Date

Ch-4

D- and F- Block elements.

* D- block element.

- The d-block element lies in group 3 to 12 column wise
- D- block elements are called transition element
- In d- block element containing four series.

1st series.

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

$[Kr]^{36} 5s^2 4d^1$ 2nd series. [Also Rla Catalyst group]

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

$[Xe]^{54} 6s^2 5d^1$ 3rd series

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

4th series -

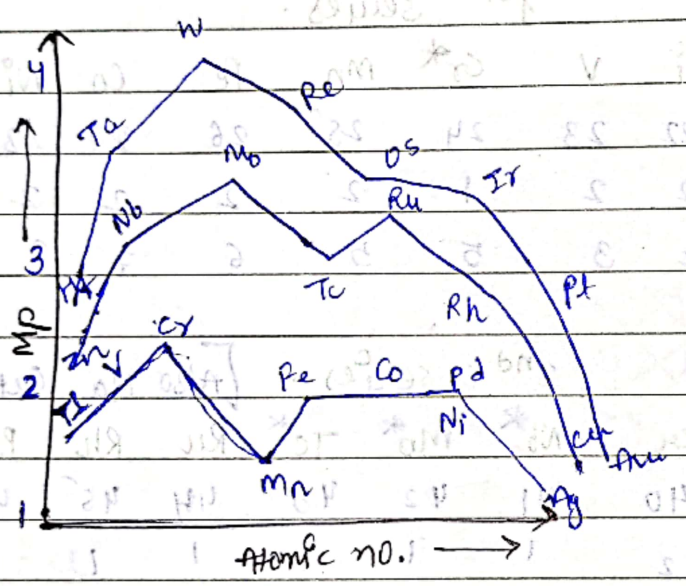
	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn
Z	89	104	105	106	107	108	109	110	111	112
7s	2	2	2	2	2	2	2	2	1	2
6d	1	2	3	4	5	6	7	8	10	10

- General configuration = $(n-1)^{1-10} ns^{1-8}$

Physical Properties

- All transition element display typical metallic property such as high tensile strength, ductility, malleability, high thermal & electric conductivity.

⇒ Trends in melting points of transition elements.



⇒ Lattice structure :

- Important element and its lattice structure.

3d series		4-d series		5d series	
Element	L·S	Element	L·S	Element	L·S
Mn	hcp (X)/Bcc	Pd	ccp	Pt	ccp
Cr	bcc	Ag	ccp	Au	ccp
Co	ccp	Cd	hcp	Hg	hcp
Ni	ccp	Mo	bcc		
Cu	ccp				
Zn	hcp				

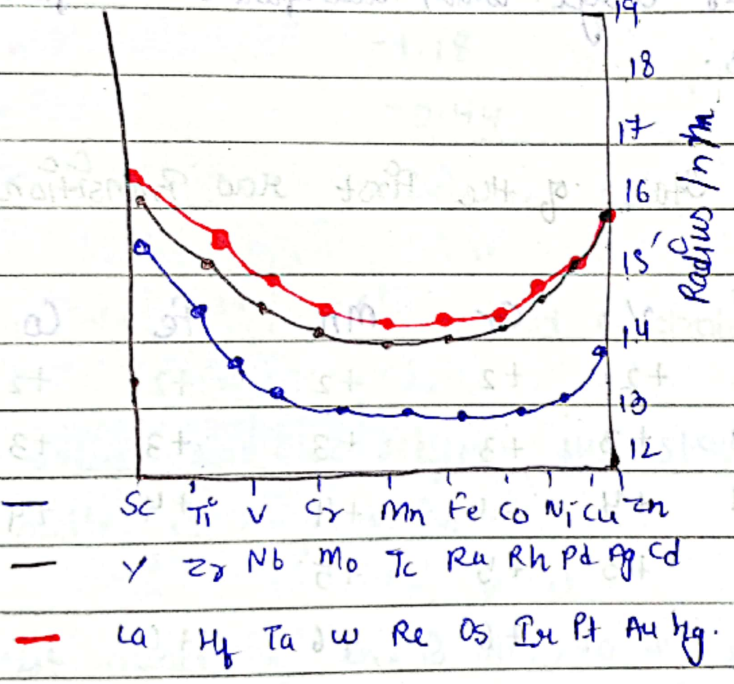
where, hcp = hexagonal close packed
ccp = cubic close packed

bcc = body centred cubic

X = a typical metal structure.

Atomic radius and ionic size of Transition metals.

- In a given series show progressive decrease in radius with increase in atomic no. This is because the new electron enters a d orbital each time the nuclear charge increases by unity.
- The outermost electron increases and the ionic radius decreases.



- Lanthanoid contraction.

a) The filling of 4f before 5d orbital results in a regular decrease in atomic radii called Lanthanoid contraction which essentially compensates for the expected increase in atomic size with increasing atomic no.

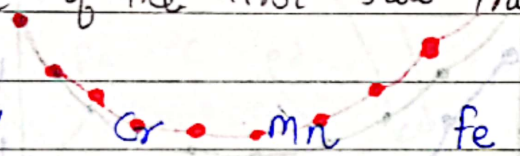
shielding of one electron by another in the same set of orbitals.

3) Metallic radius $\propto \frac{1}{Z}$

4) Ionisation Enthalpies. [$\Delta i_1 H$ or ΔH_i]

- There is increase in ionisation enthalpy along each series of the transition elements from left to right due to an increase in nuclear charge which accompanies the filling of the inner d-orbitals.

5) Oxidation State of the First row Transition metal.



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 element which gives greatest number of oxidation state occurs in or near the middle of the series. eg: Mn.
- Vary from +2 to +7 oxidation state.
- The variability of oxidation state, a characteristic of transition elements, arise due of incomplete filling of d orbitals in such a way that their O.S differ from each other by unity

- The O.S of Nickel & Iron is to be zero for complex coordination compound.
  eg:- $Ni(CO)_4$ and $Fe(CO)_5$

3) Trend in the M^{2+}/M standard electrode potentials.

- The general trend towards less negative $E^{\ominus}$ values across the series is related to the general increase in the sum of the first- and second ionisation enthalpies.

Element	E°/V
Cr	-0.90
Mn	-1.18
Fe	-0.44
Zn	-0.76

3) Trend in the M^{3+}/M^{2+} standard electrode potentials.

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

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

- The comparatively low value for V is related to the stability of V^{2+}

⇒ Trends in stability of higher oxidation states.

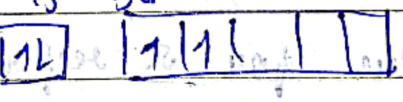
- The stable halides of the 3d series of transition metals.
- The highest oxidation no. are achieved in TiX_4, VF_5 and CrF_6
- The ability of fluorine to stabilise the highest oxidation state is due to either higher lattice energy as in the case of CoF_3, or higher bond enthalpy terms for the higher covalent compounds.

⇒ Magnetic properties.

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

n = no. of unpaired e^-

eg: Ti^{0}_{22} = $4s^2$ $3d^2$



$n = 2$

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

$$\mu = \sqrt{8}$$

$$\mu = 2 \times 1.1114$$

- Diamagnetism: The substance repel to B
- Paramagnetism: Attracted to B
- Ferromagnetism: strongly attracted to B

3) Catalytic properties.

- Transition metals and their compounds are known for their catalytic activity
- The effect of increasing the concentration of the reactant at the catalyst surface & also weakening of the bonds in the reacting molecules.
  Because the transition metal ion can change their oxidation state

3) Formation of interstitial compounds.

- These are the compounds which formed when small atoms like H, C are trapped inside the crystal lattice of metal

Characteristics of interstitial compounds.

- They have high melting points, higher than those of pure met
- They are very hard, eg: Diamond
- They retain metallic conductivity.
- They are chemically inert.

4) Alloy formation.

- It is a blend of metals prepared by mixing of componen
- eg: copper - zinc (brass), copper - tin (bronze).

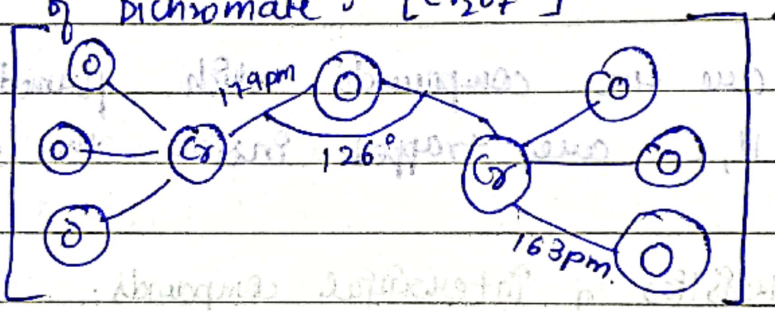
4) formation of coloured Ions

* Formation of complex compounds -

* Some important compounds of Transition elements -

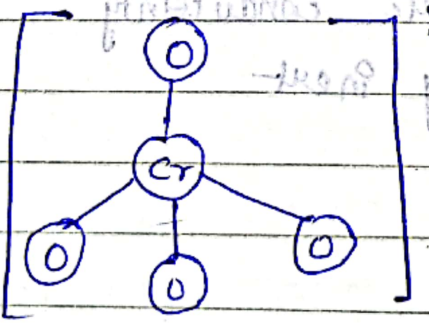
(1) Potassium Dichromate $[K_2Cr_2O_7]$.

- Acidic in nature
- Structure of Dichromate : $[Cr_2O_7^{2-}]$



Orange

- Structure of chromate. $[CrO_4^{2-}]$



Yellow

- Application of $K_2Cr_2O_7$:

- In leather industry, as a oxidising agent, as a oxidant

✱ Preparation of $K_2Cr_2O_4$:

STEP I

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

(chromite ore)

STEP II

$$2Na_2CrO_4 + 2H^+ \longrightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$$

STEP III

$$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$$

Acidic medium.

$$2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-}$$

Basic medium

$$Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$$

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

$6I^- \longrightarrow 3I_2 + 6e^-$ $\quad$ $3Sn^{2+} \longrightarrow 3Sn^{4+} + 6e^-$

$3H_2S \longrightarrow 6H^+ + 3S + 6e^-$ $\quad$ $6Fe^{2+} \longrightarrow 6Fe^{3+} + 6e^-$

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

✱ Potassium permanganate [$KMnO_4$]

✱ Preparation.

I $\quad 2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$

II $\quad 3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + 2H_2O + MnO_2$

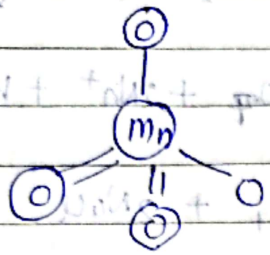
III $\quad 2MnO_4^- + K^+ \longrightarrow KMnO_4$

Commercially

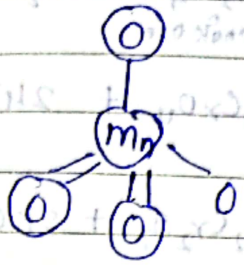
$$MnO_2 \xrightarrow[KNO_3]{KOH} MnO_4^{2-}$$

$$MnO_4^{2-} \xrightarrow[\text{oxidation}]{\text{electrolytic}} MnO_4^-$$

Laboratory: $2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \longrightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$



Manganate ion
$[MnO_4^{2-}]$
⇒ green
⇒ Paramagnetic



Permanganate ion
$[MnO_4^-]$
⇒ Purple
⇒ Diamagnetic

* In acid solution:

(a) Iodine is liberated from potassium iodide:

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

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

$$5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$$

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

$$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$$

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

$$H_2S \rightarrow 2H^+ + S^{2-}$$

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

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

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

(f) Nitrite is oxidised to nitrate:

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

* In neutral or faintly alkaline solutions:

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

$$2MnO_4^- + H_2O + I^- \longrightarrow 2MnO_2 + 2OH^- + IO_3^-$$

(b) zinc sulphate is oxidised almost quantitatively to sulphate :

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

(c) Manganous salt is oxidised to MnO_2, the presence of zinc sulphate or zinc oxide catalyses the oxidation.

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \longrightarrow 5MnO_2 + 4H^+$$

The inner transition elements [f - block]

- f - block element is also called as inner transition elements.
- electronic configuration : $[n-2]f^{0-14}(n-1)d^{0-10}ns^2$
- 2 series
  - Lanthanoid series $[Z = 57 \text{ to } 71]$
  - Actinoid series $[Z = 89 \text{ to } 103]$

	Lanthanoid		Actinoid	
57	Lanthanum	$5d^1 6s^2$	Actinium	$6d^1 7s^2$
58	Cerium	$4f^1 5d^1 6s^2$	Thorium	$6d^2 7s^2$
59	Praseodymium	$4f^3 6s^2$	Protactinium	$5f^2 6d^1 7s^2$
60	Neodymium	$4f^4 6s^2$	Uranium	$5f^3 6d^1 7s^2$
61	Promethium	$4f^5 6s^2$	Neptunium	$5f^4 6d^1 7s^2$
62	Samarium	$4f^6 6s^2$	Plutonium	$5f^6 7s^2$
63	Europium	$4f^7 6s^2$	Americium	$5f^7 7s^2$
64	Gadolinium	$4f^7 5d^1 6s^2$	Curium	$5f^7 6d^1 7s^2$
65	Terbium	$4f^9 6s^2$	Berkelium	$5f^9 7s^2$
66	Dysprosium	$4f^{10} 6s^2$	Californium	$5f^{10} 7s^2$
67	Holmium	$4f^{11} 6s^2$	Einsteinium	$5f^{11} 7s^2$
68	Erbium	$4f^{12} 6s^2$	Fermium	$5f^{12} 7s^2$
69	Thulium	$4f^{13} 6s^2$	Mendelevium	$5f^{13} 7s^2$
70	Ytterbium	$4f^{14} 6s^2$	Nobelium	$5f^{14} 7s^2$
		$4f^{14} 5d^1 6s^2$	Lawrencium	$5f^{14} 6d^1 7s^2$

* General characteristics : [Lanthanoid].

⇒ All the lanthanoids are silvery white soft metals & tarnish rapidly in air

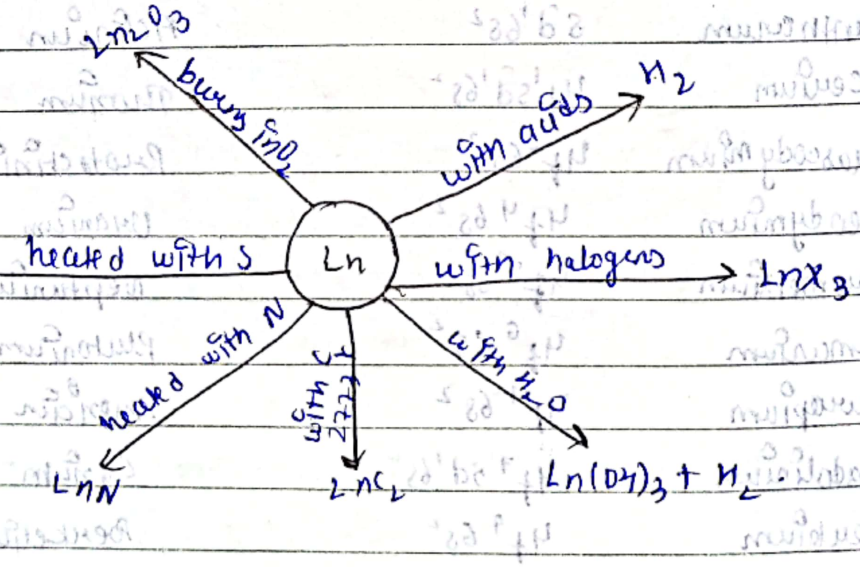
⇒ The hardness increases with increasing atomic no., Samarium (Sm) being steel hard.

⇒ The m.p & b.p = 100 K to 1200 K
But m.p & b.p of samarium (Sm) = 1623 K.

⇒ Lanthanoid series element good conductor of electricity or heat.

⇒ Many trivalent lanthanoid ions are coloured. in aqueous

* Chemical reactions of the lanthanoids.



* Ionic size

⇒ Ionic size decrease across the series due to lanthanoid contraction or lanthanoid contraction

* Highest oxidation state.
Neptunium & Pu ⇒ +7

Note: Magnum is explosive, used in nuclear reactor.

* Comparison.

Lanthanoid series	Actinoid series.
• Atomic no. = [Z = 57 to 71]	• Atomic no. ; Z = 89 to 103
• Lanthanoid contraction is less	• Actinoid contraction is more due to poor shielding effect of electron.
• Lanthanoids are low reactive metal	• Actinoids are high reactive metals.
• The magnetic property is simple	• The magnetic property is complex.
• It appears silvery white	• Silvery white but different varities of structure

* Some applications of Lanthanoid & Actinoid.
• Iron & steel are most important construction material.
• It also used in removal of impurities from metal. like Cr, Mn, Ni
• $TiCl_4$ & $Al(CH_3)_3$ forms the basis of Ziegler catalyst, used to manufacture polyethene.
• Iron catalyst are used in Haber process for production of ammonia
• Ni catalyst are used in hydrogenation, also used in polymerization
• The photographic industry relies on special light sensitive property of