Revision & Getting READY in PCM for IIT JEE 2012

INORGANIC CHEMISTRY

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Alkali and Alkaline Earth Metals

Sodium Oxide It is obtained by burning sodium at 180°C in a limited supply of air or oxygen and distilling off the excess of sodium in vacuum and by heating sodium peroxide, nitrate or nitrate with sodium. It is white amorphous mass. It decomposes at 400°C into sodium peroxide and sodium.

$$2Na_2O \xrightarrow{400°C} Na_2O_2 + 2Na$$

Sodium Peroxide It is formed by heating the metal in excess of air or oxygen at 300°, which is free from moisture and CO_2.

$$2Na + O_2 \longrightarrow Na_2O_2$$

It is a pale yellow solid, becoming white in air from the formation of a film of NaOH and Na_2CO_3.

It reacts with CO_2, giving sodium carbonate and oxygen and hence its use for purifying air in a confined space *e.g.*, submarine, ill-ventilated room,

$$2Na_2O_2 + 2CO_2 \longrightarrow 2Na_2CO_3 + O_2$$

It is an oxidizing agent and oxidizes charcoal, CO, NH_3, SO_2.

$$2NH_3 + 3Na_2O_2 \longrightarrow 6NaOH + N_2$$

Oxides of Potassium

K_2O, K_2O_2, K_2O_3 KO_2 and KO_3

Colours White White Red Bright-yellow Orange solid

Passage of O_2 through a blue solution of K in liquid NH_3 yields oxides K_2O_2 (white), K_2O_3 (red) and KO_2 (deep yellow) *i.e.*,

$$\text{K in liq. } NH_3 \xrightarrow{O_2} \underset{\text{White}}{K_2O_2} \longrightarrow \underset{\text{Red}}{K_2O_3} \longrightarrow \underset{\text{Yellow}}{KO_2}$$

$$KO_3 : KOH + O_3 \text{ (ozonized oxygen)} \xrightarrow{-10° \text{ to } -15°C} KO_3$$

(Dry powdered) (Orange solid)

Magnesium Oxide It is white powder. It is also called magnesia and obtained by heating natural magnesite.

$$MgCO_3 \longrightarrow MgO + CO_2$$

Calcium Oxide It is commonly called as quicklime or lime. It is white amorphous powder of m.p. 2570°C. It is a basic oxide and combines with some acidic oxide *e.g.*,

$$CaO + SiO_2 \longrightarrow CaSiO_3$$
$$CaO + CO_2 \longrightarrow CaCO_3$$

It combines with water to produce slaked lime.

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

Sodium Hydroxides

Caustication of Na_2CO_3 (Gossage's method)

$$NaCO_3 + \underset{\text{(Suspension)}}{Ca(OH)_2} \longrightarrow 2NaOH + CaCO_3 \downarrow$$

Since, the K_{sp} $(CaCO_3) < K_{sp}$ $(Ca(OH)_2$, the reaction shifts towards right.

It is white crystalline, deliquescent, highly corrosive solid.

$$NH_4Cl + NaOH \longrightarrow NaCl + NH_3 \uparrow + H_2O$$
$$FeCl_3 + 3NaOH \longrightarrow \underset{\text{Brown ppt.}}{Fe(OH)_3 \downarrow} + 3NaCl$$
$$ZnCl_2 + 2NaOH \longrightarrow Zn(OH)_2 \downarrow + 2NaCl$$
$$Zn(OH)_2 \downarrow + 2NaOH \xrightarrow{\text{Excess}} \underset{\text{soluble}}{Na_2ZnO_2} + 2H_2O$$

[Same with $AlCl_3$, $SnCl_2$, $PbCl_2$]

Acidic and amphoteric oxides gets dissolved easily *e.g.*,

$$CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O$$
$$Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$$

Aluminum and Zn metal gives H_2 from NaOH

$$2Al + 2NaOH + 2H_2O \longrightarrow 3H_2 + 2NaAlO_2$$

Several non-metals such as P, S, Cl etc. yield a hydride instead of hydrogen. *e.g.*,

$$4P + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$$

(Disproportionation reaction)

Potassium Hydroxide It is a stronger base compared to NaOH. Solubility in water is more compared to NaOH.

In alcohol, NaOH is sparingly soluble but KOH is highly soluble.

As a reagent KOH is less frequently used but in absorption of CO_2, KOH is preferably used compared to NaOH.

Sodium Carbonate

Leblanc Process :

$$NaCl + H_2SO_4 \text{ (conc)} \xrightarrow{\text{Mild heating}} NaHSO_4 + HCl$$
$$NaCl + NaHSO_4 \xrightarrow[\text{heated}]{\text{Strongly}} Na_2SO_4 + HCl$$
$$Na_2SO_4 + 4C \longrightarrow \underset{\text{(Salt cake)}}{Na_2S} + 4CO \uparrow$$
$$Na_2S + CaCO_3 \longrightarrow Na_2CO_3 + CaS$$

Solvay Process :

$$NH_3 + H_2O + CO_3 \longrightarrow NH_4HCO_3$$
$$NaCl + NH_4HCO_3 \longrightarrow NaHCO_3 + NH_4Cl$$
$$2NaHCO_3 \xrightarrow{150°C} Na_2CO_3 + H_2O + CO_2$$

Anhydrous Na_2CO_3 is called as soda ash, which doesn't decompose on heating but melts at 852°C. Na_2CO_3 absorbs

CO_2 yielding sparingly soluble sodium bicarbonate which can be calcined at 250°C to get pure sodium carbonate.

$$Na_2CO_3 + H_2O + CO_2 \overset{250°C}{\rightleftharpoons} 2NaHCO_3$$

Potassium Carbonate By Leblanc process, it can be prepared but by Solvay process it can't be prepared because $KHCO_3$ is soluble in water.

Calcium Carbonate It occurs in nature as marble, limestone, chalk, coral, calcite etc. It is prepared by dissolving marble or limestone in HCl and removing iron and aluminium present, by precipitating with NH_3 and then adding $(NH_4)_2CO_3$ to the solution.

$$CaCl_2 + (NH_4)_2CO_3 \longrightarrow CaCO_3 + 2NH_4Cl$$

It dissociates above 1000°C as follows :

$$CaCO_3 \longrightarrow CaO + CO_2$$

It dissolves in water containing CO_2 forming $Ca(HCO_3)_2$, but is precipitated from solution by boiling.

$$CaCO_3 + H_2O + CO_2 \underset{\text{boiling}}{\rightleftharpoons} Ca(HCO_3)_2$$

Sodium Chloride Prepared from brine containing 25% NaCl.

It is non-hygroscopic but the presence of $MgCl_2$ in common salt renders it hygroscopic.

It is used to prepare freezing mixture in laboratory [Ice-common salt mixture is called freezing mixture and temperature goes down to –23° C.]

Magnesium Chloride It crystallizes as hexahydrate. $MgCl_2 \cdot 6H_2O$

It is deliquescent solid.

This hydrate undergoes hydrolysis as follows :

$$MgCl_2 \cdot 6H_2O \longrightarrow Mg(OH)Cl + HCl + 5H_2O$$
$$Mg(OH)Cl \longrightarrow MgO + HCl$$

Hence, anhydrous $MgCl_2$ cannot be prepared by heating this hydrate.

Anhydrous $MgCl_2$ can be prepared by heating a double salt like. $MgCl_2 \cdot NH_4Cl \cdot 6H_2O$ as follows :

$$MgCl_2 \cdot NH_4Cl \cdot 7H_2O \xrightarrow{-H_2O} MgCl_2 \cdot NH_4Cl$$
$$\xrightarrow{\text{Strongly heated}} MgCl_2 + NH_3 + HCl$$

Sorel Cement It is a mixture of MgO and $MgCl_2$ (paste-like) which set to hard mass on standing. This is used in dental filling, flooring etc.

Calcium Chloride It is deliquescent crystals.

Anhydrous $CaCl_2$ is used in drying gases and organic compounds but not NH_3 or alcohol due to the formation of $CaCl_2 \cdot 8NH_3$ and $CaCl_2 \cdot 4C_2H_5OH$.

Sodium Sulphate It is formed in the first step of Leblanc process by heating common salt with sulphuric acid.

$$2NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2HCl$$

Thus, the salt cake formed is crystallized out from its aqueous solution as $Na_2SO_4 \cdot 10H_2O$. This called as **Glauber's salt**.

One interesting feature of the solubility of Glauber's salt is; when crystallized at below 32.4°C, then $Na_2SO_4 \cdot 10H_2O$ is obtained but above 32.4°C, Na_2SO_4 (anhy) comes out.

Magnesium Sulphate It is obtained by dissolving kieserite. $MgSO_4 \cdot H_2O$ in boiling water and then crystallizing the solution as a hepta hydrate *i.e.*, $MgSO_4.7H_2O$. It is called as **Epsom salt**.

Calcium Sulphate It occurs as anhydrite $CaSO_4$ and as the dihydrate $CaSO_4 \cdot 2H_2O$, gypsum, alabaster or satin-spar.

$$\underset{\text{Gypsum}}{(CaSO_4 \cdot 2H_2O)} \overset{120°C}{\underset{+H_2O}{\rightleftharpoons}} 2CaSO_4 \cdot H_2O \text{ (plaster of Paris)}$$
$$\downarrow 200°C$$
$$\text{(Anhydrous) } CaSO_4 \text{ Dead burnt plaster}$$

Solubility of $CaSO_4$ at first increases up to a certain point and then decreases with rise of temperature.

Boron Family

Heating of Boric Acid

$$H_3BO_3 \xrightarrow{100°C} \underset{\text{Metaboric acid}}{HBO_2} \xrightarrow{140°C}$$

$$\underset{\text{Pyroboric acid}}{H_2B_4O_7} \xrightarrow[\text{red hot}]{\Delta} \underset{\text{Glassy mass}}{B_2O_3}$$

$$H_3BO_3 + H_2O_2 \longrightarrow (H_2O) + (HO)_2$$
$$+ B{-}O{-}O{-}H \xrightarrow{NaOH}$$
$$Na_2\left[(HO)_2B\begin{matrix}O{-}O\\O{-}O\end{matrix}B(OH)_2\right] \cdot 6H_2O$$

Sodium peroxy borate used in washing powder.

Preparation of Borax

$$\underset{\text{Colemanite}}{2CaO \cdot 3B_2O_3} + 2Na_2CO_3 \longrightarrow$$
$$2CaCO_3 \downarrow + Na_2B_4O_7 + 2NaBO_2$$
$$\downarrow \text{Filtered } -CaCO_3 \text{ (as residue)}$$
$$NaBO_2 + [Na_2B_4O_7 \cdot 10H_2O] \xleftarrow[\text{and allowed to crystallize out and filtered}]{\text{Concentrated}} \underbrace{Na_2B_4O_7 + NaBO_2}_{\text{in solution}}$$
$$\text{in Filterate}$$
$$\downarrow CO_2 \text{ passed and crystallize out again}$$
$$[4NaBO_2 + CO_2 \longrightarrow Na_2B_4O_7 + Na_2CO_3]$$
$$Na_2B_4O_7 \cdot 10H_2O \downarrow$$

as 2nd crop. of the reaction

$$\underset{\text{(over heated)}}{2Al} + 6HCl\,(vap) \xrightarrow[\text{Dry}]{} 2AlCl_3\,(vap) + 3H_2$$

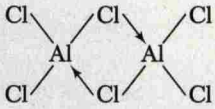
$$Al_2O_3 + 3C + 3Cl_2 \xrightarrow[1000°C]{\Delta} 2AlCl_3(vap) + 3CO$$

$\downarrow$ Cooled

Solid anhy. $AlCl_3$

$AlCl_3$

It is deliquescent and fumes in air. It sublimes at 180°C. It is covalent and exists in the form of dimer even if in non-polar solvents *e.g.*, alcohol, ether, benzene, where it is soluble in fair extent.



Alums $M_2SO_4, M_2(SO_4)_3 \cdot 24H_2O$

Props Swelling characteristics.

where, $M = Na^+, K^+, Rb^+, Cs^+, As^+, Tl^+, NH_4^+$

$M' = Al^{3+}, Cr^{3+}, Fe^{3+}, Mn^{3+}, Co^{3+}$

$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$	Potash alum
$(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$	Ammonium alum
$K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$	Chrome alum
$(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$	Ferric alum

Alums are used for coagulant, purification of water, Tanning of leather, Mordant in dying, antiseptic.

Carbides

Covalent Carbide SiC and B_4C

Interstitial Carbide *MC* (Transition element or inner transitional elements forms this kind of carbide.)

Interstitial carbide formation doesn't affect the metallic lusture and electrical conductivity. (∵ No chemical bond is present, no change in property.)

Fe_3C : Cementite

Carbon Family

SiC $SiO_2 + 2C\,(coke) \xrightarrow{2000\text{ to }2500°C} Si + 2CO\uparrow$

$Si + C \xrightarrow{2000\text{ to }2500°C} SiC$ diamond-like structure colourless to yellow solid in room temperature

$\downarrow$

When impurity is present

Properties

- It is very hard and is used in cutting tools and abrasive powder (polishing material).
- It is very much inert. It is not being affected by any acid except H_3PO_4.
- It reacts with NaOH in presence of air.

$$SiC + 2NaOH + O_2 \longrightarrow Na_2SiO_3 + CO_2 + H_2O$$

Producer gas : $CO + N_2 + H_2$

Water gas : $CO + H_2$

Water gas is having higher calorific value than producer gas. Therefore, in water gas, both CO and H_2 burns while in producer gas N_2 doesn't burn.

Silicon

Silica is found in the free state in sand, flint and quartz and in the combined state as silicates like

(i) Feldspar	–	$K_2O \cdot Al_2O_3 \cdot 6SiO_2$
(ii) Kaolinite	–	$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$
(iii) Asbestos	–	$CaO \cdot 3MgO \cdot 4SiO_2$

Elemental silicon is obtained by the reduction of silica (SiO_2) with high purity coke in an electric furnace.

$$SiO_2(s) + 2C(s) \longrightarrow Si(s) + 2CO(g)$$

From silicon tetrachloride ($SiCl_4$) or silicon chloroform ($SiHCl_3$) : Silicon of very high purity required for making semiconductors is obtained by reduction of highly purified silicon tetrachloride or silicon chloroform with dihydrogen followed by purification by zone refining.

$$SiCl_4(l) + 2H_2(g) \longrightarrow Si(s) + 4HCl(g)$$

$$SiHCl_3(s) + H_2(g) \longrightarrow Si(s) + 3HCl(g)$$

Elemental silicon is very hard having diamond-like structure.

Silicon is particularly unreactive at room temperature towards most of the elements except fluorine.

Silicon combines with carbon at 2500 K forming silicon carbide (SiC) known as **carborundum**.

$$Si(s) + C(s) \xrightarrow{2500\text{ K}} SiC(s)$$

Silicones

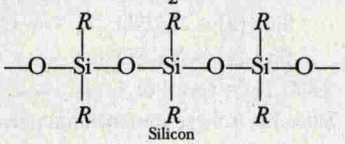
It is organic silicon polymer

$$CCl_4 + H_2O \longrightarrow \text{No hydrolysis}$$

but $CCl_4 + H_2O \longrightarrow COCl_2 + 2HCl$

$$SiCl_4 + H_2O \xrightarrow{\text{super heated steam}} Si(OH)_4 + 4HCl \xrightarrow[-2H_2O]{\Delta} SiO_2$$

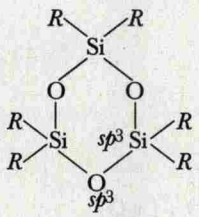
$$R_2SiCl_2 + H_2O \xrightarrow[-2HCl]{} R_2Si(OH)_2 \xrightarrow[H_2O]{\Delta}$$



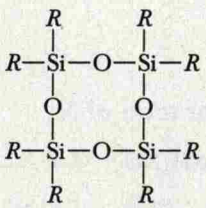
Silicon

$$R_2CCl_2 + H_2O \xrightarrow[\text{losses } H_2O \text{ readily}]{-2HCl} R_2C(OH)_2 \xrightarrow{-H_2O} R{-}\overset{\overset{O}{\|}}{C}{-}R$$

Silicons may have the cyclic structure also having 3, 4, 5 and 6 numbers of silicon atoms within the ring. Alcohol analog of silicon is known as *silanol*.

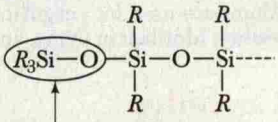


Not planar



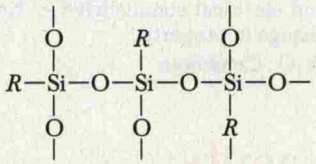
$$R_3SiCl \xrightarrow{-H_2O} \underset{\text{Silanol}}{R_3SiOH} \xrightarrow[\Delta]{-H_2O} R_3Si{-}O{-}SiR$$

$$R_2SiCl_2 + R_3SiCl \xrightarrow[\text{Hydrolysis}]{H_2O} \xrightarrow[\text{Heating condensation}]{-H_2O}$$



This end of the chain can't lie extended, hence using R_3SiCl in a certain proportion we can control the chain length of the polymer.

$$RSiCl_3 + H_2O \longrightarrow R{-}Si(OH)_3 \xrightarrow{\Delta}$$



3-dimensional network

It provides the crosslinking among the chain making the polymer more hard and hence controlling the proportion of $RSiCl_2$ we can control the hardness of polymer.

Silica

Pure silica is colourless, but sand is usually coloured yellow or brown due to the presence of ferric oxide as an impurity.

Silicon dioxide is insoluble in water and all acids except hydrofluoric acid.

$$SiO_2(s) + 4HF(l) \longrightarrow SiF_4(l) + 2H_3O(l)$$

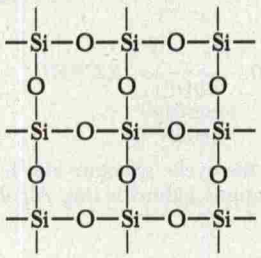
It is also combines with metallic oxides at high temperature giving silicates *e.g.*,

$$SiO_2(s) + CaO(s) \xrightarrow{\Delta} CaSiO_3(s)$$

When silica is heated strongly with metallic salts, silicates are formed and the volatile oxides are driven off as vapours.

$$SiO_2(s) + Na_2CO_3(s) \longrightarrow Na_2SiO_3(s) + CO_2(g)$$
$$SiO_2(s) + Na_2SO_4(s) \longrightarrow Na_2SiO_3(s) + SO_3(g)$$
$$3SiO_2(s) + Ca_3(PO_4)_2(s) \longrightarrow 3CaSiO_3(s) + P_2O_5(g)$$

Silica has a three-dimensional network structure :



$SnCl_2$ and $SnCl_4$

$$Sn + 2HCl\ (\text{hot conc.}) \longrightarrow SnCl_2 + H_2\uparrow$$

$$SnCl_2 \cdot 2H_2O \xrightarrow{\Delta} Sn(OH)Cl + HCl\uparrow + H_2O\uparrow$$

$\Rightarrow$ Hence, anhy. $SnCl_2$ (*Cannot be obtained.*)

$$\downarrow$$

$$SnO + HCl\uparrow \{SnCl_2 + 4H_2O \longrightarrow Sn(OH)_4 + 4HCl\uparrow \text{ fumes comes out}\}$$

$$SnCl_2 + HCl \longrightarrow \underbrace{HSnCl_3 \xrightarrow{HCl} H_2SnCl_4}_{\text{Chlorostannous acid}}$$

$$SnCl_4 + 2HCl \longrightarrow H_2SnCl_6$$

(Hexachloro stannic (IV) acid)

$$SnCl_4 + 2NH_4Cl \longrightarrow (NH_4)_2SnCl_6$$

(*Colourless crystalline compound known as "pink salt".*)

Reduction Properties of $SnCl_2$

$$Sn^{+2} + 2Fe^{+3} \longrightarrow 2Fe^{+2} + Sn^{+4}$$
$$2Cu^{+2} + Sn^{+2} \longrightarrow 2Cu^{+} + Sn^{+4}$$
$$Hg^{+2} + Sn^{+2} \longrightarrow Hg\downarrow + Sn^{+4}$$
$$PhNO_3 + SnCl_2/HCl \longrightarrow PhNH_2 + Sn^{+4}$$
$$K_2Cr_2O_7 + SnCl_2 + HCl \longrightarrow Cr^{+3} + Sn^{+4} + KCl + H_2$$

Formation of $SnCl_4$

(i) $\underset{(molten)}{Sn} + \underset{(dry)}{Cl_2\ (excess)} \longrightarrow SnCl_4$

(ii) $2HgCl_2 + Sn \longrightarrow 2Hg\downarrow + SnCl_4$

(iii) Sn + Aq. regia $\longrightarrow SnCl_4 + NO + H_2O$

- $SnCl_4 \cdot 5H_2O$ is known as butter of tin $\Rightarrow$ Are used as mordant.

$(NH_4)_2 \cdot SnCl_6$ is known as 'pink salt' $\Rightarrow$ Used as calico printing.

Pb_3O_4 : $6PbO + O_2 \underset{>470°C}{\overset{340°C}{\rightleftharpoons}} 2Pb_3O_4$ {*In the same way, prove that its formula is* $2PbO \cdot PbO_2$.}

$$Pb_3O_4 + 4HNO_3\ (\text{Cold conc.})$$
$$\text{or (hot dil.)} \longrightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$$
$$\text{But } 2Pb_3O_4 + 6H_2SO_4 \longrightarrow 6PbSO_4 + 6H_2O + O_2$$
$$Pb_3O_4 + 8HCl \longrightarrow 3PbCl_2 + 4H_2O + Cl_2$$

PbO_2 : Insoluble in water and HNO_3, But, reacts with $HCl + H_2SO_4$ (hot conc.) and in hot NaOH/KOH.

(i) $Pb_3O_4 + HNO_3 \longrightarrow$

(ii) $Pb(OAc)_2 + Ca(OCl)Cl + H_2O \longrightarrow$

$$PbO_2\ [\text{Brown (dark)}] + CaCl_2 + 2CH_3CO_2H$$

Excess bleaching powder is being removed by stirring with HNO_3.

Reaction $PbO_2 + 4HCl \longrightarrow PbCl_2 + Cl_2 + 2H_2O$

$$2PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O + O_2$$
$$PbO_2 + 2NaOH \longrightarrow Na_2PbO_3 + H_2O$$

Nitrogen Family

Preparation of N_2

- $NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$
- $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + 4H_2O + Cr_2O_3$
- $Ba(N_3)_2 \xrightarrow{\Delta} Ba + 3N_2$
  $2NaN_3 \xrightarrow{\Delta} 2Na + 3N_2$

  Purest N_2 obtained by this method.
- $2NH_3 + 3NaOCl \longrightarrow N_2 + 3NaCl + 3H_2O$

$$2NO + 2Cu \longrightarrow \underset{\text{(red, overheated)}}{2CuO} + \underset{\text{(Black)}}{N_2}$$

- Cl_2 passed into ligour NH_3

$$3Cl_2 + 2NH_3 \longrightarrow N_2 + 6HCl$$
$$6NH_3 + 6HCl \longrightarrow 6NH_4Cl$$

$$3Cl_2 + 8NH_3 \longrightarrow N_2 + 6NH_4Cl$$

In this method, NH_3 conc. should not be lowered down beyond a particular limit.

$$3Cl_2 + NH_3 \longrightarrow \underset{\text{(Tremendously explosive)}}{NCl_3} + HCl$$

Properties of N_2

Nitrogen is inert due to high bond energy.

It is absorbed by hot metal like Ca, Mg, Al etc.

$$3Ca + N_2 \longrightarrow Ca_3N_2$$
$$\text{Bright hot } 2Al + N_2 \longrightarrow 2AlN$$
$$Al_2O_3 + 3C + N_2 \xrightarrow{\Delta} 2AlN + 3CO$$

$(BN)_x$ Inorganic graphile

White slippery solid having 2D-sheet structure.

$$(BN)_x \xrightarrow{3000°C} (BN)_x$$

3-D network structure similar to diamond (Borazon) which is harder than diamond and used for diamond cutting.

$$Na_2B_4O_7 + 2NH_4Cl \xrightarrow{\Delta} 2NaCl + 2NH_3 + 2B_2O_3 + H_2O$$
$$B_2O_3 + 2NH_3 \longrightarrow 2BN + 3H_2O$$

N_2 can be absorbed by calcium carbide at the temp around 1000°C CaC_2

$$\underset{\text{Cyanamide ion}}{CaC_2} + N_2 \xrightarrow{1000°C} \underbrace{CaCNN + C}_{\text{Nitrolim}}$$

NH_3

Ammonia can be prepared by nitrate or nitrite reduction.

$$NO_3^-/NO_2^- + Zn \text{ or } Al + NaOH \longrightarrow NH_3 + [Zn(OH)_4]^{2-} \text{ or } [Al(OH)_4]^-$$

Metal nitride hydrolysis

$$N^{3-} + 3H_2O \longrightarrow NH_3\uparrow + 3OH^-$$

Haber's process $N_2 + 3H_2 \xrightarrow[\text{200-1000 atm}]{450°C} 2NH_3$

Fe/Mo

NH_3 can't dried by H_2SO_4, P_2O_5 and anhy. $CaCl_2$ because they from adduct

$$CaCl_2 + 8NH_3 \longrightarrow CaCl_2 \cdot 8NH_3$$

Properties

It dissolves several electropositive metals like Li, Na, K, Rb, Cs, Sr, Ba etc.

Eg. K in liq NH_3 ⇒

(i) blue in colour

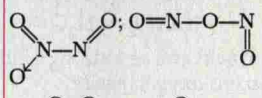
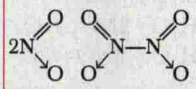
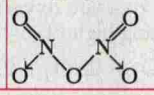
(ii) conducts electricity

(iii) having reducing property

$$K \longrightarrow \underset{\downarrow}{K^+} + \underset{\downarrow}{e^-} \quad \left.\begin{matrix} \\ \end{matrix}\right\} \text{it is the cause for above property}$$
$$K^+(NH_3)_n \quad (NH_3)_x$$

$$\underset{\text{Square planar complex}}{K_2[Ni(CN)_4]} \xrightarrow[NH_3]{\text{K in liq}} \underset{\text{Tetrahedral complex}}{K_4[Ni(CN)_4]}$$

Oxides of Nitrogen

Oxides of nitrogen	Structure	Physical state	Colour of gas
N_2O	$\bar{N}\equiv\overset{+}{N}-O$	Gas	Colourless
NO	$:N=O:$ or $:N\equiv O:$	Gas	Colourless
N_2O_3		Gas	Blue liquid (– 30°C)
NO_2		Gas	Brown
N_2O_5		Colourless solid	– (No existence is gas)

Reaction with H_2O and NaOH

	H_2O	NaOH
(i)	N_2O : Fairly soluble in water and produces neutral solution	.....
(ii)	NO : Sparingly soluble in water and produces the neutral solution.	.....
(iii)	$N_2O_3 : 2HNO_2$ Hence, it is known as anhydride of HNO_2.	$NaNO_2$
(iv)	$NO_2 : HNO_2 + HNO_3$	
(v)	Called mixed anhydride $N_2O_5 : 2HNO_3$ called as anhydride of HNO_3	$NaNO_2 + NaNO_3$ $NaNO_3$

Nitric acid, HNO_3

It was named aqua forties (means strong water) by alchemists.

Preparation

Laboratory Method

$$KNO_3 + \text{conc. } H_2SO_4 \longrightarrow KHSO_4 + HNO_3(\text{vap})$$

Vapours of nitric acid evolved are condensed in a glass receiver.

Industrial Preparation

(A) **Birkeland Eyde Process or arc process**

Step 1 $N_2 + O_2 \xrightarrow[\text{Electric arc}]{3000°C} 2NO - \text{heat}$

Step 2 $NO + O_2 \longrightarrow NO_2$

Step 3 $NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$

Step 4 $HNO_2 \longrightarrow HNO_3 + NO + H_2O$

(B) **Ostwald's Process**

Step 1

$$NH_3 + O_2 \xrightarrow[700-800°C]{\text{Pt.gauze}} NO + H_2O + \text{heat}$$

Step 2 $NO + O_2 \longrightarrow NO_2$

Step 3 $NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$

Step 4 $HNO_3 \longrightarrow HNO_2 + NO + H_2O$

Properties

Physical

Nitric acid usually acquires yellow colour due to its decomposition by sunlight into NO_2.

$$4HNO_3 \xrightarrow{\text{Sunlight}} 4NO_2 + 2H_2O + O_2$$

Chemical

- It is very strong acid. It reacts with basic oxides, carbonates, bicarbonates and hydroxides forming corresponding salts.

$$CaO + 2HHO_3 \longrightarrow Ca(NO_3)_2 + H_2O$$
$$Na_2CO_3 + 2HNO_3 \longrightarrow 2NaNO_3 + H_2O + CO_2$$
$$NaOH + HNO_3 \longrightarrow NaNO_3 + H_2O$$

Oxidizing nature Nitric acid acts as a strong oxidizing agent as it decomposes to give nascent oxygen easily.

$$2HNO_3 \longrightarrow H_2O + 2NO_2 + O$$

or

$$2HNO_3 \longrightarrow H_2O + 2NO + 3O$$

Oxidation of non-metals The nascent oxygen oxidizes various non-metals to their corresponding highest oxy acids.

$$S + 6HNO_3 \xrightarrow[\text{conc. and hot}]{} H_2SO_4 + 6NO_2 + 2H_2O$$
$$C + 4HNO_3 \longrightarrow H_2CO_3 + 4NO_2 + 2H_2O$$
$$2P + 10HNO_3 \xrightarrow[\text{conc. and heat}]{} 2H_3PO_4 + 10NO_2 + 2H_2O$$
$$I_2 + 10HNO_3 \xrightarrow[\text{conc. and heat}]{} 2HIO_3 + 10NO_2 + 4H_2O$$

Metalloids like non-metals also form highest oxy acids.

$$2As + 10HNO_3 \longrightarrow 2H_3AsO_4 + 10NO_2 + 2H_2O$$

or

$$As + 5HNO_3 \xrightarrow[\text{conc. and hot}]{} H_3AsO_4 + 5NO_2 + H_2O$$

Action on Metals Primary action of nitric acid is to produce hydrogen in the nascent form. Before this hydrogen is allowed to escape, it reduces the nitric acid into number of products like NO_2, NO, N_2O, N_2 or NH_3 according to the following reactions:

$$\text{Metal} + HNO_3 \longrightarrow \text{Nitrate} + H$$
$$2HNO_3 + 2H \longrightarrow 2NO + 2H_2O$$
$$2HNO_3 + 6H \longrightarrow 2NO + 4H_2O$$
$$2HNO_3 + 10H \longrightarrow N_2 + 6H_2O$$
$$2HNO_3 + 16H \longrightarrow 2NH_3 + 6H_2O$$

The progress of the reaction is controlled by a number of factors:

(a) The nature of the metal,
(b) The concentration of the acid,
(c) The temperature of the reaction,
(d) The presence of other impurities.

Concentration of Nitric Acid	Metal	Main Products
Very dilute HNO_3 (6%)	Mg, Mn	H_2 + Metal nitrate
	Fe, Zn, Sn	NH_4NO_3 + metal nitrate + H_2O
	Pb, Cu, Ag, Hg	NO + metal nitrate + H_2O
Dilute HNO_3 (20%)	Fe, Zn	N_2O + metal nitrate + H_2O
	Sn	NH_4NO_3 + $Sn(NO_3)_2$
Conc. HNO_3 (70%)	Zn, Fe, Pb, Cu Ag	NO_2 + metal nitrate + H_2O
	Sn	NO_2 + H_2SnO_3 Metastannic acid

Oxygen Family

Sulphur

Allotropes

(i) Rhombic or α-sulphur. (ii) Monoclinic or β-sulphur.
(iii) α-sulphur

$$S(\alpha) \underset{\text{above } 95.5^\circ C}{\overset{95.5^\circ C}{\rightleftharpoons}} S(\beta)$$
below 95.5°C

Amorphous forms are

(i) Plastic sulphur (ii) Milk of sulphur (iii) Colloidal sulphur

Viscosity of 'S' with temperature show irregular variation:

(m.p of S $\longrightarrow$ 112.8°C).

(i) > 112.8°C to 160°C $\Rightarrow$ slow decreases due to S_8 rings slip and roll over one another easily.
(ii) > 160°C, increases sharply due to breaking of S_8 rings into chains and polymerses into large size chain.
(iii) 190°C, again large chains are being broken into small chain.

- **Milk of Sulphur**

Powdered 'S' + $Ca(OH)_2$ suspension $\longrightarrow$ Solution $\xrightarrow{\text{Acidified}}$ Milk of S

$$12S + 3Ca(OH)_2 \longrightarrow 2CaS_5 + CaS_2O_3 + 3H_2O$$
$$2CaS_5 + CaS_2O_3 + 6HCl \longrightarrow 3CaCl_2 + 12S + 3H_2O$$

- **Colloidal Sulphur**

$$Na_2S_2O_3 + 2HCl \longrightarrow 2NaCl + H_2O + SO_2 + S\downarrow$$

$$2H_2S + SO_2 \longrightarrow 3S\downarrow + 2H_2O$$

H_2S

- Fused $CaCl_2$, Al_2O_3 (dehydrated)

P_2O_5 etc. are used as drying agent for this gas but not H_2SO_4, because

$$H_2SO_4 + H_2S \longrightarrow 2H_2O + SO_2 + S$$

Reducing nature

$$KMnO_4 + H_2S + H_2SO_4 \longrightarrow S + Mn^{2+}$$
$$H_2Cr_2O_7 + H_2S + H_2SO_4 \longrightarrow Cr^{3+} + S +$$
$$HNO_3 + H_2S \longrightarrow S + NO_2 + H_2O$$

Absorbent: NaOH, KOH, $PbNO_3$ solution

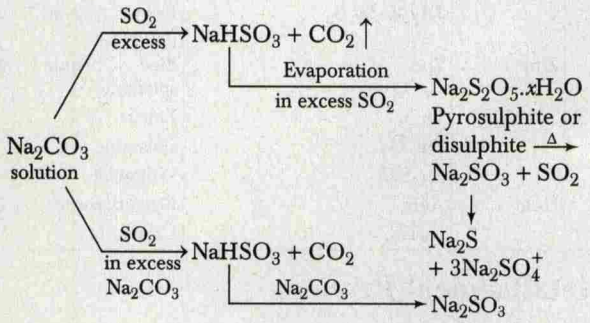
$$Pb(NO_2)_3 + H_2S \longrightarrow 2HNO_3 + PbS \text{ (black)}$$

SO_2

$$Cu + 2H_2SO_4 \text{ (conc.)} \longrightarrow CuSO_4 + 2H_2O + SO_2$$
$$Hg + H_2SO_4 \longrightarrow HgSO_4 + H_2O + SO_2$$
$$2Ag + H_2SO_4 \longrightarrow Ag_2SO_4 + H_2O + SO_2$$
$$S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$$
$$\text{(Charcoal) } C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$$
$$NaHSO_3 + H_2SO_4 \longrightarrow NaHSO_4 + H_2O + SO_2$$

Properties (i) Incombustible gas, but heated K burns in SO_2

$$4K + 3SO_2 \longrightarrow K_2SO_3 + K_2S_2O_3$$



$$\overbrace{SO_2 + Cl_2}^{\text{Both gas}} \longrightarrow SO_2Cl_2$$

$$H_2SO_4 + 2PCl_5 \longrightarrow SO_2Cl_2 + 2POCl_3 + 2HCl$$

Use of H_2SO_4 as nitrating mixture

good chlorinating agent

- P_2O_5 is stronger dehydrating agent than H_2SO_4 :

$$H_2SO_4 + P_2O_5 \longrightarrow 2HPO_3 + SO_3$$

Properties of H_2SO_4

- Dissociation At 444°C $H_2SO_4 \rightleftharpoons H_2O + SO_3$
- Acidic nature $NaOH + H_2SO_4 \rightleftharpoons NaHSO_4$

$$+ H_2O \overset{NaOH}{\rightleftharpoons} Na_2SO_4 + H_2O$$

- $CO_3^{2-} + H_2SO_4 \longrightarrow SO_4^{2-} + H_2O + CO_2$
- $HCO_3^- + H_2SO_4 \longrightarrow H_2SO_4^- + H_2O + CO_2$

Carbonates or bicarbonates are getting decomposed whereas

- $Zn/Fe + H_2SO_4 \longrightarrow ZnSO_4$ and $FeSO_4 + H_2$

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$$

$$2Ag + 2H_2SO_4 \longrightarrow Ag_2SO_4 + SO_2 + 2H_2O$$

$$Hg + 2H_2SO_4 \longrightarrow HgSO_4 + SO_4 + 2H_2O$$

Oxidising property

$$HBr/HCl + H_2SO_4 \longrightarrow Br_2/Cl_2 + SO_2 + H_2O$$

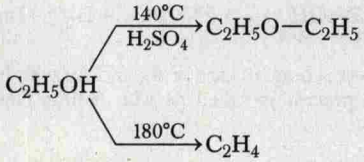
$$C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$$

$$S + 2H_2SO_4 \longrightarrow 3SO_2 + H_2O$$

$$2P + 5H_2SO_4 \longrightarrow H_3PO_4 + 5SO_2$$

Dehydrating agent

$$C_{12}H_{22}O_{11} \xrightarrow[-11H_2O]{H_2SO_4} 12\,C$$



$$C_6H_{12}O_6 \xrightarrow[-6H_2O]{H_2SO_4} 6\,C$$

$$(COOH)_2 \xrightarrow[-H_2O]{H_2SO_4} CO + CO_2$$

$$PhH \xrightarrow{H_2SO_4} PhSO_3H$$

$$HCO_2H \xrightarrow[-H_2O]{} CO$$

Sodium Thiosulphate

Preparation

$$Na_2SO_3\,sol^n. + S\ (powder) \xrightarrow{\text{Boiling}}$$

$$Na_2S_2O_3 \xrightarrow{\text{Eavporation}} Na_2S_2O_3 \cdot 5H_2O, \text{ monoclinic crystal}$$

Na_2CO_3 excess

SO_2 passed

$$\begin{cases} Na_2CO_3 + 2SO_2 + H_2O \longrightarrow 2NaHSO_3 + CO_2 \\ 2\,NaHSO_3 + Na_2CO_3 \longrightarrow Na_2SO_3 + H_2O + CO_2 \end{cases}$$

Properties

(i) $4Na_2S_2O_3 \xrightarrow{\Delta} Na_2S_5 + 3Na_2SO_4$

(ii) $Na_2S_2O_3 + 2H^+ \xrightarrow{\Delta} H_2S_2O_3 \longrightarrow H_2O + SO_2 + S\downarrow$

(White turbidity)

Reaction

(i) $Na_2S_2O_3 + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$

Cl_2 – water $\longrightarrow SO_4^{2-} + S + 2HCl$

Br_2 – water $\longrightarrow SO_4^{2-} + S + 2HBr$

But no suitable indicator {reaction may occur in alkaline}

$$4OI^- + 2OH^- \longrightarrow 2SO_4^{2-} + 4I^- + H_2O$$

$$4Cl_2 + 5H_2O \longrightarrow Na_2SO_4 + 8HCl + H_2SO_4$$

H_2O_2

- $Na_2O_2 + H_2O$ (ice cold water) $\rightarrow 2NaOH + H_2O_2$
- $BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$

Insulated of H_2SO_4, H_3PO_4 is prepared now-a-days because H_2SO_4 catalyses the decomposition of H_2O_2 whereas H_3PO_4 favours restore it.

$$3BaO_2 + 2H_3PO_4 \longrightarrow Ba_3(PO_4)_2 + 3H_2O_2$$

and $Ba_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 3BaSO_4 + 2H_3PO_4$

(reused again)

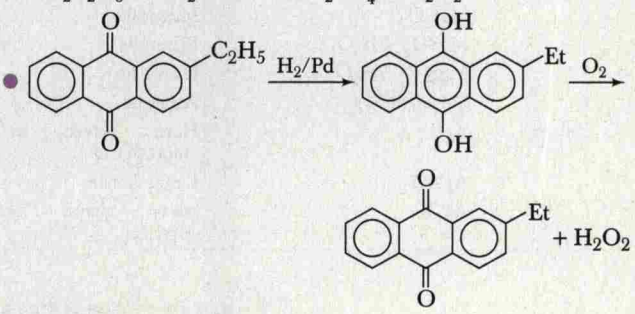
Electrolysis of 50% H_2SO_4 using high current density.

$$2H_2SO_4 \rightleftharpoons 2H^+ + 2H_2SO_4^-$$

$$2H_2SO_4^- \longrightarrow H_2S_2O_8 + 2e^- \quad \text{[At anode]}$$

$$2H^+ + 2e^- \longrightarrow H_2 \quad \text{[At cathode]}$$

$$H_2S_2O_8 + 2H_2O \longrightarrow 2H_2SO_4 + H_2O_2$$

- 

Properties

Acidic nature $H_2O_2 + 2NaOH \longrightarrow Na_2O_2 + H_2O$

It is oxidant as well as reductant.

$$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O \quad \text{[reaction in acidic medium]}$$

$$H_2O_2 + 2e^- \longrightarrow 2OH^- \quad \text{[reaction in alkali medium]}$$

Oxidizing Properties

$$PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$$
$$2KI + H_2O_2 \longrightarrow 2KOH + I_2$$
$$[X_2 + H_2O \longrightarrow 2HX + O_2, X = Cl, Br.]$$
[S.R.P order of $Cl_2 > Br_2 > H_2O_2 > I_2$]
$$H_2S + H_2O_2 \longrightarrow S\downarrow + 2H_2O$$

Reducing Properties

$$Ag_2O + H_2O_2 \longrightarrow 2Ag + H_2O + O_2$$
$$O_3 + H_2O_2 \longrightarrow H_2O + 2O_2$$
$$MnO_2 + H_2O_2 + H_2SO_4 \longrightarrow MnSO_4 + 2H_2O + O_2$$
$$X_2 + H_2O_2 \longrightarrow 2HX + O_2 \ [X = Cl, Br]$$
$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 \longrightarrow 2MnSO_4 + K_2SO_4 + 5O_2 + 8H_2O$$
$$NaOCl + H_2O_2 \longrightarrow NaCl + H_2O + O_2$$
$$NaIO_4 + H_2O_2 \longrightarrow NaIO_3 + H_2O + O_2$$

Metallurgy

Metals and Their Ores/Minerals

1.	Iron	FeS_2	Iron pyrite
		$FeCO_3$	Siderites
		Fe_2O_3	Red haematite
		$2Fe_2O_3 \cdot 3H_2O$	Brown haematite or limonite
		Fe_3O_4	Magnetite
2.	Tin	SnO_2	Tin stone or cassiterite
		$Cu_2S \cdot FeS \cdot SnS_2$	Stannite
3.	Lead	PbS	Galena
		$PbCO_3$	Anglesite
		$2\,Pb(OH)_2 \cdot PbCO_3$	White lead
4.	Copper	Cu_2O	Cuprite
		$CuFeS_2$	Copper pyrite
		Cu_2S	Copper glance
5.	Aluminium	$Al_2O_3 \cdot 2H_2O$	Bauxite
		Al_2O_3	Corundum
		$KAlSi_3O_6$	Feldspar
		$2\,NaF \cdot AlF_3$ or Na_3AlF_6	Cryolite
		$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$	Alum
		$K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$	Mica
6.	Magnesium	$KCl \cdot MgCl_2 \cdot 6H_2O$	Carnalite
		$MgCO_3 \cdot CaCO_3$	Dolomite
		$MgCO_3$	Magnesite
		$MgSO_4 \cdot 7H_2O$	Epsomite
		$MgSO_4 \cdot 7H_2O$	Kiesserite
		$CaMg(SiO_3)_4$	Asbestos
7.	Silver	AgCl	Horn silver or chloropyrite
		$AgNO_3$	Lunar caustic
		Ag_2S	Silver glance or Argentite
		$3Ag_2S \cdot Sb_2S_3$	Ruby silver or pyrogyrite
8.	Zinc	ZnS	Zinc blende or sphalerite
		ZnO	Zincite
		$ZnCO_3$	Calamine
		Zn_2SiO_4	Willmenite
9.	Gold	AuBi	Bismuth surite
		$AuTe_2$	Calaverite

Metallurgical Process

Concentration

1. **Gravity separation or levigation** Oxides and carbonates ore are concentrated by this method.
2. **Magnetic separation** The impurities are magnetic in nature. *e.g.*, SnO_2 (Non-magnetic) in Fe_3O_4 (magnetic).
3. **Froth floatation process** The process is best suitable for sulphide ores. Activator in this process is $CuSO_4$ while that of depressant in NaCN.
4. **Electrostatic concentration** This is used to separate PbS and ZnS which are found together in nature.

B. Chemical Method

1. Calcination The concentrated ore is heated in absence of air to remove water or moisture from a hydrated oxide and CO_2 from a carbonate ore at a temperature below their melting point, is called calcination

$$Al_2O_3 \cdot 2H_2O \xrightarrow{\Delta} Al_2O_3 + 2H_2O$$
$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$
$$Fe_2O_3 \cdot 3H_2O \xrightarrow{\Delta} Fe_2O_3 + 3H_2O$$

2. Roasting The process in which the concentrated ore is heated in blast of air (or excess of O_2) and ore gets converted into oxide and impurities like sulphur, arsenic are also oxidized in forms of oxide and is removed, are called roasting. It requires very high temperature and specialized furnace like bassemer or reverberatory furnace.

$$S + O_2 \longrightarrow SO_2\uparrow$$
$$4AS + 3O_2 \longrightarrow 2As_2O_3$$
$$4FeO + O_2 \longrightarrow 2Fe_2O_3$$
$$2Cu_2S + 3O_2 \longrightarrow Cu_2O + 2SO_2$$
$$2ZnO + 3O_2 \longrightarrow 2ZnO + 2SO_2$$

3. Leaching It involves treatment of ore with leaching agents (like NaOH, NaCN, KCN or other reagents) due to which ore becomes soluble and their impurities remain insoluble. The leaching process is basically done in extraction of Al by Al_2O_3 (Alumina).

$$\underset{\text{with impurities}}{Al_2O_3} + \underset{\text{Leaching agant}}{2NaOH} \longrightarrow \underset{\text{Soluble}}{2NaAlO_3} + H_2O + \underset{\text{Insoluble}}{\text{Impurities}}$$

If leaching process is done in case of Ag and Au with NaCN (0.4 to 0.8%) then the process is called as Mac-Arthur Forrest cyanide process.

Coordination Compounds

Ligands

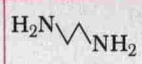
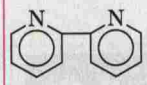
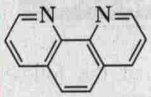
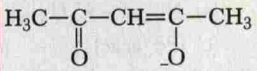
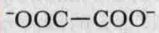
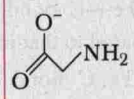
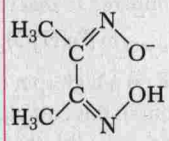
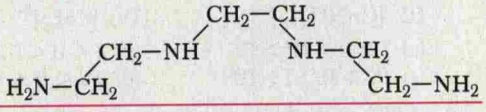
1. Neutral unidentate

$\underline{N}H_3$, $\underline{C}O$, $H_2\underline{O}$, $P\underline{P}h_3$,  (pyridine, py)

2. Univalent unidentate F^-, Cl^-, Br^-, I^-, OH^-, CN^-
3. Neutral bidentate : en, bipy, phen
4. Univalent bidentate acac, DMG, Glycine
5. Bivalent bidentate : Oxalate, sulphate, carbonate
6. Multidentate or Flexidentate : Dien, Tren, EDTA

7. Ambidentate : NCS^-, NO_2^-, CN^-
8. Bridging : Cl^-, OH^-, NH_2^-, CO, NCS^-

Polydentate Ligands

Name	Abbreviation	Structure
Ethylenediamine	en	
2, 2-bipyridyl	bipy	
1, 10-phenanthroline (phen)	phen	
Acetylacetanato	Acac	
Oxalate	Ox	
Glycinato	gly	
Dimethylglyoximate	DMG	
Diethylenetriamine	dien	
Triethylenetetramine	tren	

Isomerism

Structural Isomerism

(i) **Polymerization isomerism** *Example* $[Pt(NH_3)_2Cl_2]$, $[Pt(NH_3)_4][PtCl_4]$, $[Pt(NH_3)_4][Pt(NH_3)Cl_3]_2$.

(ii) **Ionization isomerism** $[Co(NH_3)_5Br]SO_4$ is red-violet. while $[Co(NH_3)_5SO_4]Br$ is red.

(iii) **Hydrate isomerism** Three isomers of $CrCl_3.6H_2O$ are known. From conductivity measurements and quantitative precipitation of the ionized chlorine, they are confirmed.

Complex $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$
$[Cr(H_2O)_4]Cl_2 \cdot Cl \cdot 2H_2O$

Conc. H_2SO_4 removes lattice water and not the coordinated water molecules.

(iv) **Linkage isomerism** Two different complexes $[CO(NH_3)_5(NO_2)]Cl_2$ and $[Co(NH_3)_5(ONO)]Cl_2$ have been prepared, each containing the NO_2^- group in the complex ion with different head.

(v) **Coordination isomerism** When both cation and anion are complex ions, then the ligands can exchange position between the cation and the anion.

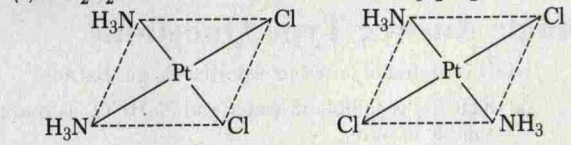
$[Cr(NH_3)_6][Co(CN)_6]$ and $[Co(NH_3)_6][Cr(CN)_6]$
$[Co(en)_3][Cr(C_2O_4)_3]$ and $[Co(en)_2(C_2O_4)][Cr(en)(C_2O_4)_2]$

Stereo Isomerisms

(i) **Geometrical isomerism or *cis-trans* isomerism** It occurs when ligands can assume different positions around rigid bounds with the metal ion.

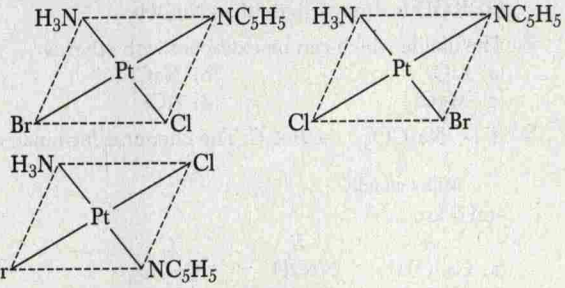
1. For square planar complexes Ma_4, Ma_3b or Mab_3 where, a and b are monodentate ligands, the geometrical isomerism is not possible. The square planar complexes, Ma_2b_2 Ma_2bc, *Mabcd* and $M(AA)_2$, $M(AB)_2$ where AA and AB represent symmetrical and unsymmetrical chelating ligands given geometrical isomers.

(a) Ma_2b_2 $Pt(HN_3)_2Cl_2$

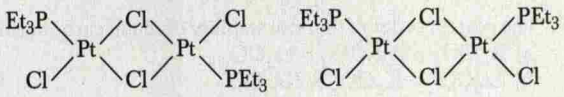


(b) Ma_2bc $[Pt(NH_3)_2(Cl)(Br)]$

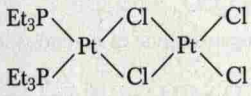
(c) *Mabcd* $[Pt(NH_3)(C_5H_5N)(Cl)(Br)]$



(d) Bridged binuclear planar complexes like $[Pt(PEt_3)Cl_2]_2$ may exist in three isomeric forms :



Trans- *Cis-*



Unsymmetrical

(ii)

1. Six coordinated octahedral complexes of the type Ma_4b_2, Ma_3b_3, Ma_3b_2c, Ma_3bcd, Ma_2b_2cd, Ma_2bcde *Mabcdef* would all give geometrical isomers. Systems with one or two bidentate ligands and rest monodentate would also give geometrical isomers.
2. A number of isomers are possible whether they can be isolated or separated is a different question which depends on so many factors. As we increase the number of different ligands, the possible number of isomers increases.
3. Ma_4b_2 type of complex would give only two isomers *cis* and *trams*.
4. Ma_3b_3 gives two isomers *facial* (*fac-*) and *meridional* (*mer-*) isomers. In the former (*fac-*) three ligands of one type form one triangular face of the octahedron and the other three on the opposite face. In the latter (*mer-*) one set of these ligands are arranged around an edge of the octahedron whereas the other set occupies the opposite edge as shown in figure.
5. *Mabcdef* is expected to give 15 isomers. ($6C_2$). a to f are unidentate ligands.