DAY TWENTY

Hydrogen

Learning & Revision for the Day

- Position of Hydrogen in Periodic Table
- Dihydrogen
- Hydrides
- Isotopes of Hydrogen
- Water (H₂O)
- + Hard and Soft water
- Hydrogen Peroxide (H₂O₂)

Dihydrogen (H_2) is the most abundant element in the universe (70% of the total mass of the universe) and is the principal element in the solar atmosphere. The giant planets Jupiter and Saturn consist of mainly hydrogen. It is the lightest element known.

Position of Hydrogen in Periodic Table

The position of hydrogen in periodic table is uncertain as it shows resemblance with alkali metals as well as with halogens. However, on the basis of electronic configuration $(1s^1)$, it is placed above lithium in the periodic table but still, it is not considered as the member of that group. On the other hand, like halogens (with ns^2 , np^5 configuration), it is short by one electron to the corresponding noble gas configuration but it is still not considered as the member of seventeenth group. Thus, it has unique behaviour and is therefore best placed separately in the periodic table.

Isotopes of Hydrogen

- Hydrogen has three isotopes, i.e. protium $\binom{1}{1}$ H), deuterium or heavy hydrogen $\binom{2}{1}$ H or D) and tritium $\binom{3}{1}$ H or T). Out of these isotopes, only tritium is radioactive and emits low energy β^{-} particles.
- The three isotopes have different masses and different enthalpy of bond dissociation hence, their rates of reaction and equilibrium constants are different. This is known as **isotopic effect**. They have same electronic configuration and chemical properties.
- **NOTE** Allotropes of hydrogen are *ortho*-hydrogen (*o*-H₂) (in which proton spin is in same direction) and *para*-hydrogen (*p*-H₂) (in which proton spin is in opposite direction). Similarly, deuterium and tritium also exhibit spin isomerism and exist in *ortho*-and *para*-forms.





Atomic Hydrogen

Hydrogen gas dissociates into atoms when it is subjected to an electric discharge under low pressure.

 $\underset{(Atomic hydrogen)}{H_2} \xrightarrow{Electric discharge} \xrightarrow{2H} (Nascent hydrogen)$

Atomic hydrogen is very reactive and can be used as a reducing agent as well as oxidising agent.

Reducing power of atomic hydrogen is more than that of nascent hydrogen.

Dihydrogen

It is the principal element in the solar atmosphere. In the combined form, it occurs in plant and animal tissues.

Preparation of Dihydrogen

Laboratory preparation of dihydrogen are as follows :

 (i) It is prepared by the action of dilute hydrochloric acid on metals that are more reactive than hydrogen granulated zinc, iron, magnesium, etc.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2^{\uparrow}$$

(ii) Certain metals like Zn, Sn, Al etc., react with NaOH to liberate $\rm H_2$

 $Zn + 2NaOH \longrightarrow \underset{Sodium \ zincate}{Na_2ZnO_2} + H_2 \uparrow$

Commercially used processes for the preparation of dihydrogen are as:

• Electrolysis of acidified water using platinum electrodes give dihydrogen.

$$\begin{array}{c} 2H_2O(I) & \xrightarrow{\text{Traces of acid/base}} 2H_2(g) + O_2(g) \\ \text{Containing small} & \text{(At cathode)} & \text{(At anode)} \end{array}$$

- Dihydrogen of high purity (> 99.95%) is obtained by electrolysing warm aqueous barium hydroxide solution between nickel electrodes.
- The mixture of CO and H₂ is called **water gas.** As this mixture is used for the synthesis of methanol and a number of hydrocarbons, it is also called **synthesis gas** or *syn* gas. Now-a-days, '*syn* gas' is produced from sewage, scrap wood, newspapers etc. The process of producing '*syn* gas' from coal is called coal gasification. (Bosch process)

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

$$Water gas$$

$$CO(g) + H_2O(g) \xrightarrow[\text{CO}_2(g)]{673 \text{ K}} CO_2(g) + H_2(g)$$

$$CO(g) + H_2O(g) \xrightarrow[\text{CO}_2(g)]{673 \text{ K}} CO_2(g) + H_2(g)$$

 CO_2 is removed by passing the mixture through water at very high pressure. (CO_2 is dissolved completely in water). This reaction is known as water-gas shift reaction (WGSR)

• Lane's process involves decomposition of steam over heated Fe (550° – 800°C). This reaction is known as gassing reaction.

 $3\text{Fe} + 4\text{H}_2\text{O} \longrightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2\uparrow$; $\Delta H = -160.7 \text{ kJ}$ By the action of water gas, Fe_3O_4 is again reduced to iron. This process is known as **vivifaction**.

$$\begin{array}{l} \mathrm{Fe_3O_4} + 4\mathrm{CO} \longrightarrow \mathrm{3Fe} + 4\mathrm{CO_2} \\ \mathrm{Fe_3O_4} + 4\mathrm{H_2} \longrightarrow \mathrm{3Fe} + 4\mathrm{H_2O} \end{array}$$

• Dihydrogen is obtained as a byproduct of brine electrolysis process for the manufacturing of NaOH, petroleum cracking plants and many electrolytic reactions.

Properties of Hydrogen

- Hydrogen is colourless, tasteless, odourless gas. It is lightest and slightly soluble in water.
- It is a neutral and highly combustible gas, so in the presence of air, it burns with pale blue flame to form water.
- **Reducing action** Hydrogen reduces the oxides of less electropositive elements but cannot reduce the oxides of alkali metals and alkaline earth metals.

$$\operatorname{ZnO}(s) + \operatorname{H}_2(g) \longrightarrow \operatorname{Zn} + \operatorname{H}_2O$$

$$\operatorname{Fe}_{3}O_{4}(s) + 4\operatorname{H}_{2}(g) \longrightarrow 3\operatorname{Fe} + 4\operatorname{H}_{2}(g)$$

Hydrogenation

Vegetable oil + $H_2 \xrightarrow{Ni/473K}$ Vanaspati ghee

$$CH_2 = CH_2 + H_2 \xrightarrow{\text{Ni or } Pt/\Delta} CH_3 \longrightarrow CH_3$$

- Reaction with CO CO (g) + $2H_2(g) \xrightarrow{\text{ZnO/Cr}_2O_3} \text{CH}_3\text{OH}(l)$
- With dinitrogen, it forms ammonia (Haber's process). $N_2(g) + 3H_2(g) \xrightarrow{673 \text{ K}, 200 \text{ atm}} 2\text{NH}_2(g)$

$$I_2(g) + 3H_2(g) \xrightarrow{\text{OVO IN} 200 \text{ dum}} 2NH_3(g)$$

Fe, Mo

Uses of Hydrogen

- In hydrogenation of oils.
- In preparation of synthetic petrol.
- In oxy-hydrogen flame.
- In hydrogen-oxygen fuel cells to produce electricity.
- In a fuel cell, electrical energy is generated by the reaction of H₂ and O₂without evolution of heat (cold combustion).
- Liquid hydrogen is used as rocket fuel.
- As a reducing agent in extraction of metals.

Hydrides

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

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Classification of Hydrides

The hydrides are classified into four categories.

- 1. Ionic or Saline or Salt-like Hydrides
- These hydrides are stoichiometric compounds of dihydrogen formed with most of the *s*-block elements which are highly electropositive in character, e.g. LiH, BeH₂ and MgH₂.
- In fact, BeH₂ and MgH₂ are polymeric in structure. Due to their high reactivity with water, ionic hydrides are used to remove traces of water from organic solvents.

2. Covalent or Molecular Hydrides

- Dihydrogen forms molecular compounds with most of the p-block elements. Most familiar examples are CH_4 , NH_3 , H_2O and HF etc.
- Molecular hydrides are further classified, according to the relative number of electrons and bonds in their Lewis structure into following types:
 - (i) **Electron deficient hydrides** have incomplete octet, so behave as Lewis acids, i.e. are electron acceptors. e.g. B_2H_6 . These hydrides are formed by the elements of group 13.
- (ii) **Electron precise hydrides** have required number of electrons to write their Lewis structure. These are obtained from elements of group 14 (e.g. CH_4) which are tetrahedral in geometry.
- (iii) Electron rich hydrides have excess electrons, which are present as lone pairs. Elements of group 15-17 form such type of hydrides. e.g. NH₃ (1 lone pair), H₂O (2 lone pairs)

and HF (3 lone pairs)

3. Metallic or Non-stoichiometric or Interstitial Hydrides

- These are formed by many *d*-block and *f*-block elements, however the metals of group 7, 8 and 9 do not form hydride (hydride gap).
- These hydrides are mainly formed by
 (i) transition metals of group 3, 4, 5 of *d*-block
- (ii) Cr metal from group 6
- (iii) *f*-block elements, e.g. LaH_{2.87}, YbH_{2.55} etc.
- Metallic hydrides are non-stoichiometric. They have metallic lattice and hydrogen is present at the interstitial sites. These conduct heat and electricity just like metals except hydrides of Eu and Yb. (EuH₂ and YbH₂ are ionic and stoichiometric)

4. Polymeric Hydrides and Complex Hydrides

- Polymeric hydrides are formed by elements having electronegativity in the range 1.4 to 2.0, e.g. $(BeH_2)_n$, $(AlH_3)_n$ etc.
- In complex hydrides, H⁻acts as ligand and is attached to central metal atom, e.g. LiAlH₄, LiBH₄ etc.

Water (H₂O)

The water molecules contains one oxygen and two hydrogen atoms connected by covalent bonds. The physical and chemical properties of water are given below:

Physical Properties

- Water (H₂O) is polar in nature. It exists in liquid state at room temperature due to intermolecular hydrogen bonding.
- HOH bond angle is 104.5° and O—H bond length is 95.7 pm. H_2O (ice) has four hydrogen bonds per molecule and hence, has a highly ordered three dimensional cage-like structure.
- Ice has low density than $\rm H_2O$ (liquid) but $\rm H_2O$ has maximum density at 3.98°C.

Chemical Properties

(i) Water is amphoteric in nature.

$$\begin{array}{rcl} \mathrm{H}_{2}\mathrm{O}(l) + & \mathrm{HCl}(aq) & \Longrightarrow & \mathrm{H}_{3}\mathrm{O}^{+}(aq) + & \mathrm{Cl}^{-}(aq) \\ & & \mathrm{Base} & & \mathrm{Acid} & & \mathrm{Base} \\ \mathrm{H}_{2}\mathrm{O}(l) + & \mathrm{NH}_{3}(aq) & \Longrightarrow & \mathrm{NH}_{4}^{+}(aq) + & \mathrm{OH}^{-}(aq) \\ & & \mathrm{Acid} & & \mathrm{Base} & & & \mathrm{Acid} & & \mathrm{Base} \end{array}$$

(ii) Water react with metals and non-metals both.

$$2\operatorname{Na}(s) + 2\operatorname{H}_2\operatorname{O}(l) \longrightarrow 2\operatorname{Na}\operatorname{OH}(aq) + \operatorname{H}_2(g)$$
$$2\operatorname{F}_2(g) + 2\operatorname{H}_2\operatorname{O}(l) \longrightarrow 4\operatorname{H}^+(aq) + 4\operatorname{F}^-(aq) + \operatorname{O}_2(g)$$

- (iii) In hydrated salts, water may remain in five types such as coordinated water, hydrogen bonded water, lattice water, clathrate water and zeolitic water.
 - Zeolites are the hydrated sodium aluminium silicate that contains cavities or certain channels in which H_2O molecules get trapped.
 - **Clathrate** contains host molecules that crystallises with an open structure containing water molecules.
- (iv) A number of compounds such as calcium hydride, calcium phosphide etc., undergo hydrolysis with water. The hydrolysis of hydrides with H_2O is highly exothermic and may be explosive as H_2 catches fire. CO_2 is reduced by hot metal hydride, so it cannot use to extinguish such fire.

Hard and Soft Water

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The water which lathers with soap is soft, if not, is hard. Hardness of water is of two types:

- 1. Temporary Hardness of Water is due to the presence of magnesium and calcium hydrogen carbonates. It can be removed either by **boiling**, through which the soluble $Mg(HCO_3)_2$ is converted into insoluble $Mg(OH)_2$ and $Ca(HCO_3)_2$ is changed into insoluble $CaCO_3$. These precipitates can be removed by filtration
- 2. **Permanent Hardness of Water** is due to the presence of soluble salts of magnesium and calcium in the form of chlorides and sulphates.

Permanent hardness can be removed by the following methods:

(i) Calgon's Method Sodium hexametaphosphate
 (Na₆P₆O₁₈), commercially called calgon, when added to hard water, the calcium and magnesium ions present in hard water react with calgon and form

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soluble complex salts which does not cause any hinderance in other information.

$$\begin{array}{ll} 2M^{2+} + \mathrm{Na_2[Na_4(PO_3)_6]} &\longrightarrow \ [\mathrm{Na_2}M(\mathrm{PO_3)_6}]^{2-} + 4 \ \mathrm{Na^+} \\ & \mathrm{Soluble} \\ & [M^{2+} = \mathrm{Ca^{2+}}, \mathrm{Mg^{2+}}] \end{array}$$

(ii) **Ion-exchange Method or Permutit or Zeolite process** is also used to remove permanent hardness. $2\operatorname{Na} Z(s) + M^{2+}(aq) \longrightarrow MZ_2(s) + 2\operatorname{Na}^+(aq)_{(M = Mg, Ca)}$

where, NaZ is sodium aluminium silicate (NaAlSiO₄). This is also known as sodium zeolite. It is regenerated for further use by treating with an aqueous NaCl solution (brine). $MZ_2(s) + 2NaCl(aq) \longrightarrow 2NaZ(s) + MCl_2(aq)$

(iii) Synthetic Resins Method Now a days hard water is softened by using synthetic cation exchangers. Cation exchange resins contain large organic molecules with —SO₃H group and are water insoluble. Ion-exchange resin (RSO_3H) is changed to RNa by treating it with NaCl.

$$2R\mathrm{Na} + M^{2+}(aq) \longrightarrow R_2 M(s) + 2\mathrm{Na}^+(aq) \ (M^{2+} = \mathrm{Ca}^{2+}, \mathrm{Mg}^{2+})$$

The resin can be regenerated by adding aqueous NaCl solution.

Heavy Water (D₂O)

- It has quite similar physical and chemical properties to those of H_2O . Dielectric constant of D_2O is lower than that of H_2O and rate of reactions are much slower than H_2O .
- It is used as a moderator in nuclear reactions, as trace compound for studying reaction mechanism for the preparation of deuterium.

For e.g.
$$CaC_2 + 2D_2O \longrightarrow C_2D_2 + Ca(OD)_2$$

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

Hydrogen Peroxide (H₂O₂)

- Hydrogen peroxide is a compound with an oxygen-oxygen single bond. It is also a strong oxidiser.
- Hydrogen peroxide has a non-polar structure. The molecular dimensions in solid and gas phase are as follows:



Preparation of H₂O₂

• It can be prepared by treating BaO_2 in presence of acid at high temperature.

 $BaO_2 \cdot 8H_2O(s) + H_2SO_4(aq) \longrightarrow$

 $BaSO_4(s) + H_2O_2(aq) + 8H_2O(l)$

• Industrially, it is prepared by the auto-oxidation of 2-alkylanthraquinols.

Chemical Properties

- It acts as an oxidising as well as reducing agent in both acidic and alkaline media.
- Oxidising action in acidic medium,
- $2Fe^{2+}(aq) + 2H^{+}(aq) + H_2O_2(aq) \longrightarrow 2Fe^{3+}(aq) + 2H_2O(l)$ $PbS(s) + 4H_2O_2 \longrightarrow PbSO_4(s) + 4H_2O(l)$
- Oxidising action in basic medium, $\mathrm{Mn}^{2+} + \mathrm{H_2O_2} {\longrightarrow} \mathrm{Mn}^{4+} + \mathrm{2OH^-}$
- Reducing action in acidic medium,

$$2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$$

• Reducing action in basic medium,

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

• Many reactions of H_2O_2 are radical reactions, therefore a mixture of H_2O_2 and Fe (II) is a source of hydroxyl radicals for organic reactions.

Uses of H_2O_2

- Aqueous solution of H_2O_2 is used as germicide, antiseptic, preservative for milk and wine, bleaching agent for soft materials. 30% H_2O_2 is called perhydrol. Its volume strength is 100 and molarity is 8.8.
- It is used as an antichlor and in refreshing old oil paintings which became black.

NOTE H_2O_2 decomposes slowly on exposure to light,

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

In the presence of metal surfaces or traces of alkali (present in glass containers), the above reaction is catalysed. It is therefore, stored in wax lined glass or plastic vessels in dark. Urea can be added as a stabiliser.

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(DAY PRACTICE SESSION 1)

FOUNDATION QUESTIONS EXERCISE

(a

(c

- 1 Ortho and para hydrogen differ in the
 - (a) number of protons

(b) molecular weight

- (c) nature of spins of protons
- (d) nature of spins of electrons
- **2** The metal, which gives hydrogen on treatment with acid as well as sodium hydroxide is

(a) Fe	(b) Zn
(c) Cu	(d) None of these

3 Which of the following reactions increases production of dihydrogen from synthesis gas?

 $\begin{array}{l} \text{(a) } \mathsf{CH}_4(g) + \mathsf{H}_2\mathsf{O}(g) \xrightarrow[1270 \text{ K}]{} \mathsf{K} \mathsf{CO}(g) + 3\mathsf{H}_2(g) \\ \text{(b) } \mathsf{C}(s) + \mathsf{H}_2\mathsf{O}(g) \xrightarrow[1270 \text{ K}]{} \mathsf{CO}(g) + \mathsf{H}_2(g) \\ \text{(c) } \mathsf{CO}(g) + \mathsf{H}_2\mathsf{O}(g) \xrightarrow[673 \text{ K}]{} \mathsf{CO}_2(g) + \mathsf{H}_2(g) \\ \text{(d) } \mathsf{C}_2\mathsf{H}_6 + 2\mathsf{H}_2\mathsf{O} \xrightarrow[1270 \text{ K}]{} \mathsf{K} \overset{\mathsf{Co}}{} \mathsf{2}\mathsf{CO} + 5 \mathsf{H}_2 \end{array}$

- **4** In context with the industrial preparation of hydrogen from water gas (CO+H₂), which of the following is the correct statement?
 - (a) CO is oxidised to CO₂ with steam in the presence of catalyst followed by absorption of CO₂ in alkali
 - (b) CO and H₂ are fractionally separated using differences in their densities
 - (c) CO is removed by absorption in aqueous $\rm Cu_2\rm Cl_2$ solution (d) $\rm H_2$ is removed through occlusion with Pd
- **5** H₂ gas is liberated at anode by electrolysis of which of the following aqueous solution?

(a)	NaH	(b)	HCOO ⁻ Na
(C)	NaCl	(d)	LiH

- **6** Very pure hydrogen (99.9) can be made by which of the following processes?
 - (a) Reaction of methane with steam

(b) Mixing natural hydrocarbons of high molecular weight

- (c) Electrolysis of water
- (d) Reaction of salts like hydrides with water
- **7** In which of the following reactions does dihydrogen act as oxidising agent?

(a) Ca + H ₂ \longrightarrow	(b) $H_2 + O_2 \longrightarrow$
$(c) H_2 + F_2 \longrightarrow$	(d) CuO + H ₂ \longrightarrow

8 The maximum possible number of hydrogen bonds in a water molecule can form in ice is

(a) 1	(b) 2	(c) 3	(d) 4
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- 9. Which one is used as propellants for rockets?
 - (a) Liq. H_2 + Liq. O_2 (b) Liq. N_2 + Liq. O_2 (c) Liq. H_2 + Liq. N_2 (d) Liq. O_2 + Liq. air
- **10** Hydrogen exists in atomic state in which of the following compounds?

Metallic hydrides)	(b) Ionic hydrides
Molecular hydrides)	(d) H ₂ O

- **11** Which of the following is electron precise hydride? (a) B₂H₆ (b) NH₃ (c) H₂O (d) CH₄
- **12** The hydrides of the first elements in groups 15-17 namely NH_3 , H_2O and HF respectively show abnormally high values for melting and boiling points. This is due to
 - (a) small size of N, O and F
 - (b) the ability to form extensive intermolecular H-bonding
 - (c) the ability to form extensive intramolecular H-bonding
 - (d) effective van der Waals' interaction
- 13 Ice floats on water because
 - (a) its density is less than that of water
 - (b) crystal structure of ice has empty space
 - (c) Both of the above
 - (d) None of the above
- 14 When zeolite, which is hydrated sodium aluminium silicate is treated with hard water, the sodium ions are exchanged with

(a)H ⁺ ion	(b) Ca ²⁺ ion
(c) SO_4^{2-} ion	(d) OH [_] ion

- 15 Which one of the following statements about water is false? → JEE Main 2016
 - (a) Water can act both as an acid and as a base
 - (b) There is extensive intramolecular hydrogen bonding in the condensed phase
 - (c) Ice formed by heavy water sinks in normal water
 - (d) Water is oxidised to oxygen during photosynthesis
- **16** Which one of the following processes will produce hard water?
 - (a) Saturation of water with CaSO
 - (b) Saturation of water with $CaCO_3$
 - (c) Addition of Na₂SO₄ to water
 - (d) Saturation of water with MgCO₃
- **17.** Which of the following is responsible for the permanent hardness of water?

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- (a) Calcium bicarbonate
- (b) Sodium chloride
- (c) Magnesium bicarbonate
- (d) Calcium sulphate
- 18. Permutit is chemically
 - (a) hydrated sodium aluminium silicate
 - (b) sodium hexaphosphate
 - (c) sodium bicarbonate
 - (d) calcium hydroxide

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19. The hardness of water sample containing 0.002 mole of magnesium sulphate dissolved in a litre of water is expressed as

(a) 20 ppm	(b) 200 ppm
(c) 2000 ppm	(d) 120 ppm

20 Hydrogen peroxide is used as

(a) an oxidant only	(b) a reductant only
(c) an acid only	(d) All of these

21 Decomposition of H₂O₂ is favoured by

1	~	2	,
(a) traces of acids			(b) alcohol
(c) acetanilide			(d) MnO

- 22 In aqueous solution, hydrogen peroxide oxidises H₂S to
 (a) sulphur
 (b) sulphuric acid
 - (c) Caro's acid (d) Marshall's acid
- 23 30 volume hydrogen peroxide means
 - (a) 30% of H_2O_2 solution
 - (b) 30 cm^3 of the solution contains 1g of H₂O₂
 - (c) 1 cm^3 of the solution liberates 30 cm^3 of O_2 at STP
 - (d) 30 cm^3 of the solution contains 1 mole of H₂O₂
- **24** Which of the following statements is not correct ?
 - (a) H_2O_2 oxidises Fe (II) to Fe (III)
 - (b) H_2O_2 can be obtained by electrolysis of dil. H_2SO_4 (c) H_2O_2 reduces Mn (VII) to Mn (II)
 - $(d)H_2O_2$ is a weak base
- 25 Acidified solution of chromic acid on treatment with $\rm H_2O_2$ yields
 - (a) $CrO_3 + H_2O + O_2$ (b) $Cr_2O_3 + H_2O + O_2$ (c) $CrO_5 + H_2O + K_2SO_4$

(d)
$$H_2Cr_2O_7 + H_2O + O_2$$

- **26** Hydrogen peroxide when added to a solution of potassium permanganate acidified with H₂SO₄.
 - (a) forms water only
 - (b) acts as an oxidising agent
 - (c) acts as a reducing agent
 - (d) reduces sulphuric acid
- 27 Consider the following reactions :
 - I. $H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$
 - II. $H_2O_2 + Ag_2O \longrightarrow 2Ag + H_2O + O_2$

Role of hydrogen peroxide in the above reactions is respectively

- (a) oxidising in I and reducing in II(b) reducing in I and oxidising in II(c) reducing in I and II
- (d) oxidising in I and II
- **28.** Hydrogen peroxide oxidises $[Fe(CN)_6]^{4-}$ to $[Fe(CN)_6]^{3-}$ in acidic medium but reduces $[Fe(CN)_6]^{3-}$ to $[Fe(CN)_6]^{4-}$ in alkaline medium. The other products formed are, respectively. → JEE Main 2015 (a) $(H_2O + O_2)$ and H_2O (b) $(H_2O + O_2)$ and $(H_2O + OH^-)$ (c) H_2O and $(H_2O + O_2)$ (d) H_2O and $(H_2O + OH^-)$
- 29. From the following statements regarding H₂O₂, choose the incorrect statement. → JEE Main 2018
 - (a) It can act only as an oxidising agent
 - (b) It decomposed on exposure to light
 - (c) It has to be stored in plastic or wax lined glass bottles in dark
 - (d) It has to be kept away from dust

Direction (Q. Nos. 30-32) In the following questions, Assertion (A) followed by a Reason (R) is given. Choose the correct answer out of the following choices.

- (a) Assertion and Reason both are correct and Reason is the correct explanation of the Assertion
- (b) Assertion and Reason both are correct but Reason is not the correct explanation of the Assertion
- (c) Assertion is correct and Reason is incorrect
- (d) Both Assertion and Reason are incorrect
- **30.** Assertion Density of ionic hydrides such as LiH is greater than that of metals from which they are formed.
 Reason Small H⁻ (hydride ions) occupy holes in the lattice of metal without distorting metal lattice.
- **31.** Assertion Melting point of D₂O is higher than that of H₂O.
 Reason Heavy water is more viscous than ordinary water, H₂O.
- **32.** Assertion H_2O_2 acts as an oxidising agent as well as reducing agent.

Reason $In H_2O_2$, oxygen has -1 oxidation state and it can increase or decrease its oxidation state.



(DAY PRACTICE SESSION 2)

PROGRESSIVE QUESTIONS EXERCISE

- 1 Out of LiH, MgH₂ and CuH
 - (a) all are ionic hydrides
 - (b) LiH, MgH₂ are ionic and CuH covalent hydride
 - (c) all are covalent hydrides
 - (d) LiH is ionic, $\mathrm{MgH}_{\mathrm{2}}$ and CuH are intermediate hydrides
- **2** The hydride ion H⁻ is stronger base than its hydroxide ion OH⁻. Which of the following reactions will occur if sodium hydride (NaH) is dissolved in water?

(a) $2H^+(aq) \longrightarrow H_2 + 2e^-$ (b) $H^-(aq) + H_2O(l) \longrightarrow OH^- + H_2$ (c) $H^- + H_2O(l) \longrightarrow$ No reaction

- (d) None of the above
- **3** The compound sodium polymeta phosphate $Na_2[Na_4(PO_3)_6]$ is called Calgon because
 - (a) it was developed by the scientist
 - (b) it was developed first in California
 - (c) it refers to calcium gone
 - (d) it is based on the name of the company which developed
- **4** Which of the following statements concerning protium, deuterium and tritium is not true?
 - (a) They are isotopes of each other
 - (b) They have similar electronic configurations
 - (c) They exists in the nature in the ratio of 1 : 2 : 3 respectively
 - (d) Their mass numbers are in the ratio 1 : 2 : 3 respectively
- **5** Select the incorrect statement.
 - (a) Ortho and para hydrogen are different due to difference in their nuclear spins
 - (b) Ortho and para hydrogen are different due to different in their electron spins
 - (c) Para hydrogen has a lower internal energy than that of ortho hydrogen
 - (d) Para hydrogen is more stable at lower temperature
- **6** Which one of the following statements is incorrect with regard to *ortho* and *para* dihydrogen?
 - (a) They are nuclear spin isomers
 - (b) The *ortho* isomer has zero nuclear spin whereas the *para* isomer has one nuclear spin
 - (c) The para isomer is favoured at low temperatures
 - (d) The thermal conductivity of the *para* isomer is 50% greater than that of the *ortho* isomer
- 7 H₂ can be obtained from
 - (a) water gas (CO + H₂) by liquefaction of CO at low temperature under pressure

- (b) water gas by oxidation of CO into $\rm CO_2$ (by steam) which can be easily removed by dissolving in $\rm H_2O$
- (c) electrolysis of water
- (d) All the above methods can be used to obtain H_2
- **8** Which one of the following pairs of substances will not produce hydrogen when reacted together?
 - (a) Copper and conc. nitric acid
 - (b) Ethanol and metallic sodium
 - (c) Magnesium and steam
 - (d) Phenol and metallic sodium
- 9 Metal hydrides are ionic, covalent or molecular in nature. Among LiH, NaH, KH, RbH, CsH, the correct order of increasing ionic character is
 - (a) LiH > NaH > CsH > KH > RbH
 - (b) LiH < NaH < KH < RbH < CsH
 - (c) RbH > CsH > NaH > KH > LiH
 - (d) NaH > CsH > RbH > LiH > KH
- **10** Which of the following equations depicts the oxidising nature of H₂O₂?

 $\begin{array}{l} \text{(a) } 2\text{MnO}_4^- + 6\text{H}^+ + 5\text{H}_2\text{O}_2 \longrightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 5\text{O}_2 \\ \text{(b) } 2\text{Fe}^{3+} + 2\text{H}^+ + \text{H}_2\text{O}_2 \longrightarrow 2\text{Fe}^{2+} + 2\text{H}_2\text{O} + \text{O}_2 \\ \text{(c) } 2\text{I}^- + 2\text{H}^+ + \text{H}_2\text{O}_2 \longrightarrow \text{I}_2 + 2\text{H}_2\text{O} \\ \text{(d) } \text{KIO}_4 + \text{H}_2\text{O}_2 \longrightarrow \text{KIO}_3 + \text{H}_2\text{O} + \text{O}_2 \end{array}$

11 Which of the following equation depicts reducing nature of H₂O₂?

 $\begin{array}{l} (a) \ 2[\text{Fe}(\text{CN})_6]^{4^-} + 2\text{H}^+ + \text{H}_2\text{O}_2 \longrightarrow 2[\text{Fe}(\text{CN})_6]^{3^-} + 2\text{H}_2\text{O} \\ (b) \ \text{I}_2 \ + \ \text{H}_2\text{O}_2 \ + 2\text{OH}^- \longrightarrow 2\text{I}^- + 2\text{H}_2\text{O} + \text{O}_2 \\ (c) \ \text{Mn}^{2+} \ + \ \text{H}_2\text{O}_2 \longrightarrow \text{Mn}^{4+} \ + 2\text{OH}^- \\ (d) \ \text{PbS} \ + \ 4\text{H}_2\text{O}_2 \longrightarrow \text{PbSO}_4 \ + \ 4\text{H}_2\text{O} \end{array}$

- **12** Which one of the following statements is correct for H_2O_2 ?
 - (a) It reduces ferricyanide to ferrocyanide in acidic medium
 - (b) It oxidises lead monoxide to lead dioxide
 - (c) It acts as a reducing agent in the decolourisation of acidified ${\rm KMnO}_4$
 - (d) It oxidises hydrides of chlorine and bromine to their diatomic gases
- **13** Hydrogen resembles halogens in many respects for which several factors are responsible. Of the following factors which one is most important in this respect?
 - (a) Its tendency to lose an electron to form a cation(b) Its tendency to gain a single electron in its valence shell

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- to attain stable electronic configuration (c) Its low negative electron enthalpy value
- c) its low negative electron enthalpy
- (d) Its small size

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ANSWERS

(SESSION 1)	1 (c) 11 (d) 21 (d) 31 (b)	2 (b) 12 (b) 22 (a) 32 (a)	3 (c) 13 (c) 23 (c)	4 (a) 14 (b) 24 (d)	5 (a) 15 (b) 25 (c)	6 (d) 16 (a) 26 (c)	7 (a) 17 (d) 27 (a)	8 (d) 18 (a) 28 (c)	9 (a) 19 (b) 29 (a)	10 (a) 20 (d) 30 (a)
(SESSION 2)	1 (d) 11 (b)	2 (b) 12 (c)	3 (c) 13 (b)	4 (c)	5 (b)	6 (b)	7 (d)	8 (a)	9 (b)	10 (c)

Hints and Explanations

SESSION 1

- **1** Ortho and para-hydrogens differ in the nature of spins of protons.
- **2** Zn is amphoteric metal and reacts with acids as well as alkalies to give hydrogen gas.

3 CO (g) +H₂O (g) $\xrightarrow[Catalyst]{Catalyst}$ CO₂(g) +H₂(g)

4 In this reaction, CO is oxidised to CO₂ with steam in the pressure of catalyst followed by absorption of CO₂ in alkali.

KOH→K₂CO₃

- $\begin{array}{l} \textbf{5} \ \text{H}_2 \ \text{gas is liberated at anode by} \\ \text{electrolysis of NaH aqueous solution.} \\ \text{NaH} + \text{H}_2 \text{O} \longrightarrow \text{NaOH} + \ \text{H}_2 \end{array}$
- **6** Hydrides are instant sources of hydrogen of higher purity. They react with H_2O forming H_2 gas. $CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2 \uparrow$
- 7 Calcium when reacts with hydrogen forms calcium hydride. Here, dihydrogen act as oxidising agent. Ca + H₂ → 2CaH
- 8 In ice, each H₂O molecule is surrounded tetrahedrally by four other water molecules through H-bonds.
- **9** Liquid H₂ and liquid O₂ are used as rocket propellants.
- **10** Hydrogen exists in atomic state in metallic hydrides.

- **11** The hydride which contains exact number of electrons to form normal covalent bonds are called electron precise hydrides, e.g. CH₄.
- 12 Hydrides of N, O and F because of the small size and high electronegativity of elements have ability to form extensive intermolecular, (i.e. between two molecules) hydrogen bonding. Thus, a large amount of energy is required to break these bonds, the melting and boiling points of hydrides of these elements are abnormally high.
- **13** Ice floats on water because its density is less than that of water which in turn is due to empty space in its crystal structure. Crystal structure of ice is regular hexagon with empty spaces at the centre.
- **14** Na₂Z + CaCl₂ \longrightarrow Sodium zeolite From hard water CaZ + 2NaCl Calcium zeolite [where, $Z = Al_2Si_2O_8 \cdot x H_2O$]
- **15** Water consists of extensive intermolecular H-bonding in the condensed phase.
- **16** Permanent hardness is due to the presence of chlorides and sulphates of calcium, magnesium and iron in water.
- 17 Chlorides and sulphates of calcium and magnesium are responsible for the permanent hardness of water. Hence, CaSO₄ is responsible for the permanent hardness of water.

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- **18** Permutit is chemically hydrated sodium aluminium silicate.
- **19** The hardness of water sample containing 0.002 mole of MgSO₄ dissolved in 1 L of water.

Hardness is measured in terms of ppm of $CaCO_3$.

 $MgSO_4 \equiv CaCO_3 \equiv 0.002 \text{ mol } L^{-1}$

 $CaCO_3 = 0.002 \times 100 \text{ gL}^{-1}$

= $0.002 \times 100 \text{ g in } 10^3 \text{ mL}$ = $\frac{0.002 \times 100 \times 10^6}{10^3} \text{ g in } 10^6 \text{ mL(ppm)}$

= 200 ppm

- **20** H₂O₂ acts as an oxidant, reductant and an acid (weak).
- **21** MnO catalysis the decomposition of H_2O_2 .
- **22** In aqueous solution, hydrogen peroxide oxidises H_2S to S.

 $H_2S + H_2O_2 \longrightarrow 2H_2O + S$

23 30 Volume hydrogen peroxide means 1 cm^3 of this solution produces 30 cm³ O_2 at NTP.

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

24
$$H_2O_2$$
 is not a weak base but a weak acid.

25
$$K_2Cr_2O_7 + H_2SO_4 \longrightarrow K_2SO_4$$

+
$$H_2Cr_2O_7$$

+ $H_2Cr_2O_7$ + $4H_2O_2 \longrightarrow 2CrO_5$ + $5H_2O_7$

$$\mathbf{26} \ 2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 + 5\text{H}_2\text{O}_2 \longrightarrow$$

$$K_2 SO_4 + 2 Mn SO_4 + 8 H_2 O + 5 O_2$$

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 \therefore H_2O_2 is acting as a reducing agent. It reduces KMnO_4 to Mn^{2+} ion.

27 In the reaction,

The oxidation state of oxygen in H_2O_2 changes from -1 to -2 H_2O_2 oxidises O_3 into O_2 , thus it behaves as an oxidising agent

For the reaction,

$$\begin{array}{c} \overset{+1}{H_2O_2} \overset{-1}{H_2O_2} \overset{+1}{H_2O_2} \overset{-2}{\longrightarrow} \begin{array}{c} \overset{0}{2Ag} \overset{+1}{H_2O_2} \overset{0}{\to} \begin{array}{c} \overset{+1}{H_2O_2} \overset{0}{\to} \begin{array}{c} \overset{0}{H_2O_2} \overset{0}{H_2O_2} \overset{0}{\to} \begin{array}{c} \overset{0}{H_2O_2} \overset{0}{H_2O_2} \overset{0}{H_2O_2} \overset{0}{\to} \begin{array}{c} \overset{0}{H_2O_2} \overset{0}{H_$$

In the above reaction, H_2O_2 reduces Ag_2O to Ag and the oxidation state of 0 changes from -1 to 0, hence it acts has a reducing agent.

28 Both reactions in their complete format are written below

(i) In acidic medium,

$$[Fe^{2+}(CN)_6]^{4-} + H_2O_2^{-1} + 2H^+ \longrightarrow$$

 $[Fe^{3+}(CN)_6]^{3-} + 2H_2O_2^{-2}$

(ii) In alkaline medium,

$$[Fe^{3+}(CN)_6]^{3-} + H_2 \overset{-1}{O}_2 + 2OH^- \longrightarrow$$

$$[Fe^{2+}(CN)_6]^{4-} + O_2 + 2H_2O$$

Hence, H_2O (for reaction (i)) and $O_2 + H_2O$ (for reaction (ii)) are produced as by product.

- **29** H_2O_2 acts as an oxidising as well as reducing agent, because oxidation number of oxygen in H_2O_2 is -1. So, it can be oxidised to oxidation state 0 or reduced to oxidation state -2. H_2O_2 decomposes on exposure to light. So, it has to be stored in plastic or wax lined glass bottles in dark for the prevention of exposure. It also has to be kept away from dust.
- **30** Ionic hydrides are solid with high density because small H⁻ ion occupy holes in the lattice of metal without distorting metal lattice.
- 31 D₂O shows more stronger H-bonding than H₂O and thus, shows higher melting and boiling points. Also, heavy water is more viscous than ordinary water.

32 H_2O_2 acts as an oxidising as well as

reducing agent because oxygen has -10 oxidation state, so it can be oxidised to oxidation state 0 or reduced to oxidation state -2.

$$\begin{array}{ccc} 2e^- + & O_{2^-}^{1-} & \longrightarrow 2 & O^{2-} \\ & & O_{xidant} \\ & & O_{2^-}^{1-} & \longrightarrow & O_{2^-}^{0} + 2e \\ & & \text{Reductant} \end{array}$$

SESSION 2

- **1** LiH is ionic, MgH₂ and CuH are intermediate hydrides.
- **2** Following reactions take place when NaH is dissolved in water. 2NaH(s) + $H_2O(l) \longrightarrow 2NaOH(aq)$

 $+ H_{2}(g)$

- **3** The compound sodium polymetaphosphate Na₂[Na₄(PO₃)₆] is called calgon because it refers to calcium gone.
- **4** Protium, deuterium and tritium exist in nature in the ratio of 3 : 2 : 1 respectively.
- **5** Ortho and para hydrogen are different due to difference in proton spin and not electron spin.
- **6** On the basis of spinning of protons, hydrogen has two allotropes, called *ortho* hydrogen and *para* hydrogen. In *ortho* hydrogen, spins of protons are in same direction, so the nuclear spin

 $=\frac{1}{2}+\frac{1}{2}=1$. While in *para* hydrogen,

spins of protons are in opposite direction, so the nuclear spin

$$=\frac{1}{2}+\left(-\frac{1}{2}\right)=0$$

All other statements about *ortho* and *para* hydrogens are true.

7 Hydrogen can be obtained from water gas, i.e. by liquefaction of CO and by oxidation of CO into CO₂. It can also be obtained from electrolysis of water.

Reaction involved : (i) Electrolysis of $H \cap$

$$2H_2O(l) \xrightarrow{Process}{of acid/base} 2H_2(g) + O_2(g)$$

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

 $+ H_2(g)$

 $\pmb{8}$ Copper, being less reactive, when reacts with conc. ${\rm HNO}_3,$ gives ${\rm NO}_2,$ but not ${\rm H}_2.$

$$Cu + 4HNO_3(conc.) \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O_3 + 2H$$

While Mg and NaH being very reactive give hydrogen gas with steam and water respectively.

 $\begin{array}{l} Mg+2H_2O \longrightarrow MgO+H_2\\ NaH+H_2O \longrightarrow NaOH+H_2\\ \text{Ethanol and phenol due to the}\\ \text{presence of acidic hydrogen also}\\ \text{produce hydrogen with metallic sodium.}\\ C_2H_5OH+Na \longrightarrow C_2H_5O^-Na^++H_2\\ C_6H_5OH+Na \longrightarrow C_6H_5O^-Na^++H_2\\ \end{array}$

9 Metal hydrides are ionic, covalent or molecular in nature. Ionic character increases as the size of the atom increases or the electronegativity of the atom decreases. The correct order of increasing ionic character is

LiH < NaH < KH < RbH < CsH

10 The reaction in which H₂O₂ is reduced,
 i.e. oxidation state of oxygen decreases
 from -1 to -2 depicts the oxidising
 nature of H₂O₂. e.g.

11 $\mathring{I}_2 + H_2 \mathring{O}_2 + 2OH^- \longrightarrow 2 \mathring{I}^- + 2H_2 \mathring{O} + O_2$

- depicts reducing nature of $\mathrm{H_2O_2}$
- **12** H_2O_2 reduces acidified KMnO₄ into colourless manganous salt and gets oxidised into O_2 .

$$5H_2O_2 + 2KMnO_4 + 3H_2SO_4 \longrightarrow$$

$$K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

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13 Hydrogen resemble halogens in many respects for which several factors are responsible. The most important is hydrogen (like halogens) accepts an electron readily to achieve nearest inert gas configuration.

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