

Hydrogen

Hydrogen has the simplest atomic structure among all the elements around us in Nature. In atomic form it consists of only one proton and one electron. However, in elemental form it exists as a diatomic (H_2) molecule and is called dihydrogen. It forms more compounds than any other element. The global concern related to energy can be overcome to a great extent by the use of hydrogen as a source of energy? In fact, hydrogen is of great industrial importance. It was first prepared by Sir Henry Cavendish by the action of sulphuric acid on Zinc and named by Antoine Lavoisier since it produced water on burning. (Greek : hydra= water, gennas = maker or producing).

POSITION OF HYDROGEN IN THE PERIODIC TABLE:

We know that the elements in the periodic table are arranged according to their electronic configurations.

Electronic structure is similar to that of alkali metals (ns^1) which have 1 electron in their outermost shell. It can attain the noble gas configuration of helium, by accepting one electron. This character is very much similar to that of the halogen family ($ns^2 np^5$) which are also short of one electron to complete the octet of electrons in their shells.

Moving on to the compound formation, hydrogen forms oxides, halides and sulphides resembling the alkali metals, but unlike the alkali metals it has a very high ionization enthalpy, and so it lacks metallic characteristics under normal conditions. When we look in terms of ionization enthalpy, it is found that hydrogen resembles more to halogens than alkali metals. For example, $\Delta_f H$ of lithium is 520 kJ mol^{-1} , fluorine is 1680 kJ mol^{-1} and for hydrogen, it is 1312 kJ mol^{-1} . It exists as a diatomic molecule like that of halogens (for example chlorine Cl_2); there is a single hydrogen bond when H_2 molecule is formed.

In spite of the fact that hydrogen, to a certain extent resembles both with alkali metals and halogens, it differs from them as well. Thus, it is unique in behaviour and is, therefore, best placed separately in the periodic table.

Occurrence:

Dihydrogen is the most abundant element in the universe (70% of the total mass of the universe) and is the principal element in the solar atmosphere. The giant planets Jupiter and Saturn consist mostly of hydrogen. However, due to its light nature, it is much less abundant (0.15% by mass) in the earth's atmosphere. Of course, in the combined form it constitutes 15.4% of the earth's crust and the oceans. In the combined form besides in water, it occurs in plant and animal tissues, carbohydrates, proteins, hydrides including hydrocarbons and many other compounds.

Isotopes of Hydrogen : Hydrogen has three isotopes: protium, ${}_1H^1$, deuterium, ${}_1H^2$ or D and tritium, ${}_1H^3$ or T. These isotopes differ from one another in respect of the presence of neutrons. Ordinary hydrogen, protium, has no neutrons, deuterium (also known as heavy hydrogen) has one and tritium has two neutrons in the nucleus. In the year 1934, an American scientist, Harold C. Urey, got Nobel Prize for separating hydrogen isotope of mass number 2 by physical methods. The predominant form is protium. Terrestrial hydrogen

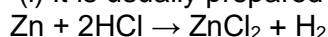
contains 0.0156% of deuterium mostly in the form of HD. The tritium concentration is about one atom per 10^{18} atoms of protium. Of these isotopes, only tritium is radioactive and emits low energy β – particles ($t_{0.5}$, 12.33 years).

Since the isotopes have the same electronic configuration, they have almost the same chemical properties. The only difference is in their rates of reactions, mainly due to their different enthalpy of bond dissociation. However, in physical properties these isotopes differ considerably due to their large mass differences.

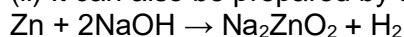
PREPARATION OF DIHYDROGEN, H_2 :

Laboratory Preparation of Dihydrogen

(i) It is usually prepared by the reaction of granulated zinc with dilute hydrochloric acid.



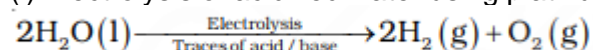
(ii) It can also be prepared by the reaction of zinc with aqueous alkali.



Commercial Production of Dihydrogen :

The commonly used processes are outlined below:

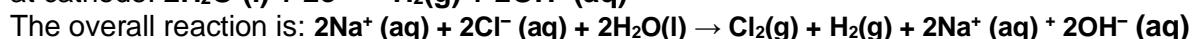
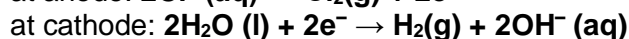
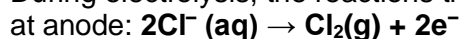
(i) Electrolysis of acidified water using platinum electrodes gives hydrogen.



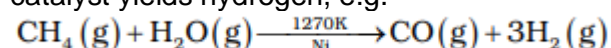
(ii) High purity (>99.95%) dihydrogen is obtained by electrolysis of warm aqueous barium hydroxide solution between nickel electrodes.

(iii) It is obtained as a byproduct in the manufacture of sodium hydroxide and chlorine by the electrolysis of brine solution.

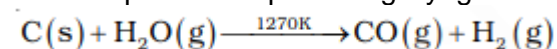
During electrolysis, the reactions that take place are:



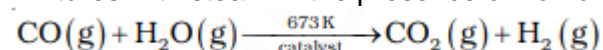
(iv) Reaction of steam on hydrocarbons or coke at high temperatures in the presence of catalyst yields hydrogen, e.g.



The mixture of CO and H_2 is called **water gas**. As this mixture of CO and H_2 is used for the synthesis of methanol and a number of hydrocarbons, it is also called synthesis gas or 'syngas'. Nowadays '**syngas**' is produced from sewage, saw-dust, scrap wood, newspapers etc. The process of producing 'syngas' from coal is called '**coal gasification**'.



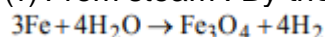
The production of dihydrogen can be increased by reacting carbon monoxide of syngas mixtures with steam in the presence of iron chromate as catalyst



This is called **water-gas shift reaction**. Carbon dioxide is removed by scrubbing with sodium arsenite solution.

Presently ~77% of the industrial dihydrogen is produced from petro-chemicals, 18% from coal, 4% from electrolysis of aqueous solutions and 1% from other sources.

(v) From steam : By the action of Fe, Sn etc.(Lane's process):



(vi) From Hydrolith (CaH_2):



DIFFERENT FORMS OF HYDROGEN :

i) Atomic Hydrogen :

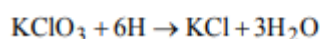
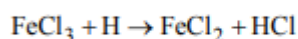
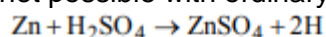


It is very reactive and its half life period is 0.33 seconds

ii) Occluded Hydrogen :

Hydrogen adsorbed by certain metals eg. Pt, Pd, Fe, Ni etc is known as occluded hydrogen. One volume of finely divided metals adsorb the following volumes of hydrogen. Palladium black 870, Platinum 49.5; Gold 46.3, Iron 15.7, Copper 4.5, Aluminium 2.7.

iii) 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.



iv) Ortho and Para hydrogen : The nucleus of the hydrogen atom also spins like a top. When in hydrogen molecule, the nuclear spins are in the same direction it is known as ortho hydrogen and when the nuclear spins are in the opposite direction it is known as para hydrogen. The two electrons in a hydrogen molecule always spin in opposite direction. At room temperature hydrogen consists of 75% ortho and 25% para. At low temperature more para is present.



Ortho-hydrogen (Parallel nuclear spin) Para-hydrogen (Anti parallel nuclear spin)

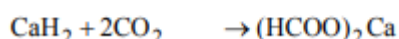
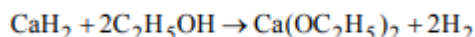
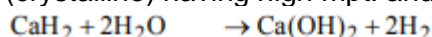
$$\text{Nuclear spin} = \frac{1}{2} + \frac{1}{2} = 1 \quad (\text{For ortho-hydrogen})$$

$$\text{Nuclear spin} = \frac{1}{2} + \left(-\frac{1}{2}\right) = 0 \quad (\text{For para-hydrogen})$$

HYDRIDES : Binary compounds of hydrogen and other elements are called hydrides. Hydrides are classified into the following four classes.

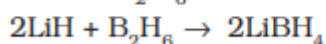
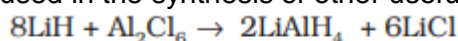
- 1) Saline or ionic hydrides.
- 2) Molecular or covalent hydrides.
- 3) Metallic or interstitial hydrides.
- 4) Polymeric hydrides.

1. Saline or ionic hydrides : These are formed by elements of group 1, 2 (Except Be and Mg) and lanthanides by heating the metal in hydrogen. These are white colourless solids (crystalline) having high mpt. and bpt. easily decomposed by water, alcohol, 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 compound.

Lithium hydride is rather unreactive at moderate temperatures with O₂ or Cl₂. It is, therefore, used in the synthesis of other useful hydrides, e.g.,



2) Molecular or covalent hydrides : These are formed by 4th , 5 th, 6th, 7th group elements and boron by sharing electrons with hydrogen atoms. eg. : NH₃ , HCl, B₂H₆ , AsH₃ . These are non electrolytes and are usually gases or liquids.

Molecular hydrides are further classified according to the relative numbers of electrons and bonds in their Lewis structure into :

- (i) electron-deficient,
- (ii) electron-precise, and
- (iii) electron-rich hydrides.

An **electron-deficient** hydride, as the name suggests, has incomplete octet. Diborane (B₂H₆) is an example. In fact all elements of group 13 will form electron-deficient compounds. They act as Lewis acids i.e., electron acceptors.

Electron-precise compounds have the complete octet without any lone pair. All elements of group 14 form such compounds (e.g., CH₄) which are tetrahedral in geometry.

Electron-rich hydrides have excess electrons which are present as lone pairs. Elements of group 15-17 form such compounds. (NH₃ has 1- lone pair, H₂O – 2 and HF –3 lone pairs). They will behave as Lewis bases i.e., electron donors. The presence of lone pairs on highly electronegative atoms like N, O and F in hydrides results in hydrogen bond formation between the molecules. This leads to the association of molecules.

3) Metallic or interstitial hydrides : The transition elements and rare earth metals combine with hydrogen to give interstitial hydrides. They exhibit metallic properties and are powerful reducing agents. They are non stoichiometric compounds and their composition varies with temperature and pressure. eg. LaH_{2.76}, TiH_{1.73} .

Earlier it was thought that in these hydrides, hydrogen occupies interstices in the metal lattice producing distortion without any change in its type. Consequently, they were termed as interstitial hydrides. However, recent studies have shown that except for hydrides of Ni, Pd, Ce and Ac, other hydrides of this class have lattice different from that of the parent metal. The property of absorption of hydrogen on transition metals is widely used in catalytic reduction / hydrogenation reactions for the preparation of large number of compounds. Some of the metals (e.g., Pd, Pt) can accommodate a very large volume of hydrogen and, therefore, can be used as its storage media. This property has high potential for **hydrogen storage** and as a source of energy.

The metals belonging to the groups 7, 8 and 9 do not form hydrides. Hence this region of the periodic table is referred to as the **hydride gap**. The hydride gap arises primarily due to the differences in electronegativity and atomic size between the elements in the region of Group 3 to Group 17. These factors influence the ability of the elements to form stable hydrides.

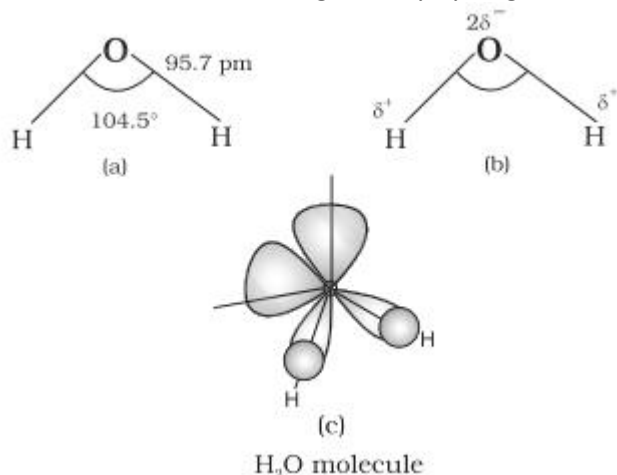
4) Polymeric hydrides : These are solids containing molecules, linked together in two or three dimensions by hydrogen bridge bonds. e.g.: $(\text{BeH}_2)_n$, $(\text{MgH}_2)_n$ and $(\text{AlH}_3)_n$

WATER:

A major part of all living organisms is made up of water. Human body has about 65% and some plants have as much as 95% water. It is a crucial compound for the survival of all life forms. It is a solvent of great importance. The distribution of water over the earth's surface is not uniform. The high heat of vaporisation and heat capacity are responsible for moderation of the climate and body temperature of living beings. It is an excellent solvent for transportation of ions and molecules required for plant and animal metabolism. Due to hydrogen bonding with polar molecules, even covalent compounds like alcohol and carbohydrates dissolve in water.

Structure of Water :

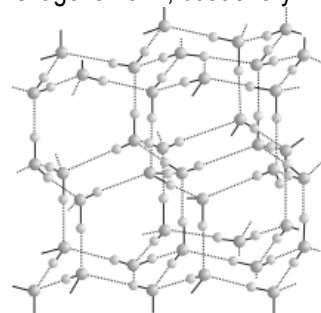
In the gas phase water is a bent molecule with a bond angle of 104.5° , and O–H bond length of 95.7 pm. It is a highly polar molecule (Dipole moment = 1.84D). In the liquid phase water molecules are associated together by hydrogen bonds.



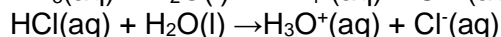
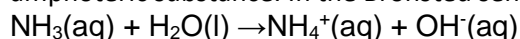
(a) The bent structure of water; (b) the water molecule as a dipole and (c) the orbital overlap picture in water molecule.

The **crystalline form** of water is ice. At atmospheric pressure ice crystallises in the hexagonal form, but at very low temperatures it condenses to cubic form. Density of ice is less than that of water. Therefore, an ice cube floats on water. In winter season ice formed on the surface of a lake provides thermal insulation which ensures the survival of the aquatic life. This fact is of great ecological significance. Ice 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 other oxygen atoms at a distance of 276 pm. Hydrogen bonding gives ice a rather open type structure with wide holes. These holes can hold some other molecules of appropriate size interstitially.

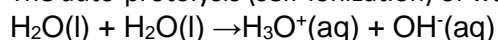
Chemical Properties of Water:



(1) Amphoteric Nature: It has the ability to act as an acid as well as a base i.e., it behaves as an amphoteric substance. In the Brönsted sense it acts as an acid with NH_3 and a base with H_2S .



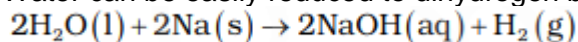
The auto-protolysis (self-ionization) of water takes place as follows



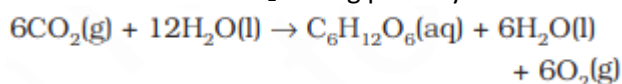
Acid-1 Base-2 Acid-2 Base-1

(2) Redox Reactions Involving Water:

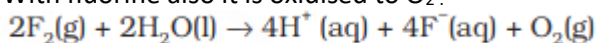
a) Water can be easily reduced to dihydrogen by highly electropositive metals.



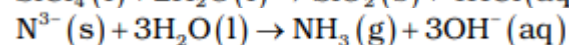
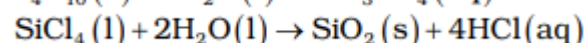
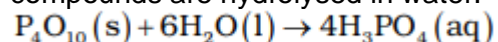
b) Water is oxidised to O_2 during photosynthesis



c) With fluorine also it is oxidised to O_2 .

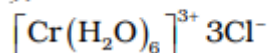


(3) Hydrolysis Reaction: Due to high dielectric constant, it has a very strong hydrating tendency. It dissolves many ionic compounds. However, certain covalent and some ionic compounds are hydrolysed in water.



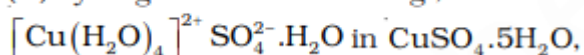
(4) Hydrates Formation: From aqueous solutions many salts can be crystallised as hydrated salts. Such an association of water is of different types .

(i) coordinated water e.g.,



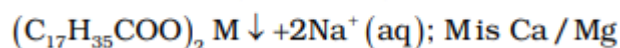
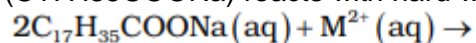
(ii) interstitial water e.g., $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$

(iii) hydrogen-bonded water e.g.,



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. p. Soap containing sodium stearate ($\text{C}_{17}\text{H}_{35}\text{COONa}$) reacts with hard water to precipitate out Ca/Mg stearate.



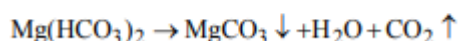
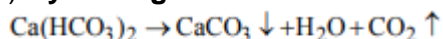
TYPES OF HARDNESS OF WATER : It is of two kinds

i) **Temporary hardness :** It is due to the presence of bicarbonates of calcium or magnesium or both.

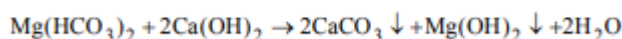
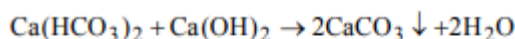
ii) **Permanent hardness :** It is due to the presence of chlorides and sulphates of calcium and magnesium.

REMOVAL OF TEMPORARY HARDNESS : It can be achieved by following methods:

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

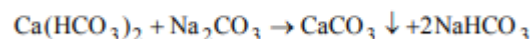
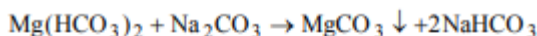


ii) **By Clark's process :** By adding lime water or milk of lime.

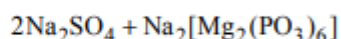
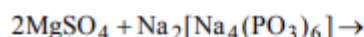
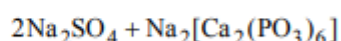
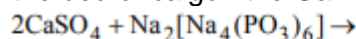


REMOVAL OF PERMANENT HARDNESS :

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

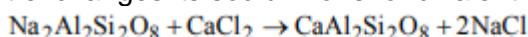


(ii) **Calgon process** : Calgon is sodium hexa metaphosphate. The water is passed through the bed of calgon the Ca^{2+} and Mg^{2+} form soluble complex.

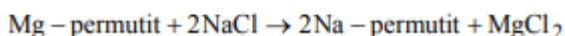
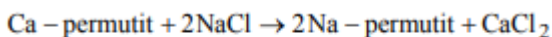


Water becomes free from Ca^{++} and Mg^{++} ions.

(iii) **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 such as Ca^{2+} and Mg^{2+} .



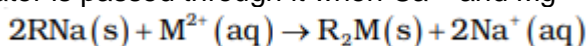
Permutit when fully exhausted can be regenerated by treating with 10% solution of sodium chloride



It is most efficient method to get water with zero degree hardness.

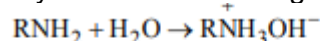
(iv) **By synthetic resins** : They are of two types :

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



The resin can be regenerated by adding aqueous NaCl solution.

b) Anion exchange resins : These are also giant molecules and can exchange anions. They contain an amino group.



Pure de-mineralised (**de-ionized**) water free from all soluble mineral salts is obtained by passing water successively through a cation exchange (in the H^+ form) and an anionexchange (in the OH^- form) resins.

The exhausted cation and anion exchange resin beds are regenerated by treatment with dilute acid and alkali solutions respective.

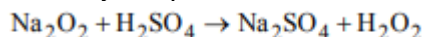
DEGREE OF HARDNESS : The hardness of water is expressed in terms of ppm of calcium carbonates.

HYDROGEN PEROXIDE (H₂O₂) :

Hydrogen peroxide is an important chemical used in pollution control treatment of domestic and industrial effluent.

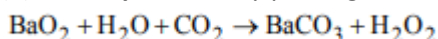
Preparation:

(i)) Acidifying Metallic peroxides by the action of ice cold dil. H₂SO₄ . and removing excess water by evaporation under reduced pressure gives hydrogen peroxide.



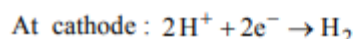
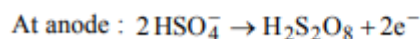
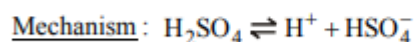
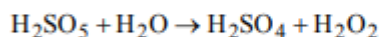
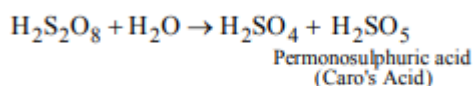
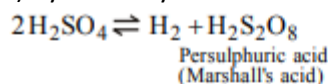
HNO₃ is not used since it will oxidise H₂O₂ .

(ii) **Merck process** : By passing CO₂ through a suspension of BaO₂ in ice cold water

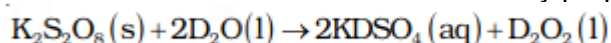


Manufacture :

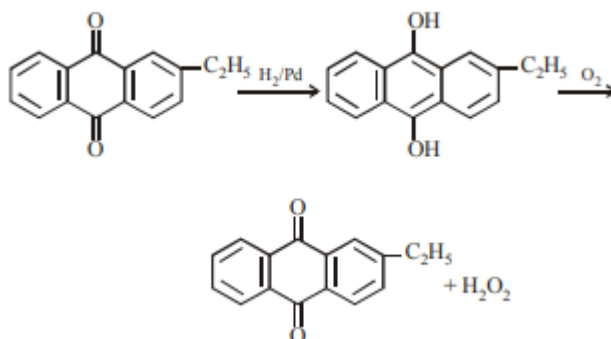
(1) By electrolysis of 50% ice cold H₂SO₄



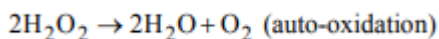
This method is now used for the laboratory preparation of D₂O₂.



(2) **Auto oxidation** : Most recent method used in America. In this method the anthraquinone is reduced to anthraquinol by dissolving in an organic solvent and passing hydrogen in presence of Pd. On frothing, the anthraquinol derivative with air, 20% solution of H₂O₂ is obtained and anthraquinone is regenerated.



CONCENTRATION OF HYDROGEN PEROXIDE : It is very carefully concentrated since it decomposes on heating or on standing.



Decomposition is catalysed by Cu, Ag, MnO₂ etc. The methods employed for concentration are

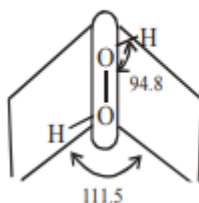
- i) Evaporation : By careful evaporation of solution on a water bath (50% H₂O₂ is obtained).
- ii) Dehydration in vacuum desiccator : The 50% H₂O₂ is dehydrated in a vacuum desiccator in presence of conc. H₂SO₄ when 90% H₂O₂ is obtained.
- iii) Vacuum distillation : The 90% H₂O₂ obtained in step (ii) is distilled under reduced pressure to get 100% H₂O₂
- iv) Cooling : The traces of water left are removed by freezing in a freezing mixture when crystals of hydrogen peroxide separate out.

STRENGTH OF HYDROGEN PEROXIDE : The strength of hydrogen peroxide is indicated in terms of the volume of oxygen at NTP that 1 volume of H₂O₂ solution gives on heating. For example "20 volume H₂O₂" means 1 volume of H₂O₂ solution at NTP will give 20 volume of oxygen.

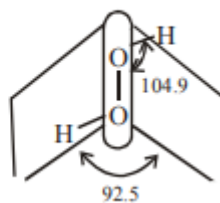
STORAGE OF HYDROGEN PEROXIDE : It is stored in presence of traces of alcohol, acetanilide or sodium pyrophosphate which slow down the rate of decomposition of hydrogen peroxide.

Structure: Hydrogen peroxide has a non-planar structure. The molecular dimensions in the liquid, gas and solid phases:

In liquid and gas form



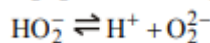
In solid form



CHEMICAL PROPERTIES :

i) Acidic nature :

It is weakly acidic in nature and pure hydrogen peroxide turns blue litmus into red. ($K_a = 1.57 \times 10^{-12}$ at 293 K). It ionises in two steps

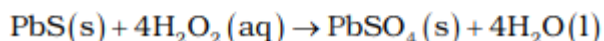
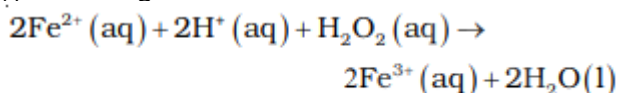


Hence it forms two series of salts eg. NaHO₂ sodium hydroperoxide and Na₂O₂ (Sodium peroxide).

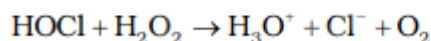
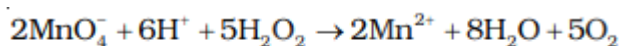
(ii) Oxidising and reducing property:

It acts as an oxidising as well as reducing agent in both acidic and alkaline media. Simple reactions are described below.

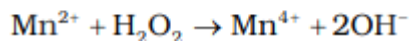
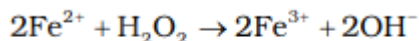
(i) Oxidising action in acidic medium:



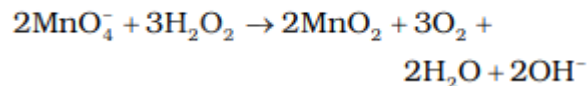
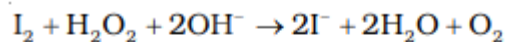
(ii) Reducing action in acidic medium:



(iii) Oxidising action in basic medium:



(iv) Reducing action in basic medium:

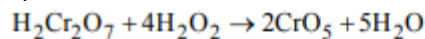


TEST for H_2O_2 :

i) It liberates I_2 from acidified KI:



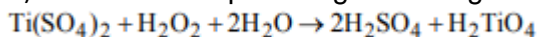
ii) Perchromic acid :



Blue colour
(chromium peroxide)

(acidified H_2O_2 + amyl alcohol + $\text{K}_2\text{Cr}_2\text{O}_7$) \rightarrow blue colour

iii) With titanous sulphate it gives orange red pertitanic acid:



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.

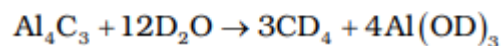
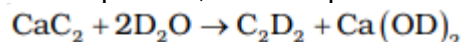
HEAVY WATER, D_2O :

It was discovered by Urey, who showed that ordinary water contains one part of heavy water in 6,000 parts of it.

PREPARATION : It is prepared by exhaustive electrolysis of water containing alkali with nickel electrodes. About 20 litres of ordinary water gives 0.5 ml of heavy water.

PROPERTIES & USES:

It is extensively used as a moderator in nuclear reactors and in exchange reactions for the study of reaction mechanisms. It can be prepared by exhaustive electrolysis of water or as a by-product in some fertilizer industries. It is used for the preparation of other deuterium compounds, for example:



It does not support life, and is injurious to living organism. It checks the growth of plants and animals. It is used as tracer compound.

DIHYDROGEN AS A FUEL : Dihydrogen releases large quantities of heat on combustion. On a mass for mass basis dihydrogen can release more energy than petrol (about three times). Moreover, pollutants in combustion of dihydrogen will be less than petrol. The only

pollutants will be the oxides of dinitrogen (due to the presence of dinitrogen as impurity with dihydrogen). This, of course, can be minimised by injecting a small amount of water into the cylinder to lower the temperature so that the reaction between dinitrogen and dioxygen may not take place. However, the mass of the containers in which dihydrogen will be kept must be taken into consideration. A cylinder of compressed dihydrogen weighs about 30 times as much as a tank of petrol containing the same amount of energy. Also, dihydrogen gas is converted into liquid state by cooling to 20K. This would require expensive insulated tanks. Tanks of metal alloy like NaNi_5 , Ti-TiH_2 , Mg-MgH_2 etc. are in use for storage of dihydrogen in small quantities.

Hydrogen Economy: The basic principle of hydrogen economy is the transportation and storage of energy in the form of liquid or gaseous dihydrogen. Advantage of hydrogen economy is that energy is transmitted in the form of dihydrogen and not as electric power. It is for the first time in the history of India that a pilot project using dihydrogen as fuel was launched in October 2005 for running automobiles. Initially 5% dihydrogen has been mixed in CNG for use in four-wheeler vehicles. The percentage of dihydrogen would be gradually increased to reach the optimum level.

Nowadays, it is also used in fuel cells for generation of electric power. It is expected that economically viable and safe sources of dihydrogen will be identified in the years to come, for its usage as a common source of energy.