

## 1. Details of Module and its structure

Module Detail	
Subject Name	Chemistry
Course Name	Chemistry 02 (Class XI, Semester 02)
Module Name/Title	Hydrogen – Part 2
Module Id	kech_20902
Pre-requisites	Hydrogen, Periodic table, Isotopes
Objectives	<p>After going through this module, the learner will be able to:</p> <ul style="list-style-type: none"><li>• Understand the structure of water and use the knowledge for explaining physical and chemical properties;</li><li>• Explain how environmental water quality depends on a variety of dissolved substances; difference between 'hard' and 'soft' water and learn about water softening;</li><li>• Acquire the knowledge about heavy water and its importance;</li><li>• Understand the structure of hydrogen peroxide, learn its preparatory methods and properties leading to the manufacture of useful chemicals and cleaning of environment;</li></ul>
Keywords	Water, Heavy water, Hardness, Hydrogen peroxide.

## 2. Development Team

Role	Name	Affiliation
National MOOC Coordinator (NMC)	Prof. Amarendra P. Behera	CIET, NCERT, New Delhi
Program Coordinator	Dr. Mohd. Mamur Ali	CIET, NCERT, New Delhi
Course Coordinator (CC) / PI	Prof. R. K. Parashar	DESM, NCERT, New Delhi
Course Co-Coordinator / Co-PI	Dr. Deepty Gupta	CIET, NCERT, New Delhi
Subject Matter Expert (SME)	Dr. (Mrs.) Komal S. Khatri	Part-Time Faculty, Applied Chemistry, G. B. Pant Institute of Polytechnic, Okhla-II, New Delhi
Review Team	Dr. Sulekha Chandra Dr Sanjeev Kumar Mishra	Zakir Husain Delhi College, University of Delhi Zakir Husain Delhi College, University of Delhi

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## Water

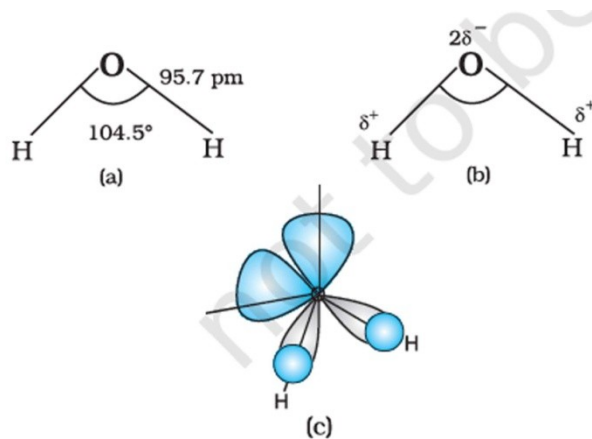
A major part of all living organisms is made up of water. Human body has about 65% and some plants have as much as 95% water. It is a crucial compound for the survival of all life forms. It is a solvent of great importance. The distribution of water over the earth's surface is not uniform. The estimated world water supply is given in Table 2.1.

**Table 2.1.** Estimated world water supply

Source	% of Total
Oceans	97.33
Saline lakes and Inland seas	0.008
Polar ice and glaciers	2.04
Ground water	0.61
Lakes	0.009
Soil moisture	0.005
Atmosphere water vapour	0.001
Rivers	0.0001

## Structure:

**Water:** In the gas phase water is a bent molecule with a bond angle of  $104.5^\circ$ , and O–H bond length of 95.7 pm as shown in Fig 2.1(a). It is a highly polar molecule, (Fig 2.1(b)). Its orbital overlap picture is shown in Fig.1(c). In the liquid phase water molecules are associated together by hydrogen bonds.

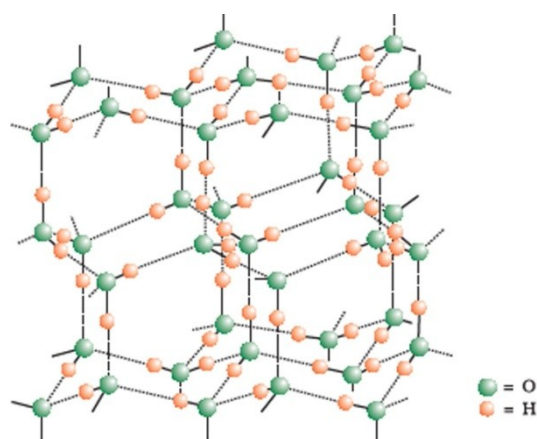


**Figure 2.1.(a)** Structure water

(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:** Ice has a highly ordered three dimensional hydrogen bonded structure as shown in Fig. 2. 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.



**Figure 2.2.** Structure of Ice

Hydrogen bonding gives ice a rather open type structure with wide holes. These holes can hold some other molecules of appropriate size interstitially.

### **Properties:**

**Physical Properties:** It is a colourless and tasteless liquid. Its physical properties are shown in Figure 2.2 along with the physical properties of heavy water.

Property	H <sub>2</sub> O	D <sub>2</sub> O
Molecular mass (g mol <sup>-1</sup> )	18.0151	20.0276
Melting point/K	273.0	276.8
Boiling point/K	373.0	374.4
Enthalpy of formation/kJ mol <sup>-1</sup>	-285.9	-294.6
Enthalpy of vaporisation (373K)/kJ mol <sup>-1</sup>	40.66	41.61
Enthalpy of fusion/kJ mol <sup>-1</sup>	6.01	-
Temp of max. density/K	276.98	284.2
Density (298K)/g cm <sup>-3</sup>	1.0000	1.1059
Viscosity/centipoise	0.8903	1.107
Dielectric constant/C <sup>2</sup> /N.m <sup>2</sup>	78.39	78.06
Electrical conductivity (293K)/ohm <sup>-1</sup> cm <sup>-1</sup>	5.7×10 <sup>-8</sup>	-

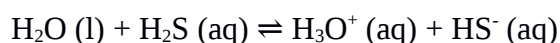
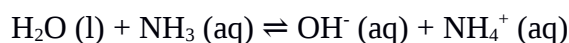
**Figure 2.2.** Physical properties of H<sub>2</sub>O and D<sub>2</sub>O

The unusual properties of water in the condensed phase (liquid and solid states) are due to the presence of extensive hydrogen bonding between water molecules. This leads to high freezing point, high boiling point, high heat of vaporisation and high heat of fusion in comparison to H<sub>2</sub>S and H<sub>2</sub>Se. In comparison to other liquids, water has a higher specific heat, thermal conductivity, surface tension, dipole moment and dielectric constant, etc. These properties allow water to play a key role in the biosphere.

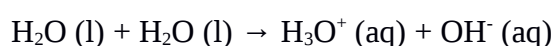
The high heat of vaporisation and heat capacity are responsible for moderation of the climate and body temperature of living beings. It is an excellent solvent for transportation of ions and molecules required for plant and animal metabolism. Due to hydrogen bonding with polar molecules, even covalent compounds like alcohol and carbohydrates dissolve in water.

**Chemical Properties:** Water reacts with a large number of substances. Some of the important reactions are given below.

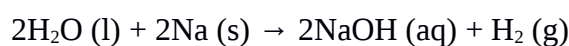
(1) **Amphoteric Nature:** It has the ability to act as an acid as well as a base i.e., it behaves as an amphoteric substance. In the Brønsted sense it acts as an acid with NH<sub>3</sub> and a base with H<sub>2</sub>S.



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



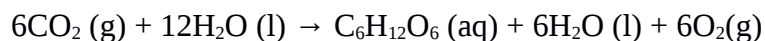
(2) **Redox Reactions Involving Water:** Water can be easily reduced to dihydrogen by highly electropositive metals.



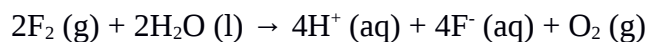
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Thus, it is a great source of dihydrogen.

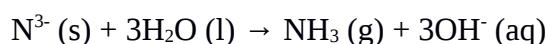
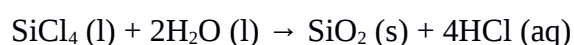
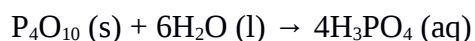
Water is oxidised to O<sub>2</sub> during photosynthesis.



With fluorine also it is oxidised to O<sub>2</sub>.



(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 viz.,

(i) coordinated water e.g.,  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+} 3\text{Cl}^-$

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

(iii) hydrogen-bonded water e.g.,  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+} \text{SO}_4^{2-} \cdot \text{H}_2\text{O}$  in  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

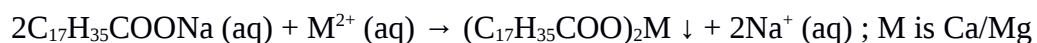
**Problem 2.1:** How many hydrogen-bonded water molecule(s) are associated in  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ?

**Solution:** Only one water molecule, which is outside the brackets (coordination sphere), is hydrogen-bonded. The other four molecules of water are coordinated.

### Hard & Soft Water:

Rain water is almost pure (may contain some dissolved gases from the atmosphere). Being a good solvent, when it flows on the surface of the earth, it dissolves many salts. Presence of calcium and magnesium salts in the form of hydrogencarbonate, chloride and sulphate in water makes water 'hard'. Hard water does not give lather with soap. Water free from soluble salts of calcium and magnesium is called Soft water. It gives lather with soap easily.

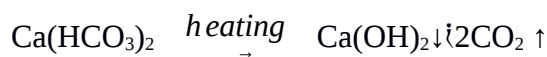
Hard water forms scum/precipitate with soap. Soap containing sodium stearate ( $\text{C}_{17}\text{H}_{35}\text{COONa}$ ) reacts with hard water to precipitate out Ca/Mg stearate.



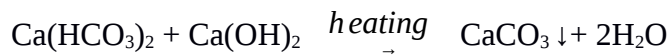
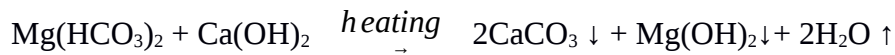
It is, therefore, unsuitable for laundry. It is harmful for boilers as well, because of deposition of salts in the form of scale. This reduces the efficiency of the boiler. The hardness of water is of two types: (i) temporary hardness, and (ii) permanent hardness.

**Temporary Hardness:** Temporary hardness is due to the presence of magnesium and calcium hydrogencarbonates. It can be removed by:

**(i) Boiling:** During boiling, the soluble  $\text{Mg}(\text{HCO}_3)_2$  is converted into insoluble  $\text{Mg}(\text{OH})_2$  and  $\text{Ca}(\text{HCO}_3)_2$  is changed to insoluble  $\text{CaCO}_3$ . It is because of high solubility product of  $\text{Mg}(\text{OH})_2$  as compared to that of  $\text{MgCO}_3$ , that  $\text{Mg}(\text{OH})_2$  is precipitated. These precipitates can be removed by filtration. Filtrate thus obtained will be soft water.

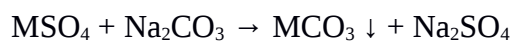
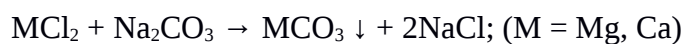


**(ii) Clark's method:** In this method calculated amount of lime is added to hard water. It precipitates out calcium carbonate and magnesium hydroxide which can be filtered off.



**Permanent Hardness:** It is due to the presence of soluble salts of magnesium and calcium in the form of chlorides and sulphates in water. Permanent hardness is not removed by boiling. It can be removed by the following methods:

**(i) Treatment with washing soda (sodium carbonate):** Washing soda reacts with soluble calcium and magnesium chlorides and sulphates in hard water to form insoluble carbonates.

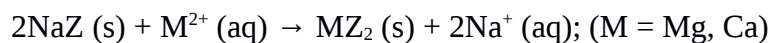


**(ii) Calgon's method:** Sodium hexametaphosphate ( $\text{Na}_6\text{P}_6\text{O}_{18}$ ), commercially called 'calgon', when added to hard water, the following reactions take place.

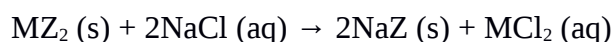


The complex anion keeps the  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions in solution.

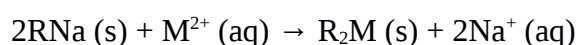
**(iii) Ion-exchange method:** This method is also called zeolite/permutit process. Hydrated sodium aluminium silicate is zeolite/permutit. For the sake of simplicity, sodium aluminium silicate ( $\text{NaAlSi}_3\text{O}_8$ ) can be written as  $\text{NaZ}$ . When this is added in hard water, exchange reactions take place.



Permutit/zeolite is said to be exhausted when all the sodium in it is used up. It is regenerated for further use by treating with an aqueous sodium chloride solution.

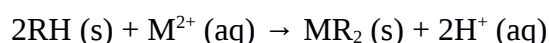


**(iv) Synthetic resins method:** Nowadays hard water is softened by using synthetic cation exchangers. This method is more efficient than zeolite process. Cation exchange resins contain large organic molecule with  $-\text{SO}_3\text{H}$  group and are water insoluble. Ion exchange resin ( $\text{RSO}_3\text{H}$ ) is changed to  $\text{RNa}$  by treating it with  $\text{NaCl}$ . The resin exchanges  $\text{Na}^+$  ions with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions present in hard water to make the water soft. Here R is resin anion.

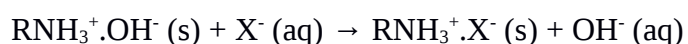
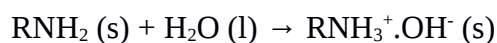


The resin can be regenerated by adding aqueous  $\text{NaCl}$  solution.

Pure de-mineralised (de-ionized) water free from all soluble mineral salts is obtained by passing water successively through a cation exchange (in the  $\text{H}^+$  form) and an anion-exchange (in the  $\text{OH}^-$  form) resins:

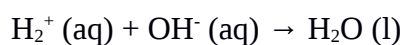


In this cation exchange process,  $\text{H}^+$  exchanges for  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and other cations present in water. This process results in proton release and thus makes the water acidic. In the anion exchange process:



$\text{OH}^-$  exchanges for anions like  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$  etc. present in water.  $\text{OH}^-$  ions, thus, liberated

neutralise the  $\text{H}^+$  ions set free in the cation exchange.



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

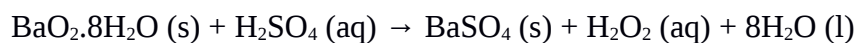
### **Hydrogen Peroxide ( $\text{H}_2\text{O}_2$ )**

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

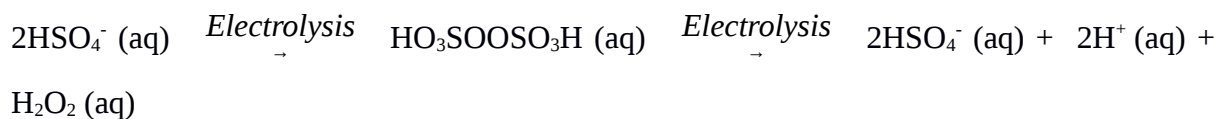
#### **Preparation:**

It can be prepared by the following methods.

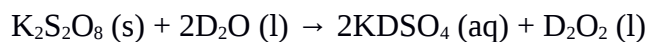
(i) Acidifying barium peroxide and removing excess water by evaporation under reduced pressure gives hydrogen peroxide.



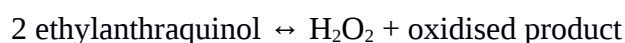
(ii) Peroxodisulphate, obtained by electrolytic oxidation of acidified sulphate solutions at high current density, on hydrolysis yields hydrogen peroxide.



This method is now used for the laboratory preparation of  $\text{D}_2\text{O}_2$ .



(iii) Industrially it is prepared by the auto oxidation of 2-Ethylantraquinone.



In this case, 1%  $\text{H}_2\text{O}_2$  is formed. It is extracted with water and concentrated to ~30% (by mass) by distillation under reduced pressure. It can be further concentrated to ~85% by careful distillation under low pressure. The remaining water can be frozen out to obtain pure  $\text{H}_2\text{O}_2$ .

### Structure:

Hydrogen peroxide has a non-planar structure. The molecular dimensions in the gas phase and solid phase are shown in Fig 2.3.

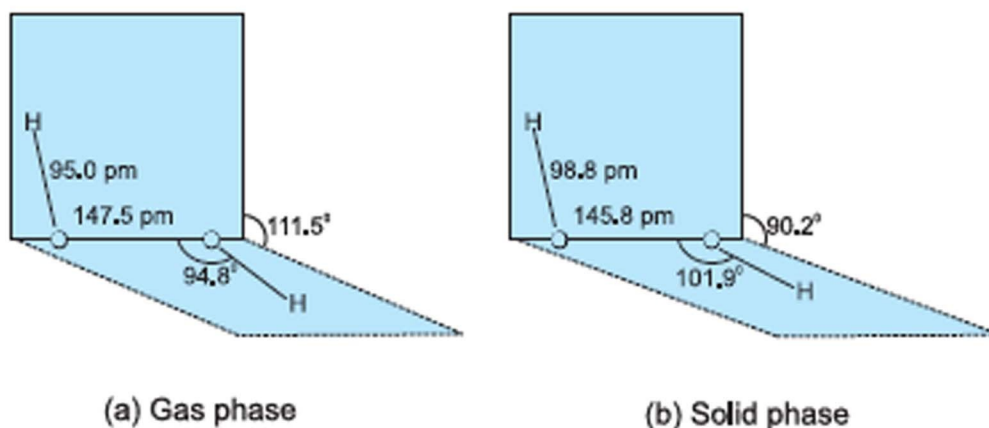


Figure 2.3. Structure of  $\text{H}_2\text{O}_2$

(Source: NCERT Chemistry Class XI, part B, p.no. 286)

### Physical Properties:

In the pure state  $\text{H}_2\text{O}_2$  is an almost colourless (very pale blue) liquid. Its important physical properties are given in Table 2.3.  $\text{H}_2\text{O}_2$  is miscible with water in all proportions and forms a hydrate  $\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$  (mp 221K). A 30% solution of  $\text{H}_2\text{O}_2$  is marketed as '100 volume' hydrogen peroxide. It means that one millilitre of 30%  $\text{H}_2\text{O}_2$  solution will give 100 mL of oxygen at



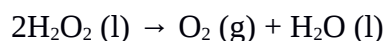
STP. Commercially marketed sample is 10 V, which means that the sample contains 3% H<sub>2</sub>O<sub>2</sub>.

**Table 2.3.** Physical properties of Hydrogen Peroxide.

Melting Point /K	272.4
Boiling Point /K	423
Vapour Pressure (298 K) /mm Hg	1.9
Density (solid at 268.5 K) /g.cm <sup>-3</sup>	1.64
Density (liquid at 298 K) /g.cm <sup>-3</sup>	1.44
Viscosity (290 K) /centipose	1.25
Dielectric constant (298 K) /C <sup>2</sup> /N m <sup>2</sup>	70.7
Electrical conductivity (298 K)/Ω <sup>-1</sup> .cm <sup>-1</sup>	5.1 × 10 <sup>-8</sup>

**Problem 2.2:** Calculate the strength of 10 volume solution of hydrogen peroxide.

**Solution:** 10 volume solution of H<sub>2</sub>O<sub>2</sub> means that 1L of this H<sub>2</sub>O<sub>2</sub> solution will give 10 L of oxygen at STP



$$2 * 34\text{g} = 68\text{g} \quad 22.4\text{L at STP}$$

On the basis of above equation 22.4 L of O<sub>2</sub> is produced from 68 g H<sub>2</sub>O<sub>2</sub> at STP

22.4 L of O<sub>2</sub> at STP is produced from H<sub>2</sub>O<sub>2</sub> = 68 g

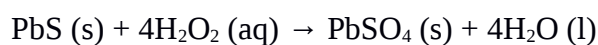
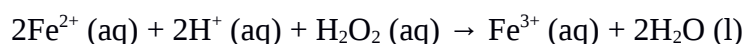
10 L of O<sub>2</sub> at STP is produced from H<sub>2</sub>O<sub>2</sub> = (68 × 10)/ 22.4 g = 30.36 g

Therefore, strength of H<sub>2</sub>O<sub>2</sub> in 10 volume H<sub>2</sub>O<sub>2</sub> solution = 30.36 gL<sup>-1</sup> = 3% H<sub>2</sub>O<sub>2</sub> solution

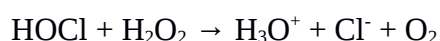
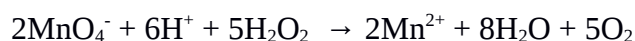
### Chemical Properties:

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

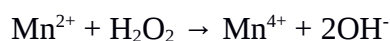
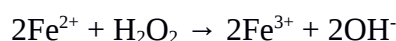
(i) Oxidising action in acidic medium



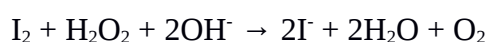
(ii) Reducing action in acidic medium



(iii) Oxidising action in basic medium



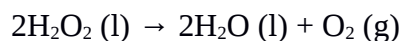
(iv) Reducing action in basic medium



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### **Storage:**

H<sub>2</sub>O<sub>2</sub> decomposes slowly on exposure to light.



In the presence of metal surfaces or traces of alkali (present in glass containers), the above reaction is catalysed. It is, therefore, stored in wax-lined glass or plastic vessels in dark. Urea can be added as a stabiliser. It is kept away from dust because dust can induce explosive decomposition of the compound.

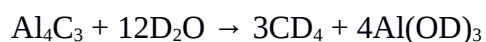
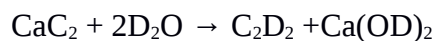
### **Uses:**

Its wide scale use has led to tremendous increase in the industrial production of H<sub>2</sub>O<sub>2</sub>. Some of the uses are listed below:

- In daily life it is used as a hair bleach and as a mild disinfectant. As an antiseptic it is sold in the market as perhydrol.
- It is used to manufacture chemicals like sodium perborate and per-carbonate, which are used in high quality detergents.
- It is used in the synthesis of hydroquinone, tartaric acid and certain food products and pharmaceuticals (cephalosporin) etc.
- It is employed in the industries as a bleaching agent for textiles, paper pulp, leather, oils, fats, etc.
- Nowadays it is also used in Environmental (Green) Chemistry. For example, in pollution control treatment of domestic and industrial effluents, oxidation of cyanides, restoration of aerobic conditions to sewage wastes, etc.

### **Heavy Water (D<sub>2</sub>O)**

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. Its physical properties are given in Table 2.2. It is used for the preparation of other deuterium compounds, for example:



### **Dihydrogen as a Fuel**

Dihydrogen releases large quantities of heat on combustion. The data on energy released by combustion of fuels like dihydrogen, methane, LPG etc. are compared in terms of the same amounts in mole, mass and volume, are shown in Table 2.3.

**Table 2.4.** The energy released by combustion of various Fuels in moles, mass and volume

Energy released on combustion in kJ state)	Dihydrogen( in gaseous state)	Dihydrogen (in liquid)	LPG	CH <sub>4</sub> gas	Octane (in liquid state)
per mole	286	285	2220	880	5511
per gram	143	142	50	53	47
per litre	12	9968	25590	35	34005

From this table it is clear that 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 minimized 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<sub>5</sub>, Ti-TiH<sub>2</sub>, Mg-MgH<sub>2</sub> etc. are in use for storage of dihydrogen in small quantities. These limitations have prompted researchers to search for alternative techniques to use dihydrogen in an efficient way.

In this view Hydrogen Economy is an alternative. 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.

### Summary

Water is the most common and abundantly available substance. It is of a great chemical and biological significance. The ease with which water is transformed from liquid to solid and to gaseous state allows it to play a vital role in the biosphere. The water molecule is highly polar in nature due to its bent structure. This property leads to hydrogen bonding which is the maximum in ice and least in water vapour. The polar nature of water makes it: (a) a very good

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solvent for ionic and partially ionic compounds; (b) to act as an amphoteric (acid as well as base) substance; and (c) to form hydrates of different types. Its property to dissolve many salts, particularly in large quantity, makes it hard and hazardous for industrial use. Both temporary and permanent hardness can be removed by the use of zeolites, and synthetic ion-exchangers.

Heavy water,  $D_2O$  is another important compound which is manufactured by the electrolytic enrichment of normal water. It is essentially used as a moderator in nuclear reactors.

Hydrogen peroxide,  $H_2O_2$  has an interesting non-polar structure and is widely used as an industrial bleach and in pharmaceutical and pollution control treatment of industrial and domestic effluents.