

This book has been prepared by the United States Department of Commerce and National Bureau of Standards in 1969 for public distribution and consumption. The purpose is to provide a basic introduction to pH and Ion Selective measurement theory and practice. As this book is now somewhat antiquated it is best suited as a historical overview for this field and a basic theoretical treatment of analytical aqueous electrochemistry.

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## FORWARD

Ion Selective Electrodes represent a major advance in analytical technique. For the first time in analytical chemistry the activities of many ions can be determined quickly and conveniently in a non-destructive manner. Unfortunately, misconceptions concerning the simplicity of the method have in the past, led to some disappointments. This could have been entirely avoided if the user had been aware of what was involved in this method of analysis. This booklet has been designed to introduce the fundamental aspects of electrochemical measurement by ion-selective electrodes. Accordingly, detailed accounts of individual electrodes are not given — references to certain electrodes are only made to illustrate general principles. Further information on ion-selective electrodes can be obtained from electrode manufacturers and from publications such as "Ion-Selective Electrodes" — this book was prepared by the United States Department of Commerce, National Bureau of Standards (1969), edited by R. Durst and is recommended to anyone intending to use ion-selective electrodes.

## MEMBRANE THEORY

### (a) MEMBRANE POTENTIALS

Certain substances, when interposed between two solutions differing in activity of a particular ionic species, allow selective migration of these ions from the solution of higher activity to the solution of lower activity. Diagram (2) shows the migration of a cation  $M^+$  through a membrane permeable to  $M^+$  but not to  $X^-$  or  $Y^-$ .

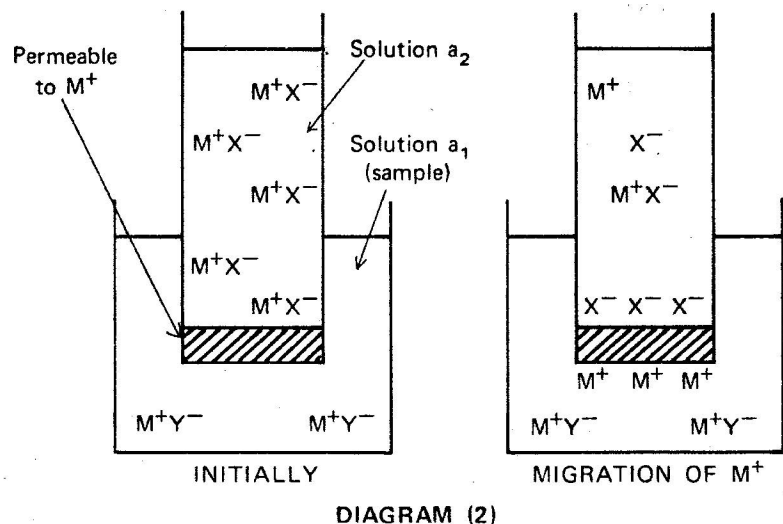


DIAGRAM (2)

Since both solutions are electrically neutral initially, the movement of a charged species across the membrane will result in a potential forming across the membrane. Migration of ions across the membrane will continue until further movement is opposed by the potential which has built up across the membrane, thus an equilibrium is established.

The Nernst equation relates the magnitude of this potential to the activities of the two solutions.

$$E = + \frac{2.303 RT}{zF} \log \frac{a_1}{a_2} \quad (5)$$

where  $z$  is the charge of the ion, including sign.

The constant  $\frac{2.303 RT}{F}$  has the following values:

6.

Temperature T (°C)	$\frac{2.303 RT}{F}$ (Millivolts)
0	54.197
10	56.181
20	58.165
25	59.157
30	60.149
50	64.118
80	70.070
100	74.038

TABLE (2)

Practically,  $a_2$  is fixed (the internal filling solution of an electrode), so that at a particular temperature, the membrane potential varies as the log of the sample activity.

$$E = b + \frac{2.303 RT}{z_i F} \log a_i \quad (6)$$

Equation (6) shows that at 25° a ten-fold change in  $a_i$  will give rise to a change in potential of:

- + 59.16 mV for a univalent cation
- 59.16 mV " " " anion
- + 29.6 mV " " " divalent cation
- 29.6 mV " " " anion

The quotient  $xmV/\text{unit decade difference in activity}$  is known as the slope of an electrode. If it reaches the value shown it is known as Nernst slope, theoretical slope or 100% slope. Most electrodes have 95–99.9% slope. An electrode with a lower slope (down to 85%) is still useable, provided it behaves reproducibly. An electrode with less than 85% slope should not be used.

### (b) TYPES OF MEMBRANES

#### (i) Glass Membranes

Some hydroscopic glasses are cation permeable. The common pH electrode is highly selective towards  $H^+$ ; a very small response to other cations e.g.  $Na^+$  only becomes apparent at very low  $H^+$  activity,

7.

i.e. high pH. Other glasses have been developed which respond to  $\text{Na}^+$  and  $\text{K}^+$ , however, these are not as highly selective (particularly towards  $\text{H}^+$ ) and certain restrictions must be placed on their use, e.g. the pH of the sample must be  $>5$ .

Glass electrodes develop a partially constant potential called an "asymmetry" potential. This may be of the order of 10mV or 0.2pX and depends on the composition of the glass of the membrane, the shape of the membrane and the way it is made, and it changes somewhat in the course of time and varies with temperature. When making measurements with a glass electrode, it is necessary to standardize at adequate intervals.

An essential part of a glass membrane is a hygroscopic glass layer which is produced by soaking the electrode prior to use. Other membrane types do not need soaking.

(ii) **Solid State Membranes**

The silver halides as well as silver sulphide are ionic conductors in which the silver ion is mobile, and all can be used to measure silver ion activity. Since a solubility product equilibrium between a particular silver halide and the halide anion in solution is established quickly, these electrodes can also be used to measure respective halide activities. (This also applies to sulphide). The sample halide activity dictates the silver ion activity at the surface of the membrane:

$$K_{sp} \text{AgX} = a_{\text{Ag}} a_{\text{X}} \quad (7)$$

This equilibrium process is carried a stage further in the case of the  $\text{Cu}^{++}$ ,  $\text{Cd}^{++}$ , and  $\text{Pb}^{++}$  electrodes. The membrane consists of the appropriate metal sulphide mixed with  $\text{Ag}_2\text{S}$ . The sample metal ion activity dictates the sulphide ion activity via

$$K_{sp} \text{MS} = a_{\text{M}} a_{\text{S}} \quad (8)$$

which in turn, dictates the silver ion activity via

$$K_{sp} \text{Ag}_2\text{S} = a_{\text{Ag}}^2 a_{\text{S}} \quad (9)$$

These electrodes show a Nernstian response to the respective  $\text{M}^{++}$ . Lanthanum fluoride is an ionic conductor in which the fluoride ion migrates, and can be used to measure fluoride ion activity.

(iii) **Liquid Membranes**

In this type of membrane, a salt of the ion of interest which is insoluble in water but soluble in a suitable organic liquid (itself insoluble in water) is used to transport the ions across the membrane.

The liquid membrane is stabilized by a porous support in contact with a reservoir of the organic exchanger (Diagram (3) ) Liquid membrane electrodes require considerable attention and most are not highly selective. Useful electrodes of this type are potassium, nitrate and calcium.

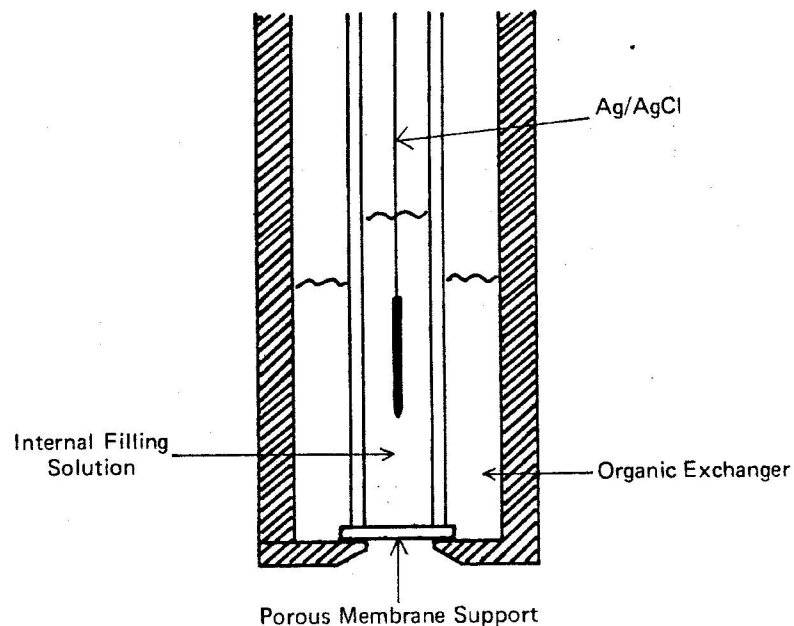


DIAGRAM (3)  
Liquid Membrane Electrode