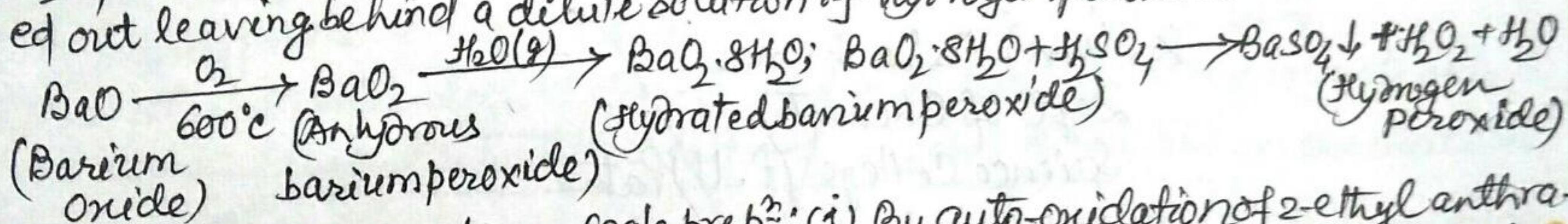


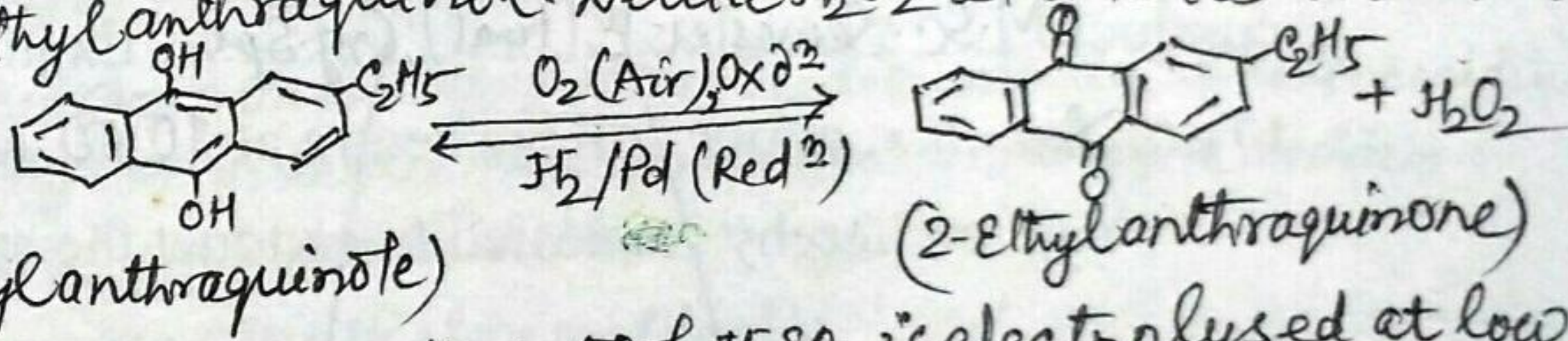
⇒ Hydrogen peroxide:

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

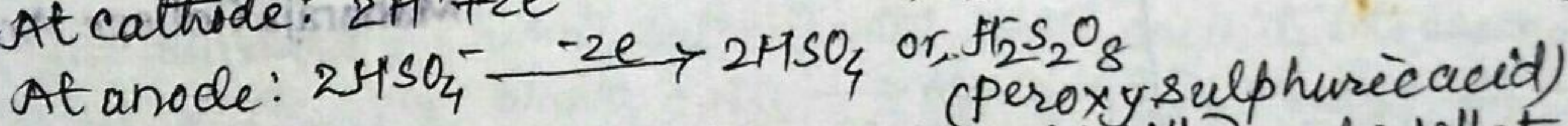
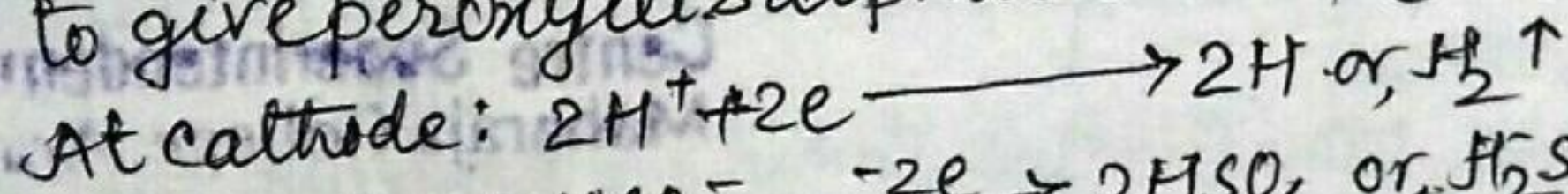
\* Preparation: 1. Laboratory method:  $H_2O_2$  is prepared in the laboratory by the action of dilute mineral acid (e.g.  $H_2SO_4$ ) on metallic peroxides preferably barium peroxide ( $BaO_2$ ) as follows: When barium oxide ( $BaO$ ) is heated in air at  $600^\circ C$ , anhydrous barium peroxide is 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 prep<sup>n</sup>: (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 method.

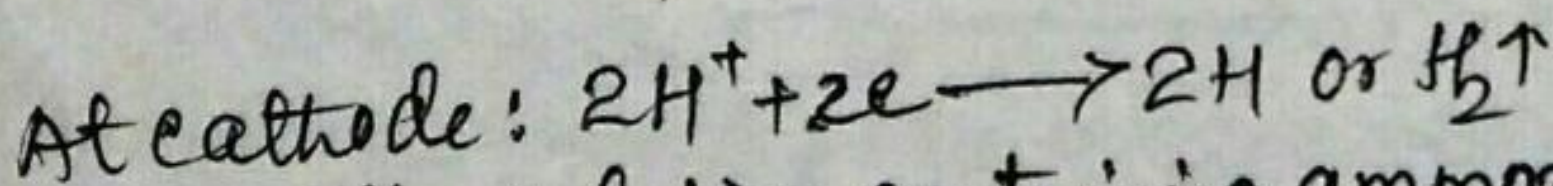
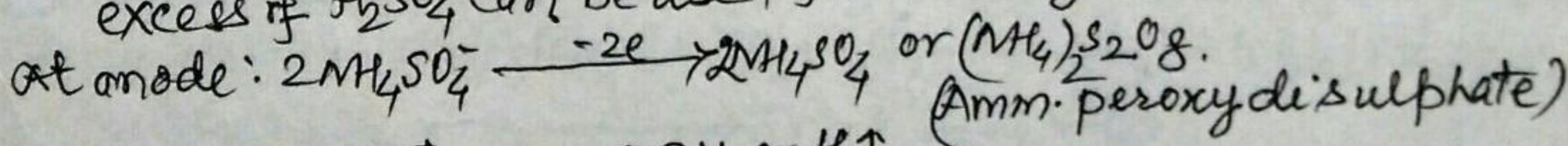


(ii) Electrolytic method: In this method, 50%  $H_2SO_4$  is electrolysed at low temperature using platinum electrodes and a current of high density to give peroxydisulphuric acid ( $H_2S_2O_8$ ).  $2H_2SO_4 \xrightarrow[\text{Current (Electrolysis)}]{\text{Electric}}$   $2H^+ + 2HSO_4^-$

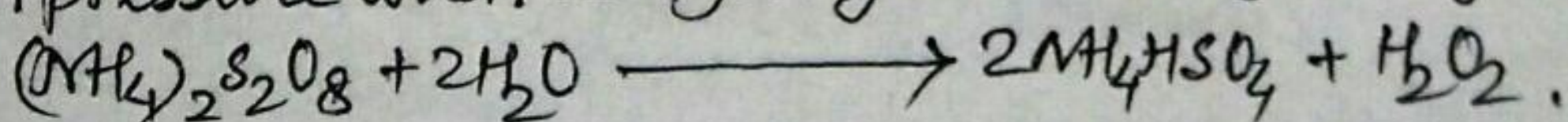


Peroxy sulphuric acid ( $H_2S_2O_8$ ) is distilled, a distillate (30%  $H_2O_2$ ) is obtained.  $H_2S_2O_8 + H_2O \xrightarrow{\text{hydrolysis}} 2H_2SO_4 + H_2O_2$  (sulphuric acid)

\* In place of 50%  $H_2SO_4$ , ammonium hydrogen sulphate dissolved in excess of  $H_2SO_4$  can be used for electrolysis.  $NH_4HSO_4 \rightleftharpoons NH_4^+ + HSO_4^-$



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



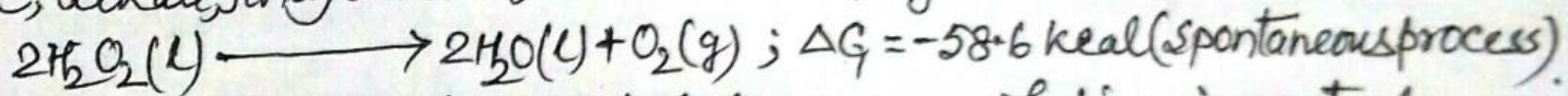


(2)

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  $H_2O_2$  obtained.

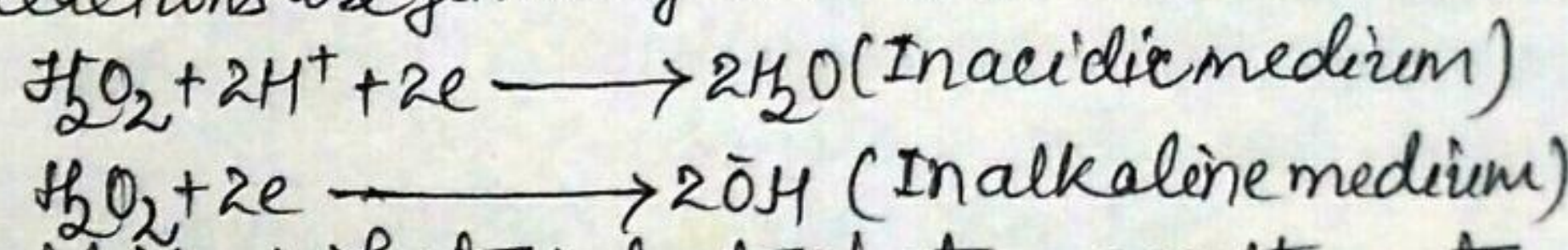
\* Properties: Physical (i) Pure anhydrous  $H_2O_2$  is pale blue syrupy liquid (density  $1.47 gm/ml$ ) (ii) Its freezing point is  $-0.89^\circ C$  and boiling point is  $85^\circ C$  at 61 mm pressure. (iii) It is soluble in water, alcohol & ether (iv) It is bitter taste liquid & injurious to skin. (v) Its dielectric constant is high (120), so it & its aqueous solution are an excellent electrolytic solvent.

\* Chemical (i) Stability: It is thermodynamically unstable. It decomposes on heating, which 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  
 $H_2O_2 \rightleftharpoons H^+ + HO_2^-$  ( $K_a = 1.5 \times 10^{-12}$  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.



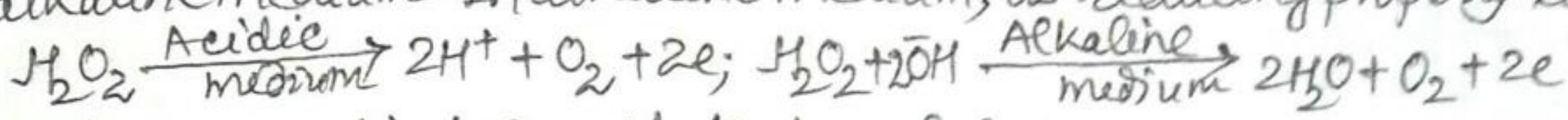
Its oxidising property is due to electron acceptor nature or nascent oxygen obtained by its decomposition.  
 $H_2O_2 \longrightarrow H_2O + O$  (Nascent oxygen)

- (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)
- $2FeSO_4 + H_2SO_4 + H_2O_2 \longrightarrow Fe_2(SO_4)_3 + 2H_2O$ ;  $Na_2AsO_3 + H_2O_2 \longrightarrow Na_2AsO_4 + H_2O$   
 (Ferrous sulphate)                      (Ferric sulphate)                      (Sod. arsenite)                      (Sod. arsenate).
- (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  $CrO_5$ .  $2K_4[Fe(CN)_6] + H_2O_2 + H_2SO_4 \longrightarrow 2K_3[Fe(CN)_6] + K_2SO_4 + 2H_2O$   
 $K_2Cr_2O_7 + H_2SO_4 + 4H_2O_2 \longrightarrow 2CrO_5 + K_2SO_4 + 5H_2O$

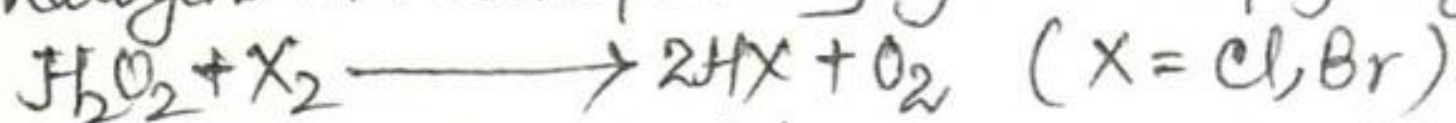
(e) It oxidises formaldehyde & benzene into formic acid and phenol respectively.  
 $HCHO + H_2O_2 \xrightarrow[\text{Pyrogallol}]{\text{Alkaline}} HCOOH + H_2$ ;  $C_6H_6 + H_2O_2 \xrightarrow{FeSO_4} C_6H_5OH$   
 (Formaldehyde)                      (formic acid)                      (Benzene)                      (Phenol)



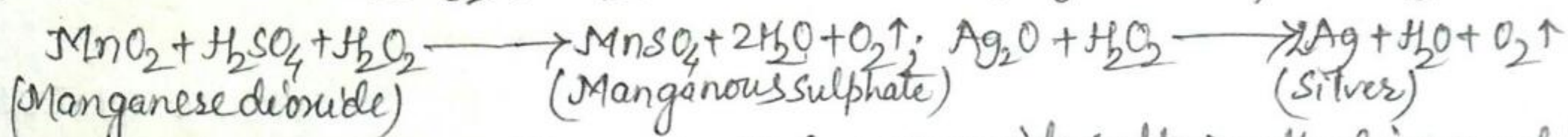
(iv) Reducing property: It acts as a reducing agent when it reacts with other oxidising agents in acidic or alkaline medium. In alkaline medium, its reducing property is more pronounced.



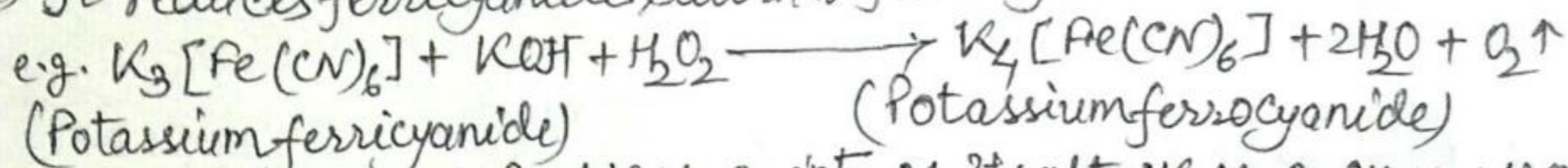
(a) It reduces halogens into corresponding hydroacids/hydrogen halides.



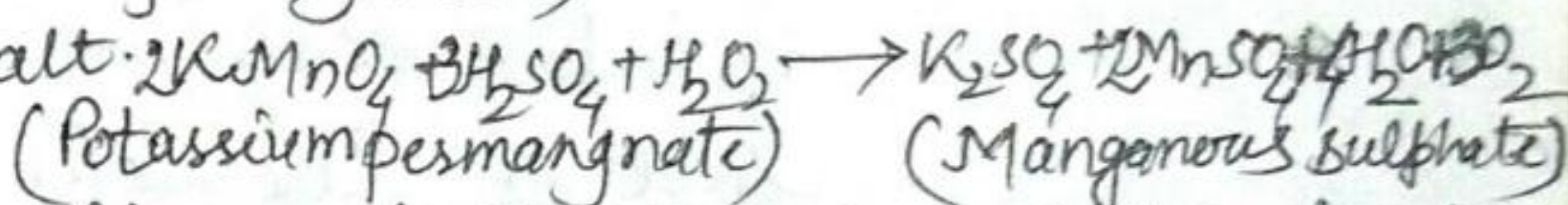
(b) It reduces  $MnO_2$ ,  $Ag_2O$ ,  $PbO_2$  etc. into  $Mn^{2+}$  salt,  $Ag$ ,  $PbO$  respectively.



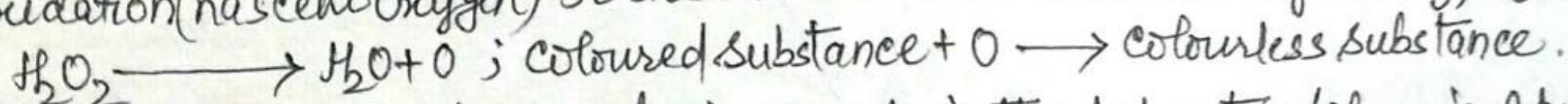
(c) It reduces ferricyanide salt into ferrocyanide salt in alkaline medium.



(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.



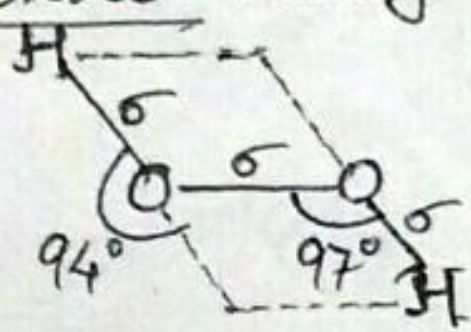
\* Uses: (i) As an oxidising & reducing agents in the laboratory/chemical processes.

(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 ( $\sigma$ ) bonds. Two O-H bond lie in different planes cross to each other.

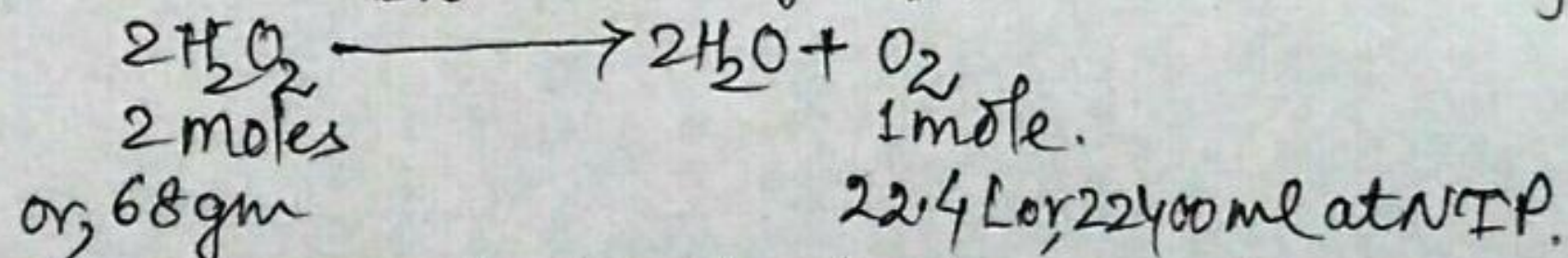
Bond length: O-O is  $1.48 \pm 0.02 \text{ \AA}$ , O-H is  $1.01 \pm 0.03 \text{ \AA}$ .

Bond angle:  $\angle HOO = 97^\circ$ ; Angle between two planes containing

H atom (i.e. O-H bond) =  $94^\circ$ . 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:

Equivalent weight of  $H_2O_2 = \frac{68}{32} \times 8 = 17$ ;

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.