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HYDROGEN

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Introduction

Hydrogen is the first element in the periodic table and is also the lightest element known. It atomic form exists only at high temperatures. In the normal element form, it exists as a diatomic molecule, i.e. H_2.

Unique Position of Hydrogen in the Periodic Table

A proper position could not be assigned to hydrogen either in the Mendeleev's periodic table or Modern periodic table because of the following reason :

In some properties, it resembles alkali metals and in some propperties it resembles halogens. So hydron can be placed both in group 1 and group 17 with alkali metals and halogen respectively.

Resemblance with Alkali Metals

1. **Electronic configuration**

Hydrogen contains one electron in the valence shell like alkali metals

H : $1s^1$

Li : $[He]2s^1$

Na : $[Ne]3s^1$

K : $[Ar]4s^1$

Rb : $[Kr]5s^1$

2. **Electropositive character**

Like alkali metal, hydrlogen also loses its only electron to form hydrogen ion, i.e., H^+

$$\underset{1s^1}{H} \longrightarrow \underset{1s^0}{H^+} + e^-$$

$$\underset{1s^2\,2s^2\,2p^6\,3s^1}{Na} \longrightarrow \underset{1s^2\,2s^2\,2p^6}{Na^+} + e^-$$

3. **Oxidation state**

Like alkalil metals, hydrogen exhibits an oxidation state of +1 in its compounds.

$H^+\ Cl^-$	$Na^+\ Cl^-$	K^+Br^-
Hydrogen chloride	Sodium chloride	Potassium chloride

4. **Reducing agent**

Alkali metals act as reducing agents because of their tendency to lose valence electron. Hydrogen is also a very good reducing agent as evident from the following reactions :

$$Fe_3O_4 + 4H_2 \xrightarrow{\Delta} 3Fe + 4H_2O$$

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

5. Combination with electronegative elements

Just llike alkali metals hydrogen combines with electronegative elements such as halogen, oxygen, sulphur, etc to form compounds with similar formulae

Halides	Oxides	Sulphides
HCl	H_2O	H_2S
NaCl	Na_2O	Na_2S

DIFFERENCE FROM ALKALI METALS

1. Ionization enthalpy

Ionization enthalpy of hydrogen (1312 kJ mol^{-1}) is very high in comparison with the ionization enthalpy of alkali metals.

2. Existence of H^+

It has been established that H^+ ion does not exist freely in aqueous solution. This is because of the fact that has a very small sixe ($\approx 1.5 \quad 10^{-3}$ pm) as compared to normal atomic and ionic size (which range from 50 to 220 pm). Thus it exists in aqueous solution in the form of hydrated roton with a formula, $H_9O^+_4$. However, for the sake of simplicity hydrated proton is represented by hydronium ion, H_3O^+.

On the other hand, the alkali metal ions mostly exist as hexahydrated ions.

3. Difference in halides

Hydrogen halides are different from the halides of alkali metals although they have similar molecular formulae. For example

(i) Pur HCl is a covalent compound while NaCl is an ionic compound.

(ii) HCl is a gaseous compound while NaCl is a solid at ordinary temperature.

Resemblance with Halogens

1. Electronic configuration

Just like halogens, hydrogen needs one electron to attain the configuration of nearest noble gas.

H	:	$1s^1$
F	:	$1s^2 2s^2 2p^5$
Cl	:	$1s^2 2s^2 2p^6 3s^2 {}_{3p}{}^5$

2. Atomicity

Like halogens, hydrogen also exists in a diatomic state. The atomicty of hydrogen as well as halogens is two.

3. Electrochemical nature

During electorlysis of LiH, CaH_2, etc, in molten state hydrogen is evolved at the anode indicating its electronegative nature. In this respect, hydrogen shows resemblance with halogens which are also liberated at the anode during electrolysis.

4. Oxidation state

Just like halogens, hydrogen also exhibit state of -1 in some of its compounds such as metal hydrides.

$Na^{+1}\ H^{-1}$ $\quad\quad$ $Na^{+}Cl^{-}$

5. Combination with alkali metals

Just like halogen, hydrogen also combines with alkali metals to form salts with similar formulae.

NaH	LiH	CaH_2
NaCl	LiCl	$CaCl_2$

6. Combination with non-metals

Just like halogens hydrogen also react with non-metals such as carbon, silicon, germanium, etc, to form covalent compounds.

Halides :	CCl_4	$SiCl_4$	$GeCl_4$
Hydrides :	CH_4	SiH_4	GeH_4

7. Ionization energy

Ionization energy of hydrogen is comparable to the ionization energies of halogens as shwon below :

Element :	H	F	Cl	Br
Ionization energies (kJ mol^{-1}):	1312	1681	1255	1121

Difference from Halogens

1. Less tendency of hydride–formation

Although hydrogen forms hydride ion (H^-) like halogens, yet its tendency to form hydride ion is very less in comparison with the halogens. It is quite clear from the fact that halogens form halides with very large number of metals but hydrogen form hydrides with only a small number metals like sodium and calcium, etc.

2. Absence of unshared electrons

There is no unshared pair of electron in hydrogen molecule (H_2) whereas halogen molecules have six unshared electron pairs as shwon below :

$$H - H \qquad :\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}} - \underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: \qquad :\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}} - \underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:$$

3. Nature of oxides

The oxides of halogen are acidic in nature whereas oxide of hydrogen is neutral

H_2O	Cl_2O_7, I_2O_5
Neutral oxide	Acidic oxides

4. Nature of compounds

The compounds of hydrogen with halogens, i.e. hydrogen halides (HF, HCl, HBr, HI) are low boiling covalent compounds whereas alkali metal halides (LiF, Nacl, KBr, CsI) are high melting ionic solids.

Isotopes of Hydrogen

It has been found by mass spectrograph that hydrogen has three isotopes namely; protium, deuterium and tritium. The relative abudance of three isotopes of hydrogen is as under.

Isotopes	${}^{1}_{1}H$	:	${}^{2}_{1}H$	:	${}^{3}_{1}H$
Abudance	1	:	$1.5\ 10^{-2}$	:	$1\ 10^{-17}$

(a) **Protium or hydrogen**

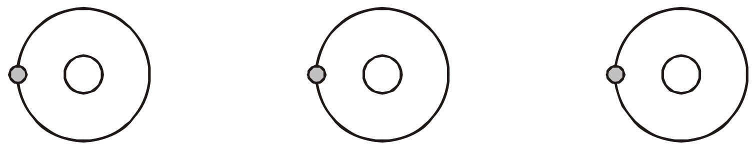
It is represented by the symbol H. Its atomic number is 1 and mass number is also 1. It has one proton (but no neutron) in its nucleas and one electron in its 1s orbital. Naturally occuring hydrgen contains 99.985% of this isotopes.

(b) **Deuterium or heavy hydrogen**

It is represented by the symbol D or ${}^{2}_{1}H$. It's atomic number is 1 and mass number is 2. It has proton and one neutron in its necleus and one electon in its 1s orbital. Naturally occuring hydrogen has 0.15% of this isotopes mostly in the form of HD.

(c) **Tritium**

It is represented by the sympbol of T or ${}^{3}_{1}H$. Its nucleus hs one proton and 2 neutron and there is one electron in its 1s orbital. It is an extremely rare isotope. Out of 10^{17} molecules of ordinary hydrogen there is just one molecule of tritium. this isotope of hydrogen is radioactive in nature and emits low energy β- particles ($t_{1/2} = 12.33\gamma$).

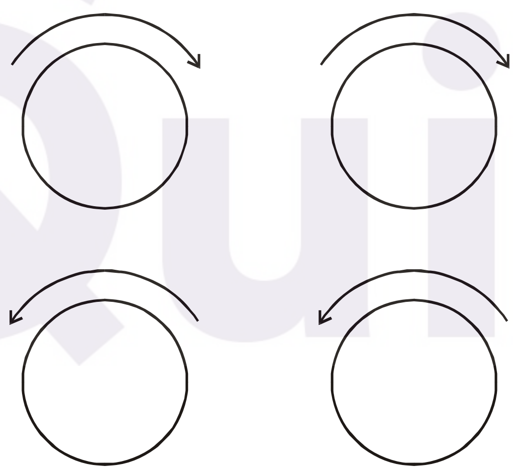


PROTIUM (^1_1H)	DUTERIUM (^2_1H)	TRITIUM (^3_1H)
(Non – Radioactive)	(Non – Radioactive)	(Radioactive)
99.985%	0.015%	10^{-15}%

It may be noted that three isotopes of hydrogen have properties because of the same electronic configuaration, $1s^1$. However due to different mass numbers they have different rates of chemical reactions. For example, reaction between protium and chlorine is 13.4 times faster than that between deuterium and chlorine. Similary electrolysis of ordinary water (H_2O) occurs more rapidly than of heavy water (D_2O). Difference in properties arising due to the difference in mass number is referred to as **isotopic effect.**

(d) **Ortho and para hydrogen**

When the spins of the nuclei are in the same direction (parallel spins), dihydrogen is called ortho hydrogen and when the spins are in the opposite direction (anti parallel spins), dihydrogen is called para hydrogen.



Total spin = $\frac{1}{2}+\frac{1}{2}=1$ **(ortho H_2)**

Total spin = $\frac{1}{2}-\frac{1}{2}=0$ **(para H_2)**

HYDRIDES

Binary compounds of the elements (metals or non-metals) with the hydrogen are called hydrides. The type of hydride which an element forms depends on its electro negativity and hence the type of bond formed. While there is no sharp divison between ionic, covalent and metallic bonding, there are classified as metallic bonding, there are classified as :

(a) Ionic or salt like hydride

(b) Covalent or molecular hydride

(c) metallic or interstitial hydride

Ionic Hydrides

When hydrogen directly combines with any alkai metal or with alkaline earth metals Ca, Sr or Ba

$$2Li(s) + H_2(g) \rightarrow 2LiH(s)$$
$$Ca(s) + H_2(g) \rightarrow CaH_2(s)$$

Covalent Hydrides

These hydrides are formed by all the true non-metals (except zero group elements) and the elements like Al, Ga, Sn, Pb, Sb , Bi, etc., which are normally metallic in nature i.e. this class includes the hydrides of p-block elements.

Molecular hydrides are further classified according to their relative numbers of electrons and bonds in their lewis structures

(i) **Electron dificient molecular hydrides :**

Diborane (B_2H_6) is an example.

(ii) **Electron-precise molecular hydrides :**

These are formed by elements of group 14. The molecules are tetrahedral. Methane (CH_4) is an example.

(iii) **Electron-rich molecular hydrides :**

NH_3, H_2O, HF etc. are examples.

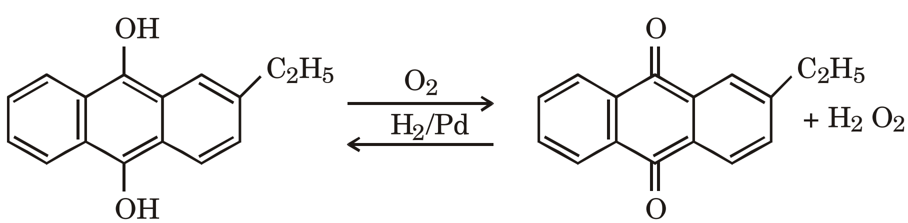
Metallic Hydrides

These hydrides are often non-stoichiometric and their composition vary with temperature and pressure. Formula of some of the hydrides of this class are :

$$TiH_{1.73},\ CeH_{2.7},\ LaH_{2.8}$$

Hydrogen Peroxide

Although the preparation of hydrogen peroxide given in NCERT book is sufficient for JEE, but here we are covering only one preparation.



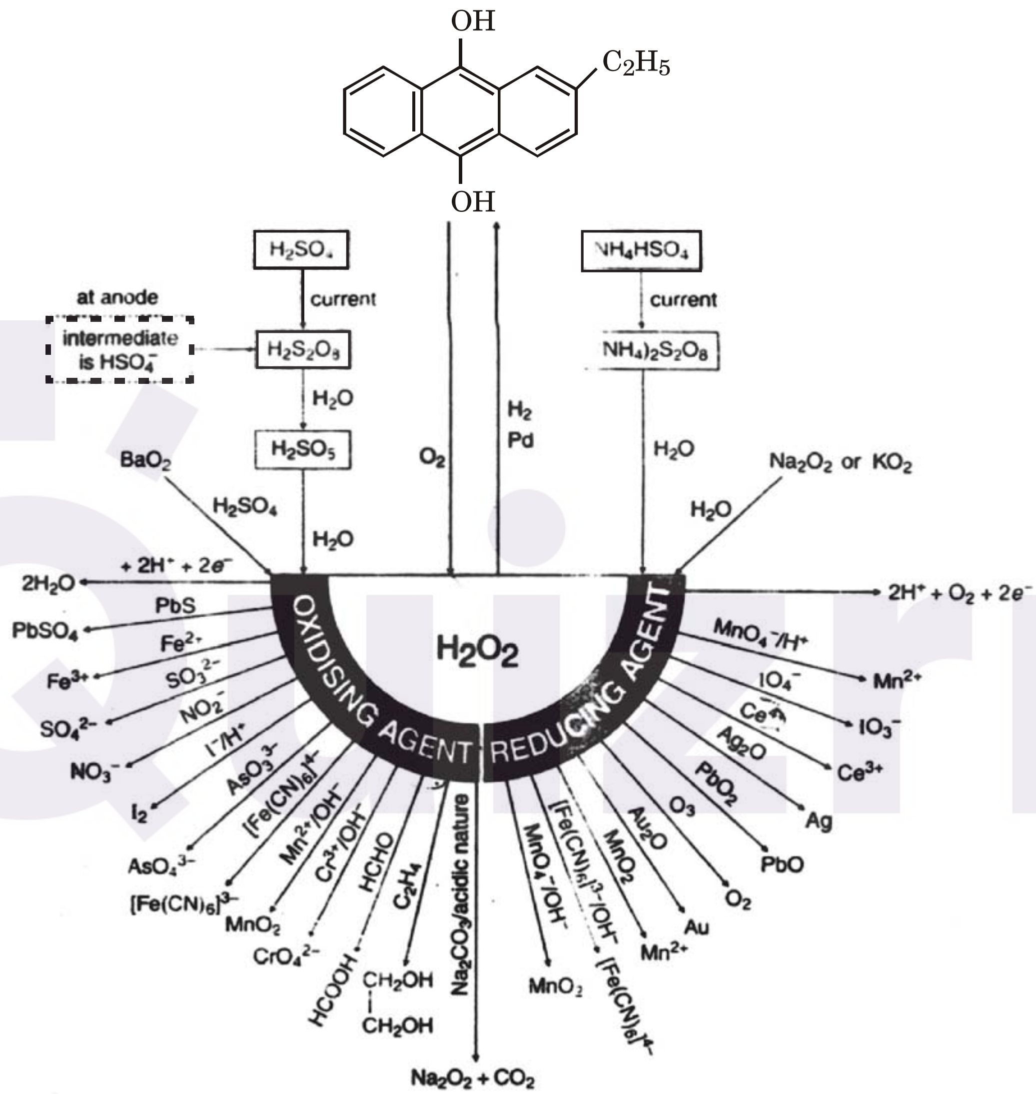
(2 ethyl anthraquinol) (2 ethyl anthraquinol)

- H_2O_2 is unstable and hence it disproportionates depending on the temperature and concentration.

$$2H_2O_2 \longrightarrow 2H_2O \quad + O_2$$

reduction

oxidation



Some more points :

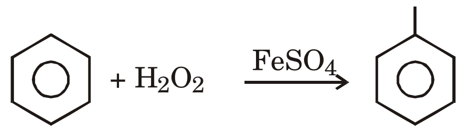
1. H_2O_2 as a bleaching agent :

Due to its oxidizing nature, it acts as a bleaching agent.

$$\text{Coloured material} + O \longrightarrow \text{Colourless.}$$

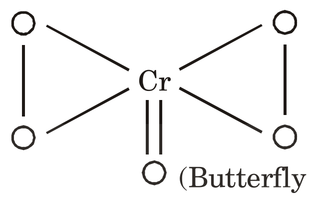
It bleaches meterials like silk, hair, ivory, cotton, wool etc.

2. Oxidizing nature

(a) 

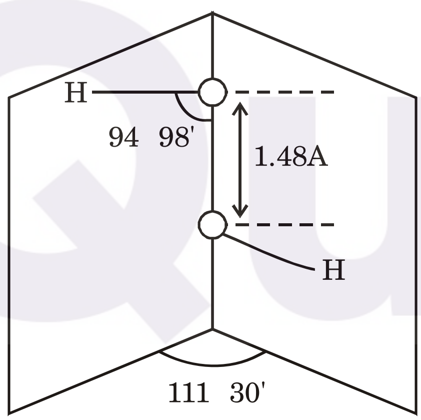
(b) A solution of chromic acid in suplhuric acid or acidified potassium dictiromate is oxidized to blue peroxide of chromium (CrO_5) which is unstable, howver, it is soluble in ether and produces blue coloured solution.

$$K_2Cr_2O_7 + H_2SO_4 + 4H_2O_2 \longrightarrow \underset{\text{(Blue)}}{2CrO_5} + K_2SO_4 + 5H_2O$$



(Butterfly Shape)

3. Structure of H_2O_2



H_2O_2 is used :

(a) as a bleaching agent

(b) as an antiseptic in surgery

(c) as a fuel for rockets

MISCELLANEOUS EXAMPLES

Example 1

(a) **Give struce O^{2-}, O_2^{2-} and O_2^-.**

(b) **What is their behaviour towards H_2O ?**

(c) **Give applications of H_2O_2 and KO_2.**

Solution

(a) $\left[:\underset{..}{\ddot{O}}:\right]^{2-}$ $\left[:\underset{..}{\ddot{O}}:\underset{..}{\ddot{O}}:\right]^{2-}$ $\left[:\underset{..}{\ddot{O}}:\underset{..}{\ddot{O}}:\right]$

(b) $\underset{\text{oxide}}{O^{2-}} + H_2O \longrightarrow 2OH^-$

$\underset{\text{peroxide}}{2O_2^{2-}} + 2H_2 \longrightarrow O_2 + 4OH^-$

$\underset{\text{superoxide}}{40_2^-} + 2H_2O \longrightarrow 3OH_2 + 4OH^-$

All the three ions are unstable towards H_2O and give alkaline solution. The decomposition of O_2^{2-} and O_2^- involve oxidation and reduction. Both of these ions, especially O_2^-, are good oxidising agents.

(c) H_2O_2 is used as :

– bleacing agent

– a substitute for Cl_2 in water and sewage treatment

– an antiseptic in curing wounds

KO_2 is used in life supports in spacecrafts, submarines and emergency breathing apparatus since it absorbs CO_2 and releases O_2.

$$4KO_2 + 2CO_2 \longrightarrow 2K_2CO_3 + 3O_2$$

Example 2

NaCl in earlier days used to manufacture NaOH and Cl_2 involving following steps. Identify (A) to (I) in the following :

$$NaCl + \text{comc } H_2SO_4 \xrightarrow{\Delta} (A) + (B) \text{ (gas)}$$

$$(B) \text{ gas} \xrightarrow{MnO_2} (C) \text{ gas}$$

$$(A) + NaCl \xrightarrow{\Delta} (D) + (B) \text{ gas}$$

$$(D) + carbon + CaCO_3 \longrightarrow (E) + (F)$$

$$CaCO_3 \xrightarrow{\Delta} (G) + (H)\ gas$$

$$(G) + H_2O \longrightarrow (I)$$

$$(I) + (E) \longrightarrow NaOH + CaCO_3$$

Solution :

$$\underset{}{NaCl} + conc.\ H_2SO_4 \longrightarrow \underset{(A)}{NaHSO_4} + \underset{(B)}{HCl}$$

$$\underset{(B)}{HCl} \xrightarrow{MnO_2} Cl_2$$

$$MnO_2 + \underset{(B)}{4HCl} \xrightarrow{\Delta} MnCl_2 + \underset{(C)}{Cl_2} + 2H_2O$$

$$\underset{(A)}{NaHSO_4} + NaCl \xrightarrow{\Delta} \underset{(D)}{Na_2SO_4} + HCI$$

$$\underset{(D)}{Na_2SO_4} + carbon + CaCO_3 \xrightarrow{\Delta} \underset{(E)}{Na_2CO_3} + \underset{(F)}{CaSO_4}$$

$$CaCO_3 \xrightarrow{\Delta} \underset{(G)}{CaO} + \underset{(H)}{CO_2}$$

$$\underset{(G)}{CaO} + H_2O \longrightarrow \underset{(I)}{Ca(OH)_2}$$

$$\underset{(I)}{Ca(OH)_2} + \underset{(E)}{Na_2CO_3} \longrightarrow 2NaOH + CaCO_3$$

Example 3

GIVE REASONS

1. Na_2SO_4 is soluble in water where as $BaSO_4$ is insoluble. Why ?

Sol: The lattice energy of Na_2SO_4 is less than the hydration energy where as the lattice energy of the $BaSO_4$ (because of bivalent charge) is very high so that hydration energy released is not sufficient to break the lattice and $BaSO_4$ remains insoluble.

2. Why potassium carbonate can not be prepared by solvay process ?

Sol: This is due to the reason that potassium bicarbonate ($KHCO_3$) formed asan intermediate (when CO_2 is passed through ammoniated solution of potassium chloride) is highly soluble in water and can not be seperated by filteration.

3. When Mg metal is burnt in air; a white powder is left behind a ash. What is the white powder ?

Sol : Mg on burning in air reacts with oxygen and nitrogen resulting in the formation of MgO and magnesium nitride.

$$2Mg + O_2 \longrightarrow MgO$$

$$3Mg + N_2 \longrightarrow Mg_3N_2$$

4. In aqueous solution Li ion has the lowest mobility. Why ?

Sol : Li ions are highly hydrated in aqueous solution which result in decrease in its mobility.

5. Explain, why lithium is kept rapped in paraffin wax and not stored in kerosene oil ?

Sol: It is because lithium is a light metal and therefore it floats at the surface of kerosene oil. To prevent its exposure to air it is kept wrapped in paraffin wax.

6. Why caesium can be used in photoelectric cell, while lithium can not be ?

Sol: Caesium has the lowest while lithium has the highest ionization energy among all the alkali metals. Hence, caesium can lose electrone very easily while lithium cannot.

7. Which alkali metal ion has the maximum polarizing power and why ?

Sol: Li ion has the maximum polarizing power among all ther alkali metal ions. Thus is due to small size of Li ion as result of which it has maximum charge/radius ratio.

8. Explain why

(i) Lithium on being heated in air mainly forms the monzide and not peroxide.

(ii) An aqueous solution of sodium carbonate gives alkaline tests.

Sol : (i) Li ion is smaller in size. It is stabilized more by smaller anion, oxide ion (O^{-2}) as compared to peroxide (O_2^{-2}).

(ii) An aqueous solution of sodium carbonate gives alkaline tests because Na_2CO_3 undergoes hydrolysis forming sodium hydroxide.

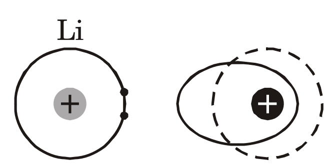
$$Na_2CO_3 + H_2O \longrightarrow NaHCO_3 + NaOH$$

Example 4

Lithium compounds have covalent character. Explain ?

Solution :

High polarising power of Li^+ ion due to its smaler size makes lithium compounds (particularly lithium halides) predominantly covalent. If Li 1 is considered fully ionic compound, its dipole moment in the saseous state would be 11.5 debye (D) but its experimental value comes out to be 3.25 D. This is due to distortion of electron charge cloud of the iodide ion by the lithium ion, which results in decrease in ionic character (hence, the decrease in dipole moment) and increase in covalent character of Lil.



Polarisation of electron charge cloud of iodide by lithium ion

Example 5

(i) An inorganic compound (A) is formed on passing a gas (B) through a concertrated liquor containing sodium sulphide and sodium sulphite.

(ii) On adding (A) into dilute solution of silver nitrate, a white precipitate appears which quickly changes into a black coloured compound (C).

(iii) On adding two or three drops of ferric chloride into the excess of solution of (A), a violet coloured compound (D) is formed. This colour disappers quickly.

(iv) On adding a solution of (A) into the solution of cupric chloride, a white precipitate is first formed which dissolves on adding excess of (A)forming a compound (E).

Identify (A) to (E) and give the chemical equations for the reactions at steps (i) to (iv).

Solution :

The reactions indicate that the compound (A) is sodium thiosulphate. It is formed in step (i) by passing gas (B) which is either I_2 or SO_2.

(i) $Na_2S + Na_2SO_3 + 3SO_3 + \underset{(B)}{I_2} \longrightarrow \underset{(A)}{Na_2S_2O_3} + 2NaI$

Or

$2Na_2S + Na_2SO_3 + 3SO_2 \longrightarrow 3Na_2S_2O_3$

(ii) $2AgNO_3 + Na_2S_2O_3 \longrightarrow \underset{\text{(White ppt.)}}{Ag_2S_2O_3} + 2NaNO_3$

$Ag_2S_2O_3 + H_2O \longrightarrow \underset{\text{(C) Black}}{Ag_2S} + H_2SO_4$

(iii) $2FeCl_3 + 3Na_2S_2O_3 \longrightarrow \underset{\text{(D) Violet}}{Fe_2(S_2O_3)_3} + 6NaCl$

$Fe_2(S_2O_3)_3 + Na_2S_2O_3 \longrightarrow \underset{\text{Colourless}}{2Fe(S_2O_3)} + 6NaCl$

(iv) $CuCl_2 + Na_2S_2O_3 \longrightarrow CuS_2O_3 + 2NaCl$

$2CuS_2O_3 + Na_2S_2O_3 \longrightarrow \underset{\text{(White ppt.)}}{CuS_2O_3} + Na_2S_4O_6$

$3Cu_2S_2O_3 + 2Na_2S_2O_3 \longrightarrow \underset{\text{(E) Soluble complex}}{Na_4[Cu_6(S_2O_3)_5]}$

Example 6

A white solid is either Na_2O or Na_2O_2. A piece of red litmus paper turns white when it is dipped into a freshly made aqueous solution of the white solid.

(i) **Identify the substance and explain with balanced equation.**

(ii) **Explain what would happen to the red liltmus if the white solid were the other compound.** **[I.I.T. 199]**

Solution :

(i) A piece of red litmus truns white when dipped into aqueous solution of white solid indicates that the solution has bleaching action on litmus. This is due to the presence of hydrogen peroxide in solution which is formed by action of water on sodium peroxide. Thus, the white solidis Na_2O_2.

$$Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$$

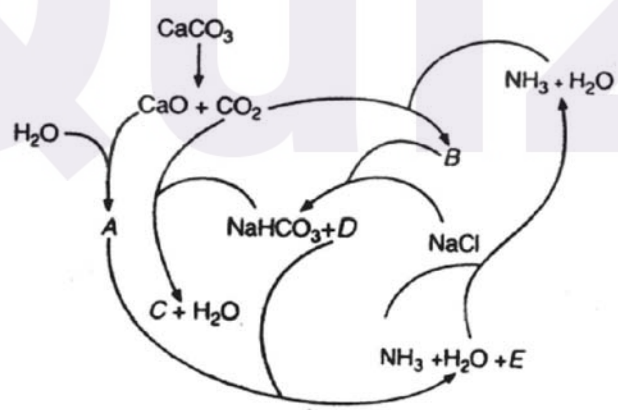
(ii) The other compound is Na_2O which gives NaOH (sodium hydroxide) with water.

$$Na_2O + H_2O \longrightarrow 2NaOH$$

The solution, thus, turns red litmus to blue.

Example 7

The Solvaly process can be represented by the following scheme :



Identify A**,** B**,** C**,** D **and** E. **[IIT 1999]**

Solution :

(A) : $Ca(OH)_2$

$$\underset{}{CaO + H_2O} \longrightarrow \underset{(A)}{Ca(OH)_2}$$

(B) : NH_4HCO_3

$$NH_3 + H_2O + CO_2 \longrightarrow \underset{(B)}{NH_4HCO_3}$$

(C) : Na_2CO_3

$$2NaHCO_3 \longrightarrow \underset{(C)}{Na_2HCO_3} + H_2O + CO_2$$

(D) : NH_4Cl

$$NH_4HCO_3 + NaCl \longrightarrow NaHCO_3 + \underset{(D)}{NH_4Cl}$$

(E) : $CaCl_2$

$$2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + 2H_2O + \underset{(E)}{CaCl_2}$$

Example 8

Aqueous solution of an inorganic compound (x) shows the following reactions :

(i) It decolourises an acidified $KMnO_4$ solution accompanied by the evolution of oxygen.

(ii) It liberates iodine from an acidifed KI solution.

(iii) It gives a brown precipitate with alkaline $KMnO_4$ solution with evolution of oxygen.

(iv) It removes black stains from old oil paintings.

Identify, (x) and give chemical equations for the ractions at steps (i) to (iv).

[roorkee 1993]

Solution :

In reaction (i) and (iii) (x) acts as a reducing agent while in reaction (ii) it acts an oxidising agent. Thus, these reactions indicate that (x) is H_2O_2 which is further confirmed from reaction (iv).

(i) $$\underset{\text{Purple coloured}}{2KMnO_4} + 3H_2SO_4 + 5H_2O_2 \longrightarrow \underbrace{-K_2SO_4 + 2MnSO_4}_{\text{Soluble,colourless}} + 8H_2O + 5O_2$$

(ii) $$2KI + H_2SO_4 + H_2O_2 \rightarrow K_2SO_4 + I_2 + 2H_2O$$

(iii) $$2KNnO_4 + 3H_2O_2 \rightarrow 2KOH + \underset{\text{Brown}}{2MnO_2} + 2H_2O + 3O_2$$

(iv) $$\underset{\text{Black}}{Pbs} + 4H_2 \rightarrow \underset{\text{White}}{PbSO_4} + 4H_2O$$

Example 9

Hydrogen peroxide acts both as an oxidising and as a reducing agent in alkaline solution towards certain first row transition metal ions. Illustrate both these properties of H_2O_2 using chemical equations. **[I.I.T. 1998]**

Solution :

Chromium hydroxide is oxidised by H_2O_2 in presence of NaOH into sodium chromate

$$[H_2O_2 \longrightarrow H_2O + O] \quad 3$$

$$2Cr(OH)_3 + 4NaOH + 3O \longrightarrow 2Na_2CrO_4 + 5H_2O$$

$$2Cr(OH)_3 + 4NaOH + 3H_2O_2 \longrightarrow 2Na_2CrO_4 + 8H_2O$$

Potassium ferricynide is reduced to ferrocyanide in presence of KOH by H_2O_2.

$$2K_3Fe(CN)_6 + 2KOH \longrightarrow 2K_4Fe(CN)_6 + H_2O + O$$

$$H_2O_2 \longrightarrow H_2O + O_2$$

$$2K_3Fe(CN)_6\ 2KOH + H_2O_2 \longrightarrow 2K_4Fe(CN)_6 + 2H_2O + O_2$$