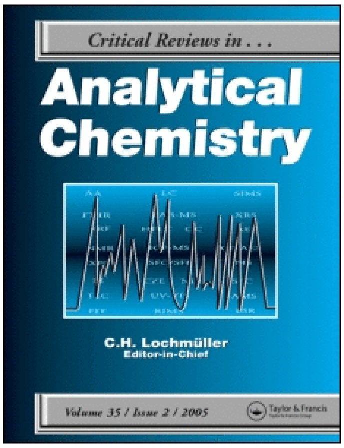

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ION-SELECTIVE ELECTRODES

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I. INTRODUCTION AND SCOPE

The term *'ion-selective electrodes'* is applied to a range of *membrane* electrodes which respond selectively toward one (or several) ionic species in the presence of others. The less-preferred term *'ion-specific'* is not favored[1] because these electrodes are rarely specific in their response to one ionic species over others, although this is a desirable property sought by the designer of new electrodes. The description *membrane* is used here in its broadest sense to denote a thin section of electrically conducting material separating two solutions and across which a potential develops. Often the term *membrane* has associated with it the notion of permeability to a species present in the flanking solutions. However, although this is undoubtedly true with certain porous biological and synthetic membranes, the actual mechanism of electrical conduction in general varies with the type of membrane material; indeed it may change within it.

The hydrogen-ion-responsive glass electrode, well-known for its use in pH measurements, falls within the definition given above. A number of reviews[2,3] and books[4,5] have dealt with its properties, use, suggested mechanism of functioning, and related studies of glass itself, so it is not the intention to devote space here to a discussion of these. Glass electrodes responsive to alkali-metal cations are a more recent development. All types of glass electrodes are, however, considered as ion-selective electrodes.

Unlike some developments in science, no startling new principle heralded the arrival of nonglass ion-selective electrodes. Indeed it is not easy to ascribe a starting date to these developments which led to the publication of several thousands of papers on this subject in the late 1960's. Rather, as shown in the next section, there was a steady increase in knowledge in related fields, which culminated in the invention of the novel lanthanum fluoride electrode,[6] and this in turn triggered off the "whole new technology of measurement." It is the purpose of this review to attempt to place in perspective claims such as this, now that the situation has stabilized, and to assess the impact on and importance for analytical chemistry of the availability of sensors for important ions that previously had not been determinable by potentiometric techniques.

A number of detailed reviews are available[7-12] but they have become dated in a period of rapid progress, particularly with regard to such ephemeral information as commercial availability of electrodes. This aspect will not be stressed here. The review papers are available from a Symposium sponsored by the National Bureau of Standards and held in Gaithersburg, Md. in January 1969. This remains a source book of much valuable information. The facts that the Symposium attracted 450 participants and that the book has had several reprintings are significant of the interest aroused. It is intended that this review will be comprehensive but not detailed in coverage and it is hoped to survey critically the principles of the subject in a way that should be comprehensible to the nonspecialist who wishes to keep abreast of developments; nevertheless, it should have something to offer the specialist.

The classification of ion-selective electrodes into (a) solid-state, (b) heterogeneous, and (c) liquid-ion-exchange types, which is based on the form of electrode fabrication, is no longer appropriate because some active materials can be used in all three of the above forms. A new classification based on the type of active material will be presented in Section III and in the following section (Section IV) different forms of electrode fabrication and construction will be discussed. Table 1 lists the ions to which the principal electrodes developed are primarily responsive, and summarizes the various systems which have been used to achieve this response. Selectivity considerations will be discussed in Section V.2.

II. HISTORICAL DEVELOPMENT

Although the current interest in ion-selective electrodes may be said to have arisen in 1966–7 with the announcement by Frant and Ross[6,14] of Orion Research Inc. of the fluoride- and calcium-responsive electrodes, in fact, these developments were the culmination of studies made by many workers and going back to the turn of the century. Cremer[15] is credited with the discovery of the hydrogen-responsive glass electrode, but the detailed study was made by Haber and Klemensiewicz.[16] Haber with his students also foreshadowed later developments in heterogeneous membrane electrodes and liquid-ion-exchange types by studying calomel dispersed in paraffin wax and the differences of potential arising from

TABLE 1

Principal Ion-selective Electrode Systems

Ion	Material/Form
H^+	Glass/bulb
Li^+	Glass/bulb
Na^+	Glass/bulb, glass/disc
K^+	Glass/bulb, Valinomycin/L or PVC or SR, Potassium tetrachlorophenylborate/L
$NH_4{}^+$	Glass/bulb, Monactin-nonactin/L
Ca^{2+}	Calcium didecylphosphate/L or PVC, Thenoyltrifluoracetone/PVC, CaF_2-LaF_3/disc
Ca^{2+}/Mg^{2+}	Calcium didecylphosphate/L (decanol)
Ba^{2+}	Nonylphenoxypolyoxyethyleneethanol/L
Cu^{2+}	Ag_2S + CuS/disc or SR, $Cu_{1.79}$ S/disc, CuS/C, Chalcogenide glass/disc, $(R\text{-}S\text{-}CH_2COO)_2Cu$/L
Fe^{3+}	Chalcogenide glass/disc
Ag^+	Glass/bulb, Ag_2S/disc
Zn^{2+}	ZnSe + Ag_2S/disc
Mn^{2+}	MnSe + Ag_2S/disc
Cd^{2+}	CdS + Ag_2S/disc
Ni^{2+}	NiSe + Ag_2S/disc
Pb^{2+}	PbS + Ag_2S/disc or SR, $(R\text{-}S\text{-}CH_2.COO)_2Pb$/L
F^-	LaF_3/single crystal or SR
Cl^-	AgCl + Ag_2S/disc, AgCl/SR, AgCl + Ag_2S/G, Dimethyldistearylammonium chloride/L
Br^-	AgBr + Ag_2S/disc, AgBr/SR, AgBr + Ag_2S/G
I^-	AgI + Ag_2S/disc, AgI/SR, I_2/G(CCl_4)
$S_2{}^-$	Ag_2S/disc, Ag_2S/SR, Ag_2S/G
$ClO_4{}^-$	Fe(II)1,10-phenanthroline perchlorate/L, Tetra-*n*-heptylammonium perchlorate/L
$NO_3{}^-$	Ni(II)1,10-phenanthroline nitrate/L or PVC, Tridodecylhexadecylammonium nitrate/L or PVC
$BF_4{}^-$	Ni(II)1,10-phenanthroline fluoroborate/L
SCN^-	AgSCN + Ag_2S/disc, AgI/SR
$SO_4{}^{2-}$	$PbSO_4$ + PbS + Ag_2S + Cu_2S/disc

Key: L Liquid-ion-exchange form
G Graphite ('Selectrode')
SR Silicone rubber heterogeneous membrane
PVC Polyvinyl chloride membrane
Systems in boldface type are available commercially.

distribution of substances such as sodium salicylate between organic and aqueous phases.[17,18] A useful summary of the work of Haber's student Beutner is given in Michaelis' classic book.[19] Much of the stimulus to this work arose from its medical and physiological implications, which were well realized by Michaelis among others. The importance of calcium ion in biological fluids inspired Tendeloo et al.[20-22] to many attempts to seek a reversible calcium sensor, but this was not achieved by Ross[14] until 30 years after Tendeloo's initial attempts[20] in 1936 with natural fluorite.

Table 2 summarizes some highlights in the development of ion-selective electrodes. It is interesting that Kolthoff and Sanders[23] made the first silver-halide-disc electrodes in 1937 and reported on their principal advantage over conventional electrodes of the second kind, that of insensitivity to oxidizing agents (potassium permanganate). They failed to reproduce Tendeloo's findings[20] with fluorite; in fact, the whole history of the subject is full of such contradictory findings. They also tried[23] coating silver chloride directly onto platinum wires and found the resulting electrode to be erratic in behavior. Again, dipped-wire

TABLE 2

Highlights in the Development of Ion-selective Electrodes

Workers	Ref. no.	Active material	Matrix	Sensitive to	Nernst slope and solution media	Selectivity	Comments
Tendeloo (1936)	20	Fluorite CaF_2	None	Ca^{2+}	Linear but not Nernstian		
Kolthoff and Sanders (1937)	23	Cast AgCl,	None	Cl^-	57.9 mV	AgI not affected by Cl^-, Br^-	Report on Pt wire coated electrodes
		AgBr		Br^-	57.4 mV	Not affected by $KMnO_4$	Could not repeat Tendeloo's work with fluorite
		AgI discs		I^-	52 mV		
Marshall (1939)	41	Natural zeolites (Chabazite Apophyllite)	None	M^+ M^{2+}	∿40 mV 20–30 mV	Not tested	Reported difficulty in sealing discs on to Pyrex with available cements
Marshall and Bergman (1941–2)	35, 36	Clay (montmorillinite bentonite)	None	K^+ NH_4^+		Interference from Na^+ but not Ca^{2+}, Mg^{2+}	Colloidal suspension dried at high temp. (490°)
Sollner (1943, 1954)	37–40	Collodion (surface oxidized in 1 *M* NaOH)	None	K^+, Na^+, NH_4^+ Mg^{2+}		Serious interferences	Useful in titration studies
Sollner (1943, 1954)	37–40	Collodion (surface treated in protamine sulfate)	None	Cl^-, Br^-, I^- ClO_4^-, NO_3^-		Serious interferences	Claimed as first anion responsive membrane electrode
Wyllie and Patnode (1950)	42	Commercial cation exchange resins	Methyl methacrylate polystyrene	Na^+	51–56 mV	Not tested	
Tendeloo and Krips (1957)	21	Ca oxalate and other calcium salts	Paraffin + nonionic detergent on gauze	Ca^{2+}	Ca nitrate	'Fairly acceptable'	Criticized by Shatkay,[30]
Parsons (1958)	43	Amberlite 120	Polystyrene	Na^+	Linear pNa 1–3 closely conforms to Nernst equation	K^+ interferes	Anion membrane also studied for titration of sulfate with barium acetate

TABLE 2 (continued)

Highlights in the Development of Ion-selective Electrodes

Workers	Ref. no.	Active material	Matrix	Sensitive to	Nernst slope and solution media	Selectivity	Comments
Fischer and Babcock (1958)	44	Ba sulfate Ba chromate	Paraffin without gauze	Ba^{2+} $SO_4{}^{2-}$	Barium chloride and hydroxide, sulfuric acid	Not perfectly selective to either anions or cations	Slow to attain equilibrium
Tendeloo and Krips (1959)	45	K tetraphenylborate	Polystyrene + gauze	K^+	Various	Not selective	
Tendeloo and van der Voort (1960)	22	Ca stearate	Paraffin as above	Ca^{2+}		Stronger response to Ca^{2+} than oxalate electrode. No response to K^+	
Cloos and Fripiat (1961)	46	Ca oxalate	Paraffin + detergent	Ca^{2+}	Various	Nonspecific, porous	Exhibit memory
Pungor and Hollos-Rokosinyi (1961)	47	Ag iodide	Paraffin	I^-		K chloride does not interfere	±5 mV reproducibility
Sollner and Shean (1964)	33	Trialkylmethyllauryl (Amberlite LA-2) amine salts	Benzene, xylene, or nitrobenzene	Cl^-, SCN^-	Within a few tenths mV of theoretical for KCl		
Pungor, Havas, and Toth (1964)	27	Ion-exchange resins	Silicone rubber	$SO_4{}^{2}$, Cl^-, OH^- H^+, K^+, Zn^{2+}, Ni^{2+}		Selective to valence type Not specific	
Pungor, Toth, and Havas (1964)	26, 27	Ba sulfate	Silicone rubber	$SO_4{}^{2-}$	K^+ sulfate (24–30 mV)	Phosphate interferes	
		Ag iodide		I^-	K^+ iodide (56–60 mV)	10^{-1} *M* KCl does not interfere	
Pungor, Havas, and Toth (1965)	28	Silver halides	Silicone rubber	Ag^+, X^-			
		Mn(III) phosphate Al oxine Ni DMG		$PO_4{}^{3-}$ Al^{3+} Ni^{2+}			

TABLE 2 (continued)

Highlights in the Development of Ion-selective Electrodes

Workers	Ref. no.	Active material	Matrix	Sensitive to	Nernst slope and solution media	Selectivity	Comments
Morazzani-Pelletier and Baffier (1965)	48	$Co(PO_4)_3$ NiDMG Mn(II) oxalate Ni(II) oxalate	Collodion Paraffin		20–23 mV in Co^{2+} chloride, bromide and nitrate. Poor response in sulfate and acetate	Leveled by K^+ chloride Li^+ sulfate	Porous membranes
Geyer and Syring (1966)	49	TiO_2, Fe_2O_3, SnO_2	Polyethylene	H^+, OH^-			Titrations only studied
		ZrO_2	Polypropylene	Na^+			
		Al_2O_3	Paraffin				
		K_2SiF_6	Agar or paper	$SiF_6{}^{2-}$ and K^+			
		$Ag_4Fe(CN)_6$ $PbWO_4$	Agar Paraffin	Both ions			
Bonner and Lunney (1966)	34	Dinonylnaphthalene sulfonate salts	Nitrobenzene + *o*-dichlorobenzene	Na^+, $NH_4{}^+$, Ca^{2+}	Less than theoretical		Useful 3×10^{-1} *M* to 3×10^{-3} *M* only
		tricaprylmethylammonium chloride (Aliquat 336)	*o*-dichlorobenzene	Cl^-			
Frant and Ross (1966)	6	LaF_3 single crystal	None	F^-	Theoretical	OH^- interferes	
Ross (1967)	14	Calcium didecylphosphate	Di-*n*-octyl Phenylphosphonate	Ca^{2+}	Theoretical	H^+, Zn^{2+} interferes	
Shatkay (1967)	30	Ca oxalate	Paraffin + nonionic Detergent + gauze	Ca^{2+}	Ca^{2+} chloride (15–20 mV)	Not completely permselective Not specific	Gauze necessary for conduction No difference between pure paraffin and paraffin + Ca oxalate
		Thenoyltrifluoracetone	PVC + tributylphosphate	Ca^{2+}	Ca^{2+} chloride (27–28 mV)	Selective up to 0.1 *M* Mg^{2+}, Na^+ chlorides	Compared well with commercial liquid-ion-exchanger electrode
Pioda, Stankova, and Simon (1969)	50	Valinomycin	Diphenylether	K^+	58.3 mV	High selectivity for K^+ over Na^+	

electrodes have recently been advocated by Freiser and co-workers.[24,25] The range of heterogeneous membrane electrodes employing silicone rubber as inert matrix introduced by Pungor, Toth, and their collaborators[8,26-29] in Hungary has its beginnings in the early efforts of Tendeloo et al.[21,22] using paraffin wax; more recent work has employed other polymers.[30,31] Often discrepant findings with precipitates and other materials imbedded in an inert matrix arise from leaky or cracked membranes. Quite stable potentials can be obtained from such systems arising from a modified liquid-junction potential. The silicone-rubber membranes impregnated with suitable precipitates devised by Pungor and his co-workers in Hungary were the first to achieve commercial viability about 1965. Halide and sulfide electrodes were the most important giving typically 56 mV/pI (iodide, pI 1–6) 55 mV/pCl (chloride, pCl 1–3). A wide range of applications was developed for these commercial forms marketed by Radelkis of Budapest, but they now appear to have been superseded by solid-state-forms. A detailed review to 1969 is available,[32] and there is a later review by Pungor and Toth.[8]

The origins of work on liquid-ion-exchange materials, culminating in the calcium-, nitrate-, and perchlorate-responsive electrodes, can be traced to two papers by Sollner and Shean[33] and by Bonner and Lunney,[34] which were notably more successful than attempts to disperse solid ion-exchange materials in a polymer matrix. The clay membranes of Marshall and Bergman[35,36] and the work on collodion membranes by Sollner et al.[37-40] are important milestones along the path of development. Sollner's collodion membranes, when oxidized in 1 *M* sodium hydroxide, showed a cation response probably due to the formation of carboxylate groups on the surface. When the membranes were conditioned in protamine sulfate instead (a preparation from trout roes, also known as clupeine, which contains arginine (10), serine (2), proline (1) and alanine (1) and valine (1) units), they showed an anion response. It seems likely that this work foreshadows the use of alkylammonium or amine salts as liquid-ion-exchangers for electrodes. Bonding new phases onto, or modifying the surface structures of, suitable materials would be a promising way of approaching the development of new electrode systems.

Students of the history of ideas might ponder why the new developments took so long. The answer probably lies in the delayed advances in related fields. Progress in the general preparative chemistry of pure materials and in understanding of the solid-state and kinetic and transport processes were all necessary, coupled with the fact that measurement of the difference of potential arising from a high-impedance source is not the difficult problem it was in the early vacuum-tube electrometer era.

No attempt has been made to give a comprehensive coverage of these early developments. The literature on membrane potentials, particularly in biological applications, is considerable. The development of heterogeneous membrane electrodes has been reviewed previously.[32] Several workers[2-5] have reviewed the development of glass electrodes.

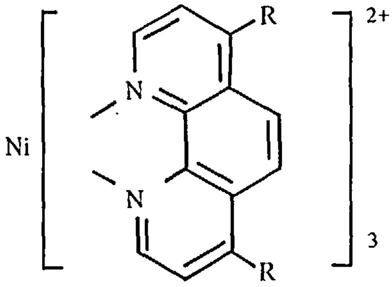
III. CLASSIFICATION OF MATERIALS

Active materials for ion-selective electrodes can be broadly classified into:

a. glass,

b. insoluble inorganic salts, such as silver sulfide and lanthanum fluoride, and

c. long-chain ion-exchange materials, such as the alkyl phosphate salts and the tetraalkyl ammonium salts, and complexing agents, often those useful for solvent extraction. These may be neutral carriers (they provide electrically neutral sites for exchange) such as 2-thenoyltrifluoroacetone, but charged sites have been used such as the nickel (II) substituted 1,10-phenanthroline complex, the active material for a nitrate-responsive electrode.



The common property shared by all these materials is their ability, when brought into contact with an electrolyte solution containing suitable ions, to set up rapidly an exchange equilibrium or ion-exchange process across the phase boundary. The exact details of this vary for the different materials. A second requisite property is the ability of the active material to conduct electricity. The conduction process may be by ionic, electronic, or defect mechanisms, or a combination of these, depending on the type of material.

1. Glass

The hydrogen-ion-responsive glass electrode was the founder member of the current family of ion-selective electrodes. By modification of the glass composition by the inclusion of alumina, it was found[51] that the alkaline error, due to a sodium-ion response at high pH, could be extended to lower pH and, hence, the electrode could be said to respond to Na^+, although H^+ ions interfered at low pH. Based principally on the studies of Eisenman and his collaborators[4,5] with these aluminosilicate glasses, a range of monovalent-cation-responsive glass electrodes is available commercially. From selectivity studies, which deal with the response of an electrode to a given ion in the presence of an interfering ion, Eisenman[4] was able to make suggestions for glass compositions giving a predominant response to certain monovalent ions. The glass composition NAS 11–18 (the first figure refers to mol% Na_2O, the second to mol% Al_2O_3 is used for sodium electrodes and NAS 27–04 or 27–06 for potassium electrodes. Boric oxide has a similar effect of enhancing the response to alkali-metal ions and is sometimes used in combination with alumina. The corresponding lithium aluminosilicates have been similarly studied and are used commercially where they have an added advantage of lower fusion temperatures. In addition to the alkali-metal ions, some glasses respond to ammonium, thallium, and silver ions, and to a much lesser extent to alkaline earth ions. All these developments have been adequately reviewed by Eisenman et al.[4,5]

As with hydrogen-ion-responsive glass electrodes, many other elements have been incorporated in glass melts to modify or enhance certain properties. For example, lithium ferrosilicate glasses show a mixed hydrogen-lithium function but on heat treatment (for 1 hr at 550°C) develop a redox function.[52] A new development along these lines that could be of great importance is the chalcogenide glass semiconducting electrodes of Baker and Trachtenburg[53] which are claimed to show Nernstian response to Cu^{2+} and Fe^{3+} *in* the range 10^{-5} to 10^{-1} mol $l.^{-1}$. The glass has the composition 60% Se, 28% Ge, and 12% Sb and is doped with 2% of metallic iron, cobalt, or nickel to increase the conductivity. The electrodes do not respond to Fe^{2+} and the presence of metallic iron in the glass is not a prerequisite for Fe^{3+} response. It is considered[53] that the glass acts as a reducing agent which generates the lower oxidation state of the redox couple and maintains it at constant activity; hence, the electrode responds to Fe^{3+} and not to Fe^{2+}.

2. Insoluble Inorganic Salts

The basic requirements of this type of material appear to be (a) a solubility below 10^{-6} mol l^{-1} (b) electrical conductivity. There is a close relationship between ion-selective electrodes fabricated from insoluble salts and electrodes of the second kind (see Section V). However, electrical conductivity of the salt is not essential for the correct functioning of electrodes of the second kind because the salt needs only to be present at saturation in the solution phase; it is just convenient to have a reservoir of material in the form of a solid coating on the metal. If this coating is closely adherent and crack-free, electrical conductivity may be necessary. This must not be taken as implying that corresponding ion-selective electrodes can only be found when a useful electrode of the second kind exists. It may not be possible to make an electrode of the second kind if the metal is unstable in the presence of air and water, for example, La/LaF_3 or $Ba/BaSO_4$. In the latter example, barium sulfate is said to be an insulator; nevertheless, a prototype heterogeneous membrane electrode was evaluated and a slope of 31 mV/decade reported.[54] When both conventional and ion-selective forms exist, the advantage claimed[23] for the latter is that the absence of the metallic phase means that any redox potential existing in the solution is not picked up. An extreme example of this comes from recent work[55] in the reviewer's laboratory where it was found that a silver-chloride disc ion-selective electrode did not cause the decomposition of chloride-containing aqueous hydrogen peroxide solutions, whereas a thermal electrolytic silver-silver chloride electrode promoted rapid catalytic decomposition and oxygen evolution.

When a choice is possible, a compacted disc or single crystal form seems to be preferable in performance. There have been few direct comparisons of these with heterogeneous membrane forms but the weight of evidence is in favor of the former type. It may not always be possible to fabricate compacted discs because of the existence of a phase transition that occurs at elevated pressure and/or temperature and whose reversal causes a compressed pellet to disintegrate some time after the pressure is decreased. It may, however, be possible to incorporate additives which remove or displace such phase transitions. An example is the incorporation of silver sulfide in silver iodide discs.[56]

For heterogeneous membrane electrodes, the correct ratio of active material to binder must be achieved[32] to ensure contact between particles to facilitate electrical conduction. Whether such conduction is achieved through or over the surface of the particles is debatable. Conduction may be enhanced by precipitation of the material with one or other of the ions present in excess. Other important factors include particle size, adhesion, surface tension, and cross-linking of the polymeric material, and especially its resistance to swelling in water. Stereoscan photographs of a section of a silver-iodide silicone-rubber-membrane electrode are shown in Figure 1. The particle size is somewhat greater than the optimum 1 to 15 μm recommended by Pungor.[57] Control of grain size can be achieved by addition of a reagent which retards secondary nucleation, as does *p*-ethoxychrysoidine for silver iodide.

In the same way as an electrode of the second kind becomes one of the third kind if a second less sparingly soluble material is incorporated, so this principle can be used for ion-selective electrodes. For example,[56] from a mixture of the sulfide of copper, lead, or cadmium with silver sulfide, membrane electrodes can be produced that are responsive to Cu^{2+}, Pb^{2+}, or Cd^{2+} by virtue of reactions such as

$$Ag_2S \rightleftharpoons 2Ag^+ + S^{2-}$$

$$Cu^{2+} + S^{2-} \rightleftharpoons CuS$$

This may be done by sintering the materials (so-called ceramic electrodes[58]) or by making heterogeneous membrane forms. Corresponding forms using PbTe or PbSe have been described as chalcogenide electrodes.[59] If $PbSO_4$ is incorporated, it is possible to make a sulfate-ion sensor.[60] A mixture of 32 mol% Ag_2S, 31 mol% PbS, 32 mol% $PbSO_4$, and 5 mol% CuS is hot-pressed at 170°C and 7,000 atm. The slope was claimed[60] to be Nernstian in the pH range 1 to 10 and the response time to be fast (1 min). The mixing of calcium fluoride with lanthanum fluoride is the basis of a calcium-responsive electrode described in a German patent[61] assigned to the Perkin Elmer Corp. Its utility is limited to calcium-ion concentrations above 1.4×10^{-4} mol $l.^{-1}$.

3. Organic Ion-exchangers and Chelating Agents

The common feature of these substances is their ability to bind certain small ions selectively, either at charged sites of opposite sign or at neutral sites of organic nature. These substances are usually, although not invariably, used with a form of a liquid membrane separating two aqueous phases; alternatively, they may be incorporated in polyvinyl chloride to give a solid membrane form (see Section IV). At the membrane interface a rapid ion-exchange process takes place between the free ions in the aqueous phases and the same ions bound to the organic groups (R). The selectivity of the electrode depends primarily on the selectivity of this ion-exchange process; that is, the site R should form a more stable complex with the particular ion in the aqueous phase than with any other.[56] Information on selectivity can be obtained from solvent-extraction data and, in fact, similar organic materials are used.

The simplest materials used are salts of long-chain organic acids such as oleates or ring-substituted salicylates, or of organic bases such as the tetraalkylammonium salts. The long hydrocarbon chains are used to render the materials insoluble in the aqueous phase. The substances are usually dissolved in a suitable organic solvent that has a low dielectric constant and is immiscible with water. Electrical conductivity in this phase is essential. Other substances used are more commonly considered to be organic chelating or sequestering agents, for example, substituted phenanthroline ligands and the important range of neutral ligands capable of complexing the alkali metals. The latter group includes the macrotetralide antibiotics[62] such as nonactin and the synthetic 'crowns' and cryptates.[63] In these cases the most useful criterion

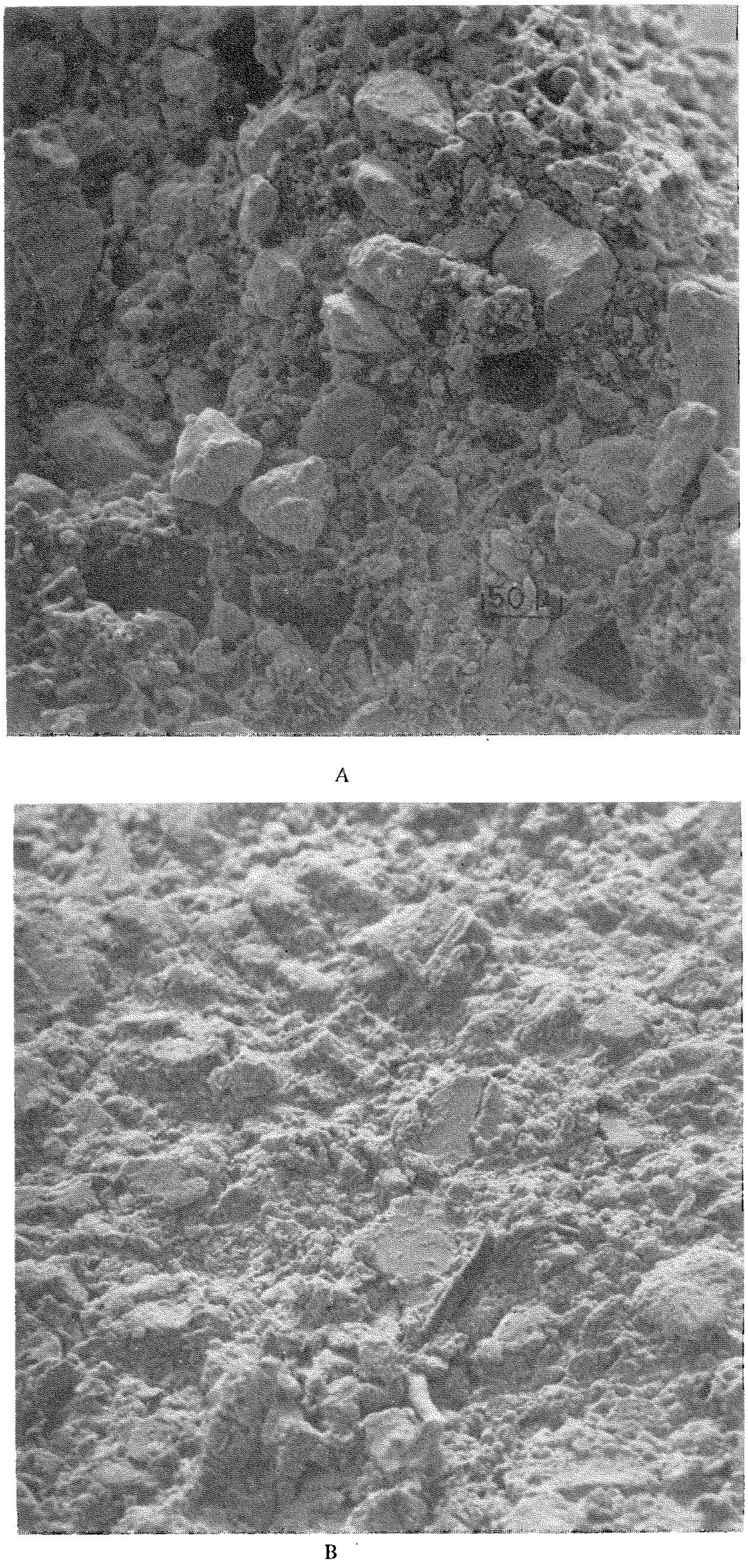


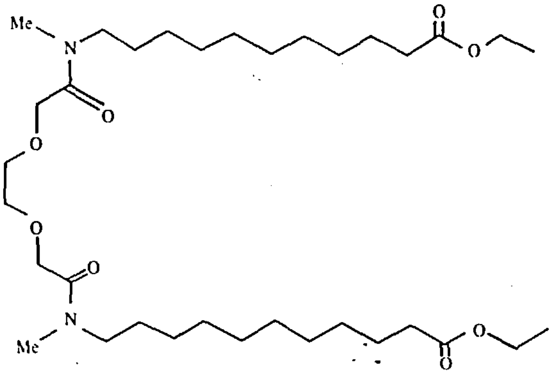
FIGURE 1 Scanning electron micrographs (Stereoscan) of a silicone-rubber-impregnated (Pungor-type) silver iodide electrode. A. Cross-section (X 200). B. Outer solution surface (X 200).

of selectivity is the stability constant for the complex or compounds formed with the ion of interest in aqueous solution compared with those for other ions. However, many groups that are interesting from a selectivity standpoint, such as most multidentate chelating groups, equilibrate too slowly to give useful electrodes with reasonable rates of response.[56] Hydrogen-ion interference will occur if mixed complexes with hydrogen ions form; this is often difficult to avoid.

Some solid-state forms that come into this category have been described, such as potassium tetraphenylborate, which has been tried in heterogeneous membrane form as an electrode for potassium.[45] It has a parallel in the use of potassium tetrachlorophenylborate in 2,3-dimethylnitrobenzene, which is the basis of liquid-ion-exchanger and PVC electrodes for potassium.[64]

Organic radical-ion salts, for example, the Ag(I) and Cu(II) salts of 7,7,8,8-tetracyanoquinodimethane,[65] are semiconducting and can be used in the form of pelletized discs or 'Selectrodes' (see Section IV). Electrodes for sulfonate[66] (crystal violet benzenesulfonate in nitrobenzene) and for salicylate[67] tetra(*n*-heptyl) salicylate in *n*-decanol have been reported. The active material[68] for an electrode selective for the acetylcholine cation, which has application for organopesticide analysis, is acetylcholine(*p*-chlorophenyl)borate in 2,3-dimethylnitrobenzene.

Most important, however, are substances of the neutral carrier class.[62] The ability of macrocyclic antibiotics to complex so selectively lies in their ability to 'wrap round' an ion and, thereby, provide a cavity of the right size. Almost comparable selectivities can be obtained with the more stable synthetic "crown" compounds[63] first synthesized by Pedersen in 1967. The affinity of these compounds for the alkali-metal cations is so great that they cannot be handled in ordinary glassware. The possibility of tailoring ligands for a particular ion of interest is an exciting prospect requiring an interdisciplinary approach. Levins[69] has described a barium-ion-selective electrode based on the barium complex of a commercially available substance, Igepal Co 880, which is a nonylphenoxypolyoxyethyleneethanol with 12 ethylene oxide units per mole of Ba^{2+}. Simon and co-workers[70] have synthesized a ligand (shown below) providing a cavity of about 1 Å diameter which is selective for Ca^{2+} over monovalent ions.



Although these electrodes could be used in aqueous organic solvent mixtures that do not enter the organic phase, their use is really restricted to pure aqueous solutions. The lower limit of detection is determined by the solubility of the organic salt or chelate in the aqueous phase, on which little information seems to be available.

IV. ELECTRODE FORMS AND CONSTRUCTION

The physical construction of an ion-selective electrode depends on the form chosen for the active material. Although, except for solid-contact types, the basic format is similar to that of the universally familiar glass electrode, only glass can be fabricated in bulb-form (Figure 2a). Some formidable sealing and glass-matching problems exist for certain glass formulations and at least one electrode type (Orion 94–11A) has a glass disc sealed into an epoxy or other plastic tube in a format similar to that shown in Figures 2b and c. This is the form of construction for single-crystal (e.g., LaF_3) and compacted disc solid-state electrodes. An ingenious adaptation allows the incorporation of the reference electrode, giving a combination electrode (Figure 2d) (Orion Model 90–02) similar to the glass-calomel combination available (e.g., Jena-Sargent S-30072-15). The Philips version is similar, except that the bottom of the electrode unscrews, and instead of the disc membrane being sealed in with suitable adhesive, it may be secured with 'O' rings (Figure 2b). A PVC membrane may be similarly secured in this type of body construction. Homemade PVC electrodes[71] usually have the membrane glued to the end of a piece of 6-mm PVC tubing with an adhesive of PVC dissolved in tetrahydrofuran. Likewise, silicone-rubber membranes are fixed to suitable glass or plastic tubing with silicone-rubber cement (e.g., GEC Silicoset). For the PVC membrane the solvent for the liquid-ion-exchanger takes on the role of plasticizer for which it may not have entirely suitable properties.[64]

The Orion liquid-ion-exchanger body (Figure 3a) allows the 0.003-in.-thick Millipore (cellulose acetate) filter to be held firmly in contact with the inner filling solution and a reservoir of liquid-ion-exchanger. Refilling is necessary every few weeks, a process that requires some practice and patience. A flow-through version is available (Figure 3b). The Corning body uses a ceramic hydrophobized porous glass) frit Figure 3. The Philips version is very similar to the solid-state model (Figure 3d). The Beckman electrode has a renewable solid ion-exchanger incorporated in a removable cap (Figure 3e).

In principle a simple U-tube construction as used by Dubini-Paglia and co-workers[72] is adequate for liquid-ion-exchange electrodes (Figure 4a), but is hardly feasible commercially. Covington and Thain[73] have described (Figure 4b) a titration-cell asembly which usefully exemplifies the principles involved for student instruction. With the 'thick' membrane layer used the response is sub-Nernstian, but useful titration curves can be obtained. The cell can be emptied using a drawn-out tube attached to a water pump. It can be cleaned by standing in dimethylsulfoxide followed by rinsing with acetone and then water.

A simplification in construction can be achieved if the support membrane is a conductor.

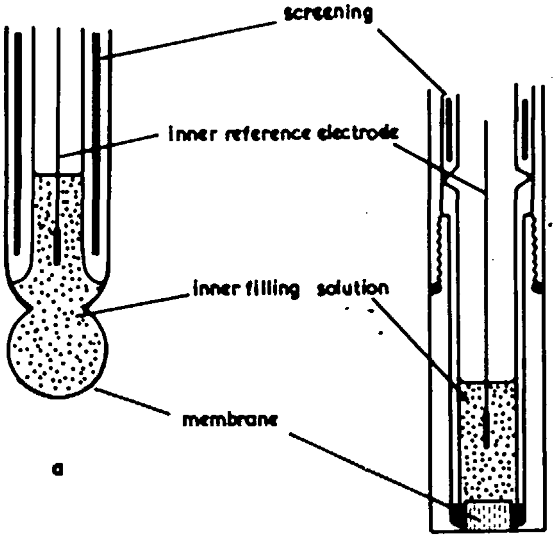
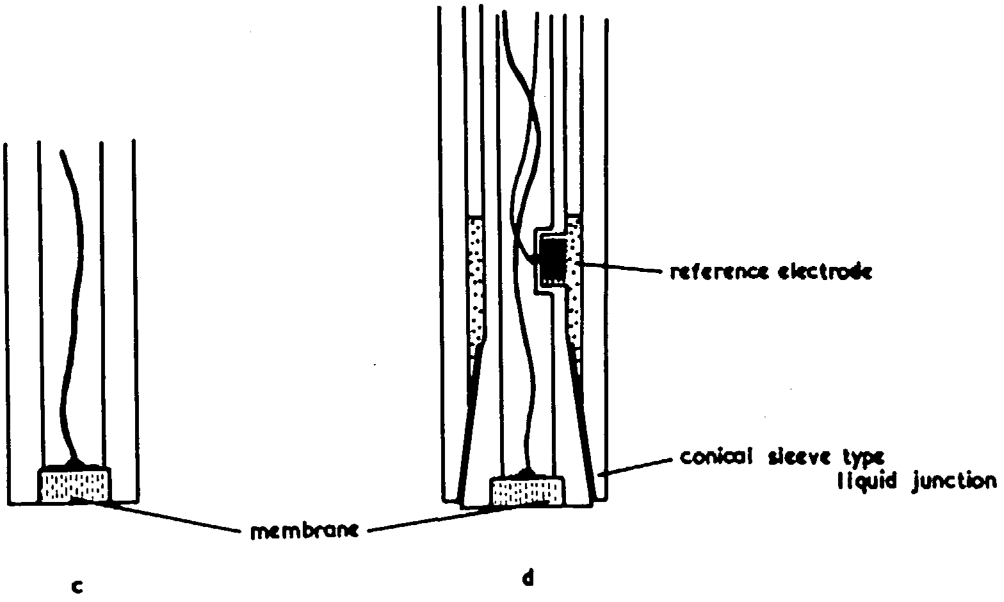


FIGURE 2. Some common forms of solid-state ion-selective electrode construction. a. Glass bulb electrode. b. Pelletized disc or single crystal form with inner filling solution (Philips). c. Pelletized disc or single crystal form with solid contact. d. Pelletized disc or single crystal form with solid contact as a combination electrode (Orion).



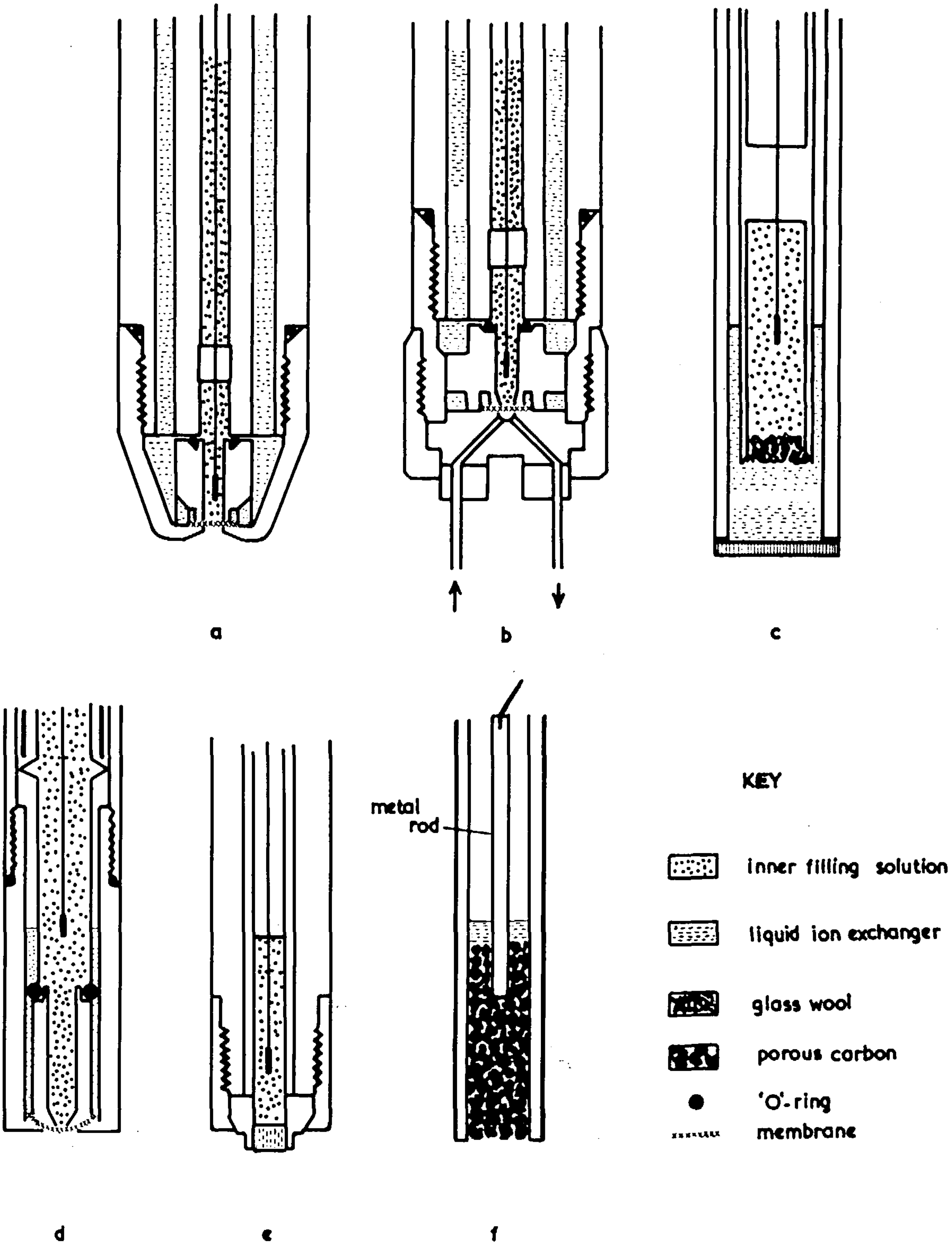
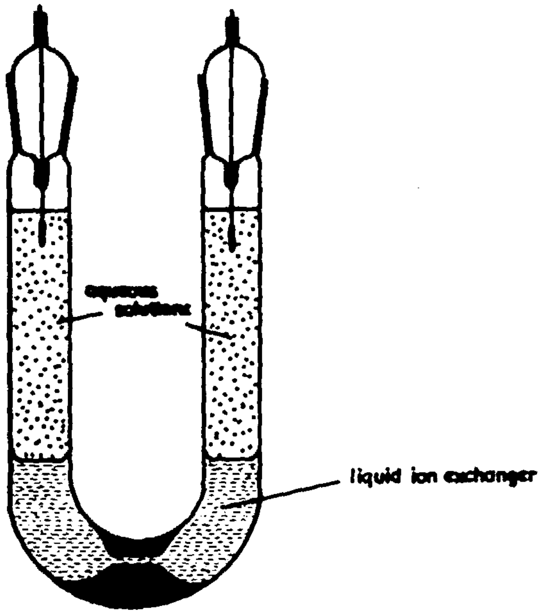


FIGURE 3. Some common forms of liquid-ion-exchanger ion-selective electrode construction. a. Millipore filter support (Orion). b. Millipore filter support as flow-through form. c. Corning porous glass form. d. Millipore filter support (Philips). e. Solid ion-sensor form (Beckman). f. "Selectrode" form (Ruzicka).



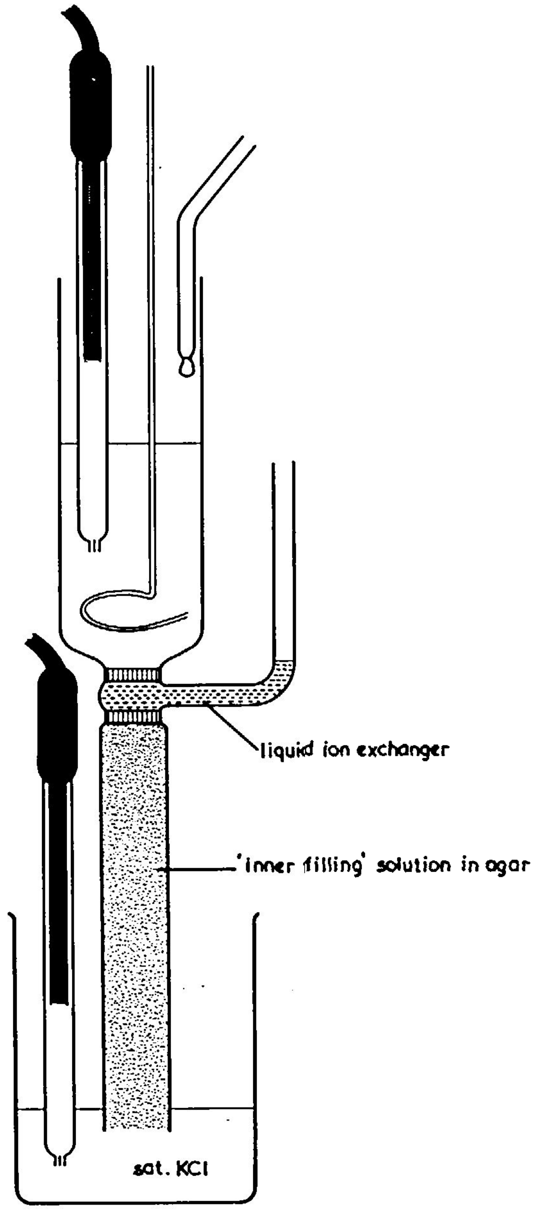


FIGURE 4. Thick membrane liquid-ion-exchanger assemblies. A. U-tube.[72] B. Titration cell assembly.[73]

The Radiometer 'Selectrode' devised by Ruzicka et al.[74-77] consists of a porous carbon or graphite rod which is made hydrophobic by treatment with Teflon® to prevent aqueous solution from soaking into it. The active material is then attached to the surface by simple rubbing or hot-dipping as appropriate. Liquid-ion-exchange electrodes can be made in this way (Figure 3f) as well as solid-state silver-halide types. Another form of electrode without inner filling solution is the simple dipped platinum-wire type which has been studied by Freiser et al.[24,25] and by Hirata and Date.[78] The active material is usually incorporated in PVC, silicone rubber, or a similar suitable polymer. One might imagine that the inner membrane solid-contact potential is not particularly well defined and that frequent standardization would be necessary, or that the electrodes would only be suitable for titrimetric purposes. If the claims made are to be believed, this does not appear to be the case. However, an improved form of the 'Selectrode' appears to use a solid pelletized calomel internal reference electrode, which includes calcium sulfate for a calcium-exchanger electrode. From experience with mercury-filled glass electrodes, these sometimes are quite reliable, but at other times inexplicable jumps of potential take place. The glass-mercury contact at the inner surface could depend on the presence of a small amount of moisture, when the inner electrode may be effectively Na(Hg) or Li(Hg)/OH^- or simply Hg/HgO/OH^-. Something similar could be responsible in certain solid-state contact electrodes. Graphite, for example, is known to have -COOH and -OH groups on its surface and it is doubtful that all water can be excluded in electrode construction, or indeed that it is desirable that this should be done. One thing is certain, however, and this is that somewhere in the vicinity of a solid-state internal connection a

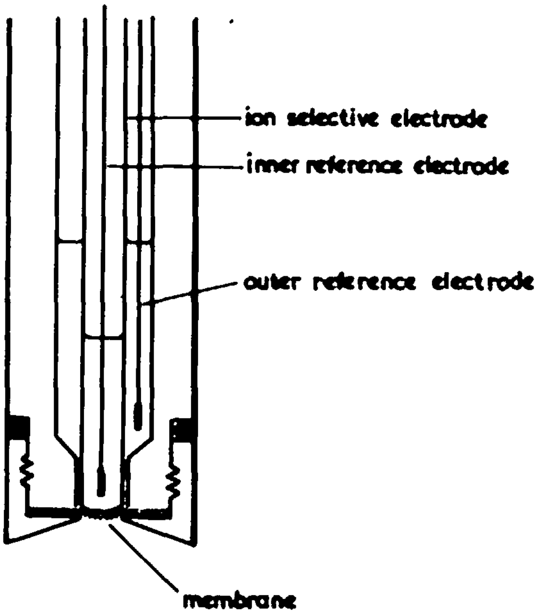


FIGURE 5. Gas-sensing electrode construction (E.I.L.).

change in conductance mechanism – electronic to ionic – must take place.

The construction of a gas-sensing electrode which permits membrane replacement is shown in Figure 5.

V. THEORETICAL CONSIDERATIONS

1. Derivation of the Nernst Relations

All potentiometric measurements are concerned with differences of e.m.f. and ratios of concentrations, although this fact is obscured by referring the e.m.f. to a standard state, which is an unreal solution with an associated e.m.f. of E°. The well-known Harned cell[79] for the evaluation of the p*K* of a weak acid HA

$$\mathrm{Pt,\ H_2|HA,\ NaA,\ NaCl|AgCl|Ag} \qquad (1)$$

requires that the standard e.m.f. of the cell

$$\mathrm{Pt,\ H_2|HCl|AgCl|Ag} \qquad (2)$$

be known. Since the hydrogen-gas electrode is used to define standard *electrode* potentials, this amounts to knowledge of the standard potential of the silver-silver chloride electrode. It is found experimentally[80] that this varies from $E^\circ = 222.4$ mV by at least ±0.2 mV, depending on the method of electrode preparation. Hence, it is suggested that for all accurate work it be redetermined by a measurement in 0.01 molal HCl. Thus, an evaluation of p*K* in effect requires a study of the double cell

$$\mathrm{Pt,\ H_2|HCl\ (0.01\ m)|AgCl|Ag\ldots}$$
$$\mathrm{Ag|AgCl|Ha,\ NaA,\ NaCl|H_2,\ Pt} \qquad (3)$$

where the silver-silver chloride electrode is being used as a "bridging electrode"[81] between the two cells.

The double cell can also be written the other way around:

$$\mathrm{Ag|AgCl|HCl\ (0.01\ m)\ |H_2,\ Pt\ldots}$$
$$\mathrm{Pt,\ H_2|HA,\ NaA,\ NaCl|AgCl|Ag} \qquad (4)$$

where the hydrogen electrode is the bridging electrode. If the glass electrode is used instead of the hydrogen-gas electrode, this procedure is mandatory, for because of its variable asymmetry potential it has to be standardized. Its standard potential has no significance.

$$\mathrm{Ag|AgCl|HCl\ (0.01\ m)\ |glass|HA,\ NaA,\ NaCl|AgCl|Ag} \qquad (5)$$

Thus, we are regarding the glass electrode as responding in each solution as a hydrogen gas electrode would, and can use cell (4), which is equivalent to cell (5), to derive the e.m.f.-concentration relation. Note that the left-hand side of cell (5) is not the internal reference electrode system of the glass electrode, which has canceled out since it makes the same contribution to each half of the double cell, as also does any asymmetry potential.

A similar treatment, based entirely on IUPAC convention for whole cells, is also applicable to any ion-selective electrode. It necessitates seeking an electrode reaction equivalent to that taking place at the outer surface of the ion-selective electrode. It is then a simple matter to write down the appropriate Nernst equation in accordance with the experimentally found cell polarities. As an example, we will take the lanthanum fluoride electrode, for which an undergraduate experiment has been devised[82] in which the dissociation constant of HF is evaluated.

The LaF_3 electrode is standardized in a solution of known fluoride concentration and the double cell is

$$Ag|AgCl|NaF\ (m_1),\ NaCl|LaF_3|NaF\ (m_2),\ HCl|AgCl|Ag \tag{6}$$

This is formally equivalent to the double cell:

$$Ag|AgCl|NaF\ (m_1),\ NaCl|LaF_3,\ La \ldots \quad La,\ LaF_3|NaF\ (m_2),\ HCl|AgCl|Ag \tag{7}$$

where the lanthanum fluoride crystal membrane has been replaced by two lanthanum-lanthanum fluoride electrodes of the second kind. It is not actually possible to make such electrodes since lanthanum metal is rapidly oxidized in contact with air. Nevertheless, this does not prevent the writing of an electrode reaction

$$La + 3F^- \longrightarrow LaF_3 + 3e \tag{8}$$

for the electrode of the right-hand cell, assuming the polarity of the silver-silver chloride electrode to be positive. Then the electrode reaction of the latter is the usual one, times three,

$$3AgCl + 3e \longrightarrow 3Ag + 3Cl^- \tag{9}$$

and adding to obtain the cell reaction, we have

$$3AgCl + La + 3F^- \longrightarrow LaF_3 + 3Ag + 3Cl^- \tag{10}$$

Hence, the Nernst equation for the right-hand cell can be written down by inspection as

$$E = E^o - k \log \frac{a_{Cl^-}}{a_{F^-}} \tag{11}$$

where k = (RT ln 10)/F. Writing a similar expression for the left-hand cell and subtracting, we have for the double cell

$$\Delta E = -k \log \frac{(a_{Cl^-})_2}{(a_{F^-})_2} + k \log \frac{(a_{Cl^-})_1}{(a_{F^-})_1}$$

$$= -k \log \frac{(a_{F^-})_1}{(a_{F^-})_2} \frac{(a_{Cl^-})_2}{(a_{Cl^-})_1} \tag{12}$$

This treatment may appear involved compared with that of writing down a Nernst equation directly for a fluoride-responsive *electrode*, but many difficulties are caused by failure to treat whole cells to which signs can be unambiguously ascribed.

If the silver-silver chloride electrode is replaced by a saturated calomel electrode, we can write a related double cell:

$$\underset{(l)}{Hg|Hg_2Cl_2|KCl\ (\underline{s})\ |NaF\ (m_1),} NaCl|LaF_3| \underset{(r)}{NaF\ (m_2),\ HCl|KCl\ (\underline{s})\ |Hg_2Cl_2|Hg} \tag{13}$$

Provided that the liquid-junction potentials at *l* and *r* are equal and opposite in sign, then a_{Cl^-} in Equation 12 is the same in both constituent cells and so

$$\Delta E = -k \log \frac{(a_{F^-})_1}{(a_{F^-})_2} \tag{14}$$

This expression would also apply to cell (7) if the activities of chloride ion (approximately, the concentrations) were the same on the two sides of the double cell. ΔE will be positive when $(a_{F^-})_{left} < (a_{F^-})_{right}$.

If $m_1 = m_2$, then this condition will not be met, for some of the fluoride ions will be complexed by hydrogen ions, so the polarity of the double cell will not be that assumed under the IUPAC convention (right-hand electrode positive polarity, unless marked otherwise).

An analogous treatment could be applied to all ion-selective electrodes. For example, for the calcium liquid-ion-exchanger (LIC) electrode:

$$\underset{m_1}{Ag|AgCl|CaCl_2|}Ca(LIC)\underset{m_2}{|CaCl_2|AgCl|Ag} \tag{15}$$

we could write an equivalent cell:

$$\underset{m_1}{Ag|AgCl|CaCl_2|}Ca(Hg)\ldots Ca(Hg)\underset{m_2}{|CaCl_2|AgCl|Ag} \tag{16}$$

with an electrode reaction at the calcium-amalgam electrode of the right-hand cell of

$$Ca(Hg) \longrightarrow Ca^{2+} + 2e \tag{17}$$

The equation corresponding to Equation 12 is

$$\Delta E = -\frac{k}{2}\log\frac{(a_{Ca}\,a_{Cl}^{2})_{2}}{(a_{Ca}\,a_{Cl}^{2})_{1}} = -\frac{3}{2}k\log\frac{(m\gamma_{\pm})_{2}}{(m\gamma_{\pm})_{1}} \quad (18)$$

and if the saturated calomel electrode is used instead of the silver-silver chloride and a cell without a liquid junction, then

$$\Delta E = -\frac{k}{2}\log\frac{(a_{Ca})_{2}}{(a_{Ca})_{1}} = \frac{k}{2}\log\frac{(a_{Ca})_{1}}{(a_{Ca})_{2}} \quad (19)$$

again with the proviso that the residual liquid-junction potential cancels. Note the opposite signs for Equation 19 referring to a cation-responsive membrane and for Equation 14 referring to an anion-responsive membrane.

2. Selectivity and Interferences

No electrode is entirely selective toward the ion specified. The presence of other ions can seriously impair electrode performance. Such interferences can take several forms, depending on the type of membrane material. The electrode behavior can be represented by an equation first used by Nicolsky[83] for the glass electrode showing a mixed response to hydrogen and sodium ions. It is sometimes called the simplified Eisenman equation:[84]

$$E = \text{constant} \pm k\log(C_i + K_{ij}C_j) \quad (20)$$

where i and j are two singly charged ions such as H^+ and Na^+; K_{ij} is called the selectivity constant. For response to an ion i only, K_{ij} must be small. For divalent ion electrodes, Equation 20 must be modified to

$$E = \text{constant} \pm \frac{k}{2}\log(C_i + K_{ij}C_j^{2}) \quad (21)$$

where i is now a divalent ion suffering an interference from a monovalent ion j. Thus, for Na^+ interference on the calcium electrode, $K_{CaNa} = 10^{-3}$ which means that the electrode is 1,000 times more responsive to Ca^{2+} than to Na^+.

The signs in Equations 20 and 21 remain ambiguous, for they are written for single electrode potentials and we have not specified whether i and j are cations or anions. These equations should be used in the form of Equations 14 or 19, that is, for double cells. This immediately suggests a way of determining the selectivity constant if one solution contains a known concentration of interfering ion while the other contains none.[85] Thus, from Equation 21

$$\Delta E = \frac{k}{2}\log\frac{(C_i + K_{ij}C_j^{2})}{C_i} \quad (22)$$

As the ratio of the concentration of the interfering ion to that of the primary ion is increased, eventually the electrode shows no response to the primary ion and a plot of potential against log C_i becomes horizontal. In the absence of interfering ion, the plot has the Nernstian slope k/2. Between these limits the plot is curved (Figure 6). By extrapolation of the constant potential to meet the extended line of Nernst slope a value of $C_{i(j)}$ can be read off, from which K_{ij} can be calculated. For example, using Equation 22 this corresponds to $\Delta E = 0$, and, therefore

$$K_{ij} = \frac{C_{i(j)}}{C_j^{2}} \quad (23)$$

where C_j is the constant concentration of the interfering ion (j). It may not be possible to establish the zero response line experimentally, in which case it can be located by extrapolating the Nernst slope to a point $\frac{k}{2}$ log 2, or about 9 mV, below the mixed response line. This arises from Equation 22 with $K_{ij}C_j^2 = C_i$ which locates the midpoint on the curve (Figure 6).

An alternative procedure is to work at constant concentration of the primary ion and vary the concentration of the interfering ion.

In Equations 20 through 23 we have deliberately replaced activities by concentrations, although Equations 20 and 21 are invariably written in the form of single ion activities. It is not very meaningful to attempt to put mean ionic activities into these equations, for the selectivity constant is only an approximate quantity. It varies with the concentration of interfering ion and that of background electrolyte if any. To emphasize this it has been suggested that the term selectivity ratio or apparent selectivity constant be used,[1] although the latter has been used for the quantity determined by an alternative method which will now be described. Often, instead of K_{ij}, its reciprocal is used.

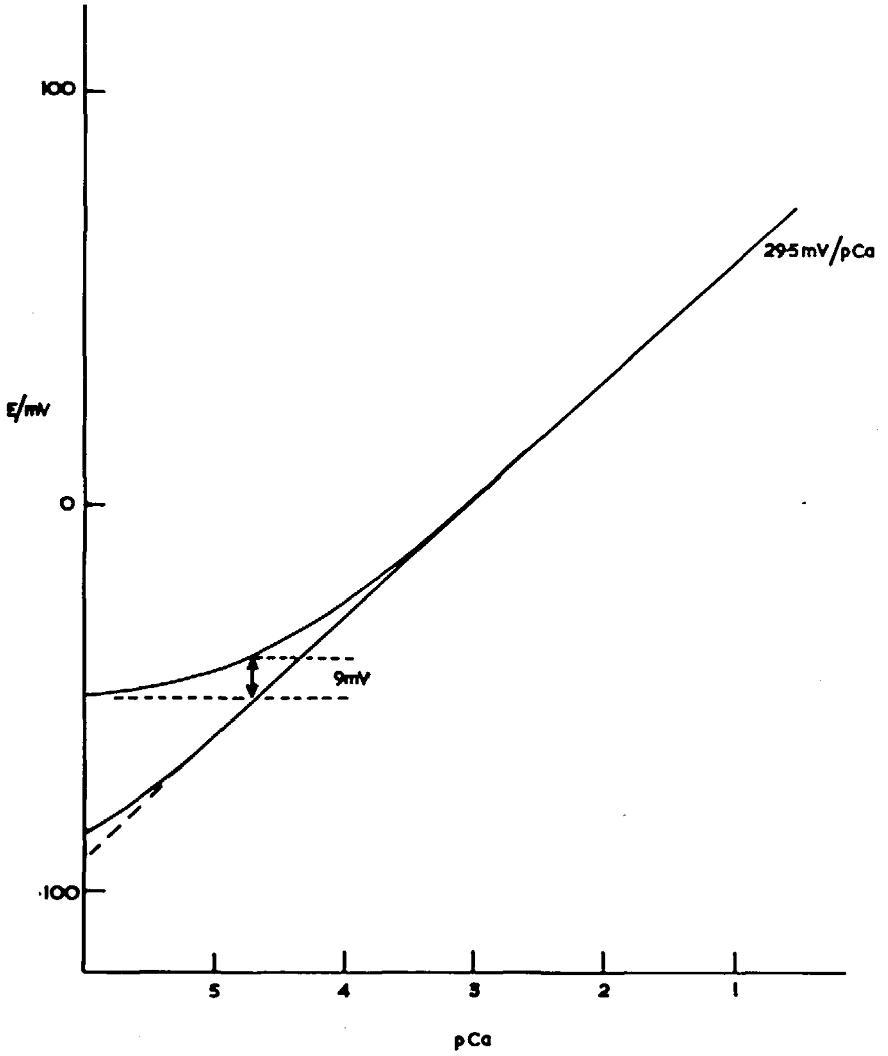


FIGURE 6. Effect of 0.2 mol $l.^{-1}$ NaCl on a calcium liquid-ion-exchange electrode in $CaCl_2$ solutions.[56]

If measurements are made in two solutions each containing one of the ions i or j only at, say $C_i = C_j = 0.1$ mol $l.^{-1}$, then, based on Equation 20:

$$\Delta E_{0.1} = \pm k \log \frac{(K_{ij}C_j)}{(C_i)} = \pm k \log K_{ij} \qquad (24)$$

From this equation arises Rechnitz's definition[86] of selectivity as the ratio of the two ionic concentrations which yield separately the same e.m.f. under otherwise identical conditions. This was the method used by Eisenman[84] to determine selectivity constants for aluminosilicate glasses showing mixed hydrogen and alkali-metal-cation response. This and the previous method are only successful if the electrode shows a true mixed response, that is, if it functions reversibly in the presence of the primary ion. Often this condition is only partly fulfilled and potentials show drift and irreproducibility in pure solutions of the interfering ion.

Obviously more complicated solutions[85] of Equations 20 or 21 are possible involving points in the region of mixed response, but whether these have significance other than computational exercises is a moot point.

For solid inorganic salt materials, the selectivity constant has a simple interpretation, as can be seen from the following considerations.[32] Let us suppose that a silver iodide electrode is placed in a solution containing bromide ions. Then at the surface of the silver iodide an exchange equilibrium

$$\mathrm{Ag\,I(s)} + \mathrm{Br}^- \rightleftharpoons \mathrm{Ag\,Br(s)} + \mathrm{I}^- \qquad (25)$$

is set up for which

$$K_{I,Br} = K_{s0}^{AgI}/K_{s0}^{AgBr} \qquad (26)$$

where K_{s0} is the solubility product.

If A_I, A_{Br} are the ionic activities in the solid, then

$$K_{I,Br} = \frac{A_{Br}}{A_I}\frac{a_I}{a_{Br}} \qquad (27)$$

From the equality of the electrochemical potentials at the electrolyte-solid interface, then following Nicolsky,[83] we have for the potential:

$$E = \text{const} + k \log \frac{a_I}{A_I} \qquad (28)$$

and substitution can be made for A_I. Writing instead concentrations for activities in the solid, then $C_{Br} = C_0 - C_I$, where C_0 is the total anion concentration (the concentration of exchangeable sites) on the surface. Therefore

$$K_{I,Br} = \frac{(C_0 - C_I)}{(C_I)}\frac{(a_I)}{(a_{Br})} \qquad (29)$$

and substituting Equation 29 into 28 gives

$$E = \text{const} + k \log (a_I + K_{I,Br}\, a_{Br}) - k \log C_0 \qquad (30)$$

which is equivalent to Equation 20 since the last term can be incorporated into the constant term. Havas and co-workers[87] have given a generalized form of Equation 20, in the case of the present example of an iodide electrode in the presence of several interfering anions j, as

$$E = \text{const} + k \log a_I \sum_j K_{I,j} \frac{(a_j)}{(a_I)} \qquad (31)$$

Equation 20 can be recovered by writing $K_{I,I} = 1$.

Selectivity constants calculated through Equation 26 from the ratio of the solubility products show reasonable agreement with those obtained by the methods previously outlined. For the example given ($K_{I,Br}$) values are 1.3×10^{-4} (calculated), 5×10^{-3} (from measurements in pure I^- and Br^- solutions), and 2×10^{-4} (from the e.m.f. curve in mixed solutions).[32]

It is only in this simple case that the selectivity constant has this interpretation. Eisenman[62] has summarized the theory of membrane potentials and shown that in general the constant K_{ij} in Equation 20 involves mobility factors for the ions in the membrane phase. In spite of these considerations, Equation 20 is best regarded as an empirical equation. Far too much significance is attributed to selectivity constants; they are useful only as guides to likely electrode performance and to the maximum concentrations of interfering ions that can be safely tolerated. They should be awarded no more respect than manufacturers' specifications for HiFi equipment. The parallel is fairly close; a variety of names are given to the same quantity for which several methods of meaurement exist. Although standard methods exist, they are not universally adopted. Strict comparison can only be effected by testing at the same time by the same method of measurement. Far too often in the literature, claims have been made for improvements to electrodes by different fabrication techniques or modifications of active material by comparison with published values for selectivity constants; direct comparisons are rare.

Table 3 lists values for selectivity constants for the principal interferences suffered by the electrodes discussed in Section VI. It cannot be too strongly emphasized that these figures are useful only as a general guide and are approximate only. However, widely discrepant values for a given sensed ion can be taken as suggesting use of a different active material; for example, the Corning K^+ electrode, based[64,88] on potassium tetra-(chlorophenyl)borate in 2,3-dimethylnitrobenzene, in comparison with the others, which have valinomycin as active material.

3. Mechanistic Considerations

It is not the intention here to review the various theories that have been developed for the establishment of membrane potentials. These have been reviewed by Eisenman,[62] and more recently by Simon and co-workers.[89] Rather, it is intended to make some general comments.

The basic approach consists of combining inter-

TABLE 3

Selectivity Constants for Some Important Electrode Systems

Electrode system	Interferences
Ca^{2+} (Beckman)	$Fe^{2+}5$, $Cu^{2+}0.33$, $Mg^{2+}0.9$, $Ba^{2+}0.1$
Ca^{2+} (Corning)	$Mg^{2+}0.01$, $Ba^{2+}0.01$, $Ni^{2+}0.01$, $Na^{+}10^{-3}$
Ca^{2+} (Orion)	$Zn^{2+}3.2$, $Fe^{2+}0.80$, $Pb^{2+}0.63$, $Cu^{2+}0.27$, $Mg^{2+}0.01$, $Ba^{2+}0.01$, $Na^{+}1.6 \times 10^{-3}$
Ca^{2+} (Philips)	$Zn^{2+}5.0$ to 0.9, $Fe^{3+}0.45$, $Cu^{2+}0.07$, $Mg^{2+}0.032$, $Ba^{2+}0.02$
$Ca^{2+} + Mg^{2+}$ (Beckman)	$Zn^{2+}1.0$, $Ba^{2+}1.0$, $Na^{2}0.01$, $K^{+}0.01$
$Ca^{2+} + Mg^{2+}$ (Orion)	$Zn^{2+}3.5$, $Fe^{2+}3.5$, $Cu^{2+}3.1$, $Ba^{2+}0.94$, $Na^{+}0.01$
NO_3^- (Beckman)	ClO_4^-100, $NO_2^-0.045$, $Cl^-0.01$, $SO_4^{2-}10^{-5}$
NO_3^- (Corning)	ClO_4^-1000, $Cl^-4 \times 10^{-3}$, $SO_4^{2-}10^{-3}$
NO_3^- (Orion)	ClO_4^-1000, $NO_2^-0.06$, $Cl^-6 \times 10^{-3}$, $SO_4^{2-}6 \times 10^{-4}$
ClO_4 (Beckman)	$I^-0.033$ NO_3 0.005, SO_4^{2-} 10^{-6}
ClO_4 (Corning)	$I^-0.001$, NO_3^- 0.001, SO_4^{2-} 0.001
ClO_4^- (Orion)	$OH^-1.0$, I^- 0.012, NO_3^- 0.0015, SO_4^{-2} 1.6×10^{-4}
K^+ (Beckman)	$Rb^+2.2$, $Cs^+0.5$, $NH_4^+0.014$, Na^+ 2×10^{-4}, 3×10^{-4}
K^+ (Corning)	Rb^+10, Cs^+20, $NH_4^+0.023$, $Na^+0.012$
K^+ (Philips)	$Rb^+1.9$, $Cs^+0.38$, $NH_4^+0.012$, $Na^+2.6 \times 10^{-4}$, Li^+ 2.1×10^{-4}
K^+ (Orion)	$Rb^+2.2$, $Cs^+0.5$, $NH_4^+0.05$, $Na^+0.09$, $Li^+0.03$
NH_4^+ (Philips)	$K^+0.12$, $Rb^+0.043$, $Cs^+0.0048$, $Li^+0.0042$, $Na^+0.002$
F^- (Beckman)	$OH^-0.1$
F^- (Orion)	$OH^-0.1$

facial potential terms (Donnan potentials) with interdiffusional terms arising from the different mobilities of the ions in the membrane. Exactly how this is done depends on the model taken for the membrane and the various simplifying assumptions necessary to solve the resulting differential equations. The theory is, thus, partly thermodynamic and partly phenomenological. It is impossible to draw, from thermodynamic considerations, any conclusions about the mechanism by which a membrane potential arises. We have already seen early in this section how, by making quite the wrong assumption that a calcium liquid-ion-exchange ion-selective electrode functions by electron transfer in the same way as a calcium-amalgam membrane, we could obtain the correct equation describing the variation of its potential with calcium-ion concentration. Furthermore, the essential requirement of any theory, that out of it should arise suggestions for further confirmatory experiments to advance the subject, is rarely met. Understanding of the mechanism of ion-selective electrode function must come from nonequilibrium type experiments.

Electrolysis-type experiments were used to elucidate conduction mechanisms in glass electrodes by Haugaard,[90] who as a result proposed the three-layer model of the glass electrode: two hydrated layers formed on the surfaces of unchanged glass by ion-exchange with water or electrolyte solutions. Similar experiments have been done with ion-selective electrodes. Durst and Ross[91] passed a current through the lanthanum fluoride electrode and showed that it can be used to generate fluoride ions electrochemically with an efficiency of 99.21 ± 0.51%. Tracer experiments are also a valuable method of investigation.

More refined electrolytic experiments are those where there is no attempt to detect gross transfer of material, but instead the effect of passage of small A.C. or D.C. currents is investigated. Some advances in understanding the complex interactions in the surface layers on glass electrodes have come about from the steady or pulsed D.C. studies of Wikby and Johanson[92,93] in Sweden. Brand and Rechnitz[94] have preferred A.C. methods. The relative merits of the two methods are not clear, but in principle the same information should be available from either. By such studies, Brand and Rechnitz[94] have concluded that the lanthanum fluoride electrode has a surface (hydrated) film like that on the glass electrode because its impedance behavior is similar. The argument, by analogy, that one type of membrane electrode behaves similarly to another, has seriously retarded advances in understanding throughout the developments reviewed in Section II. (As an example, see a recent paper.[95]) Pungor[57] imagined that the silicone rubber heterogeneous membrane electrodes developed hydrated surface layers which were essential to their functioning. While there is evidence that silicone rubber absorbs water, there is no evidence that this is beneficial or otherwise for the functioning of these electrodes. From their impedance studies, mentioned above, Brand and Rechnitz[94] drew the unlikely conclusion that there is no ionic conduction in AgI, AgBr, Ag_2S, $PgS+Ag_2S$, $CuS + Ag_2S$ solid-state electrodes, but that ion-blocking occurs and coupling occurs by a capacitative process. In AgCl it is known that Ag^+ ions are mobile; according to Ross,[56] this is true in the other halides and sulfide too.

As distinct from solid-state membranes that have fixed sites for ion exchange, in liquid-ion-exchangers the sites are assumed to be free to move within the interior of the membrane.[62] Simon and co-workers[96] have studied the transport of K^+ through PVC membranes impregnated with valinomycin in 2-octanol under the influence of a potential difference. Using ^{14}C-labeled valinomycin, it was shown that transport of K^+ is accompanied by an equivalent transport of the antibiotic consistent with the formation of a 1:1 complex. Ligand-exchange occurs during transport so a carrier relay process was proposed to account for the results.

Of particular importance in the case of neutral complexing agents, such as valinomycin and the crown compounds, is what happens to the counter anion. Some workers have assumed that the electroneutrality condition is violated within the membrane. If this unlikely event occurs, one wonders why experimentation with these systems is not a hazardous procedure! To support such membrane materials, cellulose acetate and nitrate discs (Millipore filters) are often used. Using dye-adsorption studies, Kedem et al.[97] have demonstrated that such materials are not inert, but contain residual negative charges. Tracer studies also indicate that Cl^-counter anions are taken up by the membrane. They claim[97] that Millipore filters are already ion-selective and that valinomycin simply gives improved selectivity. Similar considerations govern the choice of diphenylether for the valinomycin electrode since it is a good solvent for potassium salts.

VI. DETAILED DISCUSSION OF SOME IMPORTANT ELECTRODE SYSTEMS

1. Fluoride Electrode

The lanthanum fluoride electrode is undoubtedly the most important new potentiometric electrode discovered in the last decade. It is capable of at least ±0.1 mV accuracy. Frant[98] filed his patent application in February 1966 and announcement in the scientific literature came in December that year.[6] The search for a fluoride electrode started in conventional enough fashion among the insoluble fluorides. Calcium and barium fluorides were rejected as unsuitable since one of the aims was to measure F^-at the 1 ppm level. The first attempts with bismuth trifluoride pressed at 50,000 psi and 550°C yielded a disc which could be sealed into a PVC tube and gave the results shown in Figure 7 when tested at various F^- concentrations. The response is reasonably linear and Nerstian to pF 4 but interferences were found, from Cl^-in particular. Attention was turned to the rare earth fluorides which were available in monocrystalline form of optical quality. Results obtained with niobium, praseodymium, and cerium fluorides are shown in Figure 7, where they are compared with the response of a later model Orion LaF_3 electrode. The lanthanum fluoride crystal was stated to be doped with Eu^{2+} to improve the conductivity. While doping does lower the conductivity ($\sim 10^7\ \Omega^{-1}\ cm^{-1}$) which otherwise is a result of the mobility of F^- ions in a $LaF_2{}^+$ matrix, it now seems that it is not essential to the functioning of the electrode. Also included in Figure 7 are calibration results obtained in the reviewer's laboratory[99] with a single crystal of lanthanum fluoride (Metals Research, Ltd., Histon, Cambridge, England) sealed with epoxy cement into a tube machined from glass-fiber-filled epoxy resin. The response is not Nernstian below pF 3.5, but the electrode is eminently suitable for most purposes except that of estimating low concentrations of fluoride. Russian workers[100] have also presented results which indicate that theoretical behavior is obtained only in the range pF 0 to 3.

Unlike most of the other electrodes to be considered, the fluoride-responsive electrode does not suffer extensive interference from other ions.

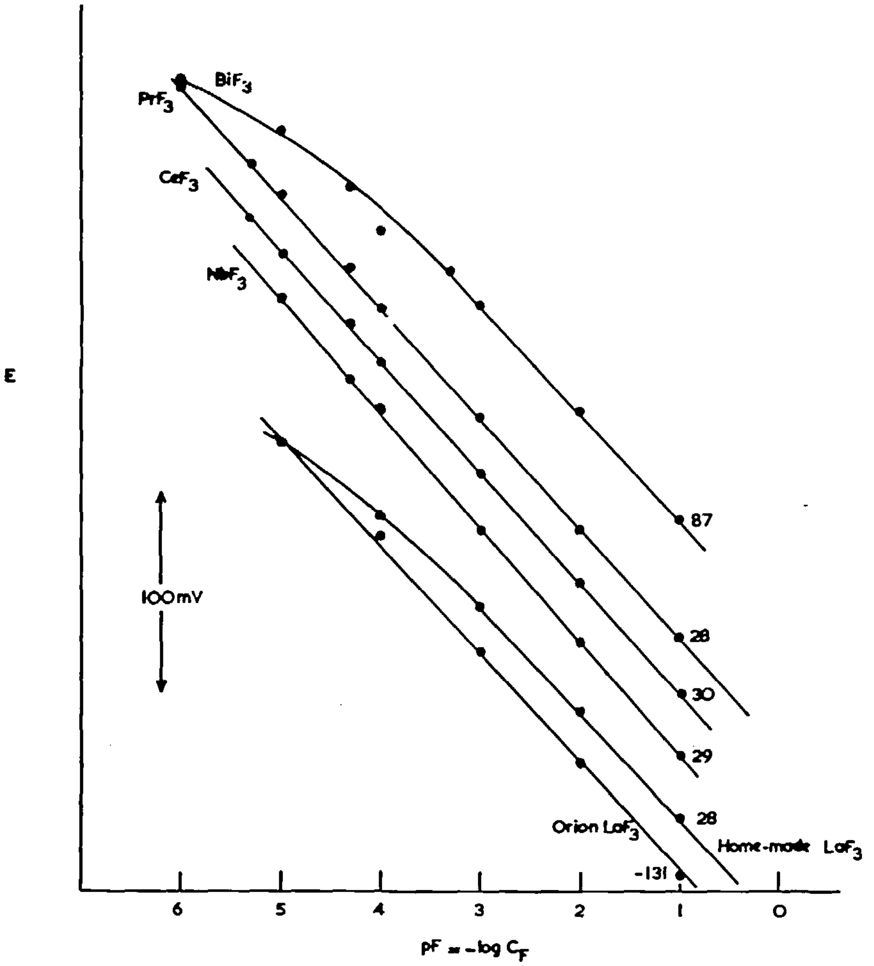


FIGURE 7. Calibration curves for various fluoride-responsive electrodes.[98,99] For clarity the curves have been displaced. The figures against points for pF = 1 refer to the reading in mV in 0.1 mol l.$^{-1}$ NaF solutions. The value observed, of course, depends on the inner filling solution concentration.

Hydroxide ion causes deviation from theoretical behavior at high pH, not, as was first thought, because of the similarity in the ionic radii of fluoride and hydroxide, but because of the formation of basic fluorides on the surface of the electrode. Acetate ion interferes similarly by the formation of solid mixed acetate and fluoride compounds of lanthanum on the electrode surface.[101] At low pH values there are also deviations from theoretical response, but this is due to the formations of HF and HF_2^-, to which the electrode does not respond.[6,56] Baumann[102] has shown (Figure 8) that the fluoride electrode responds to much lower fluoride concentrations than the limit observed by Frant and Ross[6] arising from the solubility of lanthanum fluoride. Using[102] fluoride complexing cations, such as Th^{4+} and Zr^{4+}, the electrode responds to fluoride concentration to pF 9. It seems that the fluoride ions liberated by the solution of the crystal are complexed. This dissolution from the single crystal is a slow process taking up to a fortnight to achieve an equilibrium value, which corresponded to a solubility product of 10^{-24} (mol l.$^{-1}$).[4] The solubility of the crystal is also suppressed by the presence of added lanthanum ions (Figure 8).

Lingane[103] has investigated the use of the electrode for precipitation titrations and concluded that lanthanum nitrate is a better titrant than thorium nitrate. The titration curve is im-

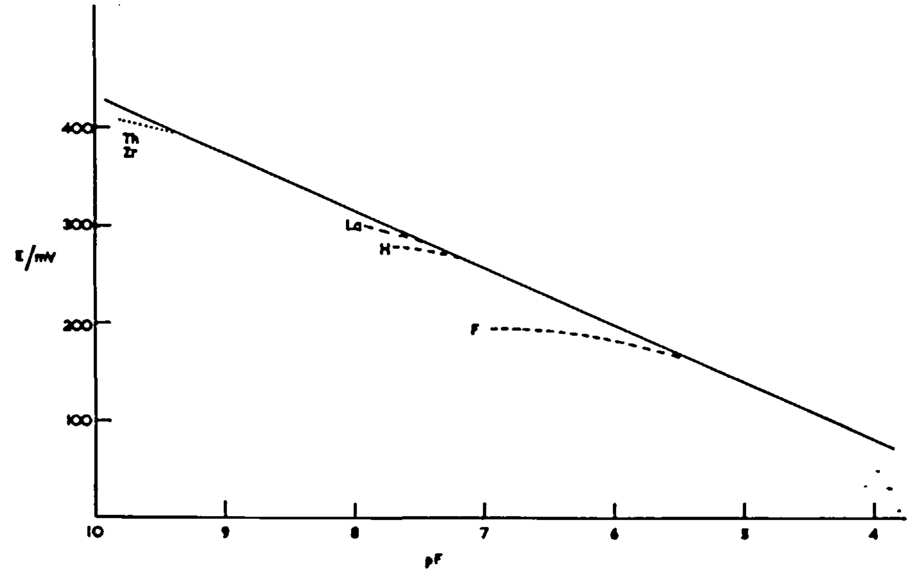


FIGURE 8. Calibration curves for the lanthanum fluoride electrode in the presence of various fluoride complexes.[102]

proved by the addition of 60 to 70% ethanol. Bazzelle[104] considers isopropanol to be even better. One difficulty in the use of this method is that the maximum rate of potential change precedes the true equivalence-point potential and, therefore, the best procedure is to standardize the titrant with standard fluoride. From the titration curves, Lingane[103] calculated the solubility product to be 10^{-18} (mol l.$^{-1}$).[4] This, however, refers to freshly precipitated lanthanum fluoride which is probably hydrated. The failure to produce a successful heterogeneous membrane fluoride electrode[105] may be related to this fact. Other workers have claimed that it is necessary to allow precipitates to age before consistent results for the solubility product are obtainable.[106] Lingane noted that the calibration curves extended linearly to higher pF values when the solution was stirred using a magnetic stirrer. He suggests that stirring prevents the accumulation of dissolved fluoride ion at the electrode surface in solutions of low fluoride ion concentration, and this is now known to be a slow process, as mentioned above. According to Ross,[56] the electrode will respond to La^{3+} in solution if finely divided LaF_3 is added to the sample.

Titration curves produced using the Orion electrode and a homemade electrode are compared in Figure 9.

2. Calcium Electrode

The search for a calcium-responsive electrode has gone on, as Table 2 shows, for many years. Ross,[14,56] in seeking an electrode with application to both biological research and water-quality analysis, argued that good selectivity for calcium in the presence of large amounts of sodium and magnesium and small levels of potassium was essential. Some guidance in the selection of liquid-ion-exchange materials can be gained from solvent-extraction studies and stability constant data for the relevant ions. It was known that phosphate and polyphosphate ions form stable complexes with calcium but not with the alkali metals. A long alkyl chain is necessary to prevent water solubility, so the easily synthesized esters of phosphoric acid containing long hydrocarbon chains were investigated. Diesters are required, for the monoesters form mixed complexes with H^+ and, hence, show some hydrogen-ion response as electrodes.

The originally announced electrode[14] used the calcium salt of didecyl phosphoric acid $[(C_{10}H_{21}O)_2PO \cdot OH]$ dissolved in di-*n*-octylphenylphosphonate $[(C_8H_{17}O)_2POC_6H_5]$. The electrode showed Nernstian response (29.4 mV/pCa) over the range pCa 1 to 5. The lower limit of detection is governed by the small solubility of the calcium phosphate ester salt in the aqueous phase. The lower limit of electrode

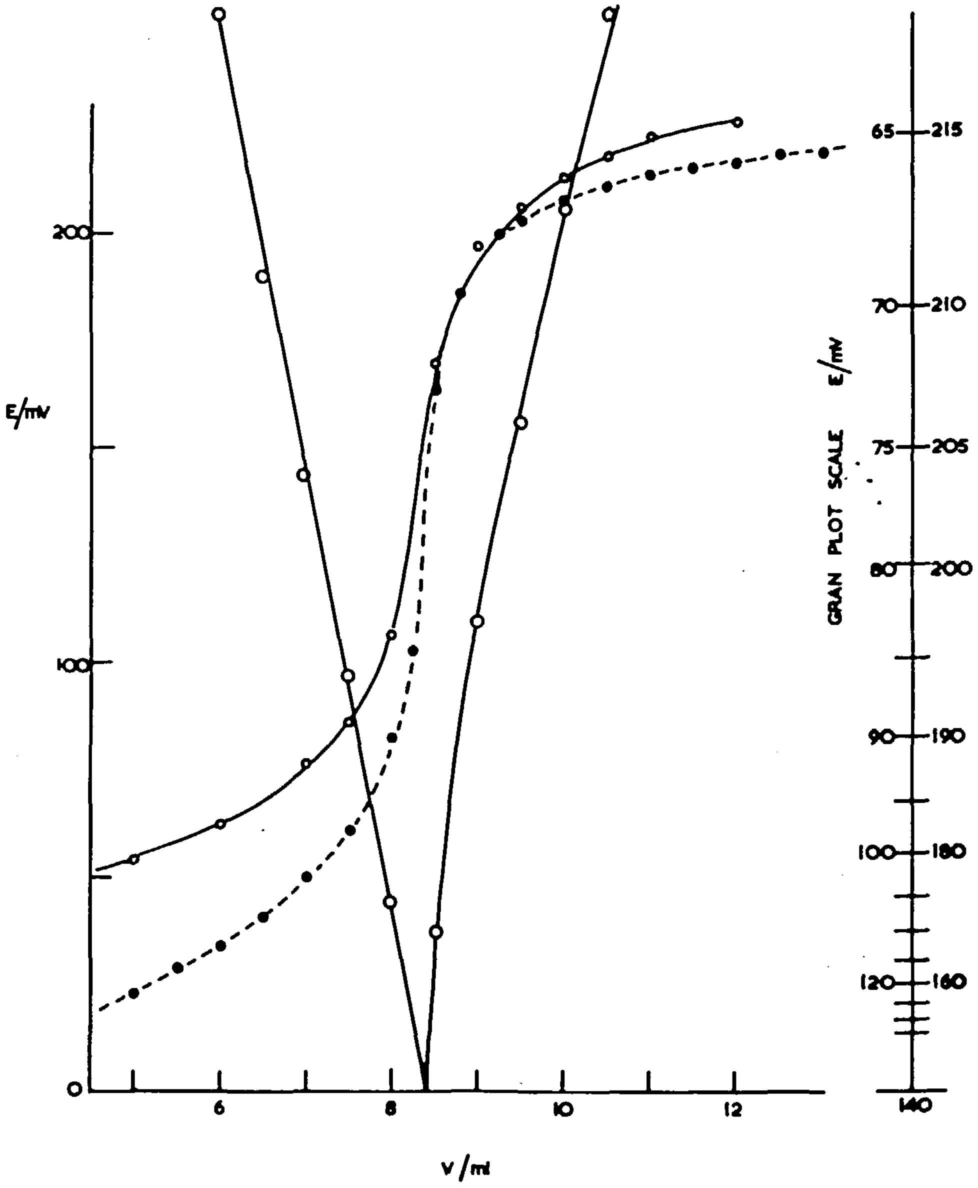


FIGURE 9. Titration curves for the titration of fluoride ion with lanthanum nitrate in aqueous solution. –o– homemade electrode –•–. Orion electrode. Gran plot for homemade electrode is superimposed.

response can be improved by increasing the length of the alkyl chain, but this may cause eventual precipitation or gelling. Alternatively, the liquid-exchanger concentration can be reduced, but this has the effect of lengthening the response time.[56] According to Bailey and Dalziel,[109] who have made ^{45}Ca tracer studies, the solubility of Orion 90-20-02 exchanger is 4 x 10^{-5} mol l^{-1} Ca^{2+} at pH 6, the value increasing in more acidic media. Good selectivity was found for calcium over magnesium and other alkaline earth ions but the electrode responds also to Zn^{2+}, Fe^{2+}, and Pb^{2+}. Some differences in selectivity can be achieved by varying the solvent polarity.[56] With 1-decanol, electrodes showed virtually identical responses to calcium and magnesium; this is the basis for the "water hardness" Ca^{2+}/Mg^{2+} electrode. Hydrogen ions cause interference at a pH lower than about 5,

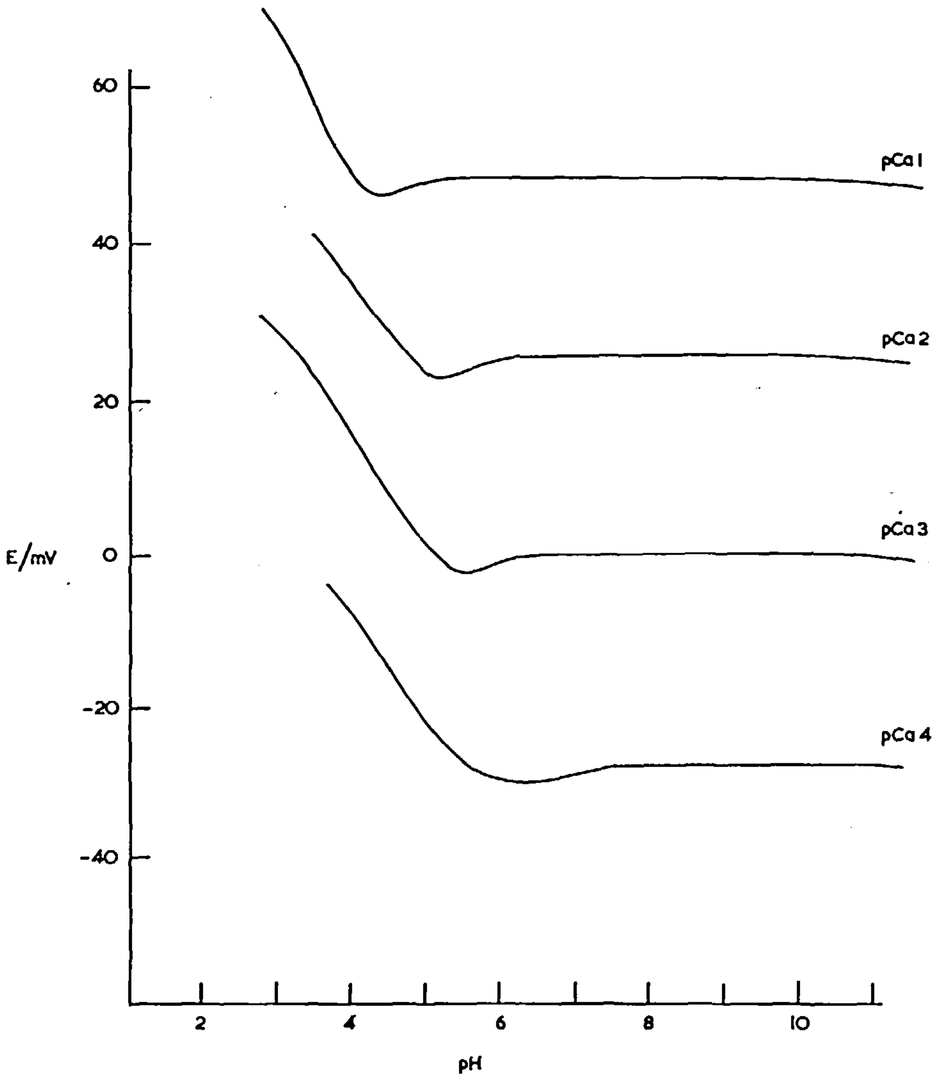
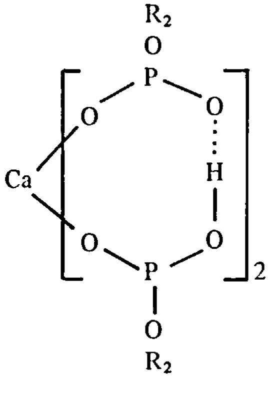


FIGURE 10. Hydrogen-ion interference of the calcium liquid-ion-exchange electrode (Orion).[56] The pH was varied with NaCl or HCl at the pCa (molarity basis) values indicated.

depending on the pCa level (Figure 10). Precipitation of calcium hydroxide and formation of $CaOH^+$ cause deviations above pH 11. Sodium interference is important only at very low pNa. Ruzicka and Tjell[107] claim to have overcome these deficiencies by changing the nature of the ion-exchanger to a mixture of organophosphate and phosphonate substituted in such a way that formation of $CaX_2 \cdot nHX$ (n = 1 to 4) is prevented; selectivity constants are, thereby, improved by several orders of magnitude and the dips visible in Figure 10 are eliminated.

Beckman workers[108] used the didecyl- or dioctylphosphate salts dispersed in collodion to give a solid form of the electrode. The salt was dissolved in about 4 parts by weight of an alcohol-ether solution of collodion and used to form a film over the end of a glass tube which was then dried at 50 to 60°C for several hours. Similarly, Moody et al.[71] have dispersed the Orion exchanger material in polyvinyl chloride membranes. A mixture of ion exchanger and PVC in appropriate proportions is dissolved in tetrahydrofuran (THF). Slow evaporation of solvent is allowed over a 2-day period to yield a 0.5-mm-thick membrane from which discs are cut and sealed on to PVC tubing, using a cement of PVC dissolved in THF. Response of both solid forms was linear over the range pCa 1 to 5 with slopes close to the expected 30 mV/decade using saturated calomel reference electrodes. Earlier, Shatkay and co-workers[30] described an electrode employing thenoyltrifluoracetone in PVC. A PVC membrane containing an Orion exchange material has been directly contacted to a graphite rod[110] and coated on to a platinum wire.[24] These electrodes without internal reference solution were claimed to be almost as good as the Orion electrode. Some improvements in selectivity claimed may just emphasize the approximate nature of selectivity constants and their variation with different methods of determination.

The exact composition of the Orion exchanger is not certain, and three serial numbers (92-20, 92-20-01, and 92-20-02) have been used. The last is a yellow liquid. Di-2-ethylhexylphosphate has been used in solvent extraction and Russian workers[111] have used this material in chlorobenzene for strontium and barium electrodes; for calcium electrodes the monoester salt calcium ethylhexylhydrogenphosphate was used;[112] this is contrary to recommendations mentioned above. Griffiths et al.[113] found that a mixture of the diester and the acid in the proportion $CaX_2 \cdot 2HX$ gives the optimum response. This was attributed to the formation of



a structure proposed by Baes[114] for extraction complexes involving dialkylphosphoric acids. In cell (15) the response was 84.6 mV over the range 10^{-1} to 5×10^{-8} mol $l.^{-1}$, but 88.2 mV over the limited range 3×10^{-2} to 10^{-4} mol $l.^{-1}$ compared with the theoretical, 88.7 mV.

Other interferences have been found in the course of its extensive use in a variety of applications. High levels of perchlorate and iodide ions alter the nature of the exchanger. Clinical workers have used triethanolamine to buffer the pH to higher values to avoid H^+ interference but it appears[115] that this substance, other bases, and even glucose and urea can have an effect on the measured calcium activity in serum samples. Whether this is due to the solution of these organic substances in the organic phase or to weak complex formation with calcium remains to be elucidated.

In his original announcement, Ross[14] tested the response of the calcium electrode in cells without liquid junction (cell (15)) to avoid "uncertainties in the reference electrode liquid-junction potential and the questionable ability of the Debye-Hückel equation to predict ionic activity coefficients" if the cell with saturated calomel reference electrode is used. Later workers have not always been similarly deterred, unfortunately. Huston and Butler,[116] however, have carried out a much more extensive series of tests with cell (15), varying also the inner filling solution and comparing their results with published mean ionic activity coefficients of $CaCl_2$. Deviations from the Nernst equation were observed whenever the test and inner filling solution were very different in concentration. With the later ion-exchange material 92-20-02 (and the flow-through electrode) test solutions up to 5 molal showed theoretical behavior, that is, agreement to within a few mV of the theoretical e.m.f. calculated from the known activity coefficients. That the electrode is capable of a higher precision than this has been shown in some recent careful studies of Briggs and Lilley[117] using cell (15). Their results are given in Table 4, which shows that the electrode is capable of ±0.15 mV precision in pure calcium chloride solutions of pCa 1.5 to 3.

3. Anion Responsive Liquid-ion-exchanger Electrodes: Nitrate, Perchlorate

Anion exchangers are either long-chain alkyl ammonium salts or salts of a nonlabile metal complex of the type ML_3X_2 where, for example, L = substituted 1,10-phenanthroline as in the Orion perchlorate and nitrate electrodes.[56]

From a systematic study of long-chain alkyl ammonium salts in ethyl bromide, tetra-*n*-heptylammonium perchlorate was singled out as a promising perchlorate electrode by Dubini-Paglia and co-workers.[72] The tetraoctylammonium salts were studied by Russian workers as exchanger

TABLE 4

Test[117] of the Calcium Liquid-ion-exchanger Electrode in Cell (15)

$10^3 m_2$/mol kg^{-1}	$\gamma\pm^a$	$\Delta E_{exp.}$/mV	ΔE_{th}(Equation 18)/mV	$\Delta E_{exp.} - \Delta E_{th.}$/mV
1.0275	0.8871	119.49	119.56	−0.07
3.2519	0.8197	78.42	78.32	+0.10
10.165	0.7286	39.05	39.21	−0.16
33.081 (m_1)	0.6185	0	0	0
99.104	0.5211	−35.68	−35.65	−0.03
295.89	0.4559	−72.64	−72.83	+0.19

^{a}(From Lietzke, M. H. and Stoughton, R. S., *J. Phys. Chem.*, 66, 508, 1962.)

materials for perchlorate and nitrate electrodes.[118,119] The Corning nitrate electrode uses tridodecylhexadecylammonium nitrate in *n*-octyl-2-nitrophenyl ether. Ishibashi and Kohara[120] concluded that quaternary ammonium salts were slightly superior to the *o*-phenanthroline complexes for perchlorate. The Orion electrodes use a substituted Fe(II)(*o*-phen)$_3$ complex for perchlorate and a Ni(II) complex for nitrate and tetrafluoroborate.[56] The patent also mentions[121] Cu(II), Co(II), and Cd(II) complexes and gives details of the preparation of a nickel complex. Substitution in the phenanthroline ring system is used to achieve water immiscibility. Solvents mentioned[121] include nitrobenzene, decanol, dioctylphenylphosphonate, and *p*-nitrocymene. Figure 11 shows[120] the results of a comparison of the responses of some Fe(II) complexes in nitrobenzene to perchlorate ions. Sharp[122] has described liquid-ion-exchanger electrodes for perchlorate based on *N*-ethylbenzothiazole-2,2-azaviolene perchlorate in 1,2-dichlorobenzene or bis(2-chloroethyl)ether, which show Nernstian response in the range pClO$_4$ 0 to 6.5 or 5.6, respectively, with an improvement over corresponding solid-state forms. The worst interferences are iodide and tetraphenylborate. Davies et al.[123] have incorporated the Orion nitrate exchanger in PVC to form a solid electrode.

Since previously no electrometric method of determining nitrate and perchlorate was available, these new electrodes are important acquisitions. Nitrate is of great interest, but perchlorate is of much less interest outside chemical laboratories where it is widely (and often erroneously) used as a noncoordinating anion. The Orion nitrate electrode was evaluated by Potterton and Shults.[124] A linear response of slope 56.6 mV/decade at 25°C was observed in the range 10^{-1} to 10^{-4} mol $1.^{-1}$ nitrate. It can be used[74] for precipitation titrations[125] using diphenylthallium (III) sulfate as titrant. A precipitation titrant for perchlorate is tetraphenylarsonium chloride.[126] Inflections are reasonably clear[73] with more than 100-mV swings (Figure 12).

4. Potassium Ions

The most important development apart from the lanthanum fluoride electrode has undoubtedly been the discovery and use of neutral carrier complexes selective toward the alkali-metal ions. These developments originate from an observation of Moore and Pressman[127] in 1964 that neutral macrocyclic antibiotics induce ion permeation in mitochondria. Electrodes based on antibiotics were first developed by Stefanac and Simon[128] in Zurich, who studied nonactin, monactin, and valinomycin (Figure 14a). Pioda, Stankova, and Simon,[129] using a dilute solution of valinomycin in diphenyl ether, obtained a slope of 58.3 mV/decade for K$^+$ with a selectivity constant of 2.5 x 10^{-4} for interference by Na$^+$. This is a great advance over cation-responsive glass electrodes (about 0.01 for Na$^+$ interference) and is of great interest for the determination of K$^+$ in body fluids, with Na$^+$ at relatively high concentrations. An ammonium-ion-selective electrode based on a mixture of nonactin and monactin in tris(2-ethylhexyl)phosphate has been described by the same group,[130] and is commercially available from Philips. A curve,[131] obtained using 25 mg of valinomycin in 0.5 g of nitrobenzene in the Orion body and 0.1 mol 1^{-1} KCl as filling solution, for the titration of 0.01 mol $1.^{-1}$ KCl with sodium tetraphenylborate solution is shown in Figure 13. Previous tests showed the electrode response to be linear in the range p*K* 0 to 3 with slope 53.3 mV/p*K*.

In 1970 Frant and Ross[132] reported on an Orion experimental electrode based on valino-

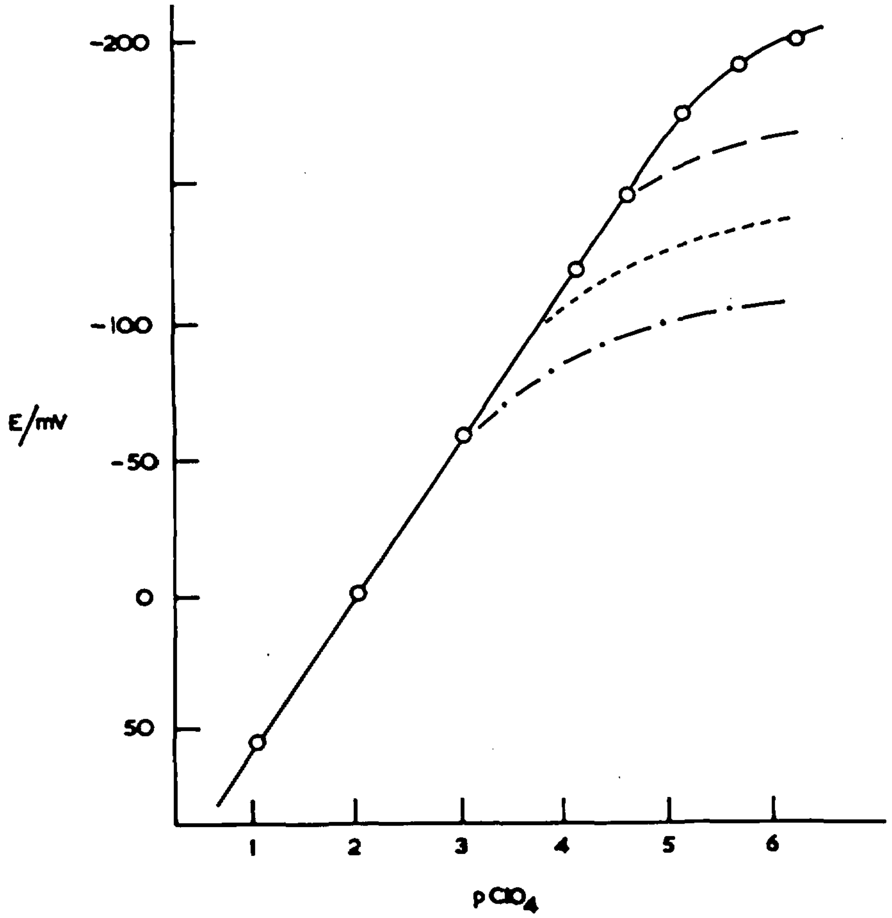


FIGURE 11. Comparison of some Fe(II) complexes as ion-selective electrodes for perchlorate. —— tris (4,7 diphenyl,1,10 phenanthroline Fe(II) perchlorate. — — tris (1,10 phenanthroline Fe(II) perchlorate. ---- a,a′ bipyridyl Fe(II) perchlorate. (All at 2.5 x 10^{-4} mol $l.^{-1}$ in nitrobenzene.) 1,10 phenanthroline Fe(II) perchlorate at 10^{-4} mol $l.^{-1}$ in 1,2-dichloroethane. Diminished linear response is probably due to increased solubility of the complex in the liquid phase.

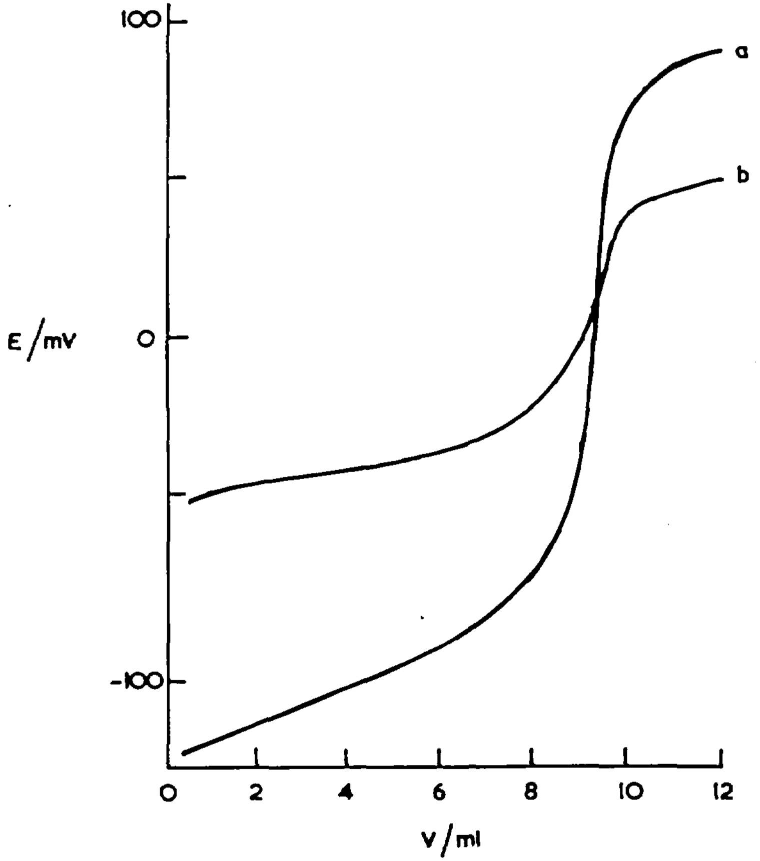


FIGURE 12. Precipitation titrations for 0.023 mol $l.^{-1}$ ammonium perchlorate.[73] a. Titration assembly (Figure 4b). b. Orion electrode.

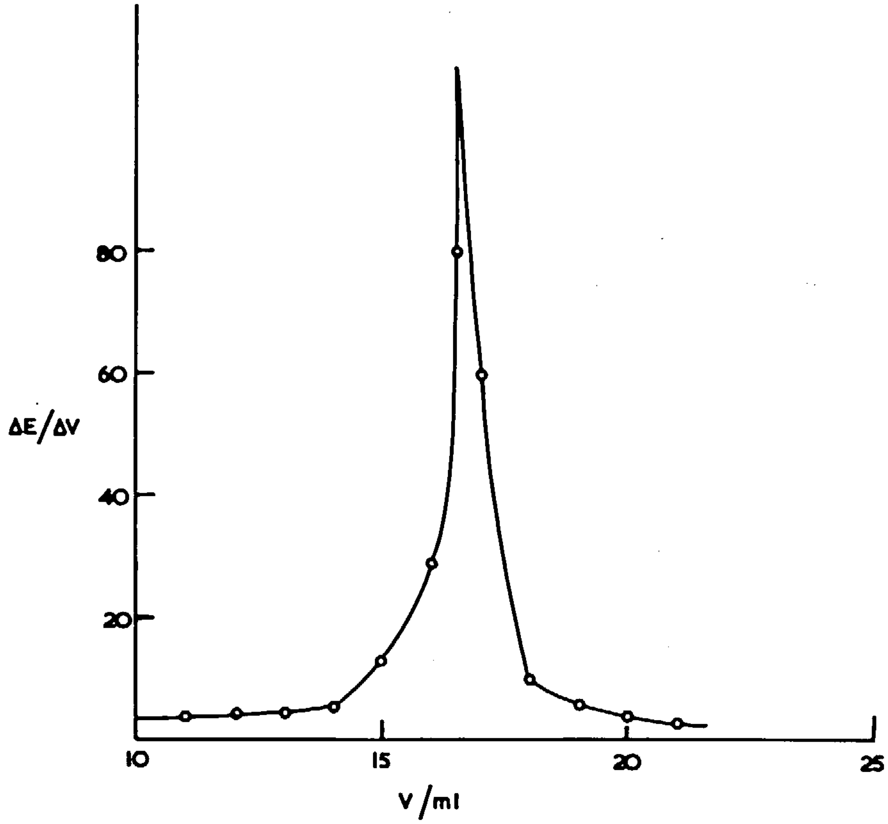
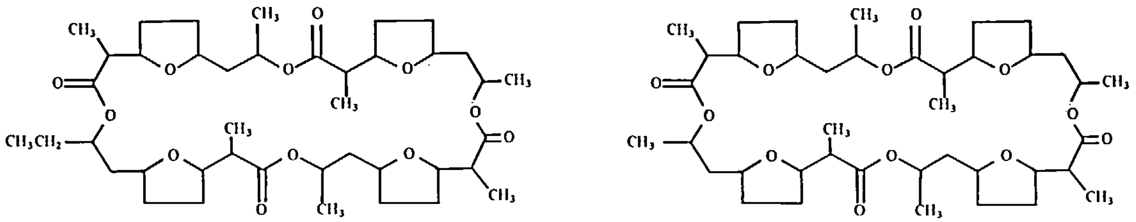


FIGURE 13. Precipitation titration of 0.01 mol $l.^{-1}$ potassium chloride with sodium tetraphenylborate solution using a valinomycin electrode,[131] plotted in differential form.

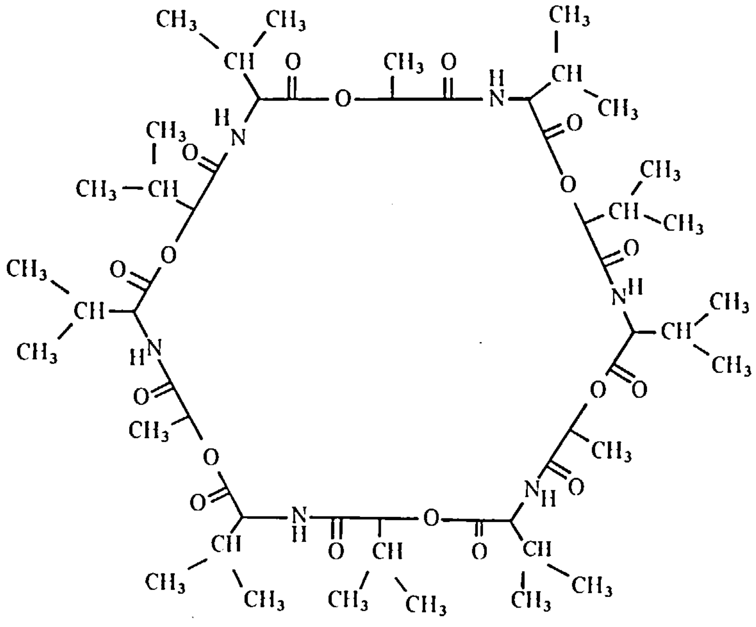
mycin (5 to 10 wt % in nitroaromatic or diphenylether solvents). Lal and Christian,[133] however, found the slope to be 52 mV over the range p*K* 1 to 4, but the selectivity constant to be only 0.09 for Na^+ interference. Valinomycin solutions are not very stable and the response can deteriorate with the solution also turning brown. Beckman workers[134] announced a solid-state potassium electrode presumably similarly based, although details were not given. More recently, valinomycin has been incorporated successfully in both PVC and silicone rubber membranes.[135] The latter electrode showed entirely comparable performance (59 mV slope, p*K* 1 to 5) to a liquid-membrane Millipore filter electrode assembly but with less drift and a life of over 1 month. The PVC electrode was less good and showed no potassium-ion response if the softener (dibutylphthalate or sebacate) was omitted.

The cyclic polyether complexes (Figure 14b), called 'Crowns' by Pedersen, appear[136] not to have such good selectivity for K^+ over Na^+ as the antibiotic valinomycin, being worse by a factor of a hundred. Rechnitz and Eyal[137] maintain that it is possible to predict selectivity properties of Crowns as electrodes on the basis of homogeneous complex formation data obtained in 50% aqueous tetrahydrofuran as solvent, but their conclusions have been criticized.[138] Electrode selectivity data were obtained using nitrobenzene as solvent, 0.1 mol l^{-1} KCl as internal filling solution, and methods described in Section V.2. Ryba and co-workers[136] have compared some Crown compounds in dipentylphthalate with valinomycin as PVC membrane electrodes. In contrast to work previously mentioned,[135] the valinomycin PVC electrode showed theoretical response in the p*K* range 1 to 5 and identical results were obtained if the material was coated onto a platinum wire provided that the coating was not more than 0.15-mm thick. Thicker coatings gave sub-Nernstian response.



Monactin

Nonactin



Valinomycin

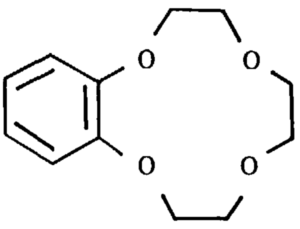
FIGURE 14A.

In further work, Petranek and Ryba[139] have attempted to improve selectivity by hydrogenation of the ring or increasing the ring size. Best results were obtained with dimethyldibenzo-30-crown-10, which X-ray analysis shows has a wrap-round structure like valinomycin (Figure 15). The reported selectivity constant for Na^+ interference is 2.8×10^{-3}, which differs now by only a factor of 10 from that originally reported for valinomycin by Simon and co-workers.[129] Selectivity constants reported[136,137,139] are usually wildly discrepant.

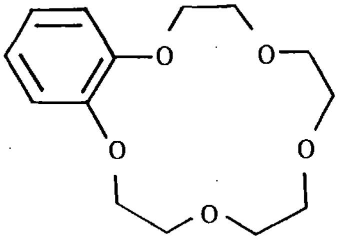
Further advances are confidently to be expected in this area. A synthetic crown compound to replace valinomycin which is fairly costly and of variable purity and doubtful stability is desirable. Although the ability to tailor the molecule to provide a cavity of the correct size to obtain optimum selectivity is clearly an important factor, it is not the only one and it is not clear yet what influence solvation has on selectivity considerations.

5. Silver Halide and Sulfide

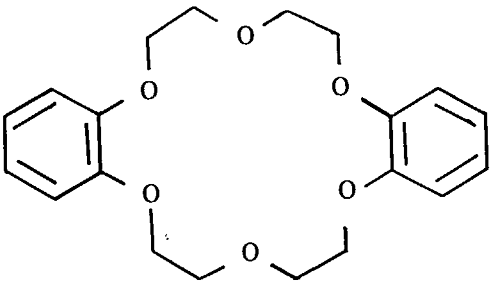
Silver halide ion-selective electrodes offer no advantages over the corresponding electrodes of the second kind apart from insensitivity to redox couples. Many of the applications claimed for those electrodes could equally well have applied to conventional types. The silver sulfide electrode,



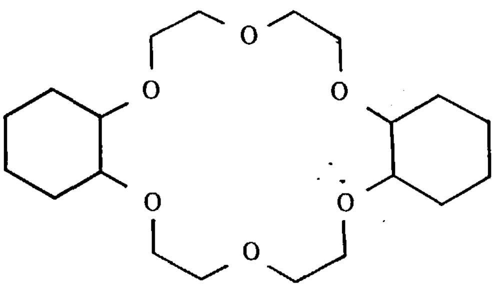
Benzo-12-crown-4



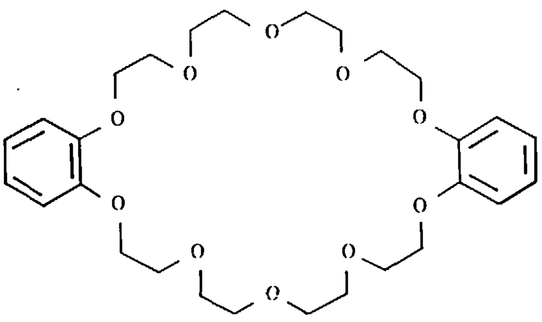
Benzo-15-crown-5



Dibenzo-18-crown-6



Dicyclohexyl-18-crown-6



Dibenzo-30-crown-10

FIGURE 14B.

however, may have advantages over the conventional form. There are advantages of using silver sulfide mixed with halide to form disc electrodes which have application to cyanide determination as described below. The addition of sulfide enhances the conductance and obviates difficulties due to light sensitivity of the halides which can introduce spurious potential effects.[56]

The lower limit of detection of the electrodes for halide ions will depend on the solubility product of the material. The problem is the same as that of excessive solubility of material from electrodes of the second kind.[32] An additional potential term k log (l+s/c) will arise, where s is the solubility of the silver halide in the halide solution of concentration c. When s = c/10 the additional term will be 2.4 mV which will be detectable as a departure from a linear calibration curve. Since approximately

$$K_{s0} = s(s + c) \tag{32}$$

then solving the quadratic gives $c = (9.1\ K_{s0})^{1/2}$. Thus, $c = 3 \times 10^{-8}$ mol $l.^{-1}$ for AgI, 2.7×10^{-6} mol $l.^{-1}$ for AgBr, and 3.8×10^{-5} mol $l.^{-1}$ for AgCl. This treatment is simpler than that given by Pungor et al.[140]

Using the Orion sulfide electrode, Hseu and Rechnitz[141] determined the solubility product of silver sulfide to be 1.48×10^{-51} (mol $l.^{-1})^3$. Hence, this electrode can be used to much lower

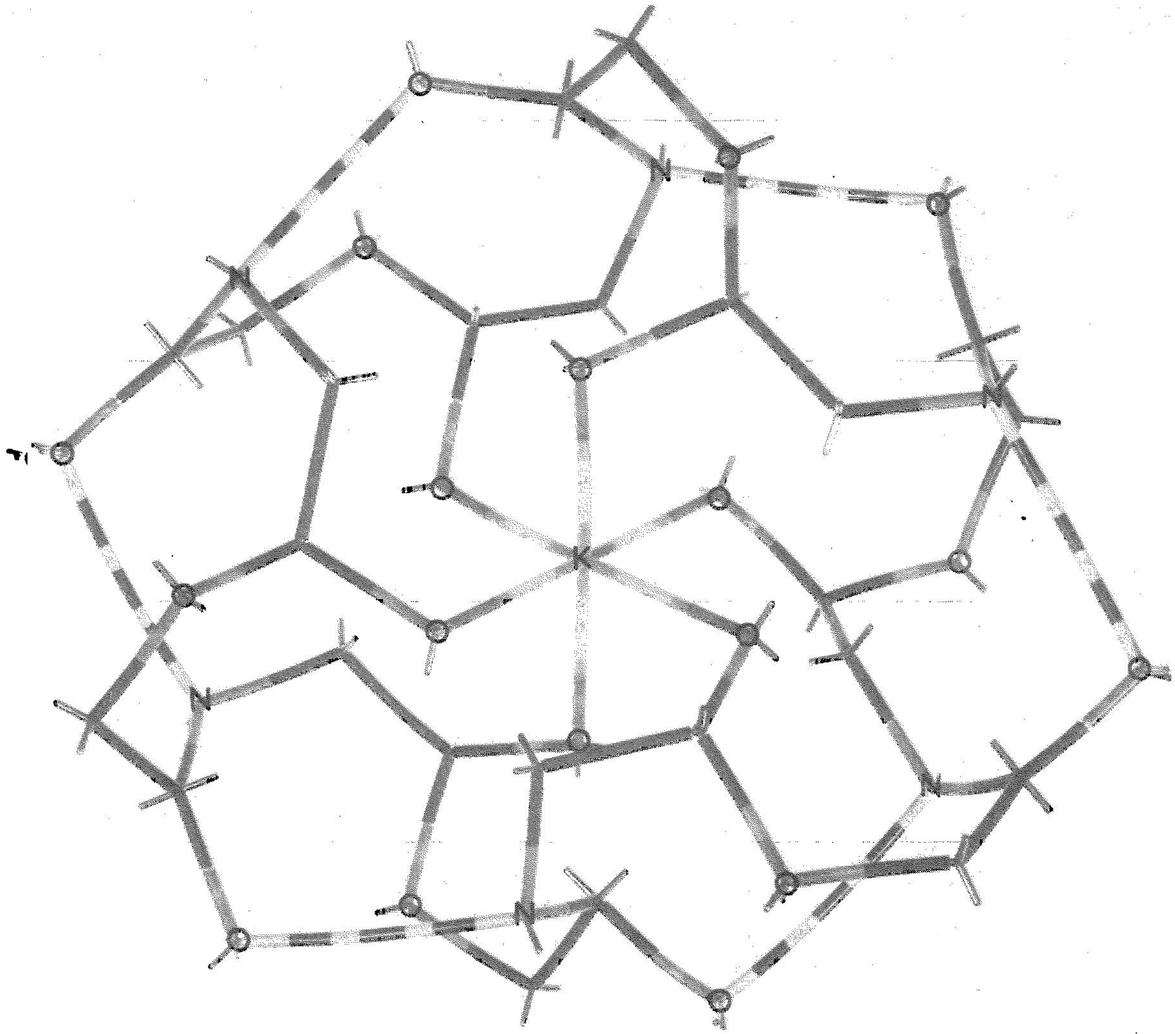


FIGURE 15. Structure of valinomycin K^+ complex. Hatched bonds indicate hydrogen bonds. Isopropyl groups are not shown.

anion concentrations. Durst[142] has shown that response to Ag^+ can be obtained to very low levels in the presence of complexed silver ion, as discussed in Section VI.1 for the fluoride electrode.

These electrodes will suffer interferences from ions which form a more insoluble silver salt.[56] For example

$$SCN^- + AgBr(s) \rightleftharpoons Ag\,SCN(s) + Br^- \qquad (33)$$

If the thiocyanate concentration is high enough, a layer of silver thiocyanate will be formed on the surface and the electrode becomes a thiocyanate electrode.

In the presence of cyanide, a silver iodide or silver iodide + sulfide membrane will tend to dissolve according to

$$Ag\,I(s) + 2CN^- \rightleftharpoons Ag\,(CN)_2^- + I^- \qquad (34)$$

Under a steady-state condition the iodide concentration sensed by the electrode is half the cyanide concentration, and the system responds in Nernstian fashion as a cyanide sensor.[56] It has the disadvantage of a short lifetime. Detailed studies by Fleet and co-workers[143,144] suggest that the mechanism is more complex than this. Nevertheless, the cyanide electrode finds wide application in water-pollution monitoring and plating-bath solution analysis.

More important is the conversion of the sulfide response to metal-ion response by incorporating the less insoluble sulfides of copper, cadmium, and lead in the pelletized disc.[56] The development of such electrodes rendered the commercially available Orion liquid-ion-exchanger electrodes for Pb (II) and Cu (II) obsolete by extending the measuring range down by three decades. The Pb (II) and Cu (II) electrodes can be used for titration of the metals with complexing agents such as EDTA. Sulfate can be determined in 50% dioxane-water (to lower the solubility of lead sulfate) by titration with lead perchlorate.[145] Rechnitz and Kenny[146] have employed the Pb (II) electrode in a variety of solvents using a cation-responsive glass electrode as reference electrode.

6. Double Membrane Electrodes

Into this new category of modified ion-selective electrodes comes a new range of gas-sensing electrodes and enzyme electrodes. The principle is similar to that of the Severinghaus carbon dioxide electrode,[147] in which CO_2 diffuses through a membrane and dissolves in a bicarbonate solution, producing a change of the hydrogen-ion activity which is detected by a pH glass electrode. A variant of this has been recently described using, instead of a glass electrode, the quinhydrone electrode.[148]

Enzyme electrodes may take a similar form in that the enzyme solution is confined by a membrane, or the enzyme may be immobilized in a polymer matrix on the surface of the sensor electrode. The enzyme catalyzes the decomposition of the sensed material to yield an ion which is detected by a suitable ion-selective electrode. For example, urea can be determined using urease; decomposition yields ammonium ions which are detected by a cation-selective glass electrode. In the first use of a nonglass ion-selective electrode, Rechnitz and Llenado[149] have coated a (silver iodide + sulfide) cyanide-responsive electrode with a polymeric coating containing β-glucosidase, which catalyzes the decomposition of amygdalin to yield glucose, benzaldehyde, and cyanide, the latter being the product detected. Guilbault[150] has reviewed enzyme electrodes.

The extension of the Severinghaus principle to ion-selective electrodes has been promoted by concern over atmospheric pollution and its control. Table 5 summarizes some of the possibilities.[151] A number of problems remain to be solved. It is essential that a steady diffusional state be created rapidly. Thus, the membrane should be readily permeable to the gas which then dissolves in a thin layer of a suitable solution confined at the surface of the electrode (see Figure 5). Usable membrane materials include low density polyethylene, microporous polyvinyl chloride, and silicone rubber. The choice of solution concentration depends on the range of gas concentration to be determined, and as with all steady-state devices, some hysteresis effects on change of concentration are unavoidable.

VII. REFERENCE ELECTRODES

All electrochemical cells require at least two electrodes. Usually interest is directed toward only one of these; the other is the reference electrode. Only if this reference electrode shows Nernstian response or is of truly invariant potential can it be disregarded, a tendency which is prevalent. The first condition can only be met by careful attention to the preparation of the reference electrode, the second never, except in the crudest measurements. The saturated (KCl) calomel electrode, which so often seems to be considered as the only reference electrode, does not meet the

TABLE 5

Gas-sensing Ion-selective Electrode Systems[151]

Gas	Reaction	Sensor
CO_2	$OH^- + CO_2 \rightarrow HCO_3^-$	H^+ – glass
NH_3	$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$	H^+ – glass
NO_2	$2NO_2 + H_2O \rightarrow NO_3^- + NO_2^- + 2H^+$	H^+ glass, nitrate
H_2S	$2OH^- + H_2S \rightarrow 2H_2O + S^{2-}$	Sulfide
HCN	$Ag(CN)_2^- \rightarrow Ag^+ + 2CN^-$	Sulfide (Silver)
HF	$HF \rightarrow H^+ + F^-$	Fluoride
Cl_2	$Cl_2 + H_2O \rightarrow 2H^+ + ClO^- + Cl^-$	H^+ – glass, chloride

second condition for variations in liquid junction potential of at least ±1 mV must be anticipated.

For most ion-selective electrodes, the effective operational range is restricted to four or five decades of concentration which corresponds to about 300 mV for a monovalent ion. A precision of 2 mV corresponds to an uncertainty of 7.5% in the concentration of a monovalent ion. Hence, it follows that the potentials of cells containing ion-selective electrodes must be measured with greater precision than is usual for most pH measurements. It may be necessary, therefore, to aim at 0.1 mV to achieve adequate accuracy in concentration determination, so variations in behavior of the reference electrode must not exceed this amount.

The problems relating to the preparation, properties, and use of reference electrodes in association with ion-selective electrodes have been surveyed elsewhere;[152] an updated summary of these considerations follows.

Apart from the solid-internal and coated-wire forms mentioned in Section IV, all ion-selective electrodes require two reference electrodes, an inner and an outer. Almost invariably, the silver-silver chloride electrode, prepared by coating silver chloride on a silver wire, is used for the internal system. The choice of outer reference system depends on the problem in hand and is one of whole cell design.[152] The various methods of use can be classified.[152]

a. Direct Comparison with a Reference Electrode Reversible to the Same Ionic Species

The e.m.f. of a cell

electrode 1 |X| electrode 2 (35)

should be constant irrespective of the concentration and nature of X provided that it contains one ionic species to which both electrodes 1 and 2 are reversible. Examples include the checking of hydrogen-ion responsive glass electrodes against the hydrogen-gas electrode and of cation-responsive glass electrodes against amalgam electrodes. The only example from nonglass ion-selective electrodes is the testing[153] of solid-state and liquid-ion-exchange chloride-responsive electrodes against conventional silver-silver chloride electrodes of the second kind (Figure 16). Since one of the most important virtues of some of the new ion-selective electrodes is their response to ions for which no potentiometric sensors were previously available, the method has limited applicability.

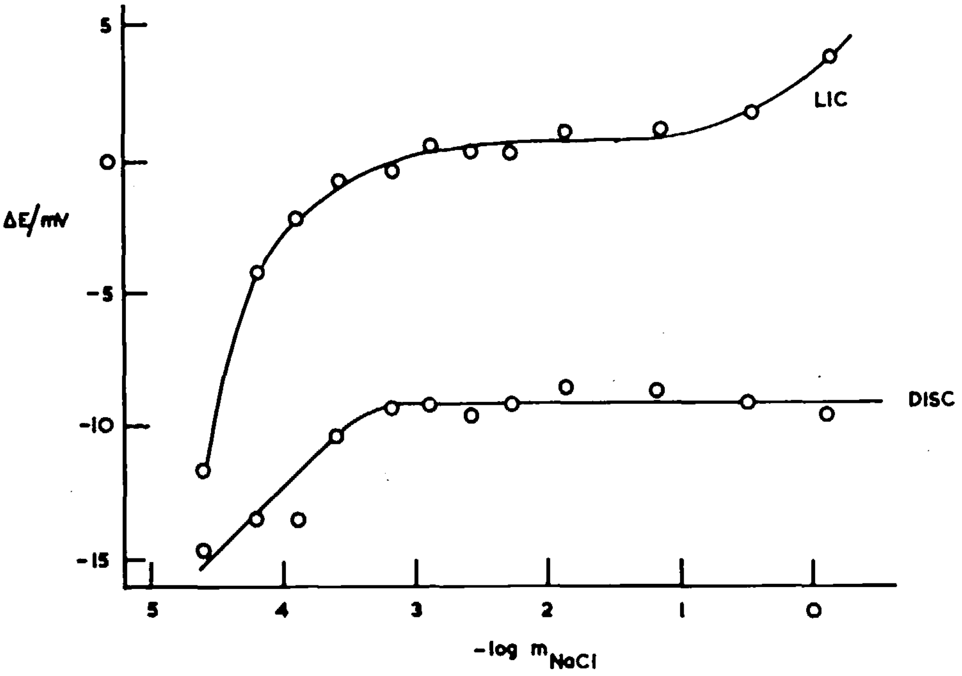


FIGURE 16. Comparison of liquid-ion-exchanger (LIC) and solid-state (disc) silver-silver chloride ion-selective electrodes with conventional electrodes of the second kind in solutions of sodium chloride.[153]

b. Use of a Reference Electrode Reversible to One of the Ions of an Added Inert Electrolyte

Since it is common practice, for several reasons, to work at an ionic strength increased by the addition of an inert electrolyte, this technique could be used more often than it is. The best example from common practice is the addition of a chloride to a buffer solution of a weak acid or base so that the reliable silver-silver chloride electrode can be used and the pK of the weak acid determined in the well-known Harned cell.[80] Often, with an ion-selective electrode, it is advantageous to buffer the solution; when this is done, the hydrogen gas, or more simply the hydrogen-ion-responsive glass electrode, could be used as a reference electrode. In fact, it is often feasible to use one ion-selective electrode as a reference electrode for another. This was done by Manahan,[154] who added fluoride to nitrate solutions and employed the lanthanum fluoride electrode in a cell for the determination of nitrate.

c. Use of a Second Ion-selective Electrode of the Same Type as its Own Reference Electrode

This technique is forced on investigators in some nonaqueous solvents where only a single type of electrode may be known to function satisfactorily, and aqueous/nonaqueous liquid junctions are anathema. The cell is a form of concentration cell with transfer. For example, Durst[155,156] has used the cell

$$LaF_3|F^-(X),KNO_3(0.1)|KNO_3(0.1)|KNO_3(0.1)F^-(S)|LaF_3 \qquad (36)$$

The left-hand side of the cell contains a solution of unknown fluoride concentration. The fluoride-ion concentration on the right-hand side (S) is varied, either by addition of fluoride or by complexing what is already there, until the e.m.f. of the cell is zero (actually adjusted to the bias potential of the two LaF_3 electrodes checked in the same solution). This technique is known as linear null-point potentiometry (LNPP) and is adaptable to very small amounts of solution (0.01 cm^3). The assumption is implicit that there is no change in liquid-junction potential.

d. Use of Reference Electrodes of (Ideally) Invariant Potential

The most commonly employed method has been deliberately left until last. It is of course the method adopted for operational pH measurements and its use for pX measurements will be discussed in Section IX.

The e.m.f. of a cell with liquid junction is, except for homo-ionic junctions (those between two solutions containing different concentrations of the same solute electrolyte), dependent on the method of forming the junction, and the subsequent interdiffusion of the two solutions. For those combinations that have been studied, the variations are not large, but knowledge is almost entirely restricted to a few simple chloride solutions. Usually the common forms of liquid junction employed (Figure 17) are those where the junction is ill-defined and diffusion takes place radially from a restraining diaphragm. These restrained flow junctions can take several forms including the porous frit or 'stone,' asbestos fiber, and ground-glass sleeve. Invariably, the basic requirement for stability, which is that the denser solution be below the less dense one, is not complied with. Too little work has been done on the reproducibility of such devices but the indications are that ±0.03 pH is not uncommon.[157] Potassium chloride, chosen because its ions are equitransferent, is messy in that it creeps. A new form of calomel assembly, the Beckman 'Permaprobe,' which consists of a porous Teflon or similar plastic tube impregnated with potassium chloride, overcomes this.

It is perhaps worthwhile summarizing the principal evidence on which the use of saturated or 3.5 mol l.$^{-1}$ KCl salt bridges is based. Guggenheim[158] showed that the e.m.f. of the whole cell

$$Hg|Hg_2Cl_2|HCl(0.1)|KCl(x)|KCl(0.1)|Hg_2Cl_2|Hg \qquad (37)$$

falls as x is increased. Second, Henderson-equation considerations suggest that if the ions are equitransferent, the ideal liquid-junction potential or diffusion potential[158] will be zero. This is meager evidence on which to stake so much so often.

Another approach to reducing liquid-junction potentials, originated by Nernst, consists of adding inert electrolyte throughout the cell, so that the potential-determining ions are present in effectively small relative concentration. The solutions in the electrode compartments may come into direct contact (single liquid junction) or an intermediate bridge may be used (double

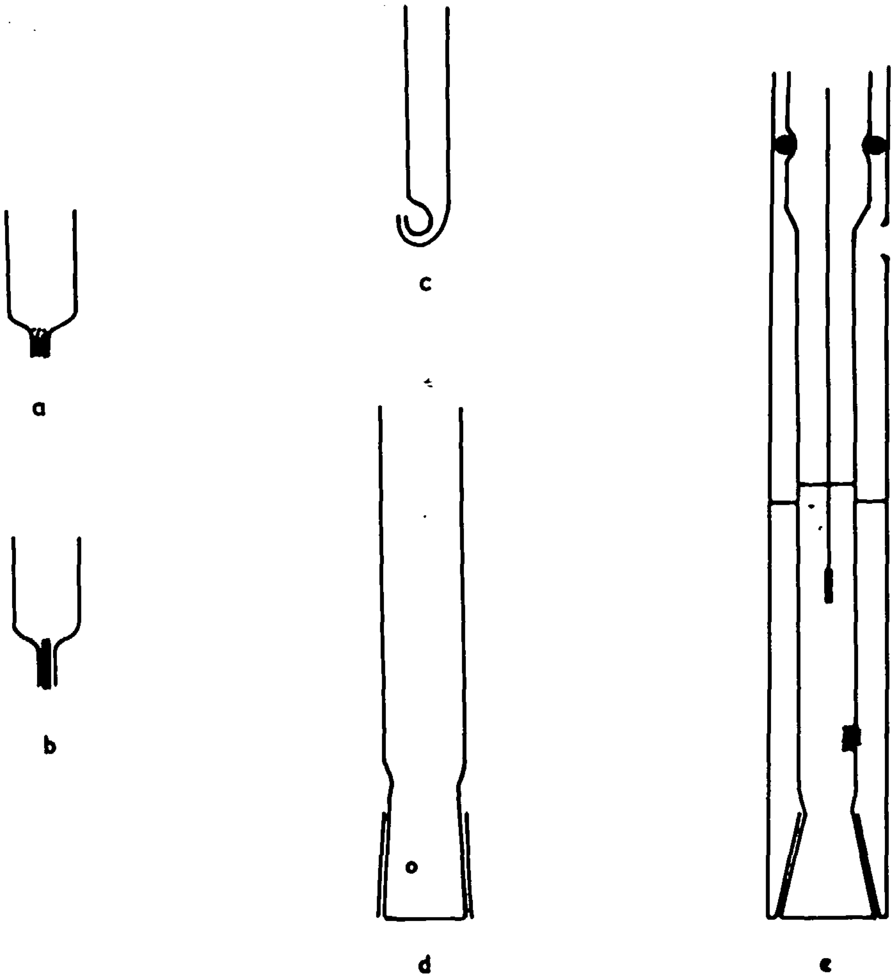


FIGURE 17. Some methods of forming the liquid junction. a. stone or porous frit. b. palladium annulus. c. J-type, favored by 'complex-ion' chemists. d. ground-glass sleeve. e. double liquid junction reference electrode form (Orion) with frit (inner) and sleeve (outer) junctions.

junction). The second is necessary if the solutions in the two electrode compartments are chemically incompatible. A double junction is used in association with the saturated calomel electrode if the seepage of chloride into the test solution cannot be tolerated. Several manufacturers market double-junction reference electrodes (Figure 17). One can get away with some chloride seepage in flow system if the reference electrode is placed downstream from the sensing electrode.

Last, other (ideally) potential invariant reference systems may be used instead of the ubiquitous calomel system. The corresponding silver-silver chloride system,

$$\mathrm{KCl(s),\ AgCl(s)\,|AgCl\,|Ag} \qquad (38)$$

is popular in the U.S. but not in Europe. The 'Thalamid' electrode[159]

$$\mathrm{KCl(s),\ TlCl(s)\,|TlCl\,|Tl(Hg)} \qquad (39)$$

does not suffer from the temperature hysteresis shown by the other two systems. It might be more widely adopted were it not that thallous chloride is poisonous and that thallium amalgams react with air necessitating a closed system. Finally, attention should be drawn to mercury-mercurous sulfate and mercury-mercurous carboxylate systems.[152]

VIII. METHODS OF USE

1. Direct Potentiometry

As was pointed out in the preceding section, an error of 2.0 mV will lead to an error of 7.5% in determination of the concentration of a monovalent ion, leaving aside any consideration of the conversion of activities to concentrations. This value is constant over the useful range of electrode function because of the logarithmic relation between potential and concentration. At low concentrations (ppm level), direct potentiometry may furnish results of at least as good accuracy as other methods, e.g., flame photometry.

Before use, the electrode has to be calibrated or checked to see if its response is theoretical. This may be done by constructing a calibration curve, as shown in Figure 7, or by using a two-point calibration, bracketing the unknown, as for pH measurements.

In order to reduce the effect of changes in liquid junction potential and with the added bonus (or pious hope) that activity coefficients will remain constant, both test and calibration solutions are brought to a fixed ionic strength by the addition of an inert electrolyte. Such solutions are available commercially for specific purposes where additionally they may contain reagents to complex ions which show interferences, and buffer components to keep the pH constant. An example is TISAB[160] which is used in the determination of fluoride in public water supplies; it contains a complexing agent such as citrate for Al^{3+} and acetate buffer to give pH 5.0 to 5.5. In view of the effect of acetate on the lanthanum fluoride electrode,[101] this choice of buffer substance is surprising.

2. Known Increment Methods[142]

This heading covers the techniques of 'spiking' of known additions, and also its reverse, addition of a reagent to complex and, hence, remove the sensed species which is sometimes called known subtraction.

The first is based on the addition of one or more aliquots of the ionic species of interest and measurement of the change of e.m.f. resulting. It is necessary that activity coefficients and the liquid junction potential do not change, so inert electrolyte is added to increase the ionic strength. If this is so

$$\Delta E = k \log \frac{C + \Delta C}{C} \qquad (40)$$

or

$$C = \frac{\Delta C}{(10^{\Delta E/k} - 1)} \qquad (41)$$

where (C + ΔC) is the increased concentration of the sensed ion produced by the addition. ΔC can be related to the concentration of the standard solution added, C_s, in aliquots of V_i to the test solution of volume V_o. Then

$$C = C_s \frac{V_i}{V_o + V_i} \left[10^{\Delta E/k} - \frac{V_o}{V_o + V_i} \right] \qquad (42)$$

It is necessary to know k either by checking whether it has its theoretical value or by calibration. It is possible, however, by making several known additions to solve the equations for k by computer.[161] The accuracy available depends on the size of ΔE; it must not be too large, otherwise the assumptions of constancy of liquid junction potential and activity coefficients will be quite invalid.

Various tables and aids[162] are available for solving Equation 42 without the tedium of using antilogarithm tables. Gran's plot[163] graph paper available from Orion Research Inc. has an antilog axis on which ΔE is plotted directly which converts it to apparent concentration. Special ruling enables volume correction (if V_i is not small compared with V_0) to be made automatically. Errors in the Gran addition method have been considered.[164] Gran's plot paper can also be used for plotting the results of potentiometric titrations, as discussed below and illustrated in Figure 9.

In the known subtraction technique, the change in e.m.f. ΔE produced by the addition of an aliquot solution containing a ligand to complex the ion species being sensed is measured. The equivalent form of Equation 42 has ΔE negative.

It is also possible to do the related pair of experiments where the ion-selective electrode is in the standard solution and the test solution is added (analate addition) or the standard solution contains an ion that reacts with the test solution (analate subtraction).

The equivalent form of Equation 42 is

$$C = C_s \left[\frac{V_o + V_i}{V_o} 10^{\Delta E/k} - \frac{V_i}{V_o} \right] \qquad (43)$$

Equations 42 and 43, of course, simplify if the volume change can be neglected.

If the ion being sensed in known addition or subtraction is partly complexed by ligands already in the test solution, it is necessary to ensure that the fraction complexed remains effectively constant on incrementation.

3. Potentiometric Titrations[142]

Examples of potentiometric titrations with ion-selective electrodes have been given in Figures 8, 9, 12, and 13. Potentiometric titrations offer an increase in accuracy over direct potentiometry and known increment methods because in the region of the equivalence point the change in e.m.f. is considerably greater than between standard and test solutions which limits the accuracy of direct potentiometry. Further problems of change in liquid-junction potential and activity coefficients are of minor importance (except in pH titrations of moderately strong acids and bases).

It is not necessary for potentiometric titrations that an indicator electrode should have theoretical slope. Provided the change in the vicinity of the equivalence point is of the order of 100 mV, the end point can be satisfactorily located. In some titrations the titration curve is not symmetrical (e.g., Figure 9). This may be due to changes in response due to solubility and the effect of interfering ions with the result that the equivalent point may not coincide with the point of maximum change of slope.[165,166] This problem can be overcome by standardizing the titrant in a preliminary titration with a known amount of analate.

Derivative titration curves ($\frac{\Delta E}{\Delta V}$ vs. V) permit a more exact location of the point of maximum change of slope (Figure 13). A method which utilizes more experimental points and overcomes possible instability of the potential at the equivalent point is the use of the Gran's plot. An example of the use of Gran's plot paper is given in Figure 9. The equivalence point is located by extrapolation of the two straight lines. Note the slopes of the two lines are not equal and opposite, indicating the sub-Nernstian response past the equivalence point.

Ion-selective electrodes may be placed in the sample solution to detect the end point on titration with a reagent which reacts with the sample as in the example above, or to respond to the titrant. An example of this, using again the lanthanum fluoride electrode, is the determination of lithium by precipitation as fluoride in alcoholic solution.[167] A third type[168,169] for titration of a metal ion M_1 utilizes competing ligand formation and involves the addition of a metal ion (M_2) which forms a more stable complex to the solution and the use of the ion-selective electrode which responds to M_2.

Titration with the complexing agent (L) first complexes virtually all M_2 and only after the first inflection does M_1L begin to form. When all M_1 has been complexed, L increases in concentration, binding the remaining M_2 and giving a second inflection. In practice it is only necessary to add a small indicator concentration of M_2L. An example is the use of Cu-EDTA indicator and EDTA to titrate Ca^{2+} and Fe^{3+}.[168,169]

Guides and summaries to the many analytical procedures that have been developed are available.[170,171]

IX. pX STANDARDS

Since the measurement of pX with an ion-selective electrode is analogous to measurement of pH,[172] if the electrode is used in conjunction with a saturated calomel electrode, then by similar arguments one should have *pX standards.* There are two important differences:

(a) With pX the mV change involved is usually much smaller than with pH

(b) A greater range of ionic strength is involved

For both reasons the residual liquid-junction potential can be sizable. As with pH, this effect may be obviated if the test and reference solution have similar composition. There is no difficulty in using a Bates-Guggenheim convention[173] for ionic strengths less than 0.1 to give the single ion activity

$$-\log \gamma_{Cl^-} = AI^{1/2}/(1 + 1.5\ I^{1/2})$$

Problems occur with higher ionic strengths. In a preliminary approach to this problem, Bates and Alfenaar[153] applied the Bates-Guggenheim (pH) convention at two trial ionic strengths, 0.1 and 1.0. This convention was intended for use at ionic strengths 0.1 and below, and its application irrespective of ionic strength does not appear reasonable. Nevertheless, pX(S) standard values were presented[153] for pNa, pCa, pCl, and pF in solutions of NaCl, $CaCl_2$, NaCl, and NaF, respectively, at ionic strengths up to 1.0 (except for NaF which is probably ion-paired at this concentration) and these have been reproduced in some manufacturers' literature. Subsequently, a different approach[174] based on the Stokes-Robinson hydration theory,[175] which is outlined in the next section, has been adopted.

1. Stokes-Robinson Hydration Theory[175,176]

The distance-of-closest approach parameter (*a*) in the Debye-Hückel theory is greater than the sum of the crystallographic radii for most salts, often by about the radius of a water molecule for each ion. This suggests that *a* should be the sum of the hydrated radii; that is, that the mean rational activity coefficient predicted by Debye-Hückel theory is that of the hydrated ions. In calculating the molality, one does not usually take into account that some of the solvent is associated with the solute. However, the chemical potential of the solute will be different from its value if the solute is considered unhydrated. The total free energy of the system is the same regardless of the way it is regarded as broken down; hence, this fact can be used to find the relationship between the activity coefficients.

Consider a quantity of solution containing one mole of solute species 2 dissolved in S moles of solvent species 1. For simplicity, attention will be restricted to a 1-1 electrolyte.

Considering the solute unsolvated, the total free energy is

$$G = S\mu_1 + \mu_2 \tag{44}$$

If the solute is solvated with *h* moles of solvent associated with 1 mole of solute

$$G = (S - h)\mu_1 + \mu_2' \tag{45}$$

where the prime ′ indicates the solvated model. Then

$$\mu_2 = \mu_2^o + 2RT \ln f_2 x_2$$

$$\mu_2' = \mu_2^{o'} + 2RT \ln f_2' x_2'$$

$$\mu_1 = \mu_1^o + RT \ln a_1$$

and

$$x_2 = \frac{1}{S + 2} \qquad x_2' = \frac{1}{S - h + 2}$$

Therefore

$$\frac{\mu_2^o - \mu_2^{o'}}{2RT} + \frac{h\mu_1^o}{2RT} + \ln f_2 + \frac{h}{2} \ln a_1 + \ln \frac{S - h + 2}{S + 2} = \ln f_2' \tag{46}$$

But at infinite dilution when S → ∞, f_2, f_2', and a_1 approach 1 and all the logarithmic terms approach zero. Hence, the first two terms involving the standard chemical potentials are zero and thus

$$\ln f_2' = \ln f_2 + \frac{h}{2} \ln a_1 + \ln \frac{S - h + 2}{S + 2} \tag{47}$$

The rational activity coefficient f_2 is more usefully expressed in terms of γ_2, the molality-scale activity coefficient, where, if M is the molecular weight of water in kg

$$f_2 = (1 + 2mM)\gamma_2 \quad \text{and} \quad S = 1/mM$$

so

$$\ln f_2' = \ln \gamma_2 + \frac{h}{2} \ln a_1 + \ln [1 + (2 - h)\, mM] \tag{48}$$

The only nonthermodynamic assumption made is that *h* is independent of concentration.

Stokes and Robinson used Equation 48 for the experimentally measured γ_2 substituting for f_2, a Debye-Hückel Equation, viz.

$$\log f_2 = - \frac{AI^{1/2}}{1 + (a/a^o)I^{1/2}} \equiv \log f_{DH} \tag{49}$$

thus

$$\log \gamma_2 = - \frac{AI^{1/2}}{1 + (a/a^o)I^{1/2}} - \frac{h}{2} \log a_1 - \log \left[1 + (2 - h) \frac{m}{55.5}\right] \tag{50}$$

is used to fit experimental data in terms of the two parameters the distance of closest approach *a*, and *h*.

Since each of the last two terms is approximately linear in *m*, and it is well known that an equation of the form

$$\log \gamma_2 = - \frac{AI^{1/2}}{1 + (a/a^o)I^{1/2}} + BI \tag{51}$$

is a good fit to activity-coefficient data up to high molalities (< 5 m), it is not surprising that the equation is remarkably successful, with the ion-size parameter *a* consistent with the likely dimensions of solvated ions and reasonable values for *h* ranging from 7.1 for LiCl to 1.9 for KCl (Figure 18).

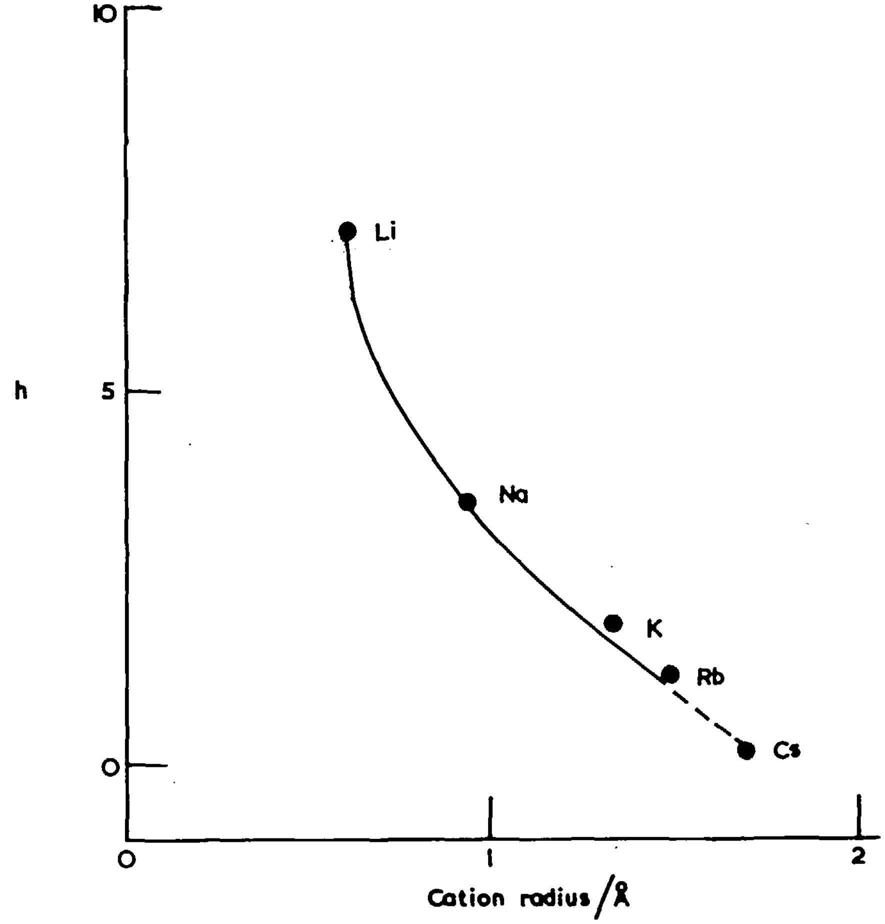


FIGURE 18. Hydration numbers of alkali metal chlorides as a function of crystallographic radii of the cations.[174] With the convention that h for the chloride ion is zero, these are also values for the cations.

2. Application to Single-ion-activity Considerations[174]

If one assumes that h for the chloride ion is *zero* (the reasonableness or unreasonableness of this assumption will not be discussed here), the ionic contribution to h appears to be additive and a for chloride becomes equal to its crystallographic radius, 1.81 Å. This choice of h for chloride ion as zero is the nonthermodynamic assumption, or convention, on which the division of the mean activity coefficients of unassociated chlorides into their ionic components has been made,[174,177] through the assignment of ionic hydration numbers.

Applying the Gibbs-Duhem Equation to a 1-1 chloride considered unhydrated, gives

$$-(55.5/m)\ d\ln a_1 = d\ln \gamma_+ m + d\ln a_- \qquad (52)$$

However, if the cation (only) is hydrated with h molecules of water, and m' is its molality in terms of unbound water, then

$$m/m' = 1 - (hm/55.5) \qquad (53)$$

and, hence

$$\begin{aligned} -(55.5/m')\ d\ln a_1 &= -(55.5/m)\ d\ln a_1 + h\ d\ln a_1 \\ &= d\ln \gamma'_+ m' + d\ln a_- \qquad (54) \end{aligned}$$

But the activity of the chloride ion is the same whether the solute is regarded as hydrated or not, so $m_-\gamma_- = m'\gamma'_-$, and

$$d\ln(\gamma_+ m) + h\ d\ln a_1 = d\ln \gamma'_+ m' \qquad (55)$$

or

$$\ln \gamma_+ = \ln \gamma_+' - h \ln a_1 - \ln [1 - (hm/55.5)] \qquad (56)$$

We now identify γ_+' with the activity coefficient given by the D-H theory corrected from the rational to the molality scale

$$\ln \gamma_+' = \ln f_{DH} - \ln [1 + (2m'/55.5)] \qquad (57)$$

and, therefore

$$\ln \gamma_+ = \ln f_{DH} - h \ln a_1 - \ln \left[1 + (2 - h) \frac{m}{55.5}\right] \qquad (58)$$

The term involving the activity of water a_1 can be elimated by introducing the osmotic coefficient ϕ defined by Equation 59

$$- \ln a_1 = 2m\phi/55.5 \qquad (59)$$

So, using also Equation 50 for the mean activity coefficient

$$\ln \gamma_+/\gamma_\pm = - \frac{h}{2} \ln a_1 = \frac{hm\phi}{55.5} \qquad (60)$$

or

$$\log \gamma_+ = \log \gamma_\pm + 0.00782\ hm\phi \qquad (61)$$

From Equation 61 it follows that

$$\log \gamma_- = \log \gamma_\pm - 0.00782\ hm\phi \qquad (62)$$

For salts of different charge types, the equations are complicated only by valence relations. For example, for an alkaline earth chloride MCl_2

$$\ln \gamma_{2+} = 4 \ln f_{DH} - h \ln a_1 - \ln\left[1 + (3 - h) \frac{m}{55.5}\right] \qquad (63)$$

from which

$$\log \gamma_{2+} = 2 \log \gamma_\pm + 0.00782\ hm\phi + \log \left[1 + (3 - h) \frac{m}{55.5}\right] \qquad (64)$$

and

$$2 \log \gamma_- = \log \gamma_\pm - 0.00782\ hm\phi - \log \left[1 + (3 - h) \frac{m}{55.5}\right] \qquad (65)$$

since

$$3 \log \gamma_\pm = \log \gamma_{2+} + 2 \log \gamma_- \qquad (66)$$

From Equations 61, 62, 64, and 65 the single-ion-activity coefficients given in Table 6 have been calculated.

TABLE 6

Single Ion Activity Coefficients Based on Bates, Staples, and Robinson[174]

Hydration Theory Approach

		$\gamma+$	$\gamma-$
0.1 molal			
	KF	0.775	0.775
	NaCl	0.783	0.773
	KCl	0.773	0.768
	$CaCl_2$	0.269	0.719
	NaBr	0.788	0.776
	KBr	0.769	0.775
	$CaBr_2$	0.283	0.729
1 molal			
	KF	0.645	0.645
	NaCl	0.697	0.620
	KCl	0.623	0.586
	$CaCl_2$	0.263	0.690
	NaBr	0.739	0.639
	KBr	0.639	0.596
	$CaBr_2$	0.378	0.748

Analysis[178] of activity data for potassium fluoride solutions using the hydration Equation 50 gives for the fluoride ion h = 1.87, almost identical to 1.9 for the K^+ ion on the basis of h for the chloride ion being zero. Sodium fluoride is probably ion-paired at concentrations above 0.1, so potassium fluoride is a better choice as a reference material;[178] moreover, it is more soluble.

If both cations and anions are hydrated, then it follows that

$$\log \gamma_+ = \log \gamma_\pm + 0.00782\ (h_+ - h_-)\ m\phi \qquad (67)$$

$$\log \gamma_- = \log \gamma_\pm + 0.00782\ (h_- - h_+)\ m\phi \qquad (68)$$

If $h_+ = h-$ for KF, then it follows that $\gamma_+ = \gamma- = \gamma_\pm$ and this is the basis for the values for KF included in Table 6.

These considerations can be extended[177,179] to binary mixtures of electrolytes with a common unhydrated anion or a common hydrated cation, one hydrated and one unhydrated anion. They can be extended to Br^- and I^- salts assuming that these anions are also unhydrated.

Tables 7 and 8 present standard reference values pX(S) for some important univalent and divalent ions calculated from the single-ion activity coefficient values given in Table 6 and values

TABLE 7

Standard Reference Values for Univalent Ions, pX(S) at 25°C Based on the Bates, Stapes, and Robinson[174], Hydration Theory Approach

Reference Material Molality/mol kg^{-1}	LiCl pLi	NaCl pNa	NaCl pCl	KCl pK	RbCl pRb	CsCl pCs	NH_4Cl pNH_4	KF pF
0.01	2.043	2.044	2.045	2.043	2.044	2.045	2.043	2.044
0.1	1.097	1.106(1.108)	1.112(1.118)	1.112	1.116	1.121	1.112	1.111
0.2	0.810	0.827	0.838	0.840	0.846	0.858	0.840	0.837
0.5	0.406	0.455	0.481	0.482	0.495	0.519	0.483	0.475
1.0	0.054	0.157(0.160)	0.208(0.204)	0.206	0.266	0.264	0.208	0.190
2.0	-0.392	-0.180	-0.072	-0.086	-0.055	0.003	-0.080	-0.119
3.0	-0.754	-0.417	-0.245	-0.274	-0.232	-0.157	-0.261	-0.325
4.0	–	-0.618	-0.374	-0.421	-0.368	-0.278	-0.397	-0.494
5.0	–	-0.804	-0.477	–	-0.481	-0.376	-0.509	–
6.0	–	-0.981	-0.563	–	–	–	-0.602	–

Values in brackets are from Bates and Alfenaar.[153]

TABLE 8

Standard Reference Values for Divalent Ions, pX(S) at 25°C Based on the Bates, Staples, and Robinson Hydration Theory Approach

Reference material Molality/mol kg^{-1}	$MgCl_2$ pMg	$CaCl_2$ pCa	$SrCl_2$ pSr	$BaCl_2$ pBa	$CaCl_2$ pCl
0.0333	1.884	1.901(1.887)	1.901	1.905	1.282(1.286)
0.1	1.554	1.570	1.575	1.587	0.842
0.2	1.321	1.349	1.360	1.389	0.562
0.333	1.123	1.165(1.105)	1.184	1.232	0.349(0.381)
0.5	0.932	0.991	1.022	1.083	0.177
1.0	0.463	0.580	0.646	0.777	-0.140
2.0	-0.459	-0.186	-0.035	0.385	-0.507

Values in brackets are from Bates and Alfenaar.[153]

pertaining to other molalities. There are some differences between these values for divalent ions and the (now superseded) values presented earlier by Bates and Alfenaar.[153] For example, at 0.1 mol kg^{-1} pNa = 1.108 compared with 1.106 in Table 7, and at 1.0 mol kg^{-1} the values are 0.160 and 0.157 with similar close agreement for pCl. However, for pCa, Bates and Alfenaar[153] give 1.887 at I = 0.1 compared with 1.901, and 1.105 compared with 1.165 at I = 1.0. The differences for the divalent ions reflect the inadequacies of the Debye-Hückel-based Bates-Guggenheim convention at high ionic strengths. The agreement of values from the two conventions is somewhat coincidental in that Bates and Alfenaar[153] chose the sodium salts on which to base their calculations; different values would be obtained if potassium salts had been chosen. As mentioned previously, KF is preferred to NaF as a standard for pF; however, the Stokes and Robinson treatment gives pF = 1.117 for NaF solutions at I = 0.1 compared with 1.124 given by Bates and Alfenaar.

To use these pX(S) values the test solution should be bracketed by two standards to make allowance for possible sub-Nernstian response. It must be strongly emphasized that the pX(S) values are only appropriate to the standard reference solution chosen (for example, pCl is different in 0.1 *M* NaCl and 0.1 *M* KCl) and are totally inapplicable to mixed electrolytes.

3. Discussion of the Problem of pX Measurements and Standards

It cannot be disputed that the ion-selective electrodes measure activity. Ross[56] argues that it is the activity of the species which most people are (or should be) interested in, but the examples he gives (e.g., corrosion of zinc in hydrochloric or acetic acid) show that it is the actual not the stoichiometric concentration of the species which is the proper quantity.

This reviewer is not convinced that it is *activity standards* that are required. Wynne-Jones has argued that it is the concentration which one really does know since quantities of HCl or NaOH, for example, can be readily measured out. Thus, in dealing with acidity in peroxide-water mixtures, Mitchell and Wynne-Jones[180] preferred to revert to the original Sϕrensen definition, $pH = -\log C_{H+}$. A pH scale for each H_2O_2-H_2O mixture was extablished using a glass electrode in the cell:

$$\text{glass electrode} \left| \begin{matrix} H_2O_2 & HClO_4 \\ H_2O & NaClO_4 \end{matrix} \right| \begin{matrix} 3.5\ \underline{M}\ KCl \\ \text{in} \\ H_2O \end{matrix} \left| \ AgCl \ \right| Ag \qquad (69)$$

The total ionic strength was held at 0.1. Then

$$pH = -\log C_{H+} = (E - E^{o} - E_J) + \log y_{H+} + \log a_{Cl^-} \qquad (70)$$

and the last two terms are constant ($I = 0.1$). y_{H+} is a molar scale activity coefficient. Therefore, the term ($E^{o} + E_J$) on the right-hand side of Equation 70, the 'standard potential,' can be determined. To use this scale sodium perchlorate has to be added to the test solution to raise the ionic strength, which could be a disadvantage.

A similar procedure could be used with ion-selective electrodes, that is, the calibration of the electrode system, on a *concentration* basis. Instead of holding I constant to keep y_X constant, some variations could possibly be allowed for with a Debye-Hückel equation correction. There are disadvantages to both methods but because of the accepted method for pH it does not follow that this is the best for pX. Indeed complex-ion chemists prefer a concentration defined "pH" scale in sodium nitrate or perchlorate solutions.[181]

A different problem arises for pX standards above values of 5 or 6. As pointed out by Hansen et al.,[77] no one, unless rigid precautions were taken, would attempt to make a buffer of pH 6 by diluting HCl, but, for example, copper nitrate solutions have been diluted to give pCu 6 to 8 when adsorption by the walls of the vessel becomes extremely important. Hansen et al.[77] advocate the use of 'metal buffers' with added complexing agent covering the range 2 to 18, an idea which goes back to Schwarzenbach. Some values for pCu at pH 4.7 using NTA or EDTA are given in Table 9. The treatment is complicated by the possible formation of several complexes and of complex formation with the buffer used to fix the pH, e.g., ammonia buffer.

pCu is defined here on a concentration basis. The ionic strength is adjusted to 0.1 *M* with potassium nitrate to reduce the residual liquid-junction potential. An analogous treatment in the calibration of the fluoride electrode down to pF 10 was discussed earlier (Figure 8).

TABLE 9

Cu(II) Ion Buffers. pCu Values[77] in Copper(II) Nitrate Solution at pH = 4.75 and Total Ionic Strength (0.1) using KNO_3

	NTA			EDTA		
Ligand ratio	10:1	1:1	1:10	10:1	1:1	1:10
pCu	6.91	7.91	8.91	10.72	11.72	12.72

NTA = nitrilotriacetate
EDTA = ethylenediaminetetracetate

X. COMPENSATION OF pX MEASUREMENTS FOR TEMPERATURE CHANGES AND ISOPOTENTIAL CONTROL

The direct scale reading of pH and pX at various temperatures requires instrumental variation of the slope factor k = (RT/F)ln10. This is, however, not the only effect of temperature if the test and standardization cells are not at the same temperature throughout, as they should always be for the most accurate measurements. The principles will be exemplified with reference to pH.[172]

The pH test cell is commonly

$$\text{glass electrode}\ |X|\ KCl_{(s)}\ |Hg_2Cl_2|Hg \qquad (71)$$

where X represents the test solution. It is necessary to standardize the electrode system in a standard buffer S of known pH_s. Then

$$pH_x - pH_s = \frac{E_x - (E'_o - E_J + E_{int})}{k}$$

$$\frac{E_s - (E'_o + E_J + E_{int})}{k} \qquad (72)$$

where E_x and E_s are the cell e.m.f.s for solutions X and S, respectively.

The term $(E'_o + E_J)$ is the standard potential of the cell (71):

$$H_2|a_{H+} = 1\ |\ KCl_{(s)}\ |Hg_2Cl_2|Hg \qquad (73)$$

incorporating the liquid-junction potential, and E_{int} is the e.m.f. of the glass electrode internal cell, which might be

$$^{+}Ag|AgCl|0.1\ M\ HCl|H_2^- \qquad E_{int} \qquad (74)$$

that is, with the inner glass surface, as well as the outer, functioning as hydrogen-ion-responsive electrodes.

If solution X does not differ markedly in composition and ionic strength from S then E_J is the same for both cells. If the temperature is the same throughout both cells then $(E'_o + E_{int})$ is also the same for both, and the residual liquid-junction potential is zero. Equation 72 then reduces to

$$pH_x - pH_s = \frac{E_x - E_s}{k} \qquad (75)$$

There are two distinct cases, which arise if the temperature of the test solution X is different from the temperature of the standard buffer S.

a. *Both* electrodes are allowed to reach temperature equilibrium in *each* solution

b. The glass electrode reaches temperature equilibrium in both solutions, but the reference electrode is remote and remains at a constant temperature; thus, there is a temperature gradient within a column of KCl solution.

For cell (71):

$$E_x = (E'_o + E_J + E_{int}) + k'T\ pH_x \qquad (76)$$

where

$$k' = (R/F)\ ln\ 10 = 0.1984\ mV\ K^{-1}$$

E'_o and E_{int} are functions of temperature which in general can be expressed as power series in temperature. Over a limited temperature range not exceeding 20°C in the neighborhood of room temperature, a simple linear expression for $(E'_o + E_J + E_{int}) = E^o$ is adequate.

Thus

$$E_x = a + bT + k'T\ pH_x \qquad (77)$$

and

$$E_x \neq f(T) \quad \text{when} \quad -bT = k'T\ pH_x$$

or

$$pH_i = -\frac{b}{k'} = -\frac{1}{k'}\frac{dE^o}{dT} \qquad (78)$$

This value pH_i, called the isopotential[182] pH, is the pH value where the lines representing the variation of E_x with pH at different temperature intersect, hence, the German, isothermenschnittpunkt, the isothermal intersection point. Because the variation with temperature is only approximately linear, the lines do not intersect at a unique pH_i-value, and slightly different pH_i-values are appropriate depending on the temperature range considered. The pH at which $E_x = 0$ is called the zero point or nullpunkt, and depends on the inner filling solution of the electrode. The value of E_x corresponding to the isopotential pH_i is sometimes tabulated. It is not the same as the zero point except for symmetrical cells, that is, those with the same type of inner and outer reference electrodes. From Equations 77 and 78

$$E_x = a - k'T\ pH_i + k'T\ pH_x + a + k(pH_x - pH_i) \qquad (79)$$

Taking case (a) first, Equation 72 becomes

$$pH_X(T_X) - pH_s(T_s) = \frac{E_{X(T_X)} - (E_o' + E_J + E_{int})_{T_X}}{k'T_X} - \frac{E_{s(T_s)} - (E_o' + E_J + E_{int})_{T_s}}{k'T_s} \qquad (80)$$

It is assumed that the only effect of the difference between test (T_X) and buffer standardization (T_s) temperatures is a change in (E_o' + E_J) and E_{int}, the so-called *zero shift*($k'pH_i$). The pH_s-value to be used with the set buffer control on the pH meter is that for the temperature T_s. Slope factor compensation is assumed.

From Equations 77 and 78, the zero shift error is given by

$$k'\, pH_i\, (T_X - T_s) \qquad (81)$$

as a potential, or in terms of pH as

$$\Delta pH_X = \frac{T_X - T_s}{T_X}\, pH_i \qquad (82)$$

In a pH meter with variable isopotential control, a bias potential equal to $k'pH_i$ is derived which automatically corrects for the zero shift. This, of course, requires the calculation of pH_i for the particular electrode system employed, which can usually be done from data for e.m.f. variation with temperature in the literature.

For example, for silver-silver chloride, 0.1 *M* HCl-glass electrode filling (cell (74)) $dE°/dT$ = +0.18 mV K^{-1} and for cell (73), $dE°/dT$ = −0.66 mV K^{-1} giving −0.48 mV K^{-1} for $d(E^{o'} + E_J + E_{int})/dT$. Hence, pH_i from Equation 78 is 2.4. The value is different if the silver-silver chloride electrode and a neutral chloride buffer is employed and depends on the molarities of the buffer (and chloride) constituents as shown below for two phosphate buffers:

$[Na_2HPO_4]$	$[KH_2PO_4]$ = [NaCl]	$dE°/dT$ (mV K^{-1})
0.04	0.026	−1.6
0.022	0.035	−1.5

The value given is for the whole cell where the reference electrode is saturated calomel. Different values are also obtained if the 3.5 or 3.8 mol $l.^{-1}$ calomel reference electrodes are employed.

Case (b) where the reference electrode is at constant temperature can be treated in a precisely similar way, involving (different) pH_i-values, by consideration of the temperature coefficients of the cells (74) and (73) combined with that of cell (83)

$$Hg|Hg_2Cl_2|KCl_{(s)}|KCl_{(s)}|Hg_2Cl_2|Hg \qquad (83)$$

(variable T) (fixed T)

This is a thermo-cell with the electrode at the higher temperature being positive. The temperature variation of the e.m.f. can also be expressed approximately by an equation linear in T. The temperature coefficient of cell (83) as written, with the variable temperature taken to be higher than the (arbitrary) fixed temperature, is −0.20 mV K^{-1}, which has to be added to −0.48 mV K^{-1} of the previous example. Hence, pH_i = 3.4 from Equation 78. Equations 81 and 82 are valid for case (b) also, but the equivalent of Equation 80 is

$$pH_X(T_X) - pH_s(T_s) = \frac{E_{X(T_X)} - (E_o' + E_J)_{T_s} - (E_{int})_{T_X}}{k'T_X} - \frac{E_{s(T_s)} - (E^{o'} + E_J)_{T_s} - (E_{int})_{T_S}}{k'T_S} \qquad (84)$$

which shows that the pH_i-value for case (b) is independent of the type of external reference electrode.

The usefulness of isopotential control can best be demonstrated by the error incurred in ignoring it. For the electrode system of the previously used example (pH_i = 2.4) and a 5° temperature difference the error by Equation 82 is 0.04. But for a neutral filled electrode (pH_i = 7.2) the error would be 0.12. Clearly sizable errors are incurred if greater temperature differences are involved.

The isopotential zero shift corrections will be in error if the pH_i-value used is approximate because the temperature range to which it is appropriate is exceeded. The concept is inherently an approximate one but is quite adequate for 20° differences in the range 0 to 50°, as can be seen from plots of E_X against temperature. Above 50° up to 95°, which is the limit of most available measurements, the plots become more curved. The error arising from doubts about which of two pH_i-values, each appropriate to 20° temperature ranges, to employ for a wider range is given from Equation 82 as

$$\Delta pH_X = \frac{T_X - T_s}{T_X} \Delta pH_i \qquad (85)$$

ΔpH_i is unlikely to exceed 0.4, so for a 50° difference ΔpH_X is not greater than 0.06.

For cell (83) a temperature coefficient as high as −0.25 mV K^{-1} has been reported so pH_i for case (b) could be 3.6 instead of 3.4 given earlier. In general, the accuracy of pH_i is ±0.1. Clearly these possible errors do not detract from the usefulness of the concept particularly for industrial measurements.

Similar considerations apply to pX measurements and have been treated by Negus and Light.[183] The following equations need modification; Equation 76 becomes

$$E_X = (E^{o'} + E_J + E_{int}) \pm \frac{k'}{n} pX_X \qquad (86)$$

where the plus sign is taken if X is a cation and the minus sign if it is an anion; *n* is the number of electrons transferred in the Nernst equation. Thus, Equation 78 becomes

$$pX_i = \pm \frac{n}{k'} \frac{dE^o}{dT} \qquad (87)$$

where the plus sign is taken if X is an anion and the minus sign if it is a cation.

Table 10 gives some illustrative isopotential values for the most important electrodes calculated from the paper of Negus and Light.[183] Attention is drawn to the notes appended to Table 10.

An application[183] of the isopotential concept to the fluoride electrode is illustrated in Figure 19. One of its most important uses is the monitoring

TABLE 10

Illustrative Isopotential Values (pX_i) for Some Ion-selective Electrodes Used with the Reference Electrode System 1 *M* KCl|AgCl|Ag

Electrode	Temperature coefficients (mV K^{-1})		Isopotential points, pX_i	
	Isothermal (a)	Nonisothermal (b)	(*a*)	(*b*)
Fluoride	+0.85	+0.61	4.29	3.08
Iodide	−0.35	−0.59	−1.76	−2.98
Sulfide	+0.46	+0.22	4.64	2.22
Cyanide	−0.25	−0.49	−1.26	2.47
Hydrogen	−1.25	−1.48	6.31	7.47
Sodium	−0.63	−0.87	3.18	4.39
Copper (II)	−0.85	−1.09	8.58	11.01
Water hardness	−0.28	−0.52	2.82	5.25

Notes

1. The temperature coefficients (dE°/dT) given here are for the whole cell with 1 *M* KCl |AgCl| Ag reference electrode. There are differences in sign between the values presented here and those of Negus and Light because these authors use different definitions and, in particular, adopt the unacceptable violation of the IUPAC Stockholm convention of calling *n*, number of electrons transferred, in the Nernst equation, a *valence factor with* sign.

2. To obtain values appropriate to the saturated calomel reference electrode −0.03 should be added to (a) temperature coefficient values. (b) values are independent of the external reference electrode.

3. The values quoted may depend on the inner reference system of the electrode, which was not specified in the original article, except for the fluoride electrode where the value refers to an adjusted filling solution as discussed in the text and not to the Orion 94–09 electrode. According to Negus and Light, the values for iodide, sulfide, and cyanide are independent of filling solution. A value for the hydrogen responsive glass electrode has been included for comparative purposes; it obviously has a phosphate buffer filling.

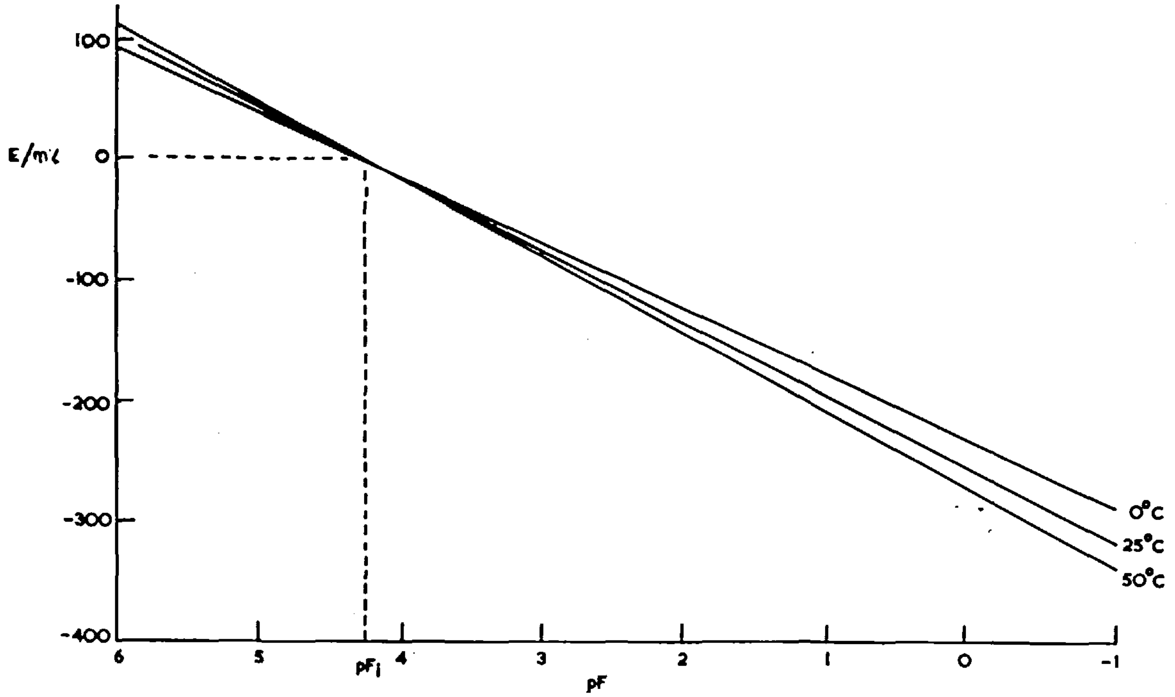


FIGURE 19. E.m.f. variation with temperature of a symmetrical lanthanum fluoride electrode cell[183] showing the isopotential point pF_i.

and control of fluoride in drinking water, which is often maintained at a mandatory level of 1 mg/l. By adjusting the inner filling solution of the Orion electrode to this level in 1 *M* KCl, and using as external reference electrode the 1 *M* KCl |AgCl| Ag system and the usual internal reference system Ag |AgCl, the whole cell is symmetrical with a zero e.m.f. at its isopotential point. The system is, therefore, independent of fluctuations of sample temperature and, moreover, the output meter can be simply calibrated in terms of positive or negative variations from the mandatory level which corresponds to zero mV output.

A detailed treatment of the design of symmetrical pH cells and choice of inner filling solutions for hydrogen glass electrodes has been given by Bates.[184] The symmetrical cell concept clearly is invalid for electrodes with solid-state connections, but it is doubtful if these electrodes are very reliable where temperature changes are involved.

XI. INSTRUMENTATION

Nonglass ion-selective electrodes usually have a lower electrical resistance than glass forms, often less than 50 MΩ rather than about ten times this, as is typical of hydrogen-responsive glass electrodes. Some digital voltmeters (DVM) have sufficiently high input impedances (of the order of 5,000 MΩ) for these to be used for measurements on cells involving ion-selective electrodes. Otherwise, a research quality pH meter reading to ±0.1 mV is necessary. The development of the new range of ion-selective electrodes has resulted in changes in pH-meter design, and research-quality models are now often described as ion-activity meters. Often these have a calibrated slope-factor control to allow for sub-Nernstian response and the meter is calibrated by the two-point method using pX standards (Section IX). In providing this facility, instrumentation engineers are ahead of research on pX standards, and it remains to be seen whether these receive widespread acceptance (Section IX.3).

The use of ion-selective electrodes as their own reference electrodes was mentioned in Section VII. Modern advances in integrated circuit D.C. amplifiers have made impedance matching to cells containing two high-impedance electrodes no problem;[185] this facility is available on some ion-activity meters where the reference electrode input can be of several megohms input impedance. Careful electrical screening and attention to grounding is still necessary.

A new modular titration apparatus designed specifically for use with ion-selective electrodes is shown in Figure 20. Slope factor control from ±10 mV/pX to ±69 mV/pX by thumb-wheel switches is provided. Output to a pulse driven recorder enables display of titration curves to preset pX end point with adjustable time delay in normal or differential forms. Use of two automatic burettes allows two-way pX-stat work to be carried out. The versatility of approach possible with this instrument makes its design at least comparable with current developments on the ion-selective electrode side.

XII. CONCLUSIONS

There is no doubt that the developments of the mid 1960's aroused considerably increased interest in potentiometric sensing devices and have stimulated much research effort in many parts of the world. Whether this amounts to the "rebirth of analytical potentiometry" or similar headlined claims is debatable. The commercial availability of electrodes selective to such important ions as fluoride, calcium, and nitrate certainly has been of great technological significance in a variety of fields relying on analytical techniques ranging from clinical through agricultural to industrial.

The stimulus given to an analytical technique by commercial developments is always large. The first commercial developments in ion-selective electrodes arose in Hungary about 1964 with the heterogeneous silicone-rubber-based electrodes developed by Pungor and his associates. Although these have now faded from the scene, their influence on developments and particularly stimulation of interest in the U.S. must not be underestimated. The principal manufacturers have been mentioned earlier in this review. These and some smaller firms market items from the range of proven systems. Patent rights appear not to be restrictive in this area. Perhaps because of the high cost of electrodes in comparison with glass pH-responsive electrodes, several groups of workers have attempted to construct their own for analytical purposes. Workers in the clinical and biological fields have never been inhibited from constructing their own, usually microversions, the applications of which are often too restrictive to be commercially viable. Most of the recent innovations have come from university laboratories some of which have liaison and formal contacts with commercial firms, links which give the academic researcher an increased sense of purpose.

In order to achieve the maximum advantage

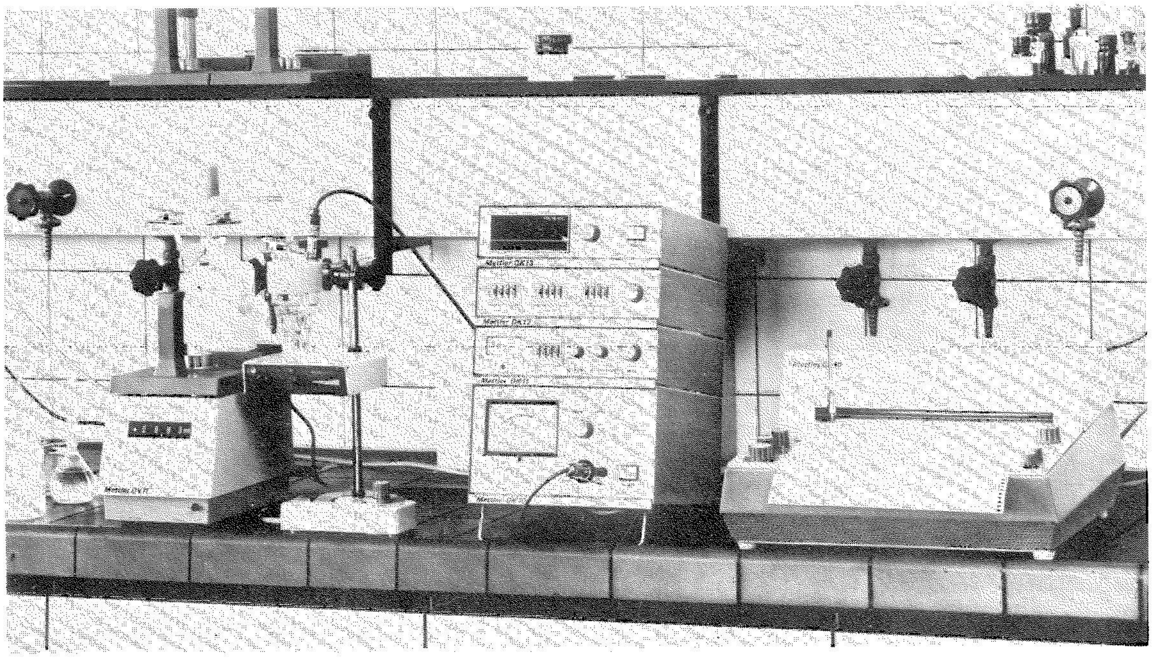


FIGURE 20. Mettler automatic titration apparatus.

from the new range of ion-selective electrodes, their limitations must be fully appreciated. The analyst's dream of inserting the required probe and pressing the appropriate button is still as far removed as the alchemist's of transmitting base metal into gold – feasible but only under very limited circumstances. Problems of inadequate selectivity can only be overcome by chemical manipulations before use of electrodes. Even so, limitations in accuracy inherent in the direct potentiometric method remain. Its principal usefulness is in continuous monitoring and control processes where the output electrical signal is a great advantage. For analytical laboratory usage, potentiometric titration, followed to a lesser extent by known increment techniques, can furnish the requisite accuracy but only after some separative chemistry.

The applications to the improvement of existing analytical techniques are many, but each has to be discussed on its own merit and it is difficult to generalize. Outstanding, however, are the application of the fluoride electrode to low level fluoride monitoring in potable water supplies, the nitrate electrode for river water analysis and measurement of fertilizer runoff, and the calcium and potassium electrodes in clinical applications. Sales of the commercial versions of these electrodes far exceed those of all the rest combined.

During the last 3 years, a process of consolidation has taken place. No radically new electrode systems have been devised. Improvements and modifications to the fabrication of electrodes and active materials have been made and the reasons are better understood, but more attention has been given to applications and devising analytical procedures. A IUPAC Group has been formed to make recommendations on the definition of terms used in the description of the properties of electrodes; the present state is one of considerable confusion especially regarding selectivity. The future requires the cooperation of chemists from different disciplines with their ingenuity harnessed toward increasing the understanding of conduction processes in the solid and liquid states, and of the selectivity shown by certain organic molecules, which could in turn be a key to understanding the importance of certain ions physiologically.

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