

## 9. HYDROGEN

9.1) Justify the position of hydrogen in the periodic table on the basis of its electronic configuration.

Hydrogen has been placed at the top of the alkali metal in group, but it is not a member of the group. Its position is not justified properly because of its electronic configuration as  $(1s^1)$ . It can be placed with alkali metals because it also has similar configuration  $(ns^1)$  as alkali metals. However, it can also be placed along with halogen in group 17 since just like halogen it can acquire inert gas configuration by accepting one electron.

9.2) Write the names of isotopes of hydrogen. What is the mass ratio of these isotopes?

The isotopes of hydrogen are Protium -  ${}^1_1\text{H}$ , Deuterium -  ${}^2_1\text{H}$ , Tritium -  ${}^3_1\text{H}$

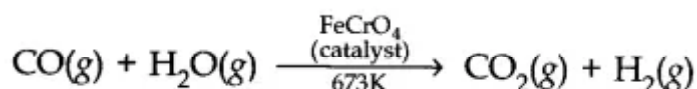
mass ratio of protium : Deuterium : Tritium = 1 : 2 : 3

9.3) Why does hydrogen occur in a diatomic form rather than in a monoatomic form under normal conditions?

The ionization enthalpy of hydrogen atom is very high ( $1312 \text{ kJ mol}^{-1}$ ). Hence, it is very hard to remove its only electron. As a result, its tendency to exist in the monoatomic form is rather low. Instead, hydrogen forms a covalent bond with another hydrogen atom and exists as a diatomic ( $\text{H}_2$ ) molecule.

9.4) How can the production of dihydrogen obtained from 'Coal gasification' be increased?

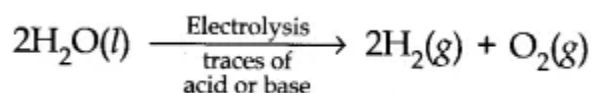
The production of dihydrogen in coal gasification can be increased by reacting CO present in syngas with steam in the presence of iron chromate catalysts.



With the removal of  $\text{CO}_2$  the reaction shifts in the forward direction and thus, the production of dihydrogen will be increased.

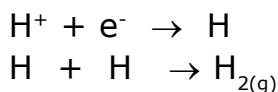
9.5) Describe the bulk preparation of dihydrogen by electrolytic method. What is the role of an electrolyte in this process?

Dihydrogen is prepared by the electrolysis of acidified or alkaline water using platinum electrodes. Generally, 15 – 20% of an acid ( $\text{H}_2\text{SO}_4$ ) or a base ( $\text{NaOH}$ ) is used.

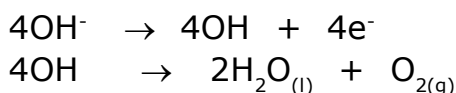


During electrolysis, dihydrogen is liberated at cathode and dioxygen is liberated at anode.

At cathode:

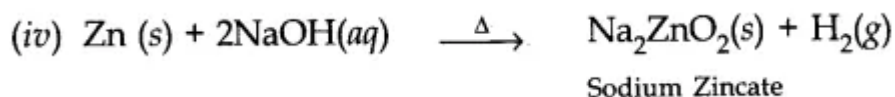
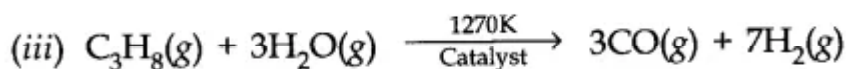
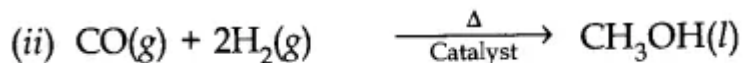
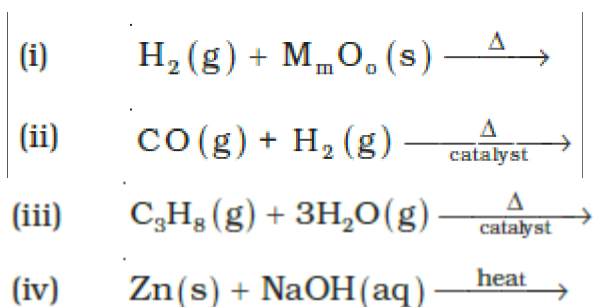


At anode:



Electrolyte is added to increase the dissociation of water.

9.6) Complete the following reactions.



9.7) Discuss the consequences of high enthalpy of H-H bond, in terms of chemical reactivity of dihydrogen.

The bond dissociation enthalpy of H-H bond is very high (435.9 kJmol<sup>-1</sup>). Due to high bond enthalpy, it is not very reactive at room temperature. However at high temperatures or in the presence of catalysts, hydrogen combines with many metals and non-metals to form hydrides.

9.8) What do you understand by (i) Electron-deficient (ii) Electron-precise (iii) Electron-rich compounds of hydrogen? Provide justification with suitable examples.

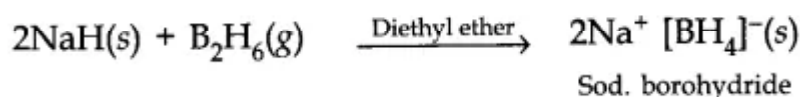
(i) Electron deficient hydrides: Compounds in which central atom has incomplete octet, are called electron deficient hydrides. For example, BeH<sub>2</sub>, BH<sub>3</sub> are electron deficient hydrides.

(ii) Electron precise hydrides: Those compounds in which exact number of electrons are present in central atom or the central atom contains complete octet are called precise hydrides e.g.,  $\text{CH}_4$ ,  $\text{SiH}_4$ ,  $\text{GeH}_4$  etc. are precise hydrides.

(iii) Electron rich hydrides: Those compounds in which central atom has one or more lone pair of excess electrons are called electron rich hydrides, e.g.,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ .

9.9) What characteristics do you expect from an electron-deficient hydride with respect to its structure and chemical reaction?

It is expected to be a Lewis acid. They are likely to accept electrons to become stable. They can form coordinate bond with electron rich compound.



9.10) Do you expect the carbon hydride of type  $\text{C}_n\text{H}_{2n+2}$  to act as Lewis acid or base? Justify your answer.

Carbon hydrides of the type  $\text{C}_n\text{H}_{2n+2}$  are electron precise hydrides. Because they have atom with exact number of electrons to form covalent bonds. Thus, they do not behave as Lewis acid or base. Since they have no tendency to accept or lose electrons.

9.11) What do you understand by the term 'non-stoichiometric hydrides'? Do you expect this type of hydrides to be formed by alkali metals? Justify your answer.

Non-Stoichiometric hydrides are hydrogen-deficient compounds formed by the reaction of dihydrogen with *d*-block and *f*-block elements. These hydrides do not follow the law of constant composition. For example:  $\text{LaH}_{2.87}$ ,  $\text{YbH}_{2.55}$ ,  $\text{TiH}_{1.5 - 1.8}$  etc.

Alkali metals being more electropositive transfer their outermost electrons to H-atom to form  $\text{H}^-$  ions. Therefore alkali metal hydrides are ionic in nature and the ratio of metal to hydrogen is always fixed (i.e) they form stoichiometric hydrides only.

9.12) How do you expect the metallic hydrides to be useful for hydrogen storage? Explain.

Metallic hydrides are hydrogen deficient, i.e., they do not hold the law of constant composition. It has been established that in the hydrides of Ni, Pd, Ce, and Ac, hydrogen occupies the interstitial position in lattices allowing further absorption of hydrogen on these metals. Metals like Pd, Pt, etc. have the capacity to accommodate a large volume of hydrogen. Therefore, they are used for the storage of hydrogen and serve as a source of energy.

9.13) How does the atomic hydrogen or oxy-hydrogen torch function for cutting and welding purposes ? Explain.

Atomic hydrogen atoms are produced by the dissociation of dihydrogen with the help of an electric arc. This releases a huge amount of energy ( $435.9 \text{ kJ mol}^{-1}$ ).

This energy can be used to generate a temperature of 4000 K, which is ideal for welding and cutting metals. Hence, atomic hydrogen or oxy-hydrogen torches are used for these purposes. For this reason, atomic hydrogen is allowed to recombine on the surface to be welded to generate the desired temperature.

9.14) Among  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  and  $\text{HF}$ , which would you expect to have highest magnitude of hydrogen bonding and why?

$\text{HF}$  is expected to have highest magnitude of hydrogen bonding since, 'F' is most electronegative. Therefore,  $\text{HF}$  is the most polar.

9.15) Saline hydrides are known to react with water violently producing fire. Can  $\text{CO}_2$ , a well known fire extinguisher, be used in this case? Explain.

No. Because if saline hydrides react with water the reaction will be highly exothermic thus the hydrogen evolved in this case can catch fire.  $\text{CO}_2$  cannot be used as fire extinguisher because  $\text{CO}_2$  will get absorbed in alkali metal hydroxides.

9.16) Arrange the following:

(i)  $\text{CaH}_2$ ,  $\text{BeH}_2$  and  $\text{TiH}_2$  in order of increasing electrical conductance.

(ii)  $\text{LiH}$ ,  $\text{NaH}$  and  $\text{CsH}$  in order of increasing ionic character.

(iii)  $\text{H-H}$ ,  $\text{D-D}$  and  $\text{F-F}$  in order of increasing bond dissociation enthalpy.

(iv)  $\text{NaH}$ ,  $\text{MgH}_2$  and  $\text{H}_2\text{O}$  in order of increasing reducing property.

(i) The electrical conductance of a molecule depends upon its ionic or covalent nature. Ionic compounds conduct, whereas covalent compounds do not.

$\text{BeH}_2$  is a covalent hydride. Hence, it does not conduct.  $\text{CaH}_2$  is an ionic hydride, which conducts electricity in the molten state. Titanium hydride,  $\text{TiH}_2$  is metallic in nature and conducts electricity at room temperature. Hence, the increasing order of electrical conductance is as follows:  $\text{BeH}_2 < \text{TiH}_2 < \text{CaH}_2$

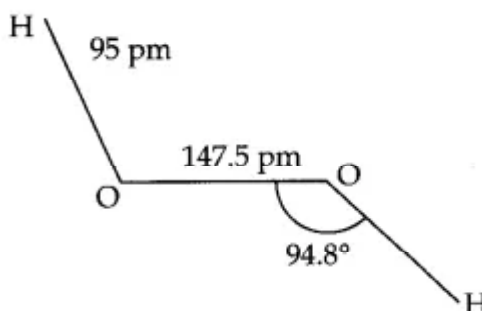
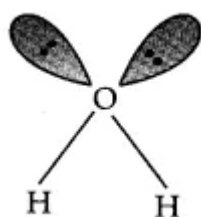
(ii) The ionic character of a bond is dependent on the electronegativities of the atoms involved. The higher the difference between the electronegativities of atoms, the smaller is the ionic character. Electronegativity decreases down the group from Lithium to Caesium. Hence, the ionic character of their hydrides will increase as:  $\text{LiH} < \text{NaH} < \text{CsH}$

(iii) Bond dissociation energy depends upon the bond strength of a molecule, which in turn depends upon the attractive and repulsive forces present in a molecule. The bond pair in  $\text{D-D}$  bond is more strongly attracted by the nucleus than the bond pair in  $\text{H-H}$  bond. This is because of the higher nuclear mass of  $\text{D}_2$ . The stronger the attraction, the greater will be the bond strength and the higher is the bond dissociation enthalpy. Hence, the bond dissociation enthalpy of  $\text{D-D}$  is higher than  $\text{H-H}$ . However, bond dissociation enthalpy is the minimum in the case of  $\text{F-F}$ . The bond pair experiences strong repulsion from the lone pairs present on each F-centre. Therefore, the increasing order of bond dissociation enthalpy is as follows:  $\text{F-F} < \text{H-H} < \text{D-D}$

(iv) Ionic hydrides are strong reducing agents.  $\text{NaH}$  can easily donate its electrons. Hence, it is most reducing in nature. Both,  $\text{MgH}_2$  and  $\text{H}_2\text{O}$  are covalent hydrides.  $\text{H}_2\text{O}$  is less reducing than  $\text{MgH}_2$  since the bond dissociation energy of  $\text{H}_2\text{O}$  is higher than  $\text{MgH}_2$ . The order is:  $\text{H}_2\text{O} < \text{MgH}_2 < \text{NaH}$

9.17) Compare the structures of  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}_2$

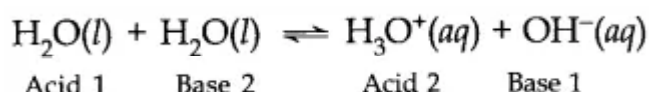
In water, Oxygen is  $\text{sp}^3$  hybridized. Due to stronger lone pair-lone pair repulsions than bond pair-bond pair repulsions, the HOH bond angle decreases from  $109.5^\circ$  to  $104.5^\circ$ . Thus water molecule has a bent structure.



$\text{H}_2\text{O}_2$  has a non-planar structure. The O—H bonds are in different planes. Thus, the structure of  $\text{H}_2\text{O}_2$  is like an open book.

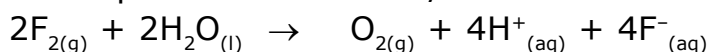
9.18) What do you understand by the term 'auto-protolysis' of water? what is its significance?

Auto-protolysis means self-ionisation of water. It may be represented as



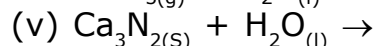
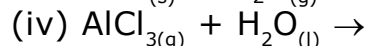
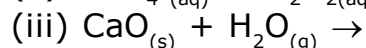
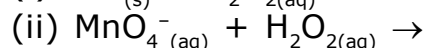
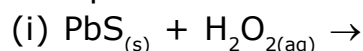
Due to auto-protolysis, water is amphoteric in nature i.e. it can act as an acid as well as base.

9.19) Consider the reaction of water with  $\text{F}_2$  and suggest, in terms of oxidation and reduction, which species are oxidised/reduced ?

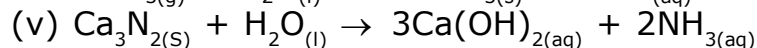
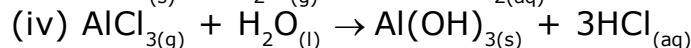
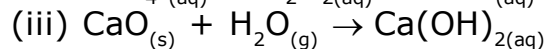
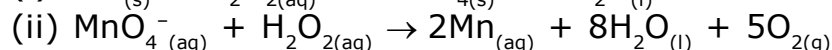
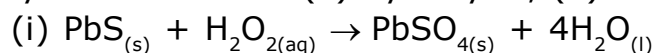


In this reaction water acts as a reducing agent and itself gets oxidised to  $\text{O}_2$  while  $\text{F}_2$  acts as an oxidising agent and hence itself reduced to  $\text{F}^-$  ions.

9.20) Complete the following chemical reactions.



Classify the above into (a) hydrolysis, (b) redox and (c) hydration reactions.

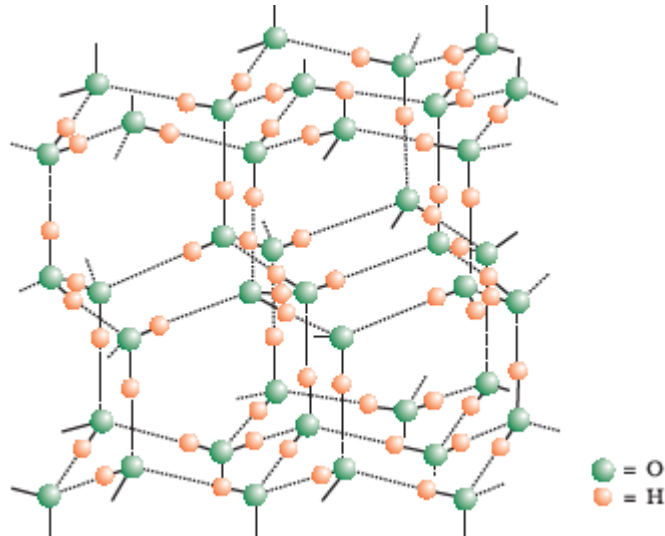


(a) Hydrolysis reactions - (iii), (iv) and (v)

(b) Redox reactions - (i), (ii)

9.21) Describe the structure of common form of ice?

Ice is the crystalline form of water. It takes a hexagonal form if crystallized at atmospheric pressure, but condenses to cubic form if the temperature is very low. The three-dimensional structure of ice is represented as:



The structure is highly ordered and has hydrogen bonding. Each oxygen atom is surrounded tetrahedrally by four other oxygen atoms at a distance of 276 pm. The structure also contains wide holes that can hold molecules of appropriate sizes interstitially.

9.22) What causes the temporary and permanent hardness of water?

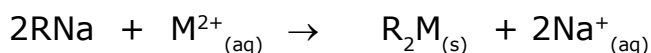
Temporary hardness of water is due to the presence of bicarbonates of calcium and magnesium in water i.e.,  $\text{Ca}(\text{HCO}_3)_2$  and  $\text{Mg}(\text{HCO}_3)_2$  in water. Permanent hardness of water is due to the presence of soluble chlorides and sulphates of calcium and magnesium i.e.,  $\text{CaCl}_2$ ,  $\text{CaSO}_4$ ,  $\text{MgCl}_2$  and  $\text{MgSO}_4$ .

9.23) Discuss the principle and method of softening of hard water by synthetic ion-exchange resins.

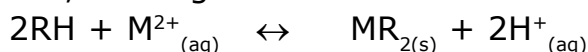
The process of treating permanent hardness of water using synthetic resins is based on the exchange of cations (e.g.,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  etc) and anions (e.g.,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$  etc) present in water by  $\text{H}^+$  and  $\text{OH}^-$  ions respectively.

Synthetic resins are of two types:

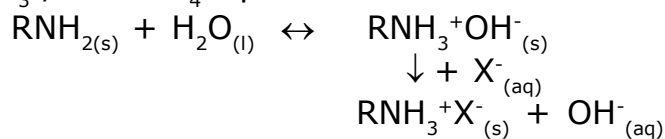
1) Cation exchange resins: Cation exchange resins are large organic molecules that contain the  $-\text{SO}_3\text{H}$  group. The resin is firstly changed to  $\text{RNa}$  (from  $\text{RSO}_3\text{H}$ ) by treating it with  $\text{NaCl}$ . This resin then exchanges  $\text{Na}^+$  ions with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions, thereby making the water soft.



There are cation exchange resins in  $\text{H}^+$  form. The resins exchange  $\text{H}^+$  ions for  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  ions.



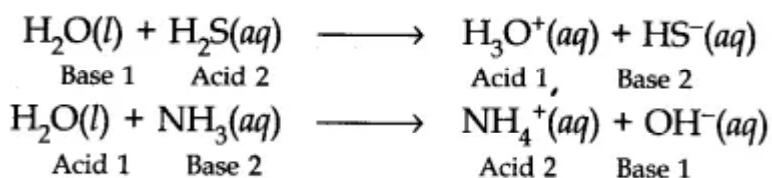
2) Anion exchange resins: Anion exchange resins exchange  $\text{OH}^-$  ions for anions like  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ , and  $\text{SO}_4^{2-}$  present in water.



During the complete process, water first passes through the cation exchange process. The water obtained after this process is free from mineral cations and is acidic in nature. This acidic water is then passed through the anion exchange process where  $\text{OH}^-$  ions neutralize the  $\text{H}^+$  ions and de-ionize the water obtained.

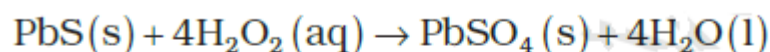
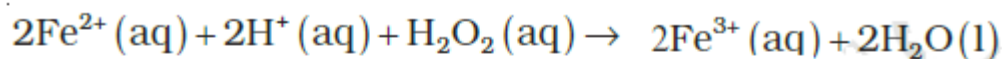
9.24) Write chemical reaction to show the amphoteric nature of water.

Water is amphoteric in nature because it acts as an acid

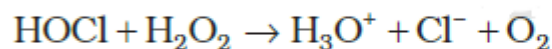
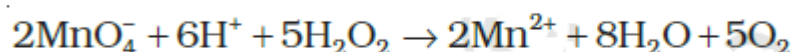


9.25) Write chemical reactions to justify that hydrogen peroxide can function as an oxidising as well as reducing agent.

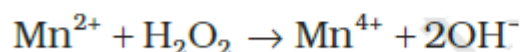
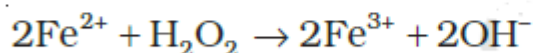
(i) Oxidising action in acidic medium



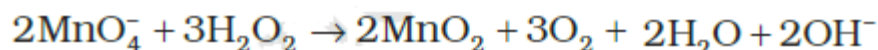
(ii) Reducing action in acidic medium



(iii) Oxidising action in basic medium



(iv) Reducing action in basic medium

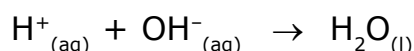


9.26) What is meant by 'demineralised water' and how can it be obtained?

Demineralised water is free from all soluble mineral salts which is obtained by passing water successively through a cation exchange (in the form of  $H^+$ ) and an anion exchange in the form of  $OH^-$  resins.

$H^+$  exchanges for  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$  and other cations present in water. This process results in release of proton which makes the water acidic.

$OH^-$  exchanges, for anions like  $Cl^-$ ,  $HCO_3^-$ ,  $SO_4^{2-}$  etc.  $OH^-$  ions thus liberated neutralize the  $H^+$  ions set free in the cation exchange process.



9.27) Is demineralised or distilled water useful for drinking purposes? If not, how can it be made useful ?

Water is an important part of life. It contains several dissolved nutrients that are required by human beings, plants, and animals for survival. Demineralised water is free of all soluble minerals. Hence, it is not fit for drinking.

It can be made useful only after the addition of desired minerals in specific amounts, which are important for growth.

9.28) Describe the usefulness of water in biosphere and biological systems.

- (i) Major part of all living system is made of water.
- (ii) It constitutes about 65 – 70% of body weights of animals and plants.
- (iii) Some properties of water like high specific heat, thermal conductivity, surface tension, high polarity allow water to play a major role in biosphere.
- (iv) Because of high heat of vaporisation it is responsible to regulate temperature of living beings.
- (v) It is an excellent fluid for the transportation of minerals and nutrients in plants.
- (vi) It is also required for photosynthesis in plants.

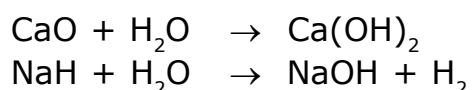
9.29) What properties of water make it useful as a solvent? What types of compound can it (i) dissolve (ii) hydrolyse?

A high value of dielectric constants ( $78.39 \text{ C}^2/\text{Nm}^2$ ) and dipole moment make water a universal solvent.

Water is able to dissolve most ionic and covalent compounds. Ionic compounds dissolve in water because of the ion-dipole interaction, whereas covalent compounds form hydrogen bonding and dissolve in water.

Water can hydrolyze metallic and non-metallic oxides, hydrides, carbides, phosphides, nitrides and various other salts. During hydrolysis,  $H^+$  and  $OH^-$  ions of water interact with the reacting molecule.

Some reactions are:



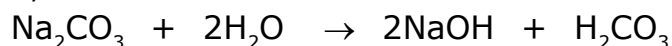


9.30) Knowing the properties of H<sub>2</sub>O and D<sub>2</sub>O, do you think D<sub>2</sub>O can be used for drinking purpose.

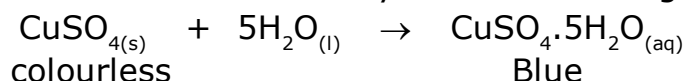
No, D<sub>2</sub>O is injurious to human beings, plants and animals. It slows down the reactions occurring in them.

9.31) What is the difference between the terms 'hydrolysis' and 'hydration'?

Hydrolysis is a chemical reaction in which a substance reacts with water under neutral, acidic or alkaline conditions.

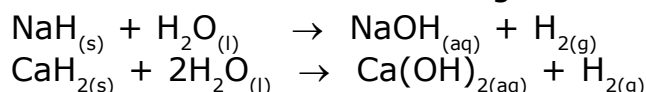


Hydration on the other hand is the property of a chemical compound to take up molecules of water of crystallisation and get hydrated.



9.32) How can saline hydrides remove traces of water from organic compounds?

Saline hydrides (CaH<sub>2</sub>, NaH etc.) react with water and form the corresponding metal hydroxide with the liberation of H<sub>2</sub> gas. Thus, these hydrides can be used to remove traces of water from the organic compounds.



9.33) What do you expect the nature of hydrides is, if formed by elements of atomic numbers 15, 19, 23 and 44 with dihydrogen? Compare their behaviour towards water.

The elements of atomic numbers 15, 19, 23, and 44 are phosphorus(P), potassium(K), vanadium(V), and ruthenium(Ru) respectively.

### 1) Hydride of Phosphorus:

Hydride of Phosphorus (PH<sub>3</sub>) is a covalent molecule. It is an electron-rich hydride owing to the presence of excess electrons as a lone pair on phosphorus.

### 2) Hydride of potassium:

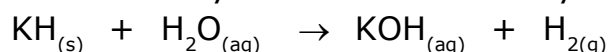
Dihydrogen forms an ionic hydride with potassium owing to the high electropositive nature of potassium. It is crystalline and non-volatile in nature.

### 3) Hydrides of Vanadium and Ruthenium:

Both vanadium and ruthenium belong to the *d*-block of the periodic table. The metals of *d*-block form metallic or non-stoichiometric hydrides. Hydrides of vanadium and ruthenium are therefore, metallic in nature having a deficiency of hydrogen.

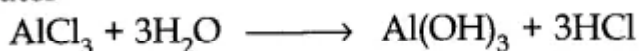
### 4) Behaviour of hydrides towards water:

Potassium hydride reacts violently with water as:



9.34) Do you expect different products in solution when aluminium (III) chloride and potassium chloride treated separately with (i) normal water (ii) acidified water (iii) alkaline water? Write equation wherever necessary.

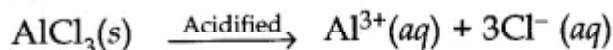
(i) In normal water



KCl will dissolve in water and ions will get hydrated.

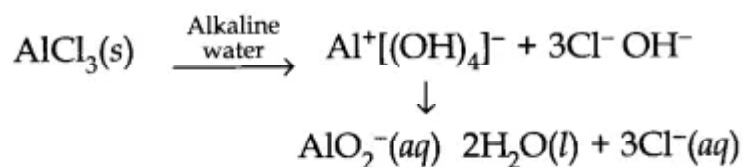
(ii) KCl will be unaffected in acidified water. While in acidic water  $\text{H}^+$  ion react with  $\text{Al}(\text{OH})_3$  to form  $\text{Al}^{3+}(\text{aq})$  ions and  $\text{H}_2\text{O}$ . Thus in acidic water  $\text{AlCl}_3$  exists as

$\text{Al}^{3+}(\text{aq})$  and  $\text{Cl}^-(\text{aq})$  ions



(iii) In alkaline water since the aqueous solution of KCl is neutral therefore, it is unaffected.

$\text{Al}(\text{OH})_3$  reacts to form soluble tetrahydroxoaluminate complex or meta-aluminate.



9.35) How does  $\text{H}_2\text{O}_2$  behave as a bleaching agent?

Bleaching action of  $\text{H}_2\text{O}_2$  is due to the oxidation of colouring matter by nascent oxygen.



The nascent oxygen combines with colouring matter which in turn gets oxidised.

9.36) What do you understand by the terms:

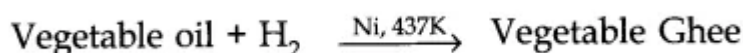
- (i) Hydrogen economy            (ii) hydrogenation            (iii) syngas  
(iv) water-gas shift reaction   (v) fuel-cell

### (i) Hydrogen economy:

Hydrogen economy is a technique of using dihydrogen in an efficient way. It involves transportation and storage of dihydrogen in the form of liquid or gas. Dihydrogen releases more energy than petrol and is more eco-friendly. Hence, it can be used in fuel cells to generate electric power. Hydrogen economy is about the transmission of this energy in the form of dihydrogen.

### (ii) Hydrogenation:

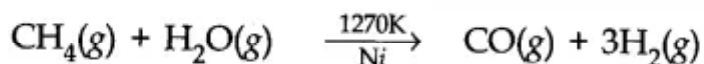
Hydrogenation is the addition of dihydrogen to another reactant. This process is used to reduce a compound in the presence of a suitable catalyst. For example, hydrogenation of vegetable oil using nickel as a catalyst gives edible fats such as vanaspati, ghee etc.



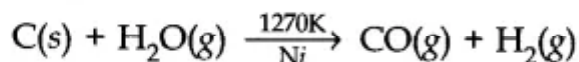
### (iii) Syngas:

Syngas is a mixture of carbon monoxide and dihydrogen. Since the mixture of the two gases is used for the synthesis of methanol, it is called syngas, synthesis gas, or water gas.

Syngas is produced on the action of steam with hydrocarbons or coke at a high temperature in the presence of a catalyst.

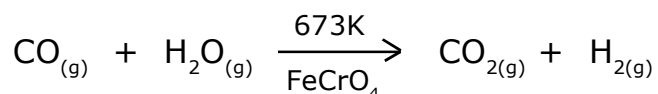


The process of producing syngas from coal is called 'Coal gasification'.



**(iv) Water shift reaction:**

It is a reaction of carbon monoxide of syngas mixture with steam to form carbon dioxide and more dihydrogen in the presence of a catalyst as:



**(v) Fuel cells:**

Fuel cells are devices for producing electricity from fuel in the presence of an electrolyte. Dihydrogen can be used as a fuel in these cells. It is preferred over other fuels because it is eco-friendly and releases greater energy per unit mass of fuel as compared to gasoline and other fuels.