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ALKALI METALS

\triangleright	Physical	properties	:	General	electronic	configuration	ns^1 .
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General oxidation state +1.

Atomic/Ionic siz	e	Li < Na < K < Rb > Cs.				
Density		Li < K < Na < Rb < Cs				
Ionisation energy	y .	Li > Na > K > Rb > Cs				
Flame colour	Li	Na	K	Rb	Cs	
	Crimsen	Golden	Pale	Reddish	Blue	
	red	yellow	violet	violet		

Basic nature increase down to the group

Reducing property : Molten Li < Na < K < Rb < Cs aqueous Li > K^{\approx} Rb > Cs > Na

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With $O_2 \Rightarrow$ Lithium forms normal oxide [Li₂O] Sodium forms peroxide (Na₂O₂) K, Rb,Cs forms superoxide KO₂,RbO₂, CsO₂

$$M_0O \longrightarrow M(OH)$$

Chemical properties :

$$M_2O_2 \xrightarrow{H_2O} M(OH) + H_2O_2$$

 $\begin{array}{l} \text{MO}_2 \xrightarrow{\text{H}_2\text{O}} \text{M(OH)} + \text{H}_2\text{O}_2 + \text{O}_2 \\ \text{With Water} \Rightarrow \text{M} + \text{H}_2\text{O} \longrightarrow \text{MOH} + \text{H}_2 \end{array}$

With Air
$$\Rightarrow$$
 $M_2O \xrightarrow{M_2O} MOH \xrightarrow{CO_2} M_2O$
 $dry air \xrightarrow{M_2O} MOH \xrightarrow{CO_2} M_2OO$
 $dry air \xrightarrow{M_2O} M_2O + M_3N$
 $only Li gives nitride$

With $\mathbf{NH}_{\mathbf{3}} \Rightarrow : M + (X + Y) \ NH_{3} \longrightarrow [Na(NH_{3})_{X}]^{+} + [e(NH_{3})_{Y}]^{-}$

ammoniated e-

Paramagnetic, blue colour excess of metal dimagnetic and copper bronze colour.

on standing
$$Li + NH_3 \longrightarrow Li_2NH$$
 (Lithmide)
 $M(Na/K/Rb/Cs) + NH_3 \longrightarrow MNH_2$ (amide)
With Halides $\Rightarrow M + X_2 \longrightarrow MX$
 K , Rb, Cs forms poly halide due to large size
Carbonates : Only Li_2CO_3 decomposes
 $Li_2CO_3 \longrightarrow Li_2O + CO_2$

Nitrates : $LiNO_3 \xrightarrow{\Delta} Li_2O + NO_2 + O_2$ $MNO_3 \xrightarrow{\Delta} MNO_2 + O_2 (M = Na/K/Rb/Cs)$



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JEE-Chemistry Handbook

- \blacktriangleright Na₂CO₃ does not impart any colour to the flame but NaCl does because the thermal ionization of Na₂CO₃ does not take place at the temperature of flame of the burner.
- In Solvay's process, CO_2 gas is passed through saturated brine (NaCl) solution when sparingly soluble NaHCO₃ separates out.

$$\begin{split} \mathsf{NH}_3 \,+\, \mathsf{H}_2\mathsf{O} \,+\, \mathsf{CO}_2 &\to \quad \mathsf{NH}_4\mathsf{HCO}_3 \\ \mathsf{NH}_4\mathsf{HCO}_3 \,+\, \mathsf{NaCl} \,\to \, \mathsf{NaHCO}_3 \,\downarrow \,+\, \mathsf{NH}_4\mathsf{Cl} \end{split}$$

The $NaHCO_3$ formed above is calcined to form Na_2CO_3

 $2NaHCO_3 \xrightarrow{Heat} Na_2CO_3 + CO_2 + H_2O$

The reactions taking place at different stages during the manufacture of Na_2CO_3 by Solvay process are given as under :

- (a) $2NH_3 + CO_2 + H_2O \rightarrow (NH_4)_2 CO_3$ MgCl₂ + $(NH_4)_2CO_3 \rightarrow MgCO_3 + 2NH_4Cl$
- or $MgCl_2 + 2NH_4OH \rightarrow Mg(OH)_2 + 2NH_4Cl$
- (b) Ammonia recovery tower

$$NH_4HCO_3 \xrightarrow{Heat} NH_3 + CO_2 + H_2O$$
$$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + CaCl_2 + 2H_2O$$

(c) Calcination of NaHCO₃ $2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O_3$

(i) Efflorescence :

 Na_2CO_3 , $10H_2O$ when exposed to air it gives out nine out of ten H_2O molecules.

$$Na_2CO_3.10H_2O \longrightarrow Na_2CO_3.H_2O + 9H_2O$$

(Monohydrate)

This process is called efflorescence. Hence washing soda losses weight on exposure to air.

(ii) Hydrolysis : Aqueous solution of Na₂CO₃ is alkaline in nature due to anionic hydrolysis.

$$Na_2CO_3 \longrightarrow 2Na^+ + CO_3^{-2}$$
 and $CO_3^{-2} + H_2O \Longrightarrow H_2CO_3 + 2OH^-$
(Carbonic acid)

- (e) Uses
- (i) For making fusion mixture $(Na_2CO_3 + K_2CO_3)$
- (ii) In the manufacture of glass, caustic soda, soap powders etc.
- (iii) In laundries and softening of water.
- (iii) NaOH is strong base

$$NaOH \xrightarrow{SiO_2} Na_2SiO_3 + H_2O$$

$$Al_2O_3 + H_2O$$

$$Al_2O_3 + H_2O$$

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(iv) Reaction with non metals : no reaction with H_2 , N_2 and C



(v) Reaction with halogens

$$\begin{array}{c} & \underset{X_2}{\text{NaOH}(\text{cold/dil})} \text{NaX} + \text{NaOX} \quad (\text{Sodium hypo halite}) \\ & \underset{X_2}{\text{NaOH}(\text{Hot/conc.})} \\ & \underset{X_2}{\text{NaOH}(\text{Hot/conc.})} \\ & \underset{X_2}{\text{NaX}} + \text{NaXO}_3 \quad (\text{Sodium Halate}) \end{array}$$

(vi) **Reaction with Metal** :







ALKALINE EARTH METALS

 \geqslant Physical properties : General electronic configuration ns². General oxidation state +2. Be < Mg < Ca < Sr < Ba Atomic/Ionic size Be > Mg > Ca > Sr > BaIonisation energy Sr & Crimson red Flame colour Ca & Brick red Ba - Apple green Basic nature increase down to the group Reducing property : Order of reducing property in aqueous and gaseous medium is $Be^{+2} \le Mg^{+2} \le Ca^{+2} \le Sr^{+2} \le Ba^{+2}$ \succ Chemical properties : With $O_2 \Rightarrow M \xrightarrow{O_2} MO \xrightarrow{O_2} MO_2$ (Be,Mg,Ca,Sr,Ba, oxide) (Ca,Sr,Ba, peroxide) With Water \Rightarrow M + 2H₂O \rightarrow M(OH)₂ + H₂ With Air \Rightarrow In moist air, except Be all the elements converts into carbonates. In dry air Be and Mg gives nitride and oxide both while other gives only oxides. With $NH_{a} \Rightarrow$: Only Ca, Sr and Ba gives blue solution of ammoniated electron. Carbonates : (i) Except $BeCO_3$, all the carbonates are stable towards heat $BeCO_3 \xrightarrow{\Delta} BeO + CO_2$ Order of decreasing stability -(ii) $BaCO_3 > SrCO_3 > CaCO_3 > MgCO_3 > BeCO_3$ Nitrates : Alkaline earth metals forms $M(NO_3)_2$ type nitrates. (M –Alkaline earth metal). (i) (ii) All alkaline metals nitrates on heating gives oxides and NO $_2$ + O $_2$ $M(NO_3)_2 \xrightarrow{\Delta} Oxides + NO_2 + O_2$

SIMILARITIES BETWEEN LITHIUM AND MAGNESIUM

(a) Both lithium and magnesium are harder and lighter than other elements in the respective groups.

- (b) Lithium and magnesium react slowly with cold water. Their oxides and hydroxides are much less soluble and their hydroxides decompose on heating. Both form a nitride by direct combination with nitrogen, Li₃N and Mg₃N₂.
- (c) The oxides, Li₂O and MgO do not combine with excess oxygen to give a peroxide or a superoxide.
- (d) The carbonates of lithium and magnesium decompose easily on heating to form the oxide and CO₂. Solid bicarbonates are not formed by lithium and magnesium.

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- Both LiCl and MgCl₂ are soluble in ethanol. (e)
- (f) Both LiCl and MgCl₂ are deliquescent and crystallise from aqueous solution as hydrates, $LiCl.2H_2O$ and $MgCl_2.8H_2O$.
- DIAGONAL SIMILARITY BETWEEN BERYLLIUM AND ALUMINIUM : In many of its properties, \succ beryllium resembles aluminium. Thus -
 - (a) The two elements have same electronegativity and their charge/ radius ratios.
 - (b) Both metals are fairly resistant to the action of acids due to a protective film of oxide on the surface. Both metals are acted upon by strong alkalies to form soluble complexes, beryllates [Be(OH)4]2and aluminates, $[Al(OH)_4]^-$.
 - The chlorides of both beryllium and aluminium (c)



have bridged chloride structures in vapour phase.

- Salts of these metals form hydrated ions, Ex. $[Be(OH_2)_4]^{2+}$ and $[Al (OH_2)_6]^{3+}$ in aqueous solutions. (d) Due to similar charge/ radius ratios of beryllium and aluminium ions have strong tendency to form complexes. For example beryllium forms tetrahedral complexes such as BeF_4 ²⁻ and $[Be(C_2 O_4)_2$ $]^{2-}$ and aluminium forms octahedral complexes like AIF₆ ³⁻ and [Al(C₂ O₄)₃]³⁻.
- Among alkaline earth metals, Be and Mg do not impart any characteristic colour to the flame due to more ionization energies.
- The stability of the carbonates of alkaline earth metals increases in the order.

 $BeCO_3 < MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$

 \geq Be_2C on treatment with H_2O forms CH_4 while CaC_2 forms C_2H_2 .

$$Be_{2}C + 2H_{2}O \rightarrow 2 BeO + CH_{4}$$

methane

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

Acetylene

- \geq BeCl₂ in the vapour phase above 900 C is monomeric ; below 900 C in the vapour exists as a mixture of monomer BeCl₂ and dimer Be₂Cl₄, in the solid state, has a polymeric structure and when dissolved in a coordinating solvent it exists as a monomer.
- \geq Anhydrous MgCl₂ cannot be prepared by the simple heating of hydrated magnesium chloride MgCl₂, 6H₂O, as it gets hydrolysed to magnesium oxide.

$$MgCl_{2}.6H_{2}O \longrightarrow MgO + 2HCl + 2H_{2}O$$

- Out of the oxides of group 2 elements only BeO is extremely hard, non volatile, has high melting point and it is amphoteric.
- \geq Anhydrous magnesium chloride (MgCl₂) cannot be prepared by heating MgCl₂.6H₂O. since on heating MgCl₂.6H₂O undergoes hydrolysis with the evolution of HCl gas.

 $MgCl_{2}.6H_{2}O \longrightarrow Mg(OH).Cl + H_{2}O$



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- Analytical detection of Mg :
 - (i) Charcoal cavity test. On heating on a charcoal cavity with one drop of $Co(NO_3)_2$, a pink colour is imparted to the residue CoO.MgO.
 - (ii) The salt solution when mixed with NH_4Cl and NH_4OH and finally treated with soluble phosphates forms a white precipitate of magnesium ammonium phosphate.

$$\label{eq:MgSO4} \begin{split} \text{MgSO}_4 \ + \ \text{Na}_2\text{HPO}_4 + \text{NH}_4\text{OH} \ \rightarrow \ \text{Mg(NH}_4)\text{PO}_4 + \text{Na}_2\text{SO}_4 \ + \ \text{H}_2\text{O} \\ \end{split} \\ \end{split} \\ \end{split} \\ \end{split} \\ \begin{split} \text{white ppt.}$$

- \blacktriangleright Hydrolith (CaH₂) is calcium hydride.
- Calcium cyanamide (CaCN₂) is prepared by heating a mixture of CaC₂ in an atmosphere of N₂ at 1270–1370K with CaF₂.

 $CaC_2 + N_2 \xrightarrow{CaF_2} CaCN_2 + C$

Its trade name is Nitrolim.

Calcium cyanamide (CaCN₂) is a slow acting manure and is preferred to soluble compounds like NaNO₃ or $(NH_4)_2$ SO₄ since it confers fertility of a permanent nature. It is a nitrogenous fertiliser and undergoes a series of changes giving cyanamide, urea, NH₃ and finally the nitrates which are assimilable by plants.

$$CaCN_{2} + H_{2}O + CO_{2} \rightarrow CaCO_{3} + H_{2}NCN$$
$$H_{2}NCN + H_{2}O \rightarrow H_{2}NCONH_{2}$$
$$Urea$$
$$H_{2}NCONH_{2} + H_{2}O \rightarrow CO_{2} + 2NH_{3}$$





BORON FAMILY

- \blacktriangleright B₂O₃ and B(OH₃) are acidic, Al₂O₃ and Al(OH)₃; Ga₂O₃ and Ga(OH)₃ are amphoteric while In₂O₃ and In(OH)₃ are basic. Thus, on moving down the group, there is gradual change from acidic to amphoteric and then to basic character of the oxide and hydroxides of the elements.
- \blacktriangleright The relative Lewis acidic strength of trihalides of boron increase in the order.

 $BF_3 \leq BCl_3 \leq BBr_3 \leq BI_3$

Borazine or Borazole or inorganic benzene is $B_3N_3H_6$.



Action of heat on orthoboric acid

(i) $H_3BO_3 \xrightarrow{100^{\circ}C} HBO_2 + H_2O$

Orthoboric acid Metaboric acid

- (ii) $4HBO_2 \xrightarrow{160^{\circ}C} H_2B_4O_7 + H_2O$ Metaboric acid Tetraboric acid
- Above 160 C, it swells up giving frothy mass and finally forms boron trioxide, B_2O_3 .
- Some important ores of Boron are given as under.
 - (i) Boric acid, H_3BO_3
 - (ii) Borax , $Na_2B_4O_7.10H_2O$
 - (iii) Colemanite, $Ca_2B_4O_{11}.5H_2O$
- Some important minerals of aluminium are given as under.
 - (i) Corundum, Al₂O₃
 - (ii) Bauxite, Al₂O₃.2H₂O
 - (iii) Cryolite, Na₃AlF₆
 - (iv) Felspar, KAlSi₃O₈
- Melting and boiling points of halides of boron decrease in the order

$$BI_3 > BBr_3 > BCl_3 > BF_3$$

Boric acid is a weak monobasic acid

$$B(OH)_{3} + 2H_{2}O \iff H_{3}O^{\oplus} + [B (OH)_{4}]^{-1}$$

pKa = 9.25

It is difficult to titrate boric acid against NaOH solutions and the end point cannot be located correctly However, it can be successfully titrated in the presence of polhydroxy alcohols (e.g. Glycerol, marinital, catechol or sugar). The presence of these compounds greatly increase the acidity of boric acid.

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Boron is complex by these compounds. These complex ions cannot interact with H^+ ions as boron atom has already acquired it's maximum covalency of four. Consequently, boric acid in presence of polyhydroxy alcohols can be titrated against NaOH to a definite end point.

Borax, which is normally written as $Na_2B_4O_7 \cdot 10H_2O$, contains tetranuclear units $[B_4O_5(OH)_4]^{2-}$ comprising BO_4 and BO_3 units. Thus, borax should have been formulated as

Na₂[B₄O₅(OH)₄].8H₂O

- Aluminium trifluoride (AIF₃) is different from other trihalides of Al in being insoluble and nonvolatile. In AIF_3 , the coordination number of Al is six, in $AICI_3$ the coordination number of Al changes from 6 to 4 as it melts while in $AIBr_3$ and AII_3 the coordination number remains four. In AIF_3 each Al is surrounded by a distorted octahedron of 6F atoms and 1 : 3 stoichiometry is achieved by the sharing of corner fluorine atoms between two octahedra.
- Aluminium chloride $(AlCl_3)$ in the pure and anhydrous state is a white solid but commercial samples are yellowish due to the impurity of FeCl₂.
- Anhydrous AlCl₃, in the crystalline state possesses a closely packed layer structure with six coordinated aluminium octahedral arrangement.
- Anhydrous AlCl₃ has a very high affinity for water. On treating AlCl₃ with water the Cl⁻ ions go outside the coordination sphere to form $[Al(H_2O)_6]Cl_3$ with enthalpy of solution -330 KJ mol⁻¹. Due to this strong Al O linkage hydrate cannot be dehydrated on heating to form AlCl₃.

 $2[Al(H_2O)_6] Cl_3 \xrightarrow{\Lambda} Al_2O_3 + 6HCl + 9H_2O$

- Aluminium chloride, is a polymeric solid which exists as a dimer Al_2Cl_6 between 200–400 C and then monomer up to 800 C.
- Thermite welding, Aluminium has got a very high affinity for oxygen.

$$4\text{Al} + 3\text{O}_2 \rightarrow 2\text{Al}_2\text{O}_3.$$

$$\Delta\text{H} = -3230 \text{ KJ mol}^{-1}$$

It, therefore, displaces metals less electropositive than itself from oxides. The large amount of heat produced is used in welding rails or heavy machinery without removing them from their position. This is called thermite welding or Gold Schmidt's aluminothermic process. In this process, a mixture of Ferric oxide (3 parts) and aluminium powder (1 part) called thermite is used.

- Pseudo alums are double sulphates of a divalent and a trivalent metals which crystallize with twenty four water molecules of crystallization, for example.
 - (i) $MnSO_4$. $Al_2(SO_4)_3.24H_2O$
 - (ii) FeSO₄. Al₂(SO₄)₃.24H₂O

They are not isomorphous with true alums.

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- Extraction of Aluminium. Al is usually extracted from Bauxite, $Al_2O_3 \cdot 2H_2O$. First, bauxite is purified from the impurities (Red bauxite contains Fe_2O_3 as impurity while white bauxite contains silica as impurity). Red bauxite can be purified by Baeyer's process or Hall's process while white bauxite is purified by Serpeck's process.
- **Baeyer's process**, involves the roasting of the ore to convert FeO to Fe_2O_3 and then digested at 423K with conc. NaOH solution for a few hours when Al_2O_3 gets dissolved to give a solution of $[Al(OH)_4]^{-1}$ The basic oxide impurities such as Fe_2O_3 are not affected.

 $Al_2O_3 + 2OH^{-1} + 3H_2O \rightarrow 2Al(OH)_4^{-1}$

Aluminate ion

 Fe_2O_3 left undissolved is filtered off. The treatment of $Al(OH)_4^{-1}$. solution with a weak acid precipitate pure $Al(OH)_3$.

$$Al(OH)_4^{-1} + H^+ \rightarrow Al(OH)_3 + H_2O$$

(White ppt.)

The Al(OH)₃ precipitate is removed by filtration and ignited to get alumina, Al₂O₃.

Hall's process, Involves the fusion of the ore with Na_2CO_3 when soluble sodium meta aluminate, $NaAlO_2$ is produced. This is extracted with water when Fe_2O_3 is left as a residue.

 $Al_2O_3 + Na_2CO_3 \rightarrow 2NaAlO_2 + CO_2$

Sodium meta aluminate

The water extract is heated upto 333K and CO_2 is passed through it. Al(OH)₃ is precipitated due to hydrolysis and is ignited to get alumina, Al_2O_3 .

 $2NaAlO_2 + 3H_2O + CO_2 \rightarrow 2Al(OH)_3 + Na_2CO_3$

Serpeck's process involves the heating of bauxite with coke in a current of N_2 at 2075K. The SiO₂ present in the ore is reduced to silicon which volatilizes off and alumina gives aluminium nitride. This can be hydrolysed to Al (OH)₃ which on fusion gives alumina.

 $SiO_2 + 2C \rightarrow Si\uparrow + 2CO\uparrow$

 $Al_2O_3 + 3C + N_2 \rightarrow 2AlN + 3CO$

Aluminium nitride

$$AIN + 3H_2O \rightarrow AI(OH)_3 + NH_3$$

Electrolysis of Al_2O_3 to from aluminium. Pure alumina is dissolved in fused cryolite, Na_3AlF_6 at 1225 K by current of 100 amperes and 6 – 7 volts to get Al. The Al obtained is purified by Hoope's process.

- Boron nitride (BN), has a structure similar to that of graphite.
- Green edged flame test for borate (BO₃³⁻) ion. A mixture of C_2H_5OH and BO₃³⁻ salt with conc. H_2SO_4 burns with green edge flame due to the formation of ethyl borate.

$$\mathrm{H_{3}BO_{3}}\ +\ \mathrm{3C_{2}H_{5}OH}\ \rightarrow\ \mathrm{B}\ (\mathrm{OC_{2}H_{5}})_{3}\ +\ \mathrm{3H_{2}O}$$

Ethyl borate

Charcoal cavity test for aluminium. On heating with Na_2CO_3 and a drop of cobalt nitrate solution a blue coloured residue to cobalt metaaluminate (Thenard's blue) is obtained.

$$2Al^{3+} + Co(NO_3)_2 + O_2 \rightarrow Co (AlO_2)_2 + 2NO_2$$

Blue residue



CARBON FAMILY

- Inert pair effect the reluctance of ns electrons to take part in bond formation is called inert pair effect. This effect is more pronounced in heavier elements and that too for 13, 14 and 15 group. It results in the decrease in oxidation state by 2 units. For examples, Tl is more stable in oxidation state + 1 than the oxidation state +3.
- Gold dissolves in aqua regia forming $H[AuCl_{a}]$ while Pt dissolves forming H_{2} [PtCl₂].
- \blacktriangleright CO₂ is a gas while SiO₂ is a solid at room temperature.
- Frimethylamine (CH₃)₃N is pyramidal while Trisilylamine N(SiH₃)₃ is planar due to back bonding.
- SiCl₄ is a Lewis acid but CCl_4 is not because carbon cannot expand it's octet due to the absence of vacant d-orbitals.
- White Lead is chemically $Pb(OH)_2$. $2PbCO_3$ and Red lead is Pb_3O_4 .

Silicones are polymeric organosilicon compounds containing Si-O-Si linkage. They have high thermal stability of Si-O-Si chains and are also called high temperature polymers.

General formula : $(R_2SiO)_n$. Where $R = -CH_3$, $-C_2H_5$, $-C_6H_5$

Catenation is the unique tendency of 14 group elements to form long chains of different sizes and shapes. The tendency to show catenation is directly related to the strength of bond. The bond energies of 14 group elements decrease as under :

	C-C	Si-Si	Ge-Ge	Sn-Sn	Pb-Pb
Bond energy (KJ mole ⁻¹)	348	222	167	155	-

This is the reason why carbon forms many chains, Si, a few and Ge and Sn form practically no chains.

Carbon suboxide (C_3O_2) is an foul smelling gas which can be prepared by the dehydration of malonic acid with P_4O_{10} .

$$3CH_{2} \begin{pmatrix} COOH \\ COOH + P_{4}O_{10} \end{pmatrix} \rightarrow 3C_{3}O_{2} + 4H_{3}PO_{4} \\ Carbon \\ Malonic acid \\ suboxide \end{pmatrix}$$

On heating upto 200 C, it decomposes into \rm{CO}_2 and carbon.

 $C_3O_2 \xrightarrow{200^{\circ}C} CO_2 + 2C$

The molecule is throught to have a linear structure.

$$O = C = C = C = O$$

- Silicon polymers or silicones are polymeric organosilicon compounds containing Si O Si linkages. Their general formula is $(R_{p}SiO)_{p}$. They may be linear, cyclic or cross linked polymers.
- Mosaic gold (SnS_2) . Stannic sulphide exists in yellow glistening scales which is used for decorative purposes under and the name mosaic gold. It is prepared by heating mixture of tin fillings, sulphur and NH_4Cl in a retort.

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 $\begin{array}{rcl} \mathrm{Sn} &+& 4\mathrm{NH_4Cl} \rightarrow & (\mathrm{NH_4})_2 & \mathrm{SnCl_4} + \mathrm{H_2} + & 2\mathrm{NH_3} \\ \\ \mathrm{2(NH_4)_2} & \mathrm{SnCl_4} + & 2\mathrm{S} \rightarrow & \mathrm{SnS_2} + & (\mathrm{NH_4})_2 & \mathrm{SnCl_6} + & 2\mathrm{NH_4Cl} \end{array}$

- Tin Cry. Tin metal when bent produces a cracking noise due to rubbing of metal crystals over one another.
- Action of conc. HNO_3 on tin
 - (a) Dilute HNO₃

 $4\text{Sn} + 10\text{HNO}_3 \rightarrow 4 \text{Sn}(\text{NO}_3)_2 + \text{NH}_4\text{NO}_3 + 3\text{H}_2\text{O}_3$

(b) Hot conc. HNO₃

$$Sn + 4HNO_3 \rightarrow H_2SnO_3 + 4NO_2 + H_2O$$

Metastannic acid

- Red lead $(Pb_{3}O_{4})$ is considered to be mixture of lead monoxide and lead dioxide and it is written as $(PbO_{2}.2PbO)$.
- \blacktriangleright Lead dioxide (PbO₂). It is a brown powder obtained by the treatment of red lead with HNO₃.

 $Pb_{3}O_{4} + 4HNO_{3} \rightarrow 2Pb(NO_{3})_{2} + PbO_{2} + H_{2}$

It is used as an active material of the positive plate in storage cells and finds use in match industry as an oxidizing agent.

- The main ores of lead are
 - (i) Glena, PbS
 - (ii) Cerrusite, PbCO₃
 - (iii) Anglesite, PbSO₄

 $SnCl_2.2H_2O$ on heating undergoes to form it's basic chloride Sn(OH).Cl. The anhydrous salt, therefore, be obtained by heating the hydrated salt.

Stannous chloride reduces mercuric chloride $(HgCl_2)$ to a white precipitate of mercurous chloride (Hg_2Cl_2) which finally turns to metallic mercury (dark grey or black).

 $2\text{Hg}^{2+} + 3\text{Cl}^- + \text{Sn}^{2+} \rightarrow \text{Hg}_2\text{Cl}_2 + \text{Sn}^{+4}$

Mercurous chloride

 $\begin{array}{rl} \mathrm{Hg_2Cl_2} + \mathrm{SnCl_2} \rightarrow & \mathrm{2Hg} \ \downarrow & + \ \mathrm{SnCl_4} \\ & & \mathrm{Black} \end{array}$

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NITROGEN FAMILY

Holme's signals. A mixture of Ca_3P_2 and CaC_2 on treatment with H_2O forms PH_3 and P_2H_4 along with C_2H_2 . The mixture burns with a bright luminous flame and it acts as a signal for approaching ships.

 $\begin{array}{rl} \text{Ca}_{3}\text{P}_{2} + 6\text{H}_{2}\text{O} + 3\text{Ca}(\text{OH})_{2} + 2\text{PH}_{3} \\ \text{Ca}\text{C}_{2} + \text{H}_{2}\text{O} \rightarrow & \text{Ca}(\text{OH})_{2} + \text{C}_{2}\text{H}_{2} \end{array}$

 \blacktriangleright The strength and solubilities of oxyacids of 15 group elements are given as under.

HNO ₃	$H_{3}PO_{4}$	$H_{3}AsO_{4}$	$H_{3}SbO_{4}$	$H_{3}BiO_{3}$
Strong	Weak	Weaker	Amphoteric	Basic
(Soluble)	(Soluble)	(Soluble)	(Insoluble)	(Insoluble)

- Acidity of oxides and the solubility of 15 group oxides decreases from N to Bi. For example, N_2O_3 , N_2O_5 , P_4O_6 , P_4O_{10} , As_4O_6 and As_4O_{10} are acidic and dissolve water forming acids. Sb_4O_6 and Sb_4O_{10} are weakly acidic and insoluble in water Bi_2O_3 is a basic oxide and is insoluble in water.
- \succ The oxoacids of phosphorus are given as under :

Formula	Name of acid	Oxidation of	Comments about
	No.	phosphorus	acidic nature
H ₃ PO ₂	Hypophosphorus	+ 1	Weak, monobasic
	acid		strong reducing
			agent.
H ₃ PO ₃	Phosphorus acid	+ 3	Dibasic acid, strong
	reducing agent.		
$H_4P_2O_6$	Hypophosphoric	+ 4	Tetrabasic
	acid		
H ₃ PO ₄	Orthophosphoric	+ 5	Tribasic
	acid		
$H_4P_2O_7$	Pyrophosphoric	+ 5	Tetrabasic
	acid		
HPO ₃	Metaphorphoric	+ 5	Monobasic
	acid		

 \blacktriangleright NCl₃ is hydrolysed with H₂O to NH₃ and HOCl.

$$\text{NCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{NH}_3 + 3\text{HOCl}$$

 \blacktriangleright PCl₃ is hydrolysed with water to form phosphorus acid, H₃PO₃.

 $\begin{aligned} & \text{PCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_3 + 3\text{HCl} \\ & \text{AsCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{H}_3\text{AsO}_3 + 3\text{HCl} \\ & \text{SbCl}_3 + \text{H}_2\text{O} \blacksquare \blacksquare \blacksquare \text{SbOCl} + 2\text{HCl} \end{aligned}$

 \blacktriangleright PCl₅ on hydrolysis forms phosphoric acid, H₃PO₄.

$$PCl_{5} + 4H_{2}O \rightarrow H_{3}PO_{4} + 5HCl$$

With Nessler's reagent K_2 HgI₄, ammonium salts give a reddish brown ppt. of Million's base HgO.Hg(NH₂)I

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ALLEN Materials



- Phosphorescence is the glowing of white phosphorus in the dark.
- Some main point of difference between white phosphorus and red phosphorus are given as under.

	Property	White phosphorus	Red phosphorus
(i)	Physical state	Pale yellow soft solid, Can be cut with knife. White when freshly cut.	Red Phosphorus Dark and brittle powder
(ii) (iii) (iv) (v)	Odour Density Solubility Ignition temp.	Garlic 1.8 g/cm ³ Soluble in CS ₂ 303K (melts under water at 317K)	Odourless 2.1 g/cm ³ Insoluble 533 K(does not melt but sublimes)
(vi)	With hot caustic soda	Dissolves and $PH_{_3}$ is evolved	No action

Smoke screens, involve the use of calcium phosphide, Ca_3P_2 . The PH_3 gas obtained from Ca_3P_2 catches fire to give the needed smoke.

Phosphatic slag or Thomas slag or Basic slag is obtained as a biproduct in the manufacture of steel and is probably a double salt of tricalcium phosphate and calcium silicate.

 \blacktriangleright On heating, phosphorus acid, H_3PO_3 decomposes into phosphine (PH₃) and phosphoric acid (H_3PO_4).

 $4H_{_3}PO_{_3} \xrightarrow{_{Heat}} 3H_{_3}PO_{_4} + PH_{_3}$





OXYGEN FAMILY

 \blacktriangleright Tailing of mercury is due to the formation of mercury oxide when Hg reacts with ozone.

$$2Hg + O_3 \rightarrow Hg_2O + O_2$$

As a result of it, mercury looses it's meniscus and starts sticking to the glass.

- The bleaching action of ozone and H_2O_2 is permanent and is due to oxidation while that of SO_2 is temporary and is due to reduction.
- Temporary hardness of water is due to the presence of bicarbonates of Ca and Mg and Permanent hardness is due to the presence of sulphates and chlorides of Ca and Mg.
- Calgon is a trade name given to sodium polymetaphosphate $Na_2[Na_4(PO_3)_6]$. It is generally employed for softening of hard water.
- \blacktriangleright 10V H₂O₂ means that one mole of that H₂O₂ at N.T.P. evolves 10ml. of oxygen gas.
- H_2O_2 is to restore the colour of old lead paintings which have been blackened due to the formation of PbS by the action of H_2S present in the air.

$$\begin{array}{ll} H_2O_2 \rightarrow & H_2O + [O] \\ PbS + 4[O] \rightarrow & PbSO_4 \\ PbS + 4H_2O_2 \rightarrow & PbSO_4 + 4H_2O \\ Black & White \end{array}$$

Antichlor action of H_2O_2 is due to its tendency to reduce the excess of chlorine from bleaching powder to HCl.

$$H_2O_2 + Cl_2 \rightarrow 2HCl + O_2$$

SO₂ gas is dried by bubbling the mixture through conc. H_2SO_4 . It is not dried over quick lime (CaO) as it react with it to form calcium sulphite.

$$CaO + SO_2 \rightarrow CaSO_3$$

- Sodium thioshlphate $Na_2S_2O_3.5H_2O$ is prepared by the following methods :
 - (a) By boiling sodium sulphite with sulphur.

 $Na_2SO_3 + S \xrightarrow{Boil} Na_2S_2O_3$

(b) By boiling sulphur with NaOH

$$4S + 6NaOH \longrightarrow Na_2S_2O_3 + 2Na_2S + 3H_2O$$

(c) By passing SO_2 into Na_2S solution.

$$3Na_2S + 3SO_2 \xrightarrow{Boil} 2Na_2S_2O_3 + S$$

(d) By spring's reaction

$$Na_2S + Na_2SO_3 + I_2 \xrightarrow{Heat} Na_2S_2O_3 + 2NaI$$

Concentrated $Na_2S_2O_3$ does not give a white ppt. with $AgNO_3$. This is because silver thiosulphate formed is readily soluble in excess of sodium thiosulphate forming soluble complex.

$$3S_2O_3^{2-} + Ag_2S_2O_3 \rightarrow 2[Ag(S_2O_3)_2]^3$$

soluble

Sodium thiosulphate is oxidized by Cl_2 to sodium sulphate.

$$Na_2S_2O_3 + Cl_2 + H_2O \rightarrow Na_2SO_4 + 2HCl + S$$

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Sodium thiosulphate is oxidized to sodium tetrathionate $Na_2S_4O_6$ by I_2

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$

This reaction forms the basis of iodometric estimation of $Cr_2O_7^{2-}$ and Cu^{2+} salts.

Sodium thiosulphate reacts with $FeCl_3$ solution to form a violet coloured solution of ferric thiosulphate.

+
$$2Fe^{3+} \Leftrightarrow Fe_2(S_2O_3)$$

Violet

The violet colour disappears quickly due to the reduction of ferric chloride by $S_2O_3^{2-}$ ions,

$$2Fe^{3+} + 2S_2O_3^{2-} \rightarrow 2Fe^{+2} + S_4O_6^{2-}$$

Sodium thiosulphate reduces cupric salts to cuprous salts.

$$2CuCl_2 + 2Na_2S_2O_3 \rightarrow 2CuCl + Na_2S_4O_6 + 2NaCl$$

Sodium thiosulphate reduces auric salts to aurous salt.

3S2032-

$$\begin{aligned} &\text{AuCl}_{3} + 2\text{S}_{2}\text{O}_{3}^{2-} \rightarrow \text{AuCl} + \text{S}_{4}\text{O}_{6}^{2-} + 2\text{Cl} \\ &\text{AuCl} + 2\text{S}_{2}\text{O}_{3}^{2-} \rightarrow [\text{Au} (\text{S}_{2}\text{O}_{3})_{2}]^{3-} + \text{Cl}^{-} \end{aligned}$$

- Neutral oxides are those which are neutral towards litmus e.g., carbon monoxide (CO), water (H_2O), nitrous oxide (N_2O) and nitric oxide (NO).
- \triangleright Ozone is heavier than air and is slightly soluble in water but is more soluble in turpentine oil, glacial acetic acid and CCl_a.
- \blacktriangleright H₂S gas is dried by passing over CaCl₂ or P₂O₅.
- Sulphur trioxides (SO₃) is a white crystalline solid with melting point 290K and boiling point 318K.
- SO₃ is prepared by the direct oxidation of SO₂ with atmospheric oxygen in presence of finally divided Pt or V_2O_5 at a pressure of 2atm. and temperature 700K.

 $2SO_2(g) + O_2(g) = 2SO_3(g)$

 \blacktriangleright SO₃ reacts with water to produce H₂SO₄ and large amount of heat is evolved.

 $SO_3 + H_2O \rightarrow H_2SO_4 + heat$

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HALOGEN FAMILY

Some of the example of polyhalides are :

 $ICl_{2}^{-},\ IBr_{2}^{-},\ BrCl_{2}^{-},\ ClF_{2}^{-},\ ICl_{4}^{-},\ BrF_{4}^{-},\ IF_{6}^{-},\ BrF_{6}^{-}$

 ICl_2^+ , IBr_2^+ , BrF_2^+ , IF_4^+ , ClF_4^+ , BrF_4^+ , IF_6^+ , BrF_6^+ , ClF_6^+ (Polyhalogen cation)

- Pseudo halides are uninegative groups which show certain characteristics of halide ions. For example Cyanide (CN⁻), Cyanate (OCN⁻), Thiocyanate (SCN⁻), Selencyanate (SeCN⁻), Azide (N_3^{-}), Aziothio carbonate (SCSN₃⁻) and isocyanate (ONC⁻).
- \blacktriangleright The electron affinity values (in KJ mol⁻¹) for 17 group element are given below :

F	Cl	Br	Ι
333	349	325	296

The bond energies (in KJ mol⁻¹) for halogens are :

F ₂	Cl_2	Br_2	I_2
158.8	242.6	192.8	151.1

AgF is soluble in water while AgCl, AgBr and AgI are insoluble.

Test for chlorine :

- (a) It is a greenish yellow gas with irritating smell.
- (b) It turns starch iodide paper blue.
- (c) It bleaches litmus paper and indigo solution.
- \blacktriangleright Iodine is slightly soluble in water but much more soluble in KI due to the formation of KI₃.

 $KI + I_2 \rightarrow KI_3$

The solution behaves as a simple mixture of KI and I_2 .

Action of silica and glass. Strong solution of HF attacks glass readily forming silicon fluoride which gives complex fluosilicic acid, H_2SiF_6 with excess HF.

 $SiO_2 + 2H_2F_2 \rightarrow SiF_4 + 2H_2O$

$$SiF_4 + H_2F_2 \rightarrow H_2SiF_2$$

This is called etching of glass.

 \blacktriangleright The acidic strength of the oxoacids of halogen decreases in the following order.

HClO₄ > HClO₃ > HClO₂ > HClO

The chlorine oxyanion in which the central atoms has highest oxidation number will have maximum number of oxygen atoms for participation in the extension of the π -bond. Thereby the charge on the ion is delocalized which greatly stabilizes the ion and thus decreases its tendency to accept a proton i.e., causes the ion to be very weak base with the result that the strength of the acid increases.

The acidity of oxoacids of different halogens having the same oxidation number decreases with the increases in atomic numbers of the halogen

HClO > HBrO > HIO

SOME REAGENTS OR MIXTURES

- Lithophone : A mixture of $ZnS + BaSO_4$ used as white paint.
- Nitrolium : Calcium cyanamide + graphite used as fertilizer.

JEE-Chemistry Handbook



NOBEL GAS

The most important source of noble gases is atmosphere in which they are present in following proportions by volume and mass:

Element	Percentage	Percentage
	by volume	by mass
He	0.0006	0.000037
Ne	0.0015	0.001
Ar	0.932	1.285
Kr	0.0001	0.00028
Xe	0.00001	0.00004

- \blacktriangleright Helium is present to the extent of 2% in natural gas found in the united states and Canada.
- Helium is also present in the minerals of radioactive elements uranium and thorium Ex. clevite, uranite, thorianite, monazite, pichblende etc.
- The sixth member of the zero group was discovered in 1900 by Dorn as one of the disintegration products of radium and was named radon or nitron.
- \blacktriangleright In Dewar's method, the separation of noble gases are summerized below



> The viscosity of He is extermely low, about $1/100^{\text{th}}$ of hydrogen gas.

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METALLURGY

Bunch of process to extract metal from their respective ore
 Ore : Minerals from which metal can be extracted economically :



ALLEN Materials



5. Reduction : To obtains metal (95 to 98%) from metal oxide.



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- The graphical representation of Gibbs energy was first used by H.I.T. Ellingham. This provide a sound basis for considering te choice of reducing agent in the reduction of oxides. this is known as Ellingham diagram such diagram help us in predicting the feasibility of thermal reduction of an ore.
- The critesion of feasibility is that at a given temperatue, Gibbs energy of reaction must be negative.
- At high temperature 'C' is the best reducing agent.
- At low temperature 'CO' is the best redusing agent.
- In blast fornace reduction takes plae at low temperature i.e. why CO is the reducing agent.

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ALLEN Materials

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A summary of the occurence and Extraction of some Metals is presented in the following table :

Metal	Occurrence	Common method of extraction	Reffining	Remarks
Aluminium E =-1.66	1. Bauxite, Al ₂ O ₃ .xH ₂ O 2. Cryolite, Na ₃ AlF ₆	Electrolysis of Al ₂ O ₃ dissolved in molten Na ₃ AlF ₆ + CaF ₂	Electrolytic refining by Hoop's cell	For the extraction, a good source of electricity is required
Iron E =-0.44	 Haematite, Fe₂O₃ Magnetite, Fe₃O₄ Limonite, Fe₂O₃.3H₂O Siderite, FeCO₃ 	Reduction of the oxide with CO and coke in Blast furnace	Bessemerization (impurites has more affinity for O ₂ as compare to Fe)	Temperature approaching 2170K is required
Copper E =-0.34	 Copper pyrites, CuFeS₂ Copper glance, Cu₂S Malachite, CuCO₃.Cu(OH)₂ Cuprite, Cu₂O Azurite, 2CuCO₃.Cu(OH)₂ 	Roasting of sulphide partially and reduction	(i) Polling (ii) Electrolytic method.	It is self reduction in a specially designed converted. The reduction takes place easily. Sulphuric acid leaching is also used in hydrometallurgy from low grade ores.
Zinc E =-0.76	 Zinc blende or Sphalerite, ZnS Calamine, ZnCO₃ Zincite, ZnO 	Roasting of sulphide ore or calcination of ZnCO ₃ of followed by reduction with coke	The metal may be purifed by fractional distillation	For ZnO, carbon is better reducing agent then Cu and Zn is obtain in vapours form ZnO+C ^{1673K} → Zn +CO
Mg E =-2.36	1. Carnallite, KCl.MgCl ₂ .6H ₂ O 2. Magnesite, MgCO ₃	Electrolysis of fused MgCl ₂ with KCl	-	MgCl ₂ .6H ₂ O is heated in the excess current of dry HCl gas to produce anhydrous MgCl ₂
Sn E =-0.14	1. Cassiterite ,SnO ₂ (Tin stone)	Reduction of the SnO_2 with carbon. SnO_2 +2C \rightarrow Sn+2CO	Polling and Liquidation	Ore contain impurity of wolframite, FeWO ₄ + MnWO ₄ (magnetic substance)
Pb E =-0.13	1. Galena , PbS	Roasting, then self reduction or Reduction of PbO (Roasted ore) with carbon PbS+2PbO→3Pb+SO ₂ PbO+C→Pb+CO	Liquadation & electrolytic method.	-
Ag E =0.80	1. Argentite- Ag ₂ S, native Silver	Hydro metallurgy $Ag_2S + 4NaCN \rightarrow$ $2NaAg(CN)_2 + N_2S$ $2NaAg(CN)_2 + Zn →$ $Na_2Zn(CN)_4 + 2Ag$	Cuplation & electrolytic method	In hydro mettallurgy Ag obtain in the form of dark amorphous ppt.
Au E =1.40	Native ore	1. Amalgamation. 2.Cynide process	Cuplation & electrolysis method.	In hydro mettallurgy Au obtain in the form of dark amorphous ppt.

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COORDINATION CHEMISTRY

 \checkmark Double salt \rightarrow completely furnish into their consituents ions

Addition compound

Complex compound \rightarrow Do not furnish completely

Representation of complex compound

Central metal ion (accept e^{-} pair) Co-ordination sphere $\rightarrow [ML_x] A \leftarrow$ Counter ion (where co-ordinate bond forms)

- Co-ordination number (property of metal = no. of e^- pair accept by metal ion.
- > Denticity (property of ligand) = no. of e^- pair donate by ligand
- Polydentate ligand forms rings with central metal ion, ring is known as chelate ring & ligand are called chelating ligand.
- Ligand which have two doner sites (atoms) but at a time only one site (atom) donates are known as ambidentate ligand. They are

CN	NO_2	SCN	(CNO	$S_2O_2^2$	[SeCN
NC	ONO	ans-	NCO	OSO_2S^2	NCSe

Ex. CN^{-} can coordinate through either the nitrogen or the carbon atom to a central metal ion.

Ligands which have two or more than two donor sites but sometimes in complex formation they do not use all donor sites this type of ligands are called flexidentate ligand.

Ex. SO_4^{2-} , CO_3^{2-} .

Structural isomerism :

- (i) **Ionisation isomerism :** Counter ion as a ligand & ligand act as counter ion. $[Co (H_2O)_5CI] SO_4 \quad \leftrightarrow \ [Co(H_2O)_5 SO_4] CI$
- (ii) **Hydrate isomersim :** Number of water molecule inside & outside the co-ordinate sphere are different.

$$[Cr(H_2O)_{c}]Cl \leftrightarrow [Cr(H_2O)_{5}Cl] Cl_2 . H_2O \leftrightarrow [Cr(H_2O)_{4}Cl_{2}] Cl.2H_2O$$

- (iv) Linkage : when ambidentate ligand is present in co-ordination sphere. $[NC \rightarrow Ag \leftarrow CN]^{-} \leftrightarrow [NC \rightarrow Ag \leftarrow NC]^{-} \leftrightarrow [CN \rightarrow Ag \leftarrow NC]^{-}$
- (iv) **Co-ordination isomerism :** In cationic anionic complex when ligand/metal ion interchange $[Pt(NH_3)_4] [PtCl_4] \leftrightarrow [Pt(NH_3)_3Cl] [Pt(NH_3)Cl_3]$

Stereo isomerism :

(i) Geometrical isomerism :

C.N. = 4

- Tetrahedral does not show
- Square planar $M_{a_{2}b_{2}}$, $M_{a_{2}bc}$, M_{abcd} , $M_{(AB)_{2}}$, $M_{(AB)_{2}ab}$. Show geometrical isomerism.



C.N. = 6

- \blacktriangleright M_{abodef} have 15 geometrical isomerism.
- Ma₃b₃ have 2 geometrical isomerism [fac-Mer]
- (ii) **Optical isomerism** : (does not have plane of symmetry)

$$C.N. = 4$$

- (i) Tetrahedral M_{abcd} is optically active
- (ii) Generally square planar is not optically active but in some case depend on ligand.
- C.N. = 6

(i)

M_{abcdef} optically active.

- (ii) $M_{(AA)_2b_2}$ cis is optically active but trans does not.
- (iii) $M_{(AA)_3}$ optically active.

Theories of co-ordination compound :

(i) Werner theory -

(a) Oxidation state of central metal ion is called primary valency satisfies by anions, represent by dotted line.(b) Co-ordination number of central metal ion is called secondary valency satisfies by neutral molecule or anions, represent by solid line.

(ii) Sidwik EAN Rule :

EAN = atomic number (Z) of the metal - oxidation state of metal ion + number of electrons gained from the donor atoms of the ligands.

(iii) Valence bond theory :

- (i) The metal provides vacant orbitals only after the process of hybridisation, thus vacant hybrid orbitals are provided by the metal ion.
- (ii) The empty 'd' orbitals involved in hybridisation may be inner (n-1)d or outer "nd" orbitals and these complexes are called as **Inner orbital complexes** and **Outer orbital complexes** respectively.
- (iii) If inner 'd' orbitals are involved in hybridisation, then it is through only the pairing of unpaired electrons in the 'd' orbitals of metal ion.
- (iv) Then such type of complexes will be **diamagnetic** or **less paramagnetic** and will be called as **Low spin complexes**.
- (v) All outer orbital complexes have **paramagnetic** nature and they are called as **High spin complexes**.

(iv) Crystal Field Theory :

In the electric field of these negative charges, the five d orbitals of the metal atom no longer have exactly same energy. Splitting of five degenerate d-orbitals of the metal ion into sets of orbitals having different energies is called crystal field splitting.

In octahedral



Orbitals which have same energy in a subshell are known as degenerate orbitals.





< edta⁴⁻ < NH_3 < en < CN^- < CO(strongest)

- Paramagnetism $\mu = \sqrt{n(n+2)}$ B.M.
- Complementry colour relationship :



For example complementry colour of red is green.





d-BLOCK

The f-blocks elements differ from those of d-blocks elements in that they have unstable electroconfiguration \geq 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

- \geq The colour in d-block elements is due to d-excitation while in f-block element, it is due to f-f transitions.
- \succ They show variable oxidation state due to less energy difference between ns and (n-1) d sub shell.
- \geq 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 = $TiCl_4 + (C_2H_5)_3$ Al

Phenton reagent = $FeSO_4 + H_2O_2$

Hydrogenation of Alkene = Ni/Pd

Decomposition of $KClO_3 = MnO_2$

Wilkinsion catalyst = $RhCl + PPh_3$

- \geq Action of heat on copper sulphate $CuSO_4.5H_2O \xrightarrow{Exposure} CuSO_4. 3H_2O \xrightarrow{373K} CuSO_4.H_2O \xrightarrow{500K} CuSO_4$ Bluish green
- \geq 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)

White

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

Ammonium dichromate Chromium sesquioxide





 $\blacktriangleright \qquad \text{Reactions of } \operatorname{Cr}_2 \operatorname{O}_7^{-2}:$



 \blacktriangleright Reaction of MnO₄⁻







SALT ANALYSIS

Definition :

The branch of chemical analysis which aims to find out the constituents of a mixture of compound is known as Qualitative Analysis.

The identification of a substances usually involves its conversion into a new substance possessing characteristic properties with the help of one or more substance of known composition. The substance which is used to bring about such change is called a Reagent.



<u>GROUP 'A' RADICALS</u> : (Decomposition by dil.HCl/dil.H₂SO₄)

(1) RADICALS DETECTED WITH DILUTE HCI/DILUTE H2SO4

(I) CARBONATE (CO_3^{2-})

All carbonates except those of alkali metals and ammonium are insoluble in H_2O .

(i) Dilute HCl

With dilute HCl, it decomposes with effervescences due to the evolution of carbon dioxide. $CO_3^{2-} + 2H^+ \longrightarrow CO_2^{\uparrow} + H_2O$

The gas produces white turbidity with lime water, Ca(OH)₂ or baryta water, Ba(OH)₂.

$$CO_2^{\uparrow} + Ca^{2+} + 2OH^- \longrightarrow CaCO_3^{\downarrow} + H_2O$$

White turbidity

 $CaCO_{3}\downarrow + CO_{2}\uparrow + H_{2}O \longrightarrow Ca(HCO_{3})_{2}$

Soluble

(II) BICARBONATE (HCO_3)

Dilute HCl

With dilute HCl, all bicarbonates gives effervescences due to the evolution of CO_2 . $HCO_3^- + H^+ \longrightarrow CO_2^+ + H_2O$ The gas gives white turbidity with lime water or baryta water.

$$\text{CO}_2^{\uparrow} + \text{Ca(OH)}_2 \longrightarrow \text{CaCO}_3^{\downarrow} + \text{H}_2^{O}$$

(III) SULPHIDE (S²⁻)

(i) Dilute HCl or Dilute H_2SO_4 $S^{2^-} + 2H^+ \longrightarrow H_2S\uparrow$ $(CH_3COO)_2Pb + H_2S\uparrow \longrightarrow PbS\downarrow + 2CH_3COOH$ Shining black $H_2S\uparrow + Cd^{2^+} \longrightarrow CdS\downarrow + 2H^+$ Yellow ppt

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(ii) Sodium Nitroprusside Solution

With sodium nitroprusside solution, ionic sulphide gives a purple colour in alkaline medium.

$$Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow Na_4[Fe(CN)_5NOS]$$

Purple colour

No reaction occurs with solutions of hydrogen sulphide or free gas. If however, filter paper moistened with a solution of the reagent is made alkaline with sodium hydroxide or ammonia solution, a purple colouration is produced with free hydrogen sulphide also.

(IV) SULPHITE (SO₃²⁻)

Only the sulphites of alkali metals and ammonium are soluble in water.

Dilute HCl or Dilute H₂SO₄

Dilute HCl or H_2SO_4 decomposes sulphites with the evolution of sulphur dioxide.

$$SO_3^{2-} + 2H^+ \longrightarrow SO_2^{\uparrow} + H_2O$$

The gas can be identified

- (a) By suffocating odour of burning sulphur.
- (b) By green colour formation, when passed through acidified $K_2Cr_2O_7$ solution. $3SO_2\uparrow + Cr_2O_7^{2-} + 2H^+ \longrightarrow 3SO_4^{2-} + 2Cr^{3+} + H_2O$

Green colour

(V) NITRITE (NO_2^{-})

All other nitrites except $AgNO_2$ (sparingly soluble) are soluble in H_2O .

(i) Dilute HCl

 $NO_{2}^{-} + H^{+} \longrightarrow HNO_{2}$ $2HNO_{2} \longrightarrow H_{2}O + N_{2}O_{3}$ $3HNO_{2} \longrightarrow HNO_{3} + 2NO^{\uparrow} + H_{2}O$ $2NO^{\uparrow} + O_{2}^{\uparrow} \longrightarrow 2NO_{2}^{\uparrow}$

Raddish-brown

(ii) Brown ring test

When the nitrite solution is added carefully to a concentrated solution of iron (II) sulphate acidified with dilute acetic or dilute sulphuric acid, a brown ring appears due to the formation of $[Fe(H_2O)_5NO]SO_4$ at the junction of the two liquids. If the addition has not been made slowly and caustiously, a brown colouration results.

$$NO_{2}^{-} + CH_{3}COOH \longrightarrow HNO_{2} + CH_{3}COO^{-}$$

$$3HNO_{2} \longrightarrow H_{2}O + HNO_{3} + 2NO^{+}$$

$$FeSO_{4} + 6H_{2}O \longrightarrow [Fe(H_{2}O)_{6}]SO_{4}$$

$$[Fe(H_{2}O)_{6}]SO_{4} + NO^{+} \longrightarrow [Fe(H_{2}O)_{5}NO]SO_{4} + H_{2}O$$
Brown ring

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(2) RADICALS DETECTED WITH CONCENTRATED H_2SO_4

(I) CHLORIDE (Cl⁻)

(i) Concentrated H_2SO_4

With concentrated H_2SO_4 , chlorides gives vapours of HCl.

$$Cl^{-} + H_2SO_4 \longrightarrow HCl^{\uparrow} + HSO_4^{-}$$

Vapour evolved

- (a) Turns blue litmus paper red
- (b) Gives white fumes of NH_4Cl when a glass rod moistened with aqueous ammonia solution is brought close to the mouth of test tube.

(ii) Chromyl Chloride Test

When a mixture containing chloride ion is heated with $K_2Cr_2O_7$ and concentrated H_2SO_4 , deep orange-red fumes of chromyl chloride (CrO_2Cl_2) are formed.

 $\begin{array}{rl} K_2 Cr_2 O_7 \,+\, 4NaCl \,+\, 6H_2 SO_4 \longrightarrow 2KHSO_4 \,+\, 4NaHSO_4 \,+\, 2CrO_2 Cl_2 \uparrow \,+\, 3H_2 O \\ & Orange\mbox{-red} \end{array}$

fumes

When chromyl chloride vapours are passed into sodium hydroxide solution, a yellow solution of sodium chromate is formed, which when treated with lead acetate gives yellow precipitate of lead chromate.

$$CrO_2Cl_2\uparrow + 2NaOH \longrightarrow Na_2CrO_4 + 2HCl$$

Yellow solution
 $Na_2CrO_4 + (CH_3COO)_2Pb \longrightarrow 2CH_3COONa + PbCrO_4\downarrow$
Yellow pp

This test is given by ionic chlorides only. Chlorides of Hg_2^{2+} , Hg_2^{2+} , Pb^{2+} , Ag^+ , Sn^{4+} and Sb^{3+} do not respond to chromyl chloride test due to their covalent character, which allows them to ionise only slightly.

(II) BROMIDE (Br⁻)

(i) Concentrated H_2SO_4

If concentrated sulphuric acid is poured in a bromide solution, first a reddish-brown solution is formed, later reddish-brown vapours of bromine accompany the hydrogen bromide.

$$2KBr + H_2SO_4 \longrightarrow K_2SO_4 + 2HBr\uparrow$$

$$2HBr + H_2SO_4 \longrightarrow 2H_2O + SO_2\uparrow + Br_2\uparrow$$

Reddish-brown

(ii) Manganese dioxide and Concentrated Sulphuric Acid

 $2KBr + MnO_2 + 2H_2SO_4 \longrightarrow Br_2^{\uparrow} + K_2SO_4 + MnSO_4 + 2H_2O$ Reddish-brown

(iii) Chlorine Water

When chlorine water is added to a solution of bromide, free bromine is liberated which colours the solution orange-red. If CS_2 , $CHCl_3$ or CCl_4 is added to the solution and the liquid shaken, the bromine dissolves in the organic solvent and after allowing to stand forms a reddish-brown solution below the colourless aqueous layer.

$$2\text{KBr} + \text{Cl}_2(\text{water}) \longrightarrow 2\text{KCl} + \text{Br}_2$$

 $Br_2^{\uparrow} + Cl_2^{\uparrow} \longrightarrow 2BrCl$

Pale yellow solution



(III) IODIDE (I⁻) Concentrated H_2SO_4 (i) $2I^{-} + 2H_2SO_4 \longrightarrow I_2^{\uparrow} + SO_4^{2-} + 2H_2O + SO_2^{\uparrow}$ Violet vapours (ii) Chlorine Water $2KI + Cl_2 \longrightarrow I_2 + 2KCl$ I_2 + Chloroform \longrightarrow Violet solution (IV) NITRATE (NO_3^{-}) Concentrated H₂SO₄ (i) $4\mathrm{NO}_3^- + 2\mathrm{H}_2\mathrm{SO}_4 \longrightarrow 4\mathrm{NO}_2^- + 2\mathrm{SO}_4^{2-} + 2\mathrm{H}_2\mathrm{O} + \mathrm{O}_2^{\uparrow\uparrow}$ Reddish-brown vapours (ii) Brown Ring Test $2\mathrm{NO}_{3}^{-} + 4\mathrm{H}_{2}\mathrm{SO}_{4} + 6\mathrm{F}e^{2+} \longrightarrow 6\mathrm{F}e^{3+} + 2\mathrm{NO}^{\uparrow} + 4\mathrm{SO}_{4}^{2-} + 4\mathrm{H}_{2}\mathrm{O}^{2-}$ $FeSO_4 + 6H_2O \longrightarrow [Fe(H_2O)_6]SO_4$ $[Fe(H_2O)_6]SO_4 + NO^{\uparrow} \longrightarrow [Fe(H_2O)_5NO]SO_4 + H_2O^{\bullet}$ Brown ring (V) ACETATE (CH_3CO_2) Dilute Sulphuric Acid On adding a small quantity of dilute H_2SO_4 to the acetate salt, acetic acid is produced, which can be easily recognized by its vinegar-like odour $CH_{2}COO^{-} + H^{+} \longrightarrow CH_{2}COOH$ Vinegar like odour OXALATE $(C_2 O_4^{2-})$ (VI) Potassium Permanganate Solution Potassium permanganate solution gets decolourized when warmed in acid solution with an oxalate salt to 60 C. Many other organic compounds also effect the bleaching of permanganate but if the evolved carbon dioxide is tested by the lime water reaction, the test becomes specific for oxalates. $5(\text{COO})_2^{2-} + 2\text{MnO}_a^- + 16\text{H}^+ \longrightarrow 10\text{CO}_2^+ + 2\text{Mn}^{2+} + 8\text{H}_2\text{O}$ **GROUP 'B' RADICALS** SULPHATE (SO₄²⁻)

Sulphates of barium, strontium and lead are practically insoluble in water, those of calcium and mercury(II) are slightly soluble and most of the remaining metallic sulphates are soluble.

Barium Chloride Solution

On adding BaCl₂ solution to a sulphate salt solution, a white precipitate of barium sulphate $(BaSO_d)$ insoluble in warm dilute hydrochloric acid and in dilute nitric acid but moderately soluble in boiling concentrated hydrochloric acid is formed.

 $SO_{a}^{2-} + Ba^{2+} \longrightarrow BaSO_{a} \downarrow$

White ppt



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ANALYSIS OF CATIONS

(1) Dry Tests

Borax Bead Test :

 $Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + B_2O_3$

$$CuO + B_aO_a \longrightarrow Cu(BO_a)$$

Copper (II) metaborate

Microcosmic Salt Bead Test

 $Na(NH_4)HPO_4 \xrightarrow{\Delta} NaPO_3 + H_2O\uparrow + NH_3\uparrow$ transparent beat $NaPO_3 + CoO \longrightarrow NaCoPO_4$

(blue bead)

Sodium Carbonate Bead Test

The sodium carbonate bead is prepared by fusing a small quantity of sodium carbonate on a platinum wire loop in the Bunsen flame; a white, opaque bead is produced. If this is moistened, dipped into a little KNO_3 and then into a small quantity of a manganese salt (for example) and the whole heated in the oxidising flame, a green bead of sodium manganate (Na_2MnO_4) is formed.

 $MnO + Na_2CO_3 + O_2 \xrightarrow{\Delta} Na_2MnO_4 + CO_2$

A yellow bead is obtained with chromium salt due to formation of sodium chromate $(Na_{2}CrO_{4})$

 $2\mathrm{Cr}_{2}\mathrm{O}_{3} + 4\mathrm{Na}_{2}\mathrm{CO}_{3} + 3\mathrm{O}_{2} \longrightarrow 4\mathrm{Na}_{2}\mathrm{CrO}_{4} + 4\mathrm{CO}_{2}$

(2) Flame Tests

Paste of the salt and con. HCl is taken into the lower oxidising zone and colour imparted to the flame by salts is observed; salts, particularly of group V(Ba²⁺, Ca²⁺, Sr²⁺), are identified by colours of the flame and summariesed in table.

Colour	Cation
Golden yellow	Na^+
Violet (Lilac)	K^{+}
Carmine-red	Li^+
Brick-red	Ca ²⁺
Apple-green	Ba ²⁺ , Mo ²⁺
Green	Cu^{2+} , (BO ₃ ³⁻), Tl^{3+}
Crimson-red	Sr^{2^+}





(3) Qualitative Analysis of Cation mixtures :

Group		Group Reagent	Cations	ppt/colour
I		Dil. HCl	$Ag^{+}, Hg_{2}^{2+}, Pb^{2+}$	AgCl Hg ₂ Cl ₂ White PbCl ₂
II	IIA	dil. HCl/H ₂ S	$Pb^{+2}, Cu^{2+}, Bi^{3+}, Hg^{2+}, Cd^2$	PbS CuS, Bi_2S_3 , HgS, CdS $\downarrow \qquad \downarrow \qquad \downarrow \qquad \downarrow \qquad \downarrow$ Black Black Brown Black Yellow
	IIB	dil. HCl/H ₂ S	As ³⁺ , As ⁵⁺ , Sb ³⁺ , Sb ⁵⁺ ,Sn ²⁺ , Sn ⁴⁺	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
III		NH ₄ Cl/NH ₄ OH	$Al^{3_{+}}, Cr^{3_{+}}, Fe^{3_{+}}$	$\begin{array}{ccc} Al(OH)_{3} & Cr(OH)_{3} & Fe(OH)_{3} \\ \downarrow & \downarrow & \downarrow \\ White & Green & Brown \end{array}$
IV		NH ₄ Cl/NH ₄ OH/ H ₂ S	Ni^{2+} , Co^{2+} , Mn^{2+} , Zn^{2+}	NiS CoS MnS ZnS $\downarrow \qquad \downarrow \qquad \downarrow \qquad \downarrow$ Black Black Pink/Buff/Skin Dirty white
V		NH ₄ Cl/NH ₄ OH/ (NH ₄) ₂ CO ₃	Ba ²⁺ , Sr ²⁺ , Ca ²⁺	$\begin{array}{cccc} BaCO_{3} & SrCO_{3} & CaCO_{3} \\ \downarrow & \downarrow & \downarrow \\ White & White & White \end{array}$
VI		No common group reagent	Na^{*} , Mg^{2*} , K^{*}	No common ppt
Zero		No common group reagent	⊕ NH₄	No common ppt (Generally identify by Nessler's reagent)

PREPARATION OF ORIGINAL SOLUTION

Transparent, aqueous solution of salt is known as original solution and it is prepared by dissolving salt/ mixture in suitable solvent. To prepare original solution, following solvents are used strictly in the order given below:

(i) Cold Water	(ii)	Hot water
----------------	------	-----------

(iii) Dilute HCl (iv) Conc. HCl

(A) Group I (Pb^{2+} , Ag^+ , Hg_2^{2+}) RADICALS :

On adding dilute HCl to the salt solution if white precipitate is obtained, it indicates the presence of Pb^{2*} , Ag^* or Hg_2^{2*} ion in the solution.





1 LEAD (II)

(i) Sodium Hydroxide Solution

 $Pb^{2+} + 2OH^{-} \longrightarrow Pb(OH)_{2} \downarrow$ White ppt $Pb(OH)_{2} \downarrow + 2OH^{-} \longrightarrow [Pb(OH)_{4}]^{2-}$ Soluble

(ii) Ammonia Solution

 $Pb^{+2} + 2NH_4OH \longrightarrow Pb(OH)_2 + 2NH_4^+$ White ppt

(iii) Potassium Chromate Solution

 $PbCl_2$ is soluble in hot water and gives a yellow precipitate with K_2CrO_4 . The precipitate obtained is insoluble in acetic acid but soluble in NaOH and nitric acid.

 $PbCl_2 + K_2CrO_4 \longrightarrow PbCrO_4 \downarrow + 2KCl$

Yellow ppt (chrome yellow)

$$PbCrO_4 \downarrow + 4NaOH \longrightarrow Na_2[Pb(OH)_4] + Na_2CrO$$

$$2PbCrO_{4}\downarrow + 2H^{+} \longrightarrow 2Pb^{2+} + Cr_{2}O_{7}^{2-} + H_{2}O_{7}^{2-}$$

2. SILVER (I)

(i) Dilute Hydrochloric Acid

With dilute hydrochloric acid (or soluble chlorides), a white precipitate of silver chloride is formed.

 $Ag^{+} + Cl^{-} \longrightarrow AgCl \downarrow$

White ppt

With concentrated hydrochloric acid precipitation does not occur. After decanting the liquid from over the precipitate. It can be dissolved in concentrated hydrochloric acid, when a dichloroargentate complex is formed.

 $AgCl^{-} + Cl^{-} \implies [AgCl_2]^{-}$

Soluble

On dilution with water, the equilibrium shifts back to the left and the precipitate reappears. Dilute ammonia solution dissolves the precipitate to form the diamineargentate(I) complex ion.

 $AgCl\downarrow + 2NH_3 \implies [Ag(NH_3)_2]^+ + Cl^-$ Soluble

(ii) Ammonia solution

 $2Ag^{+} + 2NH_{3} + H_{2}O \implies Ag_{2}O\downarrow + 2NH_{4}^{+}$ Brown ppt $Ag_{2}O\downarrow + 4NH_{3} + H_{2}O \longrightarrow 2[Ag(NH_{3})_{2}]^{+} + 2OH^{-}$

Soluble

(iii) Potassium Iodide Solution

 $Ag^{+} + I^{-} \longrightarrow AgI \downarrow$ Yellow ppt

$$AgI\downarrow + 2CN^{-} \longrightarrow [Ag(CN)_{2}]^{-} + I^{-}$$

$$AgI\downarrow + 2S_{2}O_{3}^{2-} \longrightarrow [Ag(S_{2}O_{3})_{2}]^{3-} + I^{-}$$

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3. MERCURY (I)

(i) Sodium Hydroxide Solution

 $Hg_2^{+2} + 2OH^- \longrightarrow Hg_2O\downarrow + H_2O$ Black ppt

 $Hg_{2}O\downarrow \longrightarrow HgO\downarrow + Hg\downarrow$

(ii) Ammonia Solution

$$2Hg_2Cl_2 + 4NH_4OH \longrightarrow \underbrace{HgO.Hg}_{Q} \underbrace{ NH_2}_{Q} + 2Hg\downarrow + 3NH_4Q + 3H_2O$$

Amido mercuric chloride (black)

- (iii) Potassium Iodide Solution
 - $\begin{array}{cccc} Hg_2^{+2} + 2I^- & \longrightarrow & Hg_2I_2 \\ & & & & & \\ Hg_2I_2 \downarrow + 2I^- & \longrightarrow & [HgI_4]^{2^-} + Hg \downarrow \\ & & & & & \\ Hg_2I_2 \downarrow & \longrightarrow & HgI_2 \downarrow & + & Hg \downarrow \\ & & & & \\ Hg_2I_2 \downarrow & \longrightarrow & HgI_2 \downarrow & + & Hg \downarrow \\ & & & & \\ Red & ppt & & \\ Black & ppt \end{array}$
- (iv) Potassium Chromate Solution

$$\begin{array}{ccc} Hg_2^{+2} + CrO_4^{2-} & \longrightarrow Hg_2CrO_4 \downarrow \\ & Red \ ppt \\ Hg_2CrO_4 \downarrow + 2OH^- & \longrightarrow Hg_2O \downarrow + CrO_4^{2-} + H_2O \\ & Black \ ppt \end{array}$$

(B) Group II A (Pb²⁺, Hg²⁺, Cu²⁺, Bi³⁺, Cd²⁺) RADICALS :

The precipitates of group IIA are insoluble in yellow ammonium sulphide.

1. MERCURY (II)

HgS precipitated dissolves in aqua regia forming undissociated HgCl₂.

$$3HgS\downarrow + 6HCl + 2HNO_3 \longrightarrow 3HgCl_2 + 3S\downarrow + 2NO\uparrow + 4H_2O$$

(i) Potassium Iodide Solution

$$\begin{array}{ccc} \operatorname{Hg}^{2^{+}} + 2I^{-} & \longrightarrow \operatorname{HgI}_{2} \downarrow \\ & & \operatorname{Scarlet \ red \ ppt} \\ \operatorname{HgI}_{2} + 2I^{-} & \longrightarrow \left[\operatorname{HgI}_{4}\right]^{2^{-}} \text{ or \ HgI}_{2} + 2\operatorname{KI} & \longrightarrow \operatorname{K}_{2}[\operatorname{HgI}_{4}] \\ & & \operatorname{Soluble} \end{array}$$

(ii) Tin(II) Chloride Solution

 $\begin{array}{rcl} 2\mathrm{Hg}^{^{2+}} + \mathrm{SnCl}_2 & \longrightarrow \mathrm{Hg}_2\mathrm{Cl}_2 & \downarrow + \mathrm{Sn}^{4+} \\ & & \mathrm{White \ Silky \ ppt} \\ \mathrm{Hg}_2\mathrm{Cl}_2 & \downarrow + \mathrm{SnCl}_2 & \longrightarrow 2\mathrm{Hg} & \downarrow + \mathrm{SnCl}_4 \end{array}$

(iii) Cobalt(II) Thiocyanate Test $Hg^{2^+} + Co^{2^+} + 4SCN^- \longrightarrow Co[Hg(SCN)_4] \downarrow$

Deep-blue ppt



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2. COPPER (II)

Hot, concentrated nitric acid dissolves copper(II) sulphide, leaving behind sulphur as a white precipitate. $3CuS\downarrow + 8HNO_3 \longrightarrow 3Cu^{2+} + 6NO_3^- + 3S\downarrow + 2NO\uparrow + 4H_2O$

White ppt

When boiled for long sulphur is oxidised to H_2SO_4 and a clear blue solution is obtained.

 $S\downarrow$ + 2HNO₃ \longrightarrow 2H⁺ + SO₄²⁻ + 2NO[†]

Ammonia Solution (i)

When ammonia solution is added to solution of Cu^{2+} , a blue precipitate of a basic copper sulphate is obtained, which is soluble in excess reagent giving deep-blue colouration of tetreamminecopper(II) sulphate.

 $2Cu^{2+} + SO_4^{2-} + 2NH_3 + 2H_2O \longrightarrow Cu(OH)_2.CuSO_4 \downarrow + 2NH_4^+$ Blue ppt $Cu(OH)_2.CuSO_4 \downarrow + 8NH_3 \longrightarrow 2[Cu(NH_3)_4]^{2+} + SO_4^{2-} + 2OH^{-1}$ Deep-blue colouration

Potassium Iodide (ii)

 $2Cu^{2+} + 5I^- \longrightarrow Cu_2I_2\downarrow + I_3^-$

White ppt

 $I_3^- + 2S_2O_3^{2-} \longrightarrow 3I^- + S_4O_6^{2-}$

Potassium Hexacyanoferrate(II) solution (iii)

 $\text{Cu}^{2\text{+}}$ ions give chocolate–brown precipitate with $K_4[\text{Fe}(\text{CN})_6]$ solution.

 $2Cu^{2+} + K_{a}[Fe(CN)_{6}] \longrightarrow Cu_{2}[Fe(CN)_{6}]\downarrow + 4K^{+}$

Chocolate-brown ppt

(iv) Test by NaCN & KCN

 $2Cu^{2+} + 4CN^{-} \longrightarrow 2Cu^{I}CN + (CN)_{2}$ Cyanogen

 $CuCN + 3CN^{-} \longrightarrow [Cu^{I}(CN)_{4}]^{3-}$

3. **BISMUTH** (III)

Sodium Hydroxide (i)

Bi³

With NaOH solution, Bi^{3+} give a white precipitate of bismuth(III) hydroxide.

$$^{+}$$
 + 3OH⁻ \longrightarrow Be(OH)₃

White ppt

The precipitate is soluble in acids.

$$Bi(OH)_{3}\downarrow + 3H^{+} \longrightarrow Bi^{3+} + 3H_{2}O$$

When boiled, the precipitate loses water and turns yellowish-white.

 $Bi(OH)_{3}\downarrow \longrightarrow BiO.OH\downarrow + H_{2}O$

Yellowish-white ppt

Bi(OH)₃ when reduced by tetrahydroxostannate(II) ions give black precipitate of bismuth metal. $2\text{Bi}(\text{OH})_3 \downarrow + 3[\text{Sn}(\text{OH})_4]^{2-} \longrightarrow 2\text{Bi} \downarrow + 3[\text{Sn}(\text{OH})_6]^{2-}$

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(ii) Potassium Iodide

 $\begin{array}{rcl} \operatorname{Bi}^{3^{+}}+\operatorname{3I}^{-} & \longrightarrow & \operatorname{BiI}_{3} \downarrow \\ & & & & & \\ & & & & \\ \operatorname{BiI}_{3} \downarrow \, + \, \operatorname{I}^{-} & & & & \\ & & & & \\ & & & & \\ \operatorname{BiI}_{3} \downarrow \, + \, \operatorname{H}_{2} O & \longrightarrow & \operatorname{BiOI} \downarrow \, + \, 2\operatorname{H}^{+} \, + \, 2\operatorname{I}^{-} \\ & & & & \\ & & & \\ & & & & & \\ & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & & \\ & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & &$

(iii) Water

 $Bi^{3^+} + NO_3^- + H_2O \xrightarrow{diluation} BiO(NO_3) \downarrow + 2H^+$ White ppt

$$Bi^{3^+} + Cl^- + H_2O \xrightarrow{\text{diluation}} BiOCl \downarrow + 2H^+$$

White ppt

4. CADMIUM (II)

(i) Ammoniaum Hydroxide

$$Cd^{2+} + 2NH_4OH \implies Cd(OH)_2 \downarrow + 2NH_4^+$$

White ppt

 $Cd(OH)_{2} \downarrow + 4NH_{3} \longrightarrow [Cd(NH_{3})_{4}]^{2^{+}} + 2OH^{-}$

(ii) Potassium Cyanide

 $Cd^{2^{+}} + 2CN^{-} \longrightarrow Cd(CN)_{2}\downarrow$ White ppt $Cd(CN)_{2}\downarrow + 2CN^{-} \longrightarrow [Cd(CN)_{4}]^{2^{-}}$ $[Cd(CN)_{4}]^{2^{-}} + H_{2}S \longrightarrow CdS\downarrow + 2H^{+} + 4CN^{-}$

The marked difference in the stabilities of the copper and cadmium tetracyanato complexes serves as the basis for the separation of Cu^{2+} and Cd^{2+} ions.

(C) Group III (Fe^{3+} , Al^{3+} , Cr^{3+})

1. IRON (III)

 $2Fe^{3^{+}} + 3S^{2^{-}} \longrightarrow 2FeS\downarrow + S\downarrow$ Black ppt $FeS\downarrow + 2H^{+} \longrightarrow H_{2}S\downarrow + Fe^{2^{+}}$ $4FeS\downarrow + 6H_{2}O + 3O_{2} \longrightarrow 4Fe(OH)_{3}\downarrow + 4S\downarrow$ $2Fe^{3^{+}} + 3S^{2^{-}} \longrightarrow Fe_{2}S_{3}\downarrow$ $Fe_{2}S_{3}\downarrow + 4H^{+} \longrightarrow 2Fe^{2^{+}} + 2H_{2}S\uparrow + S\downarrow$

(ii) Sodium Hydroxide Solution

With sodium hydroxide solution, a reddish-brown precipitate of iron(III) hydroxide, insoluble in excess of the reagent (distinction from aluminium and chromium) is obtained.

 $\text{Fe}^{3+} + 3\text{OH}^{-} \longrightarrow \text{Fe}(\text{OH})_{3} \downarrow$

Reddish-brown ppt



(iii) Potassium Hexacyanoferrate(II)

 $4Fe^{3+} + 3[Fe(CN)_6]^{4-} \longrightarrow Fe_4[Fe(CN)_6]_3 \downarrow$ Prussian blue $\operatorname{Fe}_{4}[\operatorname{Fe}(\operatorname{CN})_{6}]_{3}\downarrow + 12\operatorname{OH}^{-} \longrightarrow 4\operatorname{Fe}(\operatorname{OH})_{3}\downarrow + 3[\operatorname{Fe}(\operatorname{CN})_{6}]^{4-}$

Raddish-brown ppt

Potassium Hexacyanoferrate(III) (iv)

 $\operatorname{Fe}^{3^+} + [\operatorname{Fe}(\operatorname{CN})_6]^{3^-} \longrightarrow \operatorname{Fe}[\operatorname{Fe}(\operatorname{CN})_6]$

Brown colouration

Ammonium Thiocyanate Solution (v)



2. ALUMINIUM (III)

Sodium Hydroxide Solution

$$Al^{3^{+}} + 3OH^{-} \longrightarrow Al(OH)_{3} \downarrow$$
White ppt
$$Al(OH)_{3} + OH^{-} \rightleftharpoons [Al(OH)_{4}]^{-}$$
Soluble
$$[Al(OH)_{4}]^{-} + NH_{4}^{+} \longrightarrow Al(OH)_{3} \downarrow + NH_{3} \uparrow + H_{2}O$$

$$[Al(OH)_{4}]^{-} + H^{+} \rightleftharpoons Al(OH)_{3} \downarrow + H_{2}O$$

$$Al(OH)_{3} + 3H^{+} \downarrow \rightleftharpoons Al^{3^{+}} + 3H_{2}O$$

3. CHROMIUM (III)

(i) Sodium Hydroxide Solution

$$Cr^{3^+} + 3OH^- \longrightarrow Cr(OH)_3 \downarrow$$

 $Green ppt$
 $Cr(OH)_3 + OH^- \rightleftharpoons [Cr(OH)_4]^-$
 $excess$ Soluble

(ii) Ammonia Solution

 $CrCl_3 + 3NH_4OH \longrightarrow Cr(OH)_3 \downarrow + 3NH_4Cl$ Bluish-green ppt $Cr(OH)_{3}\downarrow$ + $6NH_{3} \longrightarrow [Cr(NH_{3})_{6}]^{3+} + 3OH^{-1}$ Pink colouration Excess

(iii) Chromium Pentoxide (Chromium Peroxide, Peroxochromic Acid) Test

On acidifying the solution with dilute sulphuric acid, adding few drops of ether or amyl alcohol to the mixture and finally adding some hydrogen peroxide, blue colouration is formed, which can be extracted into the organic phase by gently shaking. During the reaction, chromium pentoxide is formed.

 $\operatorname{CrO}_{4}^{2-} + 2\operatorname{H}^{+} + 2\operatorname{H}_{2}\operatorname{O}_{2} \longrightarrow \operatorname{CrO}_{5} +$ 3H₂O Blue colouration in ether layer



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Chromium pentoxide has the following structure : $\bigcup_{i=1}^{O} \bigcup_{j=1}^{O} \bigcup_{i=1}^{O} \bigcup_{$

Because of the two peroxide groups, the compound is often called chromium peroxide. The name peroxochromic acid is less appropriate, because the compound does not contain hydrogen at all. In aqueous solution, the blue colour fades rapidly, because chromium pentoxide decomposes to chromium(III) and oxygen.

$$4 \text{CrO}_5 + 12 \text{H}^+ \longrightarrow 4 \text{Cr}^{3+} + 7 \text{O}_2 \uparrow + 6 \text{H}_2 \text{O}_3 \uparrow$$

(D) Group IV $(Zn^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+})$

(i) Sodium Hydroxide Solution

$$Zn^{2^{+}} + 2OH^{-} \longrightarrow Zn(OH)_{2}\downarrow$$

White gelatinous ppt
$$Zn(OH)_{2}\downarrow + 2H^{+} \longrightarrow Zn^{2^{+}} + 2H_{2}O$$

$$Zn(OH)_{2}\downarrow + 2OH^{-} \longrightarrow [Zn(OH)_{4}]^{2^{-}}$$

excess

(ii) Ammonia Solution

$$Zn^{2^{+}} + 2NH_{3} + 2H_{2}O \longrightarrow Zn(OH)_{2}\downarrow + 2NH_{4}^{+}$$

White ppt
$$Zn(OH)_{2}\downarrow + 4NH_{2} \longrightarrow [Zn(NH_{2})_{4}]^{2^{+}} + 2OH^{-}$$

(iii) Potassium Hexacyanoferrate(II)

$$3Zn^{2+} + 2K^{+} + 2[Fe(CN)_{6}]^{4-} \longrightarrow K_{2}Zn_{3}[Fe(CN)_{6}]_{2} \downarrow$$
White ppt

$$K_2 Zn_3 [Fe(CN)_6]_2 + 12OH^{-} \longrightarrow 2[Fe(CN)_6]^{4-} + 3[Zn(OH)_4]^{2-} + 2K^{-}$$

(iv) Ammonium tetrathiocyanatomercurate(II)

 $Zn^{2+} + [Hg(SCN)_4]^{2-} \longrightarrow Zn[Hg(SCN)_4] \downarrow$

White ppt

2. MANGANESE (II)

(i) Sodium Hydroxide Solution

With sodium hydroxide solution, an initially white precipitate of manganese(II) hydroxide is obtained.

$$Mn^{2+} + 2OH^{-} \longrightarrow Mn(OH)_{2} \downarrow$$

The precipitate is insoluble in excess reagent. It rapidly oxidizes on exposure to air, becoming brown, when hydrated manganese dioxide, $MnO(OH)_2$, is formed.

 $2Mn(OH)_2 \downarrow + O_2 \longrightarrow 2MnO(OH)_2 \downarrow$ Brown ppt

(ii) Ammonia Solution

With NH_3 solution, Mn^{2+} gives a white precipitate of manganese (II) hydroxide.

$$\mathrm{Mn}^{2^+} + 2\mathrm{NH}_3 + 2\mathrm{H}_2\mathrm{O} \implies \mathrm{Mn}(\mathrm{OH})_2 \downarrow + 2\mathrm{NH}_4^+$$

White ppt

The precipitate is soluble in ammonium salts, when the reaction proceeds towards the left.

(iii) Lead dioxide and Concentrated Nitric Acid $5PbO_2 + 2Mn^{2+} + 4H^+ \longrightarrow 2MnO_4^- + 5Pb^{2+} + 2H_2O$

Purple colour

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Sodium Bismuthate (NaBiO₃) Solution (iv) $2Mn^{2^+} + 5NaBiO_3 + 14H^+ \longrightarrow 2MnO_4^- + 5Bi^{3^+} + 5Na^+ + 7H_2O^-$ Purple colour 3. NICKEL (II) The black precipitate of NiS(II) is insoluble in cold dilute HCl and in acetic acid but dissolves in hot concentrated nitric acid and in aqua regia with the separation of sulphur. $NiS \downarrow + 2HNO_3 + 6H^{+} \longrightarrow 3Ni^{2+} + 3S \downarrow + 2NO^{\uparrow} + 4H_2O$ $NiS\downarrow + HNO_3 + 3HCI \longrightarrow Ni^{2+} + S\downarrow + NOCI\uparrow + 2CI^- + 2H_2O$ (i) Sodium Hydroxide Solution $Ni^{2+} + 2OH^{-} \longrightarrow Ni(OH)_{2} \downarrow$ Green ppt $Ni(OH)_{2}\downarrow + 6NH_{3} \longrightarrow [Ni(NH_{3})_{6}]^{2+} + 2OH^{-}$ Deep-blue colouration $Ni(OH)_{2}\downarrow + 6NH_{4}^{+} + 4OH^{-} \longrightarrow [Ni(NH_{2})_{6}]^{2+} + 6H_{2}O$ Deep-blue colouration Ammonia Solution (ii) $Ni^{2+} + 2NH_3 + 2H_2O \longrightarrow Ni(OH)_2 \downarrow + 2NH_4^+$ Green ppt $Ni(OH)_2 \downarrow + 6NH_3 \longrightarrow [Ni(NH_3)_6]^{2+}$ + 20H⁻ Deep-blue colouration (E) Group V $(Ba^{2+}, Sr^{2+}, Ca^{2+})$ 1. BARIUM (II) (i) Potassium Chromate Solution $Ba^{2+} + K_2CrO_4 \longrightarrow BaCrO_4 \downarrow + 2K^+$ Yellow ppt $2CrO_4^{2-} + 2H^+ \implies Cr_2O_7^{2-} + H_2O$ Ammonium Sulphate Solution (ii) $\operatorname{Ba}^{2^+} + (\operatorname{NH}_4)_2 \operatorname{SO}_4 \longrightarrow \operatorname{BaSO}_4 \downarrow + 2\operatorname{NH}_4^+$ White ppt $BaSO_4 \downarrow + H_2SO_4(conc.) \longrightarrow Ba^{2+} + 2HSO_4^{-}$ (iii) Ammonium Oxalate Solution Ba^{2^+} + $(\operatorname{NH}_4)_2\operatorname{C}_2\operatorname{O}_4 \longrightarrow \operatorname{Ba}\operatorname{C}_2\operatorname{O}_4 \downarrow + 2\operatorname{NH}_4^+$ White ppt 2. STRONTIUM (II) (i) Ammonium Sulphate Solution $Sr^{2^+} + (NH_4)_2SO_4 \longrightarrow SrSO_4 \downarrow + 2NH_4^+$ White ppt (ii) Ammonium Oxalate Solution Sr^{2^+} + (NH₄)₂C₂O₄ \longrightarrow $\mathrm{SrC}_2\mathrm{O}_4\downarrow$ + 2NH₄⁺ White ppt



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3. CALCIUM (II)

(i) Ammonium Oxalate Solution $Ca^{2^+} + (NH_4)_2C_2O_4 \longrightarrow CaC_2O_4 \downarrow + 2NH_4^+$

White ppt

- (ii) Potassium Hexacyanoferrate(II) Solution $Ca^{2^+} + K_4[Fe(CN)_6] \longrightarrow K_2Ca[Fe(CN)_6] \downarrow + 2K^+$
- (F) Group VI (Na⁺, K⁺, Mg²⁺)

1. MAGNESIUM (II)

- (i) Ammonia Solution $Mg^{2^+} + 2NH_4OH \longrightarrow Mg(OH)_2 \downarrow + 2NH_4^+$ White ppt
- (ii) Ammonium Carbonate Solution $5Mg^{2^+} + 6CO_3^{2^-} + 7H_2O \longrightarrow 4MgCO_3.Mg(OH)_2.5H_2O\downarrow + 2HCO_3^-$

White ppt

(iii) NH₄⁺ + CO₃²⁻ \longrightarrow NH₃ + HCO₃⁻ (iii) Disodium hydrogen phosphate Solution Mg²⁺ + NH₃ + HPO₄²⁻ \longrightarrow Mg(NH₄)PO₄ \downarrow White ppt Mg²⁺ + HPO₄²⁻ \longrightarrow MgHPO₄ \downarrow

White ppt

(G) Group Zero (NH_4^+)

1. AMMONIUM (NH_4^+)

(i) Sodium Hydroxide Solution

All ammonium salts on heating with alkali (NaOH) gives smell of NH₃.

 $NH_4^+ + OH^- \longrightarrow NH_3^+ + H_2O$

- (a) The gas evolved can be detected by its smell.
- (b) Gas evolved gives white fumes of NH_4Cl with HCl.

 $NH_3 + HCl \longrightarrow NH_4Cl^{\uparrow}$

White fumes

(c) Paper soaked in $CuSO_4$ solution, becomes deep-blue by NH_3 due to the complex formation. $CuSO_4 + 4NH_3 \longrightarrow [Cu(NH_3)_4]SO_4$

Deep-blue colouration

(d) Gas can be identified by its ability to turn filter paper moistened with mercury(I) nitrate solution black.

$$2NH_{3} + Hg_{2}^{2+} + NO_{3}^{-} \longrightarrow Hg(NH_{2})NO_{3} \downarrow + Hg \downarrow + NH_{4}^{+}$$

Mercury(II) amidonitrate Black ppt
white ppt

(ii) Nessler's Reagent

With Nesseler's reagent (an alkaline solution of potassium tetraiodomercurate(II), ammonium salts form a brown precipitate or brown or yellow colouration is produced depending on the amount of NH_4^+ ions present in the solution. The precipitate is a basic mercury(II) amido-iodine.



(i)





Prussian blue

(iv) Ammonium thiocyanate Solution

With ammonium thiocyanate solution, no colouration is obtained with pure iron(II) salts (distinction from (III) ions)

(v) Dimethylglyoxime Reagent

With dimethylglyoxime reagent soluble red iron(II) dimethyl glyoxime is obtained in ammoniacal solution. Iron(III) salts give no colouration, but nickel, cobalt and large quantities of copper salts interfere and must be absent.





Important Notes





Important Notes





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Regards from Learnaf team

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