**GROUP ONE**

**CHE 441**

**PLANT DESIGN AND PROCESS ECONOMICS I**

 **ASSIGNMENT 1**

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# QUESTION

Write, in detail, three processes descriptions for hydrogen production.

# ANSWERS

1. **ELECTROLYSIS OF SULPHUROUS ACID AND WATER**

When electrodes are placed in an electrolyte and a voltage is applied, the electrolyte will conduct electricity. Lone electrons normally cannot pass through the electrolyte; instead, a chemical reaction occurs at the cathode, providing electrons to the electrolyte. Another reaction occurs at the anode, consuming electrons from the electrolyte. As a result, a negative charge develops in the electrolyte around the cathode, and a positive charge develops around the anode. The ions in the electrolyte neutralize these charges, enabling the electrons to keep flowing and the reactions to continue.

Sulphurous acid comes from the decomposition of sulphuric acid; H2SO4.

H2SO4(l) SO2(g) + O2(g) + H2O(l). [1]

The sulphuric acid industrial production (H2SO4) was produced by the following steps;

S(s) + O2(g) SO2(g) [2]

SO2(g) + O2(g) SO3(g)  [3]

Adding water directly to SO3 yields a very exothermic reaction and forms acidic vapour other than liquid, only little amounts react with water, forming concentrated sulphuric acid. Hence, SO3 is dissolved in concentrated H2SO4 forming oleum which reacts with water to form concentrated H2SO4.

SO3(g) + H2O(l) H2SO4 [4]

SO3(g) + H2SO4(l) H2S2O7 [5]

 H2S2O7 + H2O(l). H2SO4(l)  [6]

This is the Contact Process, and it uses vanadium(IV)oxide as catalyst to speed up the rate of reaction.

But during the production of sulphuric acid, there is always an emission of SO2 into the atmosphere. Sulphur dioxide is an atmospheric pollutant which needs to be treated, hence it under goes electrolysis with water, to give off hydrogen.

SO2(l) + 2H2O­(l) H2SO4(l) + H2(g) [7]

## 1.1 Purification

This includes the dusting tower, cooling pipes, scrubbers, drying tower, arsenic purifier and testing box. Sulphur dioxide has many impurities such as vapours, dust particles and arsenous oxide. Therefore, it must be purified to avoid catalyst poisoning (i.e.: destroying catalytic activity and loss of efficiency). In this process, the gas is washed with water, and dried by sulphuric acid. In the dusting tower, the sulphur dioxide is exposed to a steam which removes the dust particles. After the gas is cooled, the sulphur dioxide enters the washing tower where it is sprayed by water to remove any soluble impurities. In the drying tower, sulphuric acid is sprayed on the gas to remove the moisture from it. Finally, arsenic oxide is removed when the gas is exposed to ferric hydroxide.

## 1.2 Double Absorption

The next step to the Contact Process is **Double Absorption**. In this process, the product gases (SO2) and (SO3) are passed through absorption towers twice to achieve further absorption and conversion of SO2 to SO3 and production of higher grade sulphuric acid.

SO2-rich gases enter the catalytic converter, usually a tower with multiple catalyst beds, and are converted to SO3, achieving the first stage of conversion. The exit gases from this stage contain both SO2 and SO3 which are passed through intermediate absorption towers where sulphuric acid is trickled down packed columns and SO3 reacts with water increasing the sulphuric acid concentration. Though SO2 too passes through the tower it is unreactive and comes out of the absorption tower.

The unreacted SO2 further undergoes electrolysis with water to extract hydrogen **(Novel Process)**



**Figure 1: schematic representation of the Novel Process**

## 1.3 Electrolysis of Sulphur(Iv)Oxide

Water is the electrolyte used.

Electro-oxidation of sulphur dioxide at the anode of the electrolyser:

S02(aq) +2H20(l) → H2SO4(aq) + 2H+ (aq)+2e [8]

Electro-reduction of hydrogen ions at the cathode of the electrolyser:

2H+(aq) + 2e → H2(g)  [9]

Net electrochemical reaction at 80 - 120 °C (Equations [8] + [9]):

SO2 (aq) + 2H2O(l) → H2SO4 (aq) + H2(g)  [10]

Net cycle reaction (Equations 1 + 10):

H20(l) → H2(g) + 1/2O2(g) [9]

Therefore, hydrogen gas is given off at the cathode.

If both hydrogen and oxygen gasses are combined during the electrolysis process, there will be a substantial risk of explosion. Mixtures of between 4 and 75% hydrogen in air and 4 and 94% of hydrogen in pure oxygen are explosive. If the hydrogen content is less than 4% or greater than 75% in air the mixture will not explode but combustion will take place. Electrolysers are designed with separators (also called membranes or diaphragms) between the anode and cathode to keep the hydrogen and oxygen from combining and also to allow ions to be transferred in the liquid electrolyte. For this reason, the space between electrodes should be minimized. The separator must be permeable to liquids but not permit gasses to pass. Artificial fibre cloth, rubber cloth, or metallic mesh may also be used for the **membrane**.

1. **HYDROGEN FROM HYDROCARBON**

A preheated mixture of steam and hydrocarbon, usually natural gas, is passed through tubes containing a nickel-based catalyst, which are heated in a furnace primarily by radiant heat transfer. Typical conditions would be 30 bar pressure, a 3 to 1 steam-to carbon ratio and a tube outlet temperature of about 900°C. The reaction products are primarily **CO** (carbon monoxide) and **H2 (hydrogen gas)** together with steam, **CO2(carbon(IV)oxide)** and a little unconverted methane. The gas mixture is passed through a waste heat boiler, which cools the gas to about 350°C to 400°C and gives off an amount of steam used to preheat the feed. The gases then pass through a catalytic reactor where the shift reaction converts **CO** and steam to **CO2** and **H2.**

**C3H8(g) + 6H2O(l) 3CO2(g) +10H2(g)** [1]

**CO(g) + H2O(g) ⇌ CO2(g) + H2(g)** [2]

 The gases are cooled and **H2** is separated in a complex pressure swing adsorber **(PSA) (using pressure adsorbents such as silica gel, activated charcoal to adsorb gases; different gases are adsorbed at adsorbed at different pressures)** installed to produces pure **CO2**, pure **H2** and a waste gas stream. The hydrogen purity can be **>99.99%** with a typical recovery of **90%** from the feed gas. **CO2** recovery from the feed gas would be **>95%.** The waste combustion products from the furnace, which are at a temperature of about **1000°C**, pass through a convection heat exchange section (to lower the temperature) where they are used to preheat the reformer feed and produce steam. The hydrogen finally undergoes **methanation** to remove all traces of methane present and give off pure hydrogen as final product.

1. **ELECTROLYSIS OF BRINE**

Hydrogen is a by-product in the brine (aqueous sodium chloride) electrolysis process. It uses water as the electrolyte, and it has a permeable membrane which allows only ion pass through it. Saturated brine is passed into the first chamber of the cell where it separates into sodium and chloride ions. Chloride ions are oxidised at the anode, losing electrons to become chlorine gas and leaving the sodium ions (Na+) in the solution;

**2Cl− → Cl2(g) + 2e− [1]**

At the cathode, positive hydrogen ions from water molecules are reduced by the electrons provided by the electrolytic current, to hydrogen gas, releasing hydroxide ions into the solution.

**2H2O(l) + 2e− → H2(g) + 2OH− [2]**

The ion-permeable [membrane](https://en.wikipedia.org/wiki/Ion_exchange_membrane) at the centre of the cell allows the sodium ions (Na+) to pass to the second chamber where they react with the hydroxide ions to produce caustic soda (NaOH).

The overall reaction for the electrolysis of brine is thus:

**2NaCl(s) + 2H2O(l) → Cl2(g) + H2(g) + 2NaOH(aq)  [3]**



**Figure 2: Electrolysis setup for Brine**

**REFERENCES**

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