

**BACHLEOR OF SCIENCE**  
**SEMESTER-III**  
**PAPER NO.: US03CICH01 (3 CREDITS, 70 MARKS)**  
**(HEAVY AND FINE CHEMICALS)**

**Unit-5:**

Electrochemical industries: Anhydrous magnesium, Magnesium chloride, Magnesium oxide, hydrogen peroxide, Potassium permanganate, Hydroxyl amine.

**MAGNESIUM**

Magnesium is a silvery white metal, which soon becomes dull in air. Its melting point is 651°C and boiling point is 1100°C. It is light metal with a specific gravity of 1.75

**Raw material**

Magnesium metal is extracted by either of the following processes:

1. By the electrolysis of fused anhydrous carnallites, KCl, MgCl<sub>2</sub>.6H<sub>2</sub>O
2. By the electrolysis of fused anhydrous MgCl<sub>2</sub> containing fused CaCl<sub>2</sub> and NaCl
3. Carbo thermal process (Reduction of MgO by carbon or calcium carbide)
4. Pidgeon or Silico thermal process (Reduction of MgO with silicon)

It is well evident that magnesium is either obtained from MgCl<sub>2</sub> or MgO. These two may be obtained from

1. Carnallite (KCl, MgCl<sub>2</sub>.6H<sub>2</sub>O)
2. MgCl<sub>2</sub> present in saline's, brine wells and sea water
3. Magnesite MgCO<sub>3</sub>
4. Dolomite, (CaCO<sub>3</sub>MgCO<sub>3</sub>)

Preparation of anhydrous MgCl<sub>2</sub> from carnallite

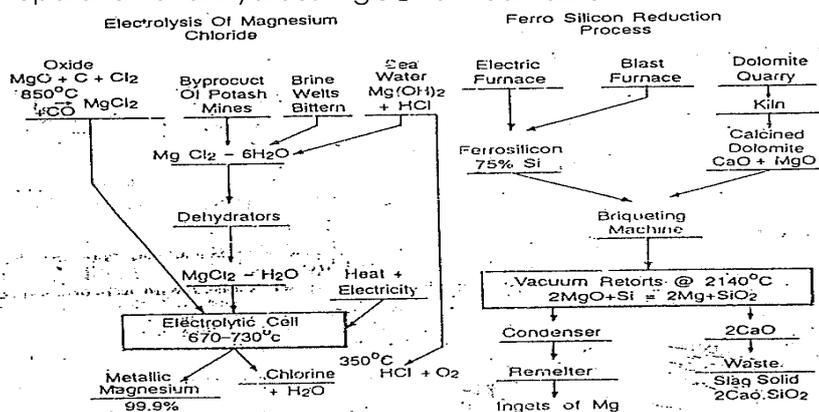


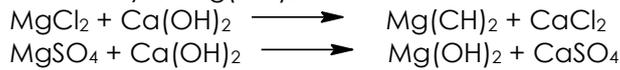
Fig. 6. Outline of processes for production of magnesium.

The mineral carnallite is first dissolved in water and then the solution is filtered and evaporated to get crystalline KCl; MgCl<sub>2</sub>. 6H<sub>2</sub>O. The crystals are then calcined in a current of HCl gas to get anhydrous KCl, MgCl<sub>2</sub>. The mother liquor obtained after separation of KCl crystals from carnallite solution contains MgCl<sub>2</sub>. The mother liquor is removed and concentrated to get MgCl<sub>2</sub>. The latter is subjected to self drying by hot air to get MgCl<sub>2</sub> 3/2H<sub>2</sub>O. It is used as an electrolyte in electrolytic process.

**PREPARATION OF MgCl<sub>2</sub> FROM SEA WATER**

A tonne of sea water contains about 61b of magnesium. Sea water is therefore a practical and very important source of magnesium. Sea water which contains about 4.2

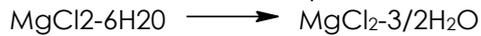
gram/litre of  $MgCl_2$  is first clarified and then treated with slaked lime (it is prepared from the calcium oxide, which is obtained by calcining pure calcium carbonate available in the form of oyster shells from the sea) as a result of reaction, magnesium hydroxide gets precipitated, because solubility of  $Mg(OH)_2$  is small.



The precipitate of  $Mg(OH)_2$  is allowed to settle and then separated by filtration. The magnesium hydroxide thus obtained is treated with 10% hydrochloric acid, prepared at high temperature from water and chlorine liberated from the cells or from chlorine by burning hydrogen or natural gas in chlorine.



The resulting solution of magnesium chloride contains some  $CaCl_2$ , which is removed as  $CaSO_4$  by treating with requisite amount of  $H_2SO_4$ . After removal of  $CaSO_4$ , the solution of magnesium chloride is evaporated to get solid magnesium chloride,  $MgCl_2 \cdot 6H_2O$ . The hexa hydrate is dehydrated in direct fixed evaporators followed by shelf drying until the water contents has fallen to the composition of hemihydrate,  $MgCl_2 \cdot 3/2 H_2O$ .



The dehydration of soil, without hydrolysis is possible only up to this stage.

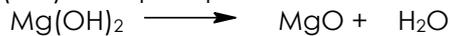
### **PREPARATION OF MgO FROM MAGENSITE**

Magnesite or  $MgCO_3$  when calcined at about  $700^\circ C$  gives  $MgO$ ,



### **PREPARATION OF MgO FROM DOLOMITE**

Dolomite ( $CaCO_3 + MgCO_3$ ) is first calcined at  $1000^\circ C$ , when a mixture of  $CaO + MgO$  is formed. The latter is dissolved in hydrochloric acid when a solution of  $CaCl_2 + MgCl_2$  is obtained. From this solution most of the  $CaCl_2$  is removed as  $CaSO_4$  by adding requisite amount of  $H_2SO_4$  the solution of  $MgCl_2$  containing some  $CaCl_2$  is precipitated with  $Ca(OH)_2$ . The  $Mg(OH)_2$  thus precipitated is filtered and then calcined to get  $MgO$ .



$Mg(OH)_2$  may also be converted into  $MgCl_2$  by dissolving 10%  $KCl$  as described above.

Anhydrous  $MgCl_2$  may be obtained by the action of chlorine on  $MgO$  in presence of coke at a very high temperature.



### **Manufacture**

The cheapest and the best method of manufacturing magnesium is by the electrolytic process. Magnesium is obtained by the electrolysis of fused  $MgCl_2$ .

The dehydrated magnesium chloride obtained from sea water is fused with anhydrous  $CaCl_2$  and sodium chloride so that the mixture contains 25%  $MgCl_2$ , 15%  $CaCl_2$  and 60%  $NaCl$ . The presence of sodium chloride decreases the melting point and increases the conductivity. The electrolysis is carried out at  $710^\circ C$ , which is greater than melting point of magnesium ( $651^\circ C$ ). The decomposition voltage of magnesium chloride is 2.25 volts  $750^\circ C$  and the voltage applied is 5-6 volts. Energy requirement is 8 kwhs/pound of magnesium produced.

Two types of cells have been used in the manufacture of magnesium by the electrolysis of fused  $MgCl_2$ .

One of cell is a closed top smaller cell made of steel. It consists of centrally placed graphite electrode surrounded by a perforated porcelain tube. The inner surface of the steel cell acts as the cathode and vertical graphite rod as the anode. The bottom and lower sides the cells are lined with ceramic material. A large number of such cells are joined in series. As a result of passage of electricity electrolysis takes place and  $Cl_2$  is liberated at the anode. The metal floats on the surface of the bath and protected from oxidation circulating coal gas. The chlorine gas is collected from the top and molten metal is collected also from the top. The mixture of salt ( $MgCl_2$ ,  $CaCl_2$  and  $NaCl$ ) which acts as an electrolyte is kept in molten state by the electric current used and by the external heat supplier gas fired outside furnaces. It processed also maintains the temperature of the bath at about  $710^\circ C$ . The decomposition voltage of  $MgCl_2$  is least (2.25 volts at  $750^\circ C$ ) among  $CaCl_2$  (2.74 at

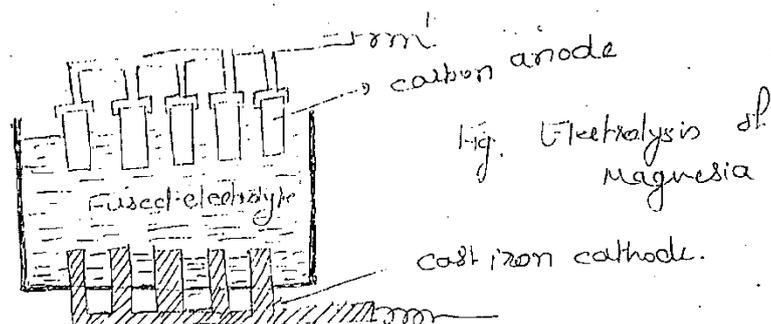
750°C) and NaCl (2.62 volts at 750°C) and hence only  $MgCl_2$  undergoes electrolysis under these conditions.

The other type of cell is known as Dow electrolytic cell. The cells are large rectangular ceramic covered steel tanks 5ft. wide; 11ft. long at 6 ft. deep and hold about 10 tonnes of fused magnesium chloride and salts. The internal parts of the cell act as the cathode and graphite anodes (about 22) suspended vertically in the top of the cell act as anodes. The temperature of the cell maintained at about 710°C (which is greater than the M.P. of magnesium, 651°C) by the electric current and by external heat supply by gas fired outside furnaces. Each self operate at about 6 volts and 80000 to 100000 amps. with current efficiency of about 80%. Power consumption is about 8 kwhr/lb. Of magnesium produced the molten magnesium liberated at the cathode rises up to the bath surface and tapped off From time to time. The chlorine liberated as a by product is separately reacted with hydrogen (liberated from the electrolysis of water) to form HCl. The latter is use again for dissolving more magnesium hydroxide in the second step.

Magnesium obtained by this method is 99% pure. It further refined by subliming at 600°C under a pressure of 1 m.m. of Hg.

### MAGNESIUM FROM ELECTROLYSIS OF MAGNESIA

Magnesium is also commercially prepared by electrolysis of magnesium oxide obtained from the calcination of the ore, magnesite,  $MgCO_3$ .

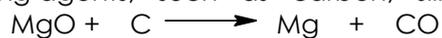


Magnesia ( $MgO$ ) is dissolved in a mixture of Magnesium, barium and sodium in a steel tank at about 900-950°C. The steel, tank acts as the electrolytic cell in which cast iron cathodes project into the electrolyte from below and the carbon anodes are suspended from above. On passing an electric current molten electrolyte forms a solid crust at the surface of the molten mass and the molten magnesium, being lighter, rises up and collects below the crust. The magnesium is thus protected from being oxidized.

### CARBO-THERMAL PROCESS

#### **Magnesium from Thermal Reduction of Magnesia**

Magnesium can also be prepared by thermal reduction of magnesia ( $MgO$ ) with reducing agents, such as carbon, silicon, calcium carbide etc.

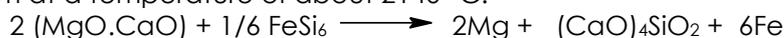


When magnesium oxide is allowed to heat with reducing agent (say carbon) in vacuum at about 2000°C, the oxide is reduced to metallic magnesium. If the mixture of magnesium and carbon monoxide vapours is cooled down slowly the reverse reaction takes place. In other words, the equilibrium is chilled, if the temperature is suddenly decreased from 2000-200°C, so that the metal separates out in the form of a condensate. To achieve this mixture of magnesium vapour and carbon monoxide vapour from the reaction chamber is brought in contact with sufficiently cooled hydrogen to chill the mixture to a temperature

of about 220°C. The solid condensate of magnesium thus obtained is purified by redistillation in vacuum.

### Silicothermal or Pidgeon process

In this process a mixture of ground dead burnt dolomite, ground ferrosilicon (70-80%) and fluorspar (1%) is charged into a furnace made of chrome alloys and equipped with a condenser tube with a removable lining. The reaction is carried out under high vacuum at a temperature of about 2140 °C.



The magnesium is collected on the lining of the condenser, the furnace is partly cooled after the run and magnesium is removed, from the condenser and remelted in the remelt furnace. It is further refined by subliming at 600°C under pressure.

### Uses

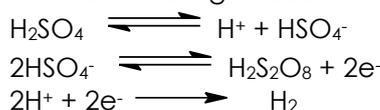
Magnesium is used in making a number of alloys which are used in automobile industry, making of air craft's and optical instruments etc. the magnesium powder mixed with potassium chlorate is used for flash bulbs in photography. It has also been used as a deoxidiser for removing last traces of oxygen from copper, steel etc. Magnesium is used in making Grignard reagents which are used for the synthesis of large number of organic compounds. Magnesium also finds its use in the extraction of boron, silicon etc.

## HYDROGEN PEROXIDE

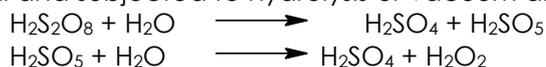
Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is manufactured by either electrolytic method or by organic oxidation method. The electrolytic method is, however, cheap and the best

### Electrolytic method

Hydrogen peroxide to the extent of a 30% solution can be prepared by the electrolysis of a 50% sulphuric acid solution, which is fed into a typical cell maintained at 35°C or below. The first product of the electrolysis is persulphuric acid H<sub>2</sub>S<sub>2</sub>O<sub>8</sub> which subsequently reacts with water during vacuum distillation or hydrolysis to form hydrogen peroxide.



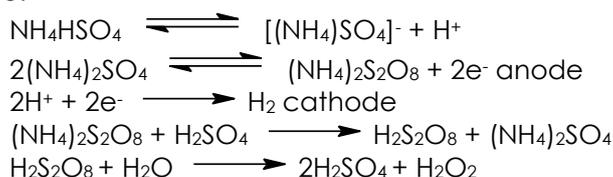
The anode solution consisting of perdisulphuric acid is immediately withdrawn from the cell and subjected to hydrolysis or vacuum distillation to yield hydrogen peroxide.



Hydrogen peroxide and water distil over and are condensed to produce dilute hydrogen peroxide. The residual liquid containing sulphuric acid is cooled and recycled to the electrolytic cell. Thus only water and electric current are consumed during the electrolysis and the overall reaction of the process may be represented as,



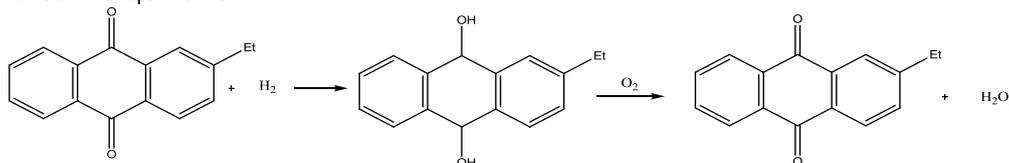
The manufacture of hydrogen peroxide can also be carried out by the electrolysis of an aqueous solution of ammonium sulphate and sulphuric acid in molecular proportions in a diaphragm cell at low temperature. Use of sulphuric acid alone as the electrolyte is not desirable because it has low current efficiency of 70-75%, while ammonium sulphate alone, and causes crystallization problems. A mixture of sulphuric acid and ammonium sulphate gives a current efficiency of 80% or higher and crystallization problem is also avoided. As a result of electrolysis, ammonium, per sulphate, NH<sub>4</sub>HSO<sub>4</sub> is obtained in anode compartment, which is quickly removed from the cell and distilled with sulphuric and under reduced pressure.



Sulphuric acid and ammonium sulphate according to the above reactions are separated and used again for the manufacture of H<sub>2</sub>O<sub>2</sub>. Electrolytic process gives only 30 – 35 % H<sub>2</sub>O<sub>2</sub>.

## Organic Oxidation Process

In this method, anthraquinone dissolved in organic solvent is catalytically hydrogenated to the hydroquinone, which on subsequent aeration produces H<sub>2</sub>O<sub>2</sub> and regenerates the quinone.



The H<sub>2</sub>O<sub>2</sub> is water extracted and concentrated. The quinone is and used again.

## Concentration of H<sub>2</sub>O<sub>2</sub> Solution

Concentration of H<sub>2</sub>O<sub>2</sub> solution is a dangerous operation, because impurities may catalyse its explosive decomposition. However the solution of H<sub>2</sub>O<sub>2</sub> obtained by above methods is concentrated by any of the following method

1. Hydrogen peroxide may be concentrated to strength of 40-45% by care full evaporation of the solution in a smooth platinum basin preferable under reduce pressure on a water bath and using a fractionating column. Hydrogen Peroxide, being appreciably less volatile then water, looses water of evaporation till a 30% solution is obtained. It is, however, not advisable to concentrated beyond 30% because it results in concentration of impurities in the product. These impurities may cause decomposition.

Further concentration is carried out by distilling the solution in a distillation flask provided with thermometer dipping into the liquid. The distillation is done at about 60°C under a pressure of 15 mm. In the beginning, the temperature is maintained at about 25°C, when water first distilled and passes over. As soon as temperature rises to 60 – 65°C and distillation is temporarily stopped and the receiver is changed to collect the later fraction containing H<sub>2</sub>O<sub>2</sub>. The distillate consists of about 90% H<sub>2</sub>O<sub>2</sub>.

2. More concentrated and pure H<sub>2</sub>O<sub>2</sub> can also be obtained by cooling till crystallization sets in. The crystals which are richer in H<sub>2</sub>O<sub>2</sub> are separated and the solution left behind. The crystal are again melted carefully and refrozen to effect further concentration. This process is repeated several times to get more and more concentrated solution of H<sub>2</sub>O<sub>2</sub>.

3. The concentration of H<sub>2</sub>O<sub>2</sub> obtained by hydrolysis of the electrolysate never exceeds 55%. The hydrolysate with 30% H<sub>2</sub>O<sub>2</sub>, following an ammonia treatment (which, decreases the concentration of free H<sub>2</sub>SO<sub>4</sub>) is mixed with small quantity of ammonium pyrophosphate as stabilizer and sent to a two stage distillation plant, each consisting of a steam heated still, a separator and a rectifier (as condenser).

During heating in the first still, the concentration of H<sub>2</sub>O<sub>2</sub> gradually increases to 73%, while the vapours consisting of about 30% H<sub>2</sub>O<sub>2</sub> and steam is fractionated in the separator rectifier to get H<sub>2</sub>O<sub>2</sub> of 65% strength in the first rectifier. It is sent to second rectifier, where strength increase to 80% by controlled and continuous distillation. The vapours in the second still, after fractionation gives a solution of 50% H<sub>2</sub>O<sub>2</sub> which is again sent to second still to get about 80% solution by continued distillation. The 80% H<sub>2</sub>O<sub>2</sub> is taken out periodically. The operating temperatures in the first and second still are 66 and 75°C respectively

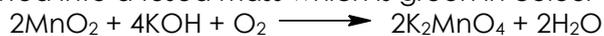
## Uses

H<sub>2</sub>O<sub>2</sub> is a mild bleaching agent and is particularly used for bleaching delicate materials. It is also used for oxidation, power generation for the manufacture of peroxide chemicals and other organic compounds. It is also used in liquid fuel rockets and also as a monopropellant. Di lute solution of H<sub>2</sub>O<sub>2</sub> is used in medicine.

## POTASSIUM PERMANGANATE

### Preparation of K<sub>2</sub>MnO<sub>4</sub>

The ore pyrolusite is crushed and ground in ball mills to 100mesh and then fused with caustic potash and some potassium nitrate. The mixture is then calcined strongly on the hearth of a coal fired furnace with constant stirring by rabbles to allow the air to come in contact with the hot mixture. As a result of heating in contact with air and alkali, on MnO<sub>2</sub> is concerted into a fused mass which is green in colour due to the formation of K<sub>2</sub>MnO<sub>4</sub>



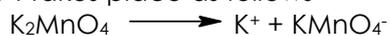
Potassium nitrate also liberates oxygen



The dark green mass is extracted with water and filtered. The unreacted one is recycled after filtration. The weight of KOH used depends upon the analysis of ore. The ratio of ore to KOH is usually 1:2

### Preparation of $\text{KMnO}_4$

The green coloured solution of potassium permanganate (formed above) is then oxidized in an electrolytic diaphragm cell provided with nickel sheets placed in the anode compartment. These sheets act as anode. The green solution is taken in the cathode compartment and a dilute KOH solution in the cathode compartment. The ionization of  $\text{K}_2\text{MnO}_4$  takes place as follows



The  $\text{K}^+$  ions migrate to the cathode and discharged there forming KOH and  $\text{H}_2$ . Oxygen is formed on the anode by the discharge of  $\text{OH}^-$  ions of the anode.

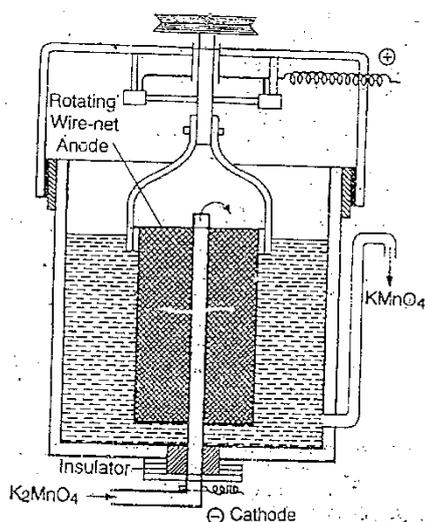
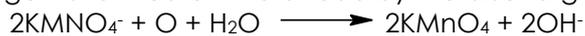


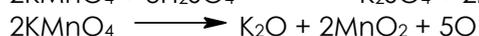
Figure: Production of  $\text{KMnO}_4$

The purple solution containing potassium permanganate is formed in the anode compartment and concentration of KOH increases in the cathode compartment.

The purple solution is evaporated under controlled conditions, whereby  $\text{KMnO}_4$  crystallises out in the form of dark purple crystals with metallic lustre. The crystals are dried and packed.

$\text{KMnO}_4$  is a power full oxidizing agent and the available oxygen differs with the medium in which oxygen occurs.

### In acid medium



That is 5 atoms of oxygen become available from two molecules of  $\text{KMnO}_4$ .

### In neutral medium



That is 3 atoms of oxygen become available from 2 molecules of  $\text{KMnO}_4$

### Uses

Primary  $\text{KMnO}_4$  is used as a powerful oxidizing agent and a good disinfectant. It is a popular analytical reagent both in qualitative and quantitative analysis. In qualitative analysis it is used for the detection of various radicals, such as chloride, bromide, iodide and oxalate. 1% solution of  $\text{KMnO}_4$  in alkaline medium is called Baeyer's reagent which is used in detecting double bonds in organic compounds. In qualitative analysis ferrous salts,

oxalic acid and oxalates are estimated by  $\text{KMnO}_4$  solution in acid medium. It is used as a source of reactive form of manganese dioxide in place of pyrolusite in making dry cells.

### Evaluation of pyrolusite

The pyrolusite purity may be checked on the basis of its  $\text{MnO}_2$  content. The methods of determining the purity of pyrolusite (which contains  $\text{MnO}_2$ ,  $\text{FeO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ ) are based on the oxidizing nature of  $\text{MnO}_2$ . The latter oxidizes conc.  $\text{HCl}$  to chlorine, ferrous sulphate to ferric sulphate and oxalic acid (in acid medium) to water and carbon dioxide.

### Concentrated HCl method

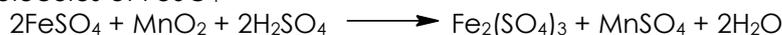
In this method a known amount of pyrolusite material is heated with conc.  $\text{HCl}$  in a flask fitted with an exit tube for the evolution of  $\text{Cl}_2$  gas which is allowed to pass through a  $\text{KI}$  solution. The liberated in this manner is then titrated against standard sodium thiosulphate solution using starch as an indicator.

One mole of  $\text{MnO}_2$  liberates one mole of iodine.



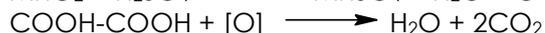
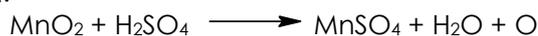
### Ferrous sulphate method

In this method, a known amount of pyrolusite is heated in a flask with excess of standard ferrous sulphate solution acidified with sulphuric acid. The amount of unreacted ferrous sulphate is determined by standard  $\text{KMnO}_4$  solution. One molecule of  $\text{KMnO}_4$  oxidizes two molecules of  $\text{FeSO}_4$



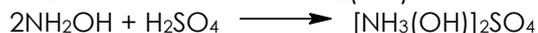
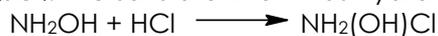
### Oxalic acid method

In this method, known weight of pyrolusite is treated in a flask with excess of standard solution of oxalic acid acidified with sulphuric acid. The contents are boiled so that the reaction is complete. A part of oxalic acid is oxidized to water and  $\text{CO}_2$  by  $\text{MnO}_2$  and the unreacted amount of oxalic acid is determined by titrating against standard solution of  $\text{KMnO}_4$ .



### Hydroxylamine

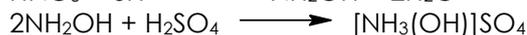
Hydroxylamine ( $\text{NH}_2\text{OH}$ ), an unstable monoacid base may be regarded as  $\text{NH}_3$ , in which one hydrogen atom has been replaced by  $-\text{OH}$  group. It forms stable salts with  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$ . The salts are known as hydroxylammonium salts.



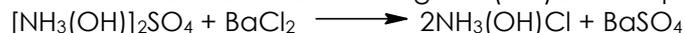
### Electrolytic method

Electrolytically hydroxylamine may be prepared by electrolysis of 50%  $\text{H}_2\text{SO}_4$ . The electrolysis is carried out in a divided diaphragm cell which consists of cylindrical lead anode separated by an asbestose cement pot from the amalgamated lead beaker acting as cathode. The whole cell is kept in an outer big vessel containing ice. The lead anode is also kept cooled. The anode compartment is within the diaphragm and the cathode compartment (provided with an outlet tap for removing hydroxylamine sulphate) is outside the diaphragm. 50%  $\text{H}_2\text{SO}_4$  is kept as an electrolyte in both the compartment.

As the current is allowed to pass, 50%  $\text{HNO}_3$  solution is added simultaneously and drop by drop in the cathode compartment. As a result of electrolysis of aqueous acid, nascent hydrogen is at once reduced to hydroxylamine. The latter with  $\text{H}_2\text{SO}_4$  to form hydroxylamminium sulphate in solution.



The hydroxylamminium sulphate solution is taken out from the cathode compartment through the exit of outlet pipe and treated with barium chloride, whereby precipitate of  $\text{BaSO}_4$  is formed. The solution containing  $\text{NH}_3(\text{OH})\text{Cl}$  is evaporated and crystallized.



Free anhydrous hydroxylamine in laboratory can be prepared by adding solution of sodium methoxide in methyl alcohol to a solution of hydroxylamine chloride in methyl alcohol. Good results are obtained if the two solutions are treated under reduced pressure. The precipitated  $\text{NaCl}$  is filtered off and the excess of alcohol is removed by distillation at 44mm Hg (reduced pressure).  $\text{CH}_3\text{OH}$  distils first and then solution of  $\text{NH}_2\text{OH}$  which is then cooled to  $11^\circ\text{C}$  as a result of which hydroxylamine crystallizes out.



### By Product

Today hydroxylamine is obtained as a byproduct in the manufacture of acetic acid from ethane present in natural gas. Ethane is nitrated in the vapour phase by nitrogen dioxide and the resulting nitroethane is treated with 80%  $\text{H}_2\text{SO}_4$



The reduction may also be carried out by nascent hydrogen produced by the action of  $\text{HCl}$  (sp. gr. 1.12) on granulated tin.



### Properties

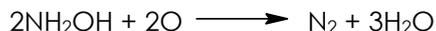
At room temperature pure  $\text{NH}_2\text{OH}$  forms colourless, odourless and deliquescent crystals (sp. Gr. 1.35, m.p.  $33^\circ\text{C}$ ) soluble in alcohol or water.

Hydroxylamine is extremely unstable and slowly decomposes liberating  $\text{N}_2$ ,  $\text{NO}$  and  $\text{NH}_3$  in aqueous solution, it is a proton acceptor.



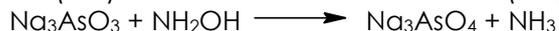
### Reducing Action

$\text{NH}_2\text{OH}$  and its salts are powerful reducing agents. For example, they reduce cuprous oxide ( $\text{Cu}_2\text{O}$ ) from alkaline copper solution (Fehling solution), ferric salts to ferrous salts in acid solution and iodine to iodide ion in alkaline medium.



### Oxidation Action

It oxidise quantitatively the ferrous hydroxide to ferric hydroxide and sodium arsenite to sodium arsenate.



In the above reaction  $\text{NH}_2\text{OH}$  also reduces to  $\text{NH}_3$ .

### Uses

Hydroxylamine is used as a reducing agent as a reagent to form oximes (aldoximes, ketoximes) and to form explosives. The latter prepared by the action of anhydrous  $\text{NH}_2\text{OH}$  on  $\text{Ca}(\text{OH})_2$  or  $\text{Ca}$ .

The resulting compounds explode on heating.



Hydroxylamine itself may also be used as an explosive, because explodes at  $60\text{-}70^\circ\text{C}$  in vapour form) in contact with air.

