CY 8292 - Chemistry for Technologists

UNIT IV ; Chemicals and Auxiliaries

(1) Discuss the preparation, properties and uses of bleaching powder.

Manufacture

Calcium hypochlorite is manufactured by the action of Cl_2 on dry slaked lime, $Ca(OH)_2$.

$$2Ca(OH)_2 + 2Cl_2 \longrightarrow 2Ca(ClO)Cl + 2H_2O$$

(or)

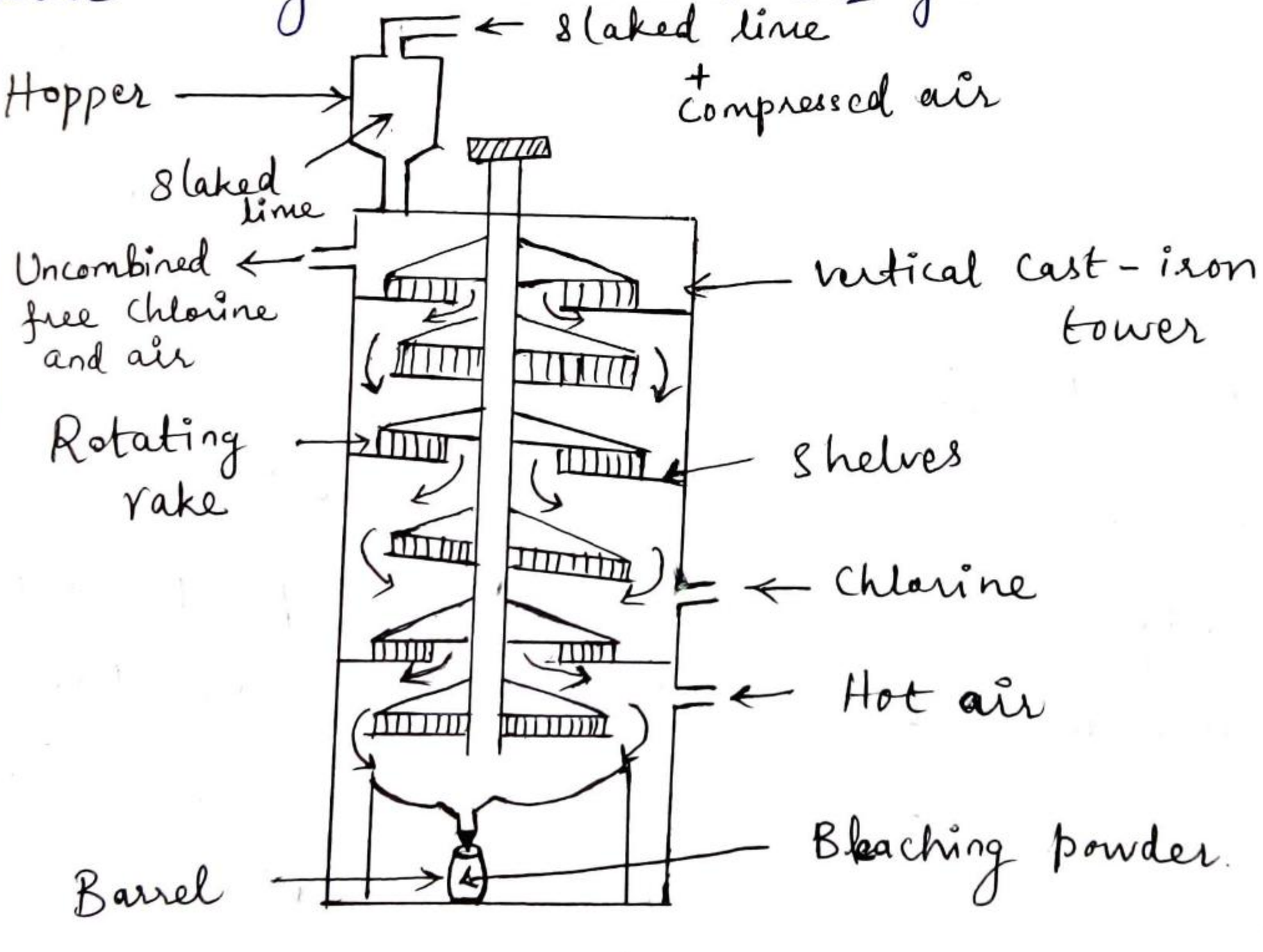
$$Ca(OH)_2 + Cl_2 \longrightarrow Ca(ClO)Cl + H_2O$$

Beckmann's plant (modern process)

⇒ The Beckmann's plant consists of a long Chlorinating tower, made up of cast iron. There are two inlet pipes, near the bottom of the tower, one for passing Cl_2 gas and the other for passing current of hot air. There is one outlet near the top of the tower, through which the unreacted Cl_2 and waste gases (air) go out. Inside the tower, it is provided with number of trays, each tray contains rotating rake.

⇒ One hopper is provided at the top of tower,

through which dry slaked lime is slowly added into the tower. Hot air and Cl_2 gas are also being passed in from the bottom of the tower. As the trays rotate, slake lime moves down and it meets the up coming Cl_2 gas. $Ca(OH)_2$ reacts with Cl_2 gas to form $CaOCl_2$, which collects in the vessel placed at the bottom of the tower. Hot air is introduced to drive away the unreacted to drive away the unreated Cl_2 gas.



Oxidising and bleaching properties

⇒ Calcium hypochlorite liberates nascent oxygen in presence of small amount of dilute acids.

$$2\,CaOCl_2 + H_2SO_4 \longrightarrow CaCl_2 + CaSO_4 + 2HCl + 2[O]$$

nascent Oxygen

⇒ The liberation of nascent oxygen shows that, $CaOCl_2$ exhibit oxidising as well as bleaching properties.

Oxidising properties

As we said above, $CaOCl_2$ oxidises various substances in presence of dilute acids. When $CaOCl_2$ oxidises a certain substance, its hypochlorite ion (ClO^-) is reduced to Cl^- ion.

$$ClO^{\ominus} + 2e^- + 2H^+ \longrightarrow Cl^- + H_2O$$

$(Cl = +1)$ $\qquad$ $(Cl = -1)$

Examples:

(i) Oxidation of KI solution in presence of CH_3COOH or HCl to I_2 by $Ca(ClO)Cl$.

$$Ca(ClO)Cl + 2KI + 2HCl \longrightarrow 2KCl + I_2 + H_2O + CaCl_2$$

$$Ca(ClO)Cl + 2KI + 2CH_3COOH \rightarrow 2KCl + I_2 + H_2O + Ca(CH_3COO)_2$$

(ii) Oxidation of Na_3AsO_3 to Na_3AsO_4 by $Ca(ClO)Cl$

$$Na_3AsO_3 + Ca(ClO)Cl \longrightarrow Na_3AsO_4 + CaCl_2$$

(or)

$$AsO_3^{3-} + ClO^- \longrightarrow AsO_4^{3-} + Cl^-$$

iii) Oxidation of pbO to pbO_2 and MnO to MnO_2

$$MO + Ca(Clo)Cl \longrightarrow MO_2 + CaCl_2$$

(or)

$$MO + ClO^- \longrightarrow MO_2 + Cl^-$$

$\therefore (M = pb, Mn)$

(iv) Oxidation of H_2S to sulphur.

$$Ca(Clo)Cl + H_2S \longrightarrow CaCl_2 + H_2O + S$$

(or)

$$ClO^- + H_2S \longrightarrow Cl^- + H_2O + S$$

(v) Oxidation of NH_3 to N_2

$$3\,Ca(Clo)Cl + 2NH_3 \longrightarrow 3\,CaCl_2 + 3H_2O + N_2$$

(or)

$$3\,ClO^- + 2NH_3 \longrightarrow 3Cl^- + 3H_2O + N_2$$

Bleaching properties

Nascent oxygen produced by the action of little amount of dilute acids on calcium hypochlorite converts the coloured matter into Colourless matter.

Coloured matter + [O] ⟶ Colourless matter.

Thus, the calcium hypochlorite also shows bleaching properties. It is effective only in acidic medium.

Uses

1.) Bleaching of cotton clothes

In textile industry, cotton clothes are mainly bleached with the help of $CaOCl_2$.

$$CaOCl_2 + HCl \longrightarrow CaCl_2 + HCl + [O]$$

(or)

$$CaOCl_2 + 2HCl \longrightarrow CaCl_2 + H_2O + Cl_2$$

Nascent oxygen produces above bleaches the cloth.

2) It acts as a disinfectant, germicide and an oxidising agent.

3.) Chloroform ($CHCl_3$) is manufactured by the interaction of $CaOCl_2$ + acetone + ethyl alcohol.

4) It is also used for making wool unshrinkable.

(2) I) How the strength of H_2O_2 is prepared ?

II) How ClO_2 is prepared in the laboratory ?

I) strength of Hydrogen peroxide (H_2O_2)

principle :

Hydrogen peroxide reacts with excess potassium iodide in the presence of an ammonium molybdate catalyst to produce tri iodide ions, which are further titrated with standard thiosulphate solution.

$$H_2O_2 + 2KI + H_2SO_4 \longrightarrow I_2 + K_2SO_4 + 2H_2O$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI.$$

procedure

A. Standardisation of Sodium thiosulphate (0.1N)

20 ml of potassium iodate solution is pipetted out in a clean conical flask. 100 ml of distilled water and mixed well.

Now 25 ml of acid mixture is added to the reaction mixture and waited for 5 minutes. Then it is titrated against sodium thiosulfate solution taken in the burette using starch as an indicator. Disappearance of blue colour is the end point.

* Normality of sodium thiosulphate

$$= \frac{(\_\_ g\ KIO_3) \times (\_\_ ml\ KIO_3)}{(\_\_ ml\ Na_2S_2O_3) \times (35.67\ g.\ Lit.\ eq.)}$$

B. Determination of H_2O_2

⇒ 3 grams of the given sample is taken in a conical flask. 200 ml of distilled water, 20 ml of potassium iodide solution and 25 ml of the acid mixture are added in-to it. The mixture is now shaken well and allowed to stand for five minutes.

⇒ Now the above solution is titrated against Standard sodium thiosulphate solution taken in the burette using starch indicator. The disappearance of blue colour is the end point. Let the volume of sodium thiosulphate be V ml.

Calculation

% of hydrogen peroxide

$$= \frac{\_\_(V)\ ml \times N \times 1.1007}{Sample\ weight.}$$

Where, V ⇒ Volume of thio consumed
N ⇒ Normality of thio.

II) How ClO_2 is prepared in the laboratory?

Preparation:

(i) Chlorine dioxide is prepared, when a mixture of powdered potassium chlorate ($KClO_3$) and Con. H_2SO_4 is heated.

$$3KClO_3 + 3KHSO_4 + HClO_4 + H_2O + 2ClO_2$$

(ii) ClO_2 is obtained when $KClO_3$ is treated with oxalic acid ($H_2C_2O_4$).

$$2KClO_3 + 2H_2C_2O_4 \longrightarrow K_2C_2O_4 + 2CO_2 + 2H_2O + 2ClO_2.$$

(iii) ClO_2 is obtained when dry Cl_2 is passed over $AgClO_3$ heated to 90°C.

$$Cl_2 + AgClO_3 \longrightarrow AgCl + O_2 + Cl_2O.$$

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3) Explain with reaction about the production of H_2O_2 in industries. [Refer Q. No. 1]

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4) Determine the strength of available chlorine in the hypochlorite bleach solution.

⇒ Bleach is used as a disinfectant,

because of its ability to oxidise the cell membranes of bacteria. It is also used to remove stains in clothing. The colours of many dyes and stains are due to the presence of multiple (double or triple) bonds in organic molecules.

⇒ The colours of the dye or stain is due to the ability of e^-s in these multiple bonds to absorb and emit electromagnetic radiation in the visible region of the electromagnetic Spetrum.

⇒ When the sodium hypochlorite in bleach comes in contact with these organic molecule it oxidizes them forming new products. The new products no longer have multiple bonds, so the colour of the dye or Strain looks white.

principle:

⇒ The percentage 'available Chlorine' is used to denote the strength of bleaching agent. It is the ratio of the mass of Cl_2 to the mass of the bleach mixture.

⇒ So available Chlorine is defined as the percentage of Chlorine made available by the

the material (bleaching powder, sodium hypochlorite) when treated with dilute acids.

⇒ The available chlorine present in hypochlorite bleach liquor is determined iodometrically by treating it with an excess of KI solution and 10 ml of dil. H_2SO_4 are added. The liberated I_2 is titrated with Hypo solution using Freshly prepared Starch Solution.

Procedure:

⇒ The given hypochlorite bleaching liquor is transferred in a 100ml standard flask and made upto the mark using distilled water.

⇒ Now 20 ml of the above prepared solution is pipetted out in a conical flask. 10 ml of 10% KI Solution and 10 ml of dil. H_2SO_4 are added. The liberated I_2 is titrated against standard hypo solution using starch indicator. The end point is the disappearance of blue colour. The above titration is repeated 2-3 times so as to get the concordant values.

Calculations

(i) Normality of hypochlorite bleach liquor.

$$V_1N_1 = V_2N_2$$

$$20 \times N_1 = 20 \times 0.10$$

$$N_1 = \frac{20 \times 0.10}{20}$$

$$N_1 = 0.10\ N$$

$V_1 \rightarrow$ volume of bleach
$N_1 \rightarrow$ Normality of bleach
$V_2 \rightarrow$ volume of hypo solution
$N_2 \Rightarrow$ Normality of hypo solution.

(ii) Amount of Chlorine present in 1 litre of the solution.

$= N_1 \times$ eq. wt. of Chlorine

iii) Amount of Chlorine present in 100 ml of the solution.

$$\% \text{ of available chlorine} = \frac{N_1 \times \text{eq. wt. of Chlorine} \times 100}{1000}$$

$\therefore$ Chlorine content should be 35-40%. in a bleach liquor.

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(5) I) Discuss the manufacturing process of H_2O_2 and NaOCl,

II) Discuss the advantages of H_2O_2 compared to other bleaching agents.

Manufacture process of H_2O_2 (Refer Q. No. 1)

Manufacture process of NaOCl

$\Rightarrow$ Sodium hypochlorite (NaOCl) is prepared

by the electrolysis of a solution of NaCl at 24°C. Sodium hydroxide (Liberated at the cathode) reacts with chlorine (liberated at anode) to give sodium hypochlorite.

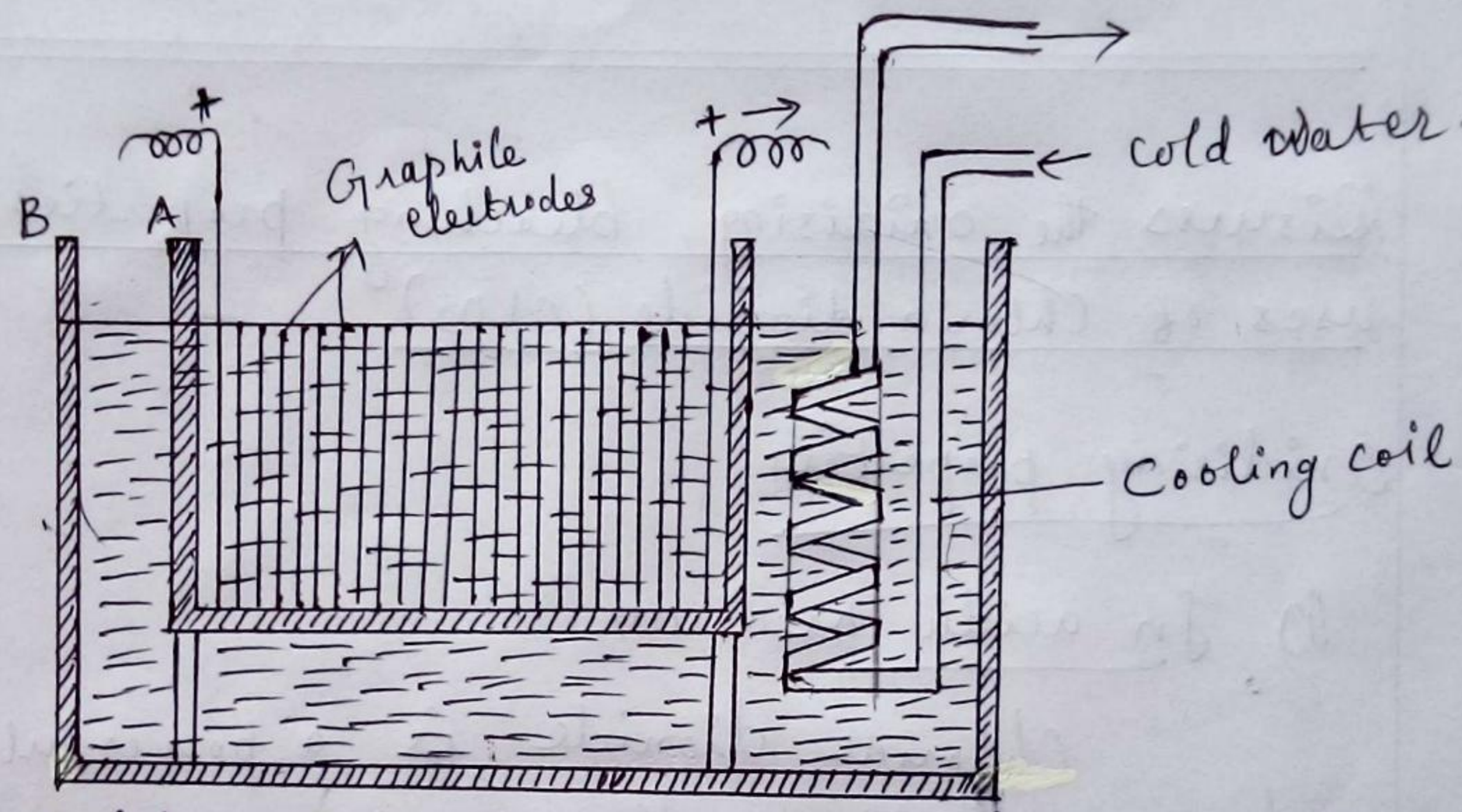
$$2NaOH + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$$

⇒ This cell consist of two semiporcelain rectangular vessels A and B, one placed inside the other. Nearly 30 graphite electrodes are placed inside the inner small vessel A as shown in the figure. These electrodes are close to one another, joined in series. The extreme electrodes are connected with the positive and negative terminals of a power supply.

⇒ The inner vessel A is placed in the outer big vessel B containing pure NaCl solution, so that the two vessels are almost completely filled up with the solution of NaCl. Cold water is circulated (to maintain temperature below 24°C) through a cooling coil immersed in the big vessel B.

⇒ On passing electric current, NaOH and H_2 are formed on the cathodes and Cl_2 is formed at the anode. Since the cell is undivided, NaOH (liberated at cathode) reacts

with Chlorine (liberated at anode) gives a mixture of NaOCl and NaCl (called bleaching mixture). It is effective in alkaline medium.



Electrolytic cell for the preparation of bleaching solutions.

II) Discuss the advantages of H_2O_2 Compared to the other bleaching agent

⇒ H_2O_2 is universal bleaching agent and can be used to bleach cotton, wool, silk, and jute.

⇒ Weight loss is less as Compared to hypochlorite bleaching.

⇒ It is very fast.

⇒ possesses better absorbency.

⇒ Chemical degeadation of cotton is less.

⇒ yellowing tendency after process is less.

(6) Explain the bleaching action of sodium hypochlorite on cotton fibre. [Refer Q. No. 4 & 5I]

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(7) Discuss the onidising, bleaching properties and uses of Chlorin dioxide. (ClO_2) ....

Onidising properties:

(i) In acidic medium

Chlorine dioxide is a powerful onidising agent in acidic medium.

$$ClO_2 + 4H^+ + 5e^- \longrightarrow Cl^- + 2H_2O$$

(ii) In alkalis

ClO_2 in presence of alkalis gives a mixture of chlorite and chlorate.

$$2ClO_2 + 2KOH \longrightarrow KClO_2 + KClO_3 + H_2O$$

(iii) Decomposition

Both liquid and solid ClO_2 are slowly decomposed in dark, but when exposed to light it decomposes rapidly.

$$ClO_2 \longrightarrow ClO + [O]$$

$$2ClO + H_2O \longrightarrow HCl + HClO_3$$

(iv) P, S and many organic compounds spontaneously catch fire in the gaseous ClO_2.

(v) Explosion

ClO_2 liquid explodes above $-40^\circ C$. The gas explodes by an electric spark. on heating it gives Cl_2 and O_2.

$$2ClO_2 \longrightarrow Cl_2 + 2O_2$$

(vi) Action with water

ClO_2 dissolves in water and gives a mixture of chlorous acid ($HClO_2$) and chloric acid ($HClO_3$).

$$2ClO_2 + H_2O \longrightarrow HClO_2 + HClO_3$$

(vii) ClO_2 oxidises phenol to quinone and maleic acid.

2.) Bleaching property

(a) Since ClO_2 is a powerful oxidising and chlorinating agent, large quantities of ClO_2 is used for bleaching wood pulp and cellulose and also for purifying drinking water.

(b) It is 30 times as effective as chlorine in bleaching flour.

(c) It is effective in acidic medium.
