

UNIT 9

HYDROGEN

- ◆ Most abundant & lightest in the universe [Earth O₂]
- ◆ Combines with all others except noble gases
- ◆ Largest no. of compounds than others
- ◆ 1st isolated by - Henry Cavendish
- ◆ Name given by - Lavoisier
- ◆ Hydrogen means - Water generator

Atomic structure

- ◆ Simplest of all
- ◆ Has a proton and an electron
- ◆ No neutrons

Attainment of stability

1) **By gaining** – $H + 1e^- \rightarrow H^-$

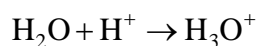
NaH, CaH₂, MgH₂ etc

2) **By sharing** – By covalent bonding

H₂O, NH₃, CH₄ etc

3) **By losing** – $H \rightarrow H^+ + 1e^-$

- H⁺ is
- Highly polar
 - Equivalent to a proton
 - Associated with others



Polar – can make distortion in electron cloud of other molecules / ions

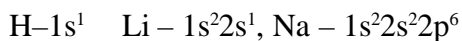
Position in the periodic table

– 1st element – Not in any group

Has similarities with alkali metal and halogens

Similarities with Alkali metals**1) Electric configuration**

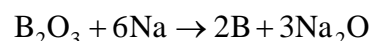
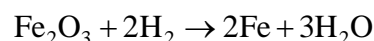
- Both have ns^1 as general valence shell configuration.

**2) Electro positive**

- Release an electron to form unipositive ions.

3) Liberation at cathode

- During electrolysis of Halides of both, H^+ and Alkali metal ions liberate at cathode

**4) Reducing power**

- Both are good reducing agents

5) Affinity for electro -ve elements

- Both have great affinity towards non metals.
- Form compounds like HCl , H_2O , H_2S etc similar to $NaCl$, Na_2O , Na_2S etc

Differences:-**1) Alkalimetals – Typical Metals**

Hydrogen – Non metal

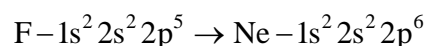
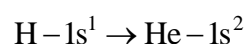
2) H_2 has high I.E

$H - 1312 \text{ KJ/mol}$

$Li - 520 \text{ KJ/mol}, Na - 495 \text{ KJ/mol}, K - 418 \text{ KJ/mol}$

3) H^+ has small size**4) H^+ is equivalent to a proton****Resemblance with Halogens****1) Electronic configuration**

- Both have valence electrons 1 less than nearest noble gas

**2) Atomicity**

$H_2, F_2, Cl_2, Br_2, I_2$ Both are diatomic

3) Ionization enthalpy

$H_2 - 1312 \text{ kJ/mol}$, $F - 1681 \text{ KJ/mol}$, $Cl - 1256 \text{ KJ/mol}$, $Br - 1143 \text{ KJ/mol}$, $I - 1009 \text{ KJ/mol}$

Both have comparable I.E

4) Electro negative character

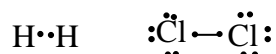
Both accept an electron to form monovalent anions

5) Liberation at Anode

On electrolysis of metal hydride and metal halides, both H^- and Halide ions move towards anode

Differences

- H_2 has smaller tendency to form H^- than halogens.
- Absence of non bonded electrons in H_2 [but halogens have]

**Dihydrogen (H_2)**

Various forms of Hydrogen

- Universe – most abundant 70%
- 90% solar atmosphere
- Doesn't occur in earth's atmosphere
- Seen as combined form

1) Isotopic Forms**1) Protium (P)**

- Normal hydrogen
- Represented as H_1^1
- e-1 P-1 n-0
- Atomic No-1
- Mass No - 1
- Abundance -99.98%

2) Deuterium (D)

- Heavy hydrogen
- Represented as H_1^2
- e-1 P-1 n-1
- Atomic No -1

- Mass No – 2
- Abundance – 0.0156%

3) Tritium (T)

- Radio active (β – rays)
- Represented as H_1^3
- e–1 p–1 n–2
- Atomic No–1
- Mass No – 3
- Abundance – $4 \times 10^{-15} \%$

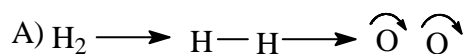
Chemical properties:-

- Identical
- Due to same no. of e^-
- physical properties
- Different
- Due to different masses

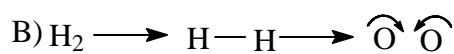
1) Isotopic effect

Property difference due to difference in mass no.

2) Isomeric forms



- Same nuclear spin direction.
- Called ortho hydrogen
- More stable
- Abundance - 75% at 300 K



- Opposite nuclear spin direction.
- Called para hydrogen
- Less stable
- Abundance - 25% at 300 K

3) Molecular hydrogen – H_2

- Most stable form
- Least Reactive form

4) Nascent hydrogen $2[H]$

- Newly formed

- Nascent hydrogen Just displaced from a compound
- More reactive than H_2
- Less stable than H_2

5) Atomic hydrogen -H

- By splitting of H_2
- Exist only at high T (4000-5000K)
- Least stable
- Most reactive
- Used in atomic hydrogen torch

Preparation of H_2

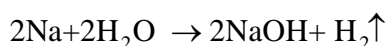
a) Laboratory preparation

By decomposing water, acids, alkalis etc.

A) From water

1) Alkali metals – Violent reaction

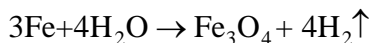
With water $\rightarrow H_2$ gas



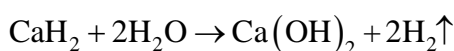
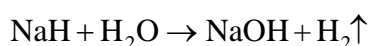
2) Alkaline earth metals – slow reaction with water $\rightarrow H_2$ gas



3) Metals decompose steam to produce their oxides by liberating H_2 gas.

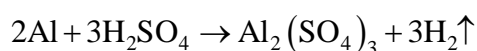
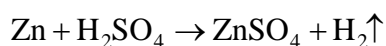
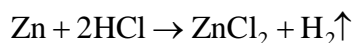


b) Hydrides of alkali metals and alkaline earth metals, when dissolved in H_2O produce $H_2\uparrow$



B) From acids

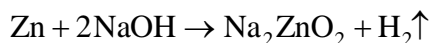
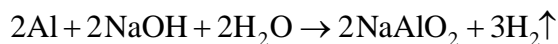
- Metal like Zn, Mg, Fe liberate H_2 gas from acids



* Reactive metals to be used

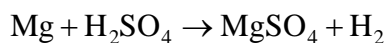
* Dil. acid to be used

If con. H_2SO_4 – SO_2 produced instead of H_2 gas

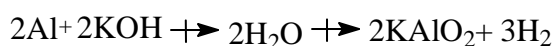
C) From Alkalis

Note:- High pure hydrogen (99.95)

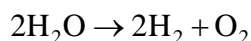
- Dil. H_2SO_4 + Mg Ribbon



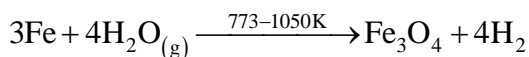
- Electrolysis of warm $\text{Ba}(\text{OH})_2$
- Water + NaH
- KOH + Scarp Al

**Industrial preparation**

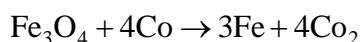
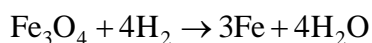
- a) Electrolysis of acidified H_2O



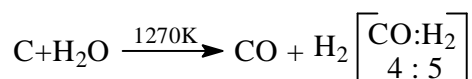
- Pt as electrodes
- b) Lanes process
- Steam passed through sponge iron



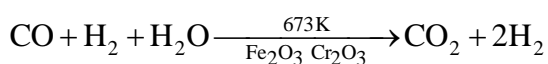
FeO_4 – Ferrosoferric oxide

Reduction Step**2) Bosch Process**

- Super heated steam passed through Red hot coke
- Water gas is formed



- Water gas again mixed with steam in the presence of Fe_2O_3 and Cr_2O_3



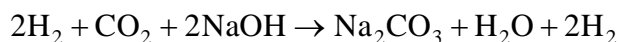
Fe_2O_3 – Catalyst

Cr_2O_3 – Promoter

$\text{CO}_2 + \text{H}_2\text{O}$ – Passed through water at high P

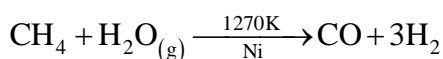
CO_2 – dissolve in H_2O

H_2 – Collected by absorbing in an alkali



4) Hydrocarbon steam process

- Modern method
- Principal source of H_2
- Natural gas [CH_4] mixed with steam



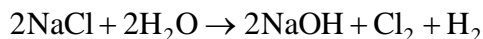
- H_2 collected as in Bosch process.

As a Biproduct

- Obtained on a large scale as a biproduct in the manufacture of many industrially important compounds

Eg : NaOH

Electrolysis of Brine



Physical Properties of H_2

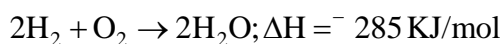
- Colourless
- Odourless
- Slightly soluble in H_2O
- Liquified only at very low T ($T_c = -253^\circ\text{C}$)
- H_2 – Non planar
- High thermal stability

Chemical Properties

- H_2 molecule – Thermally stable
- Very difficult to break at normal temperature [Highly exothermic]

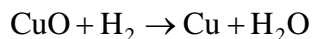
a) Combustibility

- Highly combustible gas
- Burns in air to form H_2O

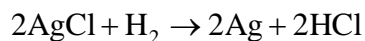


b) Reducing Property

- Metal oxides –heated with H_2^m reduced – metal is formed



Some chlorides are also reduced

**c) Reaction with non metals.**

→ with dioxygen → H_2O

→ with dinitrogen → NH_3

→ with halogens → HX



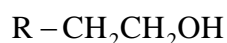
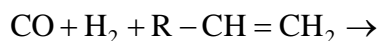
with F–Reacts even at dark

with I – needs a catalyst

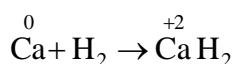
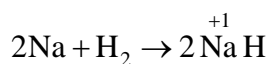
d) Reaction with organic compound**1) Hydrogenation**

- With unsaturated organic compounds, forms saturated $C_2H_4 \xrightarrow{Ni} C_2H_6$

Hydrogen gas – pass through veg. oils – converted to fat – vanaspati ghee –

2) Hydroformylation

Hydroformylation – addition of a hydrogen atom and a formyl group ($-CHO$) to a $C=C$

e) Reaction with metals

Shows oxidising property of H_2

Uses of H_2 gas

- 1) Manufacture of HCl , NH_3 , CH_3OH , HNO_3 etc
- 2) Hydrogenation of oil
- 3) Filling aeroplane tyres [85% He +15% H_2]

- 4) Atomic hydrogen torch
- 5) As a rocket fuel
- 6) Fuel cell
- 7) Reducing agent

Compounds of hydrogen

Hydrides

- Binary compounds of H_2 with other elements
- Three type

(1) Ionic | salt like | Saline

- Formed by S - Blocks
- NaH , CaH_2 , etc
- electro -veity < 2.1
- O.S of the $H_2 = -1$
- Crystalline solids
- Non volatile [stable]
- Solid form – Non conducting
- Molten/aqueous – conduct
- with $H_2O \rightarrow$ Alkaline soln and H_2 gas.

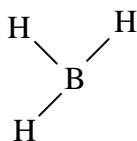
(2) Covalent /Molecular hydrides

- With p –block [13–17]
- H_2O , NH_3 , CH_4 , etc
- Covalent bonding
- Prepared by:
 - Direct reaction of non-metals with hydrogen $N_2 + 3H_2 \xrightarrow{Fe} 2NH_3$
- Three type

(1) Group 13 hydrides

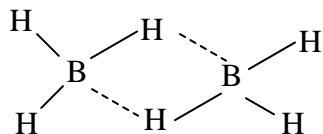
Eg: BH_3/B_2H_6 - Diborane

- Central atom - Boron (5)
- Configuration – 2, 3
- Valence electrons - 3



- Central atom has only 6 e^- .

- Electron deficient
- Act as electron acceptors
- Lewis acids

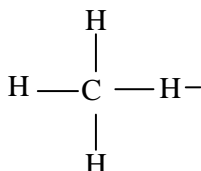


- Exist as dimeric form
- (Polynuclear hydrides)

Group-14

Eg: CH₄

Central atom – C(6). 2, 4

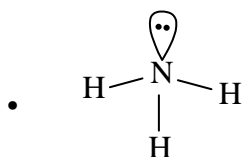


- Central atom surrounded by 8 e⁻
- Known as e⁻ precise

Group -15, 16, 17

Eg: NH₃

Central atom – N(7) 2, 5



- Central atom has compair
- Also known as e⁻ ns
Act as e⁻ donours in reactions
- Lewis bases

3) Metallic hybrides or

Interstitial/non–stoichiometric

- On heating hydrogen reacts with many transition metals, lanthanides and actinides (d & f - block)
- Such hybrides have metallic appearance
- These are less dense than parent metal
- Conduct heat and electricity [not well as parent metal]

- Here, hydrogen atoms seen inside the interstitial spaces of parent metals
- Do not obey law of constant proportion.



- Such hydrides are widely used in catalytic reduction and hydrogenation reaction
- Metals like Ni, Pt, Pd, etc can accommodate a large amount of hydrogen gas

Intermediate hydrides

Hydride gap

elements of group 7, 8 and 9 do not form hydrides

Mn	Fe	Co
7,	8,	9

- Region of periodic table from 7, 8, 9 is referred to as hydride gap
- These have low affinity to hydrogen in their normal oxidation states.

Water [H₂O]

Most important substance known to man

Abundantly found on earth.

Found as -

- 1) Ice in mountains
 - 2) Water in oceans, etc
 - 3) Vapour in atmosphere
- Covers about 3 quarters of earth
 - About 70% of human body is water

Physical Properties

Colourless, odourless, tasteless in pure form

Molar mass – 18 g /mol

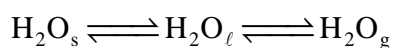
- MP – 273 K

BP – 373 K

Density – 1g/cm³

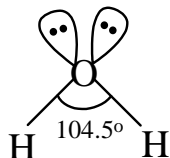
Triple point

- H₂O exist in 3 phases
- At 0.0098°C and 4.58 mmHg



Structure of water**In the gaseous phase**

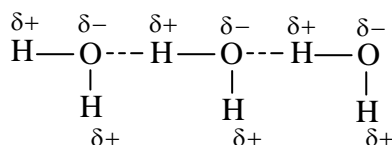
A water molecule consists of two hydrogen atoms joined to an oxygen atom by covalent bonds



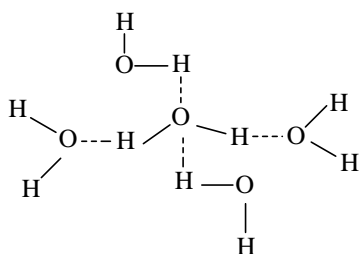
- Oxygen has 6 valence \bar{e}
- Valence s and p orbitals undergo sp^3 hybridization
- 4 sp^3 hybrid orbitals
- 2 will overlap with 1s orbitals of 2H atoms
- Due to the presence of 2 lone pairs in O_2 , bond angle of H–O–H bond will be reduced to 104.5° ($109^\circ 28'$)
- Hence structure of water is Angular /bend.

Polarity of water

- O_2 is more electronegative than H_2
- Pull the shared electron pairs more towards it.
- Hence , H–O bond acquires polarity
- Polarity result in association of water molecules
- Gives a liquid phase with high BP,

**Liquid phase water**

- H_2O molecules are held by inter molecular hydrogen bonds



- One water molecule is surrounded by 4 other water molecules
- Co-ordination no. of a water molecule is 4

Solid Phase

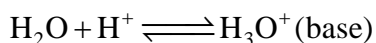
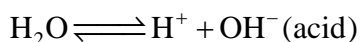
- Crystalline form
- By 2 ways
- At atm pressure – crystallises into hexagonal form
- Each oxygen is surrounded by 4 other oxygen atoms
- At very low T- crystallises into cubic form.

During crystallisation – \uparrow in No. of H bonds – \uparrow in volume \rightarrow \downarrow in density – floats on water surface

During melting – breaking of H bonds, \downarrow in volume of water, with \uparrow in Temp – per min.
Volume at 4°C - max. density of 1 g/ml at 4°C

Chemical Properties of H₂O**1) Amphoteric (Amphiprotic)**

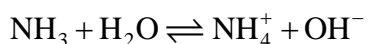
- Can donate H⁺ (acid) as well as accept H⁺ (base)



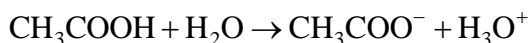
- Hence, water acts as a Lowry Bronsted Acid & Base
- Substance behaving as acid and base - “Amphoteric”

Substance that can give as well as can accept a proton – Amphiprotic

As an acid

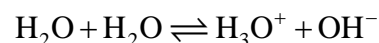


As a base :

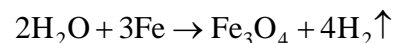
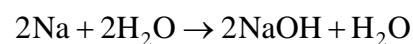


- Anion formed (OH⁻) due to the loss of H⁺ \rightarrow conjugate base
- Cation formed (H₃O⁺) due to the given of H⁺ \rightarrow conjugate acid

Autoprotolysis also take place as

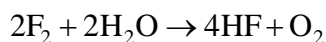
**2) Redox Reactions with water**

Water reacts with highly electropositive metals



In above reactions, Na, Fe, etc got oxidised and H_2O is reduced.

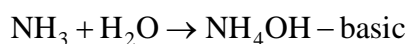
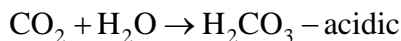
Fluorine can oxidise water.



Hydrolysis

Interaction of a cation or an anion or both with water.

An acidic, basic or a neutral solution is formed.



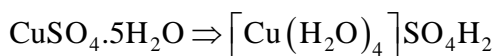
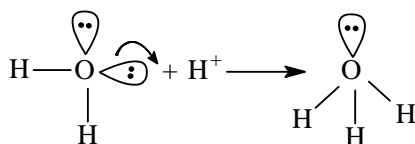
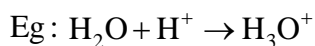
Sugar solution – Neutral

Hydration : Attraction of negative charged oxygen atom allows them to congregate around +ve ions

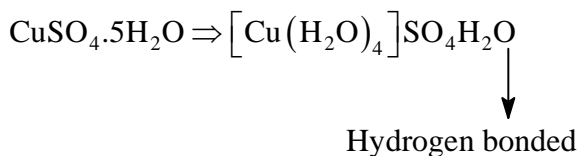
\Rightarrow +ve charged hydrogen atoms gather around –ve ions

- Water may exist as associated with other molecules or ions
- 3 ways
 - a) As co-ordinated
 - b) As hydrogen bonded
 - c) As interstitial

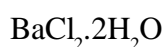
a) Co-ordinated water

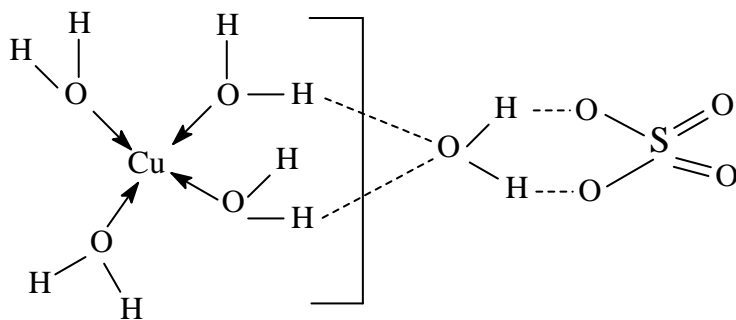


b) Hydrogen bonded water



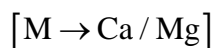
c) Interstitial water



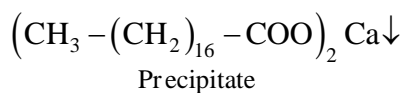
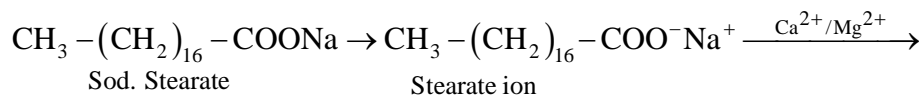


HARDNESS

- ★ Purest form of water is rain water ($p^H = 7$)
- ★ Due to the presence of soluble salts of Ca/Mg
- ★ As $M(HCO_3)_2$, MCl_2 , MSO_4 , etc



- ★ Soap do not form lather with hard water
- ★ Forms a precipitate



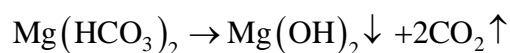
Removal of Hardness

A) If $M(HCO_3)_2$ is present

- ★ Less stable compounds
- ★ Easy to Remove
- ★ Known as Temporary hardness

Removal

1. Boiling



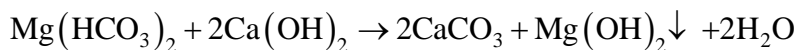
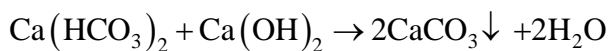
Note

If $Mg(OH)_2$ – Concentration of Mg^{2+} is only cube root of solubility product

In $\text{MgCO}_3 - \text{Mg}^{2+}$ concn. is square root of K_{sp}

2. Clark's Method

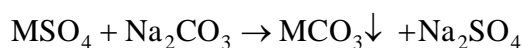
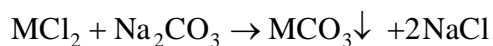
Calculated amount of lime is added to water



B) If MCl_2 , MSO_4 , etc

- * Stable compounds
- * Not easy to Remove
- * Special methods are used

1. Treatment with Na_2CO_3



2. Permutit Process

- * Zeolite is added to water $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2 \cdot x\text{H}_2\text{O}$

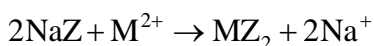
$$n = 5-13$$

$$x = 3-4$$

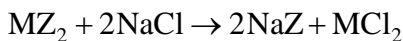
- * These are hydrated sodium aluminium silicates.



- * Ca^{2+} and Mg^{2+} ions are replaced by Na^+ ions

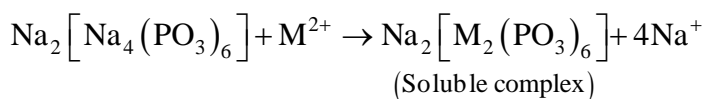
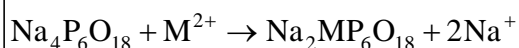
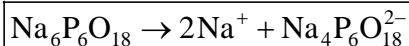


- * Zeolites can be regenerated by treating exhausted zeolite with NaCl



3. Calgon Process

- * $\text{Na}_2[\text{Na}_4(\text{PO}_3)_6]$ – Sodium hexametaphosphate is added to water



- * Ca^{2+} and Mg^{2+} ions in water are rendered ineffective by calgon, forming their soluble complexes in water – sequestration
- * This method is preferred for getting soft water for laundry purpose

4. Organic ion exchange Resin

Resin - Long chain Hydrocarbons

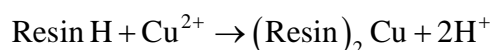
- * Both cations and anions can be removed from water
- * 2 steps

Step I

a) Using Cation Exchange Resin

Long chain hydrocarbon, attached to an acidic group

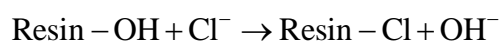
Eg. $\text{R}-\text{COOH}$



b) Using Anion Exchange Resin

Long chain H.C, attached to a basic group (OH^-)

Eg: $\text{R}-\text{NH}_4\text{OH}$



- * Resultant water \rightarrow free from cation and anions.
- * Known as demineralized or deionized water

Measurement of Hardness

- * Represented as degree of Hardness
- * Expressed in terms of amount of CaCO_3 , equivalent present in 10^6 parts of water
- * Unit - Parts Per Million (ppm)

Disadvantages of Hardness

- 1) Poor cleansing effect of soap
- 2) Boiler scale

Heavy water (D_2O)

- * Oxide of D_2
- * Present in H_2O (0.0156%)
- * 1st isolated by Harold.C. Urey
- * By prolonged electrolysis of H_2O containing small amount of NaOH
- * H_2O decomposes 1st

- * Resulting solution is rich in D_2O

Properties

- 1) Colourless, odourless, tasteless
- 2) Most of physical constants are higher than H_2O

	H_2O	D_2O
BP	$100^\circ C$	$101.42^\circ C$
MP	$0^\circ C$	$3.8^\circ C$

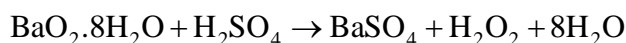
- 3) Harmful to plants & animal

Uses

- * Source of D_2
- * Moderator in nuclear reactors (controls fast moving neutrons)
- * Disinfectant

Hydrogen Peroxide (H_2O_2)

- 1) 1st prepared by J.L. Thenard
- 2) Action of dil. H_2SO_4 and Barium Peroxide



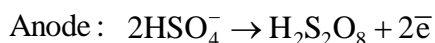
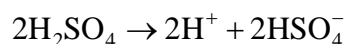
————→ Thenard process

- 3) White ppt of $BaSO_4$ can be removed by filtration
- 4) About 5% H_2O_2 is obtained
- 5) Anhydrous $BaSO_4$ cannot be used because it forms a layer over BaO_2 to reduce the reaction rate

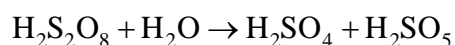
Other Preparation Methods

Electrolysis

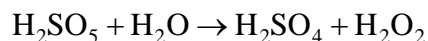
Cold solution of 50% H_2SO_4 is electrolysed



Peroxodisulphuric acid, ($H_2S_2O_8$) is hydrolysed to get H_2O_2

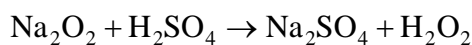


(H_2SO_5 – Peroxomonosulphuric acid)



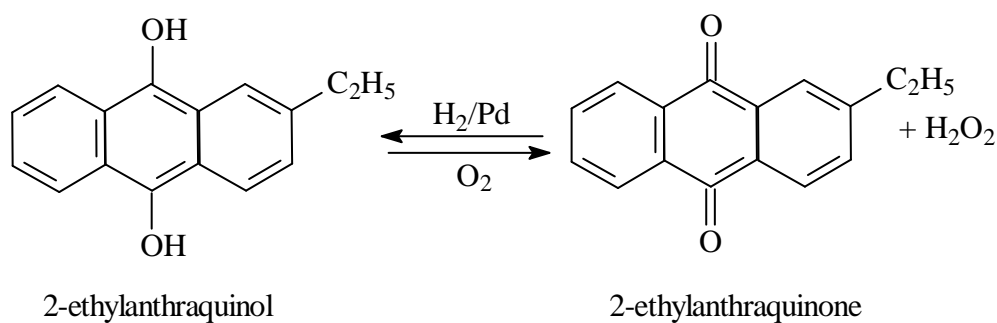
Merck's Process:

Calculated amount of Na_2O_2 is gradually added to ice cold dil. H_2SO_4 (20–80%)



Industrial

Oxidation and reduction of 2-ethylanthraquinol

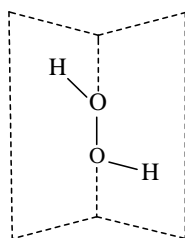


Physical Properties

- ✱ Pale blue liquid in pure form
- ✱ More dense and viscous than water (more H₂ bonds)
- ✱ Smell like HNO₃
- ✱ Completely miscible in water, alcohol and ether

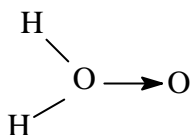
Structure

- ✱ Non planar, non-linear
- ✱ Open book like
- ✱ O₂ in SP³ hybridisation

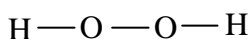


Dihedral/ inter planar
angle : solid - 90.2°
Liquid - 111.5°

Kingzett structure



Baeyer's structure

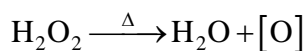


Chemical Properites

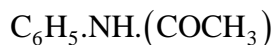
1) Stability

- Highly unstable
- due to -1 O.S of O_2

- Readily decomposes to water and nascent oxygen
- Accelerated by heat, dust, metal pieces, light, rough surface, etc



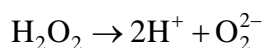
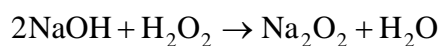
- Preservatives: Glycerol, Urea, Acetanilide, H_3PO_4 , etc



- Kept in wax coated plastic bottles
- Alkaline oxides present in glass may ↑ decomposition

Acidic Nature

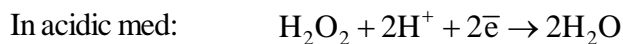
- * Dibasic acid
- * Give 2 H^+ ions



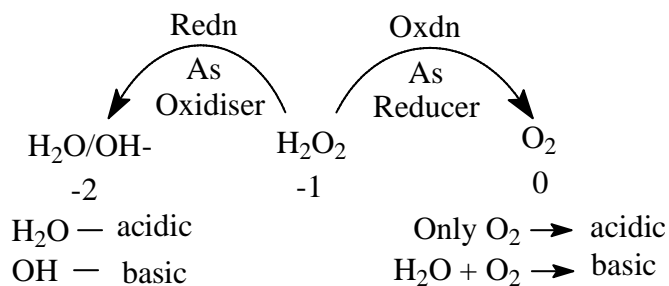
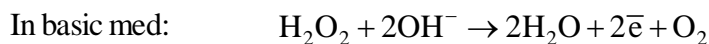
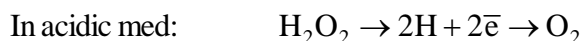
Oxidising & Reducing Nature

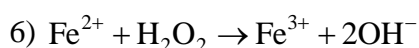
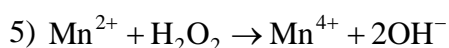
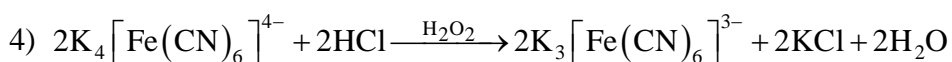
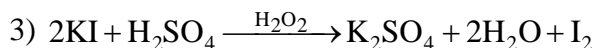
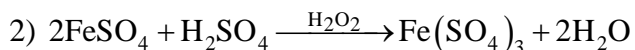
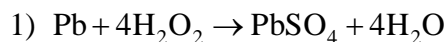
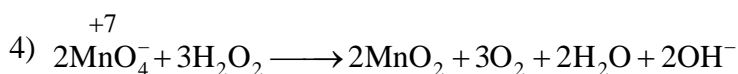
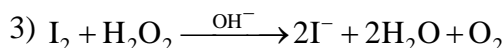
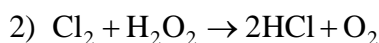
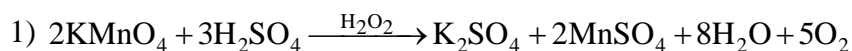
- * Can act as both
- * both in acidic & basic media
- * Due to -1 O.S. of O_2

As an oxidiser:



As a reducer:

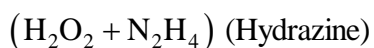


Oxidiser:**Reducer:****Bleaching Property**

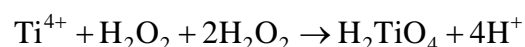
- Can produce Nascent O_2
- Used to bleach hair, feather, silk, wool etc

Uses of H_2O_2

- 1) Bleaching agent for delicate materials (silk, wool, hair, feather, etc)
- 2) Antiseptic
- 3) Manufacture of chemicals like sodium perborate Per carbonate, etc - in high quality detergents
- 4) Synthesis of pharmaceuticals , food products like tartaric acid etc.
- 5) To control air pollution (restore aerobic condition in sewage)
- 6) 93% H_2O_2 – Oxidant for Rocket fuel

**Test for H_2O_2** **1) Perchromic acid test**

Treated with acidified Ti salt solution – Yellow/Orange



2) Blue colour with starch solution**3) Perchromic acid Test**

dil.soln. of H_2O_2 is shaken with acidified soln. of chromium salt \rightarrow Blue colour $[\text{CrO}_5]$

Concentration of H_2O_2

* Expressed as volume strength

* Represents the volume of O_2 liberated from unit volume of H_2O_2 at NTP.

Eg: 10 V, 20 V, 30 V etc.

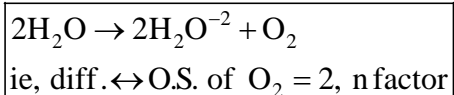
10 V means – 1 ml H_2O_2 liberates 10 ml O_2

(100 V H_2O_2 – Perhydrol)

Relations for problem solving

Normality = Molarity \times n fact

(For H_2O_2 n factor = 2)



$$\text{Molarity} = \frac{n}{\text{vol.in L}}$$

$$\text{Molarity} = \frac{\text{Vol. str}}{11.2}$$

$$\text{Strength} = \frac{\text{Vol. str} \times 1.7}{5.6}$$

$$\% \text{ Strength} = \frac{\text{Vol. str} \times 17}{56}$$

Degree of Hardness:

$$\text{If ppm of compound is given, ppm in terms of } \text{CaCO}_3 = \frac{\text{ppm of compound}}{\text{m.mass of compound}} \times 100$$