HYDROGEN PEROXIDE

- H_2O_2 was discovered by Thenard.
- H_2O_2 is also known as oxygenated water.
- (O^- - O^-) bond is known as Peroxy bond.
- H_2O_2 is a weak dibasic acid. Its molecular weight is 34 and its equivalent weight is 17.
- Substances containing peroxy linkage are H_2O_2, Na_2O_2, BaO_2, $NaHO_2$, H_2SO_5, $H_2S_2O_8$, HNO_4, H_3PO_5, CrO_5, H_2TiO_4
- Perchloric acid ($HClO_4$), MnO_2, PbO_2, TeO_2, $KMnO_4$ etc are not true peroxides as they do not contain peroxy bond.

Laboratory preparation of H_2O_2:

i) In the laboratory H_2O_2 is prepared by the action of ice cold dil. H_2SO_4 on Na_2O_2 (or) hydrated Barium Peroxide [$BaO_2.8H_2O$].

ii) H_2O_2 can also be obtained by passing CO_2 gas through a suspension of Barium peroxide in water.

- In the preparation of H_2O_2 from BaO_2, phosphoric acid is preferred to dil H_2SO_4. This is because H_3PO_4 stabilizes the formation of H_2O_2.

Auto - oxidation process:

- In auto oxidation method the starting substance is 2 - ethyl anthraquinone.
- 2 - ethyl anthraquinone is reduced to
  2 - ethyl anthraquinol with H_2/Pd.
- On aerial oxidation 2-ethyl anthraquinol gives H_2O_2 and 2-ethyl anthraquinone back.

Electrolytic Method:

- H_2O_2 is manufactured by the electrolysis of 50% H_2SO_4 (or) a mixture of $(NH_4)_2SO_4$ + dil. H_2SO_4 using platinum anode and lead cathode.
- Electrodes are separated by porous stoneware diaphragm.
- The product at anode is $H_2S_2O_8$ and at cathode is H_2 gas.

a) $2H_2SO_4 \xrightarrow{Ionisation} 2H^+ + 2HSO_4^-$

<u>At cathode</u>

$2H^+ + 2e^- \xrightarrow{Reduction} H_2$

<u>At anode</u>

$2HSO_4^- \xrightarrow{Oxidation} H_2S_2O_8 + 2e^-$

b) Peroxy disulphuric acid (Marshall's acid) on distillation gives H_2O_2.

Caro's acid (H_2SO_5) is intermediate product.

$$H_2S_2O_8 + H_2O \rightarrow H_2SO_4 + H_2SO_5 \text{ (Caro's acid)}$$

$$H_2SO_5 + H_2O \rightarrow H_2SO_4 + H_2O_2$$

- During the electrolysis of 50% H_2SO_4, the pH of the solution increases because the concentration of acid decreases.

Concentration of H_2O_2: H_2O_2 obtained above is very dilute and so it is to be concentrated. Hydrogen peroxide is unstable and decomposes easily. If organic impurities are present, they catalyze the decomposition of H_2O_2 which may lead to explosion.

$\therefore$ H_2O_2 solution is concentrated carefully in the following 3 stages.

- The stages present in the concentration of H_2O_2 are

  a) Freezing of water

  b) Evaporation of water

  c) Distillation under reduced pressure

  d) Crystallisation of H_2O_2
- 20 - 30% H_2O_2 is obtained by evaporating dilute H_2O_2 on water bath at reduced pressure, using fractionating column.
- H_2O_2 decomposes below it's boiling point if it is distilled at ordinary pressure therefore, the above 20 - 30% H_2O_2 is distilled at reduced pressure i.e. 15mm Hg (vaccum distillation at 70°C) and 90% H_2O_2 is obtained.
- 100% H_2O_2 is obtained by crystallisation of 90% H_2O_2 by using a freezing mixture of solid CO_2 and diethyl ether. (from this needle shaped crystals of 100% pure H_2O_2 separate out).

Physical properties of H_2O_2:

It is colorless syrupy liquid concentrated H_2O_2 has bluish tinge.

It forms stronger H - bonds than H_2O.

It's B.P is higher and M.P is lower then compared with H_2O.

It is completely miscible with water.

It is feebly acidic and will not blue litmus to red.

- The strength of H_2O_2 can be expressed in

  a) Volumes b) Molarity

  c) Normality

  d) Weight - Volume Percentage
- The volume of O_2 gas at S.T.P. obtained by the decomposition of 1 c.c. of H_2O_2 solution is known as its volume strength. It is denoted by V.

Sample of H_2O_2	% strength (w/v)	Molarity, M	Normality, N
5.6 vol. H_2O_2	1.7% w/v	0.5 M	1 N
11.2 vol. H_2O_2	3.4% w/v	1 M	2 N
22.4 vol. H_2O_2	6.8% w/v	2 M	4 N
10 vol. H_2O_2	3% w/v	0.89 M	1.78 N
100 vol. H_2O_2	30% w/v	8.9 M	17.8 N

- Perhydol is 30% (w/v). Its Morality is 8.9M Normality is 17.8 N and it contains 300g/lit (or) 0.3g/ml.
- On long standing or on heating H_2O_2 undergoes decomposition. The equation for the decomposition of H_2O_2 is

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

- The substances which retard the decomposition of H_2O_2 are Acetanilide, Glycerol, Urea, Alcohol, H_3PO_4, sodium stannate Pyrophosphates etc. They act as negative catalysts. They are known as inhibitors (or) stabilisers.
- Alkalies, silica, MnO_2, metals(Fe Mn), graphite, alumina etc. catalyse the decomposition of H_2O_2
- Dilute aqueous solution of H_2O_2 is fairly stable in acid Medium of alcohol or ester. Alkaline solution of H_2O_2 are selectively not very stable.
- Precautions to be taken in storing H_2O_2.
  a) The glass bottle must have wax coating on the inner side, so that the surface is smooth.
  b) Plastic bottles are preferred to glass bottles. It is because the Na_2O in glass being alkaline, catalyses the decomposition of H_2O_2
  c) A small quantity of acetanilide or urea is added as a stabiliser.
- 90% H_2O_2 is used as an oxidant for rocket fuel with hydrazine.
- The boiling point of H_2O_2 is 152^0C.
- Anhydrous H_2O_2 and dilute solutions of H_2O_2 are neutral to Litmus. They do not turn blue litmus to red colour. But Conc. H_2O_2 turns blue litmus to red colour.
- H_2O_2 exhibits a) Oxidising properties
  b) Reducing properties
  c) Bleaching property
  d) Acidic Property

  It doesn't exhibit dehydrating property.
- H_2O_2 has greater reactivity in basic medium. It is because bases catalyses the decomposition of H_2O_2.
- H_2O_2 is a stronger oxidizing agent and a weaker reducing agent.

- The antiseptic action and the bleaching action of H_2O_2 involve the oxidizing properties

Chemical properties of H_2O_2:

- **Stability:** H_2O_2 is unstable and decomposes easily. $2H_2O_2 \rightarrow 2H_2O + O_2$
  Metals, graphite, MnO_2, silica, alkalies are positive catalysis.
  Urea, Glycerol, acetanilide, alcohol, H_3PO_4, Pyrophosphates are negative catalyses or Inhibitors.
- Acidic nature: Pure H_2O_2 is weak dibasic acid. It gives two types of salts with alkalies.

$$H_2O_2 + NaOH \rightarrow NaHO_2 + H_2O$$

$$H_2O_2 + 2NaOH \rightarrow Na_2O_2 + 2H_2O$$

- During decomposition, H_2O_2 undergoes disproportionation.
- When H_2O_2 acts as an oxidising agent it undergoes reduction.
- The reaction in which H_2O_2 acts as a reducing agent, there will be the liberation of O_2.
- $H_2O_2 \rightarrow 2H^+ + O_2 + 2e^-$ $E^0 = -0.67V$ represents the reducing property of H_2O_2.
- The fundamental equation for oxidising property of H_2O_2 is **$H_2O_2 \rightarrow H_2O + (O)$**
- The oxidising properties of H_2O_2 in both acidic and basic media are due to

acidic medium

H_2O_2 Oxidant → $2H^+ + 2e^- + O_2$ ($E^0 = +1.77v$)

H_2O_2 Oxidant → $O_2 + 2H_2O + 2e^-$ ($E^0 = +0.87v$)

basic medium

- The standard reduction potential values indicate that H_2O_2 is a strong oxidising agent in acidic medium and weak oxidising agent in basic medium.

Oxidising properties of H_2O_2:

H_2O_2

- $\xrightarrow{blackPbS} H_2O + PbSO_4$ white
- $\xrightarrow[FeSO_4+H_2SO_4]{\text{Ferrous salts}} Fe_2(SO_4)_3 + H_2O$
- $\xrightarrow{KI+H_2O} l_2 + KOH$
- $\xrightarrow[\text{Sod.sulphite}]{Na_2SO_3} H_2O + Na_2SO_4$
- $\xrightarrow[\text{Pot.Nitrite}]{KNO_2} H_2O + KNO_3$
- $\xrightarrow[\text{sod. Arsenite}]{Na_3AsO_3} H_2O + Na_3AsO_4$
- $\xrightarrow[\text{pot.Ferrocyanide}]{K_4[Fe(CN)_6]} H_2O + K_3[Fe(CN)_6]$

potassium ferri-cyanide

$$\xrightarrow[(\text{or})chromicacid]{\text{acidified } K_2Cr_2O_7} \text{blue coloured } CrO_5 \text{ in ether}$$

$$\xrightarrow[\text{alkaline pyrogallol}]{HCHO} HCOOH + H_2\uparrow$$

$$\xrightarrow{C_6H_6/FeSO_4} C_6H_5OH + H_2O$$

- The bleaching action of H_2O_2 is due to its oxidising nature. **$H_2O_2 \rightarrow H_2O + (O)$**
- H_2O_2 is used to bleach silk, wool, ivory and hair.
- H_2O_2 is used to bleach black hair to golden yellow colour under the common name Auricome.
- The fundamental equation for reducing property of H_2O_2 is

  $H_2O_2 + (O) \rightarrow H_2O + O_2$
- In both acidic and basic media, H_2O_2 shows reducing properties as

$$H_2O_2 \xrightarrow[(\text{acidic})]{(\text{oxidation})} O_2 + 2H^+ + 2e^-(E° = -0.67V)$$

$$2OH^- + H_2O_2 \xrightarrow[(\text{basic})]{(\text{oxidation})} O_2 + 2H_2O + 2e^-$$

$$(E° = +0.08V)$$

The reducing properties of H_2O_2 are

H_2O_2 →
- acidified $KMnO_4$ → $Mn^{2+} + O_2$
- Cl_2 → $HCl + O_2$
- Br_2 → $HBr + O_2$
- moist Ag_2O → $Ag + O_2$
- alkaline $K_3[Fe(CN)_6]$ → $K_4[Fe(CN)_6] + O_2$ (pot Ferrocyanide)
- NaOCl → $NaCl + O_2$
- NaOBr → $NaBr + O_2$
- PbO_2 → $PbO + O_2$
- acidified MnO_2 (black) → $Mn^{2+} + O_2$
- alkaline Fe^{3+} (Ferricsalts) → Fe^{2+} (Ferrous) $+ O_2$
- O_3 (disproportionation) → $O_2 + H_2O$

Formation of addition compounds:

It forms addition compounds with some organic and inorganic compounds.

On adding H_2O, these addition compounds give back H_2O_2.

i) $H_2O_2.Na_2HPO_4$

ii) $H_2O_2.(NH_4)_2\ SO_4$

iii) $H_2O_2.(NH_2)_2\ CO$ (Hyperol)

Tests for H_2O_2:

i) H_2O_2 oxidises acidified $K_2Cr_2\ O_7$ solution to blue CrO_5 in ether.

ii) H_2O_2 turns acidifed TiO_2 solution to orange coloured pertitanic acid $[H_2TiO_4]$

iii) H_2O_2 turns starch - Iodide paper to blue colour.

iv) It decolorises $KMnO_4$ in acid medium.

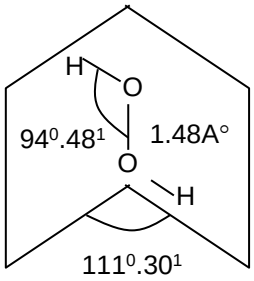
- Bleaching property : It's bleaching action is due to it's oxidising nature.

$$H_2O_2 \rightarrow H_2O + \text{'O'}$$

$$\text{'O'} + \text{color} \rightarrow \text{colorless}$$

- Disinfectant action: It's antiseptic properties are also due to its oxidising behaviour.

- The structure of H_2O_2. in **gaseous state** can be shown as:



Open book structure of H_2O_2

The H – O – O bond angle is $94^o\ 48^1$

- The dihedral angle is 111^o30^1
- The O - O bond length is $1.48A^o$ and the O - H is $0.97A^o$
- In liquid and solid states the bond lengths and bond angles are slightly changed due to hydrogen bonding.
- In crystalline H_2O_2 the dihedral angle is reduced to 90^0

Uses Of H_2O_2:

As disinfectant and germicide

In cleaning of wounds

As bleaching agent for textiles, silk, wool, wood pulp etc.

Mixture of H_2O_2 and hydrazine is used as rocket fuel.

To restore color of old oil paints

As Oxidising agent

Mixture of H_2O_2 and NH_3 solution is used to bleach humain hair into golden yellow color.