

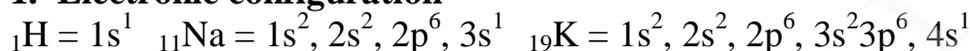
## CHAPTER 9 HYDROGEN

### ☛ Position of Hydrogen in Periodic Table

- Lightest element known having atomic number 1.
- Dihydrogen
- It resembles both alkali metals and halogens and therefore, its position is anomalous.
- In modern periodic table it is located separately

### ☆ Resemblance with alkali metals:-

#### 1. Electronic configuration



#### 2. Electropositive character: $\text{H}^+$ , $\text{Na}^+$ , $\text{K}^+$ etc.

#### 3. Oxidation state: +1

#### 4. Combination with electronegative elements: form binary compounds with electronegative elements like alkali metals.

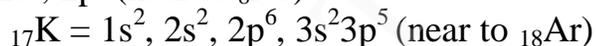
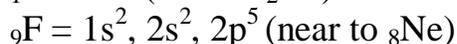
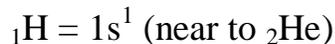
Halides:  $\text{HCl}$ ,  $\text{NaCl}$ ,  $\text{KCl}$  etc

Sulphides:  $\text{H}_2\text{S}$        $\text{Na}_2\text{S}$ ,  $\text{K}_2\text{S}$     etc

### ☆ Resemblance with halogens:-

#### 1. Electronic configuration:

Both contain one electron less than the nearest noble gas configuration



#### 2. Non-metallic character: like halogens, hydrogen is non-metallic in nature.

#### 3. Atomicity: Diatomic molecules.

#### 4. Formation of similar types of compounds:

- i. Halides:  $\text{CCl}_4$ ,  $\text{SiCl}_4$ ,  $\text{GeCl}_4$
- ii. Hydrides:  $\text{CH}_4$ ,  $\text{SiH}_4$ ,  $\text{GeH}_4$

#### 5. Oxidation state: -1



### ☆ Difference from alkali metals:-

- 1) **Ionization enthalpy:** - the ionization enthalpy of hydrogen is very high in comparison to alkali metals.
- 2) **Non-metallic character:** alkali metals are typical metals while hydrogen is non-metal
- 3) **Atomicity:** hydrogen is diatomic while alkali metals are monoatomic.
- 4) **Nature of compounds:** the compounds of hydrogen are predominantly covalent while those of alkali metals are ionic. For example:  $\text{HCl}$  is covalent while  $\text{NaCl}$  is ionic.

The oxides of alkali metals are basic while hydrogen oxide is neutral.

★ **Difference from halogens:-**

- 1) **Less tendency for hydride formation:** Hydrogen has less tendency to take up electron to form hydride ion (H<sup>-</sup>) as compared to the halogens which form halide ions (X<sup>-</sup>) very easily.
- 2) **Absence of unshared pairs of electrons :**
- 3) **Nature of oxides:** The oxides of halogens are acidic while hydrogen oxide is neutral.

⊛ **Occurrence of Hydrogen:**

- Hydrogen, the most abundant element in the universe and the third most abundant on the surface of the globe, is being visualised as the major future source of energy

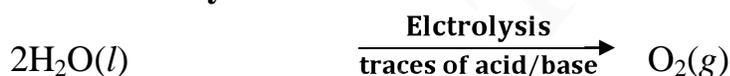
⊛ **Isotopes of hydrogen:-**

S.N.	Property	Protium	Deuterium	Tritium
1	Relative abundance	99.985 %	0.015 %	10 <sup>-15</sup> %
2	Relative atomic mass	1.007825	2.014102	3.016
3	Radioactive stability	Non-radioactive	Non-radioactive	Radioactive t <sub>1/2</sub> = 12.334 yrs

⊛ **Preparation:**

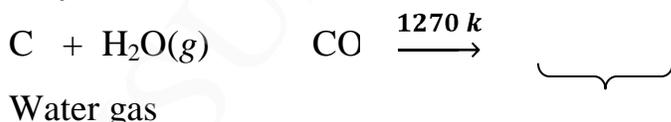
★ **Methods for commercial production of dihydrogen**

1. **Electrolysis of water**

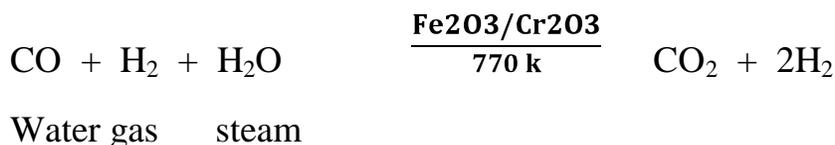


- The hydrogen prepared by this method is of very high purity. However, this method is not commonly used because it is very expensive. This method can be used only at those places where the electricity is cheap.

2. **By the reaction of steam on coke :-**



- Since the mixture of CO and H<sub>2</sub> is used for the synthesis of methanol and a number of hydrocarbons, it is also called synthesis gas or syn gas.
- The process of producing syn gas from coal or coke is called coal gasification.



- This reaction is called water gas shift reaction.

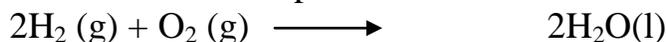
**⊙ Properties of Hydrogen:-**

**★ Physical Properties:-**

- 1) It is slightly soluble in water (about 2 %)
- 2) It is highly combustible and therefore should be handled carefully.
- 3) It lightest substance. The weight of one litre hydrogen at NTP is only 0.0899 g.

**★ Chemical properties:-** Not very reactive due to high bond dissociation energy (435.88 kJ mol<sup>-1</sup> at 298.2 K)

**(i) Combustion:** - It burns with pale blue flame

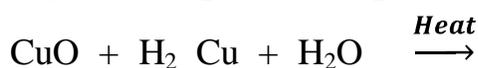
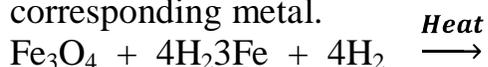


**(ii) Reaction with metals:-** Reactive metals like Na, K, Ca, Li and form hydrides.

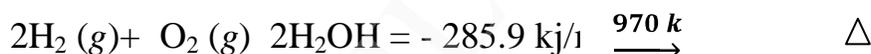
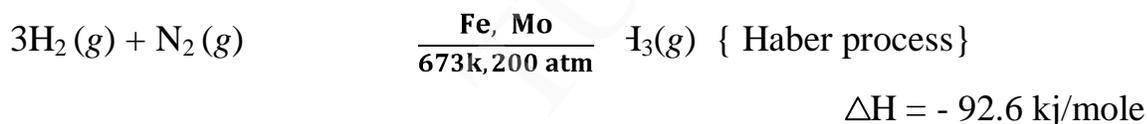


➤ Metals like Pt, Pd, Ni (elements of d block) form interstitial hydrides by absorbing large volume of hydrogen. Such hydrogen is called ‘occluded hydrogen and this property of adsorption of a gas by a metal is called occlusion.

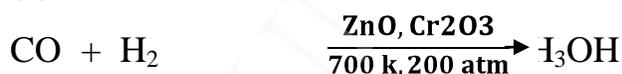
**(iii) Reaction with metal oxides:-** Hydrogen reduces oxides of less active metals to corresponding metal.



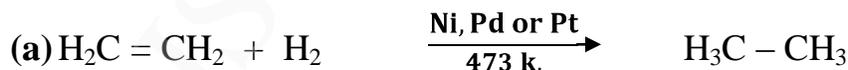
**(iv) Reaction with non-metals:-**



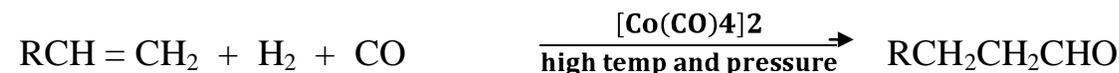
**(v) Reaction with carbon monoxide:-**



**(vi) Reaction with unsaturated Hydrocarbons:-**



**(b) Hydroformylation of olefins to aldehydes:** Hydroformylation or Oxo process



**(c) Hydrogenation of oils:-** Vegetable oils are polyunsaturated in nature. The C = C bonds in oils can easily undergo oxidation and the oil becomes rancid i.e.,

unpleasant in taste. Hydrogenation reduces the number of double bonds but completely.

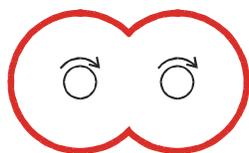


☛ **Uses of Hydrogen:-** it is used ..

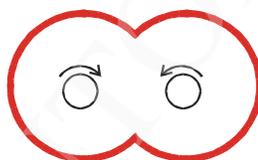
1. as a reducing agent.
2. In the manufacture of vanaspati fat, ammonia, metal hydrides, methanol, fertilizers such as urea etc.
3. In the manufacture of synthetic petrol.
4. In the atomic hydrogen torch and oxy hydrogen torches for cutting and welding. Dihydrogen is dissociated with the help of an electric arc and the hydrogen atoms produced are allowed to recombine on the surface to be welded. High temperature of about 4000 k is generated.
5. In the fuel cell for generating electrical energy.



☛ **Ortho and parahydrogens:-** A molecule of dihydrogen .....abc



**Ortho hydrogen**

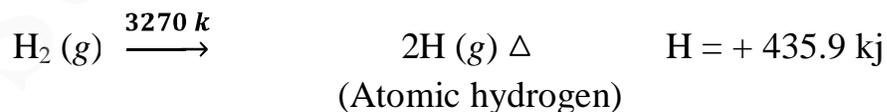


**Para hydrogen**

- They show different physical properties. For example :
  - (i) The thermal conductivity of para hydrogen is about 50 % greater than that of ortho hydrogen.
  - (ii) The melting point of para hydrogen is 0.15 k below that of hydrogen containing 75% ortho hydrogen.
- They show similar chemical properties.

☛ **Atomic hydrogen:-**

- Because of high H—H bond enthalpy, atomic hydrogen is produced only at high temp in an electric arc or under ultraviolet radiation.



- Highly reactive.
- Half life period is 0.3 sec and therefore, it immediately gets converted into the molecular form liberating a large amount of energy which is used for cutting and welding purposes.

⊛ **Nascent hydrogen:**-The hydrogen produced in contact with the substance to be reduced is known as 'nascent hydrogen'. It is very reactive form of hydrogen. Better reducing agent than ordinary dihydrogen.

⊛ **Hydrides:**-Under certain conditions  $H_2$  combines with almost all the elements, except noble gases to form compounds called hydrides.

- There are three types of hydrides, they are
  - (i) Ionic or saline hydrides
  - (ii) Covalent or molecular hydrides
  - (iii) Metallic or non-stoichiometric hydrides

**Ionic or saline hydrides:-**

- These are the compounds of  $H_2$  formed with most of the s-block elements which are highly electro positive.

**(ii) Covalent or molecular hydrides:-**These are the compounds of hydrogen formed with most of the p-block elements

**[a] Electron deficient:-** The hydrides which do not have sufficient number of electrons to form normal covalent bonds is called electron deficient hydride. For example, hydride of group 13 ( $BH_3$ ,  $AlH_3$ , etc.). They are known as Lewis acids i.e., electron acceptors. To make up their deficiency they generally exist in polymeric forms such as  $B_2H_6$ ,  $Al_2H_6$ , etc.

**[b] Electron precise:-**The hydrides which have sufficient number of electrons required for forming covalent bonds is called electron precise hydride. For example, hydrides of group 14 ( $CH_4$ ,  $SiH_4$ ,  $GeH_4$ ,  $SnH_4$ ,  $PbH_4$  etc.) they have tetrahedral geometry.

**[c] Electron rich hydrides:-**The hydrides which have excess electrons as required to form normal covalent bonds is called electron rich hydride. For example, hydrides of group 15 to 17 ( $NH_3$ ,  $PH_3$ ,  $H_2O$ ,  $H_2S$ ,  $H_2Se$ ,  $H_2Te$ ,  $HF$  etc.)

**(iii) Metallic or non-stoichiometric hydrides:-**

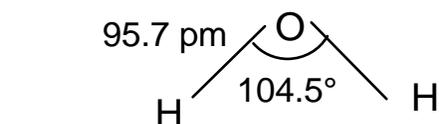
- These are formed by many d-block and f-block elements
- These hydrides conduct heat and electricity though not efficient.

⊛ **Water:** -Water! It is the major part of all living organisms. Water is also known as the river of life.

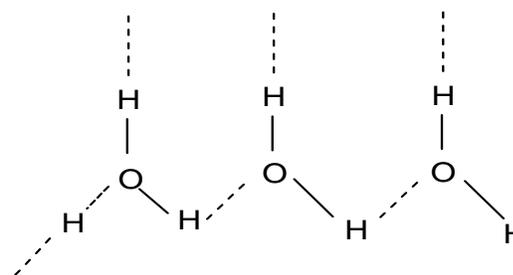
- Human body has about 65% and some plants have as much as 95% water.

❖ **STRUCTURE OF WATER:-**

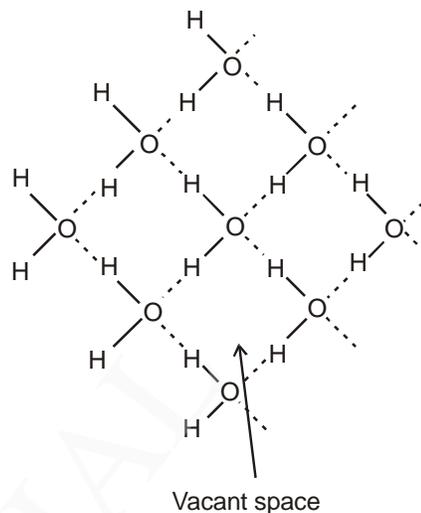
- In a gas phase water is bent molecule with a bond angle of  $104.5^\circ$  and O-H bond length of  $95.7\text{pm}$ . It is highly polar molecule.



Solid state



- ❖ **Structure of ice:-**Ice has a highly ordered 3D hydrogen bonded structure. Each oxygen atom is surrounded tetrahedrally by four other oxygen atoms at a distance of 276 pm



★**Chemical Properties of water:-**

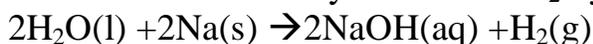
**[i] AMPHOTERIC NATURE:-**It has the ability

.it acts as an acid with  $\text{NH}_3$  and as a base with  $\text{H}_2\text{S}$

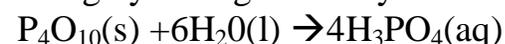


**[ii] REDOX REACTIONS INVOLVING WATER:-**

➤ Water can be easily reduced to  $\text{H}_2$  by highly electropositive metals



**[iii] HYDROLYSIS REACTION:-**Due to high dielectric constant, it has a very strong hydrating tendency .it dissolves many ionic compounds



**[iv] HYDRATES FORMATION:-**From the aqueous solutions many salts can be crystallized as hydrated salts. It of different types.

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

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

(3) 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  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

⊗**Hard & Soft Water:-**

- The water which contains dissolved salts of bicarbonates, sulphates and chlorides of calcium and magnesium is called hard water. Hard water does not produce lather with soap solution.
- Soft water is free from bicarbonates, sulphates and chlorides of calcium and magnesium. It produces lather with soap solution easily. e.g., distilled water, rain water..

★**Types of hardness:-**The hardness of water is of two types

**(i)Temporary hardness**

- Due to presence of soluble bicarbonates of calcium and magnesium.
- Can be removed by simple boiling.

**(ii)Permanent hardness**

- Due to presence of chlorides and sulphates of calcium and magnesium.
- Requires treatment of water to remove this type hardness.
- **Do you know?**

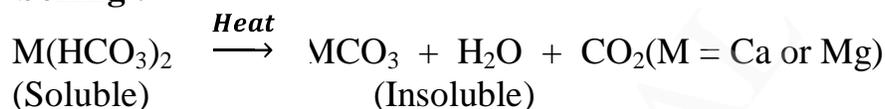
Temporary hardness is also called carbonate hardness &

Permanent hardness is also called non-carbonate hardness

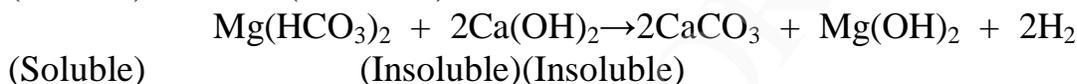
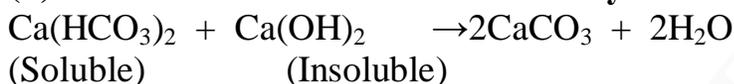
★ **Softening of water:-** The process of removal of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions from water is called softening of water.

❖ **Removal of temporary hardness:-**

(i) **By boiling :**

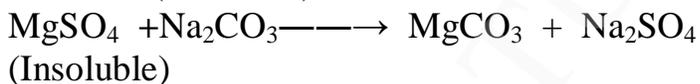
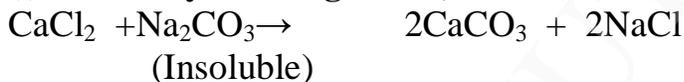


(ii) **Clark's method or calcium hydroxide method**

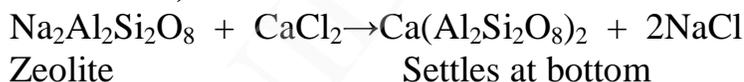


❖ **Removal of permanent hardness:-**

(i) **By washing soda ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ) treatment:**



(ii) **By using inorganic cation exchanger (permutit method or Zeolite method):**



The zeolite can be regenerated by treatment with sodium chloride solution.

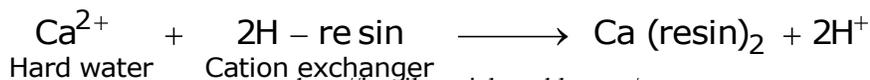


(iii) **By organic ion exchanger or synthetic resins (ion exchange resins):-**

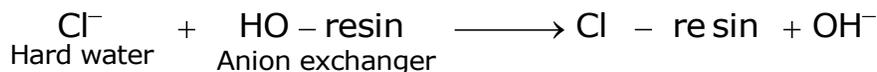
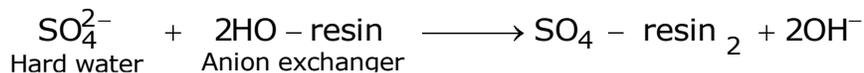
- Synthetic resins are the insoluble polymeric solids having giant hydrocarbon network containing reactive acidic or basic groups. These are superior to Zeolite because they can remove all types of cations as well as anions present in water. This resulting water is known as demineralised or deionised water.

- These are two types:

- (a) **Cation exchanger resins:** they have acidic groups such as  $\text{COOH}$  or  $\text{SO}_3\text{H}$ . they may be represented as **resin— $\text{H}^+$**



- (b) **Anion exchanger resins:** they have basic groups such as  $-\text{OH}^-$  or  $-\text{NH}_2$ . they may be represented as **resin— $\text{OH}^-$**  or **resin— $\text{NH}_3^+\text{OH}^-$**



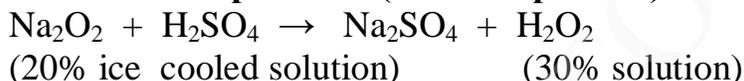
### Regeneration of resiners:



❖ **Hydrogen peroxide [ $\text{H}_2\text{O}_2$ ]:-** discovered by French chemist J.L. Thenard

#### ❖ Methods of preparation

- 1) **From sodium peroxide (Merck's process):-**



2. **From Barium peroxide:-**

- Hydrogen peroxide was first prepared by J. L. Thenard in 1818 by acidifying barium peroxide and removal of excess water by evaporation under reduced pressure.



- Barium sulphate is filtered off leaving behind  $\text{H}_2\text{O}_2$ .

#### Store of Hydrogen peroxide:-

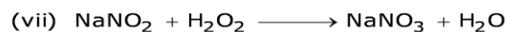
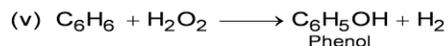
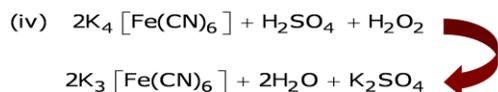
- It must be kept in wax lined coloured bottles because the rough glass surface causes its decomposition.
- A small amount of phosphoric acid, glycerol or acetanilide is generally added which retard the decomposition of  $\text{H}_2\text{O}_2$ . These are also called negative catalysts.

#### ❖ Physical properties of Hydrogen peroxide:-

- In the pure state  $\text{H}_2\text{O}_2$  is an almost colourless (very pale blue) liquid.
- $\text{H}_2\text{O}_2$  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 V of oxygen at STP. Commercially, it is marketed as 10 V, which means it contains 3%  $\text{H}_2\text{O}_2$ .

#### Chemical properties of Hydrogen peroxide:-

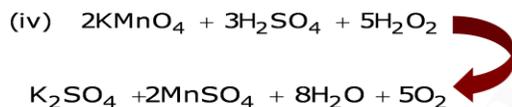
### Oxidising properties



### Reducing properties



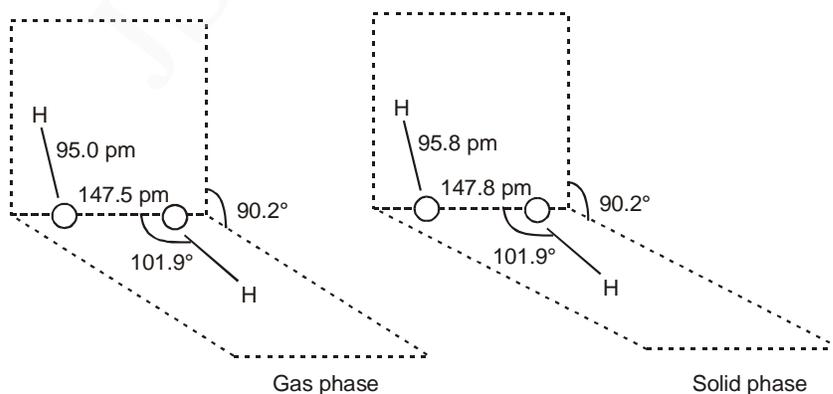
### Reducing properties



### ❖ Uses of hydrogen peroxide

- 1) For bleaching silk, wool, hair and leather
- 2) As rocket fuel

### ❖ Structure of hydrogen peroxide



### Hydrogen economy (Hydrogen as fuel)

- ☞ The electricity cannot be stored to run automobiles. It is not possible to store and transport nuclear energy. Hydrogen is an alternative source of energy and hence called as 'hydrogen economy'. Hydrogen has some advantages as fuel
- ☞ Available in abundance in combined form as water.
- ☞ On combustion produces  $H_2O$ . Hence pollution free.
- ☞  $H_2-O_2$  fuel cell give more power.
- ☞ Excellent reducing agent. Therefore can be used as substitute of carbon in reduction for processes in industry.

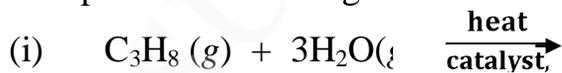
### ❖ Obstacles in hydrogen economy

#### ☞ Transportation:

- ☞ Hydrogen gas is explosive and hence it is difficult to store and transport.
- ☞ Formation of hydrogen from  $H_2O$ :
- ☞ The cheaper production of the hydrogen is basic requirement of hydrogen economy which is not possible now.
- ☞ The main aim and advantage of hydrogen economy is to transmit energy in form of hydrogen.

### One mark question:

1. What is meant by 10 volume hydrogen peroxide?
2. Why is dihydrogen gas not preferred in balloons?
3. Name the constituents of water gas.
4. Name one compound each in which hydrogen exists in (i) positive oxidation state, and (ii) Negative oxidation state.
5. What type of elements form interstitial hydrides?
6. How many hydrogen bonded water molecule(s) are present in  $CuSO_4 \cdot 5H_2O$ ?
7. What happens when heavy water is added to calcium carbonate?
8. Concentrated sulphuric acid cannot be used for drying  $H_2$ . Why?
9. Complete the following reactions?



10. How heavy water is obtained from ordinary water?

### Solutions:

1. It means that 1 ml of  $H_2O_2$  will give 10 ml of oxygen at N.T.P.
2. Dihydrogen gas is combustible in nature. Therefore, it may react with oxygen highly violently. Thus, it is not used in balloons.
3. Carbon monoxide and hydrogen.

4. (i) HCl (ii) NaH
5. Elements of d-and f-block.
6. In  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , there is one hydrogen bonded water molecule which is outside the coordination sphere. The other four molecules of water are coordinated.
7. Deutero acetylene is formed.  

$$\text{CaC}_2 + 2\text{D}_2\text{O} \longrightarrow \text{Ca(OD)}_2 + \text{C}_2\text{D}_2$$
8. Conc.  $\text{H}_2\text{SO}_4$  on absorbing water from moist  $\text{H}_2$  produces so much heat that  $\text{H}_2$  catches fire.
9.
  - (i)  $\text{C}_3\text{H}_8(g) + 3\text{H}_2\text{O}(l) \xrightarrow[\text{catalyst}]{\text{heat}} 3\text{CO} + 7\text{H}_2(g)$
  - (ii)  $\text{Zn}(s) + \text{NaOH}(aq) \xrightarrow{\text{heat}} \text{Na}_2\text{ZnO}_2(aq) + \text{H}_2(g)$
10. Heavy water is obtained from ordinary water by repeated electrolysis in the presence of 3% NaOH.

### Two mark question

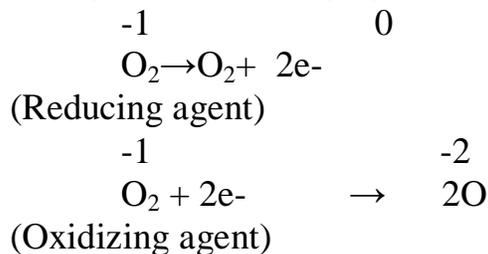
1. Can we use concentrated sulphuric acid and pure zinc in the preparation of dihydrogen?
2. Write the chemical reactions to show the amphoteric nature of water.
3. Why is hydrogen peroxide stored in wax-lined plastic coloured bottles?
4.  $\text{H}_2\text{O}_2$  acts as an oxidizing agent as well as reducing agent. Why?
5. What causes the temporary and permanent hardness of water?

### Solutions:

1. (a) Conc.  $\text{H}_2\text{SO}_4$  cannot be used because it acts as oxidizing agent also and gets reduced to  $\text{SO}_2$ .  

$$\text{Zn} + \text{dil H}_2\text{SO}_4 \longrightarrow \text{ZnSO}_4 + 2\text{H}_2\text{O} + \text{SO}_2$$
- (b) Pure Zn is not used because it is non-porous and reaction will be slow. The impurities in Zn help in constitute of electrochemical couple and speed up reaction.
2. Water is amphoteric in nature and it behaves both as an acid as well as a base. With acids stronger than itself (eg.,  $\text{H}_2\text{S}$ ) it behaves as a base and with bases stronger than itself (eg.  $\text{NH}_3$ ) it acts as an acid.
  - (i) As a base:  $\text{H}_2\text{O}(l) + \text{H}_2\text{S}(aq) \rightarrow \text{H}_3\text{O}^+(aq) + \text{HS}^-(aq)$
  - (ii) As an acid:  $\text{H}_2\text{O}(l) + \text{NH}_3(aq) \rightarrow \text{OH}^-(aq) + \text{NH}_4^+(aq)$
3. The decomposition of  $\text{H}_2\text{O}_2$  occurs readily in the presence of rough surface (acting as catalyst). It is also decomposed by exposure of light. Therefore, wax-lined smooth surface and coloured bottles retard the decomposition of  $\text{H}_2\text{O}_2$ .

4. In  $H_2O_2$ , oxygen has -1 oxidation state which lies between maximum (0 or +2 in  $OF_2$ ) and minimum -2. Therefore, oxygen can be oxidized to  $O_2$  (zero oxidation state) acting as reducing agent or can be reduced to  $H_2O$  or  $OH^-$  (-2 oxidation state) acting as an oxidizing agent.



5. Temporary hardness is due to presence of soluble bicarbonates of calcium and magnesium. On the other hand, permanent hardness is due to presence of chlorides and sulphates of calcium and magnesium.

**Three mark question:**

1. Hard water is unsuitable for laundry, washing and dyeing. Explain.
2. What do you understand by (i) electron-deficient, (ii) electron-precise, and (iii) electron-rich compounds of hydrogen? Provide justification with suitable examples.
3. Compare the structures of  $H_2O$  and  $H_2O_2$ .

Solutions:

1. Ans: - since we know that the soap are the sodium salts of higher fatty acids like stearic acid ( $C_{17}H_{35}COOH$ ), oleic acid ( $C_{17}H_{33}COOH$ ) or palmitic acid ( $C_{17}H_{31}COOH$ ). When soap is added to hard water, the anions of soap combine with  $Ca^{+2}$  and  $Mg^{+2}$  ions to form calcium and magnesium salt which are insoluble in water.



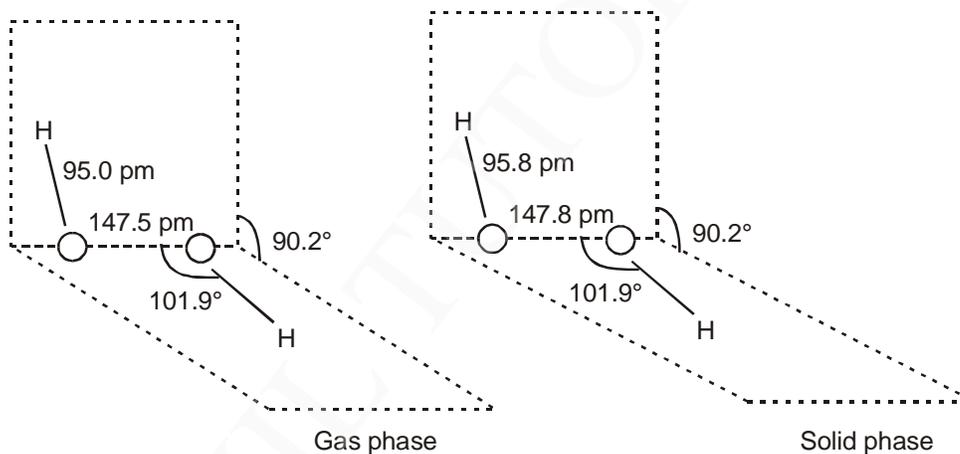
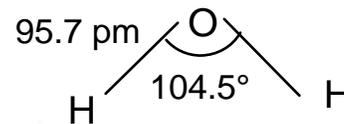
Therefore, no lather is produce until all the calcium and magnesium ions are precipitated. This also results into wastage of lot of soap. So hard water is unsuitable for laundry, washing and dyeing.

2. [a] **Electron deficient**:- The hydrides which do not have sufficient number of electrons to form normal covalent bonds is called electron deficient hydride. For example, hydride of group 13 ( $BH_3$ ,  $AlH_3$ , etc.).
- [b] **Electron precise**:- The hydrides which have sufficient number of electrons required for forming covalent bonds is called electron precise hydride. For

example, hydrides of group 14 ( $\text{CH}_4$ ,  $\text{SiH}_4$ ,  $\text{GeH}_4$ ,  $\text{SnH}_4$ ,  $\text{PbH}_4$  etc.) they have tetrahedral geometry.

**[c] Electron rich hydrides:**-The hydrides which have excess electrons as required to form normal covalent bonds is called electron rich hydride. For example, hydrides of group 15 to 17 ( $\text{NH}_3$ ,  $\text{PH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$ ,  $\text{H}_2\text{Te}$ ,  $\text{HF}$  etc.)

3. In water, O atom is  $\text{sp}^3$  hybridised and there are two O—H bonds and two  $\text{sp}^3$  hybrid orbitals occupy lone pairs of electrons. Stronger lone pair-lone pair repulsions than bond pair-bond pair repulsions, the H-O-H bond decreases from  $109.5^\circ$  to  $104.5^\circ$ . Therefore, water molecule is a bent or angular molecule.  $\text{H}_2\text{O}_2$  has non-planar structure. In this structure, two O—O oxygen atoms are bonded to each other by a single covalent bond and each O atom is further bonded to a hydrogen atom by a single covalent bond. The two O—H bonds are in different planes in  $111.50^\circ$  in the gas phase.



**Structure of hydrogen peroxide**