

INORGANIC CHEMISTRY

ENTHUSIAST | LEADER | ACHIEVER

GROUPS

d-Block

4	5	6	7	8	9	10	11	12	13	14	15
22 Ti $3d^2 4s^2$	23 V $3d^3 4s^2$	24 Cr $3d^5 4s^1$	25 Mn $3d^5 4s^2$	26 Fe $3d^6 4s^2$	27 Co $3d^7 4s^2$	28 Ni $3d^8 4s^2$	29 Cu $3d^{10} 4s^1$	30 Zn $3d^{10} 4s^2$	31 Ga $4s^2 4p^1$	32 Ge $4s^2 4p^2$	33 As $4s^2 4p^3$
40 Zr $4d^2 5s^2$	41 Nb $4d^4 5s^1$	42 Mo $4d^5 5s^1$	43 Tc $4d^5 5s^2$	44 Ru $4d^7 5s^1$	45 Rh $4d^8 5s^1$	46 Pd $4d^{10}$	47 Ag $4d^{10} 5s^1$	48 Cd $4d^{10} 5s^2$	49 In $5s^2 5p^1$	50 Sn $5s^2 5p^2$	51 Sb $5s^2 5p^3$
72 Hf $4f^{14} 5d^2 6s^2$	73 Ta $5d^3 6s^2$	74 W $5d^4 6s^2$	75 Re $5d^5 6s^2$	76 Os $5d^6 6s^2$	77 Ir $5d^7 6s^2$	78 Pt $5d^9 6s^1$	79 Au $5d^{10} 6s^1$	80 Hg $5d^{10} 6s^2$	81 Tl $6s^2 6p^1$	82 Pb $6s^2 6p^2$	83 Bi $6s^2 6p^3$
104 Rf $6d^2 7s^2$	105 Db $6d^3 7s^2$	106 Sg $6d^4 7s^2$	107 Bh $6d^5 7s^2$	108 Hs $6d^6 7s^2$	109 Mt $6d^7 7s^2$	110 Ds $6d^9 7s^2$	111 Rg $6d^{10} 7s^1$	112 Uub $6d^{10} 7s^2$	113 Uut $7s^2 7p^1$	114 Uuq $7s^2 7p^2$	115 Uup $7s^2 7p^3$

f-block

59 Pr $4f^5 5d^1 6s^2$	60 Nd $4f^4 5d^1 6s^2$	61 Pm $4f^5 5d^0 6s^2$	62 Sm $4f^6 5d^0 6s^2$	63 Eu $4f^7 5d^0 6s^2$	64 Gd $4f^7 5d^1 6s^2$	65 Tb $4f^9 5d^0 6s^2$	66 Dy $4f^{10} 5d^0 6s^2$	67 Ho $4f^{11} 5d^0 6s^2$	68 Er $4f^{12} 5d^0 6s^2$	69 Tm $4f^{13} 5d^0 6s^2$	70 Yb $4f^{14} 5d^0 6s^2$
91 Pa $5f^3 6d^1 7s^2$	92 U $5f^3 6d^1 7s^2$	93 Np $5f^4 6d^1 7s^2$	94 Pu $5f^6 6d^1 7s^2$	95 Am $5f^7 6d^1 7s^2$	96 Cm $5f^7 6d^2 7s^2$	97 Bk $5f^9 6d^1 7s^2$	98 Cf $5f^{10} 6d^1 7s^2$	99 Es $5f^{11} 6d^1 7s^2$	100 Fm $5f^{12} 6d^1 7s^2$	101 Md $5f^{13} 6d^1 7s^2$	102 No $5f^{14} 6d^1 7s^2$

STUDY MATERIAL

d and f-Block Elements

ENGLISH MEDIUM

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d & f-BLOCK ELEMENTS

2.0 INTRODUCTION :

- (i) d-block elements are often called as 'transition elements' because their position in periodic table is between the s-block and p-block elements.
- (ii) Their properties are transitional between the highly reactive metallic elements of s-block (which form ionic compounds) and the elements of p-block (which form covalent compounds).
- (iii) Typically the transition elements have an incompletely filled d-orbital. A transition element may be defined as the element whose atom in ground state or in one of common oxidation states, has partly filled d-sub shell i.e. having electrons between 1 to 9.
- (iv) Group 12 (the zinc group) elements have completely filled d-orbitals in the ground state as well as in their common oxidation states. Therefore, they are not regarded as transition elements.
- (v) The general electronic configuration of d-block elements is $(n-1) d^{1-10} ns^{1-2}$, where n is the outer most shell. However, palladium does not follow this general electronic configuration. It has electron configuration $[Kr]^{36} 4d^{10} 5s^0$.
- (vi) Zn, Cd and Hg are involved in transition series but they are called non transition elements due to completely filled d-orbitals.

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
3d	1	2	3	5	5	6	7	8	10	10

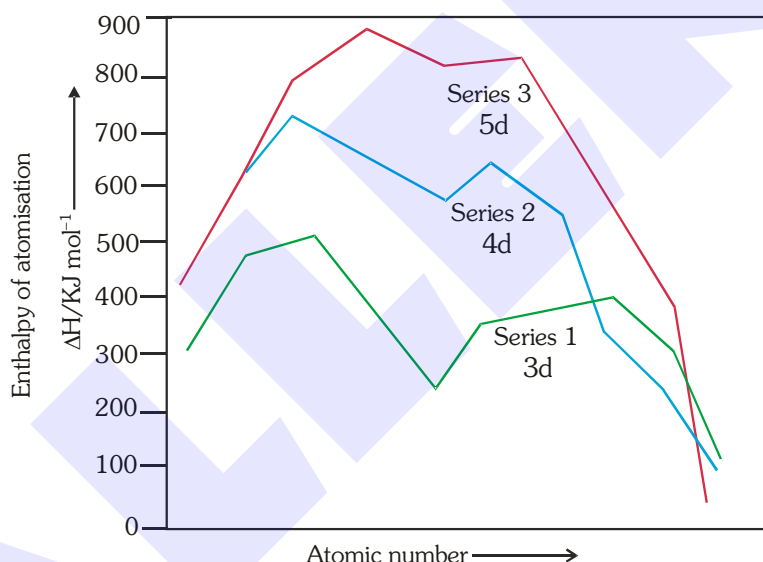
2nd Series										
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Z	39	40	41	42	43	44	45	46	47	48
5s	2	2	1	1	1	1	1	0	1	2
4d	1	2	4	5	6	7	8	10	10	10

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

2.1 GENERAL TRENDS IN THE CHEMISTRY OF TRANSITION ELEMENTS.

(A) Metallic character :

- (i) In d-block elements the penultimate shell of electrons is expanding. Thus they have many physical and chemical properties in common.
- (ii) Nearly all the transition elements display typical metallic properties such as high tensile strength, ductility, malleability, high thermal and electrical conductivity and metallic lustre.
- (iii) Most transition elements have ccp/hcp type structures.
- (iv) The transition elements are very much hard and have low volatility.
- (v) Cr, Mo and W have maximum number of unpaired electrons and therefore, these are very hard metals and have maximum enthalpies of atomisation in their respective period.
- (vi) The metals with very high enthalpy of atomisation tend to be noble in their reactions.
- (vii) The metals of the 4d and 5d series have greater enthalpies of atomisation than the corresponding elements of the 3d and this is an important factor indicating for the occurrence of much more frequent metal-metal bonding in compounds of the heavy transition metals.

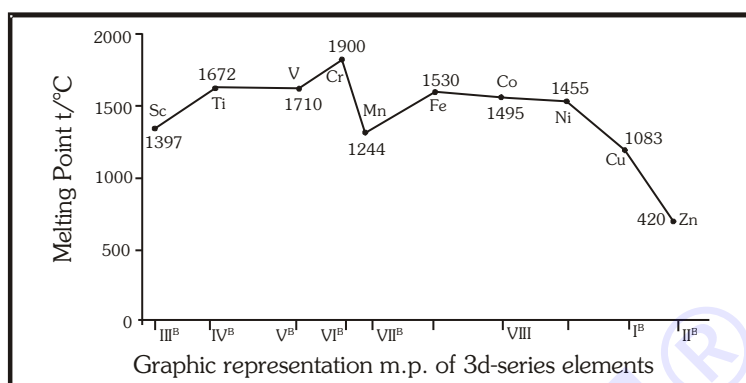


Graph showing Trends in enthalpies of atomisation of transition elements

(B) MELTING AND BOILING POINTS

- (i) Melting and boiling point of d-block elements is more than that of s block elements.
Reason : Stronger metallic bond formed by present unpaired d-electrons.
- (ii) In Zn, Cd, and Hg there is no unpaired electron present in d-orbital, hence due to absence of covalent bond, melting and boiling point are very low in series. (Volatile metals Zn, Cd, Hg)
- (iii) In 3d series, the melting points of metals rise to a maximum at d^5 except for anomalous value of Mn and Fall regularly as the atomic number increases.
- (iv) As the number of unpaired d-electron increases, the number of covalent bond and bond energy between the atoms is expected to increase up to Cr family where each of the d-orbital has only unpaired electron and the opportunity for covalent sharing is greatest.

- (v) Mn and Tc have comparatively low melting point, due to weak metallic bond because of stable Half filled (d^5) configuration.
- (vi) Lowest melting point Hg (-38°C) ; Highest melting point W (3400°C)



Illustrations

Illustration 1 : Why do the transition elements have higher boiling & melting points ?

Solution Because of having larger number of unpaired electrons in their atoms, they have stronger interatomic interaction which causes strong metallic bonds between the atoms of these elements attributing to their high melting and boiling points.

(C) DENSITY :

- The atomic volumes of the transition elements are low compared with the elements of group 1 and 2. This is because the increased effective nuclear charge. Consequently the densities of the transition metals are high.
- Across a period from left to right atomic volumes decrease and atomic masses increase. Hence the densities increase across a period.

$$\text{Sc} \leq \text{Ti} \leq \text{V} \leq \text{Cr} \leq \text{Mn} \leq \text{Fe} \leq \text{Co} \leq \text{Ni} \approx \text{Cu} > \text{Zn}$$
 (Zn has lower density because of its large atomic volume)
- $3d < 4d < 5d$; order of density in a group.
- Maximum density : $\text{Ir} \geq \text{Os}$

(D) Ionisation energies or Ionisation enthalpies :

- They have high IE as compared to group 1 and group 2 metals due to their high z_{eff} .
- The first ionisation energy of Zn, Cd, and Hg are very high because of their fully filled $(n-1)d^{10}ns^2$ configuration.

(E) Variable oxidation states :

- The transition metals exhibit a large number of oxidation states. These different oxidation states are related to the electronic configuration of their atoms.
- The existence of the transition elements in different oxidation states is due to the participation of inner $(n-1)d$ -electrons in addition to outer ns -electrons because, the energies of the ns and $(n-1)d$ -subshells are nearly same.
- In general oxidation state of d-block element is given as
 minimum oxidation state = number of ' ns ' electrons
 maximum oxidation state = number of ' ns ' electrons + unpaired ' $(n-1)d$ ' electron

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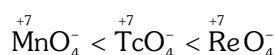
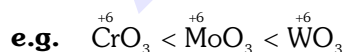
- (iv) Different oxidation states of first transition series (the most common ones are in bold types).

Element	Outer electronic configuration	Oxidation states
Sc	$3d^1 4s^2$	+3
Ti	$3d^2 4s^2$	+2, +3, +4
V	$3d^3 4s^2$	+2, +3, +4, +5
Cr	$3d^5 4s^1$	+2, +3 , +4, +5, +6
Mn	$3d^5 4s^2$	+2 , +3, +4, +5, +6, +7
Fe	$3d^6 4s^2$	+2 , +3 , +4, +5, +6
Co	$3d^7 4s^2$	+2 , +3 , +4
Ni	$3d^8 4s^2$	+2 , +3, +4
Cu	$3d^{10} 4s^1$	+1, +2
Zn	$3d^{10} 4s^2$	+2

- (v) Highest oxidation state in d-block = +8 (Os, Ru)
 (vi) Transition elements show zero oxidation state in metal carbonyls e.g. $[\text{Ni}(\text{CO})_4]$, $[\text{Fe}(\text{CO})_5]$
 (vii) Relative stability of oxidation state :

$\text{Sc}^{+2} < \text{Sc}^{+3}$	inert gas stable configuration
$\text{Ti}^{+3} < \text{Ti}^{+4}$	
$\text{Mn}^{+6} < \text{Mn}^{+7}$	
$\text{V}^{+4} < \text{V}^{+5}$	
$\text{Mn}^{+3} < \text{Mn}^{+2}$	d^5 stable configuration
$\text{Cr}^{+2} < \text{Cr}^{+3}$	d^3 is more stable than d^4 in aq. solution
$\text{Ni}^{+2} > \text{Ni}^{+4}$	
$\text{Pt}^{+2} < \text{Pt}^{+4}$	On the basis of sum of first four I.P's.

- (viii) On moving in a period stability of higher oxidation state decreases
e.g. $\text{VO}_3^- > \text{CrO}_4^{2-} > \text{MnO}_4^-$
 (ix) On moving down the group stability of higher oxidation state increases

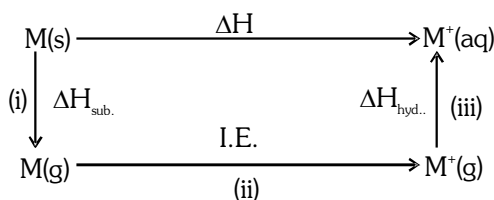


(F) ELECTRODE POTENTIALS :

In addition to ionisation enthalpy, the other factors such as enthalpy of sublimation, hydration enthalpy etc. determine the stability of a particular oxidation state in solution. This can be explained in terms of their electrode potential values. The oxidation potential of a metal involves the following process:



This process actually takes place in the following three steps as given in following flowchart :



The oxidation potential which gives the tendency of the overall change to occur, depends upon the net effect of these three steps. The overall energy change is $\Delta H = \Delta H_{\text{sub}} + \Delta H_{\text{I.E.}} + \Delta H_{\text{hyd}}$

If SOP is +ve that means oxidation will be easy

If SRP is +ve that means reduction will be easy.

Some important examples :

1. $E^0_{\text{M}^{+2}/\text{M}} \Rightarrow$ +ve only for Cu among 3d elements because hydration energy of Cu^{+2} is not enough to compensate for sublimation energy, IE_1 and IE_2 for Cu.

2. $E^0_{\text{M}^{+3}/\text{M}^{+2}}$

(a) $E^0_{\text{Cr}^{+3}/\text{Cr}^{+2}} = -ve$

that means Cr^{+2} acts as a reducing agent because Cr^{+3} has t_{2g} half filled stable configuration.

(b) $E^0_{\text{Mn}^{+3}/\text{Mn}^{+2}} = +ve$

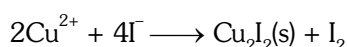
that means Mn^{+3} acts as an oxidising agent due to stability of half filled (d^5) configuration.

(G) TRENDS IN STABILITY OF HIGHER OXIDATION STATES

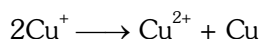
The highest oxidation states are shown generally among halides and oxides of transition elements.

(a) In halides of transition elements

- (i) The transition elements react with halogens at high temperatures to form transition metal halides.
- (ii) Since fluorine is the most electronegative element, the transition metals show highest oxidation states with fluorine. The highest oxidation states are found in TiX_4 (tetrahalides, X = F, Cl, Br and I), VF_5 and CrF_6 .
- (iii) The +7 oxidation state for Mn is not shown by simple halides. However, MnO_3F is known in which the oxidation state of Mn is +7.
- (iv) The tendency of fluorine to stabilise the highest oxidation state is due to either higher lattice enthalpy as in case of CoF_3 or higher bond enthalpy terms for the higher covalent compounds. eg. VF_5 and CrF_6 .
- (v) Fluorides are relatively unstable in their low oxidation states. For example, vanadium form only VX_2 (X = Cl, Br or I) and copper can form CuX (X = Cl, Br, I). On the other hand all copper (II) halides are known except the iodide. This is because, Cu^{2+} oxidises I^- to I_2 .



- (vi) It has been observed that many copper (I) compounds are unstable in aqueous solution and they undergo disproportionation



Copper in +2 oxidation state is more stable than in +1 oxidation state. This can be explained on the basis of much larger negative hydration enthalpy (ΔH_{hyd}) of Cu^{2+} (aq) than Cu^{+} , which is sufficiently high to compensate second ionisation enthalpy of copper.

(b) IN METAL OXIDES AND OXOCATIONS.

- (i) The ability of oxygen to stabilize the highest oxidation state is demonstrated in their oxides. The highest oxidation states in their oxides coincides with the group number. For example, the highest oxidation state of scandium of group 3 is +3 in its oxides, Sc_2O_3 whereas the highest oxidation state of manganese of group 7 is +7, in Mn_2O_7 .
- (ii) Besides the oxides, oxocation of the metals also stabilise higher oxidation states. For example, V^V as VO_2^+ , V^{IV} as VO^{2+} and Ti^{IV} as TiO^{2+} .
- (iii) It may be noted that the ability of oxygen to stabilise these high oxidation states exceeds that of fluorine. For example, manganese forms highest fluoride as MnF_4 whereas the highest oxide is Mn_2O_7 . This is due to the fact that oxygen has ability to form multiple bonds to metals.
- (iv) The transition elements in the +2 and +3 oxidation states mostly form ionic bonds whereas with higher oxidation states, the bonds are essentially covalent e.g. in MnO_4^- all bonds are covalent. In these higher oxides the acidic character is predominant. Thus CrO_3 gives H_2CrO_4 and $\text{H}_2\text{Cr}_2\text{O}_7$ and Mn_2O_7 gives HMnO_4 . **V_2O_5 is, however amphoteric though mainly acidic and with alkalis as well as acids gives VO_4^{3-} and VO_2^+ respectively.**

(H) MAGNETIC PROPERTIES

When a magnetic field is applied to substances mainly two type of magnetic behaviour is observed.

- (i) **Paramagnetic substances.** The substances which are attracted by magnetic field are called paramagnetic substances and this character arises due to the presence of unpaired electrons in the atomic orbitals.
- (ii) **Diamagnetic substances.** The substances which are repelled by magnetic field are called diamagnetic substances and this character arises due to the presence of paired electrons in the atomic orbitals.

Most of the transition metal ions or their compounds have unpaired electrons in d-sub-shell (from configuration d^1 to d^9) and therefore, they give rise to paramagnetic character.

- (iii) The magnetic moment arise only from the spin of the electrons. This can be calculated from the relation $\mu = \sqrt{n(n+2)}$ B.M. n = Number of unpaired electrons

Table : Calculated and Observed Magnetic Moments (BM)

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	

(I) FORMATION OF INTERSTITIAL COMPOUNDS

Transition metals form interstitial compounds with elements such as hydrogen, boron, carbon and nitrogen. The small atoms of these non-metallic elements (H, B, C, N, etc.) get trapped in vacant spaces of the lattices of the transition metal atoms as shown below.

e.g. TiC, Fe₃H, TiH_{1.70}, VH_{0.56}, Mn₄N etc.

Properties :

- (1) They are generally non-stoichiometric compound.
- (2) Neither typically ionic nor typically covalent
- (3) Harder than pure metal
- (4) High melting point than pure metal
- (5) They retain metallic conductivity
- (6) They are chemically inert

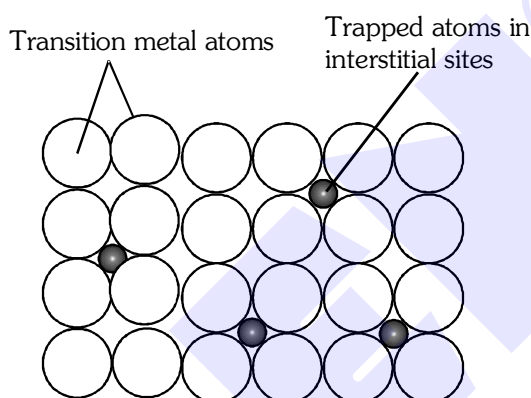


Figure showing formation of interstitial compounds

(J) CATALYTIC PROPERTIES

d-block metals or their compound act as catalyst in many reaction due to :

- (i) Possibility of variable oxidation state
- (ii) Presence of free valencies over metal surface (adsorption power)
- (iii) Presence of vacant d-orbital

e.g. Iron (III) catalyses the reaction between iodide and per sulphate ions.

**Explanation :**

Other examples of catalyst are : Finely divided iron (in Haber process), nickel (in catalytic hydrogenation)

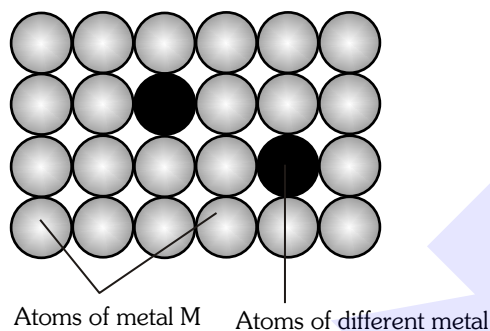
(K) ALLOY FORMATION :

- (1) Alloys are homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other metal.
- (2) The alloys are generally formed by those atoms which have metallic radii within about 15% of each other.
- (3) Transition metals form a large number of alloys because transition metals are quite similar in size and therefore the atoms of one metal can substitute the atoms of other metal in its crystal lattice.
- (4) The alloys so formed are very hard and have often high melting points.
- (5)

1. Bronze	-	Cu + Sn
2. Brass	-	Cu (60%) + Zn (40%)
3. Gun metal	-	(Cu + Zn + Sn)

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4. German Silver - Cu (25-30%) + Zn (25-30%) + Ni (40-50%)
5. Nichrome - (Ni + Cr + Fe)
6. Alloys of steel
 - (a) Chromium steel Cr (2-4%)
 - (b) Nickel Steel Ni (3-5%)
 - (c) Stainless steel Cr (12-14%) & Ni (2-4%) Cr forms oxide layer & Protects Iron From Rusting
 - (d) Invar Ni (36%)
- (6) Amalgm is a semisolid alloy which is formed by mixing a metal with Hg. Fe, CO, Ni do not form amalgam due to large difference in size.


Alloy formation
BEGINNER'S BOX-1

1. Transition elements exhibit variable oxidation states in their compounds due to
 - (1) strong shielding of (n-1) d-electrons
 - (2) very small energy difference between (n-1)d and ns orbitals
 - (3) presence of unpaired electrons
 - (4) high energy difference between (n-1)d and ns orbitals
2. Which element do not show more than one oxidation state

(1) Mn	(2) Cr	(3) Fe	(4) Sc
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3. Consider the ions Fe^{2+} , Fe^{3+} , Cr^{2+} , Cr^{3+} , Mn^{2+} , Mn^{3+}
 - (i) Strongest oxidising ion is

(1) Fe^{2+}	(2) Cr^{3+}	(3) Mn^{3+}	(4) Mn^{2+}
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 - (ii) Strongest reducing ion is

(1) Fe^{+3}	(2) Mn^{2+}	(3) Cr^{2+}	(4) Mn^{3+}
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4. Which compound does exist

(1) MnO_3F	(2) $\text{K}_2[\text{CuI}_4]$	(3) MnF_7	(4) CrF_7
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5. In the form of dichromate, Cr(VI) is a strong oxidising agent in acidic medium but Mo(VI) in MoO_3 and W(VI) in WO_3 are not, because
 - (1) Cr(VI) is more stable than Mo(VI) & W(VI)
 - (2) Mo(VI) and W(VI) does not exist at all
 - (3) H.O.S. of heavier members of group 6 of transition metals are more stable
 - (4) L.O.S. of heavier members of group 6 of transition metals are more stable

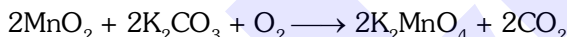
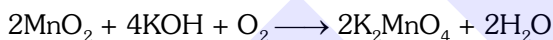
6. Which of the following show +8 oxidation state.
 (1) Fe, Ru (2) Fe, Os (3) Ru, Os (4) Mo, W
7. Which catalyst is used in contact process ?
 (1) Ni (2) V_2O_5 (3) Fe (4) $AlCl_3 + TiCl_4$
8. The element with maximum and minimum melting points in second transition series respectively.
 (1) Cr and Zn (2) Cr and Hg (3) Cr and Cd (4) Mo and Cd
9. Which of the following metal ions is expected to be paramagnetic?
 (1) Zn^{2+} (2) Ti^{3+} (3) Sc^{3+} (4) Ti^{4+}
10. Which of the element have highest density –
 (1) W (2) Os (3) Tc (4) Mo

2.2 COMPOUNDS OF d-BLOCK ELEMENTS :

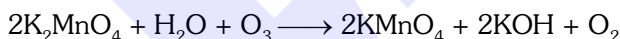
(I) POTASSIUM PERMANGANATE ($KMnO_4$) :

(a) Preparation

It is prepared by fusing pyrolusite (MnO_2) either with KOH or K_2CO_3 in presence of atmospheric oxygen or any other oxidising agent such as KNO_3 . The fused mass turns green with the formation of potassium manganate, K_2MnO_4 .

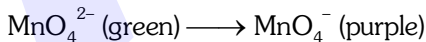
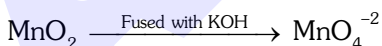


The fused mass is extracted with water and the solution is now treated with a current of chlorine or ozone or carbon dioxide to convert manganate into permanganate.

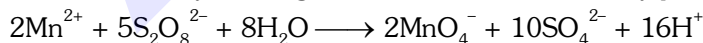


(disproportionate in acidic medium)

Commercially it is prepared by fusion of MnO_2 with KOH followed by electrolytic oxidation of manganate.



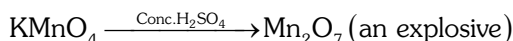
In the laboratory, a manganese(II) ion salt is oxidised by peroxodisulphate to permanganate



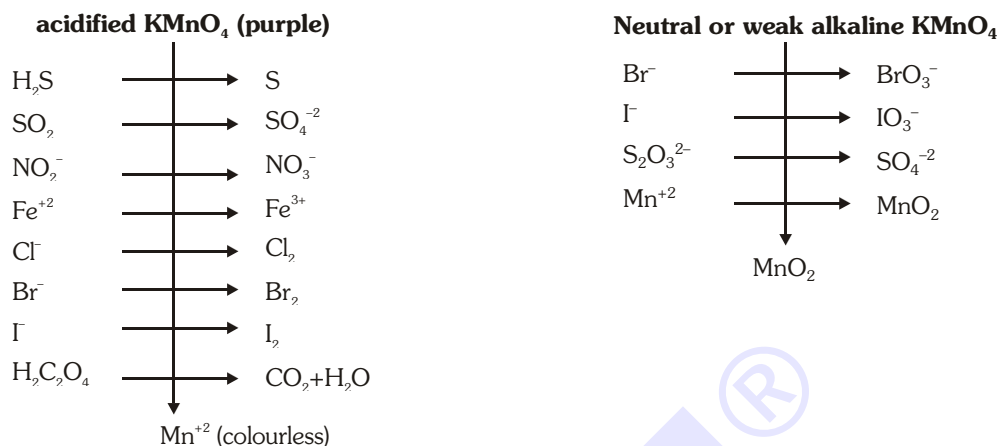
(b) **Physical property :** It is purple coloured crystalline compound. It is moderately soluble in water at room temperature.

(c) Chemical property:

- **Effect of heating** $2KMnO_4 \xrightarrow{513K} K_2MnO_4 + MnO_2 + O_2$
- On treatment with concentrated H_2SO_4 ($KMnO_4$ is taken in excess), it forms manganese heptoxide which decomposes explosively on heating.



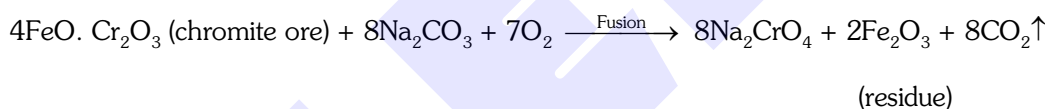
- **Potassium permanganate acts as an oxidising agent in weak alkaline, neutral or acidic solutions.**



Note :- Hydrochloric acid is not used for acidification of KMnO_4 because KMnO_4 oxidises HCl to Cl_2 .

(II) POTASSIUM DICHROMATE ($\text{K}_2\text{Cr}_2\text{O}_7$) :

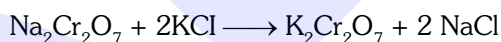
- (a) **Preparation :** The chromite ore is fused with sodium carbonate in presence of air.



The yellow solution of Na_2CrO_4 is filtered and acidified with sulphuric acid to give a solution from which orange sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$) can be crystallised.



Sodium dichromate is more soluble than potassium dichromate so $\text{K}_2\text{Cr}_2\text{O}_7$ is prepared by treating solution of $\text{Na}_2\text{Cr}_2\text{O}_7$ with KCl .

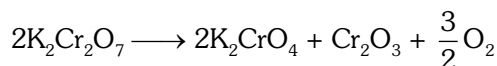


- $\text{K}_2\text{Cr}_2\text{O}_7$ is preferred over $\text{Na}_2\text{Cr}_2\text{O}_7$ as a primary standard in volumetric analysis (titration) because $\text{Na}_2\text{Cr}_2\text{O}_7$ is hygroscopic in nature but $\text{K}_2\text{Cr}_2\text{O}_7$ is not.
- $\text{CrO}_4^{-2} \xrightleftharpoons[\text{OH}^-]{\text{H}^+} \text{Cr}_2\text{O}_7^{-2}$
 Yellow Orange

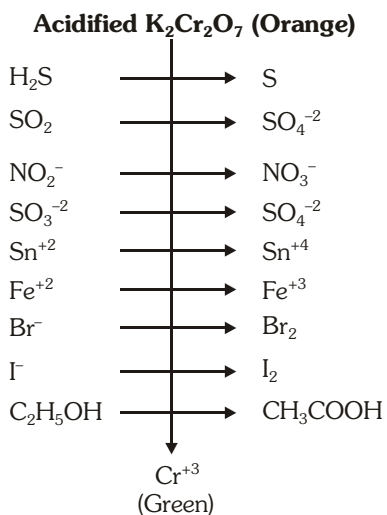
- (b) **Physical property :** It is orange-red coloured crystalline compound. It is moderately soluble in cold water but freely soluble in hot water. It melts at 398°C .

- (c) **Chemical property :**

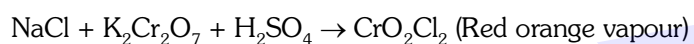
- **Effect of heating :** On strongly heating, it decomposes with liberating oxygen.



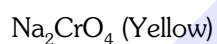
In acidic medium $\text{K}_2\text{Cr}_2\text{O}_7$ acts as an oxidising agent.



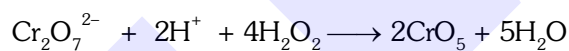
1. Chromyl chloride test (used to identify ionic chlorides)



↓ NaOH solution



2. Acidified $K_2Cr_2O_7$ solution reacts with H_2O_2 in a ethereal solution to give a deep blue solution due to the formation of CrO_5 .



f-BLOCK ELEMENTS

2.3 INNER TRANSITION ELEMENTS

The elements in which the last electron enters in $(n - 2)f$ orbitals are called **inner transition elements** or **f-block elements**.

Position in the Periodic Table

f-block elements consist of two series Lanthanoids ($\text{Ce}_{58} - \text{Lu}_{71}$), Actinoids ($\text{Th}_{90} - \text{Lr}_{103}$)

These 28 elements are present in 3^{rd} / III^{rd} B group and placed separately in lower part of periodic table.

2.4 LANTHANIDES (Rare Earths or Lanthanones)

- (i) Lanthanides are reactive elements so do not found in free state in nature.
- (ii) Most important minerals for lighter Lanthanides are – Monazite, cerites and orthite and for heavier lanthanoids – Gadolinite and Xenotime

(a) Electronic configuration

- (i) The general configuration of lanthanides may be given as $[\text{Xe}] 4f^{1-14} 5s^2 5p^6 5d^{0-1} 6s^2$.

Atomic No.	Element	Symbol	Outer electronic configuration	
			Atomic	+3 ion
58	Cerium	Ce	$4f^1 5d^1 6s^2$	$4f^1$
59	Praseodymium	Pr	$4f^3 6s^2$	$4f^2$
60.	Neodymium	Nd	$4f^4 6s^2$	$4f^3$
61.	Promethium	Pm	$4f^5 6s^2$	$4f^4$
62.	Samarium	Sm	$4f^6 6s^2$	$4f^5$
63.	Europium	Eu	$4f^7 6s^2$	$4f^6$
64.	Gadolinium	Gd	$4f^7 5d^1 6s^2$	$4f^7$
65.	Terbium	Tb	$4f^9 6s^2$	$4f^8$
66.	Dysprosium	Dy	$4f^{10} 6s^2$	$4f^9$
67.	Holmium	Ho	$4f^{11} 6s^2$	$4f^{10}$
68.	Erbium	Er	$4f^{12} 6s^2$	$4f^{11}$
69.	Thulium	Tm	$4f^{13} 6s^2$	$4f^{12}$
70.	Ytterbium	Yb	$4f^{14} 6s^2$	$4f^{13}$
71.	Lutecium	Lu	$4f^{14} 5d^1 6s^2$	$4f^{14}$

- (ii) It is to be noted that filling of 4f orbitals in the atoms is not regular. A 5d electron appears in gadolinium ($Z = 64$) with an outer electronic configuration of $4f^7 5d^1 6s^2$ (and not $4f^8 6s^2$). This is because the 4f and 5d electrons are at about the same potential energy and that the atoms have a tendency to retain stable half filled configuration.
- (iii) On the other hand, the filling of f-orbitals is regular in tripositive ions.
- (iv) **Pm** is the only synthetic radioactive lanthanide.

(b) Oxidation states

- (i) In lanthanides +3 oxidation state is most common.
- (ii) **Ce, Tb, Nd, Dy, Pr** also exhibit +4 oxidation state.
- (iii) **Sm, Eu, Tm, and Yb**, also exhibit +2 oxidation state.
- (iv) Ce^{+4} is a strong oxidising agent while Eu^{+2} is a strong reducing agent.

(c) Magnetic Properties

- In tripositive lanthanide ions the number of unpaired electrons regularly increases from lanthanum to Gadolinium (0 to 7) and then continuously decreases upto lutecium (7 to 0).
- lanthanum and lutecium ions are diamagnetic, while all other tripositive lanthanide ions are paramagnetic. (Exception – Neodymium is the most paramagnetic lanthanide).
- Ce^{+4} and Yb^{+2} are also diamagnetic ions.

(d) Colour

- The lanthanoid ions have unpaired electrons in their 4f orbitals. Thus these ions absorb visible region of light and undergo f–f transition and hence exhibit colour.
- The colour exhibited depends on the number of unpaired electrons in the 4f orbitals.
- The ions often with $4f^n$ configuration have similar colour to those ions having $4f^{14-n}$ configuration.
- lanthanide ions having $4f^0$, $4f^{14}$ are colourless.

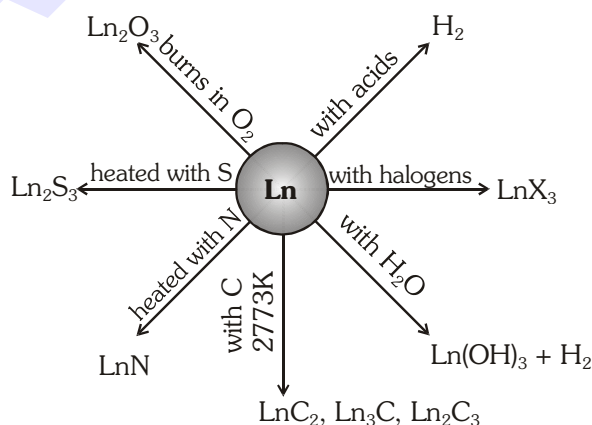
(e) Lanthanide Contraction

- In the lanthanide series with increasing atomic number, there is a progressive decrease in the size from lanthanum to lutecium or from La^{+3} to Lu^{+3} . This contraction in size is known as lanthanide contraction.
- The general electronic configuration of these elements is $4f^{1-14}5s^2 6p^0-1 6s^2$. Due to very poor shielding effect of 4f electrons, they exert very little screening effect on the outermost $6s^2$ electrons.

Hence with increasing atomic number, the enhanced nuclear charge leads to contraction in the size of atoms and ions.

APPLICATIONS OF LANTHANIDE CONTRACTION

- Atomic size :** The ionic radii of Zr^{+4} is about 9% more than Ti^{+4} . Similar trend is not maintained on passing from the second to third transition series. The ionic radius of Hf^{+4} , instead of increasing (because of inclusion of one more electronic shell), decreases (or is virtually equal to Zr^{+4}) as a consequence of the lanthanoid contraction. This explains the close similarities between the members of the second and third transition series than between the elements of the first and second series.
- Basic nature of hydroxide :** Basic nature of hydroxide regularly decreases.
- Similarity in properties of lanthanide :** Due to small difference in size the chemical properties of lanthanoids are similar and their separation is difficult.

(f) Important reactions of Lanthanides

Misch metal is an alloy of lanthanides (Mainly cerium) and iron.

2.5 ACTINIDES OR (5f - SERIES)

- The elements in which the last electron enters 5f-orbitals of $(n - 2)$ th shell are known as actinides.
- The man-made eleven elements $\text{Np}_{93} - \text{Lr}_{103}$ are placed beyond uranium in the periodic table and are collectively called trans-uranic elements.
- Th, Pa and U first three actinides are natural elements.

(a) Electronic Configuration

The general configuration of actinides may be given as $[\text{Rn}] 5f^{0-14} 6d^{0,1,2} 7s^2$.

Atomic No.	Elements	Symbol	Outer Electronic Configuration	
			Atomic	+3 ion
90	Thorium	Th	$6d^2 7s^2$	$5f^1$
91	Proactenium	Pa	$5f^2 6d^1 7s^2$	$5f^2$
92	Uranium	U	$5f^3 6d^1 7s^2$	$5f^3$
93	Neptunium	Np	$5f^4 6d^1 7s^2$	$5f^4$
94	Plutonium	Pu	$5f^6 6d^0 7s^2$	$5f^5$
95	Americium	Am	$5f^7 6d^0 7s^2$	$5f^6$
96	Curium	Cm	$5f^7 6d^1 7s^2$	$5f^7$
97	Berkellium	Bk	$5f^9 6d^0 7s^2$	$5f^8$
98	Californium	Cf	$5f^{10} 6d^0 7s^2$	$5f^9$
99	Einsteinium	Es	$5f^{11} 6d^0 7s^2$	$5f^{10}$
100	Fermium	Fm	$5f^{12} 6d^0 7s^2$	$5f^{11}$
101	Mandeleevium	Md	$5f^{13} 6d^0 7s^2$	$5f^{12}$
102	Nobellium	No	$5f^{14} 6d^0 7s^2$	$5f^{13}$
103	Lowrencium	Lr	$5f^{14} 6d^1 7s^2$	$5f^{14}$

(b) Oxidation states

- In actinoids +3 oxidation state is the most common.
- In actinides there is a greater range of oxidation states which is due to very less energy difference between 5f, 6d and 7s energy levels.
- Highest oxidation states in the actinoids is +7 exhibited by Np_{93} & Pu_{94} , it is unstable.
- Highest stable oxidation state is +6 shown by ${}_{92}\text{U}$.

Other Properties

- Physical appearance** : Actinides are silvery white metals.
- Density** : All the actinides except **thorium** and **americium** have high densities.
- Colour** : Actinide ions are generally coloured. The colour of actinide ions depends upon the number of 5f-electrons. The ions containing no unpaired 5f-electrons (exactly full filled f-subshell) are colourless, as expected.
- Ionisation energies** : Ionisation energies values of early actinides are lower than early lanthanoids.
- Electropositive character** : All the known actinide metals are **highly electropositive**. They resemble lanthanide series in this respect.
- Melting and Boiling properties** : They have **high melting and boiling points**. They do not follow regular gradation of melting or boiling points with increase in atomic number.

- **Magnetic properties** : The actinide elements are paramagnetic due to the presence of unpaired electrons.
- **Radioactive nature** : All the actinoids are radioactive in nature.
- **Actinide contraction** : The size of atom/cation decrease regularly along the actinoids series. The steady decrease in ionic radii with increase in atomic number is referred to as **actinide contraction**. This is due to poor shielding of 5f-electrons.

Comparison of Lanthanides and Actinides

Points of Resemblance :

- Both lanthanoids and actinides show a common oxidation state of +3.
- Both are electropositive and act as strong reducing agents.
- Cations with unpaired electrons in both of them are paramagnetic.
- Most of the cations of lanthanides and actinoids are coloured.
- Both of them show a steady decrease in their ionic radii along the series. Thus, lanthanides show **lanthanide contraction** and actinides show **actinide contraction**.

POINTS OF DISTINCTION

Lanthanides	Actinides
1. Besides the most common oxidation state of +3 lanthanides show +2 and +4 oxidation states in case of certain elements.	Besides the most common oxidation state of +3, actinides show +4, +5 and +6 oxidation states in case of certain elements.
2. Lanthanides have less tendency towards complex formation.	Actinides have a stronger tendency towards complex formation.
3. Except promethium, they are non radioactive.	All the actinides are radioactive.
4. Oxides and hydroxide of lanthanides are less basic.	Oxides and hydroxides of actinides are more basic

Some important uses of actinides are as follows –

Thorium : Thorium is used in atomic reactors as fuel rods and in the treatment of cancer.

Uranium : Uranium is used as nuclear fuel. Its salts are used in glass industry (for imparting green colour). textile industry and also in medicines.

Plutonium : Plutonium is used as fuel for atomic reactors as well as in atomic bombs.

BEGINNER'S BOX-2

- $$X \xrightarrow[\text{K}_2\text{Cr}_2\text{O}_7]{\text{conc. H}_2\text{SO}_4} \text{red brown vapours. X can be}$$

(1) NaI (2) NaBr (3) Both (1) & (2) (4) None of these
- $$\underset{\text{black coloured ore}}{X} \xrightarrow[\text{air}]{\text{KOH}} \underset{\text{dark green}}{Y} \xrightarrow[\text{an oxidising agent}]{\text{H}^+} Z + X$$

True statement is

(1) X can't be MnO_2 (2) Y can be KMnO_4
 (3) Z can be K_2MnO_4 (4) X is MnO_2 and Y is K_2MnO_4
- $$X \xrightleftharpoons[\text{OH}^-]{\text{H}^+} Y; Y \xrightarrow{\text{SO}_2} Z + \text{SO}_4^{2-}$$

X and Y are oxy anion of Cr than oxidation state of Cr in X, Y, Z will be respectively

(1) +3, +6, +6 (2) +6, +3, +6 (3) +6, +6, +6 (4) +6, +6, +3

4. When KMnO_4 solution is added to oxalic acid solution, the decolourisation is slow in beginning but become instantaneous after some time because
- (1) CO_2 is a by product (2) Mn^{2+} acts as a catalyst
 (3) reaction is exothermic (4) MnO_4^- catalyzes the reaction
5. The elements from cerium (At.No. 58) to lutetium (At.No. 71) in which 4f energy levels are filled up are known as :
- (1) lanthanides (2) rare earth metals (3) lanthanones (4) all the above
6. Which of the following is radioactive element :
- (1) Ce (2) Lu (3) Eu (4) Pm
7. Which of the following ion is paramagnetic ?
- (1) Ce^{+4} (2) Lu^{+3} (3) Yb^{+2} (4) Eu^{+2}
8. Which of the following ion do not show colour?
- (1) Lu^{3+} (2) Pm^{3+} (3) Eu^{3+} (4) Dy^{3+}
9. Which type of hydroxide generally formed by Lanthanoids ?
- (1) $\text{Ln}(\text{OH})_3$ (2) $\text{Ln}(\text{OH})_2$ (3) $\text{Ln}(\text{OH})_4$ (4) $\text{Ln}(\text{OH})_6$
10. Highest oxidation state +7 shown by which actinoids ?
- (1) Np, Pu (2) Pa, U (3) Am, Cm (4) Cf, Es

ANSWER'S KEY

BEGINNER'S BOX-1	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	2	4	3,3	1	3	3	2	4	2	2

BEGINNER'S BOX-2	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	2	4	4	2	4	4	4	1	1	1

NCERT QUESTIONS (REASONING)

Q.1 Why do the transition elements have higher boiling & melting points ?

Ans. Because of having larger number of unpaired electrons in their atoms, they have stronger interatomic interaction. Hence strong metallic bonds between the atoms of these elements attribute to their high melting and boiling points.

Q.2 Give the main difference in oxidation states of transition elements & p-block elements.

Ans. (i) The variation of oxidation state in transition elements is in such a way that their oxidation state differ from each other by unity e.g. V^{+2} , V^{+3} , V^{+4} , V^{+5} . While in p block elements oxidation states normally differ by two due to inert pair effect.

(ii) Stability of higher oxidation state in transition elements increase down the group

e.g. Pt^{+4} is more stable than Pt^{+2}

While in p block elements lower oxidation state become increasingly stable down the group as result of inert pair effect. eg. Pb^{+2} is more stable than Pb^{+4}

Q.3 Explain why Cu^+ ion is not stable in aqueous solutions.

Ans. Cu^+ ions in aqueous solution undergoes disproportionation.



This is because that hydration energy of $Cu^{+2}(aq)$ ions is sufficiently high to compensate IE_2 of Cu.

Q.4 Which is a stronger reducing agent Cr^{+2} or Fe^{+2} and why ?

Ans. Cr^{+2} is stronger reducing agent than Fe^{+2}

Reason : $d^4 \longrightarrow d^3$ occurs in case of $Cr^{+2} \longrightarrow Cr^{+3}$ but $d^6 \longrightarrow d^5$ occurs. In case of $Fe^{+2} \longrightarrow Fe^{+3}$ in a medium like water d^3 is more stable as compared to d^5 (on the basis of CFSE value)

Q.5 In first transition series (3d series) the enthalpy of atomisation of zinc is lowest, why ?

Ans. In the formation of metallic bonds no e^- from 3d subshell is involved in case of Zn because all 3d orbitals are fullfilled. Which decrease strength of metallic bond as well as enthalpy of atomisation of Zn.

Q.6 How iron (III) catalyses the reaction between iodide & persulphate?
