Selectivity coefficient is actually a measure of the interference that the charged species of the solution cause to the cations of the membrane in potentiometric developments and, thus, can vary from zero to any arbitrarily large value. If there are several cations in the solution, multiplying charged species with activities α_{sj} and, with charges carried by the ions are q_{sj}, the generalized form of E_b is given by

$$E_b = E_b^0 + \left(\frac{0.0591}{q_m}\right)\log\left[\alpha_m + \sum_{j=1}^{n} K_{sj}\left(\frac{\mu_{sj}}{\mu_m}\right)(\alpha_{sj})\frac{q_m}{q_{sj}}\right] \tag{6.32}$$

where q_m is the charge carried by the ion of activity α_m.

The pH sensor: The non-crystalline membranes are glasses and liquids. The discussion in the previous subsection although, is very general, pertains largely to glass electrodes. It is, in fact, the first membrane electrode to be developed. One of the purposes of a special type glass 'membrane' electrode is to sense pH, the negative logarithm of hydrogen ion concentration to indicate the amount of acidity or basicity. One such typical electrode sensor is shown in Fig. 6.8. A thin specially made pH-sensitive glass tip is sealed to the heavy-walled glass tubing as shown. The bulb so formed is filled with a buffer solution or a solution of 0.1 M HCl saturated with AgCl. A silver wire immersed in the solution forms reference electrode 2 of Fig. 6.7. Reference electrode for the complete cell is a calomel electrode. The overall measurement system, thus, requires two reference electrodes and a measuring glass electrode as a membrane.

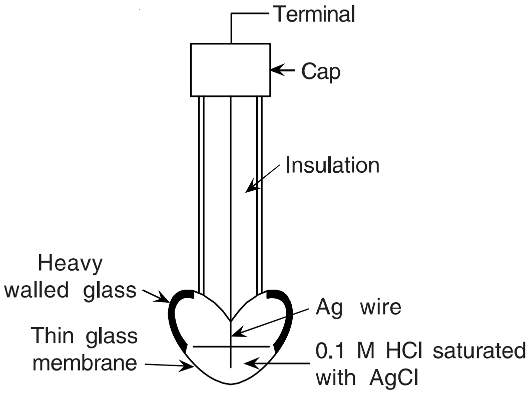

Fig. 6.8 The pH electrode.

The glass that is used for this membrane is, in general, the soda lime glass with $Na_2O(22)$, $CaO(6)$, and $SiO_2(72)$. It is quite selective for pH upto a value 9. Above this, lithium all purpose glass is more suitable which can be made when Na is replaced by Li and Ca by Ba in various proportions. This change increases the lifetime of the electrode as well. For pH sensing, the electrode needs to be hydrated. Hydration helps the ion-exchange reaction when singly charged cations of the glass are exchanged for protons of the solution. The reaction is given as

$$H^+ + Na^+G^- \rightleftharpoons Na^+ + H^+G^- \tag{6.33}$$

where G^- indicates one cation bonding site in the glass surface.

If the glass membrane has identical solutions on the two sides, it will have $E_{m1} - E_{m2} = 0$. But this is not always true and a small potential is seen to exist in some membranes which is termed as asymmetry potential. It is believed to develop because of strains within the two surfaces during manufacturing stage and contamination of the outer surface during continuous use. Frequent calibration with standard buffers eliminates this potential.

In an alkaline solution, the cation is the same kind as the Na^+ in the soda lime glass membrane; this condition reduces the selectivity and a negative error develops in the measured pH value which is called the *alkaline error*. Basically, the glass responds not only to H^+ but also to alkaline metal ions. It can be reduced to a certain extent using lithium all purpose glass. The error for different glasses is shown in Fig. 6.9(a). The alkaline error has been confirmed by taking test analytes of 1 M Na and 0.1 M Na. The error is seen to reduce by 60% from the former to the latter. As seen, there is an acid error also which has been obtained by testing with acid solutions but the cause is yet to be explained properly.

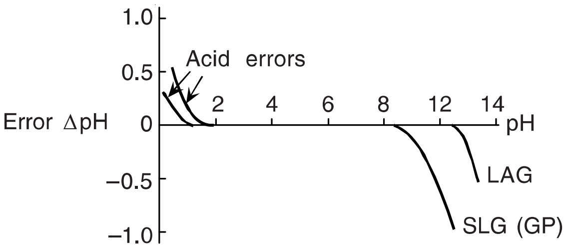

Fig. 6.9(a) Error curves for different pH-sensitive glass membranes.

The pH electrode is now available in a combination form with the reference calomel electrode integrally designed in a single casing as shown in Fig. 6.9(b).

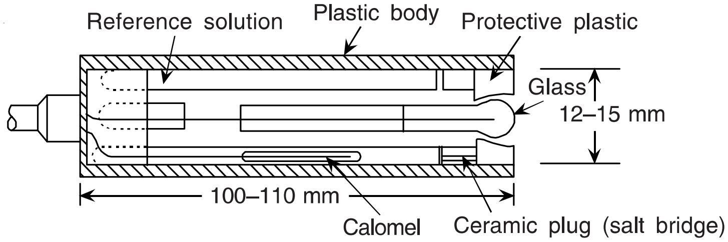

Fig. 6.9(b) The integrated PH-sensor.

Liquid membrane electrodes: Also called liquid ion exchanger membranes, liquid membrane electrodes are formed from immiscible liquids that are selective in bonding and give rise to potentials with activities of some polyvalent cations and some other singly charged cations and anions. The schematic diagrams of the electrode is given in Fig. 6.10.

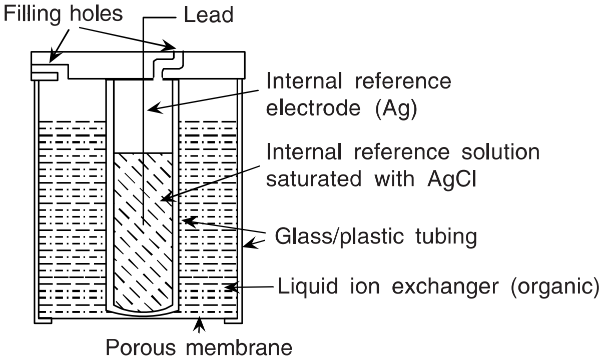

Fig. 6.10 Liquid ion exchanger membrane electrode.

As shown, the inner tube contains the internal reference electrode and solution saturated with AgCl, it also contains the aqueous standard solution of, say, MCl_x where M^{x+} is the cation whose activity is to be determined. The outer tube contains an organic ion exchanger liquid. The ion exchanger liquid and the inner liquid are held in place by a porous membrane usually made from some form of cellulose with pore diameter of around 100 nm. The membrane is made hydrophobic by chemically treating it. The ion exchanger liquid comes in contact with and permeates the membrane—actually wick action causes the pores to be filled with this liquid. With water repelled, only the cations M^{x+} from the inner tube liquid can be exchanged with the organic liquid producing a characteristic potential. However, proper choice of the exchanger liquid is essential. Such liquids consist of polar ionic sites in relatively large non-polar organic molecules. These sites are negative in a cation exchanger and positive in anion exchanger. For Ca^{++} and Mg^{++}, the exchanger is $(RO)_2\ PO_2^-$, structure is shown in Fig. 6.11, and for Cu^{++} and Pb^{++}, this is $RSCH_2COO^-$; where R is an aliphatic group. Some of these are p-(1, 1, 3, 3-tetramethylbutyl)-phenyl, p-(n-octyl)-phenyl, and so on. With $MgCl_2$ in the analyte solution in internal tube, the ion exchange liquid separates the solution from the reference $MgCl_2$ solution establishing at each interface, the equilibrium which is represented as

$$[(RO)_2\ PO_2]_2Mg \rightleftharpoons 2(RO)_2\ PO_2^- + Mg^{++} \tag{6.34}$$

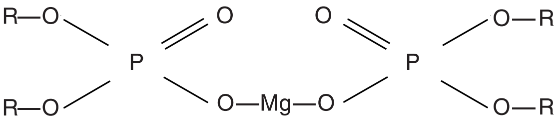

Fig. 6.11 The $(RO)_2PO_2^-$ structure.

In recent times, the liquid ion exchanger outer tube has been dispensed with by forming a membrane which has the ion exchanger immobilized in a polyvinyl chloride membrane. This membrane and the exchanger liquid are dissolved in an appropriate solvent such as tetrahydrofuran. When it is evaporated, a flexible membrane is obtained which behaves as a membrane with the ion exchanger liquid held in the pores. This new type of ion exchanger is actually being used extensively and is termed as immobilized liquid in rigid polymer.

The liquid membranes may have three types of active substances such as (i) cation exchangers, (ii) anion exchangers, and (iii) neutral macrocyclic compounds which are complex carriers and are used for cations being very selective. Selectivity for a particular ion depends on the ability of the electrode to extract the ion into the membrane. Basically, it is the ability of the ion to form a complex with the neutral carrier. After complexation and extraction, the species in such a membrane has the same charge as the extracted ion and this is the reason why it is called neutral carrier. Some typical neutral carriers are vanilonycin (for K^+), O-nitrophenyl-n-octylether (for Ca^{++}), and so on.

Crystalline membrane electrodes: Sometimes referred to as solid membrane electrodes, crystalline membrane electrodes may be single crystals or polycrystalline. A typical arrangement is shown in Fig. 6.12 with internal reference electrode. Crystalline membranes may be homogeneous or heterogeneous. Homogeneous crystalline membranes can be made cutting a single crystal or can be made as discs or pellets from the finely grounded crystalline solid by high pressure or by casting from a melt. The membrane is fitted by sealing to an inert plastic tube like teflon or polyvinyl chloride as shown in Fig. 6.12.

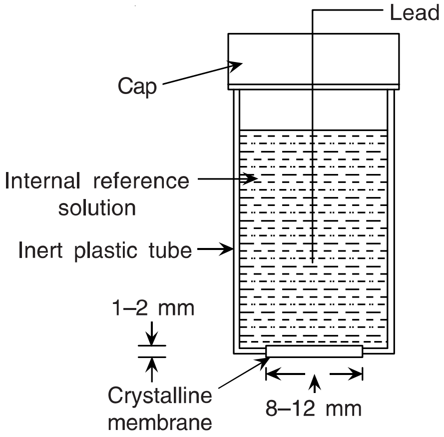

Fig. 6.12 Crystalline membrane electrode.

The heterogeneous variety is made from sparingly soluble salts. Finely grounded crystalline solids are dispersed/embedded in an inert matrix such as silicone rubber, paraffin, polyvinyl chloride and so on. Such membranes are selective to one of the ions present in the dispersed solid. If barium sulphate is dispersed in the matrix, it becomes selective to Ba ions as well as sulphate ions.

Most ionic crystals have very poor electrical conductivity at ordinary temperature. Some of which are conductive, have ions that are mobile in the solid phase such as Ag ions in silver halides and sulphides, fluoride ions in some rare-earth fluorides, and copper ions in cuprous sulphide. In such materials, the conducting ions jump to holes present as defect in the crystal lattice leaving oppositely charged holes. Only single kind of ions can participate in such a process because of mobility restriction in a solid crystal and hence, crystal membranes are so very selective.

As mentioned, single crystal membranes made from Ag halides become selective to silver and halide ions. If silver halides are mixed with crystalline silver sulphides in 1:1 molar ratio, the homogeneous membranes so prepared show good conductivity because of better mobility of silver ions in sulphide matrix. Silver sulphide in combination with Cd, Cu, and Pb sulphides also are used for selectivity of Cd^{++}, Cu^{++}, and Pb^{++}.

While Br^-, Cl^-, and I^- ions are determined by AgS–AgBr, AgS–AgCl, and AgS–AgI membranes; for detecting fluoride ions, LaF_3 has been found to be most suitable. LaF_3, or fluorides of neodymium and praseodymium are good conductors but their conductivity is further improved by doping with EuF_2. The single crystal formed is then cut according to the required size. The solid crystal membrane behaves as a glass electrode for pH measurement with charges created on the two surfaces by ionization with guiding equation

$$LaF_3 \rightleftharpoons LaF_2^+ + F^- \tag{6.35}$$

The potential across the membrane has its positive end where lower fluoride ion concentration occurs. Such membrane can be used for a concentration as low as 10^{-6} M in a temperature range of 0–80°C.

Metal salts with high electrical conductivity can be used directly in electrode form. This is called solid state electrode and has been reconsidered in recent years. Even pH electrodes have been developed on this basis. Figure 6.13 depicts such an electrode where an alumina (Al_2O_3) rod