

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.

COMPLETION OF THE CIRCUIT

(a) REFERENCE ELECTRODES

The membrane potential described in the previous section is measured by making electrical contact to the inner solution of the sensing electrode and to the sample solution by means of two suitable reference electrodes and measuring the potential difference with a voltmeter.

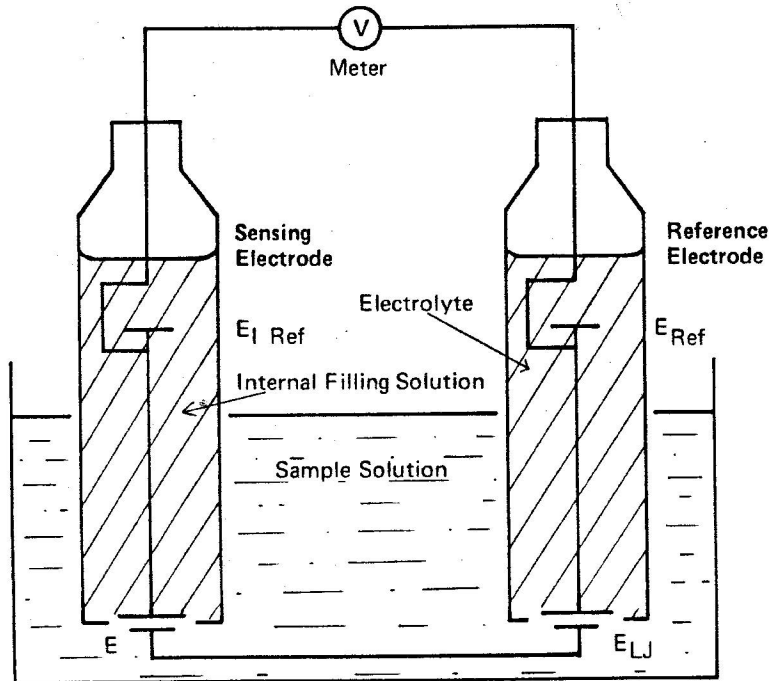


DIAGRAM (4)

$E_{I \text{ Ref}}$ and E_{Ref} are the potentials of two reversible, reproducible and stable half cells with minimal temperature hysteresis. Many cells have been devised and two in wide use are:-

- (i) The silver/silver chloride reference electrode which consists of a silver or silver plated platinum wire coated with silver chloride in contact with a chloride containing electrolyte. The cell reaction is given by $\text{AgCl} + e^- \rightarrow \text{Ag} + \text{Cl}^-$ and is chloride ion reversible.

- (ii) The mercury-mercurous chloride (calomel) reference electrode — Cl^- , Hg_2Cl_2 (s); Hg (l) which is also chloride ion reversible.

The activity of the internal filling solution of the measuring electrode will influence the "b" term of equation (6), and hence the **ISOELECTRIC POINT** of a particular electrode, which is simply the activity of the sample solution (usually in pX or M) which produces zero volts on the meter (with no offset potentials). Many pH electrodes, for example, have an isoelectric point at pH7, however, some others have isoelectric points near pH2 or pH4. If a meter will accommodate only a small variation in isoelectric point (say ± 1 pH unit) then obviously it will be important to select an electrode with the right isoelectric point for the meter (or vice versa), otherwise a section of the measuring range will be "off-scale".

(b) THE LIQUID JUNCTION POTENTIAL

Electrical contact between the electrolyte of the reference electrode and the sample solution is made via a "salt-bridge" which usually takes the form of a porous constriction at the bottom of the reference electrode. The electrolyte slowly seeps out of the chamber inside the reference electrode into the sample solution, thus the reference electrode has a continuously renewable boundary layer which is free from contamination of former samples. Since electrolyte is lost to the samples, the reference electrode requires refilling with electrolyte periodically.

As the electrolyte diffuses out into the sample solution, a "liquid junction potential" E_{LJ} will arise if the cations and anions of the electrolyte have significantly different mobilities.

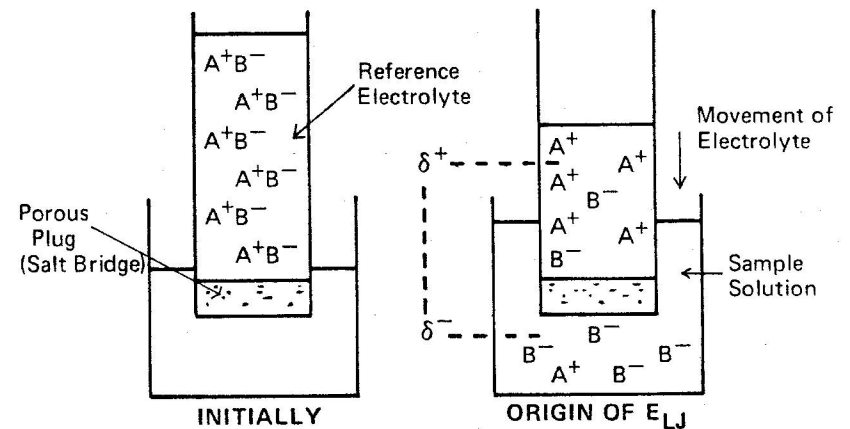


DIAGRAM (5)

The liquid junction potential can be minimized by selecting an electrolyte whose anions and cations have similar mobilities, e.g., KCl. Even so, small potentials arise, but by suitable construction of the salt bridge to ensure an even flow of electrolyte, E_{LJ} can be made fairly constant and consequently can be incorporated with the reference potential into a single constant potential term

$$c = E_{LJ} + E_{Ref}$$

$$E = b + c + \frac{2.303 RT}{z_i F} \log a_i$$

$$E = d + \frac{2.303 RT}{z_i F} \log a_i \quad (10)$$

i.e. $E \propto \log a_i$ at a given T.

Since the reference electrolyte contaminates the sample solution, it is necessary that the electrolyte does not contain ions which can be detected by the sensing electrode, either directly or as interference. It would be pointless, for example, to use a chloride selective electrode in conjunction with a reference electrode containing KCl as electrolyte. One way of overcoming this problem is to use a "double junction" reference electrode in which contact is made between the reference electrolyte and the sample solution via another "indifferent" electrolyte, e.g. 1N KNO_3

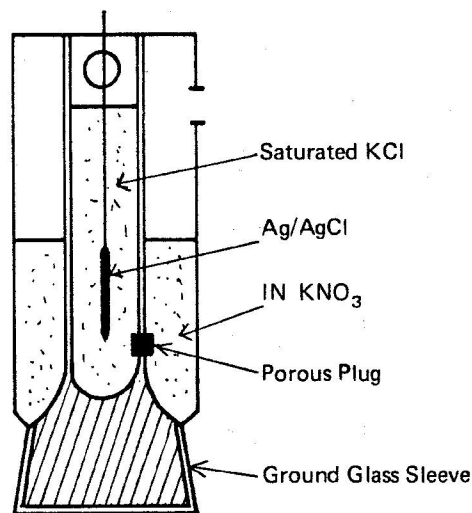


DIAGRAM (6)

Double Junction Reference Electrode.

K^+ and NO_3^- are chosen for their similar mobilities, and because neither of these ions interfere with most selective ion electrodes. There is no "universal" reference electrode and the type of reference electrode used and the nature of the electrolyte used will depend on the chemical composition of the sample. It is desirable (in order to minimize LJ effects) to have the indifferent electrolyte at the same pH as the sample. In fact, it is best to make the indifferent electrolyte as near as possible to the same composition as the sample.

(c) THE MEASURING DEVICE

The meter in Diagram (4) is a high impedance voltmeter (membranes often have large resistances – up to 500 M Ω) and usually features the following:–

(i) Display

- linear mV or pX integral or digital with or without antilog conversion (electrical or calibrated scale) for direct reading of activity. Meter types have an expanding scale to accommodate accurate measurements over small ranges and employ an **OFFSET POTENTIAL** to zero a small range.

(ii) Temperature Compensation

- either **manual** (i.e. incorporates a dial which is set at the same temperature as the sample solution) or **automatic** which has a temperature sensor in the sample and corrects electrically. Both correct for the T term of the Nernst equation.

(iii) Assymetry Potential, Slope, $\frac{1}{z}$

- Meter types employ slope and $\frac{1}{z}$ control functions to utilize full meter scale in the case of non-Nernstian slope or $|z| \neq 1$. The assymetry potential control is an offset potential to correct for an assym. potential.