

Hydrogen

Dihydrogen

- In elemental form, hydrogen exists as diatomic molecule (H_2) and this H_2 is called dihydrogen.
- Hydrogen is the first element in the periodic table.
- Electronic configuration is $1s^1$.

Resemblance of Hydrogen with Alkali Metals and Halogens

• Resemblance With Alkali Metals

- Similar outer electronic configuration – ns^1
- Lose one electron to form unipositive ions
- Form oxides, halides, and sulphides

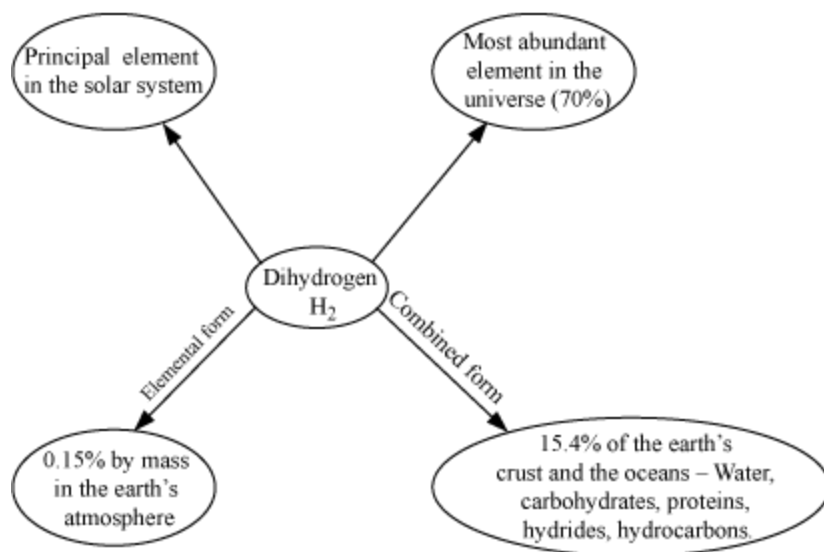
• Resemblance With Halogens

- Short by one electron to the corresponding noble gas configuration
- Gain one electron to form uninegative ions
- High ionization enthalpies
- Form diatomic molecules
- Combine with other elements to form hydrides and a large number of covalent compounds
- In many cases, hydrogen also differs from alkali metals and halogens.

Reason for Separately Placing In the Periodic Table

- Due to unique behaviour, H^+ ion does not exist freely. It exists in association with other atoms or molecules.

Occurrence

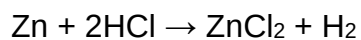


Isotopes of hydrogen

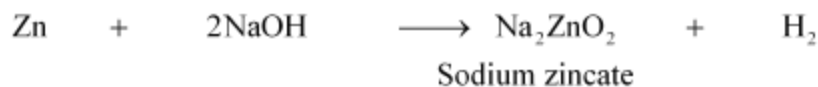
- Three isotopes
- Protium (${}^1_1\text{H}$)
- Deuterium (${}^2_1\text{H}$ or D)
- Tritium (${}^3_1\text{H}$ or T)
- Only tritium is radioactive and emits β^- particles.
- The isotopes have similar chemical properties. (exception – rates of reactions due to different bond dissociation enthalpy)
- They have different physical properties due to large differences in their masses.

Preparation of Dihydrogen (H_2)

- **Laboratory Preparation**
- By the reaction of granulated zinc with dilute HCl

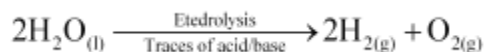


- By the reaction of zinc with aq. alkali

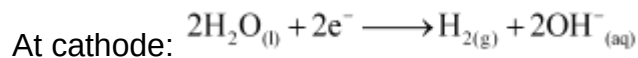
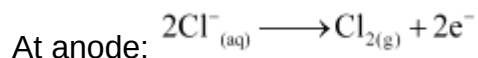


- **Commercial Production**

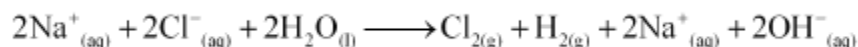
- By electrolysis of acidified water using platinum electrodes



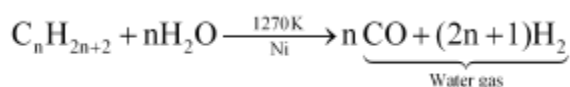
- By electrolysis of warm aqueous Ba (OH)₂ solution between nickel electrodes to obtain highly pure (99.95%) dihydrogen
- As a by-product in the electrolysis of brine solution (saturated NaCl solution) to obtain sodium hydroxide and chlorine



The overall reaction is



- By the reaction of hydrocarbons or coke with steam at high temperatures in the presence of catalyst



Water Gas – Mixture of CO and H₂

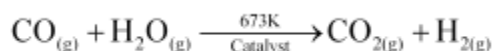
Also called synthesis gas or syngas – as it is used in the synthesis of methanol and a large number of hydrocarbons

Produced from coal, sewage, saw-dust, scrap-wood, newspaper etc.

- Coal gasification – Production of water gas from coal



- Water-gas shift reaction – increased production of dihydrogen by the reaction of carbon monoxide of syngas mixtures with steam in the presence of iron chromate (FeCrO_4) as a catalyst



The formed solution is scrubbed with sodium arsenite solution to remove carbon dioxide.

Properties of Dihydrogen

- **Physical Properties**

- Colourless, odourless, tasteless, combustible gas
- Lighter than air
- Insoluble in water

- **Chemical Properties**

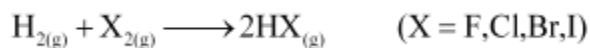
- Relatively inert at room temperature due to high H–H bond enthalpy
- Undergoes chemical reactions by either of the following ways:

(i) Losing the electron to form H^+ ion

(ii) Gaining an electron to form H^- ion

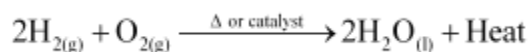
(iii) Sharing electrons to form a single covalent bond

- Reacts with halogens to give halides

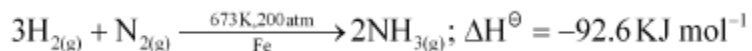


H_2 reacts with F_2 in dark also, but with I_2 only in the presence of catalyst.

- Reacts with dioxygen to form water with evolution of heat



- Reacts with dinitrogen to form ammonia (Haber's process)



- Reacts with many metals at high temperature to give hydrides



- Reduces some metal ions in aqueous solution



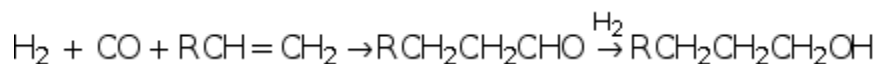
- Reduces oxides of some metals less reactive than iron



- Reactions with organic compounds:

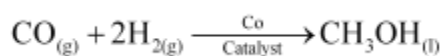
(i) Hydrogenation of vegetable oils in the presence of nickel as a catalyst to give edible fats such as margarine and vanaspati ghee

(ii) Hydroformylation of olefins (alkenes) to give aldehydes and then alcohols



Use of Dihydrogen

- In the synthesis of ammonia
- In the manufacture of vanaspati fat by hydrogenation of vanaspati oils
- In the manufacture of methanol



- In the manufacture of metal hydrides
- In the production of hydrogen chloride
- To reduce heavy metal oxides to metals in metallurgical processes

- In atomic hydrogen and oxy-hydrogen torches, which are used in cutting and welding purposes

Atomic hydrogen atoms recombine with the surface to be welded to raise the temperature to 4000 K.

- As a rocket fuel
- In fuel cells to generate electricity

It does not produce pollution and has more fuel efficiency than gasoline and other fuels.

The only pollutants – Oxides of nitrogen due to the presence of dinitrogen as impurity

Minimization of pollutants – By injection of small amount of water into the cylinder to lower the temperature

As a result, dinitrogen will not react with dioxygen.

Hydrogen Economy

- Technique of using dihydrogen in an efficient way
- Transmission of energy in the form of dihydrogen
- Involves transportation and storage of dihydrogen in the form of liquid or gas

Hydrides

Hydrides – Binary compounds with other elements except noble gases

Example – EH_x or E_mH_n (E = element)

Classification

Three categories:

- Ionic or saline or salt-like
- Covalent or molecular
- Metallic or non-stoichiometric or interstitial

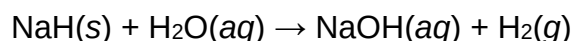
Ionic or Saline or Salt-like Hydrides

- Stoichiometric compounds with highly electropositive s-block elements (Exception – Lighter metal hydrides such as LiH, BeH₂, MgH₂ are covalent in nature)
- Crystalline and non-volatile
- Non-conducting in solid state, but conducting in molten state

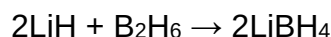
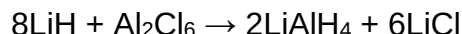
On electrolysis, liberate H₂ gas at anode



- React violently with water to produce dihydrogen gas



- Lithium hydride is used in the synthesis of some useful hydrides as lithium hydride does not react with oxygen and chlorine at moderate temperatures.



Covalent or Molecular Hydrides

- Compounds with p-block elements such as CH₄, NH₃, H₂O, HF
- Volatile in nature
- Further classified into three categories on the basis of the relative numbers of electrons and bonds in their Lewis structure :
 - Electron-deficient hydrides
 - Electron-precise hydrides
 - Electron-rich hydrides

Electron-deficient hydrides :

- Have few electrons to write their conventional Lewis structure
- All group 13 elements form electron deficient compounds. Example – Diborane (B₂H₆)
- Act as Lewis acids (Electron acceptors)

Electron-precise hydrides :

- Have as many numbers of electrons as required to write their conventional Lewis structure
- All group 14 elements form electron-precise compounds that are tetrahedral in shape. Example – Methane (CH_4)

Electron-rich hydrides :

- Have excess electrons present as lone pairs
- Group 15 – 17 elements form electron-rich hydrides.

Example –

Compounds	Number of lone pairs
NH_3	1
H_2O	2
HF	3

- Act as Lewis Bases (electron donors)
- Undergo intermolecular H-bonding as a result of lone pairs of electrons on highly electronegative atoms such as N, O, and F. This leads to the association of molecules and hence, there is an increase in boiling point. Higher the electronegativity, stronger is the H-bond and hence higher is the boiling point.

Metallic or non-stoichiometric or interstitial hydrides

- Many *d*-block and *f*-block elements (except group 7, 8, and 9) form these hydrides (only Cr of group 6 forms CrH).
- Conduct heat and electricity
- Non-stoichiometric

Example – $\text{LaH}_{2.87}$, $\text{YbH}_{2.55}$, $\text{PdH}_{0.6 - 0.8}$

- Called interstitial hydrides as it was earlier thought that in these compounds, hydrogen occupies interstitial sites in the metal lattice producing distortion without changing the type of the lattice.

However later, it was found that the lattices of these hydrides are different from their metal lattices. (Exception – Ni, Pd, Ce, and Ac)

- The transition metals which can absorb hydrogen are used as catalysts in reduction/hydrogenation reactions.
- Some metals such as Pd, Pt are used as storage media of hydrogen as they can accommodate a large volume of hydrogen. This property has a high potential for hydrogen storage and thus, these metals act as a source of energy.

Phosphorus exhibits +3 and +5 oxidation states. However, it forms PH_3 only, not PH_5 . This is because the exhibition of highest oxidation state (+5) of P is not favoured by high $\Delta_a H$ value of dihydrogen and $\Delta_{eg} H$ value of hydrogen.

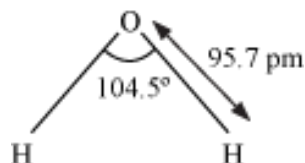
Water

Physical properties

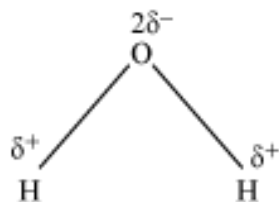
- Colourless and tasteless liquid
- Consequences of extensive intermolecular H – bonding in water:
 - High freezing point
 - High boiling point
 - High heat of vapourisation
 - High heat of fusion
- Water has the following properties higher than other liquids.
 - Specific heat
 - Thermal conductivity
 - Surface tension
 - Dipole moment
 - Dielectric constant
- Reasons for moderation of climate and temperature of living body:
 - High heat of vaporisation of water
 - High heat capacity of water
- Very good solvent for ion and molecule transporting purpose, required for plant and animal metabolism
- Miscible with alcohol and carbohydrates due to H – bonding

Structure of Water

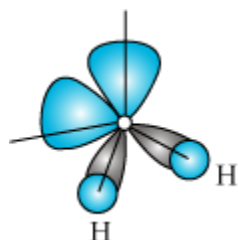
- Bent molecule with bond angle 104.5° and O – H bond length 95.7 pm.



- Highly polar molecule



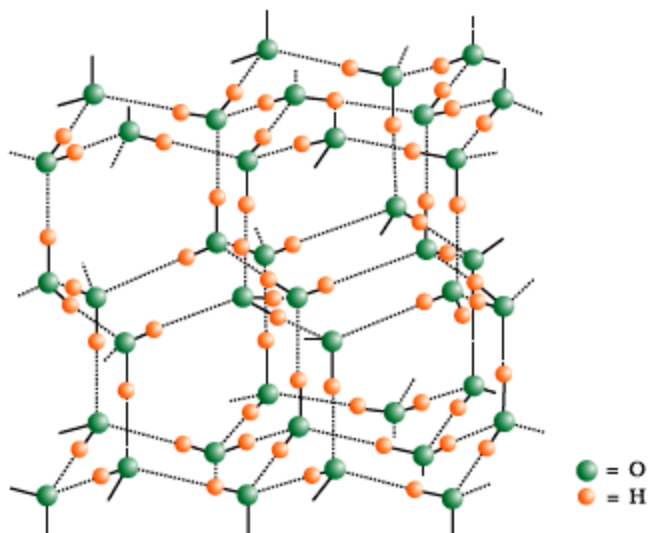
- The orbital overlap picture of water molecule is



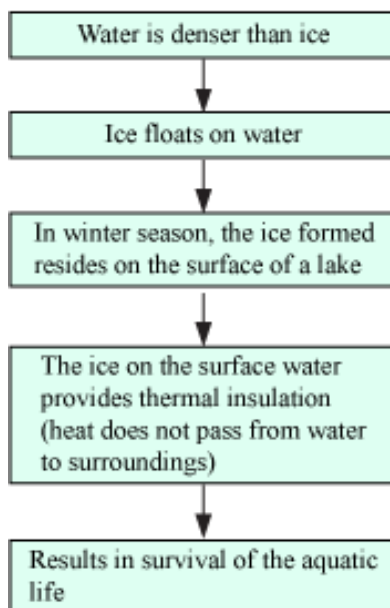
- In liquid state, water molecules are associated together by undergoing intermolecular H – bonding.

Structure of ice

- Ice – crystalline form of water
- Crystallises in hexagonal form at atmospheric pressure
- Crystallises in cubic form in lower temperature
- The highly ordered three-dimensional hydrogen bonded structure of ice is



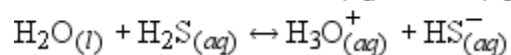
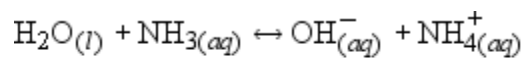
- X-ray study of ice crystals – Each oxygen atom is tetrahedrally surrounded by four other oxygen atoms at 276 pm distance.



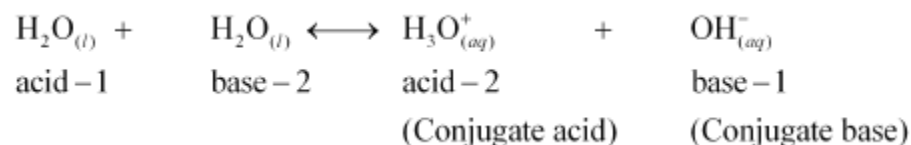
Chemical properties

- Amphoteric in nature (acts both as acid and base)

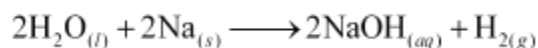
Example: Bronsted sense – Acts as acid with NH_3 while as base with H_2S



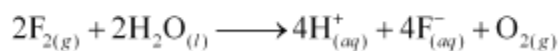
Example – Auto-protolysis (self-ionization) of water



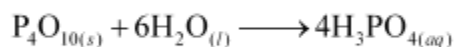
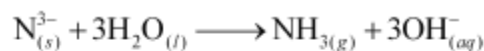
- Redox reactions
- Reduced to dihydrogen by highly electropositive metal



- Oxidized to O₂ during photosynthesis and with fluorine



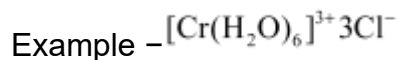
- Many ionic compounds and certain covalent compounds are hydrolysed in water.



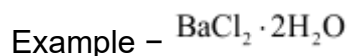
- Hydrates are formed during crystallization of some salts from aqueous solution.

Different types of such association of water:

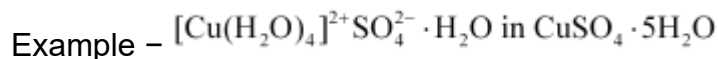
- Coordinated water



- Interstitial water



- Hydrogen-bonded water



Here, only one molecule of water (outside the brackets i.e. the coordination sphere) is hydrogen bonded in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The other four molecules of water (inside the bracket) are coordinated.

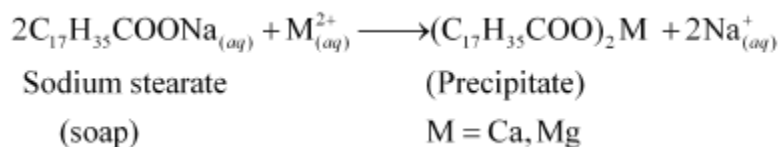
Hard and soft water

Hard water

- Water containing calcium and magnesium salts in the form of hydrogen carbonate, chloride, and sulphate
- Does not give lather with soap

Soft water

- Water free from soluble salts of calcium and magnesium
- Gives lather with soap easily
- Hard water forms scum/precipitate with soap



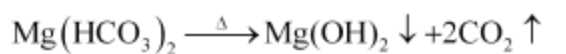
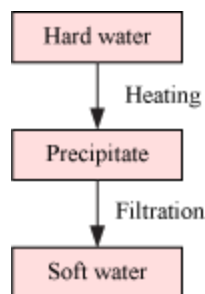
- Hard water is
- not effective in washing
- harmful for boilers – as salts are deposited in the form of scale which causes reduction of efficiency of the boiler
- Hardness of water – two types:

Temporary hardness

Permanent hardness

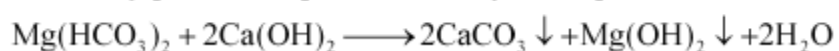
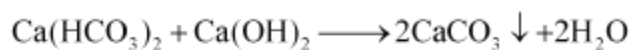
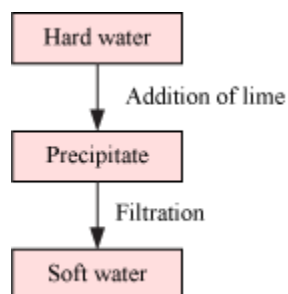
Temporary Hardness

- Cause – Presence of magnesium and calcium hydrogen carbonate
- Methods of removal:
- Boiling



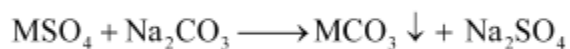
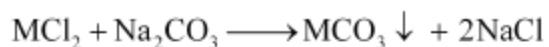
$\text{Mg}(\text{HCO}_3)_2$ is converted to $\text{Mg}(\text{OH})_2$ and not to MgCO_3 because the solubility product of $\text{Mg}(\text{OH})_2$ is greater than MgCO_3 . Therefore, $\text{Mg}(\text{OH})_2$ gets precipitated.

Clark's method



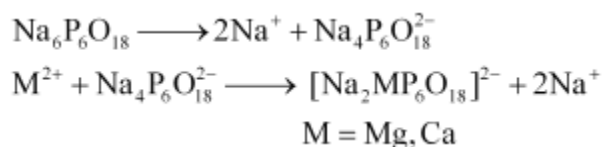
Permanent Hardness:

- Cause – Presence of soluble salts of magnesium and calcium salts as chlorides and sulphates
- Methods of removal:
- By treating with washing soda (Na_2CO_3) to form precipitate and then removing the precipitate

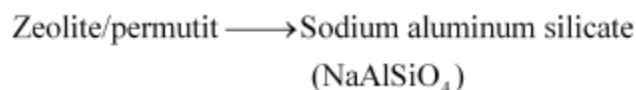


M = Mg, Ca

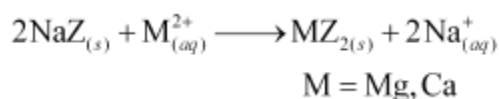
- Calgon's method – By treating with calgon (sodium hexametaphosphate, $\text{Na}_6\text{P}_6\text{O}_{18}$) to form complex anion, which keeps the Mg^{2+} and Ca^{2+} ions in solution



- Ion-exchange method (also called zeolite/permutit process) – Exchange of ions takes place.



For simplicity, NaAlSiO_4 is written as NaZ .



Regeneration of zeolite/permutit –



- Synthetic resins method – Ion exchange resins (RSO_3H) is changed to RNa by treating it with NaCl . Then, RNa exchanges Na^+ ions with Ca^{2+} and Mg^{2+} ions present in hard water and as a result, hard water is softened.

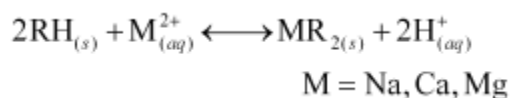


Regeneration of resin –



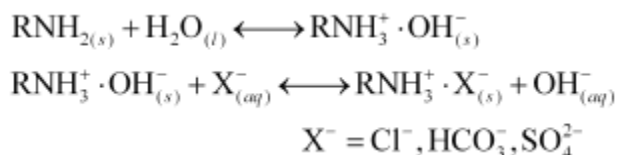
Hard water is passed successively through a cation exchange (in the H^+ form) and an anion exchange (in the OH^- form) resins to obtain pure de-ionized water, free from all soluble mineral salts.

In cation exchange process,

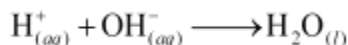


This process involves releasing of proton, making the water acidic.

In anion exchange process,



The liberated OH^- ions neutralise the H^+ ions released in the cation exchange process.

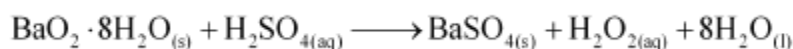


The cation and anion resins can be regenerated by adding dilute acid and alkali solutions respectively.

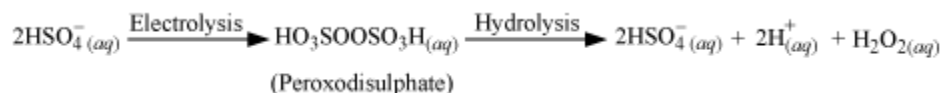
Hydrogen Peroxide (H_2O_2)

Preparation

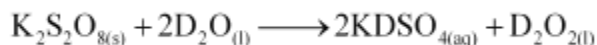
- By acidification of barium peroxide and removal of excess water by evaporation under reduced pressure



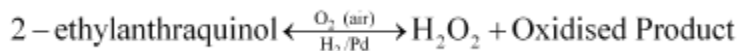
- Electrolytic oxidation of acidified sulphate solution gives peroxodisulphate, which on hydrolysis gives hydrogen peroxide.



- This method is also used in laboratory preparation of D_2O_2 .



- Industrial preparation – By the auto-oxidation of 2-ethylanthraquinol to form 1% H_2O_2



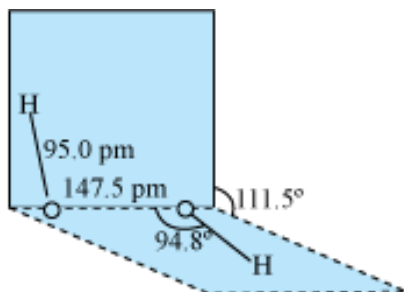
The formed H_2O_2 is concentrated by the following successive processes.

- Extraction with water and then by distillation under reduced pressure to obtain ~30% (by mass) H_2O_2

- Further distillation under low pressure to obtain ~ 85% (by mass) H_2O_2
- Freezing of remaining water to obtain pure H_2O_2

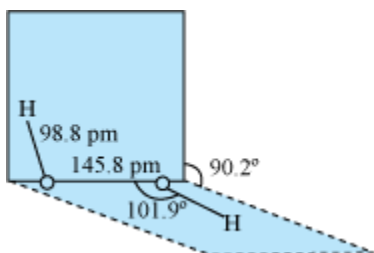
Structure

- Non-planar
- The structure of H_2O_2 in gas phase is shown below.



Dihedral angle is 111.5° .

- The structure of H_2O_2 in solid phase at 110K is shown below.



Dihedral angle is 90.2° .

Physical Properties

- Very pale blue (almost colourless) in pure state
- Miscible with water and forms a hydrate $\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$
- A 30% solution of H_2O_2 is marketed as '100 volume'.
- H_2O_2 – This means 1L of this H_2O_2 will give 100 L of oxygen at STP.
- Commercially, H_2O_2 is marketed at '10 volume'. This means it contains 3% H_2O_2 .

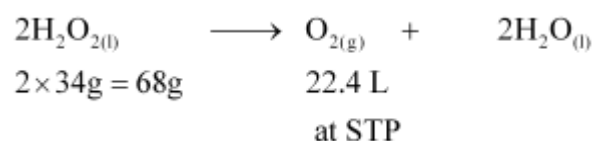
Example

If a H_2O_2 solution is marketed as 15 V, then what is its strength?

Solution

15 V H_2O_2 solution means that 1 L of this H_2O_2 solution will give 15 L of oxygen at STP.

H_2O_2 gives O_2 according to the following reaction.



That is, at STP, 22.4 L of O_2 is produced from 68 g of H_2O_2 .

Therefore, at STP, 15 L of O_2 is produced from $\frac{68\text{g} \times 15 \text{ L}}{22.4 \text{ L}}$ of H_2O_2
= 45.54 g of H_2O_2

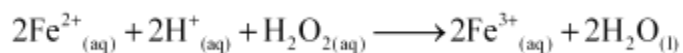
Hence, the strength of H_2O_2 solution marketed as 15 V is 45.54 g/L.

Chemical Properties

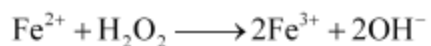
Acts as both oxidizing and reducing agents in both acidic and alkaline medium

- **As Oxidizing Agent**

- In acidic medium

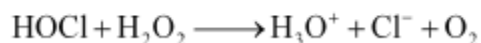


- In basic medium



- **As Reducing Agent**

- In acidic medium

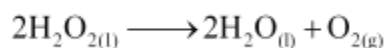


- In basic medium



Storage

- Stored in wax-lined glass or plastic vessels in dark – because it slowly decomposes when exposed to light



And, metal surfaces or traces of alkali (present in glass containers) catalyse this reaction.

- Urea is added as stabilizer.
- Kept away from dust – because dust can induce explosive decomposition of H_2O_2

Uses

- As bleaching agent in industries
- As hair bleach, antiseptic in daily life
- In the synthesis of hydroquinone, pharmaceuticals (Cephalosporin), and food products such as tartaric acid
- In the manufacture of chemicals such as sodium perborate and per-carbonate, which are important constituents of high quality detergents

- In environmental chemistry for pollution control treatment of domestic and industrial effluents, oxidation of cyanides, and the restoration of aerobic conditions to sewage wastes

This use has led to tremendous increase in the industrial production of H_2O_2 .

Detection of Hydrogen Peroxide

Heavy Water (D_2O)

Heavy water, also known as deuterium oxide (D_2O), is formed when deuterium reacts with oxygen. It has a freezing point of 3.82°C and a boiling point of 101.42°C .

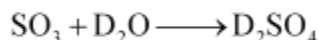
Preparation

- By exhaustive electrolysis of water
- As a by-product in some fertilizer industries

Uses

- As a moderator in nuclear reactors
- In exchange reactions for the study of reaction mechanisms
- In the preparation of deuterium compounds

Examples:



Disadvantages of Using Heavy Water:

- Injurious to living organisms
- Unfit for agricultural practices
- Mildly toxic in nature