# Wisdom Education Academy

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It was discovered by Henry Cavendish in 1766 by the action of dilute H<sub>2</sub>O<sub>4</sub> on iron. It was named 'inflammable air', Lavoisier gave it the name hydrogen (Creek: Hydra = water, gennas = producer]. It occurs in free state as well as in combined state.

#### Position of Hydrogen in the Periodic Table

Hydrogen resembles with alkali metals (group I) as well as halogens (group 17), At the same time, it differs from both in certain characteristics. That is why hydrogen if; called "rogue element".

However, it has been placed in group 1 on the basis of its configuration 1s<sup>1</sup>, which is the basis of modern classification of elements.

#### **Isotopes of Hydrogen**

Hydrogen exists in the form of three sotopes:

Name	Symbol	Atomic number	Relative a atomic mass	Density	Relative abundance	Nature
Protium	H or H	1	1.0078	0.09	99.98%	Non-radioactive
Deuterium	<sup>2</sup> H or D	1	2.0141	0.18	0.0156%	Non-radioactive
Tritium	³H or T	1	3.016	0.27	10 <sup>-15</sup> %	Radioactiva (emits 3 rays) $t_{1/2} = 12.33$ year)

Dihdrogen [H<sub>2</sub>]

**Methods of Preparation** 

(a) Lab pletbods

(i) 
$$Zn+H_2SO_4(aq) \longrightarrow ZnSO_4(aq)+H_2(g)$$
  
dilute

Metals which have reduction potential lesser than H, can liberate H<sub>2</sub> from acids.

Pure zinc is not used because it reacts slowly. The presence of some impurities increases the rate of reaction due to the

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formation of electrochemical couples Cone sulphuric acid is also not used because it oxidises, H<sub>2</sub>formed into H<sub>2</sub>O.

 $Zn + 2H_2SO_4(conc.) \rightarrow ZnSO_4 + SO_2 + 2H_2O$ 

(ii) It can also be prepared by the reaction of zinc with aqueous alkali.

$$Zn + 2NaOH \xrightarrow{\Lambda} Na_2ZnO_2 + H_2$$
sodium zincate

- b) Commercial production of dihydrogen
- (i) By the electrolysis of acidified water

$$H_2O \rightleftharpoons H^+ + OH^-$$
 (Ionisation)

At cathode,  $H^+ + e^- \longrightarrow H^*$  (Reduction)

 $H^* + H^* \longrightarrow H_2$ 

At anode,  $4OH^- \longrightarrow 4OH + 4e^-$  (Oxidation)

 $4OH \longrightarrow 2H_2O + O_2$ 

ii) From water gas (Bosch process)

$$\underbrace{\text{CO} + \text{H}_2}_{\text{water gas}} + \underbrace{\text{H}_2\text{O}}_{\text{steam}} \xrightarrow{\text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3} \text{CO}_2 \uparrow + 2\text{H}_2$$

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

(iii) From steam (Lane's process) Super heated steam is passed over iron filings heated to about 1023-1073 K when hydrogen is formed.

$$3\text{Fe} + 4\text{H}_2\text{O} \text{ (steam)} \xrightarrow{1023-1078 \text{ K}} \text{Fe}_3\text{O}_4 + 4\text{H}_2$$

- (iv) Highly pure (> 99.95%)dihydrogen is obtained by electrolysing warm aqueous barium hydroxide solution between nickel electrodes.
- (v) From hydrocarbons by partial oxidation

$$CH_4$$
 +  $H_2O$   $\xrightarrow{\text{Ni-Cr catalyst}}$   $CO + 3H_2$ 

vi) It is also obtained as a by-product in the manufacture of NaOH and chlorine hy the electrolysis of brine solution.

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During electrolysis, the reactions that take place are

At anode, 
$$2Cl(aq) \longrightarrow Cl_2(g) + 2e^-$$

At cathode, 
$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$$

The overall reactions by adding spectator Na ions,

$$2Na^{+}(aq) + 2Cl(aq) + 2H_2O(l) \longrightarrow$$

$$Cl_2(g) + H_2(g) + 2Na^+ + 2OH(aq)$$

#### **Physical Properties of Dihydrogen**

Dihydrogen is a colourless, odourless, tasteless, combustible gas. It is lighter than air and insoluble in water. It is neutral to litmus.

#### **Chemical Properties of Dlhydrogen**

(i) **Reactivity** The relative inertness of dihydrogen at room temperature is because of Its high enthalpy of H-H bond i.e., high bond dissociation energy. So its reactions take place under specific conditions only (at high temperature).

(ii) Action with non-metals

$$2H_2 + O_2 \xrightarrow{970 \text{ K}} 2H_2O(l); \Delta H^\circ = -285.9 \text{ kJ mol}^{-1}$$

$$N_2 + 3H_2 \xrightarrow{673 \text{ K/200 atm}} 2NH_3(g); \Delta H^\circ = -92.6 \text{ kJ mol}^{-1}$$

$$H_2 + X_2 \xrightarrow{Dark} 2HX$$
 (where, X represents halogens)

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Order of reactivity of halogens:

$$F_2 > Cl_2 > Br_2 > I_2$$

(iii) Reaction with metals Here H<sub>2</sub> acts as oxidising agent.

$$2Na + H_2 \xrightarrow{\Delta} 2NaH$$

$$Ca + H_2 \xrightarrow{\Delta} CaH_2$$
 (Hydrolith)

(iv) Reducing action of dihydrogen

$$CuO + H_2 \xrightarrow{\Delta} Cu + H_2O$$

(v) Reactions with metal ions and metal oxides

$$H_2(g) + Pd^{2+}(aq) \longrightarrow Pd(s) + 2H^+(aq)$$
  
 $yH_2(g) + M_xO_y(s) \longrightarrow xM(s) + yH_2O(l)$ 

(vi) Reaction with organic compounds

(i) Veg. oil + H<sub>2</sub> 
$$\xrightarrow{\text{Ni/400K}}$$
 Veg. ghee  
(ii)  $R$ —CH =CH<sub>2</sub> + H<sub>2</sub> + CO  $\xrightarrow{\text{[Co(CO)}_4]_2}$   $R$ CH<sub>2</sub>CH<sub>2</sub>CHO  
 $R$ CH<sub>2</sub>CH<sub>2</sub>CHO + H<sub>2</sub>  $\xrightarrow{\text{Ni}}$   $R$ CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH

Uses of Dihydrogen

- 1. It is used in the manufacture of CH<sub>3</sub>OH.
- 2. It produces temperature of 2850°C and oxy-atomic hydrogen flame produces a temperature of 4000°C, so it is used in oxy-hydrogen flame.
- 3. The largest single use of H<sub>2</sub> is in the synthesis of NH<sub>3</sub> which is used in the manufacture of HNO<sub>3</sub> and fertilizers.
- 4. Liquid hydrogen (LH<sub>2</sub>) is used as rocket fuel.
- 5. H<sub>2</sub> is used as a reducing agent in extraction of metals.
- 6. H<sub>2</sub> is used in fuel cell for generating electrical energy.
- 7. Hydrogen is used in the manufacture of synthetic petrol.

(By heating H<sub>2</sub> with coal and heavy oils under very high pressure in the presence of catalyst.)

### **Different Forms of Hydrogen**

**Atomic Hydrogen** 

$$H_2 \xrightarrow{\text{Electric arc}} 2H; \qquad \Delta H = 105.4 \text{ kcal mol}^{-1}$$

It is very reactive and its half-life period is 0.33 s.

#### **Nascent Hydrogen**

Freshly prepared hydrogen is known as nascent hydrogen and is more reactive than ordinary hydrogen. It causes the reduction of certain compounds which IS not possible with ordinary hydrogen. It can never be isolated.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + 2[H]$$

Activity of nascent H depends upon the reaction by which it is obtained.

#### **Adsorbed Hydrogen**

Adsorption of hydrogen at the metal surface is called occlusion. This hydrogen brings out many chemical changes such as reduction and hydrogenation. Occlusion decreases with rise in temperature.

#### Ortho and Para Hydrogen

When in hydrogen molecule, the nuclear spins are in the same direction, it is known as ortho hydrogen. On the other hand when the nuclear spins arc in the opposite direction, it is known as para hydrogen. At room temperature hydrogen consists of 75% ortho and 25% para hydrogen.

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Para hydrogen

#### **Hydrogen Economy**

Hydrogen economy is the use of liquid hydrogen as an alternate source of energy. The technology involves the production, transportation and storage of energy in the form of liquid hydrogen. Large scale production of hydrogen can be done by electrolysis of water or by thermochemical reaction cycle. Storage of hydrogen in liquid form can be done in vacuum insulated cryogenic tanks or in a metal or in all alloy like iron-titanium alloy as interstitial hydride. Hydrogen fuel has many advantage over conventional fuels in that it is non-polluting and it liberates large amount of energy on combustion.

Photohydrogen is used to obtain renewable energy from sunlight by using microscopic organism such as bacteria or algae.

#### **Hydrides**

The compounds of hydrogen with metals and non-metals are called hydrides.

#### **Ionic Hydrides**

These are formed by elements of group I, II, (except Be and Mg) by heating them in hydrogen.

These are white colourless solids (crystalline) having high m.p. and b.p. easily decomposed by water, CO<sub>2</sub> or SO<sub>2</sub>.

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

 $CaH_2 + 2CO_2 \rightarrow (HCOO)_2Ca$ 

They are strong reducing agents. Alkali metal hydrides are used for making LiAlH<sub>4</sub>, NaBH<sub>4</sub>, etc and for removing last traces of water from organic compounds.

#### **Molecular or Covalent Hydrides**

These are formed by elements of p-block having higher electronegativity than hydrogen.

- 1. **Electron deficient hydrides** These are the hydrides which do not have sufficient number of electrons needed to form normal covalent bonds, e.g., BH<sub>3</sub>, AlH<sub>3</sub>, etc.
- 2. **Electron precise hydrides** These are the hydrides which have exact number of electrons needed to form normal covalent bonds. e.g. hydrides of group 14 (CH<sub>4</sub>, SiH<sub>4</sub>, etc.)
- 3. **Electron rich hydrides** These are the hydrides which have greater number of electrons than required to form normal covalent bonds. e.g., hydrides of group 15, 16, 17, (NH<sub>3</sub>, PH<sub>3</sub>, H<sub>2</sub>S, HF, HCl, etc). The excess electrons in these hydrides are present as lone pairs of electrons.

#### **Metallic or Interstitial Hydrides**

The transition metals and rare earth metals combine with hydrogen to from interstitial hydrides. They exhibit metallic properties and are powerful reducing agents. They are non-stoicluometric hydrides and their composition varies with temperature and pressure for e.g., LaH<sub>2.76</sub>, TiH<sub>1.73</sub>.

Metals of group 7, 8 and 9 do not form hydrides and this region of the Periodic Table is called hydride gap.

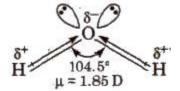
#### **Polymeric Hydrides and Complex Hydrides**

Polymeric hydrides are formed by' elements having electronegativity in the range 1.4 to 2.0, e.g., (BeH<sub>2</sub>)<sub>n</sub>, (AlH<sub>3</sub>)<sub>n</sub>, etc. In complex hydrides H<sup>-</sup> acts as ligand and is attached to central metal atom, e.g., LiAlH<sub>4</sub>, LiBH<sub>4</sub>, etc.

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Water

Water is the most abundant and widely distributed on the earth. It occurs in all the three physical states. H<sub>2</sub>O is a covalent molecule in which oxygen is sp<sup>3</sup> hybridised. It has bent structure.



#### **Physical Properties of Water**

- 1. Water is a colourless, odourless, tasteless liquid. It has abnormally high b.p., f.p., heat of vaporisation due to hydrogea bonding.
- 2. Pure water is not a good conductor so it is made conductor by adding small amount of acid or alkali.
- 3. Density of ice (which is mass per unit volume) is lesser than that of water and it floats over water.
- 4. Water has maximum density at 4°0.
- 5. Water is a highly polar solvent with high dielectric constant 78.39. It interacts with polar or ionic substances effectively with the release of considerable amount of energy due to ion dipole interaction. The dissolution of covalent compounds like urea, glucose and C<sub>2</sub>H<sub>5</sub>OH, etc is due to the tendency of these molecules to form hydrogen bond with water.

#### **Chemical Properties of Water**

1. Water is amphoteric in nature.

$$H_2O(l) + HCl(aq) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$$
base acid acid base

 $H_2O(l) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ 
acid base acid base

2. In redox reactions, water reacts with metals and non- metals both.

$$2\text{Na}(s) + 2\text{H}_2\text{O}(l) \longrightarrow 2\text{NaOH}(aq) + \text{H}_2(g)$$
  
 $2\text{F}_2(g) + 2\text{H}_2\text{O}(l) \longrightarrow 4\text{H}^+ + 4\text{F}^- + \text{O}_2(g)$ 

- 3. **In hydrated salts**, water may remain in five types such as coordinated water, hydrogen bonded water, lattice water, clathrate water and zeolite water.
- 4. A number of compounds such as calcium hydride, calcium phosphide. etc., undergo hydrolysis with water.

#### **Purification of Water**

It involves two processes

- 1. Removal of suspended impurities
- 2. Destroying the bacteria.

Suspended particles are removed by coagulation with alum followed by filtration.

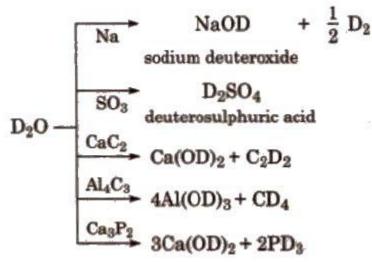
Exposure to sunlight, boiling, chlorination (treatment with liquid Cl<sub>2</sub> or bleaching powder), ozonisation and addition of CuSO<sub>5</sub> are some processes which are employed to destroy bacteria.

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Heavy Water [D<sub>2</sub>O]

It was discovered by Urey in 1932. It can be prepared by exhaustive electrolysis of ordinary water using nickel electrodes. It is colourless, odourless, tasteless liquid.

#### **Chemical Reactions of Heavy Water**



#### **Usesof Heavy Water**

It is used

- 1. in nuclear reactors to slow down the speed of neutrons and called moderator.
- 2. as a tracer compound to study the mechanisms of many reactions.

#### **Soft and Hard Water**

The water which produces large amount of lather with soap is known as soft water and which forms a scum with soap is known as hard water.

#### **Typesof Hardness of Water**

- **Temporary hardness** It is due to the presence of bicarbonates of calcium and magnesium.
- **Permanent hardness** Tt is due to the presence of chlorides and sulphates of calcium and magnesium.

#### **Removal of Temporary Hardness**

It can be achieved:

(a) By boiling The soluble bicarbonates are converted into insoluble carbonates.

$$M(HCO_3)_2 \longrightarrow MCO_3 \downarrow + H_2O + CO_2 \uparrow$$
  
(where,  $M = Ca$ , Mg)

(b) By Clark's process By adding lime water or milk of lime.

$$M(HCO_3)_2 + Ca(OH)_2 \longrightarrow MCO_3 \downarrow + 2H_2O + CaCO_3$$

#### **Removal of Permanent Hardness**

(i) By adding washing soda The calcium or magnesium salts are precipitated as carbonates.

(ii) By adding caustic soda The temporary and permanent hardness can be removed by adding caustic soda.

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$$CaSO_4 + 2NaOH \longrightarrow Ca(OH)_2 \downarrow + Na_2SO_4$$
  
 $MgCl_2 + 2NaOH \longrightarrow Mg(OH)_2 \downarrow + 2NaCl$ 

(iii) By adding sodium phosphate (Na<sub>3</sub>PO<sub>4</sub>) The phosphates of calcium and magnesium are precipitated.

$$3CaCl_2 + 2Na_3PO_4 \longrightarrow Ca_3(PO_4)_2 \downarrow + 6NaCl$$
  
 $3CaSO_4 + 2Na_3PO_4 \longrightarrow Ca_3(PO_4)_2 \downarrow + 3Na_2SO_4$ 

Similarly, magnesium also precipitate out in the form of magnesium phosphate, Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>.

(iv) Calgon's process Calgon is sodium hexa metaphosphate (Na<sub>6</sub>P<sub>6</sub>O<sub>18</sub>). This calgon when added to hard water form soluble complex.

$$2CaSO_4 + Na_2[Na_4(PO_3)_6] \longrightarrow 2Na_2SO_4 + Na_2[Ca_2(PO_3)_6]$$
calgon
soluble

Similarly.  $Mg^{2+}$  can also precipitate as  $Na_2[Mg_2(PO_3)_6]$  and water becomes free from  $Ca^{2+}$  and Mg2+ Ions. (v) **Permutit process** Permutit is hydrated sodium aluminium silicate  $Na_2Al_2Si_2O_8.xH_2O$ . It exchanges its sodium ions for divalent ions  $Ca^{2+}$  and  $Mg^{2+}$ .

$$Na_2Al_2Si_2O_8 + MCl_2 \longrightarrow MAl_2Si_2O_8 + 2NaCl(M = Ca \text{ or Mg})$$

Permutit when fully exhausted can be regenerated by treating with 10% solution of sodium chloride. It is most efficient method to gel water with zero degree of hardness.

#### (vi) By synthetic resins

These are of two types:

(a) Cation exchange resins are big molecules containing sulphonic acid group (-SO<sub>3</sub>H). It is first changed into sodium salt with the general formula RNa. The hard water is passed through it so Ca<sup>2+</sup> and M<sup>2+</sup> are exchanged and removed.

$$2R^-\text{Na}^+ + \text{Ca}^{2+} \longrightarrow R_2\text{Ca} + 2\text{Na}^+$$
  
 $2R^-\text{Na}^+ + \text{Mg}^{2+} \longrightarrow R_2\text{Mg} + 2\text{Na}^+$ 

The resins like permutit can be regenerated with a solution of NaCl.

(b) Anion exchange resins are also big molecules and can exchange anions. They contain an amino group.

$$RNH_2 + H_2O \longrightarrow RNH_3 OH$$
  
 $2RNH_3^+ \ddot{O}H + CO_3^{2-} \rightleftharpoons (RNH_3^+)_2CO_3 + 2OH^-$   
 $2RNH_3^+ OH^- + CI^- \rightleftharpoons RNH_3^+ CI^- + OH^-$ 

The water is first passed through cation resins and then through anion tesin and pure distilled water is obtained.

#### **Measurement of Degree of Hardness**

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

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Degree of hardness (in ppm) = (wt. of  $CaCO_3$  (g)/ wt. of hard water (g)) x  $10^6$ 

The molecular wt. of Ca(HCO<sub>3</sub>)<sub>2</sub>, Mg(HCO<sub>3</sub>)<sub>2</sub>, CaCl<sub>2</sub>, MgCl<sub>2</sub>, CaSO<sub>4</sub> and MgSO<sub>4</sub> is 162, 146, 111, 95, 136 and 120 respectively. The mol. wt. of CaCO<sub>3</sub> is 100.

Thus, 162 g Ca(HCO<sub>3</sub>)<sub>2</sub>, 146 g Mg(HCO<sub>3</sub>)<sub>2</sub>, 111 gCaCl<sub>2</sub>, 95 g MgCl<sub>2</sub> 136 g CaSO<sub>4</sub> and 120 g MgSO<sub>4</sub> are equivalent to 100 g CaCO<sub>3</sub>.

Hydrogen Peroxide [H<sub>2</sub>O<sub>2</sub>]

H<sub>2</sub>O<sub>2</sub> was discovered by J.L. Thenard in 1818. It is an important compound used in pollution control treatment of domestic and industrial effluents.

#### **Methods of Preparation**

(i) 
$$BaO_2 \cdot 8H_2O(s) + H_2SO_4(aq)$$

(ii) 
$$2HSO_4^-(aq) \xrightarrow{\text{Electrolysis}} HO_8SOOSO_3H(aq) \xrightarrow{H_2O} Hydrolysis$$

$$2HSO_{4}^{-}(aq) + 2H^{+}(aq) + H_{2}O_{2}(aq)$$

(iii) 2-ethylanthraquinol 
$$\xrightarrow{O_2 \text{ (air)}} H_2O_2 + \text{oxidised product}$$

#### Strength of Hydrogen Peroxide

The most common method to express the strength of  $H_2O_2$  is in terms of the volume (in mL) of oxygen liberated at NTP by decomposition or 1 mL of that sample of H Z 0 2. A solution of  $H_2O_2$  labelled as '10 volume' actually means "1 mL of such a solution of  $H_2O_2$  on decomposition by heat produces 10 mL of oxygen at NTP".

(i) Strength of H<sub>2</sub>O<sub>2</sub> in terms of normality

$$(68 \text{ x } \text{ X}/22.4) = 17 \text{ x } \text{N} \Rightarrow \text{X} = 5.6 \text{ x } \text{N}$$

where, X is volume strength of H<sub>2</sub>O<sub>2</sub>.

- (ii) % strength = (17/56) x volume strength
- (iii) X = 11.2 x molarity.

#### Storage of Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>)

It is stored in the presence of traces of alcohol, acetanilide or sodium pyrophosphate which slow down the rate of decomposition of hydrogen peroxide.

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Chemical Properties of H<sub>2</sub>O<sub>2</sub>

- 1. Acidic nature It is weakly acidic in nature and pure hydrogen peroxide turns blue litmus red.
- 2. **Oxidising agent** It acts as a strong oxidising agent in acidic as well as in basic medium.

$$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$$
  
 $H_2O_2 + OH^- + 2e^- \longrightarrow 3OH^-$ 

e.g., oxidising action of HzOz is

$$2Cr^{3+} + 3H_2O_2 + 10OH^- \longrightarrow 2CrO_4^{2-} + 8H_2O$$
  
 $Mn^{2+} + H_2O_2 + 2OH^- \longrightarrow MnO_2 + 2H_2O$ 

#### (iii) Reducing agent

(a) In acidic medium

$$2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$$
  
 $Cr_2O_7^{2-} + 8H^+ + 3H_2O_2 \longrightarrow 2Cr^{3+} + 7H_2O + 3O_2$ 

(b) In basic medium

$$2K_3$$
 [Fe(CN)<sub>6</sub>] + 2KOH +  $H_2O_2 \longrightarrow 2K_4$  [Fe(CN)<sub>6</sub>] +  $2H_2O + O_2$ 

(iv) Bleaching properties Its bleaching action is due to oxidation by atomic oxygen and permanent.  $H_2O_2$  rarr;  $H_2O + [O]$  dye  $+ [O] \rightarrow$  dye is oxidised and bleached

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## Thank You

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