

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.

(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	$7 \times 10^{-13}$	CuSCN	$1 \times 10^{-11}$
AgBrO <sub>3</sub>	$5 \times 10^{-5}$	FeS	$4 \times 10^{-19}$
AgCNS	$1 \times 10^{-12}$	Hg <sub>2</sub> Br <sub>2</sub>	$5 \times 10^{-23}$
AgCl	$1 \times 10^{-10}$	Hg <sub>2</sub> Cl <sub>2</sub>	$3 \times 10^{-18}$
Ag <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	$5 \times 10^{-12}$	Hg <sub>2</sub> I <sub>2</sub>	$1 \times 10^{-28}$
AgCrO <sub>4</sub>	$2 \times 10^{-12}$	HgS	$4 \times 10^{-54}$
AgI	$1 \times 10^{-16}$	LaF <sub>3</sub>	$1 \times 10^{-24}$
AgIO <sub>3</sub>	$2 \times 10^{-8}$	MgF <sub>2</sub>	$7 \times 10^{-9}$
Ag <sub>3</sub> PO <sub>4</sub>	$2 \times 10^{-18}$	NiS	$1 \times 10^{-24}$
Ag <sub>2</sub> S	$1 \times 10^{-51}$	PbBr <sub>2</sub>	$8 \times 10^{-5}$
Ag <sub>2</sub> SO <sub>4</sub>	$8 \times 10^{-5}$	PbCl <sub>2</sub>	$2 \times 10^{-4}$
BaSO <sub>4</sub>	$9 \times 10^{-11}$	PbCrO <sub>4</sub>	$2 \times 10^{-14}$
CaCO <sub>3</sub>	$5 \times 10^{-9}$	PbF <sub>2</sub>	$4 \times 10^{-8}$
CaF <sub>2</sub>	$3 \times 10^{-11}$	PbI <sub>2</sub>	$9 \times 10^{-9}$
CaSO <sub>4</sub>	$2 \times 10^{-4}$	PbS	$5 \times 10^{-29}$
CdS	$1 \times 10^{-28}$	PbSO <sub>4</sub>	$2 \times 10^{-8}$
CoS	$3 \times 10^{-26}$	ZnS	$1 \times 10^{-23}$
CuS	$1 \times 10^{-44}$		

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 amount 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<sup>3+</sup> can be measured by adding solid LaF<sub>3</sub> to the sample and measuring the F<sup>-</sup> 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  $\text{SO}_4^{2-}$  can be titrated with  $\text{Pb}^{2+}$  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

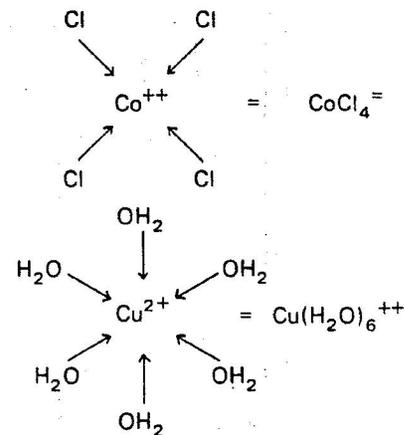
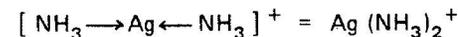
requires a separate treatment, only a few examples of the more important practical considerations that should be made are given below.

(i) **Interferences**

In cases where interfering ions do not damage an electrode membrane, allowances can be made provided the activity of interfering ion(s) is/are known and the relevant selectivity constants are known. Separation processes (partial oxidation, ion exchange, precipitation or complex formation etc.) must be used to reduce interfering 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:

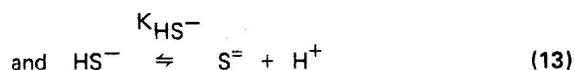
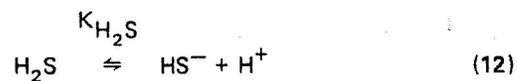


Here relatively simple ligands ( $\text{NH}_3$ ,  $\text{CN}^-$ ,  $\text{Cl}^-$ ,  $\text{H}_2\text{O}$ ) are illustrated. More complicated cases arise when the ligand is a side group of a larger molecule e.g. a protein.

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  $\text{Al}^{3+}$  (from alum used in treatment) will result in the formation of complexes between  $\text{Al}^{3+}$  and  $\text{F}^-$  (i.e.  $\text{AlF}_n^-$ ) which the fluoride electrode does not detect. The  $\text{AlF}_n^-$  complex may be destroyed, however, by adding another ligand which has a greater affinity for  $\text{Al}^{3+}$  than  $\text{F}^-$  has, e.g. citrate. The addition of a citrate solution to the sample binds the  $\text{Al}^{3+}$  and releases the  $\text{F}^-$  from the  $\text{AlF}_n^-$ . The relative affinities of the two ligands for  $\text{Al}^{3+}$  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  $\text{S}^{2-}$ ,  $\text{HS}^-$  and  $\text{H}_2\text{S}$ , depending on the pH. The dissociation constants of the two acids:



give the relationship between the three forms:

$$K_{\text{H}_2\text{S}} = \frac{[\text{HS}^-][\text{H}^+]}{[\text{H}_2\text{S}]} \quad (14)$$

$$K_{\text{HS}^-} = \frac{[\text{S}^{2-}][\text{H}^+]}{[\text{HS}^-]} \quad (15)$$

Taking  $\log_{10}$  of both sides

$$\log a_{\text{HS}^-} = \log K_{\text{HS}^-} + \log a_{\text{S}^{2-}} - \text{pH} \quad (16)$$

$$\text{and } \log a_{\text{H}_2\text{S}} = \log K_{\text{H}_2\text{S}} + \log a_{\text{HS}^-} - \text{pH} \quad (17)$$

Thus if the pH of the solution is known, as well as  $K_{\text{HS}^-}$  and  $K_{\text{H}_2\text{S}}$ ,  $a_{\text{HS}^-}$  and  $a_{\text{H}_2\text{S}}$  can be calculated, i.e. the TOTAL sulphide can be computed. Figure (1) shows the distribution of the total sulphide (= concentration) between the forms  $\text{H}_2\text{S}$ ,  $\text{HS}^-$  and  $\text{S}^{2-}$  as a function of pH.

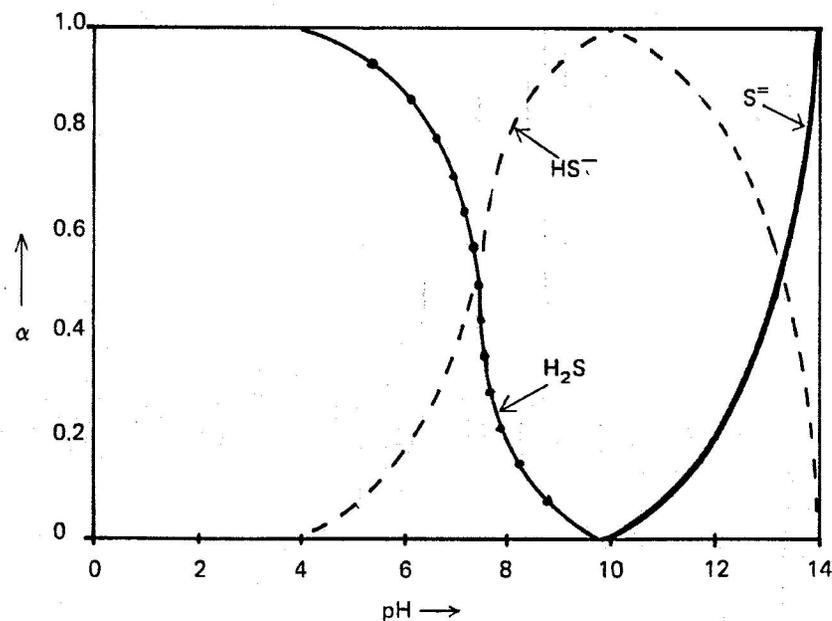


FIGURE (1)

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

(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 stirring rate.