UNIT 11

Hydrogen

SYLLABUS

Unique position in the periodic table, occurrence, isotopes.

Dihydrogen—preparation (including commercial preparation), properties, reactions and uses.

Hydrides—molecular, saline and interstitial.

Water : structure and aggregation of water molecules, physical and chemical properties, hard and soft water, water softener. Heavy water, hydrogen peroxide, hydrogen economy, use of liquid hydrogen as a fuel.

11.1. General Introduction

Hydrogen is the first element in the periodic table and is also the lightest element known. Its atomic form exists only at high temperatures. In the normal elemental form, it exists as a diatomic molecule, *i.e.* H_2. That is why it is also called *dihydrogen*. It was first discovered by *Henry Cavendish* in 1766. He prepared it by the action of dil. H_2SO_4 on iron. Its name hydrogen was proposed by *Lavoisier* because it produces water on burning with oxygen (Greek : *hydro* means water and *gene* means *producer*).

The various forms isotopes, allotropes, molecular and ionic forms are hydrogen are given in the box below :

Symbol	:	H
Atomic number, Z	:	1
Electronic configuration	:	$1s^1$
Isotopes	:	Protium, ^1H Deuterium, ^2H or D Tritium, ^3H or T
Allotropes	:	Orthohydrogen, o-H_2
	:	Parahydrogen, p-H_2 [Also o-D_2, p-D_2, o-T_2, p-T_2]
Molecular forms	:	H_2, $^2H_2$ (or D_2), $^3H_2$ (or T_2), HD, HT etc.
Ionic forms	:	$H^-, H^+, H_2^+, H_3^+ ..... H_{11}^+$ [Also corresponding ionic forms of D and T]

11.2. Unique Position of Hydrogen in the Periodic Table

Hydrogen is the first element in the periodic table. However, a proper position could not be assigned to it either in the Mendeleev's periodic table or Long form of the periodic table because of the following two reasons :

(*i*) In some properties, it resembles alkali metals. As such, it can be placed in group 1 of the periodic table along with **alkali metals.**

(*ii*) In some other properties, hydrogen resembles halogens. As such, it can be placed in group 17 along with **halogens.**

(*iii*) In some yet another properties, hydrogen differs from both alkali metals and halogens.

Thus, the position of hydrogen in the periodic table is *controversial* or *anomalous*. The main points of resemblance of hydrogen with alkali metals and halogens are briefly discussed below :

I. Resemblance with Alkali Metals. Hydrogen resembles alkali metals, *i.e.*, Li, Na, K, Rb, Cs and Fr of group I of the periodic table in the following respects :

1. Electronic configuration. Like alkali metals, hydrogen also contains one electron in its outermost (*valence*) shell :

Hydrogen, H	Lithium, Li
$1s^1$	$1s^2\ 2s^1$
Sodium, Na	Potassium, K
$1s^2\ 2s^2\ 2p^6\ 3s^1$	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$

2. Electropositive character. Like alkali metals, hydrogen also loses its only electron to form hydrogen ion, *i.e.*, H^+ (*proton*).

$$\underset{1s^1}{H} \longrightarrow \underset{1s^0}{H^+} + e^-$$

$$\underset{1s^2\,2s^2\,2p^6\,3s^1}{Na} \longrightarrow \underset{1s^2\,2s^2\,2p^6}{Na^+} + e^-$$

Thus, hydrogen like alkali metals exhibits electropositive character.

3. Oxidation state. Like alkali metals, hydrogen exhibits an oxidation state of +1 in its compounds.

$$\underset{\text{Hydrogen chloride}}{H^+\,Cl^-} \qquad \underset{\text{Sodium chloride}}{Na^+\,Cl^-} \qquad \underset{\text{Potassium bromide}}{K^+\,Br^-}$$

4. Combination with electronegative elements or non-metals. Like alkali metals, hydrogen combines with electronegative elements (*non-metals*) such as oxygen, halogens and sulphur forming their oxides, halides and sulphides respectively. For example,

Oxide : H_2O like Na_2O , K_2O etc.

Halides : HCl like NaCl, KCl etc.

Sulphide : H_2S like Na_2S , K_2S etc.

5. Liberation at the cathode. When an aqueous solution of HCl is electrolysed, H_2 is liberated at the cathode in the same way as alkali metals are liberated at the cathode during the electrolysis of their fused halides.

At cathode *At anode*

$$2HCl(aq) \xrightarrow{\text{Electrolysis}} H_2(g) + Cl_2(g)$$

$$2NaCl(l) \xrightarrow{\text{Electrolysis}} 2Na(l) + Cl_2(g)$$

6. Reducing character. Like alkali metals, hydrogen also acts as a *strong reducing agent*. For example,

$$Fe_3O_4 + 4H_2 \xrightarrow{\text{Heat}} 3Fe + 4H_2O$$

$$B_2O_3 + 6K \xrightarrow{\text{Heat}} 2B + 3K_2O$$

II. Resemblance with Halogens. Hydrogen resembles halogens, *i.e.* F, Cl, Br and I of group 17 of the periodic table in the following respects :

1. Electronic configuration : All the halogens have seven electrons in their respective outermost shells and thus have one electron less than the stable configuration of the nearest inert gas. Hydrogen, on the other hand, has one electron in the outermost shell and thus has one electron less than the stable configuration of the nearest inert gas, *i.e.*, He.

H	One electron less than	He
$1s^1$		$1s^2$
F	One electron less than	Ne
$1s^2\ 2s^2\ 2p^5$		$1s^2\ 2s^2\ 2p^6$
Cl	One electron less than	Ar
$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$		$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$.

2. Electronegative character. Halogens have a strong tendency to gain one electron to form halide ions. In a similar way, hydrogen shows some tendency to gain one electron to form hydride (H^-) ion.

$$\underset{1s^1}{H} + e^- \longrightarrow \underset{1s^2}{H^-}$$

(*He gas configuration*)

$$\underset{1s^2\,2s^2\,2p^6\,3s^2\,3p^5}{Cl} + e^- \longrightarrow \underset{1s^2\,2s^2\,2p^6\,3s^2\,3p^6}{Cl^-}$$

(*Ar gas configuration*)

3. Ionization enthalpy. The ionization enthalpy of hydrogen is quite comparable with those of halogens but much higher than those of alkali metals.

Element	*Ionization energy*
H	1312 kJ mol^{-1}
F	1681 kJ mol^{-1}
Cl	1255 kJ mol^{-1}
Li	520 kJ mol^{-1}
Na	496 kJ mol^{-1}
K	419 kJ mol^{-1}

4. Oxidation state. Just like halogens, hydrogen shows an oxidation state of −1. For example,

With sodium : $Na^+\,H^-$ like $Na^+\,Cl^-$

With calcium : $Ca^{2+}(H^-)_2$ like $Ca^{2+}(Cl^-)_2$

5. Liberation at the anode. When fused alkali metal hydrides such as lithium or sodium hydride is subjected to electrolysis, hydrogen is liberated at the anode. Similarly, halogens are liberated at the anode when fused alkali metal halides are electrolysed.

At anode *At cathode*

$$2NaH(l) \xrightarrow{\text{Electrolysis}} H_2(g) + 2Na(l)$$

$$2NaCl(l) \xrightarrow{\text{Electrolysis}} Cl_2(g) + 2Na(l)$$

6. Atomicity and non-metallic character. Just like halogens, hydrogen also exists as a diatomic molecule : H_2, F_2, Cl_2, Br_2 etc. Further, like halogens, hydrogen is also a typical non-metal.

7. Combination with metals. Hydrogen combines with highly electropositive alkali and alkaline earth metals to form metallic hydrides. In a similar way, halogens combine with these metals to form metallic halides.

With alkali metals

$$2\,Na + H_2 \longrightarrow 2NaH$$

$$2Na + Cl_2 \longrightarrow 2NaCl$$

With alkaline earth metals

$$Ca + H_2 \longrightarrow CaH_2$$

$$Ca + Cl_2 \longrightarrow CaCl_2$$

8. Formation of covalent compounds. Like halogens, hydrogen readily combines with non-metals such as carbon, silicon, nitrogen etc. to form covalent compounds.

With hydrogen : $\underset{\text{Methane}}{CH_4}\qquad \underset{\text{Silane}}{SiH_4}\qquad \underset{\text{Ammonia}}{NH_3}$

With halogens : $\underset{\text{Carbon tetrachloride}}{CCl_4}\qquad \underset{\text{Silicon tetrachloride}}{SiCl_4}\qquad \underset{\text{Nitrogen trichloride}}{NCl_3}$

9. Replacement or Substitution reactions. In many compounds of carbon, hydrogen can be replaced by halogens and halogens can be replaced by hydrogen. For example,

$$\underset{\text{Methane}}{CH_4} + Cl_2 \xrightarrow{\text{Diffused sunlight}} \underset{\text{Methyl chloride}}{CH_3Cl} + HCl$$

$$\underset{\text{Methyl chloride}}{CH_3Cl} + 2[H] \xrightarrow[\text{or Zn/HCl}]{\text{Sn/HCl}} \underset{\text{Methane}}{CH_4} + HCl$$

III. Difference from Alkali Metals and Halogens. Hydrogen differs from both alkali metals and halogens in the following respects :

1. Hydrogen is comparatively *less electropositive than alkali metals* and less *electronegative than halogens*. For example, hydrogen has less tendency to form H^+ ions as compared to alkali metals which readily form monovalent cations. Similarly, hydrogen has less tendency to form H^- ions as compared to halogens which readily form halide (X^-) ions.

2. *Unlike halogens and alkali metals, hydrogen contains only one proton (but no neutrons) in its nucleus and only one electron in the extranuclear part.*

3. Nature of oxides. The nature of oxides of alkali metals, halogens and hydrogen is quite different. *The oxides of alkali metals are* **basic** *while those of halogens are* **acidic** *but the oxide of hydrogen, i.e., H_2O is* **neutral**. Thus,

$$\underset{\textit{Neutral}}{H_2O}\qquad \underbrace{Li_2O,\ Na_2O,\ K_2O\ \text{etc}}_{\textit{Basic}}\qquad \underset{\textit{Acidic}}{Cl_2O_7}$$

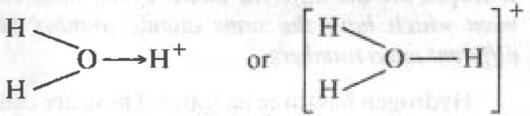
4. Absence of unshared pairs of electrons. The hydrogen atoms in hydrogen molecule do not possess any unshared pairs of electrons whereas halogen atoms in halogen molecule possess three unshared pairs of electrons as shown below :

$$H:H \qquad :\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:$$

5. Nature of compounds. The compounds of hydrogen with halogans, *i.e.* hydrogen halides (HF, HCl, HBr, HI) are *low boiling covalent comounds* whereas alkali metal halides (LiF, NaCl, KBr, CsI) are *high melting ionic solids*.

6. Size of ions. The size of H^+ ions ($\sim 1\cdot5 \times 10^{-3}$ *pm*) is much smaller than those of alkali metals. Similarly, the size of H^- ions (220 pm) is much smaller as compared to halide ions.

7. Structure of hydrates. H^+ ion exists in aqueous solution as hydrated proton having the formula, $[H_9O_4]^+$ in which four H_2O molecules are tetrahedrally arranged around the H^+ ion. However, it is generally written as $[H_3O^+]$ and called **hydronium ion.** Alkali metal cations also exist as hydrates but the extent of hydration decreases as the size of alkali metal cation increases. Thus



Hydronium ion

$$[Li(H_2O)_6]^+$$

Lithium hexahydrate cation

Halide ions, also exist in aqueous solutions as hydrated ions but their structures are not well established. That is why, they are usually represented as $X^-(aq)$ where X = F, Cl, Br or I.

Conclusion. From the above discussion, it follows that hydrogen is unique in its behaviour because it not only resembles alkali metals and halogens in certain properties but at the same time it differs from both of them in certain other properties. Therefore, it is not justified to include *hydrogen either along with alkali metals of group 1 or halogens of group 17.* In other words, *the position of hydrogen in the periodic table is anomalous or controversial.* That is why hydrogen is sometimes referred to as a *'rogue element'*.

11.3. Occurrence of Hydrogen

Hydrogen is the most abundant element in the universe (70% of the total mass of the universe). The giant planets such as Jupiter and Saturn contain mostly hydrogen. Hydrogen constitutes about half of the mass of the sun and stars.

The extremely high temperature of the sun brings about fusion of hydrogen atoms liberating large amount of energy

$$4\,{}^{1}_{1}\text{H} \longrightarrow \underset{\textit{Helium}}{{}^{4}_{2}\text{He}} + \underset{\textit{Positron}}{2\,{}^{0}_{1}e} + \text{Energy}$$

It is the third most abundant element on the surface of the globe. In the combined form, it constitutes 15·4% of the earth's crust and the oceans. However, on the earth, it, is the **ninth element** in order of abundance and forms 0·9% of the earth's crust by weight. In the crustal rocks, it is 10th in order of abundance approx. 0·15% by weight. Hydrogen is also the essential constituent of water, coal, petroleum, clay and all animal and vegetable matter.

Earth does not possess enough gravitational pull to retain the light H_2 molecules, therefore, it is not found in our atmosphere.

11.4. Isotopes of Hydrogen

Isotopes ***are the different atoms of the same element which have the same atomic number but different mass numbers.***

Hydrogen has three isotopes. These are called **protium, deuterium and tritium.**

Representation. The isotopes of an element are usually represented by putting the atomic number as the subscript and their mass number as the superscript on the symbol of the element. Thus, the three isotopes of hydrogen are represented as ${}^{1}_{1}H$, ${}^{2}_{1}H$ or D and ${}^{3}_{1}H$ or T.

Occurrence. The most abundant isotope of hydrogen is protium. This occurs in natural hydrogen to an extent of 99·9844% ; the remaining 0·0156% being deuterium mostly in form of HD. Tritium being unstable because of its radioactive nature occurs only in traces (one in 10^{18} parts) *i.e.* the natural abundances of ${}^{1}_{1}H$, ${}^{2}_{1}H$ and ${}^{3}_{1}H$ are in the ratio of $1 : 1{\cdot}56 \times 10^{-2} : 1 \times 10^{-18}$.

Some important characteristics of these isotopes are given in Table 11.1.

TABLE 11.1. Atomic Properties of Isotopes of Hydrogen

Property	H	D	T
Relative atomic mass	1·007825	2·014102	3·016049
Nuclear spin quantum number	1/2	1	1/2
Radioactive stability	Non-radioactive stable	Non-radioactive stable	Radioactive, emits low energy β-particles, $t_{1/2}$=12·33y

Electronic structure. All the three isotopes of hydrogen have the same atomic number (Z = 1), therefore, all have only one electron in their only shell (*i.e.*, K–shell) and one proton in the nucleus. Since the mass numbers of the three isotopes are different, therefore, they differ from one another in the number of neutrons in the nucleus as shown in Fig. 11.1.

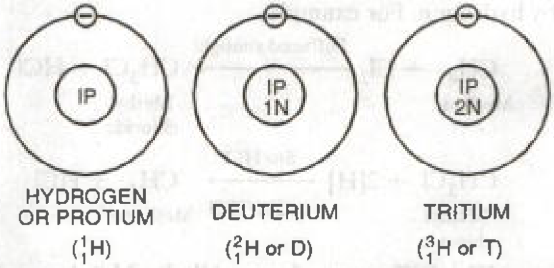


FIGURE 11.1. Isotopes of Hydrogen.

(*i*) **Protium or ordinary hydrogen [${}^{1}_{1}H$].** This is the most abundant isotope of hydrogen. Since its atomic number is 1 and mass number is also 1, its nucleus has *only one proton (but no neutron)* and one electron is revolving around the nucleus in its only shell, *i.e.* K-shell.

(*ii*) **Deuterium or heavy hydrogen [${}^{2}_{1}H$ or D].** Its natural abundance is 0.0156% . It is usually prepared by the electrolysis of heavy water (D_2O). Since its atomic number is 1 and its mass number is

2, therefore, its nucleus has *one proton and one neutron* while one electron is present in the K-shell. It is generally denoted by the symbol D.

(*iii*) **Tritium [^3_1H or T].** It is the least abundant ($10^{-16}\%$) of all the isotopes of hydrogen and is formed in the upper atmosphere by reactions induced by cosmic rays. It is *radioactive* with a short half-life of 12·33 years. It decays by β-emission with no γ-radiations

$$^3_1H \longrightarrow ^3_2He + ^0_{-1}e$$

It is prepared artificially by the bombardment of nitrogen or an isotope of lithium with neutrons:

$$^{14}_7N + ^1_0n \longrightarrow ^{12}_6C + ^3_1H$$

$$^6_3Li + ^1_0n \longrightarrow ^4_2He + ^3_1H$$

Since its mass number is 3 and atomic number is 1, its nucleus has *one proton and two neutrons* while one electron is present in the K-shell. It is usually represented by the symbol T.

Thus, the three isotopes of hydrogen differ from one another only in the number of neutrons in the nucleus.

Properties – Isotope Effect. Since the three isotopes of hydrogen have the same atomic number and electronic configuration ($1s^1$), they have similar chemical properties. But owing to their different masses, the rates or equilibrium constants of these reactions are different. For example, reaction between protium and chlorine is 13.4 times faster than between deuterium and chlorine ; protium is adsorbed more rapidly than deuterium on activated charcoal. Similarly, electrolysis of ordinary water (H_2O) occurs more rapidly than that of heavy water (D_2O).

***This type of difference in properties due to difference in atomic masses is called* isotope effect.**

Further, due to different masses, the physical properties of these isotopes are quite different.

Some common physical properties of H_2 (dihydrogen), D_2 (dideuterium) and T_2 (ditritium) are given in Table 11.2.

TABLE 11.2. Physical constants of H_2, D_2 and T_2

PROPERTY	H_2	D_2	T_2
Molecular mass (a.m.u.)	2·016	4·028	6·03
Melting point (K)	13·957	18·73	20·63
Boiling point (K)	20·39	23·67	25·00
Enthalpy of fusion (kJ mol^{-1})	0·117	0·197	0·250
Enthalpy of vaporization (kJ mol^{-1})	0·904	1·226	1·393
Enthalpy of dissociation (kJ mol^{-1} at 298·2 K)	435·88	443·35	446·9
Internuclear distance (pm)	74·14	74·14	—

Uses of Tritium. Tritium is used to make thermonuclear devices and for carrying out researches in fusion reactions as a means of producing energy. Tritium gas is usually stored by making UT_3, which on heating to 673 K releases T_2.

$$2\,UT_3 \xrightarrow{673\text{ K}} 2\,U + 3\,T_2$$

It is widely used as a *radioactive tracer* since it is relatively cheap and easy to work with.

11.5. Preparation of Dihydrogen

The important sources of dihydrogen are water, alkalies and acids.

I. From water. Dihydrogen may be obtained from water by any of the following methods :

1. By the action of water on metals

(*i*) *Cold water.* Very active metals, *i.e.*, alkali and certain alkaline earth metals like Na, K, Ca etc. react with water at room temperature evolving dihydrogen.

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$

$$2K + 2H_2O \longrightarrow 2KOH + H_2$$

$$Ca + 2H_2O \longrightarrow Ca(OH)_2 + H_2$$

The reaction with alkali metals is so vigorous and exothermic that the hydrogen evolved catches fire. In order to slow down the reaction, amalgams (alloys with mercury) of these metals are generally used. In these amalgams, only a small surface area of the metal comes in contact with water and, therefore, the reaction is slowed down.

With calcium, the reaction is not so vigorous and hence can be easily controlled.

(*ii*) *Boiling water.* Less active metals like Zn, Mg, Al etc. decompose boiling water liberating dihydrogen.

$$Zn + H_2O \xrightarrow{\text{Heat}} ZnO + H_2$$

$$Mg + H_2O \xrightarrow{\text{Heat}} MgO + H_2$$

$$2Al + 3H_2O \xrightarrow{\text{Heat}} Al_2O_3 + 3H_2$$

(*iii*) *Steam.* Still less reactive metals like Fe, Sn, Ni etc. decompose steam at high temperatures evolving dihydrogen.

$$3\,Fe + \underset{(\textit{Steam})}{4\,H_2O} \longrightarrow \underset{\text{Magnetic oxide}}{Fe_3O_4} + 4H_2$$

2. By electrolysis of water. Dihydrogen of high purity is usually obtained by the electrolysis of water in presence of small amount of an acid or a base. During electrolysis, dihydrogen is collected at cathode while dioxygen is liberated at anode as shown below :

$$2\,H_2O(l) \xrightarrow{\text{Electrolysis}} 2\,H_2(g) + O_2(g)$$

Pure water is only weakly ionized (*i.e.* is a bad conductor of electricity) but in presence of an acid or a base, the degree of ionization increases.

$$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq)$$

At cathode : $H^+(aq) + e^- \longrightarrow H\cdot$

$$H\cdot + \cdot H \longrightarrow H_2(g)$$

At anode : $OH^-(aq) \longrightarrow OH + e^-$

$$4\,OH \longrightarrow 2H_2O(l) + O_2(g)$$

Although dihydrogen prepared by this method is of high purity, yet this method is not commercially viable since it is quite expensive. However, where electricity is cheap, this method can be used.

II. From Alkalies. Metals like beryllium, zinc, tin and aluminium etc. react with boiling alkali solutions liberating dihydrogen.

$$Be + 2NaOH \xrightarrow{\text{Heat}} \underset{\text{Sod. beryllate}}{Na_2BeO_2} + H_2$$

$$Zn + 2NaOH \xrightarrow{\text{Heat}} \underset{\text{Sod. zincate}}{Na_2ZnO_2} + H_2$$

$$Sn + 2NaOH \xrightarrow{\text{Heat}} \underset{\text{Sod. stannite}}{Na_2SnO_2} + H_2$$

$$2Al + 2NaOH + 2H_2O \longrightarrow \underset{\text{Sod. meta-aluminate}}{2NaAlO_2} + 3H_2$$

III. From Acids. Metals which are more electropositive than hydrogen *i.e.*, lie above hydrogen in the electrochemical series) such as zinc, iron, magnesium etc. react with dilute mineral acids (dil HCl and H_2SO_4) to liberate dihydrogen gas.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2$$

$$Mg + 2HCl \longrightarrow MgCl_2 + H_2$$

Metals like copper, silver, mercury etc. which are less electropositive than hydrogen (*i.e.*, lie below hydrogen in the electrochemical series) do not liberate dihydrogen from acids.

11.5.1. Laboratory Preparation of Dihydrogen

In the laboratory, dihydrogen is prepared by action of dil. H_2SO_4 on granulated zinc.

$$Zn + H_2SO_4\,(\textit{dil.}) \longrightarrow ZnSO_4 + H_2$$

Granulated pieces of zinc are placed in a Woulfe's bottle and are covered with water. The bottle is fitted with a thistle funnel and a delivery tube as shown in Fig. 11.2.

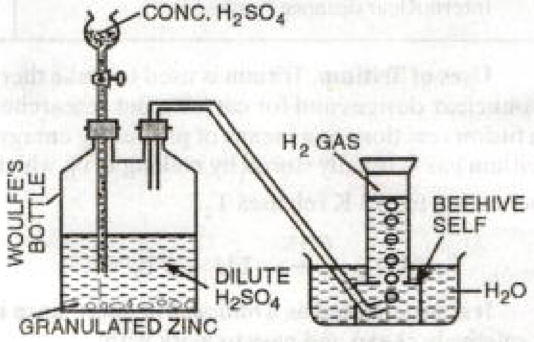


FIGURE 11.2. Preparation of dihydrogen gas in the laboratory.

Conc. H_2SO_4 is poured slowly through the thistle funnel. As the acid falls in the Woulfe's bottle, it gets diluted and then reacts with zinc evolving dihydrogen gas. It is collected by downward displacement of water.

It has been observed that sometimes the bubbles of dihydrogen produced stick to the surface of the zinc metal preventing the further reaction of the acid on the metal. Such a situation can, however, be avoided by adding a few crystals of copper sulphate to the reaction mixture.

Notes. The following points must be noted while preparing dihydrogen gas in the laboratory.

1. Pure zinc is not used for the preparation of gas because it reacts very slowly with dil. H_2SO_4. *The presence of impurities, however, increases the rate of reaction due to the formation of electrochemical couples.*

2. Concentrated sulphuric acid is not used for the preparation of dihydrogen gas because zinc reacts with concentrated acid to form SO_2 *gas instead of* H_2 *gas.*

$$\underset{(conc.)}{Zn + 2H_2SO_4} \longrightarrow ZnSO_4 + SO_2 + 2\,H_2O$$

Preparation of pure dihydrogen gas. In case *very pure dihydrogen* (> 99·95%) gas is required it may be obtained as follows :

(*i*) By the action of pure dilute sulphuric acid on magnesium ribbon.

$$Mg + H_2SO_4\,(dil.) \longrightarrow MgSO_4 + H_2$$

(*ii*) By the electronlysis of a warm solution of barium hydroxide using platinum or nickel electrodes.

(*iii*) By the action of water on sodium hydride.

$$NaH + H_2O \longrightarrow NaOH + H_2$$

(*iv*) By the action of KOH on scrap aluminium **(Uyeno's method).**

This method is used for military purposes.

$$2\,Al + 2\,KOH + 2\,H_2O \longrightarrow 2\,KAlO_2 + 3\,H_2$$

11.5.2. Commercial preparation or Manufacture of Dihydrogen

Dihydrogen can be prepared on a commercial scale by the following methods :

(i) From water gas. When super heated steam is passed over red hot coke at 1270 K, a mixture of carbon monoxide (CO) and dihydrogen (H_2) called water gas is produced.

$$C(s) + H_2O(g) \xrightarrow{1270\text{ K}} \underbrace{CO(g) + H_2(g)}_{\text{Water gas}} - 121\cdot3\text{kJ}$$

Dihydrogen is removed from water gas by any one of the following two methods :

(*i*) *Liquefaction Process.* Carbon monoxide liquefies at 83 K while dihydrogen at 42 K. Thus, when water gas is cooled under pressure, CO liquefies while H_2 passes out.

(*ii*) *By Bosch Process.* In this process, water gas is mixed with twice its volume of steam. The mixture is then passed over a heated catalyst (containing oxides of iron, chromium and cobalt) at 773 K when a mixture of carbon dioxide and dihydrogen is produced.

$$\underbrace{CO(g) + H_2(g)}_{\text{Water gas}} + H_2O(g) \xrightarrow[773\text{ K}]{Fe_2O_3/Cr_2O_3} CO_2(g) + 2H_2(g)$$

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

2. From steam and water gas – Lane's Process. Dihydrogen is manufactured by passing alternate currents of steam and water gas over red hot iron. The method, in fact, consists of two stages.

(*i*) *Oxidation stage.* Super heated steam is passed over iron filings heated to about 1023 – 1073 K when hydrogen is formed and magnetic oxide of iron is left behind (Fig. 11.3).

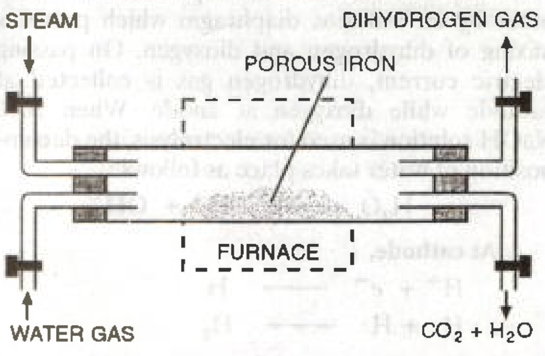


FIGURE 11.3. Manufacture of dihydrogen by Lane's process.

$$\underset{(steam)}{3Fe + 4H_2O} \longrightarrow \underset{\substack{\text{Magnetic}\\\text{oxide}}}{Fe_3O_4} + 4H_2 + 160.7\text{ kJ}$$

(ii) Reduction stage. When the whole of iron has been oxidised, the steam supply is cut off and a stream of water gas (H_2 + CO) is passed to reduce Fe_3O_4 back to iron.

$$Fe_3O_4 + 4H_2 \longrightarrow 3Fe + 4H_2O$$

$$Fe_3O_4 + 4CO \longrightarrow 3Fe + 4CO_2$$

Thus by passing steam and water gas alternately over heated iron, dihydrogen gas can be manufactured from a small quantity of iron.

3. By the electroysis of water. This is the best method of manufacturing dihydrogen where electricity is cheap. A small quantity (15 – 25%) of acid or alkali is added to water to make it a good conductor and electrolysed in a cell as shown in Fig. 11.4.

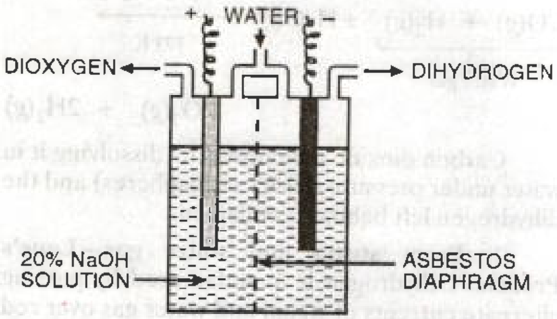


FIGURE 11.4. Electrolysis of water for commercial preparation of dihydrogen.

In this cell, iron sheet is used as a cathode while nickel plated iron sheet acts as anode.

The two electrodes are separated from each other by an asbestos diaphragm which prevents mixing of dihydrogen and dioxygen. On passing electric current, dihydrogen gas is collected at cathode while dioxygen at anode. When 20% NaOH solution is used for electrolysis, the decomposition of water takes place as follows :

$$H_2O \longrightarrow H^+ + OH^-$$

At cathode,

$$H^+ + e^- \longrightarrow H\cdot$$

$$H\cdot + H\cdot \longrightarrow H_2$$

At anode,

$$4\,OH^- \longrightarrow 4\,OH + 4e^-$$

$$4\,OH \longrightarrow 2\,H_2O + O_2$$

4. From hydrocarbons. One of the most recent methods developed for manufacture of dihydrogen involves either partial oxidation of hydrocarbons obtained from petroleum or thermal cracking of natural gas.

(i) Partial oxidation of hydrocarbons or coke. A mixture of hydrocarbons (say crude naphtha) is mixed with steam and passed over a heated Ni – Cr catalyst at 1270 K.

$$\underset{\text{Naphtha}}{C_nH_{2n+2}} + \underset{\text{Steam}}{nH_2O} \xrightarrow[1270\text{ K}]{\text{Ni}-\text{Cr}} nCO + (2n+1)H_2$$

In this process, instead of crude naphtha, natural gas may also be used.

$$\underset{\text{Natural gas}}{CH_4\,(g)} + \underset{\text{Steam}}{H_2O\,(g)} \xrightarrow[1270\text{ K}]{\text{Ni}-\text{Cr}} CO\,(g) + 3H_2\,(g)$$

Similarly,

$$C_3H_8\,(g) + 3\,H_2O\,(g) \xrightarrow[1270\text{ K}]{\text{Ni}-\text{Cr}} 3\,CO\,(g) + 7\,H_2\,(g)$$

$$C\,(s) + H_2O\,(g) \xrightarrow{1270\text{ K}} C\,(s) + H_2\,(g)$$

CO is converted to CO_2 by passing the gases and steam over an iron oxide or cobalt oxide catalyst at 673 K resulting in the generation of more H_2.

$$CO + H_2O \xrightarrow[673\text{ K}]{Fe_2O_3\text{ or }Cr_2O_3} CO_2 + H_2$$

This is called the **water gas shift reaction.**

Relatively small amounts of dihydrogen (1 – 17 m^3h^{-1}) are obtained by passing a 1 : 1 molar mixture of vapourised methanol and water over a **base-metal chromite type catalyst** at 673 K. The mixture of hydrogen and carbon monoxide thus obtained is made to react with steam to give CO_2 and more dihydrogen .

$$CH_3OH \xrightarrow[\text{Catalyst}]{673\text{ K}} CO + H_2$$

$$CO + H_2O \xrightarrow[\text{Catalyst}]{673\text{ K}} CO_2 + H_2$$

5. As a by-product. Large quantities of dihydrogen are obtained as a by-product in various industries. For example,

(i) From petroleum cracking plants, *(ii)* Manufacture of sodium hydroxide by brine electrolysis, *(iii)* From coke oven gas.

(ii) Thermal cracking of natural gas. Dihydrogen may also be obtained by thermal cracking of natural gas.

$$CH_4 \xrightarrow[\text{catalyst}]{1270\text{ K}} C + 2H_2$$

Presently above 77% of the industrial hydrogen is produced from petrochemicals, 18% from coal, 4% from electrolysis of aqueous solutions and 1% from other sources.

11.6. Properties of Dihydrogen

(*a*) **Physical properties.** 1. It is a *colourless, tasteless* and *odourless* gas

2. It is the lighest substance known. For example, one litre of dihydrogen at N.T.P. weighs 0·0899 g. Its density is approx. 1/14 th of that of air.

3. It is slightly soluble in water since its molecules are non- polar.

4. It can be liquefied under low temperature and high pressure.

Some important physical constants of dihydrogen alongwith dideuterium and ditritium are given in Table 11.2.

ADD TO YOUR KNOWLEDGE

Ortho and Para Hydrogen. Dihydrogen has two nuclear spin isomers called ortho and para dihydrogen. When two hydrogen atoms combine to form a molecule of dihydrogen, the two electrons always spin in the opposite directions (*Pauli's exclusion principle*) as otherwise the molecule will not be stable. However, the spins of the protons (nuclei) may either be in the same direction or in the opposite direction.

When the spins of the nuclei are in the same direction (parallel spins), dihydrogen is called **ortho hydrogen** *and when the spins are in the opposite directions (antiparallel spins), dihydrogen is called* **para hydrogen.**

The two forms of dihydrogen are shown in Fig. 11.5.

Conversion of one isomer into the other is a slow process. Para isomer with low energy is favoured at low temperatures.

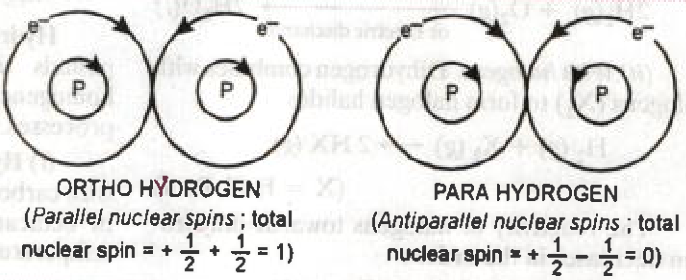


FIGURE 11.5. Ortho and Para dihydrogen.

At room temperature, ordinary dihydrogen contains 75% of ortho hydrogen and 25% of para hydrogen. As the temperature is lowered, the percentage of ortho hydrogen in the mixture decreases while that of the para hydrogen increases and at about 20K, it is pure para hydrogen. In contrast, when a sample of ordinary dihydrogen is heated say to 400 K or above, the ratio of ortho and para hydrogen remains to be the same (3 : 1). Thus, *it is possible to obtain pure para hydrogen but it is not possible to obtain pure ortho hydrogen.*

The physical properties of dihydrogen are not greatly affected by nuclear spin isomerism. However, some of the notable differences are :

(*i*) Thermal conductivity of p-H_2 is 50% greater than that of o-H_2 and

(*ii*) The melting point of p-H_2 is 0·15 K lower than that of hydrogen containing 75% o-H_2.

(*b*) **Chemical properties.** Some important chemical properties of dihydrogen are discussed below :

1. Neutral character. It is neutral to litmus.

2. Combustibility. It is a highly *combustible gas* and burns in air or dioxygen with a pale blue flame to form water. However, it is not a supporter of combustion.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

3. Dissociation. Owing to its high bond dissociation enthalpy (435·88 kJ mol⁻¹), dihydrogen is quite stable. Significant decomposition of H_2 into its atoms occurs only above 2000 K (0·081% which increases to 95·5% at 5000 K)

$$H_2(g) \xrightarrow[95\cdot5\%]{5000\text{ K}} 2H(g)$$

4. Action with metals. Dihydrogen reacts with strongly electropositive metals like sodium, potassium, calcium etc. to form salt-like (*electrovalent or ionic*) metal hydrides, in which the oxidation state of hydrogen is −1. For example,

$$2Na + H_2 \xrightarrow{573\text{ K}} \underset{\text{Sod. hydride}}{2\,Na^+H^-}$$

$$Ca + H_2 \xrightarrow{573\text{ K}} \underset{\text{Cal. hydride}}{Ca^{2+}(H^-)_2}$$

5. Action with non-metals. Because of its high bond dissociation energy (435·88 kJ mol^{-1}), dihydrogen is not particularly reactive. However, at high temperatures or in presence of catalysts, it combines with many non-metals to form covalent or molecular hydrides. For example,

(i) With dioxygen, H_2 forms H_2O. The reaction is strongly exothermic

$$2H_2(g) + O_2(g) \xrightarrow[\text{or Electric discharge}]{970\text{ K}} 2H_2O(l)$$

(ii) With halogens. Dihydrogen combines with halogens (X_2) to form halogen halides

$$H_2(g) + X_2(g) \longrightarrow 2HX(g)$$

$$(X = F, Cl, Br, I)$$

The reactivity of halogens towards dihydrogen decreases in the order :

$$F_2 > Cl_2 > Br_2 > I_2.$$

Thus, flourine reacts in dark, chlorine in presence of diffused sunlight, while the reaction with bromine and iodine occurs on heating in presence of a catalyst.

(vi) With dintrogen, it forms ammonia.

$$N_2(g) + 3H_2(g) \xrightarrow[\text{Fe, Mo}]{673\text{K, 200 atm.}} \underset{\text{Ammonia}}{2NH_3(g)}\,;$$

$$\Delta H = -\,92{\cdot}6\text{ kJ mol}^{-1}$$

This reaction is used for the manufacture of ammonia.

6. Reduction of metal oxides and ions. *Dihydrogen acts as a reducing agent* and hence reduces oxides of certain less electropositive metals such as those of Cu, Zn, Pb, Fe etc. to the corresponding metals. For example,

$$CuO + H_2 \xrightarrow{\text{Heat}} Cu + H_2O$$

$$ZnO + H_2 \xrightarrow{\text{Heat}} Zn + H_2O$$

$$PbO + H_2 \xrightarrow{\text{Heat}} Pb + H_2O$$

$$Fe_3O_4 + 4H_2 \xrightarrow{\text{Heat}} 3Fe + 4H_2O$$

The oxides of strongly electropositive metals such as those of alkali and alkaline earth metals are not reduced by this method.

Dihydrogen also reduces some metal ions in aqueous solutions. For example,

$$Pd^{2+}(aq) + H_2(g) \longrightarrow Pd(s) + 2H^+(aq)$$

7. Hydrogenation of unsaturated hydrocarbons. Unsaturated hydrocarbons such as alkenes and alkynes add dihydrogen in presence of a catalyst to form saturated hydrocarbons.

$$\underset{\text{Ethene}}{CH_2=CH_2} + H_2 \xrightarrow[473\text{ K}]{\text{Ni or Pt or Pd}} \underset{\text{Ethane}}{CH_3-CH_3}$$

$$\underset{\text{Acetylene}}{HC\equiv CH} + 2H_2 \xrightarrow[473\text{ K}]{\text{Ni or Pt or Pd}} \underset{\text{Ethane}}{CH_3-CH_3}$$

Hydrogenation of unsaturated organic compounds in presence of heterogenous and homogeneous catalysts is used in many industrial processes. For example,

(i) **Hydroformylation of olefins.** Olefins react with carbon monoxide and dihydrogen in presence of octacarbonyl dicobalt as catalyst under high temperature and pressure to form aldehydes.

$$\underset{\text{Alkene}}{RCH=CH_2} + H_2 + CO \xrightarrow[\text{High temp., pressure}]{[Co(CO)_4]_2} \underset{\text{Aldehyde}}{RCH_2CH_2CHO}$$

This reaction is called **hydroformylation** or the **oxo-process.** The aldehydes thus obtained on subsequent catalytic reduction give alcohols.

$$\underset{\text{Aldehyde}}{RCH_2CH_2CHO} + H_2 \longrightarrow \underset{\text{Alcohol}}{RCH_2CH_2CH_2OH}$$

(ii) **Hydrogenation of oils.** The vegetable oils such as soyabean oil, cotton seed oil, groundnut oils are called polyunsaturated oils since they contain many C = C bonds. When these oils are exposed to air for prolonged periods, the double bonds present in them undergo oxidation and the oils become **rancid,** *i.e,* develop unpleasant taste. To avoid this, double bonds are reduced. For this purpose, dihydrogen is bubbled through edible oils in presence of finely divided nickel of 473 K when the oils are converted into solid fats.

$$\underset{(Liquid)}{\text{Edible oil}} + H_2 \xrightarrow{\text{Ni, 473 K}} \underset{(Solid)}{\text{Edible fat}}$$

This process is called **hydrogenation** or **hardening of oils** and is used in the manufacture of vegetable ghee like Dalda, Gagan, Rath etc. from vegetable oils. It may, however, be noted that *hydrogenation reduces the number of double bonds but does not completely eliminate them.*

11.7. Uses of Dihydrogen

Dihydrogen is used

(*i*) in the manufacture of ammonia (by Haber's process) which is used for the production of various fertilizers like urea, ammonium sulphate, calcium ammonium nitrate (CAN) etc.

(*ii*) in the hydrogenation of vegetable oils to form solid fats, *i.e.*, Vanaspati Ghee.

(*iii*) in the manufacture of bulk chemicals such as methanol

$$CO\,(g) + 2\,H_2\,(g) \xrightarrow[\text{Cobalt catalyst}]{\text{700 K, 200 atm.}} CH_3OH\,(l)$$

(*iv*) in the manufacture hydrogen chloride

$$H_2\,(g) + Cl_2\,(g) \xrightarrow{h\nu} 2\,HCl\,(g)$$

(*v*) in the manufacture of metal hydrides (refer to sec 11.7).

(*vi*) in metallurgy to reduce heavy metal oxides to metals.

(*vii*) in the *atomic hydrogen* (produces temperatures around 4000 K) and *oxy-hydrogen torches* (produces temperature between 2270-2770 K) for cutting and welding. Dihydrogen is dissociated with the help of an electric arc and the hydrogen thus obtained are allowed to recombine on the surface to be welded. As a temperature of around 4000 K is generated.

(*viii*) Liquid hydrogen (mixed with liquid oxygen) is used as a rocket fuel in space research. It is also used in fuel cells and in bubble chambers for study of high energy particles.

ADD TO YOUR KNOWLEDGE

1. Hydrogen under very high pressure is expected to behave like a metal.
2. The name **dihydrogen** is commonly used for H_2 molecule, but while referring to the isotopic mixture with natural abundance for H and D, the name **diprotium is preferred.**
3. The name **proton** is used for H^+ but while referring to the isotopic mixture of H^+, D^+ and T^+, the name **hydron** is preferred.
4. Heavy hydrogen or deuterium was separated from liquid hydrogen by fractional evaporation by H.C. Urey. For this great contribution, he was awarded the Nobel Prize in Chemistry in 1934.

11.8. Hydrides

Dihydrogen combines with a number of elements to form binary compounds called *hydrides.* Their general formula being MH_x where M represents the element and *x* the number of hydrogen atoms. The various elements which form hydrides are :

(*i*) All the main group elements except those of noble gases and probably indium and thallium.

(*ii*) All lanthanides and actinides.

(*iii*) Transition metals – Sc, Y, La, Ac, Tc, Zr, Hf, Pd and to a lesser extent V, Nb, Ta, Cr, Cu and Zn.

Depending upon the physical and chemical properties, the hydrides have been divided into the following three broad categories :

1. *Ionic or Salt-like or Saline hydrides*
2. *Metallic or Interstitial hydrides*
3. *Molecular or Covalent hydrides*

1. Ionic hydrides. These are formed by those metals whose electronegativity values are appreciably lower than that of hydrogen (2·1). Thus, all elements of group 1, *i.e.*, alkali metals and group 2, *i.e.*, alkaline earth metals on heating at high temperatures (595 – 973 K) form ionic hydrides. However, BeH_2 and MgH_2 have covalent polymeric structures.

Properties. Some important properties of ionic hydrides are listed below :

(i) These are formed by transfer of electrons from the metals to the hydrogen atoms and thus contain hydride ion, H^-. For example, lithium hydride, Li^+H^- and calcium hydride, $Ca^{2+}(H^-)_2$.

(ii) These are white crystalline solids and their crystal structures consist of ions.

Alkali metal hydrides (*i.e.* ; LiH, NaH, KH, RbH and CsH) have rock salt structures. Their thermal stability, however, decreases from LiH to CsH due to the reason that the lattice energies of these hydrides decrease progressively as the size of the metal cation increases from Li^+ to Cs^+. In a similar way, the stabilities of hydrides of alkaline earth metals decrease in the order : $CaH_2 > SrH_2 > BaH_2$.

(iii) The density of these hydrides is higher than those of the metals from which they are formed. This is because that the H^- ions occupy holes in the lattice of the metal without distorting the metal lattice.

(iv) They have high melting and boiling points and conduct electricity in the fused state, liberating dihydrogen at the anode.

$$\text{At anode : } 2\,H^-(l) \longrightarrow H_2(g) + 2\,e^-$$

$$\text{At cathode : } Na^+(l) + e^- \longrightarrow Na(l)$$

(v) They have high heats of formation and are always stoichiometric.

(vi) Except LiH, they burn in air on strong heating (675 – 775 K) due to their decomposition into hydrogen which is inflammable

$$CaH_2 \xrightarrow{675-775\text{ K}} Ca + H_2$$

(vii) They react violently with water to form the corresponding metal hydroxides with the liberation of dihydrogen. Thus they act as strong bases.

$$NaH(s) + H_2O(l) \longrightarrow NaOH(aq) + H_2(g)$$

$$CaH_2(s) + 2\,H_2O(l) \longrightarrow Ca(OH)_2(aq) + 2\,H_2(g)$$

Because of the exothermic nature of the reaction, the evolved H_2 catches fire. The fires so produced cannot be extinguished by CO_2 because it gets reduced by the hot metal hydride. However, sand is useful since it a highly stable solid.

(viii) They are powerful reducing agents, especially at high temperatures

$$2\,CO + NaH \longrightarrow HCOONa + C$$

$$SiCl_4 + 4\,NaH \longrightarrow SiH_4 + 4\,NaCl$$

$$PbSO_4 + 2\,CaH_2 \longrightarrow PbS + Ca(OH)_2$$

However, their reactivity towards H_2O limits their usefulness as reducing agents in aqueous solutions.

(ix) They form complexes such as lithium aluminium hydride ($LiAlH_4$) and sodium borohydride ($NaBH_4$) which are widely used as reducing agents in organic synthesis.

$$4\,LiH + AlCl_3 \longrightarrow LiAlH_4 + 3\,LiCl$$

$$4\,NaH + B(OCH)_3 \longrightarrow NaBH_4 + 3\,CH_3ONa$$

2. Metallic or Interstitial hydrides. *d*-Block elements of groups 3, 4, 5 (Sc, Ti, V, Y, Zr, Nb, La, Hf, Ta, Ac etc.) 10, 11, 12 (Pd, Cu, Zn etc.) and *f*-block elements (Ce, Eu, Yb, Th, U etc.) on heating with H_2 under pressure form hydrides. In group 6, Cr alone forms the hydride, CrH. The metals of group 7, 8 and 9 do not form hydrides. In fact, the region of the periodic table from groups 7—9 which do not form hydrides is referred to as the **hydride gap.** Some important examples of hydrides of groups 3 to 5 are : ScH_2, YH_2, YH_3, LaH_2, LaH_3, TiH_2, ZrH_2, HfH_2, VH, VH_2, NbH, NbH_2, TaH. These hydrides generally have properties similar to those of the parent metals and hence are called **metallic hydrides.** In these hydrides, hydrogen atoms being small in size, occupy some (but not all the interstitial sites) in the metallic lattice. That is why these hydrides are also called **interstitial hydrides.**

These interstitial hydrides may also be regarded either as alloys or interstitial solid solutions of hydrogen in metals. However, it is not certain whether the hydrogen is present in the interstitial sites as hydrogen atoms or H^+ ions with delocalized electrons.

Properties. Some important properties of these hydrides are listed below :

(i) They are hard, have a metallic lustre, conduct electricity and have magnetic properties.

(ii) The density of these hydrides is lower than those of metals from which they are formed since the crystal lattice expands due to inclusion of H_2.

(iii) These hydrides are often **non stoichiometric** (ZrH_x where X = 1·30 – 1·75, TiH_x where X = 1·8 – 2·0, $ZrH_{1\cdot9}$, $PdH_{0\cdot7}$, $VH_{1\cdot6}$, $LaH_{2\cdot57}$, $YbH_{2\cdot55}$, $CeH_{2\cdot7}$). *Further the*

ratio of H-atoms to the metal atoms in these hydrides is not fixed but varies with the temperature and the pressure.

Uses. Due to interstitial hydride formation, these metals absorb large volumes of hydrogen on their surface. *This property of adsorption of a gas by a metal is known as* **occlusion.**

The amount of hydrogen occluded depends upon the nature and physical state of the metal, *i.e., colloidal palladium > palladium > platinum > gold > nickel.*

If red hot Pd is cooled in H_2, it absorbs or occludes about 935 times its own volume of H_2 gas. This may be used to separate H_2 or D_2 from He and other gases. However, on strong heating, the occluded hydrogen is liberated. Further metals which can dissolve varying amounts of hydrogen in this way can act as catalysts for hydrogenation reactions. Metallic hydrides can also be used as hydrogen storage media.

3. Molecular or Covalent hydrides. These are mainly formed by *p*-block elements and some *s*-block elements (Be and Mg) primarily due to the reason that the electronegativity difference between these elements and the hydrogen atom is quite small. Their general formula is either XH_n (for *s*-block elements) or XH_{8-n} (for *p*-block elements) where n is the number of electrons in valence shell. *These hydrides usually consist of discrete covalent molecules which are held together by weak van der Waals' forces of attraction and hence are called* **covalent or molecular hydrides.**

Nomenclature. The systematic names of molecular hydrides are usually derived from the name of the element and the suffix – *ane*. For example, **phosphane** for PH_3, **oxidane** for H_2O and **azane** for NH_3. However, common names like phosphine, water and ammonia are more commonly used.

Preparation. These are prepared by a number of different methods :

(*i*) *By direct combination of elements with dihydrogen*. For example,

$$N_2\,(g) + 3\,H_2\,(g) \xrightarrow[\text{Fe, Mo}]{\text{673 K, 200 atm}} 2\,NH_3\,(g)$$

$$2\,H_2\,(g) + O_2\,(g) \xrightarrow{\text{Electric discharge}} 2\,H_2O\,(g)$$

$$H_2\,(g) + S\,(l) \xrightarrow{\text{713 K}} H_2S\,(g)$$

$$H_2\,(g) + F_2\,(g) \xrightarrow[\text{23 K}]{\text{Dark, little moisture}} HF\,(l)$$

(*ii*) *By reduction of a suitable halide with $LiAlH_4$ in dry ether*

$$4\,BCl_3 + 3\,LiAlH_4 \longrightarrow 2\,B_2H_6 + 3\,AlCl_3 + 3\,LiCl$$

$$SiCl_4 + LiAlH_4 \longrightarrow SiH_4 + AlCl_3 + LiCl$$

(*iii*) *By action of acids on suitable binary compounds.*

$$\underset{\text{Mag. boride}}{2\,Mg_3B_2} + 4\,H_3PO_4 \longrightarrow B_4H_{10} + 2\,Mg_3(PO_4)_2 + H_2$$

$$\underset{\text{Aluminium carbide}}{Al_4C_3} + 12\,HCl \longrightarrow 3\,CH_4 + 4\,AlCl_3$$

$$FeS + H_2SO_4 \longrightarrow H_2S + FeSO_4$$

$$\underset{\text{Cal. phosphide}}{Ca_3P_2} + 3\,H_2SO_4 \longrightarrow 2\,PH_3 + 3\,CaSO_4$$

(*iv*) *By reduction of an oxoacid with $NaBH_4$ in aqueous solution*

$$4\,H_3AsO_3 + 3\,NaBH_4 \longrightarrow 4\,AsH_3 + 3\,H_3BO_3 + 3\,NaOH$$

Classification. Depending upon the number of electrons and bonds present in their Lewis structures, molecular hydrides have been classified as *electron-deficient, electron-exact* and *electron rich hydrides.*

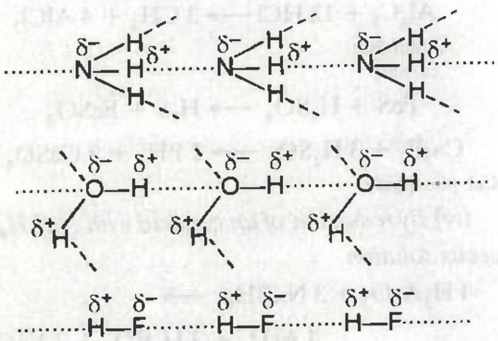
Properties. Some important properties of covalent hydrides are discussed below :

(*i*) *Covalent hydrides are usually volatile compounds having low melting and boiling points and also do not conduct electricity.*

(*ii*) *Hydrides of group 13 (i.e. BH_3, AlH_3 etc.). do not have sufficient number of electrons to form normal covalent bonds and hence are called* **electron-deficient hydrides.** They generally exist in polymeric forms such as B_2H_6, B_4H_{10}, $(AlH_3)_n$ etc.

(*iii*) *Hydrides of group 14 (i.e. CH_4, SiH_4, GeH_4, SnH_4, PbH_4) have exact number of electrons to form normal covalent bonds and hence are called* **electron precise hydrides.** All these hydrides have tetrahedral shapes. Their bond lengths increase from CH_4 to PbH_4 as the size of the element increases from C to Pb.

(iv) Hydrides of group 15, 16 and 17 (i.e., NH_3, PH_3, H_2O, H_2S, HF, HCl etc.) have more electrons than required to form normal covalent bonds and hence are called **electron-rich hydrides.** The excess electrons in these hydrides are present as lone pairs of electrons. For example, group 15 hydrides have *one lone pair*, group 16 hydrides have *two lone pairs* while group 17 hydrides have *three lone pairs of electrons.* The presence of these lone pairs of electrons on the highly electronegative O, N and F atoms result in the formation of *inter-molecular H-bonds.* As a result of these inter-molecular H-bonds, these hydrides exist as associated molecules as shown below :



Consequently, the hydrides of first elements of groups 15, 16 and 17 (i.e. NH_3, H_2O, HF) have abnormally high boiling points as compared to the boiling points of the hydrides of the second element of each group (i.e. PH_3, H_2S, HCl). The boiling points of the hydrides of the rest of the elements of each group, however, increase as the atomic number of the element or the molecular mass of the hydride increases down the group as shown in the following table.

Group 15		Group 16		Group 17	
Hydride	b.p. (K)	Hydride	b.p. (K)	Hydride	b.p. (K)
NH_3	238·5	H_2O	373	HF	292·4
PH_3	185·5	H_2S	213	HCl	188·0
AsH_3	210·6	H_2Se	231	HBr	205·9
SbH_3	254·6	H_2Te	270·8	HI	237·5

(iv) The lighter elements of group 14, 15 and 16 form polynuclear hydrides in which two or more atoms of the same element are linked together. This property of self-linking of atoms is called **catenation** *and is maximum for carbon,* (C_2H_6, C_3H_8, C_4H_{10} .... etc.), followed by nitrogen (N_2H_4, NH_3), oxygen (H_2O_2, H_2O_3) and sulphru (H_2S_x where $x = 2-6$).

ADD TO YOUR KNOWLEDGE

Besides three main categories of hydrides, *i.e.*, ionic, interstitial and covalent, certain hydrides are better known as polymeric hydrides and complex hydrides. For example,

(i) Polymeric hydrides. These are formed by elements having electronegativity in the range 1·40 – 2·0. These usually exist is the polymeric form in which the monomer molecules are held together in two or three dimensions by hydrogen bridges. Some common examples are :

$(BeH_2)_n$, $(AlH_3)_n$, $(InH_3)_n$, $(GaH_3)_n$, $(SiH_4)_n$ etc.

These are amorphous solids which decompose above 523 K to evolve H_2 gas.

Structure. Beryllium hydride exists in the polymeric form involving three-centre-two electron bonds as shown below :

(ii) Complex hydrides. In these hydrides, the hydride ion (H^-) acts as the ligand and is attached to the central metal atom by coordinate bonds. These are formed both by transition and non-transition elements. Among the non-transition elements, the most important complex hydrides are formed by elements of group 13. These are sodium borohydride ($NaBH_4$), lithium borohydride ($LiBH_4$) and lithium aluminium hydride ($LiAlH_4$).

These are versatile reducing agents and are widely used for reduction of organic compounds.

11.9. Water

Occurrence. Water is essential to all forms of life but distribution of water over the earth's surface is not uniform. Whereas deserts have no permanent surface water, oceans cover vast areas ($1{\cdot}61 \times 10^8$ km^2), *i.e.*, 78% of the earth's surface. Of the total estimated global supply of about $1{\cdot}4 \times 10^9$ km^3, the oceans and the inland saline water bodies hold 97·3% and the fresh water amounts to less than 2·7%. Most of the fresh water ($2{\cdot}5 - 2{\cdot}9 \times 10^7$ km^3) is locked up in Antartica and Artica glaciers. Fresh water lakes contain $1{\cdot}25 \times 10^5$ km^3 of water, more than half of which is in the four largest lakes : Baikal (26000 km^3), Tanganyika (2000 km^3), Nayassa (13000 km^3) and Superior (12000 km^3). Other major sources of fresh water are : ground water, springs and rivers. The fraction of fresh water readily available for human use is only 0·006% of the total global water supply.

In nature, water is found is all the three phases, *i.e.* solid, liquid and gas.

11.9.1. Structure of Water Molecule and its Aggregates

In H_2O molecule, the oxygen is sp^3-hybridized and hence has four sp^3-hybridized orbitals. Two of these sp^3-orbitals are half-filled and hence overlap with $1s$-orbitals of hydrogen to firm two sp^3-s, O–H, σ-bonds while the other two contain a lone pair of electrons each. Since the oxgyen atom is sp^3-hybridized, therefore, the geometry of H_2O molecule should be tetrahedral and the $\angle$HOH bond angle should be 109.5°. But experimentally, it has been determined that the actual $\angle$HOH bond angle is 104.5°. This may be explained as follows :

In H_2O, the oxgyen atom is surrounded by two shared pairs, and two lone pairs of electrons. But according to VSEPR (Valence Shell Electron Pair Repulsion) theory, *lone pair – lone pair* repulsions are greater than *bond pair – bond pair* repulsions. As a result, the $\angle$HOH bond angle in water is slightly lower than the regular tetrahedral angle of 109.5°. The actual bond angle is 104·5° and each O–H bond has a bond length of 95.7 pm.

In the *gaseous state*, water exists as discrete molecules and hence the structure of H_2O molecule in the gaseous state may be depicted as in Fig. 11.6(*a*).

The electronegativity of oxygen (3.5) is much higher (next only to fluorine) than that of hydrogen (2.1) and hence the shared pairs of electrons in the O–H bonds are attracted slightly more towards the oxygen atom. As a result, oxygen carries a partial negative charge (δ-) and hydrogen atoms carry a partial positive charge ($\delta+$) as shown in Fig. 11.6(*b*). Since these two dipoles are inclined to each other at an angle of 104.5, therefore, H_2O is a highly polar molecule. Its actual dipole moment is 1.84 D (Fig. 11.6(*c*)).

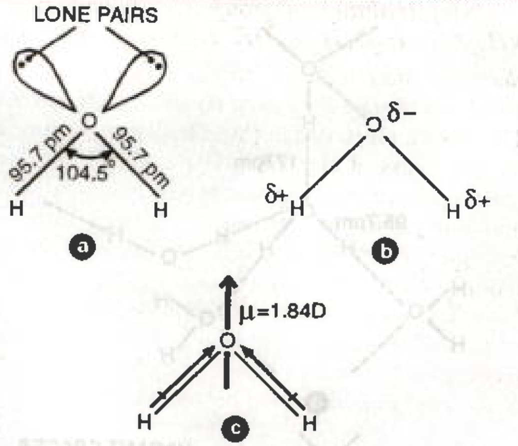


FIGURE 11.6. (*a*) Structure of H_2O in the gas phase (*b*) Polar nature of H_2O molecule (*c*) Resultant dipole moment of water molecule.

Hydrogen bonding in water and ice. *In the liquid state*, the H_2O molecules are held together by *intermolecular H-bonds.* Each oxygen atom can form two H- bonds by using each of its two lone pairs of electrons. In other words, each water molecule is generally H-bonded to four other water molecules as shown in Fig. 11.7(*a*). Thus in the liquid state, H_2O exists as an associated liquid. Experimental studies suggest that *liquid water consists of aggregates of varying number of water molecules held together by H-bonds and free water molecules in a dynamic equilibrium with the aggregates continually forming, collapsing and reforming.*

Ice, the solid form of water, can exist in nine structurally different crystalline forms depending on the conditions employed for freezing the water. At atmospheric pressure, ice crystallizes in the normal hexagonal form (I_n) but at very low temperatures, it condenses to cubic form. In the normal hexagonal ice, each oxygen atom is terahedrally surrounded by four other oxygen atoms *i.e.*. there

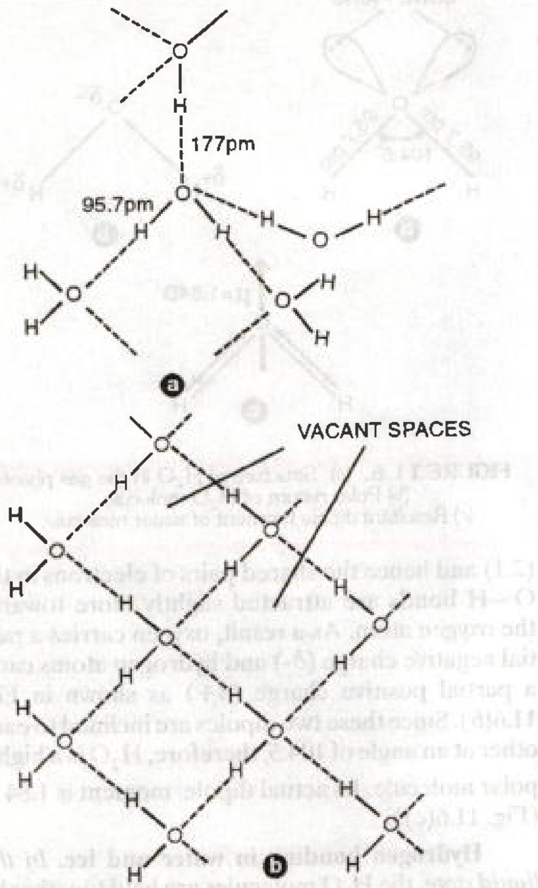


FIGURE 11.7. (a) Structure of water in the liquid state (b) Tetrahedral arrangement of oxygen atoms in ice.

is a hydrogen atom between each pair of oxygen atoms. This gives ice an *open cage like structure* as shown in Fig. 11.7(*b*). From the Fig. 11.7(*b*), it is clear that each oxygen is surrounded by four hydrogen atoms, two by strong covalent bonds (shown by solid lines) and two by weak hydrogen bonds (shown by dotted lines). Since the H-bonds are longer (177 pm) than covalent bonds (95.7 pm), the molecules of water are not closely packed in the crystal lattice. In other words, there exists a number of vacant spaces in the crystal lattice and hence the density of *ice is lower than that of liquid water*. When ice melts, some of the H-bonds are broken and the cage like structure partially collapses. In other words, some of the vacant spaces disappear which are now occupied by some of the water molecules. Therefore, for the same mass of water, the volume decreases and hence the density increases. In other words, the density of liquid water at 273 K is higher than that of ice and hence *ice floats over liquid water*.

As the temperature is raised gradually above 273 K, more and more of H-bonds break consequently more and more H_2O molecules start coming closer resulting in decrease in volume and hence increase in density. This goes on till 277 K (precisely 276·98 K). As the temperature is raised above 277K, *the increase in volume due to expansion of liquid water becomes much more than the decrease in volume due to breaking of H-bonds.* Therefore, above 277 K, there is a net increase in volume on heating thereby resulting in decrease in density. *Hence density of water is maximum at 277 K.*

This property of maximum density at 277 K helps aquatic animals to survive during winter months. In severe cold, the upper layer of sea water freezes while the water (with maximum density at 277 K) remains as liquid under the surface of ice. As a result, aquatic animals can live safely in water even during severe cold weather.

11.9.2. Properties of Water

(a) Physical properties. Most of the unique properties of water are due to the presence of H-bonding between its molecules. Some of the physical constants of liquid water (H_2O) and its deuterium analogue, *i.e.*, heavy water (D_2O) are listed in Table 11.4.

Some of the important physical properties are discussed below :

(*i*) The freezing point, boiling point, heat of fusion and heat of vaporization of water are abnormally higher than those of the hydrides of the other elements of the same group (16) such as H_2S, H_2Se, H_2Te etc. *This is due to the presence of intermolecular hydrogen bonding in H_2O molecules which is, however, absent among the molecules of H_2S, H_2Se, H_2Te etc.*

(*ii*) Water has a higher specific heat, thermal conductivity and surface tension than most other liquids. These properties allow water to play a vital role in the biosphere. For example, the high heat of vaporization and the high heat capacity of water are responsible for moderation of the climate and body temperature of living organisms.

(*iii*) *Water because of its high dielectric constant (78·39) has the ability to dissolve most of the inorganic (ionic) compounds and is, therefore, regarded*

TABLE 11.4. Some physical constants of H_2O and D_2O.

PROPERTY	H_2O	D_2O
Molecular mass (g mol^{-1})	18·015	20.0276
Melting point (K)	273·0	276·8
Boiling point (K)	373·0	374·4
Temperature of maximum density (g/cm^3)	276·98	284·2
Maximum density (298 K) (g/cm^3)	1·000	1·106
Density (298 K) (g/cm^3)	1·0000	1·1059
Enthalpy of formation, $\Delta H_f°$ (kJ mol^{-1})	–285·9	–294·6
Enthalpy of vaporisation (373 K) (kJ mol^{-1})	40·66	41·61
Enthalpy of fusion (kJ mol^{-1})	6·01	6·28
Specific heat ($Jg^{-1} K^{-1}$)	4·177	——
Ionisation constant $[H^+][OH^-]$ (mol^2 L^{-2})	$1·008 \times 10^{-14}$	$1·95 \times 10^{-15}$
Dielectric constant	78·39	78·06
Viscosity at 293 K (in centipoise)	0·8903	1·107
Electrical conductivity (293 K/ohm^{-1} cm^{-1})	$5·7 \times 10^{-8}$	

as a **universal solvent. Whereas solubility of ionic** compounds takes place due to **ion- dipole interactions** (*i.e. solvation of ions*), the solubility of covalent compounds such as alcohols, amines, urea, glucose, sugar etc. takes place due to the tendency of these molecules to **form hydrogen bonds** with water.

(*iii*) Heavy water (D_2O) has slightly higher values of physical constants because of its higher molecular mass as compared to that of ordinary water (H_2O).

(b) Chemical properties. Water displays a wide range of reactions. It behaves as *an acid, a base, an oxidant, a reductant* and as a *ligand to metal ions*. Some of these properties are discussed below:

1. Stability. Due to high negative heat of formation (ΔH_f = 285.9 kJ mol^{-1}), water is quite stable at ordinary temperature but decomposes into its elements at very high temperature. The extent of decomposition is, however, not appreciable. Even at 1500 K, it is only 2% .

$$2H_2O(g) \xrightarrow{1500\text{ K}} 2H_2(g) + O_2(g)$$

Water also decomposes into its elements, when electricity is passed through it in presence of a small amount of an acid or an alkali.

$$2H_2O(l) \xrightarrow{\text{Electric current}} \underset{(At\ cathode)}{2H_2(g)} + \underset{(At\ anode)}{O_2(g)}$$

2. Acid-base character – Amphoteric character. Water is a weak electrolyte, *i.e.*, it undergoes ionization to a small extent to give $H_3O^+(aq)$ and $OH^-(aq)$ ions. As a result, *pure water has very low electrical conductivity.*

$$H_2O(l) + H_2O(l) \longrightarrow H_3O^+(aq) + OH^-(aq)\ ;$$

$$K_w = 1.0 \times 10^{-14}\ mol^2\ L^{-2} \text{ at 298 K.}$$

Thus, water acts both as an acid and as a base and hence is said to be amphoteric in character. For example, it can act as an acid towards NH_3 and as a base towards H_2S :

$$\underset{\text{Acid}}{H_2O\ (l)} + \underset{\text{Base}}{NH_3\ (aq)} \longrightarrow \underset{\text{Acid}}{NH_4^+\ (aq)} + \underset{\text{Base}}{OH^-\ (aq)}$$

$$\underset{\text{Base}}{H_2O\ (l)} + \underset{\text{Acid}}{H_2S\ (aq)} \longrightarrow \underset{\text{Acid}}{H_3O^+\ (aq)} + \underset{\text{Base}}{HS^-\ (aq)}$$

In general, *water can act as a base towards acids stronger than itself and as an acid towards a base stronger than it.* Thus, in terms of its amphoteric nature, **auto-protolysis** of water may be represented as follows :

$$\underset{\text{Acid}}{H_2O\ (l)} + \underset{\text{Base}}{H_2O\ (l)} \rightleftharpoons \underset{\text{Acid}_2}{H_3O^+\ (aq)} + \underset{\text{Base}_2}{OH^-\ (aq)}$$

3. Oxidation-reduction or Redox reactions. Besides, acid-base reactions, water also undergoes oxidation-reduction reactions.

(i) As an oxidising agent. Water reacts with number of active metals like Na, Ca etc. whose electrode potential is less than -0.83 V liberating dihydrogen gas.

$$[2H_2O(l) + 2e^- \longrightarrow 2\,OH^-(aq) + H_2(g) \;;\quad E^\circ = -0{\cdot}83\text{ V}]$$

$$\underset{(Reductant)}{2Na(s)} + \underset{(Oxidant)}{2H_2O(l)} \longrightarrow 2NaOH(aq) + H_2(g)$$

Similarly, when steam is passed over red hot coke (1273 K), water gas is formed.

$$\underset{(Reductant)}{C(s)} + \underset{Oxidant)}{H_2O(g)} \xrightarrow{1273\text{ K}} \underbrace{CO(g) + H_2(g)}_{\text{Water gas}}$$

In all these reactions, *water acts as an oxidising agent and hence itself gets reduced to dihydrogen gas.*

(ii) As a reducing agent. Water reacts with highly electronegative elements like fluorine whose electrode potential is higher than $+1{\cdot}23$ V liberating dioxygen and trioxygen.

$$[O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l) \;;\quad E^\circ = +\,1{\cdot}23\text{ V}]$$

$$\underset{(Oxidant)}{2F_2(g)} + \underset{(Reductant)}{2H_2O(l)} \longrightarrow O_2(g) + 4\,H^+(aq) + 4F^-(aq)$$

$$\text{or } 3F_2(g) + 3H_2O(l) \longrightarrow O_3(g) + 6F^-(aq) + 6H^+(aq)$$

In these reactions, water acts as a reducing agent and hence itself gets oxidised to either O_2 or O_3. Similarly, during photosynthesis, water is oxidised to dioxygen.

$$xCO_2 + yH_2O \xrightarrow[\text{Chlorophyll}]{\text{Sunlight}} C_x(H_2O)_y + xO_2$$

4. Hydrolytic reactions. Water can hydrolyse many oxides (metallic and non-metallic), hydrides, carbides, nitrides, phosphides and other salts. In these reactions, H^+ and OH^- ions of water interact with the anions and cations of the compound respectively leading to the formation of an acid or a base or both as shown below :

$$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(aq)$$

$$SO_2(g) + H_2O(l) \longrightarrow \underset{\text{Sulphurous acid}}{H_2SO_3(aq)}$$

$$P_4O_{10}(s) + 6\,H_2O(l) \longrightarrow \underset{\text{Phosphoric acid}}{4\,H_3PO_4(aq)}$$

$$\underset{\text{Calcium hydride}}{CaH_2(s)} + 2H_2O(l) \longrightarrow Ca(OH)_2(aq) + 2H_2(g)$$

$$SiCl_4(l) + 4H_2O(l) \longrightarrow SiO_2.2\,H_2O(s) \text{ or } Si(OH)_4 + 4HCl(aq)$$

$$AlCl_3(s) + 6\,H_2O(l) \longrightarrow [Al(OH_2)_6]^{3+}(aq) + 3\,Cl^-(aq)$$

$$\underset{\text{Calcium carbide}}{CaC_2(s)} + 2H_2O(l) \longrightarrow Ca(OH)_2(aq) + \underset{\text{Acetylene}}{HC \equiv CH(g)}$$

$$\underset{\text{Aluminium carbide}}{Al_4C_3(s)} + 12H_2O(l) \longrightarrow 4Al(OH)_3(aq) + \underset{\text{Methane}}{3CH_4(g)}$$

$$\underset{\text{Calcium nitride}}{Ca_3N_2(s)} + 6H_2O(l) \longrightarrow 3Ca(OH)_2(aq) + \underset{\text{Ammonia}}{2NH_3(g)}$$

$$\underset{\text{Aluminium nitride}}{AlN(s)} + 3H_2O(l) \longrightarrow Al(OH)_3(aq) + NH_3(g)$$

$$\underset{\text{Calcium phosphide}}{Ca_3P_2(s)} + 6H_2O(l) \longrightarrow 3Ca(OH)_2(aq) + \underset{\text{Phosphine}}{2PH_3(g)}$$

$$Na_2CO_3(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2CO_3(aq)$$

Since the hydrolysis of Na_2CO_3 produces a strong base (NaOH) and a weak acid (H_2CO_3), therefore, *an aqueous solution of Na_2CO_3 is alkaline in nature.*

In contrast, the hydrolysis of $CuSO_4$ produces a weak base *i.e.*, $Cu(OH)_2$ and a strong acid (H_2SO_4), therefore, *an aqueous solution of $CuSO_4$ is acidic in nature.*

$$CuSO_4(s) + 2H_2O(l) \longrightarrow Cu(OH)_2(aq) + H_2SO_4(aq)$$

5. Hydrate formation. Many ionic compounds crystallise from water with one or more molecules of water associated with them. For example, $BaCl_2.2H_2O$, $CuSO_4.5H_2O$, $FeSO_4.7H_2O$,

$Na_2SO_4.10H_2O$ etc. *This water in combination with ionic salts is called water of crystallisation and such crystals are called hydrated salts or simply hydrates.* These hydrates can be classified into the following three categories :

(*i*) *Water molecules are coordinated to the central metal ion to form complex ions.* For example, in nickel nitrate hexahydrate, and lithium chloride hexahydrate, the six water molecules are linked to the central ion Ni^{2+}, Fe^{3+} or Cr^{3+} ion by coordinate bonds.

$$[Ni(OH_2)_6]^{2+}(NO_3^-)_2,\ [Fe(OH_2)_6]^{3+}\ 3\,Cl^-,$$
$$[Cr(OH_2)_6]^{3+}\ 3\,Cl^-$$

(*ii*) *Water molecules are linked to some oxygen containing anions by hydrogen bonding.* For example, in copper sulphate pentahydrate, $CuSO_4.5H_2O$, four H_2O molecules are linked to the central Cu^{2+} ion by coordinate bonds while the fifth H_2O molecule is linked to the sulphate (SO_4^{2-}) ion by H-bonding.

(*iii*) *Water molecules are present in interstitial sites or voids in the crystal lattice.* For example, in barium chloride dihydrate, $BaCl_2.2H_2O$, the two H_2O molecules occupy the voids in the crystal lattice.

11.10. Hard and Soft Water

Natural water contains dissolved salts. Depending upon its behaviour towards soap solution *w.r.t.* lather formation, water may be classified as *soft water* and *hard water*.

Soft water. *Water that produces lather with soap readily is called soft water.* Examples of soft water are : rain water, distilled water and demineralised water.

Hard water. *Water which does not produce lather with soap readily is called hard water.* A few examples of hard water are : sea water, river water, spring water, lake water and well water.

Cause of Hardness of Water. It has been established that *hardness of water is due to the presence of bicarbonates, chlorides and sulphates of calcium and magnesium in it.* Hard water does not produce lather with soap readily. This may be explained as under :

Soap is sodium or potassium salt of certain higher fatty acids such as *stearic acid, palmitic acid, oleic acid etc.* When hard water is treated with soap solution, Ca^{2+} and Mg^{2+} ions present in hard water react with the anions of fatty acids present in soaps to form curdy white precipitates. As a result, hard water does not produce lather with soap immediately.

$$\underset{\substack{\text{Sodium stearate}\\ (\textit{Soap})}}{2C_{17}H_{35}COO^-\,Na^+} + CaCl_2 \longrightarrow \underset{\substack{\text{Calcium stearate}\\ (\textit{Curdy white ppt.})}}{(C_{17}H_{35}COO)_2Ca\downarrow} + 2NaCl$$

$$\underset{\substack{\text{Sodium stearate}\\ (\textit{Soap})}}{2C_{17}H_{35}COO^-\,Na^+} + MgSO_4 \longrightarrow \underset{\substack{\text{Magnesium stearate}\\ (\textit{Curdy white ppt.})}}{(C_{17}H_{35}COO)_2Mg\downarrow} + Na_2SO_4$$

However, when all the Ca^{2+} and Mg^{2+} ions **present in hard water have been precipitated by addition of sufficient amount of soap, the resulting water becomes *soft* and thus readily produces lather with soap. *Thus, hard water is not suitable for washing purposes since lot of soap is wasted in precipitating out Ca^{2+} and Mg^{2+} ions present in hard water.***

11.10.1. Types of Hardness of Water

Hardness of water is of two types :

(*a*) *Temporary hardness* and

(*b*) *Permanent hardness*

(a) Temporary hardness. Temporary hardness of water is due to the presence of bicarbonates of calcium and magnesium, *i.e.* $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$. It is called temporary hardness since it can be easily removed by simply boiling and filtering the water. Termporary hardness is also called **carbonate hardness.**

(b) Permanent hardness. Permanent hardness of water is due to the presence of soluble chlorides and sulphates of calcium and magnesium, *i.e.,* $CaCl_2$, $CaSO_4$, $MgCl_2$ and $MgSO_4$. This type of hardness is called permanent hardness since it cannot be removed simply by boiling the water. Permanent hardness is also called **non-carbonate hardness.**

11.10.2. Methods of Removing Hardness of Water – Softening of Hard Water

***The process of removing hardness i.e. soluble bicarbonates, chlorides and sulphates of calcium and magnesium from hard water is called softening of water.* Depending upon the nature of the dissolved salts, hard water can be softened by the following methods.**

I. For temporary hard water. The temporary hardness of water is due to the presence of bicarbonates of calcium and magnesium. It can be removed by any one of the following methods :

1. By boiling. When temporary hard water is boiled, bicarbonates of calcium and magnesium decompose to form insoluble calcium and magnesium carbonates respectively.

$$\underset{\textit{(Temporary hardness)}}{Ca(HCO_3)_2} \xrightarrow{\Delta} \underset{\text{Cal. carbonate}}{CaCO_3\downarrow} + CO_2 + H_2O$$

$$\underset{\textit{(Temporary hardness)}}{Mg(HCO_3)_2} \xrightarrow{\Delta} \underset{\text{Mag. carbonate}}{MgCO_3\downarrow} + CO_2 + H_2O$$

These insoluble carbonates are removed by filtration and the water is rendered soft.

2. By Clark's Process. This process is used on a commercial scale. In this process, calculated quantity of *quick lime* is added. The bicarbonates present in the temporary hard water react with lime to form insoluble calcium and magnesium carbonates which can be easily filtered off.

$$\underset{\text{Quick lime}}{CaO(s)} + H_2O \longrightarrow \underset{\text{Slaked lime}}{Ca(OH)_2}$$

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + 2H_2O$$

$$Mg(HCO_3)_2 + Ca(OH)_2 \longrightarrow CaCO_3\downarrow + MgCO_3\downarrow + 2H_2O$$

However, if excess of lime is added, water will again become hard due to absorption of CO_2 from the atmosphere by unused slaked lime to form soluble calcium bicarbonate.

$$Ca(OH)_2 + 2\,CO_2 \longrightarrow Ca(HCO_3)_2$$

II. For permanent hard water. The following methods are used for the removal of permanent hardness of water.

Washing soda process. In this process, hard water is treated with a calculated amount of washing soda (Na_2CO_3) when chlorides and sulphates of calcium and magnesium present in hard water get precipitated as insoluble calcium and magnesium carbonates which can be easily filtered off. The water thus becomes soft.

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + 2NaCl$$

$$MgSO_4 + Na_2CO_3 \longrightarrow MgCO_3\downarrow + Na_2SO_4$$

III. For both temporary and permanent hard waters. The following methods are used.

1. Lime-soda process. This method is employed for the softening of hard water which contains both temporary and permanent hardness. In this method, calculated quantities of slaked lime, $Ca(OH)_2$ and sodium carbonate are used. Whereas, slaked lime removes temporary hardness, sodium carbonate removes permanent hardness.

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + 2H_2O$$

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + 2NaCl$$

$$MgSO_4 + Na_2CO_3 \longrightarrow MgCO_3\downarrow + Na_2SO_4$$

2. Ion exchange method. This is the most modern method for softening of hard water. In this method, the Ca^{2+} and Mg^{2+} ions present in hard water are exchanged by those present in complex inorganic and organic compounds called *ion exchangers*. Ion exchangers are mainly of two types :

(a) Inorganic ion exchangers – Permutit method. Compelx inorganic salts like hydrated sodium aluminium silicates, $Na_2Al_2Si_2O_8 \cdot xH_2O$ have the interesting property of exchanging Ca^{2+} and Mg^{2+} ions present in hard water with sodium present in complex salts. The naturally occurring complex salts are called *zeolites*. These may also be prepared artificially by fusing strongly a mixture of washing soda (Na_2CO_3), alumina (Al_2O_3) and silica (SiO_2). The fused mass is washed with water to remove soluble impurities and the porous mass thus obtained is called *permutit*. Both zeolite and permutit can be represented by the general formula, Na_2Z where $Z = Al_2Si_2O_8 . xH_2O$.

The zeolite or permutit is loosely packed over layers of gravel and sand in a big tank (Fig. 11.8).

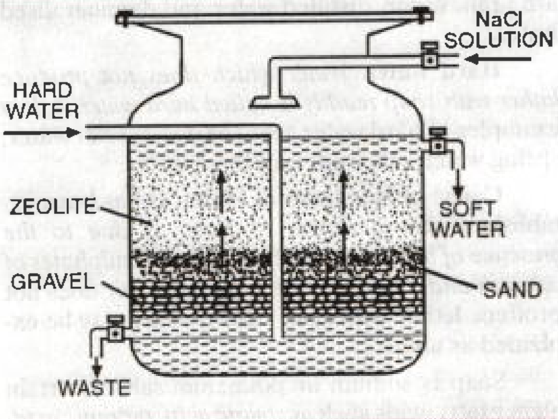


FIGURE 11.8. Permutit process for water softening.

Hard water is introduced from the top into the base of the tank. From the bottom, water rises up through the gravel and sand layers and finally percolates through the bed of the permutit. During the process, the Ca^{2+} and Mg^{2+} ions are exchanged by sodium ions in the permutit.

$$\underset{\text{Sodium zeolite}}{Na_2Z} + \underset{\textit{(From hard water)}}{CaCl_2} \longrightarrow \underset{\substack{\text{Calcium zeolite}\\ \textit{(left in the tank)}}}{CaZ} + 2NaCl$$

where $Z = Al_2Si_2O_8 . xH_2O$.

Similarly,

$$\underset{\text{Sod. zeolite}}{Na_2Z} + \underset{\textit{(From hard water)}}{MgCl_2} \longrightarrow \underset{\substack{\text{Magnesium zeolite}\\ \textit{(left in the tank)}}}{MgZ} + 2\,NaCl$$

As a result, Ca^{2+} and Mg^{2+} ions get attached to the zeolite and the water which rises above the permutit layer is reasonably soft. The softened water still contains sodium salts. But these sodium salts do not precipitate soap and hence do not prevent the lather formation.

After some time, the whole of permutit gets exhausted due to the conversion of sodium zeolite into calcium and magnesium zeolite. It can, however, be regenerated by passing a 10% solution of NaCl through it.

$$\underset{\substack{\textit{(Exhausted}\\ \textit{permutit)}}}{CaZ} + 2NaCl \longrightarrow \underset{\substack{\textit{(Regenerated}\\ \textit{permutit)}}}{Na_2Z} + CaCl_2$$

$$\underset{\substack{\textit{(Exhausted}\\ \textit{permutit)}}}{MgZ} + 2NaCl \longrightarrow \underset{\substack{\textit{(Regenerated}\\ \textit{permutit)}}}{Na_2Z} + MgCl_2$$

The soluble calcium and magnesium salts thus formed are washed away by water and the regenerated permutit can be used again.

Advantages of the Permutit Process

(*i*) It is an efficient process.

(*ii*) This is a very cheap process since during the process only sodium chloride is consumed which is quite cheap.

(*iii*) It can be used to remove both temporary and permanent hardness completely.

(b) Organic ion exchangers. One of the major drawbacks of the inorganic ion exchangers (permutit process) is that these can remove only Ca^{2+} and Mg^{2+} ions present in hard water. However, recently it has been found that certain synthetic organic exchangers also called **ion exchange resins** are even superior to zeolites since they can remove not only all types of cations but also anions present in hard water. The resulting water is called **demineralised water or deionised water** and is as good as distilled water.

Ion exchange resins are giant organic molecules of high molecular masses. These are essentially of two types :

(i) Cation exchange resins. These resins consist of giant hydrocarbon framework attached to acidic groups such as $-COOH$ (*carboxyl*) or $-SO_2OH$ (*sulphonic acid*) groups. They may be represented by the general formula $R-COOH$ or $R-SO_2OH$ where R represents the giant hydrocarbon framework.

Since these resins can exchange H^+ ions with cations such as Ca^{2+} and Mg^{2+} ions present in hard water, they are called **cation exchange resins** or **simply cation exchangers.**

(*ii*) **Anion exchange resins.** These resins consist of giant hydrocarbon framework attached to basic groups such as OH^- (hydroxide) ions usually in form of substituted ammonium hydroxides. These may be reprsented by the general formula, $R-\overset{+}{N}H_3OH^-$ where R denotes the giant hydrocarbon framework. *Since these resins can exchange OH^- ions with anions such as Cl^- and SO_4^{2-} ions present in hard water, they are called* **anion exchange resins** or *simply* **anion exchangers.**

Let us now explain the working of these resins in demineralization of hard water.

First of all, hard water is passed though a tank packed with cation exchange resins supported over gravel (Fig. 10.13). All the cations present in hard water will exchange with H^+ ions furnished by resins as shown below :

$$\underset{\textit{(Cation exchange resin)}}{2\,R-COO^-H^+} + \underset{\textit{(From hard water)}}{CaCl_2} \longrightarrow \underset{\textit{(Exhausted resin)}}{(RCOO)_2Ca} + 2H^+ + 2Cl^-$$

$$\underset{\textit{(Cation exchange resin)}}{2\,R-COO^-H^+} + \underset{\textit{(From hard water)}}{MgSO_4} \longrightarrow \underset{\textit{(Exhausted resin)}}{(RCOO)_2Mg} + 2H^+ + SO_4^{2-}$$

Thus, the water which comes out from the bottom of the first tank is richer in H^+ ions. This water is then passed through a second tank which is packed with anion exchange resins supported over gravel (Fig. 11.9). Here, the Cl^- and SO_4^{2-} ions present in hard water exchange with OH^- ions of the esins.

$$\underset{\text{(Anion exchange resin)}}{\mathrm{R-\overset{+}{N}H_3OH^-}} + \underset{\text{(in water)}}{\mathrm{Cl^-}} \longrightarrow \underset{\text{(Exhausted resin)}}{\mathrm{R-\overset{+}{N}H_3Cl^-}} + \mathrm{OH^-}$$

$$\underset{\text{(Anion exchange resin)}}{\mathrm{2R-\overset{+}{N}H_3OH^-}} + \underset{\text{(in water)}}{\mathrm{SO_4^{2-}}} \longrightarrow \underset{\text{(Exhausted resin)}}{\mathrm{(R-\overset{+}{N}H_3)_2SO_4^{2-}}} + \mathrm{2OH^-}$$

Simultaneously, the H^+ ions coming from the first tank combine with OH^- ions liberated in the second tank to form water.

$$\mathrm{H^+ + OH^- \longrightarrow H_2O}$$

Thus, the water obtained by this method is free from all types of cations as well as anions. Therefore, this method is particularly useful for obtaining drinking water from sea water and also for obtaining pure water for laboratory purposes.

Regeneration of resins. The exhausted resin in the first tank is regenerated by treatment with moderately concentrated H_2SO_4 or HCl.

$$\underset{\text{(Exhausted resin)}}{\mathrm{Ca(OOCR)_2}} + \mathrm{2H^+Cl^-} \longrightarrow \underset{\text{(Regenerated resin)}}{\mathrm{2RCOO^-H^+}} + \mathrm{Ca^{2+} + 2Cl^-}$$

Similarly, the exhausted resin in the second tank is regenerated by treatment with moderately strong NaOH solution.

$$\underset{\text{(Exhausted resin)}}{\mathrm{R-\overset{+}{N}H_3Cl^-}} + \mathrm{Na^+OH^-} \longrightarrow \underset{\text{(Regenerated resin)}}{\mathrm{R-\overset{+}{N}H_3OH^-}} + \mathrm{Na^+ + Cl^-}$$

Thus, the cation and anion exchangers can be used over again and again. It makes this process both efficient and cheap.

3. Calgon process (*sequestration*). In this process, Ca^{2+} and Mg^{2+} ions present in hard water are rendered ineffective (sequestrated) by treatment with sodium polymetaphosphate, $(NaPO_3)_x$ where *x* is as high as 100, or more commonly with sodium hexametaphosphate. $Na_2[Na_4(PO_3)_6]$. The trade name for sodium hexametaphosphate is calgon (which means calcium gone).

When calgon is added to hard water, the Ca^{2+} and Mg^{2+} ions present in it combine with sodium hexametaphosphate to form soluble complex of calcium and magnesium salts.

$$\underset{\text{(From hard water)}}{\mathrm{2CaCl_2}} + \underset{\text{Sod. hexametaphosphate}}{\mathrm{Na_2[Na_4(PO_3)_6]}} \longrightarrow \underset{\text{Complex salt}(\textit{soluble})}{\mathrm{Na_2[Ca_2(PO_3)_6]}} + \mathrm{4NaCl}$$

$$\underset{\text{(From hard water)}}{\mathrm{2MgSO_4}} + \underset{\text{Sod. hexametaphosphate}}{\mathrm{Na_2[Na_4(PO_3)_6]}} \longrightarrow \underset{\text{Complex salt}(\textit{soluble})}{\mathrm{Na_2[Mg_2(PO_3)_6]}} + \mathrm{2Na_2SO_4}$$

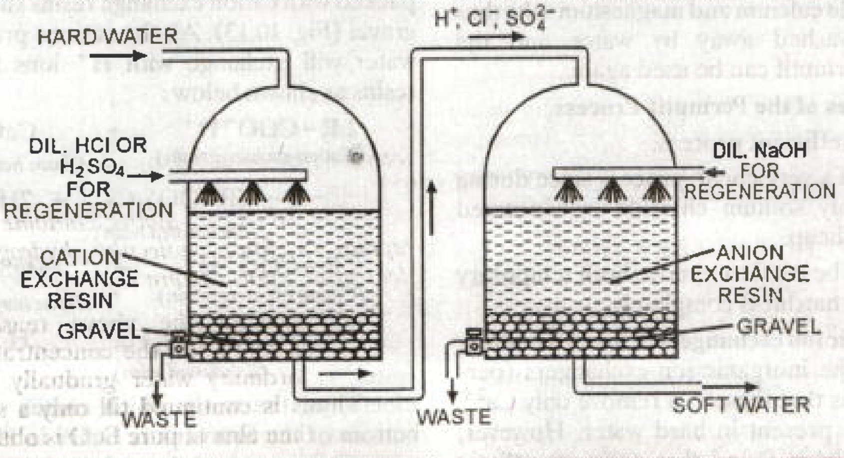


FIGURE 11.9. Ion exchange process involving organic resins.

The complex calcium and magnesium ions do not form any precipitate with soap and hence readily produce lather with soap solution.

The water softened by the above process can be used for laundry and household washing purposes and also for raising steam in boilers. Calgon is also used in synthetic detergents to check the wastage of soap during washing of clothes and also for removing *boiler scales*.

ADD TO YOUR KNOWLEDGE

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

EXAMPLE. *One litre of a sample of hard water contains 1 mg of $CaCl_2$ and 1 mg of $MgCl_2$. Find out the total hardness in terms of parts of $CaCO_3$ per 10^6 parts of water by mass.*

Solution. (*i*) Mol. mass of $CaCl_2 = 111$

Now, 111 *g* of $CaCl_2$ = 100 *g* of $CaCO_3$

$$\therefore \quad 1 \text{ mg of } CaCl_2 = \frac{100}{111} \times 1 \text{ mg of } CaCO_3 = 0{\cdot}9 \text{ mg of } CaCO_3$$

(*ii*) Mol. mass of $MgCl_2 = 95$

Now 95 *g* of $MgCl_2$ = 100 *g* of $CaCO_3$

$$\therefore 1 \text{ mg of } MgCl_2 = \frac{100}{95} \times 1 \text{ mg of } CaCO_3 = 1{\cdot}05 \text{ mg of } CaCO_3$$

Thus, 1 litre of hard water contains $= 0{\cdot}90 + 1{\cdot}05 = 1{\cdot}95$ mg of $CaCO_3$

One litre of water $= 10^3\ g = 10^6$ mg

$\therefore$ Degree of hardness $= 1{\cdot}95$ ppm.

2. **Estimation of hardness of water.** The hardness of water due to Ca^{2+} and Mg^{2+} ions is usually estimated volumetrically. A known volume of hard water containing buffer solution of *p*H 10 is titrated against a standard solution of EDTA (ethylenediamine tetraacetic acid disodium salt) using Eriochrome Black T as indicator. Under these conditions, Ca^{2+} and Mg^{2+} ions form complexes with EDTA. When all the Ca^{2+} and Mg^{2+} ions are consumed. The next drop of EDTA changes the colour of the indicator from wine red to blue.

11.11. Heavy Water

Chemically heavy water is deuterium oxide (D_2O). It was discovered by Urey, an American Chemist in 1932. He showed that ordinary water contains traces (1 part in 6000 parts) of D_2O.

11.11.1. Preparation of Heavy Water

Heavy water is mainly prepared from ordinary water either by exhaustive electrolysis or by fractional distillation.

1. By exhaustive electrolysis. This method is based upon the principle that when ordinary water is electrolysed, protium (or hydrogen) is liberated much more readily than deuterium (D_2) because of the following reasons :

(*i*) *Being smaller in size, H^+ ions have greater mobility (or speed) as compared to D^+ ions.*

(*ii*) *Because of lower discharge potential, H^+ ions are discharged at the cathode more easily than D^+ ions.*

(*iii*) *Hydrogen atoms combine much more rapidly to form molecular hydrogen than do deuterium atoms to form D_2.*

In view of the above reasons, as the electrolysis continues, the concentration of heavy water in ordinary water gradually increases. If electrolysis is continued till only a small volume remains, then almost pure D_2O is obtained. About 29,000 litres of water must be electrolysed to get one litre of 99% pure D_2O.

The electrolytic cell designed by Brown, Degget and Urey for the preparation of heavy water is shown in Fig. 11.10.

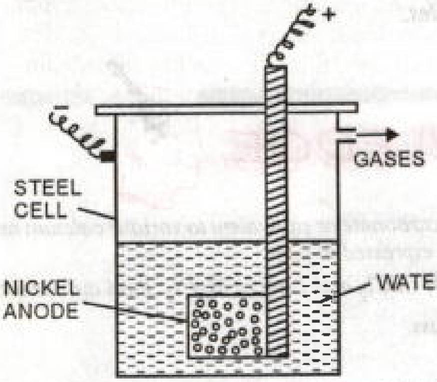


FIGURE 11.10. Electrolytic cell for the preparation of heavy water.

It consists of a steel cell (45 cm. long and 10 cm. in diameter) which acts as a cathode. The anode is a cylindrical sheet of nickel with a number of holes punched in it. In actual practice a large number of such cells are employed for electrolysis of water in a number of stages. The gases obtained from each stage are burnt separately and water thus produced is returned to the previous stage. As a result, the concentration of heavy water goes on increasing slowly in the residual water. Generally, the whole process is carried out in five stages as described below :

First Stage. In all, thirty electrolytic cells of the type described above are employed in the first stage. Each cell is charged with three litres of a three per cent solution of NaOH in ordinary water. A current of 110 volts is used for electrolysis which is carried out for nearly 72 hours. The gases evolved (protium and oxygen) in this stage are discarded. After the first stage, the charge is reduced to about 15 litres and contains about 2·5 per cent heavy water.

Second Stage. In this stage, the residue from the first stage is electrolysed in a battery of six cells. The electrolysis is continued till heavy water content increases to about 12 per cent. The gases obtained are burnt and returned to the cells in the first stage.

Third Stage. The residue obtained in the second stage is further electrolysed to raise the heavy water content in it to about 60 per cent. The gases evolved are burnt and returned to the cells in the second stage.

Fourth Stage. The residue from the third stage is electrolysed again in order to increase its heavy water content to about 99 per cent. The gases evolved are burnt as usual and sent to cells in the third stage.

Fifth Stage. The heavy water obtained as above is contaminated with impurities of alkali and ordinary water. It is subjected to distillation and the distillate is electrolysed when pure deuterium is obtained. This is burnt separately with oxygen when 100 per cent pure D_2O is obtained.

A flow sheet diagram for the preparation of heavy water by this method is given in Fig. 11.11.

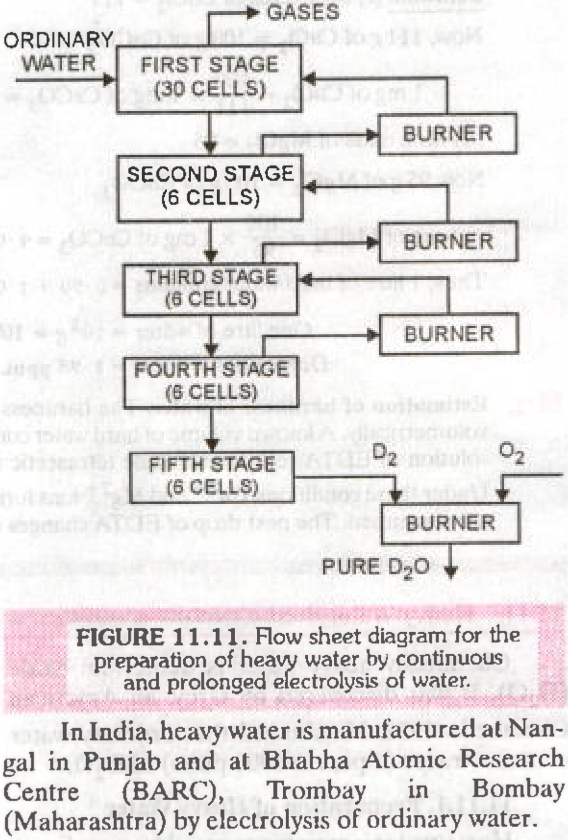


FIGURE 11.11. Flow sheet diagram for the preparation of heavy water by continuous and prolonged electrolysis of water.

In India, heavy water is manufactured at Nangal in Punjab and at Bhabha Atomic Research Centre (BARC), Trombay in Bombay (Maharashtra) by electrolysis of ordinary water.

2. By fractional distillation. At normal atmospheric pressure, the boiling points of ordinary and heavy water are 373 K and 374·42 K respectively. This small difference in their boiling points forms the basis of preparation of heavy water by fractional distllation of ordinary water. In actual practice, fractionating columns of the order of about 12 metres height are employed.

11.11.2. Properties of Heavy Water

(*a*) Physical Properties. It is a colourless, odourless and tasteless mobile liquid heavier than water. Because of higher molecular mass, there is a marked difference in physical properties of ordinary water and heavy water as shown in Table 11.4.

Further since dielectric constant of D_2O is lower than that of H_2O, therefore, ionic compounds are less soluble in D_2O than in H_2O.

(*b*) Chemical Properties. the chemical properties of heavy water are quite similar to those of ordinary water. However, the reactions of heavy water with most of the substances proceed at a much slower rate as compared to ordinary water. Some important chemical properties of heavy water are described below :

1. *Electrolysis.* When heavy water is electrolysed, deuterium is obtained at the cathode.

$$2\,D_2O \longrightarrow \underset{\text{Deuterium}}{2\,D_2} + O_2$$

2. *Action with alkali and alkaline earth metals.* Heavy water reacts slowly with alkali and alkaline earth metals producing deuterium.

$$2\,Na + 2\,D_2O \longrightarrow \underset{\text{Sodium deuteroxide}}{2\,NaOD} + D_2$$

$$Ca + 2\,D_2O \longrightarrow \underset{\text{Calcium deuteroxide}}{Ca(OD)_2} + D_2$$

3. *Action with metallic oxides.* The oxides of active metals like sodium and calcium react slowly with heavy water to form their respective deuteroxides.

$$Na_2O + D_2O \longrightarrow 2\,NaOD$$

$$CaO + D_2O \longrightarrow Ca(OH)_2$$

4. *Action with non-metalic oxides.* Non-metallic oxides such as phosphorus pentoxide (P_2O_5), sulphur troxide (SO_3) etc. readily dissolve in heavy water forming their corresponding deuteroacids.

$$P_2O_5 + 3\,D_2O \longrightarrow \underset{\text{Deuterophosphoric acid}}{D_3PO_4}$$

$$SO_3 + D_2O \longrightarrow \underset{\text{Deuterosulphuric acid}}{D_2SO_4}$$

5. *Action with metallic carbides.* Heavy water reacts with metallic carbides forming deuterohydrocarbons.

$$\underset{\text{Aluminium Carbide}}{Al_4C_3} + 12\,D_2O \longrightarrow 4\,Al(OD)_3 + \underset{\text{Deuteromethane}}{CD_4}$$

$$\underset{\text{Calcium carbide}}{CaC_2} + 2\,D_2O \longrightarrow Ca(OD)_2 + \underset{\text{Deuteroacetylene}}{DC \equiv CD}$$

6. *Action with metallic nitrides, phosphides and arsenides.* Heavy water reacts with metallic nitrides, phosphides and arsenides liberating deuteroammonia, deuterophosphine and deuteroarsine respectively.

$$\underset{\text{Cal. nitride}}{Mg_3N_2} + 6\,D_2O \longrightarrow 3\,Mg(OD)_2 + \underset{\text{Deuteroammonia}}{2\,ND_3}$$

$$\underset{\text{Cal. phosphide}}{Ca_3P_2} + 6\,D_2O \longrightarrow 3\,Ca(OD)_2 + \underset{\text{Deuterophosphine}}{2\,PD_3}$$

$$\underset{\text{Sod. arsenide}}{Na_3As} + 3\,D_2O \longrightarrow 3\,NaOD + \underset{\text{Deuteroarsine}}{AsD_3}$$

7. *Formation of deuterates.* Like ordinary water, heavy water also combines with many compounds as heavy water of crystallization. The heavy hydrates thus obtained are called *deuterates.* For example, $CuSO_4 . 5\,D_2O$; $Na_2SO_4 . 10\,D_2O$; $MgSO_4 . 7\,D_2O$, $NiCl_2 . 6\,D_2O$, $CoCl_2 . 6\,D_2O$ etc.

8. *Exchange reactions.* When treated with heavy water, many compounds exchange their active hydrogen atoms either partially or completely with deuterium. Some of these exchange reactions are given below :

$$HCl + D_2O \rightleftharpoons DCl + HOD$$

$$NaOH + D_2O \rightleftharpoons NaOD + HOD$$

$$\underset{\text{Chloroform}}{CHCl_3} + D_2O \rightleftharpoons \underset{\text{Deuterochloroform}}{CDCl_3} + HOD$$

$$NH_4Cl + D_2O \rightleftharpoons NH_3DCl + HOD$$

$$NH_3DCl + D_2O \rightleftharpoons NH_2D_2Cl + HOD$$

$$NH_2D_2Cl + D_2O \rightleftharpoons NHD_3Cl + HOD$$

$$NHD_3Cl + D_2O \rightleftharpoons ND_4Cl + HOD$$

9. *Biological properties.* Heavy water is injurous to human beings, plants and animals since it slows down the rates of reactions occurring in them. Thus heavy water does not support life so well as does ordinary water.

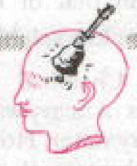
11.11.3. Uses of Heavy Water

1. As a moderator. Heavy water is extensively used as a moderator in nuclear reactions since it slows down the fast moving neutrons and thus helps in controlling the nuclear reactions.

2. As a trace compound. Heavy water is widely used as a tracer compound for studying the mechanism of many reactions. For example, when hypophosphorus acid (H_3PO_2) is treated with D_2O, only one H-atom is found to exchange with deuterium. This suggests that H_3PO_2 has only one ionizable H-atom and hence *it is a monobasic acid.*

3. For the preparation of deuterium. Heavy hydrogen or deuterium is produced by the electrolysis of heavy water or by its decomposition by Na metal.

ADD TO YOUR KNOWLEDGE



1. **Deuterium peroxide** is prepared by the action of D_2SO_4 dissolved in H_2O on BaO_2.

$$BaO_2 + D_2SO_4 \longrightarrow BaSO_4 + D_2O_2$$

2. **Deuterium chloride** may be prepared by any one of the following methods :

$$2\,AgCl + D_2 \longrightarrow 2\,Ag + 2\,DCl$$

$$2\,NaCl + D_2SO_4 \longrightarrow Na_2SO_4 + 2\,DCl$$

$$SOCl_2 + 2\,D_2O \longrightarrow D_2SO_3 + 2\,DCl$$

11.12. Hydrogen Peroxide

Hydrogen peroxide was discovered by the French Chemist *J.L. Thenard* in 1818. Its molecular formula is H_2O_2.

11.12.1. Preparation of Hydrogen Peroxide

1. From sodium peroxide (Merck's method). Calculated amount of sodium peroxide (Na_2O_2) is gradually added to an ice-cold solution of 20% H_2SO_4.

$$\underset{\text{Sodium peroxide}}{Na_2O_2} + H_2SO_4 \longrightarrow Na_2SO_4 + \underset{\text{Hydrogen peroxide}}{H_2O_2}$$

Upon cooling, crystals of $Na_2SO_4.10H_2O$ separate out and the resulting solution contains about 30% H_2O_2. The solution also contains some dissolved Na_2SO_4 but it does not interfere with the reactions of H_2O_2. A pure sample of H_2O_2 may, however, be prepared by vacuum distillation.

2. From barium peroxide – Laboratory method of preparation. Hydrogen peroxide is prepared from barium peroxide by the following methods :

(a) By the action of dilute sulphuric acid. A thin paste of hydrated barium peroxide ($BaO_2.8H_2O$) is prepared in ice-cold water and then added slowly to an ice-cold solution of 20% H_2SO_4.

$$\underset{\text{Hydrated barium peroxide}}{BaO_2.8H_2O\,(s)} + H_2SO_4\,(aq) \longrightarrow BaSO_4\,(s) + \underset{\text{Hydrogen peroxide}}{H_2O_2\,(aq)} + 8H_2O\,(l)$$

The white precipitate of $BaSO_4$ is removed by filtration leaving behind a dilute solution (5%) of H_2O_2. *In this method, anhydrous barium peroxide cannot be used since the precipitated $BaSO_4$ forms a protective layer around unreacted barium peroxide thereby preventing the further reaction.*

Limitation. Hydrogen peroxide prepared by this method contains appreciable quantities of Ba^{2+} ions (in the form of dissolved barium persulphate) which catalyse the decomposition of H_2O_2. Therefore, H_2O_2 prepared by this method cannot be stored for a long time.

Further, H_2SO_4 also acts as a catalyst for decomposition of H_2O_2 therefore, the use of weaker acids such as CO_2(or H_2CO_3) and H_3PO_4 are preferred to H_2SO_4.

(b) By the action of carbon dioxide or carbonic acid. When a rapid stream of CO_2 is bubbled through a thin paste of BaO_2 in ice-cold water, H_2O_2 and $BaCO_3$ are produced :

$$BaO_2 + H_2O + CO_2 \longrightarrow BaCO_3 \downarrow + H_2O_2$$

The insoluble barium carbonate is removed by filtration leaving behind a dilute solution of H_2O_2.

(*c*) *By the action of phosphoric acid.* Hydrogen peroxide can also be prepared by the action of phosphoric acid on barium peroxide :

$$3BaO_2 + 2H_3PO_4 \longrightarrow Ba_3(PO_4)_2 \downarrow + 3H_2O_2$$

This method has the advantage over $BaO_2 - H_2SO_4$ method since almost all the heavy metal (*e.g.* Pb etc.) impurities present in BaO_2 and which catalyse the decomposition of H_2O_2 are removed as insoluble phosphates. As a result, the resulting solution of H_2O_2 has good keeping properties.

11.12.2. Manufacture of Hydrogen Peroxide

1. By electrolysis of 50%. H_2SO_4. Hydrogen peroxide is manufactured by the electrolysis of a cold 50% solution of H_2SO_4 in an electrolytic cell using platinum as anode and graphite as cathode. The reactions taking place are :

$$2H_2SO_4 \longrightarrow 2H^+ + 2HSO_4^-$$

$$\textit{At cathode} : 2H^+ + 2e^- \longrightarrow H_2 \uparrow$$

$$\textit{At anode} : 2HSO_4^- \longrightarrow \underset{\text{Peroxodisulphuric acid}}{H_2S_2O_8} + 2e^-$$

Peroxydisulphuric acid formed around anode is withdrawn and then distilled with water under reduced pressure. The low boiling H_2O_2 distils over along with water leaving behind high boiling H_2SO_4 which is recovered and recycled.

$$\underset{\text{Peroxodisulphuric acid}}{H_2S_2O_8} + H_2O \longrightarrow \underset{\text{Peroxomonosulphuric acid}}{H_2SO_5} + H_2SO_4$$

$$\underset{\text{Peroxomonosulphuric acid}}{H_2SO_5} + H_2O \longrightarrow H_2SO_4 + H_2O_2$$

Modification. Recently, it has been observed that if instead of 50% H_2SO_4, an equimolar mixture of H_2SO_4 and ammonium sulphate is electrolysed, a more concentrated solution of H_2O_2 is obtained. The reactions taking place are :

$$(NH_4)_2SO_4 + H_2SO_4 \longrightarrow \underset{\text{Amm. hydrogen sulphate}}{2NH_4HSO_4}$$

$$2NH_4HSO_4 \longrightarrow 2H^+ + 2NH_4SO_4^-$$

$$\textit{At cathode} : 2H^+ + 2e^- \longrightarrow H_2 \uparrow$$

$$\textit{At anode} : 2NH_4SO_4^- \longrightarrow \underset{\textbf{Amm. persulphate}}{(NH_4)_2S_2O_8} + 2e^-$$

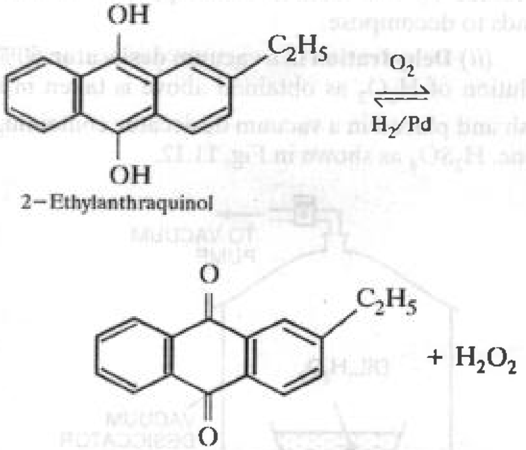
Ammonium persulphate formed around anode is withdrawn and distilled with water to give H_2O_2.

$$(NH_4)_2S_2O_8 + 2H_2O \longrightarrow 2NH_4HSO_4 + H_2O_2$$

This process is now used only for the laboratory preparation of D_2O_2, *i.e.* ;

$$K_2S_2O_8 + 2D_2O \longrightarrow 2KDSO_4 + D_2O_2$$

2. By autoxidation of 2-ethylanthraquinol. This is a new method and is widely used in U.S.A. In this process, air is bubbled through a 10% solution of 2-ethylanthraquinol in benzene and cyclohexane when 2-ethylanthraquinol is oxidised to 2-ethylanthraquinone and H_2O_2 is formed according to the following equation.



2−Ethylanthraquinol

2−Ethylanthraquinone

The H_2O_2 thus formed (about 1%) is extracted with water and the aqueous solution is concentrated by distillation under reduced pressure to give 30% (by weight) H_2O_2 solution.

2-Ethylanthraquinone formed in the process is reduced with H_2 in presence of Pd catalyst to give back 2-ethylanthraquinol which is used again. Thus, in this process, only atmospheric oxygen and hydrogen are used up which are inexpensive. Therefore, this method is quite cheap and is widely used for the manufacture of H_2O_2.

11.12.3. Concentration of Hydrogen Peroxide solution

Hydrogen peroxide prepared by any of the above methods is in the form of dilute aqueous solution. Quite often for a large number of reactions, we need a concentrated solution of H_2O_2. It cannot be concentrated simply by distillation since it decomposes much below its boiling point to give H_2O and O_2

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

Further, the process of decomposition is catalysed by presence of heavy metal ion impurities, dust and rough surfaces. In view of these difficulties, concentration of H_2O_2 is carried out carefully in a number of stages as follows :

(*i*) **Evaporation on a water bath.** The dilute aqueous solution of hydrogen peroxide is taken in a large shallow evaporating dish and is heated on a water bath. Slow evaporation of water continues until the solution contains about 50% hydrogen peroxide. Further concentration of hydrogen peroxide by this method is not possible since it tends to decompose.

(*ii*) **Dehydration in a vacuum desiccator.** 50% solution of H_2O_2 as obtained above is taken in a dish and placed in a vacuum desiccator containing conc. H_2SO_4 as shown in Fig. 11.12.

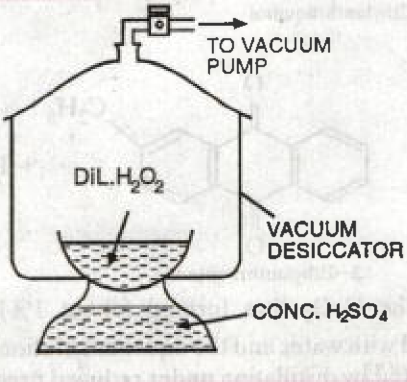


FIGURE 11.12. Vacuum Desiccator.

Pressure inside the desiccator is reduced by connecting it to a vacuum pump. As a result of low pressure, water readily evaporates and the water vapours thus produced are absorbed by conc. H_2SO_4. In this way, hydrogen peroxide of about 90% concentration is produced.

(*iii*) **Distillation under reduced pressure.** The 90% solution of hydrogen peroxide as obtained above is subjected to distillation under reduced pressure (10 – 15 mm). During this process, water distils over between 303 – 313 K leaving behind almost pure (99%) hydrogen peroxide.

(*iv*) **Removal of last traces of water.** The last traces of water in hydrogen peroxide are removed by freezing it in a freezing mixture consisting of *dry* ice (solid carbon dioxide) and ether when crystals of hydrogen peroxide separate out. These crystals are removed, dried and melted to give pure hydrogen peroxide.

Storage of hydrogen peroxide. The following precautions are taken while storing hydrogen peroxide solution.

(*i*) Hydrogen peroxide cannot be stored in glass bottles since the rough surface of glass, alkali oxides present in it, and exposure to light catalyse its decomposition. Therefore, H_2O_2 is usually stored in *coloured paraffin wax coated plastic or teflon bottles.*

(*ii*) To further check the decomposition of H_2O_2, some stabilizer or **negative catalyst*** such as glycerine, acetanilide, phosphoric acid etc. must also be added.

11.12.4. Strength of Hydrogen Peroxide solution

The strength of an aqueous solution of hydrogen peroxide is usually expressed in the following two ways :

(*a*) **Percentage strength.** It expresses the amount of H_2O_2 by weight present in 100 ml of the solution. For example, a 30% aqueous solution (w/v) of H_2O_2 implies that 30 grams of H_2O_2 are present in 100 ml of the solution.

(*b*) **Volume strength.** The most common method of expressing the strength of an aqueous solution of hydrogen peroxide is *in terms of the volume (in ml) of oxygen liberated at N.T.P. by the decomposition of 1 ml of that sample of hydrogen peroxide.* Thus, the aqueous solutions of hydrogen peroxide sold in the market are labelled as *10 volume, 20 volume, 30 volume, 100 volume etc. A solution of hydrogen peroxide labelled as* 10 volume actually means that *1 ml of such a solution of hydrogen peroxide on decomposition by heat produces 10 ml of oxygen at N.T.P.*

---

*A negative catalyst retards or decreases the rate of a chemical reaction.

Simiarly, 1 ml of *20 volume, 30 volume and 100 volume* H_2O_2 solutions produce 20 ml, 30 ml and 100 ml of oxygen at N.T.P. respectively.

Let us now calculate the percentage strength of a *10 volume* H_2O_2 solution.

Hydrogen peroxide decomposes on heating according to the equation :

$$\underset{2 \times 34\ \text{g}}{2H_2O_2} \longrightarrow 2H_2O + \underset{\substack{22\cdot4\ \text{litres at N.T.P.} \\ \text{or } 22400\ \text{cm}^3 \text{ at N.T.P.}}}{O_2}$$

From the equation,

22.4 litres of O_2 at N.T.P. are obtained from 2×34 or 68 g of H_2O_2.

∴ 10 ml of O_2 at N.T.P. will be obtained from $\frac{68}{22400} \times 10$ g of H_2O_2

But 10 ml of O_2 at N.T.P. are produced from 1 ml of *10 volume* H_2O_2 solution

Thus, 1 ml of *10 volume* H_2O_2 solution contains $\frac{68}{22400} \times 10$ g of H_2O_2

∴ 100 ml of *10 volume* H_2O_2 solution will contain $\frac{68}{22400} \times \frac{10}{1} \times 100 = 3.035$ g

Thus, a *10 volume* H_2O_2 solution is approx. 3%

NUMERICAL PROBLEMS ON THE STRENGTH OF HYDROGEN PEROXIDE SOLUTIONS

EXAMPLE 11.1. *Calculate the normality of 20 volume hydrogen peroxide solution.*

Solution. **Step 1.** *To calculate the strength in g/l of 20 volume H_2O_2 solution.*

By definition, 1 litre of 20 volume H_2O_2 solution on decomposition gives 20 litres of oxygen at N.T.P.

Consider the chemical equation,

$$\underset{2 \times 34 = 68\ \text{g}}{2H_2O_2} \longrightarrow 2H_2O + \underset{22.4\ \text{litres at N.T.P.}}{O_2}$$

Now 22.4 litres of O_2 at N.T.P. will be obtained from $H_2O_2 = 68$ g

∴ 20 litres of O_2 at N.T.P. will be obtained from

$$H_2O_2 = \frac{68 \times 20}{22.4}\ \text{g} = 60.7\ \text{g}$$

Thus, the strength of 20 volume H_2O_2 solution $= 60\cdot7$ *g/l*

Step 2. *To calculate the equivalent weight of H_2O_2.*

Consider the chemical equation,

$$\underset{68\ \text{parts by weight}}{2H_2O_2} \longrightarrow 2H_2O + \underset{32\ \text{parts by weight}}{O_2}$$

From the above equation,

32 parts by wt. of oxygen are obtained from 68 parts by wt. of H_2O_2

∴ 8 parts by wt. of oxygen will be obtained from

$$\frac{68}{32} \times 8 = 17 \text{ parts by wt. of } H_2O_2$$

∴ Eq. wt. of $H_2O_2 = 17$

Step 3. *To calculate the normality of 20 volume H_2O_2 solution.*

Now we know that, $\text{Normality} = \frac{\text{Strength}}{\text{Eq. wt.}}$

$$= \frac{60.7}{17} = 3\cdot57$$

Hence the normality of 20 volume H_2O_2 solution $= 3\cdot57$ N

EXAMPLE 11.2. *Find the volume strength of 1.6 N H_2O_2 solution.*

Solution. We know that strength

= Nrmality × Eq. wt.

and Eq. wt. of $H_2O_2 = 17$

∴ Strength of $1\cdot6$ N H_2O_2 solution

$= 1\cdot6 \times 17$ *g/l*

Now 68 g of H_2O_2 gives 22400 ml O_2 at N.T.P.

∴ 1.6×17 g of H_2O_2 will give

$\frac{22400}{68} \times 1.6 \times 17 = 8960$ ml of O_2 at N.T.P.

But 1.6×17 g of H_2O_2 are present in 1000 ml of H_2O_2 solution.

Hence 1000 ml of H_2O_2 solution gives 8960 ml of O_2 at N.T.P.

∴ 1 ml of H_2O_2 solution will give $= \frac{8960}{1000}$

$= 8\cdot96$ ml of O_2 at N.T.P.

Hence the volume strength of $1\cdot 6$ N H_2O_2 solution $= \mathbf{8\cdot 96}$ **volume**

EXAMPLE 11.3. *Calculate the volume strength of a 3% solution of H_2O_2.*

Solution. Step 1. *To calculate the amount of H_2O_2 present in one litre of 3% solution.*

100 ml of H_2O_2 solution contain H_2O_2

$$= 3\text{ g}$$

$\therefore$ 1000 ml of H_2O_2 solution will contain

$$H_2O_2 = \frac{3}{100} \times 1000 = \mathbf{30\ g}$$

Step 2. *To calculate the volume strength*

Consider the chemical equation,

$$\underset{2 \times 34 = 68\text{ g}}{2\,H_2O_2} \longrightarrow 2\,H_2O + \underset{22\cdot 4\text{ litres at N.T.P.}}{O_2}$$

Now 68 g of H_2O_2 give O_2 at N.T.P.

$$= 22\cdot 4 \text{ litres}$$

$\therefore$ 30 g of H_2O_2 will give O_2 at N.T.P.

$$= \frac{22\cdot 4}{68} \times 30 = 9\cdot 88 \text{ litres}$$

$$= 9880 \text{ ml.}$$

But 30 g of H_2O_2 are present in 1000 ml of H_2O_2.

Hence 1000 ml of H_2O_2 solutioin gives O_2 at N.T.P. = 9880 ml

$\therefore$ 1 ml of H_2O_2 solution will give O_2 at N.T.P. $= \frac{9880}{1000} = 9\cdot 88$ ml.

Hence the volume strength of 3% H_2O_2 solution $= \mathbf{9\cdot 88}$

EXAMPLE 11.4. *What is the mass of hydrogen peroxide present in 1 litre of 2M solution ? Calculate the volume of oxygen at STP liberated upon complete decomposition of 100 cm³ of the above solution.*

Solution. Step 1. *To calculate the mass of H_2O_2 in 1 litre of 2M solution.*

Molecular mass of $H_2O_2 = 2 \times 1 + 2 \times 16$

$$= 34 \text{ a.m.u.}$$

By definition, 1 litre of 1M H_2O_2 contains 34 g of H_2O_2

$\therefore$ 1 litre of 2M H_2O_2 will contain H_2O_2

$$= 34 \times 2 = \mathbf{68\ g}$$

Step 2. *To calculate the volume of O_2 liberated at STP from 100 cm³ of 2M solution.*

1 litre of 2M H_2O_2 solution contains H_2O_2

$$= 68\text{g}$$

$\therefore$ 100 cm³ of 2M H_2O_2 solution will contain H_2O_2

$$= \frac{68}{1000} \times 100 = 6.8\text{ g}$$

The equation representing the decomposition of H_2O_2 is

$$\underset{2 \times 34 = 68\text{ g}}{2H_2O_2} \longrightarrow 2H_2O + \underset{22400\text{ cm}^3\text{ at STP}}{O_2}$$

Now 68 g of H_2O_2 at STP give O_2

$$= 22400 \text{ cm}^3$$

$\therefore$ 6.8 g of H_2O_2 at STP will evolve O_2

$$= \frac{22400}{68} \times 6.8 = 2240 \text{ cm}^3$$

$$= \mathbf{2.24\ litres}$$

EXAMPLE 11.5. *30 ml of a H_2O_2 solution after acidification required 30 ml of N/10 $KMnO_4$ solution for complete oxidation. Calculate the percentage and volume strength of H_2O_2 solution.*

Solution. Step 1. *To determine the normality of H_2O_2 solution.* From the given data,

For H_2O_2, $V_1 = 30$ ml, $N_1 = ?$

For $KMnO_4$, $V_2 = 30$ ml, $N_2 = N/10$

Applying normality equation, $N_1V_1 = N_2V_2$

i.e., $30 \times N_1 = 30 \times 1/10$

$\therefore \quad N_1 = 0\cdot 1$ N

Thus, the normality of H_2O_2 solution $= \mathbf{0\cdot 1\ N}$.

Step 2. *To determine the percentage strength of H_2O_2 solution,*

We know that, $H_2O_2 \longrightarrow 2\,H^+ + O_2 + 2\,e^-$

$\therefore$ Eq. wt. of $H_2O_2 = 34/2 = 17$

Hence strength of H_2O_2 solution

$$= \text{Normality} \times \text{Eq. wt.}$$

$$= 0\cdot 1 \times 17 = 1\cdot 7 \text{ g/litre}$$

$$\therefore \quad \%\text{ Strength of } H_2O_2 = \frac{1\cdot 7 \times 100}{1000}$$

$$= \mathbf{0\cdot 17\%}.$$

Step 3. *To determine the volume strength of H_2O_2 solution.*

Consider the chemical equation,

$$\underset{68\text{ g}}{2\,H_2O_2} \longrightarrow 2\,H_2O + \underset{22400\text{ ml at N.T.P.}}{O_2}$$

Now 68 g of H_2O_2 give O_2 at N.T.P.

$$= 22400\text{ ml}$$

$\therefore$ 1·7 g of H_2O_2 will give O_2

$$= \frac{22400}{68} \times 1\cdot7 = \mathbf{560\ ml}$$

But 1·7 g of H_2O_2 are present in 1000 ml of H_2O_2 solution.

Hence 1000 ml of H_2O_2 solution gives 560 ml of O_2 at N.T.P.

$\therefore$ 1 ml of H_2O_2 solution will give

$$= \frac{560}{1000} = 0\cdot56\text{ ml of } O_2 \text{ at N.T.P.}$$

$\therefore$ Volume strength of H_2O_2 solution

$$= \mathbf{0\cdot56.}$$

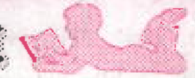
ADD TO YOUR KNOWLEDGE

Problems on percentage strength, normality, molarity and volume strength of H_2O_2 can be easily solved by the application of the following relations.

1. Volume strength $= 5\cdot6 \times$ **Normality** $= 5\cdot6 \times \dfrac{\textbf{Percentage strength}}{\textbf{Eq. wt. of } \mathbf{H_2O_2} \textbf{ (i.e. 17)}} \times 10$

2. Volume strength $= 11\cdot2 \times$ **Molarity**

PROBLEMS FOR PRACTICE



1. Calculate the concentration in gram/litre of a 20 volume H_2O_2 solution. [60·7g/l]
2. Find the volume strength of 2N H_2O_2 solution. [**11.2 volume**]
3. Calculate the normality of a solution of 1 litre of hydrogen peroxide labelled 30 volumes. [5·357 N]
4. Calculate the amount per litre of 10 ml of a solution of hydrogen peroxide labelled 20 volumes. [60·7g/litre]

11.12.5. Properties of Hydrogen Peroxide

(a) Physical properties.

1. Pure hydrogen peroxide is a thick syrupy liquid with pale blue colour.

2. It has a bitter taste.

3. Hydrogen peroxide is more dense (1·44 g/cm³) and more viscous than water. This is due to the reason that the molecules of H_2O_2 are even more highly associated through H-bonds than H_2O molecules.

4. Its m.p. is 272.4 K. Since it decomposes vigorously on heating, it is not possible to determine its b.p. at atmospheric pressure. However, its b.p. has been determined to be 423·2 by extrapolation method.

5. It is completely miscible with water, alcohol and ether in all proportions.

6. The dipole moment of H_2O_2 is little more (2·1 D) than that of H_2O (1·84 D).

TABLE 11.5. Some Physical Characteristics of H_2O_2.

Melting point (K)	272·4	Density (liquid at 298 K) ($g\ cm^{-3}$)	1·4425
Boiling point (extrapolated) (K)	423	Viscosity at 298 K (*Centipoise*)	1·245
Vapour pressure at 298 K (*mm Hg*)	1·9	Dielectric constant of 298 K	70·7
Density (solid at 268·5) ($g\ cm^{-3}$)	1·6434	Electrical conductivity at 298 K ($\Omega^{-1}\ cm^{-1}$)	$15\cdot1 \times 10^{-8}$

(b) Chemical properties. 1. Decomposition. Pure hydrogen peroxide is an unstable liquid and decomposes into water and oxygen on long standing or heating.

$$2H_2O_2 \longrightarrow 2H_2O + O_2 \ ; \ \Delta H = -196.0 \text{ kJ}$$

It is an example of *auto-oxidation* and *auto-reduction*.

The decomposition is further accelerated by the presence of certain metal ions (*e.g.* Fe^{2+}), metal powders (Co, Au, Ag, Pt etc), and metal oxides (*e.g.* MnO_2). Even carbon, rough surfaces and light also catalyse its decomposition.

2. Acidic nature. Pure hydrogen peroxide turns *blue litmus red* but its dilute solution is *neutral to litmus*. It thus behaves as a *weak acid*. Its dissociation constant is $1{\cdot}55 \times 10^{-12}$ at 293 K which is only slightly higher than that of water ($1{\cdot}0 \times 10^{-14}$). *Thus, hydrogen peroxide is only a slightly stronger acid than water.* Since hydrogen peroxide has two *ionizable H- atoms*, it forms two series of salts, *i.e.*, *hydroperoxides (acidic salts)* and *peroxides (normal salts)*.

$$H_2O_2 \rightleftharpoons H^+ + HO_2^- \quad (\textit{hydroperoxide ion})$$

$$H_2O_2 \rightleftharpoons 2H^+ + O_2^{2-} \quad (\textit{peroxide ion})$$

The acidic nature of hydrogen peroxide is shown by its neutralization reactions with hydroxides and carbonates.

$$NaOH + H_2O_2 \longrightarrow \underset{\text{Sod. hydroperoxide}}{NaHO_2} + H_2O$$

$$2NaOH + H_2O_2 \longrightarrow \underset{\text{Sod. peroxide}}{Na_2O_2} + 2H_2O$$

$$Ba(OH)_2 + H_2O_2 \longrightarrow BaO_2 + 2H_2O$$

3. Oxidising and reducing character. Hydrogen peroxide behaves as an oxidising as well as a reducing agent in both acidic and alkaline solutions. The oxidation state of oxygen in hydrogen peroxide is -1. It can be oxidised to O_2 (zero oxidation state) or reduced to H_2O or OH^- (-2 oxidation state for oxygen). However, *hydrogen peroxide is a powerful oxidising agent but a weak reducing agent.*

(a) Oxidising character. Hydrogen peroxide acts as an oxidising agent both in acidic as well as in alkaline medium.

In acidic medium,

$$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$$

In basic medium,

$$H_2O_2 + OH^- + 2e^- \longrightarrow 3OH^-$$

Some important reactions in which hydrogen peroxide acts as an oxidising agent are given below:

1. Oxidising action in acidic medium.

(*i*) It oxidises acidified *ferrous sulphate to ferric sulphate*

$$H_2O_2 \longrightarrow H_2O + [O]$$

$$2FeSO_4 + H_2SO_4 + [O] \longrightarrow Fe_2(SO_4)_3 + H_2O$$

$$2FeSO_4 + H_2SO_4 + H_2O_2 \longrightarrow Fe_2(SO_4)_3 + 2H_2O$$

$$\text{or } 2Fe^{2+} + H_2O_2 + 2H^+ \longrightarrow 2Fe^{3+} + 2H_2O$$

(*ii*) It oxidises acidified *potassium ferrocyanide to potassium ferricyanide*

$$H_2O_2 \longrightarrow H_2O + [O]$$

$$2K_4[Fe(CN)_6] + H_2SO_4 + [O] \longrightarrow 2K_3[Fe(CN)_6] + K_2SO_4 + H_2O$$

$$2K_4[Fe(CN)_6 + H_2SO_4 + H_2O_2 \longrightarrow 2K_3[Fe(CN)_6] + K_2SO_4 + 2H_2O$$

$$\text{or } 2[Fe(CN)_6]^{4-} + H_2O_2 + 2H^+ \longrightarrow 2Fe(CN)_6^{3-} + 2H_2O$$

(*iii*) It liberates *iodine from acidified potassium iodide solution*

$$H_2O_2 \longrightarrow H_2O + [O]$$

$$2KI + H_2SO_4 + [O] \longrightarrow K_2SO_4 + I_2 + H_2O$$

$$2KI + H_2SO_4 + H_2O_2 \longrightarrow K_2SO_4 + I_2 + 2H_2O$$

$$\text{or } 2I^- + H_2O_2 + 2H^+ \longrightarrow I_2 + 2H_2O$$

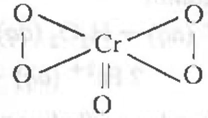
(*iv*) *Hydrogen peroxide oxidises ice-cold acidified potassium dichromate solution (containing ether) to chromium pentoxide which dissolves in ether producing a blue colouration.*

$$H_2O_2 \longrightarrow H_2O + [O] \times 4$$

$$K_2Cr_2O_7 + H_2SO_4 + 4[O] \longrightarrow K_2SO_4 + 2CrO_5 + H_2O$$

$$K_2Cr_2O_7 + H_2SO_4 + 4H_2O_2 \longrightarrow K_2SO_4 + \underset{\text{Chromium pentoxide}}{2CrO_5} + 5H_2O$$

Chromium pentoxide is actually a peroxide having the structure



(*v*) Hydrogen peroxide oxidises *lead sulphide to lead sulphate*

$$H_2O_2 \longrightarrow H_2O + [O] \times 4$$

$$PbS + 4[O] \longrightarrow PbSO_4$$

$$\underset{\substack{\text{Lead sulphide}\\ (\textit{Black})}}{PbS} + 4H_2O_2 \longrightarrow \underset{\substack{\text{Lead sulphate}\\ (\textit{White})}}{PbSO_4} + 4H_2O$$

This reaction is used in restoring the white colour of lead paintings which have blackened due to the formation of lead sulphide by the action of H_2S present in the air. On treatment with H_2O_2, lead sulphide (black) changes into lead sulphate (white) and thus the colour of lead paintings is restored.

(*vi*) Hydrogen peroxide *oxidises H_2S to sulphur and sulphurous acid to sulphuric acid.*

$$H_2S + H_2O_2 \longrightarrow 2\,H_2O + S$$

$$H_2SO_3\,(g) + H_2O_2\,(aq) \longrightarrow H_2SO_4\,(aq) + H_2O\,(l)$$

(*vii*) It oxidises *mercury to mercuric oxide in acidic medium*

$$Hg + H_2O_2 \xrightarrow{\text{Dil. } H_2SO_4} HgO + H_2O$$

2. Oxidising action in alkaline medium

(*i*) It oxidises *sulphites, nitrites and arsenites to sulphates, nitrates and arsenates respectively in alkaline medium.*

$$\underset{\text{Sod. sulphite}}{Na_2SO_3} + H_2O_2 \longrightarrow \underset{\text{Sod. sulphate}}{Na_2SO_4} + H_2O$$

$$\underset{\text{Pot. nitrite}}{KNO_2} + H_2O_2 \longrightarrow \underset{\text{Pot. nitrate}}{KNO_3} + H_2O$$

$$\underset{\text{Sod. arsenite}}{Na_3AsO_3} + H_2O_2 \longrightarrow \underset{\text{Sod. arsenate}}{Na_3AsO_4} + H_2O$$

(*ii*) It oxidises *manganese salts to manganese dioxide in alkaline medium.*

$$\underset{\text{Manganese sulphate}}{MnSO_4} + H_2O_2 + 2\,NaOH \longrightarrow Na_2SO_4 + \underset{\text{Manganese dioxide}}{MnO_2} + 2\,H_2O$$

or $$Mn^{2+} + H_2O_2 + 2\,OH^- \longrightarrow MnO_2 + 2\,H_2O$$

(*iii*) It oxidises *chromium salts to chromates in alkaline medium.*

$$\underset{\text{Chromium sulphate}}{Cr_2(SO_4)_3} + 3\,H_2O_2 + 10\,NaOH \longrightarrow \underset{\text{Sod. chromate}}{2\,Na_2CrO_4} + 3\,Na_2SO_4 + 8\,H_2O$$

or $$2\,Cr^{3+} + 3\,H_2O + 10\,OH^- \longrightarrow 2\,CrO_4^{2-} + 8\,H_2O$$

(*iv*) It oxidises *formaldehyde to formic acid*

$$\underset{\text{Formaldehyde}}{HCHO} + H_2O_2 \longrightarrow \underset{\text{Formic acid}}{HCOOH} + H_2O$$

(*v*) It oxidises *benzene to phenol in alkaline medium*

$$\underset{\text{Benzene}}{C_6H_6} + H_2O_2 \longrightarrow \underset{\text{Phenol}}{C_6H_5OH} + H_2O$$

(b) Reducing character. In presence of strong oxidising agents, hydrogen peroxide behaves as a reducing agent both in acidic as well as alkaline medium. In all these reactions, molecular oxygen is always produced by the combination of H_2O_2 with the oxygen atom released by the strong oxidising agent :

$$H_2O_2 + \underset{\substack{\text{from oxidising}\\ \text{agent}}}{[O]} \longrightarrow H_2O + O_2$$

Acidic medium,

$$H_2O_2 \longrightarrow 2\,H^+ + O_2 + 2\,e^-$$

Alkaline medium

$$H_2O_2 + 2OH^- \longrightarrow 2\,H_2O + O_2 + 2\,e^-$$

Some important reactions in which hydrogen peroxide behaves as a reducing agent are given below :

1. Reducing action in acidic medium

(*i*) *It reduces acidified potassium permanganate solution*. As a result of this reaction, *the pink colour of $KMnO_4$ solution is discharged*

$$2\,KMnO_4 + 3\,H_2SO_4 \longrightarrow K_2SO_4 + 2\,MnSO_4 + 3\,H_2O + 5\,[O]$$

$$H_2O_2 + [O] \longrightarrow H_2O + O_2] \times 5$$

$$2\,KMnO_4 + 3\,H_2SO_4 + 5\,H_2O_2 \longrightarrow K_2SO_4 + 2\,MnSO_4 + 8\,H_2O + 5\,O_2$$

$$\text{or } 2\,MnO_4^- + 6\,H^+ + 5\,H_2O_2 \longrightarrow 2\,Mn^{2+} + 8\,H_2O + 5\,O_2$$

(ii) It reduces acidified potassium dichromate solution. As a result of this reaction, *the orange colour of $K_2Cr_2O_7$ changes to green due to the formation of chromium salt.*

$$K_2Cr_2O_7 + 4\,H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4\,H_2O + 3\,[O]$$

$$H_2O_2 + [O] \longrightarrow H_2O + O_2] \times 3$$

$$K_2Cr_2O_7 + 4\,H_2SO_2 + 3\,H_2O_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7\,H_2O + 3\,O_2$$

$$\text{or } Cr_2O_7^{2-} + 8\,H^+ + 3\,H_2O_2 \longrightarrow 2Cr^{3+} + 7\,H_2O + 3\,O_2$$

(iii) It reduces manganese dioxide to manganese sulphate in presence of dil H_2SO_4.

$$MnO_2 + H_2SO_4 \longrightarrow MnSO_4 + H_2O + [O]$$

$$H_2O_2 + [O] \longrightarrow H_2O + O_2$$

$$MnO_2 + H_2SO_4 + H_2O_2 \longrightarrow MnSO_4 + 2\,H_2O + O_2$$

(iv) It reduces ozone to dioxygen

$$O_3 \longrightarrow O_2 + [O]$$

$$H_2O_2 + [O] \longrightarrow H_2O + O_2$$

$$H_2O_2 + O_3 \longrightarrow H_2O + 2\,O_2$$

(v) Chlorine and bromine are reduced to HCl and HBr respectively. This property is called **Antichlor.**

$$Cl_2 + H_2O \longrightarrow 2\,HCl + [O]$$

$$H_2O_2 + [O] \longrightarrow H_2O + O_2$$

$$H_2O_2 + Cl_2 \longrightarrow 2\,HCl + O_2$$

$$\text{and } H_2O_2 + Br_2 \longrightarrow 2\,HBr + O_2$$

(vi) It reduces hypohalous acid to halide ion in acidic medium

$$HOCl\,(aq) + H_2O_2\,(aq) \longrightarrow H_3O^+\,(aq) + Cl^-\,(aq) + O_2\,(g)$$

2. Reducing action in alkaline medium

(i) It reduces potassium permanganate to manganese dioxide in alkaline medium.

$$2\,KMnO_4\,(aq) + 3\,H_2O_2\,(aq) \longrightarrow 2\,MnO_2\,(s) + 2\,KOH\,(aq) + 3\,O_2\,(g) + 2\,H_2O\,(l)$$

(ii) It reduces ferric salts to ferrous salts in alkaline medium

$$2\,Fe^{3+}\,(aq) + H_2O_2\,(aq) + 2\,OH^-\,(aq) \longrightarrow 2\,Fe^{2+}\,(aq) + O_2\,(g) + 2\,H_2O\,(l)$$

(iii) It reduces alkaline potassium ferricyanide to potassium ferrocyanide

$$2\,K_3[Fe(CN)_6] + 2\,KOH \longrightarrow 2\,K_4[Fe(CN)_6] + H_2O + [O]$$

$$H_2O_2 + [O] \longrightarrow H_2O + O_2$$

$$\underset{\text{Pot. ferricyanide}}{2\,K_3[Fe(CN)_6]} + 2\,KOH + H_2O_2 \longrightarrow \underset{\text{Pot. ferrocyanide}}{2\,K_4[Fe(CN)_6]} + 2\,H_2O + O_2$$

$$\text{or } 2\,[Fe(CN)_6]^{3-} + 2\,OH^- + H_2O_2 \longrightarrow 2\,[Fe(CN)_6]^{4-} + 2\,H_2O + O_2$$

(iv) It reduces metal oxides to metals, i.e., silver oxide to silver in the alkaline medium. However, lead dioxide is reduced to lead monoxide.

$$Ag_2O + H_2O_2 \longrightarrow 2\,Ag + H_2O + O_2$$

$$\underset{\text{Lead dioxide}}{PbO_2} + H_2O_2 \longrightarrow \underset{\text{Lead monoxide}}{PbO} + H_2O + O_2$$

(v) It reduces hypohalites to halides in alkaline medium

$$\underset{\text{Sod. hypobromite}}{NaOBr} + H_2O_2 \longrightarrow NaBr + H_2O + O_2$$

$$\underset{\text{Bleaching powder}}{CaOCl_2} + H_2O_2 \longrightarrow CaCl_2 + H_2O + O_2$$

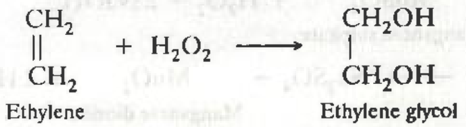
4. Bleaching action. The bleaching action of hydrogen peroxide is due to the *nascent oxygen* which it liberates on decomposition.

$$H_2O_2 \longrightarrow H_2O + [O]$$

The nascent oxygen combines with colouring matter which, in turn, gets oxidised. Thus, *the bleaching action of H_2O_2 is due to the oxidation of colouring matter by nascent oxygen.* It is used for the bleaching of delicate materials like ivory, feather, silk, wool etc.

$$\text{Colouring matter} + [O] \longrightarrow \text{Colourless matter}$$

5. Addition reactions. *Hydrogen peroxide reacts with alkenes to form glycols.*



$$\underset{\text{Ethylene}}{\begin{array}{c}CH_2\\ \|\\ CH_2\end{array}} + H_2O_2 \longrightarrow \underset{\text{Ethylene glycol}}{\begin{array}{c}CH_2OH\\ |\\ CH_2OH\end{array}}$$

11.12.6. Uses of Hydrogen Peroxide

(*i*) The most important industrial use of H_2O_2 is as a bleaching agent for delicate materials like textiles (silk, wool), paper pulp, straw, leather, ivory, oils and fats.

(*ii*) Domestically, it is used as a hair bleach and as a mild disinfectant.

(*iii*) It is extensively used to manufacture inorganic chemicals like sodium perborate and percarbonate which are important constituents of good quality detergents.

(*iv*) It is used in the production of epoxides, proplyene oxide and polyurethanes.

(*v*) H_2O_2 is also used in the synthesis of hydroquinone, pharmaceuticals like cephalosoporin and food products like tartaric acid.

(*vi*) H_2O_2 is increasingly being used in environmental chemistry to control pollution by (*i*) treatment of domestic and industrial effluents (*ii*) oxidation of cyanides and restoration of aerobic conditions to sewage wastes.

(*vii*) It is used as an antiseptic under the name *perhydrol* for washing wounds, teeth and ears.

(*viii*) It is used for restoring the colour of lead paintings which have blackened due to the action of H_2S present in the air on lead paints.

(*ix*) It is used in the laboratory for detecting the presence of chromium, titanium and vanadium salts with which it yields peroxides of characteristic colours.

(*x*) 93% H_2O_2 solution is used as an oxidant for rocket fuel and as a propellant for torpedoes and submarines.

(*xi*) It is used as antichlor (to remove Cl_2) in textile industry to remove excess of chlorine after bleaching operations.

11.12.7. Tests of Hydrogen Peroxide

(*i*) H_2O_2 on treatment with an acidifed solution of titanium salt gives a yellow or organe colour due to the formation of pertitanic acid (H_2TiO_4)

$$Ti(SO_4)_2 + H_2O_2 + 2\,H_2O \longrightarrow H_2TiO_4 + 2\,H_2SO_4$$

(*ii*) It liberates iodine from KI solution which, in turn, gives blue colour with starch solution,

(*iii*) When an ethereal solution of H_2O_2 is shaken with acidified solution of $K_2Cr_2O_7$, blue colour appears in the ethereal layer due to the formation of chromium pentoxide (CrO_5)

(*iv*) When brought in contact with H_2O_2 solution, a filter paper with black stain of PbS turns white.

(*v*) It decolourizes acidified $KMnO_4$ solution.

ADD TO YOUR KNOWLEDGE

1. **Peroxides.** *Metallic oxides which on treatment with dilute acids produce hydrogen peroxide are called peroxides.* For example, Na_2O_2 and BaO_2. In these peroxides, the two oxygen atoms are linked by a single bond and each oxygen atom has an oxidation state of —1. In other words, all peroxides contain a peroxide ion (O_2^{2-}) having the structure $^{-}:\underset{\cdot\cdot}{\ddot{O}}-\underset{\cdot\cdot}{\ddot{O}}:^{-}$. In this structure, all the electrons are paired and hence all peroxides are **diamagnetic.**

   There are certain other oxides like PbO_2 and MnO_2 which may be mistaken as peroxides. These compounds, however, do not give H_2O_2 on treatment with dilute acids. As such these compounds do not contain a peroxide ion (O_2^{2-}) and hence they cannot be called as peroxides. Actually in these compounds the two oxygen atoms are linked to the metal atom by a double bond and hence are called dioxides, *i.e.,* $O = Pb = O$ (lead dioxide) and $O = Mn = O$ (mangenses dioxide). In dioxides, the oxidation state of each oxygen atom is –2.

2. **Superoxides.** Besides peroxides, alkali metals also form higher oxides called superoxides. For example, potassium superoxide (KO_2), rubidium superoxide (RbO_2), cesium superoxide (CsO_2) etc. All these superoxides contain a superoxide ion, *i.e.* O_2^- having the structure, $:\underset{\cdot\cdot}{\ddot{O}}-\underset{\cdot}{\ddot{O}}:^{-}$. Thus all superoxides contain an odd number of electrons (*i.e.* 13) and hence are **paramagnetic.**

ADD TO YOUR KNOWLEDGE CONTD.

3. **Classification of oxides on the basis of oxygen content.**
On the basis of oxygen content, oxides can be calssified into the following types :
(i) Normal oxides. Those oxides in which the oxidation number of the element (M) can be deduced from the empirical formula M_xO_y by taking the oxidation number of oxygen as –2 are called normal oxides. For example, H_2O, Na_2O, MgO Al_2O_3, CO_2 etc. All these oxides contain M—O bonds.
(ii) Polyoxides. These oxides contain more oxygen than would be expected from the oxidation number of the element (M). These have been further classified into peroxides, and superoxides.

11.12.8. Structure of Hydrogen Peroxide.

Hydrogen peroxide is a non-planar molecule (Fig. 11.13). The two oxygen atoms are linked to each other by a single covalent bond (*i.e.*, peroxide bond) and each oxygen is further linked to a hydrogen atom by a single covalent bond. The two O–H bonds are, however, in different planes due to repulsions between different bonding and anti-bonding orbitals. The dihedral (interplanar) angle between the two planes being 111·5° (Fig. 11.13*a*) in the gas phase but reduces to 90·2° (Fig. 11.13*b*) in the crystalline state due to hydrogen bonding. The other molecular dimensions of hydrogen peroxide in the gas phase and the crystalline state are shown in Fig. 11.13.

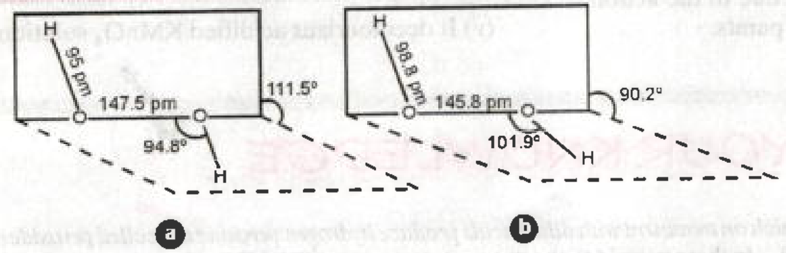


FIGURE 11.13. Structure of H_2O_2 (*a*) in the gas phase dihedral angle = 111·5° and (*b*) in the solid phase at 110 K, dihedral angle = 90·2°.

11.13. Hydrogen Economy

The coal and petroleum reserves of the world are limited and are fast dwindling. Therefore, the fundamental problem which concerns the mankind today is the search for alternative sources of energy. Nuclear power has recently posed severe health and environmental problems and even if these problems are solved it cannot be used for running cars, trains and propelling aeroplanes. One proposed way to meet the need for new energy sources is to burn hydrogen as a fuel in industry and power plants and possibly also in homes and motor vehicles. This proposal is referred to **hydrogen economy.**

There are several advantages of hydrogen economy. Burning of hydrogen in air or dioxygen not only liberates large amount of energy but yields water as the only product. In other words, in contrast to burning coal in power stations, or petrol or deisel in motor engines, burning of hydrogen produces no pollutants like SO_2 and oxides of nitrogen that are responsible for acid rain, nor CO_2 that is responsible for the green house effect, nor carcinogenic hydrocarbons, nor lead compounds.

However, there are two major barriers in achieving the goal of hydrogen economy. The first is to find out a cheap method for large scale production of H_2. Two methods which have been proposed are : electrolysis of water and the thermochemical reaction cycle. The first method is not economically viable since the cost of production of H_2 by electrolysis of H_2O is so high that almost all H_2 is obtained from natural gas which itself is in short supply. The other method involves series of thermochemical reactions in which the only things consumed are water and heat and the only products are hydrogen and oxygen while all other species are recycled. One such thermochemical reaction cycle is

$$3\,FeCl_2 + 4\,H_2O \xrightarrow{775\text{ K}} Fe_3O_4 + 6\,HCl + H_2] \times 2$$

$$2\,Fe_3O_4 + 12\,HCl + 3\,Cl_2 \xrightarrow{475\text{ K}} 6\,FeCl_3 + 6\,H_2O + O_2$$

$$2\,FeCl_3 \xrightarrow{725\text{ K}} 2\,FeCl_2 + Cl_2] \times 3$$

$$2\,H_2O \longrightarrow 2\,H_2 + O_2$$

Whether any of the methods listed above can produce H_2 cheaply enough to make its use practicable is a most distant possibility. The other problem is to find out an effective means of stroring H_2. The gaseous H_2, because of its bulk, is difficult to store, but liquid H_2 can be stored relatively easily and safely in cryogenic tanks (already in use for space programme in U.S.A.). It is also feasible to transport liquid H_2 by road or rail tankers of 20,000 US gallons capacity. It can also be stored in underground tanks and transported by pipelines. However, it may not be convenient to store liquid H_2 in a home or a car since the boiling point of H_2 is very low (20·4 K) In either case (gaseous or liquid form) H_2 must be kept out of contact with oxygen or air with which it forms explosive mixtures. The only alternative left is to store H_2 in a metal or in an alloy (such as iron-titanium alloy, $LaNi_5$, $Mg-MgH_2$, $Ti-TiH_2$ etc.) as interstitial hydride.

The gas can then be released on mild heating. In an automobile, for example, this storage system would replace the gasoline tank. The heat required to release H_2 from the metal hydride could come from the exhaust gases from the engine.

If the problems discussed above can be solved, not only can H_2 be used to substitute gasoline as a fuel for transportation, but it could also replace natural gas for space heating. Moreover, because H_2 is a good reducing agent, it could replace carbon (as coal or coke) in many metallurgical processes. And, of course, it would be abundantly available for reaction with N_2 to produce NH_3 for fertilizer manufacture and other uses. Hydrogen can also be used as a direct substitute for electricity which can be generated by wide spread use of fuel cells. The fuel cells are rountinely used as power source on spacecraft. A 4·5 megawatt fuel cell power plant (with conversion efficiency of 70-85%) has been established in Tokyo. Unfortunately such fuel cells are too expensive to be used in consumer oriented applications in developing countries like India.

The combination of all these potential uses of hydrogen could bring a fundamental change in our way of life, giving rise to what is called **hydrogen economy.**

11.14. Use of Liquid Hydrogen as a Fuel

Use of hydrogen as an automobile fuel has many advantages :

(*i*) First the heat of combustion of H_2 is by far the largest, *i.e.*, 115 megajoules per kilogram (MJ/kg) as against 43 MJ/kg for a typical unleaded gasoline, 39 MJ/kg for ethanol and 20 MJ/kg for methanol. Thus, an automobile engine is 25 – 50% more efficient when it uses H_2 rather than gasoline.

(*ii*) The exhaust is free from pollutants like CO, CO_2, NO_x, SO_2, hydrocarbons, aldehydes and lead compounds.

(*iii*) Combustion product is water with some traces of nitrogen oxides.

(*iv*) Internal combustion engine can be easily modified for use of hydrogen as fuel.

The most effective means of storing hydrogen is in the liquid form. The liquid H_2 is widely used as a rocket fuel since it gives higher thursts than most of the other fuels.

The range of supersonic aircraft could be increased if the aircraft used liquid H_2 as a fuel. Further hypersonic aircrafts would also become possible if liquid H_2 is used as a fuel.

Conceptual Questions

Q. 1. **Which isotope of hydrogen is used as a tracer in organic reactions.**

Ans. Hydrogen has three isotopes, *viz.*, H, D and T. Due to difference in masses, the rate constants of these isotopes with the same substrate are different. In other words, both D and T show *isotope effect.* But since T is not only radioactive but is also least abundant hydrogen isotope, therefore, D is used as a tracer to study the mechanism of organic reactions.

Q. 2. **Name one example of a reaction in which dihydrogen acts (i) as an oxidising agent and (ii) as a reducing agent.**

Ans. (*i*) In the reaction of dihydrogen with metals to form metal hydrides, it acts as an oxidising agent.

$$2\,Na\,(s) + H_2\,(g) \xrightarrow{\text{Heat}} 2\,Na^+H^-\,(s)$$

Here, Na has been oxidised to Na^+ while dihydrogen has been reduced to hydride (H^-) ion.

(*ii*) In the reaction of heated cupric oxide with dihydrogen to form H_2O and copper metal, dihydrogen acts as a reducing agent.

$$CuO\,(s) + H_2\,(s) \xrightarrow{\text{Heat}} Cu\,(s) + H_2O\,(g)$$

Here, CuO is reduced to Cu while dihydrogen is oxidised to H_2O

Q. 3. Hydrogen forms three types of bonds in its compounds. Describe each type of bonding using suitable examples. **(*N.C.E.R.T.*)**

Ans. Hydrogen forms compounds in three different ways:

(*i*) *by loss of electrons* as in the reactions of H_2 with metal oxides, *i.e.*, heated CuO and Fe_3O_4.

$$CuO\,(s) + H_2\,(g) \xrightarrow{\text{Heat}} Cu\,(s) + H_2O\,(g)\ ;$$

$$Fe_3O_4\,(s) + 4\,H_2\,(g) \xrightarrow{\text{Heat}} 3\,Fe\,(s) + 4\,H_2O\,(g)$$

(*ii*) *by gain of electrons* as in the reactions of H_2 with metals.

$$Na\,(s) + H_2\,(g) \xrightarrow{\text{Heat}} 2\,Na^+H^-\,(s)\ ;$$

$$Ca\,(s) + H_2\,(g) \xrightarrow{\text{Heat}} Ca^{2+}\,(H^-)_2$$

(*iii*) *by sharing of electrons* as in the reactions of H_2 with halogens :

$$H_2\,(g) + F_2\,(g) \xrightarrow[\text{23 K}]{\text{Dark}} 2\,H{-}F\,(l)\ ;$$

$$H_2\,(g) + Cl_2\,(g) \xrightarrow[\text{sunlight}]{\text{Diffused}} 2\,H{-}Cl\,(g)$$

Q. 4. Conc. H_2SO_4 cannot be used for drying H_2. Why ?

Ans. Conc. H_2SO_4 on absorbing H_2O from moist H_2 produces so much heat that hydrogen catches fire.

Q. 5. Why is dioxygen paramagnetic ?

Ans. M.O. diagram shows that O_2 has two *unpaired electrons* and thus shows paramagnetism.

Q. 6. Can marine species live in distilled water ?

Ans. No, because distilled H_2O does not contain dissolved O_2.

Q. 7. A sample of hard water is allowed to pass through an anion exchanger. Will it produce lather will soap easily ?

Ans. No. Ca^{2+} and Mg^{2+} ions are still present and these will react with soap to form curdy white ppt. Therefore, it will not produce lather with soap easily.

Q. 8. Can distilled water be called as deionised water ?

Ans. Yes. Distilled water does not contain any cations and anions and hence can be called as deionized water.

Q. 9. Explain why oxide ion is called a hard ion ?

Ans. Oxide ion is very small in size and thus cannot be easily polarized and hence it is called a hard ion.

Q. 10. Anhydrous BaO_2 is not used for preparing H_2O_2. Why ?

Ans. Anhydrous BaO_2 is not used because the $BaSO_4$ formed during the reaction forms a protective layer around unreacted BaO_2 and the reaction stops after some time.

Very Short Answer Questions CARRYING 1 MARK

Q. 1. Which isotope of hydrogen (*i*) does not contain neutrons, (*ii*) contains equal number of protons and neutrons, (*ii*) is radioactive.

Ans. (*i*) protium (*ii*) deuterium (*iii*) tritium.

Q. 2. Why is dihydrogen not prefered in balloons these days ?

Ans. Dihydrogen is highly combustible and hence is likely to catch fire in presence of excess of air

Q. 3. Name one compound each in which hydrogen exists in (*i*) +1 and (*ii*) –1 oxidation state.

Ans. (*i*) HCl or H_2O or NH_3 (*ii*) NaH or CaH_2

Q. 4. What is the importance of heavy water with regard to nuclear power generation ?

Ans. It is used as a moderator to slow down the neutrons produced as a result of fission and thus helps to control the nuclear reactions.

Q. 5. How is heavy water produced from ordinary water ?

Ans. It is obtained by repeated electrolysis of ordinary water containing 3% NaOH.

Q. 6. What do you mean by 15 volume H_2O_2 solution ?

Ans. 1 cm^3 of a 15 volume H_2O_2 solution gives 15 ml of O_2 at NTP.

Q. 7. Name two compounds which retard the decomposition of H_2O_2 solution.

Ans. Acetanilide, glycerol.

Q. 8. Calculate the amount of H_2O_2 present in 10 ml of 25 volume H_2O_2 solution.

Ans. 10 ml of 25 volume H_2O_2 liberate $O_2 = 10 \times 25 = 250$ ml at NTP

$$\underset{68\text{ g}}{2H_2O_2} \longrightarrow 2H_2O + \underset{22400\text{ ml at NTP}}{O_2}$$

$\therefore$ Amount of H_2O_2 that will liberate 250 ml of O_2 at NTP $= \frac{68 \times 250}{22400} = \mathbf{0{\cdot}759\ g}$

Q. 9. Hydrogen peroxide is used to restore the colour of old oil paintings containing lead oxide. Write a balanced equation of the reaction that takes place in this process.

Ans. Refer to Ans. to Q. 2. of C.B.S.E.-P.M.T. (MAINS) SPECIAL on page 11/47.

Q. 10. 10 ml of a given solution of H_2O_2 contains 0·91 g of H_2O_2. Express its strength in volume.

Ans. 68 *g* of H_2O_2 produce O_2 = 22400 ml at NTP

$\therefore$ 0·91 *g* of H_2O_2 will produce $O_2 = \frac{22400 \times 0{\cdot}91}{68} = 300$ ml at NTP

$\therefore$ Volume strength $= \frac{300}{10} = 30$

Q. 11. What is the chemical composition of zeolite ?

Ans. Hydrated sodium aluminium silicate, $Na_2Al_2Si_2O_8 . xH_2O$.

Q. 12. What is water gas ? How is it prepared ?

Ans. An equimolar mixture of CO and H_2 is called water gas. It is prepared by passing steam over red hot coke,

$$C(s) + H_2O(g) \xrightarrow{1270\text{ K}} CO(g) + H_2(g)$$

Q. 13. Name one example of a reaction in which dihydrogen acts (*i*) as an oxidising agent (*ii*) as a reducing agent.

Ans. Oxidising agent : $2Na + H_2 \longrightarrow 2Na^+ H^-$

Reducing agent : $CuO + H_2 \xrightarrow{\text{Heat}} Cu + H_2O$.

Q. 14. What happens when heavy water is added to calcium carbide ?

Ans. Deuteroacetylene is formed, $CaC_2 + 2D_2O \longrightarrow Ca(OD)_2 + DC \equiv CD$

Q. 15. What is demineralized water ? How is it obtained ?

Ans. Water which does not contain cations and anions is called demineralized water. It is obtained by passing ordinary water through ion exchange resins.

Q. 16. The boiling point of H_2O is higher than that of H_2S. Explain.

Ans. Due to extensive intermolecular H-bonding in H_2O, the b.p. of H_2O is much higher than that of H_2S.

Q. 17. What is hydrolith ? How is it prepared ?

Ans. $Ca + H_2 \xrightarrow{\Delta} CaH_2$ (hydrolith).

Q. 18. Write the structures of two complex metal hydrides which are used as reducing agent is organic synthesis.

Ans. $LiAlH_4$ and $NaBH_4$.

Q. 19. What type of elements form interstitial hydrides ?

Ans. *d*- and *f*-block elements.

Q. 20. Write two uses of interstitial hydrides.

Ans. (*i*) Storing H_2 and (*ii*) catalysts for hydrogenation reactions.

Q. 21. What happens when chloroform is treated with heavy water in presence of an alkali ?

Ans. Deuterochloroform ($CDCl_3$) is formed. $CHCl_3 + D_2O \xrightarrow{OH^-} CDCl_3 + DOH$.

Q. 22. Why is sodium chloride less soluble in heavy water than in ordinary water ?

Ans. Due to lower dielectric constant of D_2O over H_2O, NaCl is less soluble in D_2O than in H_2O.

Q. 23. Explain why beryllium forms a covalent hydride while calcium forms an ionic hydride.

Ans. Because of higher electronegativity (E.N. = 1·5), Be forms covalent hydride while due to lower electronegativity (E.N. = 1·0) Ca forms ionic hydride.

Q. 24. Give two advantages of using hydrogen as a fuel over gasoline.

Ans. High heat of combustion and no pollutants like SO_2, NO_2, CO_2 etc.

Q. 25. Explain why electrolysis of ordinary water occurs faster than heavy water ?

Ans. Due to lower bond dissociation energy of protium bonds in H—O—H than deuterium bonds in D—O—D, electrolysis of H_2O occurs much faster than that of D_2O.

Q. 26. What is meant by autoprotolysis of water ? *(N.C.E.R.T.)*

Ans. Autoprotolysis of water means that two molecules of water react with each other through proton transfer *i.e.* one acts as the acid while the other acts as the base. The molecule which accepts a proton is converted into H_3O^+ while that which loses a proton is converted into OH^- ion.

Thus, $$\underset{\text{acid}_1}{H_2O\,(l)} + \underset{\text{base}_2}{H_2O\,(l)} \qquad \underset{\text{acid}_2}{H_3O^+\,(aq)} + \underset{\text{base}_1}{OH^-\,(aq)}$$

Q. 27. What is understood by hydrogenation ? *(N.C.E.R.T.)*

Ans. Hydrogenation means addition of H_2 in presence of a catalyst to multiple bonds to form saturated compounds.

For example, $$\underset{\text{Ethene}}{CH_2 = CH_2} + H_2 \xrightarrow[\text{473 K}]{\text{Ni or Pt or Pd}} \underset{\text{Ethane}}{CH_3 - CH_3}$$

Q. 28. Is it correct to say that hydrogen can behave as a metal ? State the conditions under which such behaviour can be possible ? *(N.C.E.R.T.)*

Ans. Yes, H_2 can act as a metal under very very high pressures.

Q. 29. Ionic hydrides are frequently used to remove traces of water from organic compounds. What is underlying basis of this process ? *(N.C.E.R.T.)*

Ans. H^- is a strong Bronsted base and hence reacts with H_2O readily liberating H_2 gas

$$H_2O\,(l) + H^-\,(s) \longrightarrow H_2\,(g) + OH^-\,(aq)$$

Q. 30. Although D_2O resembles H_2O, chemically yet it is a toxic substance. Explain. *(N.C.E.R.T.)*

Ans. D_2O is toxic since, D^+ reacts at a much slower rate as compared to H^+ in enzyme-catalyzed reactions.

Q. 31. Give an example each of an ionic hydride and a covalent hydride. *(N.C.E.R.T.)*

Ans. Ionic : NaH or CaH_2.

Covalent : H_2O, B_2H_6, CH_4 etc.

Q. 32. What is the difference between hydrolysis and hydration ? *(N.C.E.R.T.)*

Ans. Interaction of H^+ and OH^- ions of H_2O with the anion and the cation of a salt respectively to give the original acid and the original base is called hydrolysis. For example

$$\underset{\text{Salt}}{Na_2CO_3} + 2\,H_2O \longrightarrow \underset{\text{Base}}{2\,NaOH} + \underset{\text{Acid}}{H_2CO_3}$$

Hydration, on the other hand, means addition of H_2O to ions or molecules to form hydrated ions or hydrated salts. For example,

$$\underset{\text{Salt}}{Na^+Cl^-} + H_2O \longrightarrow Na^+\,(aq) + Cl^-\,(aq)$$

$$\underset{\text{(Colourless)}}{CuSO_4} + 5\,H_2O \longrightarrow \underset{\text{(Blue)}}{CuSO_4 \cdot 5\,H_2O}$$

Short Answer Questions CARRYING 2 or 3 MARKS

Sec. 11.1. to 11.2.

1. Discuss the characteristics in which hydrogen resembles halogens.
2. Discuss two characteristics in which hydrogen resembles alkali metals.
3. Explain why hydrogen is best placed separately in the periodic table of elements. *(N.C.E.R.T.)*

Sec. 11.1. to 11.7.

4. How is dihydrogen prepared (*i*) from water by using a reducing agent (*ii*) in the laboratory in pure form and (*iii*) hydrocarbons ? *(N.C.E.R.T.)*
5. What is meant by 'water gas shift reaction' ? Describe its use for the preparation of dihydrogen. *(N.C.E.R.T.)*
6. Describe the industrial applications of hydrogen dependent on :
   (*i*) the heat liberated when the atoms are made to combine on the surface of a metal.
   (*ii*) its effect on unsaturated organic systems in presence of a catalyst.
   (*iii*) its ability to combine with nitrogen under specific conditions. *(N.C.E.R.T.)*
7. Explain the correct context in which the following terms are used.
   (*i*) diprotium (*ii*) dihydrogen (*iii*) proton and (*iv*) hydron. *(N.C.E.R.T.)*
8. Name the isotopes of hydrogen. What is the importance of the heavier isotopes of hydrogen ? *(N.C.E.R.T.)*
9. How will you prepare heavy hydrogen is the laboratory ?
10. How many allotropes of dihydrogen are known ? What is their importance ? *(N.C.E.R.T.)*
11. Complete the following reactions :
    (*i*) $CuO\,(s) + H_2\,(g) \longrightarrow$ (*ii*) $CO\,(g) + H_2\,(g) \longrightarrow$ *(N.C.E.R.T.)*

Sec. 11.3. to 11.7.

12. How is dihydrogen obtained from
    (*i*) water (*ii*) dilute acids (*iii*) alkalies ?
13. How does dihydrogen react with
    (*i*) Blue litmus solution (*ii*) chlorine (*iii*) flourine (*iv*) nitrogen (*v*) sulphur (*vi*) carbon (*vii*) sodium (*viii*) ferric-ferro oxide (magnetic oxide) (*ix*) carbon monoxide ?

14. How is dihydrogen obtained from
(*a*) dilute sulphuric acid (*b*) sodium hydroxide (*c*) water ? Give one equation in each case.
15. Give one method (other than electrolysis) for large scale preparation of dihydrogen.
16. Name the different ways in which hydrogen forms compounds ? Give examples.

Sec. 11.8. 17. What are metallic/interestitial hydrides ? How do they differ from molecular hydrides ? *(N.C.E.R.T.)*
18. Hydrogen forms compounds with elements having atomic numbers : 9, 11, 12 and 17. What are their chemical formulae ? Compare their chemical behaviour. *(N.C.E.R.T.)*
[Hint. HF, NaH, MgH_2 and HCl]
19. Name the class of hydrides to which H_2O, B_2H_6, NaH and LaH_3 belong. What is understood by hydride gap ? *(N.C.E.R.T.)*
20. Distinguish between salt like and covalent hydrides.
21. Discuss briefly the variation in boiling points among the hydrides of groups 15, 16 and 17.
22. What are interstitial hydrides ? Discuss their important uses.
23. Discuss briefly the characteristics of salt like hydrides.

Sec. 11.9. to 11.11. 24. Explain why water has high boiling and melting points as compared to H_2S. *(N.C.E.R.T.)*
25. Explain the structure of the common form of ice. *(N.C.E.R.T.)*
26. Hydrogen forms three types of bonds in its compounds. Describe each type of bonding using suitable examples. *(N.C.E.R.T.)*
27. Explain the amphoteric nature of water. *(N.C.E.R.T.)*
28. Describe some unusual properties of water. *(N.C.E.R.T.)*
29. What is the difference between hydrolysis and hydration *(N.C.E.R.T.)*
30. Why do lakes freeze from top towards bottom ? *(N.C.E.R.T.)*
31. Why is ice less dense than water and what kind of attractive forces must be overcome to melt ice ? *(N.C.E.R.T.)*
32. Complete the following reactions :
(*i*) $CaO(s) + H_2O(l) \longrightarrow$ (*ii*) $Na_2O(s) + H_2O(l) \longrightarrow$ (*iii*) $Fe(s) + H_2O(g) \longrightarrow$ *(N.C.E.R.T.)*
33. Elements with atomic numbers 17 and 20 form compounds with hydrogen. Write the formulae of these compounds and compare their chemical behaviour in water. *(N.C.E.R.T.)*
[Hint. HCl, CaH_2]
34. Distinguish between (*i*) hard and soft water and (*ii*) temporary and permanent hardness. *(N.C.E.R.T.)*
35. Discuss the principle and method of softening of hard water by organic ion exchange resins. *(N.C.E.R.T.)*
36. Discuss the importance of heavy water in nuclear reactors. *(N.C.E.R.T.)*
37. Explain : (*i*) water has maximum density at 277 K. (*ii*) ice floats over water.
38. Describe permutit process for softening of hard water.
39. Discuss briefly demineralisation and deionisation of water by ion exchange resins.
40. Describe the principle of sequestration for softening of hard water.
41. Calculate the hardness of a water sample which contains 0·001 mole of $MgSO_4$ dissolved per litre of the solution. **[Ans. = 100 ppm]**
42. What is the action of water on (*i*) Calcium carbide (*ii*) Calcium phosphide (*iii*) Magnesium nitride ?
43. What are the ways in which water molecules are bonded to the anhydrous salt to form hydrate.
44. Why is water an excellent solvent for ionic or polar compounds ?
45. How is heavy water prepared from normal water ? *(N.C.E.R.T.)*
46. Discuss the importance of heavy water is nuclear reactors. *(N.C.E.R.T.)*
47. How is heavy water prepared ? Compare its physical properties with that of ordinary water.

48. What is the action of heavy water on
(*i*) sodium (*ii*) sodium hydroxide (*iii*) ammonium chloride and (*iv*) sulphur trioxide ?

49. Name the following compounds and write down how can they be prepared from heavy water
(*i*) $CDCl_3$ (*ii*) DCl (*iii*) D_2 (*iv*) C_2D_2 and (*v*) CD_4.

50. Write the structures of six varieties of heavy water differing in atomic mass of oxygen atom and their molecular masses.

Sec 11.12. **51.** Compare the structures of H_2O and H_2O_2. *(N.C.E.R.T.)*

52. Compare the chemical properties of H_2O and H_2O_2. *(N.C.E.R.T.)*

53. Show by proper chemical reactions how hydrogen peroxide can function both as an oxidising and a reducing agent. *(N.C.E.R.T.)*

54. Complete the following equations :
(*i*) $PbS\,(s) + H_2O_2\,(aq) \longrightarrow$ (*ii*) $MnO_4^-\,(aq) + H_2O_2\,(aq) \longrightarrow$ *(N.C.E.R.T.)*

55. What happens when H_2O_2 is treated with
(*a*) acidified potassium parmanganate
(*b*) lead sulphide
(*c*) alkaline potassium ferricyanide
(*d*) acidified ferrous sulphate
(*e*) sulphurous acid ?
(*f*) sodium arsenite ?

56. What happens when
(*a*) Barium peroxide is treated with cold dilute sulphuric acid.
(*b*) Sodium peroxide is treated with cold dilute sulphuric acid and the resulting mixture is cooled below 273 K
(*c*) Barium peroxide is treated with phosphoric acid
(*d*) Hydrogen peroxide is treated with sodium carbonate
(*e*) Hydrogen iodide is added to hydrogen peroxide?

57. Write equations for the following reactions : —
(*a*) A solution of 2-ethylanthraquinol in a mixture of benzene and cyclohexanel is oxidised
(*b*) The organic product obtained in (*a*) is treated with hydrogen in the presence of palladium catalyst.
(*c*) Peroxydisulphuric acid is hydrolysed
(*d*) Chlorine is passed through hydrogen peroxide solution
(*d*) Sodium hydroxide is treated with hydrogen peroxide.

58. Give ion electron equations for the following reactions :—
(*a*) Oxidation of ferrous ions to ferric ions by hydrogen peroxide
(*b*) Oxidation of iodide ion to iodine by hydrogen peroxide
(*c*) Oxidation of acidified permanganate ion by hydrogen peroxide
(*d*) Reduction of alkaline ferricyanide ions to ferrocyanide ions
(*e*) Oxidation of ferrocyanide ions to ferricyanide ions in acidic medium.

59. "Hydrogen peroxide is a strong oxidising agent both in acid and alkaline medium." Justify giving suitable reactions.

60. How is a solution of H_2O_2 prepared by electrolysis of an aqueous solution of ammonium sulphate and H_2SO_4 ?

61. How is a solution of H_2O_2 concentrated ? Why cannot it be concentrated by distillation at ordinary pressure ?

62. Justify the statement "An aqueous solution of hydrogen peroxide is weakly acidic".

63. In the preparation of hydrogen peroxide, the use of phosphoric acid has an advantage over dilute sulphuric acid. Explain.

64. Name the compound of hydrogen and oxygen which acts both as an oxidising as well as a reducing agent. Give one method for its preparation.

65. How does H_2O_2 act as a bleaching agent ?

66. Give three uses of hydrogen peroxide.

67. Explain :

(*i*) H_2O has a higher boiling point than water.

(*ii*) H_2O_2 cannot be stored for prolonged periods.

68. Hydrogen peroxide is used to restore the colour of old oil paintings containing lead oxide. Write a balanced equation for the reaction which takes place in this process.

Sec. 11.13. to 11.14. 69. What is understood by hydrogen economy ? *(N.C.E.R.T.)*

70. What are advantages of using hydrogen as a fuel over gasoline or coal ? *(N.C.E.R.T.)*

71. Give one thermochemical cycle of chemical reactions depicting the decomposition of water.

72. Discuss two methods for storing hydrogen.

73. Discuss the use of liquid hydrogen as a fuel.

Long Answer Questions CARRYING 5 or more MARKS

Sec. 11.1. to 11.4. 1. Discuss the position of hydrogen in the periodic table.

2. What are isotopes ? Discuss briefly the structure, properties and uses of isotopes of hydrogen.

Sec. 11.5. to 11.7. 3. How is dihydrogen prepared from :
(*i*) water (*ii*) acids and (*iii*) alkalies. Discuss its various uses.

4. How is dihydrogen prepared on a commercial scale ? Give one convenient method for preparing dihydrogen in the laboratory.

5. Give equations to show the reactions of dihydrogen with : Na, Ca, CO, N, S, Cl and CuO.

Sec. 11.8. 6. What are hydrides ? Discuss their various types. How are they formed ?

7. Discuss briefly the properties and uses of different types of hydrides.

Sec. 11.9. to 11.12. 8. What do you mean by hard water ? What are the different methods used for softening of hard water ? Briefly explain the principle of each method.

9. Discuss the structure of (*a*) water in the gaseous and liquid states (*b*) ice. Explain why water expands on freezing ?

10. Give the equation for the auto-oxidation of 2-ethylanthraquinol to produce H_2O_2. Why is the process called auto-oxidation ? What is the advantage of this process ? Give one example of a reaction with equation in which ozone acts as an oxidant but no oxygen is produced. Which element is a stronger oxidant than ozone ? *(West Bengal J.E.E. 2001)*

11. How is hydrogen peroxide prepared in the laboratory and on a commercial scale ? Giving four reactions of each type justify the statement that hydrogen peroxide acts both as an oxidising as well as a reducing agent.

Sec. 11.13. to 11.14. 12. Write notes on :
(*a*) Hydrogen economy and (*b*) Liquid hydrogen as a fuel of the future.

COMPETITION FOCUS

ADDITIONAL USEFUL INFORMATION

1. Atomic hydrogen is produced when molecular hydrogen is passed through an electric arc struck between tungsten electrodes (3773—4273 K).

$$H_2 \xrightarrow{\text{Electric arc, } 3773 - 4273 \text{ K}} 2H \; ; \; \Delta H = 435 \cdot 9 \; kJ \; mol^{-1}$$

The life time of atomic hydrogen is 0·3 sec.

and hence it immediately gets converted into the molecular form liberating a large amount of energy which is used for welding purposes in form of **atomic hydrogen torch Fig. 11.14.**

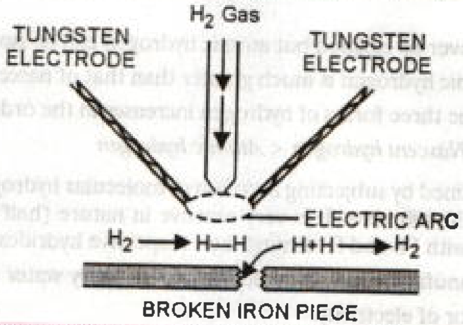


FIGURE 11.14. Atomic Hydrogen Torch.

Atomic hydrogen is very reactive and hence it acts as a powerful reducing agent. It reduces, oxides, chlorides, sulphides and sulphates of heavy metals and many alkali metal salts other than chlorides and sulphates.

$$CuO + 2H \longrightarrow Cu + H_2O \quad ; \quad AgCl + H \longrightarrow Ag + HCl$$

$$Cu_2S + 2\,H \longrightarrow 2\,Cu + H_2S \quad ; \quad BaSO_4 + 8\,H \longrightarrow BaS + 4\,H_2O$$

It also reduces oxides of non-metals. For example,

$$CO_2 + 2H \longrightarrow HCOOH$$

$$CO + 2H \longrightarrow HCHO$$

$$P_4O_{10} + 32\,H \longrightarrow 4\,PH_3 + 10\,H_2O$$

ADDITIONAL USEFUL INFORMATION contd.

It combines with O_2, Ag and Hg at low temperatures to form their respective hydrides.

$$O_2 + 2\,H \longrightarrow H_2O_2 \quad ; \quad Ag + H \longrightarrow AgH$$

2. Nascent hydrogen. *The hydrogen produced in contact with the substance to be reduced is called nascent hydrogen.* In other words, it is the hydrogen at the moment of its generation. That is why it is also sometimes called as *newly born hydrogen. It is much more reactive and a much more powerful reducing agent than the ordinary (molecular) hydrogen.* For example, ordinary hydrogen cannot reduce permanganate, ferric, dichromate and chlorate ions. But, if a small zinc piece is added to such solutions, these ions are reduced to manganous, ferrous, chromic and chloride ions respectively.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + 2\,H \quad \textit{(nascent hydrogen)}$$

$$2\,MnO_4^- + 6\,H^+ + 10\,H \longrightarrow 2\,Mn^{2+} + 8\,H_2O$$

$$Fe^{3+} + H \longrightarrow Fe^{2+} + H^+$$

$$Cr_2O_7^{2-} + 8\,H^+ + 6\,H \longrightarrow 2\,Cr^{3+} + 7\,H_2O$$

$$ClO_3^- + 6\,H \longrightarrow Cl^- + 3\,H_2O$$

Some common sources of nascent hydrogen are : (*i*) a mixture of zinc and dil. H_2SO_4, (*ii*) a mixture of tin and conc. HCl, (*ii*) metallic sodium and absolute alcohol and (*iv*) Zinc-copper couple and H_2O or alcohol.

The activity of nascent hydrogen may be due to :

(*i*) its atomic nature because atoms are more reactive than molecules, (*ii*) its association with a part of chemical energy liberated during the reaction thereby making it hyperreactive (*iii*) its liberation in form of tiny bubbles having high internal pressure. However, none of these theories is entirely satisfactory to explain the behaviour of nascent hydrogen.

3. Comparison between Atomic and Nascent hydrogen. Main points of difference are :

(*i*) Nascent hydrogen can be produced even at room temperature but atomic hydrogen is produced at elevated temperatures.

(*ii*) Nascent hydrogen can never be isolated but atomic hydrogen can be isolated.

(*iii*) Reducing power of atomic hydrogen is much greater than that of nascent hydrogen.

In general,the reactivity of the three forms of hydrogen increases in the order :

Molecular hydrogen (H_2) *< Nascent hydrogen < Atomic hydrogen*

4. Active hydrogen. It is obtained by subjecting a stream of molecular hydrogen at ordinary temperatures to silent electric discharge at about 30,000 volts. It is very reactive in nature (half life = 0·33 sec) and combines directly at ordinary temperatures with Pb and S forming their respective hydrides.

5. Heavy hydrogen. It is manufactured by the electrolysis of heavy water containing a little of H_2SO_4 or NaOH to make it a good conductor of electricity.

$$\underset{\text{Heavy water}}{2\,D_2O(l)} \xrightarrow{\text{Electrolysis}} \underset{\text{(At }\textit{cathode}\text{)}}{2\,D_2(g)} + \underset{\text{(At }\textit{anode}\text{)}}{O_2(g)}$$

In the laboratory, it can be prepared by the action of heavy water on sodium metal.

$$2\,D_2O(l) + 2\,Na(s) \longrightarrow 2\,NaOD(aq) + D_2(g)$$

C.B.S.E.-P.M.T. (MAINS) SPECIAL

A. SUBJECTIVE QUESTIONS (Common with I.I.T.)

Q. 1. **The process 1/2 H_2 (g) + e^- $\longrightarrow$ H^- (g) is endothermic ($\Delta H = +151$ kJ mol^{-1}), yet salt like hydrides are known. How do you account for this?**

Ans. It is true that formation of hydride (H^-) ion is an endothermic process, yet alkali and alkaline earth metals form salt like hydrides. This is due to the reason that high lattice energy released (energy released during the formation of solid metal hydrides from their corresponding gases ions, *i.e.*, M^+ and H^-) more than compensates the energy needed for the formation of H^- ions from H_2 gas.

Q. 2. **Statues coated with white lead on long exposure to atmosphere turn black and the original colour can be restored on treatment with H_2O_2. Why?** ***(Roorkee 1987)***

Ans. On long exposure to atmosphere, white lead is converted into black PbS due to the action of H_2S present in the atmosphere. As a result, statues turn black.

$$PbO_2 + 2H_2S \longrightarrow PbS + 2H_2O$$

On treatment of these blackened statues with H_2O_2, the black PbS gets oxidised to white $PbSO_4$ and the colour is restored.

$$PbS + 4\,H_2O_2 \longrightarrow PbSO_4 + 4\,H_2O$$

Q. 3. **A mixture of hydrazine and H_2O_2 with Cu (II) catalyst is used as a rocket propellant. Why?**

Ans. The reaction between hydrazine and H_2O_2 is highly exothermic and is accompanied by a large increase in the volume of the products and hence this mixture is used as a rocket propellant.

$$NH_2—NH_2\,(l) + 2\,H_2O_2\,(l) \xrightarrow{Cu\,(II)} N_2\,(g)\uparrow + 4\,H_2O\,(g)\uparrow$$

Q. 4. **Hydrogen peroxide acts both as an oxidising agent and as a reducing agent in alkaline solution towards certain first row transition metal ions. Illustrate both these properties of H_2O_2 using chemical equations.** ***(I.I.T. 1998)***

Ans. Oxidising agent :

$$2\,Cr(OH)_3 + 4\,NaOH + 3\,H_2O_2 \longrightarrow 2\,Na_2CrO_4 + 8\,H_2O$$

Here, Cr^{3+} gets oxidised to Cr^{6+}.

Reducing agent :

$$2\,K_3[Fe(CN)_6] + 2\,KOH + H_2O_2 \longrightarrow 2\,K_4\,[Fe(CN)_6] + 2\,H_2O + O_2$$

Here Fe^{3+} gets reduced to Fe^{2+}.

Q. 5. **A white solid is either Na_2O or Na_2O_2. A piece of red litmus paper turns white when it is dipped into a freshly made aqueous solution of the white solid.**

(*i*) Identify the substance and explain with balanced equation

(*ii*) Explain what would happen to the red litmus if the white solid were the other compound. ***(I.I.T. 1999)***

Ans. (*i*) $Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$

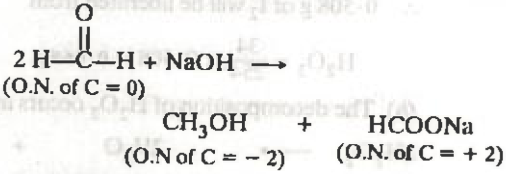
H_2O_2 thus produced turns red litmus paper white due to its bleaching action.

(*ii*) $Na_2O + H_2O \longrightarrow 2NaOH$

NaOH thus produced will turn red litmus blue.

Q. 6. **An element has its maximum and minimum oxidation states as + *m* and −*m* respectively and it does not have the possibility of undergoing disproportionation in any of its compounds. What is the value of *m* ?** ***(West Bental J.E.E. 2003)***

Ans. Hydrogen has maximum and minimum oxidation states as + 1 and − 1 respectively. Elements of group 14, *i.e.*, C, Si, Ge, Sn & Pb can also have maximum and minimum oxidation states of + 4 and −4 respectively. But all these elements undergo disproportionation reactions in some of their compounds. For example,



$$\underset{\text{(O.N. of C = 0)}}{2\,H—\overset{\overset{\Large O}{\|}}{C}—H} + NaOH \longrightarrow \underset{\text{(O.N of C = − 2)}}{CH_3OH} + \underset{\text{(O.N. of C = + 2)}}{HCOONa}$$

Therefore, the value of *m* is 1.

Q. 7. **(a) Is it possible to remove completely by boiling the temporary hardness due to $Mg(HCO_3)_2$?**

(b) Calculate the molarity strength of H_2O_2 solution marked '30 volume'. ***(West Bengal J.E.E. 2004)***

Ans. (*a*) Temporary hardness of H_2O due to $Mg(HCO_3)_2$ can be completely removed by boiling because soluble $Mg(HCO_3)_2$ is converted into insoluble $MgCO_3$ which can be removed by filtration

$$\underset{(Soluble)}{Mg(HCO_3)_2} \xrightarrow{Boil} \underset{(Insoluble)}{MgCO_3\downarrow} + CO_2\uparrow + H_2O$$

(*b*) Molarity = Volume strength/11·2

$$= \frac{30}{11\cdot2} = \mathbf{2\cdot68\ M.}$$

B. PROBLEMS

Problem 1. **Calculate the volume of 10 volume H_2O_2 solution that will react with 200 ml of 2 N $KMnO_4$ in acidic medium :**

Solution. Normality of 10 volume H_2O_2

$$= \frac{10 \times 68}{22\cdot4 \times 17} = \frac{10}{5\cdot6}\,N$$

Applying normality equation,

$$\underset{(H_2O_2)}{N_1V_1} = \underset{(KMnO_4)}{N_2V_2}$$

$$\frac{10}{5\cdot6} \times V_1 = 2 \times 200$$

or $$V_1 = \frac{2 \times 200 \times 5\cdot6}{10}$$

$$= \mathbf{224\ cm^3}.$$

Problem 2. **The degree of hardness of a given sample of hard water is 40 ppm. If the entire hardness in due to $MgSO_4$, how much of $MgSO_4$ is present per kg of water ?**

Solution. Degree of hardness of H_2O is 40 ppm

i.e., 10^6 *g* of water contain $CaCO_3$ = 40 g

Since 1 mole of $CaCO_3 \equiv$ 1 mole of $MgSO_4$

$\therefore$ 100 g of $CaCO_3 \equiv$ 120 g of $MgSO_4$

$\therefore$ 10^6 *g* of water contain $MgSO_4 = \frac{40 \times 120}{100}$

$= 48\ g$

or 10^3 *g* of water will contain $MgSO_4$

$$= \frac{48 \times 10^3}{10^6} \times 10^3\ mg$$

or 1 kg of water will contain $MgSO_4$ = **48 mg**

I.I.T. (MAINS) SPECIAL

Q. 1. **A 5·0 cm^3 solution of H_2O_2 liberates 0·508 g of iodine from an acidified KI solution. Calculate the strength of H_2O_2 solution in terms of volume strength at STP** (*I.I.T. 1995*)

Ans. (*a*) $2KI + H_2SO_4 + H_2O \longrightarrow K_2SO_4 + 2H_2O + I_2$

From the above equation, $H_2O_2 \equiv I_2$

34 g of $H_2O_2 \equiv$ 254 g of I_2

$\therefore$ 0·508 g of I_2 will be liberated from

$$H_2O_2 = \frac{34}{254} \times 0\cdot508 = \mathbf{0\cdot068\ g}$$

(*b*) The decomposition of H_2O_2 occurs as

$$\underset{2\times34=68\ g}{2H_2O_2} \longrightarrow 2H_2O + \underset{22400\ cm^3\ at\ NTP}{O_2}$$

$\therefore$ 0·068 of H_2O_2 upon decomposition will give

$$O_2 = \frac{22400}{68} \times 0\cdot068 = 22\cdot4\ ml$$

(*c*) Now 5·0 cm^3 of H_2O_2 solution gives

$$O_2 = 22\cdot4\ cm^3 \text{ at NTP}$$

$\therefore$ 1·0 cm^3 of H_2O_2 solution will give

$$O_2 = \frac{22\cdot4}{5} = 4\cdot48\ cm^3 \text{ at NTP}$$

Thus, volume strength of given H_2O_2 solution

= **4·48.**

Q. 2. **To a 25 ml H_2O_2 solution, excess of acidified solution of potassium iodide was added. The iodine liberated required 20 ml of 0·3 N sodium thiosulphate solution. Calculate the volume strength of H_2O_2 solution.** (*I.I.T. 1997*)

Ans. **Step 1.** *To determine the normality of H_2O_2 solution.*

Let the normality of the H_2O_2 solution be N_1

According to the question,

25 ml of N_1 H_2O_2 = 20 ml of 0·3 N $Na_2S_2O_3$ solution

or $25 \times N_1 = 20 \times 0\cdot3$

or $$N_1 = \frac{20 \times 0\cdot3}{25} = \mathbf{0\cdot24\ N}$$

Thus, the normality of the given H_2O_2 solution

= **0·24 N**

Step 2. *To determine the amount of H_2O_2 in 25 ml solution*

1000 ml of 1 N H_2O_2 solution contain H_2O_2

= 17 g

∴ 25 ml of 0·24 N H_2O_2 solution will contain

$$H_2O_2 = \frac{17 \times 25 \times 24}{1000 \times 100} = \mathbf{0 \cdot 102\ g}$$

Step 3. *To determine the volume strength of H_2O_2 solution.*

Consider the chemical equation,

$$2\,H_2O_2 \longrightarrow 2\,H_2O + O_2$$

$$2 \times 34 = 68\,g \qquad\qquad 22\cdot4 \text{ litres at N.T.P.}$$

68 *g* of H_2O_2 give O_2 = 22·4 litres at N.T.P.

∴ 0·102 *g* of H_2O_2 will give

$$O_2 = \frac{22\cdot4 \times 1000 \times 0\cdot102}{68}$$

$$= 33\cdot6 \text{ ml at N.T.P.}$$

Now, 25 ml of H_2O_2 solution give

$$O_2 = 33\cdot6 \text{ ml at N.T.P.}$$

∴ 1 ml of H_2O_2 solution will give O_2

$$= \frac{33\cdot6}{25} = 1\cdot344$$

Thus, the volume strength of the given H_2O_2 solution = 1·344

Q. 3. **Hydrogen peroxide solution (20 ml) reacts quantitatively with a solution of $KMnO_4$ (20 ml) acidified with dilute H_2SO_4. The same volume of $KMnO_4$ solution is just decolourised by 10 ml of $MnSO_4$ in neutral medium simultaneously forming a dark brown precipitate of hydrated MnO_2. The brown precipitate is dissolved in 10 ml of 0·2 M sodium oxalate under boiling condition in the presence of dilute H_2SO_4. Write the balanced equations involved in the reactions and calculate the molarity of H_2O_2.**

(I.I.T. 2001)

Ans. Step 1. *To write balanced equations for the reactions involved.*

(*i*) **In acidic medium,** *MnO_4^-* oxidises *H_2O_2* to *O_2*.

$$MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + 4\,H_2O] \times 2$$

$$H_2O_2 \longrightarrow O_2 + 2\,H^+ + 2\,e^-] \times 5$$

$$2\,MnO_4^- + 5\,H_2O_2 + 6\,H^+ \longrightarrow 2\,Mn^{2+} + 5\,O_2 + 8\,H_2O$$

(*ii*) **In neutral medium,** *MnO_4^- oxidises Mn^{2+} to MnO_2.*

$$MnO_4^- + 2\,H_2O + 3\,e^- \longrightarrow MnO_2 + 4\,OH^-] \times 2$$

$$Mn^{2+} + 4\,OH^- \longrightarrow MnO_2 + 2\,H_2O + 2\,e^-] \times 3$$

$$2\,MnO_4^- + 3\,Mn^{2+} + 4\,OH^- \longrightarrow 5\,MnO_2 + 2\,H_2O$$

(*iii*) **In acidic medium,** *MnO_2 oxidises sodium oxalate to CO_2*

$$MnO_2 + 4\,H^+ + 2\,e^- \longrightarrow Mn^{2+} + 2\,H_2O$$

$$C_2O_4^{2-} \longrightarrow 2\,CO_2 + 2\,e^-$$

$$MnO_2 + C_2O_4^{2-} + 4\,H^+ \longrightarrow Mn^{2+} + 2\,CO_2 + 2\,H_2O$$

$$\text{or } 5\,MnO_2 + 5\,C_2O_4^{2-} + 20\,H^+ \longrightarrow 5\,Mn^{2+} + 10\,CO_2 + 10\,H_2O \quad ...(iv)$$

From the above three balanced equations, it follows that

(*iv*) $5\,C_2O_4^{2-} \equiv 2\,MnO_4^- \equiv 5\,H_2O_2$

Step 2. *To determine the number of moles of $C_2O_4^{2-}$ present in 10 ml of 0·2 M sodium oxalate.*

No. of moles of sodium oxalate

= Molarity × volume in litres

$$= 0\cdot2 \times \frac{10}{1000} = 2 \times 10^{-3} \text{ mole}$$

Step 3. *To calculate the molarity of H_2O_2*

From Eq. (*iv*), it follows that $5\,C_2O_4^{2-} \equiv 5\,H_2O_2$

or 2×10^{-3} mole of $C_2O_4^{2-} \equiv 2 \times 10^{-3}$ mole of H_2O_2

Now 2×10^{-3} mole of H_2O_2 is present in 10 ml of H_2O_2

$$\therefore \text{Molarity } H_2O_2 = \frac{2 \times 10^{-3}}{10} \times 1000$$

$$= \mathbf{0 \cdot 2\ M}$$

MULTIPLE CHOICE QUESTIONS

For CBSE-PMT (Preliminary), AIIMS, AFMC, DPMT, CPMT, BHU and other Medical Entrance Examinations

1. Which of the following statements is most applicable to hydrogen ? It can act
   (*a*) as a reducing agent
   (*b*) as an oxidising agent
   (*c*) both as oxidising and reducing agents
   (*d*) neither as an oxidising nor as a reducing agent.

2. Hydrogen combines with other elements by
   (*a*) losing an electron
   (*b*) gaining an electron
   (*c*) sharing an electron
   (*d*) losing, gaining and sharing of an electron.

3. The first ionization energy (kJ mol^{-1}) for H, Li, F, Na has one of the following values : 1681, 520, 1312, 495. Which of these values corresponds to that of hydrogen ?
   (*a*) 1681 (*b*) 1312
   (*c*) 520 (*d*) 495.

4. The correct increasing order of the acidity of CO_2, H_2O and H_2O_2 is
   (*a*) $CO_2 < H_2O_2 < H_2O$
   (*b*) $H_2O < H_2O_2 < CO_2$
   (*c*) $H_2O < H_2O_2 > CO_2$
   (*d*) $H_2O_2 > CO_2 > H_2O$

5. The volume of 10 volume H_2O_2 solution that decolourises 200 ml of 2N $KMnO_4$ solution in acidic medium is :
   (*a*) 112 ml (*b*) 336 ml
   (*c*) 200 ml (*d*) 224 ml.

6. Which of the following metals cannot be used for liberating dihydrogen from dilute hydrochloric acid?
   (*a*) Zinc (*b*) Copper
   (*c*) Iron (*d*) Magnesium.

7. Which of the following is used as a moderator in nuclear reactors ?
   (*a*) Hard water (*b*) Heavy water
   (*c*) Deionized water (*d*) Mineral water.

8. The temporary hardness of water due to calcium bicarbonate can be removed by adding
   (*a*) $CaCO_3$ (*b*) $Ca(OH)_2$
   (*c*) $CaCl_2$ (*d*) HCl.

9. In the calgon process of softening of water, which of the following is used ?
   (*a*) Sodium polymetaphosphate
   (*b*) Hydrated sodium aluminium silicate
   (*c*) Cation exchange resins
   (*d*) Anion exchange resins.

10. Hydrogen will not reduce
    (*a*) heated cupic oxide (*b*) heated ferric oxide
    (*c*) heated stannic oxide
    (*d*) heated aluminium oxide. *(I.I.T. 1985)*

11. The oxidation states exhibited by hydrogen in its various compounds are
    (*a*) −1 only (*b*) zero only
    (*c*) +1, −1 and zero (*d*) +1 only
    (Pb. J.E.T. 1988)

12. The oxidation states of the most electronegative element in the products of the reaction, BaO_2 with dil. H_2SO_4 are
    (*a*) 0 and −1 (*b*) −1 and −2
    (*c*) −2 and 0 (*d*) −2 and +1.
    (I.I.T. 1991)

13. 30 volumes H_2O_2 means
    (*a*) 30% H_2O_2
    (*b*) 30 cm^3 of the solution contains 1g of H_2O_2
    (*c*) 1 cm^3 of the solution liberates 30 cm^3 of O_2 at STP
    (*d*) 30 cm^3 of the solution contain one mole of H_2O_2.
    (Haryana C.E.E.T. 1992)

14. An oxide which gives H_2O_2 on treatment with dilute acid is
    (*a*) PbO_2 (*b*) Na_2O_2
    (*c*) MnO_2 (*d*) TiO_2.
    (A.F.M.C. 1994)

15. Nascent hydrogen consists of
    (*a*) Hydrogen atoms with excess energy

ANSWERS

1. *c* **2.** *d* **3.** *b* **4.** *b* **5.** *d* **6.** *b* **7.** *b* **8.** *b* **9.** *a* **10.** *d*
11. *c* **12.** *b* **13.** *c* **14.** *b*

(*b*) Hydrogen molecules with excess energy

(*c*) Hydrogen ions in the excited state

(*d*) Solvated protons. *(A.I.I.M.S. 1994)*

16. The oxidation number of O in H_2O_2 is :

(*a*) —2 (*b*) —1

(*c*) +1 (*d*) +2.

(M.L.N.R. Allahabad 1994)

17. The O—O—H bond angle in H_2O_2 is

(*a*) 106° (*b*) 109° 28′

(*c*) 120° (*d*) 94·8°.

(C.B.S.E. P.M.T. 1994)

18. Hydrolysis of one mole of peroxodisulphuric acid produces

(*a*) two moles of sulphuric acid

(*b*) two moles of peroxomonosulphuric acid

(*c*) one mole of sulphuric acid and one mole of peroxomonosulphuric acid

(*d*) one mole of sulphuric acid, one mole of peroxomonosulphuric acid and one mole of hydrogen peroxide. *(I.I.T. 1996)*

19. Which contains both polar and non-polar bonds ?

(*a*) NH_4Cl (*b*) HCN

(*c*) H_2O_2 (*d*) CH_4 *(I.I.T. 1997)*

20. The critical temperature of water is higher than that of O_2 because the H_2O molecule has

(*a*) Fewer electrons than oxygen

(*b*) Two covalent bonds (*c*) V-shape

(*d*) Dipole moment *(I.I.T. 1997)*

21. Among KO_2, AlO_2^-, BaO_2 and NO_2^+, unpaired electron is present in

(*a*) NO_2^+ and BaO_2 (*b*) KO_2 and AlO_2^-

(*c*) KO_2 only (*d*) BaO_2 only

(I.I.T. 1997)

22. Which of the following statements is *correct* ?

(*a*) Hydrogen has same ionization potential as alkali metals

(*b*) H^- has same electronegativity as halogens

(*c*) H^- has oxidation number of –1

(*d*) H^- will not be liberated at anode

(A.F.M.C. 1997)

23. What is heavy water ?

(*a*) $H_2^{18}O$ (*b*) $H_2^{16}O$

(*c*) H_2O_3 (*d*) D_2O *(A.F.M.C. 1997)*

24. The high density of water as compared to ice is due to

(*a*) Hydrogen bonding interactions

(*b*) Dipole-dipole interactions

(*c*) Dipole-induced dipole interactions

(*d*) Induced dipole induced dipole interactions

(C.B.S.E. P.M.T. 1997)

25. The volume strength of 1·5 N H_2O_2 solution is

(*a*) 4·8 (*b*) 5·2

(*c*) 8·8 (*d*) 8·4

(I.I.T. 1991, C.B.S.E. P.M.T. 1997)

26. The hydride ion H^- is a stronger base than hydroxide ion. Which of the following reactions will occur if sodium hydride (NaH) is dissolved in water?

(*a*) $H^-(aq) + H_2O(l) \longrightarrow H_3O^+(aq)$

(*b*) $H^-(aq) + H_2O(l) \longrightarrow OH^-(aq) + H_2(g)$

(*c*) $H^- + H_2O \longrightarrow$ No reaction

(*d*) None of these. *(C.B.S.E. P.M.T. 1997)*

27. When a substance A reacts with water, it produces a combustible gas B and *a* solution of substance C in water. When another substance D reacts with this solution of C, it produces the same gas B on warming but D can produce gas B on reaction with dilute sulphuric acid at room temperature. A imparts a deep golden yellow colour to a smokeless flame of Bunsen burner. A, B, C and D respectively are :

(*a*) Na, H_2, NaOH, Zn

(*b*) K, H_2, KOH, Al

(*c*) Ca, H_2, $Ca(OH)_2$, Sn

(*d*) CaC_2, C_2H_2, $Ca(OH)_2$, Fe.

(C.B.S.E. P.M.T. 1998)

28. Which of the following pairs of substances on reaction will not evolve H_2 gas ?

(*a*) Fe and H_2SO_4 (aqueous)

(*b*) Copper and HCl (aqueous)

(*c*) Sodium and ethyl alcohol

(*d*) Iron and steam. *(C.B.S.E. P.M.T. 1998)*

29. Acidified solution of chromic acid on treatment with H_2O_2 yields

(*a*) $CrO_3 + H_2O + O_2$ (*b*) $Cr_2O_3 + H_2O + O_2$

A N S W E R S

15. *b* **16.** *b* **17.** *d* **18.** *c* **19.** *c* **20.** *d* **21.** *c* **22.** *c* **23.** *d* **24.** *a*
25. *d* **26.** *b* **27.** *a* **28.** *b*

(*c*) $CrO_5 + H_2O$ (*d*) $H_2Cr_2O_7 + H_2O + O_2$.

(*M.P.C.E.E. 1999*)

30. Amongst H_2O, H_2S, H_2Se and H_2Te, the one wih the highest boiling point is

(*a*) H_2O because of hydrogen bonding

(*b*) H_2Te because of higher molecular weight

(*c*) H_2S because of hydrogen bonding

(*d*) H_2Se because of lower molecular weight

(*I.I.T. 2000*)

31. *Para* and *ortho* hydrogen differ in

(*a*) atomic number (*b*) atomic mass

(*c*) spins of protons (*d*) number of neutrons

(*A.F.M.C. 2001*)

32. Heavy water is obtained by

(*a*) boiling water

(*b*) fractional distillation of H_2O

(*c*) prolonged electrolysis of H_2O

(*d*) heating H_2O_2 (*A.F.M.C. 2001*)

33. Polyphosphates are used as water softening agents because they

(*a*) form soluble complexes with anionic species

(*b*) precipitate anionic species

(*c*) form soluble complexes with cationic species

(*d*) precipitate cationic species

(*I.I.T. 2002*)

34. Action of water or dilute mineral acids on metals can give

(*a*) Monohydrogen (*b*) Tritium

(*c*) Dihydrogen (*d*) Trihydrogen

(*e*) D_2 (*Kerala M.E.E. 2002*)

35. Which one of the following processes will produce permanent hard water ?

(*a*) Addition of Na_2SO_4 to water

(*b*) Saturation of water with $CaCO_3$

(*c*) Saturation of water with $MgCO_3$

(*d*) Saturation of water with $CaSO_4$

(*A.I.E.E.E. 2003*)

36. The reagent commonly used to determine hardness of water titrimetrically is

(*a*) Oxalic acid (*b*) Disodium salt of EDTA

(*c*) Sodium citrate (*d*) Sodium thiosulphate

(*A.I.E.E.E. 2003*)

37. The structure of H_2O_2 is

(*a*) planar (*b*) non-planar

(*c*) spherical (*d*) linear.

(*C.B.S.E. P.M.T. 1999*)

38. H_2O_2 acts as an oxidising agent in

(*a*) Neutral medium (*b*) Acidic medium

(*c*) Alkaline medium

(*d*) Alkaline and neutral medium

(*e*) Acidic and alkaline medium

(*Kerala M.E.E. 2004, A.F.M.C. 2004*)

39. Commercial 11·2 volume H_2O_2 solution has a molarity of

(*a*) 1·0 (*b*) 0·5

(*c*) 11·2 (*d*) 1·12

(*e*) 0·75 (*Kerala E.E.E. 2004*)

HINTS/EXPLANATIONS to Multiple Choice Questions

3. IE of H is more than that of alkali metals but less than that of F.

4. A stronger acid displaces a weaker acid from its salts.

$$\underset{\text{Stronger acid}}{BaO_2 + H_2O + CO_2} \longrightarrow BaCO_3 + \underset{\text{Weaker acid}}{H_2O_2}$$

5. Refer to Problem 1 on page 11/48 for answer.

10. Al—O bond is very strong

12. $BaO_2 + H_2SO_4 \longrightarrow BaS\overset{-2}{O_4} + H_2\overset{-1}{O_2}$

15. Hydrogen molecules with excess energy.

18. $\underset{\text{Peroxodisulphuric acid}}{HO—SO_2—O—O—SO_2—OH} + H_2O \longrightarrow \underset{\text{Sulphuric acid}}{HOSO_2OH} + \underset{\text{Permono-sulphuric acid}}{HOOSO_2OH}$

19. O—O bond is non-polar while O—H bonds are polar.

21. $K^+ [\,{}^-:\underset{..}{\ddot{O}} - \underset{..}{\dot{O}}:]$

25. Multiply normality by 5.6. *i.e.* 5·6 × 1·5 = 8·4.

ANSWERS

29. *c* **30.** *a* **31.** *c* **32.** *c* **33.** *c* **34.** *c* **35.** *d* **36.** *b* **37.** *b* **38.** *e*

39. *a*

27. $\underset{A}{2\,Na} + 2\,H_2O \longrightarrow \underset{B}{H_2} + \underset{C}{2\,NaOH}$

and $\underset{D}{Zn} + \underset{C}{2\,NaOH} \longrightarrow Na_2ZnO_2 + \underset{B}{H_2}$

33. Sodium hexametaphosphate—a polyphosphate, combines with cations (*i.e.*, Ca^{2+}, Mg^{2+}) to form soluble complexes.

$$2\,Ca^{2+} + Na_2\,[Na_4\,(PO_3)_6] \longrightarrow 4\,Na^+ + \underset{\text{complex (soluble)}}{Na_2\,[(Ca_2\,(PO_3)_6]}$$

35. Saturation of water with $CaSO_4$ produces hardness

39. Molarity = Volume strength/11·2

= 11·2/11·2 = 1·0

ADDITIONAL QUESTIONS

For All Competitive Examinations

Assertion-Reason Type Questions

The following questions consist of two statements each, printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following four responses.

(*a*) If both Assertion and Reason are true and the Reason is a correct explanation of the Assertion.

(*b*) If both Assertion and Reason are true but Reason is not a correct explanation of the Assertion.

(*c*) If Assertion is true but the Reason is false. **(*d*) If both Assertion and Reason are false.**

	Assertion	**Reason**
1.	Water is a good solvent for ionic compounds but poor for covalent compounds.	Hydration energy of ions releases sufficient energy to overcome lattice energy and break hydrogen bonds in water while covalently bonded compounds interact so weakly that even van der Waals' forces between molecules of covalent compounds cannot be broken.
2.	H_2O_2 liberates O_2 when it reacts with acidified $KMnO_4$ solution.	$KMnO_4$ oxidises H_2O_2 to O_2.
3.	H_2O_2 has higher boiling point than water.	The dipole moment of H_2O_2 is little more than that of H_2O.
4.	Beryllium hydride is a covalent hydride.	The electronegativity difference between Be and H is very high.
5.	D_2O is called hard water.	Its degree of dissociation is high.
6.	The O–O bond length is H_2O_2 is shorter than that of O_2F_2	H_2O_2 is on ionic compound. *(A.I.I.M.S. 2003)*

True/False Statements

Which of the following statements are true and which are false ?

1. Water can act as an oxidising as well as a reducing agent.
2. Sequestration of Ca^{2+} and Mg^{2+} ions present in hard water is carried out by using zeolites.
3. Complete hydrolysis of one mole of peroxydisulphuric acid gives one mole of H_2O_2 and two moles of H_2SO_4.
4. During electrolysis of aqueous hydrochloric acid, dihydrogen is liberated at the anode.
5. When treated with H_2O_2, lead dioxide is reduced to lead metal.
6. In copper sulphate pentahydrate, all the water molecules are attached to the Cu^{2+} ion by coordinate covalent bonds.
7. Zinc hydroxide dissolves in excess of NaOH solution to evolve dihydrogen gas.
8. Lead dioxide on reaction with dil. H_2SO_4 gives H_2O_2.
9. Deuterium is an isomer of protium.
10. Water cannot be used to extinguish petrol fire.

Fill In The Blanks

1. Dihydrogen acts a reducing agent in its reaction with .... while it acts as an oxidising agent in its reaction with ....
2. In the reaction of F_2 with H_2O, water acts as a ....
3. The bleaching action of hydrogen peroxide is due to ....
4. Temporary hardness of water is due to ....
5. Hydrogen peroxide turns starch-potassium iodide paper blue due to the liberation of ....
6. The chemical formula of permutit is ....
7. Hydrogen gas is liberated by the action of aluminium with a concentrated solution of .... *(I.I.T. 1987)*
8. The electrolysis of molten sodium hydride liberates .... gas at the anode. *(I.I.T. 1989)*
9. Calgon is the trade name of...........
10. Hydrogen has.......isotopes and......nuclear isomers.

Matching Type Questions

Match items of column I with appropriate items of column II

Column-I	**Column-II**
1. Deuterates are salts with	(*a*) Dihydrogen
2. Cation exchange resins contain	(*b*) Nuclear reactors
3. Palladium hydride	(*c*) D_2O as water of crystallization.
4. Zn dissolves in NaOH	(*d*) Sod. polymetaphosphate
5. Calgon	(*e*) Non stochiometric.
6. Heavy water	(*f*) acidic groups such as $-COOH$ and $-SO_3H$

ANSWERS

ASSERTION-REASON TYPE QUESTIONS

1. (*a*) **2.** (*a*) **3.** (*b*) **4.** (*c*) **5.** (*d*) **6.** (*d*)

TRUE/FALSE STATEMENTS

1. T **2.** F, sod. polymetaphosphate **3.** T **4.** F, at the cathode **5.** F, PbO **6.** F, four are bonded to Cu^{2+} by coordinate bonds while the fifth one is bonded to SO_4^{2-} ion by H-bonds **7.** F, $Zn(OH)_2 + 2NaOH \longrightarrow Na_2ZnO_2 + 2H_2O$ **8.** F, PbO_2 is not a peroxide since it does not contain $^-O-O^-$ ion and hence it does not evolve H_2O_2 on treatment with dil. H_2SO_4, **9.** F, deuterium is an isotope of protium **10.** Being ligher, petrol floats over water.

FILL IN THE BLANKS

1. heated CuO or Fe_3O_4 ; Na or Ca, **2.** reducing agent, **3.** nascent oxygen. **4.** bicarbonates of Ca^{2+} & Mg^{2+} **5.** I_2 **6.** $Na_2Al_2Si_2O_8 . xH_2O$ **7.** sodium hydroxide **8.** dihydrogen **9.** sodium hexametaphosphate **10.** three (H, D, T), two (ortho and para).

MATCHING TYPE QUESTIONS

1. (*c*) **2.** (*f*) **3.** (*e*) **4.** (*a*) **5.** (*d*) **6.** (*b*).

HINTS/EXPLANATIONS to Assertion-Reason Type Questions

3. *Correct explanation* : The extent of H-bonding in H_2O_2 is higher than that in H_2O.

4. *Correct reason* : The electronegativity difference between Be (1·5) and H (2·1) is small.

5. *Correct assertion* : D_2O is called heavy water.

Correct reason : Due to stronger D—O bonds, the degree of dissociation of D_2O is lower than that of H_2O.

Correct assertion : The O—O bond length in H_2O_2 is much longer than that of O_2F_2.

6. *Correct reason* : The lone pairs of electrons on the O atoms are strongly attracted by the electronegative F atoms. As a result, lone pair–lone pair repulsion of the two oxygen atoms is far less in.O_2F_2 than in H_2O_2. As a result, O—O) bond length is O_2F_2 (1·22 Å) is much shorter than in H_2O_2 (1·48 Å)