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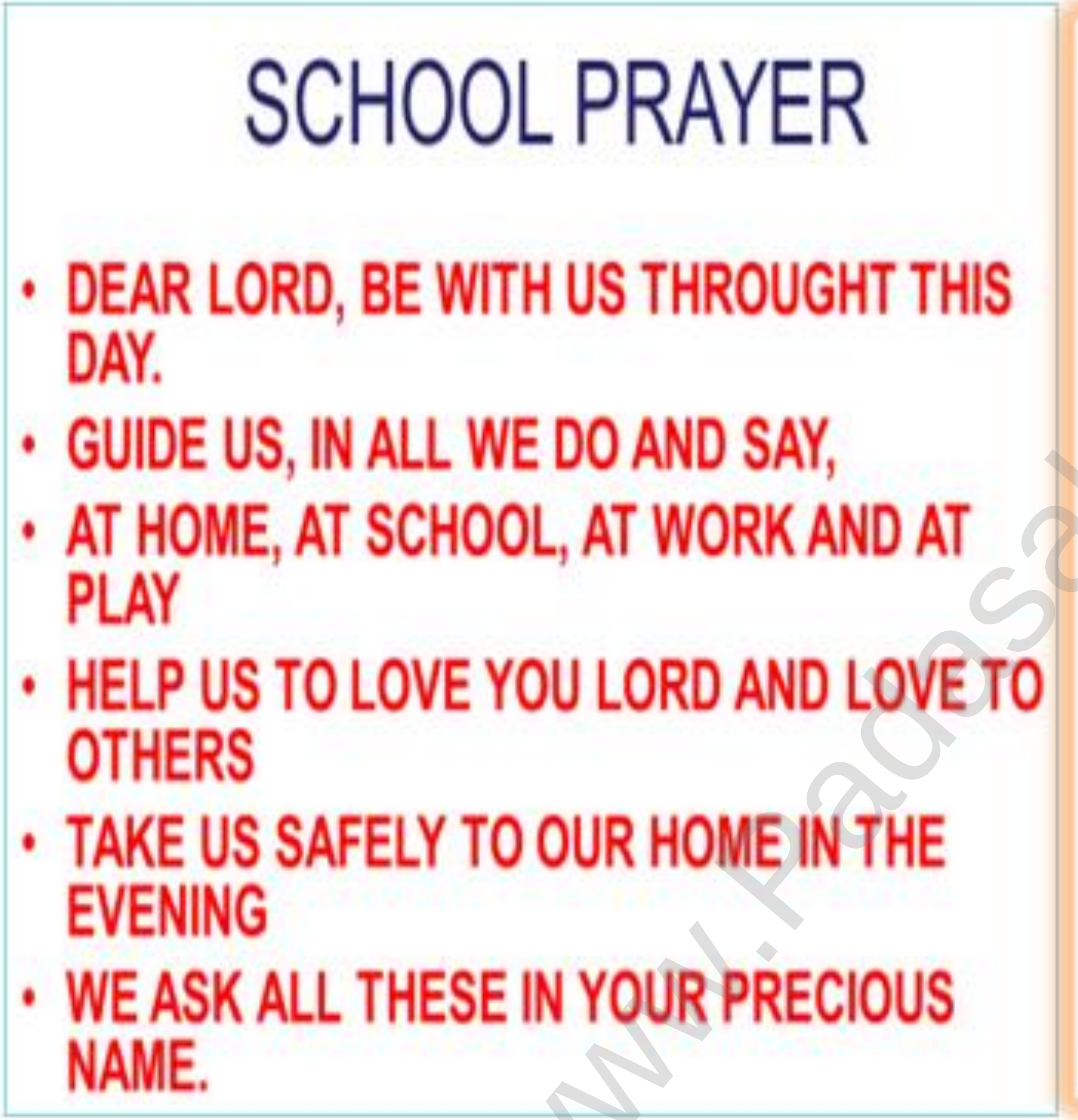
UNIT
4

TRANSITION AND INNER TRANSITION ELEMENTS



SCHOOL PRAYER

- DEAR LORD, BE WITH US THROUGHT THIS DAY.
- GUIDE US, IN ALL WE DO AND SAY,
- AT HOME, AT SCHOOL, AT WORK AND AT PLAY
- HELP US TO LOVE YOU LORD AND LOVE TO OTHERS
- TAKE US SAFELY TO OUR HOME IN THE EVENING
- WE ASK ALL THESE IN YOUR PRECIOUS NAME.

Introduction:

- **Generally the metallic elements that have incompletely filled d or f sub shell in the neutral or cationic state are called transition metals. This definition includes lanthanides and actinides.**
- **However, *IUPAC defines transition metal as an element whose atom has an incomplete d sub shell or which can give rise to cations with an incomplete d sub shell.***
- **They occupy the central position of the periodic table, between s and p block elements, and their properties are transitional between highly reactive metals of s block and elements of p block which are mostly non metals.**
- **Except group- 11 elements all transition metals are hard and have very high melting point.**

Importance of d- block elements:

- Transition metals, iron and copper play an important role in the development of human civilization.

- Many other transition elements also have important applications such as

Tungsten in light bulb filaments.

Titanium in manufacturing artificial joints.

Molybdenum in boiler plants.

Platinum in catalysis.

- They also play vital role in living system, for example iron in hemoglobin, cobalt in vitamin B_{12} etc.,

Position of d- block elements in the periodic table:

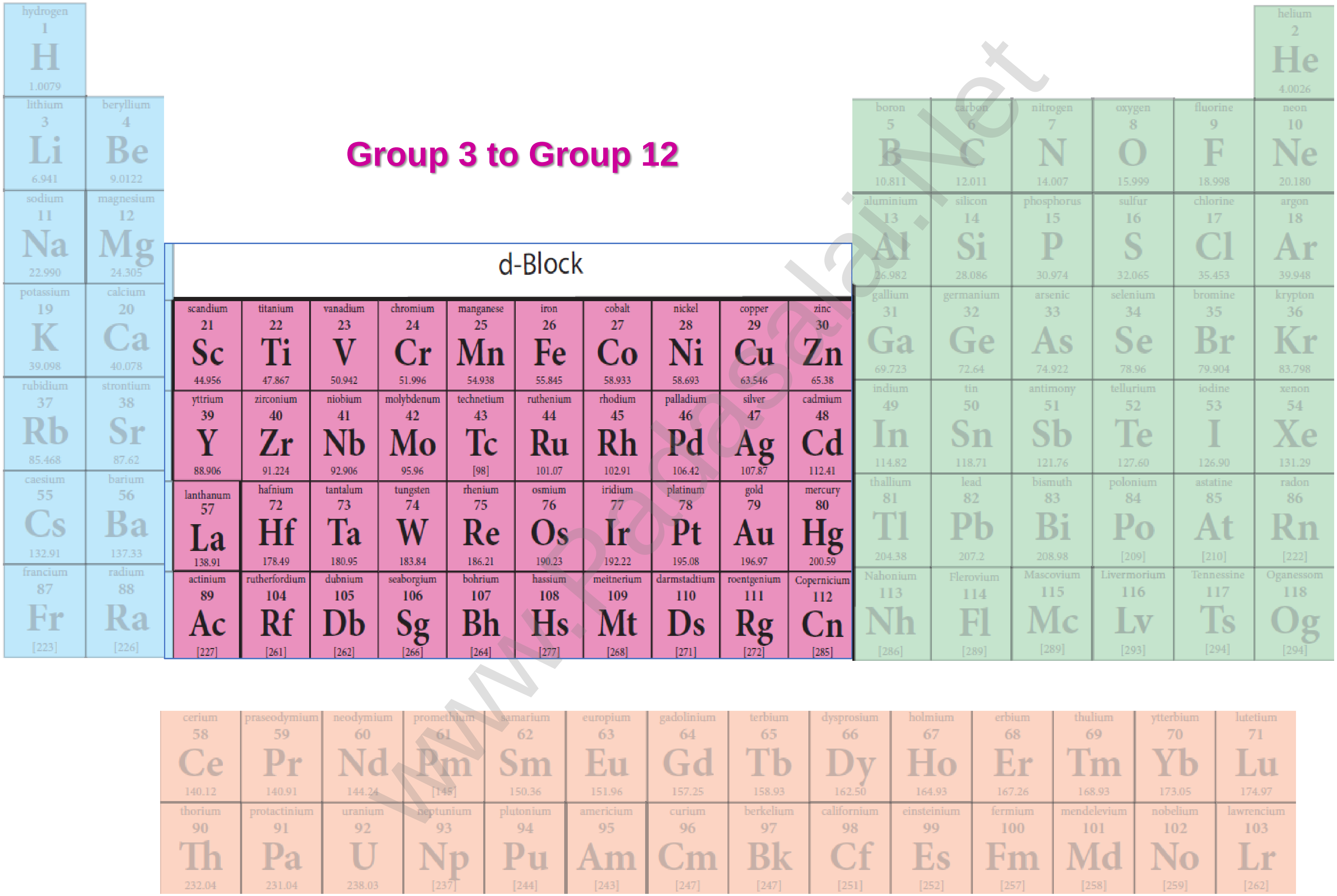
- d-block elements:
  The elements of periodic table belonging to group 3 to 12 are known as d-Block elements. because in these elements last electron enters in d sub shell or d orbital .

- The d -block elements lies in between s- and p-block elements in the long form of periodic table s-Block

p-Block

Group 3 to Group 12

d-Block

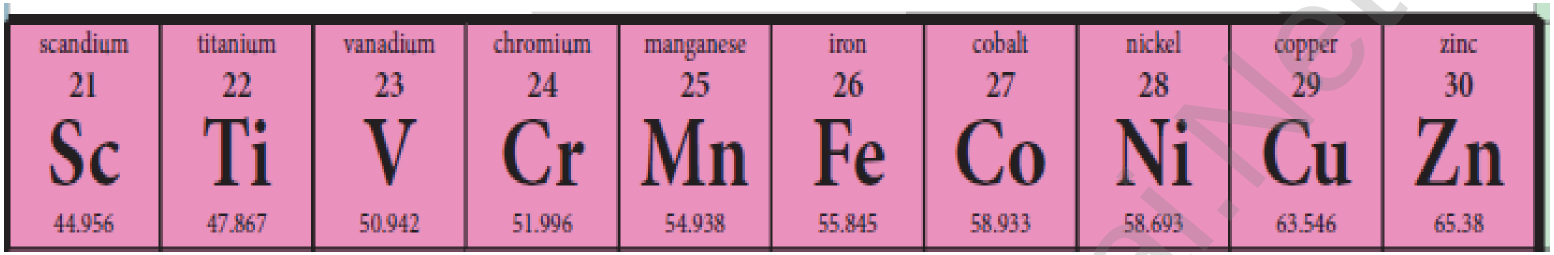


hydrogen 1 H 1.0079																	helium 2 He 4.0026
lithium 3 Li 6.941	beryllium 4 Be 9.0122											boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305											aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.38	gallium 31 Ga 69.723	germanium 32 Ge 72.64	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.798
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.96	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
caesium 55 Cs 132.91	barium 56 Ba 137.33	lanthanum 57 La 138.91	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr [223]	radium 88 Ra [226]	actinium 89 Ac [227]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [277]	meitnerium 109 Mt [268]	darmstadtium 110 Ds [271]	roentgenium 111 Rg [272]	Copernicium 112 Cn [285]	Nahonium 113 Nh [286]	Flerovium 114 Fl [289]	Mascovium 115 Mc [289]	Livermorium 116 Lv [293]	Tennessine 117 Ts [294]	Oganessom 118 Og [294]

cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.05	lutetium 71 Lu 174.97
thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]	lawrencium 103 Lr [262]

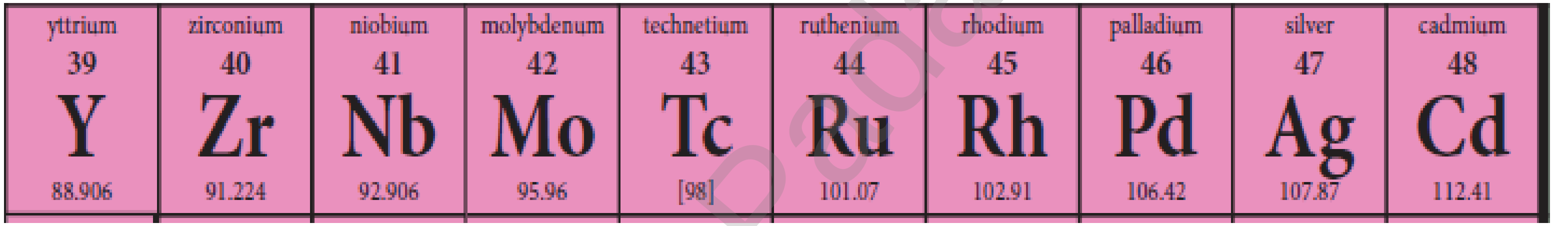
d- Block elements composed of

3d series (4th period) Scandium to Zinc (10 elements)



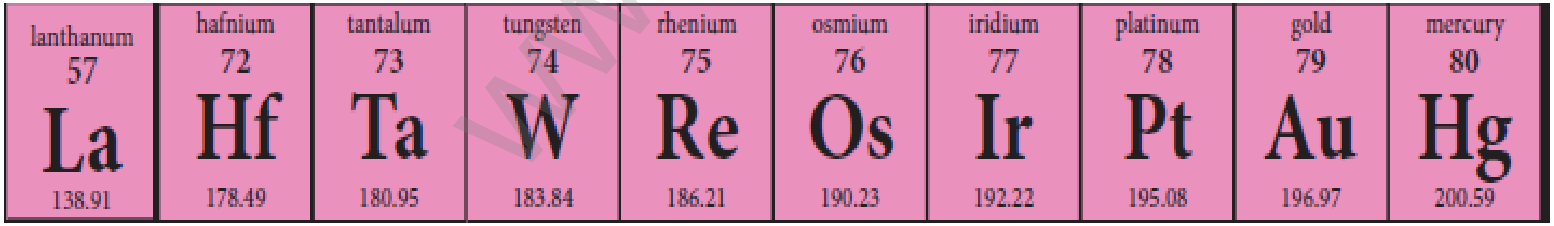
scandium	titanium	vanadium	chromium	manganese	iron	cobalt	nickel	copper	zinc
21	22	23	24	25	26	27	28	29	30
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
44.956	47.867	50.942	51.996	54.938	55.845	58.933	58.693	63.546	65.38

4dseries (5th period) Yttrium to Cadmium (10 elements)



yttrium	zirconium	niobium	molybdenum	technetium	ruthenium	rhodium	palladium	silver	cadmium
39	40	41	42	43	44	45	46	47	48
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
88.906	91.224	92.906	95.96	[98]	101.07	102.91	106.42	107.87	112.41

5d series (6th period) Lanthanum , Haffinium to mercury.



lanthanum	hafnium	tantalum	tungsten	rhenium	osmium	iridium	platinum	gold	mercury
57	72	73	74	75	76	77	78	79	80
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
138.91	178.49	180.95	183.84	186.21	190.23	192.22	195.08	196.97	200.59

How are d - Block Elements & Transition elements different?

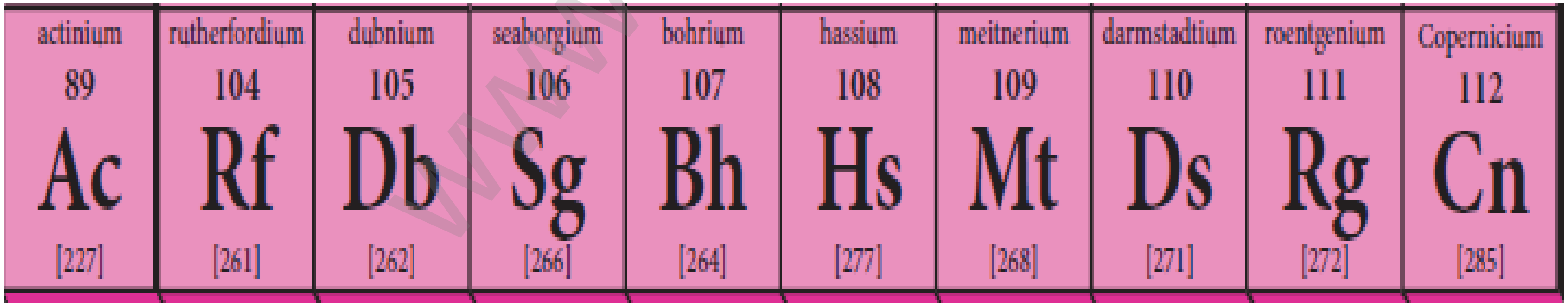
All d block elements are not transition elements but all transition elements are d-block elements

All d block elements are not transition elements because d block elements like Zinc have full d^{10} configuration in their ground state as well as in their common oxidation state.which is not according to definition of transition elements.

we know that the group-12 elements **Zinc, Cadmium and Mercury** do not have partially filled d-orbital either in their elemental state or in their normal oxidation states. However they are treated as transition elements, because their properties are an extension of the properties of the respective transition elements.

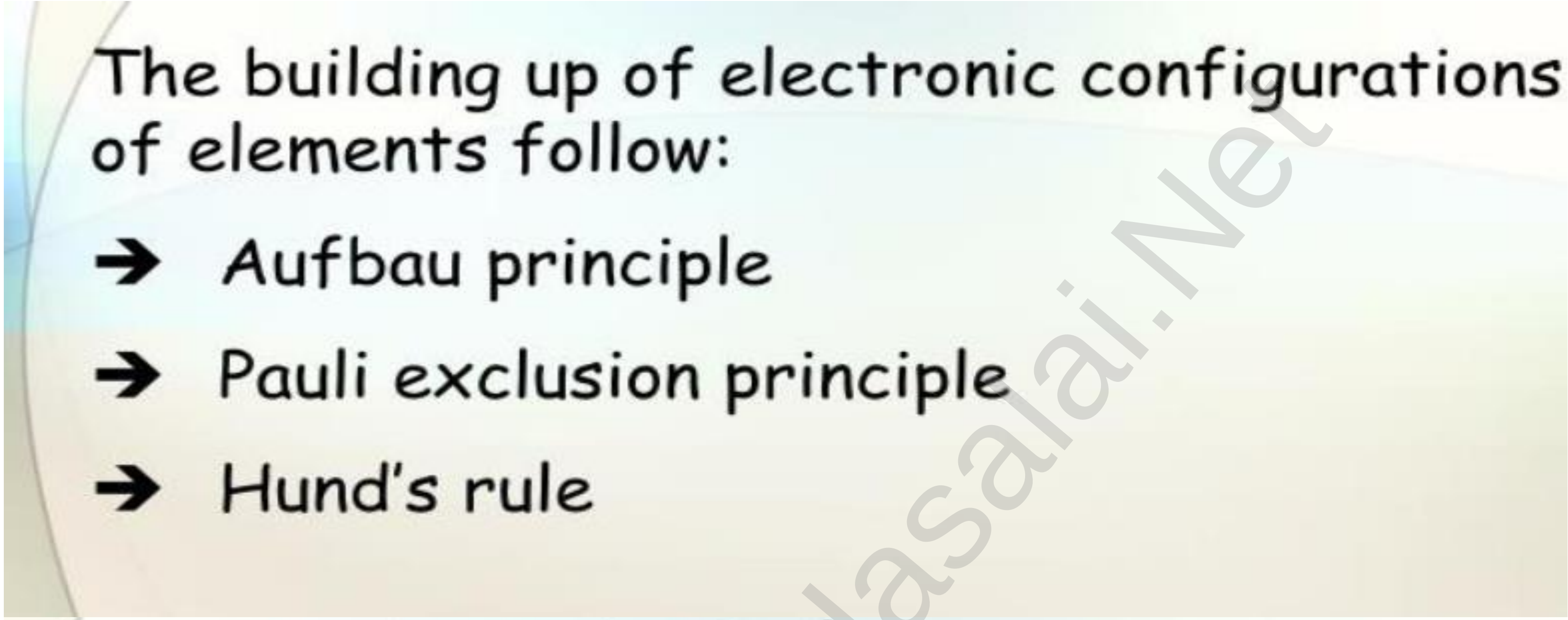
As per the IUPAC definition,

- The seventh period elements, starting from Ac, Rf to Cn also belong to transition metals. **(6d series – in complete)**
- All of them are radioactive.
- Except Actinium; all the remaining elements are synthetically prepared and have very low half life periods



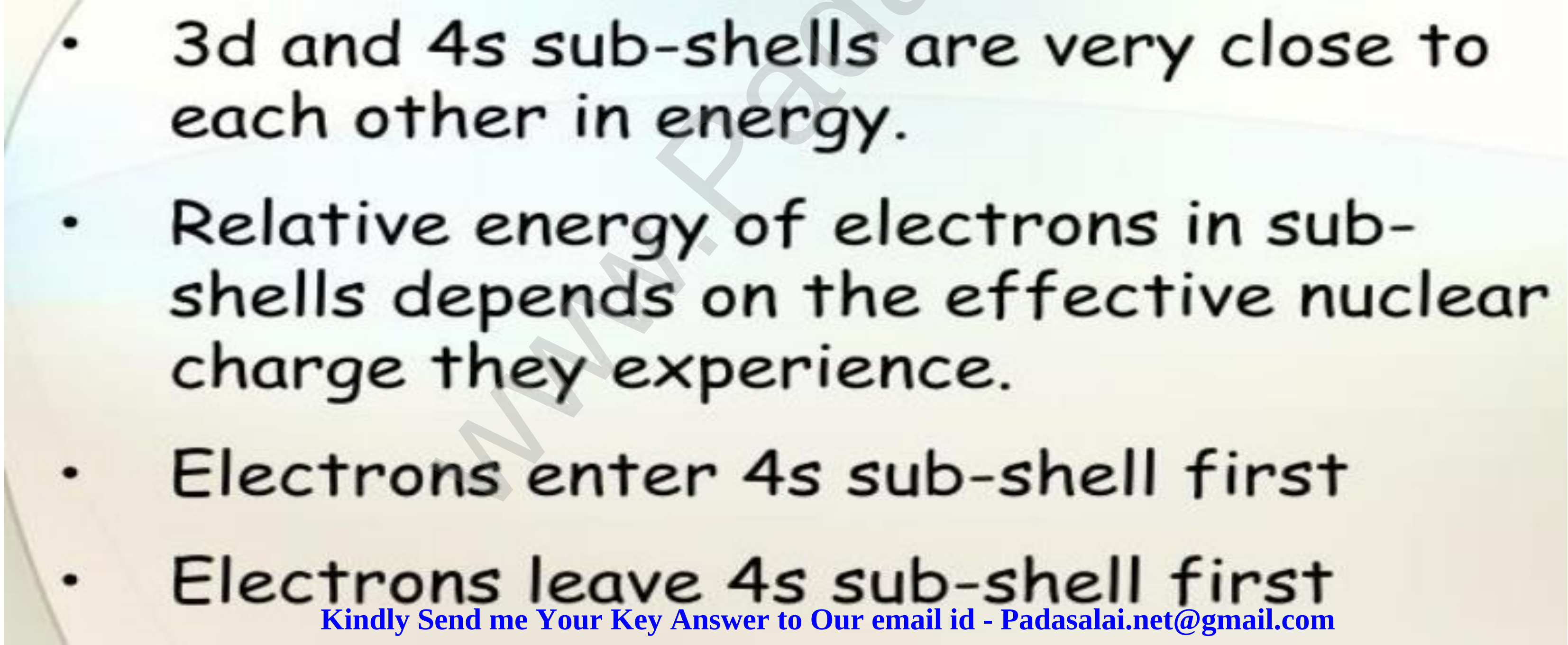
actinium	rutherfordium	dubnium	seaborgium	bohrium	hassium	meitnerium	darmstadtium	roentgenium	Copernicium
89	104	105	106	107	108	109	110	111	112
Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn
[227]	[261]	[262]	[266]	[264]	[277]	[268]	[271]	[272]	[285]

Electronic configuration:



The building up of electronic configurations of elements follow:

- ➔ Aufbau principle
- ➔ Pauli exclusion principle
- ➔ Hund's rule



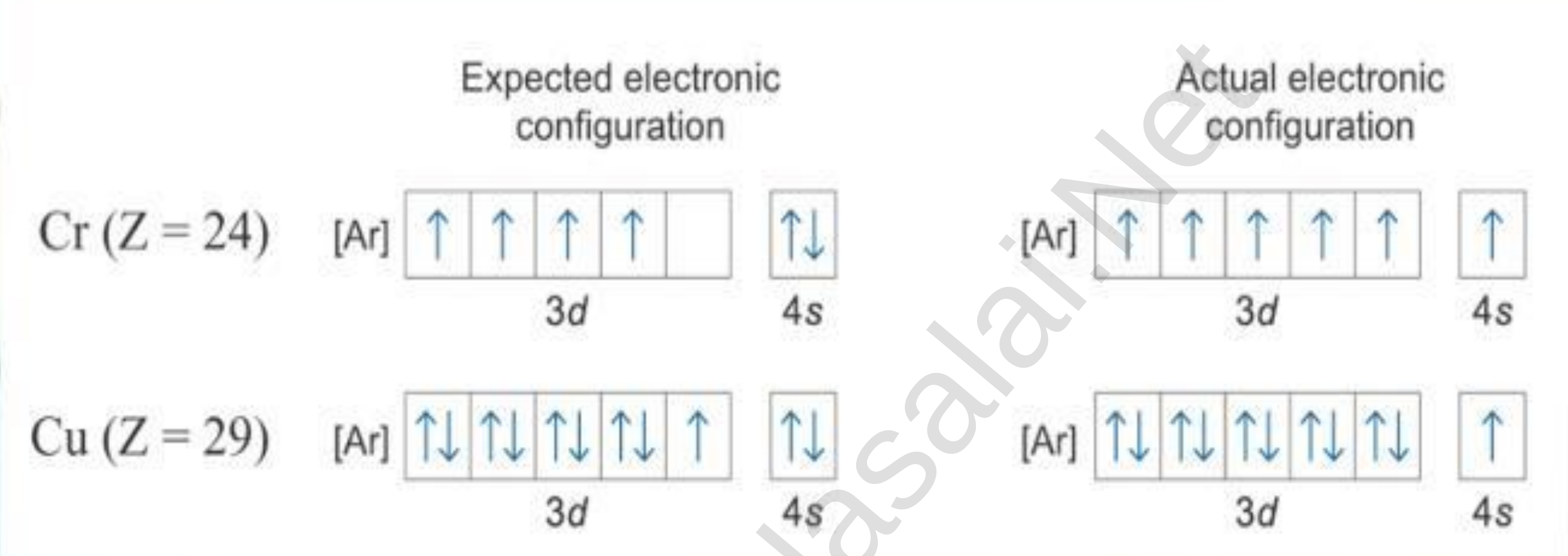
- 3d and 4s sub-shells are very close to each other in energy.
- Relative energy of electrons in sub-shells depends on the effective nuclear charge they experience.
- Electrons enter 4s sub-shell first
- Electrons leave 4s sub-shell first

Electronic Configurations

- Valence electrons in the inner 3d orbitals
- Examples:
  - ➔ The electronic configuration of scandium: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$
  - ➔ The electronic configuration of zinc: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$

Electronic configurations of the first series of the *d*-block elements

Element	Atomic number	Electronic configuration
Scandium	21	$[Ar]\,3d^{1}4s^{2}$
Titanium	22	$[Ar]\,3d^{2}4s^{2}$
Vanadium	23	$[Ar]\,3d^{3}4s^{2}$
Chromium	24	$[Ar]\,3d^{5}4s^{1}$
Manganese	25	$[Ar]\,3d^{5}4s^{2}$
Iron	26	$[Ar]\,3d^{6}4s^{2}$
Cobalt	27	$[Ar]\,3d^{7}4s^{2}$
Nickel	28	$[Ar]\,3d^{8}4s^{2}$
Copper	29	$[Ar]\,3d^{10}4s^{1}$
Zinc	30	$[Ar]\,3d^{10}4s^{2}$



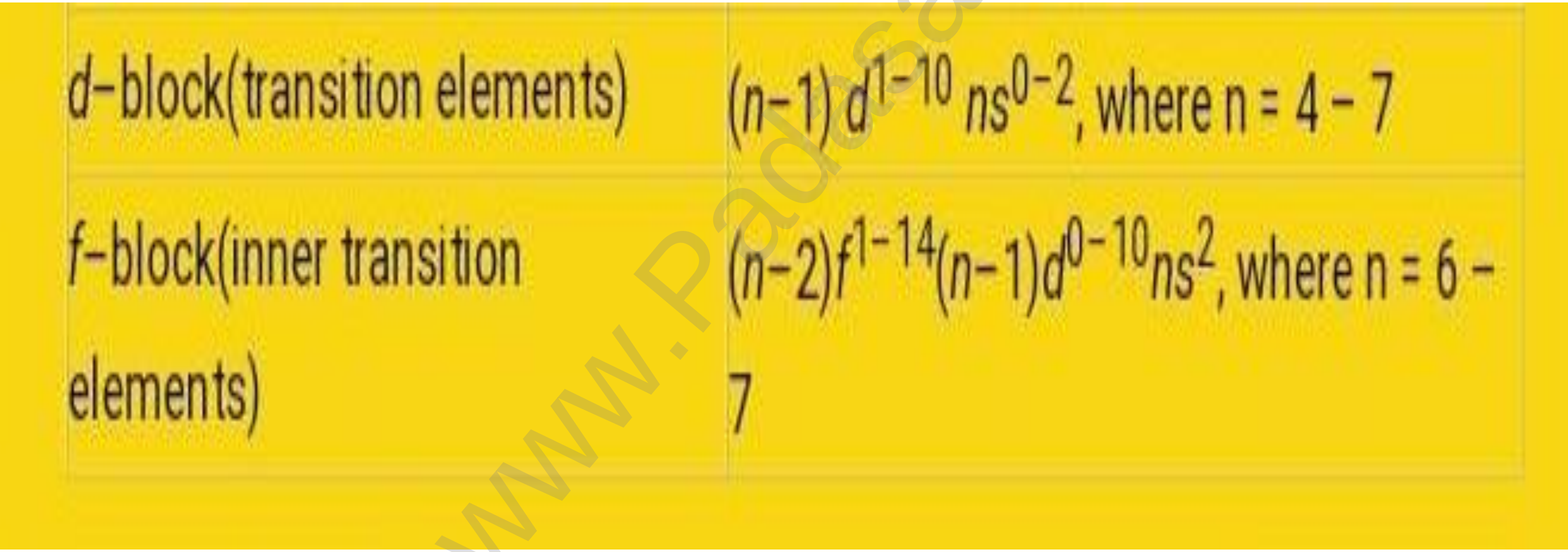
- A half-filled or fully-filled d sub-shell has extra stability

The general electronic configuration of d- block elements can be written as

$[\text{Noble gas}]\ (n -)d^{1\text{-}10}\ ns^{1\text{-}2}$ **Here, n = 4 to 7 .**

In periods 6 and 7, (except La and Ac) the configuration includes ((n −2) f orbital

$[\text{Noble gas}]\ (n-2)f^{14}\,(n-1)d^{1-10}ns^{1-2}$



d-block(transition elements)	$(n-1)\,d^{1-10}\,ns^{0-2}$, where n = 4 – 7
f-block(inner transition elements)	$(n-2)f^{1-14}(n-1)d^{0-10}ns^{2}$, where n = 6 – 7

Outer electronic configuration of d – block elements:

1st Series

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Z	21	22	23	24	25	26	27	28	29	30
4*s*	2	2	2	1	2	2	2	2	1	2
3*d*	1	2	3	5	5	6	7	8	10	10

2nd Series

	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Z	39	40	41	42	43	44	45	46	47	48
5*s*	2	2	1	1	1	1	1	0	1	2
4*d*	1	2	4	5	6	7	8	10	10	10

3rd Series

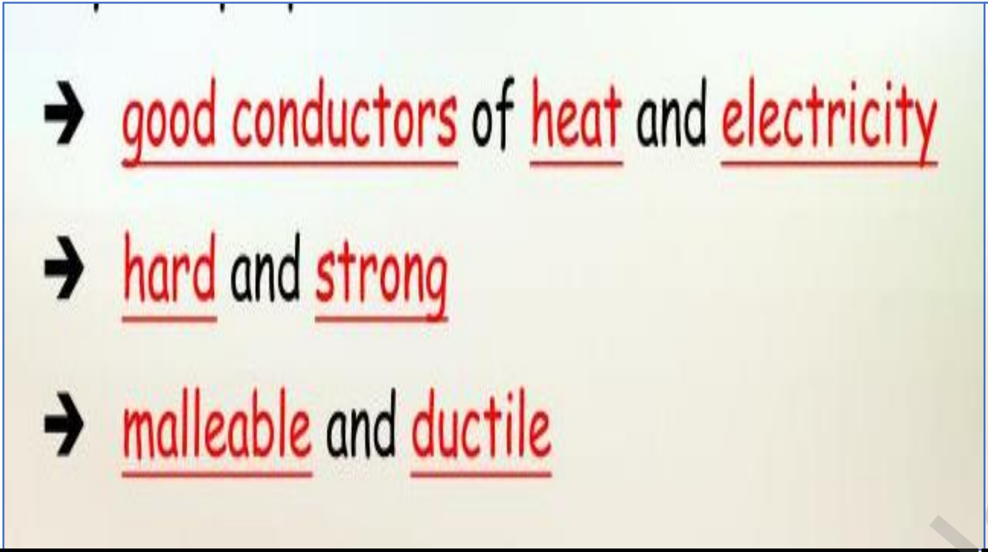
	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Z	57	72	73	74	75	76	77	78	79	80
6*s*	2	2	2	2	2	2	2	1	1	2
5*d*	1	2	3	4	5	6	7	9	10	10

4th Series

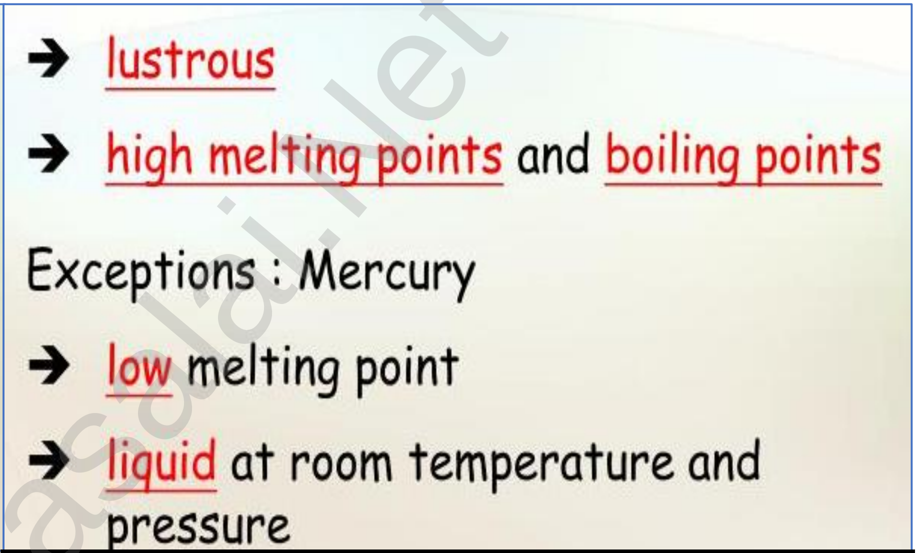
	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub
Z	89	104	105	106	107	108	109	110	111	112
7*s*	2	2	2	2	2	2	2	2	1	2
6*d*	1	2	3	4	5	6	7	8	10	10

General trend in properties:

Metallic behaviour:



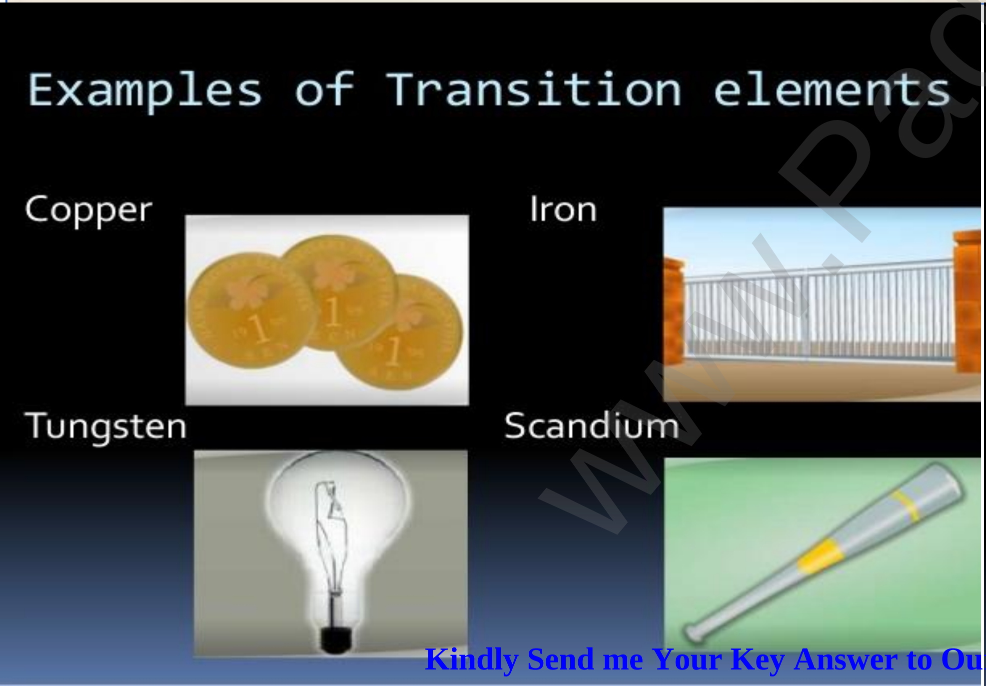
- good conductors of heat and electricity
- hard and strong
- malleable and ductile



- lustrous
- high melting points and boiling points

Exceptions : Mercury

- low melting point
- liquid at room temperature and pressure



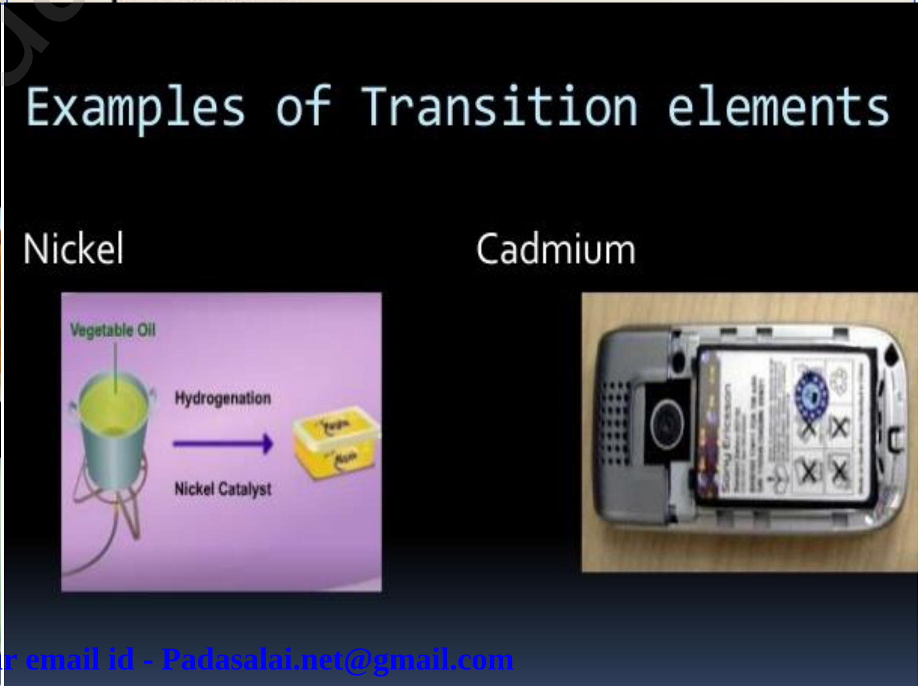
Examples of Transition elements

Copper

Iron

Tungsten

Scandium



Examples of Transition elements

Nickel

Cadmium

Most of the transition elements are hexagonal close packed, cubic close packed or bod
centrered cubic which are the characteristics of true metals.

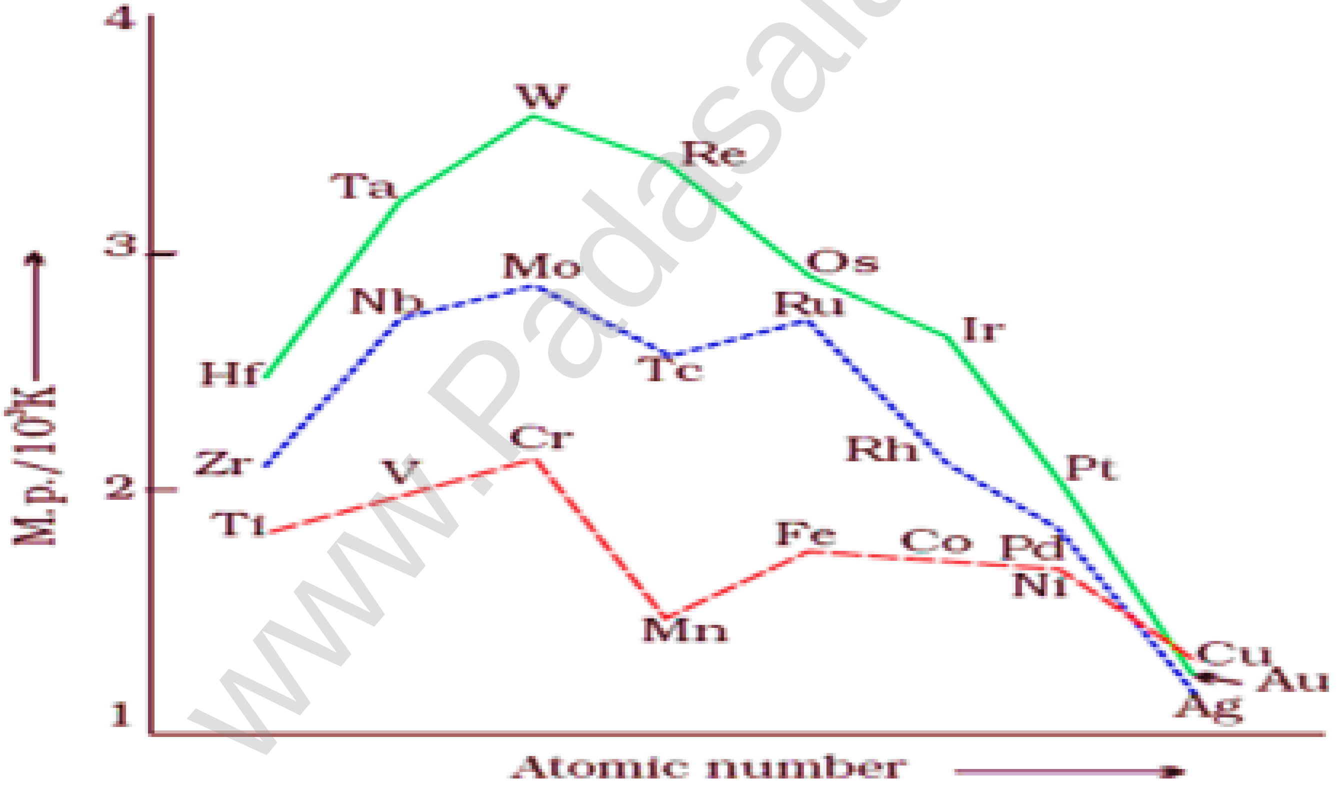
21 Sc HCP	22 Ti HCP	23 V BCC	24 Cr BCC	25 Mn BCC	26 Fe BCC	27 Co HCP	28 Ni FCC	29 Cu FCC	30 Zn HCP
39 Y HCP	40 Zr HCP	41 Nb BCC	42 Mo BCC	43 Tc HCP	44 Ru HCP	45 Rh FCC	46 Pd FCC	47 Ag FCC	48 Cd HCP
57* La DHCP	72 Hf HCP	73 Ta BCC/ TETR	74 W BCC	75 Re HCP	76 Os HCP	77 Ir FCC	78 Pt FCC	79 Au FCC	80 Hg RHO
89** Ac FCC	104 Rf [HCP]	105 Db [BCC]	106 Sg [BCC]	107 Bh [HCP]	108 Hs [HCP]	109 Mt [FCC]	110 Ds [BCC]	111 Rg [BCC]	112 Cn [BCC]

lattice structures of 3d, 4d and 5d transition metals

MELTING POINT AND BOILING POINT

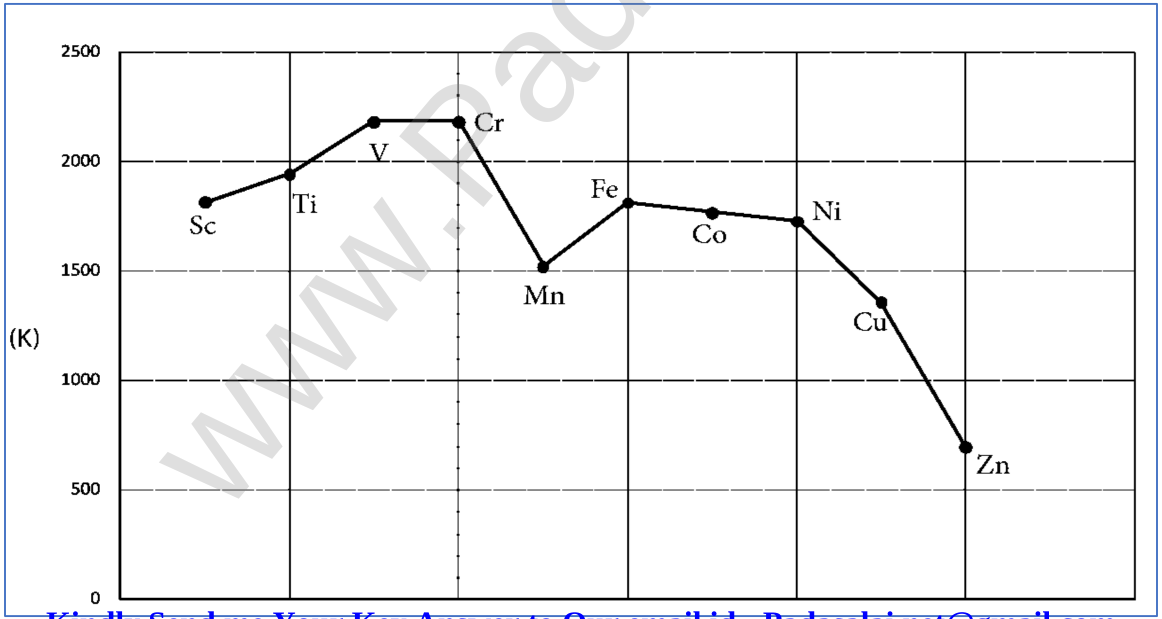
- High M.P and B.P - Due to strong metallic bond and the **presence of half filled d-orbitals**
- Involvement of greater number of electrons from (n-1)*d* in addition to the ns electrons in the inter atomic metallic bonding.
- Because of stronger interatomic bonding, transition elements have high M.P and B.P

- In moving along the period from left to right, the M.P of these metals first **INCREASES** to MAXIMUM and the **DECREASES** regularly towards the end of the period.



Trends in melting points of transition elements

- For example, in the first series the melting point increases from Scandium (m.pt 1814K) to a maximum of 2183 K for vanadium, which is close to 2180K for chromium.
- However, manganese in 3d series and Tc in 4d series have low melting point.
- The maximum melting point at about the middle of transition metal series indicates that d^5 configuration is favorable for strong interatomic attraction.
- The following figure shows the trends in melting points of transition elements.



Variation of atomic and ionic size:

- The Atomic/ionic radii first **DECREASES** till the middle, becomes **almost constant** and then **INCREASES** towards the end of the period.
- New electron enters a *d* orbital each time the nuclear charge increases by unity, But the shielding effect of a *d* electron is not that effective, hence the net electrostatic attraction between the nuclear charge and the outermost electron increases and the ionic radius decreases

- However the increased nuclear charge is partly cancelled by the **increased screening effect of electrons in the d – orbitals** of penultimate shell.
- When the increased nuclear charge and increased Screening effect balance each other, the atomic radii becomes almost constant.
- Increase in atomic radii towards the end may be attributed to the **electron – electron repulsion**.
- In fact the pairing of electrons in d – orbitals occurs after d^5 configuration.
- The **repulsive interaction** between the **paired electron** causes Increase in Atomic/ ionic radii

- It is generally expected a steady decrease in atomic radius along a period as the nuclear charge increases and the extra electrons are added to the same sub shell.

- But for the 3d transition elements, the expected decrease in atomic radius is observed from Sc to V , thereafter up to Cu the atomic radius nearly remains the same.

- As we move from Sc to Zn in 3d series the extra electrons are added to the 3d orbitals, the added 3d electrons only partially shield the increased nuclear charge and hence the effective nuclear charge increases slightly.

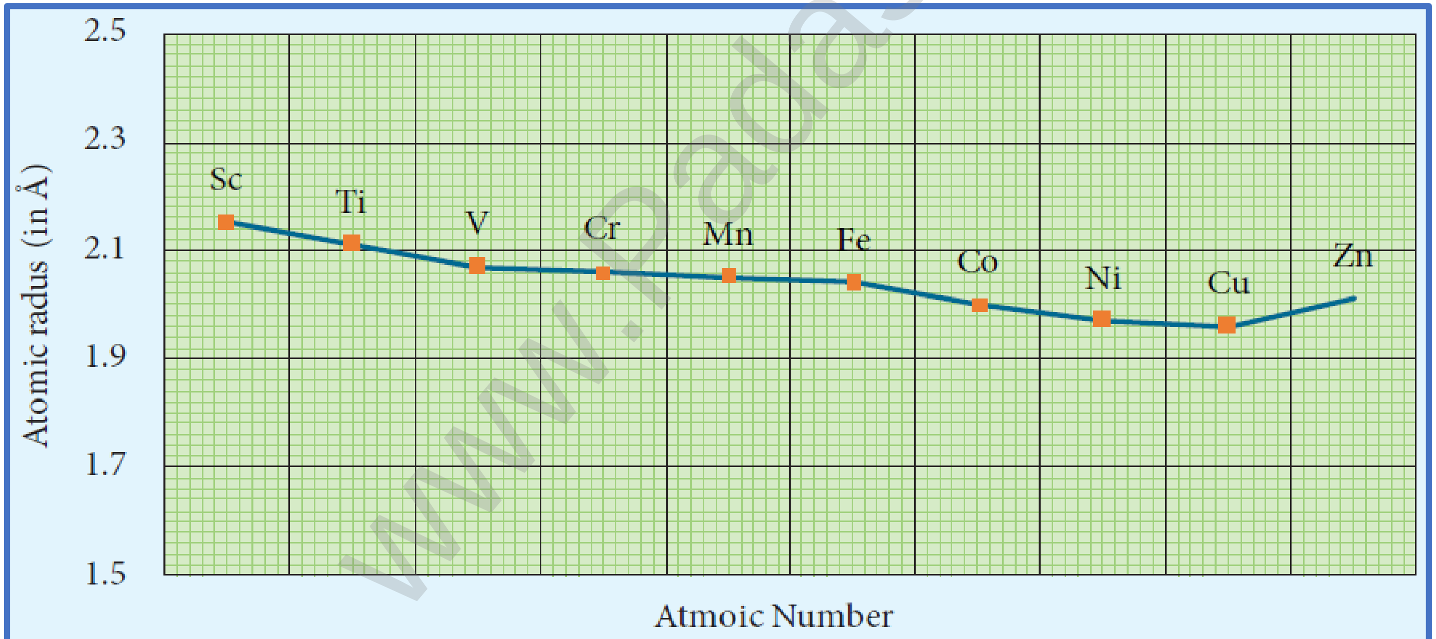
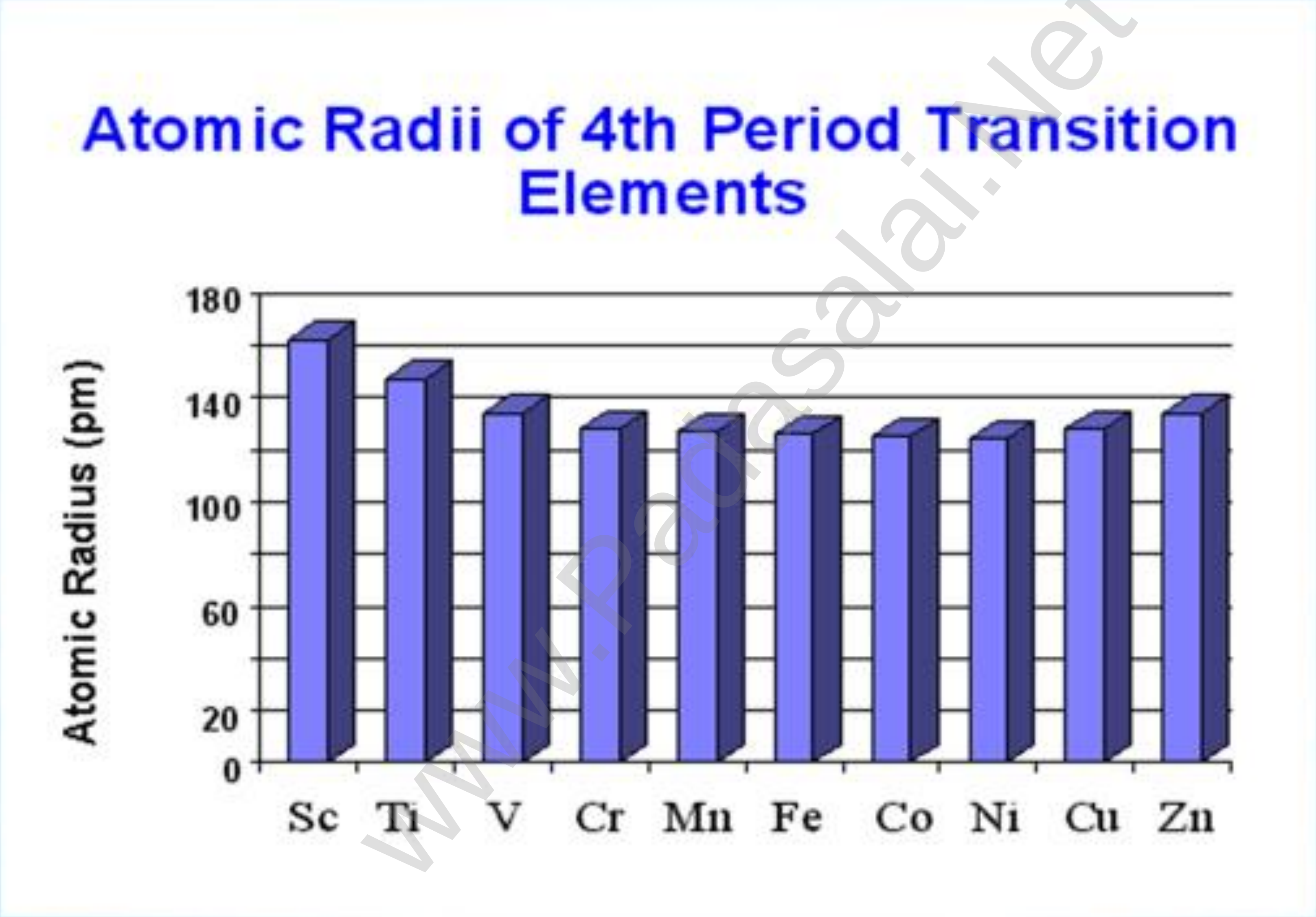


Figure 4.4 (a) Atomic radius of 3d Elements

ATOMIC & IONIC SIZE



- **However, the extra electrons added to the 3d sub shell strongly repel the 4s electrons and these two forces are operated in opposite direction and as they tend to balance each other, it leads to constancy in atomic radii.**

- **At the end of the series, d – orbitals of Zinc contain 10 electrons in which the repulsive interaction between the electrons is more than the effective nuclear charge and hence, the orbitals slightly expand and atomic radius slightly increases.**

- **Generally as we move down a group atomic increases, the same trend is expected d block elements also. As the electrons are added to the 4d sub shell the atomic radii of the 4d elements are higher than the corresponding of the 3d series. However there is an unexpected observation in the atomic radius of 5d elements which have nearly same atomic radius as that of corresponding 4d elements. Th is is due to lanthanoide contraction which is to be discussed later in this unit under inner transition elements.**

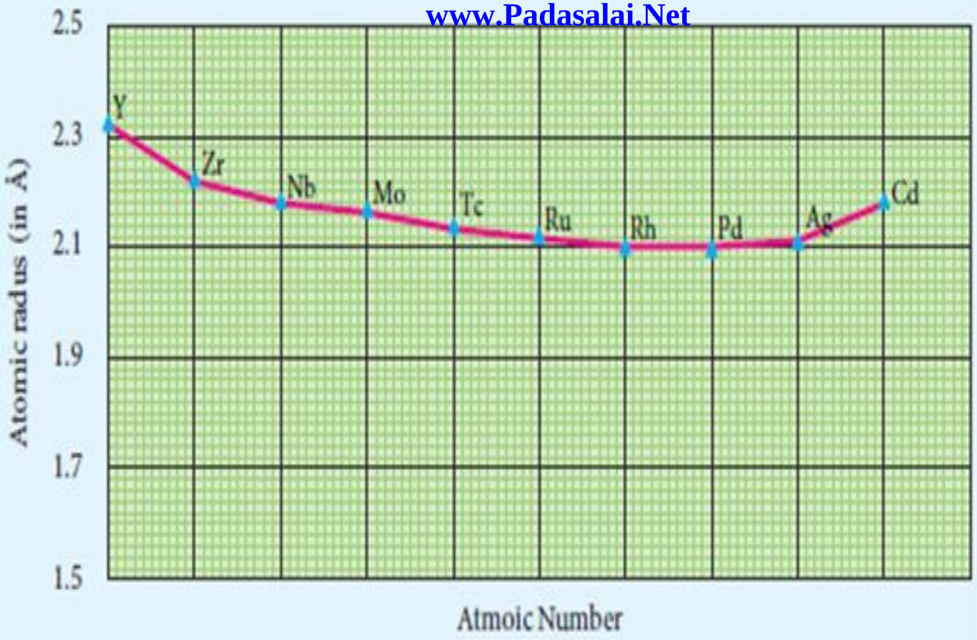


Figure 4.4 (b) Atomic radius of 4d Elements

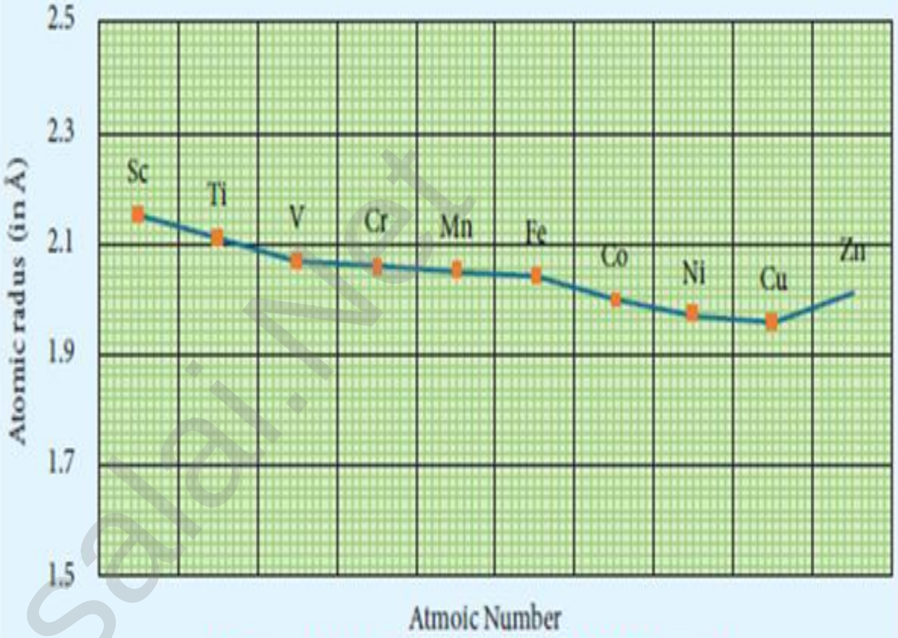


Figure 4.4 (a) Atomic radius of 3d Elements

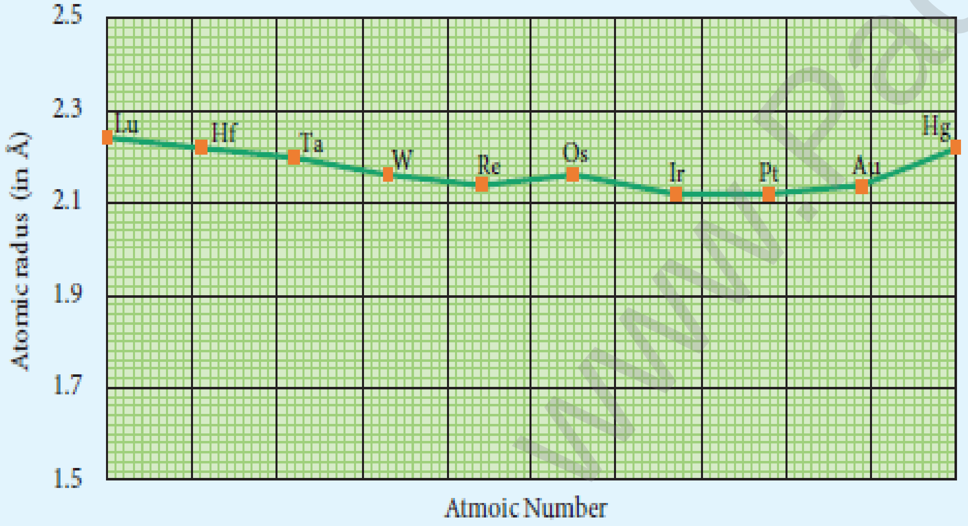
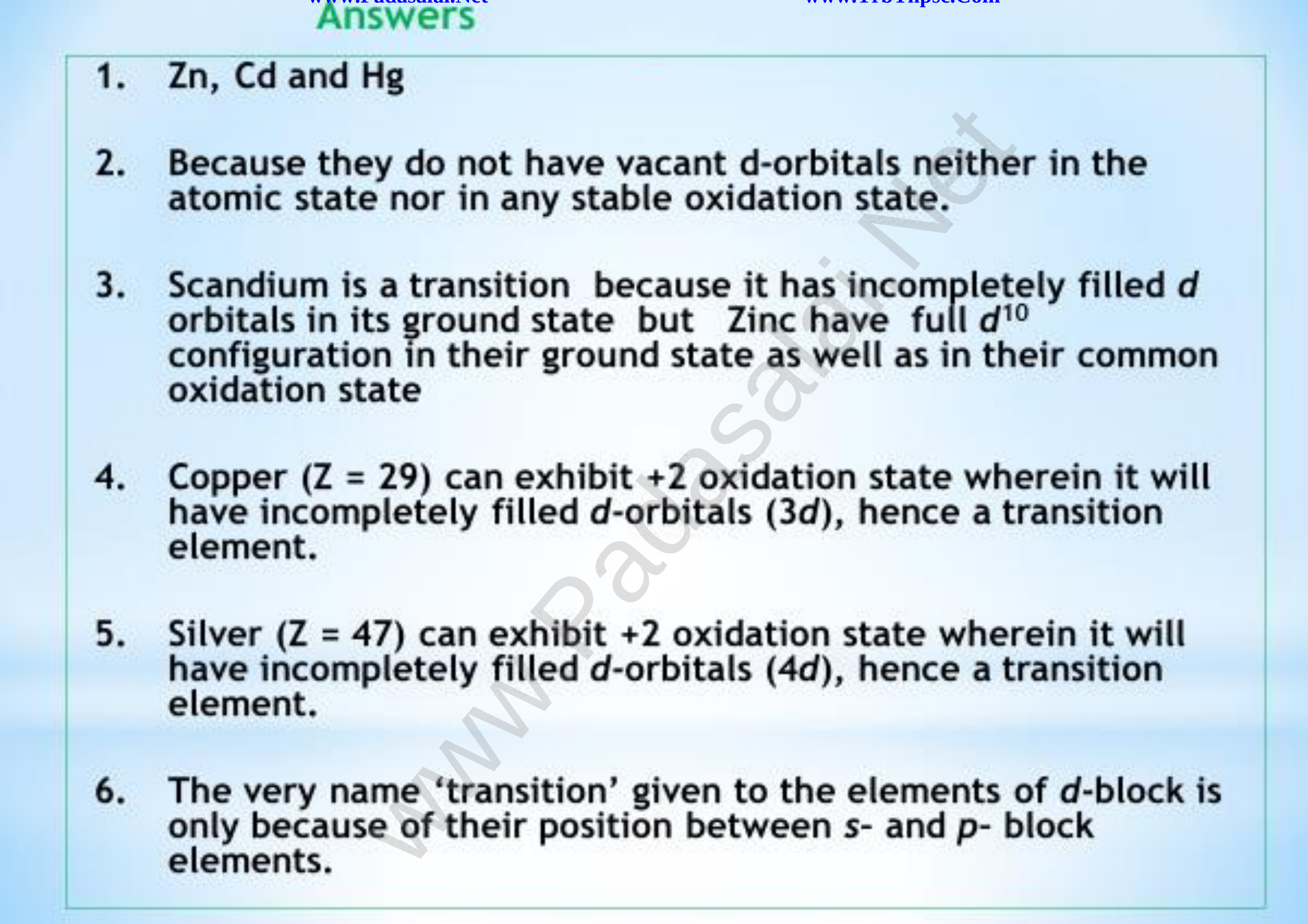


Figure 4.4 (c) Atomic radius of 5d Elements

1. Which of the d-block elements may not be regarded as the transition elements?
2. Why Zn, Cd and Hg are not considered as transition elements.
3. Why Scandium is a transition element but Zinc is not.
4. Copper atom has completely filled d orbital ($3d^{10}$) in its ground state, yet it is transition element. Why
5. Silver atom has completely filled d orbital ($4d^{10}$) in its ground state, yet it is transition element. Why
6. Why the very name 'transition' given to the elements of *d*-block .

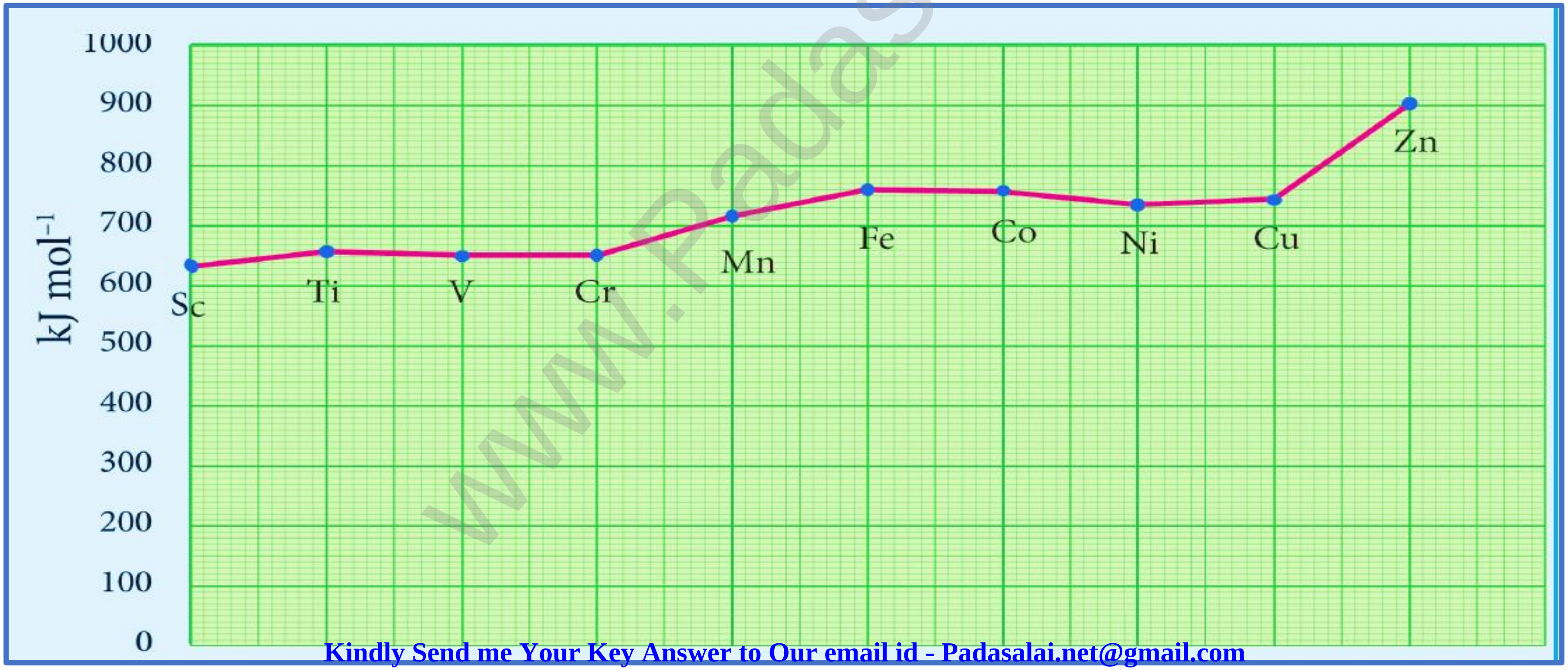


Answers

1. Zn, Cd and Hg
2. Because they do not have vacant d-orbitals neither in the atomic state nor in any stable oxidation state.
3. Scandium is a transition because it has incompletely filled *d* orbitals in its ground state but Zinc have full d^{10} configuration in their ground state as well as in their common oxidation state
4. Copper (Z = 29) can exhibit +2 oxidation state wherein it will have incompletely filled *d*-orbitals (3*d*), hence a transition element.
5. Silver (Z = 47) can exhibit +2 oxidation state wherein it will have incompletely filled *d*-orbitals (4*d*), hence a transition element.
6. The very name 'transition' given to the elements of *d*-block is only because of their position between *s*- and *p*- block elements.

Ionization enthalpy.

- Ionization energy of transition element is intermediate between those of s and p block elements.
- As we move from left to right in a transition metal series, the ionization enthalpy increases as expected.
- This is due to increase in nuclear charge corresponding to the filling of d electrons.
- The following figure show the trends in ionisation enthalpy of transition elements.



- The increase in first ionisation enthalpy with increase in atomic number along a particular series is not regular.
- The added electron enters (n-1)d orbital and the inner electrons act as a shield and decrease the effect of nuclear charge on valence ns electrons.
- Therefore, it leads to variation in the ionization energy values.
- The ionisation enthalpy values can be used to predict the thermodynamic stability of their coumponds.

- Let us compare the ionisation energy required to form Ni^{2+} and Pt^{2+} ions.

$$\text{For Nickel,} \quad IE_1 + IE_2 = (737 + 1753) = 2490\ \text{kJmol}^{-1}$$

$$\text{For Platinum,} \quad IE_1 + IE_2 = (864 + 1791) = 2655\ \text{kJmol}^{-1}$$

- Since, the energy required to form Ni^{2+} is less than that of Pt^{2+}, Ni(II) compounds are thermodynamically more stable than Pt(II) compounds.

Relation between I.E and Stability of a metal in a given oxdn state

- With the help of I.E, we can predict which of the two metals in a given oxdn state is thermodynamically more stable.

Eg

- When a metal M (0) is converted into M(11), the energy required is equal to **$I_1 + I_2$**

  Similerly **M (IV) = $I_1 + I_2 + I_3 + I_4$**

- Ni (0) $\longrightarrow$ Ni (II) $I_1 + I_2 = 2.49 \times 10^3$ kJ mol $^{-1}$
- Pt (0) $\longrightarrow$ Pt (II) $I_1 + I_2 = 2.66 \times 10^3$ kJ mol $^{-1}$
- Ni (0) $\longrightarrow$ Ni (IV)

  $I_1 + I_2 + I_3 + I_4 = 11.299 \times 10^3$ kJ mol $^{-1}$
- Pt (0) $\longrightarrow$ Pt (IV)

  $I_1 + I_2 + I_3 + I_4 = 9.36 \times 10^3$ kJ mol $^{-1}$

$I_1 + I_2$ for Ni (II) is less than $I_1 + I_2$ for Pt (II). So Ni (II) is more stable

Similarly Pt (IV) is more stable

Oxidation state:

The first transition metal Scandium exhibits only +3 oxidation state, but all other transition elements exhibit variable oxidation states

Reason : *by loosing electrons from (n-1)d orbital and ns orbital as the energy difference between them is very small.*

Let us consider the 3d series; the following table summarizes the oxidation states of the 3d series elements

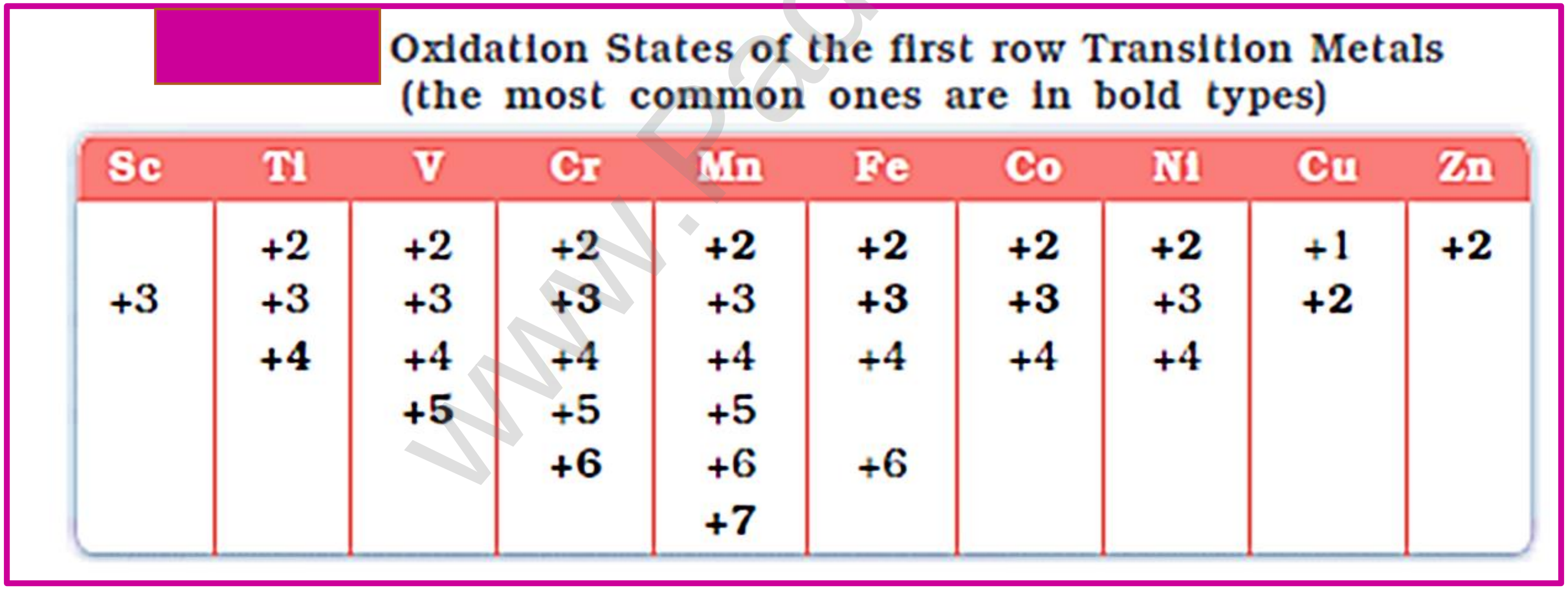
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
				+7				
			+6	+6	+6			
		+5	+5	+5				
	+4	+4	+4	+4	+4	+4	+4	
+3	+3	+3	+3	+3	+3	+3	+3	
	+2	+2	+2	+2	+2	+2	+2	+2
								+1

- At the beginning of the series, +3 oxidation state is stable but towards the end +2 oxidation state becomes stable.
- The number of oxidation states increases with the number of electrons available, and it decreases as the number of paired electrons increases.
- Hence, the first and last elements show less number of oxidation states and the middle elements with more number of oxidation states.

- ***For example,***
- The first element Sc has only one oxidation state +3;

  The middle element Mn has six different oxidation states from +2 to +7.

  The last element Cu shows +1 and +2 oxidation states only.



Oxidation States of the first row Transition Metals
(the most common ones are in bold types)

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

- The relative stability of different oxidation states of 3d metals is correlated with the extra stability of half filled and fully filled electronic configurations.

Example: Mn^{2+} ($3d^5$) is more stable than Mn^{4+} ($3d^3$)

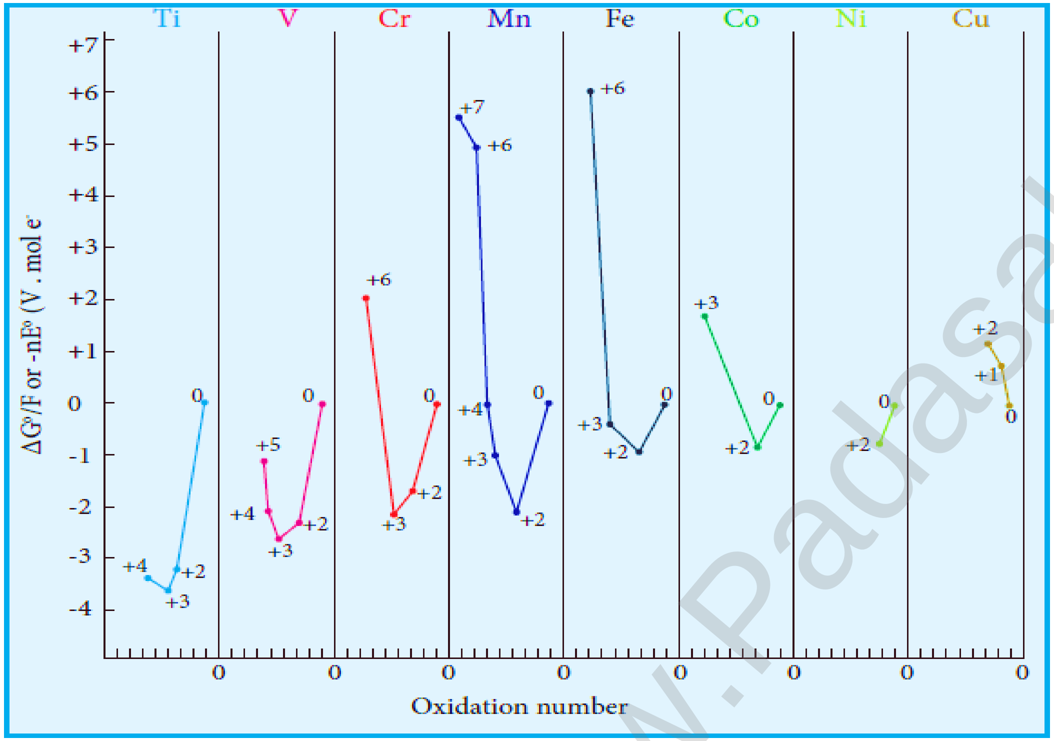
- The oxidation states of 4d and 5d metals vary from +3(for Y and La) to +8 (for Ru and Os).

- The highest oxidation state of 4d and 5d elements are found in their compounds with the higher electronegative elements like O, F and Cl. for example: RuO_4, OsO_4 and WCl_6.

- In $Ni(CO)_4$ and $Fe(CO)_5$, the oxidation state of nickel and iron is zero.

- Generally in going down a group, a stability of the higher oxidation state increases while that of lower oxidation state decreases.

- It is evident from the Frost diagram (ΔG^0 vs oxidation number) as shown below,



A Frost diagram or Frost–Ebsworth diagram is a type of graph used by inorganic chemists in electrochemistry to illustrate the relative stability of a number of different oxidation states of a particular substance. The graph illustrates the free energy vs oxidation state of a chemical species.

- For titanium , vanadium and chromium, the most thermodynamically stable oxidation state is +3.
- For iron, the stabilities of +3 and +2 oxidation states are similar.

Copper is unique in 3d series having a stable +1 oxidation state. It is prone to disproportionate to the +2 and 0 oxidation states.

Standard electrode potentials of transition metals

- **Redox reactions** involve transfer of electrons from one reactant to another. Such reactions are always coupled, which means that when one substance is oxidized, another must be reduced.
- The substance which is oxidised is a reducing agent and the one which is reduced is an oxidizing agent.
- The oxidizing and reducing power of an element is measured in terms of the standard electrode potentials.
- **Standard electrode potential** is the value of the standard emf of a cell in which molecular hydrogen under standard pressure (1atm) and temperature (273K) is oxidised to solvated protons at the electrode.
- If the standard electrode potential (E_0), of a metal is large and negative, the metal is apowerful reducing agent, because it loses electrons easily.
- Standard electrode potentials (reduction potential) of few first transition metals are given in the following table.

Reaction	Standard reduction potential (V)
$Ti^{2+} + 2e^- \longrightarrow Ti$	−1.63
$V^{2+} + 2e^- \longrightarrow V$	−1.19
$Cr^{2+} + 2e^- \longrightarrow Cr$	−0.91
$Mn^{2+} + 2e^- \longrightarrow Mn$	−1.18
$Fe^{2+} + 2e^- \longrightarrow Fe$	−0.44
$Co^{2+} + 2e^- \longrightarrow Co$	−0.28
$Ni^{2+} + 2e^- \longrightarrow Ni$	−0.23
$Cu^{2+} + 2e^- \longrightarrow Cu$	+0.34
$Zn^{2+} + 2e^- \longrightarrow Zn$	−0.76

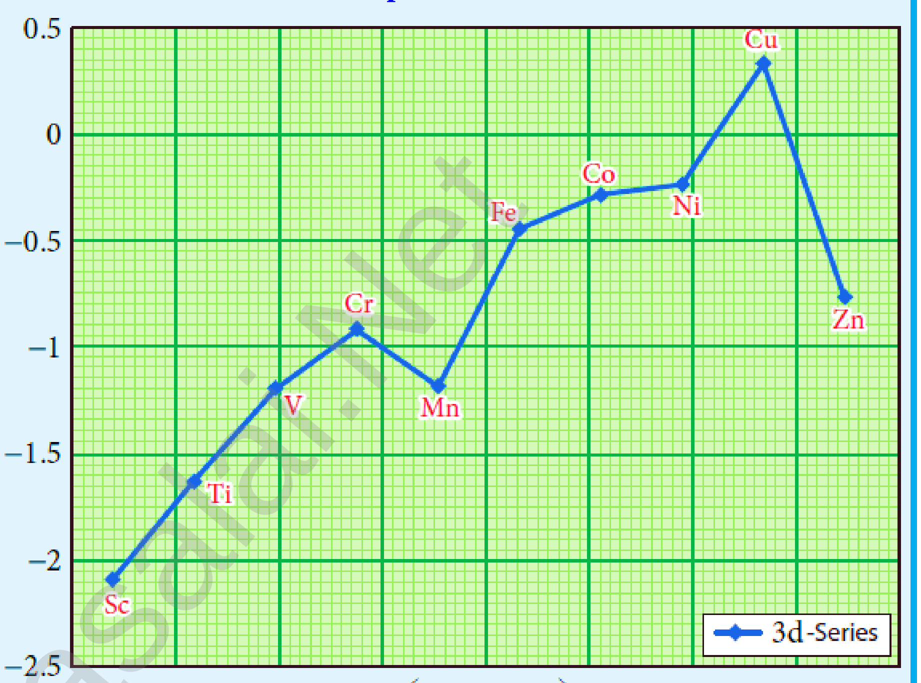


Figure 4.7 (a) $\left(E^0_{M^{2+}/M}\right)$ -3d series

- In 3d series as we move from Ti to Zn, the standard reduction potential $(E^o_{M^{2+}/M})$ value is approaching towards less negative value and copper has a positive reduction potential. i.e., elemental copper is more stable than Cu^{2+}.

There are two deviations.,

- **In the general trend, Fig shows that ($E^0_{M^{2+}/M}$) value for manganese and zinc are more negative than the regular trend. It is due to extra stability which arises due to the half filled d^5 configuration in Mn^{2+} and completely filled d^{10} configuration in Zn^{2+}.**

- **Transition metals in their high oxidation states tend to be oxidizing .**

  For example,

- **Fe^{3+} is moderately a strong oxidant, and it oxidises copper to Cu^{2+} ions.**
- **The feasibility of the reaction is predicted from the following standard electrode potential values.**

$$Fe^{3+}(aq) + e^- \rightleftharpoons \mathrm{Fe}^{2+} \quad \mathrm{E}^0 = 0.77\mathrm{V}$$

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons \mathrm{Cu(s)} \quad \mathrm{E}^0 = +0.34\ \mathrm{V}$$

The standard electrode potential for the M^{3+}/M^{2+} half-cell gives the relative stability between M^{3+} and M^{2+}. The reduction potential values are tabulated as below.

Reaction	Standard reduction potential (V)
$Ti^{3+} + e^- \longrightarrow Ti^{2+}$	–0.37
$V^{3+} + e^- \longrightarrow V^{2+}$	–0.26
$Cr^{3+} + e^- \longrightarrow Cr^{2+}$	–0.41
$Mn^{3+} + e^- \longrightarrow Mn^{2+}$	+1.51
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	+0.77
$Co^{3+} + e^- \longrightarrow Co^{2+}$	+1.81

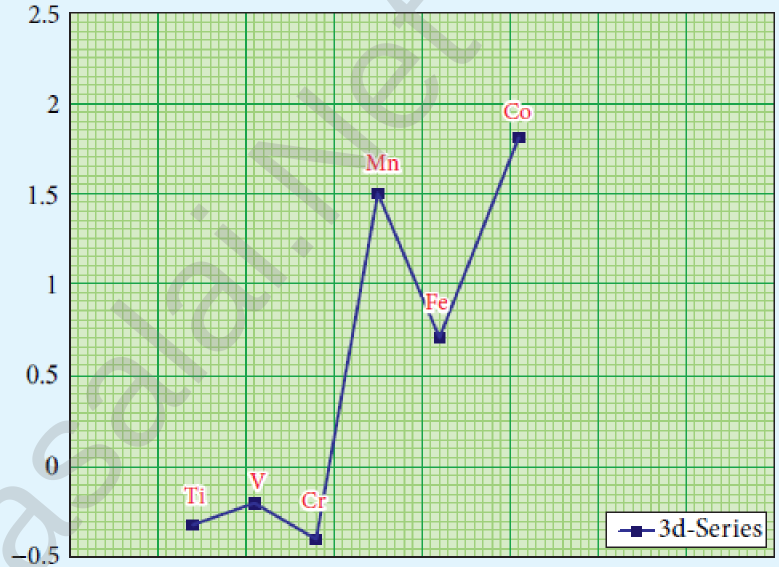


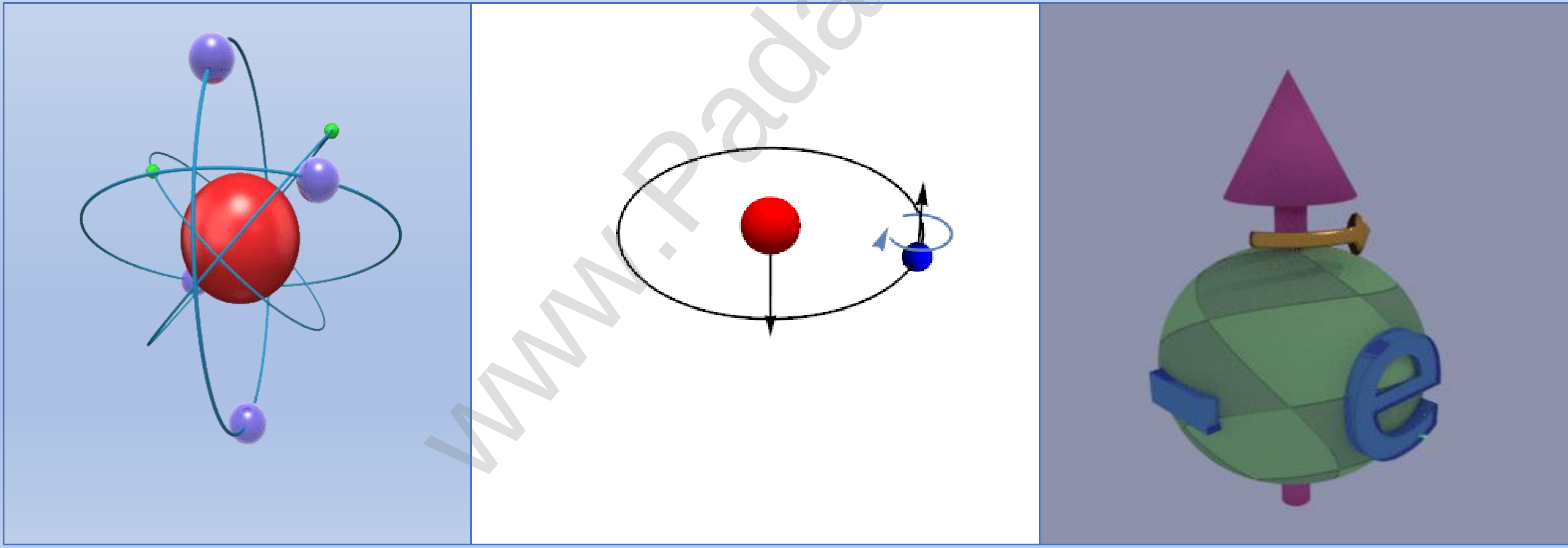
Figure 4.7 (b) M^{3+}/M^{2+} -3d series

The negative values for titanium, vanadium and chromium indicate that the higher oxidation state is preferred. If we want to reduce such a stable Cr^{3+} ion, strong reducing agent which has high negative value for reduction potential like metallic zinc $\left(E^0 = -0.76\ V\right)$ is required.

The high reduction potential of Mn^{3+}/Mn^{2+} indicates Mn^{2+} is more stable than Mn^{3+}. For Fe^{3+}/Fe^{2+} the reduction potential is 0.77V, and this low value indicates that both Fe^{3+} and Fe^{2+} can exist under normal conditions. The drop from Mn to Fe is due to the electronic structure of the ions concerned. Mn^{3+} has a $3d^4$ configuration while that of Mn^{2+} is $3d^5$. The extra stability associated with a half filled d sub shell makes the reduction of Mn^{3+} very feasible ($E^0 = +1.51V$).

Magnetic properties

Th electron is spinning around its own axis, in addition toe its orbital motion around the nucleus. Due to these motions, a tiny magnetic field is generated and it is measured in terms of magnetic moment.



Magnetic properties

Paramagnetic

Substances which contain electrons in their orbitals – PARAMAGNETIC.

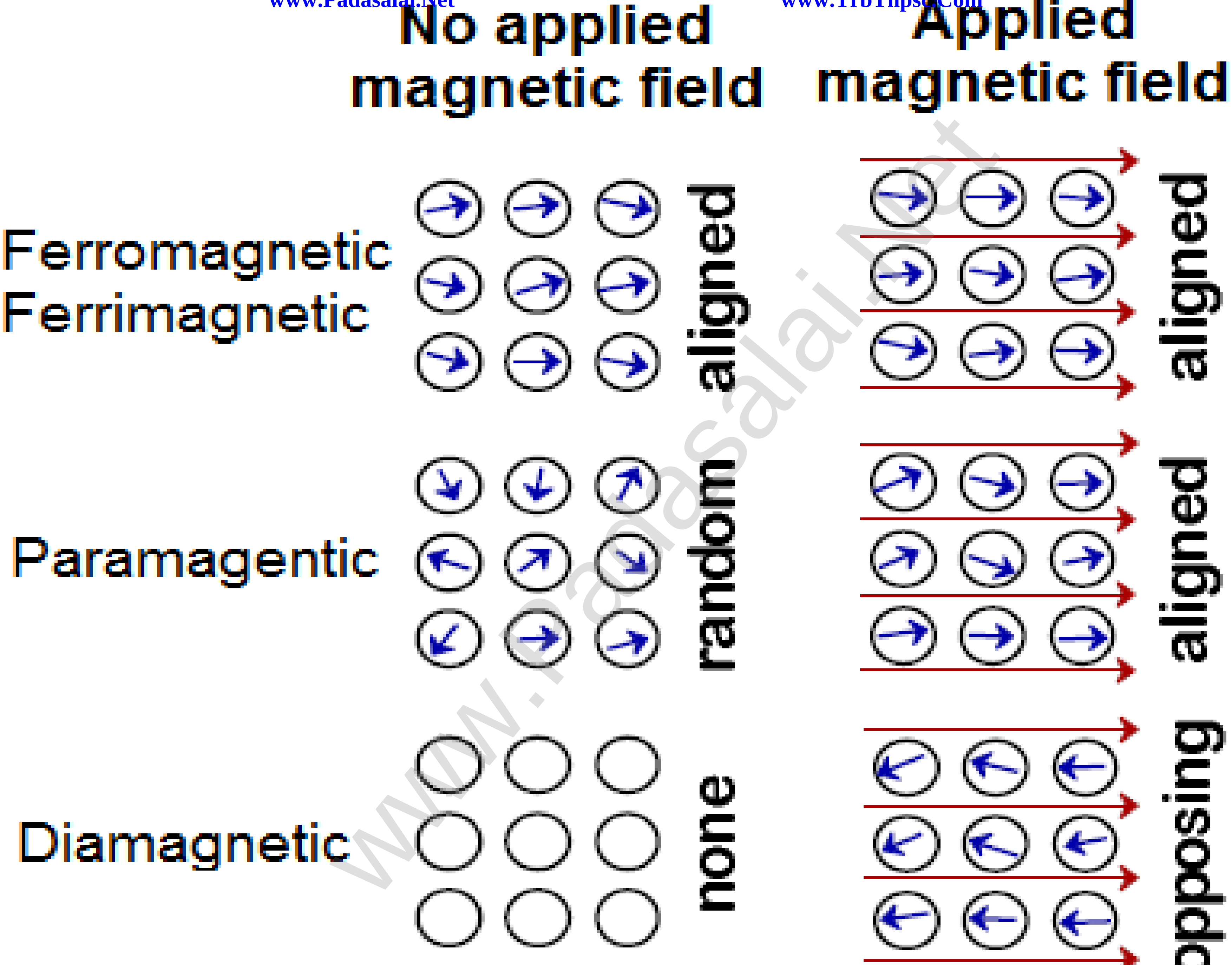
- PARAMAGNETIC SUBSTANCES are weakly attracted by the magnetic field.

Diamagnetic

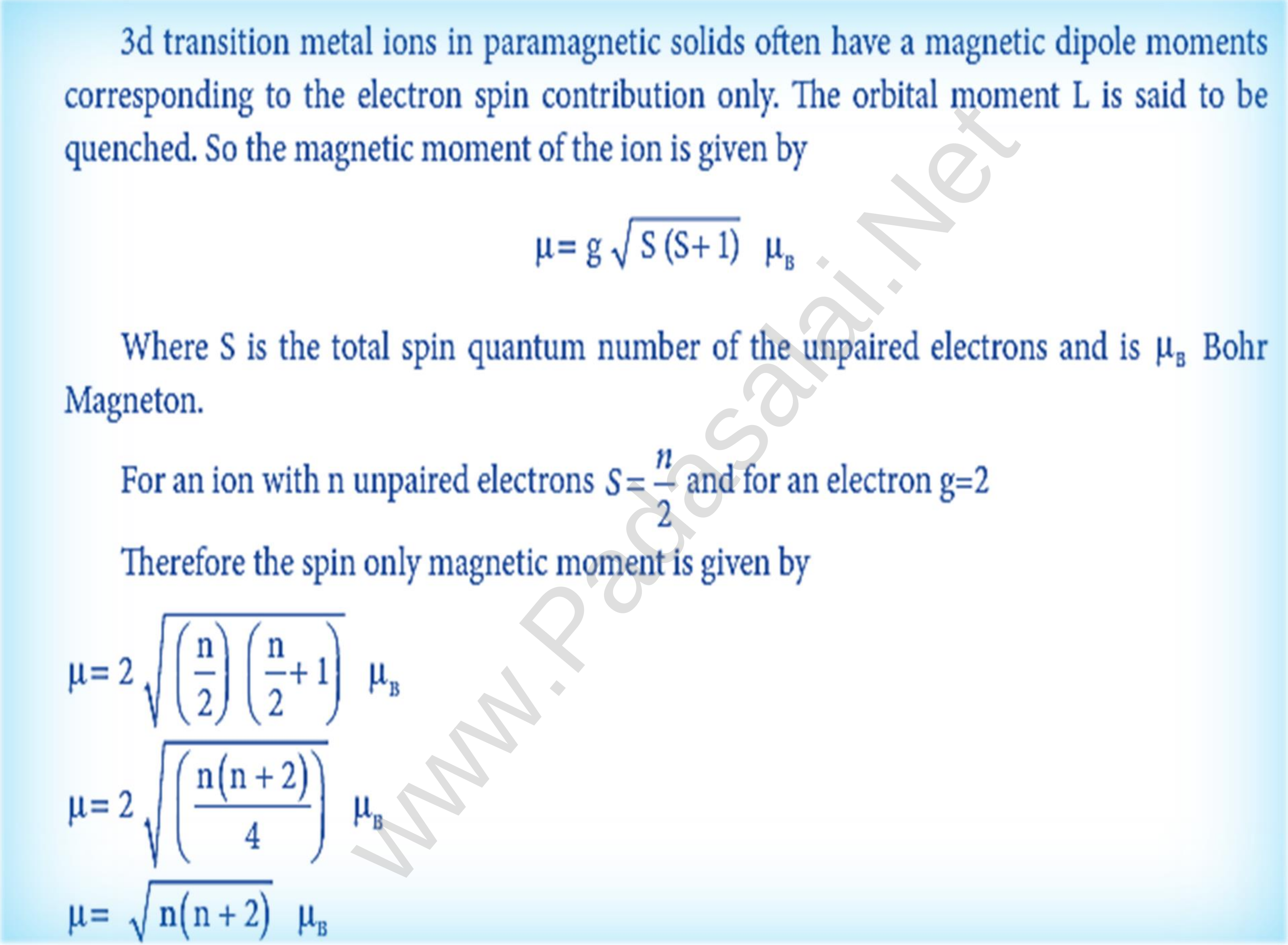
Substances which do not contain any unpaired electrons and are repelled my magnetic field _ DIAMAGNETIC.

- Substances which are attracted very strongly are said to be *ferromagnetic.*

- In fact, ferromagnetism is an extreme form of paramagnetism.


No applied magnetic field
Applied magnetic field
Ferromagnetic
Ferrimagnetic
aligned
aligned
Paramagentic
random
aligned
Diamagnetic
none
opposing

- ❑ Most of the transition elements and their compounds show paramagnetism.
- ❑ Paramagnetism arises from the presence of unpaired electrons, each such electron have a magnetic moment.
- ❑ The magnetic moment of any transition element or its compound/ion is given by (assuming no contribution from the orbital magnetic moment).
- ❑ $\mu_s = \sqrt{n(n+2)}$ BM
- ❑ Here n is the number of unpaired electrons



3d transition metal ions in paramagnetic solids often have a magnetic dipole moments corresponding to the electron spin contribution only. The orbital moment L is said to be quenched. So the magnetic moment of the ion is given by

$$\mu = g\sqrt{S(S+1)}\ \mu_B$$

Where S is the total spin quantum number of the unpaired electrons and is μ_B Bohr Magneton.

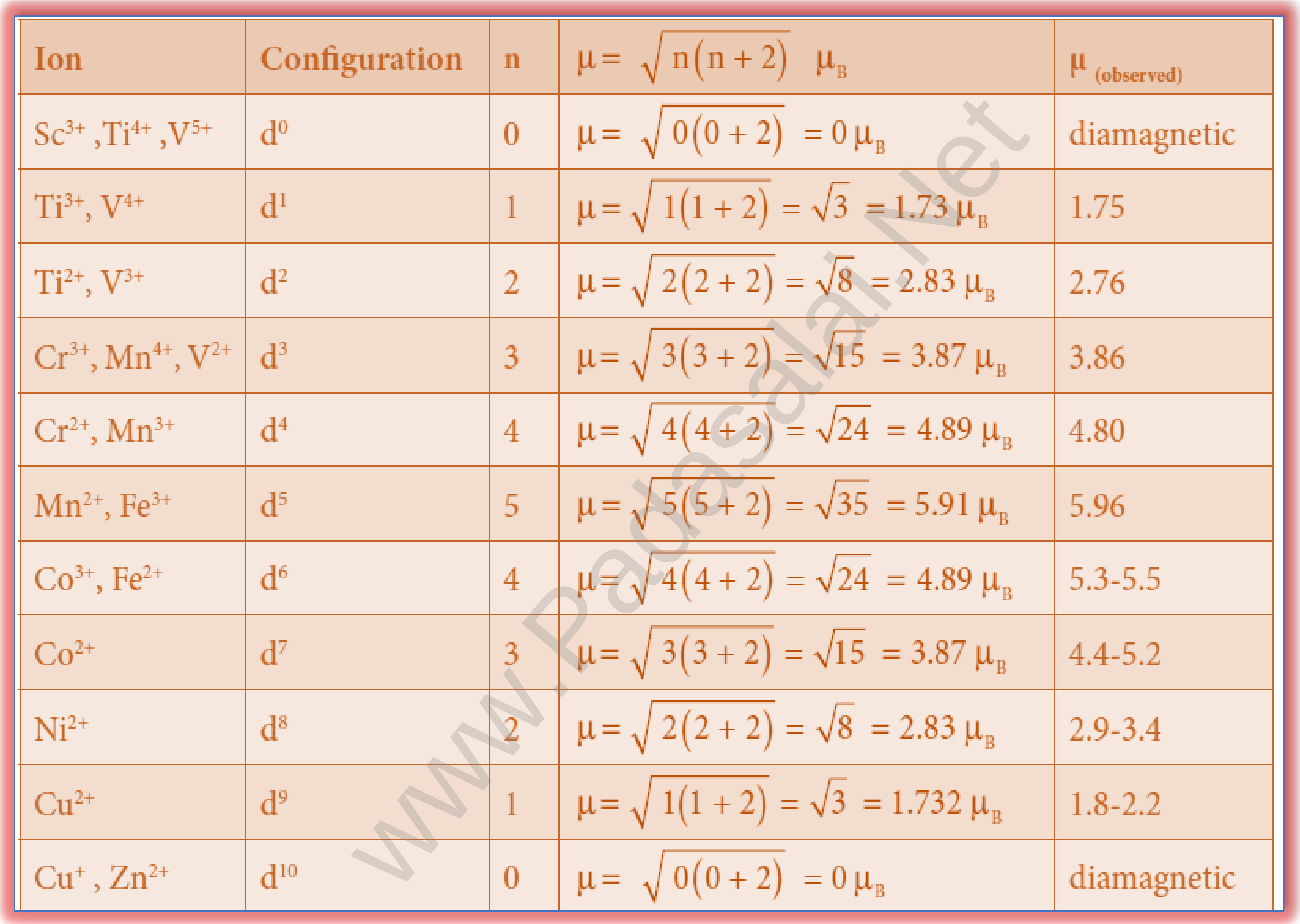
For an ion with n unpaired electrons $S = \frac{n}{2}$ and for an electron g=2

Therefore the spin only magnetic moment is given by

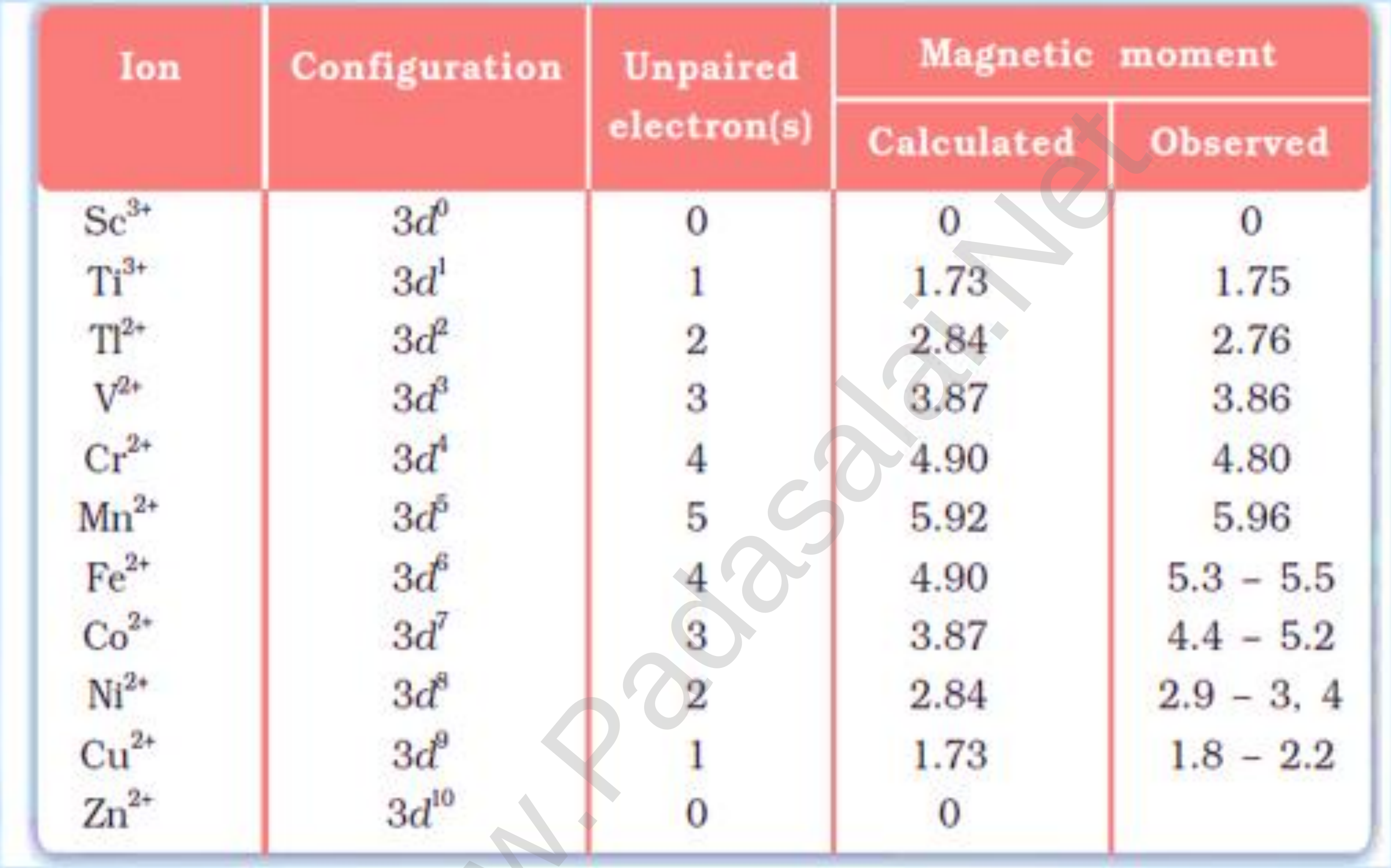
$$\mu = 2\sqrt{\left(\frac{n}{2}\right)\left(\frac{n}{2}+1\right)}\ \mu_B$$

$$\mu = 2\sqrt{\left(\frac{n(n+2)}{4}\right)}\ \mu_B$$

$$\mu = \sqrt{n(n+2)}\ \mu_B$$



Ion	Configuration	n	$\mu = \sqrt{n(n+2)}\ \mu_B$	$\mu_{\text{(observed)}}$
Sc^{3+} ,Ti^{4+} ,V^{5+}	d^0	0	$\mu = \sqrt{0(0+2)} = 0\,\mu_B$	diamagnetic
Ti^{3+}, V^{4+}	d^1	1	$\mu = \sqrt{1(1+2)} = \sqrt{3} = 1.73\,\mu_B$	1.75
Ti^{2+}, V^{3+}	d^2	2	$\mu = \sqrt{2(2+2)} = \sqrt{8} = 2.83\,\mu_B$	2.76
Cr^{3+}, Mn^{4+}, V^{2+}	d^3	3	$\mu = \sqrt{3(3+2)} = \sqrt{15} = 3.87\,\mu_B$	3.86
Cr^{2+}, Mn^{3+}	d^4	4	$\mu = \sqrt{4(4+2)} = \sqrt{24} = 4.89\,\mu_B$	4.80
Mn^{2+}, Fe^{3+}	d^5	5	$\mu = \sqrt{5(5+2)} = \sqrt{35} = 5.91\,\mu_B$	5.96
Co^{3+}, Fe^{2+}	d^6	4	$\mu = \sqrt{4(4+2)} = \sqrt{24} = 4.89\,\mu_B$	5.3-5.5
Co^{2+}	d^7	3	$\mu = \sqrt{3(3+2)} = \sqrt{15} = 3.87\,\mu_B$	4.4-5.2
Ni^{2+}	d^8	2	$\mu = \sqrt{2(2+2)} = \sqrt{8} = 2.83\,\mu_B$	2.9-3.4
Cu^{2+}	d^9	1	$\mu = \sqrt{1(1+2)} = \sqrt{3} = 1.732\,\mu_B$	1.8-2.2
Cu^{+} , Zn^{2+}	d^{10}	0	$\mu = \sqrt{0(0+2)} = 0\,\mu_B$	diamagnetic



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

- The paramagnetism first increases in any transition element series, and then decreases. The maximum paramagnetism is seen around the middle of the series.

Questions-

Q. 1: Which ion has maximum magnetic moment

(a) V^{3+} (b) Mn^{3+}

(c) Fe^{3+} (d) Cu^{2+}

Ans: c

Q.2. What is the magnetic moment of Mn^{2+} ion (Z= 25) in aqueous solution ?

Ans.- With atomic number 25, the divalent Mn^{2+} ion in aqueous solution will have d^5 *configuration (five unpaired electrons).Hence, The magnetic moment, μ is*

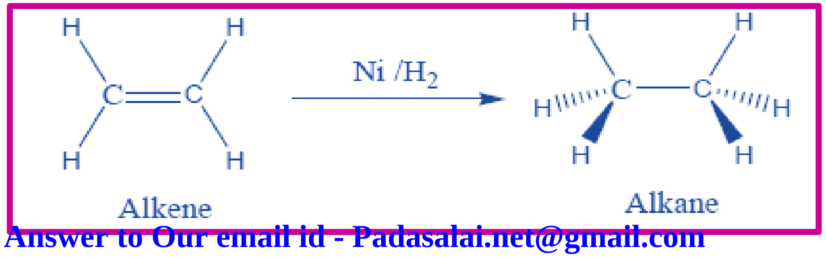
$$\mu = \sqrt{5(5 + 2)} = 5.92 BM$$

Catalytic properties

- ☐ The chemical industries manufacture a number of products such as polymers, flavours, drugs etc., Most of the manufacturing processes have adverse effect on the environment so there is an interest for eco friendly alternatives.
- ☐ In this context, catalyst based manufacturing processes are advantageous, as they require low energy, minimize waste production and enhance the conversion of reactants to products.
- ☐ Many industrial processes use transition metals or their compounds as catalysts.
- ☐ Transition metal has energetically available d orbitals that can accept electrons from reactant molecule or metal can form bond with reactant molecule using its d electrons.

For example,

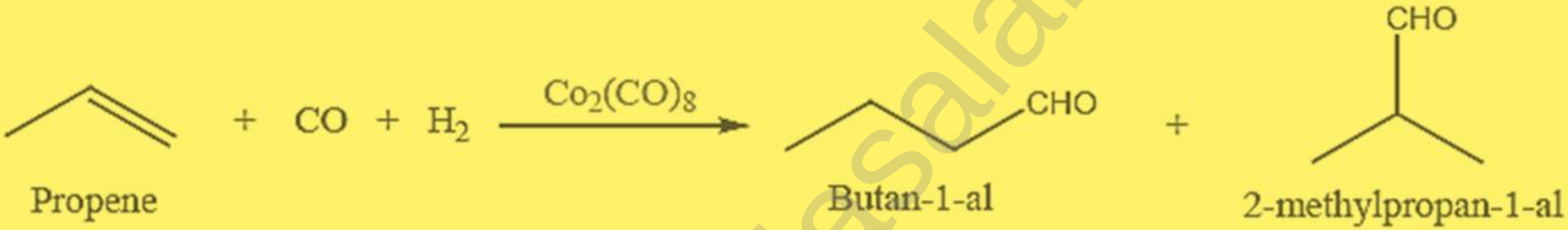
- ☐ Ithe catalytic hydrogenation of an alkene, the alkene bonds to an active site by using its π electrons with an empty d orbital of the catalyst.
- ☐ The σ bond in the hydrogen molecule breaks, and each hydrogen atom forms a bond with a d electron on an atom in the catalyst.
- ☐ The two hydrogen atoms then bond with the partially broken π -bond in the alkene to form an alkane.



- In certain catalytic processes the variable oxidation states of transition metals find applications.
- For example, in the manufacture of sulphuric acid from SO_3, vanadium pentoxide (V_2O_5) is used as a catalyst to oxidise SO_2. In this reaction V_2O_5 is reduced to vanadium (IV) Oxide (VO_2).

Some more examples are discussed below,

(i) Hydroformylation of olefins



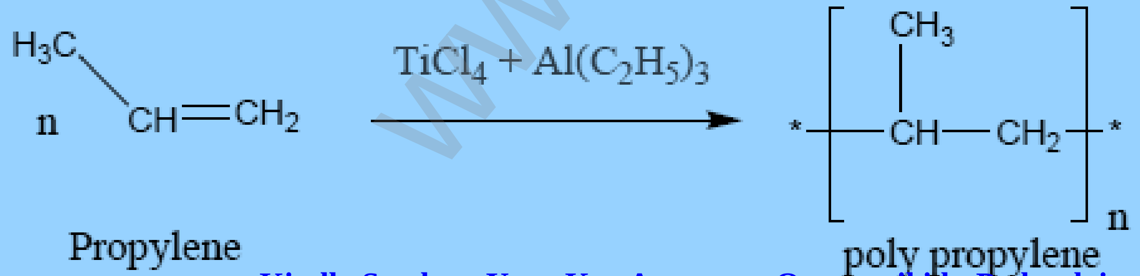
(ii) Preparation acetic acid from acetaldehyde.

$$CH_3\text{-}CHO + CO \xrightarrow{\text{Rh / Ir complex}} CH_3\text{-}COOH$$

Acetaldehyde
Acetic acid

(iii) Zeigler – Natta catalyst

A mixture of TiCl4 and trialkyl aluminium is used for polymerization.



Alloy formation

- An alloy is formed by blending a metal with one or more other elements.

- The elements may be metals or non-metals or both.

- The bulk metal is named as solvent, and the other elements in smaller portions are called solute.

According to Hume-Rothery rule

- To form a substitute alloy the difference between the atomic radii of solvent and solute is less than 15%.
- Both the solvent and solute must have the same crystal structure and valence and their electro negativity difference must be close to zero.
- Transition metals satisfying these mentioned conditions form a number of alloys among themselves, since their atomic sizes are similar and one metal atom can be easily replaced by another metal atom from its crystal lattice to form an alloy.
- The alloys so formed are hard and often have high melting points.

Examples:

Ferrous alloys, gold – copper alloy, chrome alloys etc.,

Alloys

- Transition metals are often mixed with other metals or non-metals to form **alloys**. This changes the property of the metal so it is better suited for a particular purpose.
  - **Steel** is an alloy of **iron** and other elements, such as **carbon**, **nickel**, **manganese** and **chromium**. There are many different types of steel, each with different properties.
  - **Brass** is an alloy of 70% **copper** and 30% **zinc**.
  - **Bronze** is an alloy of 90% **copper** and 10% **tin**.
  - **Cupronickel** is an alloy of 75% **copper** and 25% **nickel** – it is used in 'silver' coins.

Formation of interstitial compounds

- An interstitial compound or alloy is a compound that is formed when small atoms like hydrogen, boron, carbon or nitrogen are trapped in the interstitial holes in a metal lattice.
- They are usually non-stoichiometric compounds.
- Transition metals form a number of interstitial compounds such as TiC, $ZrH_{1.94}$, Mn_4N etc .

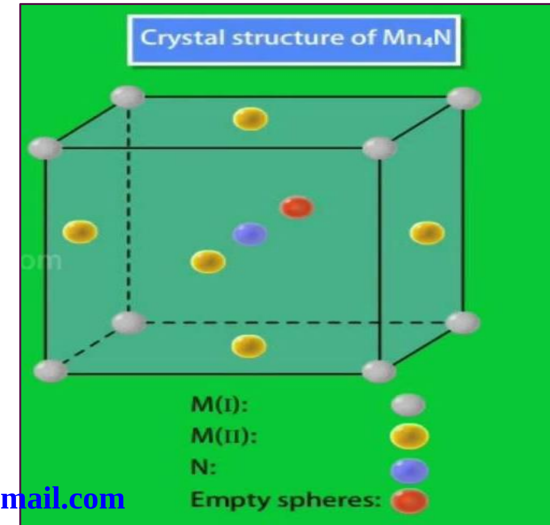
The elements that occupy the metal lattice provide them new properties.

(i) They are hard and show electrical and thermal conductivity

(ii) They have high melting points higher than those of pure metals

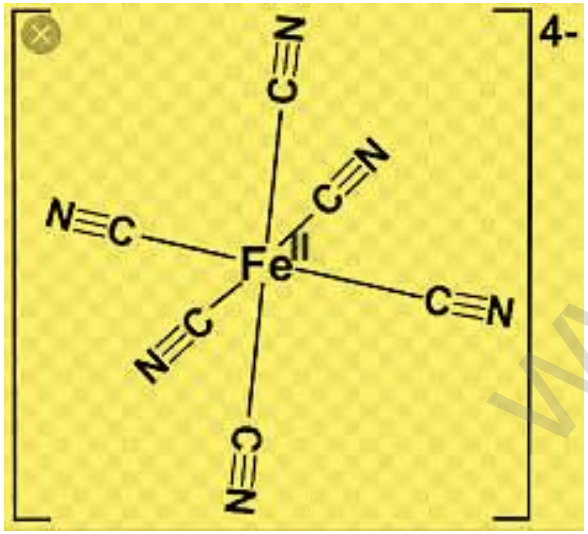
(iii) Transition metal hydrides are used as powerful reducing agents

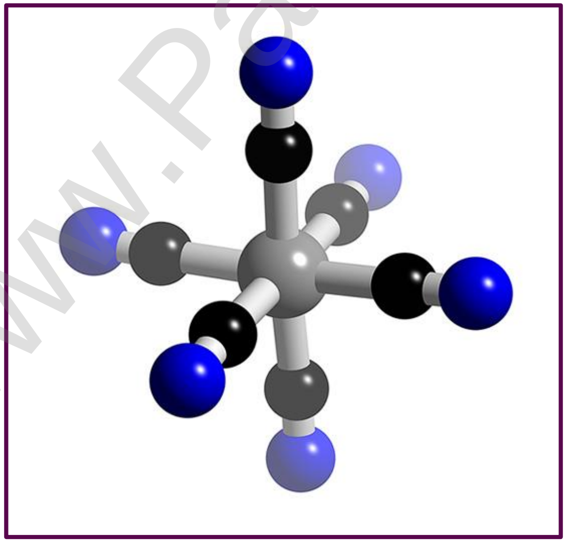
(iv) Metallic carbides are chemically inert.



Formation of complexes

- **Transition elements have a tendency to form coordination compounds with a species that has an ability to donate an electron pair to form a coordinate covalent bond.**
- ***Transition metal ions are small and highly charged and they have vacant low energy orbitals to accept an electron pair donated by other groups. Due to these properties, transition metals form large number of complexes.***
- **Examples: $[Fe(CN)_6]^{4-}$, $[Co(NH_3)_6]^{3+}$,**





Important compound of Transition elements

Oxides and Oxoanions of Metals:

- Generally, *transition metal oxides are formed by the reaction of transition metals with molecular oxygen at high temperatures.*
- Except the first member of 3d series, Scandium, all other transition elements form ionic metal oxides.
- The oxidation number of metal in metal oxides ranges from +2 to +7.
- As the oxidation number of a metal increases, ionic character decreases, for example, Mn_2O_7 is covalent. Mostly higher oxides are acidic in nature, Mn_2O_7 dissolves in water to give permanganic acid ($HMnO_4$) , similarly CrO_3 gives chromic acid (H_2CrO_4) and dichromic acid ($H_2Cr_2O_7$).
- Generally lower oxides may be amphoteric or basic, for example, Chromium (III) oxide - Cr_2O_3, is amphoteric and Chromium(II) oxide, CrO, is basic in nature.

Oxides and Oxoanions of Metals

- The elements of first transition series form variety of oxides of different oxidation states having general formula MO, M_2O_3, M_3O_6, MO_2, MO_3.
- Theses oxides are generally formed by heating the metal with oxygen at high temperature.

- In general

  lower oxidation state metal – BASIC

  Higher oxidation state metal – ACIDIC

  Intermediate oxidation state - AMPHOTERIC
- Example

MnO (+2)basic, **Mn_2O_3** (+3)Basic, **Mn_3O_4** (+8/3)Ampho,

MnO_2 (+4) Ampho, **Mn_2O_7** (+7)Acidic

Sc – **Sc_2O_3** Basic

Ti – **TiO** Basic, **Ti_2O_2** Basic, **TiO_2** Amphoteric

V – **VO** Basic, **V_2O_3** Basic, **VO_2** Ampho, **V_2O_5** Acidic

Cr – **CrO** Basic, **Cr_2O_3** Ampho, **CrO_2** Ampho,
CrO_3Acidic

Mn – **MnO** basic, **Mn_2O_3** Basic, **Mn_3O_4** Ampho,
MnO_2 Ampho, **Mn_2O_7** Acidic

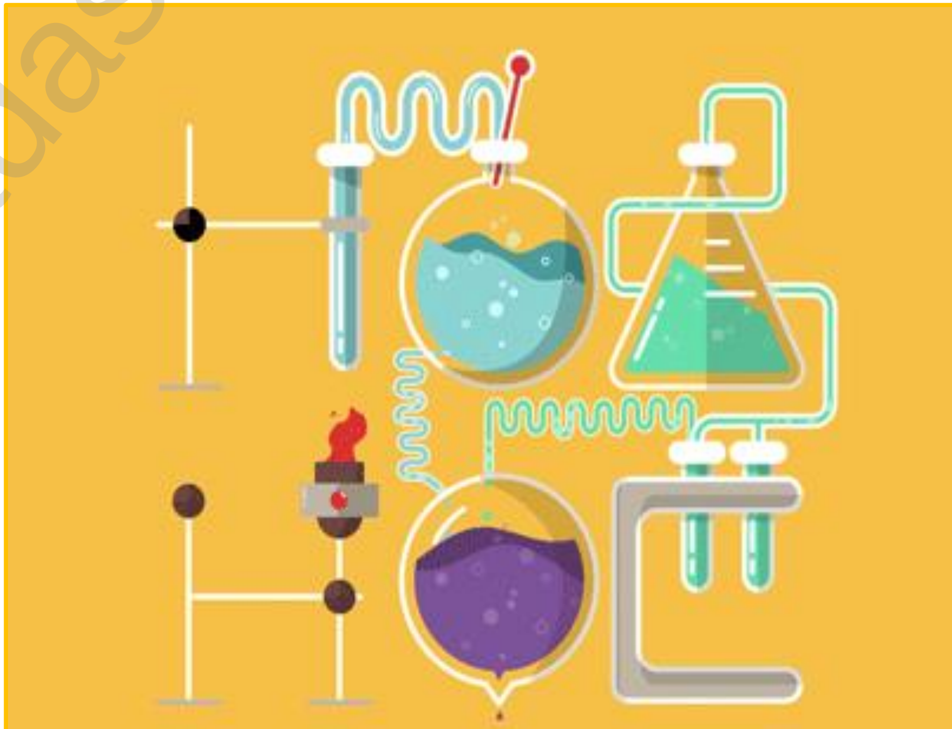
Fe – **FeO** Basic, **Fe_2O_3** Amph, **Fe_3O_4** Basic

Co – **CoO** Basic

Ni – **NiO** Basic

Cu – **Cu_2O** Basic, **CuO** Ampho

Zn – **ZnO** Ampho



POTASSIUM DICHROMATE($K_2Cr_2O_7$)

$K_2Cr_2O_7$

Preparation:

STEP 1: Conversion of Chromate ore into potassium di chromate :

Potassium dichromate is prepared from chromate ore. The ore is concentrated by gravity separation. It is then mixed with excess sodium carbonate and lime and roasted in a reverberatory furnace.

$$4\,FeCr_2O_4 + 8\,Na_2CO_3 + 7\,O_2 \xrightarrow{900 - 1000^0C} 8\,Na_2CrO_4 + 2\,Fe_2O_3 + 8\,CO_2 \uparrow$$

STEP 2 : Conversion of Sodium chromate to Sodium di chromate:

The roasted mass is treated with water to separate soluble sodium chromate from insoluble iron oxide.

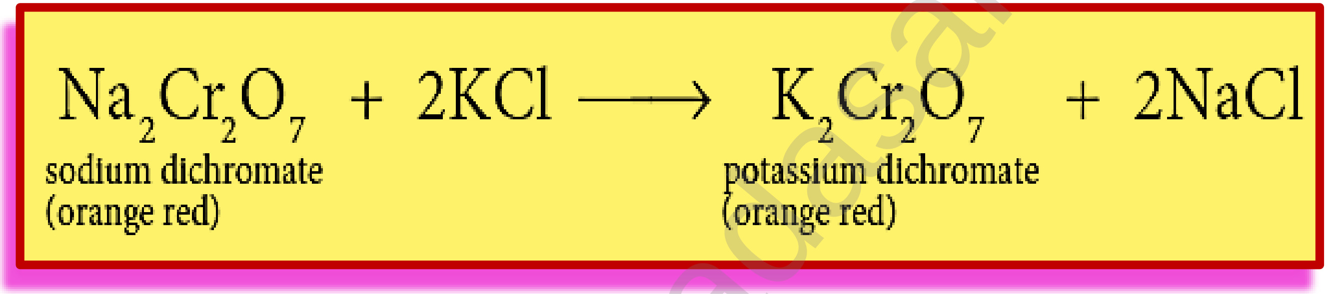
The yellow solution of sodium chromate is treated with concentrated sulphuric acid which converts sodium chromate into sodium dichromate.

$$\underset{\substack{\text{sodium chromate}\\\text{(yellow)}}}{2\,Na_2CrO_4} + H_2SO_4 \longrightarrow \underset{\substack{\text{sodium dichromate}\\\text{(orange red)}}}{Na_2Cr_2O_7} + Na_2SO_4 + H_2O$$

STEP 3: Conversion of Sodium di chromate to Potassium di chromate:

The above solution is concentrated to remove less soluble sodium sulphate. The resulting solution is filtered and further concentrated. It is cooled to get the crystals of $Na_2SO_4.2H_2O$.

The saturated solution of sodium dichromate in water is mixed with KCl and then concentrated to get crystals of NaCl. It is filtered while hot and the filtrate is cooled to obtain $K_2Cr_2O_7$ crystals.



$$\underset{\substack{\text{sodium dichromate}\\\text{(orange red)}}}{Na_2Cr_2O_7} + 2KCl \longrightarrow \underset{\substack{\text{potassium dichromate}\\\text{(orange red)}}}{K_2Cr_2O_7} + 2NaCl$$

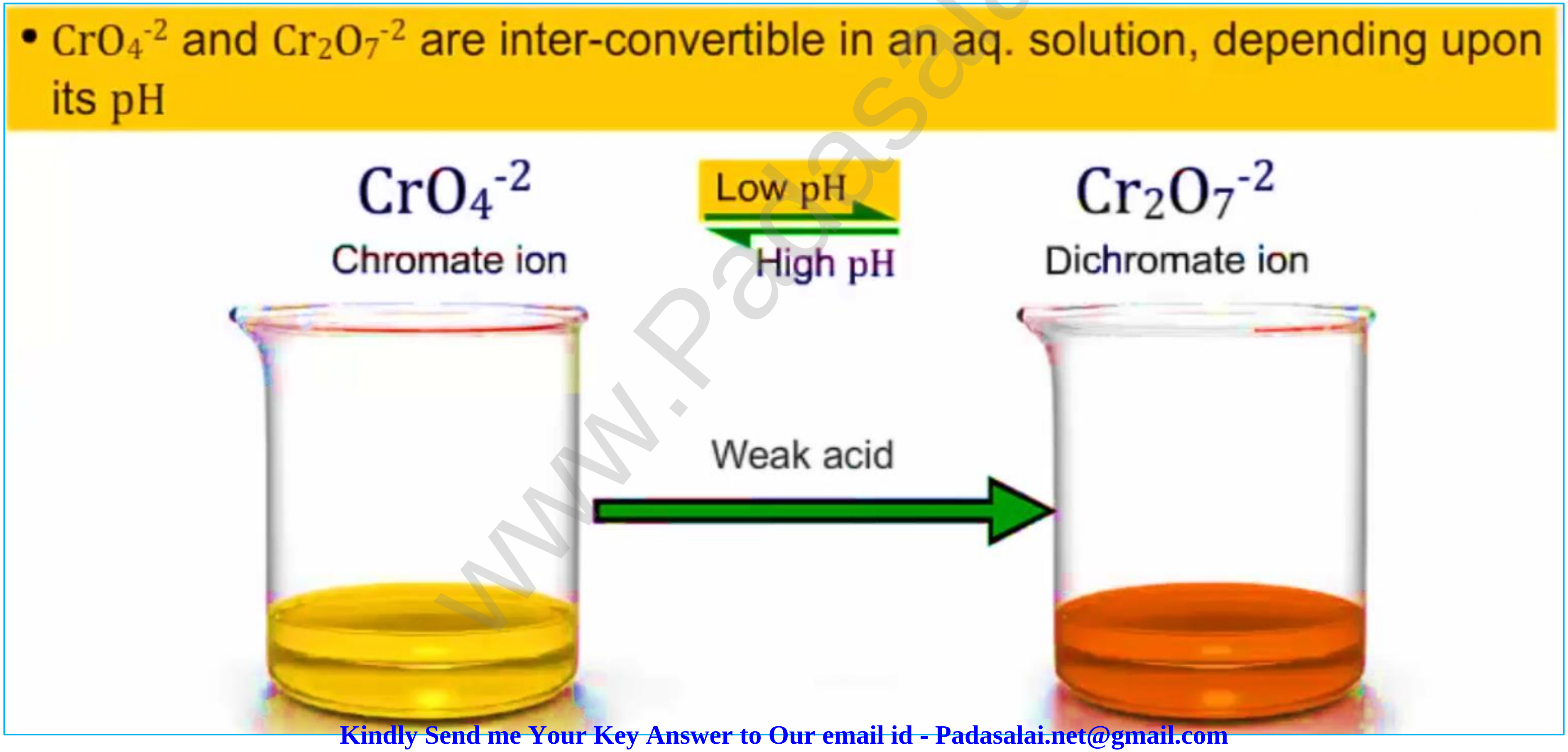
Physical properties Of $K_2Cr_2O_7$:

- Potassium dichromate is an **orange red crystalline solid** which melts at 671K and it is moderately soluble in cold water, but very much soluble in hot water.

- **On heating it decomposes and forms Cr_2O_3 and molecular oxygen. As it emits toxic chromium fumes upon heating, it is mainly replaced by sodium dichromate.**

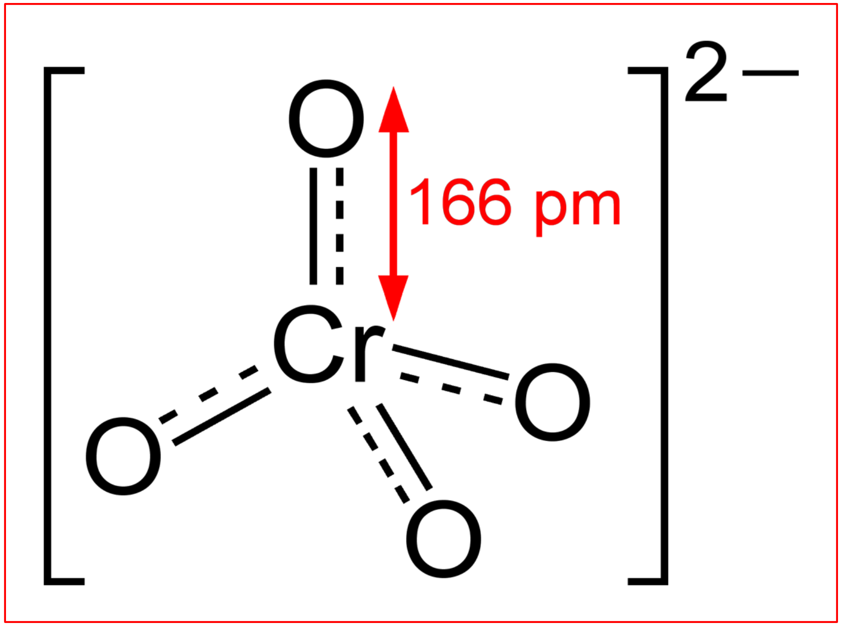
$$\underset{\text{potassium dichromate}}{4\ K_2Cr_2O_7} \xrightarrow{\Delta} \underset{\text{potassium chromate}}{4\ K_2CrO_4} + \underset{\text{chromium(III) oxide}}{2\ Cr_2O_3} + 3O_2\uparrow$$

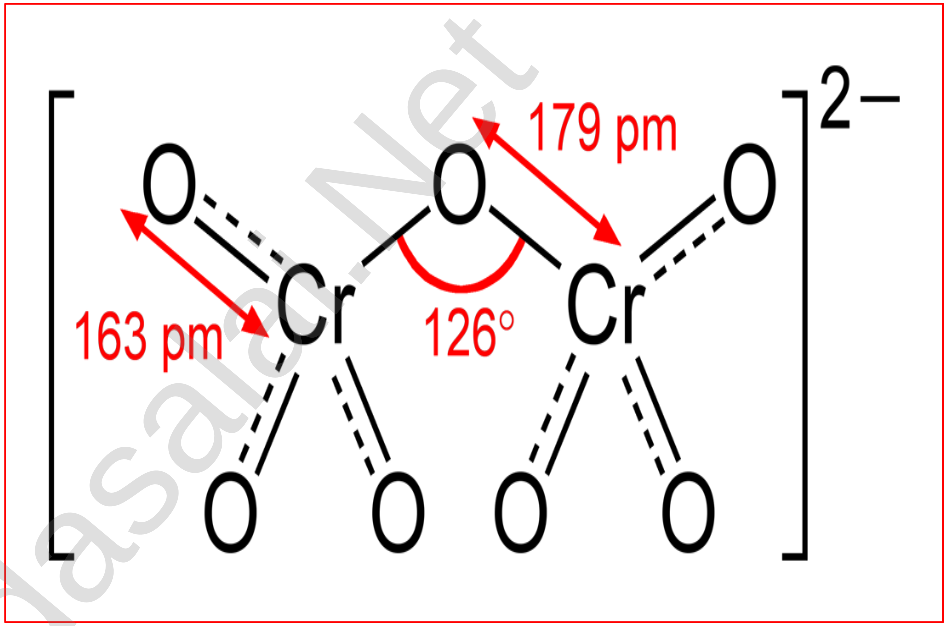
- Both chromate and dichromate ion are oxo anions of chromium and they are moderately strong oxidizing agents.
- In these ions chromium is in +6 oxidation state.
- In an aqueous solution, chromate and dichromate ions can be interconvertible, and in an alkaline solution chromate ion is predominant, whereas dichromate ion becomes predominant in acidic solutions.

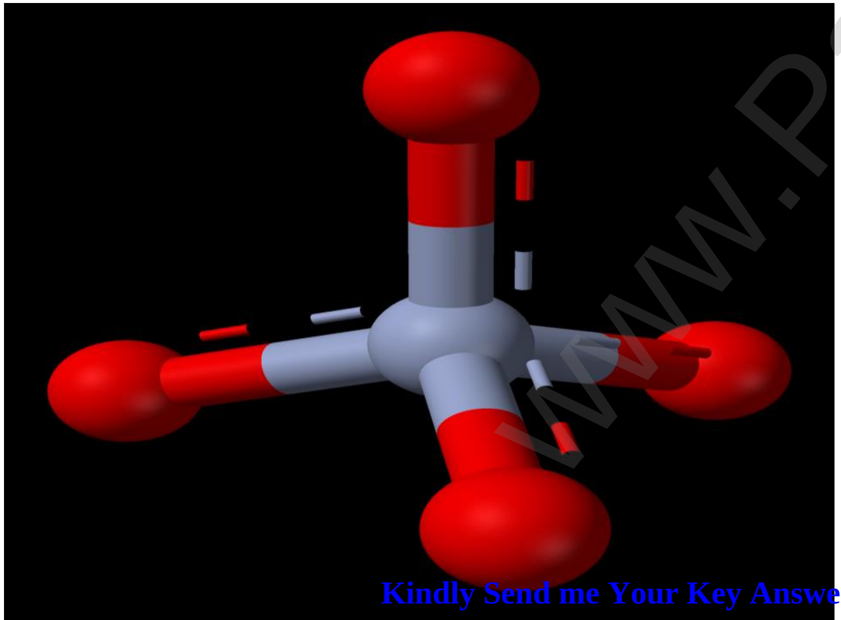


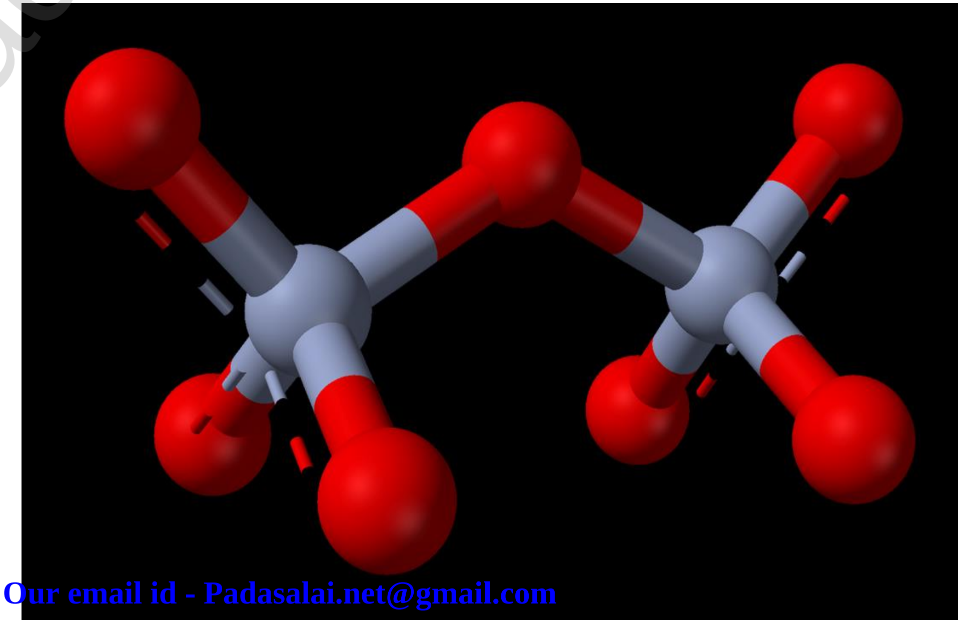
- CrO_4^{-2} and $Cr_2O_7^{-2}$ are inter-convertible in an aq. solution, depending upon its pH

Structure of dichromate ion:









Chemical properties of $K_2Cr_2O_7$

1. Oxidation

- Potassium dichromate is a powerful oxidising agent in acidic medium. Its oxidising action in the presence of H^+ ions .
- You can note that the change in the oxidation state of chromium from Cr^{6+} to Cr^{3+}.
- Its oxidising action is shown below.

$$\boxed{Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7\,H_2O}$$

- The oxidising nature of potassium dichromate (dichromate ion) is illustrated in the following examples.

(i) It oxidises ferrous salts to ferric salts:

$$\boxed{Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O}$$

(ii) It oxidises iodide ions to iodine:

$$\boxed{Cr_2O_7^{2-} + 6I^- + 14H^+ \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O}$$

(iii) It oxidises sulphide ion to Sulphur :

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

(iv) It oxidises sulphur dioxide to sulphate ion :

$$Cr_2O_7^{2-} + 3SO_2 + 2H^+ \longrightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O$$

(v) It oxidises stannous salts to stannic salt :

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

(vi) It oxidises alcohols to acids:

$$2K_2Cr_2O_7 + 8H_2SO_4 + 3CH_3CH_2OH \longrightarrow 2K_2SO_4 + 2Cr_2(SO_4)_3 + 3CH_3COOH + 11H_2O$$

2. Chromyl chloride test:

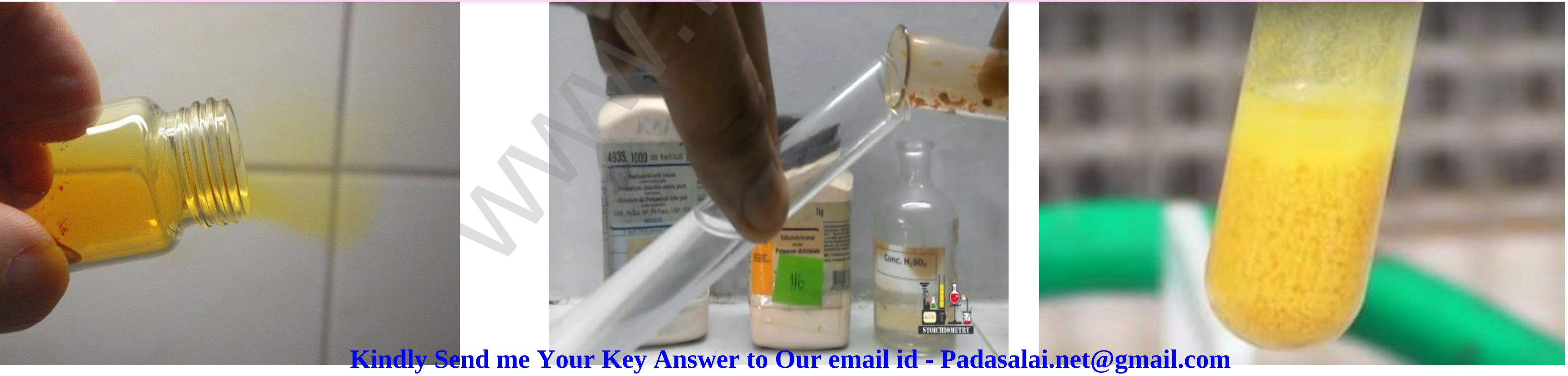
- When *potassium dichromate is heated with any chloride salt in the presence of Conc H_2SO_4, orange red vapours of chromyl chloride (CrO_2Cl_2) is evolved.* This reaction is used to confirm the presence of chloride ion in inorganic qualitative analysis.

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \longrightarrow 2KHSO_4 + 4NaHSO_4 + \underset{\text{Chromyl chloride}}{2CrO_2Cl_2} \uparrow + 3H_2O$$

- The chromyl chloride vapours are dissolved in **sodium hydroxide solution** and then acidified with acetic acid and treated with lead acetate. A yellow precipitate of lead chromate is obtained.

$$CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O$$

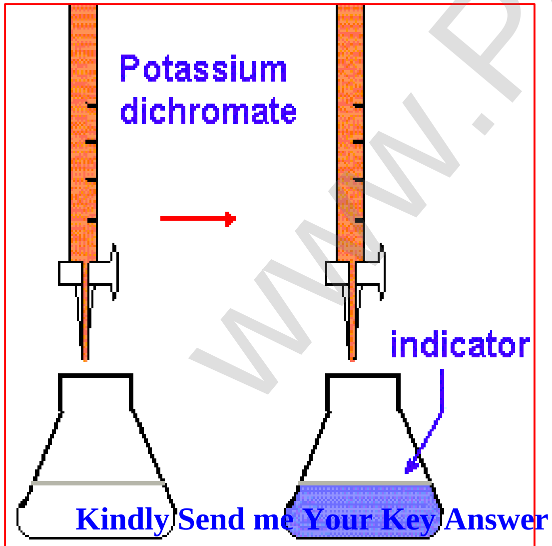
$$Na_2CrO_4 + (CH_3COO)_2Pb \longrightarrow \underset{\substack{\textit{Leadchromate} \\ (\textit{Yellowprecipitate})}}{PbCrO_4} \downarrow + 2CH_3COONa$$



Uses of potassium dichromate:

Some important uses of potassium dichromate are listed below.

1. It is used as a strong oxidizing agent.
2. It is used in dyeing and printing.
3. It used in leather tanneries for chrome tanning.
4. It is used in quantitative analysis for the estimation of iron compounds and iodides.



Potassium permanganate - $KMnO_4$

$KMnO_4$

Preparation:

- Potassium permanganate is prepared from pyrolusite (MnO_2) ore.
- The preparation involves the following steps.

(i) Conversion of MnO_2 to potassium manganate:

- Powdered ore is fused with KOH in the presence of air or oxidising agents like KNO_3 or $KClO_3$.
- A green coloured potassium manganate is formed.

$$2MnO_2 + 4KOH + O_2 \longrightarrow \underset{\substack{\text{potassium manganate}\\ \text{(Green)}}}{2K_2MnO_4} + 2H_2O$$

(ii) Oxidation of potassium manganate to potassium permanganate:

- Potassium manganate thus obtained can be oxidised in two ways , either by chemical oxidation or electrolytic oxidation.

Chemical oxidation:

In this method potassium manganate is treated with ozone (O_3) or chlorine to get potassium permanganate.

$$2MnO_4^{2-} + O_3 + H_2O \longrightarrow 2MnO_4^{-} + 2OH^{-} + O_2$$

$$2MnO_4^{2-} + Cl_2 \longrightarrow 2MnO_4^{-} + 2Cl^{-}$$

Electrolytic oxidation

In this method aqueous solution of potassium manganate is electrolyzed in the presence of little alkali.

$$K_2MnO_4 \rightleftharpoons 2K^{+} + MnO_4^{2-}$$

$$H_2O \rightleftharpoons H^{+} + OH^{-}$$

Manganate ions are converted into permanganate ions at anode.

$$\underset{\text{Green}}{2MnO_4^{2-}} \rightleftharpoons \underset{\text{purple}}{2MnO_4^{-}} + 2e^{-}$$

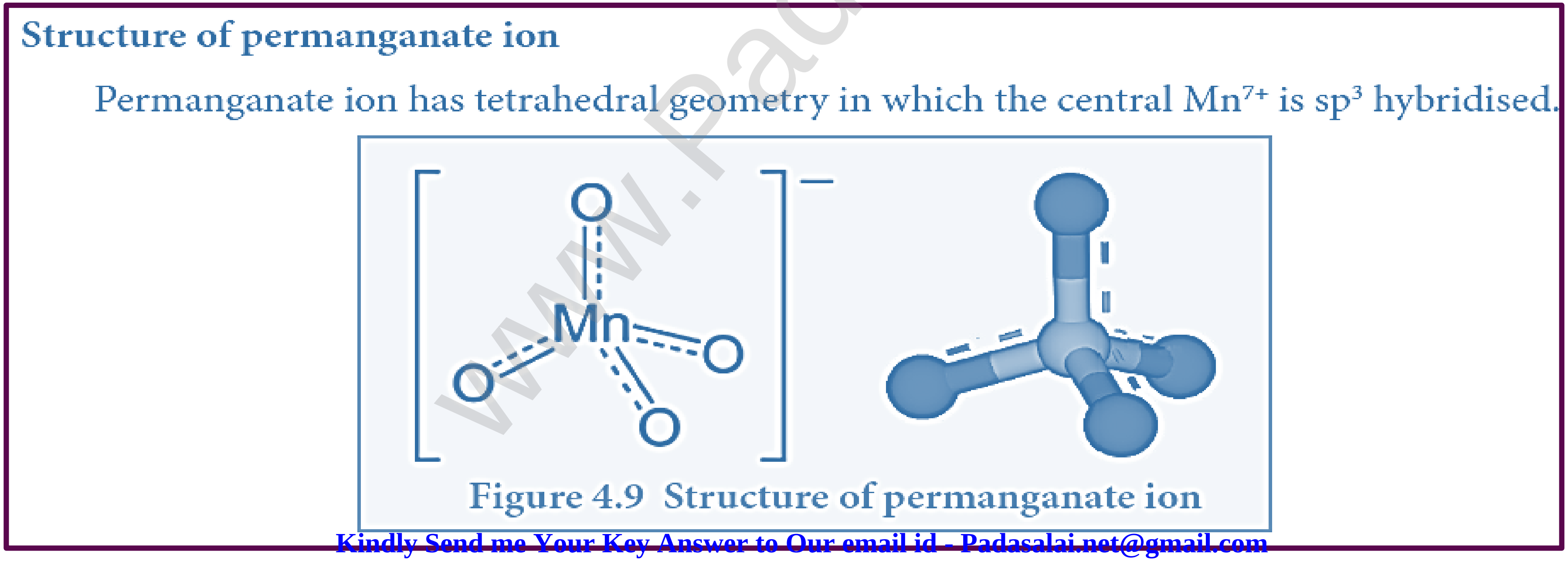
H_2 is liberated at the cathode.

$$2H^{+} + 2e^{-} \longrightarrow H_2 \uparrow$$

The purple coloured solution is concentrated by evaporation and forms crystals of potassium permanganate on cooling.

Physical properties:

- **Potassium permanganate exists in the form of dark purple crystals which melts at 513 K. It is sparingly soluble in cold water but, fairly soluble in hot water.**



Structure of permanganate ion

Permanganate ion has tetrahedral geometry in which the central Mn^{7+} is sp^3 hybridised.

Figure 4.9 Structure of permanganate ion

Chemical properties:

1. Action of heat:

- When heated, potassium permanganate decomposes to form potassium manganate and dioxide.

$$2KMnO_4 \longrightarrow 2K_2MnO_4 + MnO_2 + O_2$$

2. Action of conc H_2SO_4 :

- On treating with cold conc H_2SO_4, it decomposes to form manganese heptoxide, which subsequently decomposes explosively.

$$\underset{\text{(cold)}}{2KMnO_4 + 2H_2SO_4} \longrightarrow Mn_2O_7 + 2KHSO_4 + H_2O$$

$$2Mn_2O_7 \xrightarrow{\Delta} 4MnO_2 + 3O_2$$

But with hot conc H_2SO_4, potassium permanganate give $MnSO_4$

$$\underset{\text{(hot)}}{4KMnO_4 + 6H_2SO_4} \longrightarrow 4MnSO_4 + 2K_2SO_4 + 6H_2O + 5O_2$$

3. Oxidising property:

- Potassium permanganate is a strong oxidising agent, its oxidising action differs in different reaction medium

a) In neutral medium:

- In neutral medium, it is reduced to MnO_2

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$$

(i) It oxidises H_2S to Sulphur:

$$2MnO_4^- + 3H_2S \longrightarrow 2MnO_2 + 3S + 2OH^- + 2H_2O$$

(ii) It oxidises thiosulphate into sulphate:

$$8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 6SO_4^{2-} + 8MnO_2 + 2OH^-$$

b) In alkaline medium:

In the presence of alkali metal hydroxides, the permanganate ion is converted into manganate.

$$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$$

This manganate is further reduced to MnO_2 by some reducing agents.

$$MnO_4^{2-} + H_2O \longrightarrow MnO_2 + 2OH^- + [O]$$

So the overall reaction can be written as follows.

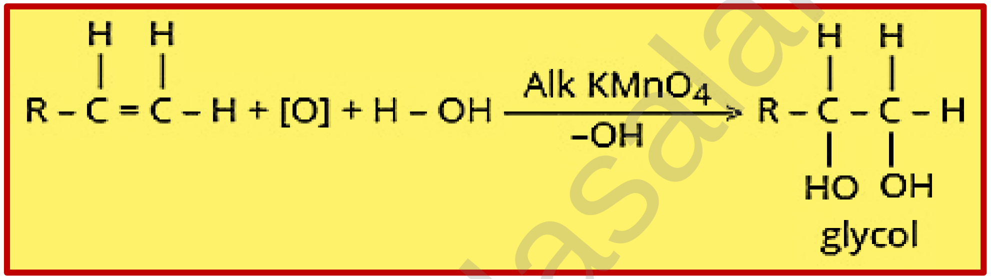
$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$$

This reaction is similar as that for neutral medium.

Bayer's reagent:

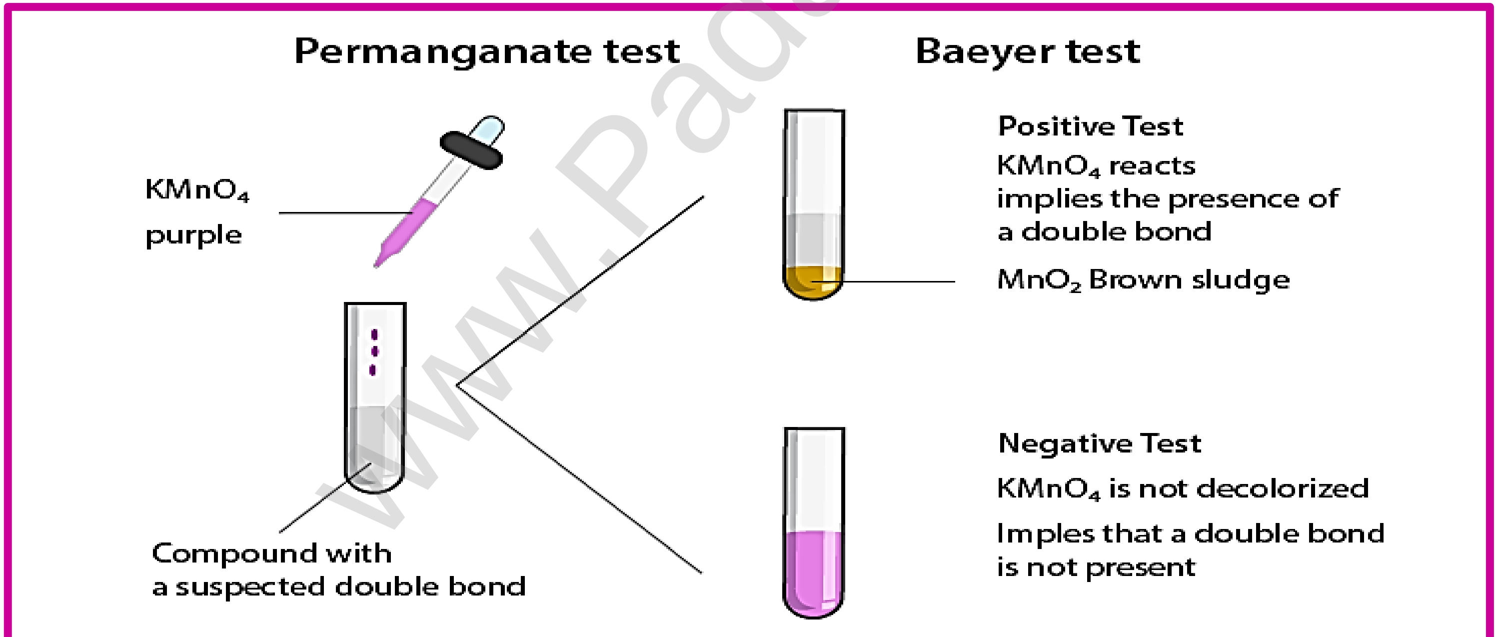
- Cold dilute alkaline $KMnO4$ is known as Bayer's reagent. It is used to oxidise alkenes into diols.

- For example, ethylene can be converted into ethylene glycol and this reaction is used as a test for unsaturation.



$$R-\overset{H}{C}=\overset{H}{C}-H+[O]+H-OH \xrightarrow[-OH]{\text{Alk } KMnO_4} R-\underset{HO}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-H$$

glycol



Positive Test

$KMnO_4$ reacts implies the presence of a double bond

MnO_2 Brown sludge

Negative Test

$KMnO_4$ is not decolorized

Imples that a double bond is not present

c) In acid medium:

- In the presence of dilute sulphuric acid, potassium permanganate acts as a very strong oxidising agent. Permanganate ion is converted into Mn^{2+} ion.

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

The oxidising nature of potassium permanganate (permanganate ion) in acid medium is illustrated in the following examples.

(i) It oxidises ferrous salts to ferric salts.

$$2MnO_4^- + 10Fe^{2+} + 16H^+ \longrightarrow 2Mn^{2+} + 10Fe^{3+} + 8H_2O$$

(ii) It oxidises iodide ions to iodine

$$2MnO_4^- + 10\,I^- + 16H^+ \longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O$$

(iii) It oxidises oxalic acid to CO_2 :

$$2MnO_4^- + 5(COO)_2^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

(iv) It oxidises sulphide ion to Sulphur :

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

(v) It oxidises nitrites to nitrates:

$$2MnO_4^- + 5NO_2^- + 6H^+ \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$$

(vi) It oxidises alcohols to aldehydes :

$$2KMnO_4 + 3H_2SO_4 + 5CH_3CH_2OH \longrightarrow K_2SO_4 + 2MnSO_4 + 5CH_3CHO + 8H_2O$$

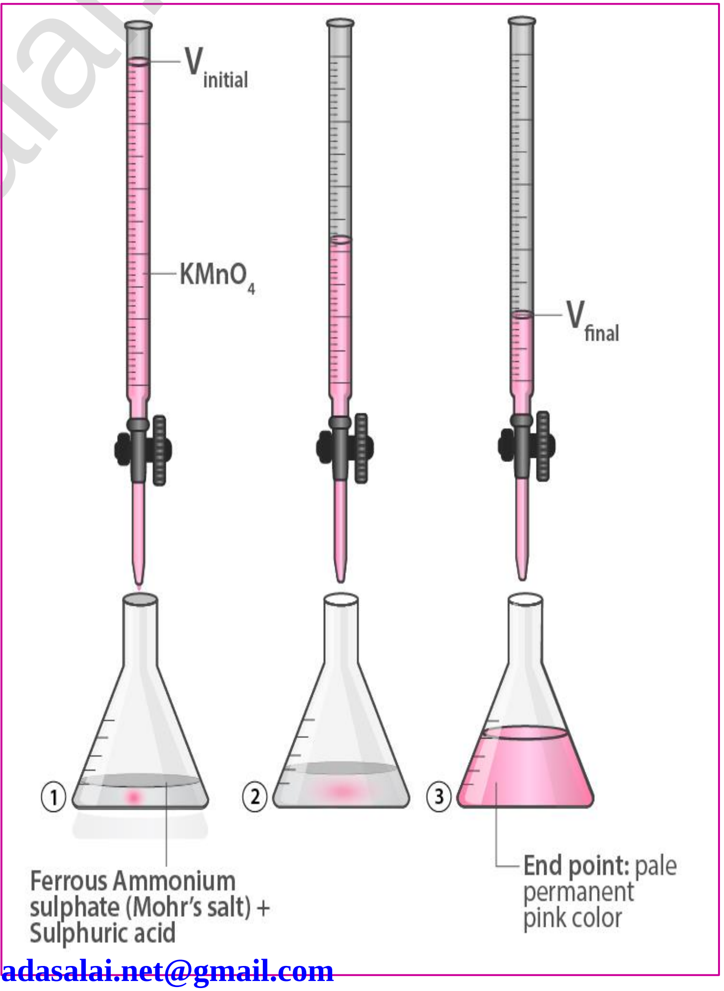
(vii) It oxidises sulphite to sulphate :

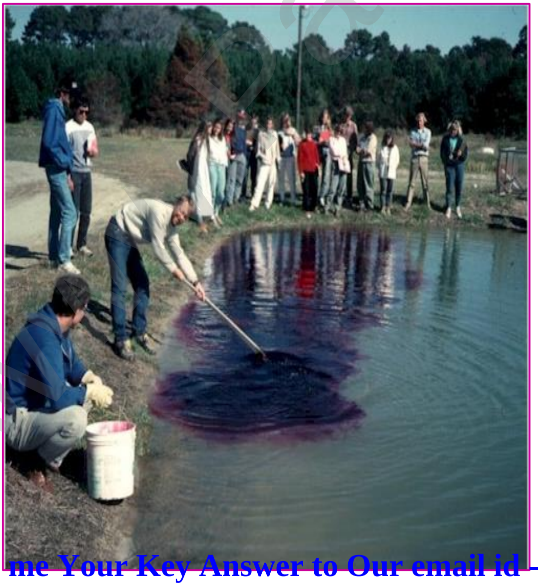
$$2MnO_4^- + 5SO_3^{2-} + 6H^+ \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$$

Uses of potassium permanganate:

Some important uses of potassium permanganate are listed below.

1. It is used as a strong oxidizing agent.
2. It is used for the treatment of various skin infections and fungal infections of the foot.
3. It used in water treatment industries to remove iron and hydrogen sulphide from well water.
4. It is used as Bayer's reagent for detecting unsaturation in an organic compound.
5. It is used in quantitative analysis for the estimation of ferrous salts, oxalates, hydrogen peroxide and iodides.





Note HCl cannot be used for making the medium acidic since it reacts with $KMnO_4$ as follows.

$$2MnO_4^- + 10\,Cl^- + 16H^+ \longrightarrow 2Mn^{2+} + 5Cl_2 + 8H_2O$$

HNO_3 also cannot be used since it is good oxidising agent and reacts with reducing agents in the reaction.

However, H_2SO_4 is found to be most suitable since it does not react with potassium permanganate.

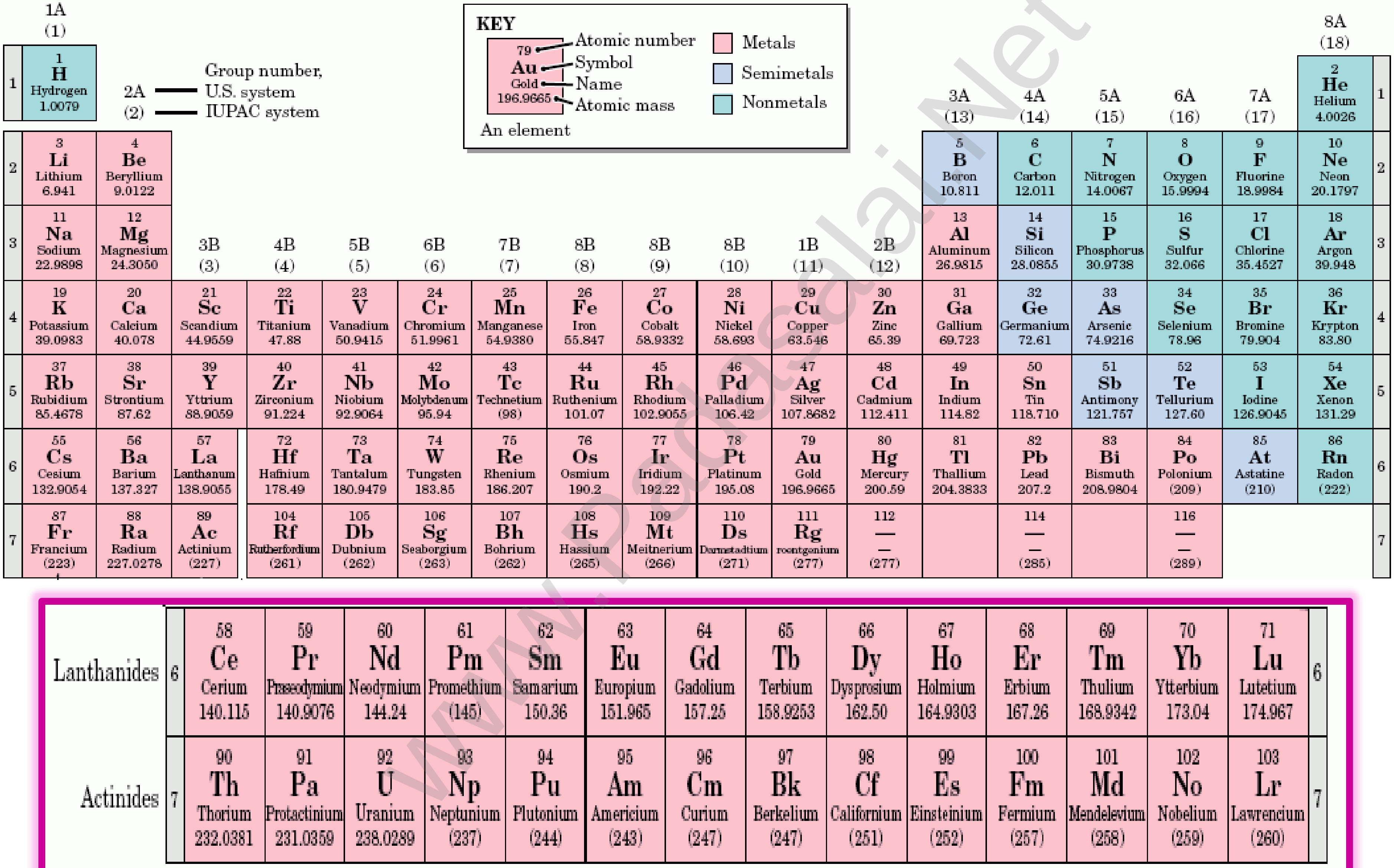
Note

$$\text{Equivalent weight of KMnO}_4\text{ in acid medium} = \frac{\text{Molecular weight of KMnO}_4}{\text{no of mols of electrons transferred}} = \frac{158}{5} = 31.6$$

$$\text{Equivalent weight of KMnO}_4\text{ in basic medium} = \frac{\text{Molecular weight of KMnO}_4}{\text{no of mols of electrons transferred}} = \frac{158}{1} = 158$$

$$\text{Equivalent weight of KMnO}_4\text{ in neutral medium} = \frac{\text{Molecular weight of KMnO}_4}{\text{no of mols of electrons transferred}} = \frac{158}{3} = 52.67$$

INNER TRANSITION ELEMENTS(f BLOCK ELEMENTS)



KEY

79 — Atomic number
Au — Symbol
Gold — Name
196.9665 — Atomic mass

An element

🟥 Metals
🟦 Semimetals
🟩 Nonmetals

2A — Group number, U.S. system
(2) — IUPAC system

	1A (1)	2A (2)	3B (3)	4B (4)	5B (5)	6B (6)	7B (7)	8B (8)	8B (9)	8B (10)	1B (11)	2B (12)	3A (13)	4A (14)	5A (15)	6A (16)	7A (17)	8A (18)	
1	1 **H** Hydrogen 1.0079																	2 **He** Helium 4.0026	1
2	3 **Li** Lithium 6.941	4 **Be** Beryllium 9.0122											5 **B** Boron 10.811	6 **C** Carbon 12.011	7 **N** Nitrogen 14.0067	8 **O** Oxygen 15.9994	9 **F** Fluorine 18.9984	10 **Ne** Neon 20.1797	2
3	11 **Na** Sodium 22.9898	12 **Mg** Magnesium 24.3050											13 **Al** Aluminum 26.9815	14 **Si** Silicon 28.0855	15 **P** Phosphorus 30.9738	16 **S** Sulfur 32.066	17 **Cl** Chlorine 35.4527	18 **Ar** Argon 39.948	3
4	19 **K** Potassium 39.0983	20 **Ca** Calcium 40.078	21 **Sc** Scandium 44.9559	22 **Ti** Titanium 47.88	23 **V** Vanadium 50.9415	24 **Cr** Chromium 51.9961	25 **Mn** Manganese 54.9380	26 **Fe** Iron 55.847	27 **Co** Cobalt 58.9332	28 **Ni** Nickel 58.693	29 **Cu** Copper 63.546	30 **Zn** Zinc 65.39	31 **Ga** Gallium 69.723	32 **Ge** Germanium 72.61	33 **As** Arsenic 74.9216	34 **Se** Selenium 78.96	35 **Br** Bromine 79.904	36 **Kr** Krypton 83.80	4
5	37 **Rb** Rubidium 85.4678	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.9059	40 **Zr** Zirconium 91.224	41 **Nb** Niobium 92.9064	42 **Mo** Molybdenum 95.94	43 **Tc** Technetium (98)	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.9055	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.8682	48 **Cd** Cadmium 112.411	49 **In** Indium 114.82	50 **Sn** Tin 118.710	51 **Sb** Antimony 121.757	52 **Te** Tellurium 127.60	53 **I** Iodine 126.9045	54 **Xe** Xenon 131.29	5
6	55 **Cs** Cesium 132.9054	56 **Ba** Barium 137.327	57 **La** Lanthanum 138.9055	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.9479	74 **W** Tungsten 183.85	75 **Re** Rhenium 186.207	76 **Os** Osmium 190.2	77 **Ir** Iridium 192.22	78 **Pt** Platinum 195.08	79 **Au** Gold 196.9665	80 **Hg** Mercury 200.59	81 **Tl** Thallium 204.3833	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.9804	84 **Po** Polonium (209)	85 **At** Astatine (210)	86 **Rn** Radon (222)	6
7	87 **Fr** Francium (223)	88 **Ra** Radium 227.0278	89 **Ac** Actinium (227)	104 **Rf** Rutherfordium (261)	105 **Db** Dubnium (262)	106 **Sg** Seaborgium (263)	107 **Bh** Bohrium (262)	108 **Hs** Hassium (265)	109 **Mt** Meitnerium (266)	110 **Ds** Darmstadtium (271)	111 **Rg** roentgenium (277)	112 **—** — (277)		114 **—** — (285)		116 **—** — (289)			7

		58	59	60	61	62	63	64	65	66	67	68	69	70	71	
Lanthanides	6	58 **Ce** Cerium 140.115	59 **Pr** Praseodymium 140.9076	60 **Nd** Neodymium 144.24	61 **Pm** Promethium (145)	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.965	64 **Gd** Gadolium 157.25	65 **Tb** Terbium 158.9253	66 **Dy** Dysprosium 162.50	67 **Ho** Holmium 164.9303	68 **Er** Erbium 167.26	69 **Tm** Thulium 168.9342	70 **Yb** Ytterbium 173.04	71 **Lu** Lutetium 174.967	6
Actinides	7	90 **Th** Thorium 232.0381	91 **Pa** Protactinium 231.0359	92 **U** Uranium 238.0289	93 **Np** Neptunium (237)	94 **Pu** Plutonium (244)	95 **Am** Americium (243)	96 **Cm** Curium (247)	97 **Bk** Berkelium (247)	98 **Cf** Californium (251)	99 **Es** Einsteinium (252)	100 **Fm** Fermium (257)	101 **Md** Mendelevium (258)	102 **No** Nobelium (259)	103 **Lr** Lawrencium (260)	7

INNER TRANSITION ELEMENTS (Rare earths)

- The elements which have partly tilled (n-2) f-orbitals are df-block elements.
- Since their inner subshells (4f and 5f) are successively filled with electrons, these electrons are called transition elements. These are two series of inner transition elements.

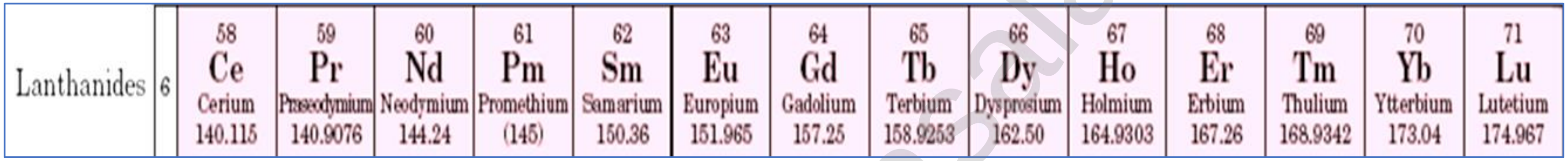
They are

- **Lanthanide series (4f-block elements)**
- **Actinide series (5f-block elements)**

1) Lanthanoids (previously called lanthanides)

- Lanthanoid series consists of fourteen elements from Cerium ($_{58}$Ce) to Lutetium ($_{71}$Lu) following Lanthanum ($_{57}$La).

- These elements are characterised by the preferential filling of 4f orbitals,

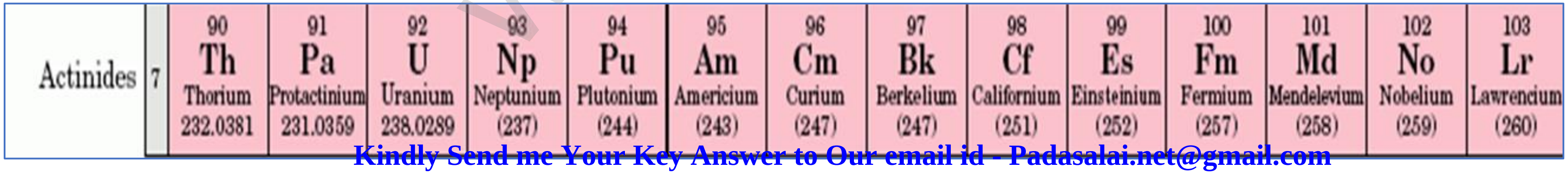


Lanthanides	6	58 Ce Cerium 140.115	59 Pr Praseodymium 140.9076	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.965	64 Gd Gadolium 157.25	65 Tb Terbium 158.9253	66 Dy Dysprosium 162.50	67 Ho Holmium 164.9303	68 Er Erbium 167.26	69 Tm Thulium 168.9342	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967

2) Actinoids (previously called actinides)

- Actinoids consists of 14 elements from Thorium ($_{90}$Th) to Lawrencium ($_{103}$Lr) following Actinium ($_{89}$Ac).

- These elements are characterised by the preferential filling of 5f orbital.



Actinides	7	90 Th Thorium 232.0381	91 Pa Protactinium 231.0359	92 U Uranium 238.0289	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (260)

The position of Lanthanoids in the periodic table

- The actual position of Lanthanoids in the periodic table is at **group number 3 and period number 6.**
- However, in the sixth period after lanthanum, the electrons are preferentially filled in inner 4f sub shell and these **fourteen elements following lanthanum** show similar chemical properties.
- Therefore these elements are grouped together and **placed at the bottom of the periodic table.** This position can be justified as follows.

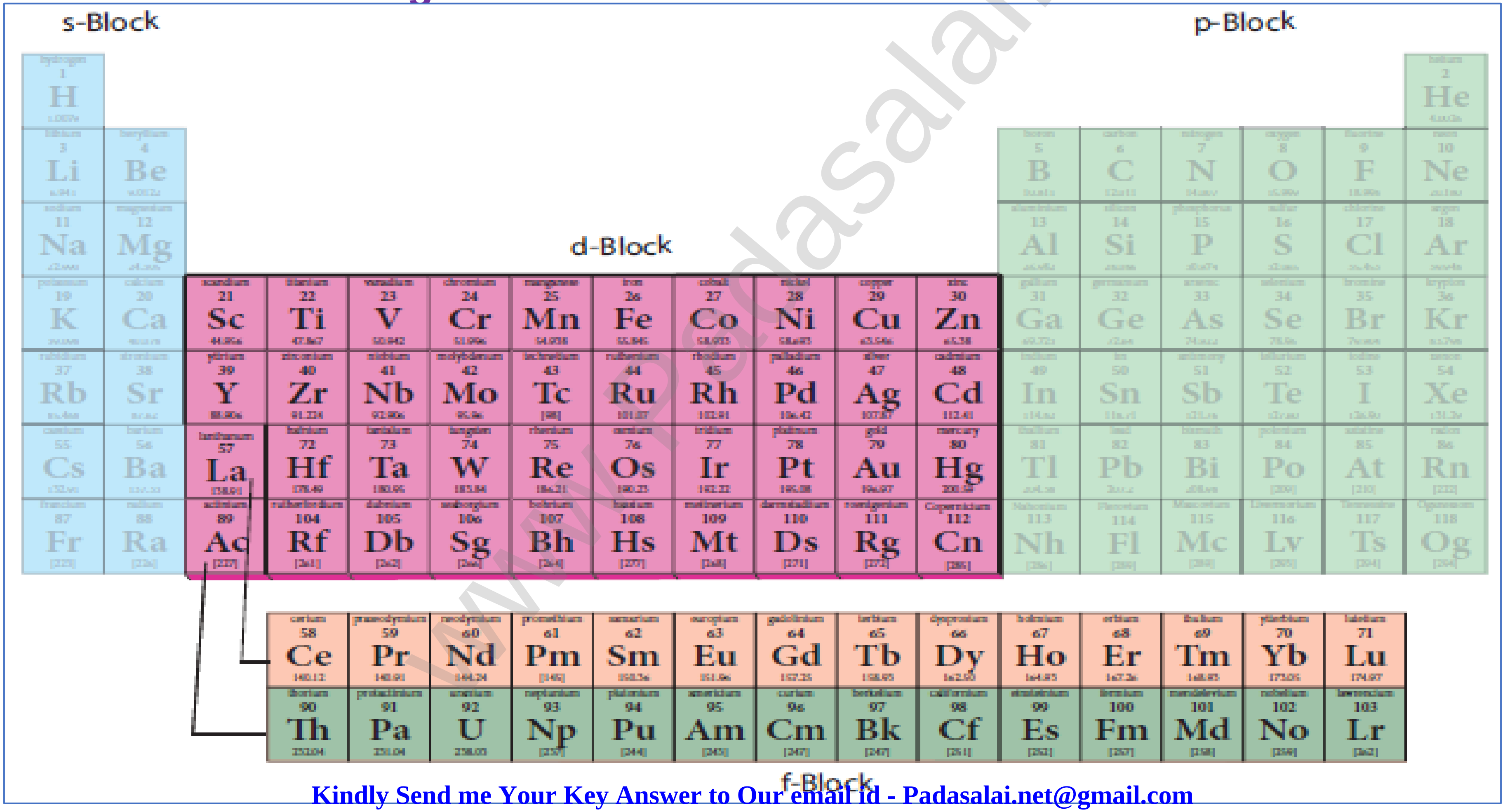
1. Lanthanoids have general electronic configuration

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

2. The common oxidation state of lanthanoides is +3

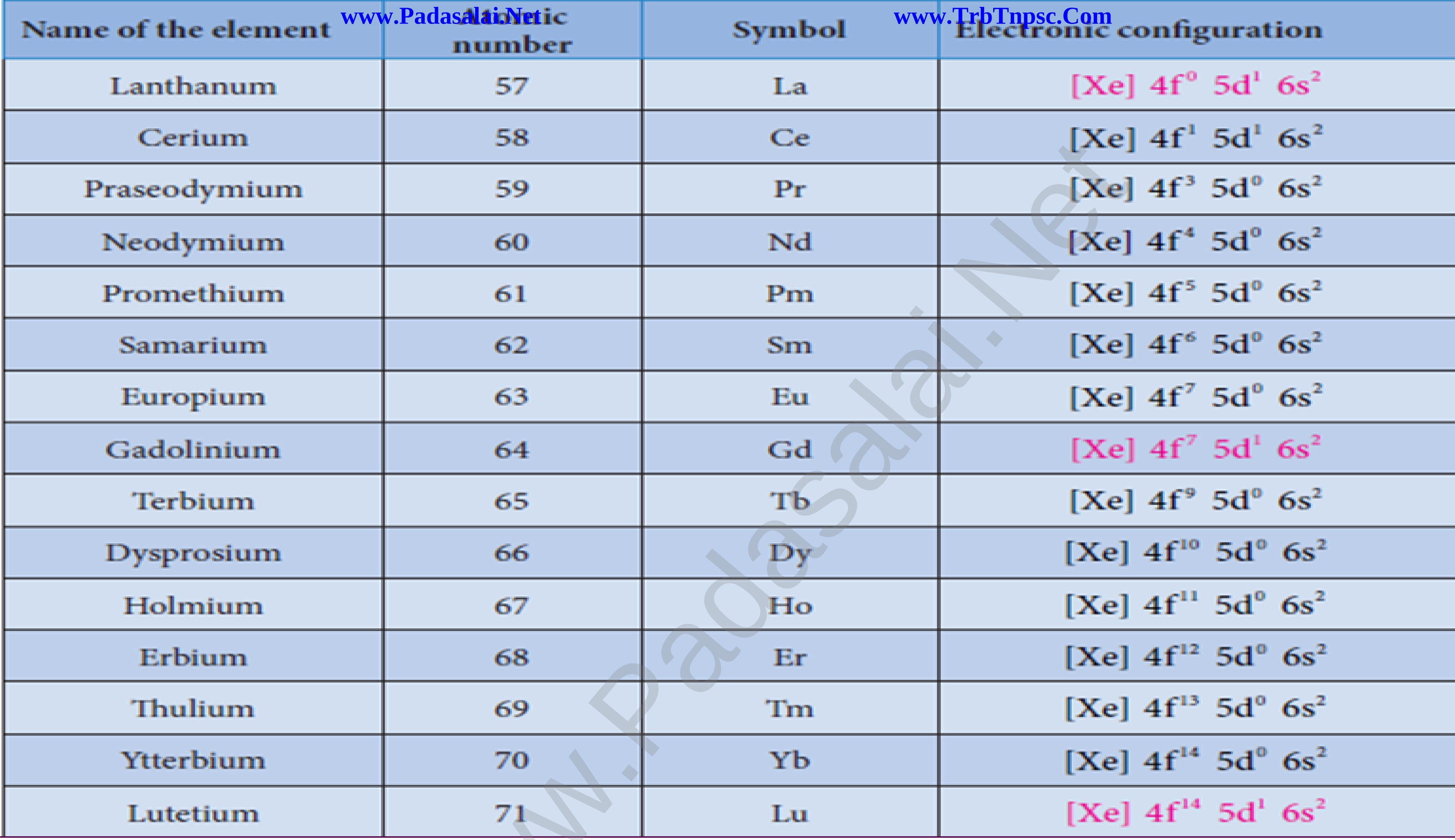
3. All these elements have similar physical and chemical properties.

- ☐ Similarly the fourteen elements following actinium resemble in their physical and chemical properties.
- ☐ If we place these elements after Lanthanum in the periodic table below 4d series, the properties of the elements belongs to a group would be different and it would affect the proper structure of the periodic table.
- ☐ Hence a separate position is provided to the inner transition elements as shown in the figure.



Electronic configuration of Lanthanoids:

- ❑ We know that the electrons are filled in different orbitals in the order of their increasing energy in accordance with Aufbau principle.
- ❑ As per this rule after filling 5s,5p and 6s and 4f level begin to fill from lanthanum, and hence the expected electronic configuration of Lanthanum(La) is [Xe] $4f^1 5d^0 6s^2$ but the actual electronic configuration of Lanthanum is[Xe] $4f^0 5d^1 6s$ and it belongs to d block.
- ❑ Filling of 4f orbital starts from Cerium (Ce) and its electronic configuration is [Xe] $4f^1 5d_1 6s^2$.
- ❑ As we move from Cerium to other elements the additional electrons are progressively filled in 4f orbitals as shown in the table.



Name of the element	Atomic number	Symbol	Electronic configuration
Lanthanum	57	La	$[Xe]\ 4f^{0}\ 5d^{1}\ 6s^{2}$
Cerium	58	Ce	$[Xe]\ 4f^{1}\ 5d^{1}\ 6s^{2}$
Praseodymium	59	Pr	$[Xe]\ 4f^{3}\ 5d^{0}\ 6s^{2}$
Neodymium	60	Nd	$[Xe]\ 4f^{4}\ 5d^{0}\ 6s^{2}$
Promethium	61	Pm	$[Xe]\ 4f^{5}\ 5d^{0}\ 6s^{2}$
Samarium	62	Sm	$[Xe]\ 4f^{6}\ 5d^{0}\ 6s^{2}$
Europium	63	Eu	$[Xe]\ 4f^{7}\ 5d^{0}\ 6s^{2}$
Gadolinium	64	Gd	$[Xe]\ 4f^{7}\ 5d^{1}\ 6s^{2}$
Terbium	65	Tb	$[Xe]\ 4f^{9}\ 5d^{0}\ 6s^{2}$
Dysprosium	66	Dy	$[Xe]\ 4f^{10}\ 5d^{0}\ 6s^{2}$
Holmium	67	Ho	$[Xe]\ 4f^{11}\ 5d^{0}\ 6s^{2}$
Erbium	68	Er	$[Xe]\ 4f^{12}\ 5d^{0}\ 6s^{2}$
Thulium	69	Tm	$[Xe]\ 4f^{13}\ 5d^{0}\ 6s^{2}$
Ytterbium	70	Yb	$[Xe]\ 4f^{14}\ 5d^{0}\ 6s^{2}$
Lutetium	71	Lu	$[Xe]\ 4f^{14}\ 5d^{1}\ 6s^{2}$

In Gadolinium (Gd) and Lutetium (Lu) the 4f orbitals, are half-filled and completely filled, and one electron enters 5d orbitals. Hence the general electronic configuration of 4f series of elements can be written as

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

Oxidation state of lanthanoids:

- The common oxidation state of lanthanoids is +3.
- In addition to that some of the lanthanoids also show either +2 or +4 oxidation states.
- Gd^{3+} and Lu^{3+} ions have extra stability, it is due to the fact that they have exactly half filled and completely filled f-orbitals respectively, their electronic configurations are

$$\boxed{\begin{aligned} Gd^{3+} &: [Xe]4f^{7} \\ Lu^{3+} &: [Xe]4f^{14} \end{aligned}}$$

- Similarly Cerium and terbium attain $4f^0$ and $4f^7$ configurations respectively in the +4 oxidation states.
- Eu^{2+} and Yb^{2+} ions have exactly half filled and completely filled f orbitals respectively.

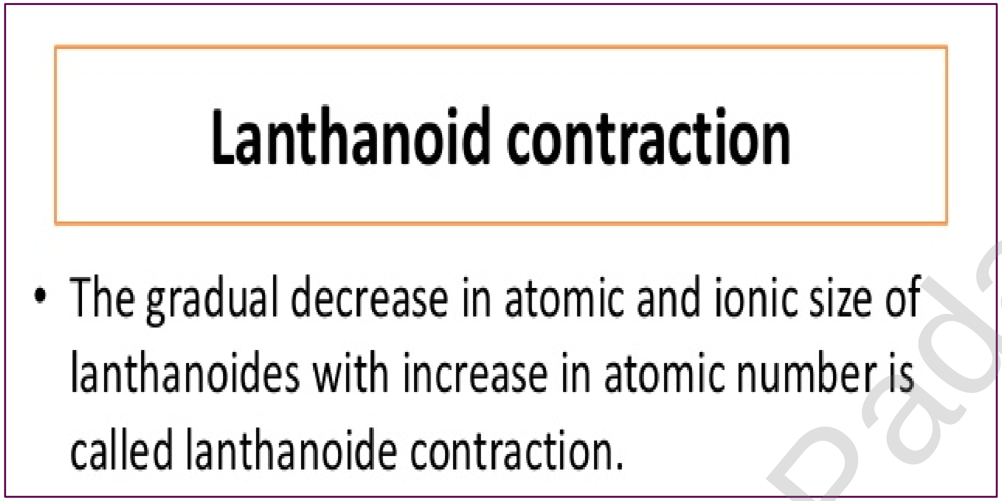
- **The stability of different oxidation states has an impact on the properties of these elements.**

- **The following table shows the different oxidation states of lanthanoids.**

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
		+2		+2	+2						+2	+2	
+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3
+4	+4	+4					+4	+4					

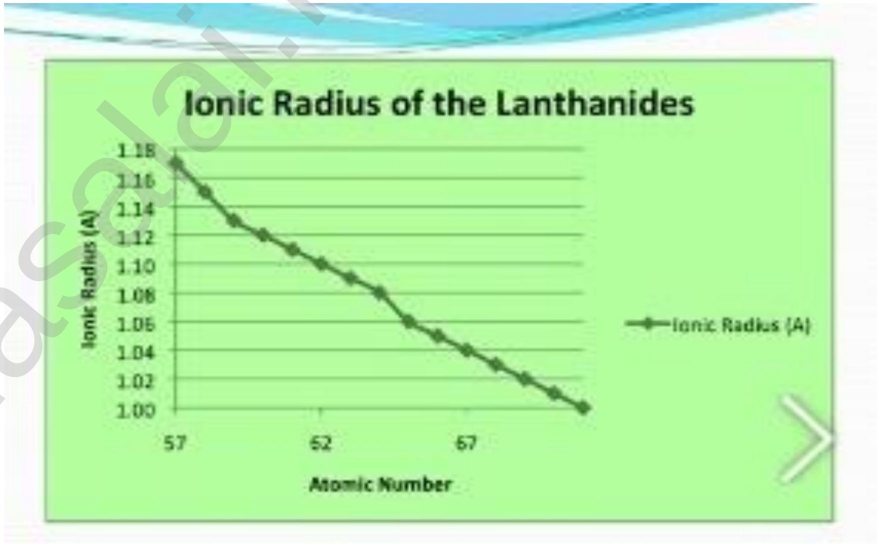
Atomic and ionic radii

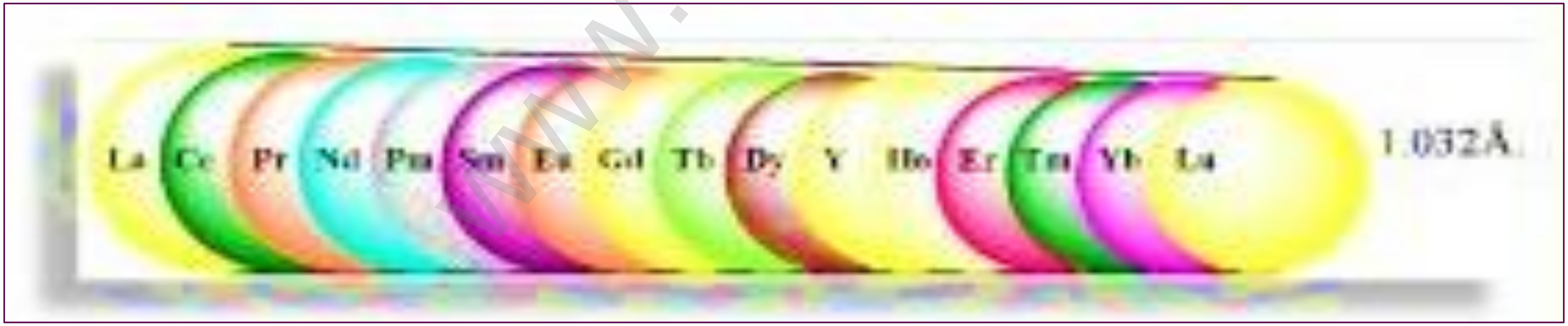
As we move across 4f series, the atomic and ionic radii of lanthanoids show gradual decrease with increase in atomic number. This decrease in ionic size is called lanthanoid contraction.



Lanthanoid contraction

- The gradual decrease in atomic and ionic size of lanthanoides with increase in atomic number is called lanthanoide contraction.





Cause of lanthanoid contraction:

- ☐ As we move from one element to another in 4f series (Ce to Lu) the nuclear charge increases by one unit and an additional electron is added into the same inner 4f sub shell.
- ☐ We know that 4f sub shell have a diffused shapes and therefore the shielding effect of 4f electrons relatively poor. Hence, with increase of nuclear charge, the valence shell is pulled slightly towards nucleus.
- ☐ As a result, the effective nuclear charge experienced by the 4f electrons increases and the size of Ln^{3+} ions decreases.
- ☐ Lanthanoid contraction of various lanthanoids is shown in the graph

Consequences of lanthanoid contraction:

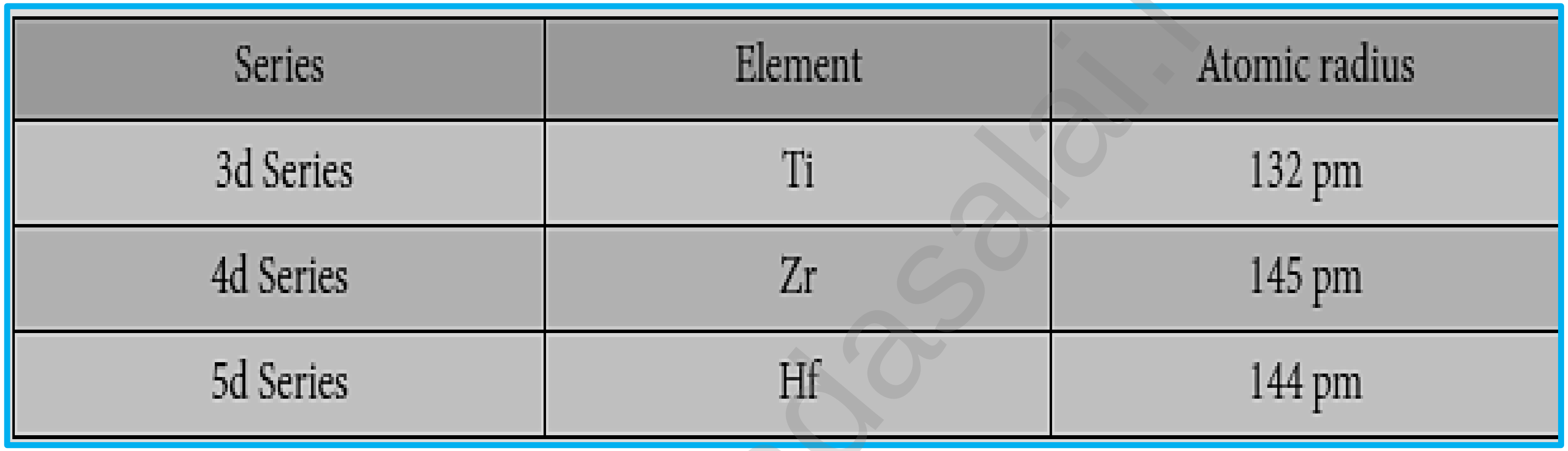
1. Basicity differences

As we from Ce^{3+} to Lu^{3+} , the basic character of Ln^{3+} ions decrease. Due to the decrease in the size of Ln^{3+} ions, the ionic character of Ln −OH bond decreases (covalent character increases) which results in the decrease in the basicity.

2. Similarities among lanthanoids:

In the complete f - series only 10 pm decrease in atomic radii and 20 pm decrease in ionic radii is observed. because of this very small change in radii of lanthanoids, their chemical properties are quite similar.

The elements of the second and third transition series resemble each other more closely than the elements of the first and second transition series. For example



Series	Element	Atomic radius
3d Series	Ti	132 pm
4d Series	Zr	145 pm
5d Series	Hf	144 pm

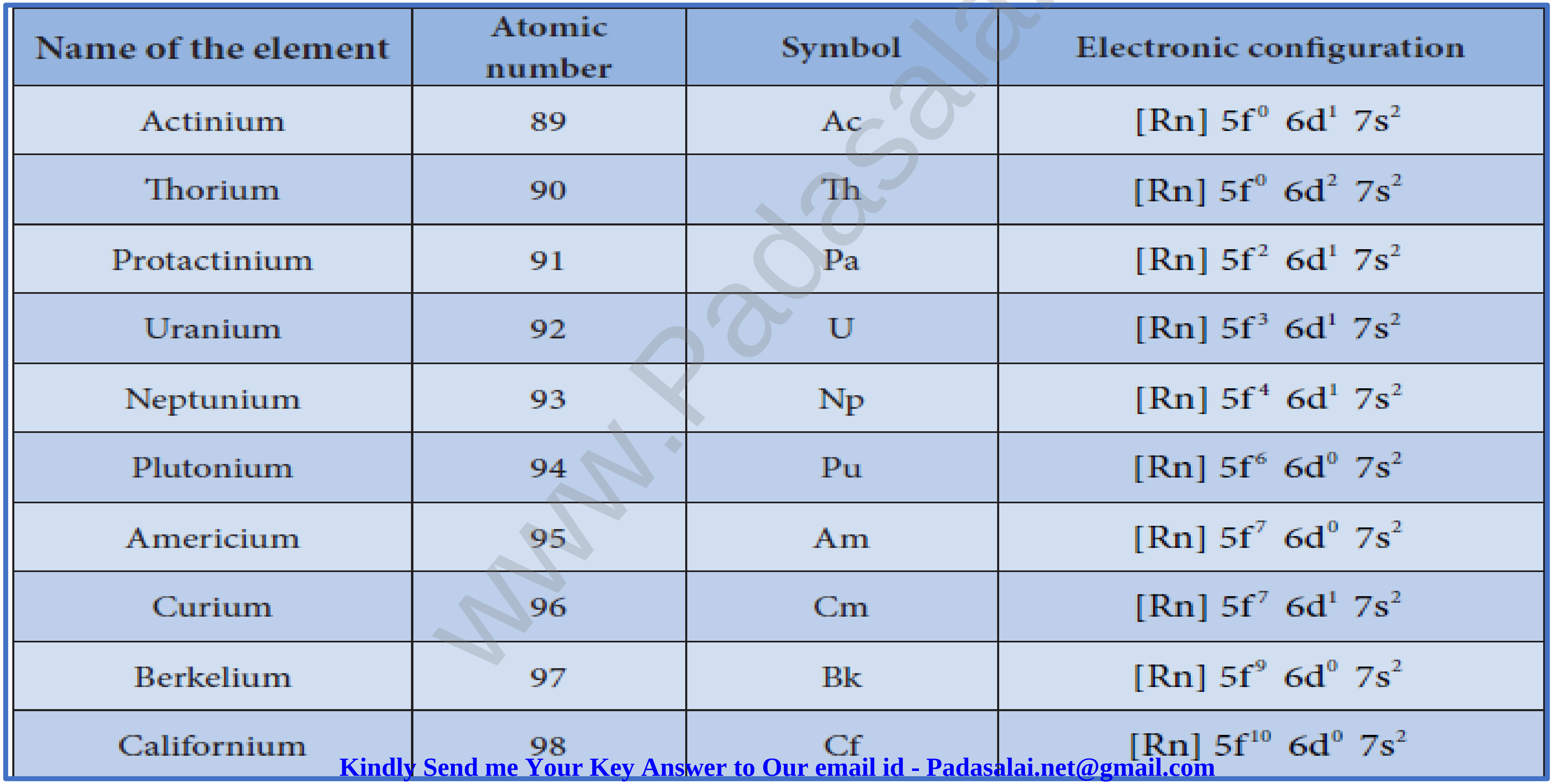
Actinoids:

- ❑ The fourteen elements following actinium ,i.e., from thorium (Th) to lawrentium (Lr) are called actinoids.
- ❑ Unlike the lanthanoids, all the actinoids are radioactive and most of them have short half lives.
- ❑ Only thorium and uranium(U) occur in significant amount in nature and a trace amounts of Plutonium(Pu) is also found in Uranium ores.
- ❑ Neptunium(Np) and successive heavier elements are produced synthetically by the artificial transformation of naturally occuring elements by nuclear reactions.
- ❑ Similar to lanthanoids, they are placed at the bottom of the periodic table.

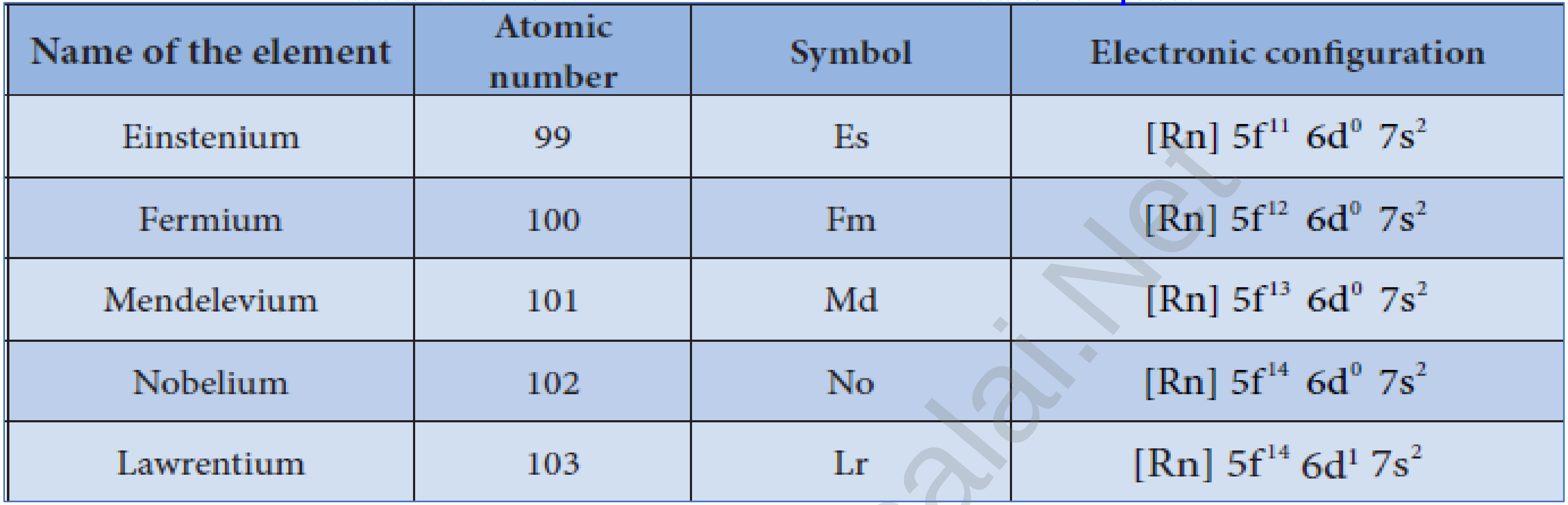
Electronic configuration:

- ❑ The electronic configuration of actinoids is not definite.
- ❑ The general valence shell electronic configuration of 5f elements is represented as $[Rn]5f^{0-14}\ 6d^{0-2}\ 7s^{2}$.

The following table show the electronic configuration of actinoids.



Name of the element	Atomic number	Symbol	Electronic configuration
Actinium	89	Ac	$[Rn]\ 5f^0\ 6d^1\ 7s^2$
Thorium	90	Th	$[Rn]\ 5f^0\ 6d^2\ 7s^2$
Protactinium	91	Pa	$[Rn]\ 5f^2\ 6d^1\ 7s^2$
Uranium	92	U	$[Rn]\ 5f^3\ 6d^1\ 7s^2$
Neptunium	93	Np	$[Rn]\ 5f^4\ 6d^1\ 7s^2$
Plutonium	94	Pu	$[Rn]\ 5f^6\ 6d^0\ 7s^2$
Americium	95	Am	$[Rn]\ 5f^7\ 6d^0\ 7s^2$
Curium	96	Cm	$[Rn]\ 5f^7\ 6d^1\ 7s^2$
Berkelium	97	Bk	$[Rn]\ 5f^9\ 6d^0\ 7s^2$
Californium	98	Cf	$[Rn]\ 5f^{10}\ 6d^0\ 7s^2$



Name of the element	Atomic number	Symbol	Electronic configuration
Einstenium	99	Es	[Rn] $5f^{11}$ $6d^0$ $7s^2$
Fermium	100	Fm	[Rn] $5f^{12}$ $6d^0$ $7s^2$
Mendelevium	101	Md	[Rn] $5f^{13}$ $6d^0$ $7s^2$
Nobelium	102	No	[Rn] $5f^{14}$ $6d^0$ $7s^2$
Lawrentium	103	Lr	[Rn] $5f^{14}$ $6d^1$ $7s^2$

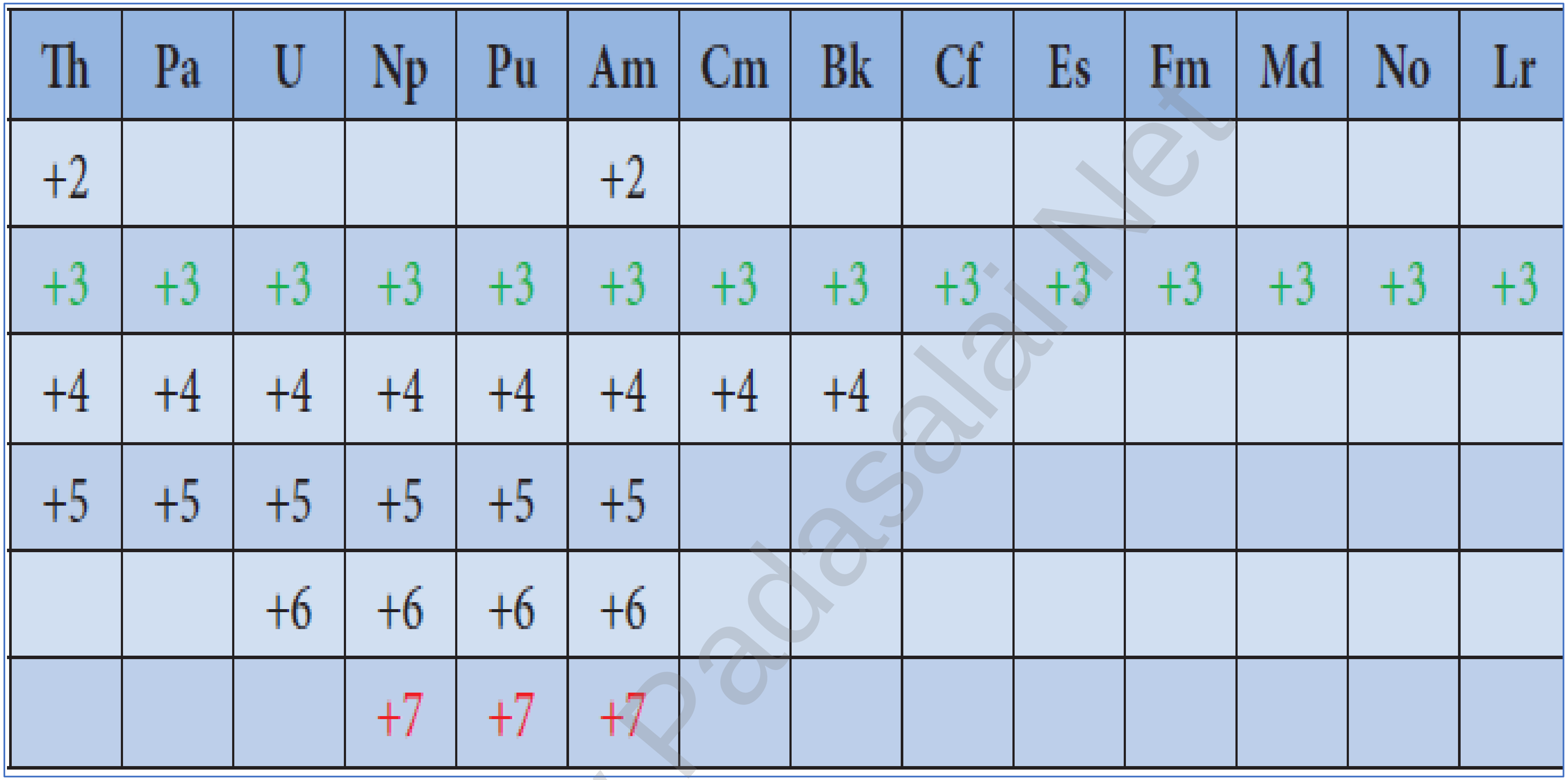
Oxidation state of actinoids:

☐ Like lanthanoids, the most common state of actinoids is +3.

☐ In addition to that actinoids show variable oxidation states such as +2 , +3 , +4 ,+5,+6 and +7.

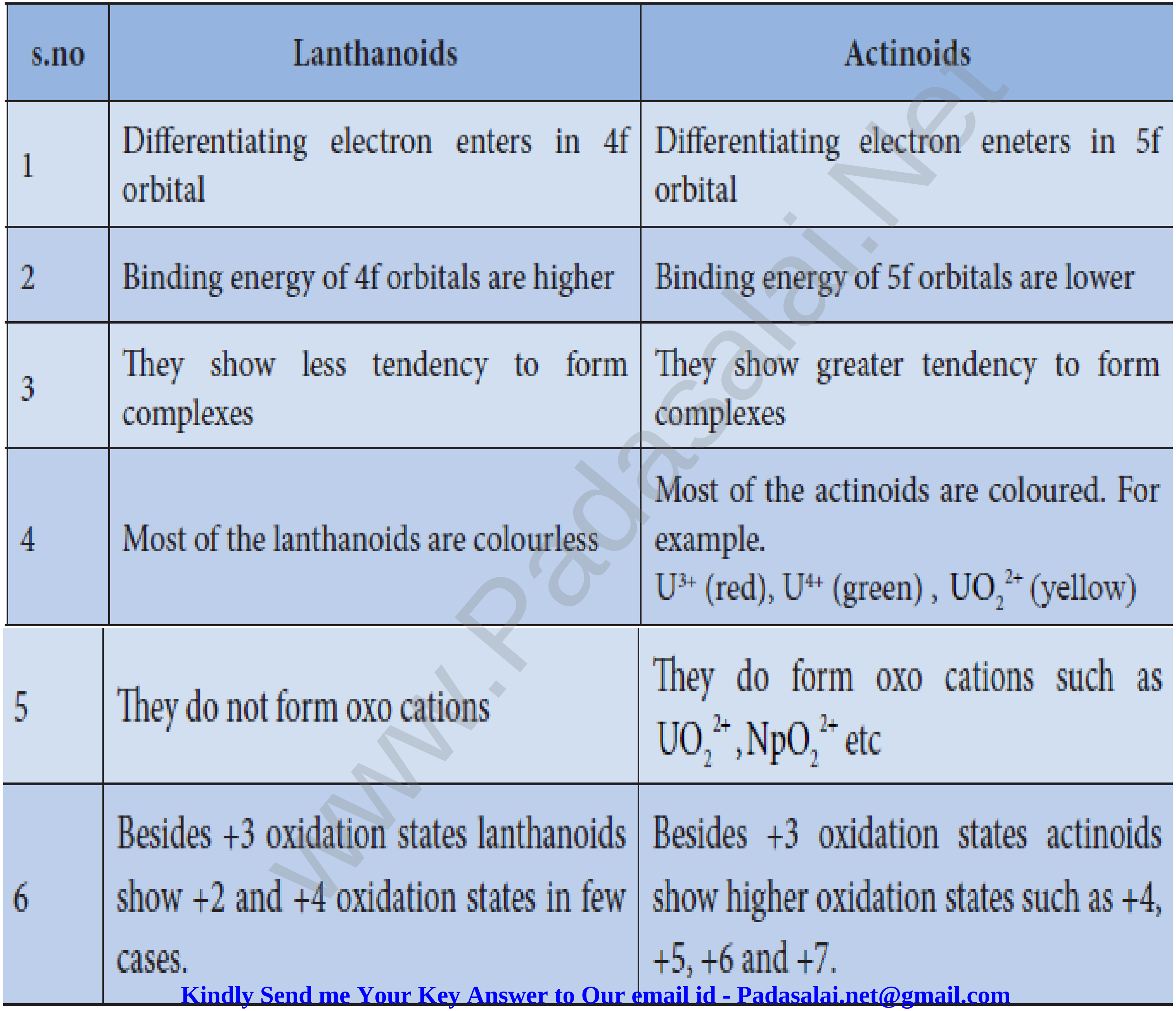
☐ The elements Americium(Am) and Thorium (Th) show +2 oxidation state in some compounds , for example thorium iodide (ThI_2).

☐ The elements Th , Pa, U ,Np , Pu and Am show +5 oxidation states. Np and Pu exhibit +7 oxidation state.



Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
+2					+2								
+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3
+4	+4	+4	+4	+4	+4	+4	+4						
+5	+5	+5	+5	+5	+5								
		+6	+6	+6	+6								
			+7	+7	+7								

Differences between lanthanoids and actinoids:



s.no	Lanthanoids	Actinoids
1	Differentiating electron enters in 4f orbital	Differentiating electron eneters in 5f orbital
2	Binding energy of 4f orbitals are higher	Binding energy of 5f orbitals are lower
3	They show less tendency to form complexes	They show greater tendency to form complexes
4	Most of the lanthanoids are colourless	Most of the actinoids are coloured. For example. U^{3+} (red), U^{4+} (green) , UO_2^{2+} (yellow)
5	They do not form oxo cations	They do form oxo cations such as UO_2^{2+}, NpO_2^{2+} etc
6	Besides +3 oxidation states lanthanoids show +2 and +4 oxidation states in few cases.	Besides +3 oxidation states actinoids show higher oxidation states such as +4, +5, +6 and +7.

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