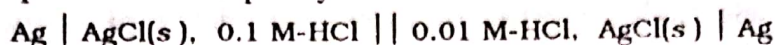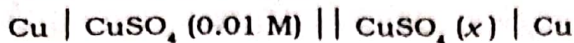3. Calculate the e.m.f. of the following cell at 25°C, assuming that the liquid junction potential is completely eliminated :

$$Ag \mid AgCl(s), \ 0.1 \ M\text{-}HCl \mid\mid 0.01 \ M\text{-}HCl, \ AgCl(s) \mid Ag$$

(Rajasthan B. Sc. 1987)
[Ans. 0.0591 volt]

4. The e.m.f. of the cell,

$$Cu \mid CuSO_4 \ (0.01 \ M) \mid\mid CuSO_4 \ (x) \mid Cu$$

at 25°C is 0.02955 volt, calculate the value of x.

(Magadh B. Sc., 1986)
[Ans. 0.1]

12. REFERENCE ELECTRODES

It is impossible to measure the value of single electrode potential by using a voltmeter or potentiometer. Therefore, it is necessary to assemble first a cell by coupling the given electrode with another electrode, whose potential is either arbitrarily fixed or exactly known. *This type electrode of standard potential, with which we can compare the potentials of all other electrodes, is called a* **reference electrode.** Thus, by knowing the e.m.f. of the assembled cell and the electrode potential in question can easily computed. The best reference electrode used is *standard hydrogen electrode.* By convention, *the electrode potential of standard hydrogen electrode at all temperatures is taken as zero.* However, in view of the difficulties encountered in setting up of a hydrogen electrode, various **subsidiary reference electrode** are also used. Importants reference electrodes are :

(1) **Hydrogen electrode.** It consists of a small platinised platinum foil (about 0.5 cm square), which is sealed through the end of a glass tube. This
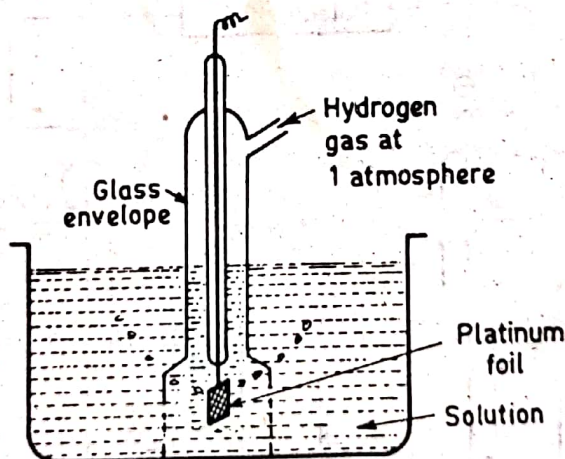

Fig. 11. Hydrogen electrode.

tube is surrounded by another co-axial tube, which is sealed to the inner glass tube at the top. The outer glass tube is provided with a side-arm for passing hydrogen gas into the in-between space. The bottom of the outer tube is flared into a bell, around the platinum electrode. Openings in the bell allow the escape of hydrogen gas. The platinum foil is coated with a layer finely divided platinum (called *platinum black*), which adsorbs the hydrogen gas and it also speeds up the equilibrium between hydrogen gas and the hydrogen ions (H^+ or H_3O^+). This electrode when dipped in a 1 N-HCl and when hydrogen at 1 atmosphere is passed through, a *normal or standard*

hydrogen electrode is formed. The e.m.f. of such a cell has arbitrarily been fixed at zero.

Hydrogen electrode may be employed to find the pH value of an unknown solution. For this, the solution whose pH is to be determined is taken in a vessel and a platinum electrode is half-dipped in it. A slow current of hydrogen gas at 1 atmosphere is bubbled through the solution. The platinum catalyses the following electrochemical reaction at the electrode,

$$H^+ + e^- \rightleftharpoons \tfrac{1}{2} H_2(g)$$

and this couses the electrode to develop a definite potential, depending on the H^+ ion concentration on the solution under-test.

$$E = E^\circ - \frac{2.303}{nF} \log \frac{[H_2]^{1/2}}{[H^+]}$$

$$= 0 - \frac{0.0591}{1} \log \frac{[H_2]^{1/2}}{[H^+]} \qquad \text{(At 25°C)}$$

$$= -0.0591 \log \frac{1}{[H^+]}$$

(∵ Activity of hydrogen gas at 1 atm = 1)

or $\qquad\qquad E = -0591 \text{ pH.}$

...(i)

The above half-cell so-formed is conncected to a standard or normal hydrogen electrode (i.e. having a solution of 1 N-HCl). The two solutions are
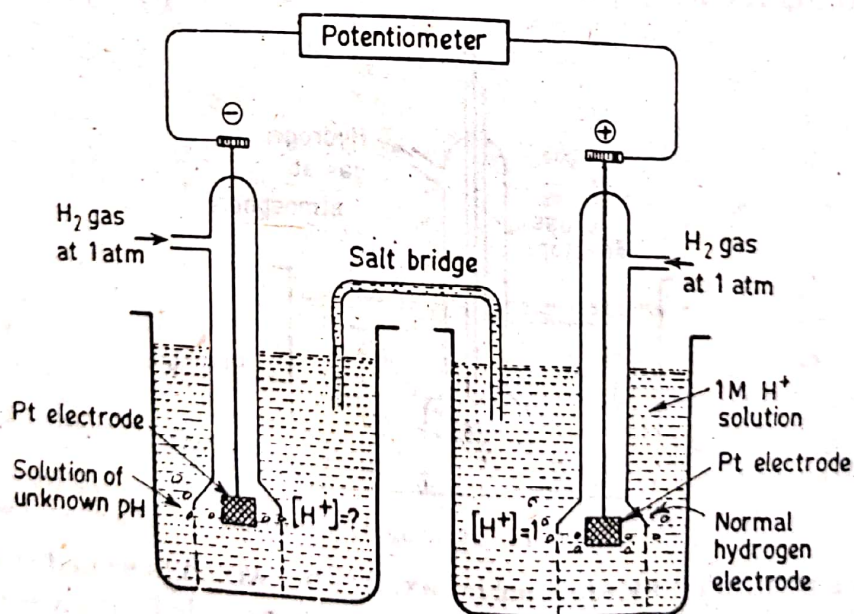

Fig. 12. Measurement of pH by hydrogen electrode.

separated by a salt bridge to eliminate liquid junction potential. The e.m.f. of the full cell is then determined by means of a potentiometer. Since e.m.f. of reference electrode is zero, therefore, the observed e.m.f. gives directly the e.m.f. of half cell containing the solution under-test.

$$\therefore \qquad E_{cell} = E_{right} - E_{left}$$

or

$$E_{cell} = 0 - (-0.0591 \text{ pH}) = 0.0591 \text{ pH}$$

$$\therefore \qquad pH = -\frac{E_{cell}}{0.0591} \qquad \qquad ...(ll)$$

Limitations : (1) The hydrogen electrode is readily affected by compounds of Hg, As, S and oxidising agents like, Fe^{3+}, MnO_4^-, $Cr_2O_7^{2-}$, etc., and consequently, this electrode cannot be used in solutions containing these ions.

(2) It cannot be used in the presence of ions of many metals.

(3) It cannot be used in solutions containing redox systems.

(4) It is quite cumbersome to set up a hydrogen gas electrode.

(2) **Calomel electrode** is the most commonly used subsidiary reference electrode. It is the *mercury-merecurous chloride electrode.* It can be conveniently set up and used for a long time, without any subsequent attention. *The potential of the calomel electrode, on the hydrogen scale, has been found to vary with the concentration of the potassium chloride solution used.* The reduction potentials for the various KCl concentrations at 25°C are :

KCl concentration	0·1-N	1·0-N	Saturated
Electrode potential (in volt)	0·3335	0·2810	0.2422

When the KCl solution is 0.1-N, 1.0-N and saturated, it is called respectively as *decinormal, normal* (NCE) and *saturated calomel electrode* (SCE).

The electrode reactions taking place in this half-cell is :

$$Hg_2Cl_2(s) + 2e^- \longrightarrow Hg(l) + 2Cl^-.$$
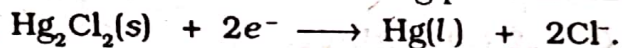
The potential of this electrode is thus, due to the *reduction of mercurous ions to mercury.* Its value is equal to the e.m.f. of the cell.

$$- \text{Pt, H}_2 \text{ (1 atm)} \mid H^+ \text{ (1 M)} \mid\mid \text{KCl (0.1 N or or satd.)} \mid Hg_2Cl_2. Hg^+$$

since potential of hydrogen electrode is zero.

Construction. It consists of a tube in the bottom of which is a layer of mercury, over which is placed a paste of $Hg + Hg_2Cl_2$. The remaining

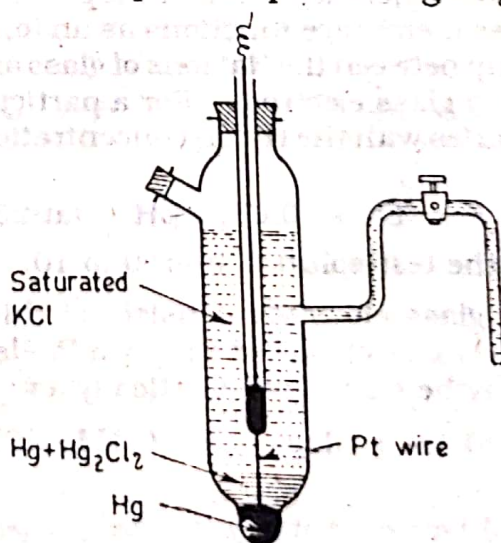
Saturated KCl

$Hg+Hg_2Cl_2$

Pt wire

Hg

Fig. 13. Saturated calomel electrode.

portion of cell is filled with a solution of normal or decinormal or saturated solution of KCl. A platinum wire, dipping into the mercury layer, is used for making electrical contact. The side-tube is used for making electrical contact with a salt bridge. The saturated calomel electrode is formulated as :

$$Hg.Hg_2Cl_2(s), \ KCl \ (satd. \ solution).$$

The electrode can be coupled with hydrogen electrode containing solution of unknown pH.

$$Pt. \ H_2 \ (1 \ atm) \ || \ H^+ = ? \ || \ Hg_2 \ Cl_2(s) \ | \ Hg^+.$$
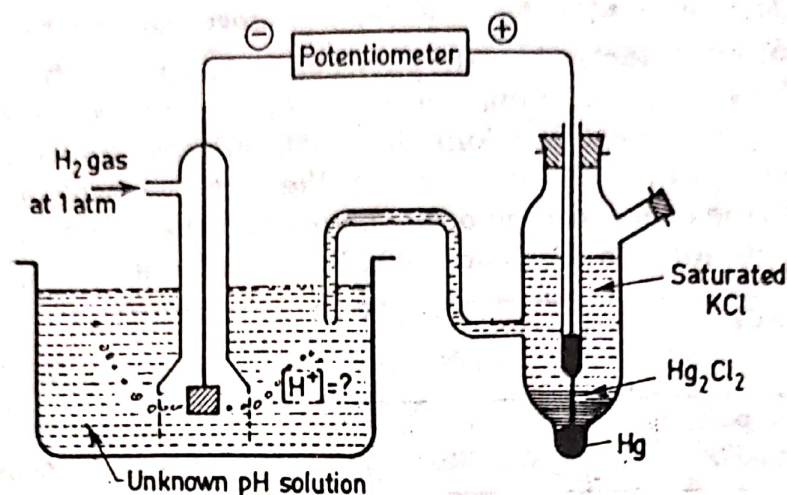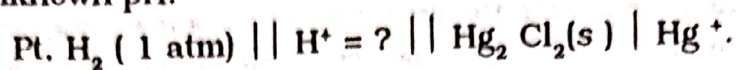
Fig. 14. Determination of pH value of a solution.

The e.m.f. the cell,

$$E_{cell} = E_{right} - E_{left}$$

$$= 0.2422 + 0.0591 \ pH$$

$$\therefore \qquad pH = \frac{E_{cell} - 0.2422}{0.0591} \qquad \qquad ...(iii)$$

(3) **Glass electrode.** It has been found experimentally that *when two solutions of different pH values are separated by a thin glass membrance, there develops a difference of potential between the two surfaces of the membrace. The potential difference developed is proportional to the difference in pH value.* The glass membrace functions as an ion-exchange resin, and an equilibrium is set up between the Na^+ ions of glass and H^+ ions in solution. This forms the basis of glass electrode. For a particular type of glass, the potential difference varies with the H^+ ion concentration, and is given by the expression :

$$E = E^\circ + 0.0591 \ pH \qquad (at \ 25°C) \qquad ...(iv)$$

over a range of pH of the test-solution from 0 to 10.

·*Construction.* A glass electrode consists of thin-walled glass bulb* containing AgCl-coated Ag electrode or simply a Pt electrode in 0.1 M-HCl. The glass electrode may be shown schematically as :

- $Ag \ | \ AgCl(s), \ HCl \ (0.1M \ | \ Glass \ or \ Pt, \ 0.1M \ HCl \ | \ Glass^+$

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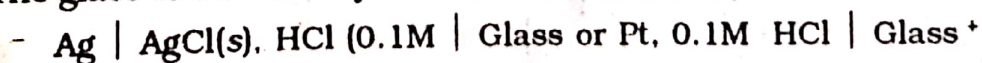
*The glass is of a special type of relatively low melting point and high electrical conductivity.

HCl in the bulb furnishes a constant H^+ ion concentration. Thus, it is a silver-silver chloride, electrode reversible with respect of chloride ions.
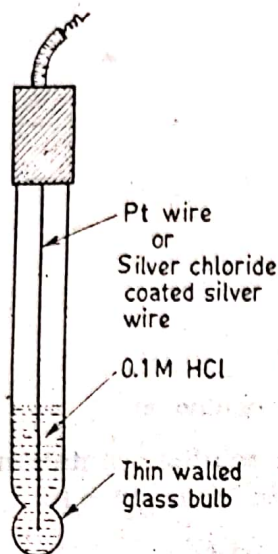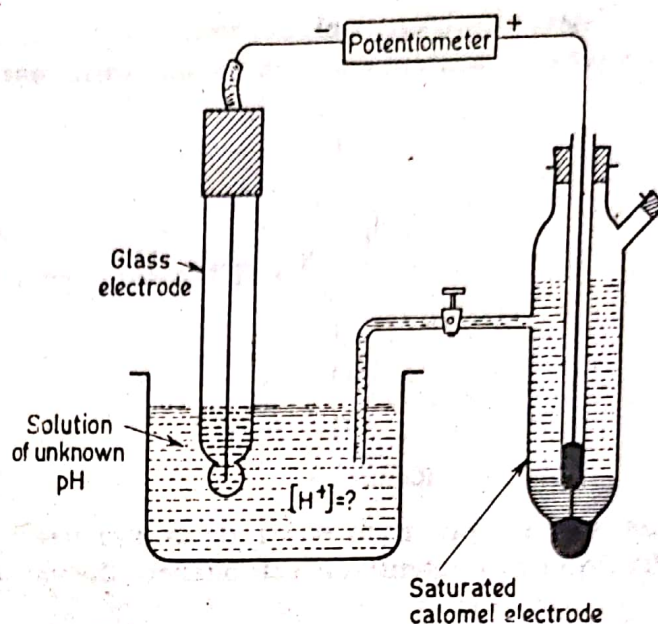

Fig. 15. Glass electrode.

Fig. 16. Determination of pH by glass electrode.

Glass electrode is, usually, used as the "internal reference electrode". It is mostly used for determining the pH of solutions, especially coloured solutions containing oxidizing or reducing agents. Usually, calomel electrode is used as the second electrode. In order to determine the pH of a solution, the glass electrode is placed is the solution under-test and this half-cell is coupled with saturated calomel electrode (see Fig. 16). The e.m.f. of the cell is measured. Since the resistance is very high, so special electron-tube voltmeters are used to measure the e.m.f. of the above cell. The e.m.f. of the complete cell is given by :

$$E_{cell} = E_{right} - E_{lect}$$

$$= 0.2422 - [E^{\circ}_G + 0.0591 \text{ pH}] \qquad \text{(At 25°C)}$$

whence,

$$\boxed{\text{pH} = \frac{0.2422 - E_{cell} - E^{\circ}_G}{0.0591}}\qquad ...(v)$$

The E°_G value of a glass electrode can be determined by using a solution of known pH.

Advantages of glass electrode : (1) It is simple and can easily be used, (2) Equilibrium is rapidly achieved. (3) The results are accurate. (4) It is not easily poisoned.

Limitations : (1) The glass electrode can be used in solutions with pH range of 0 to 10. Electrodes composed of special glasses can be used for measurements up to a pH of 12. However, above 12 pH, cations of solution affect the glass interface and render the electrode useless.

(2) Although glass membrance of electrode is very thin, yet its resistance is extemely high (of the order of 10 to 100 million ohms), which can not be measured