

d-BLOCK ELEMENTS

1. 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 p-block 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 $(n-1)d^{1-10} ns^0, 1 \text{ or } 2$
- (e) These elements either in their atomic state or in any of their common oxidation state have partly filled $(n-1)d$ orbitals of $(n-1)^{\text{th}}$ main shell.
- (f) The transition elements have an incompletely filled d-level. Since Zn, Cd, Hg elements have d^{10} configuration and are not considered as transition elements but they are d-block elements.

ELECTRONIC CONFIGURATION

I st Transition Series										
Symbol	Sc	Ti	V	Cr	Mn	Fe	Co	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										
II nd 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 electronic configuration Nb, Mo, Ru, Rh, Pd, Ag										
III rd Transition Series										
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 electronic configuration W, Pt, Au										

- □ The irregularities in the observed configuration of Cr ($3d^5 4s^1$ 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.

2. 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.

- (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.

3. METALLIC CHARACTER

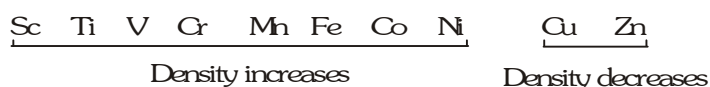
- (a) All the d-block elements are metals as the numbers of electrons in the outer most shell are one or two.
- (b) They are hard, malleable and ductile (except Hg). IB group elements Cu, Ag and Au are most ductile and soft.
- (c) These are good conductor of heat and electricity (due to free e^-) Elements 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.

4. 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.

5. 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 gm cm^{-3}) and Ir (22.61 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.** $Ti < Zr \ll Hf$
- (d) **In 3d series**

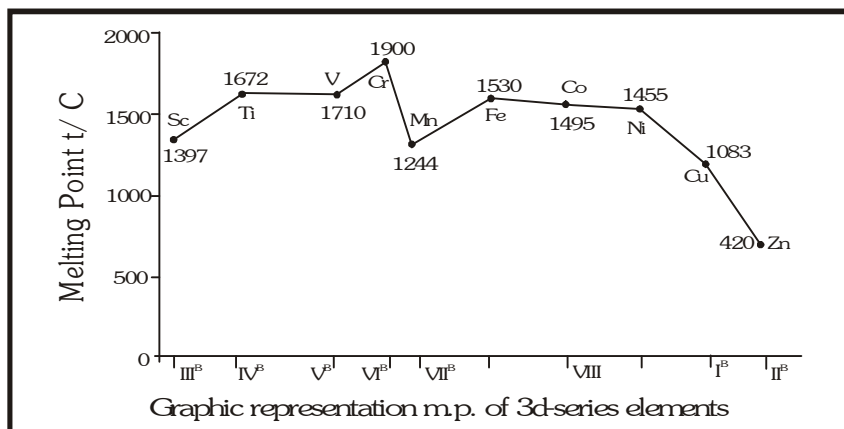


- (e) In 3d series highest density – Cu lowest density – Sc
- (f) Some important orders of density
- $Fe < Ni < Cu$ $Fe < Cu < Au$ $Fe < Hg < Au$

6. 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 (d^5) configuration

- (f) Lowest melting point Hg (– 38 C), Highest melting point W (\approx 3400 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. | | |

7. 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 ¹ 4s ²	<div> <div>↑</div> <div></div> <div></div> <div></div> <div></div> </div> <div>3d</div> <div> <div>↑↓</div> </div> <div>4s</div>	+ 3
Ti	3d ² 4s ²	<div> <div>↑</div> <div>↑</div> <div></div> <div></div> <div></div> </div> <div>3d</div> <div> <div>↑↓</div> </div> <div>4s</div>	+ 2 + 3 + 4
V	3d ³ 4s ²	<div> <div>↑</div> <div>↑</div> <div>↑</div> <div></div> <div></div> </div> <div>3d</div> <div> <div>↑↓</div> </div> <div>4s</div>	+ 2 + 3 + 4 + 5
Cr	3d ⁵ 4s ¹	<div> <div>↑</div> <div>↑</div> <div>↑</div> <div>↑</div> <div>↑</div> </div> <div>3d</div> <div> <div>↑</div> </div> <div>4s</div>	+ 1 + 2 + 3 + 4 + 5 + 6
Mn	3d ⁵ 4s ²	<div> <div>↑</div> <div>↑</div> <div>↑</div> <div>↑</div> <div>↑</div> </div> <div>3d</div> <div> <div>↑↓</div> </div> <div>4s</div>	+ 2 + 3 + 4 + 5 + 6 + 7
Fe	3d ⁶ 4s ²	<div> <div>↑↓</div> <div>↑</div> <div>↑</div> <div>↑</div> <div>↑</div> </div> <div>3d</div> <div> <div>↑↓</div> </div> <div>4s</div>	+ 2 + 3 + 4 + 6
Co	3d ⁷ 4s ²	<div> <div>↑↓</div> <div>↑↓</div> <div>↑</div> <div>↑</div> <div>↑</div> </div> <div>3d</div> <div> <div>↑↓</div> </div> <div>4s</div>	+ 2 + 3 + 4
Ni	3d ⁸ 4s ²	<div> <div>↑↓</div> <div>↑↓</div> <div>↑↓</div> <div>↑</div> <div>↑</div> </div> <div>3d</div> <div> <div>↑↓</div> </div> <div>4s</div>	+ 2 + 3 + 4
Cu	3d ¹⁰ 4s ¹	<div> <div>↑↓</div> <div>↑↓</div> <div>↑↓</div> <div>↑↓</div> <div>↑↓</div> </div> <div>3d</div> <div> <div>↑</div> </div> <div>4s</div>	+ 1 + 2
Zn	3d ¹⁰ 4s ²	<div> <div>↑↓</div> <div>↑↓</div> <div>↑↓</div> <div>↑↓</div> <div>↑↓</div> </div> <div>3d</div> <div> <div>↑↓</div> </div> <div>4s</div>	+ 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.
- (l) 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.

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 $3d$, $3d^5$ & $3d^{10}$ 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) $Mo^{VI}O_4^{2-}$ (oxidation state of Mo is +6), $Mo^{VI}O_4^{2-}$ (4d series) & $W^{VI}O_4^{2-}$, $Re^{VII}O_4^-$ (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 Iodide. **Ex.**

- (i) V (Vanadium) react with halogens to form VF_5 , VCl_5 , VBr_3 , but doesn't form VBr_5 or VI_5 because in +5 oxidation state Vanadium is strong oxidizing agent thus convert Br^- & I^- to Br_2 & I_2 respectively, So VBr_3 & VI_3 are formed but not VBr_5 & VI_5 .

- (ii) On the other hand VF_5 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.

Diffrent oxidation state of chloride & oxides compound

+2	+3	+4	+5	+6	+7
TiCl ₂	TiCl ₃	TiCl ₄			
VOCl ₂	VOCl ₃	VOCl ₄	VOCl ₃		
(Ionic, basic)	Less ionic (Amphoteric)	Covalent and Acidic (Strong lewis acid)			
TiO	Ti ₂ O ₃	TiO ₂			
VO	V ₂ O ₃		V ₂ O ₅		
CrO	Cr ₂ O ₃			CrO ₃	
MnO	Mn ₂ O ₃	MnO ₂		MnO ₃	Mn ₂ O ₇
Ionic, basic	Less Ionic (Amphoteric)			Acidic, covalent	

- (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. $[\text{Ni}(\text{CO})_4]$, $[\text{Ag}(\text{CN})_2]^-$, $[\text{Ag}(\text{NH}_3)_2]^+$

8. COLOUR PROPERTY

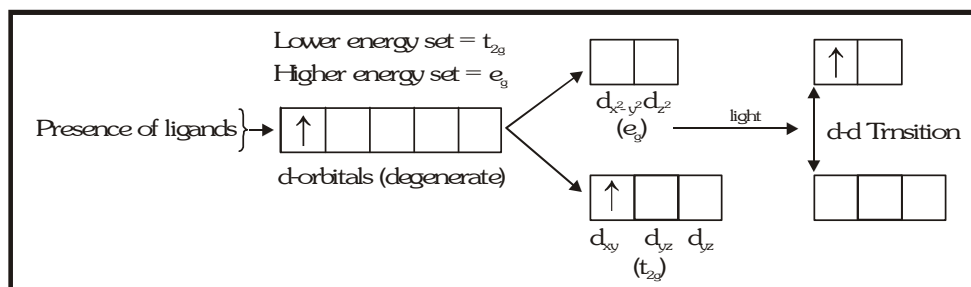
- (a) Most of the transition metal ions exhibit colour property.
 (b) This is due to d-d transition of unpaired electrons in their t_{2g} and e_g sets of 'd' orbitals.
 (c) They require less amount of energy to undergo excitation of electrons. Hence they absorb visible region of light exhibiting colour.

Ex. $\text{Sc}^{+2} : [\text{Ar}]3d^1$, $\text{Ti}^{+2} : [\text{Ar}]3d^2$, $\text{V}^{+2} : [\text{Ar}]3d^3$

- (d) Transition metal ions which do not have any unpaired electrons in their 'd' orbitals like $3d^0$ and $3d^{10}$ configurations, do not exhibit any colour property.

Ex. $\text{Sc}^{+3} : [\text{Ar}]3d^0$, $\text{Cu}^{+1} : [\text{Ar}]3d^{10}$, $\text{Ti}^{+4} : [\text{Ar}]3d^0$ etc are colourless ions.

- (e) A transition metal ion absorbs a part of visible region of light and emmits 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 the transition metal ions exhibit colour property.



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.

$$\Delta_0 \propto \frac{1}{\lambda(\text{Wavelength of light absorb})}$$

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

Ex. Complex ions	$[\text{Co}(\text{H}_2\text{O})_6]^{3+}$	$[\text{Co}(\text{NH}_3)_6]^{3+}$	$[\text{Co}(\text{CN})_6]^{3-}$
Ligand field strength	$\text{H}_2\text{O} <$	NH_3	$< \text{CN}^-$
Magnitude of Δ_0	$\Delta_0(\text{H}_2\text{O}) <$	$\Delta_0(\text{NH}_3) <$	$\Delta_0(\text{CN}^-)$
Magnitude of λ	$\lambda(\text{H}_2\text{O}) <$	$\lambda(\text{NH}_3) <$	$\lambda(\text{CN}^-)$
Colour of the transmitted	orange	Green-blue	violet
Colour of absorbed light Light (I.e. colour of the complex	Green-blue	Orange	Yellow-green

- (d) KMnO_4 (dark pink), $\text{K}_2\text{Cr}_2\text{O}_7$ (orange) having d configuration but they are coloured due to charge transfer spectrum and charge is transferred from anion to cation.

Example of Some coloured metal ions :

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	

9. 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.** $\text{Ti}^{+2} [\text{Ar}]3d^2$, $\text{Ti}^{+3} [\text{Ar}]3d^1$, $\text{V}^{+2}[\text{Ar}]3d^3$, $\text{Cr}^{+3}[\text{Ar}]3d^3$
- (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.

$$\mu = \text{Magnetic moment in Bohr Magnetons (B.M.)}$$
- (g) The magnetic moment of diamagnetic substances will be zero.
- (h) Transition metal ions having d^5 configuration will have maximum number of unpaired electrons therefore they will be maximum paramagnetic in nature.

10. CATALYTIC PROPERTY

- 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.
- 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.
- Transition metals and their compounds exhibiting catalytic properties in various processes are-

Catalyst	Used
TiCl ₃	Used as the Ziegler-Natta catalyst in the production of polythene.
V ₂ O ₅	Convert SO ₂ to SO ₃ in the contact process for making H ₂ SO ₄
MnO ₂	Used as a catalyst to decompose KClO ₃ to give O ₂
Fe	Promoted iron is used in the Haber-Bosch process for making NH ₃
FeCl ₃	Used in the production of CCl ₄ from CS ₂ and Cl ₂
FeSO ₄ and H ₂ O ₂	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 ₃ CHO + 2HCl + Pd.
Pd	Used for hydrogenation (e.g. phenol to cyclohexanone).
Pt/PtO	Adams catalyst, used for reductions.
Pt	Formerly used for SO ₂ → 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 (CH ₃) ₂ SiCl ₂ used to make silicones.
Cu/V	Oxidation of cyclohexanol/cyclohexanone mixture to adipic acid which is used to make nylon-66
CuCl ₂	Deacon process of making Cl ₂ from HCl
Ni	Raney nickel, numerous reduction processes (e.g. manufacture of hexamethylenediamine, production of H ₂ from NH ₃ , reducing anthraquinone to anthraquinol in the production of H ₂ O ₂)

11. FORMATION OF ALLOY

- Transition elements have maximum tendency to form alloys.
- 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.
- In the alloys, ratio of component metals is fixed.
- These are extremely hard and have high melting point.

SOME IMPORTANT ALLOY

(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	
	$\frac{2}{21}$ Vanadium steel	V (0.2 - 1 %)
	$\frac{2}{21}$ Chromium steel	Cr (2 - 4 %)
	$\frac{2}{21}$ Nickel steel	Ni (3 - 5 %)
	$\frac{2}{21}$ Manganese steel	Mn (10 - 18 %)
	$\frac{2}{21}$ Stainless steel	Cr (12 - 14 %) & Ni (2 - 4 %)
	$\frac{2}{21}$ Tungustoon steel	W (10 - 20 %)
	$\frac{2}{21}$ Invar	Ni (36 %)
(j)	14 Carat Gold	54 % Au + Ag (14 to 30 %) + Cu (12 - 28 %)
(k)	24 Carat Gold	100 % Au
(l)	Solder	Pb + Sn
(m)	Magnellium	Mg (10%) + Al (90%)
(n)	Duralumin	(Al + Mn + Cu)
(o)	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

12. FORMATION OF INTERSTITIAL COMPOUNDS

- Transition elements form interstitial compounds with smaller sized non metal elements like hydrogen, carbon, boron, nitrogen etc.
- The smaller sized atoms get entrapped in between the interstitial spaces of the metal lattices.
These interstitial compounds are nonstoichiometric in nature and hence cannot be given any definite formula.
- The smaller sized elements are held in interstitial spaces of transition elements by weak Vander Waals forces of attractions.
- 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.

13. NONSTOICHIOMETRY

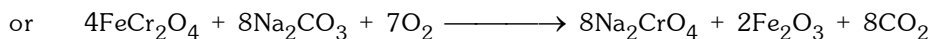
- (a) The transition elements sometimes form nonstoichiometric compounds due to variable valency.
- (b) These are the compounds of indefinite structure & proportion.
- (c) For example, Iron (II) Oxide FeO should be written as a bar over the formula $\overline{\text{FeO}}$ to indicate the ratio of Fe & O atom is not exactly 1:1 ($\text{Fe}_{0.94}\text{O}$ & $\text{Fe}_{0.84}\text{O}$), $\overline{\text{VSe}}$ ($\text{VSe}_{0.98}\text{VSe}_{1.2}$).
- (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.

14. POTASSIUM DICHROMATE ($\text{K}_2\text{Cr}_2\text{O}_7$)**Preparation**

It is prepared from Chromite ore or Ferrochrome or Chrome iron. ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$ or FeCr_2O_4). The various steps involved are.

- (a) **Preparation of sodium chromate (Na_2CrO_4) :**

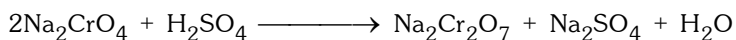
The powdered chromite ore is fused with sodium hydroxide or sodium carbonate in the presence of air in a reverberatory furnace.



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 ($\text{Na}_2\text{Cr}_2\text{O}_7$) from sodium chromate (Na_2CrO_4) :**

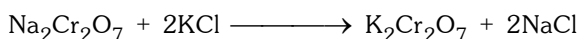
The solution of sodium chromate is filtered and acidified with dil./con. H_2SO_4 acid giving its dichromate.



On cooling, sodium sulphate being less soluble crystallizes out as $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and is removed. The resulting solution contains sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$).

- (c) **Formation of potassium dichromate from sodium dichromate :**

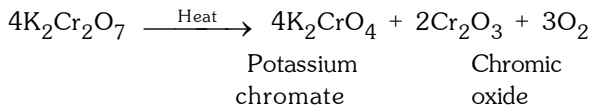
The hot concentrate solution of sodium dichromate is heated with calculated amount of KCl.



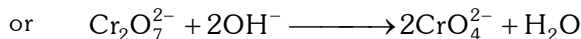
Sodium chloride, being the least soluble precipitates out from the hot solution and is removed by filtration. Orange red crystals of potassium dichromate separate out from mother liquid on cooling.

Properties

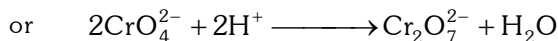
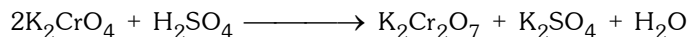
- (a) **Colour and Melting Point :-** Orange red crystals. 670 K
- (b) **Solubility :-** Moderately soluble in cold water but readily soluble in hot water.
- (c) **Action of Heat :-** It decompose on heating to give potassium chromate, chromic oxide and oxygen.



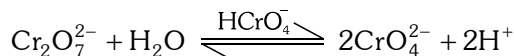
- (d) **Action of Alkalies :-** On heating with alkalies the orange colour of dichromate solution changes to yellow due to the formation of chromate ions.



This chromate on acidifying reconverts into dichromate.

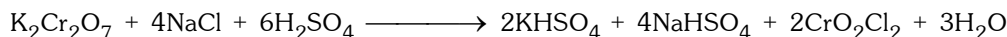


The interconversion is explained by the fact that dichromate ion and chromate ion exist in equilibrium at a pH of about 4.

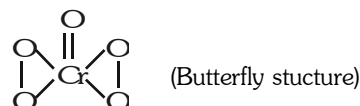
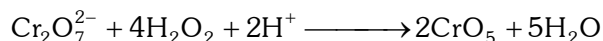


When alkali added, H^+ consumed so forward direction. When acid added, H^+ increases so backward direction.

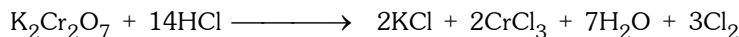
- (e) **Chromyl chloride Test :-** When potassium dichromate is heated with conc. H_2SO_4 acid and a soluble metal chloride (ex. NaCl) orange red vapours of chromyl chloride (CrO_2Cl_2) are formed.



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

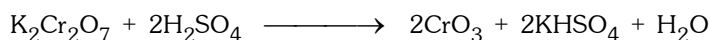


- (g) **Action with HCl :-** Potassium dichromate reacts with hydrochloric acid and evolves chlorine.



- (h) **Action of con. H_2SO_4**

- (i) In cold, red crystals of chromic anhydride are formed.

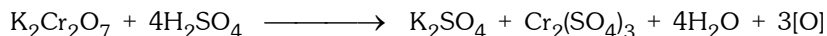


- (ii) On heating the mixture oxygen is evolved.

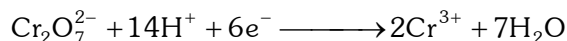


- (i) **Oxidising properties**

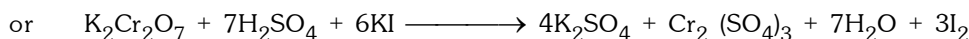
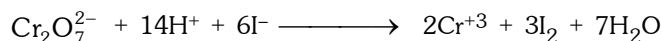
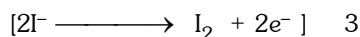
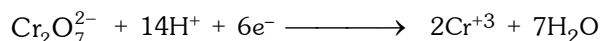
The dichromates act as powerful oxidising agent in acidic medium. In presence of dil H_2SO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$ liberates Nascent oxygen and therefore acts as an oxidising agent.



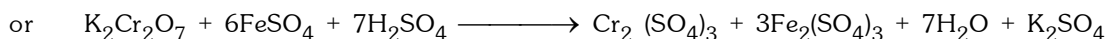
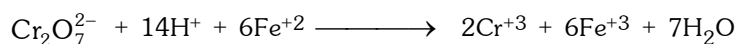
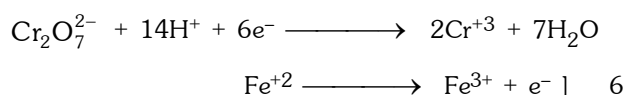
In terms of electronic concept the $\text{Cr}_2\text{O}_7^{2-}$ ion takes up electrons in the acidic medium and hence acts as an oxidising agent.



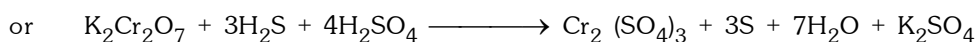
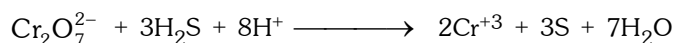
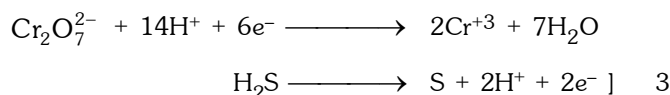
- (i) **It oxidises iodides to iodine :-**



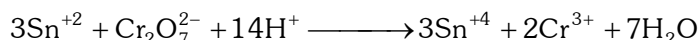
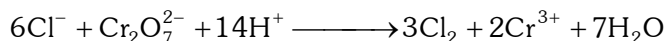
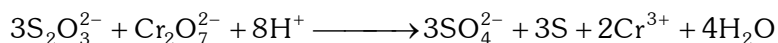
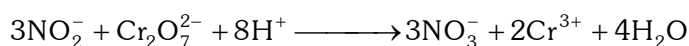
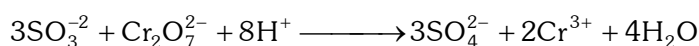
(ii) **Acidified ferrous sulphate to ferric sulphate**



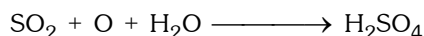
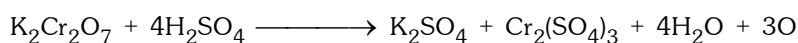
(iii) **Oxidises H_2S to sulphur**



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.



It oxidises SO_2 to sulphuric acid.

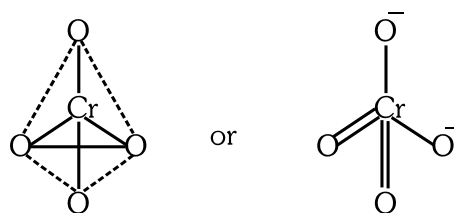


Uses

- For volumetric estimation of ferrous salts, iodides and sulphites.
- For preparation of other chromium compounds such as chrome alum ($\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$), chrome yellow (PbCrO_4) and chrome red ($\text{PbCrO}_4 \cdot \text{PbO}$).
- Used in photography for hardening of gelatin film.
- It is used in leather industry (chrome tanning)
- Chromic acid mixture is used for cleaning glassware, consist of $\text{K}_2\text{Cr}_2\text{O}_7$ and Con. H_2SO_4 .
- In organic chemistry, it is used as an oxidising agent.
- In dyeing and calico printing.

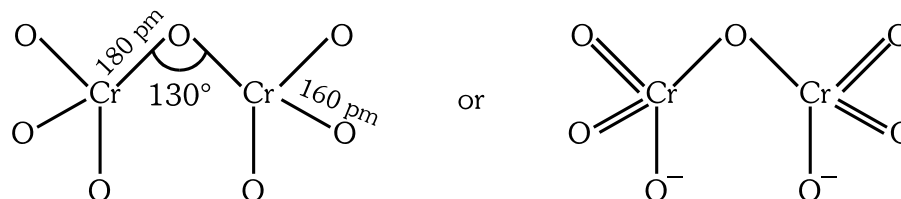
Structure

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.



Dichromate ion

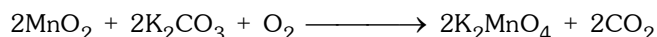
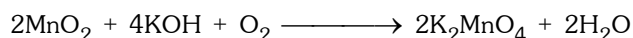
15. POTASSIUM PERMANGANATE (KMnO₄)

Preparation

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

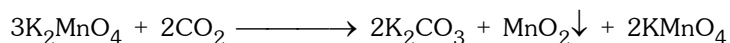
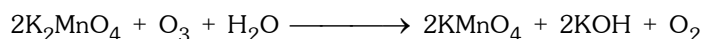
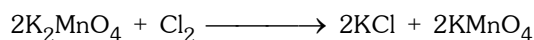
(a) **Conversion of pyrolusite ore to potassium manganate**

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 (K₂MnO₄).



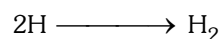
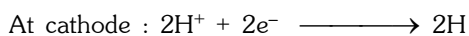
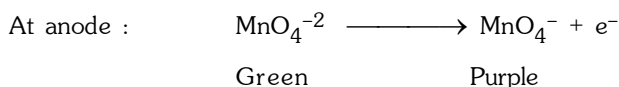
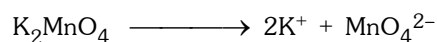
(b) **Oxidation of potassium manganate to potassium permanganate**

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 seperate out.



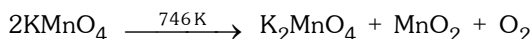
Alternatively, alkaline potassium manganate is electrolytically oxidised.

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.

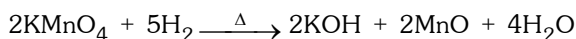


Properties

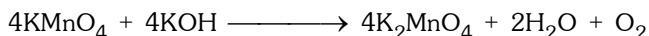
- (a) **Colour and M.P.** :- Dark violet crystalline solid, M.P. 523 K
- (b) **Solubility** :- Moderately soluble at room temperature, but fairly soluble in hot water giving purple solution.
- (c) **Heating** :- When heated strongly it decomposes at 746 K to give K_2MnO_4 and O_2 .



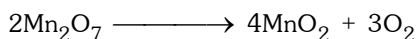
Solid $KMnO_4$ gives KOH , MnO and water vapours, when heated in current of hydrogen.



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

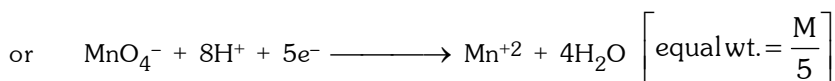
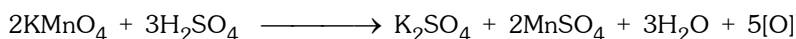


- (e) **Action of con. H_2SO_4** :- With cold H_2SO_4 , it gives Mn_2O_7 which on heating decomposes into MnO_2 .

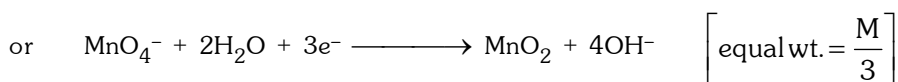
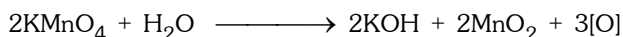


- (f) **Oxidising character** :- $KMnO_4$ acts as powerful oxidising agent in neutral, alkaline or acidic solution because it liberates nascent oxygen as :-

Acidic solution :- Mn^{+2} ions are formed



Neutral solution :- MnO_2 is formed



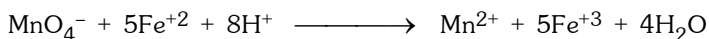
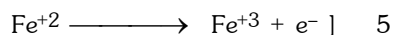
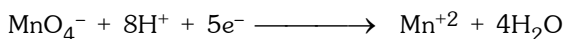
During the reaction the alkali produced generates the alkaline medium even if we start from neutral medium.

Alkaline medium :- Manganate ions are formed.

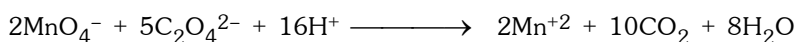
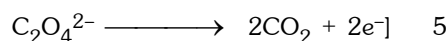
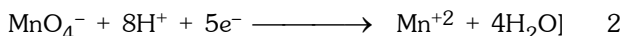


Reactions in Acidic Medium : In acidic medium $KMnO_4$ oxidizes -

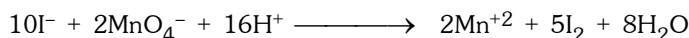
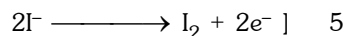
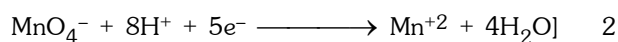
- (a) **Ferrous salts to ferric salts**



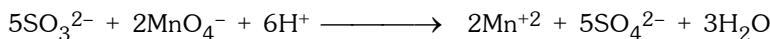
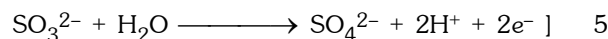
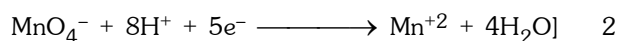
- (b) **Oxalates to CO_2** :



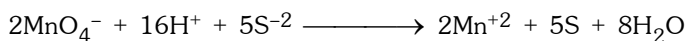
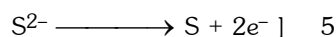
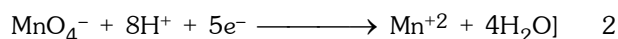
(c) **Iodides to Iodine**



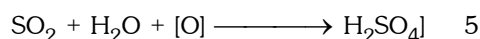
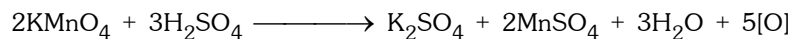
(d) **Sulphites to sulphates**



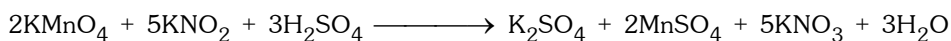
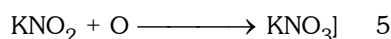
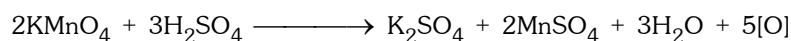
(e) **It oxidizes H_2S to S**



(f) **It oxidizes SO_2 to sulphuric acid**

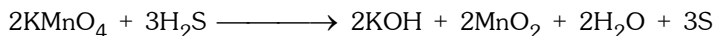
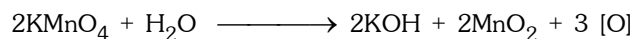


(g) **It oxidizes Nitrites to nitrates**

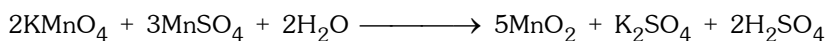
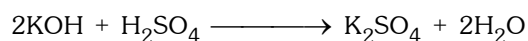
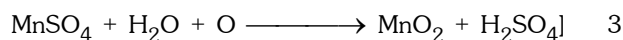
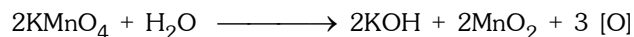


Reactions in Neutral Medium :

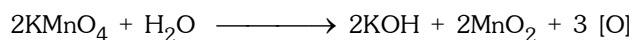
(a) **It oxidizes H_2S to sulphur :**



(b) **It oxidizes Manganese sulphate (MnSO_4 to MnO_2) manganese dioxide :**

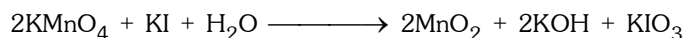
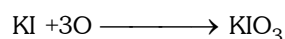
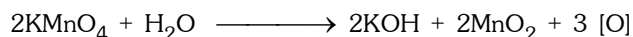


- (c) It oxidizes Sodium thiosulphate to sulphate and sulphur :

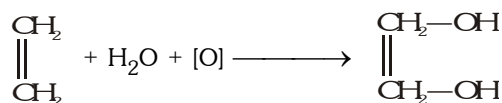


Reactions in alkaline Medium

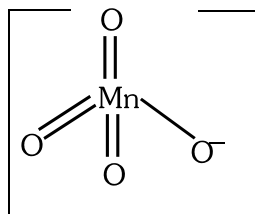
- (a) It oxidizes Iodides to Iodates in alkaline medium :



- (b) Alkaline KMnO_4 (Baeyers reagent) oxidizes ethylene to ethylene glycol.



Structure

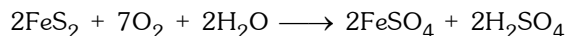


Uses

- 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.
- It is used as strong oxidising agent in the laboratory as well as industry.
- As disinfectant and germicide.
- In dry cells.
- A very dilute solution of KMnO_4 is used for washing wounds.

16. COMPOUNDS OF IRON

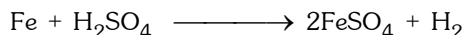
FERROUS SULPHATE (GREEN VITRIOL), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$: This is the best known ferrous salt. It occurs in nature as copper and is formed by the oxidation of pyrites under the action of water and atmospheric air.



It is commonly known as harakasis.

Preparation

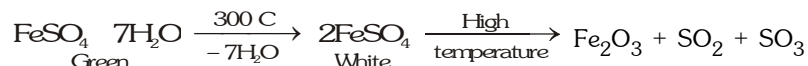
It is obtained by dissolving scrap iron in dilute sulphuric acid.



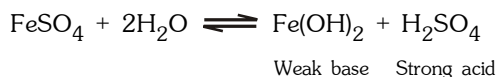
The solution is crystallised by the addition of alcohol as ferrous sulphate is sparingly soluble in it.

Properties

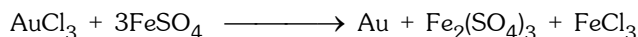
- (a) **Action of heat** : At 300 C, it becomes anhydrous. The anhydrous ferrous sulphate is colourless. The anhydrous salt when strongly heated, breaks up to form ferric oxide with the evolution of SO_2 and SO_3 .



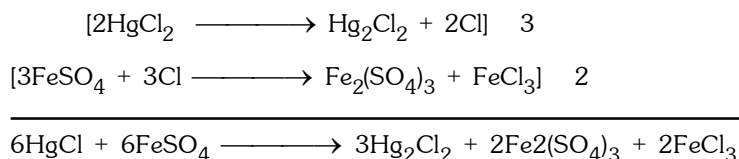
- (b) The aqueous solution of ferrous sulphate is slightly acidic due to its hydrolysis.



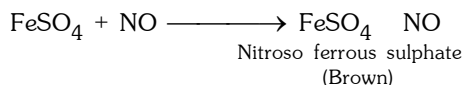
- (c) It reduces gold chloride to gold.



- (d) It reduces mercuric chloride to mercurous chloride.



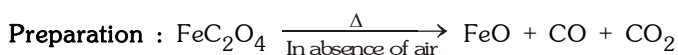
- (e) A cold solution of ferrous sulphate absorbs nitric oxide forming dark brown addition compound, nitroso ferrous sulphate.



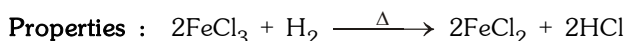
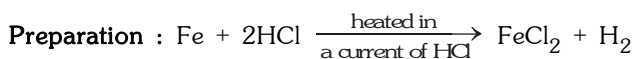
The NO gas is evolved when the solution is heated.

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)

Properties : It is stable at high temperature and on cooling slowly disproportionates into Fe_3O_4 and iron

Ferrous chloride (FeCl₂)

- (a) It is deliquescent in air like FeCl_3
 (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 Fe_2Cl_4 . 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
- $$\text{FeCl}_2 \cdot 2\text{H}_2\text{O} \longrightarrow \text{colourless}$$
- $$\text{FeCl}_2 \cdot 4\text{H}_2\text{O} \longrightarrow \text{pale green}$$
- $$\text{FeCl}_2 \cdot 6\text{H}_2\text{O} \longrightarrow \text{green}$$

17. COMPOUND OF ZINC

Zinc oxide (ZnO) zinc white

Preparation

- (a) ZnO is formed when ZnS is oxidised
- $$2\text{ZnS} + 3\text{O}_2 \longrightarrow 2\text{ZnO} + 2\text{SO}_2$$
- (b) $\text{Zn}(\text{OH})_2$ on strongly heating gives ZnO
- $$\text{Zn}(\text{OH})_2 \xrightarrow{\Delta} \text{ZnO} + \text{H}_2\text{O}$$
- (c) Zinc on burning in air gives ZnO (commercial method)
- $$2\text{Zn} + \text{O}_2 \longrightarrow 2\text{ZnO}$$

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.
- $$\text{ZnO} + 2\text{H}^+ \longrightarrow \text{Zn}^{2+} + \text{H}_2\text{O}$$
- $$\text{ZnO} + 2\text{OH}^- + \text{H}_2\text{O} \longrightarrow [\text{Zn}(\text{OH})_4]^{2-} \text{ or } \text{ZnO}_2^{2-}$$
- zincate ion
- $$\text{ZnO} + 2\text{HCl} \longrightarrow \text{ZnCl}_2 + \text{H}_2\text{O}$$
- $$\text{ZnO} + 2\text{NaOH} \longrightarrow \text{Na}_2\text{ZnO}_2 + \text{H}_2\text{O}$$
- sodium zincate
- (c) $\text{ZnO} + \text{C} \xrightarrow[\text{>1000 C}]{\Delta} \text{Zn} + \text{CO}$
- $$\text{ZnO} + \text{CO} \xrightarrow{\Delta} \text{Zn} + \text{CO}_2$$

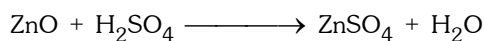
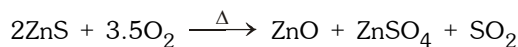
It is preferred to white lead as it is not blackened by H_2S . It is also used in medicine and in the preparation of Rinman's green (ZnCo_2O_4)

Zinc Sulphate (ZnSO_4)

Preparation

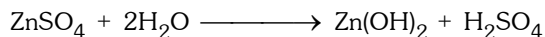
- (a) $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (also called white vitriol) is formed by decomposing ZnCO_3 with dil. H_2SO_4
- $$\text{ZnCO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{ZnSO}_4 + \text{H}_2\text{O} + \text{CO}_2$$

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



Properties

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



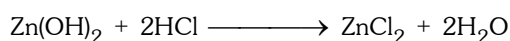
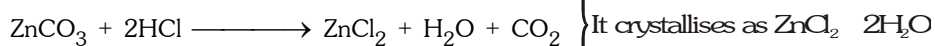
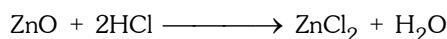
- (b) $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O} \xrightarrow[\Delta]{100^\circ\text{C}} \text{ZnSO}_4 \cdot 6\text{H}_2\text{O} \xrightarrow[\Delta]{280^\circ\text{C}} \text{ZnSO}_4 \xrightarrow{T > 760^\circ\text{C}} \text{ZnO} + \text{SO}_3$

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 $\text{BaS} + \text{ZnSO}_4$ and is used as white pigment).

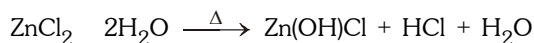
Zinc chloride (ZnCl_2)

Preparation

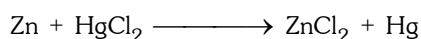
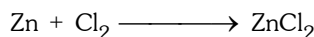


} It crystallises as $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$

Anhydrous ZnCl_2 cannot be made by heating $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$ because



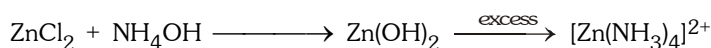
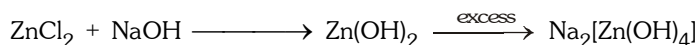
To get anhydrous ZnCl_2



Properties

- (a) It is deliquescent white solid (when anhydrous)

- (b) $\text{ZnCl}_2 + \text{H}_2\text{S} \longrightarrow \text{ZnS}$

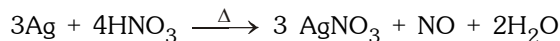


Uses

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

18. COMPOUND OF SILVER**Silver Nitrate (Lunar Caustic) AgNO_3** **Preparation**

- (a) When Ag is heated with dil HNO_3 , AgNO_3 is formed. Crystals separate out on cooling the concentrated solution of AgNO_3

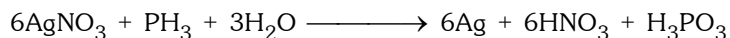
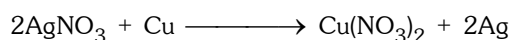


Colourless crystalline compound soluble in H_2O and alcohol ; m.p. 212°C

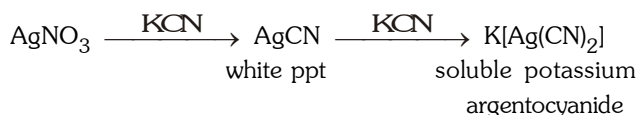
- (b) When exposed to light, it decomposes hence, stored in a brown coloured bottle:

**Properties**

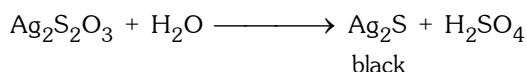
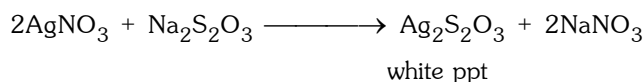
- (a) It is reduced to metallic Ag by more electropositive metals like Cu, Zn, Mg and also by PH_3 .



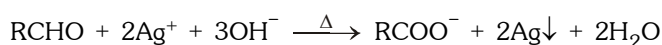
- (b) It dissolves in excess of KCN:



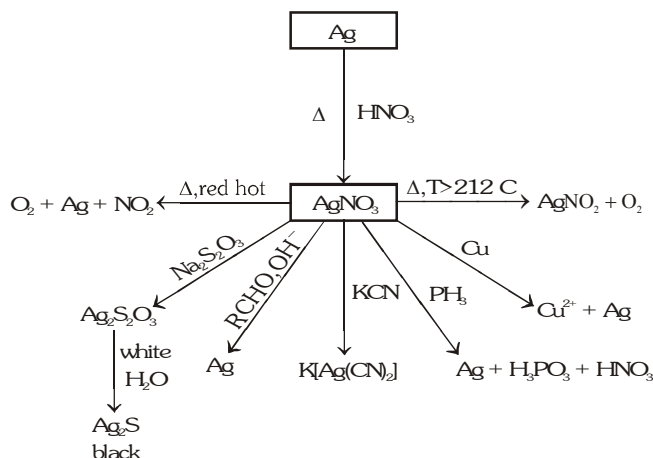
AgNO_3 gives white precipitate with $\text{Na}_2\text{S}_2\text{O}_3$; white precipitate changes to black.



- (c) Ammoniacal AgNO_3 is called Tollen's reagent and is used to identify reducing sugars (including aldehydes):



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

Some important reaction of AgNO_3 

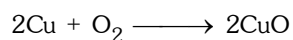
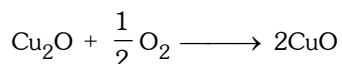
19. COMPOUND OF COPPER

Cupric oxide (CuO)

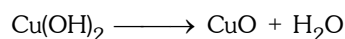
It is called black oxide of copper and is found in nature as tenorite.

Preparation

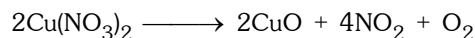
- (a) By heating Cu_2O in air or by heating copper for a long time in air (the temperature should not exceed above 1100°C)



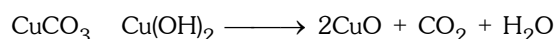
- (b) By heating cupric hydroxide,



- (c) By heating copper nitrate,



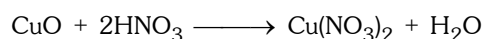
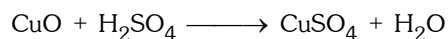
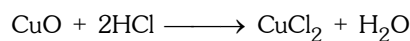
- (d) On a commercial scale, it is obtained by heating malachite which is found in nature.



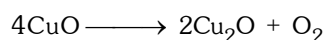
Properties

- (a) It is black powder and stable to moderate heating.

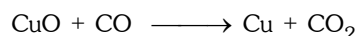
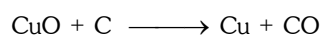
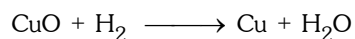
- (b) The oxide is insoluble in water but dissolves in acids forming corresponding salts.



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



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



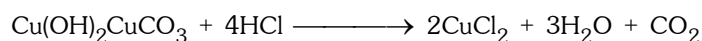
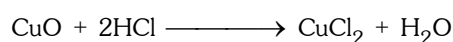
Uses

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

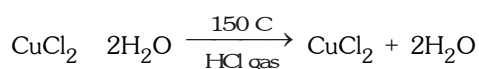
Cupric Chloride, ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$)

Preparation

- (a) $2\text{Cu} + 4\text{HCl} + \text{O}_2 \longrightarrow 2\text{CuCl}_2 + 2\text{H}_2\text{O}$



- (b) $\text{Cu} + \text{Cl}_2 \longrightarrow \text{CuCl}_2$



Properties

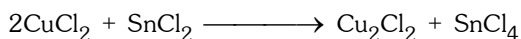
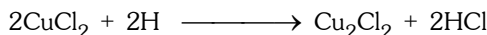
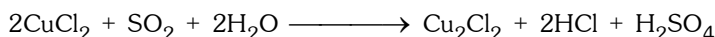
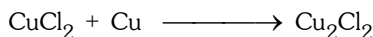
- (a) The aqueous solution is acidic due to its hydrolysis.



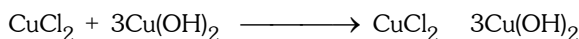
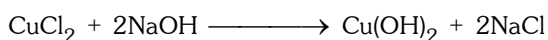
- (b) The anhydrous salt on heating forms Cu_2Cl_2 and Cl_2



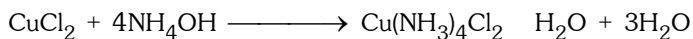
- (c) It is readily reduced to Cu_2Cl_2 by copper turnings or SO_2 gas, or hydrogen (Nascent—obtained by the action of HCl on Zn) or SnCl_2 .



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



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



Uses

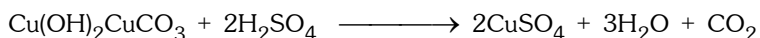
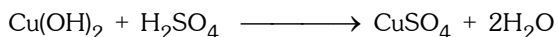
It is used as a catalyst in Deacon's process. It is also used in medicines and as an oxygen carrier in the preparation of organic dyestuffs.

Copper Sulphate (Blue Vitriol), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

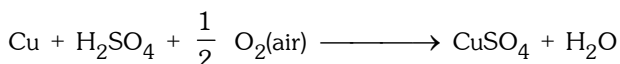
Copper sulphate is the most common compound of copper. It is called as blue vitriol or nila thotha.

Preparation

- (a) $\text{CuO} + \text{H}_2\text{SO}_4 \longrightarrow \text{CuSO}_4 + \text{H}_2\text{O}$



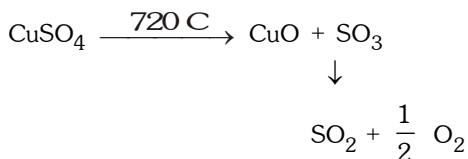
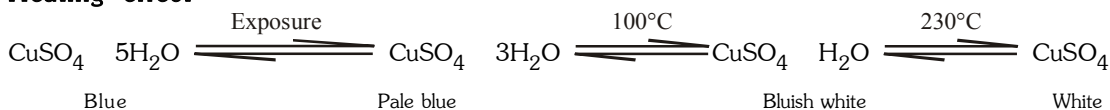
- (b) **On commercial scale :** it is prepared from scrap copper. The scrap copper is placed in a perforated lead bucket which is dipped into hot dilute sulphuric acid. Air is blown through the acid. Copper sulphate is crystallised from the solution.



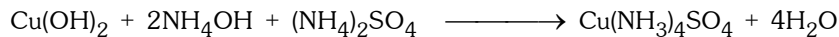
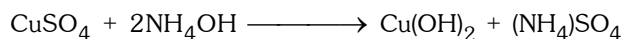
Properties

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

- (b) **Heating effect**



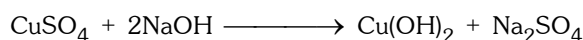
- (c) **Action of NH_4OH** : With ammonia solution, it forms the soluble blue complex. First it forms a precipitate of $\text{Cu}(\text{OH})_2$ which dissolves in excess of ammonia solution



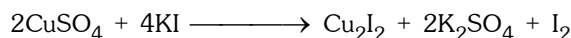
Tetrammine cupric
sulphate

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

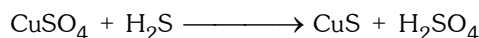
- (d) **Action of alkalis** : Alkalies form a pale blue precipitate of copper hydroxide.



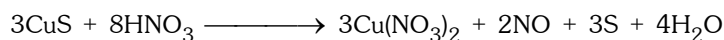
- (e) **Action of potassium iodide** : First cupric iodide is formed which decomposes to give white cuprous iodide and iodine.



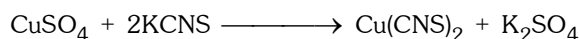
- (f) **Action of H_2S** : When H_2S is passed through copper sulphate solution, a black precipitate of copper sulphide is formed.



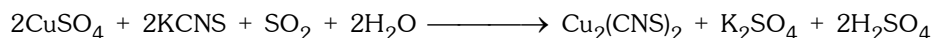
The black precipitate dissolves in conc. HNO_3



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

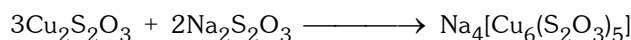
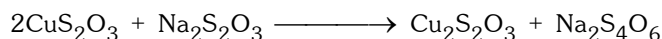
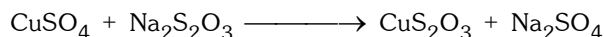


If SO_2 is passed through the solution, a white precipitate of cuprous sulphocyanide is formed.



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

- (h) **Action of sodium thiosulphate etc.**



Sodium cuprothiosulphate

Uses

- Copper sulphate is used for the preparation of other copper compounds.
- It is used in agriculture as a fungicide and germicide.
- It is extensively used in electric batteries.