OTHER REFERENCE ELECTRODES

The standard hydrogen electrode (SHE) is not the most convenient standard electrode to use in the laboratory. The gas has to be carefully controlled and hydrogen gas can form explosive mixtures with air. Any other electrode system whose potential has been determined relative to the SHE can also be used as **Secondary standard electrode.**

(1) The Standard Silver-Silver Electrode

In this electrode system, silver wire (or strip) is covered with silver chloride (a highly insoluble substance). It is dipped in potassium chloride solution in which the concentration of Cl^- ion is 1 M This electrode can be represented as

$$Ag, AgCl \,|\, Cl^- (1\ M)$$

The half-cell reaction of the Ag-AgCl electrode is

$$AgCl + e^- \longrightarrow Ag + Cl^-$$

We can set up a cell involving this electrode and the hydrogen electrode

$$Pt\ ,\ H_2 \,|\, H^+ (1\ M) \,\|\, Cl^- (1\ M) \,|\, AgCl, Ag$$

with a KCl salt bridge connecting the two solutions. The emf of the combined cell is found to be 0.2224 V. Thus the standard electrode potential for the silver-silver chloride electrode is 0.2224 V.

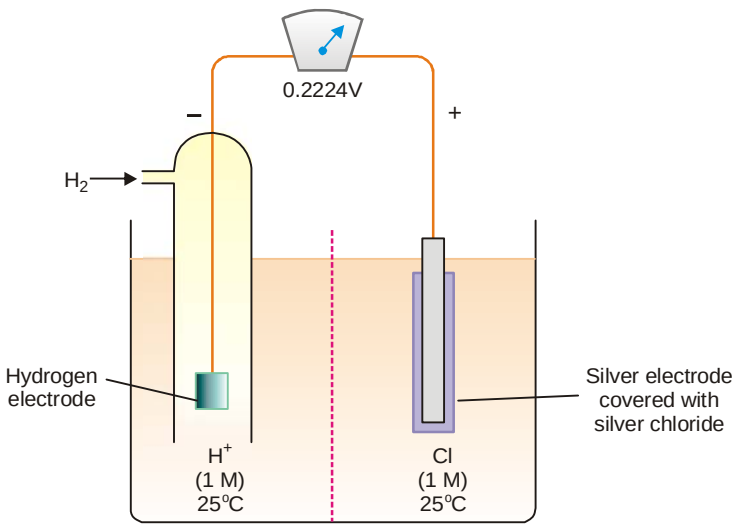

Figure 29.13
Schematic diagram of Ag-AgCl electrode coupled with SHE (salt bridge replaced by porous partition).

(2) The Calomel Electrode

It is the most commonly used secondary standard reference electrode. The standard calomel electrode, **SCE,** consists of a wide glass-tube with a narrow side-tube. It is set up as illustrated in Fig. 29.14. A platinum wire is dipping into liquid mercury covered with solid mercurous chloride (Hg_2Cl_2, calomel). The tube is filled with a 1 M solution of KCl (or saturated KCl solution). The side-tube containing KCl solution provides the salt bridge which connects the electrode to any other electrode.

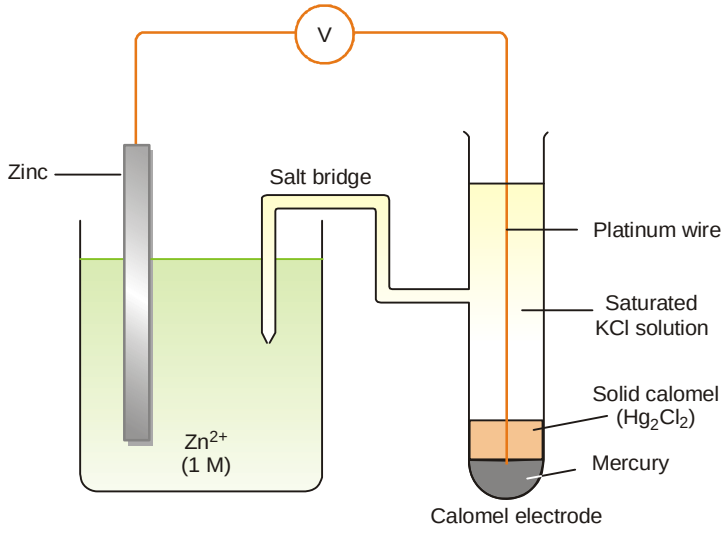

Figure 29.14
The calomel electrode coupled with zinc electrode to determine its emf.

The calomel electrode is represented as

$$Cl^-\,(1M)\,|\,Hg_2Cl_2,\,Hg$$

and the half-cell reaction is

$$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$$

The emf of the cell

$$Pt\,,\,H_2\,|\,H^+\,\|\,KCl\,(1\,M)\,|\,Hg_2Cl_2\,,\,Hg$$

at 25°C is + 0.280 V. That is, the calomel electrode emf with respect to the standard hydrogen electrode is + 0.280 V. This means that **0.280 must be added to any electrode potential measured against a calomel electrode.** This would give the standard potential on the standard hydrogen scale.

Note. The potential of the calomel electrode depends on the concentration of KCl solution taken in the half-cell. Thus for 0.1M KCl solution emf is 0.3338 Volt; for 1M solution emf is 0.2800 Volt; and for saturated KCl solution emf is 0.2415 Volt.

Determination of emf of the standard zinc half-cell using calomel electrode

The zinc half-cell is connected with the standard calomel electrode as shown in Fig. 29.14. The emf of the complete cell is then measured with the help of a voltmeter. It is found to be 1.040 V. Since zinc forms the negative electrode of the cell, its emf with respect to calomel electrode will be – 1.040 V. The addition of 0.280 gives the standard electrode potential of zinc.

$$(-1.040 + 0.280) = -0.76\ V$$

The dipping calomel electrode

For many purpose, a calomel electrode is manufactured as a self-contained unit. It is used by simply dipping the tip of the electrode in the solution of another electrode whose emf is to be determined. This type of electrode is often referred as the dipping calomel electrode (Fig. 29.15).

The mercury and calomel (Hg_2Cl_2) are held in a narrow central tube by a porous cotton wool plug. A platinum wire dips into the mercury. The KCl saturated solution contained in the electrode makes contact with the other electrode solution through a sintered glass disc. This disc functions as a 'salt bridge' between the two electrode solutions. Thus a galvanic cell is set up and its emf is measured with the help of a voltmeter.

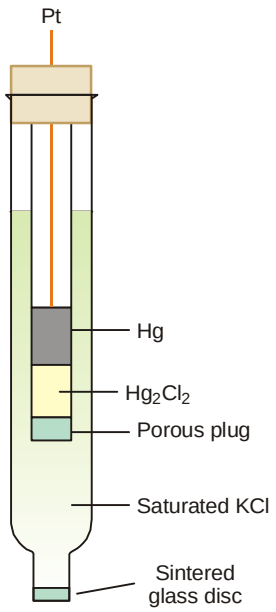

Figure 29.15
A dipping calomel electrode.

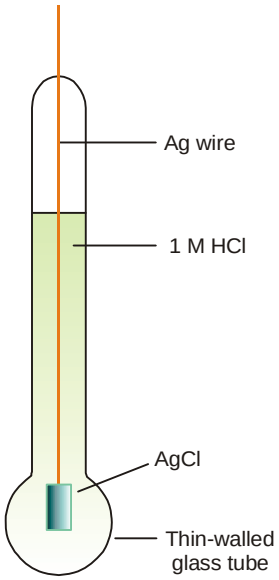

Figure 29.16
Glass electrode

The Glass Electrode

A commonly used secondary standard electrode is the so-called glass electrode. Its emf is determined by coupling with a standard calomel electrode (SCE). The glass electrode provides one of the easiest methods for measuring the pH of a given solution.

A simple type of glass electrode (Fig. 29.16) consists of a glass tube having a thin-walled bulb at the lower end. The bulb contains a 1M HCl solution. Sealed into the glass-tube is a silver wire coated with silver chloride at its lower end. The lower end of this silver wire dips into the hydrochloric acid, forming silver-silver chloride electrode. The glass electrode may be represented as

$$Ag, AgCl \mid 1\ M\ HCl \vdots H^+ \text{ (Test Solution)}$$

When placed in a solution, the potential of the glass electrode depends on the H^+ ion concentration of the solution. The potential develops across the glass membrane as a result of a concentration difference of H^+ ions on the two sides of the membrane. This happens much in the same way as the emf of a concentration cell develops.

The potential of a glass electrode can be determined against a standard calomel electrode (SCE).

Quinhydrone Electrode

It is a widely used secondary standard electrode. It involves the redox reaction between quinone (Q) and hydroquinone (QH_2),