

Hydrogen



Hydrogen, third most abundant on the surface of the Universe, is being visualised as the major feature source of energy



Antoine - Laurent de Lavoisier
(1743-1794)

He recognised and named hydrogen and oxygen. He introduced a new system for chemical nomenclature in 1787

Learning Objectives

After studying this unit, the students will be able to

- Justify the position of hydrogen in the periodic table
- Recognise the different isotopes of hydrogen
- Explain the methods of preparation of hydrogen.
- Explain the properties of hydrogen
- Appraise the uses of hydrogen
- Differentiate various types of hydrides
- Translate the knowledge of structure of water for explaining its physical and chemical properties
- Differentiate hard and soft water and select the suitable method for water softening.
- Recognise heavy water and explain its properties.
- Explain the preparation and properties of hydrogen peroxide
- List the uses of hydrogen peroxide

4.1 Introduction

Hydrogen is the simplest atom which contains one electron and one proton. In contrast to other elements (except helium) its valence electron is directly in the sphere of action of the nucleus. It is invariably present in most of the compounds we come across in our daily life such as water, carbohydrate, proteins etc. As it has an unpaired electron, it is reactive and exists as a diatomic molecule (H_2). However, the abundance of hydrogen gas in the earth's atmosphere is very small.

4.1.1 Position in Periodic Table

The hydrogen has the electronic configuration of $1s^1$ which resembles with ns^1 general valence shell configuration of alkali metals and shows similarity with them as follows:

1. It forms unipositive ion (H^+) like alkali metals (Na^+ , K^+ , Cs^+)
2. It forms halides (HX), oxides (H_2O), peroxides (H_2O_2) and sulphides (H_2S) like alkali metals (NaX , Na_2O , Na_2O_2 , Na_2S)
3. It also acts as a reducing agent.

However, unlike alkali metals which have ionization energy ranging from 377 to 520 kJ mol^{-1} , the hydrogen has 1,314 kJ mol^{-1} which is much higher than alkali metals.

Like the formation of halides (X) from halogens, hydrogen also has a tendency to gain one electron to form hydride ion (H^-) whose electronic configuration is similar to the noble gas, helium. However, the electron affinity of hydrogen is much less than that of halogen atoms. Hence, the tendency of hydrogen to form hydride ion

is low compared to that of halogens to form the halide ions as evident from the following reactions:



Since, hydrogen has similarities with alkali metals as well as the halogens; it is difficult to find the right position in the periodic table. However, in most of its compounds hydrogen exists in +1 oxidation state. Therefore, it is reasonable to place the hydrogen in group 1 along with alkali metals as shown in the latest periodic table published by IUPAC.

4.1.2 Isotopes of Hydrogen

Hydrogen has three naturally occurring isotopes, viz., protium (${}_1H^1$ or H), deuterium (${}_1H^2$ or D) and tritium (${}_1H^3$ or T). Protium (${}_1H^1$) is the predominant form (99.985 %) and it is the only isotope that does not contain a neutron.

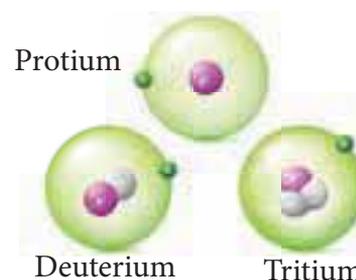


Figure 4.1 Isotopes of hydrogen

Deuterium, also known as heavy hydrogen, constitutes about 0.015 %. The third isotope, tritium is a radioactive isotope of hydrogen which occurs only in traces (~ 1 atom per 10^{18} hydrogen atoms). Due to the existence of these isotopes naturally occurring hydrogen exists as H_2 , HD , D_2 , HT , T_2 and DT . The properties of these isotopes are shown in Table 4.1.

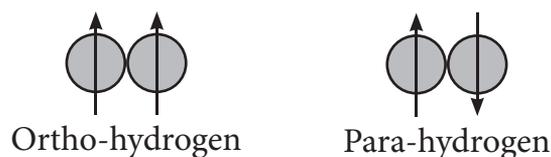
Table 4.1 Properties of Hydrogen, Deuterium and Tritium molecules.

Property	Protium	Deuterium	Tritium
Atomic Hydrogen			
	H	D	T
Atomic mass (<i>amu</i>)	1.008	2.014	3.016
No of electron / protons / neutrons	1 / 1 / 0	1 / 1 / 1	1 / 1 / 2
Nuclear stability	Stable	Stable	Radioactive ($t_{1/2}=12.3$ yrs)
Molecular Hydrogen	H ₂	D ₂	T ₂
Abundance (%)	99.985	0.015	$\sim 10^{-16}$
Molecular mass (<i>amu</i>)	2.016	4.028	6.032
Melting point (K)	13.96	18.73	20.62
Boiling point (K)	20.30	23.67	25.04
Internuclear distance (<i>pm</i>)	74.14	74.14	74.14
Critical Temperature (K)	33.19	38.35	40.60
Enthalpy of dissociation (<i>kJ/mol</i>) [†]	435.9	443.4	446.9

[†] Bond dissociation energy

4.1.3 Ortho- and Para-Hydrogen:

In the hydrogen atom, the nucleus has a spin. When molecular hydrogen is formed, the spins of two hydrogen nuclei can be in the same direction or in the opposite direction as shown in the figure. These two forms of hydrogen molecules are called *ortho* and *para* hydrogens respectively.



At room temperature, normal hydrogen consists of about 75% ortho-form and 25% para-form. As the ortho-form is more stable than para-form, the conversion of one isomer into the other is a slow process. However, the equilibrium shifts in favour of para hydrogen when the temperature is lowered. The para-form can be catalytically transformed into ortho-form using platinum or iron. Alternatively, it can also be converted by passing an electric discharge, heating above 800°C and mixing with paramagnetic molecules such as O₂, NO, NO₂ or with nascent/atomic hydrogen.

Ortho and para hydrogen are similar in chemical properties but differ in some of the physical properties. For example, the melting point of para hydrogen is 13.83 K while that of ortho-H₂ 13.95 K; boiling point of para hydrogen is 20.26 K while that of ortho hydrogen 20.39 K. Since the nuclear spins are in opposite directions the magnetic moment of para hydrogen is zero and ortho hydrogen has magnetic moment twice that of a proton.

4.2 Preparation of Hydrogen

High purity hydrogen (>99.9 %) is obtained by the electrolysis of water containing traces of acid or alkali or the electrolysis of aqueous solution of sodium hydroxide or potassium hydroxide using a nickel anode and iron cathode. However, this process is not economical for large-scale production.

At anode : $2 \text{OH}^- \rightarrow \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 + 2\text{e}^-$

At cathode : $2 \text{H}_2\text{O} + 2 \text{e}^- \rightarrow 2 \text{OH}^- + \text{H}_2$

Overall reaction : $\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2$

4.2.1 Laboratory Preparation

Hydrogen is conveniently prepared in laboratory by the reaction of metals, such as zinc, iron, tin with dilute acid.

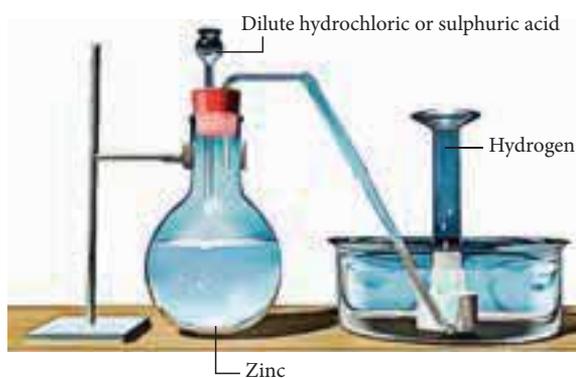
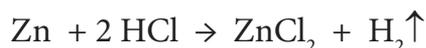


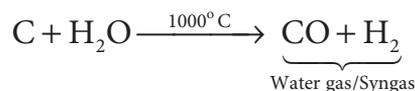
Figure 4.2 Laboratory preparation of hydrogen

4.2.2 Industrial Production

In the large-scale, hydrogen is produced by steam-reforming of hydrocarbons. In this method hydrocarbon such as methane is mixed with steam and passed over nickel catalyst in the range 800-900 °C and 35 atm pressures.

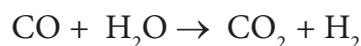


In an another process, steam is passed over a red-hot coke to produce carbon monoxide and hydrogen. The mixture of gases produced in this way is known as *water gas* ($\text{CO} + \text{H}_2$). This is also called *syngas* (Synthetic gas) as it is used in the synthesis of organic compounds such as methanol and simple hydrocarbons.



Conversion of Carbon monoxide in water gas to Carbon dioxide:

The carbon monoxide of the water gas can be converted to carbon dioxide by mixing the gas mixture with more steam at 400°C and passed over a shift converter containing iron/copper catalyst. This reaction is called as *water-gas shift reaction*.



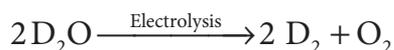
The CO₂ formed in the above process is absorbed in a solution of potassium carbonate.



4.2.3 Preparation of Deuterium:

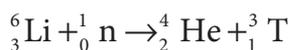
Electrolysis of heavy water:

Normal water contains 1.6×10^{-4} percentage of heavy water. The dissociation of protium water (H_2O) is more than heavy water (D_2O). Therefore, when water is electrolysed, hydrogen is liberated much faster than D_2 . The electrolysis is continued until the resulting solution becomes enriched in heavy water. Further electrolysis of the heavy water gives deuterium.



4.2.4 Preparation of Tritium:

As explained earlier the tritium is present only in trace amounts. So it can be artificially prepared by bombarding lithium with slow neutrons in a nuclear fission reactor. The nuclear transmutation reaction for this process is as follows.



4.3 Properties of Hydrogen

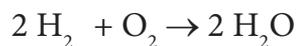
4.3.1 Physical Properties:

Hydrogen is a colorless, odorless, tasteless, lightest and highly flammable gas. It is a non-polar diatomic molecule. It can be liquefied under low temperature and high pressure. Hydrogen is a good reducing agent. Various physical constants of hydrogen molecule are listed in Table 4.1.

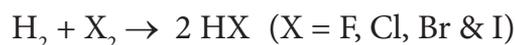
4.3.2 Chemical Properties:

Hydrogen reacts with oxygen to give water. This is an explosive reaction and

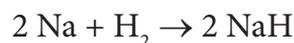
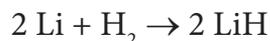
releases lot of energy. This is used in fuel cells to generate electricity.



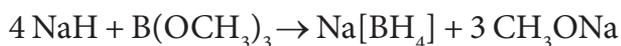
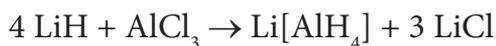
Similarly, hydrogen also reacts with halogens to give corresponding halides. Reaction with fluorine takes place even in dark with explosive violence while with chlorine at room temperature under light. It combines with bromine on heating and reaction with iodine is a photochemical reaction.



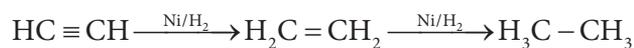
In the above reactions the hydrogen has an oxidation state of +1. It also has a tendency to react with reactive metals such as lithium, sodium and calcium to give corresponding hydrides in which the oxidation state of hydrogen is -1.



These hydrides are used as reducing agents in synthetic organic chemistry. It is used to prepare other important hydrides such as lithium aluminium hydride and sodium boro hydride.

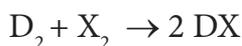
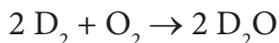


Hydrogen itself acts as a reducing agent. In the presence of finely divided nickel, it adds to the unsaturated organic compounds to form saturated compounds.



4.3.3 Chemical properties of Deuterium

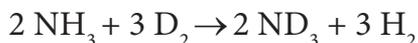
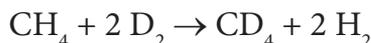
Like hydrogen, deuterium also reacts with oxygen to form deuterium oxide called heavy water. It also reacts with halogen to give corresponding halides.



(X = F, Cl, Br & I)

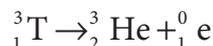
Deuterium exchange reactions:

Deuterium can replace reversibly hydrogen in compounds either partially or completely depending upon the reaction conditions. These reactions occur in the presence of deuterium or heavy water.



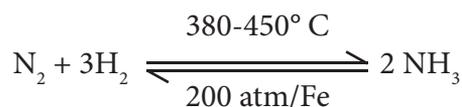
4.3.4 Properties of Tritium

It is a β -emitter with a half-life period of 12.3 years .



4.4 USES OF HYDROGEN

1. Over 90 % hydrogen produced in industry is used for synthetic applications. One such process is Haber process which is used to synthesis ammonia in large scales. Ammonia is used for the manufacture of chemicals such as nitric acid, fertilizers and explosives.

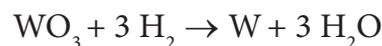
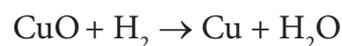


2. It can be used to manufacture the industrial solvent, methanol from carbon monoxide using copper as catalyst.



3. Unsaturated fatty oils can be converted into saturated fats called Vanaspati (margarine) by the reduction reaction with Pt/H₂.

4. In metallurgy, hydrogen can be used to reduce many metal oxides to metals at high temperatures.



5. Atomic hydrogen and oxy-hydrogen torches are used for cutting and welding.

6. Liquid hydrogen is used as a rocket fuel.

7. Hydrogen is also used in fuel cells for generating electrical energy. The reversible uptake of hydrogen in metals is also attractive for rechargeable metal hydride battery.

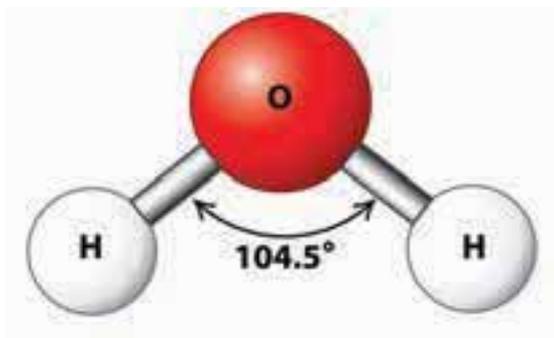


Figure 4.3: Application of rocket fuel

4.5 Compounds of Hydrogen

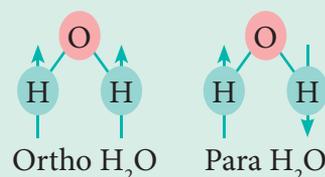
4.5.1 Water

Water is one of the most abundant compounds of hydrogen and our earth's surface contains approximately 70 % of ocean which is the major source of water. However, sea water contains many dissolved salts hence it can not be used directly. Water is essential for all living things and our body contains about 65% water.



Ortho-H₂O and Para-H₂O

Water exists in the interstellar clouds, in proto-planetary disks, in the comets and icy satellites of the solar system. In particular, the ortho-to-para ratio (OPR) of water in space has recently received attention. Like hydrogen, water can also be classified into ortho-H₂O, in which the spin directions of the nuclei of the hydrogen atoms are parallel, and para-H₂O, in which the directions are antiparallel. At the temperature conditions of the earth (300 K), the OPR of H₂O is 3. However, at low temperatures (< 50 K) the amount of para-H₂O increases. It is known that the OPR of water in interstellar clouds and comets has more para-H₂O (OPR = 2.5) than on Earth.



4.5.2 Physical Properties:

Water is a colourless and volatile liquid. The peculiar properties of water in the condensed phases are due to the presence of inter molecular hydrogen bonding between water molecules. Hydrogen bonding is responsible for the high melting and boiling points of water. Some of the physical parameters of water are listed in Table 4.2.

Table 4.2 Properties of water, heavy water and super heavy water[†].

Property	H ₂ O	D ₂ O	T ₂ O
Molecular weight	18.015	22.028	22.0312
Melting point (K)	273.0	276.8	277.5
Boiling point (K)	373.0	374.4	374.5
Temperature of maximum density (K)	277.0	284.2	286.4
Maximum density (g/cm ³)	1.000	1.106	1.215
Density (g/cm ³)	0.997	1.104	1.214
Vapour pressure (mm Hg)	23.75	20.51	19.80
Viscosity (cP)	0.890	1.107	---
Dielectric constant	78.39	78.06	---
Enthalpy of formation (kJ/mol)	- 285.9	- 294.6	---
Enthalpy of vaporization (kJ/mol)	40.66	41.61	---

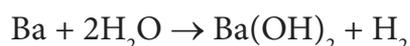
[†]Unless otherwise stated, all data are at 298 K.

4.5.3 Chemical Properties:

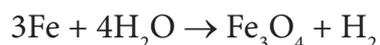
Water reacts with metals, non-metals and other compounds differently. The most reactive metals are the alkali metals. They decompose water even in cold with the evolution of hydrogen leaving an alkali solution.



The group 2 metals (except beryllium) react in a similar way but less violently. The hydroxides are less soluble than those of Group 1.

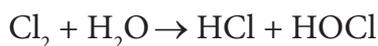


Some transition metals react with hot water or steam to form the corresponding oxides. For example, steam passed over red hot iron results in the formation of iron oxide with the release of hydrogen.

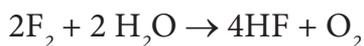


Lead and copper decompose water only at a white heat. Silver, gold, mercury and platinum do not have any effect on water. In the elemental form, the non-metals such as carbon, sulphur and phosphorus normally do not react with water. However, as we have seen earlier, carbon will react with steam when it is red (or white) hot to give *water gas*.

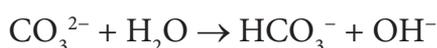
On the other hand, the halogens react with water to give an acidic solution. For example, chlorine forms hydrochloric acid and hypo chlorous acid. It is responsible for the antibacterial action of chlorine water, and for its use as bleach.



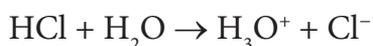
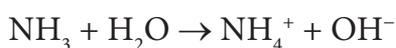
Fluorine reacts differently to liberate oxygen from water.



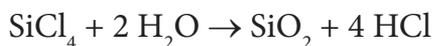
In a similar way, compounds of non-metals react with water to give acidic or alkaline solutions. For example, solutions of carbonates are slightly alkaline.



Water is an amphoteric oxide. It has the ability to accept as well as donate protons and hence it can act as an acid or a base. For example, in the reaction with HCl it accepts proton whereas in the reaction with weak base ammonia it donates proton.



Water dissolves ionic compounds. In addition, it also hydrolyses some covalent compounds.



Many salts crystallized from aqueous solutions form hydrated crystals. The water in the hydrated salts may form co-ordinate bond or just present in interstitial positions of crystals.

Examples: $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ – All six water molecules form co-ordinate bond

$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ – Both the water molecules are present in interstitial positions.

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ – In this compound four water molecules form co-ordinate bonds while the fifth water molecule, present outside the co-ordination, can form intermolecular hydrogen bond with another molecule. $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$

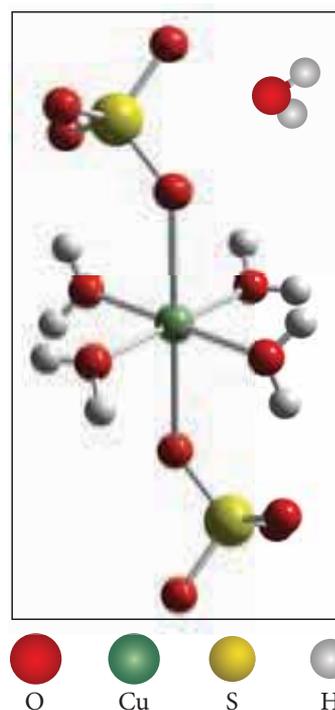


Figure 4.4 structure of copper sulphate pentahydrate

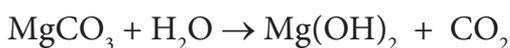
4.5.4 Hard and Soft Water:

Hard water contains high amounts of mineral ions. The most common ions found in hard water are the soluble metal cations such as magnesium & calcium, though iron, aluminium, and manganese may also be found in certain areas. Presence of these metal salts in the form of bicarbonate,

chloride and sulphate in water makes water 'hard'. When hard water is boiled carbonates of magnesium and calcium present in it gets precipitated. On the other hand, water free from soluble salts of calcium and magnesium is called soft water. The hardness of water is of two types, viz., temporary hardness and permanent hardness.

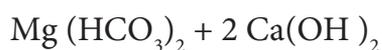
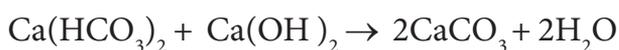
Temporary Hardness and its removal:

Temporary hardness is primarily due to the presence of soluble bicarbonates of magnesium and calcium. This can be removed by boiling the hard water followed by filtration. Upon boiling, these salts decompose into insoluble carbonate which leads to their precipitation. The magnesium carbonate thus formed further hydrolysed to give insoluble magnesium hydroxide.

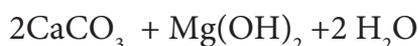


The resulting precipitates can be removed by filtration.

Alternatively, we can use Clark's method in which, calculated amount of lime is added to hard water containing the magnesium and calcium, and the resulting carbonates and hydroxides can be filtered-off.

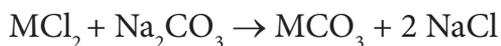


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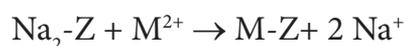


Permanent Hardness:

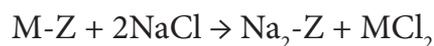
Permanent hardness of water is due to the presence of soluble salts of magnesium and calcium in the form of chlorides and sulphates in it. It can be removed by adding washing soda, which reacts with these metal (M = Ca or Mg) chlorides and sulphates in hard water to form insoluble carbonates.

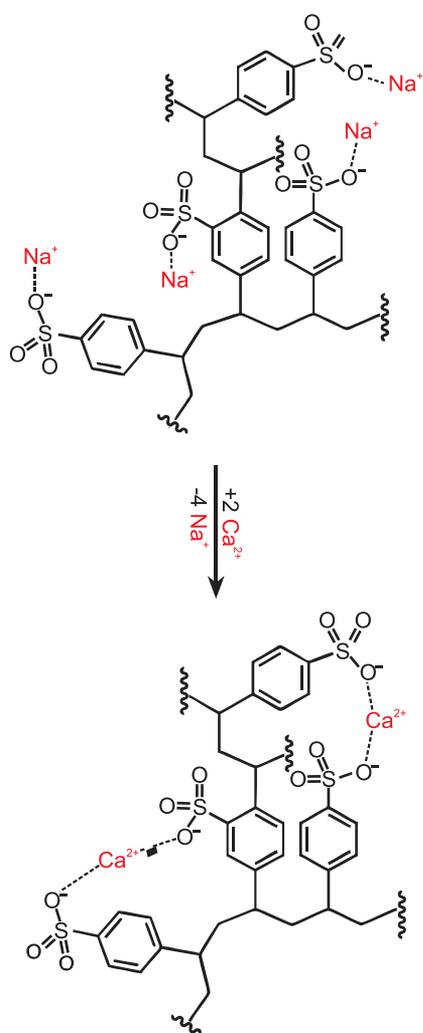
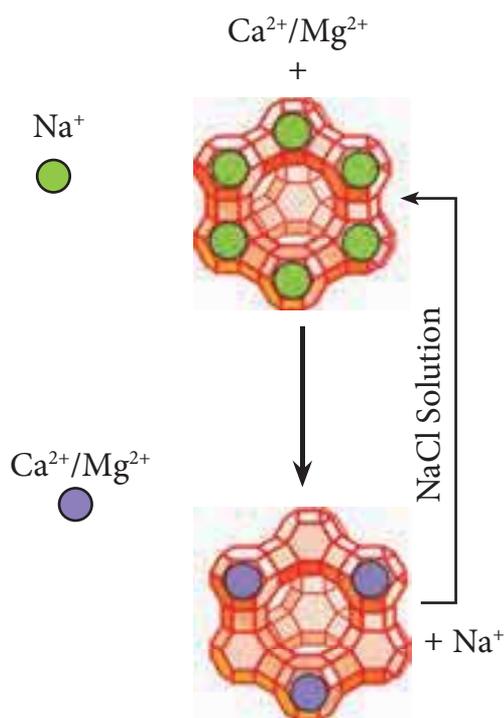


In another way to soften the hard water is by using a process called ion-exchange. That is, hardness can be removed by passing through an ion-exchange bed like zeolites or column containing ion-exchange resin. Zeolites are hydrated sodium aluminosilicates with a general formula, $\text{NaO} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$ ($x = 2$ to 10 , $y = 2$ to 6). Zeolites have porous structure in which the monovalent sodium ions are loosely held and can be exchanged with hardness producing metal ions (M = Ca or Mg) in water. The complex structure can conveniently be represented as $\text{Na}_2\text{-Z}$ with sodium as exchangeable cations.



When exhausted, the materials can be regenerated by treating with aqueous sodium chloride. The metal ions (Ca^{2+} and Mg^{2+}) caught in the zeolite (or resin) are released and they get replenished with sodium ions.





4.6 Heavy Water:

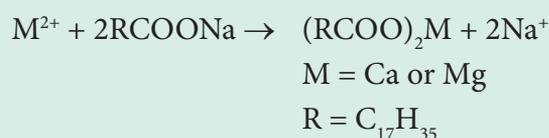
Heavy water (D_2O) is the oxide of heavy hydrogen. One part of heavy water is present in 5000 parts of ordinary water. It is mainly obtained as the product of electrolysis of water, as D_2O does not undergo electrolysis as easily as H_2O .

D_2O is a colorless, odorless and tasteless liquid. However, there is a marked difference between physical properties of water and heavy water as shown in Table 4.2.



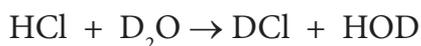
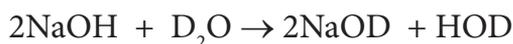
Hard water produces less foam with detergents. Do you know why?

The cleaning capacity of soap is reduced when used in hard water. Soaps are sodium or potassium salts of long chain fatty acids (e.g., coconut oil). When soap is added to hard water, the divalent magnesium and calcium ions present in hard water react with soap. The sodium salts present in soaps are converted to their corresponding magnesium and calcium salts which are precipitated as scum/precipitate.



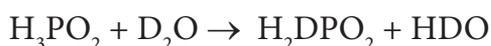
4.6.1 Chemical properties of heavy water:

When compounds containing hydrogen are treated with D_2O , hydrogen undergoes an exchange for deuterium

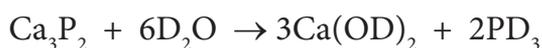
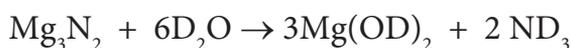
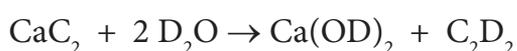
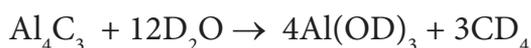


These exchange reactions are useful in determining the number of ionic hydrogens present in a given compound.

For example, when D_2O is treated with of hypo-phosphorus acid only one hydrogen atom is exchanged with deuterium. It indicates that, it is a monobasic acid.



It is also used to prepare some deuterium compounds:

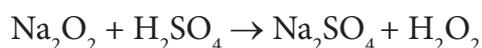
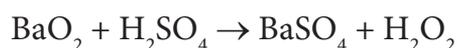


4.6.2 Uses of heavy water:

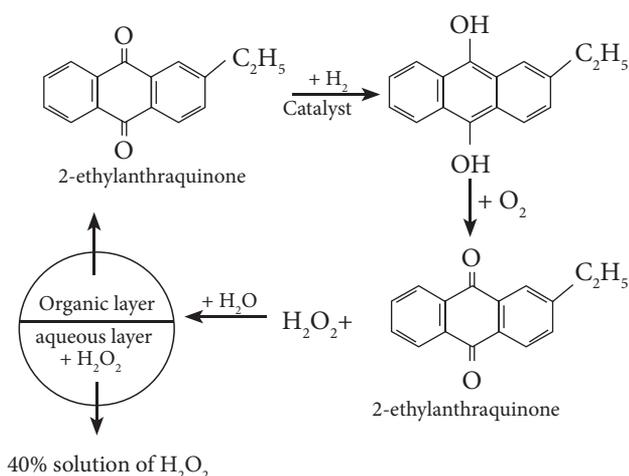
1. Heavy water is widely used as moderator in nuclear reactors as it can lower the energies of fast neutrons
2. It is commonly used as a tracer to study organic reaction mechanisms and mechanism of metabolic reactions
3. It is also used as a coolant in nuclear reactors as it absorbs the heat generated.

4.7 Hydrogen Peroxide:

Hydrogen peroxide (H_2O_2) is one of the most important peroxides. It can be prepared by treating metal peroxide with dilute acid.



On an industrial scale, hydrogen peroxide is now prepared exclusively by autoxidation of 2-alkyl anthraquinol.



4.7.1 Physical properties:

Pure hydrogen peroxide is almost a colorless liquid (pale blue), less volatile and more viscous than water.

A 30 % solution of hydrogen peroxide is marketed as '100-volume' hydrogen peroxide indicating that at S.T.P., 100 ml of oxygen is liberated by 1 ml of this solution on heating.

4.7.2 Chemical properties:

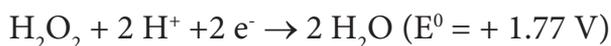
Hydrogen peroxide is highly unstable and the aqueous solution spontaneously

disproportionates to give oxygen and water. The reaction is, however, slow but is explosive when catalyzed by metal. If it is stored in glass container, it dissolves the alkali metals from the glass, which catalyzes the disproportionation reaction. For this reason, H_2O_2 solutions are stored in plastic bottles.



Hydrogen peroxide can act both as an oxidizing agent and a reducing agent. Oxidation is usually performed in acidic medium while the reduction reactions are performed in basic medium

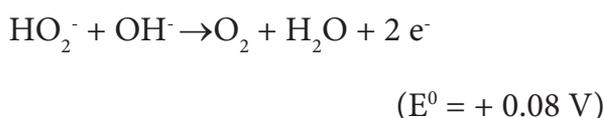
In acidic conditions:



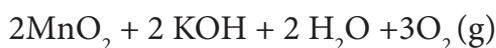
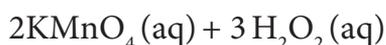
For example



In basic conditions:



For Example,

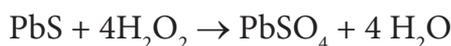


4.7.3 Uses of hydrogen peroxide:

The oxidizing ability of hydrogen peroxide and the harmless nature of its products, i.e., water and oxygen, lead to its many applications. It is used in water treatment to oxidize pollutants, as a mild

antiseptic, and as bleach in textile, paper and hair-care industry.

Hydrogen peroxide is used to restore the white colour of the old paintings which was lost due to the reaction of hydrogen sulphide in air with the white pigment $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$ to form black colored lead sulphide. Hydrogen peroxide oxidises black coloured lead sulphide to white coloured lead sulphate, there by restoring the colour.



4.7.4 Structure of hydrogen peroxide:

Both in gas-phase and liquid-phase, the molecule adopts a skew conformation due to repulsive interaction of the OH bonds with lone-pairs of electrons on each oxygen atom. Indeed, it is the smallest molecule known to show hindered rotation about a single bond.

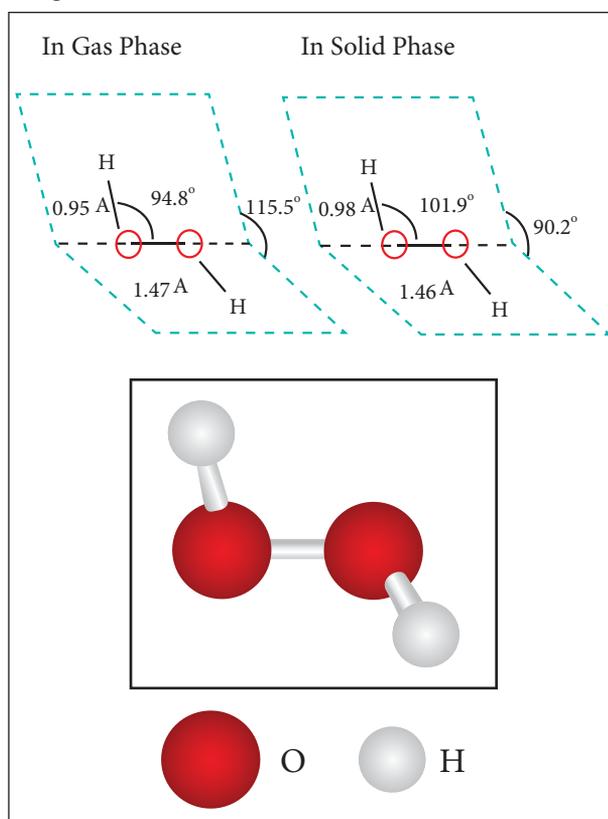


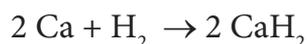
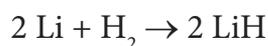
Figure 4.5 structure of H_2O_2

H_2O_2 has a non-polar structure. The molecular dimensions in the gas phase and solid phase differ as shown in figure 4.5. Structurally, H_2O_2 is represented by the dihydroxyl formula in which the two OH groups do not lie in the same plane. One way of explaining the shape of hydrogen peroxide is that the hydrogen atoms would lie on the pages of a partly opened book, and the oxygen atoms along the spine. In the solid phase of molecule, the dihedral angle reduces to 90.2° due to hydrogen bonding and the O-O-H angle expands from 94.8° to 101.9° .

4.8 Hydrides

Hydrogen forms binary hydrides with many electropositive elements including metals and non-metals. It also forms ternary hydrides with two metals. E.g., LiBH_4 and LiAlH_4 . The hydrides are classified as ionic, covalent and metallic hydrides according to the nature of bonding. Hydrides formed with elements having lower electronegativity than hydrogen are often ionic, whereas with elements having higher electronegativity than hydrogen form covalent hydrides.

Ionic (Saline) hydrides: These are hydrides composed of an electropositive metal, generally, an alkali or alkaline-earth metal, except beryllium and magnesium, formed by transfer of electrons from metal to hydrogen atoms. They can be prepared by the reaction of elements at about 400°C . These are salt-like, high-melting, white crystalline solids having hydride ions (H^-) and metal cations (M^{n+}).



Covalent (Molecular) hydrides: They are compounds in which hydrogen is attached to another element by sharing of electrons. The most common examples of covalent hydrides of non-metals are methane, ammonia, water and hydrogen chloride. Covalent hydrides are further divided into three categories, viz., electron precise (CH_4 , C_2H_6 , SiH_4 , GeH_4), electron-deficient (B_2H_6) and electron-rich hydrides (NH_3 , H_2O). Since most of the covalent hydrides consist of discrete, small molecules that have relatively weak intermolecular forces, they are generally gases or volatile liquids.

Metallic (Interstitial) hydrides: Metallic hydrides are usually obtained by hydrogenation of metals and alloys in which hydrogen occupies the interstitial sites (voids). Hence, they are called interstitial hydrides; the hydrides show properties similar to parent metals and hence they are also known as metallic hydrides. Most of the hydrides are non-stoichiometric with variable composition ($\text{TiH}_{1.5-1.8}$ and $\text{PdH}_{0.6-0.8}$), some are relatively light, inexpensive and thermally unstable which make them useful for hydrogen storage applications. Electropositive metals and some other metals form hydrides with the stoichiometry MH or sometimes MH_2 ($\text{M} = \text{Ti, Zr, Hf, V, Zn}$).

4.9 Hydrogen Bonding

Hydrogen bonding is one of the most important natural phenomena occurring in chemical and biological sciences. These interactions play a major role in the

structure of proteins and DNA. When a hydrogen atom (H) is covalently bonded to a highly electronegative atom such as fluorine (F) or oxygen (O) or nitrogen (N), the bond is polarized. Due to this effect, the polarized hydrogen atom is able to form a weak electrostatic interaction with another electronegative atom present in the vicinity. This interaction is called as a hydrogen bond ($20\text{-}50\text{ kJ mol}^{-1}$) and is denoted by dotted lines (...).

It is weaker than covalent bond ($> 100\text{ kJ mol}^{-1}$) but stronger than the van der Waals interaction ($< 20\text{ kJ mol}^{-1}$). Hydrogen bond has profound effect on various physical properties including vapour pressure (H_2O and H_2S), boiling point, miscibility of liquids (H_2O and $\text{C}_2\text{H}_5\text{OH}$), surface tension, densities, viscosity, heat of vaporization and fusion, etc. Hydrogen bonds can occur within a molecule (*intramolecular hydrogen bonding*) and between two molecules of the same type or different type (*intermolecular hydrogen bonding*).

Intramolecular Hydrogen Bond

Intramolecular hydrogen bonds are those which occur within a single molecule.

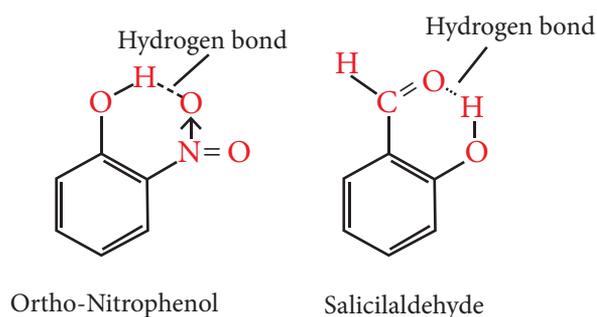


Figure 4.6 Intramolecular hydrogen bonding

Intermolecular hydrogen bond

Intermolecular hydrogen bonds occur between two separate molecules. They can occur between any numbers of like or unlike molecules as long as hydrogen donors and acceptors are present in positions which enable the hydrogen bonding interactions. For example, intermolecular hydrogen bonds can occur between ammonia molecule themselves or between water molecules themselves or between ammonia and water.

Water molecules form strong hydrogen bonds with one another. For example, each water molecule is linked to four others through hydrogen bonds. The shorter distances (100 pm) correspond to covalent bonds (solid lines), and the longer distances (180 pm) correspond to hydrogen bonds (dotted lines).

In ice, each atom is surrounded tetrahedrally by four water molecules through hydrogen bonds. That is, the presence of two hydrogen atoms and two lone pairs of electron on oxygen atoms in each water molecule allows formation of a three-dimensional structure. This arrangement creates an open structure, which accounts for the lower density of ice compared with water at 0°C . While in liquid water, unlike ice where hydrogen bonding occurs over a long-range, the strong hydrogen bonding prevails only in a short range and therefore the denser packing.

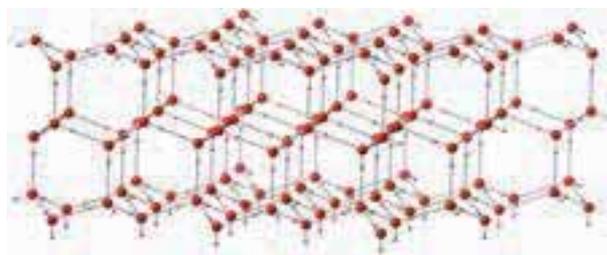


Figure 4.7 (a) Structure of Ice

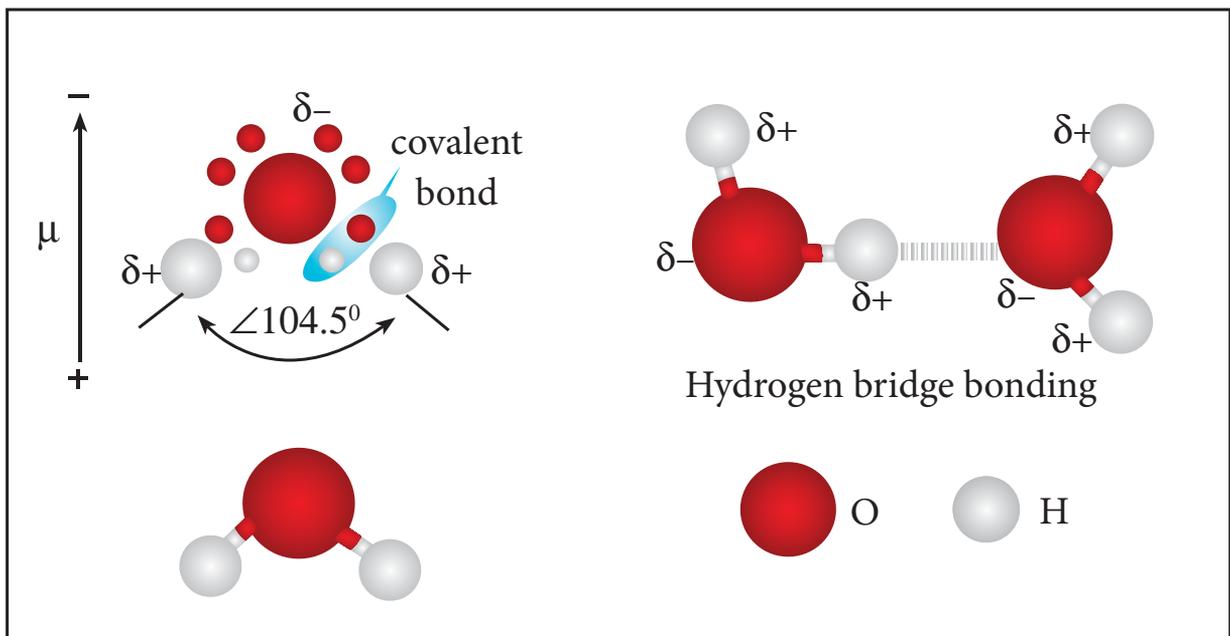


Figure 4.7 (b) Hydrogen bonding in water

Hydrogen bond occurs not only in simple molecules but also in complex biomolecules such as proteins, and they are crucial for biological processes. For example, hydrogen bonds play an important role in the structure of deoxyribonucleic acid (DNA), since they hold together the two helical nucleic acid chains (strands).

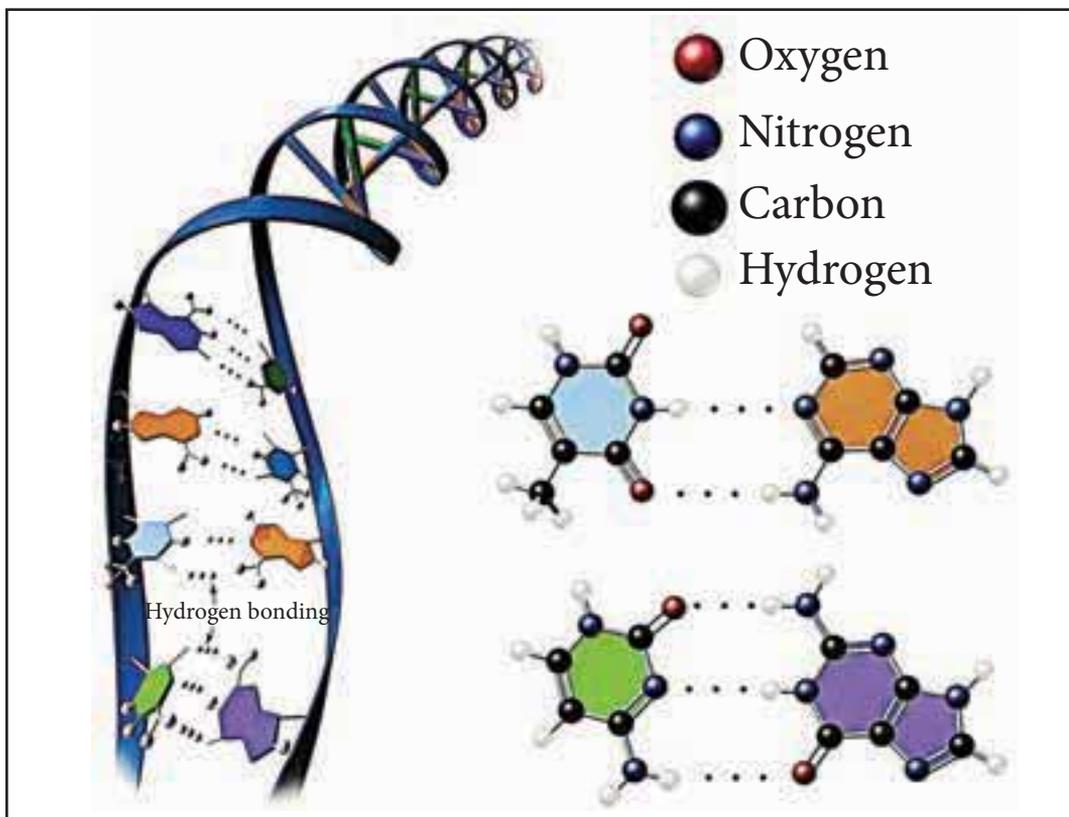


Figure 4.8 Hydrogen bonding in DNA molecules



Significant developments related to hydrogen

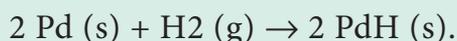
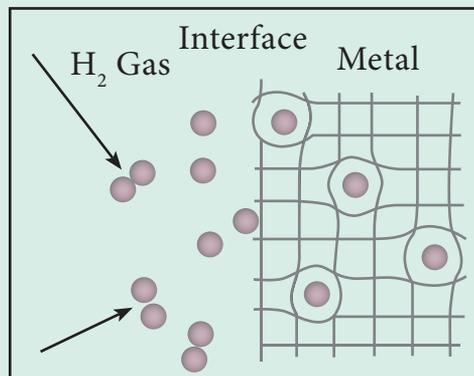
1670	Robert Boyle produced flammable gas by reacting metals with acid.
1700	Nicolas Lemery showed that the gas produced in the sulphuric acid/iron reaction was explosive in air.
1766	Henry Cavendish, discovered hydrogen by reacting zinc metal with hydrochloric acid and isolated a gas.
1780	Felice Fontana discovered the water-gas shift reaction
1783	Antoine Lavoisier named the element hydrogen (Greek meaning – water former).
1800	William Nicholson and Anthony Carlisle decomposed water into hydrogen and oxygen by electrolysis.
1801	Humphrey Davy discovered the concept of the Fuel Cell.
1806	François I. de Rivaz built the first internal combustion engine powered by a mixture of hydrogen and oxygen.
1811	Humphrey Davy discovered gas hydrates ($\text{Cl}_2 \cdot 7\text{H}_2\text{O}$).
1818	J.L. Thenard recognized and prepared hydrogen peroxide from BaO_2 .
1834	Michael Faraday published Faraday's laws of electrolysis
1866	T. Graham discovered solubility/absorption of hydrogen on palladium.
1897	Paul Sabatier facilitated the use of hydrogenation with the discovery of the Sabatier reaction.
1898	James Dewar liquefied hydrogen.
1909	S.P.L. Sorensen introduced the pH scale for hydrogen ion concentration.

1910	Fritz Haber patented the Haber process.
1913	Niels Bohr explained the Rydberg formula for the spectrum of hydrogen by imposing a quantization condition on classical orbits of the electron in hydrogen
1924	R. Mecke discovered ortho- and para-hydrogen.
1931	Harold C. Urey discovered deuterium.
1932	Harold C. Urey discovered heavy water
1932	L.P. Hammett proposed acidity function (H_0) for very strong acids.
1934	Ernest Rutherford, Mark Oliphant, and Paul Harteck discovered tritium.
1935	Eugene Wigner and H.B. Huntington predicted metallic hydrogen.
1947	A.E. Finholt, A.C. Bond and H.I. Schlesinger discovered LiAlH_4 and subsequently shown to be a versatile reducing agent.
1950	V. Faltings and P. Harteck detected first tritium in atmosphere.
1967	Akira Fujishima discovered the phenomenon of photocatalytic water decomposition.
1971	Alexandr I. Kloss and Boris I. Tsenter patented the Nickel-Hydrogen battery.
1990	Solar-Wasserstoff-Bayern, The first solar-powered hydrogen production plant became operational.
2000	Peter Toennies demonstrated superfluidity of hydrogen at 0.15 K.

METAL HYDRIDE (HYDROGEN SPONGE)



The best studied binary hydrides are the palladium-hydrogen system. Hydrogen interacts with palladium in a unique way, and forms a limiting monohydride, PdH. Upon heating, H atoms diffuse through the metal to the surface and recombine to form molecular hydrogen. Since no other gas behaves this way with palladium, this process has been used to separate hydrogen gas from other gases:



The hydrogen molecule readily adsorb on the palladium surface, where it dissociates into atomic hydrogen. The dissociated atoms dissolve into the interstices or voids (octahedral/tetrahedral) of the crystal lattice.

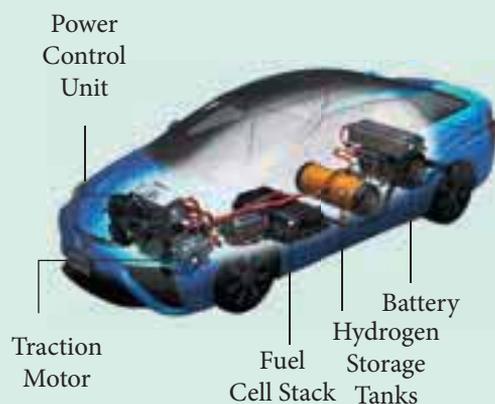
Technically, the formation of metal hydride is by chemical reaction but it behaves like a physical storage method, i.e., it is absorbed and released like a water sponge. Such a reversible uptake of hydrogen in metals and alloys is also attractive for hydrogen storage and for rechargeable metal hydride battery applications.

The Hydrogen – Future Fuel



The depletion of fossil fuel reserves and the threat of global warming make the world to shift toward alternative fuels. In this regard, hydrogen is often considered as a potential candidate for this purpose as it is a clean burning fuel as it does not produce any pollutants upon burning. Hence, hydrogen can directly be used as a fuel and can replace existing gasoline (petrol)/diesel/kerosene powered engines, and/

or indirectly be used with oxygen in fuel cells to generate electricity. However, there are some difficulties needs to be overcome. The production cost is high and also uses more fossil fuels. Due to its volatile and flammable nature in its native form, it is difficult to store and transport. Being the smallest molecule it is prone to leakage.



SUMMARY

Hydrogen is the simplest atom which contains one electron and one proton. It has three isotopes namely protium, deuterium and tritium. The hydrogen exists as diatomic gaseous molecule. The molecule has two nuclear spin isomers namely ortho and para-hydrogen. Elemental hydrogen having an electronic configuration of $1s^1$, has properties similar to alkali metals as well as halogens. Based on its electronic configuration and existence of the +1 oxidation state in most of the compounds it is placed in group 1 along with alkali metals.

Hydrogen is prepared by the action of metal with mineral acids in laboratory. In industrial scale, hydrogen is produced by the steam-reforming of hydrocarbons. Deuterium can be synthesized by the electrolysis of heavy water, while the radioactive tritium is prepared by the nuclear transmutation reaction of lithium with slow neutrons.

Hydrogen reacts with nonmetals like oxygen and halogens to form water and hydrogen halides respectively. It reacts with metals to form metal hydrides. It acts as good reducing agent. Deuterium undergoes

exchange reactions with hydrogen. Tritium with a half-life period of 12.4 years and emits β -particles spontaneously. Hydrogen has many uses including in the preparation of ammonia, methanol, and hydrogenation of oils and reduction of metal oxides. It can also be used as fuel.

Water is an important amphoteric oxide of hydrogen and used a universal solvent. It hydrolyses oxides and forms metal hydroxides with metals such as sodium and barium. Due to the presence of soluble salts of calcium and magnesium in water, the water shows hardness. Clark's method can be used to remove temporary hardness. Like water, another important oxide is hydrogen peroxide. It is used as a mild antiseptic and as a bleaching agent in textile and paper industries. Hydrogen bound to strong electronegative atoms such as fluorine, nitrogen or oxygen atoms, forms a peculiar type of electrostatic interactions with another strong electronegative atom. This is called hydrogen bond. This is one of important interactions observed in many biological molecules such as proteins, DNA etc...

EVALUATION



- Which of the following statements about hydrogen is incorrect ? (NEET - 2016)
 - Hydrogen ion, H_3O^+ exists freely in solution.
 - Dihydrogen acts as a reducing agent.
 - Hydrogen has three isotopes of which tritium is the most common.
 - Hydrogen never acts as cation in ionic salts.
- Water gas is
 - H_2O (g)
 - $\text{CO} + \text{H}_2\text{O}$
 - $\text{CO} + \text{H}_2$
 - $\text{CO} + \text{N}_2$
- Which one of the following statements is incorrect with regard to ortho and para dihydrogen ?
 - They are nuclear spin isomers
 - Ortho isomer has zero nuclear spin whereas the para isomer has one nuclear spin
 - The para isomer is favoured at low temperatures
 - The thermal conductivity of the para isomer is 50% greater than that of the ortho isomer.
- Ionic hydrides are formed by
 - halogens
 - chalogens
 - inert gases
 - group one elements
- Tritium nucleus contains
 - 1p + 0 n
 - 2 p + 1n
 - 1p + 2n
 - none of these
- Non-stoichiometric hydrides are formed by
 - palladium, vanadium
 - carbon, nickel
 - manganese, lithium
 - nitrogen, chlorine

7. Assertion : Permanent hardness of water is removed by treatment with washing soda.
Reason : Washing soda reacts with soluble calcium and magnesium chlorides and sulphates in hard water to form insoluble carbonates
- a) Both assertion and reason are true and reason is the correct explanation of assertion.
b) Both assertion and reason are true but reason is not the correct explanation of assertion.
c) Assertion is true but reason is false
d) Both assertion and reason are false
8. If a body of a fish contains 1.2 g hydrogen in its total body mass, if all the hydrogen is replaced with deuterium then the increase in body weight of the fish will be
- a) 1.2 g b) 2.4 g c) 3.6 g d) $\sqrt{4.8}$ g
9. The hardness of water can be determined by volumetrically using the reagent
- a) sodium thio sulphate b) potassium permanganate
c) hydrogen peroxide d) EDTA
10. The cause of permanent hardness of water is due to
- a) $\text{Ca}(\text{HCO}_3)_2$ b) $\text{Mg}(\text{HCO}_3)_2$ c) CaCl_2 d) MgCO_3
11. Zeolite used to soften hardness of water is, hydrated
- a) Sodium aluminium silicate b) Calcium aluminium silicate
c) Zinc aluminium borate d) Lithium aluminium hydride
12. A commercial sample of hydrogen peroxide marked as 100 volume H_2O_2 , it means that
- a) 1 ml of H_2O_2 will give 100 ml O_2 at STP
b) 1 L of H_2O_2 will give 100 ml O_2 at STP
c) 1 L of H_2O_2 will give 22.4 L O_2
d) 1 ml of H_2O_2 will give 1 mole of O_2 at STP

13. When hydrogen peroxide is shaken with an acidified solution of potassium dichromate in presence of ether, the ethereal layer turns blue due to the formation of
- a) Cr_2O_3 b) CrO_4^{2-} c) $\text{CrO}(\text{O}_2)_2$ d) none of these
14. For decolourisation of 1 mole of acidified KMnO_4 , the moles of H_2O_2 required is
- a) $\frac{1}{2}$ b) $\frac{3}{2}$ c) $\frac{5}{2}$ d) $\frac{7}{2}$
15. Volume strength of 1.5 N H_2O_2 is
- a) 1.5 b) 4.5 c) 16.8 d) 8.4
16. The hybridisation of oxygen atom in H_2O and H_2O_2 are, respectively
- a) sp and sp^3 b) sp and sp c) sp and sp^2 d) sp^3 and sp^3
17. The reaction $\text{H}_3\text{PO}_2 + \text{D}_2\text{O} \rightarrow \text{H}_2\text{DPO}_2 + \text{HDO}$ indicates that hypo-phosphorus acid is
- a) tribasic acid b) dibasic acid c) mono basic acid d) none of these
18. In solid ice, oxygen atom is surrounded
- a) tetrahedrally by 4 hydrogen atoms
- b) octahedrally by 2 oxygen and 4 hydrogen atoms
- c) tetrahedrally by 2 hydrogen and 2 oxygen atoms
- d) octahedrally by 6 hydrogen atoms
19. The type of H-bonding present in ortho nitro phenol and p-nitro phenol are respectively
- a) inter molecular H-bonding and intra molecular H-bonding
- b) intra molecular H-bonding and inter molecular H-bonding
- c) intra molecular H - bonding and no H - bonding
- d) intra molecular H - bonding and intra molecular H - bonding

20. Heavy water is used as
- a) modulator in nuclear reactions b) coolant in nuclear reactions
- c) both (a) and (b) d) none of these
21. Water is a
- a) basic oxide b) acidic oxide
- c) amphoteric oxide d) none of these

II. Write brief answer to the following questions:

22. Explain why hydrogen is not placed with the halogen in the periodic table.
23. An ice cube at 0° C is placed in some liquid water at 0° C, the ice cube sinks - Why ?
24. Discuss the three types of Covalent hydrides.
25. Predict which of the following hydrides is a gas and which is a solid (a) HCl (b) NaH. Give your reason.
26. Write the expected formulas for the hydrides of 4th period elements. What is the trend in the formulas? In what way the first two numbers of the series differ from the others ?
27. Write chemical equation for the following reactions.
- i) reaction of hydrogen with tungsten (VI) oxide WO_3 on heating.
- ii) hydrogen gas and chlorine gas.
28. Complete the following chemical reactions and classify them into (a) hydrolysis (b) redox (c) hydration reactions.
- 1) $\text{KMnO}_4 + \text{H}_2\text{O}_2 \rightarrow$
- 2) $\text{CrCl}_3 + \text{H}_2\text{O} \rightarrow$
- 3) $\text{CaO} + \text{H}_2\text{O} \rightarrow$
29. Hydrogen peroxide can function as an oxidising agent as well as reducing agent. substantiate this statement with suitable examples.

30. Do you think that heavy water can be used for drinking purposes ?
31. What is water-gas shift reaction ?
32. Justify the position of hydrogen in the periodic table ?
33. What are isotopes? Write the names of isotopes of hydrogen.
34. Give the uses of heavy water.
35. Explain the exchange reactions of deuterium.
36. How do you convert parahydrogen into ortho hydrogen ?
37. Mention the uses of deuterium.
38. Explain preparation of hydrogen using electrolysis.
39. A group metal (A) which is present in common salt reacts with (B) to give compound (C) in which hydrogen is present in -1 oxidation state. (B) on reaction with a gas (C) to give universal solvent (D). The compound (D) on reacts with (A) to give (B), a strong base. Identify A, B, C, D and E. Explain the reactions.
40. An isotope of hydrogen (A) reacts with diatomic molecule of element which occupies group number 16 and period number 2 to give compound (B) is used as a modulator in nuclear reaction. (A) adds on to a compound (C), which has the molecular formula C_3H_6 to give (D). Identify A, B, C and D.
41. NH_3 has exceptionally high melting point and boiling point as compared to those of the hydrides of the remaining element of group 15 - Explain.
42. Why interstitial hydrides have a lower density than the parent metal.
43. How do you expect the metallic hydrides to be useful for hydrogen storage ?
44. Arrange NH_3 , H_2O and HF in the order of increasing magnitude of hydrogen bonding and explain the basis for your arrangement.
45. Compare the structures of H_2O and H_2O_2 .



CONCEPT MAP

