

Hydrogen



The electronic configuration: 1s¹

It has 1 proton and 1 electron but no neutron.

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

The point of similarities of hydrogen with alkali metals

- 1. Electronic configuration: The electronic configuration of hydrogen is 1s¹ which is similar to the outmost electronic configuration of alkali metals (ns¹). So it is placed with alkali metals in group1.
- **2. Electropositive character:** Hydrogen can from unipositive ion by losing one electron like alkali metals. e.g. $H \longrightarrow H^+ + e^-$

$$Na \longrightarrow Na^+ + e^-$$

- **3.** Oxidation state: Hydrogen exhibits oxidation state of + 1 ion the compounds of hydrogen which is similar to alkali metals.
- **4. Valency:** Valency of hydrogen is 1 like alkali metals.
- 5. Reaction with Non-metals: Like alkali metals, hydrogen forms binary compounds with non-metal.
- **6. Reducing nature :** Hydrogen is a good reducing agent like alkali metals.

The points of similarities between Hydrogens and Halogens

(Practice Question in the End, Q.2,4)

1. Both hydrogen and halogens(X) require one electron in order to attain a stable electronic configuration. $H:1s^1 \xrightarrow{e^-} H^-:1s^2$

$$X: ns^2 np^5 \xrightarrow{e^-} X^-: ns^2 np^6$$

- 2. They both are non-metallic in nature with respect to metals.
- 3. Both have high electronegativity as compared to metals.
- 4. When coupled with metals, both hydrogen, as well as halogens, behave as negative ions.

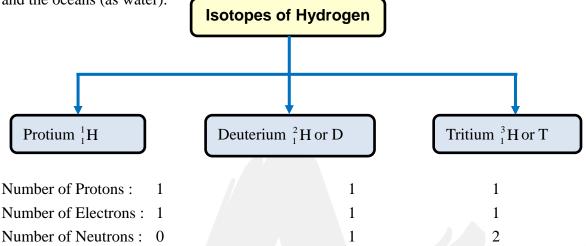
5. Both Hydrogen and elements of halogens exist as diatomic species in nature such as hydrogen gas (H₂) and halogens (F₂, Cl₂, Br₂, I₂).

DIHYDROGEN, H₂

Occurrence

Dihydrogen is the most abundant element in the universe (70% of the total mass of the universe) and is the principal element in the solar atmosphere. The giant planets Jupiter and Saturn consist

mostly of hydrogen. However, due to its light nature, it is much less abundant (0.15% by mass) in the earth's atmosphere. Of course, in the combined form it constitutes 15.4% of the earth's crust and the oceans (as water).



- The predominant form is protium.
- Only tritium is radioactive and emits low energy β^- particles. It is because of high n/p ratio of tritium which makes nucleus unstable.

$$_{1}^{3}H \longrightarrow _{2}^{3}He + _{-1}^{0}e$$
 (Practice Question in the End, Q.8)

PREPARATION OF H2

Laboratory Preparation of H2

1. The reaction of zinc with dilute hydrochloric acid.

$$Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$$

2. The reaction of zinc with aqueous alkali.

$$Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2$$

sodium zincate

Commercial Production of H₂

1. Electrolysis of acidified water using platinum electrodes.

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

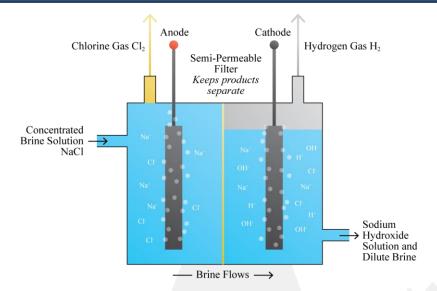
- 2. High purity (> 99.95%) dihydrogen is obtained by electrolysing warm aqueous barium hydroxide solution between nickel electrodes.
- 3. It is obtained as a byproduct in the manufacture of sodium hydroxide and chlorine by the electrolysis of brine solution. During electrolysis, the reactions that take place are:

At anode:
$$2Cl^{-}(aq) \longrightarrow Cl_{2}(g) + 2e^{-}$$

At cathode:
$$2H_2O(1) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$$

The overall reaction:

$$2Na^{+}(aq) + 2Cl^{-}(aq) + 2H_{2}O(l) \longrightarrow Cl_{2}(g) + H_{2}(g) + 2Na^{+}(aq) + 2OH^{-}(aq)$$



4. Reaction of steam on hydrocarbons or coke at high temperatures in the presence of catalyst yields hydrogen.

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

Water gas: CO + H₂

Syngas: CO and H₂ is used for the synthesis of methanol and a number of hydrocarbons, it is also called synthesis gas or 'syngas'. Nowadays 'syngas' is produced from sewage, saw-dust, scrap wood, newspapers etc. The process of producing 'syngas' from coal is called 'coal gasification'.

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

Water – gas shift reaction:

The production of dihydrogen can be increased by reacting carbon monoxide of syngas mixtures with steam in the presence of iron chromate as catalyst.

$$CO(g) + H_2O(g) \xrightarrow{673K} CO_2(g) + H_2(g)$$

CO₂ gas is removed by scrubbing with sodium arsenite solution.

- Q. How can the production of dihydrogen, obtained from 'coal gasification', be increased?

 [NCERT Exercise]
- **Sol.** The production of dihydrogen in coal gasification can be increased by reacting CO(g) present in syngas with steam in the presence of iron chromate catalysts.

$$C + H_2O \xrightarrow{heat} CO + H_2 \uparrow (syn gas)$$

$$H_2O \longrightarrow FeCrO_4(Catalyst) CO_2 + H_2$$

With the removal of CO_2 the reaction shifts in the forward direction and thus, the production of dihydrogen will be increased.

PROPERTIES OF DIHYDROGEN

Physical Properties:

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

- (i) loss of the only electron to give $H^+ H^{-e^-} \to H^+$
- (ii) gain of an electron to form H⁻ $H \xrightarrow{e^-} H^-$
- (iii) sharing electrons to form a single covalent bond. H•—•Cl

Reaction with halogens:

It reacts with halogens, X2 to give hydrogen halides, HX,

$$H_2(g) + X_2(g) \longrightarrow 2HX(g) (X = F, Cl, Br, I)$$

While the reaction with fluorine occurs even in the dark, with iodine it requires a catalyst.

Reaction with dioxygen:

It reacts with dioxygen to form water. The reaction is highly exothermic.

$$2H_2(g) + O_2(g) \xrightarrow{\text{catalyst or heating}} 2H_2O(l)$$

Reaction with dinitrogen:

With dinitrogen it forms ammonia.

$$3H_2(g) + N_2(g) \xrightarrow{673K.200atm} 2NH_3(g);$$

This is the method for the manufacture of ammonia by the Haber process.

Reactions with metals:

With many metals it combines at a high temperature to yield the corresponding hydrides

$$H_2(g) + 2M(g) \longrightarrow 2MH(s)$$
; where M is an alkali metal.

Reactions with metal ions and metal oxides:

It reduces some metal ions in aqueous solution and oxides of metals (less active than iron) into corresponding metals.

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

$$yH_2(g) + M_xO_y(s) \longrightarrow xM(s) + yH_2O(l)$$

Reactions with organic compounds:

- 1. Hydrogenation of vegetable oils using nickel as catalyst gives edible fats (margarine and vanaspati ghee)
- 2. Hydroformylation of olefins yields aldehydes which further undergo reduction to give alcohols.

$$\begin{aligned} \mathbf{H_2} + \mathbf{CO} + \mathbf{R} - \mathbf{CH} &= \mathbf{CH_2} - \mathbf{R} - \mathbf{CH_2} - \mathbf{CH_2} - \mathbf{C} - \mathbf{H} \\ \mathbf{O} & \mathbf{O} - \mathbf{H} \\ \mathbf{H_2} + \mathbf{R} - \mathbf{CH_2} - \mathbf{CH_2} - \mathbf{C} - \mathbf{H} \longrightarrow \mathbf{R} - \mathbf{CH_2} - \mathbf{CH_2} - \mathbf{C} - \mathbf{H} \\ \mathbf{H} & \mathbf{H} - \mathbf{CH_2} - \mathbf{CH_2} - \mathbf{C} - \mathbf{H} - \mathbf{H} - \mathbf{C} - \mathbf{C} - \mathbf{H} - \mathbf{C} - \mathbf{C} - \mathbf{H} - \mathbf{C} - \mathbf{C} - \mathbf{C} - \mathbf{H} - \mathbf{C} - \mathbf{C} - \mathbf{C} - \mathbf{H} - \mathbf{C} -$$

Q. Comment on the reactions of dihydrogen with (i) chlorine, (ii) sodium, and (iii) copper(II) oxide. [NCERT Example]

Sol.

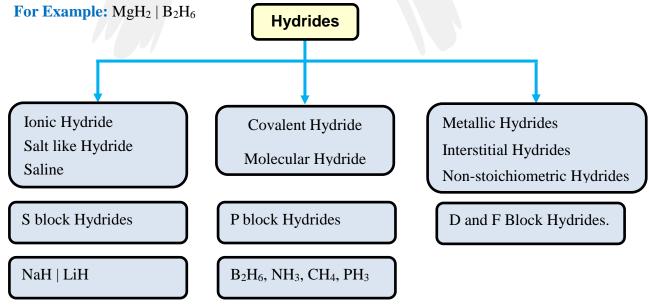
- 1. $H_2 + Cl_2 \longrightarrow 2HCl$ Dihydrogen reduces chlorine into chloride (Cl⁻) ion and itself gets oxidised to H⁺ ion by chlorine to form hydrogen chloride. An electron pair is shared between H and Cl leading to the formation of a covalent molecule.
- 2. $H_2 + 2Na \longrightarrow 2NaH$ Dihydrogen is reduced by sodium to form NaH. An electron is transferred from Na to H leading to the formation of an ionic compound, Na^+H^- .
- 3. $H_2 + \text{CuO} \longrightarrow \text{Cu} + H_2\text{O}$ Dihydrogen reduces copper(II) oxide to copper in zero oxidation state and itself gets oxidised to $H_2\text{O}$, which is a covalent molecule.

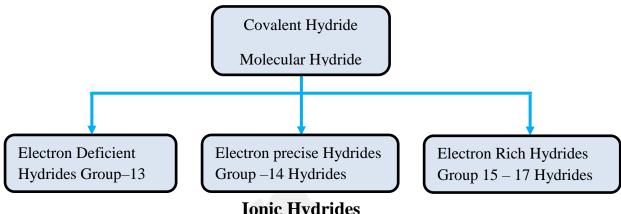
Uses of H₂

- The largest single use of dihydrogen is in the synthesis of ammonia which is used in the manufacture of nitric acid and nitrogenous fertilizers.
- Dihydrogen is used in the manufacture of vanaspati fat by the hydrogenation of polyunsaturated vegetable oils like soyabean, cotton seeds etc.
- It is used in the manufacture of bulk organic chemicals, particularly methanol. $CO(g) + 2H_2(g) \xrightarrow{\text{cobalt} \atop \text{catalyst}} CH_3OH(l)$
- It is used as a rocket fuel in space research.
- Dihydrogen is used in fuel cells for generating electrical energy. It has many advantages over the conventional fossil fuels and electric power. It does not produce any pollution and releases greater energy per unit mass of fuel in comparison to gasoline and other fuels.

Hydrides (Practice Question in the End, Q.1,5,7,9)

Dihydrogen, under certain reaction conditions, combines with almost all elements, except noble gases, to form binary compounds, called hydrides.





Ionic Hydrides

The ionic hydrides are crystalline, non-volatile and non-conducting in solid state. However, their melts conduct electricity and on electrolysis liberate dihydrogen gas at anode, which confirms the existence of H⁻ion.

 $2H^{-}(melt) \xrightarrow{anode} H_{2}(g) + 2e^{-}$ Anode:

Saline hydrides react violently with water producing dihydrogen gas.

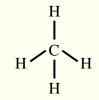
 $NaH(s) + H_2O(aq) \longrightarrow NaOH(aq) + H_2(g)$

Lithium hydride is rather unreactive at moderate temperatures with O₂ or Cl₂. It is, therefore, used in the synthesis of other useful hydrides, e.g.,

$$8\text{LiH} + \text{Al}_2\text{Cl}_6 \longrightarrow 2\text{LiAlH}_4 + 6\text{LiCl}$$

 $2\text{LiH} + \text{B}_2\text{H}_6 \longrightarrow 2\text{LiBH}_4$

- Do you expect the carbon hydride of type C_nH_{2n+2} to act as 'Lewis' acid or base? Justify 0. your answer. [NCERT Exercise]
- **Sol.** Carbon hydrides of the type C_n H_{2n+2} (e.g. CH_4) are electron precise hydrides. Because they have atom with exact number of electrons to form covalent bonds. Thus, they do not behave as Lewis acid or base. Since they have no tendency to accept or lose electrons.



- How do you expect the metallic hydrides to be useful for hydrogen storage? Explain. Q. [NCERT Exercise]
- **Sol.** In metallic hydrides, hydrogen is adsorbed as H-atoms. Due to the adsorption of H atoms the metal Lattice expands and become unstable. Thus, when metallic hydride is heated, it decomposes to form hydrogen and finely divided metal. The hydrogen evolved can be used as fuel. Metallic hydrides $\xrightarrow{\Delta} H_2 \uparrow + \text{Metal (finely divided)}$
- 0. Saline hydrides are known to react with water violently producing fire. Can CO₂, a well known fire extinguisher, be used in this case? Explain. [NCERT Exercise]
- **Sol.** No. Because if saline hydrides react with water the reaction will be highly exothermic thus the hydrogen evolved in this case can catch fire. NaH + $H_2O \longrightarrow NaOH + H_2$

Here CO_2 cannot be used as fire extinguisher because CO_2 will get absorbed in alkali metal hydroxides. NaOH $\xrightarrow{CO_2}$ Na₂CO₃

Water (Practice Question in the End, Q.3)

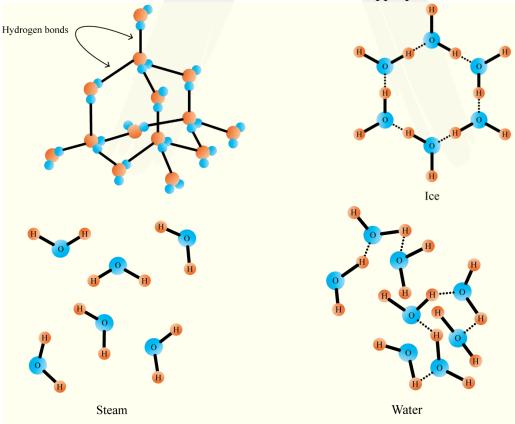
A major part of all living organisms is made up of water. Human body has about 65% and some plants have as much as 95% water.

Structure of Water

- In the gas phase water is a bent molecule with a bond angle of 104.5°, and O–H bond length of 95.7 pm.
- In the liquid phase water molecules are associated together by hydrogen bonds.
- The crystalline form of water is ice.
- At atmospheric pressure ice crystallises in the *hexagonal form*, but at *very low temperatures* it condenses to *cubic form*.
- Density of ice is less than that of water.

Structure of Ice

• Ice has a highly ordered three dimensional hydrogen bonded structure. H
Hydrogen bonding gives ice a rather open type structure with wide
holes. These holes can hold some other molecules of appropriate size interstitially.



Chemical properties of water

1. Amphoteric nature: It has the ability to act as an acid as well as a base

$$H_2O(1) + NH_3(aq) \Longrightarrow OH^-(aq) + NH_4^+(aq)$$

$$H_2O(1) + H_2S(aq) \Longrightarrow H_3O^+(aq) + HS^-(aq)$$

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

$$H_2O(1) + H_2O(1) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

(acid) (base) (conjugate acid) (conjugate base)

2. Redox Reactions Involving Water:

- Water can be easily reduced to dihydrogen by highly electropositive metals. So it is a great source of H_2 . $2H_2O(1) + 2Na(s) \longrightarrow 2NaOH(aq) + H_2(g)$
- Water is oxidised to O₂ during photosynthesis.

$$6CO_2(g) + 12H_2O(l) \longrightarrow C_6H_{12}O_6(aq) + 6H_2O(l) + 6O_2(g)$$

• With fluorine also it is oxidised to O_2 .

$$2F_2(g) + 2H_2O(1) \longrightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$$

3. Hydrolysis Reaction:

Due to high dielectric constant, it has a very strong hydrating tendency. It dissolves many ionic compounds. However, certain covalent and some ionic compounds are hydrolysed in water.

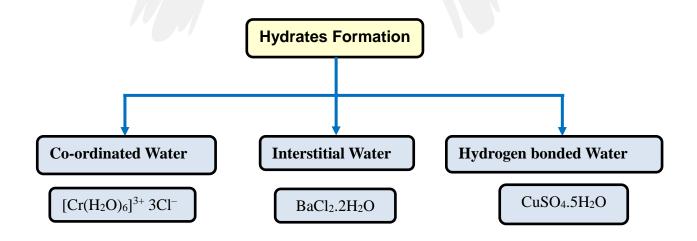
$$P_4O_{10}(s) + 6H_2O(l) \longrightarrow 4H_3PO_4(aq)$$

 $SiCl_4(l) + 2H_2O(l) \longrightarrow SiO_2(s) + 4HCl(aq)$

$$N^{3-}(s) + 3H_2O(1) \longrightarrow NH_3(g) + 3OH^-(aq)$$

4. Hydrates Formation:

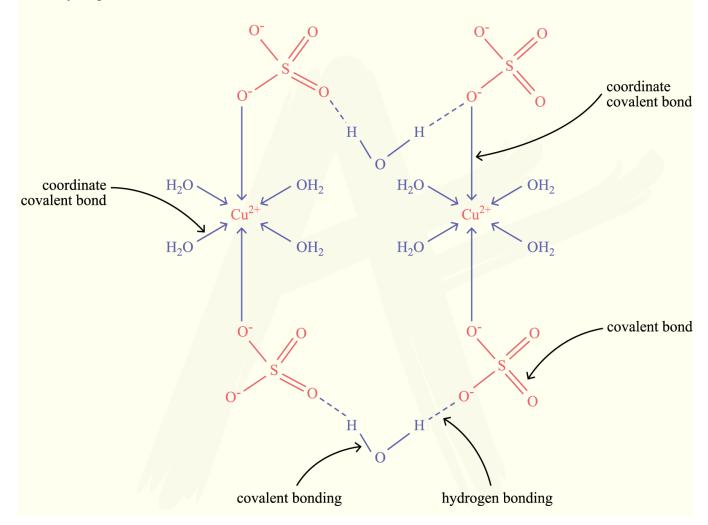
From aqueous solutions many salts can be crystallised as hydrated salts. Such an association of water is of different types viz.,



Q. How many hydrogen – bonded water molecule(s) are associated in CuSO4.5H2O? [NCERT Example]

Sol.
$$CuSO_4.5H_2O = [Cu(H_2O)_4]^{2+}SO_4^{2-}.H_2O$$

Only one water molecule, which is outside the brackets (coordination sphere), is hydrogen – bonded. The other four molecules of water coordinated.



Hard and Soft Water

Hard water: Presence of calcium and magnesium salts in the form of hydrogencarbonate, chloride and sulphate in water makes water 'hard'. Hard water does not give lather with soap.

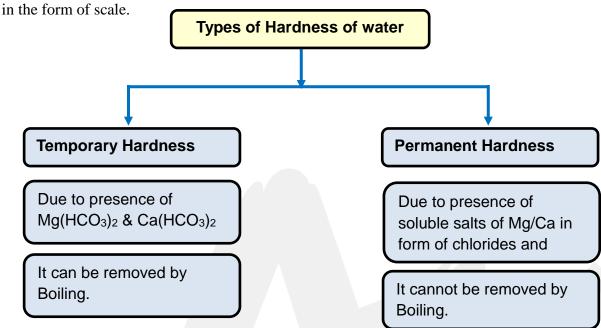
Soft water: Water free from soluble salts of calcium and magnesium is called Soft water. It gives lather with soap easily.

• Hard water forms scum/precipitate with soap. Soap containing sodium stearate (C₁₇H₃₅COONa) reacts with hard water to precipitate out Ca/Mg stearate.

$$2C_{17}H_{35}COONa(aq) + M^{2+}(aq) \longrightarrow (C_{17}H_{35}COO)_2M \downarrow +2Na^+(aq)$$
 $[M=Ca/Mg]$

APNI KAKSHA -

It is unsuitable for laundry and harmful for boilers as well, because of deposition of salts in the form of scale



Temporary Hardness

(I) Boiling:

a.
$$Mg(HCO_3)_2 \xrightarrow{Heating} Mg(OH)_2 \downarrow + 2CO_2 \uparrow$$

b.
$$Ca(HCO_3)_2 \xrightarrow{Heating} CaCO_3 \downarrow + H_2O + CO_2 \uparrow$$

Precipitates can be removed by filtration. Filtrate thus obtained will be soft wate.

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

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

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

Permanent Hardness

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

1. Treatment with washing soda (sodium carbonate):

Washing soda reacts with soluble calcium and magnesium chlorides and sulphates in hard water to form insoluble carbonates.

$$MCl_2 + Na_2CO_3 \longrightarrow MCO_3 \downarrow +2NaCl$$
 $(M = Mg, Ca)$
 $MSO_4 + Na_2CO_3 \longrightarrow MCO_3 \downarrow +Na_2SO_4$

2. Calgon's method:

Sodium hexametaphosphate ($Na_6P_6O_{18}$), 'calgon', when added to hard water, the following reactions take place.

$$Na_6P_6O_{18} \longrightarrow 2Na^+ + Na_4P_6O_{18}^{2-}$$
 (M = Mg, Ca)
 $M^{2+} + Na_4P_6O_{18}^{2-} \longrightarrow [Na_2MP_6O_{18}]^{2-} + 2Na^+$

The complex anion keeps the Mg²⁺ and Ca²⁺ ions in solution.

3. Ion-exchange method: (Zeolite/Permutit Process)

Hydrated sodium aluminium silicate ($NaAlSiO_4 = NaZ$) is zeolite/permutit. When this is added in hard water, exchange reactions take place.

$$2NaZ(s) + M^{2+}(aq) \longrightarrow MZ_2(s) + 2Na^{+}(aq) \qquad (M = Mg, Ca)$$

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

$$MZ_2(s) + 2NaCl(aq) \longrightarrow 2NaZ(s) + MCl_2(aq)$$

4. Synthetic resins method:

Nowadays hard water is softened by using synthetic cation exchangers. This method is more efficient than zeolite process.

- Cation exchange resins contain large organic molecule with SO₃H group and are water insoluble.
- Ion exchange resin (RSO₃H) is changed to RNa by treating it with NaCl. The resin exchanges Na⁺ ions with Ca²⁺ and Mg²⁺ ions present in hard water to make the water soft. Here R is resin anion.

$$2RNa(s) + M^{2+}(aq) \longrightarrow R_2M(s) + 2Na^+(aq)$$

- The resin can be regenerated by adding aqueous NaCl solution.
- Pure de-mineralised (de-ionized) water free from all soluble mineral salts is obtained by passing water successively through a cation exchange (in the H⁺ form) and an anion-exchange (in the OH⁻ form) resins:
 - (a) Cation (H⁺) Exchange $2RH(s) + M^{2+}(aq) \rightleftharpoons MR_2(s) + 2H^+(aq)$

for Na^+ , Ca^{2+} , Mg^{2+} and other cations present in water. This process results in proton release and thus makes the water acidic.

$$RNH_2(s) + H_2O(l) \rightleftharpoons RNH_3^+.OH^-(s)$$

$$RNH_3^+.OH^-(s) + X^-(aq) \Longrightarrow RNH_3^+.X^-(s) + OH^-(aq)$$

$$(X^{-} = Cl^{-} | HCO_{3}^{-} | SO_{4}^{2-})$$

• OH⁻ ions, thus, liberated neutralise the H⁺ ions set free in the cation exchange.

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(1)$$

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

HYDROGEN PEROXIDE (H₂O₂)

(Practice Question in the End, Q.6,10,11,12,13)

Preparation:

(I) Acidifying barium peroxide and removing excess water by evaporation under reduced pressure

$$BaO_2.8H_2O(s) + H_2SO_4(aq) \longrightarrow BaSO_4(s) + H_2O_2(aq) + 8H_2O(l)$$

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

This method is now used for the laboratory preparation of D_2O_2 .

$$K_2S_2O_8(s) + 2D_2O(l) \longrightarrow 2KDSO_4(aq) + D_2O_2(l)$$

(III) Industrial Method: it is prepared by the auto-oxidation of 2-alklylanthraquinols.

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

$$\begin{array}{c}
OH \\
C_2H_5 \\
OH
\end{array}$$

$$\begin{array}{c}
O \\
+O_2
\end{array}$$

$$\begin{array}{c}
O \\
+O_2
\end{array}$$

$$\begin{array}{c}
O \\
+O_2
\end{array}$$

In this case 1% H_2O_2 is formed. It is extracted with water and concentrated to ~30% (by mass) by distillation under reduced pressure. It can be further concentrated to ~85% by careful distillation under low pressure. The remaining water can be frozen out to obtain pure H_2O_2 .

Physical Properties

- In the pure state H₂O₂ is an almost colourless (very pale blue) liquid.
- H₂O₂ is miscible with water in all proportions and forms a hydrate H₂O₂. H₂O
- A 30% solution of H₂O₂ is marketed as '100 volume' hydrogen peroxide. It means that one millilitre of 30% H₂O₂solution will give 100 mL of oxygen at STP.

Q. Calculate the strength of 10 volume solution of hydrogen peroxide. [NCERT Example]

Sol. 10 volume solution of H_2O_2 means that 1 L of this H_2O_2 solution will give 10 L of oxygen at

$$2H_2O_2(l) \longrightarrow O_2(g) + H_2O(l)$$

 $2 \times 34g = 68g$ 22.7L at STP

22.7 L of O_2 is produced from 68 g H_2O_2 at STP

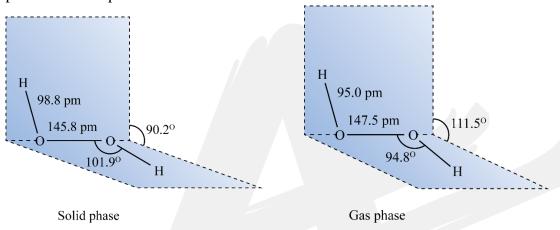
1 L of O₂ at STP is produced from =
$$\frac{68}{22.7}$$
g

10 L of O₂ at STP is produced from
$$=\frac{68\times10}{22.7}$$
g = 29.9g \approx 30gH₂O₂

Therefore, strength of H_2O_2 in 10 volume H_2O_2 solution = 30 g/L = 3% H_2O_2 solution.

Structure

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



- "(a) H₂O₂ structure in gas phase, dihedral angle is 111.5°.
- (b) H₂O₂ structure in solid phase at 110K, dihedral angle is 90.2°."

Chemical properties:

It acts as an oxidising as well as reducing agent in both acidic and alkaline media.

1. Oxidising action in acidic medium

$$2Fe^{2+}(aq) + 2H^{+}(aq) + H_2O_2(aq) \longrightarrow 2Fe^{3+}(aq) + 2H_2O(l)$$

 $PbS(s) + 4H_2O_2(aq) \longrightarrow PbSO_4(s) + 4H_2O(l)$

2. Reducing action in acidic medium

$$2MnO_{4}^{-} + 6H^{+} + 5H_{2}O_{2} \longrightarrow 2Mn^{2+} + 8H_{2}O + 5O_{2}$$

 $HOCl + H_{2}O_{2} \longrightarrow H_{3}O^{+} + Cl^{-} + O_{2}$

3. Oxidising action in basic medium

$$2Fe^{2+} + H_2O_2 \longrightarrow 2Fe^{3+} + 2OH^-$$

 $Mn^{2+} + H_2O_2 \longrightarrow Mn^{4+} + 2OH^-$

4. Reducing action in basic medium

$$I_{2} + H_{2}O_{2} + 2OH^{-} \longrightarrow 2I^{-} + 2H_{2}O + O_{2}$$

$$2MnO_{4}^{-} + 3H_{2}O_{2} \longrightarrow 2MnO_{2} + 3O_{2} + 2H_{2}O + 2OH^{-}$$

Storage:

H₂O₂ decomposes slowly on exposure to light.

$$2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)$$

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

Heavy Water, D₂O

It is extensively used as a moderator in nuclear reactors and in exchange reactions for the study of reaction mechanisms. It can be prepared by exhaustive electrolysis of water or as a by-product in some fertilizer industries.

$$CaC_2 + 2D_2O \longrightarrow C_2D_2 + Ca(OD)_2$$

 $SO_3 + D_2O \longrightarrow D_2SO_4$
 $Al_4C_3 + 12D_2O \longrightarrow 3CD_4 + 4Al(OD)_3$

- Q. Knowing the properties of H_2O and D_2O , do you think that D_2O can be used for drinking purposes? [NCERT Exercise]
- **Sol.** No, D₂O is injurious to human beings, plants and animals.

Practice Questions

Q1. Arrange the following.

[NCERT Exercise]

- (a) CaH₂, BeH₂ and TiH₂ in order of increasing electrical conductance.
- (b) LiH, NaH and CsH in order of increasing ionic character.
- (c) H-H, D-D and F-F in order of increasing bond dissociation enthalpy.
- (d) NaH, MgH2 and H2O in order of increasing reducing property.
- **Sol.** (a) $BeH_2 < TiH_2 < CaH_2$
 - (b) LiH < NaH < CsH ($Li^+ < Na^+ < Cs^+$: Ionic character by fajan's rule)
 - (c) F F < H H < D D
 - (d) $H_2O < MgH_2 < NaH$ (Reducing property $\uparrow \Rightarrow H^{\Theta}$ Donating Tendency \uparrow)
- Q2. Hydrogen resembles halogens in many respects for which several factors are responsible. Of the following factors which one is most important in this respect? [NCERT Exemplar]
 - (a) Its tendency to lose an electron to form a cation.
 - (b) Its tendency to gain a single electron in its valence shell to attain stable electronic configuration.
 - (c) Its low negative electron gain enthalpy value.
 - (d) Its small size.

Sol. (b) Halogens have the tendency to gain one electron and acquire inert gas configuration. Hydrogen also accepts one electron and acquires helium configuration.

$$F \longrightarrow Ne;$$
 $Cl \longrightarrow Ar;$ $Br \longrightarrow Kr$
 $2s^2 2p^5 2s^2 2p^6 3s^2 3p^5 3s^2 3p^6 4s24p5 4s^2 4p^6$
 $H \longrightarrow He$
 $1s^1 1s^2$

Q3. Consider the reaction of water with F2 and suggest, in terms of oxidation and reduction, which species are oxidised/reduced. [NCERT Exercise]

Sol.
$$2F_2(g) + 2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4F^-(aq)$$

In this reaction water acts as a reducing agent and itself gets oxidised to O_2 while F_2 acts as an oxidising agent and hence itself reduced to F^- ions.

- Q4. Why does H⁺ ion always get associated with other atoms or molecules? [NCERT Exemplar]
 - (a) Ionisation enthalpy of hydrogen resembles that of alkali metals.
 - (b) Its reactivity is similar to halogens.
 - (c) It resembles both alkali metals and halogens.
 - (d) Loss of an electron from hydrogen atom results in a nucleus of very small size as compared to other atoms or ions. Due to small size it cannot exist free.
- **Sol.** (d) $H \longrightarrow H^+ + e^-$

 $\rm H^+$ has a very small size (~1.5 x 10^{-3} pm) compared to normal atomic and ionic sizes of 50 to 220 pm. It does not exist freely and is always associated with other atoms or molecules.

- Q5. Metal hydrides are ionic, covalent or molecular in nature. Among LiH, NaH, KH, RbH, CsH, the correct order of increasing ionic character is [NCERT Exemplar]
 - (a) LiH > NaH > CsH > KH > RbH
 - (b) LiH < NaH < KH < RbH < CsH
 - (c) RbH > CsH > NaH > KH > LiH
 - (d) NaH > CsH > RbH > LiH > KH
- **Sol.** (b) Ionic character increases as the size of the atom increases. LiH < NaH < KH < RbH < CsH
- Q6. Complete the following chemical reactions.

[NCERT Exercise]

- (a) PbS (s) + H_2O_2 (aq) \rightarrow
- $(b)\ MnO_4^-(aq) + H_2O_2^-(aq) \rightarrow$
- (c) $CaO(s) + H_2O(g) \rightarrow$
- (d) AlCl₃ (g) + H₂O (l) \rightarrow

(e) $Ca_3N_2(s) + H_2O(l) \rightarrow$

Classify the above into (a) hydrolysis, (b) redox and (c) hydration reactions,

Sol. (a) PbS (s) + $4H_2O_2$ (aq) \longrightarrow PbSO₄(s) + $4H_2O(1)$: Redox reaction

- (b) $MnO_4^-(aq) + H_2O_2(aq) + 6H^+(aq) \longrightarrow 2Mn(aq) + 8H_2O(l) + 5O_2(g)$: Redox reaction
- (c) $CaO(s) + H_2O(g) \longrightarrow Ca(OH)_2(aq)$: Hydrolysis
- (d) $AlCl_3(g) + 3H_2O(l) \longrightarrow Al(OH)_3(S) + 3HCl(aq)$: Hydrolysis
- (e) $Ca_3N_2(s) + H_2O(1) \longrightarrow 3Ca(OH)_2(aq) + 2NH_3(aq)$: Hydrolysis
- Q7. Which of the following hydrides is electron-precise hydride?

[NCERT Exemplar]

(a) **B**₂**H**₆

(b) NH₃

(c) H₂O

- (d) CH₄
- **Sol.** (d) CH₄ is an electron precise hydride since there are exact number of electrons to form normal covalent bonds.

$$\begin{array}{c} H \\ \times \\ \cdot \\ H \times \cdot C \cdot \times H \\ \cdot \\ \times \\ H \end{array}$$

- Q8. Radioactive elements emit α , β and γ rays and are characterised by their half-lives. The radioactive isotope of hydrogen is [NCERT Exemplar]
 - (a) Protium

(b) Deuterium

(c) Tritium

- (d) Hydronium
- **Sol.** (c) Nucleides with n/p (neutron-proton) ratio > 1.5 are usually radioactive. For example, tritium (n = 2, p = 1).
- Q9. How can saline hydrides remove traces of water from organic compounds?

[NCERT Exercise]

Sol. Saline hydrides (i.e, CaH₂ NaH etc.) react with water and form the corresponding metal hydroxide with the liberation of H₂ gas. Thus, these hydrides can be used to remove traces of water from the organic compounds.

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

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

Q10. Consider the reactions (A) $H_2O_2 + 2HI \longrightarrow I_2 + 2H_2O(B)$

 $HOCl + H_2O_2 \longrightarrow H_3O^+ + Cl^- + O_2$ Which of the following statements is correct about H_2O_2 with reference to these reactions? Hydrogen perioxide is . [NCERT Exemplar]

- (a) an oxidising agent in both (A) and (B)
- (b) an oxidising agent in (A) and reducing agent in (B)
- (c) a reducing agent in (A) and oxidising agent in (B)
- (d) a reducing agent in both (A) and (B)

O.N. of oxygen is decreased from -1 (H_2O_2) to -2 (H_2O_3), therefore, it is reduced and acts as an oxidizing agent.

$$\begin{array}{c} -1 \\ HOCl + H_2O_2 \longrightarrow H_3O^+ + Cl^- + O_2 \end{array}$$

O.N. of oxygen is increased from -1 (H_2O_2) to O (O_2), therefore, it is oxidized and acts as a reducing agent.

Q11. The oxide that gives H₂O₂ on treatment with dilute H₂SO₄ is — [NCERT Exemplar]

(a) PbO₂

(b) $BaO_2.8H_2O + O_2$

(c) MnO₂

(d) TiO₂

Sol. (b) BaO₂ .8H₂O + O₂. This oxide has peroxide linkage $\left(O_2^{2-}\right)$ when reacted with dilute H₂SO₄, it produces H₂O, however, dioxides do not produce the same products and the metal atom doesn't give out water on treatment with dilute H₂SO₄.

Q12. Which of the following equations depict the oxidising nature of H₂O₂? [NCERT Exemplar]

(a)
$$2\text{MnO}_4^- + 6\text{H}^+ + 5\text{H}_2\text{O}_2 \longrightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 5\text{O}_2$$

(b)
$$2Fe^{3+} + 2H^{+} + H_2O_2 \longrightarrow 2Fe^{2+} + 2H_2O + O_2$$

(c)
$$2I^- + 2H^+ + H_2O_2 \longrightarrow I_2 + 2H_2O$$

(d)
$$KIO_4 + H_2O_2 \longrightarrow KIO_3 + H_2O + O_2$$

Sol. (c)
$$-1 + 1 + 1 - 1 0 + 1 - 2$$

 $2I^{-} + 2H^{+} + H_{2}O_{2} \longrightarrow I_{2} + 2H_{2}O$

I ions are oxidized to I_2 (increase in O.N. from–1 to 0). Hence, H_2O_2 acts as an oxidizing agent

Q13. Which of the following equation depicts reducing nature of H₂O₂? [NCERT Exemplar]

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

(b)
$$I_2 + H_2O_2 + 2OH^- \longrightarrow 2I^- + 2H_2O + O_2$$

(c)
$$Mn^{2+} + H_2O_2 \longrightarrow Mn^{4+} + 2OH^-$$

(d) $PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$

Sol. (b) $I_2 + H_2O_2 + 2OH^- \longrightarrow 2I^- + 2H_2O + O_2$

 I_2 is reduced to I^- . Thus, H_2O_2 acts as a reducing agent.

Ab Phod Do!

