus in **Ac, Th, Pa, U** and **Np** electrons may occupy either 5d or 6f orbitals.

5f orbital extend in space, comparatively more than 4f orbital, hence 5f electrons participate in bonding to a greater extent

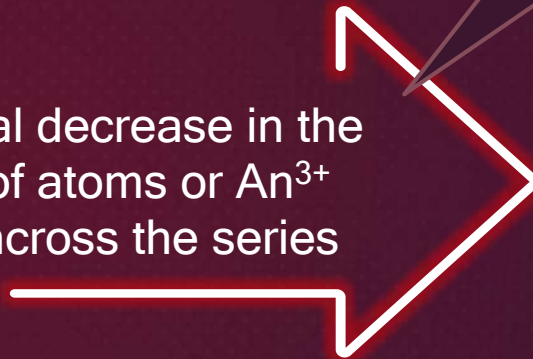


# Actinoids: Atomic and Ionic sizes



Due to **actinoid contraction**

Gradual decrease in the size of atoms or  $An^{3+}$  ions across the series





# Actinoids : General Characteristics



Physical  
properties

Actinoid metals are all silvery in appearance but display a **variety of structures.**

Due to irregularities in metallic radii which are far greater than in lanthanoids

# Actinoids : Chemical Properties



Actinoids are **highly reactive** metals

1

H<sub>2</sub>O (Boil)



2

Most non-metals



3

HCl



4

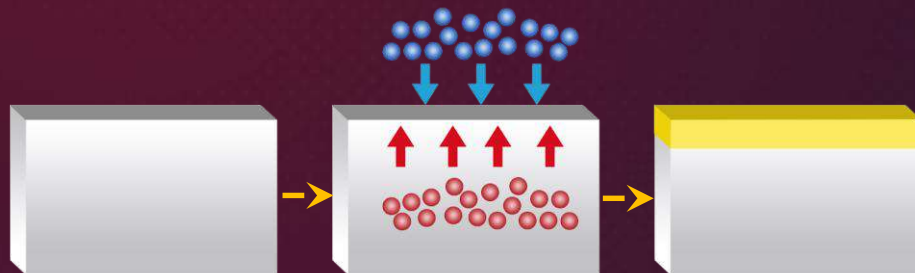
HNO<sub>3</sub>



Hydrochloric acid attacks all metals but most metals are less affected by **nitric acid**.



Due to formation of **protective oxide layer**.



# Actinoids : General Characteristics

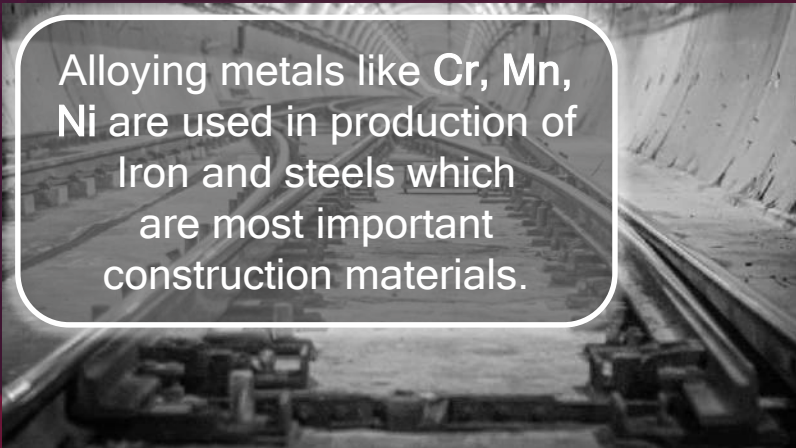


Magnetic properties




Ions are paramagnetic or diamagnetic depending upon the number of unpaired 5f electrons.


# Uses of d & f Block Elements



Alloying metals like Cr, Mn, Ni are used in production of Iron and steels which are most important construction materials.



TiO<sub>2</sub> as white pigment

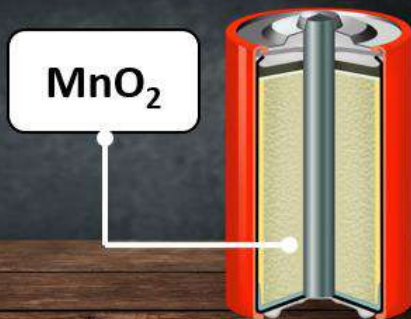


Dry cell battery

# Uses of d & f Block Elements



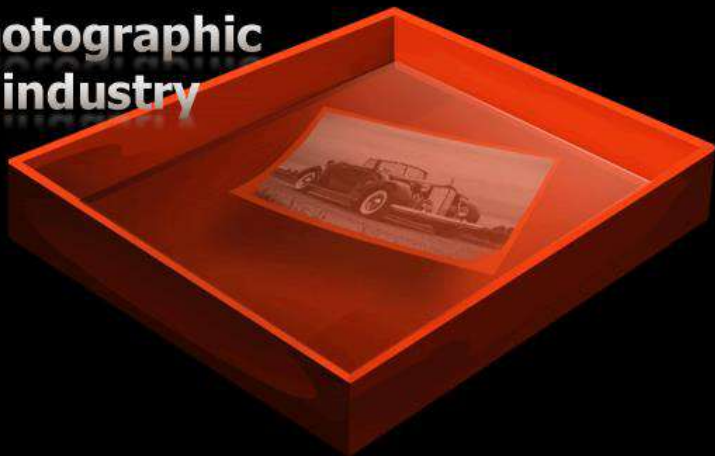
$\text{MnO}_2$  used  
in dry cell



Coinage metal



Photographic  
industry



Lightest-known  
form of uranium  
created



# Application as Catalysts



Important

Catalyst	Process
$V_2O_5$	Contact process
Ziegler catalyst [ $TiCl_4$ with $Al(CH_3)_3$ ]	Polythene manufacturing
Iron	Haber process
Nickel	Hydrogenation of fats
$PdCl_2$	Wacker process
Nickel complex	Polymerisation of alkynes and benzene