D-BLOCK

A LOT OF COMMERCIAL AND IMPORTANT METALS THAT WE USE LIKE IRON(FE), GOLD(AU), SILVER(AG), COPPER(CU) ETC ARE TRANSITION ELEMENTS.
AS ALL TRANSITION ELEMENTS ARE ESSENTIALLY METALS, THEY ARE ALSO CALLED TRANSITION METALS.

DEFINITION : Initially they were named "transition" elements because their properties were found to be transitional between s & p block elements.
However, IUPAC definition is as follows,
Transition metals are metals which have incomplete d subshell either in neutral atom or in their ions.
Thus, elements which have one or more unpaired d electrons in their ground state or in their common oxidation state can be called transition elements.

CBSE 2015

*Note – Grp-12 elements, i.e., Zn, Cd and Hg have completely filled d-orbital both in their ground state and in their Oxidation State thus they are not considered transition elements but nonetheless are studied under d-block.

CBSE 2016(2),2014

A lot of elements do not possess unpaired electrons in their ground state but this definition helps identify them as transition elements.
Eg- Copper (Cu) **CBSE 2017(2)**

Cu 's Electronic configuration is : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$
As we can see, it has a completely filled d orbital in its ground state but in its common Oxidation State i.e., +2,
Cu+2 's Electronic configuration is : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^9$
and it has an unpaired electron thus it can be called a transition element. A similar case is observed for Silver. **CBSE 2017**

The possession of unpaired d and f electrons makes transition elements different from s & p block elements and hence there study is carried out separately.

SOME IMPORTANT DEFINITIONS AND CONCEPTS:

These concepts would appear later in the chapter a lot so they should be understood before hand.

(i) ENTHALPY OF ATOMISATION (ΔHat):

It is the change in enthalpy when one mole of bonds is completely broken to obtain atoms in the gas phase.

It signifies the inter-atomic strength that the molecules of a compound possess.

Lower ΔHat ⟶ weaker bonds ⟶ easier to break them.

Melting Point, Boiling Point etc. depend hugely on ΔHat as they essentially are meant to weaken the inter-atomic attraction.

(ii) METALLIC BONDING:

It is a type of chemical bond formed between positively charged atoms in which the free electrons are shared among a lattice of cations. Strength of metallic bond depends on the size, the charge and the number of de-localisable (unpaired and not in a stable configuration) electrons that the metal has. Extent of metallic bond hugely influences ΔH_{at}. **CBSE 2017**

(iii) SCREENING EFFECT:

It is defined as the reduction in the effective nuclear charge on the electron cloud, due to a difference in the attractive forces of the electrons on the nucleus. It is a very important phenomenon used in explaining atomic size variation in transition metals. As d-orbitals exhibit bad shielding effect to the outermost s-orbital, the outermost orbital experiences a stronger nuclear attraction, hence the size of atom decreases.

(iv) LANTHANOID CONTRACTION:

The more than expected decrease in size of the lanthanoid series (from Lanthanum to Lutherium), due to the poor screening effect subjected on the outermost electrons by the f-subshell.

(v) STANDARD ELECTRODE POTENTIAL(E°):

In electrochemistry, standard electrode potential is defined as the measure of the individual potential of a reversible electrode at standard state with ions at an effective concentration of 1mol dm^{-3} at the pressure of 1 atm. Basically, it is the tendency of an ion to become a neutral atom in aqueous medium. Negative E° value reflects the fact that the reversible process which we are studying is not feasible.
E° is heavily affected by these properties and for a more negative E°:
(i) Lower Enthalpy of Atomisation is required
(ii) Lower Ionisation Enthalpy is required
(iii) Higher Hydration Enthalpy is required

(vi) OXIDATION AND REDUCTION:

IUPAC gives several different definitions of oxidation: loss of electron, increase in positive value of oxidation state, decrease in negative value of oxidation state, loss of hydrogen, or gain of oxygen.
So, gain of electron, decrease in positive value of oxidation state, increase in negative value of oxidation state, gain of hydrogen, or loss of oxygen are the various definitions of reduction.

1. ELECTRONIC CONFIGURATION:

-The general outer electronic configuration of transition metals is $(n-1)d^{1-10}ns^{1-2}$.
-Although a lot of exceptions arise to this "formula" because there is very little energy difference between the ns and (n-1)d orbitals ..

Eg – Copper(Cu) and Chromium(Cr):
-The element just before Cr is Vanadium(V)-23 and its electronic configuration is, $1s^22s^22p^63s^23p^64s^23d^3$
So according to Aufbau principle, Cr's electronic configuration should be, $1s^22s^22p^63s^23p^64s^23d^4$,but the actually found configuration is $1s^22s^22p^63s^23p^64s^13d^5$.
-This is because this configuration has a half filled d orbital which is very stable.
-A similar anomaly is found for Cu.
Nickel(Ni)-28, which is just before Cu, has the electronic configuration, $1s^22s^22p^63s^23p^64s^23d^8$,
-So the configuration of Cu should be, $1s^22s^22p^63s^23p^64s^23d^9$, but the actual configuration is, $1s^22s^22p^63s^23p^64s^13d^{10}$.
-This is because there is a fully filled d orbital in this configuration which is highly stable.

Are more influenced by the surrounding than the s &p orbitals.

Due to unpaired e–these metals:
–showcase a wide variety of Oxidation States.
–form coloured ions.
–form complexes with a variety of ligands.

CBSE 2015,2017

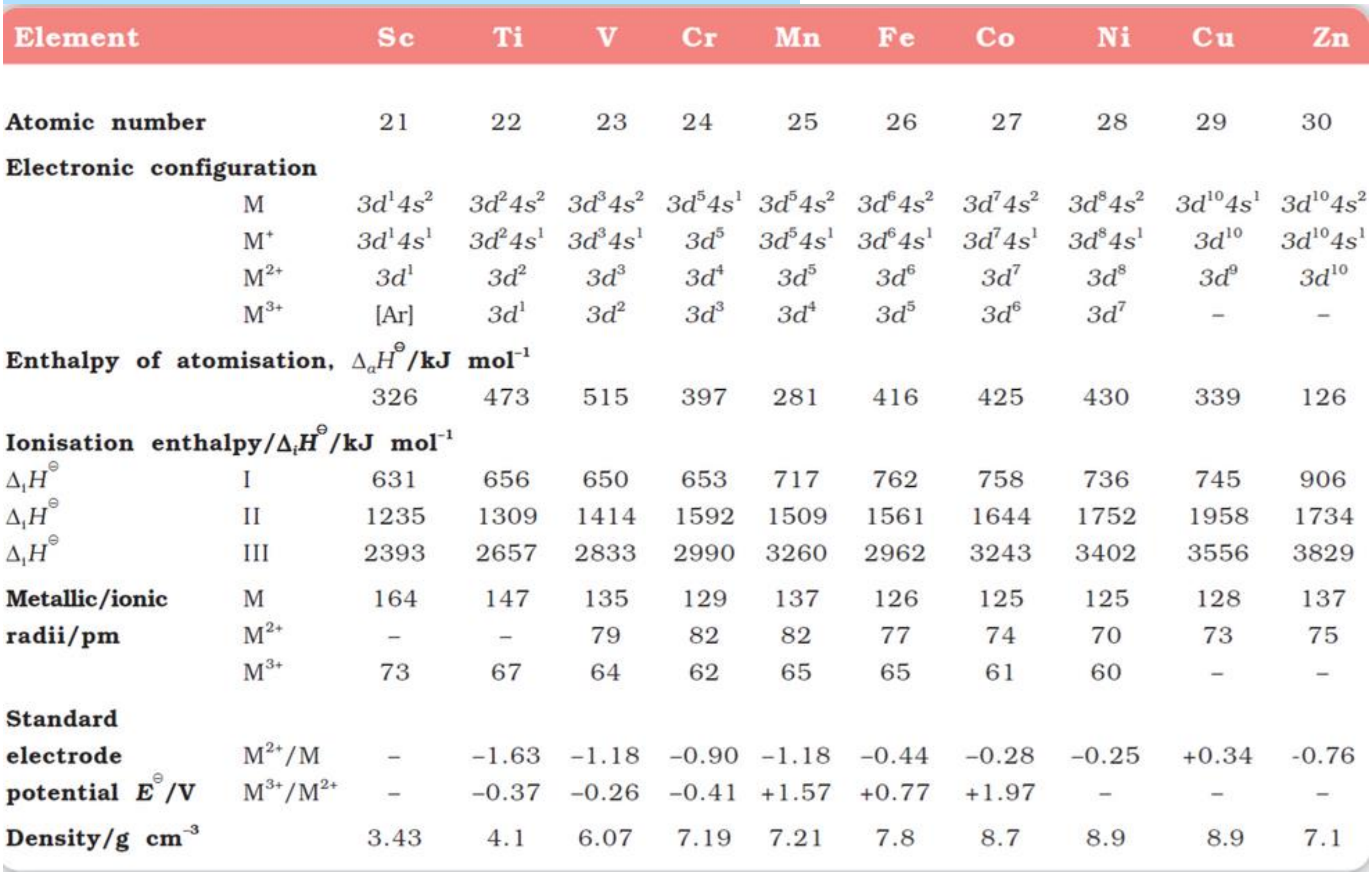
Also they influence the neighbouring atoms or molecules more as compared to s & p orbitals.

EFFECTS

Ions of same dn electronic configuration have similar magnetic and electronic properties.

Transition metals and their compounds:
– have paramagnetic property
– have catalytic property

2. GENERAL PROPERTIES :



Element		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic number		21	22	23	24	25	26	27	28	29	30
Electronic configuration											
	M	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$
	M^+	$3d^1 4s^1$	$3d^2 4s^1$	$3d^3 4s^1$	$3d^5$	$3d^5 4s^1$	$3d^6 4s^1$	$3d^7 4s^1$	$3d^8 4s^1$	$3d^{10}$	$3d^{10} 4s^1$
	M^{2+}	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^9$	$3d^{10}$
	M^{3+}	[Ar]	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	–	–
Enthalpy of atomisation, $\Delta_a H^\ominus$/kJ mol^{-1}		326	473	515	397	281	416	425	430	339	126
Ionisation enthalpy/$\Delta_i H^\ominus$/kJ mol^{-1}											
$\Delta_i H^\ominus$	I	631	656	650	653	717	762	758	736	745	906
$\Delta_i H^\ominus$	II	1235	1309	1414	1592	1509	1561	1644	1752	1958	1734
$\Delta_i H^\ominus$	III	2393	2657	2833	2990	3260	2962	3243	3402	3556	3829
Metallic/ionic radii/pm	M	164	147	135	129	137	126	125	125	128	137
	M^{2+}	–	–	79	82	82	77	74	70	73	75
	M^{3+}	73	67	64	62	65	65	61	60	–	–
Standard electrode potential $E^\ominus$/V	M^{2+}/M	–	–1.63	–1.18	–0.90	–1.18	–0.44	–0.28	–0.25	+0.34	-0.76
	M^{3+}/M^{2+}	–	–0.37	–0.26	–0.41	+1.57	+0.77	+1.97	–	–	–
Density/g cm^{-3}		3.43	4.1	6.07	7.19	7.21	7.8	8.7	8.9	8.9	7.1

All the general properties of the first transition series

(a) PHYSICAL PROPERTIES :

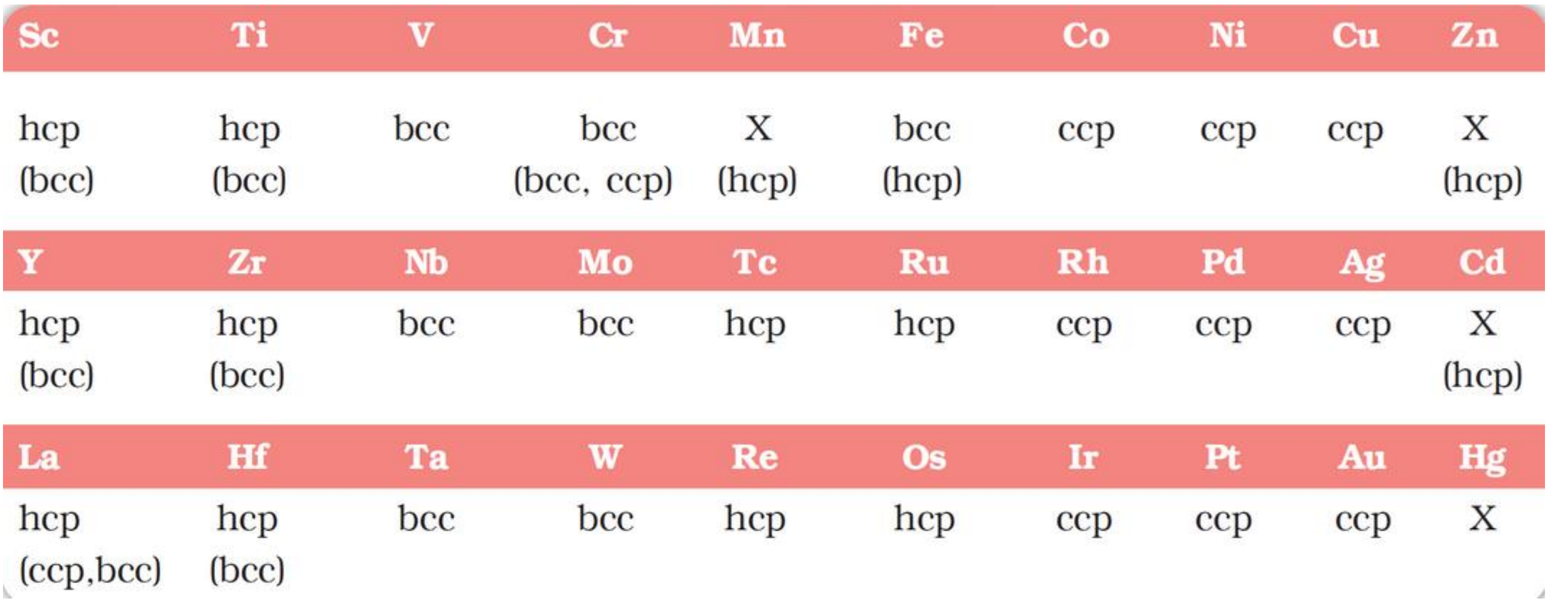
Almost all transition metals show general metallic properties like :

- ductility
- malleability
- lustre
- high tensile strength
- thermal and electrical conductance

–The elements of grp–12 (Zn, Cd, Hg), due to their fully–filled d orbitals show anomaly from the rest of the elements with respect to properties.

–This is because metallic properties are directly dependent upon the extent of metallic bond that a metal can exhibit and the extent of metallic bond in turn is directly dependent on the number of unpaired electrons that a metal possesses .

–All transition metals except Mn and Grp–12 elements, have one or more typical metallic structures at normal temperatures and all of these, except Grp–12 metals, are very hard and show very low volatility i.e. have high boiling and melting points.



Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
hcp (bcc)	hcp (bcc)	bcc	bcc (bcc, ccp)	X (hcp)	bcc (hcp)	ccp	ccp	ccp	X (hcp)
Y	**Zr**	**Nb**	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**	**Cd**
hcp (bcc)	hcp (bcc)	bcc	bcc	hcp	hcp	ccp	ccp	ccp	X (hcp)
La	**Hf**	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	**Hg**
hcp (ccp,bcc)	hcp (bcc)	bcc	bcc	hcp	hcp	ccp	ccp	ccp	X

Lattice structures of Transition metals

(b) MELTING POINT:

–Generally, transition metals have a high Melting and boiling point because of strong metallic bonds that they form using the ns and (n–1)d electrons.

-In a row, generally increases from the first element to the element with d^5 electronic configuration and then falls regularly from there to last.
-The reason attributed to this is that because the d^5 configuration forms the strongest metallic bonding, melting point becomes very high.
-Metals with very high enthalpy of atomisation tend to be noble in their reactions.

CBSE 2019 Exception – Mn & Tc 's Melting Point is less than the previous element in their respective period despite having a d^5 configuration. This is because these elements have a stable half filled configuration due to twhich these electrons do not participate in bonding ,thus the atom-atom attraction of these metals is weaker and hence its easier to break their metallic bonds leading to a low Melting Point and hence the metals preceeding these(Cr and Mo) have the highest melting points. **CBSE 2016**

(c) ENTHALPY OF ATOMISATION:

Transition metals have a high enthalpy of atomisation.
Order : 3d series <<< 4d series < 5d series
This is because 4d and 5d series' elements exhibit a stronger metallic bond(abundance of unpaired electrons) and it is more and more difficult to atomise them. **CBSE 2019**

(d) ATOMIC AND IONIC SIZE:

-Within a series/period, as expected, ionic and atomic size decreases as the atomic number increases .
-The poor shielding that the (n-1)d electrons offer, lead to further penetration of outermost ns electrons and decrease in size. Although the variation in size observed in a series is quite small.
-We observe an increase from the 3d to the 4d series of the elements but the radii of the 5d series are virtually the same as those of the corresponding members of the 4d series.

This is observed due to a phenomenon called LANTHANOID CONTRACTION. **CBSE 2017**

-Lanthanoid Contraction is caused because of the screening effect that the f-orbitals (even weaker screening than d-orbitals) exhibit which leads to a shrinking in size of the atom and thus compensates for the expected increase in size.
-This also leads to a lot of similarities in properties between the corresponding 4d and the 5d series elements.

From this information, we see that, moving left, there is an increase in the atomic mass and decrease in atomic radii among the transition elements. Thus, there is an increase in density observed as we move from Titanium(Ti)-22 to Copper(Cu)-29.

(e) IONIZATION ENTHALPIES:

-There is an increase in ionisation enthalpy along each series of the transition elements due to an increase in nuclear charge because of filling of the inner d-orbitals, although the increase observed is quite less than the increase along a period of non-transition elements.
-This is because the increase in nuclear charge is partly cancelled out by the shielding effect of the d-subshell electrons.
-The three terms responsible for the value of ionisation enthalpy are attraction of each electron towards nucleus, repulsion between the electrons and the exchange energy.
-Exchange energy is responsible for the stabilisation of energy state.
-Knowledge of Ionization Enthalpy helps us identify the most stable oxidation state of a metal and understand its ease to exist in a certain Oxidation State.

For eg-
(i) The 2nd I.E. of Cu(29) is found to have an abnormally high value. This is because in Cu^+, copper achieves the d^{10} stable configuration and a further loss of electron will lead to instability.
(ii) The 2nd I.E. of Cr(24) found to have an abnormally high value. This is because in Cr^+, chromium achieves the d^5 stable configuration and a further loss of electron will lead to instability.
(iii) The 3rd I.E. of Mn(25) is found to have an abnormally high value. This is because in Mn^{2+}, manganese achieves the d^5 stable configuration and a further loss of electron will lead to instability.
(iv) The 1st I.E. of Grp-12 elements is found to have an abnormally high value. This is because, grp-12 elements have a stable $(n-1)d^{10}$ ns^2 configuration and any loss of electron will lead to instability.

-As after the second ionization, the only left electrons left to give up are the (n-1)d subshell electrons, which shield each other very poorly because d-orbitals are aligned in different direction, generally there is a jump observed in the 2nd(or higher) ionization enthalpy of transition metals.

Exception – Fe’s 3rd and Mn’s 2nd Ionization Enthalpy is relatively low as these ionisations lead to a stable d^5 configuration for both the elements.

-The lowest common oxidation state of these metals is +2.
-To form the M^{2+} ions from the gaseous atoms, the dominant term needed is the 2nd ionisation enthalpy.

Eg-
(i) Cu and Cr prefer forming +1 rather than +2 Oxidation State because in +1 state they have very stable d^{10} and d^5 configurations, respectively and hence do not disturb this configuration.
(ii) The 2nd I.E. of Grp-12 Metals is relatively low because it leads to an extremely stable d^{10} configuration.

-Concluding, any ionisation which leads to a d^5 and d^{10} configuration brings about much stability for an element thus its I.E. is relatively lower and that Oxidation State will be preferred by that element and vice-versa

(f) OXIDATION STATE:

-One of the notable features of a transition elements is the great variety of oxidation states these may show in their compounds.
-The elements which give the greatest number of oxidation states occur in or near the middle of the series as they have more number of unpaired electrons.

Eg-Manganese, exhibits all the oxidation states from +2 to +7. **CBSE 2015**

-The lesser number of oxidation states at both the ends of a series is observed because they have either too few electrons to lose or share (eg-Sc, Ti), or too many d electrons, hence leading to fewer orbitals available in which to share electrons with others (eg-Cu, Zn).

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 most common Oxidation States are in bold types)

- Elements to the extreme left like Sc and Ti are found to exhibit only 1 O.S. or are significantly more stable in only one of them .

Eg-
(i) Sc is only found in +3 O.S., its +2 O.S. is not found. **CBSE 2016**
(ii) Ti although shows +2, +3 and +4 O.S. , +4 O.S. is way more stable.

- Elements to the extreme right like Zn, mainly exist in 1 or 2 O.S.

Eg-
Zn is found only in +2 O.S. and it never disturbs its d10 electrons.

- In the 3d series, upto Manganese, the maximum reasonably stable oxidation state that can exist corresponds to the sum of 4s and 3d electrons in the element.

Eg-
Vanadium(V)-23 : $3d^3 4s^2$.
So maximum O.S. which is stable : $2+3 = 5 \longrightarrow +5$

- Metals following Manganese, show an abrupt decrease in the most stable O.S.

Stable O.S. of the following metals are-
(i) Fe - +2 and +3
(ii) Co - +2 and +3
(iii) Ni - +2
(iv) Cu - +1 and +2
(v) Zn - +2

- The variability of oxidation states, a characteristic of transition elements, arises out of incomplete filling of d-orbitals in such a way that their oxidation states differ from each other by unity.

Eg- Vanadium-23 's O.S. : V^{+II}, V^{+III}, V^{+IV}, V^{+V}.

- This is in contrast with the variability of oxidation states of non-transition elements where oxidation states normally differ by a unit of two. **CBSE 2016**
- A striking dissimilarity arises in transition elements here. The heavier members of the d block prefer higher O.S. more than the lighter elements

Eg- In Grp-6, Cr^{+6} acts as an Oxidising agent in acidic medium because it is more stable in +3 O.S. while W^{+6} and Mo^{+6} are stable.

– Low oxidation states are found when a complex compound has ligands capable of π–acceptor character in addition to the σ–bonding.

Eg – in $Ni(CO)_4$ and $Fe(CO)_5$, the oxidation state of nickel and iron is 0.

(g) TRENDS IN THE M^{2+}/M Standard Electrode Potentials(E°):

– Transition elements have a negative E° as metals do not have a tendency to get reduced to their neutral form.

– Generally, as we move right in a series, E° becomes less –ve, i.e., metals start developing more tendency to undergo neutralisation.

– This is because the combined 1st and 2nd I.E. of the metals increase as we move rightwards in a series and thus it becomes less energy efficient for a metal to stay in the ionic form. **CBSE 2017**

*Exception – **CBSE 2017(3), 2019(2), 2018, 2020**

Cu's E° is positive i.e., it is not stable in its ionic form and it readily tries to convert back into its neutral atom.

This is because $Cu \longrightarrow Cu^{2+}$ transformation has a high value of combined 1st and 2nd I.E. and a very low Hydration Enthalpy.

*Exception –

The E° value of $Ni \longrightarrow Ni^{2+}$, $Mn \longrightarrow Mn^{2+}$ and $Zn \longrightarrow Zn^{2+}$ is higher than expected.

Reasons:

(i) Mn achieves the stable d^5 configuration with this ionisation thus it has a more negative E°. **CBSE 2017, 2019(2)**

(ii) Ni has the highest value of Hydration Enthalpy, thus it leads to a more negative E°.

IMPORTANT CASE: **CBSE 2014, 2020**

–Cr^{2+} is reducing and Mn^{3+} is oxidising but both have d^4 configuration.

–$3d^3$ configuration leads to a stable half-filled t_{2g} configuration (t_{2g} configuration is more stable than d^5 in aqueous state) **CBSE 2017(3),2016,**

–$3d^5$ configuration leads to a stable half-filled d-subshell configuration.

–So while trying to achieve stability from the d^4 configuration, can either lose an electron(to attain d^3) or gain an electron(to attain d^5).

–Cr^{2+} – $3d^4 4s^0$ with 24 protons thus losing one more electron is easier as lesser nuclear attraction. **CBSE 2017(2)**

–Mn^{3+} – $3d^4 4s^0$ with 25 protons thus losing one more electron is not easy as there is more nuclear attraction so gains one instead.

So $Cr^{2+} \longrightarrow Cr^{3+} + e^-$ ⟶ oxidation

$Mn^{3+} + e^- \longrightarrow Mn^{2+}$ ⟶ reduction

(h) TRENDS IN THE M^{3+}/M^{2+} Standard Electrode Potentials(E°):

- Sc has a negative E° value for $Sc^{3+} \longrightarrow Sc^{2+}$. This is because Sc^{3+} is an already stable ion as it has a noble gas configuration.
- Zn has a very highly positive E° value because Zn^{3+} is achieved after losing an electron from the stable d^{10} configuration.
- Fe has a low positive E° value because Fe^{3+} is a stable ion due to a stable d^5 configuration and Fe^{2+} disrupts.
- Mn has a high positive value because Mn^{2+} is a stable ion due to a d^5 configuration and Mn^{3+} disrupts this stability. **CBSE 2012,2017(3),2018**
- V has a low value because V^{2+} has a half filled t_{2g} configuration.

(i) TRENDS IN STABILITY OF HIGHER OXIDATION STATE:

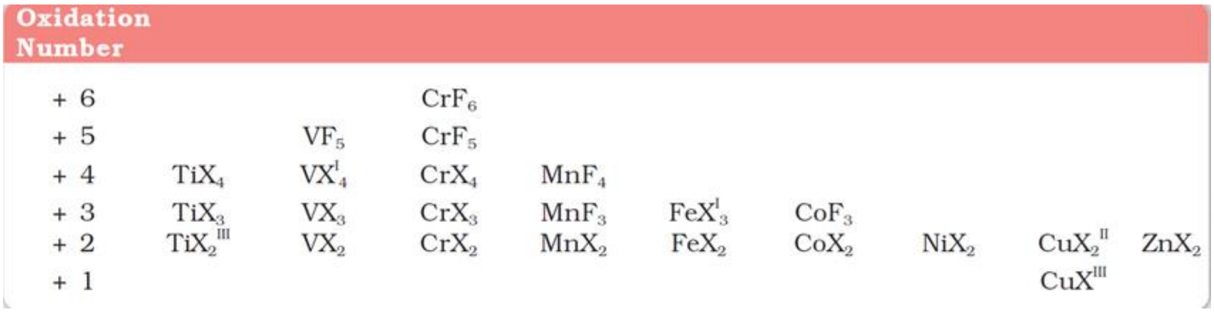
(i)HALIDES:

- Fluorine especially is able to stabilise higher Oxidation States because of either very high lattice energy (like in CoF_3) or very high bond enthalpy values for higher covalent bonds(like in VF_5 or CrF_6).

  Eg- Mn doesn't show +7 as a simple halide compound but in MnO_3F.

- After Mn, no element except Fe and Co, forms trihalides.
- Although V^{+5} is represented only by VF_5, the other halides, however, undergo hydrolysis to give oxo-halides, VOX_3.
- Another feature of fluorides is their instability in the low oxidation states.

  Eg- VX_2 and the same applies to CuX. (X= Cl, Br, I)



Oxidation Number									
+ 6			CrF_6						
+ 5		VF_5	CrF_5						
+ 4	TiX_4	VX^{I}_4	CrX_4	MnF_4					
+ 3	TiX_3	VX_3	CrX_3	MnF_3	FeX^{I}_3	CoF_3			
+ 2	TiX_2^{III}	VX_2	CrX_2	MnX_2	FeX_2	CoX_2	NiX_2	CuX_2^{II}	ZnX_2
+ 1								CuX^{III}	

Oxidation States observed in Halides

-All CuII halides are known except the iodide.

-In this case, Cu^{2+} oxidises I^- to I_2:

$$2Cu^{2+} + 4I^- \longrightarrow Cu_2I_2\,(s) + I_2$$

-However, many copper (I) compounds are unstable in aqueous solution and undergo disproportionation.

$$2Cu^+ \longrightarrow Cu + Cu^{2+}$$

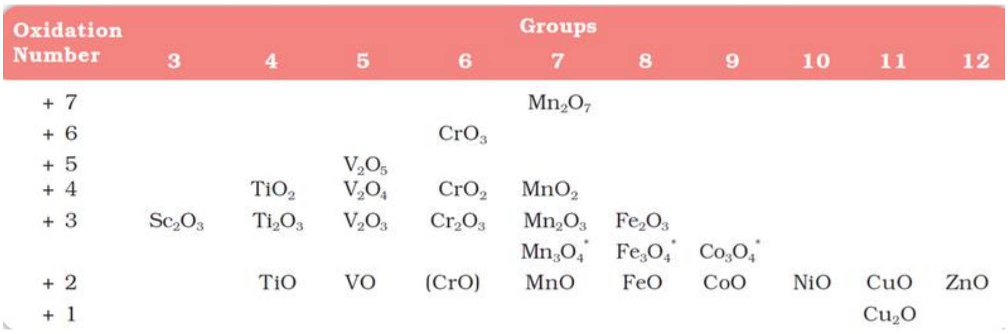
-The stability of Cu^{2+}(aq) rather than Cu^{+}(aq) is due to the much more negative hydration enthalpy of Cu^{2+}(aq) than Cu^{+}. **CBSE 2016,2018**

(ii) OXIDES:

-Oxygen has the ability to stabilise the highest Oxidation State. The highest oxidation number in the oxides coincides with the group number and is attained in Sc_2O_3 to Mn_2O_7.

-Beyond Group 7, no higher oxides of Fe above Fe_2O_3, are known, although ferrates (VI) $(FeO_4)^{2-}$, are formed in alkaline media but they readily decompose to Fe_2O_3 and O_2.

-Besides the oxides, oxo-cations stabilise V^{V} as VO_2^{+}, V^{IV} as VO^{2+} and Ti^{IV} as TiO^{2+}.



Oxidation Number	Groups 3	4	5	6	7	8	9	10	11	12
+ 7					Mn_2O_7					
+ 6				CrO_3						
+ 5			V_2O_5							
+ 4		TiO_2	V_2O_4	CrO_2	MnO_2					
+ 3	Sc_2O_3	Ti_2O_3	V_2O_3	Cr_2O_3	Mn_2O_3	Fe_2O_3				
					$Mn_3O_4^{*}$	$Fe_3O_4^{*}$	$Co_3O_4^{*}$			
+ 2		TiO	VO	(CrO)	MnO	FeO	CoO	NiO	CuO	ZnO
+ 1									Cu_2O	

Oxidation States observed in Oxides

-The ability of O to stabilise high oxidation states exceeds that of F. Thus the highest Mn fluoride is MnF_4(IV) while the highest oxide is Mn_2O_7(VII). **CBSE 2016**

-The ability of oxygen to form multiple bonds by pπ-dπ bonding with metals explains its superiority in stabilising higher O.S. of metals. **CBSE 2016, 2017**

-In the covalent oxide Mn_2O_7, each Mn is tetrahedrally surrounded by O's including a Mn–O–Mn bridge. The $[MO_4]^{n-}$ ion is tetrahedral.

-Generally, an oxide with higher oxidation state is more acidic than the compound of that element with lower oxidation state. This is because, as the oxidation state increases the charge density of that atom also increases which in turn strongly pulls electron density towards itself from other specie that comes closer or in contact with it. **CBSE 2017**

(j) CHEMICAL REACTIVITY AND E- VALUES :

-Transition metals vary widely in their chemical reactivity.

-Many of them are enough electropositive to dissolve in mineral acids, although a few are 'noble'—that is, they are unaffected by single acids.

-The first series metals with the exception of copper are reactive and are oxidised by 1M H^{+}, though the actual rate of getting oxidised is sometimes low.

Eg- Titanium and Vanadium are passive to dilute non oxidising acids.

-The E^- values for M^{2+}/M indicate a decreasing tendency to form divalent cations across the series.
This is due to the increase in the sum of the first and second ionisation enthalpies leading to less tendency to exist in the divalent state.
-The E^- values for Mn, Ni and Zn are more negative than expected from the general trend.
-This behaviour can be explained for :

(a) Nickel, due to it having the highest negative enthalpy of hydration.
(b) Manganese, due to the stability of half-filled d-subshell (d^5) in Mn^{2+}
(c) Zinc, due to the completely filled d-subshell (d^{10}) .

-From the M^{3+}/M^{2+} Standard Electrode Potentials, we conclude that:
(a)Mn^{3+} and Co^{3+} ions are strong oxidising agents in aq. solutions .
(b)Ti^{2+}, V^{2+} and Cr^{2+} are strong reducing agents .

Eg- $Cr^{2+}(aq) + 2\,H^+(aq) \longrightarrow 2\,Cr^{3+}(aq) + H_2(g)$

(k) MAGNETIC PROPERTIES:

-Most of the transition metals ions are paramagnetic.
-Paramagnetism arises from the presence of unpaired electrons, each such electron having a magnetic moment associated with its spin angular momentum and orbital angular momentum.
-For the compounds of the first series of transition metals, the magnetic moment is determined by the number of unpaired electrons and is calculated by using the 'spin-only' formula only, and that is,

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

CBSE 2017(2), 2016

'n' is the number of unpaired electrons and μ is the magnetic moment in units of Bohr Magneton (BM).

-The magnetic moment increases with the increasing number of unpaired electrons.
-Thus, the observed magnetic moment gives a useful indication about the number of unpaired electrons present in the atom, molecule or ion.

(l) FORMATION OF COLOURED COMPOUNDS:

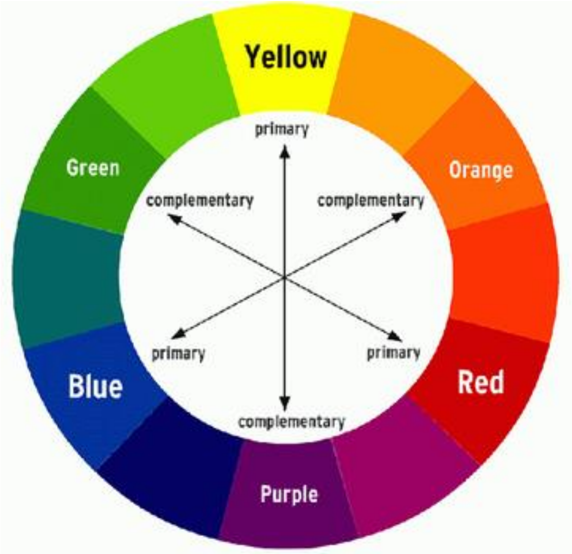
-When an electron from a lower energy d-orbital is excited to a higher energy d-orbital, the energy of excitation corresponds to the frequency of light absorbed.
-While interacting with groups called ligands, the d-orbitals lose there degeneracy and an energy difference is observed between some of them.

–Thus, for electrons to jump between two of such orbitals, energy of a certain frequency is required. **CBSE 2017, 2015**

–This required frequency generally lies in the visible region, thus transition metal compounds are generally coloured.

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

Eg– If 516 THz (frequency of Yellow colour) frequency is absorbed by a compound, it will show purple as purple is yellow's complementary.

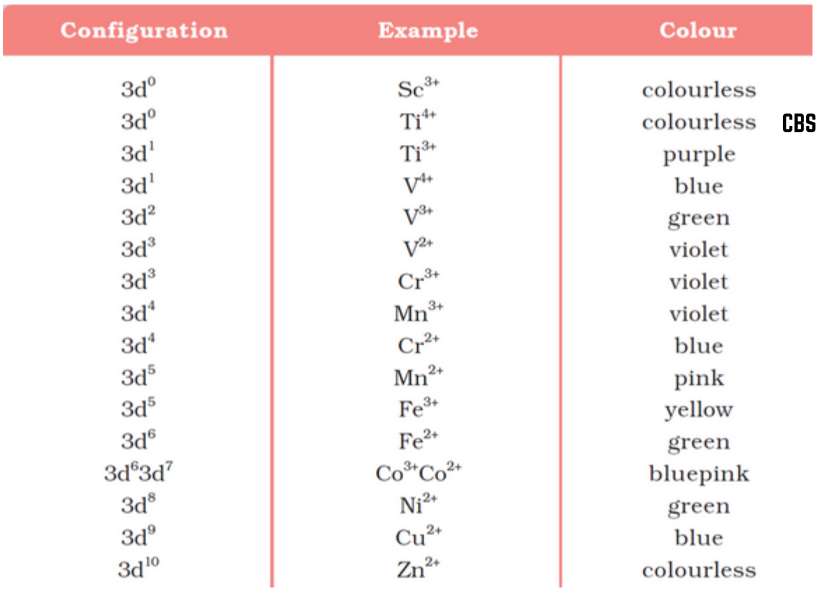


–The frequency of the light absorbed is determined by the nature of the ligand.

–Compounds of certain metal ions like Sc^{3+} and Zn^{2+} are colourless.

Sc^{3+} – $4s^0\,3d^0$: No d-electron thus, no d-d transition is possible. **CBSE 2018**

Zn^{2+} – $4s^0\,3d^{10}$: d-orbitals fully-filled,no d-d transition is possible. **CBSE 2017**



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

CBSE 2017(2)

Colours shown by metals in an aqueous solution, i.e., when water molecules act as ligands.

(m) FORMATION OF COMPLEX COMPOUNDS:

-Complex compounds are those in which the metal ions bind a number of anions or neutral molecules giving complex species.

-The transition metals form a large number of complex compounds.

-This is due to the comparatively smaller sizes of the metal ions, their high ionic charges and the availability of d orbitals for bond formation. **CBSE 2017(2),2014 2019**

Eg- $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, $[Cu(NH_3)_4]^{2+}$ and $[PtCl_4]^{2-}$.

(n) CATALYTIC PROPERTY:

-The transition metals and their compounds are known for their catalytic activity.

-This activity of theirs is ascribed to their ability to adopt multiple oxidation states and to form complexes. **CBSE 2019, 2016**

-Catalysts at a solid surface involve the formation of bonds between reactant molecules and atoms of the surface of the catalyst.

-This has the effect of increasing the concentration of the reactants at the catalyst surface and also weakening of the bonds in the reacting molecules (the activation energy is lowering).

-Also because the transition metal ions can change their oxidation states, they become more effective as catalysts.

Eg-
(i) Vanadium(V) Oxide [V_2O_5] in Contact Process.
(ii) Finely divided Iron in Haber's Process
(iii) Nickel in various hydrogenation processes.
(iv) Iron(III) catalyses the reaction between iodide and persulphate ions.

Reaction-

$$2\,I^- + S_2O_8^{2-} \longrightarrow I_2 + 2SO_4^{2-}$$

Step-1: $2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$
Step-2: $2Fe^{2+} + S_2O_8^{2-} \longrightarrow 2Fe^{3+} + 2SO_4^{2-}$

Fe^{3+} is regenerated and is just being used to create a pathway for the reaction to occur faster or have a better yield.

(o) FORMATION OF INTERSTITIAL COMPOUNDS:

-Interstitial compounds are those which are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals.
-They are usually non-stoichiometric and are neither typically ionic nor covalent.

Eg- TiC, Mn_4N, Fe_3H, $VH_{0.56}$ and $TiH_{1.7}$

-The formulas quoted above do not, of course, correspond to the oxidation state of the metal.
-Because of the nature of their composition, these compounds are referred to as interstitial compounds.
-The principal physical and chemical characteristics of these compounds are as follows:

(i) They have high melting points, higher than those of pure metals.
(ii) They are very hard, some borides approach diamond in hardness.
(iii) They retain metallic conductivity.
(iv) They are chemically inert.

(p) ALLOY FORMATION:

- 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.
-Such alloys are formed by atoms with metallic radii that are within about 15 percent of each other which works in favour of transition metals as they are very similarly sized. **CBSE 2019**
-The alloys so formed are hard and have often high melting points.
-Ferrous alloys: chromium, vanadium, tungsten, molybdenum and manganese are used for the production of a variety of steels. Transition metals also form alloys with non-transition metals such as brass (copper-zinc) and bronze (copper-tin).

3. SOME IMPORTANT COMPOUNDS OF TRANSITION METALS:

OXIDES AND OXOANIONS:

-These oxides are generally formed by the reaction of metals with oxygen at high temperatures.
-All the metals except scandium form MO oxides which are ionic.

-The highest oxidation number in the oxides, coincides with the group number and is attained in Sc_2O_3(III) to Mn_2O_7(VII). **CBSE 2017**

-Beyond group 7,no higher oxides of iron above Fe_2O_3 are known.

-Besides the oxides, the oxo-cations stabilise V^V as VO_2^+, V^{IV} as VO^{2+} and Ti^{IV} as TiO^{2+}.

-As the oxidation number of a metal increases, ionic character decreases.

-In the case of Mn, Mn_2O_7 is a covalent green oil. Even CrO_3(VI) and V_2O_5 have low melting points. **CBSE 2017**

-In these higher oxides, the acidic character is predominant. Thus, Mn_2O_7 gives $HMnO_4$ and CrO_3 gives H_2CrO_4 and $H_2Cr_2O_7$.

-V_2O_5 is, however, amphoteric though mainly acidic.

-In vanadium there is gradual change from the basic V_2O_3 to less basic V_2O_4 and to amphoteric V_2O_5.

-V_2O_4 dissolves in acids while V_2O_5 reacts with alkalies as well as acids.

-The well characterised CrO is basic but Cr_2O_3 is amphoteric.

(a) POTASSIUM DICHROMATE($K_2Cr_2O_7$):

Potassium dichromate is a very important chemical used in leather industry and as an oxidant for preparation of many azo compounds.

(i)Preparation: **CBSE 2016, 2019, 2017(2), 2020**

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

$$4\,FeCr_2O_4 + 8\,Na_2CO_3 + 7\,O_2 \longrightarrow 8\,Na_2CrO_4 + 2\,Fe_2O_3 + 8\,CO_2$$ **CBSE 2016**

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

$$2Na_2CrO_4 + 2H^+ \longrightarrow Na_2Cr_2O_7 + 2\,Na^+ + H_2O$$ **CBSE 2016**

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

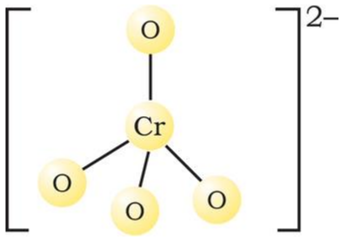
$$Na_2Cr_2O_7 + 2\,KCl \longrightarrow K_2Cr_2O_7 + 2\,NaCl$$

-Orange crystals of potassium dichromate crystallise out.

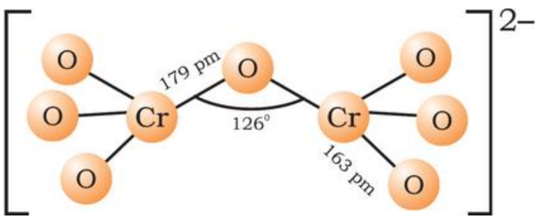
Important –
(i)The chromates(ORANGE) and dichromates(YELLOW) are interconvertible in aqueous solution depending upon pH of the solution. The oxidation state of chromium in chromate and dichromate is the same.

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

$Cr_2O_7^{2-} + 2\,OH^- \longrightarrow 2\,CrO_4^{2-} + H_2O$ **CBSE 2014, 2017(2)**



Chromate Ion



Dichromate Ion

(ii)The chromate ion is tetrahedral whereas the dichromate ion consists of two tetrahedra sharing one corner with Cr–O–Cr bond angle of 126°.

Properties

–Sodium and potassium dichromates are strong oxidising agents

Acidified potassium dichromate oxidises iodides to iodine, sulphides to sulphur, tin(II) to tin(IV) and iron(II) salts to iron(III)

$6\,I^- \longrightarrow 3I_2 + 6e^-$; **CBSE 2015, 2016**

$3\,Sn^{2+} \longrightarrow 3Sn^{4+} + 6e^-$ **CBSE 2016**

$3\,H_2S \longrightarrow 6H^+ + 3S + 6e^-$; **CBSE 2015**

$6\,Fe^{2+} \longrightarrow 6Fe^{3+} + 6\,e^-$ **CBSE 2018**

Full reaction are of the type:

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

–Potassium dichromate is used as a primary standard in volumetric analysis.

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

(b) POTASSIUM PERMANGANATE($KMnO_4$):

(i)Preparation: **CBSE 2015**

–Fusion of MnO_2 with an alkali metal hydroxide and an oxidising agent like KNO_3 produces the dark green K_2MnO_4 which disproportionates in a neutral or acidic solution to give permanganate.

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

$3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$ **CBSE 2020, 2019**

-**Commercially:** Alkaline oxidative fusion of MnO_2 followed by the electrolytic oxidation of Manganate(VI) produces Permanganate(VII)

$MnO_2 \longrightarrow MnO_4^{2-} \longrightarrow$ Fused with KOH, oxidised with air or KNO_3 **CBSE 2018**

$MnO_4^{2-} \longrightarrow MnO_4^{-} \longrightarrow$ Electrolytic oxidation in alkaline solution

-**Laboratry:** A manganese (II) ion salt is oxidised by per-oxo-disulphate to permanganate.

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

Properties

Forms dark purple (almost black) crystals isostructural with $KClO_4$. The salt is not very soluble in water, but when heated it decomposes.

$KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$

It has two physical properties of considerable interest: its intense colour and its diamagnetism along with temperature-dependent weak para-magnetism.

Hydrogen ion concentration of the solution plays a very important part in influencing the redox reactions of the permanaganate ion.

The manganate and permanganate ions are tetrahedral.
The π bonding takes place by overlap of p-orbitals of oxygen with d orbitals of manganese.

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

$KMnO_4$ should oxidise water at $[H^+]=1$ but in reality the reaction progresses very slowly unless MnO_4^{2-} is present or the solution's heated.

Oxidising reactions in ACIDIC MEDIUM:

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

(ii) $5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$ **CBSE 2018**

(iii) $5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$ **CBSE 2015**

(iv) $H_2S \longrightarrow 2H^+ + S^{2-}$ **CBSE 2017**
$5S^{2-} + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5S$

(v) $5SO_3^{2-} + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 3H_2O + 5SO_4^{2-}$ **CBSE 2015**

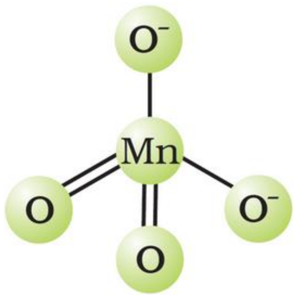
(vi) $5NO_2^- + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$ **CBSE 2015**

Oxidising reactions in NEUTRAL OR FAINTLY ALKAKLINE MEDIUM:

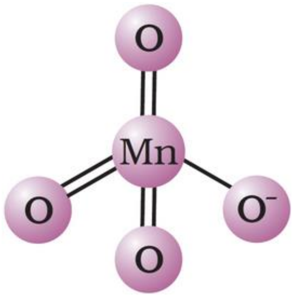
(i) $2MnO_4^- + H_2O + I^- \longrightarrow 2MnO_2 + 2OH^- + IO_3^-$ **CBSE 2018**

(ii) $8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$ **CBSE 2016**

(iii) $2MnO_4^- + 3Mn^{2+} + 2H_2O \longrightarrow 5MnO_2 + 4H^+$
-Zinc Sulphate or Zinc Oxide act as catalyst.



Manganate Ion (GREEN) Mn in +6



Permanganate Ion (PURPLE) Mn in +7

USES:

Used in analytical chemistry in the technique of titration.

Titration using $KMnO_4$ in the presence of HCl and HNO_3 often leads to unsatisfactory results as Cl^- of HCl is oxidised to Cl_2 and as HNO_3 is itself an oxidising agent, it oxidises the titrand and does not let $KMnO_4$ exhibit its oxidising property. **CBSE 2017(2)**

Used as a favourite oxidant in preparative organic chemistry.

Used for the bleaching of wool, cotton, silk and other textile fibres and for the decolourisation of oils, as a result of its strong oxidising power.

F-BLOCK

(The Inner-Transition Metals)

LANTHANOIDS
(The 14 elements following Lanthanum)

ACTINOIDS
(The 14 elements following Actinium)

INTRODUCTION:

-Lanthanum resembles the Lanthanoids, and Actinium the Actinoids, thus it is common to study them with their respective following groups.

-The lanthanoids resemble one another more than the members of ordinary transition elements in any series. They have only one stable oxidation state.

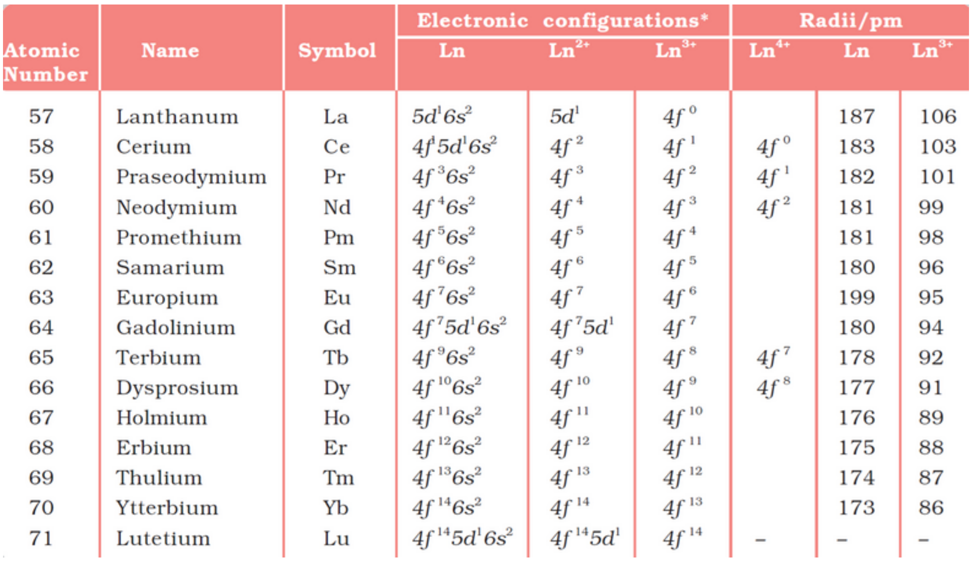
-The chemistry of the actinoids is much more complicated. The complication arises because of the occurrence of a wide range of oxidation states in these elements and because of their radioactive properties.

THE LANTHANOIDS

1. ELECTRONIC CONFIGURATION:

-In neutral state, all lanthanoids have fully-filled 6s orbital but, are found with variable occupancy of 4f and 5d subshells because the energy difference between the orbitals of these subshells is very low and electron can shift between them very easily to achieve the most stable electronic configuration.

- In X^{3+}, which is their most stable Oxidation State, they have the configuration $4f^n$ (n=1,2,3...,14).



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

Electronic Configurations and Radii of Lanthanum and Lanthanoids

2. IONIC AND ATOMIC RADII:

-There is an overall more than expected decrease in the size of lanthanoids as we move right from Lanthanum to Luterium and this is called lanthanoid contraction.

-It has consequences in the chemistry of the 5d series elements as well.

-The decrease in atomic radii is not quite regular as it is regular in M^{3+} ions.

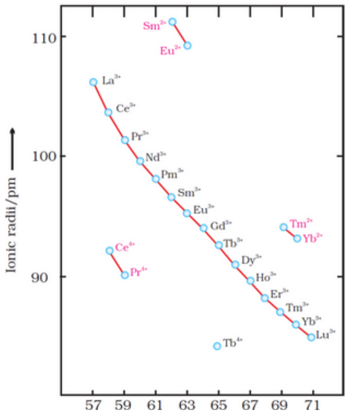
-This contraction is, of course, similar to that observed in a transition series and is attributed to the same cause, the imperfect shielding of one electron by another in the same sub-shell.

-However, the shielding of one 4f electron by another is less than one d electron by another with the increase in nuclear charge along the series.

-There is fairly regular decrease in the sizes with increasing atomic number.

-Due to Lanthanoid Contraction, the 5d series elements have a size almost equal to their corresponding group members from the 4d series.

Eg- Hf(159 pm) and Zr(160 pm) have an almost identical atomic size due to lanthanoid contraction and because of this they are found to exist together in nature and it is difficult to separate them. **CBSE 2016, 2013**



Trends in ionic radii of lanthanoids

2012,2017(2),
2016,2019(2),

3. OXIDATION STATES:

-Predominantly, they exist as X^{3+} or X^{2+} .

-However, occasionally in the solid phase or in a solution, they are found in +2 or +4 states.

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

-These reasons are also responsible for the irregular ionisation enthalpies.

Eg-

(a)The formation of Eu^{2+} and Yb^{2+} is favoured because of their half-filled and fully-filled 4f configuration respectively.

$Eu - 4f^7 6s^2 \longrightarrow Eu^{2+} - 4f^7 6s^0 \longrightarrow$ Half-filled configuration

$Yb - 4f^{14} 6s^2 \longrightarrow Yb^{2+} - 4f^{14} 6s^0 \longrightarrow$ Fully-filled configuration.

However, Eu^{2+} and Yb^{2+} are strong Reducing Agents i.e., prefer being oxidised to the +3 ion . **CBSE 2017, 2019**

(b) The formation of Tb^{4+} is favoured because of its half-filled 4f configuration.

$Tb - 4f^9 6s^2 \longrightarrow Tb^{4+} - 4f^7 6s^0 \longrightarrow$ Half-filled configuration

However, Tb^{4+} acts as an oxidising agent i.e., prefers getting reduced to the +3 state.

(c) CeIV 's formation is favoured because of its noble gas configuration.

$Ce - [Xe]\, 4f^1\, 5d^1\, 6s^2 \longrightarrow Ce^{4+} - [Xe]\, 4f^0\, 5d^0\, 6s^0 \longrightarrow [Xe]$ **CBSE 2016, 2012, 2017(2)**

$\longrightarrow$ Noble gas configuration.

Practically, Ce^{+4} acts as an Oxidising Agent, i.e. prefers being reduced to Ce^{3+}. In fact, Ce^{4+} can even oxidise water, still it is used in analytical chemistry because it is kinetically very slow. **CBSE 2019**

(d) Sm, like Eu, exhibits +2 and +3 Oxidation States.

(e) Pr, Nd, Tb and Dy also exhibit +4 state but only in oxides, MO_2.

(4) GENERAL CHARACTERISTICS:

-All the lanthanoids are silvery white soft metals and tarnish rapidly in air.

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

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

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

-Density and other properties change smoothly except for Eu and Yb.

-Many trivalent lanthanoid ions are coloured(except La^{3+} and Lu^{3+}) both in the solid state and in aqueous solutions. Colour of these ions may be attributed to the presence of f-electrons.

-The lanthanoid ions other than the f^0 type (La^{3+} and Ce^{4+}) and the f^{14} type (Yb^{2+} and Lu^{3+}) are all paramagnetic.

-The first and second ionisation enthalpies of the lanthanoids are comparable with those of calcium.

-The third ionisation enthalpies indicates that the exchange enthalpy considerations, appear to impart a certain degree of stability to empty, half-filled and completely filled orbitals .

-Chemically, the earlier members of the series are similar to calcium but, with increasing atomic number, they behave more like aluminium.

-The metals combine with hydrogen when gently heated in the gas.

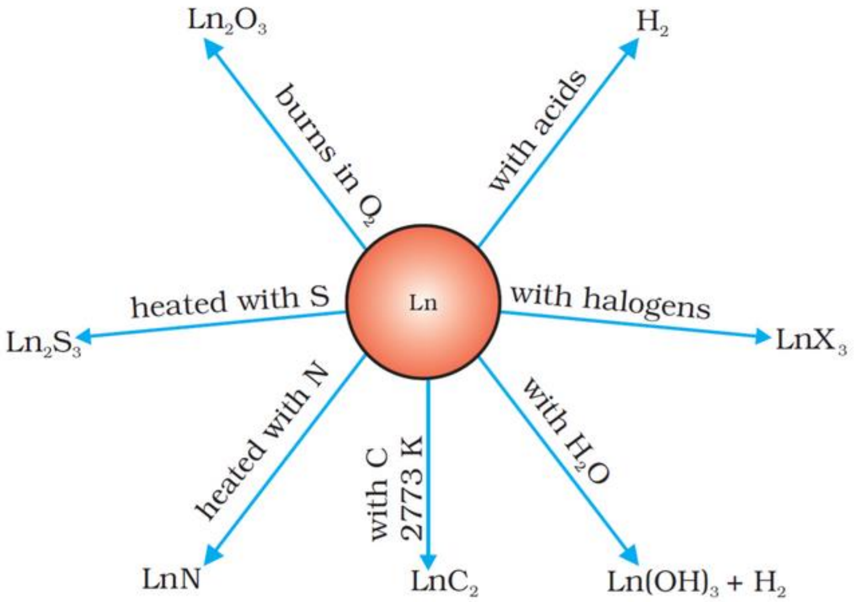
-The carbides, Ln_3C, Ln_2C_3 and LnC_2 are formed when the metals are heated with carbon.

-They liberate hydrogen from dilute acids and burn in halogens to form halides.

-They form oxides M_2O_3, sulphides M_2S_3 and hydroxides $M(OH)_3$. **CBSE 2020**

-The hydroxides are definite compounds, not just hydrated oxides. They are basic like alkaline earth metal oxides and hydroxides. The basic property of hydroxides decrease as we go from La to Lu because of decrease in size due to LANTHANOID CONTRACTION. **CBSE 2018**

- General reactions of Lanthanoids are as follows:



Chemical reactions of the lanthanoids

USES

Production of alloy steels for plates and pipes. A well known alloy is **misch-metall** which consists of a lanthanoid metal (~ 95%) and iron (~ 5%) and traces of S, C, Ca and Al. **CBSE 2016**

A good deal of Misch-metall is used in Mg-based alloy to produce bullets, shell and lighter flint.

Some individual Ln oxides are used as phosphors in television screens and similar fluorescing surfaces.

Mixed oxides of lanthanoids are employed as catalysts in petroleum cracking.

THE ACTINOIDS

- Includes the fourteen elements from Thorium to Lawrencium.
- The actinoids are radioactive and showcase a variety of oxidation states, thus their chemistry is complex. **CBSE 2017**
- As the latter members could be prepared only in nanogram quantities, they are difficult to study.

1. ELECTRONIC CONFIGURATION:

- All the actinoids are believed to have the electronic configuration of $7s^2$ and variable occupancy of the 5f and 6d subshells.
- The addition of fourteen electrons with increasing atomic numbers, is done to 5f.

*Thorium is an exception to this as the new electron that comes to it while moving from actinium(89) to it, goes to the 6d orbital.

- The irregularities in the electronic configurations of the actinoids, like those in the lanthanoids are related to the stabilities of the f^0, f^7 and f^{14} occupancies of the 5f orbitals. **CBSE 2016, 2019**

Eg- The configurations of Am and Cm are [Rn] $5f^7\ 7s^2$ and [Rn] $5f^7\ 6d^1\ 7s^2$ respectively.

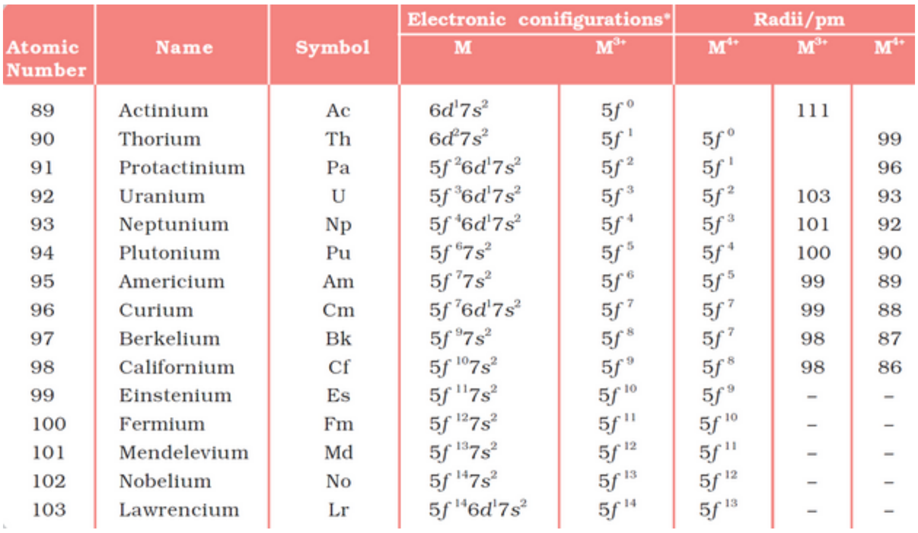
- Although the 5f orbitals resemble the 4f orbitals in their angular part of the wave-function, they are not as buried as 4f orbitals and hence 5f electrons can participate in bonding to a far greater extent.

2. IONIC SIZE:

-There is a decrease in the size of atoms or M^{3+} ions across the series.

-This may be referred to as the Actinoid Contraction.

The effect of Actinoid Contraction is greater than Lanthanoid Contraction because of even poor shielding by 5f electrons. **CBSE 2015, 2020**

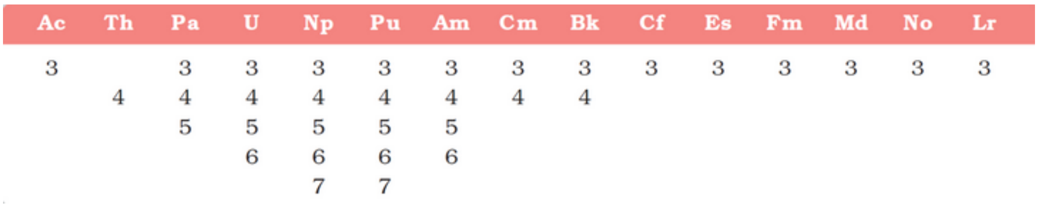


Atomic Number	Name	Symbol	Electronic conifigurations*		Radii/pm		
			M	M^{3+}	M^{4+}	M^{3+}	M^{4+}
89	Actinium	Ac	$6d^1 7s^2$	$5f^0$		111	
90	Thorium	Th	$6d^2 7s^2$	$5f^1$	$5f^0$		99
91	Protactinium	Pa	$5f^2 6d^1 7s^2$	$5f^2$	$5f^1$		96
92	Uranium	U	$5f^3 6d^1 7s^2$	$5f^3$	$5f^2$	103	93
93	Neptunium	Np	$5f^4 6d^1 7s^2$	$5f^4$	$5f^3$	101	92
94	Plutonium	Pu	$5f^6 7s^2$	$5f^5$	$5f^4$	100	90
95	Americium	Am	$5f^7 7s^2$	$5f^6$	$5f^5$	99	89
96	Curium	Cm	$5f^7 6d^1 7s^2$	$5f^7$	$5f^7$	99	88
97	Berkelium	Bk	$5f^9 7s^2$	$5f^8$	$5f^7$	98	87
98	Californium	Cf	$5f^{10} 7s^2$	$5f^9$	$5f^8$	98	86
99	Einstenium	Es	$5f^{11} 7s^2$	$5f^{10}$	$5f^9$	–	–
100	Fermium	Fm	$5f^{12} 7s^2$	$5f^{11}$	$5f^{10}$	–	–
101	Mendelevium	Md	$5f^{13} 7s^2$	$5f^{12}$	$5f^{11}$	–	–
102	Nobelium	No	$5f^{14} 7s^2$	$5f^{13}$	$5f^{12}$	–	–
103	Lawrencium	Lr	$5f^{14} 6d^1 7s^2$	$5f^{14}$	$5f^{13}$	–	–

Electronic Configurations and Radii of Actinium and Actinoids

3. OXIDATION STATES:

-There is a greater range of oxidation states exhibited by the actinoids, because of the fact that the 5f, 6d and 7s levels are of comparable energies and electrons of all these 3 subshells can interact while reacting. **CBSE 2020, 2019, 2012**



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

The known oxidation states of Actinium and Actinoids

-The actinoids generally show +3 oxidation state. The elements, in the first half of the series frequently exhibit higher oxidation states.

Eg-The maximum oxidation state increases from +4 in Th to +5 in Pa,+6 in U and +7 in Np. The successive elements show a decrease in their maximum oxidation states.

-Have more compounds in +3 state than in the +4 state. However, +3 and +4 ions tend to hydrolyse.

-The distribution of oxidation states among the actinoids is very uneven.

(4) GENERAL PROPERTIES

PHYSICAL: The actinoids are all silvery in appearance but display a variety of structures. This structural variability is obtained due to irregularities in metallic radii which are far greater than in lanthanoids

REACTIVITY:
-The actinoids when finely divided are highly reactive
Eg- With boiling water they form a mixture of oxide and hydride.
-The combination with most non-metals takes place at moderate temperatures.

ATTACK OF ACIDS AND ALKALIES: Hydrochloric acid attacks all metals but most are slightly affected by nitric acid owing to the formation of protective oxide layers. Alkalies, however have no action.

MAGNETIC PROPERTIES: The magnetic properties of the actinoids are complex. The variation in the magnetic susceptibility, with the number of unpaired 5f electrons, is roughly parallel to the corresponding results for the lanthanoids, but the latter has higher values.

IONISATION ENTHALPIES:
-The ionisation enthalpies are lower than the early lanthanoids.
-Because of the fact that the outer electrons of actinoids are less firmly held, they are available for bonding. **CBSE 2020**

5. COMPARISON WITH LANTHANOIDS: **CBSE 2017(2), 2015**

-The behavioural similarities become evident after the second half of the actinoid series. Although, like lanthanoids, even the early actinoids show close similarities with each other and gradual variation in properties not involving change in oxidation state.
-The lanthanoid and actinoid contractions, have extended effects on the sizes, thus also on the properties of the elements succeeding them in their respective periods.
-The lanthanoid contraction is more important because the chemistry of elements succeeding the actinoids are much less known and studied.

-The photographic industry relies on the special light-sensitive properties of AgBr.

Steel Production: It is based on the reduction of iron oxides, the removal of impurities and the addition of carbon and alloying metals such as Cr, Mn and Ni.

TiO is manufactured for the pigment industry and MnO_2 for use in dry battery cells.
The battery industry also requires Zn and Ni/Cd.

6. APPLICATIONS OF TRANSITION AND INNER TRANSITON METALS:

Many of the metals and/or their compounds are essential catalysts in the chemical industry:

(a) V_2O_5 catalyses the oxidation of SO_2 in the manufacture of sulphuric acid.
(b) $TiCl_4$ with $Al(CH_3)_3$ forms the basis of the Ziegler catalysts used to manufacture polyethylene (polythene).
(c)Iron catalysts are used in the Haber process for the production of ammonia from N_2/H_2 mixtures.
(d)Nickel catalysts enable the hydrogenation of fats.
(e)In the Wacker process the oxidation of ethyne to ethanal is catalysed by $PdCl_2$.
(f)Nickel complexes are useful in the polymerisation of alkynes and other organic compounds such as benzene.

The elements of Group 11 are called the coinage metals, although Ag and Au are restricted to collection items.