HYDROGEN PEROXIDE(H_2O_2)

Introduction

The credit for the discovery of hydrogen peroxide goes to the French chemist J. L. Thenard. This chemical compound holds significant importance in the realm of pollution control, particularly in the treatment of both domestic and industrial effluents.

Preparation of H_2O_2

Hydrogen peroxide can be produced through three primary methods:

(i) One method involves the reaction between sulphuric acid and hydrated barium peroxide:

$$BaO_2 \cdot 8H_2O(s) + H_2SO_4(aq) \rightarrow BaSO_4(s) + H_2O_2(aq) + 8H_2O(l)$$

The surplus water is eliminated by evaporation under reduced pressure.

(ii) Another approach entails the electrolytic oxidation of acidified sulfate solutions at high current density, yielding peroxosulphates. Subsequent hydrolysis of these peroxosulphates results in the formation of hydrogen peroxide:

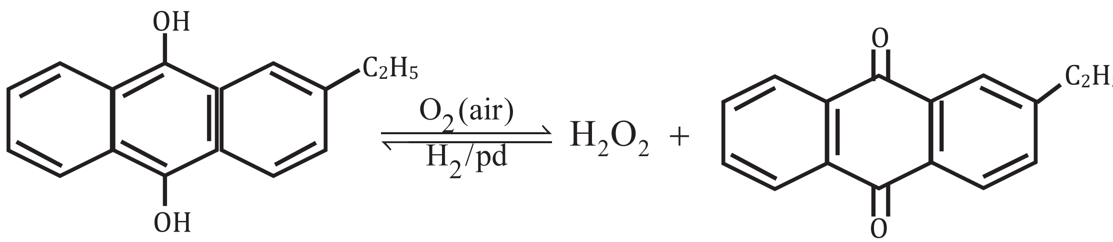
$$2HSO_4^-(aq) \xrightarrow{\text{Electrolysis}} HO_3SOOSO_3,H(aq) + 2e^-$$

$$HO_3SOOSO_3H(aq) \xrightarrow{\text{Hydrolysis}} 2HSO_4^-\ (aq) + 2H+(aq) + H_2O_2(aq)$$

This method is also employed in the laboratory preparation of heavy water (D_2O_2), as demonstrated in the reaction:

$$K_2S_2O_8(s) + 2D_2O(1) \rightarrow 2KDSO_4(aq) + D_2O_2(1)$$

(iii) On an industrial scale, hydrogen peroxide is manufactured through the auto-oxidation of 2-ethylanthraquinols.



2-ethylanthraquinol Oxidised product

Concentration of H_2O_2

In the aforementioned scenario, the hydrogen peroxide (H_2O_2) obtained initially has a concentration of 1%. Therefore, a concentration process is necessary. The first step involves extracting H_2O_2 with water and subsequently concentrating it to approximately 30%. Further concentration is achieved through distillation under reduced pressure, resulting in a concentration of 85% by mass. To obtain pure H_2O_2, the remaining water can be separated by freezing out the water content.

Physical Properties

(i) Pure hydrogen peroxide (H_2O_2) is a colorless and odorless liquid, while impure forms may exhibit a bluish tinge.

(ii) It engages in a greater number of hydrogen bonding interactions compared to water (H_2O), resulting in a higher boiling point.

(iii) Hydrogen peroxide is soluble in water, alcohol, and ether.

(iv) It possesses a bitter taste and can be harmful to the skin.

(v) Hydrogen peroxide is a weak dibasic acid.

(vi) It displays both oxidizing and reducing properties.
(vii) Hydrogen peroxide is prone to rapid decomposition when exposed to light and elevated temperatures. Therefore, it is typically stored in opaque containers and in cool locations.
(viii) A 30% solution of hydrogen peroxide is referred to as Perhydro.

Volume Strength of H_2O_2

The volume strength of a hydrogen peroxide (H_2O_2) solution is defined as the volume of oxygen (O_2) evolved at Standard Temperature and Pressure (STP) in milliliters, obtained per milliliter of the H_2O_2 solution.

For instance, if 1 liter of the H_2O_2 solution produces 10 liters of oxygen at STP, the volume strength of the H_2O_2 is considered to be 10 volumes.

Let's consider a sample of H_2O_2 labeled 'V' volume.

The decomposition reaction is represented as: $2H_2O_2 \rightarrow 2H_2O + O_2$

If 68 grams of H_2O_2 yields 22,400 ml of O_2,

then 'V' ml of O_2 is obtained from $\frac{68}{22400}$ grams of H_2O_2.

Therefore, if 1 ml of H_2O_2 corresponds to $\frac{68}{22400}$ grams of H_2O_2,

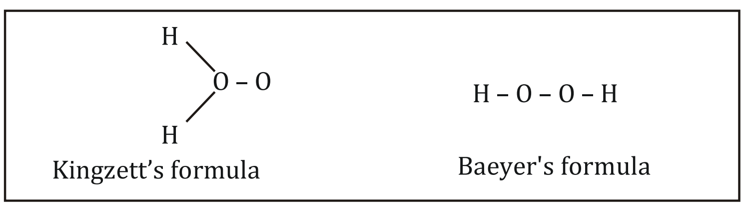
then 1000 ml (1 liter) of H_2O_2 would be equivalent to $\frac{68}{22.4}$ V grams per liter.

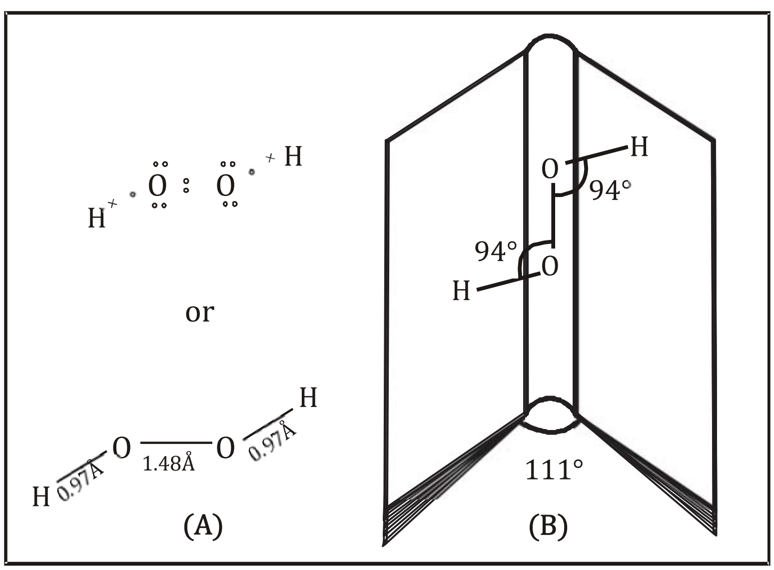
Hence, the strength of H_2O_2 is calculated as $\frac{68}{22.4}$V.

The molarity is given by $\frac{V}{11.2}$, and the normality is $\frac{V}{5.6}$.

Structure of H_2O_2

Structure Of Hydrogen Peroxide





The vapor density, determined using the Victor Meyer method at 90°C, is found to be 17. Consequently, the molecular mass of H_2O_2 is determined to be 34. Two different formulas have been proposed for hydrogen peroxide.
The calculated value of the single bond O – O distance is 1.48Å and X-ray measurements shows what in hydrogen peroxide, O–O bond distance is 1.46 + 0.03Å. The value of dipole moment of H_2O_2 is 2.1 D. This suggests that all the four atoms do not lie in the same plane. The molecule can be pictured as lying on the spine of a book open to an angle of 111°. The hydrogen atoms are present one on each cover and H–O bonds making angles of 94° with the O–O bond as shown in fig. The bond distance between O–H is 0.97Å.

Precautions

(i) Hydrogen peroxide (H_2O_2) should not be kept in regular glass containers because the uneven surface of glass, often containing alkali oxides, can be stimulated by light, leading to the decomposition of H_2O_2. Therefore, it is typically stored in colored plastic bottles that are coated with paraffin wax.

(ii) When handling hydrogen peroxide, it is advisable to include a small quantity of an inhibitor or a negative catalyst to inhibit its decomposition. Substances like H_3PO_4 (phosphoric acid) or acetanilids can serve this purpose effectively.

Question: Why is hydrogen peroxide (H_2O_2) kept away from dust?

Answer: Hydrogen peroxide (H_2O_2) is stored away from dust due to the fact that dust particles have the potential to trigger explosive decomposition of the compound.

Chemical Properties

1. Stability

It possesses inherent instability and undergoes decomposition when left undisturbed or when exposed to heat. This behavior serves as an illustration of auto-oxidation and reduction reactions.

Reaction; $H_2O_2 \longrightarrow H_2O + O$

Note: Nascent oxygen working as colourless agent Decomposition of

$$H_2O_2; 2H_2O_2 \longrightarrow 2H_2O + O_2$$

Note: This is retarded by R–OH, acetanilide, glycerol

2. Oxidizing Nature

H_2o_2 Is A Powerful oxidant in acidic as well as in alkaline medium.

(In acid) $H_2O_2 + 2H^+ + 2e \xrightarrow{\text{Fast}} 2H_2^{0}$ $E^{o}_{Rp} = 1.77V$

(In alkali) $H_2O + HO_2^- + 2e \xrightarrow{\text{Slow}} 3HO^-$ $E^{o}_{Rp} = 1.87V$

Thus, H_2O_2 is more powerful oxidant in acidic medium. The simple interpretation of H_2O_2 as oxidant can be shown by the equation.

$$H_2O_2 \longrightarrow H_2O + O$$

Following are some important examples of oxidant action of H_2O_2:

(a) H_2O_2 oxidizes black lead sulphide (PbS) to white lead sulphate ($PbSO_4$).

This reaction is used in restoring the white colour of old paintings which have blackened due to the formation of lead sulphide by the action of H_2S present in air.

$$4[H_2O_2 \longrightarrow H_2O + O]$$
$$PbS + 4O \longrightarrow PbSO_4$$
$$PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$$

(b) H_2O_2 oxidizes sulphites into sulphates.

$$H_2O_2 \longrightarrow H_2O + O$$
$$Na_2SO_3 + O \longrightarrow Na_2SO_4$$
$$Na_2SO_3 + H_2O_2 \longrightarrow Na_2SO_4 + H_2O$$

(c) H_2O_2 oxidizes nitrites to nitrates.

$$H_2O_2 \longrightarrow H_2O + O$$
$$Na_2NO_2 + O \longrightarrow NaNO_3$$
$$Na_2NO_2 + H_2O_2 \longrightarrow Na_2NO_3 + H_2O$$

(d) H_2O_2 oxidizes H_2S into sulphur.

$$H_2O_2 \longrightarrow H_2O + O$$
$$H_2S + O \longrightarrow H_2O + S$$
$$H_2S + H_2O_2 \longrightarrow 2H_2O + S$$

3. **Reducing nature**

It can also act as a reducing agent towards powerful oxidising agents.

$$H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^-$$

(a) It reduces Ag_2O to silver.

$$Ag_2O + H_2O_2 \longrightarrow 2Ag + H_2O + O_2$$

(b) It reduces ozone to oxygen.

$$H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$$

Storage and Usage of H_2O_2

Storage

Due to the catalytic decomposition of hydrogen peroxide (H_2O_2) in the presence of factors such as sunlight, metal surfaces, glass, alkali, and dust, it is imperative to store H_2O_2 in suitable containers away from sunlight. The decomposition process occurs gradually when H_2O_2 is exposed to light, leading to the formation of water and oxygen:

$$2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)$$

To mitigate the risks associated with storage, H_2O_2 is not typically stored in glass bottles, which may contain alkali metal oxides. Instead, it is stored in vessels made of wax-lined glass or plastic that offer protection from light. Additionally, urea is often added as a stabilizer to enhance the stability of H_2O_2 during storage. Moreover, precautions are taken to prevent the introduction of dust, as dust particles can induce explosive decomposition of the compound.

Uses of H_2O_2

(i) Used as a bleaching agent.
(ii) Employed in hair dyeing.
(iii) $H_2O_2 + N_2H_4$ as Rocket propellent
(iv) H_2O_2 as oxidant and reductant
(iv) Utilized as an antiseptic.