

Hydrogen

Chemical symbol-H (Atomic number = 1)

Electronic configuration $1s^1$

Hydrogen is the lightest and most abundant element in the universe [70% of the total mass of universe].

It was discovered by **Henry Cavendish** in 1766 by the action of dilute H_2SO_4 on iron. It was named 'inflammable air'. **Lavoisier** gave it the name hydrogen [Greek : *Hydra* = water, *gennas* = producer]. It occurs in free state as well as in combined state.

Position of Hydrogen in the Periodic Table

Hydrogen resembles with alkali metals (group 1) as well as halogens (group 17). At the same time, it differs from both in certain characteristics. That is why hydrogen is called "**rogue element**". However, it has been placed in group 1 on the basis of its configuration $1s^1$, which is the basis of modern classification of elements.

Isotopes of Hydrogen

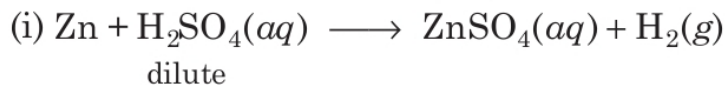
Hydrogen exists in the form of three isotopes:

Name	Symbol	Atomic number	Relative atomic mass	Density	Relative abundance	Nature
Protium	1_1H or H	1	1.0078	0.09	99.98%	Non-radioactive
Deuterium	2_1H or D	1	2.0141	0.18	0.0156%	Non-radioactive
Tritium	3_1H or T	1	3.016	0.27	$10^{-15}\%$	Radioactive (emits β -rays, $t_{1/2} = 12.33$ year)

Dihydrogen [H₂]

Methods of Preparation of Dihydrogen

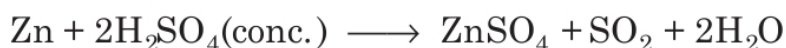
(a) Lab methods



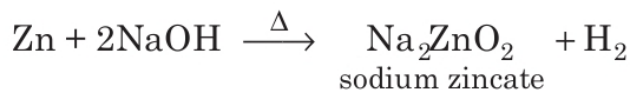
Metals which have reduction potential lesser than H, can liberate H₂ from acids.

Pure zinc is not used because it reacts slowly. The presence of some impurities increases the rate of reaction due to the formation of electrochemical couples.

Conc sulphuric acid is also not used because it oxidises, H₂ formed into H₂O.

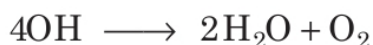
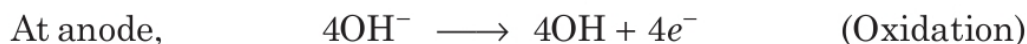
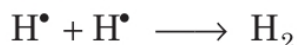
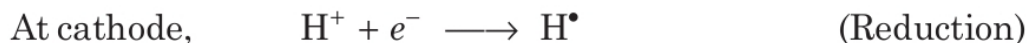
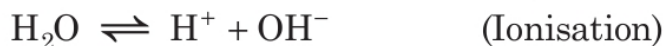


- (ii) It can also be prepared by the reaction of zinc with aqueous alkali.

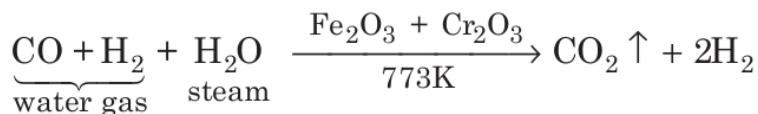


(b) Commercial production of dihydrogen

- (i) By the electrolysis of acidified water



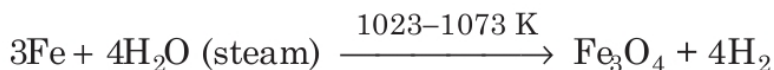
- (ii) From water gas (Bosch process)



[water gas shift reaction]

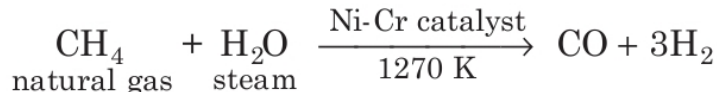
Carbon dioxide is removed by dissolving it in water under pressure (20-25 atm) and hydrogen left behind is collected.

- (iii) From steam (Lane's process)-Super heated steam is passed over iron filings heated to about 1023-1073 K when hydrogen is formed.



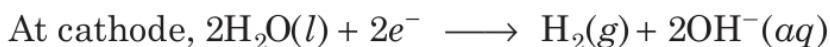
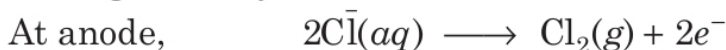
(iv) Highly pure (> 99.95%) dihydrogen is obtained by electrolysing warm aqueous barium hydroxide solution between nickel electrodes.

(v) **From hydrocarbons by partial oxidation**

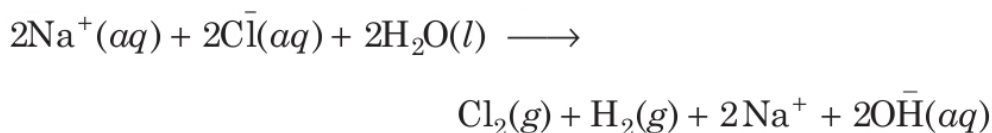


(vi) It is also obtained as a by-product in the manufacture of NaOH and chlorine by the electrolysis of brine solution.

During electrolysis, the reactions that take place are



The overall reactions by adding spectator Na^+ ions,



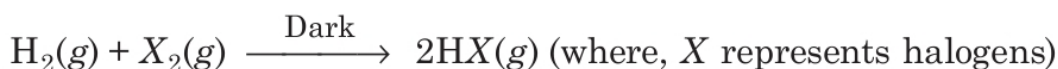
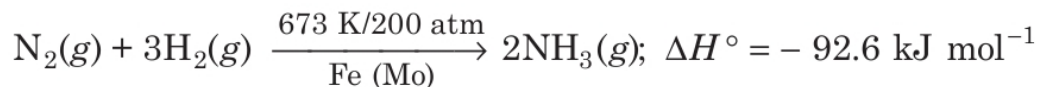
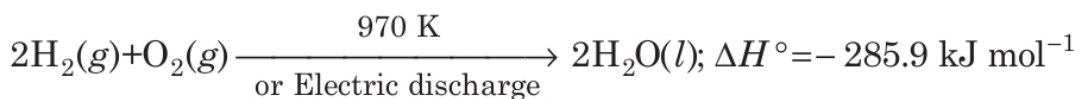
Physical Properties of Dihydrogen

Dihydrogen is a colourless, odourless, tasteless, combustible gas. It is lighter than air and insoluble in water. It is neutral to litmus.

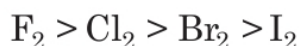
Chemical Properties of Dihydrogen

(i) **Reactivity** The relative inertness of dihydrogen at room temperature is because of its high enthalpy of H—H bond i.e. high bond dissociation energy. So its reactions take place under specific conditions only (at high temperature).

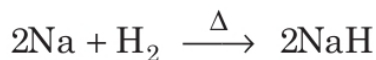
(ii) **Action with non-metals**



Order of reactivity of halogens:



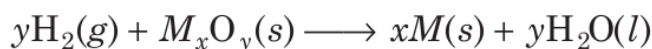
(iii) **Reaction with metals** Here H_2 acts as oxidising agent.



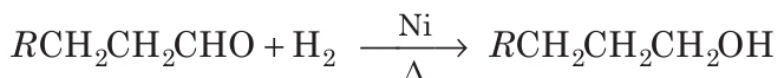
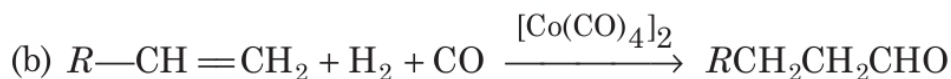
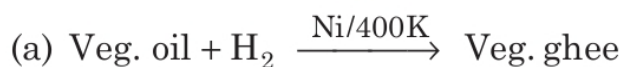
(iv) **Reducing action of dihydrogen**



(v) **Reactions with metal ions and metal oxides**

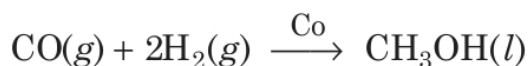


(vi) **Reaction with organic compounds**



Uses of Dihydrogen

1. It is used in the manufacture of CH_3OH .



2. It produces temperature of $2850^\circ C$ and oxy-atomic hydrogen flame produces a temperature of $4000^\circ C$, so it is used in oxy-hydrogen flame.

3. The largest single use of H_2 is in the synthesis of NH_3 which is used in the manufacture of HNO_3 and fertilizers.

4. Liquid hydrogen mixed with liquid oxygen is used as rocket fuel in space research.

5. H_2 is used as a reducing agent in extraction of metals.

6. H_2 is used in fuel cell for generating electrical energy.

7. Hydrogen is used in the manufacture of synthetic petrol. (By heating H_2 with coal and heavy oils under very high pressure in the presence of catalyst.)

8. It is use for the preparation of metal hydrides, hydrogen chloride.

9. It is used in metallurgical processes to reduce heavy metal oxides to metals.
10. Atomic hydrogen and oxy hydrogen torches find use for cutting and welding purposes.

Different Forms of Hydrogen

Atomic Hydrogen

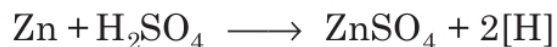
It is obtained from thermal decomposition of molecular hydrogen at high temperature and low pressure.



It is very reactive and its half-life period is 0.33 s.

Nascent Hydrogen

Freshly prepared hydrogen is known as nascent hydrogen and is more reactive than ordinary hydrogen. It causes the reduction of certain compounds which is not possible with ordinary hydrogen. It can never be isolated.



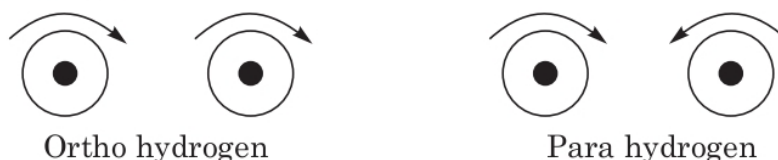
Activity of nascent H depends upon the reaction by which it is obtained.

Adsorbed Hydrogen

Adsorption of hydrogen at the metal surface is called **occlusion**. This hydrogen brings out many chemical changes such as reduction and hydrogenation. Occlusion decreases with rise in temperature.

Ortho and Para Hydrogen

When in hydrogen molecule, the nuclear spins are in the same direction, it is known as ortho hydrogen. On the other hand when the nuclear spins are in the opposite direction, it is known as para hydrogen. At room temperature hydrogen consists of 75% ortho and 25% para hydrogen.

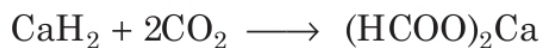
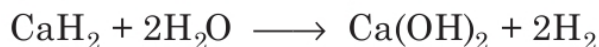


Hydrides

The compounds of hydrogen with metals and non-metals (except noble gases) are called hydrides.

Ionic or Saline Hydrides

These are formed by elements of group I, II, (except Be and Mg) by heating them in hydrogen. These are white colourless solids (crystalline) having high m.p. and b.p. easily decomposed by water, CO₂ or SO₂.



They are strong reducing agents. Alkali metal hydrides are used for making LiAlH₄, NaBH₄, etc and for removing last traces of water from organic compounds.

Molecular or Covalent Hydrides

These are formed by elements of p-block having higher electronegativity than hydrogen.

- (i) **Electron deficient hydrides** These are the hydrides which do not have sufficient number of electrons needed to form normal covalent bonds, e.g. hydrides of group 13 (BH₃, AlH₃, etc.)
- (ii) **Electron precise hydrides** These are the hydrides which have exact number of electrons needed to form normal covalent bonds, e.g. hydrides of group 14 (CH₄, SiH₄, etc.)
- (iii) **Electron rich hydrides** These are the hydrides which have greater number of electrons than required to form normal covalent bonds, e.g. hydrides of group 15, 16, 17, (NH₃, PH₃, H₂S, HF, HCl, etc). The excess electrons in these hydrides are present as lone pairs of electrons.

Metallic or Interstitial or Non-stoichiometric Hydrides

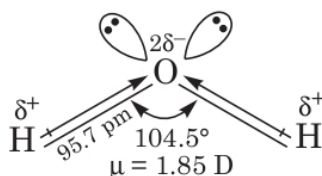
The transition metals and rare earth metals combine with hydrogen to form interstitial hydrides. They exhibit metallic properties and are powerful reducing agents. They are non-stoichiometric hydrides and their composition varies with temperature and pressure for e.g. LaH_{2.76}, TiH_{1.73}. Metals of group 7, 8 and 9 do not form hydrides and this region of the Periodic Table is called **hydride gap**.

Polymeric Hydrides and Complex Hydrides

Polymeric hydrides are formed by elements having electronegativity in the range 1.4 to 2.0, e.g. (BeH₂)_n, (AlH₃)_n, etc. In complex hydrides, H⁻ acts as ligand and is attached to central metal atom, e.g. LiAlH₄, LiBH₄, etc.

Water

Water is the most abundant and widely distributed on the earth. Human body has about 65% and some plants have as much as 95% H_2O . It occurs in all the three physical states. H_2O is a covalent molecule in which oxygen is sp^3 -hybridised. It has bent structure.



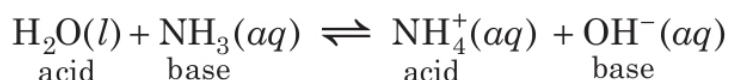
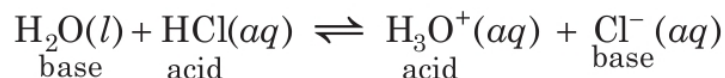
The crystalline form of water is ice. It has a highly ordered three dimensional hydrogen bonded structure. Examination of ice crystals with X-rays shows that each oxygen atom is surrounded tetrahedrally by four oxygen atom.

Physical Properties of Water

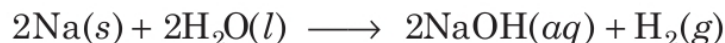
1. Water is a colourless, odourless, tasteless liquid. It has abnormally high b.p., f.p., heat of vaporisation due to hydrogen bonding.
2. Pure water is not a good conductor so it is made conductor by adding small amount of acid or alkali.
3. Density of ice (which is mass per unit volume) is lesser than that of water and it floats over water.
4. Water has maximum density at 4°C . This property of maximum density at 277 K helps aquatic animals to survive during winter months.
5. Water is a highly polar solvent with high dielectric constant 78.39. It interacts with polar or ionic substances effectively with the release of considerable amount of energy due to ion dipole interaction. The dissolution of covalent compounds like urea, glucose and $\text{C}_2\text{H}_5\text{OH}$, etc is due to the tendency of these molecules to form hydrogen bond with water.

Chemical Properties of Water

1. Water is amphoteric in nature.



2. In redox reactions, water reacts with metals and non-metals both.



3. In **hydrated salts**, water may remain in five types such as coordinated water, hydrogen bonded water, lattice water, clathrate water and zeolite water.

4. A number of compounds such as calcium hydride, calcium phosphide, etc., undergo hydrolysis with water.

Purification of Water

It involves two processes

(i) Removal of suspended impurities

(ii) Destroying the bacteria.

Suspended particles are removed by coagulation with alum followed by filtration. Exposure to sunlight, boiling, chlorination (treatment with liquid Cl_2 or bleaching powder), ozonisation and addition of CuSO_4 are some processes which are employed to destroy bacteria.

Soft and Hard Water

The water which produces large amount of lather with soap is known as soft water and which forms a scum with soap is known as hard water.

Types of Hardness of Water

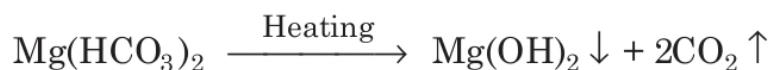
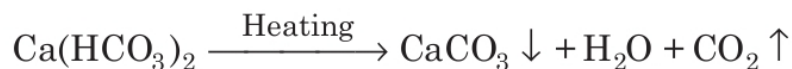
(i) **Temporary hardness** It is due to the presence of bicarbonates of calcium and magnesium.

(ii) **Permanent hardness** It is due to the presence of chlorides and sulphates of calcium and magnesium.

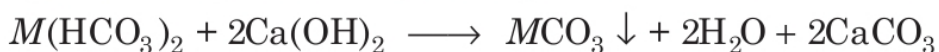
Removal of Temporary Hardness

It can be achieved :

(i) **By boiling** The soluble bicarbonates are converted into insoluble carbonates.

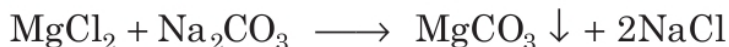


(ii) **By Clark's process** By adding lime water or milk of lime.

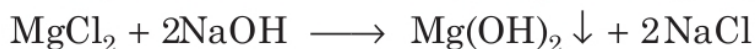
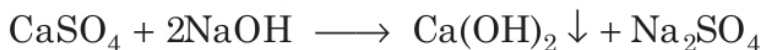


Removal of Permanent Hardness

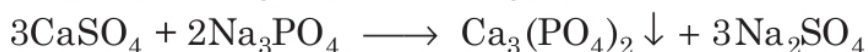
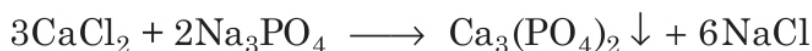
- (i) **By adding washing soda** The calcium or magnesium salts are precipitated as carbonates.



- (ii) **By adding caustic soda** The temporary and permanent hardness can be removed by adding caustic soda.

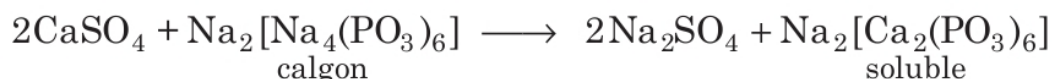


- (iii) **By adding sodium phosphate** (Na_3PO_4) The phosphates of calcium and magnesium are precipitated.



Similarly, magnesium also precipitate out in the form of magnesium phosphate, $\text{Mg}_3(\text{PO}_4)_2$.

- (iv) **Calgon's process** Calgon is sodium hexa metaphosphate ($\text{Na}_6\text{P}_6\text{O}_{18}$). This calgon when added to hard water form soluble complex.



Similarly, Mg^{2+} can also precipitate as $\text{Na}_2[\text{Mg}_2(\text{PO}_3)_6]$ and water becomes free from Ca^{2+} and Mg^{2+} ions.

- (v) **Permutit process** Permutit is hydrated sodium aluminium silicate $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot x\text{H}_2\text{O}$. It exchanges its sodium ions for divalent ions Ca^{2+} and Mg^{2+} .



Permutit when fully exhausted can be regenerated by treating with 10% solution of sodium chloride. It is most efficient method to get water with zero degree of hardness.

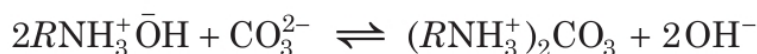
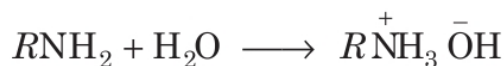
- (vi) **By synthetic resins** These are of two types:

- (a) **Cation exchange resins** are big molecules containing sulphonic acid group ($-\text{SO}_3\text{H}$). It is first changed into sodium salt with the general formula $\bar{R}\text{Na}^+$. The hard water is passed through it so Ca^{2+} and Mg^{2+} are exchanged and removed.



The resins like permutit can be regenerated with a solution of NaCl.

- (b) **Anion exchange resins** are also big molecules and can exchange anions. They contain an amino group.



The water is first passed through cation resins and then through anion resin and pure distilled water is obtained.

Measurement of Degree of Hardness

Degree of hardness is defined as the number of parts of calcium carbonate or equivalent to various calcium and magnesium salts present in one million parts of water by mass. It is expressed in ppm.

$$\text{Degree of hardness (in ppm)} = \frac{\text{wt. of CaCO}_3 \text{ (g)}}{\text{wt. of hard water (g)}} \times 10^6$$

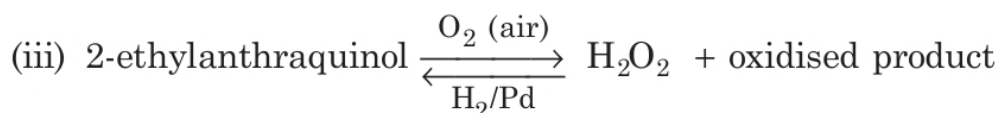
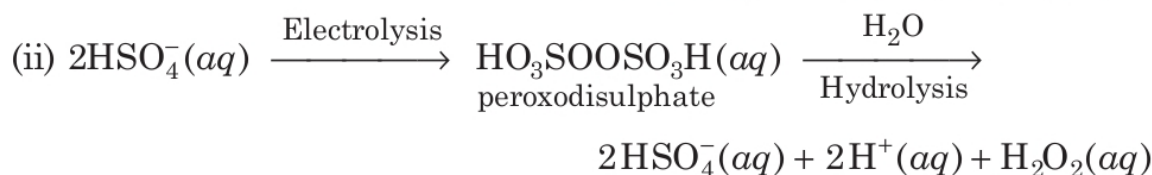
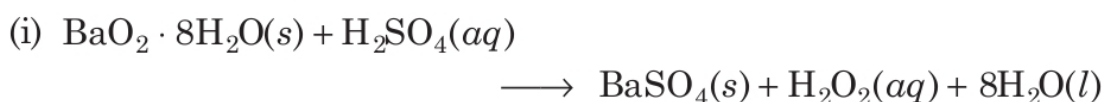
The molecular wt. of $Ca(HCO_3)_2$, $Mg(HCO_3)_2$, $CaCl_2$, $MgCl_2$, $CaSO_4$ and $MgSO_4$ is 162, 146, 111, 95, 136 and 120 respectively. The mol. wt. of $CaCO_3$ is 100.

Thus, 162 g $Ca(HCO_3)_2$, 146 g $Mg(HCO_3)_2$, 111 g $CaCl_2$, 95 g $MgCl_2$, 136 g $CaSO_4$ and 120 g $MgSO_4$ are equivalent to 100 g $CaCO_3$.

Hydrogen Peroxide [H_2O_2]

H_2O_2 was discovered by J.L. Thenard in 1818. It is an important compound used in pollution control treatment of domestic and industrial effluents.

Methods of Preparation



Physical Properties

- (i) In the pure state, H_2O_2 is almost colourless (very pale blue) liquid.
- (ii) it is miscible with water in all proportions and forms a hydrate $\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$.

Strength of Hydrogen Peroxide

The most common method to express the strength of H_2O_2 is in terms of the volume (in mL) of oxygen liberated at NTP by decomposition of 1 mL of that sample of H_2O_2 . A solution of H_2O_2 labelled as '10 volume' actually means "1 mL of 3% of a solution of H_2O_2 on decomposition by heat produces 10 mL of oxygen at NTP". Similarly, 1 mL of 20 volume, 30 volume and 100 volume H_2O_2 solution produce 20 mL, 30 mL and 100 mL of oxygen at N.T.P. respectively.

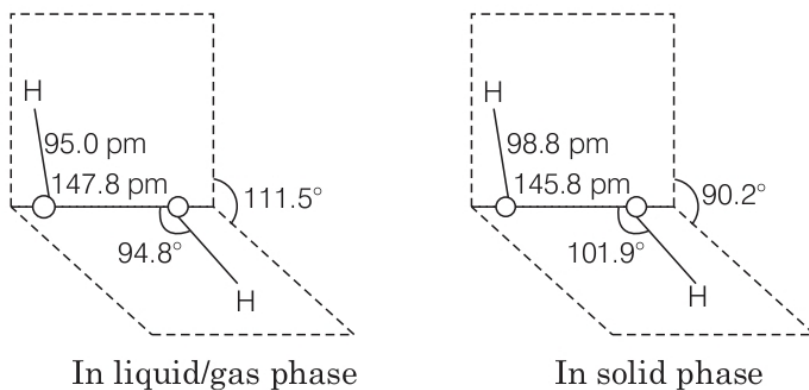
- (i) Strength of H_2O_2 in terms of normality

$$\frac{68 \times X}{22.4} = 17 \times N \Rightarrow X = 5.6 \times N$$

where, X is volume strength of H_2O_2 .

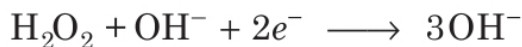
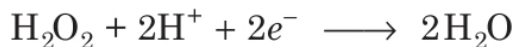
- (ii) % strength = $17/56 \times$ volume strength
- (iii) $X = 11.2 \times$ molarity.

Structure

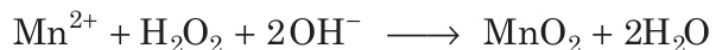


Chemical Properties of H_2O_2

- (i) **Acidic nature** It is weakly acidic in nature and pure hydrogen peroxide turns blue litmus red.
- (ii) **Oxidising agent** It acts as a strong oxidising agent in acidic as well as in basic medium.

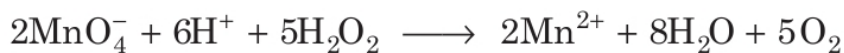


e.g. oxidising action of H_2O_2 is

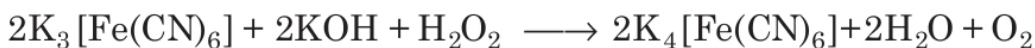


(iii) Reducing agent

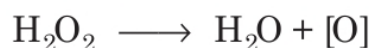
(a) In acidic medium



(b) In basic medium



(iv) **Bleaching properties** Its bleaching action is due to oxidation by atomic oxygen and permanent.



dye + [O] \longrightarrow dye is oxidised and bleached

Storage of Hydrogen Peroxide (H_2O_2)

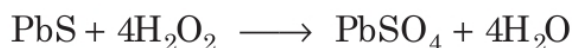
It is stored in the presence of traces of alcohol, acetanilide or sodium pyrophosphate which slow down the rate of decomposition of hydrogen peroxide.

Test

1. It liberates I_2 from acidified KI.



2. Black lead sulphide is turned white by it.



Uses

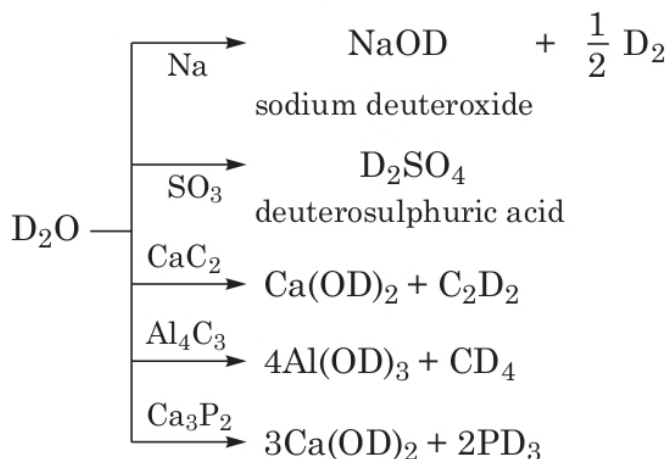
It is used as a bleaching agent, disinfectant, source of power (90% H_2O_2 as fuel in submarines, rockets and helicopters), in restoration of old paintings in which lead oxide is used as white paint.

30% H_2O_2 is called **perhydrol** which is used as an antiseptic and germicide for washing wounds, teeth and ears. (Volume strength is 100 and molarity is 8.8)

Heavy Water [D_2O]

It was discovered by Urey in 1932. It can be prepared by exhaustive electrolysis of ordinary water using nickel electrodes. It is colourless, odourless, tasteless liquid.

Chemical Reactions of Heavy Water



Uses of Heavy Water

It is used

1. in nuclear reactors to slow down the speed of neutrons and is called moderator.
2. as a tracer compound to study the mechanisms of many reactions.

Hydrogen Economy

Hydrogen economy is the use of liquid hydrogen as an alternate source of energy. The technology involves the production, transportation and storage of energy in the form of liquid or gaseous hydrogen. Large scale production of hydrogen can be done by electrolysis of water or by thermochemical reaction cycle. Storage of hydrogen in liquid form can be done in vacuum insulated cryogenic tanks or in a metal or in an alloy like iron-titanium alloy as interstitial hydride. Hydrogen fuel has many advantages over conventional fuels in that it is non-polluting and it liberates large amount of energy on combustion.

Photohydrogen is used to obtain renewable energy from sunlight by using microscopic organism such as bacteria or algae.