TRANSITION ELEMENTS (d & f block)

d-BLOCK ELEMENTS

INTRODUCTION

- (a) The element lying between s- and p-block element of the periodic table are collectively known as transition or transitional elements. (T.E'.S.)
- (b) Their properties are transitional between the highly electropositive s- block element to least electropositive pblock element.
- (c) In d- block elements, the last differentiating electron is accommodated to the penultimate shell.
- (d) The general electronic configuration of transition element is $(n-1)d^{1-10} ns^{0, 1}$ or 2
- (e) These elements either in their atomic state or in any of their common oxidation state have partly filled (n-1)d orbitals of (n-1)th main shell.
- (f) The transition elements have an incompletely filled d-level. Since Zn, Cd, Hg elements have d¹⁰ configuration and are not considered as transition elements but they are d-block elements.

Electronic Configuration

Ist Transition Series												
Symbol	Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn		
Atomic No.	21	22	23	24	25	26	27	28	29	30		
3d electrons	1	2	3	5	5	6	7	8	10	10		
4s electrons	2	2	2	1	2	2	2	2	1	2		
Irregular electronic configuration Cr, Cu												
IInd Transition Series												
Symbol	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd		
Atomic No.	39	40	41	42	43	44	45	46	47	48		
4d electrons	1	2	4	5	5	7	8	10	10	10		
5s electrons	2	2	1	1	2	1	1	0	1	2		
Irregular elect	ronic cor	nfiguratio	on Nb, M	o, Ru, Rh	, Pd, Ag							
	12		Ι	IIrd Tran	sition Ser	ies						
Symbol	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg		
Atomic No.	57	72	73	74	75	76	77	78	79	80		
5d electrons	1	2	3	4	5	6	7	9	10	10		
6s electrons	2	2	2	2	2	2	2	1	1	2		
Irregular elect	ronic co	nfigurati	on W, Pt,	Au								



(D) five

EDUBULL	KEY	POINTS
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The irregularities in the observed configuration of Cr $(3d^5 4s^1 \text{ instead of } 3d^4 4s^2)$, Cu $(3d^{10} 4s^1)$, Mo $(4d^5 5s^1)$, Pd ([Kr] $4d^{10} 5s^0$), Au ([Xe] $4f^{14} 5d^{10} 6s^1$), Ag ([Kr] $4d^{10} 5s^1$) are explained on the basis of the concept that half-filled and completely filled d-orbitals are relatively more stable than other d-orbitals.

- Ex. On what ground you can say that scandium (Z = 21) is a transition element but zinc (Z = 30) is not?
- **Sol.** On the basis of incompletely filled 3d orbitals of scandium, [Ar]¹⁸ 3d¹ 4s², and completely filled 3d orbitals of Zn, [Ar]¹⁸ 3d¹⁰ 4s², they are considered transition and non-transition elements respectively.
- **Ex.** The element with the electronic configuration $[Xe]^{54} 4f^{14} 5d^1 6s^2$ is a :
 - (A) representative element (B) d-block element
 - (C) lanthanod (D) actinoid
- Sol. After achieving $4f^{14}$ $5d^0$ $6s^2$ configuration, the next electron goes to 5d and this is the case of Lu(Z = 71) which is the last element of lanthanoid series.

Therefore, **(C)** option is correct.

Ex. The number of transition series is :

(A) two (B) three

Sol. There are four transition series ; 3d, 4d, 5d and 6d series.

Therefore, (C) option is correct.

GENERAL PROPERTIES OF D-BLOCK ELEMENTS

(a) The properties of d-block elements of any given period are not so much different from one another as those of the same period of non transition elements.

(C) four

(b) It is due to the fact that, in transition series, there is no change in number of electrons of outermost shell and only change occur in (n-1)d electron from member to member in a period.

Metallic Character

- (a) All the d-block elements are metals as the numbers of electrons in the outer most shell are one or two.
- (b) They are hard, malleable and ductile (except Hg). IB group elements Cu, Ag and Au are most ductile and soft.
- (c) These are good conductor of heat and electricity (due to free e⁻⁻) Elements of IB group are most conductive in nature. Their order of conductivity is Ag > Cu > Au > Al
- (d) Covalent and metallic bonding both exist in the atom of transition metals.
- (e) The presence of partially filled d-subshell favour covalent bonding and metallic bonding. These bonding are favourable also due to possession of one or two electron in outermost energy shell.

Reducing Power

- (a) Reducing power of d-block elements depends on their electrode potential.
- (b) Standard oxidation potential (SOP) of Cu is minimum in the 3d series so it is least reducing elements in 3d series.
- (c) Au is the least reducing element in the d-block because of highest +ve value of Standard reduction potential.
- (d) The poor reducing capacity of the transition metal is due to high heats of vaporization, high ionization potential and low heat of hydration of their ions, because reduction potential depends upon all these three factors.



Density

- (a) The atomic volume of the transition elements are low, compared with s-block, so their density is comparatively high (D = M/V)
- (b) Os $(22.57 \text{ gm cm}^{-3})$ and Ir $(22.61 \text{ gm cm}^{-3})$ have highest density.
- (c) In all the groups (except IIIB) there is normal increase in density from 3d to 4d series, and from 4d to 5d, it increases just double. Due to lanthanide contraction Ex. Ti < Zr << Hf</p>

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(d) In 3d series
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Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu Zn	
		De	nsity	incre	ases			Density decrea	ses

- (e) In 3d series highest density Cu lowest density Sc
- (f) Some important orders of density
 - Fe < Ni < Cu

Fe < Cu < Au Fe < Hg < Au

Melting and boiling points

(a) Melting and boiling point of d-block > s-block

Reason : Stronger metallic bond and presence of covalent bond formed by unpaired d-electrons.)

- (b) 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)
- (c) In 3d series Sc to Cr melting and boiling point increases then Mn to Zn melting and boiling point decreases
- (d) As the number of d-electron increases, the number of covalent bond between the atoms are expected to increase up to Cr-Mo-W family where each of the d-orbital has only unpaired electrons and the opportunity for covalent sharing is greatest.
- (e) Mn and Tc have comparatively low melting point, due to weak metallic bond because of stable Half filled (d⁵) configuration
- (f) Lowest melting point Hg $(-38^{\circ}C)$,
- Highest melting point W ($\simeq 3400^{\circ}$ C)





CHARACTERISTIC PROPERTIES OF TRANSITION ELEMENTS :

(a) Variable oxidation state	(b) Coloured ions	(c) Paramagnetic properties
(d) Catalytic properties	(e) Formation of alloys	(f) Formation of interstitial compounds
(g) Formation of complexes.		

- **Ex.** Why do the transition elements have higher boiling & melting points ?
- **Sol.** Because of having larger number of unpaired electrons in their atoms, they have stronger interatomic interaction and hence stronger bonding between atoms. Hence strong metallic bonds between the atoms of these elements attribute to their high melting and boiling points.
- **Ex.** The atomic radii of transition elements in a period are
 - (A) smaller than those of s-block as well as p-block elements.
 - (B) larger than those of s-block as well as p-block elements.
 - (C) smaller than those of s-block but larger than those of p-block elements.
 - (D) larger than those of s-block but smaller than those of p-block elements.
- **Sol.** Across the period the atomic radii generally decrease with increasing atomic number as effective nuclear charge increase.

Therefore, **(C)** option is correct.

Variable Valency or Variable Oxidation States

- (a) They exhibit variable valency due to involvement of (ns) and (n-1)d electrons. Due to less energy difference between these electrons.
- (b) The oxidation states of all transition elements of '3d' series are as follows -

Element	Conf.	Outer electronic configuration	Oxidation states
Sc	$3d^14s^2$		+3
		3d 4s	
Ti	$3d^24s^2$		+2 +3 +4
V	3d ³ 4s ²		+2 +3 +4 +5
Cr	3d ⁵ 4s ¹		+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 +6
Со	3d ⁷ 4s ²		+2 +3 +4
Ni	$3d^84s^2$		+2 +3 +4
Cu	3d ¹⁰ 4s ¹	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$	+1 +2
Zn	3d ¹⁰ 4s ²	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$	+2

- (c) Highest oxidation state of transition elements can be calculated by n + 2 where (n = number of unpaired electrons) It is not applied for Cr and Cu.
- (d) The transition metal ions having stable configuration like $d^0 d^5$ or d^{10} are more stable.

Ex. Sc^{+3} , Ti^{+4} , V^{+5} , Fe^{+3} , Mn^{+2} , Zn^{+2} etc.

- (e) In aqueous medium Cr^{+3} is stable.
- (f) Co^{+3} and Ni^{+2} are stable in complexes..
- (g) In aqueous medium due to disproportionation Cu^{+1} is less stable than Cu^{+2} while its configuration is $3d^{10}$
- (h) Most common oxidation state among the transition elements is +2.
- (i) Highest oxidation state shown by transition elements of '4d' and '5d' series is +8 by Ru (44) and Os (76).
- (j) The common oxidation state shown by elements of IIIB i.e., Sc, Y, La and Ac is +3 as their divalent compounds are highly unstable.
- (k) In lower oxidation state transition elements form ionic compounds and in higher oxidation state their compounds are covalent.
- (1) They also shows zero oxidation state in their carbonyl compounds like $Ni(CO)_4$.
- (m) Usually transition metal ions in their lower oxidation state act as reducing agents and in higher oxidation state they are oxidising agents.

Ex. Sc⁺², Ti⁺², V⁺², Fe⁺², Co⁺² etc are reducing agents

Cr⁺⁶, Mn⁺⁷, Mn⁺⁶, Mn⁺⁵, Mn⁺⁴ etc are oxidising agents.

Standard Electrode Potentials

The magnitude of ionization enthalpy gives the amount of energy required to remove electrons to form a particular oxidation state of the metal in a compound. Thus, the value of ionisation enthalpies gives information regarding the thermodynamic stability of the transition metal compounds in different oxidation states. Smaller the ionisation enthalpy of the metal, the stable is its compound. For example, the first four ionisation enthalpies of nickel and platinum are given below :

Ionisation enthalpies	Ni	Pt
$IE_1 + IE_2$	$2.49 \times 10^3 \text{ kJ mol}^{-1}$	$2.66 \times 10^3 \text{ kJ mol}^{-1}$
$IE_3 + IE_4$	$8.80 \times 10^3 \text{ kJ mol}^{-1}$	$6.70 \times 10^3 \text{ kJ mol}^{-1}$
Total	$11.29 \times 10^3 \text{ kJ mol}^{-1}$	$9.36 \times 10^3 \text{ kJ mol}^{-1}$

It is clear form the above table that the sum of first two ionization enthalpies is less for nickel than for platinum.

$Ni \longrightarrow Ni^{2+} + 2e^{-}$	I.E. = $2.49 \times 10^3 \text{kJ mol}^{-1}$
$Pt \longrightarrow Pt^{2+} + 2e^{-}$	I.E. = $2.66 \times 10^3 \text{kJ mol}^{-1}$

Therefore, ionization of nickel to Ni²⁺ is energetically favourable as compared to that of platinum. Thus, the nickel (II) compounds are thermodynamically more stable than platinum (II) compounds. On the other hand, the sum of first four ionisation enthalpies is less for platinum than for nickel as :

$Ni \longrightarrow Ni^{4+} + 2e^{-}$	I.E. = $11.29 \times 10^3 \text{kJ mol}^{-1}$
$Pt \longrightarrow Pt^{4+} + 2e^{-}$	I.E. = $9.36 \times 10^3 \text{kJ mol}^{-1}$



Thus, the platinum (IV) compounds are relatively more stable than nickel (IV) compounds. Therefore, K_PtCl, [having Pt (IV)] is a well-known compound whereas the corresponding nickel compound is not known. However, in solutions the stability of the compounds depends upon electrode potentials.

Electrode potentials :

In addition to ionisation enthalpy, the other factors such as enthalpy of sublimation, hydration enthalpy, ionisation 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:

 $M(s) \longrightarrow M^+(aq) + e^-$

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



(i) In the first step, the atoms get isolated from one another and become independent in the gaseous state. This converts solid metal to the gaseous state. The energy needed for this step is known as enthalpy of sublimation.

$$M(s) \longrightarrow M^+(g)$$
 Enthalpy of sublimation, $\Delta_{sub} H^{\Theta}$

(ii) In the second step, the outer electron is removed from the isolated atom. The energy required for this change is ionisation enthalpy.

$$M(s) \longrightarrow M^+(g) + e^-$$
 Ionisation enthalpy, IE

(iii)

In the third step the gaseous ion gets hydrated. In this process, energy known as hydration enthalpy, is liberated.

 $M^+(g) + nH_{,O} \longrightarrow M^+(aq)$ Enthalpy of hydration, $\Delta_{hvd}H$

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

 $\Delta H = \Delta_{sub} H^{\Theta} + IE + \Delta_{hvd} H$

Thus, ΔH gives the enthalpy change required to bring the solid metal, M to the monovalent ion in aqueous medium, M^+ (aq). An exactly similar cycle may be constructed for the formation of an anion in solution except that the ionization enthalpy may be replaced by electron gain enthalpy when the gaseous atom goes to gaseous anion. ΔH helps to predict the stability of a particular oxidation state. The smaller the values of total energy change for a particular oxidation state in aqueous solution, greater will be the stability of that oxidation state. The electrode potentials are a measure of total energy change. Qualitative, the stability of the transition metal ions in different oxidation states can be determined on the basis of electrode potential data. The lower the electrode potential i.e.,



more negative the standard reduction potential of the electrode, the more stable is the oxidation state of the transition metal in the aqueous solution.

The electrode potentials of different metals can also be measured by forming the cell with standard hydrogen electrode. For the measurement of electrode potential of $M^{2+} \mid 1M$, the e.m.f. of the cell in which the following reaction occurs is measured :

 $2H^+(aq) + M(s) \longrightarrow M^{2+}(aq) + H_2(g)$

Knowing the potential of $2H^+(aq) | H_2(g)$, it is possible to determine the potential of $M^{2+}(aq) | M$. For the first transition series, the E^{Θ} values of $M^{2+}(aq) | M$ are given below :

The observed values of E^{Θ} and those calculated using the data are compared in the following figure.



Thermochemical data (kJ mol⁻¹) for the first row Transition Elements and the Standard Electrode potentials for the Reduction of MII to M

Element (M)	$\Delta_{a}Hq(M)$	$\Delta_{f}H_{1}^{\theta}$	$\Delta_1 H_2^\theta$	$\Delta_{hyd} \mathbf{H}^{\theta}(\mathbf{M}^{2+})$	E ^θ /V
Ti	469	661	1310	-1866	-1.63
V	515	648	1370	-1895	-1.18
Cr	398	653	1590	-1925	-0.90
Mn	279	716	1510	-1862	-1.18
Fe	418	762	1560	-1998	-0.44
Co	427	757	1640	-2079	-0.28
Ni	431	736	1750	-2121	-0.25
Cu	339	745	1960	-2121	0.34
Zn	130	908	1730	-2059	-0.76



The results lead to the following conclusions :

- (i) There is no regular trend in these values. This is attributed to the irregular variation of ionisation enthalpies $(IE_1 + IE_2)$ and the sublimation energies in the period.
- (ii) It may be noted that the electrode potentials of transition metals are low in comparison to elements of group 2 (e.g., Ca = -2.87 V). Compared to group 2 elements, the transition elements have fairly large ionisation enthalpies and very large enthalpies of atomisation. These reduce their electrode potentials though their hydration enthalpies are large.
- (iii) Zinc has low enthalpy of atomisation and fairly large hydration energy. But it has also low electrode potential (-0.76 V) because of its very high ionisation enthalpy (IE₁ + IE₂).
- (iv) It is clear from above table and figure that copper has positive reduction potential, E^{Θ} (0.34 V) and this shows that copper is least reactive metal out of the first transition series. This unique behaviour (+ve) E value of copper) also accounts for its inability to liberate H₂ from acids. It has been observed that only oxidizing acids (such as nitric acid and hot concentrated sulphuric acid) react with copper in which the acids are reduced. The high energy required to convert Cu(s) to Cu²⁺ (aq) is not balanced by its hydration enthalpy.
- (v) In general, the value becomes, less negative across the series. This is related to the general increase in the sum of first and second ionisation enthalpies. It is interesting to note that the values of E° of Mn, Ni and Zn are more negative than expected from the general trend. The relatively more negative values of E° for Mn and Zn are due to stability of half filled d-sub-shell in Mn²⁺ (3d⁵) and the completely filled (3d¹⁰) configuration in Zn²⁺. The exceptionally high E° value of Ni from regular trend is related to the highest negative enthalpy of hydration of Ni²⁺ ion.

Trends in the M³⁺ | M²⁺ Standard Electrode Potentials

Except copper and zinc, all other elements of first transition series show +3 oxidation states also to form M^{3+} ions in aqueous solutions. The standard reduction potentials for $M^{3+} | M^{2+}$ redox couple are given below :

	Ti	V	Cr	Mn	Fe	Со
$E^{\Theta} (M^{3+}(aq) M^{2+}(aq))$ (in Volt)	-0.37	-0.26	-0.41	+1.57	+0.77	+1.97

These values reveal the following facts :

- (i) The low value of scandium reflects the stability of Sc^{3+} which has a noble gas configuration.
- (ii) The comparatively high value for Mn shows that Mn^{2+} (d⁵ configuration) is particularly stable. On the other hand comparatively low value for Fe shows the extra stability of Fe³⁺ (d⁵ configuration).
- (iii) The comparatively low value of V is related to the stability of V^{2+} (due to half filled t_{2g}^{3} energy level of 3d orbitals in octahedral crystal field spitting).
- (iv) The E^{Θ} value for Mn^{3+}/Mn^{2+} couple much more positive than for Cr^{3+}/Cr^{2+} or Fe^{3+}/Fe^{2+} . This is because of the much larger IIIrd ionisation energy of Mn (removal of electron from d⁵ configuration).



Trends in Stability of Higher Oxidation States

Standard electrode potential data provide valuable information about the stabilities of different oxidation states shown by an element. The highest oxidation states are shown generally among halides and oxides.

1. In metal halides. The transition elements react with halogens at high temperatures to form transition metal halides. These reactions have very high heat of reaction. But once the reaction starts, the heat of reaction is sufficient to continue the reaction. The halogens react in the following decreasing order ; $F_2 > Cl_2 > Br_2 > I_2$

Oxidation Number	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+6				CrF6						
+5			VF5	CrF5				A.		
+4		TiX4	VX4 ^a	CrF4	MnF4					
+3	ScX ₃	TiX3	VX3	CrF3	MnF3	FeX3 ^a	CoF3			
+2		TiX2	VX2 ^c	CrF ₂	MnX_2	FeX ₂	CoX2	NiX2	CuX2 ^b	ZnX_2
+1									CuX ^c	
			where	X = F, Cl, Bı	$r,I,X^{a}=F,C$	Cl, Br, $X^b = H$	$F, Cl, X^c = Cl$, Br, I		

Halides of first transition series

Within each of the transition groups 3 - 12, there is a difference in the stability of the various oxidation states. In general, the second and third transition series elements exhibit higher coordination number and their higher oxidation states are more stable than the corresponding first transition series elements. The following trends are observed from table regarding transition metal halides :

- (i) In general, the elements of first transition series tend to exist in low oxidation states. Chromium to zinc form stable diflourides and the other chlorides are also known.
- (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), VF₅ and CrF₆.
- (iii) The +7 oxidation state for Mn is not shown by simple halides. However, $MnO_{3}F$ is known in which the oxidation state of Mn is +7.
- (iv) After Mn, the tendency to show higher oxidation states with halogens are uncommon. Iron and cobalt form trihalides FeX_3 (X = F, Cl or Br) and CoF₃.
- (v) 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 due to higher covalent bonds e.g., VF₅ and CrF₆.
- (vi) V(V) is shown by VF₅ only. However, the other halides undergo hydrolysis to form oxohalides, VOX₃.
- (vii) 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, I). All copper (II) halides are known except the iodide. This is because, Cu^{2+} oxidises I⁻ to I₂.

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

It has been observed that many copper (I) compounds are unstable in aqueous solution and they undergo disproportionation to Cu(II) and Cu(0) as :

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



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 ($\Delta_{hyd}H^{\Theta}$) of Cu²⁺ (aq) than Cu⁺, which is much more than compensates for the large energy required to remove the second electron i.e., second ionisation enthalpy of copper.

Oxidation Number	Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn
+7					Mn ₂ O ₇					4
+6				CrO ₃						
+5			V ₂ O ₅						1	
+4		TiO2	V_2O_4	CrO ₂	MnO ₂					
+3	Sc ₂ O ₃	Ti ₂ O ₃	V ₂ O ₃	Cr ₂ O ₃	Mn ₂ O ₃	Fe ₂ O ₃	1	4		
+2		TiO	VO	(CrO)	MnO	FeO	CoO	NiO	CuO	ZnO
+1								1	Cu2O	
Mixed oxides				_	Mn ₃ O ₄	Fe ₃ O ₄	Co ₃ O ₄			

2. In metal oxides and oxocations.

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 . However beyond group 7, no higher oxides of iron above Fe_2O_3 are known. Although higher oxidation state such as +6 is shown in ferrates such as FeO_4^{2-} in alkaline medium, but they readily decompose to Fe_2O_3 and O_2 . 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+} . 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 great ability to form multiple bonds to metals. In the covalent oxide. Mn_2O_7 , each Mn is tetrahedrally surrounded by oxygen atoms and has Mn-O-Mn bridge. The tetrahedral $[MO_4]^{n-}$ ions are also known for vanadium (V), chromium (VI), manganese (VI) and manganese (VII).

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. As the oxidation number of a metal increases, the ionic character of their oxides decrease. For example, in case of Mn, Mn_2O_7 is a covalent green oil. In these higher oxides the acidic character is predominant. Thus CrO_3 gives H_2CrO_4 and $H_2Cr_2O_7$ and Mn_2O_7 gives $HMnO_4$. V_2O_5 is, however amphoteric though mainly acidic and with alkalies as well as acids gives VO_4^{3-} and VO_2^+ respectively.

Ex. For the first series of transition metals the E^{Θ} values are

 E^9 V
 Cr
 Mn
 Fe
 Co
 Ni
 Cu

 (M^{2+}/M^{+1}) -1.18 -0.91 -1.18 -0.44 -0.28 -0.25 +0.34

Explain the irregularity in the above values.

Sol. This is because of irregular variation of ionization energies $(IE_1 + IE_2)$ and also the sublimation energies which are much less for manganese and vanadium



CHEMISTRY FOR JEE MAIN & ADVANCED

Write the formulae of different oxides of manganese. What is the oxidation state of manganese in each of them ? Ex. Arrange them in order of their decreasing acidic character. $Mn^{+2}O, Mn_2^{3+}O_3, Mn^{4+}O_2, Mn_2^{7+}O_7, Mn_3O_4$ (mixed oxide of MnO and Mn_2O_3) Sol. As the oxidation state of Mn increases, the electronegativity values of the central metal ions increase. As a result of this the difference in the electronegativity values between metals and oxygen decrease. So the acidic character increases as given below. $MnO < Mn_2O_3 < MnO_2 < Mn_2O_7$ Name the oxo metal anions of the first series of the transition metals in which the metal exhibits the oxidation state Ex. equal to its group number. In $\operatorname{Cr}_{2}O_{7}^{2-}$ and $\operatorname{Cr}O_{4}^{2-}$ the oxidation state of Cr is +6 (2x + 7(-2) = -2 and x + 4(-2) = -2). The group number is equal Sol. to the number of electrons in (n-1) d and ns sub-shells for d-block elements. So group no. = 5 + 1 = 6. In MnO_4^{-} the oxidation state of Mn is +7 (2x + 7(-2) = -1). The group number is equal to the number of electrons in (n-1) d and ns sub-shells for d-block elements. So group no. = 5 + 2 = 7Ex. Zinc does not show variable valency because of : (A) complete 'd' sub-shell (B) inert pair effect (C) $4s^2$ sub-shell (D) none. $_{30}$ Zn = [Ar]¹⁸ 3d¹⁰ 4s². Zinc has completely filled d-sub-shell so removal of electron from completely filled 4d sub-Sol. shell would be quite difficult. Thus it does not show variable valency.

Therefore, (A) option is correct.

The relative stability of various oxidation states

(a) The relative stabilities of various oxidation states of 3d-series element can be correlated with the extra stability of 3d°,3d⁵ & 3 d¹⁰ configuration to some extent.

Ex. Stability of $Ti^{4+}(3d^0) > Ti^{3+}(3d^1) Mn^{2+}(3d^5) > Mn^{3+}(3d^4)$

- (b) The higher oxidation state of 4d and 5d series element are generally more stable than the elements of 3d series.
 Ex. (i) Mo^{vi}O₄⁻² (oxidation state of Mo is +6), Mo^{vi}O₄⁻² (4d series) & W^{vi}O₄²⁻, Re^{vii}O₄⁻ (5d series) are more stable due to their maximum oxidation state.
- (ii) $Cr^{vi}O_4^{-2}$ & Mn^{vii}O_4^{-}(3d-series) are strong oxidizing agents.
- (c) Strongly reducing states probably do not form fluorides or oxides, but may well form the heavier halides Conversely, strong oxidizing state form oxides & fluoride, but not Bromide and lodide. Ex.
- V (Vanadium) react with halogens to form VF₅ VCl₅, VBr₃, but doesn't form VBr₅ or VI₅ because in + 5 oxidation state Vanadium is strong oxidizing agent thus convert Br⁻ & I⁻ to Br₂ & I₂ respectively, So VBr₃ & VI₃ are formed but not VBr₅ & VI₅.
- (ii) On the other hand VF₅ is formed because V^{5+} ion unable to oxidize highly electronegative & small anion F⁻
- (iii) Similarly highly electronegative and small O^2 ion formed oxides Ex. VO_4^3 , CrO_4^{2-} & MnO_4 etc.



	Different oxid	lation state of cl	nloride & oxides	compound		
+2	+3	+4	+5	+6	+7	
TiCl ₂	TiCl ₃	TiCl ₄				
VCl ₂	VCl ₃	VCl_4	VOCl ₃			
(Ionic, basic)	Less ionic (Amphoteric)	Covalent : (Strong le	and Acidic wis acid)			
TiO	Ti ₂ O ₃	TiO ₂				
VO	V_2O_3		V_2O_5			
CrO	Cr_2O_3			CrO ₃		
MnO	Mn ₂ O ₃	MnO ₂		MnO ₃	Mn_2O_7	
Ionic, basic	Less Ionic (A	mphoteric)		Acidic, co	ovalent	

(d) Such compounds are expected to be unstable except in case where vacant d-orbitals are used for accepting lone-pair from π-bonding ligand.

Ex. $[Ni(CO)_4], [Ag(CN)_2]^-, [Ag)(NH_3)_2]^+$

- **Ex.** Zn forms only Zn^{2+} and not Zn^{3+} , why?
- Sol. In the formation of Zn^{3+} , an electron from the d^{10} configuration has to be removed which requires abnormally higher amount of energy.

Colour Property

- (a) Most of the transition metal ions exhibit colour property.
- (b) This is due to d-d transition of unpaired electrons in their t_{2g} and e_g sets of 'd' orbitals.
- (c) They require less amount of energy to undergo excitation of electrons. Hence they absorb visible region of light exhibiting colour.

Ex. Sc^{+2} : [Ar]3d¹, Ti⁺² : [Ar]3d², V⁺² : [Ar]3d³

(d) Transition metal ions which do not have any unpaired electrons in their 'd' orbitals like 3d⁰ and 3d¹⁰ configurations, do not exhibit any colour property.

Ex. Sc^{+3} : [Ar]3d⁰, Cu⁺¹: [Ar]3d¹⁰, Ti⁺⁴: [Ar]3d⁰ etc are colourless ions.

- (e) A transition metal ion absorbs a part of visible region of light and emits rest of the colours, the combination of which, is the colour of emitted light. The colour of metal ion is the colour of the emitted light.
- (f) In transition metal ion the 'd' orbitals split into lower energy set t_{2g} orbitals and higher energy set e_g orbitals. The electrons from t_{2g} set get excited to higher energy set i.e., e_g set. This excitation of electrons is called as 'd-d' transition. Due to this 'd -d' transition metal ions exhibit colour property.



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Factors affecting the colour of complex

The colour of a transition metal complex depends on-

- (a) The magnitude of energy difference between the two d-levels (Δ_0) .
- (b) An increase in the magnitude of Δ_0 decreases the wave length (λ) of the light absorbed by the complexes.

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0		A /TT7 1 1 01 1 1 1 1
		$\lambda (M)$ avelength of light abcorb)

1

(c) Thus with a decrease in the λ the colour of complex changes from Red to Violet.

Ex. Complex ions	[Co(H ₂ O) ₆] ³⁺	$[Co(NH_3)_6]^{3+}$	[Co(CN) ₆] ³ -
Ligand field strength	H ₂ O <	NH ₃ <	CN-
Magnitude of Δ_0	$\Delta_0(H_2O) <$	$\Delta_0(\mathrm{NH}_3)$ <	$\Delta_0(CN^-)$
Magnitude of λ	$\lambda(H_2O) <$	λ(NH ₃) <	λ(CN-)
Colour of the transmitted	orange	Green-blue	violet
Colour of absorbed light	Green-blue	Orange	Yellow-green
Light (i.e. colour of the			
complex			

(d) KMnO₄ (dark pink), $K_2Cr_2O_7$ (orange) having d° configuration but they are coloured due to charge trans fer spectrum and charge is transferred from anion to cation.

Ti ⁺³	Purple	Cr ⁺³	Green	Mn^{+2}	Light pink	Fe ⁺²	Green
Fe ⁺³	Yellow	Co ⁺³	Pink	Ni ⁺²	Green	Cu ⁺²	Blue
Sc ³⁺	Colourless	Ti ⁴⁺	Colourless	Ti^{3+}	Purple	V^{4+}	Blue
V^{3+}	Green	V^{2+}	Violet	Cr ²⁺	Blue	Cr ³⁺	Green
Mn ³⁺	Violet	Mn ²⁺	Pink	Fe ²⁺	Green(light)	Fe ³⁺	Yellow
Co ²⁺	Pink	Ni ²⁺	Blue	Zn^{2+}	Colourless		

Example of Some coloured metal ions :

- **Ex.** Explain the blue colour of $CuSO_4.5H_2O$.
- Sol. Cu^{2+} ion (3d⁹) absorbs red light from the visible region, for the promotion of 3d electrons, the ions reflect blue light and appear blue.

Magnetic Properties

- (a) Generally transition elements exhibits the magnetic property. A **paramagnetic** substance is one which is attracted into a magnetic field. Paramagnetism is mainly due to the presence of unpaired electrons in atoms or ions or molecules. It varies inversely with temperatures.
- (b) **Diamagnetic** substance is one which is slightly repelled by a magnetic field. It's independent of temperature.
- (c) As is evident most of the transition metal ions have unpaired electrons in their 'd' orbitals. Hence most of the transition metal ions are paramagnetic in nature. Ex. Ti⁺² [Ar]3d², Ti⁺³ [Ar]3d¹. V⁺²[Ar]3d³, Cr⁺³ [Ar]3d³



- (d) Transition metal ions having $3d^0$ and $3d^{10}$ configuration exhibit diamagnetic nature.
- (e) The total magnetic moment of a substance is the resultant of the magnetic moments of all the individual electrons.
- (f) The magnetic moment (μ) created due to spinning of unpaired electrons can be calculated by using $\mu = \sqrt{n(n+2)}$ Where - 'n' is the number of unpaired electrons in the metal ion.

 μ = Magnetic moment in Bohr Magnetons (B.M.)

- (g) The magnetic moment of diamagnetic substances will be zero.
- (h) Transition metal ions having d⁵ configuration will have maximum number of unpaired electrons therefore they will be maximum paramagnetic in nature.

Catalytic Property

- (a) Transition elements and their compounds exhibit catalytic properties. This is due to their variable valency as well as due to the free valencies on their surface.
- (b) When transition elements and their compounds are in powdered state, their catalytic properties exhibited will be to a greater extent. This is due to greater surface area available in the powdered state.
- (c) Transition metals and their compounds exhibiting catalytic properties in various processes are -

Catalyst	Used		
TiCl3	Used as the Ziegler-Natta catalyst in the production of polythene.		
MnO ₂	Used as a catalyst to decompose KClO3 to give O2		
Fe	Promoted iron is used in the Haber-Bosch process for making NH3		
FeCl ₃	Used in the production of CCl4 from CS2 and Cl2		
FeSO4 and H2O2	Used as Fenton's reagent for oxidizing alcohols to aldehydes.		
PdCl ₂	Wacker process for converting C ₂ H ₄ + H ₂ O + PdCl ₂ to		
	$CH_3CHO + 2HCl + Pd.$		
Pd	Used for hydrogenation (e.g. phenol to cyclohexanone).		
Pt/PtO	Adams catalyst, used for reductions.		
Pt	Formerly used for $SO_2 \longrightarrow SO_3$ in the contact process for making		
	H ₂ SO ₄		
Pt/Rh	Formerly used in the ostwald process for making HNO ₃ to oxidize		
	NH ₃ to NO		
Cu	Is used in the direct process for manufacture of (CH3)2SiCl2 used		
	to make silicones.		
Cu/V	Oxidation of cyclohexanol/cyclohexanone mixture to adipic acid		
11 1 A	which is used to make nylone-66		
CuCl ₂	Decon process of making Cl2 from HCl		
Ni	Raney nickel, numerous reduction processes (e.g. manufacture of		
	hexamethylenediamine, production of H2 from NH3, reducing		
	anthraquinone to anthraquinol in the production of H2O2		

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

Sol.
$$2Fe^{3+}+2I^- \longrightarrow 2Fe^{2+}+I_2$$

$$2\mathrm{Fe}^{2+} + \mathrm{S}_{2}\mathrm{O}_{8}^{2-} \longrightarrow 2\mathrm{Fe}^{3+} + 2\mathrm{SO}_{4}^{2-}$$

$$2I^{-} + S_2O_8^{2-} \xrightarrow{Fe(III)} I_2 + 2SO_4^{2-}$$



Formation of Alloy

- (a) Transition elements have maximum tendency to form alloys.
- (b) The reactivity of transition elements is very less and their sizes are almost similar. Due to this a transition metal atom in the lattice can be easily replaced by other transition metal atom and hence they have maximum tendency to form alloys.
- (c) In the alloys, ratio of component metals is fixed.
- (d) These are extremely hard and have high melting point.

SOME IMPORTANTALLOY

(a)	Bronze	Cu (75 - 90 %) +Sn (10 - 25 %)
(b)	Brass	Cu (60 - 80 %) +Zn (20 - 40 %)
(c)	Gun metal	(Cu + Zn + Sn) (87 : 3 : 10)
(d)	German Silver	Cu + Zn + Ni(2:1:1)
(e)	Bell metal	Cu (80 %) + Sn (20 %)
(f)	Nichrome	(Ni + Cr + Fe)
(g)	Alnico	(Al, Ni, Co)
(h)	Type Metal	Pb + Sn + Sb
(i)	Alloys of steel	
	• Vanadium steel	V (0.2 - 1 %)
	• Chromium steel	Cr (2 - 4 %)
	• Nickel steel	Ni (3 -5 %)
	• Manganese steel	Mn (10 - 18 %)
	• Stainless steel	Cr (12 - 14 %) & Ni (2 - 4 %)
	• Tungsten steel W (10 -	20%)
	• Invar	Ni (36 %)
(j)	14 Carat Gold	54% Au + Ag (14 to 30%) + Cu (12 - 28%)
(k)	24 Carat Gold	10 <mark>0 % Au</mark>
(l)	Solder	Pb + Sn
(m)	Magnellium	Mg (10%)+Al (90%)
(n)	Duralumin	(Al + Mn + Cu)
(0)	Artificial Gold	Cu (90 %) + Al (10%)
(p)	Constantan	Cu(60%) + Ni (40%)
	%	of Carbon in Different Type of Iron

	Name	% of C
(a)	Wrought Iron	0.1 to 0.25
(b)	Steel	0.25 to 2.0
(c)	Cast Iron	2.6 to 4.3
(d)	Pig Iron	2.3 to 4.6



TRANSITION ELEMENTS (d & f BLOCK)

Ex. Which of the following form an alloy ?

 $(\mathbf{A}) \mathbf{A}\mathbf{g} + \mathbf{P}\mathbf{b}$

 (\mathbf{C}) Pt + Hg

(D) Fe + C

Sol. Argentiferrous lead is an alloy contains Ag & Pb.

'Fe' and 'C' form an alloy called cementite, Fe₃C.

Therefore, (A) & (D) option are correct.

(B) Fe + Hg

Formation of Interstitial Compounds

- (a) Transition elements form interstitial compounds with smaller sized non metal elements like hydrogen, carbon, boron, nitrogen etc.
- (b) The smaller sized atoms get entrapped in between the interstitial spaces of the metal lattices.

These interstitial compounds are non-stoichiometric in nature and hence cannot be given any definite formula.

- (c) The smaller sized elements are held in interstitial spaces of transition elements by weak Vander Waals forces of attractions.
- (d) The interstitial compounds have essentially the same chemical properties as the parent metals but they differ in physical properties such as density and hardness.

The process of adsorption of excess of H atom by the transition metals like Pd, Pt etc is called occlusion.

Non-stoichiometry

- (a) The transition elements sometimes form nonstoichiometric compounds due to variable valency.
- (b) These are the compounds of indefinite structure & proportion.
- (c) For example, Iron (II) Oxide FeO should be written as a bar over the formula FeO to indicate the ratio of Fe & O atom is not exactly 1:1 (Fe_{0.94} O & Fe_{0.84} O), \overline{VSe} (VSe_{0.98}VSe_{1.2}).
- (d) Non stoichiometry is shown particularly among transition metal compounds of the group 16 elements (O,S,Se,Te).
- (e) Some times nonstoichiometry is caused by defect in the solid structure.

Potassium Dichromate (K₂Cr₂O₇)

PREPARATION

It is prepared from Chromite ore or Ferrochrome or Chrome iron. (FeO. Cr_2O_3 or Fe Cr_2O_4). The various steps involved are.

(a) Preparation of sodium chromate (Na_2CrO_4) :

The powdered chromite ore in fused with sodium hydroxide or sodium carbonate in the presence of air in a reverberatory furnace.

$$4FeCr_2O_4 + 16NaOH + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8H_2O$$

or $4\text{FeCr}_2\text{O}_4 + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 \longrightarrow 8\text{Na}_2\text{CrO}_4 + 2\text{Fe}_2\text{O}_3 + 8\text{CO}_2$

After the reaction the roasted mass is extracted with water. So sodium chromate is completely dissolved while ferric oxide is left behind.



(b) Formation of sodium dichromate $(Na_2Cr_2O_7)$ from sodium chromate (Na_2CrO_4) :

The solution of sodium chromate is filtered and acidified with dil./con. H₂SO₄ acid giving its dichromate.

 $2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$

On cooling, sodium sulphate being less soluble crystallizes out as Na2SO4.10H2O and is removed. The resulting solution contains sodium dichromate (Na₂Cr₂O₇).

(c) Formation of potassium dichromate from sodium dichromate :

The hot concentrate solution of sodium dichromate is heated with calculated amount of KCl.

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

Sodium chloride, being the least soluble precipitates out from the hot solution and is removed by filtration. Orange red crystals of potassium dichromate separate out from mother liquid on cooling.

PROPERTIES

- (a) Colour and Melting Point :- Orange red crystals. 670 K
- (b) Solubility :- Moderately soluble is cold water but readily soluble in hot water.
- (c) Action of Heat :- It decompose on heating to give potassium chromate, chromic oxide and oxygen.

$$4K_2Cr_2O_7 \xrightarrow{Heat} 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$$

Potassium Chromic
chromate oxide

(d) Action of Alkalies :- On heating with alkalies the orange colour of dichromate solution changes to yellow due to the formation of chromate ions.

$$K_2Cr_2O_7 + 2KOH \longrightarrow 2K_2CrO_4 + H_2O$$

$$\operatorname{Cr}_{2}\operatorname{O}_{7}^{2-} + 2\operatorname{OH}^{-} \longrightarrow 2\operatorname{Cr}\operatorname{O}_{4}^{2-} + \operatorname{H}_{2}\operatorname{O}$$

This chromate on acidifying reconverts into dichromate.

$$2K_2CrO_4 + H_2SO_4 \longrightarrow K_2Cr_2O_7 + K_2SO_4 + H_2C$$
$$2CrO_4^{--} + 2H^+ \longrightarrow Cr_2O_7^{--} + H_2O$$

or

$$rO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$$

The interconversion is explained by the fact that dichromate ion and chromate ion exist in equilibrium at a pH of about 4.

$$Cr_2O_7^{2-} + H_2O \xrightarrow{HCrO_4^-} 2CrO_4^{2-} + 2H^+$$

When alkali added, H⁺ consumed so forward direction. When acid added, H⁺ increases so backward direction.

(e) Chromyl chloride Test :- When potassium dichromate is heated with conc. H_2SO_4 acid and a soluble metal chloride (ex. NaCl) orange red vapours of chromyl chloride (CrO₂Cl₂) are formed.

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \longrightarrow 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2 + 3H_2O_2Cl_2 + +$$

Reaction with H_2O_2: - Acidified solution of dichromate ions give deep blue colour solution with H_2O_2 due to **(f)** the formation of $[CrO(O_2)_2]$ or CrO_5 . The blue colour fades away gradually due to the decomposition of CrO_5 into Cr⁺³ ions and oxygen.



(g) Action with HCl:- Potassium dichromate reacts with hydrochloric acid and evolves chlorine.

$$K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$$

- (h) Action of con. H_2SO_4
 - (i) In cold, red crystals of chromic anhydride are formed.

$$K_2Cr_2O_7 + 2H_2SO_4 \longrightarrow 2CrO_3 + 2KHSO_4 + H_2O$$

(ii) On heating the mixture oxygen is evolved.

$$2K_2Cr_2O_7 + 8H_2SO_4 \longrightarrow 2K_2SO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3O_2$$

(i) Oxidising properties

The dichromates act as powerful oxidising agent in acidic medium. In presence of dil H_2SO_4 , $K_2Cr_2O_7$ liberates Nascent oxygen and therefore acts as an oxidising agent.

In terms of electronic concept the $Cr_2O_7^{2-}$ ion takes up electrons in the acidic medium and hence acts as an oxidising agent.

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

(i) It oxidises iodides to iodine :-

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

$$[2I^- \longrightarrow I_2 + 2e^-] \times 3$$

$$\operatorname{Cr}_{2}\operatorname{O}_{7}^{2-} + 14\operatorname{H}^{+} + 6\operatorname{I}^{-} \longrightarrow 2\operatorname{Cr}^{+3} + 3\operatorname{I}_{2} + 7\operatorname{H}_{2}\operatorname{O}$$

or
$$K_2Cr_2O_7 + 7H_2SO_4 + 6KI \longrightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2$$

(ii) Acidified ferrous sulphate to ferric sulphate

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

Fe⁺² \longrightarrow Fe³⁺ + e⁻] × 6

or

 $K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O + K_2SO_4$

(iii) Oxidises H₂S to sulphur

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{+3} + 7H_2O$$
$$H_2S \longrightarrow S + 2H^+ + 2e^-] \times 3$$

 $\operatorname{Cr}_{2}\operatorname{O}_{7}^{2-} + 14\operatorname{H}^{+} + 6\operatorname{Fe}^{+2} \longrightarrow 2\operatorname{Cr}^{+3} + 6\operatorname{Fe}^{+3} + 7\operatorname{H}_{2}\operatorname{O}$

$$\operatorname{Cr}_2\operatorname{O}_7^{2-} + 3\operatorname{H}_2\operatorname{S} + 8\operatorname{H}^+ \longrightarrow 2\operatorname{Cr}^{+3} + 3\operatorname{S} + 7\operatorname{H}_2\operatorname{O}$$

$$K_2Cr_2O_7 + 3H_2S + 4H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 3S + 7H_2O + K_2SO_4$$

Similarly, it oxidises sulphites to sulphates, chlorides to chlorine, nitrites to nitrates, thiosulphates to sulphates and sulphur and stannous (Sn^{+2}) salts to stannic (Sn^{+4}) salts.



or

$$3SO_{3}^{-2} + Cr_{2}O_{7}^{2-} + 8H^{+} \longrightarrow 3SO_{4}^{2-} + 2Cr^{3+} + 4H_{2}O$$

$$3NO_{2}^{-} + Cr_{2}O_{7}^{2-} + 8H^{+} \longrightarrow 3NO_{3}^{-} + 2Cr^{3+} + 4H_{2}O$$

$$3S_{2}O_{3}^{2-} + Cr_{2}O_{7}^{2-} + 8H^{+} \longrightarrow 3SO_{4}^{2-} + 3S + 2Cr^{3+} + 4H_{2}O$$

$$6Cl^{-} + Cr_{2}O_{7}^{2-} + 14H^{+} \longrightarrow 3Cl_{2} + 2Cr^{3+} + 7H_{2}O$$

$$3Sn^{+2} + Cr_{2}O_{7}^{2-} + 14H^{+} \longrightarrow 3Sn^{+4} + 2Cr^{3+} + 7H_{2}O$$
It oxidises SO₂ to sulphuric acid.

$$K_{2}Cr_{2}O_{7} + 4H_{2}SO_{4} \longrightarrow K_{2}SO_{4} + Cr_{2}(SO_{4})_{2} + 4H_{2}O + 4$$

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O_2O_2 + O + H_2O \longrightarrow H_2SO_4$$

USES

- (a) For volumetric estimation of ferrous salts, iodides and sulphites.
- (b) For preparation of other chromium compounds such as chrome alum (K₂SO₄, Cr₂(SO₄)₃.24H₂O), chrome yellow (PbCrO₄) and chrome red (PbCrO₄.PbO).
- (c) Used in photography for hardening of gelatin film.
- (d) It is used in leather industry (chrome tanning)
- (e) Chromic acid mixture is used for cleaning glassware, consist of $K_2Cr_2O_7$ and Con. H_2SO_4 .
- (f) In organic chemistry, it is used as an oxidising agent.
- (g) In dyeing and calico printing.

STRUCTURE

The chromate ion has tetrahedral structure in which four atoms around chromium atom are oriented in a tetrahedral arrangement.



Chromate ion

The structure of dichromate ion consist of two tetrahedra sharing an oxygen atom at the common corner.





POTASSIUM PERMANGANATE (KMnO₄)

PREPARATION

Potassium permanganate is prepared from mineral pyrolusite (MnO₂). The preparation involves the following steps.

(a) Conversion of pyrolusite ore to potassium manganate

The pyrolusite MnO₂ is fused with caustic potash (KOH) or potassium carbonate in the presence of air or oxidising agents, such as KNO3 or KClO3 to give a green mass due to the formation of potassium manganate $(K_2MnO_4).$

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

$$2MnO_2 + 2K_2CO_3 + O_2 \longrightarrow 2K_2MnO_4 + 2CO_2$$

(b) Oxidation of potassium manganate to potassium permanganate

The green mass is extracted with water resulting is green solution of potassium manganate. The solution is then treated with a current of Cl₂ or ozone or CO₂ to oxidise K₂MnO₄ to KMnO₄. The solution is concentrated and dark purple crystals of KMnO₄ separate out.

$$2K_{2}MnO_{4} + Cl_{2} \longrightarrow 2KCl + 2KMnO_{4}$$
$$2K_{2}MnO_{4} + O_{3} + H_{2}O \longrightarrow 2KMnO_{4} + 2KOH + O_{2}$$
$$3K_{2}MnO_{4} + 2CO_{2} \longrightarrow 2K_{2}CO_{3} + MnO_{2} \downarrow + 2KMnO_{4}$$

Alternatively, alkaline potassium manganate is electrolytically oxidised.

Electrolytic method :- The potassium manganate solution is taken in an electrolytic cell which contains iron cathode and nickel anode. When current is passed the manganate ion in oxidised to permanganate ion at anode and hydrogen is liberated at cathode.

At anode :

$$K_{2}MnO_{4} \longrightarrow 2K^{+} + MnO_{4}^{2-}$$

$$MnO_{4}^{-2} \longrightarrow MnO_{4}^{-} + e^{-}$$
Green Purple
At cathode :

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

$$2H \longrightarrow H_{2}$$

PROPERTIES

At a

- (a) Colour and M.P. :- Dark violet crystalline solid, M.P. 523 K
- (b) Solubility :- Moderately soluble is room temperature, but fairly soluble in hot water giving purple solution.
- (c) Heating :- When heated strongly it decomposes at 746 K to give K_2MnO_4 and O_2 .

 $2KMnO_4$ 746K $K_2MnO_4 + MnO_2 + O_2$

Solid KMnO₄ gives KOH, MnO and water vapours, when heated in current of hydrogen.

 $2KMnO_4 + 5H_2 \xrightarrow{\Lambda} 2KOH + 2MnO + 4H_2O$

(d) Action of alkali :- On heating with alkali, potassium permanganate changes into potassium manganate and oxygen gas is evolved.

 $4KMnO_4 + 4KOH \longrightarrow 4K_2MnO_4 + 2H_2O + O_2$



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(e) Action of con. H_2SO_4 : - With cold H_2SO_4 , it gives Mn_2O_7 which on heating decomposes into MnO_2 .

$$2KMnO_4 + 2H_2SO_4 \longrightarrow Mn_2O_7 + 2KHSO_4 + H_2O$$
$$2Mn_2O_7 \longrightarrow 4MnO_2 + 3O_2$$

(f) Oxidising character :- KMnO₄ acts as powerful oxidising agent in neutral, alkaline or acidic solution because it liberates nascent oxygen as :-

Acidic solution :- Mn⁺² ions are formed

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

or
$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O \left[equal wt. = \frac{M}{5} \right]$$

$$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3[O]$$

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

or

During the reaction the alkali produced generates the alkaline medium even if we start from neutral medium.

equal wt. =

Alkaline medium :- Manganate ions are formed.

$$2KMnO_4 + 2KOH \longrightarrow 2K_2MnO_4 + H_2O + [O]$$

Reactions in Acidic Medium : In acidic medium KMnO₄ oxidizes -

(a) Ferrous salts to ferric salts

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

$$Fe^{+2} \longrightarrow Fe^{+3} + e^{-}] \times 5$$

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

(b) Oxalates to CO_2 :

$$MnO_4^{-} + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O] \times 2$$
$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-] \times 5$$

$$2\mathrm{MnO_4^{-+}5C_2O_4^{2-+}16H^+} \longrightarrow 2\mathrm{Mn^{+2}+10CO_2+8H_2O_2^{-+}H_2O_2^{-+}H_2O_2^{-+}}$$

(c) Iodides to Iodine

$$MnO_4^{-} + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O] \times 2$$
$$2I^- \longrightarrow I_2 + 2e^-] \times 5$$

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



(d) Sulphites to sulphates

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

$$SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2e^-] \times 5$$

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

(e) It oxidizes H₂S to S

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

 $S^{2-} \longrightarrow S^{+} 2e^{-}] \times 5$

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

(f) It oxidizes SO₂ to sulphuric acid

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

$$SO_2 + H_2O + [O] \longrightarrow H_2SO_4] \times 5$$

$$2KMnO_4 + 5SO_2 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

(g) It oxidizes Nitrites to nitrates

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$
$$KNO_2 + O \longrightarrow KNO_3] \times 5$$

$$2KMnO_4 + 5KNO_2 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5KNO_3 + 3H_2O$$

Reactions in Neutral Medium :

(a) It oxidizes H₂S to sulphur :

$$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3 [O]$$
$$H_2S + O \longrightarrow H_2O + S] \times 3$$

 $2KMnO_4 + 3H_2S \longrightarrow 2KOH + 2MnO_2 + 2H_2O + 3S$

(b) It oxidizes Manganese sulphate (MnSO₄ to MnO₂) manganese dioxide :

$$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3 [O]$$
$$MnSO_4 + H_2O + O \longrightarrow MnO_2 + H_2SO_4] \times 3$$

$$2\text{KOH} + \text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 + 2\text{H}_2\text{O}$$

 $2KMnO_4 + 3MnSO_4 + 2H_2O \longrightarrow 5MnO_2 + K_2SO_4 + 2H_2SO_4$



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(c) It oxidizes Sodium thiosulphate to sulphate and sulphur :

$$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3 [O]$$

Na₂S₂O₃ + O \longrightarrow Na₂SO₄ + S] × 3

 $2KMnO_4 + 3Na_2S_2O_3 + H_2O \longrightarrow 2MnO_2 + 3Na_2SO_4 + 2KOH + 3SO_4 + 3SO_4$

Reactions in Alkaline Medium

(a) It oxidizes Iodides to Iodates in alkaline medium :

$$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3 [O]$$
$$KI + 3O \longrightarrow KIO_3$$

 $2KMnO_4 + KI + H_2O \longrightarrow 2MnO_2 + 2KOH + KIO_3$

Alkaline KMnO₄ (Baeyer's reagent) oxidizes ethylene to ethylene glycol. **(b)**

$$\begin{array}{c} \mathrm{CH}_2 \\ \| \\ \mathrm{CH}_2 \end{array} + \mathrm{H}_2\mathrm{O} + [\mathrm{O}] \longrightarrow \qquad \begin{array}{c} \mathrm{CH}_2 \longrightarrow \mathrm{OH} \\ \| \\ \mathrm{CH}_2 \longrightarrow \mathrm{OH} \end{array}$$

STRUCTURE

 MnO_4^-



USES

- (a) Used in volumetric analysis for estimation of ferrous salts, oxalates, and other reducing agents. It is not used as primary standard because it is difficult to obtain it in the pure state.
- (b) It is used as strong oxidising agent in the laboratory as well as industry.
- (c) As disinfectant and germicide.
- (d) In dry cells.
- (e) A very dilute solution of $KMnO_4$ is used for washing wounds.

Potassium permanganate acts as an oxidant in neutral, alkaline as well as acidic media. The final products obtained from it in three conditions are respectively :

(A) MnO_4^{2-} , Mn^{3+} and Mn^{2+}

(C) MnO_2 , MnO_2^+ and Mn^{3+}

- **(B)** MnO_2 , MnO_2 and Mn^{2+} (D) MnO , MnO_2^+ and Mn^{2+}

Ex.

Sol. $3e^- + 2H_2O + MnO_4^- \longrightarrow MnO_2 + 4OH^-$ (neutral medium)

 $e^++MnO_4^- \longrightarrow MnO_4^{-2}$ (dilute alkaline medium)

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

Therefore, (B) option is correct.

POTASSIUM DICHROMATE (K₂Cr₂O₇) :

PREPARATION

The chromite ore is roasted with sodium carbonate in presence of air in a reverberatory furnace

4FeO.
$$Cr_2O_3$$
 (chromite ore) + 8Na₂CO₃ + 7O₂ $\xrightarrow{Roasting}$ 8Na₂CrO₄ + 2Fe₂O₃ + 8CO₂

The roasted mass is extracted with water when Na_2CrO_4 goes into the solution leaving behind insoluble Fe₂O₃. The solution is then treated with calculated amount of H₂SO₄.

$$2\mathrm{Na}_{2}\mathrm{CrO}_{4} + \mathrm{H}_{2}\mathrm{SO}_{4} \longrightarrow \mathrm{Na}_{2}\mathrm{Cr}_{2}\mathrm{O}_{7} + \mathrm{Na}_{2}\mathrm{SO}_{4} + \mathrm{H}_{2}\mathrm{O}_{4}$$

The solution is concentrated when less soluble Na_2SO_4 crystallises out. The solution is further concentrated when crystals of $Na_2Cr_2O_7$ are obtained. Hot saturated solution of $Na_2Cr_2O_7$ is then treated with KCl when orange red crystals of $K_2Cr_2O_7$ are obtained on crystallisation.

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

Note: K₂Cr₂O₇ is preferred over Na₂Cr₂O₇ as a primary standard in volumetric estimation because Na₂Cr₂O₇ is hygroscopic in nature but K₂Cr₂O₇ is not.

PROPERTIES

(a) Physical :

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.

(b) Chemical :

(i) Effect of heating :

On heating strongly, it decomposes liberating oxygen.

$$2K_2Cr_2O_7 \longrightarrow 2K_2CrO_4 + Cr_2O_3 + \frac{3}{2}O_2$$

On heating with alkalies, it is converted to chromate, i.e., the colour changes from orange to yellow. On acidifying, yellow colour again changes to orange.

$$K_{2}Cr_{2}O_{7} + 2KOH \longrightarrow 2K_{2}CrO_{4} + H_{2}O$$
$$Cr_{2}O_{7}^{2-} + 2OH^{-} \longrightarrow 2CrO_{4}^{2-} + H_{2}O$$

Orange

Yellow



$$2 \operatorname{CrO}_{4}^{2-} + 2 \operatorname{H}^{+} \longrightarrow \operatorname{Cr}_{2} \operatorname{O}_{7}^{2-} + \operatorname{H}_{2} \operatorname{O}$$

Yellow

Thus $\operatorname{Cr}_{A}^{2-}$ and $\operatorname{Cr}_{2}O_{7}^{2-}$ exist in equilibrium and are interconvertible by altering the pH of solution.

 $2 \operatorname{CrO}_{4}^{2-} + 2 \operatorname{H}^{+} \longrightarrow 2 \operatorname{HCrO}_{4}^{-} \longrightarrow \operatorname{Cr}_{2} \operatorname{O}_{7}^{2-} + \operatorname{H}_{2} \operatorname{O}_{4}^{2-}$

Orange

In alkaline solution, chromate ions are present while in acidic solution, dichromate ions are present.

(ii)
$$K_2Cr_2O_7 + 2H_2SO_4$$
 (conc. & cold) $\longrightarrow 2CrO_3 \downarrow$ (bright orange/red) + 2KHSO_4 + H_2O_3

$$2K_2Cr_2O_7 + 8H_2SO_4$$
 (conc. & Hot) $\longrightarrow 2K_2SO_4 + 8H_2O + 2Cr_2(SO_4)_3 + 3O_2$

(iii) Acidified $K_2Cr_2O_7$ solution reacts with H_2O_2 to give a deep blue solution due to the formation of CrO_5 .

$$\operatorname{Cr}_{2}O_{7}^{2-} + 2\mathrm{H}^{+} + 4\mathrm{H}_{2}O_{2} \longrightarrow 2\mathrm{Cr}O_{5} + 5\mathrm{H}_{2}O_{2}$$

Blue colour in aqueous solution fades away slowly due to the decomposition of CrO_5 to Cr^{3+} ions and oxygen. In less acidic solution $K_2Cr_2O_7$ and H_2O_2 give salt which is violet coloured and diamagnetic due to the formation of $[CrO(O_2)(OH)]^-$. In alkaline medium with 30% H_2O_2 , a red-brown K_3CrO_8 (diperoxo) is formed. It is tetra peroxo species $[Cr(O_2)_4]^{3-}$ and thus the Cr is in +V oxidation state. In ammoniacal solution a dark red-brown compound, $(NH_4)_3CrO_4$ - diperoxo compound with Cr(IV) is formed.

(iv) Potassium dichromate reacts with hydrochloric acid and evolves chlorine gas.

$$K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$$

(v) It acts as a powerful oxidising agent in acidic medium (dilute H_2SO_4)

$$\operatorname{Cr}_{2}O_{7}^{2-} + 14\mathrm{H}^{+} + 6\mathrm{e}^{-} \longrightarrow 2\mathrm{Cr}^{+3} + 7\mathrm{H}_{2}O. (\mathrm{E}^{\circ} = 1.33 \mathrm{V})$$

The oxidation state of Cr changes from + 6 to +3.

(a) Iodine is liberated from potassium iodide :

$$\operatorname{Cr}_{2}\operatorname{O}_{7}^{2-} + 14\operatorname{H}^{+} + 6e^{-} \longrightarrow 2\operatorname{Cr}^{3+} + 7\operatorname{H}_{2}\operatorname{Cr}^{3+}$$

$$\mathbf{2}\mathrm{I}^{-} \longrightarrow \mathrm{I}_{2} + 2\mathrm{e}^{-} \times [3]$$

 $\operatorname{Cr}_{2}\operatorname{O}_{7}^{2-} + 14\operatorname{H}^{+} + 6\operatorname{I}^{-} \longrightarrow 2\operatorname{Cr}^{3+} + 3\operatorname{I}_{2} + 7\operatorname{H}_{2}\operatorname{O}$

(b) Ferrous salts are oxidised to ferric salts :

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

(c) Sulphites are oxidised to sulphates :

$$\operatorname{Cr}_{2}\operatorname{O}_{7}^{2-} + 3\operatorname{SO}_{3}^{2-} + 8\operatorname{H}^{+} \longrightarrow 3\operatorname{SO}_{4}^{2-} + 2\operatorname{Cr}^{3+} + 4\operatorname{H}_{2}\operatorname{O}$$

(d) H₂S is oxidised to sulphur :

$$\operatorname{Cr}_{2}\operatorname{O}_{7}^{2-} + 3\operatorname{H}_{2}\operatorname{S} + 8\operatorname{H}^{+} \longrightarrow 2\operatorname{Cr}^{3+} + 7\operatorname{H}_{2}\operatorname{O} + 3\operatorname{S}$$



(e) SO_2 is oxidised to H_2SO_4 :

 $Cr_{2}O_{7}^{2-}+3SO_{2}+2H^{+}\longrightarrow 2Cr^{3+}+3SO_{4}^{2-}+H_{2}O;$

Chrome alum is obtained when acidified K₂Cr₂O₇ solution is saturated with SO₂.

 $K_2Cr_2O_7 + H_2SO_4 + 3SO_2 + 23H_2O \xrightarrow{T < 70^{\circ}C} K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$

(f) It oxidises ethylalcohol to acetaldehyde and acetaldehyde to acetic acid

 $C_2H_5OH \xrightarrow{[O]} CH_3CHO \xrightarrow{[O]} CH_3COOH$ ethyl alcohol acetaldehyde acetic acid

(g) It also oxidises nitrites to nitrates, arsenites to arsenates, HBr to Br_2 . HI to I_2 , etc.

(h)
$$K_2Cr_2O_7 + 2C$$
 (charcoal) \land $Cr_2O_3 + K_2CO_3 + CO$

(vi) Chromyl chloride test : $4\text{Cl}^- + \text{Cr}_2\text{O}_7^{2-} + 6\text{H}^+ \longrightarrow 2\text{CrO}_2\text{Cl}_2 \uparrow (\text{deep red}) + 3\text{H}_2\text{O}$

 $\operatorname{CrO}_2\operatorname{Cl}_2 + 4\operatorname{OH}^- \longrightarrow \operatorname{CrO}_4^{2-}(\operatorname{yellow}) + 2\operatorname{Cl}^- + 2\operatorname{H}_2\operatorname{O}^2$

 $\operatorname{CrO}_{4}^{2-}(\operatorname{yellow}) + \operatorname{Pb}^{2+} \longrightarrow \operatorname{Pb}\operatorname{CrO}_{4} \downarrow (\operatorname{yellow})$

(vii) $\operatorname{Cr}_2O_7^{2-}$ (concentrated solution) + 2Ag⁺ \longrightarrow Ag₂Cr₂O₇ \downarrow (reddish brown)

$$Ag_2Cr_2O_7 \downarrow + H_2O \xrightarrow{boil} Ag_2CrO_4 \downarrow + CrO_4^{2-} + 2H^+$$

(viii) $\operatorname{Cr}_{2}O_{7}^{2-} + \operatorname{Ba}^{2+} + \operatorname{H}_{2}O = 2\operatorname{Ba}\operatorname{Cr}O_{4} \downarrow + 2\operatorname{H}^{+}$

As strong acid is produced, the precipitation is only partial. But if NaOH or CH₃COONa is added, precipitate becomes quantitative.

USES

It is used :

- (i) As a volumetric reagent in the estimation of reducing agents such as oxalic acid, ferrous ions, iodide ions, etc. It is used as a primary standard.
- (ii) For the preparation of several chromium compounds such as chrome alum, chrome yellow, chrome red, zinc yellow, etc.
- (iii) In dyeing, chrome tanning, calico printing, photography etc.
- (iv) As a cleansing agent for glass ware in the form of chromic acid.
- Ex. An inorganic compound (A) has garnet red prismatic crystals.(A) is moderately soluble in water and dissolves in cold concentrated H_2SO_4 to yield red crystals (B). In presence of dilute H_2SO_4 it converts a pungent gas(C) into a yellow turbidity (D) and converts a suffocating gas (E) into a green solution (F). The gas (C) and (E) also combine to produce the yellow turbidity (D). With KI and starch in presence of dilute. H_2SO_4 (A) yields blue colour. (A) and concentrated H_2SO_4 mixture is used as a cleansing agent for glassware in the laboratory. Identify (A) and explain the reactions.
- Sol. As compound (A) has garnet red prismatic crystals which with cold conc. H_2SO_4 gives red crystals and a suffocating gas (SO₂) turns its solution in water in to green coloured solution, therefore compound (A) may be K₂Cr₂O₇.



$$K_{2}Cr_{2}O_{7} + 4H_{2}SO_{4} + 3H_{2}S \longrightarrow KHSO_{4} + 2 CrO_{3} (red crystals) + H_{2}O$$
(A)
(B)
$$K_{2}Cr_{2}O_{7} + 4H_{2}SO_{4} + 3H_{2}S \longrightarrow K_{2}SO_{4} + Cr_{2}(SO_{4})_{3} + 7H_{2}O + 3S\downarrow (Yellow)$$
(C)
(D)
$$K_{2}Cr_{2}O_{7} + H_{2}SO_{4} + 3SO_{2} \longrightarrow Cr_{2}(SO_{4})_{3} (Green solution) + K_{2}SO_{4} + H_{2}O$$
(E)
(F)
$$K_{2}Cr_{2}O_{7} + 7H_{2}SO_{4} + 6KI \longrightarrow 4K_{2}SO_{4} + Cr_{2}(SO_{4})_{3} + 7H_{2}O + 3I_{2}$$

$$I_{2} + Starch \longrightarrow Blue colour$$

COMPOUNDS OF IRON

Ferrous Sulphate (Green Vitriol), FeSO₄·7H₂O:

This is the best known ferrous salt. It occurs in nature as copper and is formed by the oxidation of pyrites under the action of water and atmospheric air.

 $2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4$

It is commonly known as harakasis.

PREPARATION

It is obtained by dissolving scrap iron in dilute sulphuric acid.

 $Fe + H_2SO_4 \longrightarrow 2FeSO_4 + H_2$

The solution is crystallised by the addition of alcohol as ferrous sulphate is sparingly soluble in it.

PROPERTIES

(a) Action of heat : At 300°C, it becomes anhydrous. The anhydrous ferrous sulphate is colourless. The anhydrous salt when strongly heated, breaks up to form ferric oxide with the evolution of SO₂ and SO₃.

$$\begin{array}{c} \operatorname{FeSO}_{4} \cdot 7\operatorname{H}_{2}\operatorname{O} \xrightarrow{300^{\circ}\mathrm{C}} - 7\operatorname{H}_{2}\operatorname{O} \xrightarrow{2\operatorname{FeSO}_{4}} \xrightarrow{\operatorname{High}} \operatorname{Fe}_{2}\operatorname{O}_{3} + \operatorname{SO}_{2} + \operatorname{SO}_{3} \\ \end{array} \xrightarrow{\text{Green}} \begin{array}{c} \operatorname{FesO}_{4} \xrightarrow{\operatorname{High}} \operatorname{Fe}_{2}\operatorname{O}_{3} + \operatorname{SO}_{2} + \operatorname{SO}_{3} \end{array}$$

(b) The aqueous solution of ferrous sulphate is slightly acidic due to its hydrolysis.

 $FeSO_4 + 2H_2O \implies Fe(OH)_2 + H_2SO_4$

Weak base Strong acid

(c) It reduces gold chloride to gold.

 $AuCl_3 + 3FeSO_4 \longrightarrow Au + Fe_2(SO_4)_3 + FeCl_3$

(d) It reduces mercuric chloride to mercurous chloride.

 $[2HgCl_2 \longrightarrow Hg_2Cl_2 + 2Cl] \times 3$

 $[3FeSO_4 + 3Cl \longrightarrow Fe_2(SO_4)_3 + FeCl_3] \times 2$

 $6HgCl + 6FeSO_4 \longrightarrow 3Hg_2Cl_2 + 2Fe2(SO_4)_3 + 2FeCl_3$



(e) A cold solution of ferrous sulphate absorbs nitric oxide forming dark brown addition compound, nitroso ferrous sulphate.

$$FeSO_4 + NO \longrightarrow FeSO_4 \cdot NO$$

Nitroso ferrous sulpha
(Brown)

The NO gas is evolved when the solution is heated.

USES

- (a) Ferrous sulphate is used for making blue black ink.
- (b) It is used as a mordant in dyeing.
- (c) It is also used as an insecticide in agriculture.
- (d) It is employed as a laboratory reagent and in the preparation of Mohr's salt.

Ferrous-Oxide FeO (BLACK)

PREPARATION: $FeC_2O_4 \xrightarrow{\Delta} FeO + CO + CO_2$

PROPERTIES: It is stable at high temperature and on cooling slowly disproportionates into Fe₃O₄ and iron

Ferrous Chloride (FeCl₂)

PREPARATION : Fe + 2HCl $\xrightarrow{\text{heated in}}$ FeCl₂ + H₂

PROPERTIES: 2FeCl₂+H₂
$$\longrightarrow$$
 2FeCl₂+2HCl

- (a) It is deliquescent in air like FeCl₃
- (b) It is soluble in water, alcohol and ether also because it is sufficiently covalent in nature
- (c) It volatilises at about 1000°C and vapour density indicates the presence of Fe₂Cl₄. Above 1300°C density becomes normal
- (d) It oxidises on heating in air

 $12\text{FeCl}_2 + 3\text{O}_2 \longrightarrow 2\text{Fe}_2\text{O}_3 + 8\text{FeCl}_3$

(e) H_2 evolves on heating in steam

 $3\text{FeCl}_2 + 4\text{H}_2\text{O} \longrightarrow \text{Fe}_3\text{O}_4 + 6\text{HCl} + \text{H}_2$

(f) It can exist as different hydrated form

 $FeCl_2 \cdot 2H_2O \longrightarrow colourless$

 $FeCl_2 \cdot 4H_2O \longrightarrow pale green$

 $FeCl_2 \cdot 6H_2O \longrightarrow green$

COMPOUND OF ZINC

Zinc Oxide (ZnO) Zinc White

PREPARATION

(a) ZnO is formed when ZnS is oxidised

 $2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$



(b) $Zn(OH)_2$ on strongly heating gives ZnO

$$Zn(OH)_2 \xrightarrow{\Lambda} ZnO + H_2O$$

(c) Zinc on burning in air gives ZnO (commercial method)

$$2Zn + O_2 \longrightarrow 2ZnO$$

PROPERTIES

- (a) ZnO is white when it is cold, a property that has given it a use as a pigment in paints. However, it changes colour, when hot, to a pale yellow. This is due to change in the structure of lattice.
- (b) ZnO is soluble both in acid and alkali and is thus amphoteric in nature.

$$ZnO + 2H^{+} \longrightarrow Zn^{2+} + H_{2}O$$

$$ZnO + 2OH^{-} + H_{2}O \longrightarrow [Zn(OH)_{4}]^{2-} \text{ or } ZnO_{2}^{2-}$$

zincate ion

 $ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$ $ZnO + 2NaOH \longrightarrow Na_2ZnO_2 + H_2O$

sodium zincate

(c)
$$ZnO + C \xrightarrow{\Delta} Zn + CO$$

$$ZnO + CO \longrightarrow Zn + CO_2$$

It is preferred to white lead as it is not blackened by H_2S . It is also used in medicine and in the preparation of Riemann's green (ZnCo₂O₄)

Zinc Sulphate (ZnSO₄)

PREPARATION

(a) $ZnSO_4 \cdot 7H_2O$ (also called white vitriol) is formed by decomposing $ZnCO_3$ with dil. H_2SO_4

 $ZnCO_3 + H_2SO_4 \longrightarrow ZnSO_4 + H_2O + CO_2$

(b) By heating ZnS (zinc blende) in air at lower temperature and dissolving the product in dil. H_2SO_4

$$2ZnS + 3.5O_2 \longrightarrow ZnO + ZnSO_4 + SO_2$$

 $ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O$

PROPERTIES

(a) Highly soluble in water and solution is acidic in nature due to hydrolysis

 $ZnSO_4 + 2H_2O \longrightarrow Zn(OH)_2 + H_2SO_4$

(b) $\operatorname{ZnSO}_4 \cdot 7\operatorname{H}_2O \xrightarrow{100^{\circ}C} \Delta ZnSO_4 \cdot 6\operatorname{H}_2O \xrightarrow{280^{\circ}C} \Delta ZnSO_4 \xrightarrow{T > 760^{\circ}C} ZnO + SO_3$

It slowly effloresces when exposed to air.

(c) It is isomorphous with Epsom salt and used in the manufacture of lithophone (which is a mixture of $BaS + ZnSO_4$ and is used as white pigment).



Zinc Chloride (ZnCl₂)

PREPARATION

 $ZnO + 2HCI \longrightarrow ZnCl_{2} + H_{2}O$ $ZnCO_{3} + 2HCI \longrightarrow ZnCl_{2} + H_{2}O + CO_{2}$ $Zn(OH)_{2} + 2HCI \longrightarrow ZnCl_{2} + 2H_{2}O$ $Anhydrous ZnCl_{2} cannot be made by heating ZnCl_{2} \cdot 2H_{2}O because$ $ZnCl_{2} \cdot 2H_{2}O \longrightarrow Zn(OH)Cl + HCl + H_{2}O$ $Zn(OH)Cl \longrightarrow ZnO + HCl$ $To get anhydrous ZnCl_{2}$ $Zn + Cl_{2} \longrightarrow ZnCl_{2}$ $Zn + 2HCl(dry) \longrightarrow ZnCl + H_{2}$ $Zn + HgCl_{2} \longrightarrow ZnCl_{2} + Hg$ PROPERTIES

- (a) It is deliquescent white solid (when anhydrous)
- **(b)** $ZnCl_2 + H_2S \longrightarrow ZnS$

 $ZnCl_2 + NaOH \longrightarrow Zn(OH)_2 \xrightarrow{excess} Na_2[Zn(OH)_4]$

$$\operatorname{ZnCl}_2 + \operatorname{NH}_4\operatorname{OH} \longrightarrow \operatorname{Zn}(\operatorname{OH})_2 \xrightarrow{\operatorname{excess}} [\operatorname{Zn}(\operatorname{NH}_3)_4]^{2^2}$$

USES

- (a) Used for impregnating timber to prevent destruction by insects
- (b) As dehydrating agent when anhydrous
- (c) $ZnO \cdot ZnCl_2$ used in dental filling

Ex. $\operatorname{Zn}(\operatorname{OH})_2 \xrightarrow{\Lambda} [X].$

Select the correct statement (s) for the compound X.

- (A) X on heating with cobalt nitrate gives green mass
- (B) X on heating alone, becomes yellow but turns white on cooling.
- (C) Solution of X in dilute HCl gives bluish white/white precipitate with excess potassium ferrocyanide.
- **(D)** X is insoluble in aqueous sodium hydroxide.

Sol. (A) X is ZnO which on heating with cobalt nitrate gives ZnO. CoO, the Riemann's green.

- (B) It turns yellow on heating and becomes white on cooling.
- (C) $ZnCl_2$ forms bluish white/white precipitate. $Zn_3K_2[Fe(CN)_6]_2$.

$$3 \operatorname{Zn}^{2+} + 2 \operatorname{K}^{+} + 2 [\operatorname{Fe}(\operatorname{CN})_6]^{4-} \longrightarrow \operatorname{K}_2 \operatorname{Zn}_3 [\operatorname{Fe}(\operatorname{CN})_6]_2 \downarrow$$

(**D**) $ZnO + 2NaOH \longrightarrow Na_2ZnO_2$ (soluble complex) + H₂O.

So options A, B & C are correct and (D) is incorrect.



COMPOUND OF SILVER

Silver Nitrate (Lunar Caustic) AgNO₃

PREPARATION

(a) When Ag is heated with dil HNO₃, AgNO₃ is formed. Crystals separate out on cooling the concentrated solution of AgNO₃

 $3Ag + 4HNO_3 \xrightarrow{\Delta} 3AgNO_3 + NO + 2H_2O$

Colourless crystalline compound soluble in H_2O and alcohol ; m.p. 212°C

(b) When exposed to light, it decomposes hence, stored in a brown coloured bottle:

$$2Ag + 2NO_2 + O_2 \xleftarrow{\Delta, red hot} 2AgNO_3 \xrightarrow{\Delta, T > 212^\circ C} 2AgNO_2 + O_2$$

PROPERTIES

(a) It is reduced to metallic Ag by more electropositive metals like Cu, Zn, Mg and also by PH₃.

$$2AgNO_3 + Cu \longrightarrow Cu(NO_3)_2 + 2Ag$$

$$6AgNO_3 + PH_3 + 3H_2O \longrightarrow 6Ag + 6HNO_3 + H_3PO_3$$

(b) It dissolves in excess of KCN:

$$\begin{array}{ccc} AgNO_3 & & \underbrace{KCN} & AgCN & & \underbrace{KCN} & K[Ag(CN)_2] \\ & & \text{white ppt} & \text{soluble potassium} \end{array}$$

argentocyanide

AgNO₃ gives white precipitate with Na₂S₂O₃; white precipitate changes to black.

$$2AgNO_3 + Na_2S_2O_3 \longrightarrow Ag_2S_2O_3 + 2NaNO_3$$

white ppt

$$Ag_2S_2O_3 + H_2O \longrightarrow Ag_2S + H_2SO_4$$

(c)

Ammoniacal AgNO₃ is called Tollen's reagent and is used to identify reducing sugars (including aldehydes):

 $\text{RCHO} + 2\text{Ag}^+ + 3\text{OH}^- \xrightarrow{\Delta} \text{RCOO}^- + 2\text{Ag} \downarrow + 2\text{H}_2\text{O}$

It is called 'silver mirror test' of aldehydes and reducing sugar (like glucose, fructose).

Some important reaction of AgNO₃





COMPOUND OF COPPER

Cupric Oxide (CuO)

It is called black oxide of copper and is found in nature as tenorite.

PREPARATION

(a) By heating Cu₂O in air or by heating copper for a long time in air (the temperature should not exceed above 1100°C)

$$Cu_2O + \frac{1}{2}O_2 \longrightarrow 2CuO$$

 $2Cu + O_2 \longrightarrow 2CuO$

(b) By heating cupric hydroxide,

 $Cu(OH)_2 \longrightarrow CuO + H_2O$

(c) By heating copper nitrate,

 $2Cu(NO_3)_2 \longrightarrow 2CuO + 4NO_2 + O_2$

(d) On a commercial scale, it is obtained by heating molachite which is found in nature.

 $CuCO_3 \cdot Cu(OH)_2 \longrightarrow 2CuO + CO_2 + H_2O$

PROPERTIES

- (a) It is black powder and stable to moderate heating.
- (b) The oxide is insoluble in water but dissolves in acids forming corresponding salts.

$$CuO + 2HCl \longrightarrow CuCl_2 + H_2O$$

 $CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$

$$CuO + 2HNO_3 \longrightarrow Cu(NO_3)_2 + H_2O$$

(c) When heated to $1100 - 1200^{\circ}$ C, it is converted into cuprous oxide with evolution of oxygen.

4CuO \longrightarrow 2Cu₂O + O₂

(d) It is reduced to metallic copper by reducing agents like hydrogen, carbon and carbon monoxide.

 $CuO + H_2 \longrightarrow Cu + H_2O$

$$CuO + C \longrightarrow Cu + CO$$

 $CuO + CO \longrightarrow Cu + CO_2$

USES

It is used to impart green to blue colour to glazes and glass.

Cupric Chloride, (CuCl₂ · 2H₂O)
PREPARATION
(a)
$$2Cu + 4HCl + O_2 \longrightarrow 2CuCl_2 + 2H_2O$$

 $CuO + 2HCl \longrightarrow CuCl_2 + H_2O$
 $Cu(OH)_2CuCO_3 + 4HCl \longrightarrow 2CuCl_2 + 3H_2O + CO_2$

(b)
$$\operatorname{Cu} + \operatorname{Cl}_2 \longrightarrow \operatorname{Cu}\operatorname{Cl}_2$$

$$\operatorname{CuCl}_{2} \cdot 2\operatorname{H}_{2}\operatorname{O} \xrightarrow[\mathrm{HCl gas}]{150^{\circ}\mathrm{C}} \operatorname{CuCl}_{2} + 2\operatorname{H}_{2}\operatorname{O}$$

PROPERTIES

(a) The aqueous solution is acidic due to its hydrolysis.

$$CuCl_2 + 2H_2O \implies Cu(OH)_2 + 2HCl$$

(b) The anhydrous salt on heating forms Cu_2Cl_2 and Cl_2

$$2\mathrm{CuCl}_2 \rightleftharpoons \mathrm{Cu}_2\mathrm{Cl}_2 + \mathrm{Cl}_2$$

(c) It is readily reduced to Cu₂Cl₂ by copper turnings or SO₂ gas, or hydrogen (Nascent-obtained by the action of HCl on Zn) or SnCl₂.

$$CuCl_2 + Cu \longrightarrow Cu_2Cl_2$$

 $2\mathrm{CuCl}_2 + \mathrm{SO}_2 + 2\mathrm{H}_2\mathrm{O} \longrightarrow \mathrm{Cu}_2\mathrm{Cl}_2 + 2\mathrm{HCl} + \mathrm{H}_2\mathrm{SO}_4$

 $2\mathrm{CuCl}_2 + 2\mathrm{H} \longrightarrow \mathrm{Cu}_2\mathrm{Cl}_2 + 2\mathrm{HCl}$

$$2CuCl_2 + SnCl_2 \longrightarrow Cu_2Cl_2 + SnCl_4$$

(d) A pale blue precipitate of basic cupric chloride, $CuCl_2 \cdot 3Cu(OH)_2$ is obtained when NaOH is added.

$$CuCl_2 + 2NaOH \longrightarrow Cu(OH)_2 + 2NaCl$$

$$\operatorname{CuCl}_2 + \operatorname{3Cu(OH)}_2 \longrightarrow \operatorname{CuCl}_2 \cdot \operatorname{3Cu(OH)}_2$$

It dissolves in ammonium hydroxide forming a deep blue solution. On evaporating of this solution deep blue crystals of tetraammine cupric chloride are obtained.

$$\operatorname{CuCl}_2 + 4\operatorname{NH}_4\operatorname{OH} \longrightarrow \operatorname{Cu(NH}_3)_4\operatorname{Cl}_2 \cdot \operatorname{H}_2\operatorname{O} + 3\operatorname{H}_2\operatorname{O}$$

USES

It is used as a catalyst in Deacon's process. It is also used in medicines and as an oxygen carrier in the preparation of organic dyestuffs.

Copper Sulphate (Blue Vitriol), CuSO₄ · 5H₂O

Copper sulphate is the most common compound of copper. It is called as blue vitriol or nila thotha.

PREPARATION

(a) $CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$

$$Cu(OH)_2 + H_2SO_4 \longrightarrow CuSO_4 + 2H_2O$$

$$Cu(OH)_2CuCO_3 + 2H_2SO_4 \longrightarrow 2CuSO_4 + 3H_2O + CO_2$$

(b) On commercial scale : it is prepared from scrap copper. The scrap copper is placed in a perforated lead bucket which the dipped into hot dilute sulphuric acid. Air is blown through the acid. Copper sulphate is crystallised from the solution.

$$Cu + H_2SO_4 + \frac{1}{2}O_2(air) \longrightarrow CuSO_4 + H_2O$$



PROPERTIES

- (a) It is a blue crystalline compound and is fairly soluble in water.
- (b) Heating effect



(c) Action of NH₄OH : With ammonia solution, it forms the soluble blue complex. First it forms a precipitate of Cu(OH)₂ which dissolves in excess of ammonia solution

$$CuSO_4 + 2NH_4OH \longrightarrow Cu(OH)_2 + (NH_4)SO_4$$
$$Cu(OH)_2 + 2NH_4OH + (NH_4)_2SO_4 \longrightarrow Cu(NH_3)_4SO_4 + 4H_2O$$
$$Tetraammine cupric$$

sulphate

The complex is known as Schwitzer's reagent which is used for dissolving cellulose in the manufacture of artificial silk.

(d) Action of alkalies : Alkalies form a pale blue precipitate of copper hydroxide.

 $CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$

(e) Action of potassium iodide : First cupric iodide is formed which decomposes to give white cuprous iodide and iodine.

 $[CuSO_4 + 2KI \longrightarrow CuI_2 + K_2SO_4] \times 2$ $2CuI_2 \longrightarrow Cu_2I_2 + I_2$

 $2\mathrm{CuSO}_4 + 4\mathrm{KI} \longrightarrow \mathrm{Cu}_2\mathrm{I}_2 + 2\mathrm{K}_2\mathrm{SO}_4 + \mathrm{I}_2$

(f) Action of H_2S : When H_2S is passed through copper sulphate solution, a black precipitate of copper sulphide is formed.

 $CuSO_4 + H_2S \longrightarrow CuS + H_2SO_4$

The black precipitate dissolves in conc. HNO3

 $3CuS + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 3S + 4H_2O$

(g) Action of potassium sulphocyanide : Cupric sulphocyanide is formed.

 $CuSO_4 + 2KCNS \longrightarrow Cu(CNS)_2 + K_2SO_4$



If SO₂ is passed through the solution, a white precipitate of cuprous sulphocyanide is formed.

$$2CuSO_4 + 2KCNS + SO_2 + 2H_2O \longrightarrow Cu_2(CNS)_2 + K_2SO_4 + 2H_2SO_4$$

[This is the general method for obtaining cuprous compounds.]

(h) Action of sodium thiosulphate etc.

$$CuSO_4 + Na_2S_2O_3 \longrightarrow CuS_2O_3 + Na_2SO_4$$

$$2CuS_2O_3 + Na_2S_2O_3 \longrightarrow Cu_2S_2O_3 + Na_2S_4O_6$$

$$3Cu_2S_2O_3 + 2Na_2S_2O_3 \longrightarrow Na_4[Cu_6(S_2O_3)_5]$$

Sodium cuprothiosulphate

USES

- (a) Copper sulphate is used for the preparation of other copper compounds.
- (b) It is used in agriculture as a fungicide and germicide.
- (c) It is extensively used in electric batteries.
- Ex. Anhydrous white solid (A) on addition of potassium iodide solution gave a brown precipitate which turned white (B) on addition of excess of hypo solution. When potassium cyanide is added to an aqueous solution of (A) a white precipitate is formed which then dissolves in excess forming (C). A solution (1%) of (A) on adding to a solution of white portion of egg produced violet colouration in alkaline medium (i.e. in presence of NaOH). Identify compound (A) and explain the reactions.
- Sol. As 1% solution of (A) produced violet colouration with white portion of egg (Biuret test) and (A) with potassium iodide gives brown precipitate which turned white on adding hypo. The (A) may be anhydrous $CuSO_4$ (White). This is further confirmed by the reaction of (A) with potassium cyanide.

$$2\text{CuSO}_4 + 4\text{KI} \longrightarrow \text{Cu}_2\text{I}_2 \downarrow \text{(white)} + \text{I}_2 \uparrow \text{(yellow or brown)} + 2\text{K}_2\text{SO}_4$$

(B)

 $I_{2} + 2Na_{2}S_{2}O_{3} \longrightarrow Na_{2}S_{4}O_{6} + 2NaI$ $2CuSO_{4} + 4KCN \longrightarrow 2Cu(CN)_{2} \downarrow (yellow) + 2K_{2}SO_{4}; 2Cu(CN)_{2} \longrightarrow 2CuCN \downarrow (white) + (CN)_{2}\uparrow$ $2CuCN + 6KCN \longrightarrow 2K_{3}[Cu(CN)_{4}] \text{ (colourless soluble complex).}$ (C)

Ex. $\operatorname{CuSO}_4.5\operatorname{H}_2O \xrightarrow{100^{\circ}C} [X](s) \xrightarrow{250^{\circ}C} [Y](s)$

(A) X and Y are $CuSO_4$. $3H_2O$ and $CuSO_4$

(B) X and Y are $CuSO_4$. $3H_2O$ and $CuSO_4$. H_2O

- (C) X and Y are $CuSO_4$. H₂O and $CuSO_4$
- (D) X and Y are CuSO₄ and CuO
- Sol. $CuSO_4.5H_2O \xrightarrow{100^{\circ}C} CuSO_4.H_2O(s) \xrightarrow{250^{\circ}C} CuSO_4(s).$

So, (C) option is correct.



f-BLOCK ELEMENTS

THE INNER TRANSITION ELEMENTS (f-BLOCK)

INTRODUCTION

The elements constituting the f-block are those in which the 4f and 5f oribitals are progressively filled. These elements are the members of group 3.

The f-block elements comprises of the two series, (i) lanthanoids (the fourteen elements following lanthanum) and (ii) actinoids (the fourteen elements following actinum). It is important to note that the lanthanoids resembles one another more closely than that of the ordinary transition elements in any series. Lanthanoids have only one stable oxidation state and their chemical properties provide the excellent opportunity to observe the effect of small changes in size and nuclear charge along a series of similar elements. On the other hand the chemistry of actinoids is much more complicated and this complication arises partly owing to the occurrence of a wide range of oxidation states in these elements and partly because of their radioactive nature.

LANTHANOIDS (4f - SERIES) :

Electronic configuration : The atoms of these elements have electronic configuration with $6s^2$ common but with variable occupancy of 4f level. However, the electronic configurations of all the tripositive ions which is the most stable oxidation state of all the lanthanoids, are of the form $4f^n$ (n = 1 to 14 with increasing atomic number)

Atomic sizes : There is decrease in atomic and ionic radii from lanthanum to lutetium due to lanthanoid contraction. The decrease in atomic radii is not quit regular as it is regular in M^{3+} ion. This contraction is of course, similar to that observed in an ordinary transition series and is attributed to the imperfect shielding of one electron by another in the same subshell. However, the shielding of one 4f electron by another is less than a 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.

The cumulative effect of the contraction of the lanthanoids series, known as lanthanoids contraction, causes the radii of the members of the third transition series to be very similar to those of the corresponding members of the second series. The almost identical radii of Zr(160 pm) and Hf(159 pm) is a result of the lanthanoid contraction. This accounts for their occurrence together in nature and for the difficulty in their separation.

Oxidation state : In the lanthaoids, La(III) and Ln(III) compounds are predominant species. However, occasionally +2 and +4 ions in solution or in solid compounds are also obtained. This irregularity (as in ionisation enthalpies) arises mainly from the extra stability of empty, half filled or filled f subshell. Thus the formation of Ce^{IV} is favoured by its noble gas configuration, but it is a strong oxidant reverting to the common +3 state. The E° value for Ce⁴⁺/Ce³⁺ is + 1.74 V which suggests that it can oxidise water. However, the reaction rate is very slow and hence Ce(IV) is a good analytical reagent; Pr Nd, Tb and and and Dy also exhibit +4 state but only in oxides, MO₂. Eu²⁺ is formed by losing the two s electrons and its f⁷ configuration accounts for the formation of this ion. However, Eu²⁺ is a strong reducing agent changing to the +3 common oxidation state. Similarly Yb⁺² which has f¹⁴ configuration is a reductant. Tb^{IV} has half filled f-orbitals and is an oxidant. The behaviour of samarium is very much like europium, exhibiting both +2 and +3 oxidation states.



GENERAL CHARACTERISTICS

All the lanthanoids are silvery white soft metals and tarnish rapidly in air. The hardness increases with increasing atomic number, samarium is hard as steel. 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 and occasionally for Sm and Tm. Many trivalent landthanoid ions are coloured both in the solid state and in aqueous solution. Colour of these ions may be attributed to the presence of f electron. Neither La³⁺ nor Lu³⁺ ion shows any colour but the rest do so. However, absorption bands are narrow, probably because of the excitation within f level.. The lanthanoids ions other than the f^0 type (La⁺³ and Ce⁴⁺) and the f^{14} type (Yb²⁺ and Lu³⁺) are all paramagnetic. The paramagnetism rises to maximum in neodyamium.

The first ionisation enthalpies of the lanthanoids are around 600 kJ mol⁻¹s, the second about 1200 kJ mol⁻¹ comparable with those of calcium. A detailed discussion of the variation of the third ionisation enthalpies indicates that the exchange enthalpy considerations (as in 3d orbitals of the first transition series), appear to impart a certain degree of stability to empty, half-filled and completely filled orbitals f level. This is indicated from the abnormally low value of the third ionisation enthalpy of lanthanum, gadolinium and lutetium.

In their chemical behaviour, in general, the earlier members of the series are quit reactive similar to calcium but, with increasing atomic number. They behave more like aluminium. Values for E^{θ} for the half reaction

 $Ln^{3+}(aq) + 3e^{-1} \rightarrow Ln(s)$

are in the range of -2.2 to -2.4 V except for Eu for which the value is -2.0 V. This is of course, a small variation. The **metals combine with hydrogen when gently heated in the gas.** They form oxides M_2O_3 and hydroxides $M(OH)_3$. The hydroxides are definite compounds, not just hydrate oxides. They are basic like alkaline earth metals oxides and hydroxides.



USES OF LANTHANOIDS

- Used for the production of alloy steels for plates and pipes. e.g mischmetall which consists of lanthanoid metal (~95%) and iron (~5%) and traces of S,C,Ca and Al. Mischmetall is used in Mg based alloy to produce bullets, shell and lighter flint.
- 2. Mixed oxides of lanthanoids are employed as catalyst in petroleum cracking.
- 3. Some individual Ln oxides are used as phosphors in television screens and similar fluorescing surfaces.
- 4. Because of their paramagnetic and ferromagnetic character, their compounds are used in making magnetic & electronic devices.
- 5. Ceric sulphate is a well knonw oxidizing agent in volumetric analysis.



ACTINOIDS (5f - SERIES) :

The actinoids include the fourteen elements from Th to Lr. The actinoids are radioactive elements and the earlier members have relatively long half lives, the latter ones have half life values ranging from a day to 3 minutes for lawrencium (Z=103).

Electronic Configuration : All the actinoids are believed to have the electronic configuration of $7s^2$ and variable occupancy of the 5f and 6d subshell. The fourteen electrons are formally added to 5f, through not in thorium (Z = 90) but from Pa onwards the 5f orbitals are complete at element 103. The irregularities in the electronic configuration of the actinoid, like those in the lanthanoids are related to the stabilities of the f^o, f⁷ and f¹⁴ occupancies of the 5f orbitals. Thus the configurations of Am and Cm are [Rn] 5f⁷ 7s² and [Rn] 5f⁷6d¹7s².

Ionic Sizes : The general trend in lanthanoids is observable in the actinoids as well. There is a gradual decrease in the size of atoms or M^{3+} ions across the series. This may be referred to as the actinoids contraction (like lanthanoids contraction). The contraction is, however, greater from elements to element in this series resulting from poor shielding by 5f electrons.

Oxidation states : There is a greater range of oxidation states, which is in part attributed to the fact that the 5f, 6d and 7s levels are of comparable energies.

The actinoids show in general +3 oxidation state. The elements, in the first half to the series frequently exhibit higher oxidation state. e.g. The maximum oxidation state increases from +4 in Th to +5, +6 and +7 respectively in Pa, U and Np but decreases in succeeding elements. The actinoids resemble the lanthanoids in having more compounds in +3 state than in the +4 state. However +3 and +4 ions tends to hydrolyse.

GENERAL CHARACTERISTICS AND COMPARISION WITH LANTHANOIDS :

- 1. The actinoids metals are all silvery white in appearance but display a variety of structures. The structural variability is obtained due to irregularities in metallic radii which are far greater than in lanthanoids.
- 2. The actinoids are highly reactive metals, especially when divided, the action of boiling water on them, for example, gives a mixture of oxide and hydride and combination with most metals takes place at moderate temperatures; hydrochloric acid attacks all metals but most are slightly affected by nitric acid owing to the formation of protective oxide layers; alkalies have no action.
- 3. It is evident from the chemistry of lanthanoids that the ionisation enthalpies of the early actinoids, though not accurately known, but are lower than for the early lanthanoids. This is quit reasonable since it is to be expected that when 5f orbitals are beginning to be occupied, they will penetrate less into the inner core of electrons. The 5f electrons, will therefore, be more effectively shielded from the nuclear charge than the 4f electrons of the corresponding lanthanoids. Because the outer electrons are less firmly held, they are available for bonding in the actinoids.
- **Note :** The lanthanoids contraction is more important because the chemistry of elements succeeding the actinoids are much less known at the present time.

USES OF ACTINOIDS :

- 1. Thorium is used in atomic reactors and in the treatment of cancer. Its salts are used in making incandescent gas mantles.
- 2. Uranium is used as a nuclear fuel. Its salts are used in glass industry (for imparting green colour), textile industry, ceramic industry and in medicines.
- 3. Plutonium it is used as a fuel for atomic reactors as well as for making atomic bombs.



CHEMISTRY FOR JEE MAIN & ADVANCED

- Ex. Name the members of the lanthanoids series which exibit +4 oxidation states and those which exhibit +2 oxidation state. Try to correlate this type of behaviour with the electronic configurations of these elements.
- **Sol.** $+ 4 = {}_{58}Ce, {}_{59}Pr, {}_{60}Nd {}_{65}Tb, {}_{66}Dy$

+ $2 = {}_{60}$ Nd, ${}_{62}$ Sm, ${}_{63}$ Eu ${}_{65}$ Tm, ${}_{66}$ Yb

+2 oxidation state is exhibited when the lanthanoid has the configuration $5d^0 6s^2$ so that 2 electrons are easily lost; +4 oxidation state is exhibited when the configuration left is close to $4f^0$ (e.g. $4f^0$, $4f^1$, $4f^2$) or close to $4f^7$ (e.g. $4f^7$ or $4f^8$).

- **Ex.** The chemistry of the actinoid elements is not so smooth as that of the lanthanoid. Justify this statement by giving some examples from the oxidation state of these elements.
- Sol. Lanthanoids show limited number of oxidation state, viz, +2, +3 and +4 (out of which +3 is most common). This is because of large energy gap between 4f, 5d and 6s subshells, the dominant oxidation state of actinoids is also +3 but they show a number of other oxidation states also, e.g. uranium (Z = 92) and plutonium (Z = 94), show +3 + 4 + 5 and +6 neptunium (Z = 94) shows +3 + 4 + 5 and +7 etc. This is due to small energy difference between 5f, 6d and 7s subshell of the actinoids



d-block

1. The f-blocks elements differ from those of d-blocks elements in that they have unstable electroconfiguration in the outer shells in comparison to that of d-blocks element.

d-block elements electronic configuration

 $(n-1)d^{1-10} ns^{1-2}$

Most common oxidation state +2

- 2. The colour in d-block elements is due to d-excitation while in f-block element, it is due to f-f transitions.
- 3. They show variable oxidation state due to less energy difference between ns and (n-1) d sub shell.
- 4. Most of the d-block compounds act as catalyst due to their variable oxidation state or complex formation tendency or adsorption on their surface. Example :

contact proecess = V_2O_5

Ostwald process = Pt/Rh

Haber process = $Fe_2O_3 + Al_2O_3 + K_2O$

Zeigter Natta = $TiCl_4 + (C_2H_5)_3Al$

Phenton reagent = $FeSO_4 + H_2O_2$

Hydrogenation of Alkene = Ni/Pd

Decomposition of $KClO_3 = MnO_2$

Wilkinsion catalyst = $RhCl + PPh_3$

5. Action of heat on copper sulphate

 $CuSO_{4}.5H_{2}O \xrightarrow{Exposure} CuSO_{4}.3H_{2}O \xrightarrow{373K} CuSO_{4}.H_{2}O \xrightarrow{500K} CuSO_{4}$ Bluish green White

6. Chemical volcano. When crystals of red coloured ammonium dichromate are heated, a violent action takes place accompained by flashes of light and nitrogen is liberated leaving behind a dark green residue of chromium sesquioxide

 (Cr_2O_3)

$$(NH_4)_2Cr_2O_7 \rightarrow N_2 + 4H_2O + Cr_2O_3$$

Ammonium dichromate Chromiun

Chromium sesquioxide



7. **Reactions of Cr_2O_7^{-2}:**



