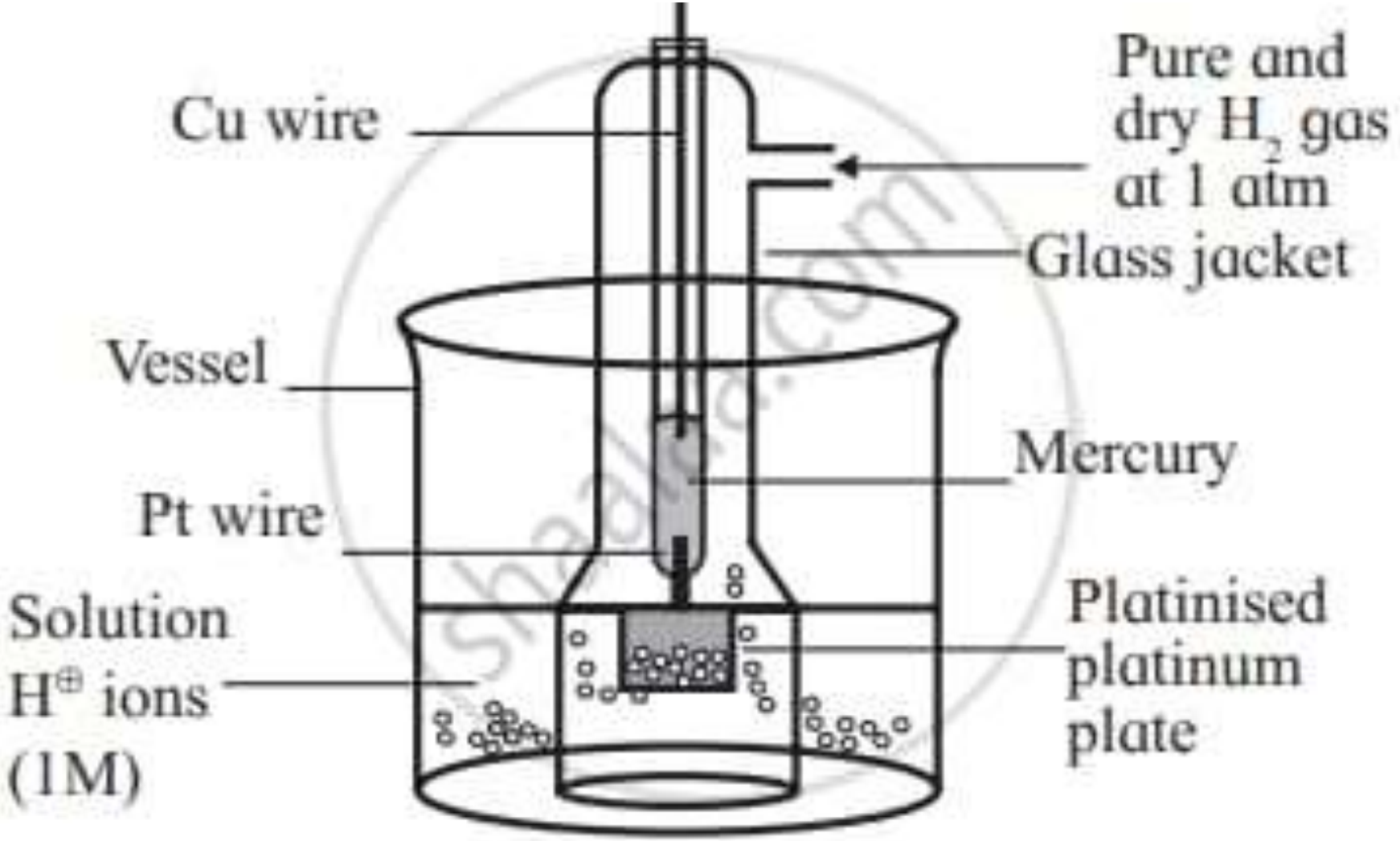
Reference Electrode

The potential of unknown electrode can be measured by coupling it with another electrode, called reference electrode whose potential is already known or arbitrarily fixed as zero. The important reference electrode is standard hydrogen electrode, whose standard electrode potential is taken as zero at all temperature. So, it is called primary reference electrode. It is very difficult to set up a hydrogen electrode. So, other electrode called secondary reference electrode (like calomel electrode) is used.

Standard Hydrogen electrode

Standard Hydrogen electrode is called a primary reference electrode because 1) The emf developed by the standard hydrogen electrode is arbitrarily fixed as zero at 1 atm pressure and the value of which is treated as constant at all temperature. 2) It is an only electrode with which the potential of all other electrodes are compared.

Construction of a Standard Hydrogen Electrode



It consists of rectangular platinum foil which is connected to a platinum wire and sealed in a glass tube. A glass jacket surrounds the tube carrying the platinum foil. The jacket is closed at the top and opened at the bottom. A side tube attached to the outer jacket is used for the injection of hydrogen gas into the cell. This electrode, when dipped in a 1 M HCl solution at 25 oC and hydrogen gas at 1 atm is passed, forms a standard hydrogen electrode.

When this electrode acts as anode, the electrode reaction is as follows :

$$H_2(g) \longrightarrow 2H^+ + 2e^- \text{ (oxidation)}$$

When this electrode acts as cathode, the electrode reaction is as follows:

$$2H^+ + 2e^- \longrightarrow H_2(g) \text{ (reduction)}$$

The standard hydrogen electrode is represented as,

$$Pt, H_2(1\ atm) / H^+ (1\ M); E^0 = 0\ V$$

Development of EMF of SHE

When hydrogen gas is bubbled through the solution, it is adsorbed by the platinum foil. Due to the adsorption of hydrogen gas, the equilibrium is established between hydrogen molecules and H+ ions. The electrode potential developed during this equilibrium is taken as zero and treated as constant at all temperature

Limitation

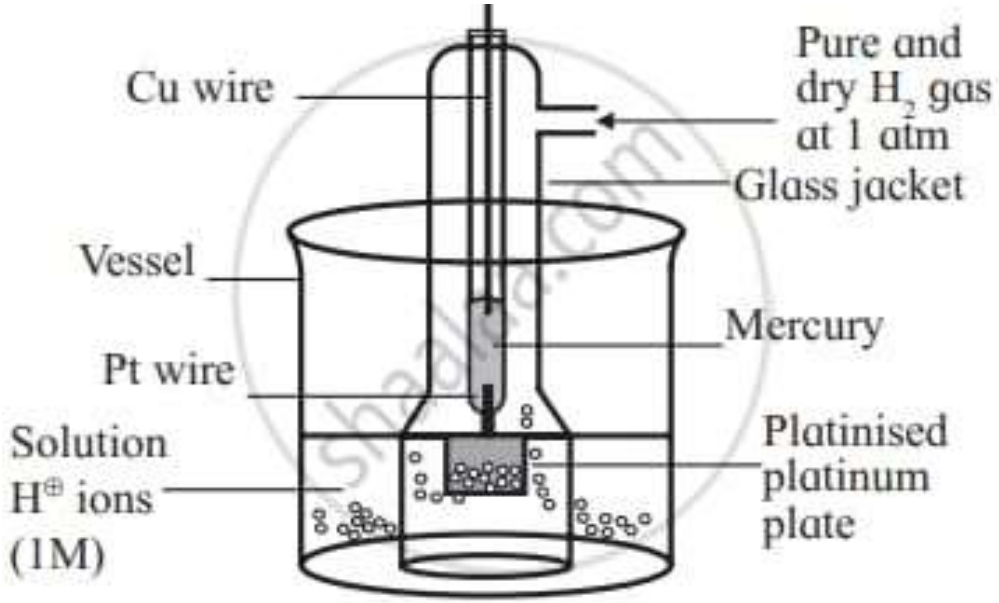
1. It requires H2 gas and is difficult to set up and transport.
2. It requires considerable volume of test solution.
3. The solution may affect the surface of the platinum electrode.
4. The potential of the electrode is altered by changing the pressure of H2 gas.

Need for Secondary Reference Electrode

1.It is very difficult to maintain the H+ ion concentration at 1 M and hydrogen gas pressure at 1 atm.

2.Platinum electrode is poisoned by the presence of impurities in the solution or gas.

Calomel Electrode or Secondary Reference Electrode



To overcome the limitations of hydrogen electrode, the calomel electrode is developed. This is called the secondary reference electrode. It consists of a glass tube. Pure mercury is placed at the bottom of the tube and is covered with a paste of mercurous chloride. The remaining portion of the tube is filled with a saturated solution of KCl. The bottom of the tube is sealed with a platinum wire .

If the electrode acts as anode, the reaction is

$$2Hg(l) \longrightarrow Hg^{2+} + 2e^-$$

$$Hg^{2+} + 2Cl^- \longrightarrow Hg\,Cl\,(s)$$

$$2Hg(l) + 2Cl^- \rightleftharpoons Hg_2Cl_2(s) + 2e^-$$

Mercury undergo oxidation to produce mercurous ion (Hg^{2+})and combines with chloride ion to give mercurous chloride(Hg_2Cl_2). Hence, the concentration of chloride ions is decreased. Calomel electrode the electrode acts as cathode, the reaction is

$$Hg\,Cl\,(s) \longrightarrow Hg^{2+} + 2Cl^-$$

$$Hg^{2+} + 2e^- \longrightarrow 2Hg(l)$$

$$Hg_2Cl_2(s) + 2e^- \longrightarrow 2Hg(l) + 2Cl^-$$

The mercurous ion present in the mercurous chloride undergoes reduction to give mercury. Hence the concentration of chloride ions is increased.

Calomel electrode is represented by Hg | Hg2Cl2(s), KCl (sat.solution).

Characteristics of calomel electrode

1) **The electrode potential of calomel electrode depends on the activity of the chloride ions. When the concentration of chloride ion decreases, the electrode potential of calomel Electrode increases. The single electrode potential of calomel electrode with various concentration of KCl on the hydrogen scale at 298 K are given below**
2) **0.1 N KCl = 0.3338 V**
3) **1 N KCl = 0.2800 V**
4) **Saturated KCl = 0.2422 V**