The Ag–AgCl electrode can be used as a reference electrode which responds to the concentration of an anion with which its ion either forms a precipitate or a stable complex ion. It is made by dipping a silver wire into a solution of specified KCl and into which AgCl is added till saturation. KCl strength may be 3.5 M or 1 M with electrode potentials 0.199 V and 0.222 V respectively at 25°C. Functional state and reaction relations can be given as

$$\text{Ag} \mid \text{AgCl (satd), KCl(kM)} \parallel \tag{6.19}$$

and

$$\text{AgCl(s)} + \text{e} \rightleftharpoons \text{Ag(s)} + \text{Cl}^- \tag{6.20}$$

Thallium electrode is not as common as the other two but has the advantage that it attains equilibrium potential much more rapidly than the others after a change in temperature. Its functional state relation is

$$\text{Tl(vo\%)} \mid \text{TlCl(satd), KCl (satd)} \parallel \tag{6.21}$$

The major source of error in the reference electrode is the contamination through the junction plugs and for this, the cell may behave erratically. Fortunately, the amount of contamination is so very negligible that it is of no concern for the electrode performance. But this leads to lower capacity cell as far as current rating is concerned.

6.8 SENSOR ELECTRODES

Sensor electrodes, or indicator electrodes as they are commonly known, are of two kinds: (a) metal, (b) membrane.

6.8.1 Metal Electrodes

Metal electrodes are similar to reference electrodes which can be subclassified to be of (i) the first kind, (ii) the second kind, (iii) the third kind, and (iv) the redox type.

(i) *The first kind electrode:* Such an electrode is in direct equilibrium with the cation derived from electrode metal. For such a case, denoting metal with μ,

$$\mu^{k+} + k\text{e} \rightleftharpoons \mu(\text{s}) \tag{6.22}$$

and the electrode potential is given by the standard equation

$$\begin{aligned} E &= E_\mu^0 - \frac{0.0591}{k} \log \frac{1}{\mu^{k+}} \\ &= E_\mu^0 - \frac{0.0591}{k} p\mu \end{aligned} \tag{6.23}$$

where $p\mu$ denotes the negative logarithm of the μ-ion concentration. The metals in this category are Cu, Zn, Ag, Hg, Cd, and Pb. They show reversible oxidation–reduction behaviour.

(ii) *The second kind electrode:* As has already been mentioned in Sec. 6.7, this electrode is responsive to the concentration of an anion and its own ion makes precipitate with it or forms a complex ion. Ag, for example, can be used as a second kind electrode with respect to halide ions and for measurement purposes, the surface layer of the analyte has to be saturated with AgCl. Then one writes

$$AgCl(s) + e \rightleftharpoons Ag(s) + Cl^- \tag{6.24}$$

and

$$E = 0.222 - 0.0591 \log[Cl^-] \tag{6.25}$$

(iii) *The electrode of the third kind:* It responds to a different cation under certain circumstances. For example, Hg-electrode can be used to determine the Ca ion concentration in solutions containing calcium. This is possible, however, by introducing a complex of calcium and maintaining a certain concentration of the complex for standardization. The chain of processes makes the electrode a third kind.

(iv) *Redox electrode:* An electrode, usually made of inert metal, is immersed in a solution containing a substance in the reduced or oxidized state; the electrode would acquire a potential depending on the tendency of the ions in the solution to pass from a higher to a lower state of oxidation or from a lower to a higher state of oxidation. If the solution has a reducing property, the ions will tend to be oxidized losing electrons to the electrode and it becomes negatively charged with respect to the solution. The case reverses if the solution has oxidizing property. The potential value of the electrode will be a measure of the oxidizing or reducing power of the solution whereas the sign of the potential gives the actual characteristic. With α_+ as the activity of the oxidized ion and α_- that of the reduced ion, electrode potential is obtained as

$$E = E^0 - \frac{0.0591}{n} \log\left(\frac{\alpha_+}{\alpha_-}\right) \tag{6.26}$$

Platinum or gold is often chosen as the electrode metal but the choice of metal depends on the solution concerned. The metal should not be attacked by the solution, nor should it catalyse side reaction. The electron transfer process must not also be too slow for a reproducible behaviour. Two typical redox electrodes are shown in Figs. 6.6(a) and (b).

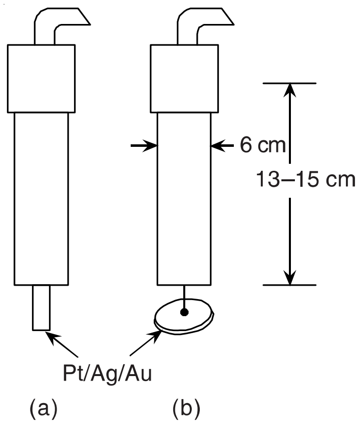

Fig. 6.6 Redox electrodes (a) rod type, and (b) plate type.

6.8.2 Membrane Electrodes

Membrane electrodes are of two different types: (a) ion-selective and (b) the molecular selective type.

The ion-selective type membrane electrode can be subdivided into two major categories: the non-crystalline membrane and the crystalline membrane. The molecular selective type has two major subgroups: the gas sensing type and the enzyme substrate type.

The ion-selective membrane electrodes

Ion-selective membranes must have some electrical conductivity which occurs, in general, due to ion transfer or exchange. The conductivity value may be quite small in some cases. The membrane should be so constituted that it must be capable of binding the analyte ion selectivity. The bindings are of three types, namely the ion-exchange, crystallization, and complexation. Complexation is not very common. The membrane should not dissolve to any extent in the analyte solution, which, in general, is aqueous in nature. This connotes that the membranes should be made of silica glasses or polymer resins or such other molecular aggregates. Some ionic inorganic compounds of low solubility can also be used mostly as crystalline membrane, single or poly- or mixed.

Conduction in a membrane cell, as has been mentioned already, takes place by ion transfer, unlike in aqueous solution where it is by migration of anions and cations or in metal electrode–liquid interface where it occurs through oxidation/reduction process. The membrane itself is ionic in nature. Some membranes are ion exchangers having numerous ionic sites which are capable of interacting with charged 'bodies' in a solution, such as silicate glass. It consists of a three dimensional 'lattice' form of oxygen atoms bonded to silicon atoms keeping open regions in the structure which can be occupied by cations and which can neutralize the negative charge of the O_2–Si network. If these cations have multiple charges as with Ca^{++} and Al^{+++} in Ca-glass and Al-glass, these positive ions are immobile but if they have single charge as in Na^+, K^+, Li^+, and the like, they exhibit mobility in the structure and this mobility allows the charge to be transferred through the glass.

There are two glass–solution interfaces and single mobile charges, like protons, are transferred once from glass to a solution at one side and from a solution to the glass at the other, making a current to flow. In fact the cation sites in the glass are mostly occupied by protons, H^+. If the current is absent, on the two sides of the membrane equilibria are reached which are due to relative hydrogen ion concentrations in the solutions on the two sides. When the positions of these equilibria differ, the surface of the membrane at which greater dissociation has occured would be negative with respect to the other surface resulting in a potential whose magnitude obviously depends on the difference in hydrogen ion concentration on the two sides of the ion-selective membrane. This can be called the *boundary potential* and can be measured in a cell for pH measurement.

Each cell consists of a membrane electrode as the indicator/sensor electrodes and a reference electrode, as has been described earlier, like calomel electrode. But the membrane is not amenable to be connected to the external circuit and hence, an internal standard solution with a second reference electrode in association with the membrane is used. The scheme is shown in Fig. 6.7. The second reference electrode has usually a different potential and its 'preparation' will largely be governed by the internal standard solution. As indicated in the figure, second reference electrode has a potential E_{r2}, between this and the membrane for the activity of the internal standard solution the potential E_{m2} is developed, on the other side of the membrane potential is E_{m1} for the activity of the analyte; first reference electrode junction has a potential E_s, and the corresponding reference electrode potential is E_{r1}. The overall potential would thus, be the algebraic sum of these potentials. The second reference electrode, the internal standard solution, and the membrane can be made a single unit and named the *measuring* or *analyte sensing electrode,* as will be discussed later.

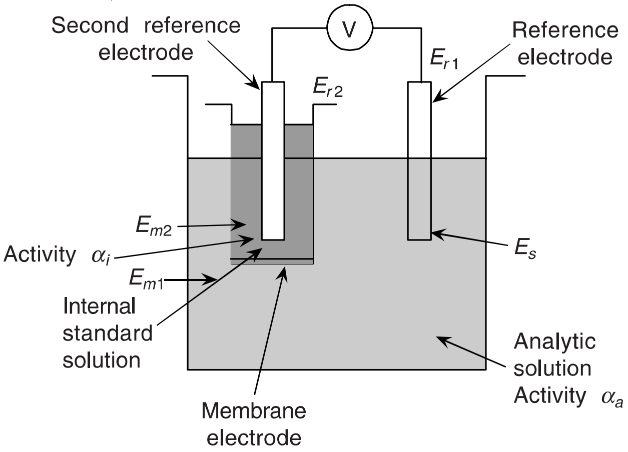

Fig. 6.7 Cell using a membrane electrode.

The potential of the entire cell is given by

$$E_c = E_{r1} + E_s - E_M^0 + \left(\frac{0.0591}{n}\right)\log\left(\frac{1}{\alpha_a}\right) \tag{6.27}$$

where E_M^0 is the value of E_M and is given as in Eq. (6.28) for $\alpha_a = 1$.

Now,

$$\begin{aligned} E_M &= E_{m1} - (E_{m2} - E_{r2}) \\ &= E_b + E_{r2} \end{aligned} \tag{6.28}$$

E_b being the boundary potential.

An important aspect of the ion-selective membrane electrodes is their selectivity. Selectivity coefficient has been defined for a membrane with respect to a specific analytic solution. Thus, if the activities of the cations of the membrane on the external side and the singly charged species of the analyte solution in it are α_m and α_s and on the surface of the membrane are α'_m and α'_s, the selectivity coefficient is given as

$$K_s = \frac{\alpha_m \alpha'_s}{\alpha'_m \alpha_s} \tag{6.29}$$

The boundary potential is then given by

$$E_b = E_b^0 + 0.0591 \log\left[\alpha_m + K_s\left(\frac{\mu_s}{\mu_m}\right)\alpha_s\right] \tag{6.30}$$

where μ_m and μ_s stand for mobilities of the membrane cations and charge species of the solution in the membrane, and

$$E_b^0 = -0.0591 \log(\alpha_m + \alpha_s) \tag{6.31}$$