

Inorganic chemistry II

Second stage / First semester

The fourth lecture

2022/2023

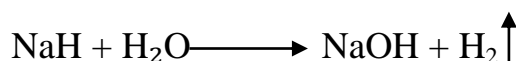
Pro. Dr. Mohammed Hamid

■ Preparation of Pure Hydrogen

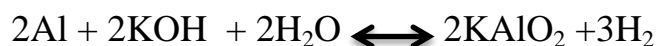
Pure hydrogen is obtained,

(i) by carrying electrolysis of barium hydroxide, $\text{Ba}(\text{OH})_2$, solution in a U-tube using platinum electrodes or nickel electrodes. The gas liberated at the cathode is passed over heated platinum gauze as to remove oxygen if present as an impurity in the form of water which is removed by passing the gas through P_2O_5 . Barium hydroxide, $\text{Ba}(\text{OH})_2$ is preferred to sodium hydroxide or potassium hydroxide because if any amount of CO_2 is absorbed, the BaCO_3 produced, being insoluble, settles down and does not interfere with electrolytic process.

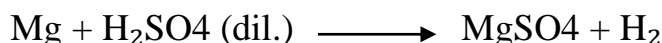
(ii) by action of water on NaH ,



(iii) by Uyeno's method,



(iv) by the action of pure dilute H_2SO_4 on magnesium ribbon.



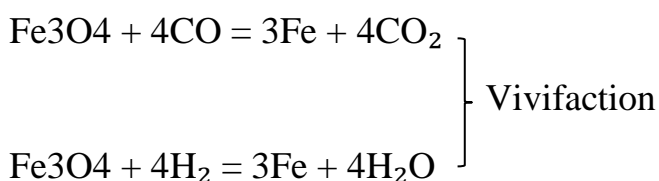
MANUFACTURE OF HYDROGEN

Large quantities of hydrogen are required these days in industry for various purposes. Water is found in abundance and is the cheapest raw material from which hydrogen can be obtained. Many methods have been proposed for the commercial production of hydrogen, among which the important ones are described below:

(i) 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 regenerated by reducing magnetic oxide with water gas ($\text{CO} + \text{H}_2$). This reaction is called vivifaction and time allotted for this reaction is about 20 minutes.



This iron is again used for decomposition of steam. In order to make the process continuous, the above two reactions are carried out alternatively using two or more furnaces.

PROPERTIES OF HYDROGEN

Physical Properties

- (a) It is a colourless, odourless and tasteless gas.
- (b) It is only slightly soluble in water, about 2 volumes in 100 volume of water at 0°C.
- (c) It is lightest of all elements.

$$\text{Density} = 0.08987 \text{ gL}^{-1}$$

- (d) It is diatomic in nature.

$$C_p/C_v = \gamma = 1.40$$

- (e) It has low melting and boiling points,

$$\text{b.pt.} = -252.5^\circ\text{C} \text{ (20.5 K)}$$

$$\text{m.pt.} = -259.0^\circ\text{C} \text{ (14.0 K)}$$

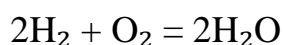
- (f) The various physical constants are :

Ionisation potential	13.54 eV or 313 kcal mol ⁻¹
Electron affinity	17.3 kcal mol ⁻¹ or 72 kJ mol ⁻¹
Electronegativity	2.1
Critical temperature	-236.9°C
Bond energy, H-H	436 kJ mol ⁻¹
Bond length, H-H	74 pm

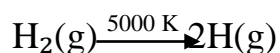
(g) Certain metals like palladium, platinum, iron, cobalt, etc., can adsorb large quantities of hydrogen. Palladium can adsorb 1000 times its own volume of hydrogen. The adsorbed hydrogen is called occluded hydrogen and is more active than ordinary hydrogen. This property can be used for the purification of hydrogen because only pure hydrogen is adsorbed.

Chemical Properties

(a) Combustion: Hydrogen is inflammable or combustible gas. It burns with blue flame in oxygen atmosphere. Hydrogen, however, does not help in burning. If a burning splinter is introduced in a jar full of hydrogen, the splinter goes out while the gas burns on the mouth of the jar. On account of hydrogen burning, water is formed.

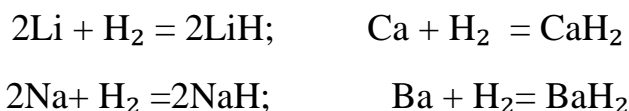


(b) Combination reactions: Hydrogen is not a very active element and does not react readily with other elements. The HH bond dissociation enthalpy (436 kJ mol) is the highest for a single bond between two atoms of any element. It's dissociation is only 0.081% at 2000 K and increases to 95.5% at 5000 K.



Therefore, most of the reactions of dihydrogen occur at high temperatures.

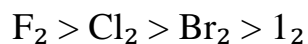
Under suitable conditions, hydrogen can be made to combine with metals and nonmetals both. (i) Alkali and alkaline earth metals (with the exception of beryllium) directly combine with hydrogen when heated in its atmosphere. The compounds formed are called hydrides.



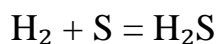
These hydrides are electrovalent compounds, conduct electricity in fused state. (ii) Non-metals like halogens, oxygen, sulphur, nitrogen, etc., directly combine with hydrogen under definite set of conditions and form stable covalent compounds. With fluorine, hydrogen combines readily even at low temperature while the combination with chlorine takes place in presence of sunlight or on heating. Similarly, with bromine it combines on heating while with iodine it combines when heated in presence of a catalyst.



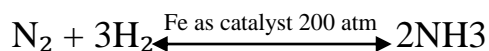
The reactivity of halogens towards dihydrogen decreases in the order:



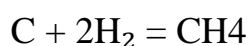
Hydrogen combines with sulphur on ignition.



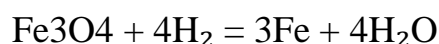
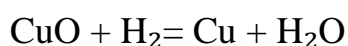
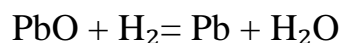
It combines with nitrogen under high pressure and in presence of a catalyst at 500°C.



It combines with carbon at about 1200°C to form methane in small amounts.

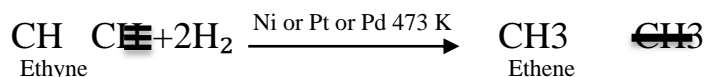
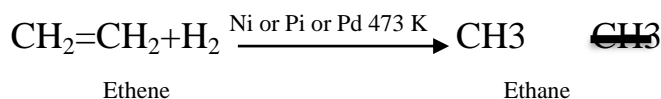
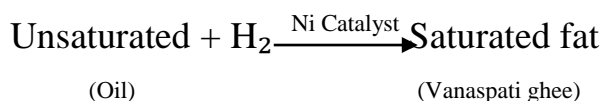


(c) Reducing nature: As hydrogen has great affinity for oxygen, it is suitable for removing oxygen. The oxides of less electropositive metals such as copper, tin, iron, lead, etc., are reduced to the metals when heated in hydrogen.

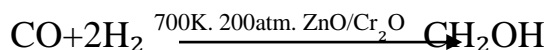


[Note: The oxides of strongly electropositive metals such as those of alkali and alkaline earth metals are not reduced by dihydrogen.]

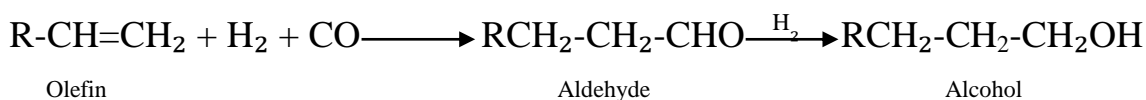
Numerous substances are reduced or hydrogenated by hydrogen in presence of suitable catalysts. The unsaturated fats are changed to saturated fats in the presence of finely divided nickel.



(d) Reaction with carbon monoxide: At about 700 K and under high pressure and in presence of a catalyst (ZnO/ Cr₂O₃), dihydrogen combines with CO to form methanol.



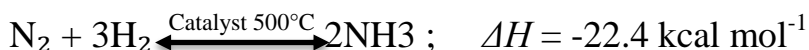
(e) Hydroformylation of olefins to aldehydes: Olefins combine with carbon monoxide and hydrogen in presence of octacarbonyldicobalt, Co₂(CO)₈, as catalyst under high temperature and pressure to form aldehydes which can be further reduced to alcohols.



INDUSTRIAL APPLICATIONS

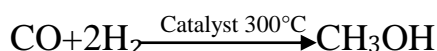
Very large quantities of hydrogen are required for synthesis of a number of products.

(a) Synthesis of ammonia: A mixture of N₂ and H₂ in ratio of 1: 3 is compressed to 200 atmospheres and passed over heated catalyst at 500°C. About 8% NH₃ is formed. It is known as Haber's process.



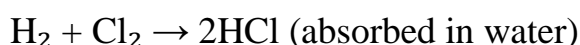
Catalyst -Freshly reduced iron having Mo as promoter.

(b) Manufacture of methyl alcohol: Water gas enriched is compressed to 200 atmospheres and then passed Catalyst ZnO and CrO₃, when CH₃OH is formed.



(c) Manufacture of hydrogen chloride: Large quantities of H₂ and Cl₂ obtained as byproducts during manufacture

of NaOH are made to combine to form HCl by burning one in the other.



(d) In food processing industry by hydrogenation of oils: Hydrogen is chiefly used in catalytic hydrogenation of unsaturated (liquid) oils into solid fats for the production of vegetable ghee.

(e) Synthetic petrol : Petrol substitutes are obtained by subjecting a paste of powdered coal in crude oil to the action of hydrogen under pressure and in presence of a catalyst.

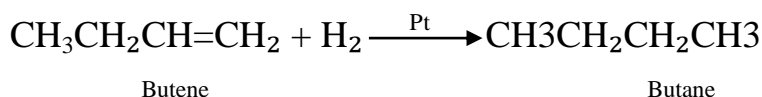
(f) Oxyhydrogen flame: Oxyhydrogen flame produces a temperature of 2800°C while oxyatomic hydrogen flame produces a temperature of 4000°C. This temperature is required for melting substances having very high melting points such as quartz, platinum, etc., and also for welding purposes.

(g) With helium, it is used for filling balloons employed for atmospheric study.

(h)Hydrogen is used for creating a reducing atmosphere in processes like annealing and deoxidising.

(i) As fuel for space shuttle's main rocket engine: The density of liquid hydrogen is very low (0.08987 gL^{-1}), which is less than one-tenth that of water. This low density makes hydrogen a very light weight but bulky fuel. Hydrogen has the highest specific enthalpy of any known fuel. The low density and highest specific enthalpy of liquid hydrogen makes it a valuable fuel for space mission, so liquid hydrogen storage tank with liquid oxygen is used to power the main rocket engine of space shuttle

(j) In petrochemical industry: One major use of hydrogen is in the petrochemical industry. In many cases the reaction is one where hydrogen is added to hydrocarbon compound containing carbon-carbon double bonds to produce compound that contain carbon-carbon single bond. For example, 1-butene can be reacted with hydrogen using a platinum or palladium catalyst to produce butane.



Butane is the constituent of petrol