

HYDROGEN & IT'S COMPOUNDS

HYDROGEN

It is the first element in the periodic table. The position of hydrogen is not definite in the periodic table because it resembles both the alkali metals as well as halogens. At the same time it differs from both in many characteristics.

Occurrence : Hydrogen occurs in nature in the free as well as combined state. The earth's crust contains nearly 1% hydrogen by weight. In free state (H_2), it occurs only in traces in the atmosphere (1 part in 10^6 parts by volume). It is mainly found in the combined state. Important sources are water, acids, alkalies, organic matter, ammonia, hydrogen sulphide, etc.

Isotopes of Hydrogen

	Protium	Deuterium	Tritium
	Ordinary hydrogen	Heavy hydrogen	Radioactive
Representation	1_1H	2_1D	3_1T
Neutrons	0	1	2
Occurrence	99.98%	0.16%	$10^{-15} \%$

- (i) H_2 , D_2 and T_2 differ with respect to their properties like (i) rates of diffusion H_2 diffuses 1.414 times faster than D_2 and H_2 diffuses 1.732 times faster than T_2 .

- (ii) **Bond energy and reactivity**

The bond energy of H – H bond is least and hence it is most reactive among the isotopes of hydrogen.

Bond energy $H_2 < D_2 < T_2$

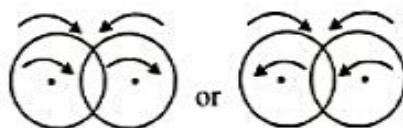
Reactivity $H_2 > D_2 > T_2$

This difference in the properties of isotopes which arises due to large difference in their atomic masses or molecular masses is called as isotopic effect.

FORMS OF HYDROGEN

Ordinary hydrogen exists in the form of diatomic molecule which is quite stable and very less reactive.

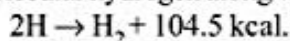
- Active hydrogen :** It is obtained by subjecting molecular hydrogen to silent electric discharge at ordinary temperature and 0.5 mm pressure. This hydrogen, so produced, has great chemical activity. The half-life period of the active hydrogen is similar to that of atomic hydrogen (0.3 sec.)
- Ortho and Para hydrogen :** When the spins of the two protons are in the same direction, the molecule is known as ortho hydrogen, while when the spins of protons are in the opposite directions, hydrogen formed is known as para hydrogen. These two allotropic forms of hydrogen are similar in chemical properties but differ in boiling point, specific heat and thermal conductivities. Ortho hydrogen is more stable than the para hydrogen. Para hydrogen mixed with atomic hydrogen gets converted into the ortho form.

(a) **Ortho hydrogen :**

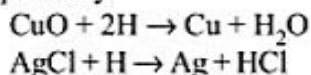
In this molecule of hydrogen both the protons in the two nuclei spin in the same direction.

(b) **Para hydrogen :**3. **Atomic hydrogen :** Molecular hydrogen undergoes thermal dissociation into atomic hydrogen at high temperatures and low pressures.

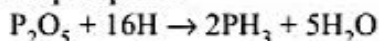
and the heat is stored up in the atoms. Atomic hydrogen, thus produced, when strikes a metallic surface, its atoms recombine to form molecular hydrogen along with the evolution of large amount of heat.

**Properties :**

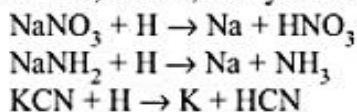
- (i) Atomic hydrogen is highly unstable (half life = 0.3 second).
- (ii) It combines readily with non metals : like S, P, As, Sb, Bi, O₂ and halogens forming corresponding hydride, H₂O and hydracids respectively.



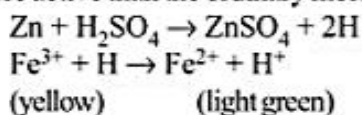
It reduces phosphorus pentoxide to phosphine



It reduces alkali metal salts like nitrates, amides, and cyanides to free metal.

**Uses :**

1. It is used as a strong reducing agent.
2. It is used in the fabrication of atomic hydrogen torch.

2. **Nascent hydrogen :** Hydrogen produced in contact with the substance to be reduced is called nascent (newly born) hydrogen. It is more active than the ordinary molecular hydrogen.

Some of the common sources of nascent hydrogens are

- | | |
|---|---|
| (i) A mixture of zinc and dil. H ₂ SO ₄ | (ii) A mixture of tin and dil. hydrochloric acid. |
| (iii) Aluminium and NaOH. | (iv) Electrolysis of acidified water. |

Illustration

1. Hydrogen :

- (A) resembles in I A since it forms mono valent cation H^+
 (B) resembles in VII A (halogen family) since it forms monovalent anion H^-
 (C) resembles in IV A (carbon family) since both have a half filled shell of electron
 (D) all correct

Ans. D

Sol. $HCl \rightarrow H$ has +1 oxidation state so it resemble I A group property
 $NaH \rightarrow H$ has -1 oxidation state so it resemble VII A group property
 $H (1s^1)$ due to half filled shell of electron it resemble IV A group property

2. Hydrogen gas will not reduce

- (A) heated cupric oxide (B) heated ferric oxide
 (C) heated stannic oxide (D) heated aluminium oxide

Ans. D

Sol. Hydrogen gas will not reduce heated aluminium oxide because ΔG for this reaction is positive.

Exercise

Q.1 Orthohydrogen and parahydrogen have

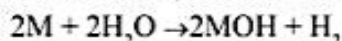
- (A) Same electronic spin, physical and chemical properties
 (B) Parallel electronic, and nuclear spin with identical physical and chemical properties.
 (C) Different electronic spin with differences in physical and chemical properties.
 (D) Opposite electronic spin, different nuclear spin and with different physical properties

Ans. D

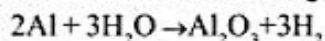
METHODS OF PREPARATION OF HYDROGEN (H_2)

1. By action of water with metals.

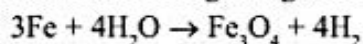
(a) Active metals like Na, K react at room temperature.



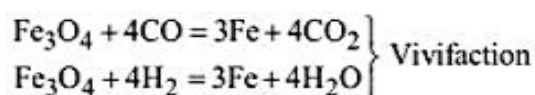
(b) Less active metals like Ca, Zn, Mg, Al liberate hydrogen only on heating.



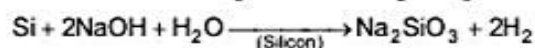
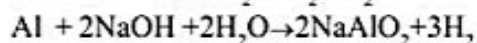
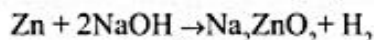
2. **Lane's process:** In this process, steam is passed over hot iron. Iron decomposes steam with the formation of magnetic oxide (Fe_3O_4) and hydrogen. The temperature of iron is maintained between 550 to 800°C. This reaction is termed *gassing reaction* and time allotted for this reaction is about 10 minutes.



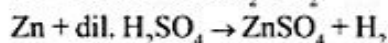
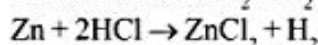
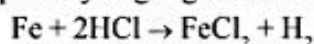
Iron is generated by reducing magnetic oxide with water gas ($CO + H_2$). This reaction is called *vivification* and time allotted for this reaction is about 20 minutes.



3. **By reaction of metals like Zn, Sn, Al with alkalis.**



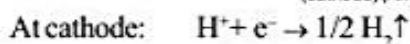
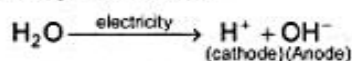
4. **By action of metals with acids.** All active metals which lie above hydrogen in electrochemical series, can displace hydrogen gas from dilute mineral acids.



It must be noted that

- (a) Pure zinc is not used for preparation.
- (b) Conc. H_2SO_4 is not used as it oxidizes the liberated H_2 and produce SO_2

5. **By electrolysis of water**



6. **Preparation of pure hydrogen.** It can be obtained by

- (a) The action of pure dil. H_2SO_4 on pure magnesium ribbon.

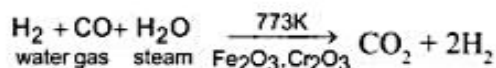
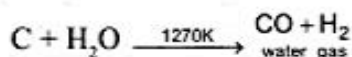
$$\text{Mg} + \text{H}_2\text{SO}_4 \rightarrow \text{MgSO}_4 + \text{H}_2$$
- (b) The electrolysis of a solution of barium hydroxide using nickel electrodes.
- (c) By the action of water on NaH.

$$\text{NaH} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{H}_2$$
- (d) Very pure form of hydrogen is obtained by the action of KOH on scrap aluminum.

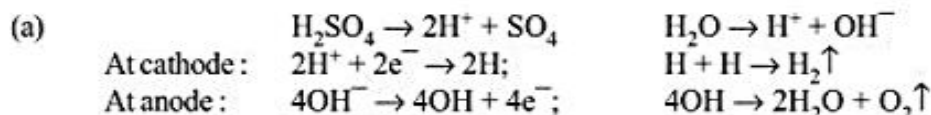
$$2\text{Al} + 2\text{KOH} + 2\text{H}_2\text{O} \rightarrow 2\text{KAlO}_2 + 3\text{H}_2 \uparrow$$

7. **Industrial preparation**

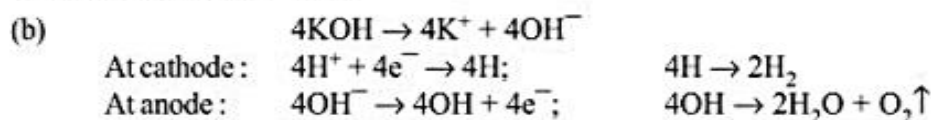
- (a) **Bosch process** - In this method water gas is mixed with steam and passed over heated catalytic mixture of Fe_2O_3 and Cr_2O_3 at 773 K when CO_2 and H_2 are obtained. The mixture is compressed to 25 atmospheric pressure and passed into water, CO_2 dissolves while H_2 is set free.



- (b) By the electrolysis of water containing a small amount (15 - 20%) of an acid or alkali. Hydrogen is liberated at the cathode (usually iron) while oxygen (a by product) is liberated at anode (usually nickel plated iron rod.) The anode and cathode are separated by an asbestos diaphragm which serves to prevent mixing of hydrogen and oxygen evolved.



It is important to note that sulphate ions are not discharged as their discharge potential is very much higher than that of OH^- ions.



Note that K^+ ions are not discharged at cathode because their discharge potential is high than that of H^+ ions.

PROPERTIES

(a) Physical Properties :

- Hydrogen is colourless, odourless and tasteless gas.
- It is the lightest element and also lightest gas. Its density with respect to air as 1 is 0.0695. One litre of the gas weighs only 0.08987 gm.
- It is sparingly soluble in water.
- Its critical temperature is very low (-236.9°C) at or below which it can be liquefied by the application of a suitable pressure. At -258.8° it can be liquified.
- Its molecule is diatomic, indicated by the ratio of its specific heats at constant pressure and constant volume ($C_p/C_v = 1.40$).
- It is adsorbed (occluded) by certain metals like Fe, Au, Pt and Pd. Palladium in the powdered state can occlude nearly 1000 times its own volume of hydrogen.

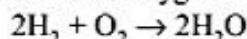
Transportation. Since critical temperature of hydrogen is very low (36.1 K) it can't be liquefied easily. Hence the gas has to be transported under pressure in steel cylinders having almost negligible mass of gas, and can be transported in either of the followed ways.

(i) In the form of hydrolith (CaH_2); 1 pound of CaH_2 gives 16.5 ft^3 of H_2 .

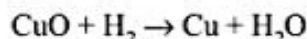
(ii) In the form of anhydrous NH_3 in light aluminium containers which on cracking gives N_2 and H_2 mixture.

(b) Chemical properties :

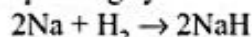
- Reactions of hydrogen are slow at room temperature but rapid at high temperatures. It is neutral towards litmus. It is combustible and burns in air or oxygen with nearly invisible pale blue flame.



- Reducing property. When hydrogen is passed over heated metallic oxides, the latter are reduced to the respective metal.

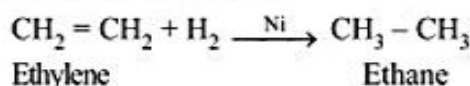


- Reaction with metals and non-metals. It combines with strongly electropositive metals (active metals) like Li, Na and Ca to form corresponding hydrides.



It combines with N, C, O, halogens, S, etc. under suitable conditions to form NH_3 , CH_4 , H_2O , HX and H_2S respectively.

- Reaction with unsaturated compounds. Hydrogen adds on the double or triple bond in the presence of finely divided Ni to form saturated compounds.



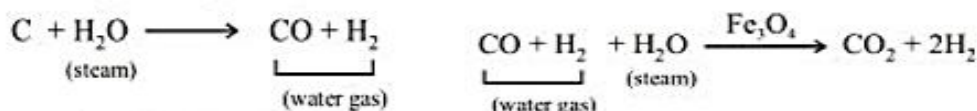
Illustration

1. Which of the following pair will not produce dihydrogen gas-
 (A) $\text{Cu} + \text{HCl}(\text{dil.})$ (B) $\text{Fe} + \text{H}_2\text{SO}_4$ (C) $\text{Mg} + \text{steam}$ (D) $\text{Na} + \text{alcohol}$

Ans. A

Sol. The less active metals which lie below hydrogen in electrochemical series can't displace hydrogen gas from dilute mineral acid.

2. The incorrect option regarding the chemical reaction is



- (A) Process is called Lane's process
 (B) Water gas acts as a reducing agent for Fe_3O_4
 (C) Fe_3O_4 shows magnetic property
 (D) Fe_3O_4 can't be concentrated by magnetic separation method

Ans. D

Sol. Fe_3O_4 is a magnetic oxide of iron and it has non-magnetic impurities, so it is concentrated by magnetic separation method.

Exercise

1. When dil. H_2SO_4 is electrolysed by using platinum electrodes, the gas evolved at the cathode is
 (A) O_2 (B) SO_2 (C) SO_3 (D) H_2

Ans. D

2. Nascent hydrogen consists of

- (A) hydrogen ions in excited state (B) hydrogen ions with excess energy
 (C) solvated protons (D) hydrogen atoms with excess energy

Ans. D

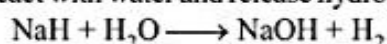
HYDRIDES

The compounds of hydrogen with metals or non-metals are called as hydrides. They are classified into different types depending upon their behaviour and nature of bonding.

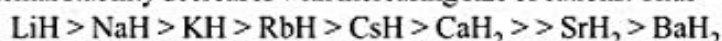
- (1) **Ionic or Saline hydrides:** Ionic hydrides or salt-like hydrides. The compounds of hydrogen with more electropositive metals like alkali metals and alkaline earth metals are ionic hydrides. They are formed by transfer of electron from metal to hydrogen.

For example: LiH , NaH , CaH_2 , SrH_2 etc.

- (a) They are crystalline solids.
 (b) They have high melting and boiling points.
 (c) They conduct electricity in molten state and release hydrogen gas at anode.
 (d) They react with water and release hydrogen gas and thus act as powerful reducing agents



The thermal stability decreases with increasing size of cations. Thus



- (2) **Covalent or Molecular Hydrides** : The compounds of hydrogen with more electronegative elements or 'p' Block elements are covalent or Molecular hydrides.

For example : HCl , H_2O , CH_4 , PH_3 etc.

- (a) They are generally soft, with less melting and boiling points.
- (b) They are poor conductors of electricity.
- (c) They release hydrogen on decomposition and thus act as reducing agents.
- (d) Some of them react with water and release hydrogen gas.



- (3) **Interstitial hydrides or Metallic hydrides** : The hydrogen atoms occupy the interstitial spaces of transition elements and hence they are interstitial hydrides. They are nonstoichiometric in nature.

Illustration

1. Which is not correct statement
 (A) s-block elements, except Be and Mg, form ionic hydride
 (B) Interstitial hydride are nonstoichiometric in nature.
 (C) p-block elements form covalent hydride
 (D) d-, f-block elements form ionic hydride

Ans. D

Sol. Hydrogen atoms occupy the interstitial spaces of d & f block elements & they form interstitial hydrides.

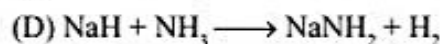
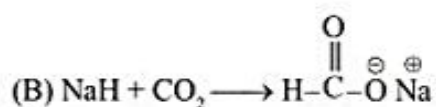
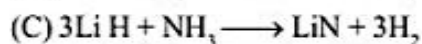
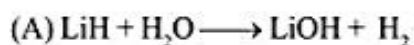
2. Which of the following easily reacts with water producing hydrogen?
 (A) PH_3 (B) B_2H_6 (C) CH_4 (D) H_2S

Ans. B

Sol. $\text{B}_2\text{H}_6 + 6\text{H}_2\text{O} \longrightarrow 2\text{B}(\text{OH})_3 + 6\text{H}_2 \uparrow$

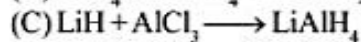
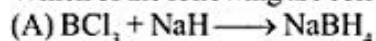
Exercise

1. Which of the following are correct



Ans. A, B, D

2. Which of the following are correct



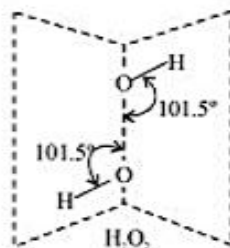
(D) All of these

Ans. D

HYDROGEN PEROXIDE (H₂O₂)

Structure :

Hydrogen peroxide is best represented as an equilibrium between following two structures. However, all the four atoms do not lie in the same plane, i.e., the H₂O₂ molecule is not planar but described as open book structure. The O–O–H bond angle is found to be nearly 101.5°. The O–O single bond distance in H₂O₂ is 1.48 Å.



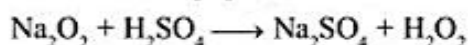
Tests of H₂O₂.

- (i) It liberates iodine from KI solution in the presence of ferrous sulphate.
- (ii) It gives orange red colour with acidified titanium oxide due to formation of pertitanic acid.

$$\text{Ti}(\text{SO}_4)_2 + \text{H}_2\text{O}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{TiO}_4 + 2\text{H}_2\text{SO}_4$$
- (iii) When brought in contact with H₂O₂ solution, a filter paper with black stain of PbS turns white.
- (iv) It decolourises acidified KMnO₄ solution.

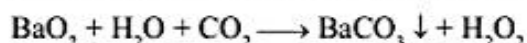
Preparations of Hydrogen peroxide

- (1) **Merck's Method :** Na₂O₂ is gradually added to 20% ice cold H₂SO₄

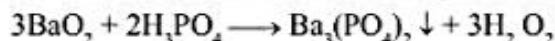


Most of Na₂SO₄·10H₂O is crystallised out by cooling.

- (2) **By the action of CO₂ on an ice cold paste of BaO₂**



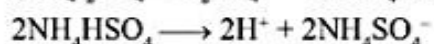
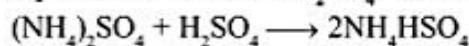
- (3) **By the action of phosphoric acid on BaO₂**



Impurities (metal ions) present in BaO₂ are removed as their phosphates.

- Reaction of BaO₂·8H₂SO₄ with H₂SO₄(ice cold) also gives H₂O₂ but the method is not used as the presence of H₂SO₄ & other metal ions (impurities of BaO₂) catalyse the decomposition of H₂O₂.

- (4) **Electrolysis of equimolar mixture of H₂SO₄ & ammonium sulphate**



At cathode: $2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2$

At anode: $2\text{NH}_4\text{SO}_4^- \longrightarrow (\text{NH}_4)_2\text{S}_2\text{O}_8 + 2\text{e}^-$
 (Ammonium persulphate)

Ammonium per sulphate is collected and distilled with water to produce H₂O₂



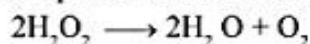
(5) Auto oxidation of 2-Ethylanthraquinol

Air is bubbled in 10% solution of 2-Ethylanthraquinol in benzene

2-Ethylanthraquinone obtained is reduced back to 2-Ethylanthraquinol. The solution is concentrated by reduced pressure distillation to get 20% H_2O_2 .

CONCENTRATION OF HYDROGEN PEROXIDE SOLUTION

Hydrogen prepared by any of the above methods is in the form of dilute aqueous solution. Quite often for a large number of reactions, we need a concentrated solution of H_2O_2 . It cannot be concentrated simply by distillation since it decomposes much below its boiling point to give H_2O and O_2



Further, the process of decomposition is catalysed by the presence by heavy metal ion impurities, dust and rough surfaces. In view of these difficulties, concentration of H_2O_2 is carried out carefully in a number of stages.

Storage of hydrogen peroxide

The following precautions are taken while storing hydrogen peroxide solution.

- (i) Hydrogen peroxide cannot be stored in glass bottles since the rough surface of glass, alkali metal oxides present in it, and exposure to light catalyse its decomposition. Therefore, H_2O_2 is usually stored in coloured paraffin wax coated plastic or teflon bottles.
- (ii) To further ; check the decomposition of H_2O_2 , some stabilizer or negative catalyst such as glycerine, acetanilide, phosphoric acid etc. Must also be added.

Strength of hydrogen peroxide solution

The strength of aqueous solution of hydrogen peroxide is usually expressed in the following two ways:

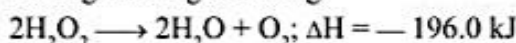
- (a) **Percentage strength :** It expresses the amount of H_2O_2 by weight present in 100 ml of the solution. For example, a 30% aqueous solution (w/v) of H_2O_2 implies that 30 grams of H_2O_2 are present in 100 ml of the solution.
- (b) **Volume strength :** The most common method of expression of the strength of an aqueous solution of hydrogen peroxide is in terms of the volume (in ml) of oxygen liberated at N.T.P. by the decomposition of 1 ml of the at sample of hydrogen peroxide.

PROPERTIES OF HYDROGEN PEROXIDE**(a) Physical properties.**

1. Pure hydrogenperoxide is a thick syrupy liquid with pale blue colour.
2. It has a bitter taste.
3. Hydrogen peroxide is more dense (1.44g/cm^3) and more viscous than water. This is due to the reason that the molecules of H_2O_2 are even more highly associated through H-bonds than H_2O molecules.
4. Its m.p. is 272.4 K. Since it decomposes vigorously on heating, it is not possible to determine its b.p. at atmosphere pressure. However, its b.p. has been determined to be 423.2 by extrapolation method.
5. It is completely miscible with water, alcohol and ether in all proportions.
6. The dipole moment of H_2O_2 is little more (2.1D) than that of H_2O (1.84D).

(b) Chemical properties.

1. **Decomposition:** pure hydrogen peroxide is an unstable liquid and decomposes into water and oxygen on long standing or heating.



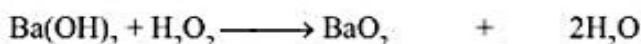
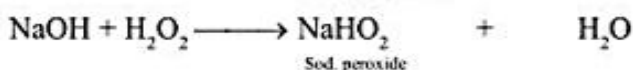
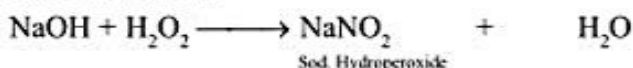
It is an example of auto-oxidation and auto-reduction.

The decomposition is further accelerated by the presence of certain metal ions (e.g. Fe^{2+}), metal powders (Co, Au, Ag, Pt etc.), and metal oxides (e.g. MnO_2). Even carbon, rough surfaces and light also catalyse its decomposition.

2. **Acidic Nature:** Pure hydrogen peroxide turns blue litmus red but its dilute solution is neutral to litmus. It thus behaves as a weak acid. Its dissociation constant is 1.55×10^{-12} at 293 K which is only slightly higher than that of water (1.0×10^{-12}). Thus, hydrogen peroxide is only a slightly stronger acid than water. Since hydrogen peroxide has two ionizable H-atoms, it forms two series of salts, i.e., hydroperoxides (acidic salts) and peroxides (normal salts).

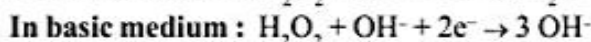
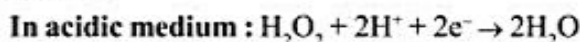


The acidic nature of hydrogen peroxide is shown by its neutralization reaction with hydroxides and carbonates.



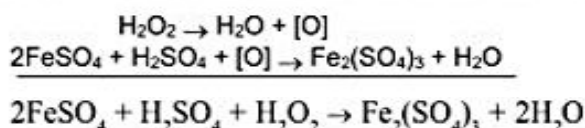
3. **Oxidising and reducing character:** Hydrogen peroxide behaves as an oxidising as well as a reducing agent in both acidic and alkaline solutions. The oxidation state of oxygen in hydrogen peroxide is -1 . It can be oxidised to O_2 (zero oxidation state) or reduced to H_2O or OH^- (-2 oxidation state for oxygen). However, hydrogen peroxide is a powerful oxidising agent but a weak reducing agent.

- (a) **Oxidising character.** Hydrogen peroxide acts as an oxidising agent both in acidic as well as in alkaline medium.

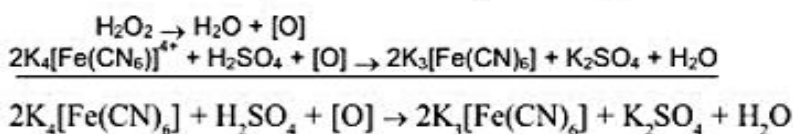


Some important reactions in which hydrogen peroxide acts an oxidising agent are given below;

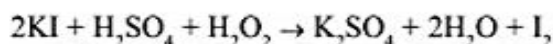
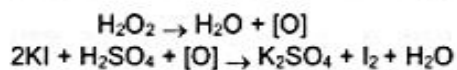
- (i) **It oxidises acidified ferrous sulphate to ferric sulphite**



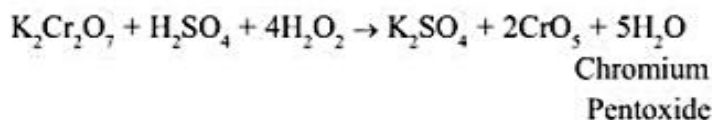
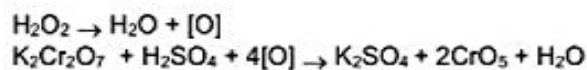
- (ii) **It oxidises acidified potassium ferrocyanide to potassium ferricyanide**



- (iii) It liberates iodine from acidified potassium iodide solution.

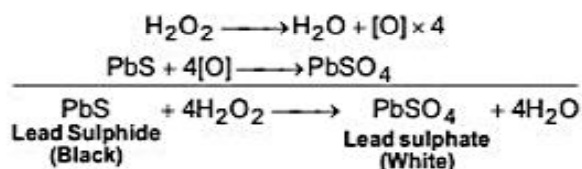


- (iv) Hydrogen peroxide oxidises ice-cold acidified potassium dichromate solution (containing ether) to chromium pentoxide which dissolves in ether producing a blue colouration.



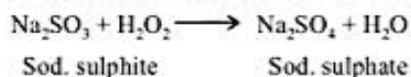
Chromium pentoxide is actually a peroxide having the structure

- (v) Hydrogen peroxide oxidises lead sulphide to lead sulphate

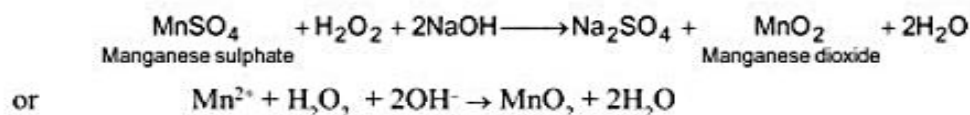


This reaction is used in restoring the white colour of lead paintings which have blackened due to the formation of lead sulphide by the action of H_2S present in the air. On treatment with H_2O_2 , lead sulphide (black) changes into lead sulphate (white) and thus the colour of lead paintings is restored.

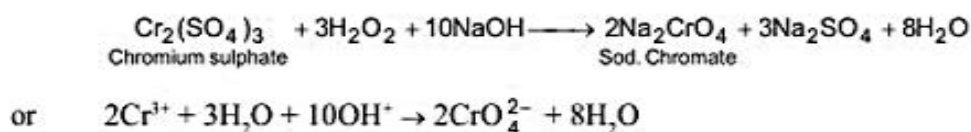
- (vi) Hydrogen peroxide oxidises H_2S to sulphur
 $\text{H}_2\text{S} + \text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{S}$
- (vii) It oxidises sulphites, nitrites and arsenites to sulphate, nitrates and arsenates respectively.



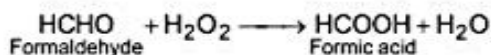
- (viii) It oxidises manganese salts to manganese dioxide in alkaline medium.



- (ix) It oxidises chromium salts to chromates in alkaline medium.



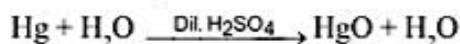
- (x) It oxidises formaldehyde to formic acid



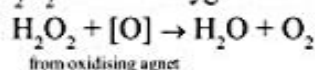
- (xi) It oxidises benzene to phenol



- (xii) It oxidises mercury to mercuric oxide in acidic medium



- (b)
- Reducing character:**
- In presence of strong oxidising agents, hydrogen peroxide behaves as a reducing agent both in acidic as well as alkaline medium. In all these reactions, molecular oxygen is always produced by the combination of
- H_2O_2
- with the oxygen atom released by the strong oxidising agent:

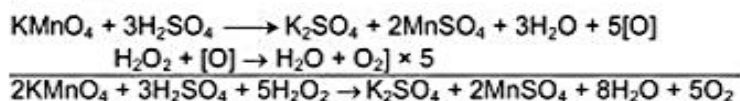


Acidic medium $\text{H}_2\text{O}_2 \rightarrow 2\text{H}^+ + \text{O}_2 + 2\text{e}^-$

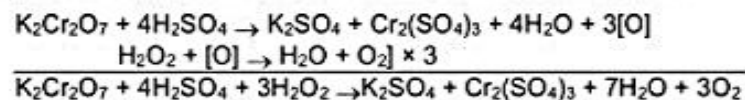
Alkaline medium $\text{H}_2\text{O}_2 + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 2\text{e}^-$

Some important reactions in which hydrogen peroxide behaves as a reducing agent are given below:

- (i) It reduces acidified potassium permanganate solution. As a result of this reaction, the pink colour of
- KMnO_4
- disappears.

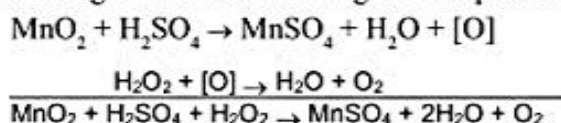


- (ii) It reduces acidified potassium dichromate solution. As a result of this reaction, the orange colour of
- $\text{K}_2\text{Cr}_2\text{O}_7$
- changes to green due to the formation of chromium salt.

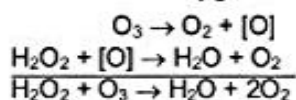


or $\text{Cr}_2\text{O}_7^{2-} + 8\text{H}^+ + 3\text{H}_2\text{O}_2 \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 3\text{O}_2$

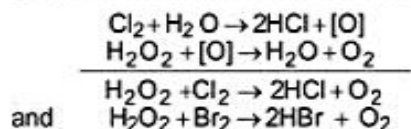
- (iii) It reduces manganese dioxide to manganese sulphate in presence of dil
- H_2SO_4
- .



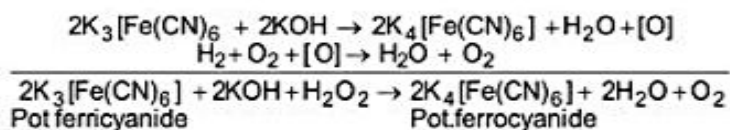
- (iv) It reduces ozone to dioxygen



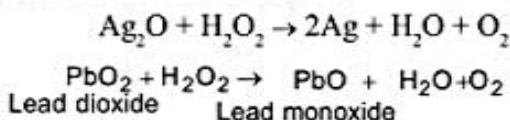
- (v) Chlorine and bromine are reduced to HCl and HBr respectively. This property is called Antichlor.



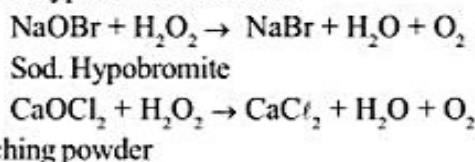
- (vi) It reduces alkaline potassium ferricyanide to potassium ferrocyanide



- (vii) It reduces metal oxides to metals, i.e., silver oxide to silver in the alkaline medium. However, lead dioxide is reduced to lead monoxide.



- (viii) It reduces hypohalites to halides

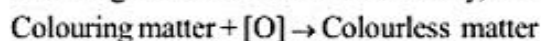


4. Bleaching Action.

The bleaching action of hydrogen peroxide is due to the nascent oxygen which it liberates on decomposition.

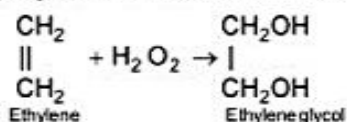


The nascent oxygen combines with colouring matter which, in turn, gets oxidised. It is used for the bleaching of delicate materials like ivory, feather, silk, wool etc.



5. Addition reactions

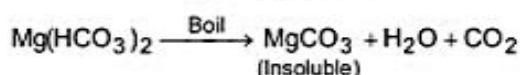
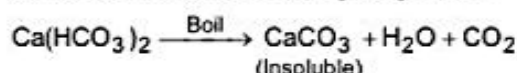
Hydrogen peroxide reacts with alkenes to form glycols.



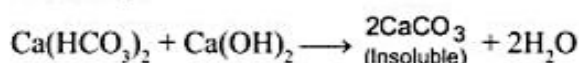
Uses of hydrogen peroxide

- It is used for bleaching delicate materials like hair, silk, wool, ivory, textile, wood and paper pulp.
- It is used as an antiseptic under the name perhydrol (30% H_2O_2) for washing wounds, teeth and ears.
- It is used for restoring the colour of lead paintings which have blackened due to the action of H_2S present in the air on lead paints.
- It is used in the laboratory for detecting the presence of chromium, titanium and vanadium salts with which it yields peroxides of characteristic colours.
- 93% H_2O_2 solution is used as an oxidant for rocket fuel and as a propellant for torpedoes and submarines.
- It is used as antichlor (to remove Cl_2) in textile industry to remove excess of chlorine after bleaching operations.
- It is used in the manufacture of many inorganic and organic (sodium perborate, epoxides) compounds.

- (a) **Temporary hardness :** This is due to the presence of bicarbonates of calcium and magnesium. Temporary hardness in water is easily removed by boiling, as the bicarbonates decompose readily and the insoluble carbonates are precipitated.



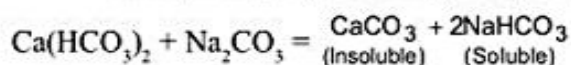
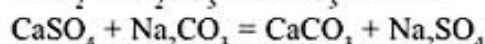
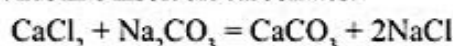
Temporary hardness can also be removed by Clark's process which involves the addition of slaked lime $[\text{Ca}(\text{OH})_2]$.



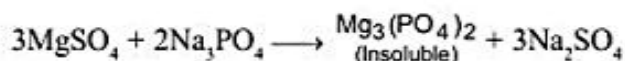
It is essential to add only the calculated amount of $\text{Ca}(\text{OH})_2$, because excess will cause artificial hardness.

- (b) **Permanent hardness :** Permanent hardness is introduced when water passes over rocks containing the sulphates or chlorides of both of calcium and magnesium. This type of hardness cannot be removed by boiling or by the addition of slaked lime. Many substances are used for the removal of this type of hardness. The substances used to remove the hardness of water are known as water softeners. The various water softeners are :

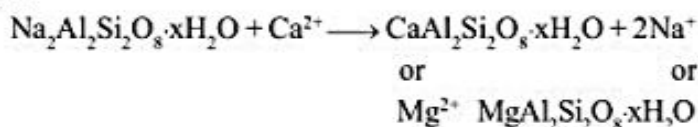
- (i) **Washing soda :** It removes both the temporary and permanent hardness by converting soluble calcium and magnesium compounds into insoluble carbonates.



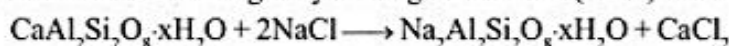
In place of sodium carbonate, caustic soda or sodium phosphate can also be used.



- (ii) **Permutit :** Permutit is the technical name given to certain hydrated silicates of aluminium and sodium. The sodium ions of permutit are exchanged with calcium and magnesium ions when hard water is passed through it.

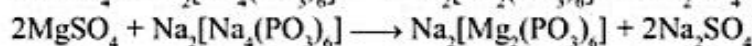


These ions can be re-exchanged by treating it with brine (NaCl) solution.



This method is useful for the removal of both temporary and permanent hardness of water.

- (iii) **Calgon** : The complex salt of metaphosphoric acid, sodium hexametaphosphate (NaPO_3)₆, is known as calgon. It is represented as $\text{Na}_6[\text{Na}_6(\text{PO}_3)_6]$.



- (iv) **Ion exchange resins :** Ion exchange resins are the most popular water softeners these days. These resins are synthetic substances. The cation exchanger consists of granular insoluble organic acid resin

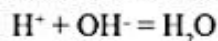
having giant molecules with $-\text{SO}_3\text{H}$ or $-\text{COOH}$ groups while the anion exchanger contains giant organic molecules with basic groups derived from amines. Ion exchange resins remove all soluble minerals from water. The hard water is first passed through a bed of cation exchanger, which removes the cations like Na^+ , Mg^{2+} , Ca^{2+} and others by exchanging with H^+ ions.



The water coming from cation exchanger is acidic on account of free H^+ ions. This water is then passed through another bed containing anion exchanger. This exchanger removes anions like Cl^- , SO_4^{2-} , NO_3^- by exchanging with OH^- ions.



The OH^- ions neutralise the H^+ ions.



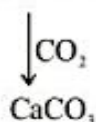
Illustration

1. Chemical A is used for water softening to remove temporary hardness. A reacts with sodium carbonate to generate caustic soda. When CO_2 is bubbled through a solution of A, it turns cloudy. What is the chemical formula of A

(A) CaCO_3 (B) CaO (C) $\text{Ca}(\text{OH})_2$ (D) $\text{Ca}(\text{HCO}_3)_2$

Ans. C

Sol. $\text{Ca}(\text{OH})_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{NaOH} + \text{CaCO}_3 \downarrow$



Exercise

1. Permanent hardness due to Mg^{2+} ions is best removed by-
(A) $\text{Ca}(\text{OH})_2$ (B) Na_2CO_3 (C) $\text{Na}_2\text{CO}_3 + \text{Ca}(\text{OH})_2$ (D) None of these

Ans. C

2. Permutit is:
(A) hydrated sodium aluminium silicate
(B) sodium hexametaphosphate
(C) sodium silicate
(D) sodium meta-aluminate

Ans. A

DEGREE OF HARDNESS

The amount of hardness causing substances (soluble salts of calcium or magnesium) in a certain volume of water measures the extent of hardness or degree of hardness. Hardness of water is always calculated in terms of calcium carbonate although this is never responsible for causing hardness of water because of its insoluble character. The reason for choosing CaCO_3 as the standard for calculating hardness of water is the ease in calculation as its molecular weight is exactly 100.

Thus the amount of various hardness causing substances in terms of CaCO_3 can be calculated on the basis of the following relations.

- (i) 1 gm mole or 162 g of $\text{Ca}(\text{HCO}_3)_2 \equiv 1$ gm mole or 100 g of CaCO_3
- (ii) 1 gm mole or 111 g of $\text{CaCl}_2 \equiv 1$ gm mole or 100 g of CaCO_3
- (iii) 1 gm mole or 136 g of $\text{CaSO}_4 \equiv 1$ gm mole or 100 g of CaCO_3
- (iv) 1 gm mole or 146 g of $\text{Mg}(\text{HCO}_3)_2 \equiv 1$ gm mole or 100 g of CaCO_3
- (v) 1 gm mole or 95 g of $\text{MgCl}_2 \equiv 1$ gm mole or 100 g of CaCO_3
- (vi) 1 gm mole or 120 g of $\text{MgSO}_4 \equiv 1$ gm mole or 100 g of CaCO_3

Thus the various types of hardnesses in a water sample may be calculated as below.

Temporary hardness = Hardness due to $\text{Ca}(\text{HCO}_3)_2$ + Hardness due to $\text{Mg}(\text{HCO}_3)_2$

Permanent hardness = Hardness due to CaCl_2 + due to CaSO_4 + due to MgCl_2 + due to MgSO_4

Degree of hardness is usually expressed as parts per million (ppm) and thus may be defined as the number of parts by weight of CaCO_3 (equivalent to calcium and magnesium salts) present in a million (10⁶) parts by weight of water. In short,

1 ppm = 1 part of CaCO_3 in 10⁶ parts of water

From the above definition, we can say that

1 MgSO_4	\equiv 1 CaCO_3	1 MgCl_2	\equiv 1 CaCO_3
120 ppm	100 ppm	95 ppm	100 ppm
1 CaSO_4	\equiv 1 CaCO_3	1 CaCl_2	\equiv 1 CaCO_3
136 ppm	100 ppm	111 ppm	100 ppm

Ex.1 Determine the degree of hardness of a sample of water containing 30 ppm of MgSO_4 .

Sol. 1 $\text{MgSO}_4 \equiv$ 1 CaCO_3
 120 ppm = 100 ppm
 \therefore 30 ppm = 25 ppm

HEAVY WATER (D_2O)

Heavy water was first discovered by chemist Urey.

Methods of preparation : Following are the methods to prepare heavy water (D_2O).

- [1] **By Fractional Distillation of water :** The boiling point of ordinary water is 100°C and the boiling point of D_2O is 101.42°C. Therefore, fractional distillation of water is performed in 40 ft high fractional columns. This process is repeated several times. Lighter part of water is removed on distillation and remaining part is basically heavy water (D_2O).

- [2] **Fractional Freezing** : In this method heavy water and ordinary water are separated by fractional freezing, because freezing point of water is 0°C and freezing point of heavy water is 3.82°C .
- [3] **Electrolysis of Water** : In this method, 99.5% heavy water is obtained after five steps on repeated electrolysis of NaOH solution in ordinary water.

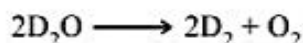
PROPERTIES

1. **Physical Properties** : Heavy water is colourless, odourless and tasteless liquid. Its physical constants, like specific gravity, viscosity, melting point, specific heat, are higher than those of ordinary water while surface tension is lower. Solubility of compounds in heavy water is lower as compared to that in ordinary water (approximately 15% lower)
2. **Chemical Properties** : Chemical reaction of H_2O and D_2O are same O–H bond of H_2O is more polar than O–D bond of D_2O . Therefore the chemical reactions of D_2O are relatively slower as compared to those of H_2O .

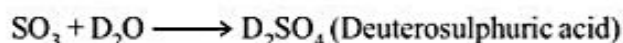
- [a] **With Alkali Metals** : Heavy water liberates D_2 on reaction with metals, like Na, K, Ca, etc.



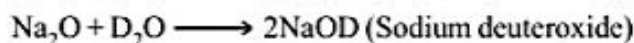
- [b] **Electrolysis** : D_2 is liberated on electrolysis of heavy water.



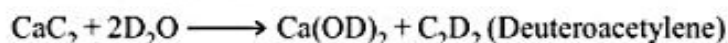
- [c] **With Acid Anhydrides** : Acids are formed on reaction with acid anhydrides, like SO_3 and P_2O_5 .



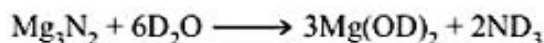
- [d] **With Metal Oxides** : Metal oxides, like Na_2O , form metal deuteroxides on reacting with heavy water.



- [e] **With Carbides** : They form deuterated hydrocarbons. Thus, calcium carbide reacts with heavy water to liberate deuteroacetylene.



- [f] **With Nitrides** : Heavy ammonia is liberated

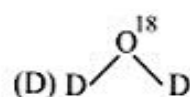
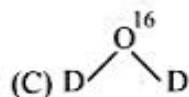
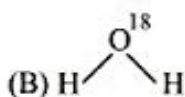
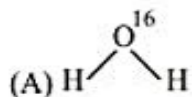


Uses of Heavy Water :

- [a] As moderator in nuclear reactors.
- [b] Electrolysis of heavy water is done for the production of deuterium.
- [c] In the form of a tracer in the studies of mechanism of biochemical reactions in living beings.

Illustration

1. In which of the following NaCl is more soluble

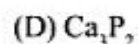
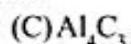
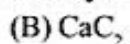
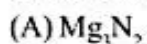


Ans. A

Sol. $\text{H}-\overset{\text{O}^{16}}{\text{O}}-\text{H}$ due to bond energy of O – H is least.

Exercise

1. Deutero methane is obtained by the deuteroysis of



Ans. C

2. Heavy water (D_2O) is

(A) A product of oxygen and hydrogen

(B) Water of mineral springs

(C) Water obtained by repeated distillation and condensation

(D) Ordinary water containing dissolved salts heavy metals

Ans. C

SOLVED EXAMPLES

Q.1 When a substance A reacts with water, it produces a combustible gas B and a solution of substance C in water. D reacts with this solution C and produces the same gas B on warming. D can also produce gas B on reaction with dilute H_2SO_4 . A imparts a deep golden yellow colour to smokeless flame. A, B, C and D respectively are

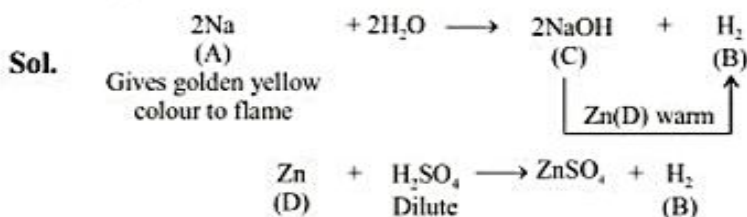
(A) Na, H_2 , NaOH, Zn

(B) K, H_2 , KOH, Al

(C) Ca, H_2 , $\text{Ca}(\text{OH})_2$, Sn

(D) CaC_2 , C_2H_2 , $\text{Ca}(\text{OH})_2$, Fe

Ans. (A)



Q.2 What is false about H_2O_2 ?

(A) Acts both as oxidising and reducing agent

(B) Two OH bonds lie in the same plane

(C) Pale blue liquid

(D) Can be oxidised by O_3

Ans. (B)

Sol. Two O-H bonds lie in the different planes.

Q.3 In which of the following reactions does hydrogen act as an oxidizing agent ?

(A) $\text{H}_2 + \text{F}_2 \longrightarrow$ (B) $\text{H}_2 + \text{SiCl}_4 \longrightarrow$ (C) $\text{Na} + \text{H}_2 \longrightarrow$ (D) $\text{CuO} + \text{H}_2 \longrightarrow$

Ans. (C)

Sol. The reaction in which hydrogen accepts the electron or its oxidation number changes from 0 to -1, it acts as an oxidizing agent. $2\text{Na} + \text{H}_2 \rightarrow 2\text{Na}^+ \text{H}^-$

Q.4 When H_2O_2 is added to ice cold solution of acidified potassium dichromate in ether and the contents are shaken and allowed to stand

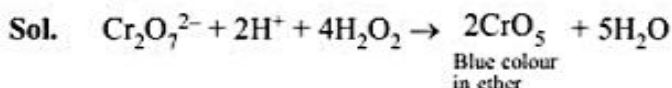
(A) a blue colour is obtained in ether due to formation of $\text{Cr}_2(\text{SO}_4)_3$

(B) a blue colour is obtained in ether due to formation of CrO_5

(C) a blue colour is obtained in ether due to formation of CrO_3

(D) chromyl chloride is formed

Ans. (B)



Q.5 Mass percentage of deuterium in heavy water is

(A) same as that of protium in water

(B) 11.1

(C) 20.1

(D) cannot be predicted

Ans. (C)

Sol. The formula of heavy water is D_2O , i.e., molecular mass = 20

$$\% \text{ of deuterium} = \frac{4}{20} \times 100 = 20$$

- Q.6** 2 g of aluminium is treated separately with excess of dilute H_2SO_4 and excess of NaOH . The ratio of volumes of hydrogen evolved under similar conditions of pressure and temperature is
 (A) 2 : 3 (B) 1 : 1 (C) 2 : 1 (D) 1 : 2

Ans. (B)

Sol. $2\text{Al} + 3\text{H}_2\text{SO}_4 \rightarrow \text{Al}_2(\text{SO}_4)_3 + 3\text{H}_2$;
 $2\text{Al} + 2\text{NaOH} + 2\text{H}_2\text{O} \rightarrow 2\text{NaAlO}_2 + 3\text{H}_2$
 Thus ratio of volumes of hydrogen evolved is 1 : 1

- Q.7** In which reaction, hydrogen peroxide neither acts as an oxidising agent nor a reducing agent ?
 (A) $\text{PbS} + \text{H}_2\text{O}_2 \rightarrow$ (B) $\text{SO}_3 + \text{H}_2\text{O}_2 \rightarrow$ (C) $\text{PbO}_2 + \text{H}_2\text{O}_2 \rightarrow$ (D) $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O}_2 \rightarrow$

Ans. (D)

Sol. H_2O_2 behaves as an acid when reacts with Na_2CO_3 .
 $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O}_2 \rightarrow \text{Na}_2\text{O}_2 + \text{CO}_2 + \text{H}_2\text{O}$

- Q.8** Which one of the following reactions does not form gaseous product ?
 (A) $\text{PbO}_2 + \text{H}_2\text{O}_2 \rightarrow$ (B) $\text{PbS} + \text{H}_2\text{O}_2 \rightarrow$ (C) $\text{Cl}_2 + \text{H}_2\text{O} \rightarrow$ (D) $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow$

Ans. (B)

Sol. $\text{PbS} + 4\text{H}_2\text{O}_2 \rightarrow \underset{\text{(Solid)}}{\text{PbSO}_4} + \underset{\text{(Liquid)}}{4\text{H}_2\text{O}}$

- Q.9** What is the degree of hardness of a sample of water containing 24 mg of MgSO_4 (molecular mass 120) per kg of water ?

(A) 10 ppm (B) 15 ppm (C) 20 ppm (D) 25 ppm

Ans. (C)

Sol. 24 mg of MgSO_4 present in 1000 g of water
 1000 g water will contain = 24000 mg of MgSO_4 = 24 g of MgSO_4
 120 g of $\text{MgSO}_4 \equiv 100$ g of CaCO_3

$$\text{So, } 24 \text{ g of } \text{MgSO}_4 = \frac{100}{120} \times 24 = 20 \text{ g of } \text{CaCO}_3$$

Hardness of water = 20 ppm

- Q.10** In alkaline medium, H_2O_2 reacts with Fe^{3+} and Mn^{2+} separately to give
 (A) Fe^{4+} and Mn^{4+} (B) Fe^{2+} and Mn^{2+} (C) Fe^{2+} and Mn^{4+} (D) Fe^{4+} and Mn^{2+}

Ans. (C)

Sol. $\text{K}_3\text{Fe}(\text{CN})_6$ is reduced by H_2O_2 in alkaline medium.
 $2\text{K}_3\text{Fe}(\text{CN})_6 + 2\text{KOH} + \text{H}_2\text{O}_2 \rightarrow 2\text{K}_4\text{Fe}(\text{CN})_6 + 2\text{H}_2\text{O} + \text{O}_2$
 $\text{Mn}(\text{OH})_2$ is oxidised by H_2O_2 in alkaline medium
 $\text{Mn}(\text{OH})_2 + \text{H}_2\text{O}_2 \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$