This book has been prepared by the United States Department of Commerce and National Burea 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.

Table of Contents for Selective Ion Electrode Paper (1969)

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.

CONTENTS

SOLUTION CHEMISTRY

(a)   **ACTIVITY VERSUS CONCENTRATION.**

An ion in solution may exist as a free iron (i.e., not bound to other ions or molecules) or it may interact with other ions or molecules in solution. The term **ACTIVITY** of an ion "X" relates to the number of free ions of X per unit volume of solution, while the **CONCENTRATION** OF X refers to the **TOTAL** number of ions of X (i.e., free **AND** bound) per unit volume of solution. Of the two, activity is much less readily defined because in many cases we are uncertain as to the extent of interaction of X with other ions. An understanding of the relationship between activity and concentration is essential in interpreting the results of electrochemical measurements because whilst we **MEASURE** activity, we can only precisely define concentration.

(b)   **ACTIVITY COEFFICIENTS.**

In solutions of electrolytes electrical forces acting between oppositely charged ions cause the activity of the ions to be reduced, and hence ions behave as if they were of lower concentration than that calculated from the stiochiometric concentration of the dissolved electrolyte. To obtain the activity of the ions, the concentration must be multiplied by a factor which will allow for the interionic attraction. This factor is termed the **ACTIVITY COEFFICIENT** because it gives the fraction of the total concentration which is effective in equilibrium reactions. If we represent the corrected concentration or activity by 'a', the activity coefficient by 'f' and the concentration by 'c' then

$$a = c \times f \qquad\qquad (1)$$

The value of the activity approaches that of the molar concentration or molarity as the solution is progressively diluted, since under these conditions the ions will be further apart and the interionic attraction will consequently become smaller. At infinite dilution the forces between the ions will be practically zero, a = c and f = I. Table (1) shows the variation of the mean activity coefficients with concentration for some electrolytes. The activity coefficient varies with valency and has the same value for all dilute solutions having the same IONIC STRENGTH, the latter being a measure of the electrical field existing in the solution. The ionic strength, designated by the symbol I, is defined as equal to one-half of the sums of the products of the total concentration of each ion multiplied by the square of its valency or $I = \frac{1}{2} \sum c_i z_i^2$ where c_i is the ionic concentration in gram moles/litre of solution.

Molar Concentration	0·001	0·01	0·05	0·1	0·2	0·5	1·0	2·0
HCl	0·966	0·904	0·830	0·796	0·767	0·758	0·809	1·01
HBr	0·966	0·906	0·838	0·805	0·782	0·790	0·871	1·17
HNO$_3$	0·965	0·902	0·823	0·785	0·748	0·715	0·720	0·78
HIO$_3$	0·96	0·86	0·69	0·58	0·46	0·29	0·19	0·10
H$_2$SO$_4$	0·830	0·544	0·340	0·265	0·209	0·154	0·130	0·12
NaOH	—	—	0·82	—	0·73	0·69	0·68	0·70
KOH	—	0·90	0·82	0·80	—	0·73	0·76	0·89
Ba(OH)$_2$	—	0·712	0·526	0·443	0·370	—	—	—
AgNO$_3$	—	0·90	0·79	0·72	0·64	0·51	0·40	0·28
Al(NO$_3$)$_3$	—	—	—	0·20	0·16	0·14	0·19	0·45
BaCl$_2$	0·88	0·72	0·56	0·49	0·44	0·39	0·39	0·44
Ba(NO$_3$)$_2$	0·88	0·71	0·52	0·43	0·34	—	—	—
CaCl$_2$	0·89	0·73	0·57	0·52	0·48	0·52	0·71	—
Ca(NO$_3$)$_2$	0·88	0·71	0·54	0·48	0·42	0·38	0·35	0·35
CdCl$_2$	0·76	0·47	0·28	0·21	0·15	0·09	0·06	—
CdSO$_4$	0·73	0·40	0·21	0·17	0·11	0·07	0·05	0·04
CuCl$_2$	0·89	0·72	0·58	0·52	0·47	0·42	0·43	0·51
CuSO$_4$	0·74	0·41	0·21	0·16	0·11	0·07	0·05	—
FeCl$_2$	0·89	0·75	0·62	0·58	0·55	0·59	0·67	—
KF	—	0·93	0·88	0·85	0·81	0·74	0·71	0·70
KCl	0·965	0·901	0·815	0·769	0·719	0·651	0·606	0·576
KBr	0·965	0·903	0·822	0·777	0·728	0·665	0·625	0·602
KI	0·965	0·905	0·84	0·80	0·76	0·71	0·68	0·69
KClO$_3$	0·967	0·907	0·813	0·755	—	—	—	—
KClO$_4$	0·965	0·895	0·788	—	—	—	—	—
K$_2$SO$_4$	0·89	0·71	0·52	0·43	0·36	—	—	—
K$_4$Fe(CN)$_6$	—	—	0·19	0·14	0·11	0·67	—	—
LiBr	0·966	0·909	0·842	0·810	0·784	0·783	0·848	1·06
Mg(NO$_3$)$_2$	0·88	0·71	0·55	0·51	0·46	0·44	0·50	0·69
MgSO$_4$	—	0·40	0·22	0·18	0·13	0·09	0·06	0·05
NH$_4$Cl	0·96	0·88	0·79	0·74	0·69	0·62	0·57	—
NH$_4$Br	0·96	0·87	0·78	0·73	0·68	0·62	0·57	—
NH$_4$I	0·96	0·89	0·80	0·76	0·71	0·65	0·60	—
NH$_4$NO$_3$	0·96	0·88	0·78	0·73	0·66	0·56	0·47	—
(NH$_4$)$_2$SO$_4$	0·87	0·67	0·48	0·40	0·32	0·22	0·16	—
NaF	—	0·90	0·81	0·75	0·69	0·62	—	—
NaCl	0·966	0·904	0·823	0·780	0·730	0·68	0·66	0·67
NaBr	0·966	0·914	0·844	0·800	0·740	0·695	0·686	0·734
NaI	0·97	0·91	0·86	0·83	0·81	0·78	0·80	0·95
NaNO$_3$	0·966	0·90	0·82	0·77	0·70	0·62	0·55	0·48
Na$_2$SO$_4$	0·89	0·71	0·53	0·45	0·36	0·27	0·20	—
NaClO$_4$	0·97	0·90	0·82	0·77	0·72	0·64	0·58	—
Pb(NO$_3$)$_2$	0·88	0·69	0·46	0·37	0·27	0·17	0·11	—
ZnCl$_2$	0·88	0·71	0·56	0·50	0·45	0·38	0·33	—
ZnSO$_4$	0·70	0·39	—	0·15	0·11	0·07	0·05	0·04

TABLE (1)

Mean Activity Coefficients of Various Electrolytes

4.

The Debye-Huckel theory of complete dissociation has provided a theoretical solution of the problem of calculating individual activities of ions in very dilute solution. The expression for the activity coefficient of an ion is:

$$\log f_i = -A z_i^2 \sqrt{I} \qquad (2)$$

where z_i = valency of ion i and A depends on the temperature and the dielectric constant of the solution. The mean activity coefficient of a dilute aqueous solution of a SALT at 25° is given by:

$$\log f = -0.509 \, z_+ z_- \sqrt{I} \qquad (3)$$

where z_+ and z_- are the valencies of the positive and negative ions respectively. The expression is a limiting one and is applicable to solutions of low ionic strength (up to about I = 0.01).

(c) **THE pX SCALE**

For many purposes, especially when dealing with small concentrations or large changes in concentration (or activities), it is cumbersome to express concentrations of ions in terms of gram equivalents per litre. A very convenient method, originally proposed for the hydrogen ion is the ion exponent (pX) defined by the relationships:

$$pX = \log_{10} [X] = \log_{10} \frac{1}{[X]} \quad \text{or} \quad [X] = 10^{-pX} \qquad (4)$$

The quantity pX is thus the logarithm of the reciprocal of the concentration (or activity) of X. In the case of the hydrogen ion, this method has the advantage that all states of acidity and alkalinity can be expressed by a series of positive numbers between 0 and 14.

When applied to the case (s) $X \neq H$, the p scale is less useful. The more usual measures of concentration M or ppm have been in wide use for a long time, and it is unlikely the p scale as applied to ions other than hydrogen will have much use.

5.

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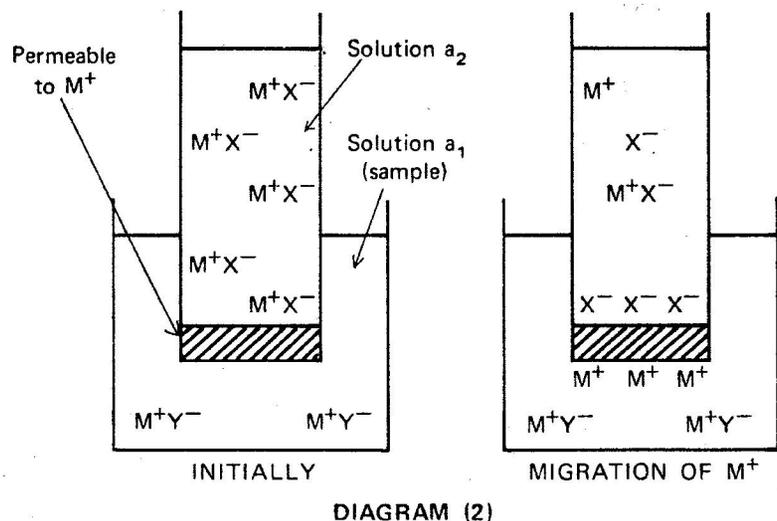
Since both solutions are electrically neutral initially, the movement of a charged species across the membrane will result in a potential forming across the membrane. Migration of ions across the membrane will continue until further movement is opposed by the potential which has built up across the membrane,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

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

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

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

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

Temperature T (O°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.

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

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

$$\begin{aligned}
& + \; 59.16 \text{ mV for a univalent cation} \\
& - \; 59.16 \text{ mV } '' \quad '' \quad '' \quad \text{anion} \\
& + \; 29.6 \;\; \text{mV } '' \quad '' \text{divalent cation} \\
& - \; 29.6 \;\; \text{mV } '' \quad '' \quad '' \quad \text{anion}
\end{aligned}$$

The quotient xmV/ unit decade difference in activity is known as the slope of an electrode. If it reaches the value shown it is known as Nerst 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,

i.e. high pH. Other glasses have been developed which respond to Na^+ and K^+, however, these are not as highly selective (particularly towards 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 "assymmetry" 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 hydroscopic 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:

$$K_{sp}AgX = a_{Ag} \, a_X \qquad (7)$$

This equilibrium process is carried a stage further in the case of the Cu^{++}, Cd^{++}, and Pb^{++} electrodes. The membrane consists of the appropriate metal sulphide mixed with Ag_2S. The sample metal ion activity dictates the sulphide ion activity via

$$K_{sp}MS = a_M \, a_S \qquad (8)$$

which in turn, dictates the silver ion activity via

$$K_{sp}Ag_2S = a^2_{Ag} a_S \qquad (9)$$

These electrodes show a Nerstian response to the respective 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.

8.

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.
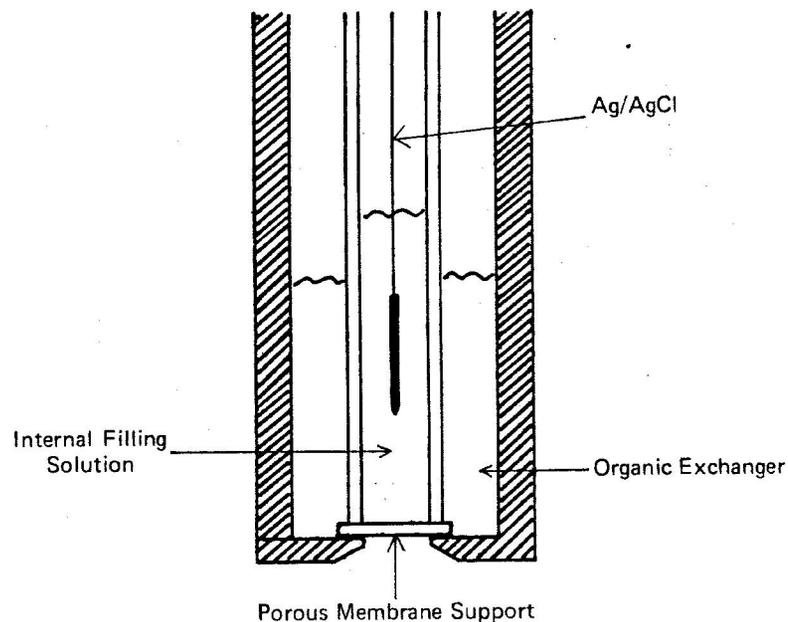

DIAGRAM (3)
Liquid Membrane Electrode

9.

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.
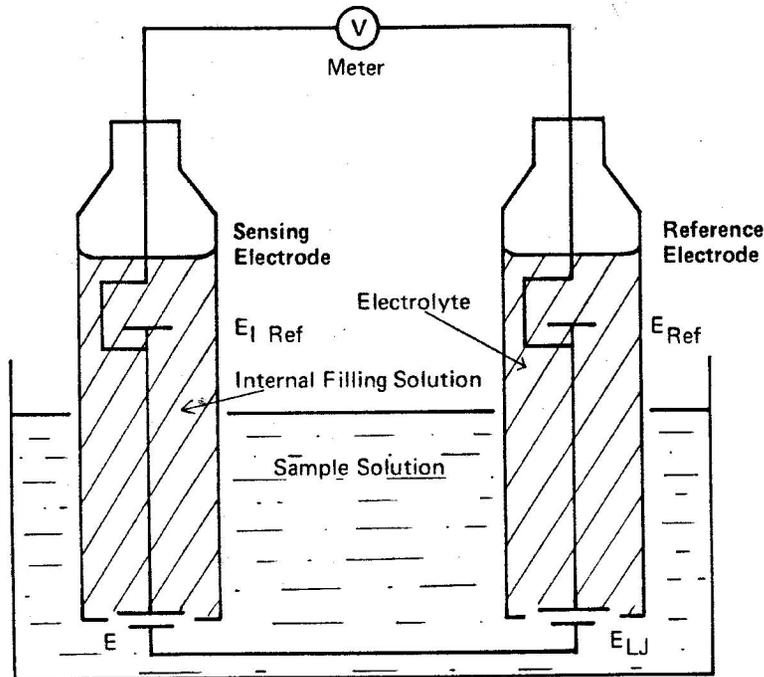
DIAGRAM (4)

E_I $_{Ref}$ 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 $AgCl + e^- \rightarrow Ag + Cl^-$ 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 $\pm$ 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.
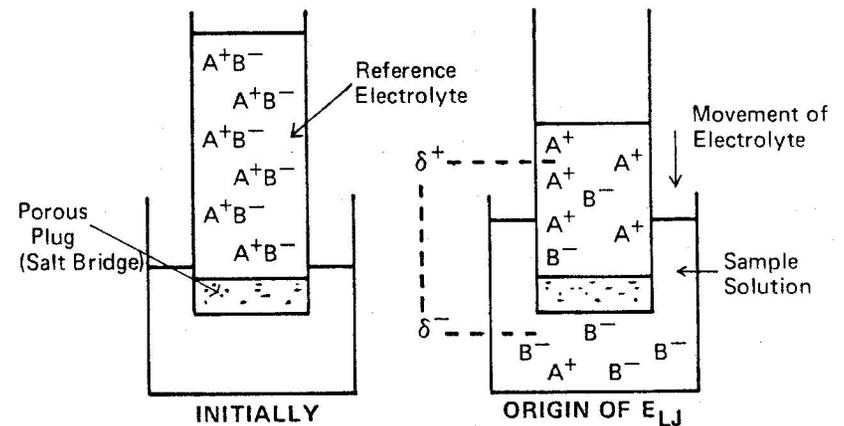
DIAGRAM (5)

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

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

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

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

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. IN KNO_3
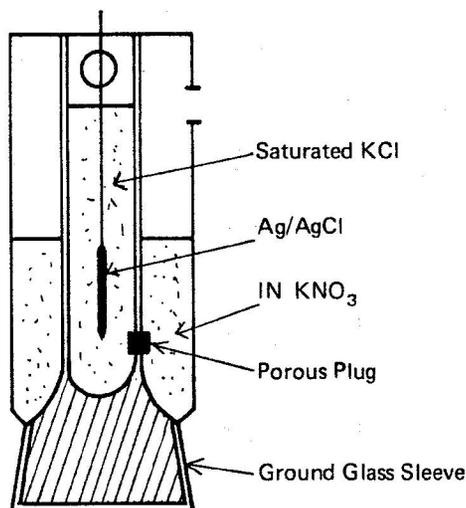

- Saturated KCl
- Ag/AgCl
- IN KNO_3
- Porous Plug
- Ground Glass Sleeve

DIAGRAM (6)
Double Junction Reference Electrode.

12.

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 Nerst 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-Nerstian slope or $|z| \neq 1$. The assymetry potential control is an offset potential to correct for an assym. potential.

13.

ELECTRODE CHARACTERISTICS

(a) DRIFT

The drift of most solid-state and glass Ion Selective Electrodes compares well to the drift of a good quality pH Electrode (typically 1-4mV/day). However, higher accuracy is frequently required for specific ion measurements than with pH, so the more frequent the recalibration with standards, the better. The exact frequency of calibration depends on the accuracy required. Liquid membrane electrodes can drift up to 8mV/day. The above comments apply of course to measurements at a constant temperature and under conditions where the membrane (or sample) is not undergoing a change.

(b) REPRODUCIBILITY

A reproducibility of 1mV/decade is a typical figure for careful measurements under ideal conditions. If special precautions are taken w.r.t. liquid junction potentials, washing techniques, shielding from external charges and if conditions of measurements are matched very closely, reproducibilities of 0.1mV can be obtained. Considerable experience in electrochemical measurements on the operator's part is a prerequisite in this case.

(c) RESPONSE TIME

When an electrode is used around the middle of its measuring range, electrochemical equilibrium is usually attained in less than 15 seconds. At the lower limit of detection, longer response times (up to 3 mins) are more usual. If an electrode has a very slow response time ($>$5 mins) or never gives a stable indication (with due consideration to the inherent drift — see notes on drift) it can mean:—

(i)   A liquid junction potential problem

(ii) The membrane surface (or sample ?) is changing in some manner, e.g. is being poisoned by interfering ions or is being coated with — say, a protein, oil or fat.

(iii) The electrode is approaching the end of its useful life.

(d) LIMIT OF DETECTION

The lower limit of detection in the case of the solid-state electrodes is governed by the solubility product of the membrane material. If an electrode is left in distilled water for sufficiently long, the membrane will equilibrate to form a saturated solution of the membrane material, so naturally, the electrode cannot sense solutions of lower activity than the activity of the membrane — saturated solution. As this process is fairly

slow (sometimes days) and as only an extremely small amount of the membrane dissolves anyway, it is quite safe to wash electrodes in distilled water and also to leave electrodes immersed in distilled water. If the membrane material is appreciably soluble in solutions of high activity of the ion of interest, an upper limit of detection is placed on its use also. This does not mean that such an electrode cannot be used in solutions of high activity, but simply that repeated use will reduce the life time of the electrode (See notes on Life Time). Examples are the Cl^- and CN^- electrodes. The solubility product of

$$Ag_2S \quad (K_{sp} \, Ag_2S \; = \; 1 \times 10^{-51})$$
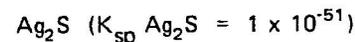
would indicate that a silver ion activity of $< 10^{-20}M$ could be detectable. In practice, it is very difficult to prepare very dilute solutions $(10^{-8}M$ without ionic absorption onto and desorption from the surfaces of the containing vessels and the electrodes. This problem is analogous to the difficulty faced by an analyst in attempting to obtain accurate pH readings in very dilute unbuffered solutions.

In the case of the liquid membrane electrodes, the lower limit of detection is defined by the solubility of the organic ion exchanger in the sample solution.

(e) ACCURACY

The logarithmic relationship between sample activity and millivolts means that electrodes give constant accuracy throughout their measuring range — measurements in solutions of very low activity are just as accurate as measurements of high activity. Divalent ion measurements are not as accurate as monovalent because the $\frac{1}{2}$ term in the Nerst equation halves the slope, but does not change the magnitude of drifts, etc.

(f) LIFE OF AN ELECTRODE

Most solid-state and glass electrodes when used in ideal solutions, under normal laboratory conditions, have a life time of 1-2 years. This time will be considerably reduced if the electrode:—

(i)   Is subjected to extremes of temperature regularly.

(ii) Is placed in solutions which irreversibly damage the membrane (see interferences — selectivity).

(iii) Is placed in a sample which is agitated and contains materials which can cause abrasive action. (Particularly important in single crystal and glass membranes).

A contracted slope and/or a sluggish response is/are the first symptoms of an electrode losing its sensing ability. Liquid type membrane electrodes

which have replaceable membranes can be used for as long as supplies of the membrane supports and ion exchanger exist.

(g) SELECTIVITY

An electrode which responds to other species of ions besides the one it is intended to measure (the primary ion) exhibits interference by these ions. **ALL** electrodes produced so far, (including the pH electrode) have this problem to some degree, electrodes are best termed "ion selective" rather than "ion specific". Some electrodes are more responsive to interfering ions than to primary ion; therefore, it is necessary to consider which ions are likely to be in a sample **BEFORE** measurements are made so that the measurements are meaningful and the membrane is not damaged.

All that is necessary in order to understand the qualitative and quantitive aspects of interference is a familiarity with the chemical properties of the membrane.

(i) Glass Membranes

Selectivity in glass membranes is determined by the relative magnitude of mobility ratios and ion exchange equilibrium constants. The only highly selective glass membrane is the H^+ responsive glass.

(ii) Solid State Membranes

As far as ionic migration is concerned, solid state membranes are very selective. The most common cause of interference in these types is simply a chemical reaction taking place on the surface of the membrane.

Two types of chemical reactions can occur:—

(a) The deposition of a layer of (relatively) insoluble material on the membrane surface which prevents membrane—solution contact.

(b) Dissolution of the membrane as a soluble reaction product.

Consider the solid state silver chloride membrane. AgCl (whether an electrode membrane or a reagent chemical) reacts with bromide ion (if in sufficient concentration)

$$AgCl + Br^- \rightarrow AgBr + Cl^-$$
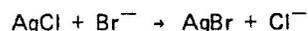
because the resultant product, silver bromide, is more insoluble ($K_{sp} = 8 \times 10^{-13}$) than silver chloride ($K_{sp} = 1 \times 10^{-10}$). The layer of silver bromide built up on the membrane surface prevents the equilibration of chloride ion in solution with the silver chloride of the membrane, consequently the electrode will no longer respond to chloride ion. Restoration of the chloride response necessitates removal of the AgBr

layer, either by abrasion or soaking in a very strong chloride solution, which favours the reverse reaction. Similarly, it would be expected that iodide ($K_{sp}AgI = 1 \times 10^{-16}$) and sulphide ($K_{sp}Ag_2S = 1 \times 10^{-51}$) would interfere. The allowable limits of Br^- I^- or $S^=$ activities (w.r.t. to a particular Cl^- activity) will depend on the ratio of the solubility product of Ag Br, AgI or Ag_2S to that of AgCl. This ratio (calculated or experimental) is known as a "selectivity constant". Silver chloride also reacts with aqueous NH_3 and CN^- to form comparatively stable soluble silver complexes, i.e., $Ag(NH_3)_2^+$ and $Ag(CN)_2^-$. Placing a chloride electrode in an ammonia or cyanide solution results in the dissolution of the membrane:

$$K_{stab\ const} = \frac{[Ag\ (NH_3)_2^+]}{[Ag^+]\ [NH_3]^2} \qquad (11)$$

The allowable levels of CN^- and NH_3 are governed by the ratio of the stability constant for the respective complex to the solubility product of AgCl. On the other hand, common cations (except Hg^{++}) would not be expected to interfere to any significant extent; neither would F^- NO_3^- and $SO_4^=$ etc. AgCl is stable in acid solutions, indicating a pH independance.

In strong Cl^- solutions () 1.0 MCl^-) AgCl is appreciably soluble, and use of a chloride electrode in such solutions for long periods of time reduces the lifetime of the electrode:

NaCl (M)	Ag^+ (M $\times 10^5$)
0.933	8.6
1.43	18.4
2.27	57.0
3.00	119.4
4.17	333.5
5.04	603.9

TABLE (3)

Effect of NaCl on the Solubility of AgCl

Essentially similar arguments can be used to predict the selectivity of all other solid-state electrodes.

(iii) Liquid Membranes

Selectivity is a function of the values of the various complex ion stability constants (primary ion: other ions) and the properties of the solvent. Selectivity constants are difficult to predict and are best determined experimentally.

Substance	K_{sp}	Substance	K_{sp}
AgBr	7×10^{-13}	CuSCN	1×10^{-11}
$AgBrO_3$	5×10^{-5}	FeS	4×10^{-19}
AgCNS	1×10^{-12}	Hg_2Br_2	5×10^{-23}
AgCl	1×10^{-10}	Hg_2Cl_2	3×10^{-18}
$Ag_2C_2O_4$	5×10^{-12}	Hg_2I_2	1×10^{-28}
$AgCrO_4$	2×10^{-12}	HgS	4×10^{-54}
AgI	1×10^{-16}	LaF_3	1×10^{-24}
$AgIO_3$	2×10^{-8}	MgF_2	7×10^{-9}
Ag_3PO_4	2×10^{-18}	NiS	1×10^{-24}
Ag_2S	1×10^{-51}	$PbBr_2$	8×10^{-5}
Ag_2SO_4	8×10^{-5}	$PbCl_2$	2×10^{-4}
$BaSO_4$	9×10^{-11}	$PbCrO_4$	2×10^{-14}
$CaCO_3$	5×10^{-9}	PbF_2	4×10^{-8}
CaF_2	3×10^{-11}	PbI_2	9×10^{-9}
$CaSO_4$	2×10^{-4}	PbS	5×10^{-29}
CdS	1×10^{-28}	$PbSO_4$	2×10^{-8}
CoS	3×10^{-26}	ZnS	1×10^{-23}
CuS	1×10^{-44}		

TABLE (4)
Table of Solubility Products at the Laboratory Temperature.

USE OF ELECTRODES

(a) METHODS OF USE

Ion Selective Electrodes can be used to measure activity by direct potentiometry (and also concentration if activity coefficients are known), or concentration by titration methods. In some applications activity is the more meaningful, particularly in biological systems. In industrial analysis, concentration is usually the parameter required. Important points of both applications will be discussed below.

(i) Direct Potentiometry.

In this, the activity of the sample is compared to measured activities of standard solutions (cf. buffer calibration in pH measurements). If the reading is in mV or pX, then an antilog conversion is required to produce a linear relationship between mV (pX) and activity. Logarithmic graph paper can be used or alternatively, a calibration curve can be constructed. A direct reading of activity is possible if the output is in the M or ppm antilog form provided the slope is corrected.

"Standard" solutions are essentially "standard" (i.e., of accurately known composition) w.r.t. **CONCENTRATION** rather than activity. This is because a standard solution is prepared by weighing out a certain quantity of compound (containing a specific amoung of the desired ion) and dissolving it in a known volume of solvent. If the solution is not dilute, it will depart from ideal and the concentration will not be the same as the activity, as shown in Section 1. Fortunately, activity coefficients or related data (see table (1)) can be obtained for many simple electrolytes and, hence, measurement of either activity **OR** concentration of a sample containing a **SINGLE** electrolyte is possible. A sample containing many electrolytes or a non-aqueous solvent presents a different problem. The **ACTIVITY** can be measured directly by comparing to standards of known activity. The **CONCENTRATION** can be obtained by making standards with identical composition to the sample w.r.t. the other electrolytes or solvent composition, and constructing a calibration curve.

Some ions, for which there are no electrodes, can be measured by adding a relatively insoluble salt (in powder form) of the ion and measuring the activity of the complementary cation or anion of the salt, the level of which will be determined by the activity of the ion via the solubility product.

La^{3+} can be measured by adding solid LaF_3 to the sample and measuring the F^- activity.

Various "standard addition" methods involving measuring the change of potential when increments of a standard reactant are added to the sample are also of use in extending the application to other systems.

(ii) **Titration**

Chemical

Ion Selective Electrodes can be used as end point indicators, just as the pH electrode can be used to detect the end point of an acid base titration. This method is particularly useful when coloured dyes or chelating agents cannot be used as indicators, as in applications where the sample is coloured or turbid.

A titration method always measures **CONCENTRATION** not activity. As a particular ionic species is consumed in the course of a titration bound ions become free because the equilibrium constant (which defines the **RATIO** of bound to free ions) must remain fixed. Thus ALL of the bound ions will become available for reaction even if there is an extremely small number of free ions (relative to bound) present initially. For most simple inorganic reactions this redistribution takes place exceedingly quickly; much faster than the time taken for the titration. The titration method is more accurate than direct potentiometry, but is more time-consuming.

The method can also be extended to measure some ions for which no electrodes exist, because either the ion to be titrated **OR** the titrating ion can be monitored.

As an example $SO_4^=$ can be titrated with Pb^{++} using a lead electrode to measure the end-point.

Generating Ion

If a potential is applied across a membrane, ions can be caused to migrate; this means that in favourable circumstances a titrant can be "generated" electrically. Sensing electrodes can be used to detect the end point, so the whole titration becomes electrochemical.

A survey of many applications both potentiometric and titration is given in "Ion Selective Electrodes" and new methods of analysis are constantly being devised. Journals such as "Analytical Chemistry" are useful sources of information on new applications.

(b) **SOME PRACTICAL CONSIDERATIONS**

The best way of deciding whether an electrode can be used for a particular application is to consult the literature (reviews, articles etc.) and to make use of information supplied by electrode manufacturers. In this way references to similar applications may be obtained. As each application
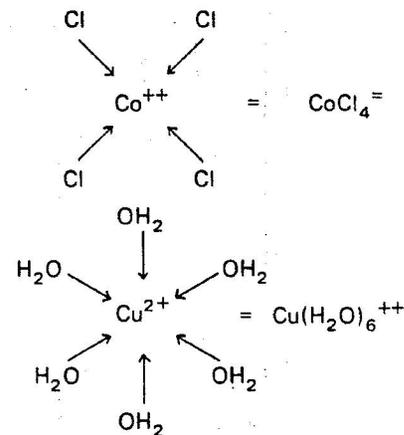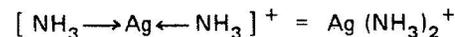
20.

requires a separate treatment, only a few examples of the more important practical considerations that should be made are given below.

(i) **Interferences**

In cases where interferring ions do not damage an electrode membrane, allowances can be made provided the activity of interferring ion(s) is/are known and the relevant selectivity constants are known. Separation processes (partial oxidation, ion exchange, precipation or complex formation etc.) must be used to reduce interferring ions to below the critical level if these ions damage the membrane. Consultation of literature reports will be a valuable guide in dealing with a specific problem.

(ii) **Complexation**

A complex consists of a central metal ion (often a transition or alkaline earth metal ion) surrounded by a number of anions or neutral molecules called ligands. The number of ligands which surround the central metal ion is determined by the **COORDINATION NUMBER** of the central metal ion and is commonly 2, 4 or 6. The complex overall may be an anion, cation or neutral molecule, depending on the charge of the central metal ion, and the charge (if any) of the ligands. Examples are:
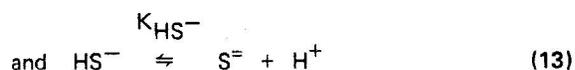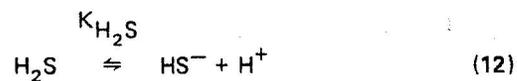
$$[NH_3 \longrightarrow Ag \longleftarrow NH_3]^+ = Ag(NH_3)_2^+$$

$$[CN \longrightarrow Ag \longleftarrow CN]^- = Ag(CN)_2^-$$

$$CoCl_4^=$$

$$Cu(H_2O)_6^{++}$$

21.

Here relatively simple ligands (NH_3, CN^-, Cl^-, H_2O) are illustrated. More complicated cases arise when the ligand is a side group of a larger molecule e.g. a protein.

It is important to know whether complexation can take place in a given sample solution if the **CONCENTRATION** of the ion is required. For example, in the measurement of the fluoride ion concentration in town water the presence of Al^{3+} (from alum used in treatment) will result in the formation of complexes between Al^{3+} and F^- (i.e. $AlF_{\overline{n}}$) which the fluoride electrode does not detect. The $AlF_{\overline{n}}$ complex may be destroyed, however, by adding another ligand which has a greater affinity for Al^{3+} than F^- has, e.g. citrate. The addition of a citrate solution to the sample binds the Al^{3+} and releases the F^- from the $AlF_{\overline{n}}$. The relative affinities of the two ligands for Al^{3+} can be obtained from the stability constants of the respective complexes. The extent of complexation is usually a function of pH, hence by suitable adjustment of the pH of the sample, complexation can be prevented.

(iii)   **pH Control**

Some anions, e.g. sulphide can exist in a variety of forms in solution, such as $S^=$, HS^- and H_2S, depending on the pH. The dissociation constants of the two acids:

$$H_2S \; \overset{K_{H_2S}}{\leftrightharpoons} \; HS^- + H^+ \qquad (12)$$

$$\text{and} \quad HS^- \; \overset{K_{HS^-}}{\leftrightharpoons} \; S^= + H^+ \qquad (13)$$

give the relationship between the three forms:

$$K_{H_2S} = \frac{[HS^-][H^+]}{[H_2S]} \qquad (14)$$

$$K_{HS^-} = \frac{[S^=][H^+]}{[HS^-]} \qquad (15)$$

22.

Taking $\log_{10}$ of both sides

$$\log a_{HS^-} = \log K_{HS^-} + \log a_{S^=} - pH \qquad (16)$$

and

$$\log a_{H_2S} = \log K_{H_2S} + \log a_{HS^-} - pH \qquad (17)$$

Thus if the pH of the solution is known, as well as K_{HS^-} and K_{H_2S}, a_{HS^-} and a_{H_2S} can be calculated, i.e. the TOTAL sulphide can be computed.   Figure (1) shows the distribution of the total sulphide (= concentration) between the forms H_2S, HS^- and $S^=$ as a function of pH.
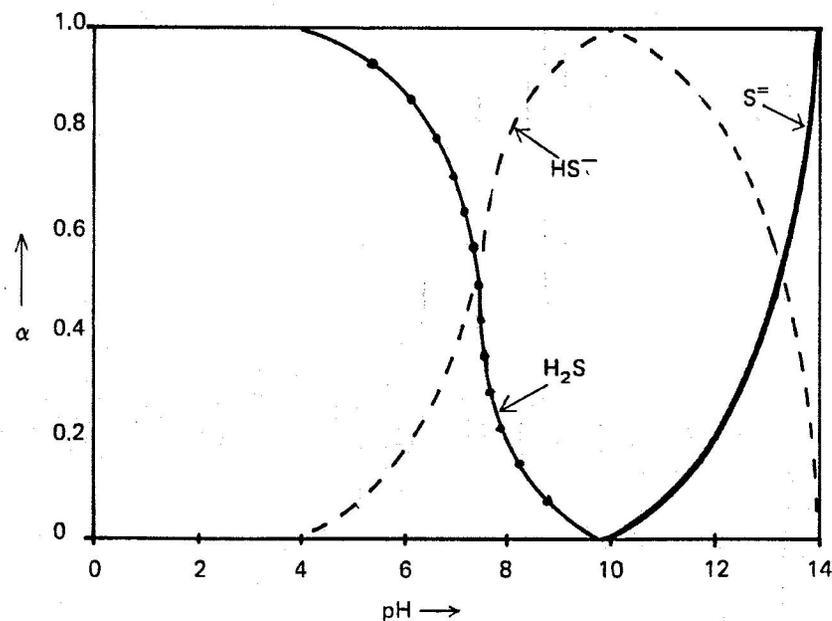

FIGURE (1)

The **DIRECT** determination of **TOTAL** sulphide involves making **BOTH** the sample and the calibration standards strongly alkaline. Cyanide, CN^- can exist as HCN whilst divalent metal ions precipitate out as hydroxides at high pH.

23.

(iv) **High Ionic Strength Medium**

By adding an inert electrolyte to the sample to produce a large increase in the ionic strength, the ionic strength contribution of the sample electrolyte can be swamped out; measurements can then be interpreted in terms of concentration rather than activity. This method has been of particular value in determining low fluoride levels.

(v) **Stirring**

Stirring samples of low ionic strength can lead to the generation of small electrokinetic potentials. Usually it is not necessary to stir when measuring with ion-selective electrodes, however if a solution has to be stirred, a uniform rate should be applied and calibration carried out at the same stiring rate.