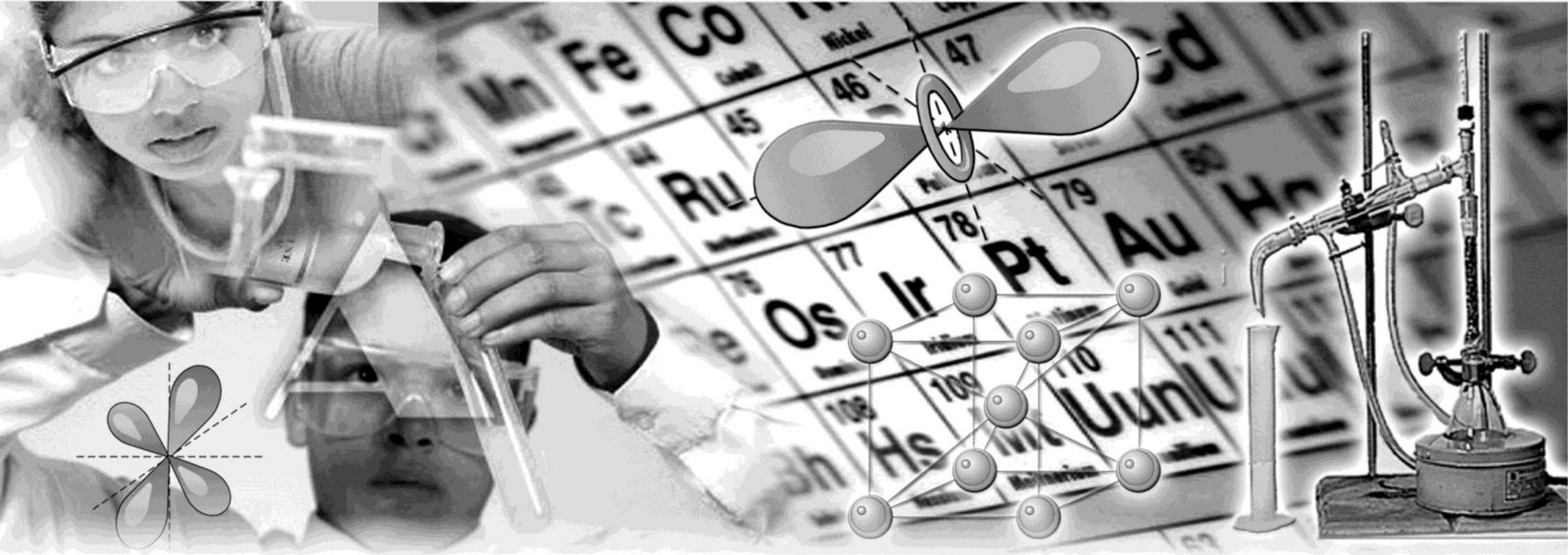


Chapter

17

Hydrogen and Its compounds

Hydrogen

(1) Position of hydrogen in the periodic table

Hydrogen is the first element in the periodic table. Hydrogen is placed in no specific group due to its property of giving electron (When H^- is formed) and also losing electron (When H^+ is formed).

(i) Hydrogen is placed in group I (Alkali metals) as,

(a) It has one electron in its (Outer) shell- $1s^1$ like other alkali metals which have (inert gas) ns^1 configuration.

(b) It forms monovalent H^+ ion like $Li^+, Na^+ \ldots$

(c) Its valency is also 1.

(d) Its oxide (H_2O) is stable as Li_2O, Na_2O.

(e) It is a good reducing agent (In atomic as well as molecular state) like $Na, Li \ldots$

(ii) Hydrogen also resembles halogens (Group VII A) as,

(a) It is also diatomic (H_2) like $F_2, Cl_2 \ldots$

(b) It also forms anion H^- like $F^-, Cl^- \ldots$ by gain of one electron.

(c) H^- has stable inert gas (He) configuration as CH_4, C_2H_6 like halogens CCl_4, SF_2Cl_2 etc.

(d) *H* is one electron short of duplet (Stable configuration) like $F, Cl, \ldots$ which are also one electron deficient than octet, $F - 2s^2 2p^5$; $Cl - 3s^2 3p^5$.

(e) (*IE*) of $H (1312\, kJ\ mol^{-1})$ is of the same order as that of halogens.

(iii) (*IE*) of *H* is very high in comparison with alkali metals. Also size of H^+ is very small compared to that of alkali metal ion. *H* forms stable hydride only with strongly electropositive metals due to smaller value of its electron affinity $(72.8\, kJ\ mol^{-1})$.

(iv) In view of the anomalous behaviour of hydrogen, it is difficult to assign any definite position to it in the periodic table. Hence it is customary to place it in group I (Along with alkali metals) as well as in group VII (Along with halogens).

(2) **Discovery and occurrence :** It was discovered by ***Henry Cavendish*** in 1766. Its name hydrogen was proposed by ***Lavoisier***. Hydrogen is the 9th most abundant element in the earth's crust.

Hydrogen exists in diatomic state but in triatomicstate it is called as Hyzone. Systematic name of water is oxidane.

(3) **Preparation of Dihydrogen :** Dihydrogen can be prepared by the following methods,

(i) *By action of water with metals*

(a) Active metals like *Na, K* react at room temperature

$$2M + 2H_2O \rightarrow 2MOH + H_2 \qquad [M = Na, K \text{ etc.}]$$

(b) Less active metals like *Ca, Zn, Mg, Al* liberate hydrogen only on heating.

$$2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2$$

(c) Metals like *Fe, Ni, Co, Sn* can react only when steam is passed over red hot metals.

$$3Fe + 4H_2O(\text{steam}) \rightarrow \underset{\text{Ferrosoferric oxide}}{Fe_3O_4} + 4H_2$$

(ii) *By the action of water on alkali and alkaline earth metals hydrides*

$$NaH + H_2O \rightarrow NaOH + H_2$$

$$CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2$$

(iii) *By reaction of metals like Zn, Sn, Al with alkalies (NaOH or KOH)*

$$Zn + 2NaOH \xrightarrow{\Delta} \underset{\text{sod. zincate}}{Na_2ZnO_2} + H_2$$

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

$$\underset{\text{Silicon}}{Si} + 2NaOH + 2H_2O \xrightarrow{\Delta} Na_2SiO_3 + 3H_2$$

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

(iv) ***By action of metal with acids*** : All active metals which lie above hydrogen in electrochemical series, can displace hydrogen gas from dilute mineral acids like *HCl*, H_2SO_4.

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

(v) *By the electrolysis of acidified water*

$$2H_2O \xrightarrow{H^+/\text{Electrolysis}} \underset{\text{At cathode}}{2H_2\uparrow} + \underset{\text{At anode}}{O_2\uparrow}$$

(vi) ***Laboratory method*** : In laboratory, it is obtained by action of granulated zinc with dilute H_2SO_4.

$$Zn + \text{dil.}H_2SO_4 \rightarrow ZnSO_4 + H_2$$

It must be noted that

(a) Pure zinc is not used for the preparation of H_2 as rate of reaction of pure *Zn* with dil. H_2SO_4 is quite slow.

(b) Conc. H_2SO_4 is not used because then SO_2 gas is evolved instead of H_2.

(vii) ***Preparation of pure hydrogen***: It can be obtained by

(a) The action of pure dil. H_2SO_4 on pure magnesium ribbon.

$$Mg + H_2SO_4 \rightarrow MgSO_4 + H_2$$

(b) Hydrogen of high purity (> 99.95%) is obtained by electrolysing warm aqueous barium hydroxide between nickel electrodes.

(c) By the action of water on sodium hydride.

$$NaH + H_2O \rightarrow NaOH + H_2\uparrow$$

(d) By the action of *KOH* (aq.) on aluminium.

$$2Al + 2KOH + 2H_2O \rightarrow 2KAlO_2 + 3H_2\uparrow$$

(viii) *Commercial production of dihydrogen*

(a) **Bosch process :** In this method, water gas is mixed with twice its volume of steam and passed over heated catalyst Fe_2O_3 in the presence of a promoter Cr_2O_3 or ThO_2 at 773 *K* when CO_2 and H_2 are obtained. CO_2 is removed by dissolving it in water under pressure (20-25 *atm*) and H_2 left undissolved is collected.

$$C + H_2O \xrightarrow{1270\ K} \underbrace{CO + H_2}_{\text{Water gas}}$$

$$H_2 + CO + H_2O \xrightarrow[Fe_2O_3,\ Cr_2O_3]{773\ K} CO_2 + 2H_2$$

About 18% of the world's production of H_2 is obtained from coal.

(b) **Lane's process :** By passing steam over spongy iron at 773-1050 *K*.

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

The ferrosoferric oxide (Fe_3O_4) so produced is reduced back to iron with water. this reaction is known as **Vivification reactions**

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

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

(c) **By electrolysis of water** : Electrolysis of acidified water using platinum electrodes is used for the bulk preparation of hydrogen.

(d) **From hydrocarbons** : Hydrocarbons (alkanes) react with steam at high temperature to produce carbon monoxide and hydrogen, *e.g.,*

$$CH_4(g) + H_2O(g) \xrightarrow[\text{Catalyst}]{1270\ K} CO(g) + 3H_2(g)$$

The mixture of *CO* and H_2 so obtained can be converted into hydrogen as in Bosch process. About 77% of the world's production of H_2 is obtained from hydrocarbons.

(e) It is also produced as a by-product of the brine electrolysis process for the manufacture of Cl_2 and *NaOH.*

(4) **Physical properties of dihydrogen :** It is a colourless, tasteless and odourless gas. It is slightly soluble in water. It is highly combustible. The Physical constants of atomic hydrogen are,

Atomic radius (pm) – 37

Ionic radius of H^- ion (pm) – 210

Ionisation energy $(kJ\ mol^{-1})$ – 1312

Electron affinity $(kJ\ mol^{-1})$ –72.8

Electronegativity – 2.1

(5) **Chemical properties of dihydrogen :** Dihydrogen is quite stable and dissociates into hydrogen atoms only when heated above 2000 K, $H_2 \xrightarrow{2000\ K} H + H$. Its bond dissociation energy is very high, $H_2 \rightarrow H + H$; $\Delta H = 435.9\ kJ\ mol^{-1}$. Due to its high bond dissociation energy, it is not very reactive. However, it combines with many elements or compounds.

(i) ***Action with metals*** : To forms corresponding hydrides.

$$2Na + H_2 \xrightarrow{Heat} 2NaH\ ;\ Ca + H_2 \xrightarrow{Heat} CaH_2.$$

With transition metals (elements of *d* – block) such as *Pd, Ni, Pt* etc. dihydrogen forms interstitial hydrides in which the small molecules of dihydrogen occupy the interstitial sites in the crystal lattices of these hydrides. As a result of formation of interstitial hydrides, these metals adsorb large volume of hydrogen on their surface. This property of adsorption of a gas by a metal is called ***occlusion.*** The occluded hydrogen can be liberated from the metals by strong heating.

(ii) ***Reaction with Non-metals***

$$2H_2 + O_2 \xrightarrow{970\ K} 2H_2O$$

$$N_2 + 3H_2 \xrightarrow[750\ K,\ \text{Pressure}]{Fe,\ Mo} 2NH_3$$

$$H_2 + F_2 \xrightarrow{Dark} 2HF$$

$$H_2 + Cl_2 \xrightarrow[673\ K,\ \text{Pressure}]{Sunlight} 2HCl$$

$$H_2 + Br_2 \rightarrow 2HBr$$

$$H_2 + I_2 \xrightarrow[Pt]{673\ K} 2HI$$

The reactivity of halogen towards dihydrogen decreases as,

$$F_2 > Cl_2 > Br_2 > I_2$$

As a result, F_2 reacts in dark, Cl_2 in the presence of sunlight, Br_2 reacts only upon heating while the reaction with I_2 occurs in the presence of a catalyst.

(iii) ***Reaction with unsaturated hydrocarbons*** : H_2 reacts with unsaturated hydrocarbons such as ethylene and acetylene to give saturated hydrocarbons.

$$\underset{Ethylene}{H_2C=CH_2}+H_2 \xrightarrow[473\ K]{Ni\ or\ Pt\ or\ Pd} \underset{Ethane}{CH_3-CH_3}$$

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

This reaction is used in the ***hydrogenation or hardening of oils***. The vegetable oils such as groundnut oil or cotton-seed oil are unsaturated in nature because they contain at least one double bond in their molecules. Dihydrogen is passed through the oils at about 473 K in the presence of catalyst to form solid fats. The vegetable ghee such as Dalda, Rath, etc. are usually prepared by this process.

$$\underset{(liquid)}{\text{Vegetable oil}}+H_2 \xrightarrow[473\ K]{Ni} \underset{(solid)}{Fat}$$

(6) **Uses of Dihydrogen**

(i) As a reducing agent

(ii) In the hydrogenation of vegetable oils

(iii) As a rocket fuel in the form of liquid H_2

(iv) In the manufacture of synthetic petrol

(v) In the preparation of many compounds such as NH_3, CH_3OH, Urea etc.

(vi) It is used in the oxy-hydrogen torch for welding if temperature around 2500°C is required. It is also used in atomic hydrogen torch for welding purposes in which temperature of the order of 4000°C is required.

Different forms of hydrogen

(1) **Atomic hydrogen :** It is obtained by the dissociation of hydrogen molecules. The atomic hydrogen is stable only for a fraction of a second and is extremely reactive. It is obtained by passing dihydrogen gas at atmospheric pressure through an electric arc struck between two tungsten rods.

The electric arc maintains a temperature around 4000 – 4500°C. As the molecules of dihydrogen gas pass through the electric arc, these absorb energy and get dissociated into atoms as

$$H_2(g) \xrightarrow[arc]{Electric} 2H(g) : \Delta H = 435.90 KJ\ mol^{-1}$$

This arrangement is also called atomic hydrogen torch.

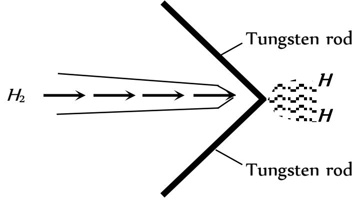


Fig. 17.1 Atomic hydrogen torch

(2) **Nascent hydrogen :** The hydrogen gas prepared in the reaction mixture in contact with the substance with which it has to react, is called nascent hydrogen. It is also called newly born hydrogen. It is more reactive than ordinary hydrogen. For example, if ordinary hydrogen is passed through acidified $KMnO_4$ (pink in colour), its colour is not discharged. On the other hand, if zinc pieces are added to the same solution, bubbles of hydrogen rise through the solution and the colour is discharged due to the reduction on $KMnO_4$ by nascent hydrogen.

$$KMnO_4 + \underset{Molecular}{H_2} + H_2SO_4 \rightarrow No\ reaction$$

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + \underset{Nascent\ hydrogen}{2[H]}$$

$$2KMnO_4 + 3H_2SO_4 + 10[H] \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O$$

(3) **Ortho and para hydrogen :** A molecule of dihydrogen contains two atoms. The nuclei of both the atoms in each molecule of dihydrogen are spinning. Depending upon the direction of the spin of the nuclei, the hydrogen is of two types,

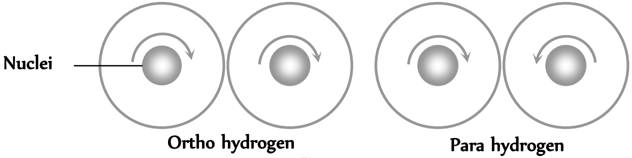


Fig. 17.2

(i) Molecules of hydrogen in which the spins of both the nuclei are in the same directions, called ortho hydrogen.

(ii) Molecules of hydrogen in which the spins of both the nuclei are in the opposite directions, called para hydrogen.

Ordinary dihydrogen is an equilibrium mixture of ortho and para hydrogen. Ortho hydrogen $\rightleftharpoons$ Para hydrogen. The amount of ortho and para hydrogen varies with temperature as,

(a) At 0°K, hydrogen contains mainly para hydrogen which is more stable.

(b) At the temperature of liquefaction of air, the ratio of ortho and para hydrogen is 1:1.

(c) At the room temperature, the ratio of ortho to para hydrogen is 3:1.

(d) Even at very high temperatures, the ratio of ortho to para hydrogen can never be more than 3:1.

Thus, it has been possible to get pure para hydrogen by cooling ordinary hydrogen gas to a very low temperature (close to 20 K) but it is never possible to get a sample of hydrogen containing more than 75% of ortho hydrogen. i.e., Pure ortho hydrogen can not be obtained.

(4) **Hydrides :** Hydrogen forms binary hydrides of the type MH_x or M_mH_n with

(a) All main group elements except noble gases and probably indium and thallium.

(b) All lanthanoids and actinoids.

(c) Transition metals (*Sc*, *Y*, *La*, *Ac*, *Tc*, *Zr*, *Hf* and to a lesser extent *V*, *Nb*, *Ta*, *Cr*, *Cu* and *Zn*). In group 6 only *Cr* forms hydride (*CrH*).

Hydrides are classified into three main categories.

(i) ***Saline or ionic hydrides*** : Most of the *s*-block metals form this type of hydrides. These are non-volatile, non-conducting crystalline solids. However, BeH_2 and MgH_2 have covalent polymeric structure. These ionic hydrides have rock-salt structure. Thermal stability of 1st and 2nd group hydrides are in the order;

$LiH > NaH > KH > RbH > CsH$

$$CaH_2 > SrH_2 > BaH_2$$

BeH_2, MgH_2 and LiH have significant covalent character.

Electrolysis of solution of saline hydride in molten alkali halide produces H_2 at anode. Saline hydrides react explosively with water.

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

The fire so produced cannot be extinguished by CO_2 as it gets reduced by the hot metal hydride. Only sand is useful, as it is a solid.

Alkali metal hydrides are used for making $LiAlH_4$, $NaBH_4$ etc. Alkali metal hydrides are also used for the removal of last traces of water from organic compounds.

(ii) ***Metallic or interstitial hydrides*** : Elements of groups 3, 4, 5 (*d*-block) and *f*-block elements form metallic hydrides. In group 6, only *Cr* forms hydride (*CrH*). Metals of group 7, 8, 9 do not form hydrides. This region of periodic table from group 7 to group 9 is known as hydride gap. Examples of hydrides of group 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

The *f*-block metals form hydrides of limiting compositions of MH_2 and MH_3. All these hydrides are non-stoichiometric with variable composition *e.g.*,

$$ZrH_x (1.30 \le x \le 1.75),\ TiH_x (1.8 \le x \le 2.0).$$

Most of these hydrides are good conductors of electricity in solid state.

Metallic hydrides can be used to store hydrogen especially in cars working on fuel cells.

(iii) ***Molecular or covalent hydrides*** : Hydrogen form molecular compounds with *p*-block elements (*B, C, N, O, F, Si, P, S, Cl, Ga, Ge, As, Sb, Br, In, Sn, Sb, Te, I, Tl, Pb, At*). common examples of such hydrides are CH_4, NH_3, H_2O, HF etc. The stability of these hydrides decreases down the group. For example, $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$. In a period the stability increases with increasing electronegativity. For example, $CH_4 < NH_3 < H_2O < HF$. Molecular hydrides are classified as electron rich, electron precise and electron deficient hydrides.

(a) *Electron rich molecular hydrides* : These hydrides have one or more lone pairs of electrons around the central more electronegative element. For example

$$H-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-H\ ,\ \ H-\overset{\cdot\cdot}{\underset{\underset{H}{|}}{N}}-H\ ,\ \ H-\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:$$

(b) *Electron precise molecular hydrides* : Elements of group 14 form such hydrides. The bond length increases on going down the group. A common example of electron precise molecular hydrides is CH_4.

(c) *Electron deficient molecular hydrides* : These hydrides have lesser number of electrons than that required for writing the conventional Lewis structure. A common example of such molecular hydride is diborane, B_2H_6.

(d) *Systematic names of molecular hydrides* : The systematic names of these hydrides are obtained from the name of the element and the suffix –ane. For example,

PH_3	H_2O	NH_3
Phosphane	oxidane	ozane

Isotopes of Hydrogen

Isotopes are the different forms of the same element, which have the same atomic number but different mass numbers.

Table 17.1 *Isotopes of hydrogen*

Name	Symbol	Atomic number	Mass number	Relative abundance	Nature radioactive or non-radioactive
Protium or Hydrogen	^1_1H or H	1	1	99.985%	Non-radioactive
Deuterium	^2_1H or D	1	2	0.015%	Non-radioactive
Tritium	^3_1H or T	1	3	10^{-15} %	Radioactive

Table 17.2 *Physical constants of H_2, D_2 and T_2*

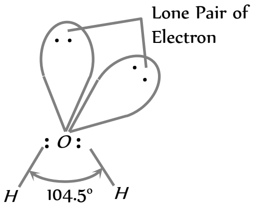
Property	H_2	D_2	T_2
Molecular mass	2.016	4.028	6.03
Melting point (*K*)	13.8	18.7	20.63
Boiling point (*K*)	20.4	23.9	25.0
Heat of fusion $(kJ\ mol^{-1})$	0.117	0.197	0.250
Heat of vaporisation $(kJ\ mol^{-1})$	0.994	1.126	1.393
Bond energy $(kJ\ mol^{-1})$	435.9	443.4	446.9

Isotopic effect : In general chemical properties of isotopes are same but quantiative differences are noticed amongst them. For example, the reaction between H_2 and Cl_2 is 13.4 times faster between D_2 and Cl_2 under similar conditions. Such differences in chemical properties, which are due to difference in the mass numbers of isotopes is known as isotopic effect.

Water

Water is the oxide of hydrogen. It is an important component of animal and vegetable matter. Water constitutes about 65% of our body. It is the principal constituent of earth's surface.

(1) **Structure :** Due to the presence of lone pairs, the geometry of water is distorted and the $H-O-H$ bond angle is 104.5°, which is less than the normal tetrahedral angle (109.5°). The geometry of the molecule is regarded as angular or bent. In water, each $O-H$ bond is polar because of the high electronegativity of oxygen (3.5) in comparison to that of hydrogen (2.1). The resultant dipole moment of water molecule is 1.84D.



In ice, each oxygen atom is tetrahedrally surrounded by four hydrogen atoms; ***two by covalent bonds and two by hydrogen bonds***. The resulting structure of ice is open structure having a number of vacant spaces. Therefore, the density of ice is less than that of water and ice floats over water. It may be noted that water has maximum density $(1 g\, cm^{-3})$ at $4°C$ $(277\ K)$.

(2) **Heavy water :** Chemically heavy water is deuterium oxide (D_2O). It was discovered by ***Urey***.

It is obtained as a by-product in some industries where H_2 is produced by the electrolysis of water.

Heavy water (D_2O) is used (a) as a moderator and coolant in nuclear reactors (b) in the study of mechanism of chemical reactions (c) as a starting material for the preparation of a number of deuterium compounds, *e.g.,*

$$SO_3 + D_2O \rightarrow \underset{\text{Deuteriosulphuric acid}}{D_2SO_4}$$

$$Al_4C_3 + 12D_2O \rightarrow \underset{\text{Deuteromethane}}{3CD_4} + 4Al(OD)_3$$

$$CaC_2 + 2D_2O \rightarrow \underset{\text{Deuterioacetylene}}{C_2D_2} + Ca(OD)_2$$

(3) **Physical properties :** Water is colourless, odourless and tasteless liquid at ordinary temperature.

At $273K$ water is in equilibrium with ice and vapour this point is known triple point.

Table 17.3 ***Some physical constants of H_2O and D_2O at 298 K***

Constant	**Ordinary water H_2O**	**Heavy water D_2O**
Molecular mass	18.015	20.028
Maximum density $(g\, cm^{-3})$	1.000	1.106
Melting point (K)	273.2	276.8
Boiling point (K)	373.2	374.4
Heat of fusion $(kJ\ mol^{-1})$ at $273K$	6.01	6.28
Heat of vaporisation $(kJ\ mol^{-1})$ at $373K$	40.66	41.61
Heat of formation $(kJ\ mol^{-1})$	– 285.9	– 294.6
Ionisation constant	1.008×10^{-14}	1.95×10^{-15}

(4) **Chemical properties :** Water shows a versatile chemical behaviour. It behaves as an acid, a base, an oxidant, a reductant and as ligand to metals.

(i) ***Dissociation of water*** : Water is quite stable and does not dissociate into its elements even at high temperatures. Pure water has a small but measurable electrical conductivity and it dissociates as,

$$H_2O + H_2O \rightleftharpoons \underset{\text{Hydronium ion}}{H_3O^+} + OH^-$$

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

(ii) ***Amphoteric nature*** : Water can act both as an acid and a base and is said to be amphoteric. However, water is neutral towards litmus and its *p*H is 7.

(iii) ***Oxidising and reducing nature*** : Water can act both as an oxidising and a reducing agent in its chemical reactions. e.g.

$$2Na + \underset{\text{Oxidising agent}}{2H_2O} \rightarrow 2NaOH + H_2$$

$$2F_2 + \underset{\text{Reducing agent}}{2H_2O} \rightarrow 4HF + O_2$$

(iv) ***Hydrolytic reactions*** : Water can hydrolyse many oxides, halides, hydrides, carbides, nitrides, phosphides, carbonates etc. to give an acid or a base or both as shown below :

$$SO_2 + H_2O \rightarrow H_2SO_3$$

$$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$$

$$CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2$$

$$CaO + H_2O \rightarrow Ca(OH)_2$$

$$Na_2CO_3 + 2H_2O \rightarrow 2NaOH + H_2CO_3$$

$$SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4HCl$$

$$Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$$

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

(v) ***Water forms hydrates with metal salts*** : There are three main types of hydrates.

(a) Compounds in which water molecule are co-ordinated to the metal ion (complex compounds) $[Ni(OH_2)](NO_3)_2$, $Fe(OH_2)_6]Cl_3$ etc.

(b) Compound in which water molecule may be hydrogen bonded to oxygen to form oxo-anion. For example in $CuSO_4.5H_2O$, 4 molecules of water are co-ordinated to Cu^{2+} while the fifth molecule is hydrogen bonded to SO_4^{2-} ion.

(c) In some compounds, water molecule occupies, interstitial sites in the crystal lattice *e.g.,* $BaCl_2.2H_2O$.

(5) **Hard and Soft water**

Water which produces lather with soap solution readily is called ***soft water***. e.g. distilled water, rain water and demineralised water.

Water which does not produce lather with soap solution readily is called ***hard water***. e.g. sea water, river water, well water and tap water.

(i) ***Cause of hardness of water*** : The hardness of water is due to the presence of bicarbonates, chlorides and sulphates of calcium and magnesium.

Hard water does not produce lather because the cations $(Ca^{+2}$ and $Mg^{+2})$ present in hard water react with soap to form insoluble precipitates,

$$\underset{\text{From hard water}}{M^{+2}} + \underset{\text{Sodium stearate(soap)}}{2C_{17}H_{35}COONa} \rightarrow \underset{\text{Metal stearate(PPt.)}}{(C_{17}H_{35}COO)_2M} + 2Na^+$$

Where *M* = *Ca* or *Mg*

Therefore, no lather is produced until all the calcium and magnesium ions are precipitated. This also results into wastage of lot of soap.

(ii) ***Type of hardness of water*** : The hardness of water is of two types,

(a) *Temporary hardness* : This is due to the presence of bicarbonates of calcium and magnesium. It is also called carbonate hardness.

(b) *Permanent hardness* : This is due to the presence of chlorides and sulphates of calcium and magnesium. It is also called non-carbonate hardness.

(iii) ***Softening of water*** : The process of the removal of hardness from water is called softening of water.

(a) *Removal of temporary hardness* : It can be removed by the following methods,

- By boiling : During boiling, the bicarbonates of *Ca* and *Mg* decompose into insoluble carbonates and give CO_2. The insoluble carbonates can be removed by filtration.

$$\underset{\text{Cal.bicarbonate}}{Ca(HCO_3)_2} \xrightarrow{Heat} \underset{\text{PPt.}}{CaCO_3} + CO_2 + H_2O$$

$$\underset{\text{Mag.bicarbonate}}{Mg(HCO_3)_2} \xrightarrow{Heat} \underset{\text{PPt.}}{MgCO_3} + CO_2 + H_2O$$

- Clark's method : This process is used on a commercial scale. In this process, calculated amount of lime $[Ca(OH)_2]$ is added to temporary hard water.

$$\underset{\text{Soluble}}{Ca(HCO_3)_2} + \underset{\text{Lime}}{Ca(OH)_2} \longrightarrow \underset{\text{Insoluble}}{2CaCO_3} \downarrow + 2H_2O$$

$$\underset{\text{Soluble}}{Mg(HCO_3)_2} + \underset{\text{Lime}}{Ca(OH_2)} \longrightarrow \underset{\text{(Insoluble)}}{MgCO_3 \downarrow + CaCO_3} \downarrow + 2H_2O$$

(b) *Removal of permanent hardness* : Permanent hardness can be removed by the following methods,

- By washing soda method : In this method, water is treated with a calculated amount of washing soda (Na_2CO_3) which converts the chlorides and sulphates of *Ca* and *Mg* into their respective carbonates which get precipitated.

$$CaCl_2 + Na_2CO_3 \longrightarrow \underset{ppt.}{CaCO_3} + 2NaCl$$

$$MgSO_4 + Na_2CO_3 \longrightarrow \underset{ppt.}{MgCO_3} + Na_2SO_4$$

- Permutit method : This is a modern method employed for the softening of hard water. hydrated sodium aluminium silicate $(Na_2Al_2Si_2O_8.xH_2O)$ is called permutit. These complex salts are also known as zeolites.

The permutit as loosely packed in a big tank over a layer of coarse sand. Hard water is introduced into the tank from the top. Water reaches the bottom of the tank and then slowly rises through the permutit layer in the tank. The cations present in hard water are exchanged for sodium ions. Therefore this method is also called ion exchange method.

$$\underset{\substack{\text{Sodium}\\ \text{zeolite}}}{Na_2Z} + \underset{\substack{\text{(From hard}\\ \text{water)}}}{Ca^{+2}} \longrightarrow \underset{\substack{\text{Cal}\\ \text{zeolite}}}{CaZ} + 2Na^+$$

$$\underset{\substack{\text{Sodium}\\ \text{zeolite}}}{Na_2Z} + \underset{\substack{\text{(From hard}\\ \text{water)}}}{Mg^{+2}} \longrightarrow \underset{\substack{\text{Magnesium}\\ \text{zeolite}}}{MgZ} + 2Na^+$$

where $Z = Al_2Si_2O_8.\ xH_2O$

Hydrogen peroxide

Hydrogen peroxide (H_2O_2) was discovered by French chemist ***Thenard***.

(1) **Preparation :** It is prepared by

(i) ***Laboratory method*** : In laboratory, H_2O_2 is prepared by Merck's process. It is prepared by adding calculated amounts of sodium peroxide to ice cold dilute (20%) solution of H_2SO_4.

$$Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$$

(ii) By the action of sulphuric acid or phosphoric acid on hydrated barium peroxide $BaO_2.8H_2O$

(a) $BaO_2.8H_2O + H_2SO_4 \rightarrow BaSO_4 \downarrow + H_2O_2 + 8H_2O$

It must be noted that anhydrous barium peroxide does not react readily with sulphuric acid (because a coating of insoluble barium sulphate is formed on its surface which stops further action of the acid). Therefore, hydrated barium peroxide, $BaO_2.8H_2O$ must be used.

(b) $3BaO_2 + 2H_3PO_4 \rightarrow Ba_3(PO_4)_2 + 3H_2O_2$

$$Ba_3(PO_4)_2 + 3H_2SO_4 \rightarrow 3BaSO_4 + 2H_3PO_4$$

Phosphoric acid is preferred to H_2SO_4 because soluble impurities like barium persulphate (from $BaO_2.8H_2O + H_2SO_4$) tends to decompose H_2O_2 while H_3PO_4 acts as preservative (negative catalyst) for H_2O_2.

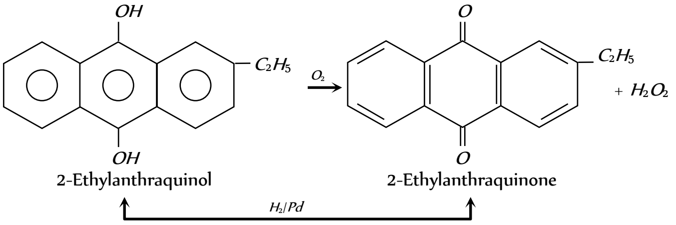
(iii) ***Industrial method*** : On a commercial scale, H_2O_2 can be prepared by the electrolysis of 50% H_2SO_4 solution. In a cell, peroxy disulphuric acid is formed at the anode.

$$2H_2SO_4 \xrightarrow[\text{Elecrolysis}]{} \underset{\substack{\text{Peroxy disulphuric}\\ \text{acid}}}{H_2S_2O_8(aq.)} + H_2(g)$$

This is drawn off from the cell and hydrolysed with water to give H_2O_2.

$H_2S_2O_8 + 2H_2O \longrightarrow 2H_2SO_4 + H_2O_2$ The resulting solution is distilled under reduced pressure when H_2O_2 gets distilled while H_2SO_4 with high boiling point, remains undistilled.

(iv) ***By redox process*** : Industrially H_2O_2 is prepared by the auto-oxidation of 2-alkylanthraquinols. The process involves a cycle of reactions. The net reaction is the catalytic union of H_2 and O_2 to give H_2O_2.



The H_2O_2 formed (about 1%) is extracted with water and concentrated.

(2) **Physical properties**

(i) Pure hydrogen peroxide is a pale blue syrupy liquid.

(ii) It freezes at $-0.5°C$ and has a density of 1.4 in pure state.

(iii) Hydrogen peroxide is diamagnetic.

(iv) It is more highly associated via hydrogen bonding than water.

(v) Although it is a better polar solvent than H_2O. However, it can't be used as such because of strong autooxidation ability.

(vi) Dipole moment of H_2O_2 is 2.1 *D*.

(3) **Chemical properties**

(i) ***Decomposition*** : Pure H_2O_2 is an unstable liquid and decomposes into water and O_2 either upon standing or upon heating,

$$2H_2O_2 \longrightarrow 2H_2O + O_2;\ \Delta H = -196.0\,kJ$$

(ii) ***Oxidising nature*** : It is a powerful oxidising agent. It acts as an oxidising agent in neutral, acidic or in alkaline medium. *e.g.*

$2KI + H_2O_2 \longrightarrow 2KOH + I_2$ [In neutral medium]

$2FeSO_4 + H_2SO_4 + H_2O_2 \longrightarrow Fe_2(SO_4)_3 + 2H_2O$ [In acidic medium]

$MnSO_4 + H_2O_2 + 2NaOH \longrightarrow MnO_2 + Na_2SO_4 + 2H_2O$ [In alkaline medium]

(iii) ***Reducing nature*** : H_2O_2 has tendency to take up oxygen from strong oxidising agents and thus, acts as a reducing agent, $H_2O_2 + \underset{\text{From oxidising agent}}{O} \longrightarrow H_2O + O_2$. It can act as a reducing agent in acidic, basic or even neutral medium.

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

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

(iv) ***Bleaching action*** : H_2O_2 acts as a bleaching agent due to the release of nascent oxygen.

$$H_2O_2 \longrightarrow H_2O + O$$

Thus, the bleaching action of H_2O_2 is due to oxidation. It oxidises the colouring matter to a colourless product, Colouring matter $+O \rightarrow$ Colour less matter.

H_2O_2 is used to bleach delicate materials like ivory, silk, wool, leather etc.

(v) ***Acidic nature*** : Anhydrous hydrogen peroxide is acidic in character $(K_a = 1.55 \times 10^{-12}$ at 298 *K*). its dissociation in aqueous solution may be given as

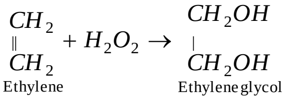
$$H_2O_2 + H_2O \rightarrow H_3O^+ + HO_2^-$$

It forms two types of salts

$$NaOH + H_2O_2 \rightarrow \underset{\substack{\text{Sod. hydroperoxide}\\ \text{(Acidic salt)}}}{NaHO_2} + H_2O$$

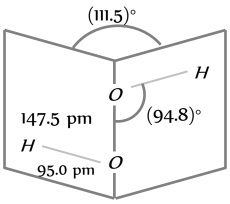
$$2NaOH + H_2O_2 \rightarrow \underset{\substack{\text{Sod. peroxide}\\ \text{(Normal salt)}}}{Na_2O_2} + 2H_2O$$

(vi) ***Addition reactions*** : Hydrogen peroxide is capable of adding itself to ethylenic linkage.

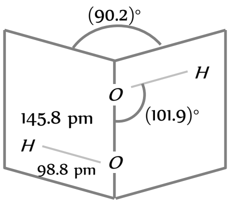


$$\underset{\text{Ethylene}}{\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix}} + H_2O_2 \rightarrow \underset{\text{Ethylene glycol}}{\begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix}}$$

(4) **Structure of H_2O_2 :** Hydrogen peroxide is non-linear, non-planar molecule. It has a open book structure. The $-O-O-$ linkage is called peroxy linkage. The structure is shown below.



In gas phase



In solid phase (110 *K*)

(5) **Concentration of H_2O_2 :** Dilute H_2O_2 is concentrated to about 50% by slow evaporation on a water bath. It is further concentrated to 90% in a vacuum desiccator using conc. H_2SO_4 as dehydrating agent. Further concentration to 99% is obtained by distillation under reduced pressure. Last traces of moisture in 99% of H_2O_2 are removed or anhydrous H_2O_2 is obtained by cooling it to 263 *K* in a cold bath of ether and dry ice followed by seeding with a few crystals of solid H_2O_2 when needle-shaped crystals of 100% H_2O_2 separate out. These crystals are removed, dried and melted to get 100% H_2O_2.

(6) **Storage of H_2O_2 :** H_2O_2 is not stored in glass bottles since the alkali metal oxides present in glass catalyse its decomposition. It is, therefore, stored in paraffin wax coated glass, plastic or teflon bottles. Small amounts of acid, glycerol, alcohol, acetanilide and H_3PO_4 are often used as stablizers to check its decomposition.

Uses of hydrogen peroxide

(i) For bleaching delicate articles like wool, hair, feather, ivory, etc.

(ii) For restoring colour of old lead paintings whose white lead has blackened due to formation of *PbS* by H_2S of atmosphere. Hydrogen peroxide converts the black lead sulphide to white lead sulphate

(iii) As an aerating agent in production of spong rubber.

(iv) As an antiseptic and germicide for washing wounds, teeth and ears, under the name of perhydrol.

(v) In the manufacture of sodium perborate, sodium percarbonate. These are used in high quality detergents.

(vi) As an antichlor.

(vii) As an oxidant for rocket fuel.

(viii) In the detection of *Ti*, *V* and *Cr* ions with which it forms peroxides of characteristics colours.

(ix) In the production of epoxides, propylene oxide and polyurethanes.

(x) In the synthesis of hydroquinone, pharmaceuticals (cephalosoporin) and food products like tartaric acid.

(xi) For pollution control of domestic effluents where it restores the aerobic conditions of sewage wastes. For pollution control of industrial effluents containing CN^- ions. H_2O_2 oxidises CN^- ions to harmless products.

T Tips & Tricks

✍ Hydrogen forms more compounds than even carbon.

✍ Metals like *Pd, Pt, Au* etc., have the property of absorbing large quantity of hydrogen at normal or higher temperature. Colloidal *Pd* can absorb 2950 times its own volume of hydrogen and *Pd* metal can absorb 900 times its own volume of hydrogen.

This phenomenon is known as occlusion of hydrogen. the occlusion property of these metals is in the order

Colloidal Palladium > Palladium > Platinum > Gold > Nickel.

✍ In solids, water molecules can also be present as zeolite water and clathrate water.

✍ Ice is a good thermal insulator.

✍ 30% H_2O_2 is called perhydrol. Its volume strength is 100 and molarity is 8.8.

OT Ordinary Thinking

Objective Questions