are 1, and the relation is

$$2H^+ + 2e^- \rightleftharpoons H_2(g) \tag{6.14}$$

A typical hydrogen electrode is presented in Fig. 6.2. The platinum electrode uses a platinum foil coated with platinum black to provide a large surface area and a reversible reaction, Eq. (6.14) rapidly proceeds, with the solution near the electrode kept saturated with respect to the gas. The electrode can be either an anode or a cathode with hydrogen being oxidized to hydrogen ions, or vice versa.

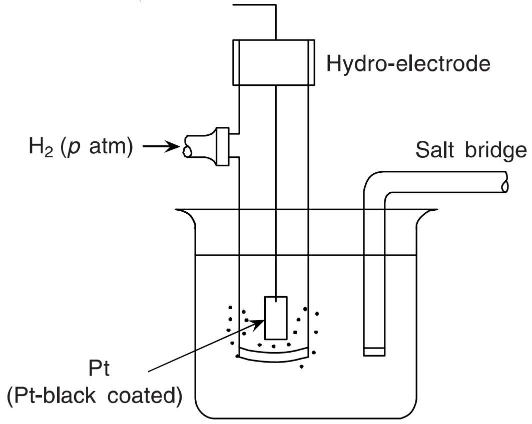

Fig. 6.2 Structure of a hydrogen electrode.

For measurement of potential using SHE or any second standard using Nernst equation, Eq. (6.12), two things are of importance, namely (i) the sign of the electrode potentials and (ii) the value of the standard electrode potential. The sign, in fact, is determined by the specific use of the electrode such as anode or cathode. If the electrode is used as an anode from which electrons flow through the external circuit to the SHE, this would be the negative terminal of the galvanic cell and its standard electrode potential (SEP) is negative; on the other hand, SEP is positive for the cathodes. International Union of Pure and Applied Chemistry (IUPAC) specifies that relative external potential is reserved for half-reactions as reductions. The magnitude of the SEP of an electrode is, as has already been mentioned, the value of the electrode potential of a half-cell reaction with respect to SHE when all reactants and products possess unit activity. Tables have been prepared by determining the SEP by actual measurements with SHE or other reference electrodes as the other half-cell.

6.5 LIQUID JUNCTIONS AND OTHER POTENTIALS

The liquid junction potential arises when two electrolyte solutions of different chemical compositions come in contact because of unequal distribution of positive (cations) ions and negative (anions) ions across the junction which, in turn, is due to the difference in their migratory speeds. The speeds are governed by the concentration difference between the electrolytes since migration occurs from higher to lower concentration of solutions. Besides, mobility is also a factor affecting migratory speeds of the ions. The two factors try to counteract and an equilibrium condition develops providing a specific potential value depending upon the above considerations, that is, half-cell specifications.

The junction potential may be quite large in value and in measurement of the cell potential, its contribution cannot be ignored. Neither can it be easily computed except in some simple situations. It can, however, be reduced by introducing a salt bridge, as has already been mentioned. Salt bridge is actually a concentrated electrolyte solution that joins the two half-cell electrolytes. Often, saturated potassium chloride is used as salt bridge because of its high concentration (4 M at room temperature) with respect to the half-cell electrolyte concentrations and its low ion mobility variation in many situations, specially with chlorides in half-cells.

Salt bridge solution should be selected in such a way that no interference occurs between this and the half-cell solutions. A typical cell structure with salt bridge is shown in Fig. 6.3.

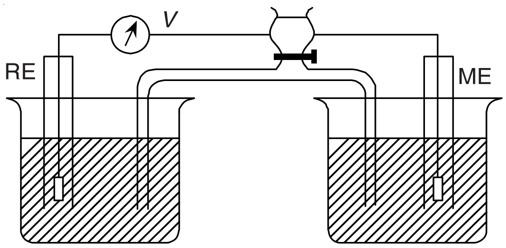

Fig. 6.3 Cell structure with salt bridge.

With a current flowing in the cell, there occurs an ohmic drop, following the Ohm's law, and the resistance of the cell contributes to the magnitude of this drop. In effect, the measured potential becomes less. The relations expressing the mechanism are as follows:

$$E_{\text{thermodynamic}} = E_{\text{cathode}} - E_{\text{anode}} \tag{6.15a}$$

$$E_{\text{cell}} = E_{\text{thermodynamic}} - IR \tag{6.15b}$$

or,

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} - IR \tag{6.16}$$

6.6 POLARIZATION

With electrode potentials being constant, as is usually the case, cell potential E_{cell} should be linearly related to cell current I as is seen from Eq. (6.16). But, sometimes this is not the situation. The nonlinearity that arises is due mainly to *polarization* which is manifested as reduction of current or corresponding overvoltage. There are four types of polarization, namely concentration polarization, reaction polarization, adsorption/desorption/crystallization polarization, and charge transfer polarization.

Concentration polarization

Oxidation–reduction at the electrode surfaces can occur normally when the movement of 'Ox' and/or 'Red' species across the bulk of the electrolyte by mass transfer is normal. If not, reaction rate decreases and correspondingly the current. This is due to what is known as concentration polarization.

Reaction polarization

If there is any intermediate chemical reaction in any half-cell for producing 'Ox' or 'Red' species that travel to electrodes and which participate in electron transfer, it is likely that formation of these species at the intermediate stage is not normal. This is known as reaction polarization.

Adsorption/desorption/crystallization polarization

Sometimes the current is limited by processes such as adsorption/desorption or crystallization of the reactants and hence, the name.

Charge transfer polarization

Charge transfer takes place from the electrode to oxidized species or from reduced species to the electrode. Often, the rate of charge transfer is reduced because of the existence of a charge surface film around the electrodes. This is called charge transfer polarization or electrical polarization. Figure 6.4 graphically shows the polarized and unpolarized conditions of a cell.

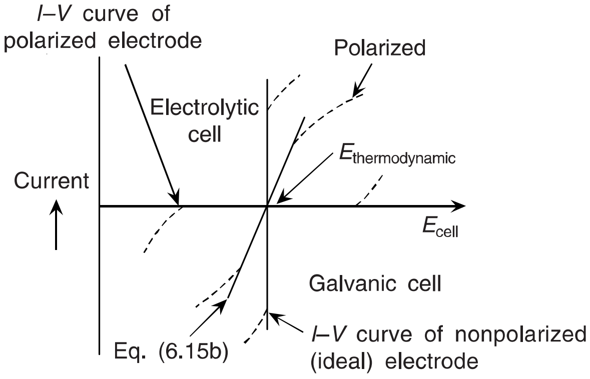

Fig. 6.4 Polarized and unpolarized conditions of a cell.

As has already been discussed, the concentration and/or type of an electrolyte solution can be measured by measuring the potential of a cell containing the solution, the cell being made up of two half-cells each with one electrode. Of these, one must be a reference electrode with, perhaps, zero electrode potential as in SHE. But, reproducible forms of reference electrodes are different than SHE. The other electrode is the measuring or indicating, or actual sensor electrode.

6.7 REFERENCE ELECTRODES

The reference electrodes are required to have a known and constant half-cell potential unaffected by solution composition. Their properties can be listed as they must

1. have known constant potential and follow Nernst equation,
2. have reversible cell-reaction,
3. have little or no hysteresis with temperature and small current cycling,
4. be non-polarized.

Some electrodes have been designed and used in practice which more or less follow these properties. The commercially used ones are:

- Saturated calomel electrode (SCE),
- Silver/silver chloride electrode, and
- Thallium/thallouschloride electrode.

Figure 6.5 shows the elements of a commercial type SCE. The chemists' nomenclature for the electrode function is given as

$$\mathrm{Hg(l)}\,|\,\mathrm{Hg_2Cl_2(satd)},\quad \mathrm{KCl(aq)}\,\| \tag{6.17}$$

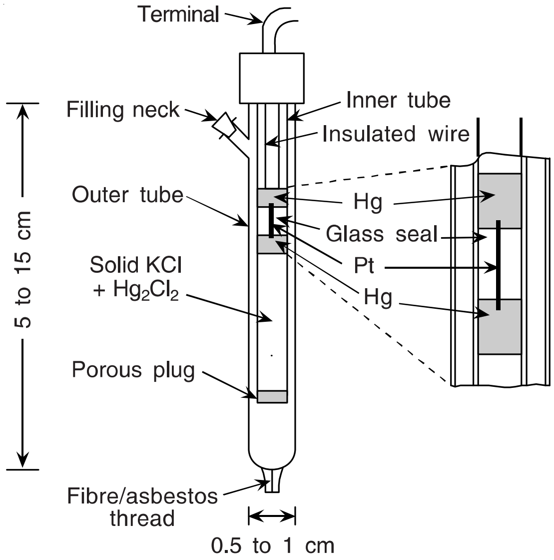

Fig. 6.5 Schematic view of a saturated calomel electrode.

The corresponding electrode reaction is

$$\mathrm{Hg_2Cl_2(s)} + 2e \rightleftharpoons 2\mathrm{Hg(l)} + 2\mathrm{Cl^-} \tag{6.18}$$

The electrode consists of an inner glass/plastic tube containing Hg, Hg_2Cl_2, and KC1. This tube dips into a saturated solution of KCl and Hg_2Cl_2(calomel) contained in an outer tube made of the same glass/plastic material. The junction to the other half-cell for electrical continuity is made through a fibre of quartz or asbestos, a crack, a ceramic plug, or a glass sleeve. Platinum wire is used for external connection. Provision for refilling with KCl/aqua is also there. A normal calomel electrode containing 1 M KCl and decinormal type with 0.1 M KCl can also be made; but the SCE, the saturated electrode is most commonly used in practice. The glass-sleeved or ceramic plug junction type design has lower impedance than the fibre type where output impedance may be as high as 3 kΩ. The electrode potential at 25°C for different concentrations of KCl is tabulated in Table 6.1.

Table 6.1 KCl concentration versus electrode potential

KCl	*Saturated*	4.0 M	3.5 M	1 M	0.1 M
E_{electro} (V)	0.244	0.246	0.250	0.280	0.336

Note: These potentials have been accurately measured with reference to SHE.