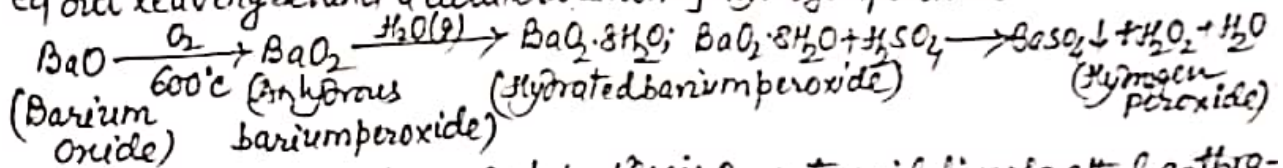


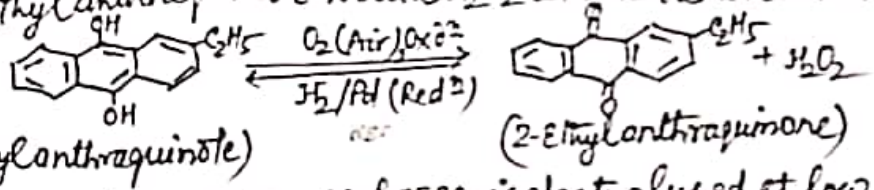
→ Hydrogen peroxide:

Hydrogen peroxide (H_2O_2) is also known as 'oxygenated water'.

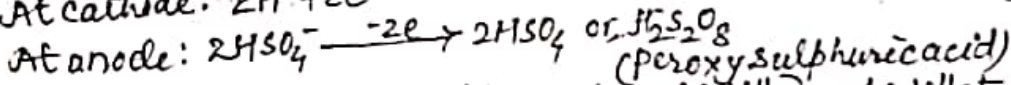
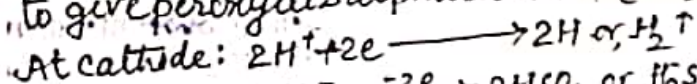
* Preparation: 1. Laboratory method: H_2O_2 is prepared in the laboratory by the action of dilute mineral acid (e.g. H_2SO_4) on metallic peroxides preferably barium peroxide (BaO_2) as follows: When barium oxide (BaO) is heated in air at $600^\circ C$, anhydrous barium peroxide is formed. This is converted into creamy hydrated barium peroxide with the help of steam. It is then added to an ice cold dilute H_2SO_4 . The solution is kept well stirred all along when white $BaSO_4$ precipitated out leaving behind a dilute solution of hydrogen peroxide.



2. Commercial method/ Large scale prepⁿ: (i) By auto-oxidation of 2-ethyl anthraquinol: This is recent method for manufacture of H_2O_2 . In this method, air is passed through 10% solution of 2-ethyl anthraquinol in a mixture of benzene and higher alcohol ($C_{11}H_{23}OH$). The resulting solution (2-ethyl anthraquinone) is then reduced by passing H_2/Pd under a pressure of 1-3 atmosphere at $4^\circ C$. This gives back 2-ethyl anthraquinol. Dilute H_2O_2 obtained is concentrated by usual methods.

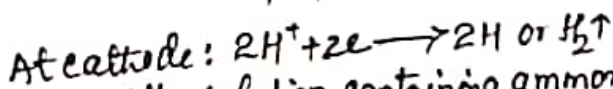
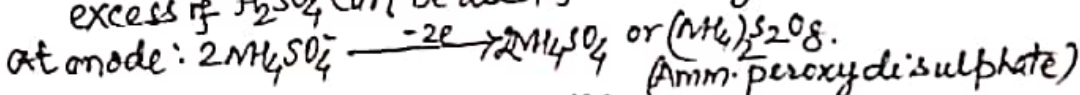


(ii) Electrolytic method: In this method, 50% H_2SO_4 is electrolysed at low temperature using platinum electrodes and a current of high density to give peroxydisulphuric acid ($H_2S_2O_8$). $2H_2SO_4 \xrightarrow[\text{Current (Electrolysis)}]{\text{Electric}}$ $2H^+ + 2HSO_4^-$

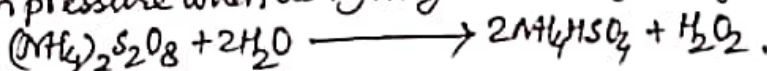


Peroxy sulphuric acid ($H_2S_2O_8$) is distilled, a distillate (30% H_2O_2) is obtained. $H_2S_2O_8 + H_2O \xrightarrow{\text{hydrolysis}} 2H_2SO_4 + H_2O_2$ (sulphuric acid)

* In place of 50% H_2SO_4 , ammonium hydrogen sulphate dissolved in excess of H_2SO_4 can be used for electrolysis. $NH_4HSO_4 \rightleftharpoons NH_4SO_4 + H^+$



The solution containing ammonium peroxydisulphate is heated at 43 mm pressure when its hydrolysis occurs forming H_2O_2 .

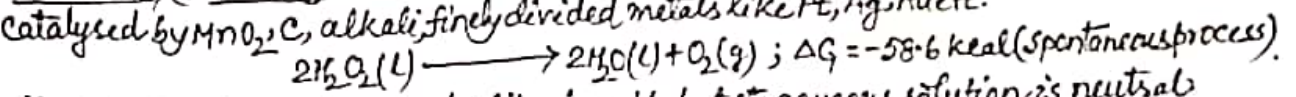


(2)

- * Concentration of H_2O_2 solution: The dilute (30%) H_2O_2 solution obtained commercially is concentrated as follows: (i) The dilute (30%) H_2O_2 solution is heated in a smooth platinum or porcelain vessel to $70^\circ C$, when 66% H_2O_2 is obtained.
 (ii) 66% H_2O_2 is then evaporated over concentrated H_2SO_4 in vacuum desiccator kept in a freezing mixture when 95% H_2O_2 is formed.
 (iii) This H_2O_2 is further purified by adding a piece of solid CO_2 to it when H_2O_2 crystallise out. The crystals are separated and distilled in vacuum under reduced pressure when 100% (approx) pure H_2O_2 is obtained.

- * Properties: Physical (i) Pure anhydrous H_2O_2 is pale blue syrupy liquid (density $1.47 g/ml$)
 (ii) Its freezing point is $-0.89^\circ C$ and boiling point is $85^\circ C$ at 61 mm pressure.
 (iii) It is soluble in water, alcohol & ether (iv) It is bitter taste liquid & injurious to skin.
 (v) Its dielectric constant is high (20), so it & its aqueous solution are an excellent electrolytic solvent.

- * Chemical (i) Stability: It is thermodynamically unstable. It decomposes on heating, which is catalysed by MnO_2 , C, alkali, finely divided metals like Pt, Ag, Au etc.



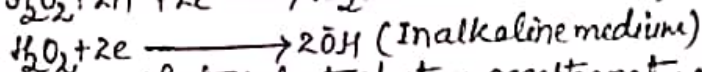
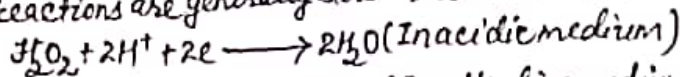
- (ii) Acidic property: It is weak dibasic acid, but its aqueous solution is neutral.

$$H_2O_2 \rightleftharpoons H^+ + HO_2^- \quad (K_a = 1.5 \times 10^{-12} \text{ at } 20^\circ C)$$

$$2NaOH + H_2O_2 \longrightarrow Na_2O_2 + 2H_2O$$
 (Sodium peroxide)
 It liberates CO_2 gas from Na_2CO_3 .

$$Na_2CO_3 + H_2O_2 \longrightarrow Na_2O_2 + H_2O + CO_2 \uparrow$$

- (iii) Oxidising property: It is strong oxidising agent in acidic as well as alkaline medium. The reactions are generally slow in acidic medium, but fast in alkaline medium.

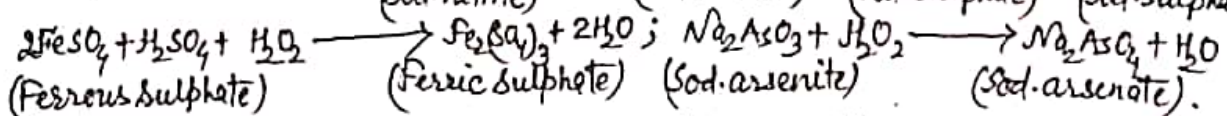


Its oxidising property is due to electron acceptor nature or nascent oxygen obtained by its decomposition.

$$H_2O_2 \longrightarrow H_2O + O \text{ (Nascent oxygen)}$$

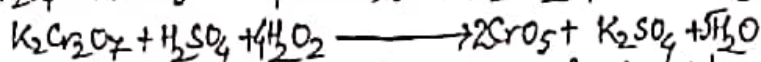
- (a) It oxidises metal sulphide into sulphate. e.g. $PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$
 lead(II) sulphide: lead(II) sulphate (white)

- (b) It oxidises nitrite into nitrate, sulphite into sulphate, arsenite into arsenate, ferrous salt into ferric salt etc. e.g. $NaNO_2 + H_2O_2 \longrightarrow NaNO_3 + H_2O$; $Na_2SO_3 + H_2O_2 \longrightarrow Na_2SO_4 + H_2O$
 (Sod. nitrite) (Sod. nitrate) (Sod. sulphite) (Sod. sulphate)

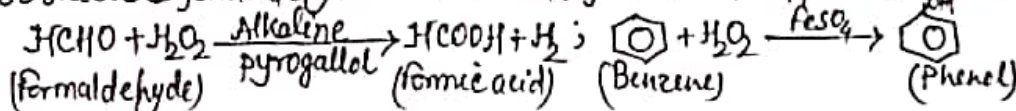


- (c) It oxidises KI into I_2 , H_2S into S etc. $H_2S + H_2O_2 \longrightarrow 2H_2O + S$; $2KI + H_2O_2 \longrightarrow 2KOH + I_2$

- (d) It oxidises acidified potassium ferrocyanide into potassium ferricyanide, acidified $K_2Cr_2O_7$ into CrO_5 . $2K_4[Fe(CN)_6] + H_2O_2 + H_2SO_4 \longrightarrow 2K_3[Fe(CN)_6] + K_2SO_4 + 2H_2O$

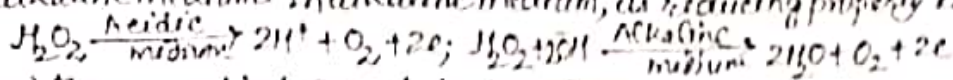


- (e) It oxidises formaldehyde & benzene into formic acid and phenol respectively.

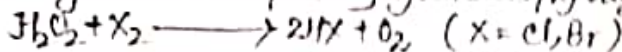


(3)

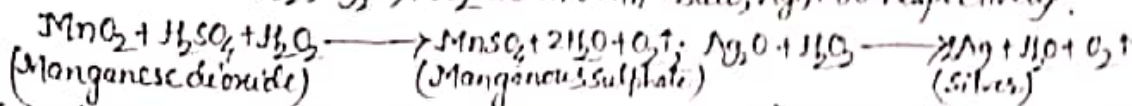
(iv) Reducing property: It acts as a reducing agent when it reacts with other oxidising agents in acidic or alkaline medium. In alkaline medium, its reducing property is more pronounced.



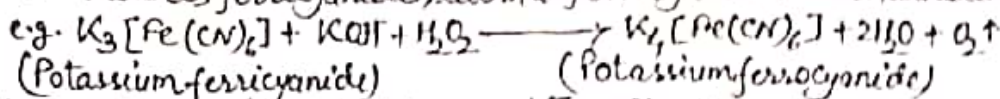
(a) It reduces halogens into corresponding hydroacids/hydrohalic acids.



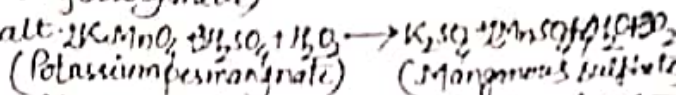
(b) It reduces MnO_2 , Ag_2O , PbO_2 etc. into Mn^{2+} salt, Ag , PbO respectively.



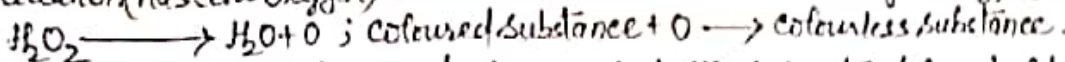
(c) It reduces ferricyanide salt into ferrocyanide salt in alkaline medium.



(d) It reduces acidified $KMnO_4$ into Mn^{2+} salt.



(v) Bleaching property: It acts as a mild bleaching agent. Its bleaching property is due to oxidation (nascent oxygen). It bleaches delicate materials e.g. ivory, cotton, wool, silk etc.



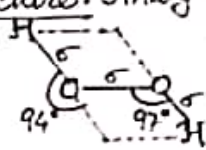
* USES: (i) As an oxidising & reducing agents in the laboratory/chemical processes.

(ii) As bleaching agent for wool, silk, cotton, ivory etc. materials.

(iii) As an antiseptic & germicide for washing wounds, teeth and ears.

(iv) As a concentrated source of O_2 required to ignite liquid fuel in jet & rocket engines.

* Structure: Analytical and spectral data suggest following structure of H_2O_2 .



Bonds O-O, O-H are single covalent (σ) bonds. Two O-H bond lie in different planes cross to each other.

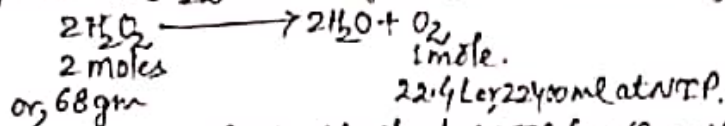
Bond lengths: O-O is $1.48 \pm 0.02 \text{ \AA}$, O-H is $1.01 \pm 0.03 \text{ \AA}$

Bond angle: $\angle HOO = 94^\circ$; Angle between two planes containing

H-atom (i.e. O-H bond) = 94° . Shape: open book

* Strength of H_2O_2 solution: The strength of H_2O_2 solution is expressed in terms of the volume of O_2 gas evolved at NTP. The volume of O_2 evolved at NTP on decomposition/heating one volume of H_2O_2 solution is called volume strength of H_2O_2 . For example, 10 volume H_2O_2 means, one volume of H_2O_2 solution gives/evolves 10 volumes of O_2 at NTP.

Sometimes, the concentration of H_2O_2 in a solution is expressed as % of H_2O_2 i.e. gm/100ml. Thus, 10% H_2O_2 means that 10 gm H_2O_2 is present in 100 ml of solution. 10 volume H_2O_2 solution is 3.035% solution of H_2O_2 i.e. 3.035 gm H_2O_2 present in 100 ml of the solution, calculated as follows:



\therefore 22400 ml of O_2 is obtained/evolved at NTP from 68 gm of H_2O_2

\therefore 10 ml " " " " $\frac{68}{22400} \times 10 = 0.03035 \text{ gm } H_2O_2$.

\therefore 1 ml of H_2O_2 solution contains 0.03035 gm H_2O_2 (By definition of volume strength of H_2O_2)

\therefore 100 ml " " $0.03035 \times 100 = 3.035 \text{ gm } H_2O_2$.

In normality (N), strength of H_2O_2 is calculated as follows: $2H_2O_2 \longrightarrow 2H_2O + O_2 \uparrow$
Equivalent weight of $H_2O_2 = \frac{68}{32} \times 2 = 17$; $32 \text{ gm } \rightarrow 22.4 \text{ L at NTP}$

No. of gm equivalent in 10 volume of H_2O_2 solution = $\frac{\text{Conc. (gm/L)}}{\text{Eq. wt.}} = \frac{30.35}{17} = 1.785$.

\therefore strength of H_2O_2 solution in normality = 1.785.