ELECTRODES - Concepts.

Electrochemistry is a branch of science that deals with conversion of chemical energy into electrical energy and vice-versa

INTRODUCTION: CONDUCTANCE: Reciprocal of Resistance

$K = \frac{1}{\rho}$ Kappa

Conductors:

A substance which allows electric current to pass through it, is called as conductor

Eg:- Metals, Graphite, aqueous solution of acids, bases, salts

Conductors are of two types:-

a) Metallic conductors: The substance which conduct electricity, but are not decomposed by it.

Eg:- Metal, Graphite

$$M \longrightarrow M^{n} + ne^{-}$$

Electrolytes:- The substance which decomposes as a result of passage of electric current is called electrolyte. and the phenomenon of decomposition of electrolyte through the passage of electricity is called electrolysis

... Bases, ElectroValent Salt (NaCl)

⇒ There will be two electrodes. one is Anode (Negative ions move towards Anode) and the other Cathode (Positive ions move (towards Cathode)

<u>Electrolyte</u>:

A substance which decomposes as a result of passage of electric current is called Electrolyte

$$AB \longrightarrow A^{+} + B^{-}$$

⇒ The properties of electrolytes depend upon the properties of ions.

<u>Specific conductance</u>:- conductivity of $1 cm^3$ of the sol

The resistance offered by a conductor to the passage of electricity through it, which is proportional to its length (l) and inversely proportional to the area of cross section [S].

Hence, Resistance (R) is given by relationship (Ohm's Law)

$$R = \frac{\rho \times l}{S}$$

ρ = constant (which depends on material of Conductor and is known as Specific Resistance)

l = Length

S = Area of cross section

when l and S are both equal to unity ($R = \rho$)

⇒ the specific resistance of an electrolyte is resistance in ohms which allows passage of electricity in $1 cm^3$ of the solution

⇒ The reciprocal of specific resistance is known as specific conductance and it is denoted by the symbol K

$$\boxed{K = \frac{l}{S} \times \frac{1}{R}}$$

The units for specific conductance is $ohm^{-1} cm^{-1}$

Hence, $K = \frac{l}{S} \times \frac{1}{R} = \frac{cm \times 1}{cm^2 \times ohm}$

$= ohm^{-1} cm^{-1}$

The reciprocal of ohms is termed as specific conductance and expressed in mhos or ohm^{-1}.

Equivalent conductance :- [λ]

The equivalent conductance is defined as Conductivities of all the ions produced from one gram equivalent of an electrolyte in the solution

The equivalent conductance at the dilution V is written as λ_v. It is equal to the product of specific conductivity and ... 1 gram equivalent of electrolyte

$$\lambda_v = K_v \times V \quad \left(V = \frac{1000}{C}\right)$$

$$\lambda_v = \frac{K_v \times 1000}{C}$$

$$\lambda_v = K_v \times V$$

$$= \frac{l}{S} \times \frac{1}{R} \times V \quad \left[\because K = \frac{l}{S} \times \frac{1}{R}\right]$$

$$= \frac{cm \times 1 \times cm^3}{cm^2 \times ohm \times equivalent}$$

$$= ohm^{-1} \, cm^2 \, equiv^{-1}$$

Molecular Conductance:

The Molecular conductance of a solution is defined as conductivity of all the ions produced by dissociation of one mole of (1g mol. wt) an electrolyte in the solution

$$\lambda_m = K_v \times V$$

$$\lambda_m = \frac{1000}{}$$

$$= K_v \times \frac{1000}{C}$$

$$= ohm^{-1} \, cm^2 \, mole^{-1}$$

Effect of Dilution on Conductance :-

As the solution becomes dilute, the number of current carrying ions present per ml of the solution become less. Hence, Specific conductance is the conductance of $1 cm^3$ of the solution. It is expected that its value will fall with dilution.

The equivalent conductance and Molecular conductance increase with dilution, on dilution more and more number of electrolyte molecules ionises.

REFFERENCE ELECTRODES

DEFINITION:

The electrode of standard potential, with which one can compare the potentials of another electrode is called reference electrode.

INTRODUCTION:

The standard hydrogen electrode is used as reference electrode for determining single electrode potentials, whose potential arbitarily taken as zero. But hydrogen electrode is not always convenient to set up this electrode on various difficulties involved in maintaining activity of hydrogen ions at unity and keeping the pressure of the gas at one atmosphere. So, some other electrodes called secondary reference electrodes have been employed.

The important reference electrodes are as follows:

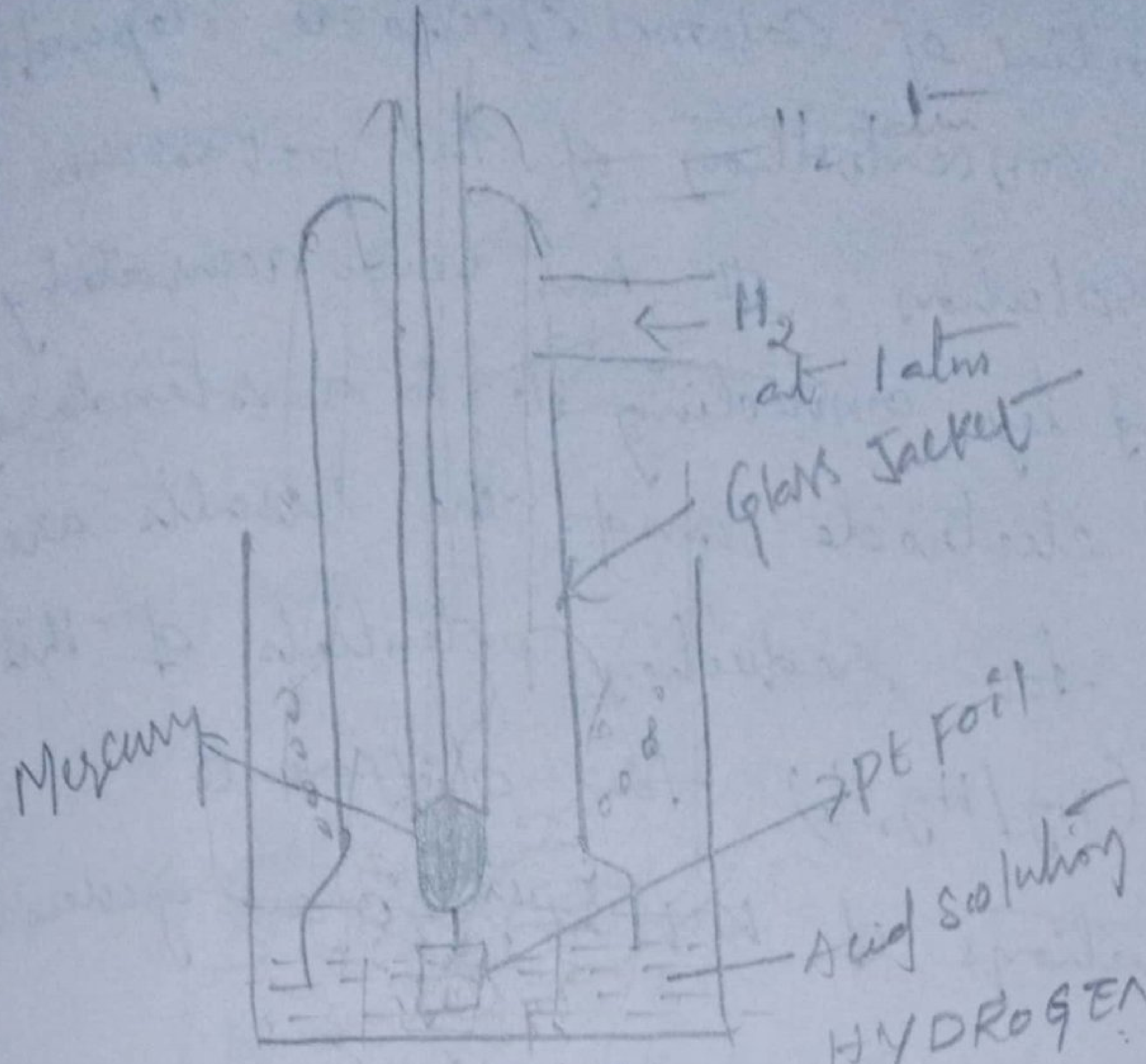
(a) Hydrogen Electrode:

⇒ It is the primary electrode. It consists of small platinum strip coated with platinum black to absorb hydrogen gas. A platinum wire welded to the electrode and sealed through a glass tube makes contact with outer circuit.

The platinum strip is surrounded by an outer glass tube which has inlet for hydrogen at top and no. of holes at the base for escape of excess gas. The electrode is placed in a dilute solution of an acid. pure hydrogen is then passed into it at one atmosphere pressure. A part of hydrogen gas adsorbed by the platinised electrode, while the excess is escapes through the lower holes. Then it results an equilibrium between the adsorbed hydrogen on the electrode surface and hydrogen ions in the solution.

$$H_2 \longrightarrow 2H^+ + 2e^-$$

The potential of standard hydrogen electrode when hydrogen at one atmosphere pressure is bubbled through a solution of hydrogen ions of unit concentration is fixed as zero. The hydrogen electrodelectro used to find the pH of a solution.



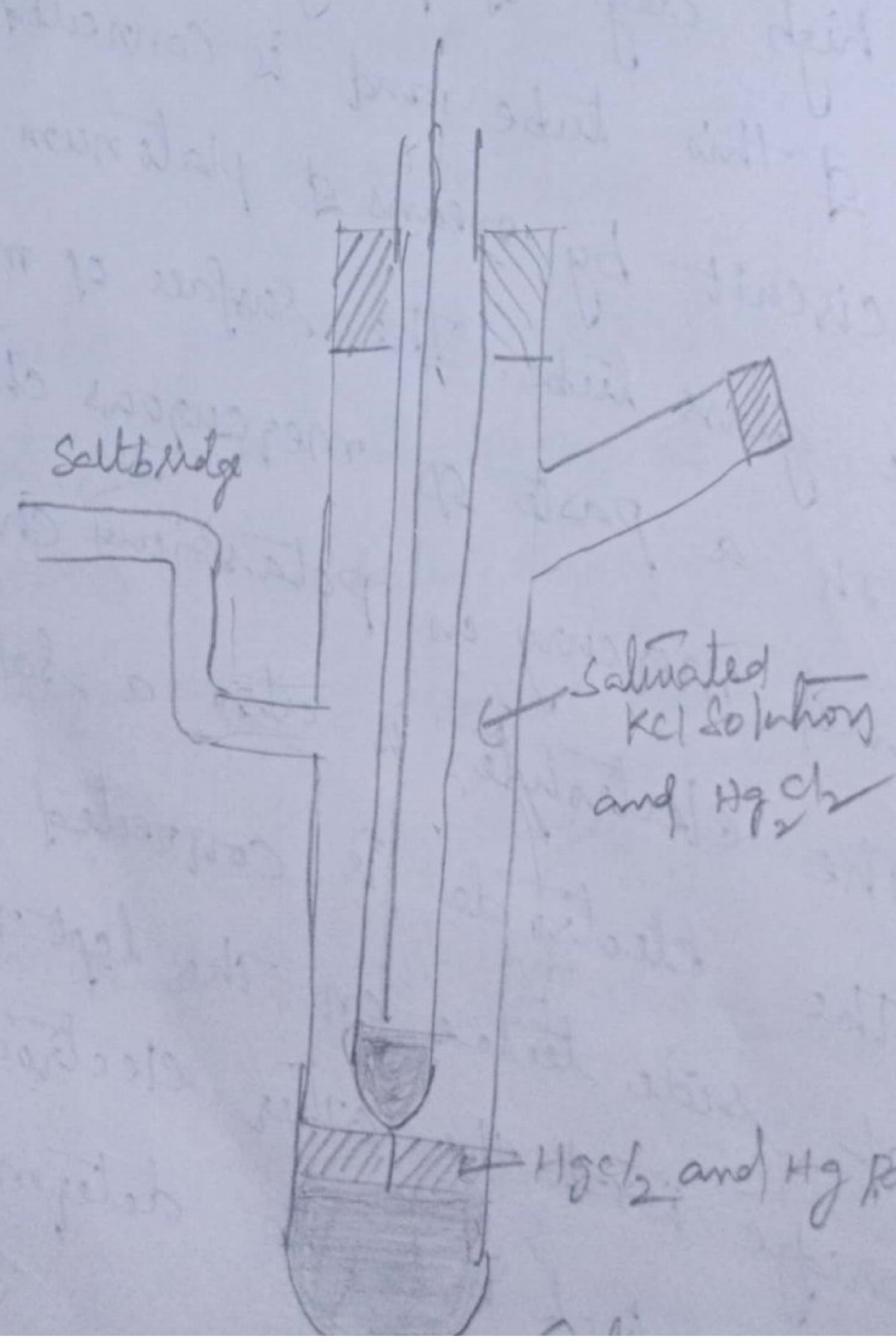
HYDROGEN ELECTRODE

b) Calomel electrode :-

It is a secondary electrode, consists of a glass tube having a side tube on each side. Mercury of high degree of purity is placed at the bottom of this tube and is connected to the other circuit by means of platinum wire sealed in a glass tube. The surface of mercury covered with a paste of mercurous chloride (Calomel) and mercury in potassium chloride solution. The electrolyte is also a solution of KCl. The electrode is connected with the help of side tube on the left through a salt bridge with the other electrode (the potential of which is to be determined)

The potential of Calomel electrode depends upon the concentration of the potassium chloride solution. It has very accurately determined by connecting it to a standard hydrogen electrode and the results are obtained for reduction potentials of this electrode (Hg/Hg_2Cl_2) for different concentrations of KCl at 24°C are given below.

For Saturated KCl solution E = + 0.2415 V

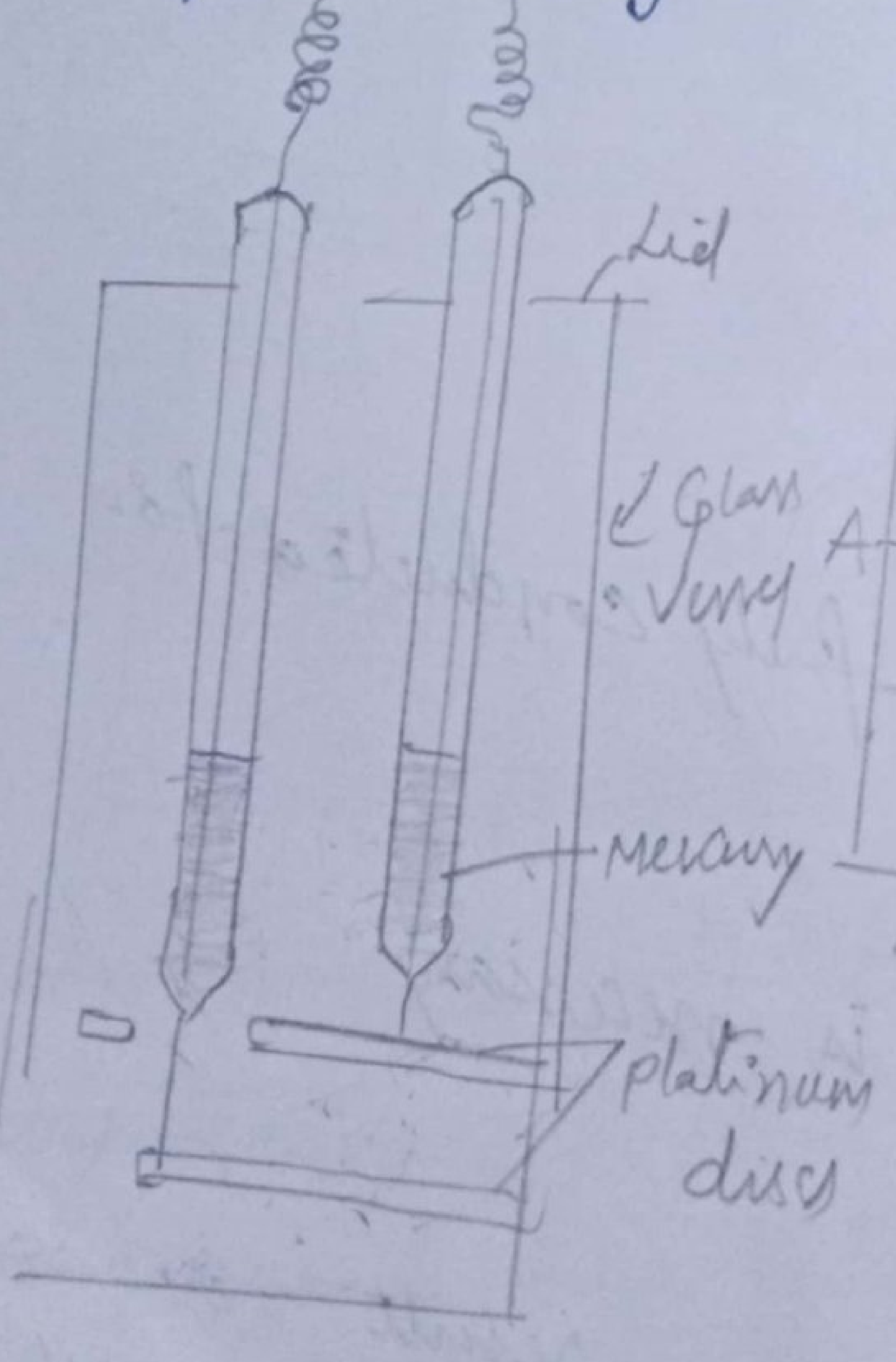


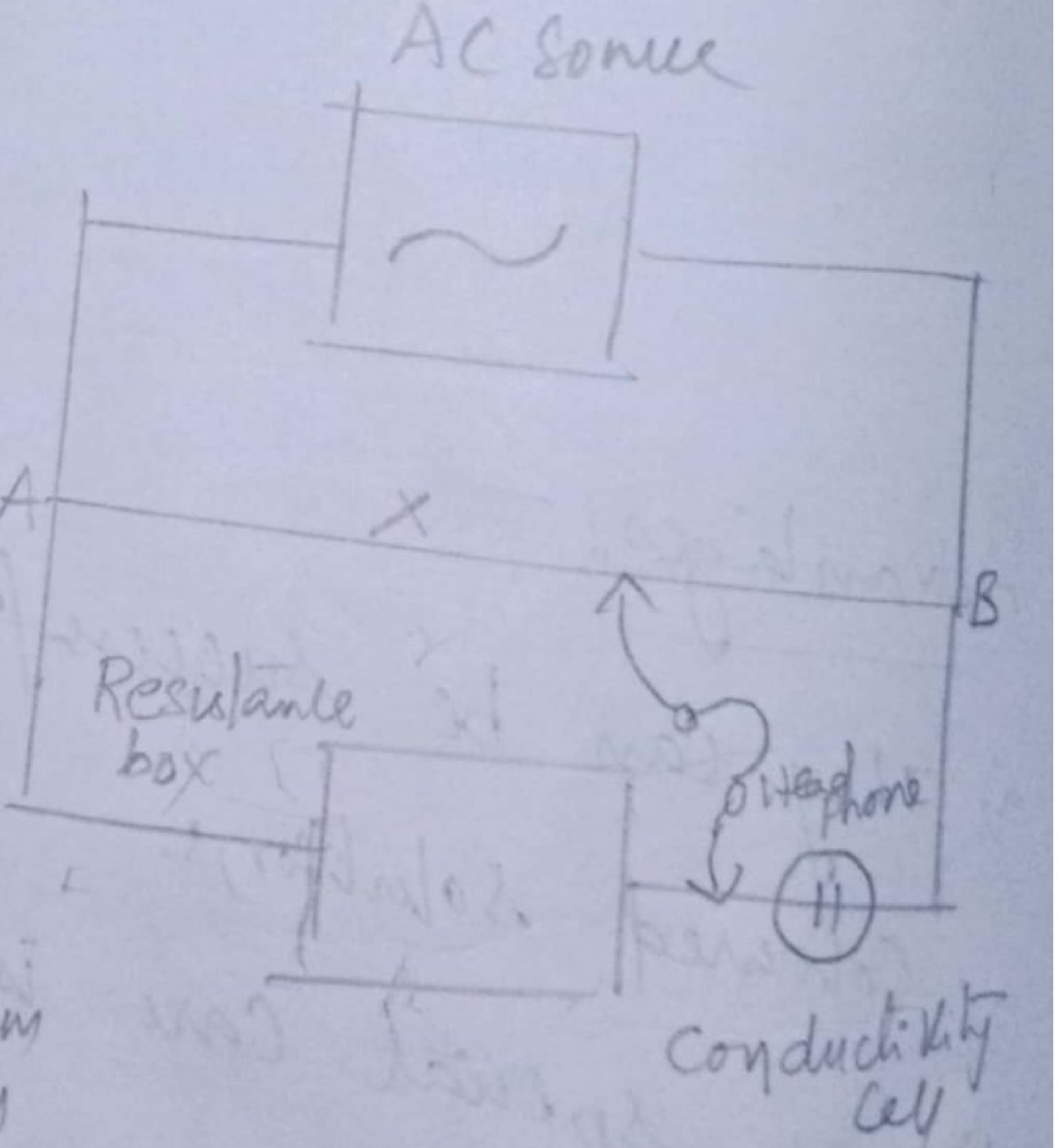
Measurement of conductance:-

Measurement of conductance is normally carried out by using a Wheatstone bridge.

The Measurement of conductivity of any electrolyte is complicated that if a direct current is used, the products of electrolysis collect at the electrodes emf i.e back polarisation which increases the resistance of electrolyte is

To avoid these complications, an alternating current is ~~used~~ employed and detecting the flow of current with a head telephone in place of galvanometer.





Working :-

The solution whose conductance is to be determined is placed in a special cell known as conductivity cell.

It is made up of special glass and fixed with two platinum electrodes, coated with platinum black and are firmly fixed in ebonite collar of cells. So that distance between the electrodes may not alter during the experiment.

$$\frac{\text{Resistance of resistance box } [R]}{\text{Resistance of solution in cell}} = \frac{AX}{XB}$$

$$\frac{1}{\text{Resistance of solution in cell}} = \frac{AX}{XB} \times \frac{1}{R} = \text{obs. conductance}$$

Now, R, AX, and XB are known, so the value of observed conductance can be calculated. This on multiplication with cell constant gives the value of specific conductivity.

Thus Specific conductivity = Observed conductivity × Cell constant

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Conductometric Titration :

The process of determining the quantity of a sample by adding measured increments of a titrant until the end-point is reached. The titration is monitored by measuring the conductance of the solution.

Conductometric Titration (Acid - Base titrations) :

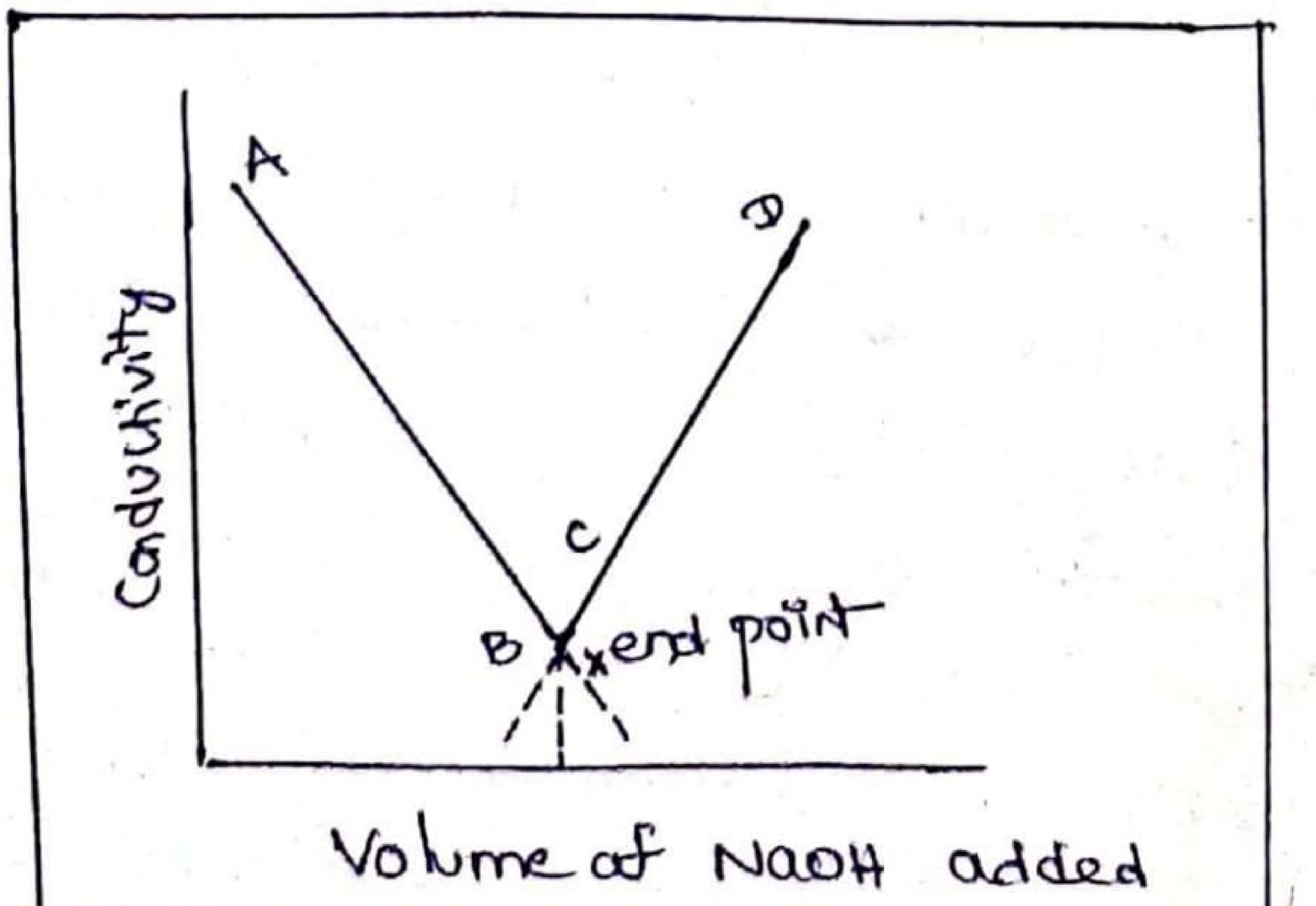
i) Strong acid with a Strong base :

Consider the titration of a strong acid (HCl) with a strong base (NaOH)

$$[H^+Cl^-] + [Na^+OH^-] \longrightarrow [Na^+ + Cl^-] + H_2O$$

→ The acid is taken into the conductivity vessel and the alkali in the burette. At the begining of the titration, the acid solution has high conductivity due to high mobile hydrogen ions.

→ The addition of each drop of NaOH solution from the burette to a solution of HCl taken in the conductivity cell, there occurs a progressive decrease in the conductance of the solution, i.e the end - point is reached.

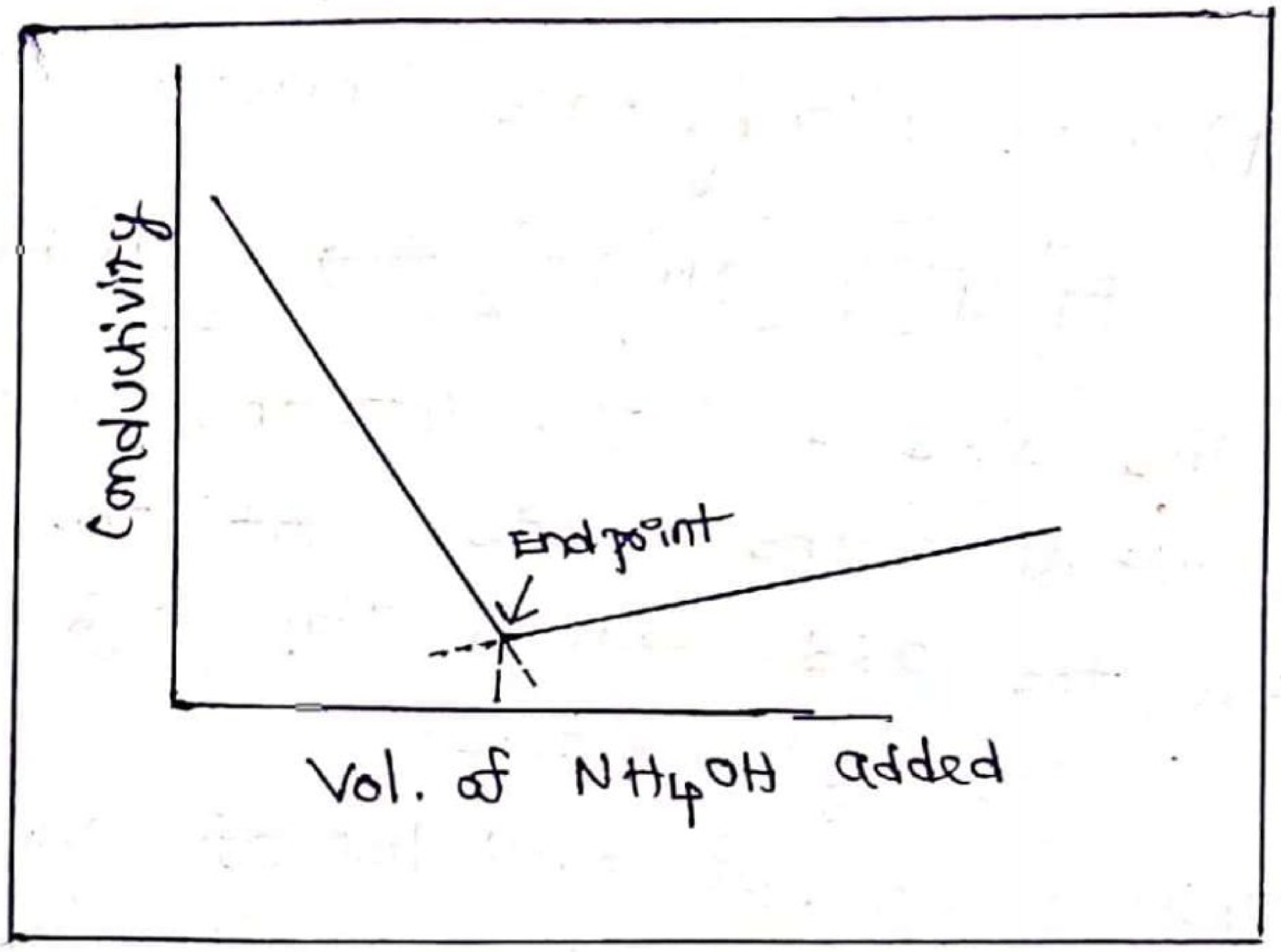


(ii) Strong acid with a weak base :

Let us consider titration of HCl (strong acid) with NH_4OH (weak base).

When Ammonium hydroxide is added to HCl, the conductivity decreases because of the replacement of the fast moving H^+ ions by slow moving NH_4^+ ions resulting in the decrease in the conductance value.

$$[H^+ Cl^-] + [NH_4^+ OH^-] \rightarrow [NH_4^+ Cl^-] + H_2O$$



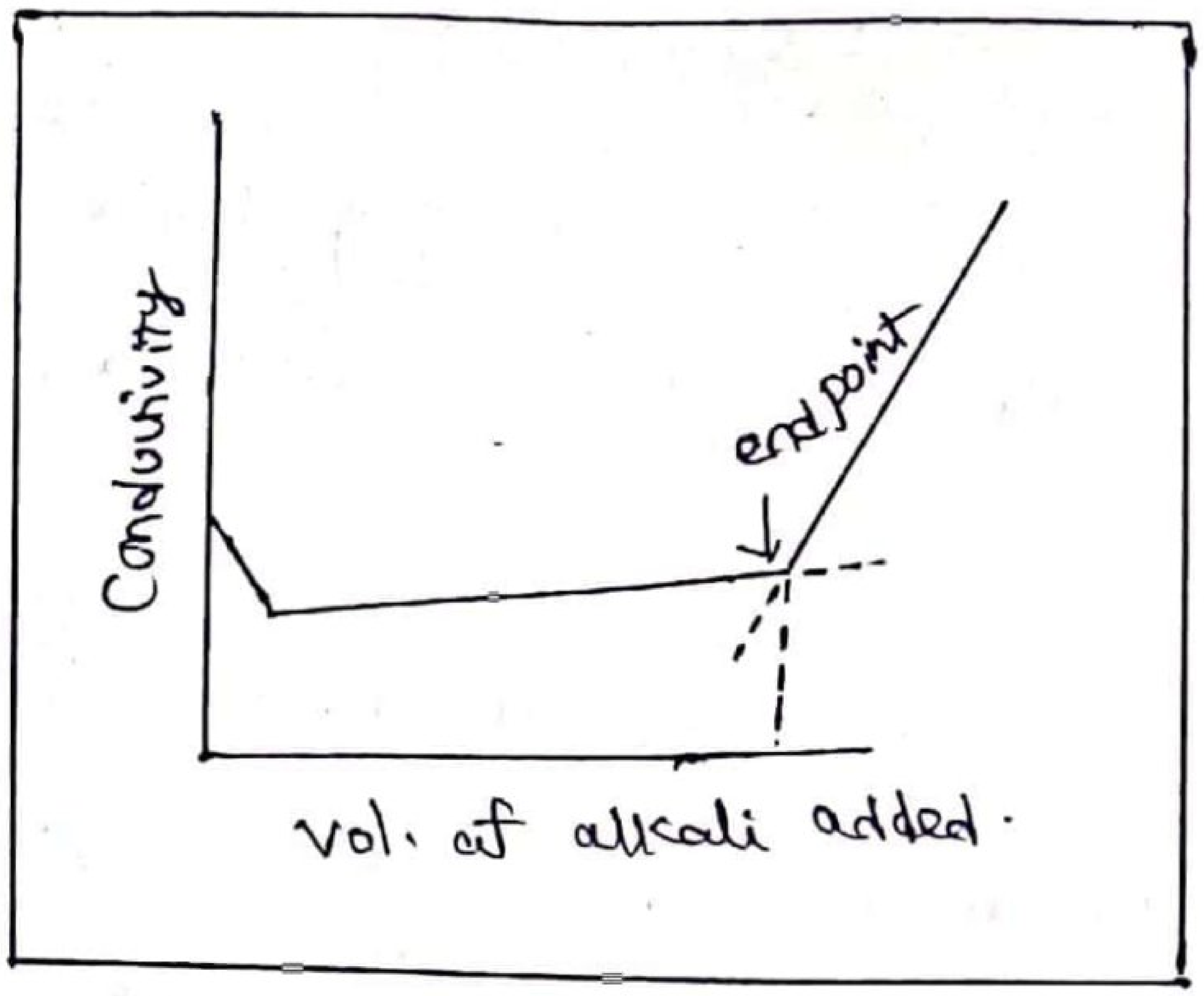
Titration of Strong acid with a weak base.

(iii) Weak acid with a Strong base :-

Let us Consider the titration of acetic acid (weak acid) with a strong base (NaOH). When small amount of NaOH is added to acetic acid, the conductivity decreases initially then increases with the further addition of NaOH.

$$[CH_3COO^- H^+] + [Na^+ OH^-] \rightarrow [CH_3COO^- Na^+] + H_2O$$

→ when neutralization of acid is completed, further addition of alkali produces excess of OH^- ions. The conductance of solution therefore begins increasing more rapidly.

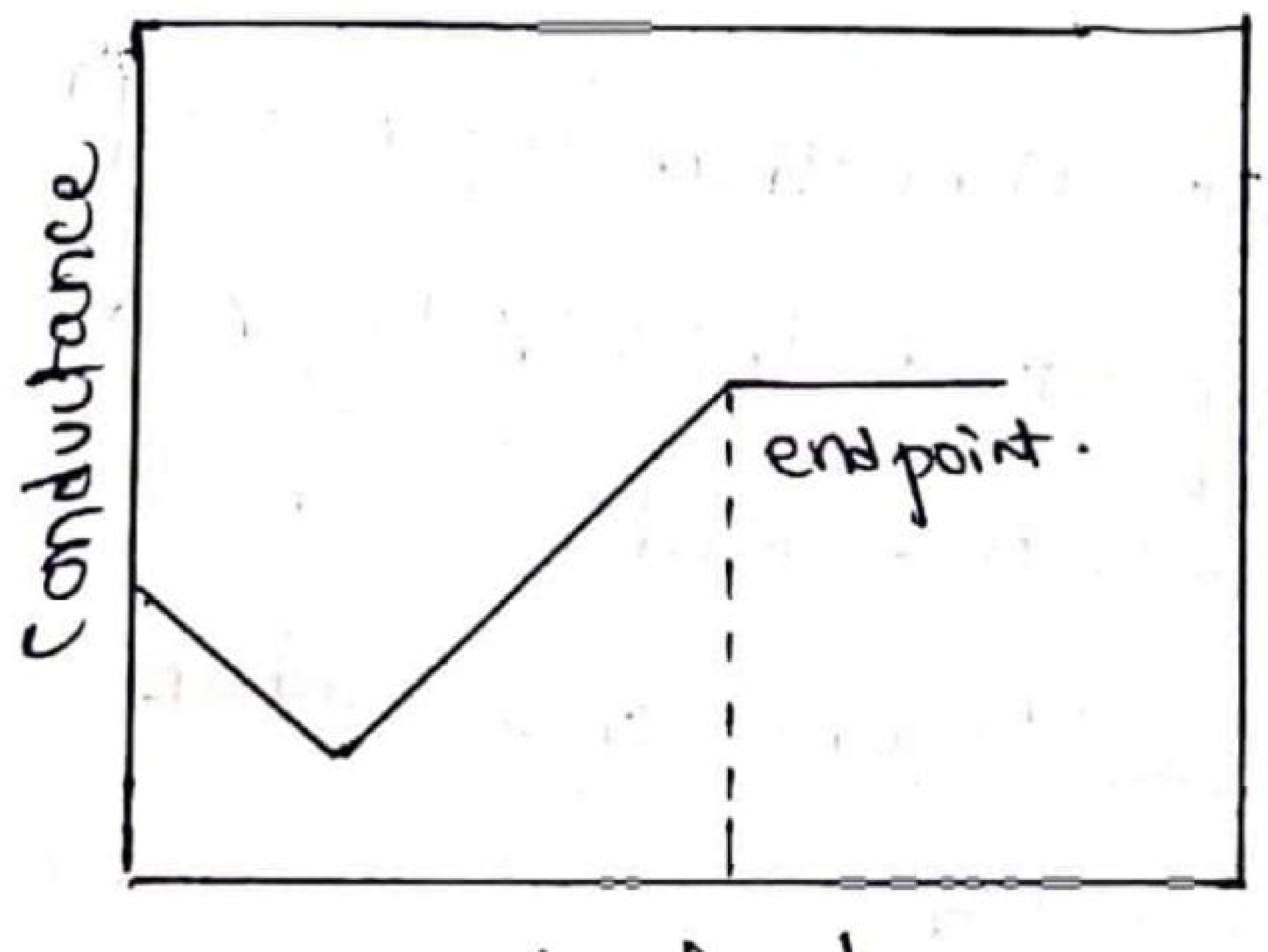


Titration of weak acid with a strong base.

iv) Weak acid with a weak base :

Let us consider the titration of weak acid (CH_3COOH) with weak base (NH_4OH).

$$[CH_3COO^- H^+] + [NH_4^+ OH^-] \longrightarrow [CH_3COONH_4] + H_2O$$



→ Now, as we add few drops of weak base, the OH^- ion consumes H^+ to form water. So, By addition of few drops of base at first, Conductance decreases slightly. Now as we ~~move further~~ add more drops of base, all H^+ ~~ion~~ is consumed and hence the dissociation of the weak acid increases which is reflected by gradual increase in conductance value.

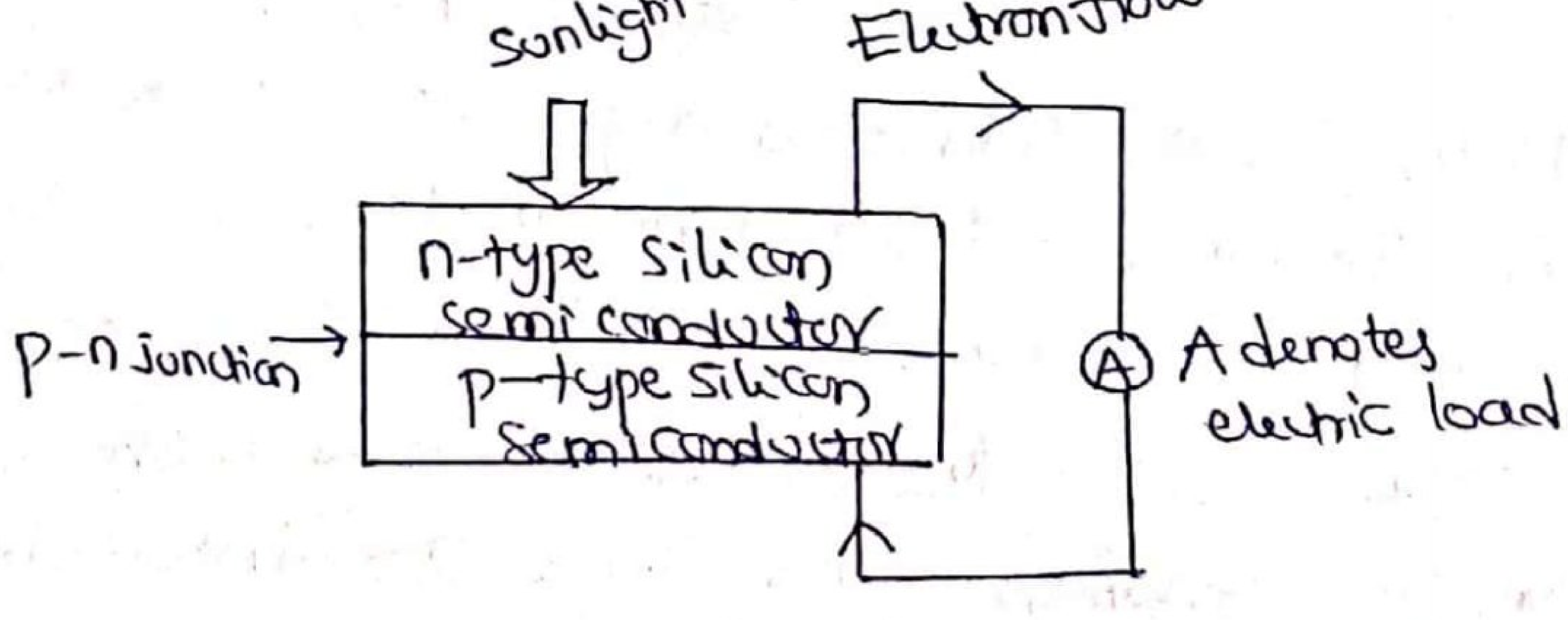
photo voltaic cell : [solar cell]

A solar cell, popularly called a photo voltaic cell, can directly convert solar radiations into electric current.

principle: Solar cells are made of various semiconducting materials, which are made electrically conducting when supplied with heat or light. The major element of such semiconducting materials is crystalline silicon. The working of photovoltaic cell is based on photoelectric effect.

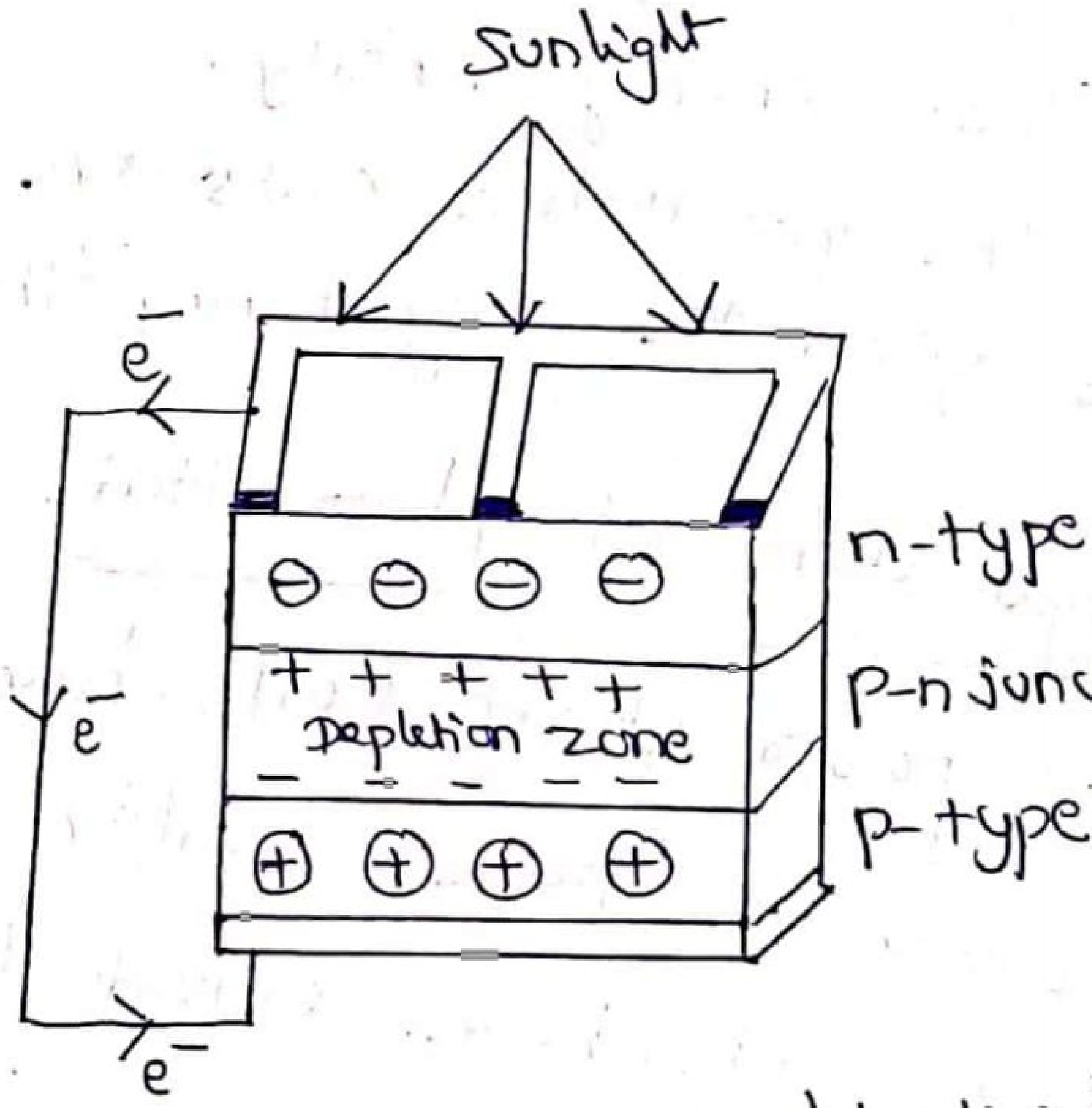
→ It consist of semiconducting device made up of a p-n junction diode, which is the presence of sunlight, generates electrical energy.

constrution: A silicon based photovoltaic cell is made of a thin wafer of ultra thin layer of phosphorous doped (n-type) silicon on top of a thicker layer of boron doped (p-type) silicon. An electric field is created at the point of contact of these layers and when light strikes the surface current is generated.



p-n junction in solar cell.

working : when Sunlight Strikes a photovoltaic cell, the energy rich ~~pho~~ photons are absorbed by the cell. The absorption of a photon results in the dislocation of an electron from the silicon atom and a positive 'hole' is Created. The free electron and positive hole together are neutral and hence need to be Separated so as to generate electricity. when photon hits the cell, free electrons tend to combine with positive holes present on the p-layer.



Working of photovoltaic cell

→ Due to the presence of p-n Junction, it allows electrons to move only in one direction. when an electrical contact is created on the front and rear of the cell connected through an external circuit, free electrons can returns to positive holes only by flowing through this external circuit thereby generating current. The electric power generated from photovoltaic cell is directly proportional to its area and intensity of the Sun's rays that Strike the cell usually measured in watts (W).

Advantages of photovoltaic cell:

1. There are no ~~emm~~ emissions of toxic Combustion products or radio active residues during operations, hence it is eco-friendly.

2. It is low on operating costs as no fuels are involved in the operation.

Disadvantages of photovoltaic cell:

1. As sunlight is diffuse in nature, it provides very low energy density.

2. The installation costs are quite high and energy can be generated only during the day time.

Applications of photovoltaic cells:

1. photo voltaic cells have been used for electric power in space. Solar-powered electric vehicles have also been devised to achieve eco-friendly transporation.

2. various communication signals such as mobiles, radio and television require amplification, and photovoltaic that run low-power transmitters are used in hilly locations.

3. In scientific and climatic studies such as seismic activity monitoring, highway conditions, meterological information, and other research activities can be powered by photovoltaic cell systems. Even portable traffic lights can be powered by these systems.

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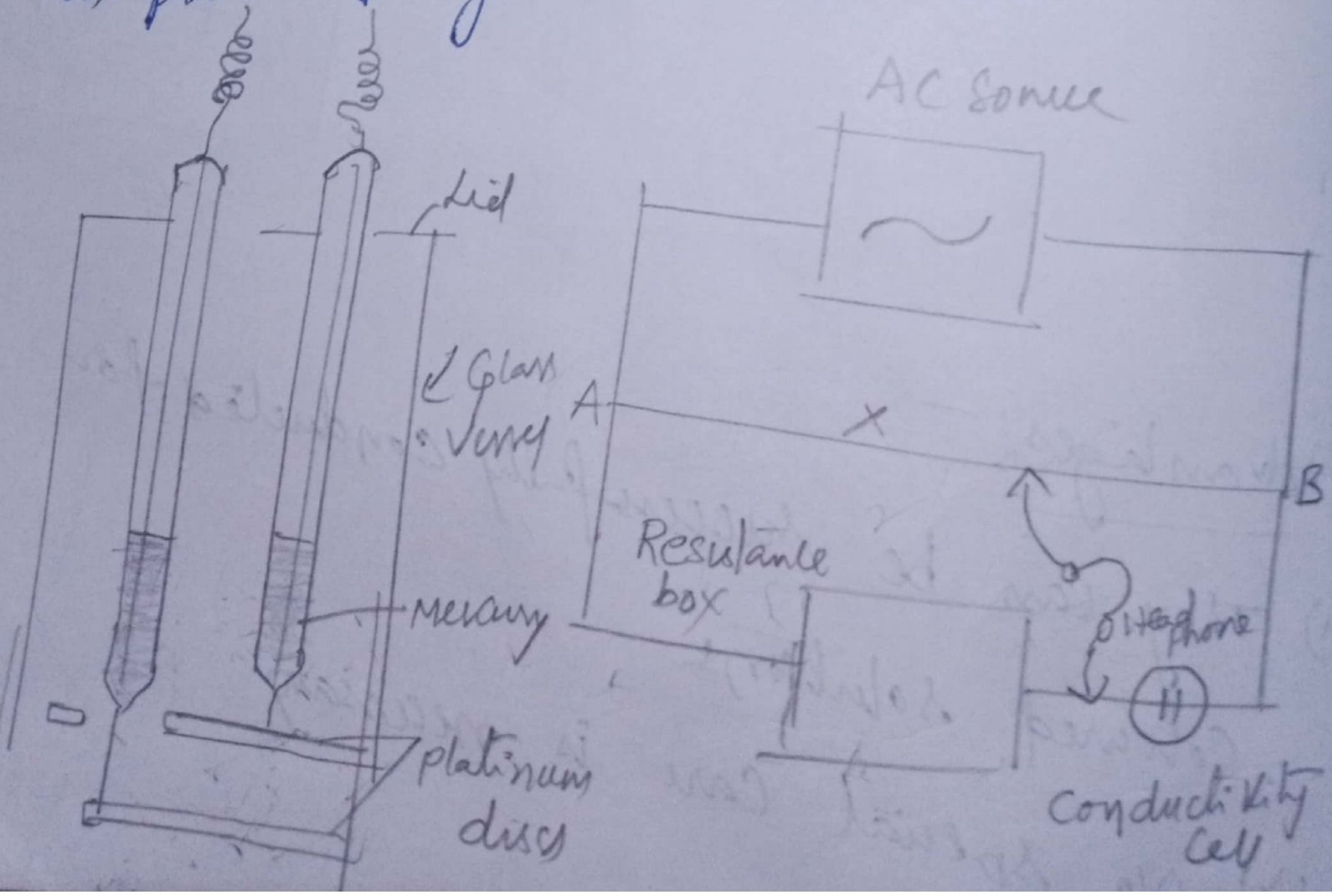

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Thus Specific conductivity = Observed conductivity × Cell consta

Fuel cells :

The galvanic cells can only produce electrical energy for a limited time because the electrod reactants are eventually depleted. fuel cells are different. They are electrochemical cells in which electr reactants are supplied continuosly and are able to operate without theoritical limit as long as the supp of reactant is maintained. This makes fuel cells an attractive source of power where long-term generation of electrical energy is needed.

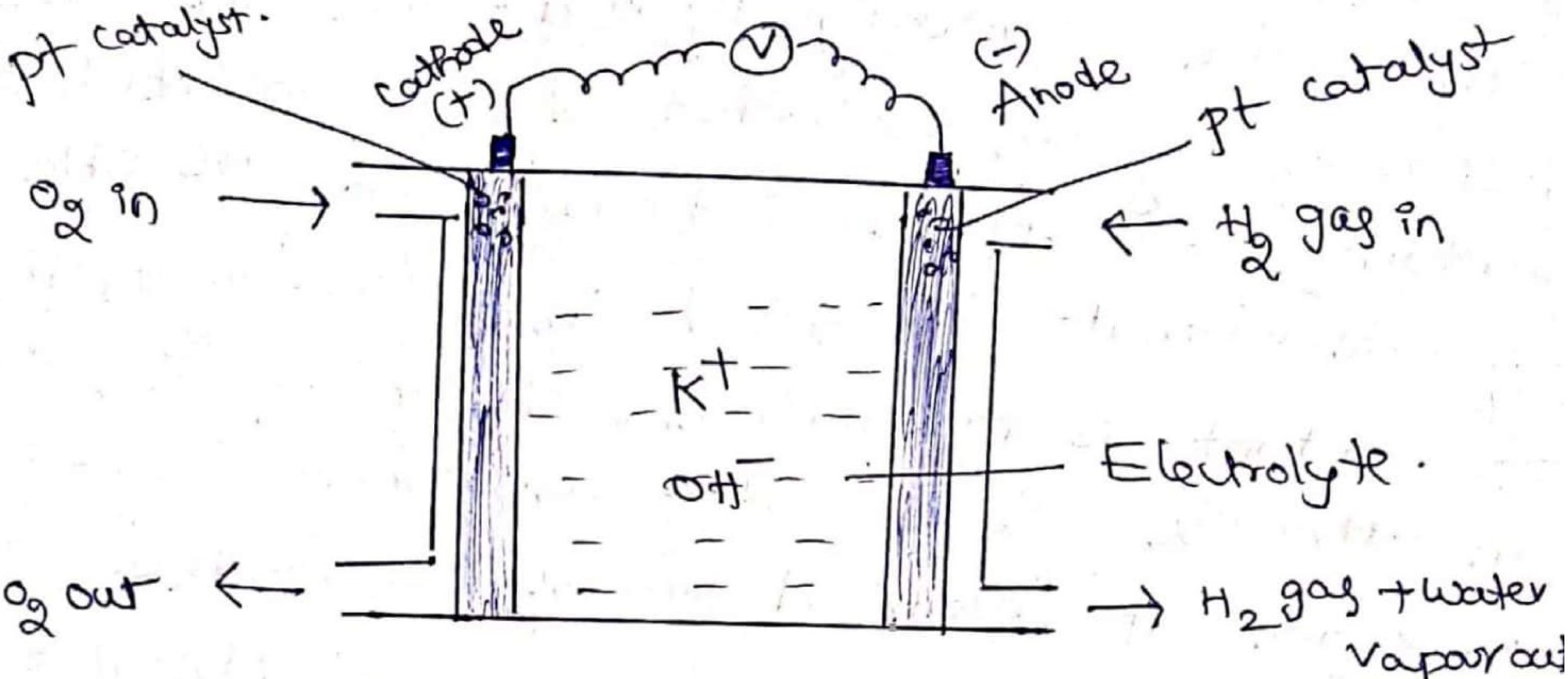
In a fuel cell, an electrical energy is obtained without combustion from oxyge and a gas that can be oxidised. A fuel cell converts the chemical energy of the fuels directl to electricity.

$$\text{Fuel} + O_2 \longrightarrow \text{oxidation product} + \text{Electricity}$$

Hydrogen - oxygen fuel cell :

It consist of ~~two~~ ~~electrolyte~~ two porous electrodes anode and cathode. These porous electrodes are made of compressed carbon containing a small amount of catalyst (pt, pd, Ag). In between the two electrodes an electrolytic solution such as KOH or NaOH is filled.

→ Hydrogen is passed through the anode compartment where it is oxidised. The oxygen is passed through the cathode compartment, where it is reduced.



Hydrogen- oxygen fuell cell

The electrode reaction are as follows.

At Anode:

Hydrogen gas, passed through the anode oxidised with the liberation of electrons, which then combine with hydroxide ions to form water

$$H_2 \rightarrow 2H^+ + 2e^-$$

$$2H^+ + 2OH^- \rightarrow 2H_2O$$

$$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$$

Multiply by 2 : $2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$

At cathode:

Oxygen passed through the cathode, where it is absorbed by oxygen and water to produce hydroxide ions.

$$O_2 + 4e^- \longrightarrow 2O^{2-}$$

$$2O^{2-} + 2H_2O \longrightarrow 4OH^-$$

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$$

Overall cell reaction:

At Anode: $2H_2 + 4OH^- \longrightarrow 4H_2O + 4e^-$

At Cathode: $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

$$2H_2 + O_2 \longrightarrow 2H_2O$$

→ The EMF of the cell = 0.8 to 1.0V.

Applications:-

1. H_2-O_2 Fuel cells are used as auxiliary energy source in space vehicles, submarines, and military vehicles.
2. In case of H_2-O_2 Fuel cells, the product of water proves to be a valuable source of fresh water to the astronauts

Methanol - oxygen Fuel cell :

Methanol - oxygen Fuel cell is made of two Fuel electrodes. one consist of porous nickel plate coated with a catalyst platinum. and other is the similar porous nickel plate coated with a silver catalyst.

In between these electrodes 25% NaOH or KOH is taken. The positive ions (H^+) are transferred across the proton Exchange membrane. Electrons are transported through an external circuit from anode to cathode, providing power to a connected device. Methanol and water are absorbed on a catalysts usually made of platinum particles and lose protons until CO_2 is formed.

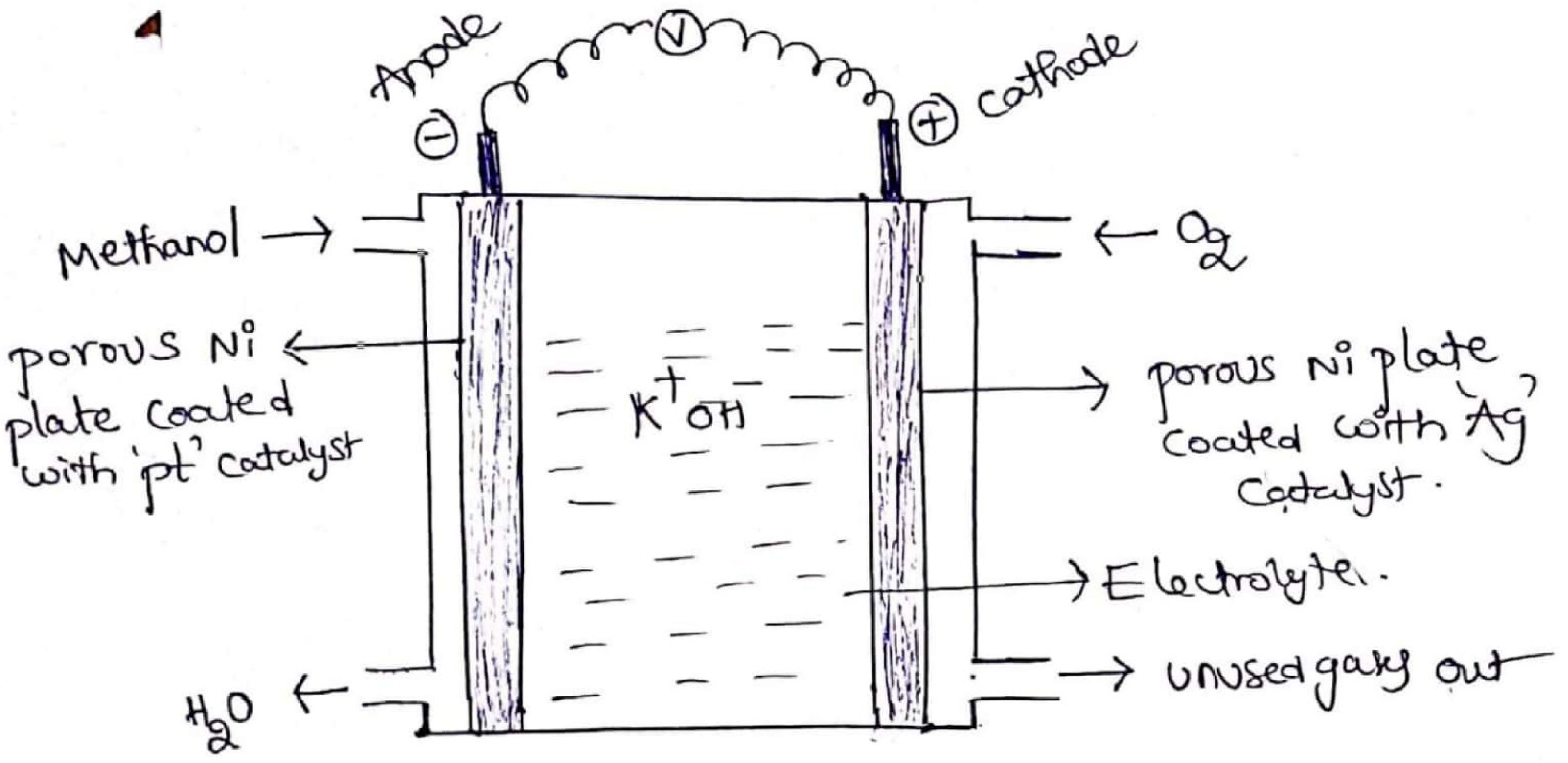
Cell reaction : The following reaction occur at each electrode.

Oxidation : $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$ (A

Reduction : $\frac{3}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$ (cathode)

Redox reaction : $CH_3OH + 3/2\, O_2 \rightarrow CO_2 + 2H_2O$

→ cell voltage 1.21 V.



Methanol – oxygen fuel cell

Limitations: 1. Methanol is toxic and flammable. Hence utmost care has to be taken.

2. Limited in the power they produce.

Advantages:

1. Storage of methanol is much easier than H_2 as it does not need high pressure or low pressure since methanol is liquid from $-97^\circ C$ to $64.7^\circ C$.

2. The energy density of methanol is an order of magnitude greater than even highly compressed hydrogen.