UNIT-4 HYDROGEN

MY REVISION TIMELINE:-

SUMMARY:-

- Hydrogen contains one proton and one electron.
- Has an unpaired electron and exists as H_2 with electron configuration as^1.
- It forms H^+, halides (HX), oxides (H_2O), peroxides (H_2O_2) and sulphides (H_2S) like alkali metals.
- It acts as reducing agent.
- Isotopes:
    - Protium ($_1H^1$)
    - Deuterium ($_1H^2$)
    - Tritium ($_1H^3$)
- In hydrogen atom, nucleus has a spin and in molecular hydrogen the spin can be in same or opposite direction (i.e.) ortho and para forms respectively.
- Physical properties of hydrogen are colourless, odourless, tasteless, lightest, highly inflammable non-polar diatomic molecule.
- Chemical properties of hydrogen is that it reacts with oxygen, halogen, reactive metals to give corresponding water, halides and hydrides respectively.
- Physical properties of heavy water are colourless, odourless and tasteless liquid.
- Chemical properties of hydrogen is that it reacts with oxygen and replace reversibly hydrogen compounds either partially or completely.
- Properties of tritium is that it is β emitter.
- Physical properties of water are colourless, volatile, high melting and boiling point. Hydrogen bonding exists.
- Chemical properties of water is that it reacts with metals, non-metals and other compounds differently. It is amphoteric oxide.
- Hard water: water with high amount of mineral ions.
- Soft water: water free from soluble salts of calcium and magnesium.
- Temporary hardness is due to the presence of soluble bicarbonates of magnesium and calcium.
- Permanent hardness is due to the presence of soluble salts of magnesium and calcium in the form of chlorides and sulphates in it.
- Physical properties of hydrogen peroxide are colourless liquid (pale blue), less volatile and more viscous than water.

- Chemical properties of hydrogen peroxide is that it is highly unstable, also disproportionates to give oxygen and water and can act as both oxidising and reducing agent.
- Hydrides:
  - Ionic (saline) hydrides eg: LiH, CaH_2 etc…
  - Covalent (molecular) hydrides eg: CH_4, C_2H_6, SiH_4 etc…
  - Metallic (interstitial) hydrides eg: $TiH_{1.5\text{-}1.8}$, $PdH_{0.6\text{-}0.8}$
- Hydrogen bonding:
  - Intramolecular hydrogen bonding (hydrogen bonding with a single molecule) eg: Ortho-nitro phenol, salicilaldehyde
  - Intermolecular hydrogen bonding (hydrogen bonding between two separate molecules) eg: H_2O, HF, NH_3 etc…

FORMULAS:-

- Normality = $\frac{Volume}{5.6}$
- Molarity = $\frac{Volume\ strength}{11.2}$
- Strength of H_2O_2 = $\frac{68 \times Volume}{22.4\ g/L}$

TEXTBOOK EVALUATION

Multiple choice questions:-

1. Which of the following statements about hydrogen is incorrect? (NEET – 2016)
(a) Hydrogen ion, H_3O^+ exists freely in solution.
(b) Dihydrogen acts as a reducing agent.
(c) Hydrogen has three isotopes of which tritium is the most common.
(d) Hydrogen never acts as cation in ionic salts.
Explanation:
Protium is the most common isotope of hydrogen.

2. Water gas is
(a) $H_2\ O_{(g)}$ (b) $CO + H_2O$
(c) $CO + H_2$ (d) $CO + N_2$

3. Which one of the following statements is incorrect with regard to ortho and para dihydrogen?
(a) They are nuclear spin isomers
(b) **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.
Explanation:
Ortho has one nuclear spin and para has zero nuclear spin.

4. Ionic hydrides are formed by
(a) halogens (b) chalogens
(c) inert gases **(d) group one elements**

5. Tritium nucleus contains
(a) 1p + 0n (b) 2p + 1n
(c) 1p + 2n (d) none of these

6. Non-stoichiometric hydrides are formed by
(a) palladium, vanadium (b) carbon, nickel
(c) manganese, lithium (d) nitrogen, chlorine
Explanation:
d-block elements form non-stoichiometric hydrides.

7. Assertion: Permanent hardness of water is removed by treatment with washing soda.
Reason: Washing soda reacts with soluble calcium and magnesium chlorides and sulphates in hard water to form insoluble carbonates
(a) Both assertion and reason are true and reason is the correct explanation of assertion.
(b) Both assertion and reason are true but reason is not the correct explanation of assertion.
(c) Assertion is true but reason is false
(d) Both assertion and reason are false

8. If a body of a fish contains 1.2 g hydrogen in its total body mass, if all the hydrogen is replaced with deuterium then the increase in body weight of the fish will be
(a) 1.2 g (b) 2.4 g
(c) 3.6 g (d) √4.8 g
Explanation:
Mass of deuterium = 2 × mass of protium
Mass of deuterium = 2 × 1.2g
Mass of deuterium = 2.4g
Increased body weight = 2.4 – 1.2
Increased body weight = 1.2g

9. The hardness of water can be determined by volumetrically using the reagent
(a) sodium thio sulphate (b) potassium permanganate
(c) hydrogen peroxide **(d) EDTA**

10. The cause of permanent hardness of water is due to
(a) $Ca(HCO_3)_2$ (b) $Mg(HCO_{3k})_3$
(c) $CaCl_2$ (d) $MgCO_3$
Explanation:
Due to the presence of soluble salts of magnesium and calcium in the form of chlorides and sulphates.

11. Zeolite used to soften hardness of water is, hydrated
(a) Sodium aluminium silicate (b) Calcium aluminium silicate
(c) Zinc aluminium borate (d) Lithium aluminium hydride

12. A commercial sample of hydrogen peroxide marked as 100 volume H_2O_2, it means that
(a) 1 ml of H_2O_2 will give 100 ml O_2 at STP
(b) 1 L of H_2O_2 will give 100 ml O_2 at STP
(c) 1 L of H_2O_2 will give 22.4 L O_2
(d) 1 ml of H_2O_2 will give 1 mole of O_2 at STP

13. When hydrogen peroxide is shaken with an acidified solution of potassium dichromate in presence of ether, the ethereal layer turns blue due to the formation of
(a) Cr_2O_3 (b) CrO_4^{2-}
(c) $CrO(O_2)_2$ (d) none of these

14. For de colorization of 1 mole of acidified $KMnO_4$, the moles of H_2O_2 required is
(a) 1/2 (b) 3/2
(c) 5/2 (d) 7/2

15. Volume strength of 1.5 N H_2O_2 is
(a) 1.5 (b) 4.5
(c) 16.8 **(d) 8.4**

Explanation:

Normality = $\frac{Volume}{5.6}$

$2H_2O_2 \rightarrow 2H_2O + O_2 \uparrow$

Volume = 5.6 × Normality

Volume = 5.6 × 1.5

Volume = 8.4

16. The hybridization of oxygen atom is H_2O and H_2O_2 are respectively
(a) sp and sp^3 (b) sp and sp
(c) sp and sp^2 **(d) sp3 and sp^3**

17. The reaction $H_3PO_2 + D_2O \rightarrow H_2DPO_2 + HDO$ indicates that hypo-phosphorus acid is
(a) tri basic acid (b) di basic acid
(c) mono basic acid (d) none of these

Explanation:

In hypo-phosphorous acid, only one hydrogen is connected to oxygen which can be removed or released. Hence it is a monobasic acid.

18. In solid ice, oxygen atom is surrounded
(a) tetrahedrally by 4 hydrogen atoms
(b) octahedrally by 2 oxygen and 4 hydrogen atoms
(c) tetrahedrally by 2 hydrogen and 2 oxygen atoms
(d) octahedrally by 6 hydrogen atoms

19. The type of H-bonding present in ortho nitro phenol and p-nitro phenol are respectively
(a) inter molecular H-bonding and intra molecular H-bonding
(b) intra molecular H-bonding and inter molecular H-bonding
(c) intra molecular H – bonding and no H – bonding
(d) intra molecular H – bonding and intra molecular H – bonding

20. Heavy water is used as
(a) modulator in nuclear reactions (b) coolant in nuclear reactions
(c) both (a) and (b) (d) none of these

21. Water is a
(a) basic oxide (b) acidic oxide
(c) amphoteric oxide (d) none of these

Write brief answers to the following questions:-

22. Explain why hydrogen is not placed with the halogen in the periodic table.

- Hydrogen resembles alkali metals as well as hydrogen but more of **alkali metals** than halogens.
- **Electron affinity** of hydrogen is much **less** than that of halogen atom. Hence the tendency to form **hydride ion** is less compared to that of halogens as evident from the following reactions.
- $\frac{1}{2} H_2 + e^- \rightarrow H^-$ $\Delta H = +36$ kcal/mol

  $\frac{1}{2} Br_2 + e^- \rightarrow Br^-$ $\Delta H = -55$ kcal/mol

- In most places its compound hydrogen exists in +**1 oxidation state** and hence it is reasonable to place the hydrogen atom in group 1 along alkali metals.

23. The cube at 0°C is placed in some liquid water at 0°C, the ice cube sinks. Why?

- In an ice cube, each atom is surrounded **tetrahedrally** by **four water molecules** through hydrogen bond and its **density** is **low**.
- Liquid water at **0°C** has the density as **999.82 kg/cm^3**. Maximum density is attained by water only at **4°C** as **1000 kg/cm^3**.
- When the temperature changed from 4°C to 0°C, the **density of water decreases** rather than increases. This is called **anomalous expansion of water**.
- The reason for this phenomenon lies in the s**tructure of ice lattice and hydrogen bonding** in water.
- At 0°C, ice cube sinks in liquid water because of the **lesser density and greater volume of water**.

24. Predict which of the following hydrides is a gas on a solid (a)HCl (b)NaH. Give your reason.

- HCl is a **gas** because the forces between the **molecule is not strong**.
- NaH is a **solid** because the forces between the **molecule is strong**.

25. Write the expected formulas for the hydrides of 4th period elements. What is the trend in the formulas? In what way the first two members of the series different from the others?

- KH, CaH_2, ……. GaH_3, GeH_4, AsH_3, H_2Se, HBr
- Trend in the formula:
  MH, MH_2----------(MH or MH_2)----------MH_3, MH_4, MH_3, MH_2, MH
  s-block d-block p-block
  (Ionic hydrides) (non-stoichiometric) (Covalent hydrides)
- First 2 members: KH & CaH_2. KH is **alkali hydride** (Grey powder). CaH_2 is an **alkaline earth hydride**.
- KH **reacts vigorously** with **water** liberating **H_2 gas**.
  $LiH_{(s)} + H_2O_{(l)} \rightarrow Li(OH)_{(aq)} + H_2$
- CaH_2 **reacts** with **water** and liberates **H_2 gas**.
  $CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2$

26. Write chemical equation for the following reactions.
i) reaction of hydrogen with tungsten (VI) oxide on heating.
ii) hydrogen gas and chlorine gas.

- $WO_3 + 3H_2 \rightarrow W + 3H_2O$
- $H_2 + Cl_2 \rightarrow 2HCl$

27. Complete the following chemical reactions and classify them in to (a) hydrolysis (b) redox (c) hydration reactions.
i) $KMnO_4 + H_2O_2 \rightarrow$
ii) $CrCl_3 + H_2O \rightarrow$
iii) $CaO + H_2O \rightarrow$

- $2KMnO_4 + 3H_2O_2 \rightarrow 2MnO_2 + 2KOH + 2H_2O + 3O_2$ (Redox reaction)
- $CrCl_3 + 6H_2O \rightarrow [Cr\ Cl_2\ (H_2O)_4]\ Cl.\ 2H_2O$ (Hydration reaction)
- $CaO + H_2O \rightarrow Ca\ (OH)_2$ (Hydrolysis reaction)

28. Hydrogen peroxide can function as an oxidising agent as well as reducing agent. Substantiate this statement with suitable examples.

- H_2O_2 act as oxidizing agent in acidic medium. For example,

$$2FeSO_4 + H_2SO_4 + H_2O_2 \rightarrow Fe_2(SO_4)_3 + 2H_2O$$

Ferrous sulphate — Ferric sulphate

- H_2O_2 act as reducing agent in basic medium. For example,

$$2KMnO_{4\,(aq)} + 3H_2O_{2\,(aq)} \rightarrow 2MnO_2 + 2KOH + 2H_2O + 3O_{2\,(g)}$$

Potassium permanganate — Manganese dioxide

29. Do you think that heavy water can be used for drinking purposes?

- Heavy water is **toxic** when taken in **large quantities**.
- Heavy water is **not radioactive**. The deuterium in it is stable, it does not decay. Nobody will be in danger at all from radiation.
- It is **heavier** than **plain water**.
- D_2O perform little different from H_2O in chemical reactions. One has to drink a lot of D_2O to kill him. Hence heavy water should not be used for drinking purposes.

30. What is water-gas shift reaction?

- The **carbon monoxide** of the water gas can be converted to **carbon dioxide** by mixing the gas mixture with more steam **400°C** and passed over a shift converter containing **iron/copper catalyst**. The reaction is called as **water-gas shift** reaction.
- $CO_2 + H_2O \rightarrow CO_2 + H_2$

31. Justify the position of hydrogen in the periodic table?

- Electronic configuration **$1s^1$** as alkali metals have ns^1.
- Hydrogen forms **unipositive H+** ion like alkali metals Na^+, K^+.
- Hydrogen form **halides** (HX), **oxides** (H_2O) **peroxide** (H_2O_2) like alkali metals (NaX, Na_2O, Na_2O_2).
- Hydrogen also acts as **reducing agent** like alkali metals.
- However, alkali metals have ionization energy ranging from 377kJ/mol to 520kJ/mol, the hydrogen has **1314kJ/mol** which is much higher than alkali metals.
- **Electron affinity** of hydrogen is much **less** than that of halogen atom. Hence the tendency to form **hydride ion** is less compared to that of halogens as evident from the following reactions.
- $\frac{1}{2} H_2 + e^- \rightarrow H^-$ $\quad \Delta H = +36$ kcal/mol

  $\frac{1}{2} Br_2 + e^- \rightarrow Br^-$ $\quad \Delta H = -55$ kcal/mol
- In most places its compound hydrogen exists in **+1 oxidation state** and hence it is reasonable to place the hydrogen atom in group 1 along alkali metals.

32. What are isotopes? Write the names of isotopes of hydrogen.

- Isotopes are atoms of the same element that have the **same atomic number** but **different mass number** (or) Isotopes are atoms that have **same number of protons** and **electrons** but **differ in number of neutrons**.
- Hydrogen has three naturally occurring isotopes namely **Protium** ($_1H^1$), **Deuterium** ($_1H^2$) and **Tritium** ($_1H^3$).

33. Give the uses of heavy water.

- Heavy water is used as **moderator** in **nuclear reactors**.
- It is used as a **tracer** to study **organic reaction mechanisms** and **mechanism of metabolic reactions.**
- It is used as a **coolant** in **nuclear reactors** as it absorbs the heat generated.

34. Explain the exchange reactions of deuterium.

- Deuterium can replace **reversibly hydrogen** in compounds either partially or completely depending upon the reaction conditions. These reactions occur in the **presence of deuterium**.
- $CH_4 + 2D_2 \rightarrow CD_4 + 2H_2$
  Methane Deutero methane
- $2NH_3 + 3D_2 \rightarrow 2ND_3 + 3H_2$
  Ammonia Deutero ammonia

35. How do you convert para hydrogen into ortho hydrogen?

- Para-form can be catalyctically transformed into ortho-form using **platinum or iron**.
- It can also be converted by passing an **electric discharge**.
- Heating above **800°C** and **mixing with paramagnetic molecules** such as O_2, NO, NO_2 or with nascent or atomic hydrogen.

36. Mention the uses of deuterium.

- To prepare **D_2O** (heavy water)
- To prepare **deuterated halides**.
- To manufacture **deuterium lamps** with quarty or UV glass bulb.

37. Explain preparation of hydrogen using electrolysis.

- **High purity of hydrogen** (>99.9%) is obtained by the electrolysis of water containing **traces of acid** or **alkali** or **electrolysis of aqueous solution** of sod**ium hydroxide** or **potassium hydroxide** using a **nickel anode** and **iron cathode**. This process is **not economical** for **large scale production**.
- At **anode** : $2OH^- \rightarrow H_2O + ½\ O_2 + 2e^-$
- At **cathode** : $2H_2O + 2e^- \rightarrow 2OH^- + H_2$
- **Overall reaction** : $H_2O \rightarrow H_2 + 14\ O_2$

38. A group-1 metal (A) which is present in common salt reacts with (B) to give compound (C) in which hydrogen is present in –1 oxidation state. (B) on reaction with a gas (C) to give universal solvent (D). The compound (D) on reacts with (A) to give (E), a strong base. Identify A, B, C, D and E. Explain the reactions.
Solution:

- Group (1) metal (A) is present in common salt is NaCl. So, (A) is sodium – Na.
- Sodium reacts with hydrogen (B) to give sodium hydride – NaH (C) in which hydrogen is in -1 oxidation state.
  $2Na + H_2 \rightarrow 2NaH$
- Hydrogen on reaction with oxygen (O_2) gas which is (C) to give a universal solvent water (D).
  $2H_2 + O_2 \rightarrow 2H_2O$
- Water (D) reacts with sodium metal (A) to give a strong base sodium hydroxide NaOH which is (E).
  $2Na + 2H_2O \rightarrow 2NaOH + H_2$

	Element or Compound	Symbol
A	Sodium	Na
B	Hydrogen	H_2
C	Oxygen	O_2
D	Water	H_2O
E	Sodium hydroxide	NaOH

39. An isotope of hydrogen (A) reacts with diatomic molecule of element which occupies group number 16 and period number 2 to give compound (B) is used as a moderator in nuclear reaction. (A) adds on to a compound (C), which has the molecular formula C_3H_6 to give (D). Identify A, B, C and D.

Solution:

- An isotope of hydrogen Deuterium (A) reacts with diatomic molecule of element belongs to group number 16 and period number 2 oxygen O_2 to give a compound (B) which is heavy water D_2O. D_2O is used as a moderator in nuclear reaction.

  $2D_2 + O_2 \rightarrow 2D_2O$

- Deuterium reacts with C_3H_6 propane (C) to give Deutero propane C_2D_6 (D).

  $3D_2 + C_3H_6 \rightarrow C_3D_6 + 3H_2$

	Element or Compound	Symbol
A	Deuterium	D_2
B	Heavy water	D_2O
C	Propane	C_3H_6
D	Deuteron propane	C_3D_6

40. NH_3 has exceptionally high melting point and boiling point as compared to those of the hydrides of the remaining element of group 15 - Explain.

It is due to **intermolecular H-bonding** which are stronger than London forces present in other hydrides. Other hydrides lack H-bonding.

41. Why interstitial hydrides have a lower density than the parent metal?

- Interstitial hydrides have **metallic bonding**.
- These are **non – stoichiometric**, their composition varies with **temperature** and **pressure**.
- The **crystal lattice** expands due to the inclusion of **dihydrogen** and there is **distortion** of **crystal lattice**. So they have lower density than parent metals.

42. How do you expect the metallic hydrides to be useful for hydrogen storage?

- Hydrogen interacts with **palladium** in a unique way and forms a limiting monohydride, PdH.
- Upon heating, H atoms diffuse through the metal to the surface and recombine to form **molecular hydrogen**.

  $2Pd\ (s) + H_2\ (g) \rightarrow 2PdH\ (s)$

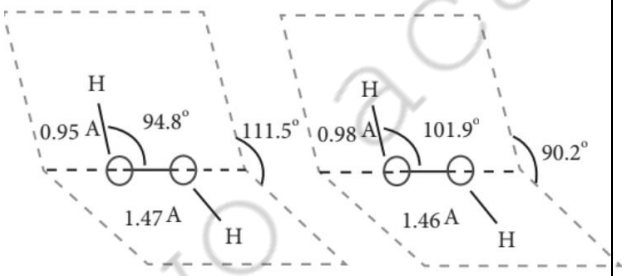
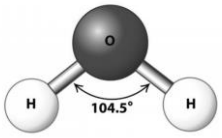
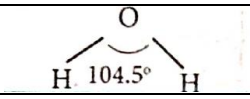
- The hydrogen molecule **readily adsorb** on the **palladium** surface, where it dissociates into atomic hydrogen.
- The dissociated atoms dissolve into the interstices or voids (**octahedral/tetrahedral**) of the crystal lattice.

- The formation of **metal hydride** is by chemical reaction but it behaves like a physical storage i.e., it is absorbed and released like a water sponge.
- Such a reversible uptake of hydrogen in metals and alloys is also attractive for **hydrogen storage** and for **rechargeable metal hydride** battery applications.

43. Arrange NH_3, H_2O and HF in the order of increasing magnitude of hydrogen bonding and explain the basis for your arrangement.

- Order: **NH_3 < H_2O < HF**
- The **strength of H-bond** depends upon the electronegativity of atom to which H-atom is covalently bonded.
- Since, electronegativity of **F > O > N**, the strength of H-bond is in the order **H-F…..H > H-O……..H > H-N…….H.**
- H-bonds are much **weaker** than **covalent bonds**.

44. Compare the structures of H_2O and H_2O_2.

	H_2O_2	**H_2O**
1. Hybridisation of oxygen	sp^3 (each 0 - atom)	sp^3
2. Structure	 Partly open book like structure with O-atom along spine.	 Bent – V Shape
3. Bond angle	H-O-O-H angle expands from 94.8° - 101.9°	
4. Bond length	H-O-bond length from 0.95 Å – 0.98 Å	H-O-bond length 0.96 Å
5. DPM	2.2D	1.85D