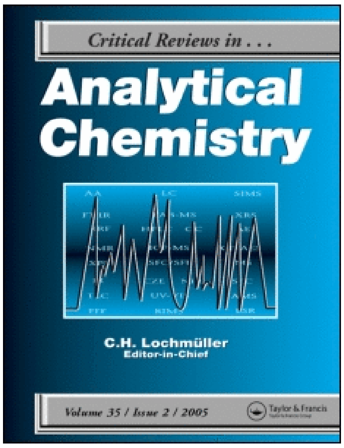

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ELECTROANALYTICAL CHEMISTRY OF MEMBRANES

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I. PERSPECTIVE ON THE ROLES OF MEMBRANE ELECTROCHEMISTRY AND ELECTROANALYTICAL CHEMISTRY

The thrust of electrochemistry in the past 25 years has been the study of electrode processes at blocked and unblocked electrodes, primarily metal/electrolyte interfaces. The vast literature which has been contributed by both physical and analytical chemists comprises a topic now known as electrodics to distinguish it from the more classical topics – electrochemical thermodynamics (the study of equilibrium and transport properties of electrochemical cells) and ionics (the study of equilibrium and transport properties of electrolyte solutions) – which occupied a significant number of chemists during the first 50 years of this century. Analytical electrochemists have found their interests expanding as they turn from analytical methodology to fundamental and applied studies within electrodics. Many practical contributions have been made in new and improved battery systems, fuel cells, electrochemical synthesis, electrolyte and redox properties in nonaqueous solvents, and electrochemical instrumentation. Electroanalytical chemists have also contributed to fundamental topics such as: double layer structure; capacitance measurements and charging kinetics; thorough characterization of inert and electroactive materials on electrodes; roles of adsorbed intermediates; kinetics of fast homogeneous reactions coupled into electron and ion transfers at electrodes; electrocatalysis; elucidation of electrochemical oxidation and reduction pathways; electrogeneration of radicals in and out of esr resonant cavities; radical annihilation reactions; electrochemiluminescence; development of ultrasensitive spectroelectrochemical techniques for detection of electrochemical intermediates; and theoretical and experimental aspects of energy transfers in connection with the rates of electron and ion transfers at electrodes.

Although these topics and application are by no means fully explored, a number of key volumes summarize the progress in considerable depth.[1-9] These are mentioned at this point to advise readers familiar with membrane technology that much fundamental and technological progress has occurred in electrochemistry in recent years – an era beginning roughly with the 1947 Discussion of the Faraday Society[10] and continuing with the "mainstream" monographs of Delahay,[11,12] Vetter,[13] Levich,[14] and Bockris and Reddy.[15] Two new books emphasizing techniques are recommended.[16,17] A major two volume set brings together solid and liquid transport theory.[18] For the readers not familiar with membrane electrochemistry, the following review will stress those concepts which are already familiar although they are applied to more complicated systems. The complication is primarily related to existing methodological limitations. Membrane electrochemistry usually involves the simultaneous study of two active interfaces since no way has yet been devised for the unequivocal electrical measurement of processes at a single membrane/solution interface.

What, then, has been the impact of modern electrochemistry or electroanalytical chemistry on membrane science? Secondly, and possibly more important in the context of this review, is the question: What is the role of membrane technology in analytical science? Electrochemistry is pertinent in membrane studies at three levels. One is the development of techniques with application to experimental phenomenology including current-voltage-time-concentration behavior. A second is the mathematical modeling implied by experiment and tested against experiment. The third level is experimental verification of models in terms of the molecular processes and properties and includes determination of theoretical parameters by electrical methods and by complementary nonelectrochemical methods: physical optical, esr, nmr, Raman, fluorescence, T-jump techniques, etc. From transient and steady state measurement of current or membrane potential as a function of chemical composition, chemical treatment, and temperature, the roles of kinetic and equilibrium parameters can be deduced or inferred. A possible approach to modeling begins with the assumption of the membrane as a linear system to which laws of network theory may be applied. Another begins by solution of basic electrodiffusion laws of transport with equilibrium or kinetic boundary conditions in order to deduce forms for system functions which satisfy the data. Other possibilities are discussed later. Finally, necessary parameters are measured independently to check the values implied by models.

The most important contribution of electrochemists to membrane electrochemistry is the transfer of perspective and wisdom to the new area. There are many *sine qua nons* in electrochemistry which have occurred through extensive studies of electrolytes and electrolyte/metal interfaces. Electrochemists have learned to subdivide systems into interfacial and bulk processes and to expect effects of dielectric constant (complex formation, ion pairing), effects of short-range forces (adsorption of charged and uncharged species with, possibly, changes in rates of interfacial processes), effects of high fields near surfaces (Wien Effect and dielectric saturation, for example), and the important effect of local potentials on rates of interfacial processes (irreversible charge transfers, psi effects, etc). Inasmuch as the presence of space charge at interfaces is a natural consequence of the continuity of potential from one phase to another, the presence of space charge and space charge mediated effects in membrane systems is anticipated. These are a few examples of phenomena at electrified interfaces which not only should be present in membrane systems but may also be crucial in providing a link between properties of membrane interfaces and the much better known and documented properties of metallic interfaces.

As a rule, electrochemists seek to generalize the uncovered principles of classical and modern electrochemistry. It is therefore understandable that less well-known systems involving interfaces of the types electrolyte/salt, electrolyte/semiconductor, electrolyte/electrolyte in a second immiscible solvent, and electrolyte/membrane (of various types) should now become targets of further research. In the past decade, many electrochemists have already turned from systems involving metals to other two-phase systems where basic electrostatic and thermodynamic principles can be applied in new ways with the goal of making the new and more complex systems interpretable and predictable. The new interest is not purely academic because the transport properties of solid (and some liquid) membranes are important in new batteries and fuel cells.

The impact of membrane technology on analytical chemistry is twofold: the development of membrane systems responding in predictable ways to ionic solution activities has already provided a new dimension in electroanalytical chemistry. This is the technology of ion selective electrodes. However, the second and possibly the major aspect of analytical chemistry affected by membrane technology is analytical separation science. In a particularly lucid table by Lakshminarayanaiah,[19] all presently known membrane phenomena are placed into categories according to the driving forces acting within or across membranes: gradients of chemical potential, electrochemical potentials, pressure, temperature, and combinations of these. This table, modified slightly, appears here as Table 1. I have starred those listings which now have analytical significance. Clearly, there are many items which may be considered as techniques of analytical separations. Among these are techniques whose development and application belong mainly in the domains of clinical and medicinal chemistry, physiology, pathology, chemical engineering, industrial chemistry, and the various ecological and public health sciences. They are nonetheless capable of practical application and extension in the analytical laboratory.

The literature in book form describing membrane technology and applications is far too extensive to mention. Instead, I have tried to restrict this review and its references to those topics which are in the realm of membrane electrochemistry. Admittedly, there must be considerable reference to other aspects of membrane technology since the preparation and characterization of membranes is common to all applications. In the case of ion exchange membranes, the bulk of the literature on these materials concerns their use for separations. Their electrochemical properties, although present and functioning, are only incidental to applications in separation science. The principal volumes containing significant sections on, or totally devoted to membrane electrochemistry are by Helfferich,[20] Cole,[21] Lakshminarayanaiah,[19,22,23] Hope,[24] Arndt and Roper,[25] Plonsey,[26] and Kotyk and Janacek.[27] Continuing series are edited by Bittar,[28] Eisenman,[29] and Danielli, Rosenberg, and Cadenhead.[30] Applications of membrane electrochemistry to yield activity sensing electrodes are amply described in books edited by Eisenman[31] and Durst.[32] However, this field has produced such a variety of new measuring devices and has opened so many analytical possibilities in terms of new analyses and new detection systems that it is very likely that additional volumes will soon appear. Numerous recent volumes are concerned, in part, with membrane electrochemistry.[33-41]

A. Some Definitions in Membrane Electrochemistry

A *passive membrane* is a region of space which separates two phases in such a way that material

TABLE 1*

Various Membrane Phenomena

Driving force	Phenomena	Membrane	Primary flow	Comments
Chemical or electrochemical potential, $\Delta\mu$ or $\Delta\bar{\mu}$	Mixing or diffusion	Ultrafilter or solution diffusion	Chemical components	Establishment of chemical equilibrium
	Membrane potential	Ion exchange	Ionic solute	Source of e.m.f.; negligible solvent flow*
	Osmosis	Ultrafilter or solution diffusion	Solvent	Solvent enters concentrated solution (osmometry)*
	Dialysis	Ultrafilter	Solute	Solute leaves concentrated solution (hemodialysis)*
	Diasolysis	Ultrafilter	More mobile component	Selective transport of more mobile species
	Osmionosis	Ion exchange	Ionic solute	Three streams of different concentration generate driving force. Similar to electrodialysis without application of external electric field
	Dufour effect	Solution diffusion	Thermal	Gives rise to ΔT
Electric field, ΔE	Electric conduction	Ion exchange	Current	Estimation of membrane resistance
	Transport number of species	Ion exchange	Fraction of current carried by species	Estimation of membrane permselectivity
	Electroosmosis	Ion exchange	Solvent	Solvent transfer
	Electrodialysis	Ion exchange	Ionic solute and/or solvent transfer	Solute removal
	Transport depletion	Usually cation exchange alternates with ultrafilter in stacks	Ionic solute	Simplified high current density electrodialysis*
	Electrophoresis	Solution or gel	Ionic solute	Separation of large molecules*
Pressure, ΔP	Filtration	Ultrafilter (microporous)	Solvent	Particulate matter retained by sieving*
	Hydraulic or mechanical permeability	Ultrafilter or solution diffusion	Solvent	Relates to space available for laminar and/or diffusional flow
	Pressure permeation	Solution diffusion	Selective transport of most mobile component	Separation of liquids and/or gases
	Ultrafiltration or reverse osmosis	Ultrafilter	Solvent	Solvent leaves and solution is concentrated*

TABLE 1* (continued)

Various Membrane Phenomena

Driving force	Phenomena	Membrane	Primary flow	Comments
Pressure, ΔP, continued	Streaming potential	Ion exchange	Solvent	Generation of e.m.f.
	Streaming current	Ion exchange	Ionic solute	Current very small: studies rare
	Piezodialysis	Mosaic ion exchange	Ionic solute	Product of reduced salinity
Vacuum	Pervaporation	Solution diffusion	Selective transport of most mobile component	Separation of liquids and/or gases
Temperature ΔT	Heat conduction	Ion exchange, ultrafilter, or solution diffusion	Heat	Thermal conductance*
	Thermoosmosis	Ion exchange, ultrafilter, or solution diffusion	Solvent	Solvent may move from hot to cold side or vice versa
	Thermo-e.m.f.	Ion exchange, ultrafilter, or solution diffusion	Ionic solute	Source of e.m.f.; studies rare
	Soret effect	Ion exchange, ultrafilter, or solution diffusion	Solute	Gives rise to $\Delta\mu$; difficult to measure
Electric field ΔE + pressure ΔP	Forced-flow electrophoresis	Ion exchange or ultrafilter	Ionic solute and solvent	Purification of blood, sewage; still in experimental stage*
Electric field ΔE + temperature ΔT	Electrodecantation	Ion exchange (cation) and ultrafilter	Ionic solute and solvent	ΔT supplied by electrical heating and/or cooling; ionic matter concentrates downward and solvent concentrates upward

*See *Encyclopaedia Polym. Sci. Technol.*, 8, 622, 1968.

(including electronic) transport between the outer phases is in some way modified or inhibited in comparison to transport between the same phases in direct contact (without the membrane). This definition may seem excessively broad, but it is based on the generality of processes which occur at a variety of membrane/outer phase interfaces and within membranes themselves. Clearly, basic electrostatic laws apply in all cases. It may not be so obvious that thermodynamic (and quasi-thermodynamic, steady state) laws of distribution of charged species and neutral species, including salts, also apply and that general laws of transport apply regardless of membrane composition. Rates of interfacial processes may also be governed by laws with similar form, regardless of membrane composition, but this point has not been verified (see Section IIIB).

Membranes may be solid, liquid, or gas,* and the outer phases are usually liquid or solid.

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*It may be surprising to some readers that gas films between electrolyte solutions qualify as membranes. Yet the classical measurement of surface potentials using the Kenrick method (Kenrick, F. B., *Z. Phys. Chem.*, 19, 625 (1896)) as modified by Randles (Randles, J. E. B., *Trans. Faraday. Soc.*, 52, 1573 (1956)) is an example of a membrane potential measurement.

Although it is frequently the case that membranes are thin in one dimension relative to the other two dimensions, this property is only functional or operational. In order to achieve a measurable chemical change or electrochemical effect and to make chemical or electrochemical measurements on a membrane system in a reasonable time, some transport related property must be susceptible to temporal change. Thus, a change in potential, flux, or concentration (among many varying and measurable quantities) requires sample thicknesses d such that $d^2/2D$ is comparable with the observation time (D is a mean diffusion coefficient). Although irregularly shaped membranes are conceivable, most theories and experiments are restricted to systems with one-dimensional or spherical symmetry such that transport occurs in one dimension, the x direction in parallel-face, planar membranes or along a radius in membranes with spherical shape.

Membranes are considered to be *porous* or *nonporous* depending upon the extent of solvent penetration.[42] At the nonporous extreme are membranes which are nonionic and contain negligible transportable species at equilibrium. Ceramics, quartz, anthracene crystals, and teflon films between metal electrodes or electrolyte bathing solutions are solid membrane examples. Organic liquid films such as hydrocarbons and fluorocarbons in contact with aqueous electrolytes are liquid membrane examples. At the other extreme are porous membranes, which can be solvated and will contain components from the outer phases. Among these are nonionic films such as cellophane, inorganic gels, and loosely compressed powders in contact with aqueous solutions. These materials absorb solvent from the surrounding media and may also extract other neutral molecules and ionic salts. More widely studied are those membranes of polyelectrolytes ("solid" ion exchangers), aqueous-immiscible organic liquid electrolytes ("liquid" ion exchangers),[19,20,22,23] and solid, ion conducting electrolytes, including silver halides, rare earth fluorides, and alkali silicate and alumino-silicate glasses.[31,32,43-45] All of these materials contain ionic or ionizable groups within the membranes which are capable of transport under diffusive or electric field forces. In addition, these materials possess the properties of porosity. Polyelectrolytes tend to swell rapidly by osmotic pressure driven uptake of solvent. Liquid ion exchangers are surprisingly slow to take up water, while the inorganic salts have no tendency to hydrate. Glass membranes are complicated by simultaneous hydrolysis of the polyelectrolyte during uptake of water. The most recent papers in this continuing area of research are by Wikby and Karlberg[46,47] and Sandifer and Buck.[48]

Depending on the dielectric constant and solvent penetration, sites are potentially, partially, or even completely ionized. A characteristic of electrolyte membranes is the presence of charged *sites.*[20] If ionic groups are fixed in a membrane as -SO_3^- and -COO^- attached to cation exchange resins, the membrane is considered to possess fixed sites, even if protons or metal ions are covalently bonded to the sites. In glasses, the fixed sites are -SiO^- and -AlO^- groups, while in anion exchange resin membranes these are $\text{-N}^+\text{-}$. Fixed sites do not contribute to the passage of either transient or steady state ionic current through the membrane. On the other hand, liquid ion exchangers which are water immiscible, such as diesters of phosphoric acid, can be viewed as mobile site membranes. The acid is trapped in the organic phase, and while protons (or other cations) can transfer into and out of the membrane, the phosphonate cannot. The uninegative groups are considered to be mobile sites which contribute to transient but not steady state current. When dissolved in a hydrophobic solvent, solid and liquid quaternary amines such as Aliquat 336 (methyl tricapryl ammonium salt) are examples of positive mobile sites. Membranes without ionizable groups contain no charge sites. It is important to know that cellulose triacetate, which is initially site free, soon develops negative sites by hydrolysis and oxidation on exposure to aqueous solutions.

The question of membrane *charge* deserves some comment. *Membrane systems* consisting of the membrane and outer phases must be overall electrically neutral when one includes adjacent regions of electrolyte bathing solutions (or metallic contacts) on either side.[49] The total region contains nonelectroneutral (space charge) sections as double layers at the interfaces and within the membrane. These space charge regions protrude outward into the outer phases and inward into the membrane. The actual width of the space charge regions is variable, but for electrolytes, the mean thickness (Debye thickness) depends inversely on the square root of electrolyte concentration. Consequently, a positive probe brought from infinity will experience space charge and dipolar fields as it is pushed from one outer phase through the membrane to the other outer phase. The existence of space charge and potential curvature are synonymous general features of membrane systems. The electrostatic character of membranes can often be legitimately ignored for the well-known reason that measurable membrane potentials are independent of space charge for the usual thick membranes, i.e., those which contain some region of electroneutrality in their bulk. However, it must be recognized that a membrane will generally be electrostatically *charged* unless the outer phases fortuitously create flat band potentials at both interfaces and the internal region is also electroneutral. Any charge in the membrane tends to reside at the interfaces. This point will be discussed in a later section.

The frequent use of "charged" and "uncharged" in the membrane literature is usually unsound electrostatically, but does provide an intuitive chemical description. For example, "charged" membranes usually refer to electrolyte membranes such as solid and liquid ion exchangers where the fixed and mobile sites are the "charges." Actually, these membranes are quasi-electroneutral in their bulk when the thickness is large compared with the Debye thicknesses at each interface. *Quasi-electroneutrality* means that in any volume element large compared with the distance between ions, the sum of ionic charges $\sum_i z_i \bar{C}_i = 0$. In the literature, "uncharged" membranes are those, like cellophane, with no fixed charges. This frequently used literature definition provides no place for lipid bilayer membranes, which are electrostatically neutral only in the absence of charge carriers and in the absence of bathing solutions whose salts possess preferential solubility of anion over cation or vice versa, but are usually electrostatically charged by an excess of ions of one sign in normal operation. Thick hydrocarbon membranes and membranes of diphenyl ether (or derivatives), phthalate, and sebacate esters are generally neutral in the presence of most bathing electrolytes, but may be charged electrostatically, depending on thickness, in the presence of neutral-carrier species which preferentially solubilize ions of one sign. The use of "charged" and "uncharged" to describe electrolyte or nonelectrolyte membranes should be discouraged unless the precise electrostatic connotation is involved.

The notion of *homogeneous* vs. *heterogeneous* membranes proves to be an important distinction from the point of view of mass transport. In the dilute solution limit, the friction coefficients for mass transport by diffusion or migration are interconvertible by Onsager reciprocal relations, and both can be related to jump distances and frequencies according to random walk models. As long as there are no preferred regions of low friction in the membrane, it is isotropic on a molecular level and is considered to be homogeneous. Uniformity of mesh on a molecular scale is another view of homogeneity. Channel free solid and liquid membranes are usually homogeneous, and two-phase membranes such as solid crystallites imbedded in a nonionic resin are clearly heterogeneous. The distinction, however, is not always essential. For example, heterogeneous membranes containing inert solid and large, random areas of immobilized solvent may be simply diluted versions of the membrane without the inert solid. If transport occurs mainly through solvent regions, potentiometric responses may not be altered by the heterogeneities. The current-voltage and conductance characteristics would be modified. Ion exchange resin membranes containing different amounts of water as a function of cross-linking may be considered heterogeneous; yet, the transport properties described in terms of empirical transport parameters obey essentially homogeneous laws, and so the distinction is not important.

Characterization of membranes in terms of their permeabilities to solvents, solutes, and individual ions is fundamentally important from the very definition of "membrane." Quantitative expression of permeability follows later. Two general descriptions apply, however. *Semipermeability* is a measure of preferential solvent transport by a membrane. The reflection coefficient (or rejection coefficient) for solutes, σ_s is defined according to:

$$1 - \sigma_s = t_s/x_s \tag{1}$$

where t_s is the transport number (volume fraction) of solute in the liquid passing through the membrane in a permeation experiment where x_s is the volume fraction of solute in the bathing solution on one side ($x_s = 0$ on the other). When $\sigma_s = 1$, only solvent permeates the membrane (solute is reflected), and the membrane is considered ideally semipermeable. When the membrane is equally permeable to solute and solvent, $\sigma_s = 0$. *Permselectivity* is a measure of the current carrying ability of ions in a membrane. Ideal cation permselectivity occurs when the cation transference number $t_c = 1$, i.e, all current is carried through the membrane by cations and $t_a = 0$. The converse definition applies to ideal anion permselectivity. This property is indispensable for the generation of membrane potentials at zero or finite current, and occurs in quasi-thermodynamic relations between potential and external ion activities.

Electrolyte membranes (liquid and solid ion exchangers) containing trapped, fixed, or mobile sites of one sign define a *counter-ion* and a *co-ion*. The former is an ion of opposite sign to the site. The co-ion is an ion in the bathing solution with the same sign as the site. At high site density, counter-ion concentration in the membrane is nearly equal to but slightly greater than the site concentration. The slight excess is compensated by co-ions which encroach from electrolyte solutions. Co-ions are excluded more effectively with increasing site concentrations. This effect, *Donnan Exclusion*, is a manifestation of the equality of electrochemical potential for each ion in equilibrium across an interface.

B. Comparison of Electroanalytical and Membrane Electrochemical Experiments

While contemporary electrodics focuses attention on single interfaces and processes occurring in their vicinities, membrane electrochemistry considers systems with at least two interfaces with processes occurring in the region between, as well as outside of the interfaces. The reasons are twofold: comparable magnitudes of parameters govern equilibria and kinetic properties at each interface, and the three-electrode techniques requiring a reversible electrode implanted *within* a membrane have, so far, not been found applicable. Thus, membrane electrochemistry basically involves two-electrode studies with all of the well-known implied limitations. Experimental techniques of the past 20 years using three electrodes, which allowed isolation and study of single metal/electrolyte interfaces by control of local relative potentials or currents, generally cannot be used.

Since this review includes membranes of ion conducting solids, mixed electronic ionic conducting solids, and thin electrolyte solutions, it must be allowed that three- and four-electrode experiments are frequently used. Four-electrode experiments, where two outer electrodes pass current and two inner probe electrodes sense potential drops between them, are important means for removing interfacial potential drops from bulk resistance measurements. Applicability requires that the probe pair be either in ionic or electronic equilibrium with the substrate. Reversible electrodes used as probes at zero current (or nearly zero current) meet the requirement.

Consider the similarity between an ideally cation permselective electrolyte membrane cell (an oil containing a liquid cation exchanger) between aqueous electrolyte bathing solutions (Figure 1) and the corresponding *thin-layer electrochemical cell* (dilute aqueous silver nitrate between silver electrodes), for example. Both systems possess interfaces across which ions of one sign, the cations, are permeable, while anions are constrained to remain in the membrane. Both systems can develop sloping (tilted) concentration profiles (concentration polarization) under application of current and voltage. Both systems may exhibit slow rates of ion transfer at the interfaces (electrochemical irreversibility and activation overpotential if the ion transfer rate is interfacial potential dependent). The membrane cell system possesses additional degrees of freedom in the sense that the exterior electrolyte solutions, as

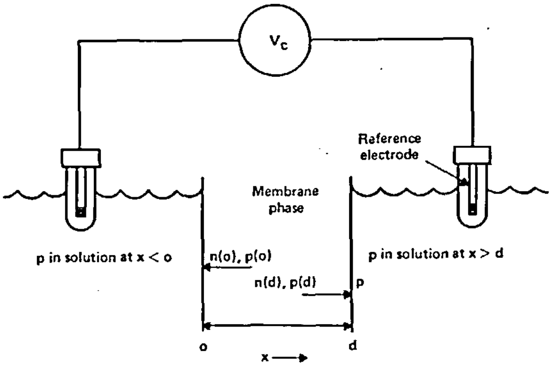

FIGURE 1. Schematic sketch of a liquid ion exchange membrane separating two aqueous solutions. The membrane of thickness d is hydrophobic and contains water-insoluble (trapped) anions n. Cations p are free to transport across and through the membrane. Low resistance reference probes reversible to anions in a junctionless configuration, or reversible to ions of either sign when used with a salt bridge, are used to measure or apply the cell potential $V_c = \Delta\varphi_m$. (From Buck, R. P., *J. Electroanal. Chem.*, 46, 1 (1973). With permission.)

well as the membrane interior, may become concentration polarized. When the mobilities of ions in a membrane exceed those in the bathing solutions or when the latter solutions are very dilute, *film diffusion* (ordinary Nernst boundary layer mass transport control, or external concentration polarization) limitations can occur. This condition arises when u_iC_i (external) < $\bar{u}_i\bar{C}_i$ (internal) for the permeable ions. A further mode of current transport in membranes is possible when co-ions (anions in the example above) from the electrolyte are not excluded from the membrane (low anion exchanger content or high electrolyte solubility in the membrane). The corresponding, but unlikely electrochemical process is oxidation of an anion concurrently with a metal to give internal currents carried by ions of both signs. A further parallel situation corresponds to the membrane bi-ionic potential which occurs when the solution on either side of the membrane in Figure 1 contains different permeable cations. One has an analogous situation in Figure 2 when the internal electrolyte is a silver nitrate, cupric nitrate mixture, while the electrode materials are Ag on one side and Cu on the other, for example.

The kinds of electrochemical experiments at constant temperature and pressure which are applicable to membrane cells are the same as those which are suitable for thin-layer cells:[16,17]

1. Controlled, applied constant current excitation – measure cell or membrane potential vs. time (response). This method includes normal potentiometry.
2. Controlled applied constant voltage (excitation) – measure cell current vs. time (response). These experiments may be step pulses, in which voltage or current is stepped from one value to a new constant value. They may also be square pulses (or other arbitrary forms) or true impulses of minimal duration. In both, the applied signal jumps to a new value and then returns to the original value. The latter mode is a charging experiment which can include charge injections of controlled magnitudes.
3. Time dependent voltage or current signals (excitations) – measure the resulting response as a function of time. These methods include ramp voltages analogous to single sweep voltammetry, repetitious ramps (sawtooth and triangular wave excitations), and square wave and sine wave sequences in time.
4. Periodic signals applied on a dc bias. When a small amplitude (20-mV peak-to-peak) ac voltage is applied across a membrane cell biased to zero dc current, a classical impedance measurement is performed. Less commonly performed is the application of an ac signal to a membrane cell under a dc bias such that a steady current is flowing. Various combinations of perturbations such as charge injection can be combined and superimposed on dc polarized cells.

In common with conventional electrochemistry, membrane electrochemistry considers current, voltage, and time responses as functions of activities of electrolytes, nonelectrolytes, and solvents which can be varied on one or both sides of a membrane. Not only is systematic variation of concentrations important for deducing membrane responses and processes, but step changes in concentration can also be achieved by rapid mixing stop flow experiments. A step concen-

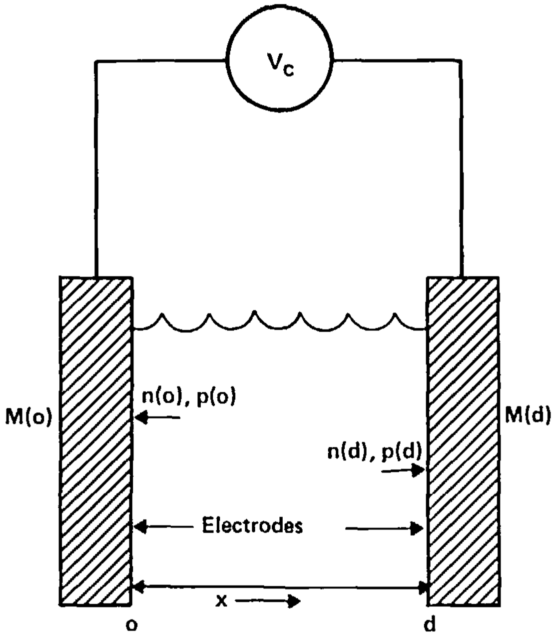

FIGURE 2. Twin parallel electrode cell with electrode spacing d. A single electrolyte contains cations p and anions n. Electrodes of metal M are reversible to cations p. Cell potentials $V_c = \Delta\varphi_m$, measured or applied, have signs determined by the inner potentials of the phases at x = 0 and x = d. (From Buck, R. P., *J. Electroanal. Chem.*, 46, 1 (1973). With permission.)

tration on one side of a membrane is equivalent to a step voltage across one interface. This experiment is the nearest equivalent to the potentiostatic step pulse method found useful in metal/electrolyte interfacial kinetic measurements.

The temperature and pressure dependences of response functions must also be determined. In contrast with thin-layer cell studies, variation of hydrostatic pressure across a membrane cell is an additional technique, in conjunction with current or flux measurements, for deducing the occurrence and prevalence of solvent transport through a membrane.

About 10 years ago, it became apparent that many details of electrochemical processes could not be interpreted or elucidated solely by electrical response measurements. This limitation became particularly acute in efforts to determine adsorbed species on electrode surfaces and intermediates in electrochemical reactions that cannot, by virtue of their short lifetimes or low concentrations, be isolated for chemical analysis. Over 100 years ago, a similar limitation on the separate identification of current carrying species in an electrolyte was recognized. Determination of transference numbers by chemical analysis of anode and cathode compartments was a solution to this problem. Similarly, radiotracer measurement of fluxes of individual species is a contemporary solution to the transference number problem in many phases, including membranes. Here, the use of tracers permits the analysis of accumulated species at much lower levels of concentration than allowed by conventional titrimetry. Atomic absorption and other spectroscopic methods are available for determining metallic species.

Spectrophotometric procedures[50,51] using absorption spectroscopy in the visible and ultraviolet regions permit identification of species in membranes. For example, picrate is a favorite "pilot" ion for monitoring the extent of cation extractions by carriers in low dielectric membranes. In the past 5 years, techniques for sensitive absorption measurements involving changes of 10^{-5} absorption units have been developed, and the instruments are now commercially available. This progress, in part, is due to the applications of signal averaging techniques with the aid of a computer. Signal processing to improve signal/noise amounts to amplification which permits the sensing and quantitative measurement of small numbers of molecules present in the vicinity of interfaces or in membranes. Other methods of great sensitivity[51] include ellipsometry, where a beam of polarized light is reflected from a surface. The variation in polarization direction (rotation) is a sensitive function of the optical parameters of materials at the reflecting surface. Totally attenuated internal reflectance measurements give enhanced signals for materials near surfaces.

At a higher level of sophistication, many of the popular, even faddish, tools of the chemical physicist have been considered or have been used to study membrane surface or bulk properties. As a rule, these techniques[50] – nmr line broadening, esr of spin labeled molecules, stimulated and resonance raman scattering, time resolved or normal fluorescence emission, and surface techniques such as Auger spectroscopy and ESCA – are sensitive to the local dynamic environment of probe molecules at membrane surfaces or in the bulk. Although interesting correlations with chemical and electrochemical properties may appear, the importance of physical measurements lies in their support of models of membranes and membrane transport suggested by electrochemical measurements. After all, in biological systems, the primary consideration for a useful, viable membrane is its delicate electrical and electrochemical balance. The pressing problem is the reduction of membrane systems of different compositions to a set of processes with parameters such as rate constants, equilibrium constants, and transport coefficients or with equivalent electrical circuit elements whose values are directly related to the parameters. Correlations of measured parameters in terms of local forces, descriptions in terms of central force models between atoms, pair distribution functions, and other statistical mechanical descriptions are ultimately important only in clarifying and unifying our accumulated knowledge of membranes.

Electrochemistry operates at a phenomenological level and relies strongly on the electrochemical equivalent of electrical network theory. Electrochemical systems are believed to have some characteristic functions associated with them, like an equation of state in thermodynamics, which describe their macroscopic behavior under various perturbing forces. In electronics, these transfer or system functions relate responses to excitations. The impedance is a typical example, although other transfer functions exist. Whereas electronic systems involve three variables, i.e., current, voltage, and time (charge and field are implicitly included), electrochemical systems involve current, voltage, *concentration*, and time for systems normally encountered at constant temperature and pressure. The electrochemist seeks to determine these functions, or at least some of them, by direct experiments in which one of the variables is controlled and the others are observed as described above. Implicit in the relationships are the characteristic parameters: rate constants, equilibrium constants, mobilities, and activity coefficients, to name the more important.

The singular problem in designing electrochemical experiments on membrane systems is the limitation imposed by the use of external perturbation: currents, concentration steps of external bathing solutions, coulostatic charges, and $\Delta\varphi$ (or ΔE) across the membrane. The responses are also measured externally. Even when the excitations are small so that linear response theory may be applied, the resulting system functions do not allow thorough diagnosis of the electrochemical condition of a membrane. One must assume a priori that the system can be, and generally will be, nonlinear, with the further assumption that additional information, such as species concentration profiles and voltage or field profiles, must be acquired before exact modeling can be done. This is a serious limitation in principle and requires that electrochemistry of membranes be supplemented with other techniques which allow a fuller knowledge of conditions, both chemical and electrochemical, which are occurring within the membrane region.

II. QUALITATIVE AND QUANTITATIVE ELECTROSTATIC FEATURES OF INTERFACES BETWEEN HOMOGENEOUS PHASES

A. Single Interface Systems

When two structureless fluids, such as immiscible liquids, containing dissolved electrolytes are contacted, the energy levels of extractable ions are most likely unequal in the two phases.[52] The following arguments which apply to electrolyte/metal interfaces are inferred to hold for other immiscible material phases capable of sustaining charge. Possible charge density, field, and potential profiles at zero current and constant temperature and pressure are shown in Figure 3. Phases I and II are electroneutral at large distances from the interface; for illustration, the dielectric constants differ $\epsilon_I < \epsilon_{II}$.

Quantitative descriptions of these profiles, at the simplest level of approximation, make the assumptions that charged species are points subject to central electrical (Coulomb's Law) force and that Poisson's equation and Gauss' Law are corollaries. Further, the charges are in thermal equilibrium and so obey a distribution function. The classical Boltzmann distribution follows from Poisson's equation and the Nernst-Planck equations of motion applied to blocked situations (neither ionic species can pass the interface). The latter equations of motion at nonzero current predict a perturbed Boltzmann distribution which reduces to the usual distribution when current is zero.[53] The distribution of charged species is considered "diffuse". Charge densities at zero current obey:

$$C_+(x) - C_-(x) = \rho(x) = \mp \frac{4RT\kappa^2\epsilon}{zF}\left[\frac{\cosh(\kappa x)}{\cosh(2\kappa x) - 1}\right]$$

where x is the distance perpendicular to the interface and is taken to be positive in either direction from an interface and κ, the reciprocal Debye thickness (the place where field, voltage, or charge decrease to 1/e of their surface values in the linearized version), is given by:

$$\kappa = \left(\frac{2z^2 F^2 \Sigma C_b}{\epsilon RT}\right)^{1/2} \tag{3}$$

In Equation 2, x cannot be zero and must be greater than the radius of an ion. This equation applies to single, symmetric electrolytes of charge z and concentration C_b in the bulk of either phase. The resulting fields and potential profiles are

$$E(x) = \pm \frac{2RT\kappa}{zF} \operatorname{cosech}(\kappa x); \tag{4}$$

and

$$\varphi(x) - \varphi_b = \mp \frac{2RT}{zF} \ln[\coth(\kappa x/2)] \tag{5}$$

where φ_b is the flat potential in either electroneutral phase. Near the potential of zero charge

$$[\varphi(0) - \varphi_b] << RT/zF \text{ volts} \tag{6}$$

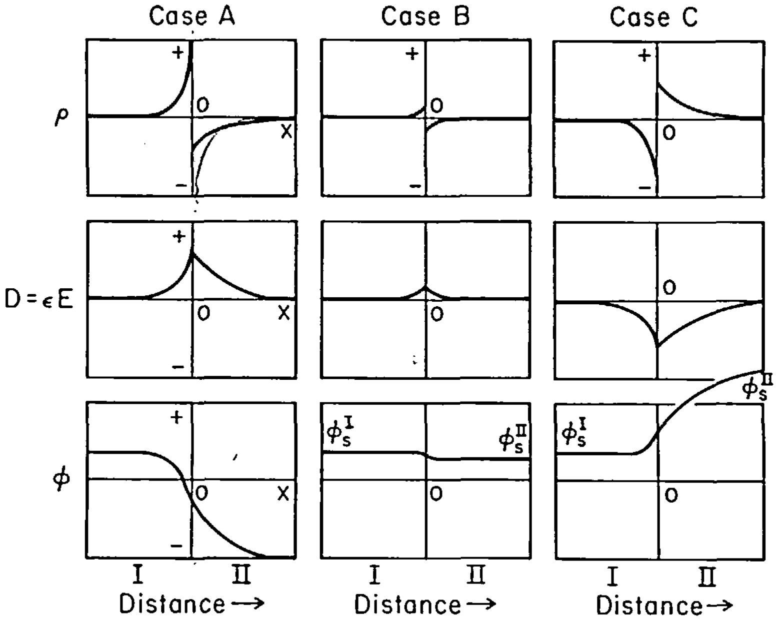

FIGURE 3. Schematic interfacial electrostatic characteristics for immiscible liquid/liquid electrolyte interfaces. The interface is located at x = 0. Electroneutrality holds in the bulk of each phase. Case A: Phase I is positively charged; Case B: nearly zero charge corresponding to nearly a flat band potential; Case C: Phase I is negatively charged. ρ = Space charge density; D = electric displacement; φ = local potential.

the linearized version of the Gouy-Chapman theory gives the internally consistent, but not particularly useful simplifications:

$$\rho(x) = \mp \frac{4RT\kappa^2}{zF} \exp(-\kappa x) \tag{7}$$

$$E(x) = \pm \frac{4RT\kappa}{zF} \exp(-\kappa x) \tag{8}$$

$$\varphi(x) - \varphi_b = \mp \frac{4RT}{zF} \exp(-\kappa x) \tag{9}$$

The quantities may be formulated in terms of total charge, surface density of charge, or in terms of each other.[12,38,51,53] The apparent capacitance per unit cross-section $C_{d.l.}$ (d.l. = double layer) of these doubly diffuse interfaces is a voltage dependent, series combination:[52]

$$C_{d.l.} = \frac{C_I C_{II}}{C_I + C_{II}} \tag{10}$$

where

$$C_I = \kappa_I \epsilon_I \cosh \{zF[\varphi(0) - \varphi_b^I]/2RT\} \tag{11}$$

and

$$C_{II} = \kappa_{II} \epsilon_{II} \cosh \{zF[\varphi(0) - \varphi_b^{II}]/2RT\} \tag{12}$$

but in the linear region $[\varphi(0) - \varphi_b] < 2RT/zF$

$$C_{d.l.} \cong \frac{\kappa_I \epsilon_I \kappa_{II} \epsilon_{II}}{\kappa_I \epsilon_I + \kappa_{II} \epsilon_{II}} \tag{13}$$

The state of affairs at a static, equilibrated membrane interface is considerably more complex than this simple model because of at least four factors:[12,54-57]

1. Ions are not point charges and cannot pile up at the surfaces to create space charge densities greater than that allowed by their finite sizes or by their salt solubilities and ion pairing constants.

2. Dipolar materials such as water solvent and oil soluble dipolar molecules in the membrane will become oriented at the two sides of the interface. Precise direction of orientation is a matter of conjecture. One intuitive approach is to assume that polar ends align with their end of sign opposite to the external phase charge nearest the

interface. These orientable molecules compete with ions for space near an interface. Rejection of ions from the first few angstroms defines the distance of closest approach of diffuse-layer ions, the Outer Helmholtz Plane (OHP).

3. Some ions in either phase may compete with oriented solvent or other dipolar molecules at the interface and become specifically adsorbed. These ions' centers are somewhat closer to the interface than those nonadsorbed ions. The specifically adsorbed plane of ion centers defines the Inner Helmholtz Plane (IHP).

4. In addition to (a) the presence of dipolar species in solutions and membranes and (b) the presence of electrolytes which are restricted to one phase or the other, there are many ionizable species, such as membrane soluble salts of organic acids and bases, whose cation and anion partition coefficients are not equal. Due to the preferential solubility of a cation or anion in one phase or the other, a double layer of charge is created from a single material. This process leads to electrostatic charging of each phase until a balance is achieved between the generated electric field and the chemical forces causing the preferential solubility of ions of one sign. The difference between surface charging in this case and that described in Item 1 or 3 above is the origin of the species composing the space charge. An example of this behavior is the lipid bilayer composed of the ionizable lipid, phosphatidylserine. The charged ends of the lipid presumably align at the interface while water soluble counter ions form a diffuse compensating charge layer. Another situation with similar consequences is the well-known interface of an ion exchanger upon contact with water. Water soluble counter ions will leave the ion exchanger phase to produce a double layer of counter ion space charge in water and the remaining fixed or mobile sites of opposite charge in the membrane phase.

The presence of dipolar layers adjacent to an interface leads to modifications of the profiles of diffuse charge, field, and potential as shown schematically in Figure 3. The potential drops through the dipolar regions are linear except at the edges of the layer where the fractional charges presumably reside. For a single dipolar layer, the classical potential (an example of a surface potential) drop through the layer is ideally

$$\Delta\varphi = n\,\mu/\epsilon_0 \qquad (14)$$

where n = number of dipoles/cm^2 and μ is the dipole moment in coulomb-cm. Since the dipole atoms occupy a finite space, their fractional charge cannot be uniformly smeared out. This results in some curvature of potential to smooth out the sharp corners (shown schematically in Figure 4). This dipolar layer rejects soluble, nonspecifically adsorbed ions from the immediate vicinity of the surface and forms a region of space with a characteristic capacitance. This capacitor is unusual in that it is an electret possessing its own potential difference in the absence of space charge. Thus, at a condition of zero charge (from bulk solution to bulk electroneutral membrane), a residual potential difference exists through the oriented dipolar layers in each phase on either side of an interface. Since the absolute potential of zero charge cannot be directly measured (only a

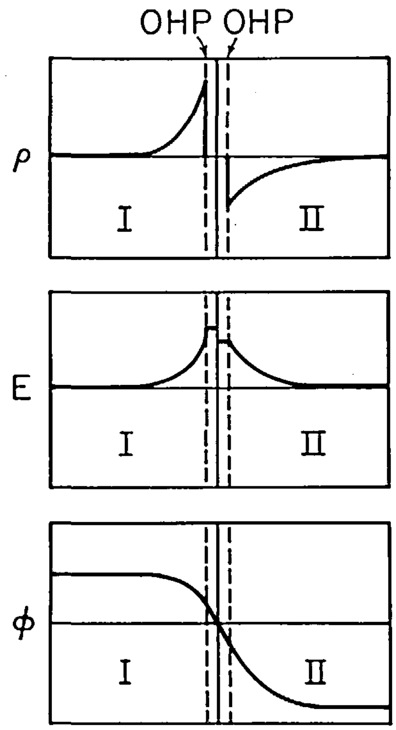

FIGURE 4. A refined schematic of interfacial electrostatic characteristics for immiscible liquid/liquid electrolyte interfaces. The additional feature illustrated, compared with Figure 3, is a region of solvent dipoles at the interface. Space charge of nonadsorbed ions approach the interface only to the OHP (Outer Helmholtz Plane) shown as dashed lines. ρ = space charge density; E = electric field magnitude; φ = local potential.

finite cell potential corresponding to zero charge can be observed), the presence of this persistent surface potential cannot be readily detected; only changes in its value have been measured, from which its sign may be deduced.[58]

To account for the adsorbed dipolar layer, and to account in part for the finite size of ions, equations for diffuse space charge density, field, and potential can be modified by introducing the distance from the interface to the OHP. Thus, the equations above give proper dependence on distance beyond the OHP when the distance variable x is replaced by $x + x_L$ where

$$x_L = \frac{1}{\kappa} \ln|\coth\{zF/4RT[\varphi(OHP) - \varphi_b]\}| - x_{OHP} \qquad (15)$$

Introduction of x_L, the Levich thickness, allows calculation of quantities in terms of the potential difference between the OHP and the bulk.[53] Calculations have meaning only for $x > x_{OHP}$. Within the dipolar region, known as the "compact" part of the double layer, the charge is zero, the field is constant, and the potential profile varies linearly with a net value given by Equation 14. The capacitance is still a series combination:

$$\frac{1}{C_{d.l.}} = \frac{1}{C_I} + \frac{1}{C_{II}} + \frac{1}{C_{cI}} + \frac{1}{C_{cII}} \qquad (16)$$

where C_I and C_{II} are capacitances of the diffuse layers given above and C_{cI} and C_{cII} are the "compact" layer contributions. When electrolyte concentrations in both phases are large, e. g., greater than about 0.1 *M*, the diffuse layer capacitance contributions are so large that only the compact layer values appear as determining factors in the overall value of $C_{d.l.}$. For those systems of blocked and nearly blocked electrodes (electrolyte/Hg, electrolyte/Pt, electrolyte/glass, and electrolyte/AgCl), it is found that the compact layer capacitances are also voltage dependent. This result has not been fully interpreted; however, electrostriction leading to change in the effective thickness of the dipolar layer, lowering of the effective dielectric constant, and possible specific adsorption have been invoked in the explanations.

Examples of the complexities introduced by the presence of specifically adsorbed ions are illustrated in Figure 5. Diffuse space charge regions still obey the modified equations above. However, the compact layers now contain charges and are no longer represented as simple capacitors in series. The relations for development of potential and field profiles are known in principle and have been verified within limitations due to the voltage and field dependences of some of the parameters, particularly the local dielectric constant. In the absence of a dipolar layer, adsorbed ions and their equal and opposite space charge are believed to create a potential profile as shown in Figure 6(b). Since the ions are not smeared out uniformly as shown in Figure 6(a), the notion of discrete size again allows a potential drop between $x = 0$ and x_{IHP} and between x_{IHP} and x_{OHP}. When solvent dipoles are included, the profiles may be similar to Figure 6(d). Figure 6(c) shows the profile for dipoles in the absence of specific adsorption. It is clear from consideration of the plots that the measured potential of a blocked electrode can depend on the extent of specific adsorption (the Esin-Markov Effect). There is a dependence of the measured p.z.c. (potential of zero charge) on the exact distribution of space charge between the diffuse layer and that which is specifically adsorbed. Serious problems remain in calculating the potential profile between OHP and interface and interpreting the measured inner layer capacitance values. One fundamental question regards the validity of the simple, smeared-out physical model of capacitors in series, in part because of discreteness of charge and secondly because of induced imaging by virtue of the closeness of adsorbed ions to the surface.[59-62] It is probable that lines of force from the interface charge terminate on both adsorbed and diffuse ions. Different models are considered by Delahay,[12] Shiffrin,[59] and most recently by Reeves.[57] Interfaces through which net current or net fluxes at zero current flow are not blocked, and the usual theories based on the Poisson-Boltzmann equations do not apply because the spatial distribution of ions, fields, and potential is perturbed by the flux.[53] At low currents and fluxes, the static results can be applied as an approximation.

The reasons for the primary importance of the electrostatic features of the membrane interface are threefold. Rates of slow ion transfers (analogous to the well-known irreversible electron transfer) may depend upon the actual concentration of transferring species at the OHP or the IHP. These values are not the same as bulk values and must be accounted for in surface kinetics (the static psi effect). Secondly, ion transfer rate constants may

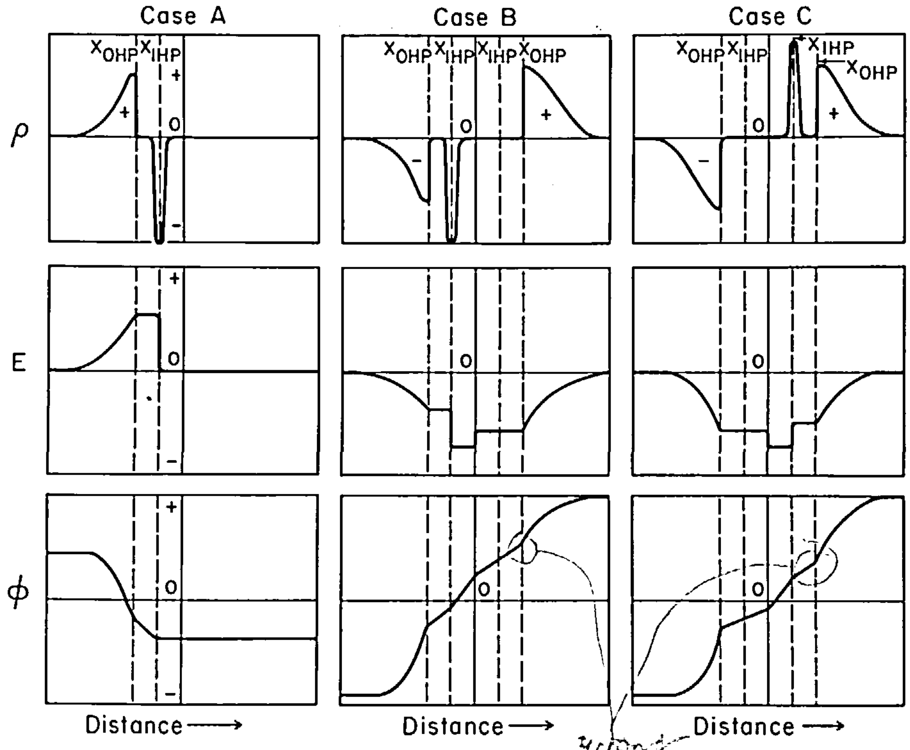

FIGURE 5. Schematic illustration of the electrostatic characteristics of immiscible liquid/liquid interfaces including specific adsorption of ions at the position of closest approach, the IHP (Inner Helmholtz Plane). Case A: specifically adsorbed anions in the left phase with compensating diffuse space charge of cations in the same phase. Case B: specifically adsorbed anions (and diffuse negative space charge) compensated by diffuse positive space charge in the second phase. Case C: specifically adsorbed cations in the right phase. ρ = Space charge density; E = Electric field magnitude; φ = Local potential.

be potential dependent, and it is necessary to know the local potential at the position of an ion transfer in order to describe the rate accurately. The combination of these factors leads to the so-called Frumkin correction in electrode kinetics. Thirdly, the transport rate of ions is modified in the space charge region by the high fields (so called dynamic psi effect). For excitable biological membranes, ion flux and current responses are sensitive functions of the membrane potential. Readjustments of space charge profiles may be crucial steps in the interpretation of the time course of ion fluxes. For reversible interfaces, where some ions are not impeded by slow surface rates but can traverse rapidly between phases, the net potential across an interface is presumably fixed on thermodynamic grounds (see below). In such cases, adsorbed ions and space charge densities adjust in such a way as to permit the net potential to be obeyed by a Nernst-type dependence on ionic bulk activities in the two phases.

In addition to specific adsorption of charged species, field and potential profiles at interfaces are affected by adsorption of uncharged molecules. The effect is primarily a change in the local dielectric constant of the compact layer. However, interpretation of nonionic adsorption as a function of species activities (adsorption isotherm) and interfacial potential or charge can be difficult.[52,55-57] The adsorption isotherm is frequently potential dependent even though the adsorbed material has no net charge.

B. Qualitative Electrostatic Features of Two-Interface Systems – Membranes

The electrostatic situation in and around membranes which are bathed in electrolytes is essentially a compounding (but not a simple superposition) of the effects already described for single interfaces. Eliminating the complications from dipolar layers and specific adsorption of charged and uncharged species, there are three

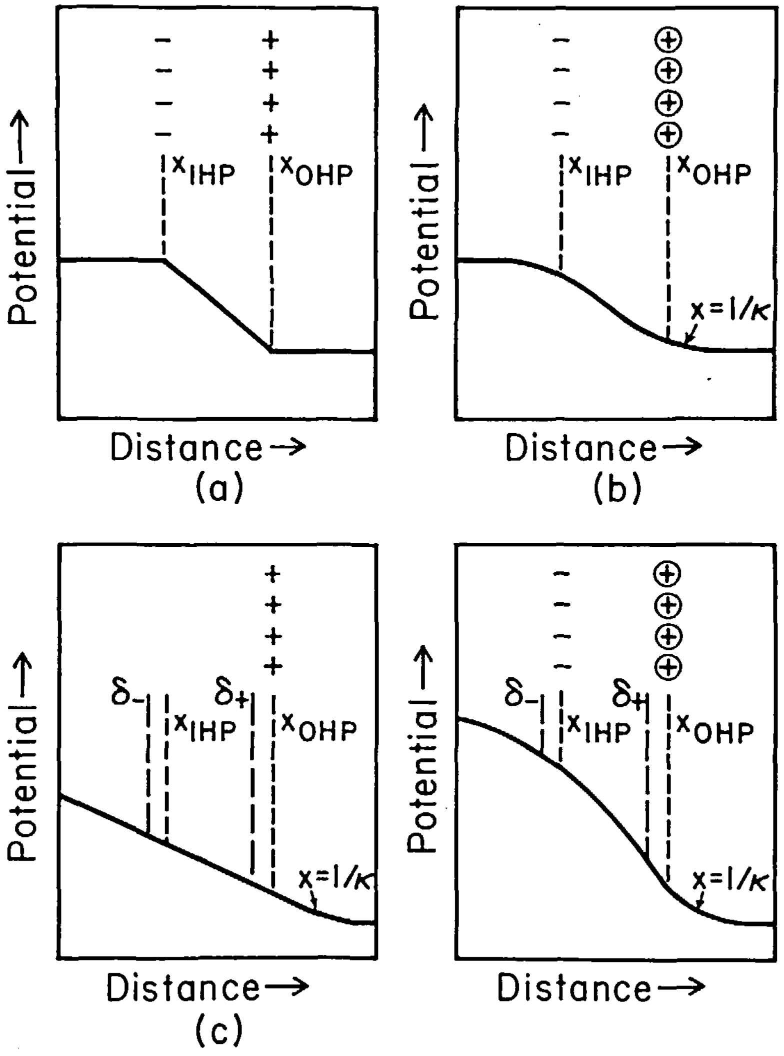

FIGURE 6. Schematic illustration of potential vs. distance profiles for the region between an interfacial surface and the OHP (a) Smeared out charge sheets at the IHP and OHP (negative ion adsorption) (b) Discreet charges in a sheet at the IHP and OHP (negative ion adsorption) (c) Adsorbed dipoles at an electrode on the negative potential side of the p.z.c. (potential of zero charge) (d) Adsorbed dipoles and specific anion adsorption. Interfacial surface is at the left of each drawing. Dipole partial charges are shown as δ_+, δ_- and are slightly displaced from x_{IHP} and x_{OHP} for clarity.

primary static cases to be described. These are shown in Figure 7.

1. Case A – A Permselective Membrane with a Region of Electroneutrality Inside

This situation prevails in a majority of the passive membranes considered as model systems for solid crystalline transport and liquid and solid ion exchange transport. For example, positive ions in a cation exchanging membrane are the permselective counter ions which are free to exchange with solution ions, while the negative ions are trapped in the membrane. Negative ion sites may consist of vacancies, fixed and mobile ion exchanger anions, and some extracted anions from the solutions. Although surface anionic sites (surface states), adsorbed anions, and nonuniform fixed sites near surfaces will complicate the picture, most anions are believed to adjust their concentrations according to some model such as

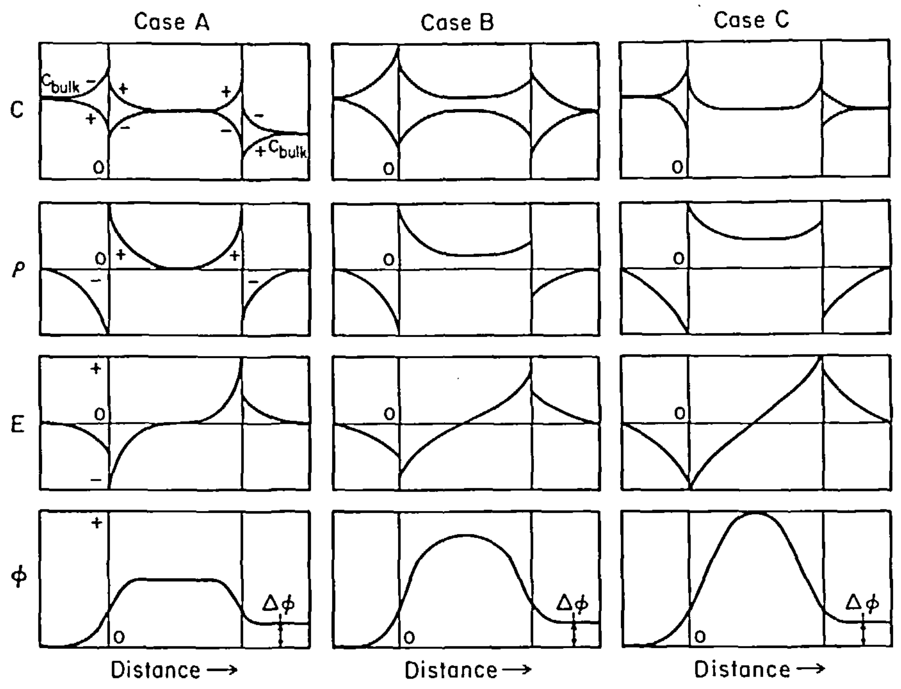

FIGURE 7. Schematic illustrations of expected electrostatic characteristics for site-free membranes. Case A: a membrane with preferential solubility of cations over anions, but non-zero values of extraction coefficients, such that electroneutrality prevails in the membrane interior. Case B: a membrane with preferential solubility of cations over anions and very small anion extraction coefficient so that electroneutrality does not prevail in the membrane interior. Case C: Membrane with exclusive solubility of cations. Anion extraction coefficient is zero.

the idealized, static, or flux modified Gouy-Chapman profiles indicated schematically in Figure 7. The illustrated arrangement of negative ions is probably most nearly appropriate for liquid ion exchanger membranes. Rejection of anions from the inner surfaces of membranes that prefer cations is believed to be a general phenomenon as deduced from the electrochemical potential concept.

At the left of Figure 7, a cation permselective membrane is bathed in two different activities of electrolyte which, after a rapid charging process which is described later, has come to a zero current steady state or equilibrium condition*. Concentration profiles of the space charge regions are governed by individual ion extraction coefficients. In the illustration, cations are favored. The space charge density $\rho = (C_+ - C_-)zF$ is exactly balanced at each interface, but there is no reason to expect that the total space charge will be identical for both interfaces except when bulk concentrations are identical. Note that the electrical fields are not constant except in the regions of electroneutrality where they will be nearly zero. Of course, this drawing is not to scale, and the illustrated space charge regions are larger than usual for clarity of presentation. A constant field in a membrane at zero current is an unusual situation and only occurs when a specific combination of permselective ion activities inside and outside exist for a given set of single ion extraction coefficients. The potential is simply the negative integral of the field along the positive-going distance parameter. The result is potential curvature in the space charge regions and slowly varying (nearly constant) potential in the electroneutral region. A net potential difference exists for unequal bathing activities of the permselective ion. This potential profile is a "barrier" to current flow. However, the profile is a function of current. Consequently, exact derivation of current vs. membrane potential relations gives results which differ from a pure activation, Eyring-type calculation, although in more nearly exact treatments,[63]

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*Equilibrium is a proper description at constant P and T only for equal permselective ion activities on both sides.

the membrane potential does appear as an exponential (but also as a multiplying factor) as it would in the absolute rate theory treatment.

2. Case B and Case C – Permselective Membranes Without Regions of Electroneutrality

The intermediate Case B shows a membrane which deviates from electroneutrality by an imbalance of positive over negative ions. No examples of this behavior are well-known. However, digital simulation of liquid ion exchange membrane electrostatics clearly allows this possibility merely by adjustment of relative single ion extraction parameters to favor cations and partially exclude anions from the membrane. Finally, Case C represents the limit of a fully charged membrane containing only cations. This situation has been exactly treated by DeLevie and Moriera[64,65] to provide quite an accurate model of site free lipid bilayer membranes in contact with oil soluble ions of one sign or the other. In these schematic drawings, roughly the same concentrations of permselective ions have been imagined in each case. Consequently, the fields become steeper and the potential barrier more pronounced (less flat-top) as one reads across from Case A to C. If we had chosen more dilute solutions, the fields could be made more nearly constant simply by adjusting the space charge to provide a desired maximum allowable curvature. Recent detailed analysis of dipolar arrangement and local potentials can be found in a book by Friedenberg.[66] Other books which deal with membrane surfaces are edited by Blank,[67] Brown,[68] and Hair.[69]

Theoretical treatments of the electrical properties of homogeneous membranes under finite flux conditions proceed via solution of transport equations with application of reversible (equilibrium) or irreversible (kinetic) boundary conditions. Electrostatic effects manifest themselves under non equilibrium (finite flux) conditions through modifications of local potential, concentration, and rate constants. We will also discuss later the proposed effect of spatially dependent mobilities and standard chemical potentials. At zero flux (equilibrium), the reversible boundary conditions can usually be applied even for systems that would show kinetic limitations under finite flux. Calculation of a static membrane potential for asymmetric bathing solutions surrounding a permselective membrane can be done by either method (even with flux) provided the components of the potential are accounted for correctly. Although these points are taken up in more detail later, suffice it to say that the membrane potential,

$$\Delta\varphi_m = \varphi(\text{b.r.}) - \varphi(\text{b.l.}) \qquad (17)^*$$

can be calculated in segments in a number of ways. Two are most important: (I) for membranes with a region of interior electroneutrality and (II) for membranes without electroneutrality.

$$\text{(I)}\quad \Delta\varphi_m = [\varphi(\text{b.r.}) - \bar{\varphi}_{\text{m.r.}}] + {} + [\bar{\varphi}_{\text{m.r.}} - \bar{\varphi}_{\text{m.l.}}] + [\bar{\varphi}_{\text{m.l.}} - \varphi_{\text{b.l.}}] \qquad (18)^*$$

or

$$\text{(II)}\quad \Delta\varphi_m = [\varphi_{\text{b.r.}} - \bar{\varphi}_{\text{s.r.}}] + [\bar{\varphi}_{\text{s.r.}} - \bar{\varphi}_{\text{s.l.}}] + [\bar{\varphi}_{\text{s.l.}} - \varphi_{\text{b.l.}}] \qquad (19)^*$$

Subdivision of the total membrane potential into segments, a concept of basic importance, was introduced into membrane electrochemistry by Teorell[69a-c] and by Meyer and Sievers[69f] in connection with their theory of concentration potentials, so-called TMS Theory. In the first case (illustrated in Figure 8), potentials just inside the membrane surface beyond the space charge layers are used since these values can be computed for reversible interfaces using the electrochemical potential concept. On the other hand, if no point in the membrane is electroneutral, or if one knows the precise space charge distributions arising from fixed and partitioned charges, then the second equation can be used. The latter has been used for

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*b.r. = Bulk solution on the right side of a membrane.
b.l. = Bulk solution on the left side of a membrane.
m.r. = Inside the right interface of a membrane beyond the space charge region.
m.l. = Inside the left interface of a membrane beyond the space charge region.
s.r. = Inside the right interface of a membrane at the inner surface.
s.l. = Inside the left interface of a membrane at the inner surface.

simple, lipid bilayer membranes which are charged by virtue of the preferential solubility of an ion of one sign.[64,65] At the same time, lipid bilayer membranes with neutral carriers which enforce preferential solubility of alkali cations have been treated by these procedures.[29,30,70-72]

In asymmetric electrolytes, some carrier mediated systems have shown deviations from expected reversible bi-ionic potential behavior.[71-74] The discovery of the dependence of membrane potential at zero current on fluxes of species is of great theoretical significance. The interpretation is similar to that of the potential dependent irreversible rates at metal electrodes. Although discussed later, the treatment uses Equation 19 with allowance for surface charge (absorbed and fixed) potentials and space dependence of standard chemical potentials. MacDonald and Bangham,[75] Ohki,[76,77] and Ehrenfest and Gilbert[78] have also invoked blocked electrode surface charge electrostatics to interpret measured membrane potentials. Massey and McColloch[79] treated surface charge in equilibrium with bulk on the basis of a Langmuir adsorption isotherm. The latter, while simple, rarely holds in electrode kinetics, and more complex isotherms are needed to express ion adsorption.[12] At this time, it appears that coupling of surface charge-surface rate limitations and transport must be simultaneously considered in nonequilibrium systems.[74]

III. IONIC PROCESSES AT INTERFACES BETWEEN HOMOGENEOUS PHASES

A. Interfacial Processes in the Equilibrium Domain

Interfacial transfer of material, single ions, neutral salts, and neutral molecules falls into two main classes of behavior depending on the rates of forward and backward transfer processes across interfaces. In the first category, reversible behavior, local thermodynamic equilibrium prevails and activity ratios of species (inside to outside the membrane) can be calculated from the equality of the species' electrochemical potential in each phase. The electrochemical potential at constant temperature and uniform pressure is

$$\tilde{\mu}_i = \mu_i^{0} + RT \ln a_i + z_i F \varphi \tag{20}$$

For neutral species, z = 0, and the usual chemical potential equality holds. For membranes permeable to solvent, the osmotic pressure p may also have to be considered. Then,

$$\tilde{\mu}_i = \mu_i^{0} + RT \ln a_i + p v_i + z_i F \varphi \tag{21}$$

Reversible interfacial "local" equilibrium means that the flux of material through the interface does not perturb local equilibrium activity ratios However, the local "surface" activities will not, in general, be bulk values. "Surface" activities are determined through flux balance by whatever slow transport processes occur in the membrane and in the external solutions near the surfaces. For example, Figure 9 shows a membrane cell with current flow. The exterior solution will be concentration polarized (depleted on the entering side and raised above bulk values on the exiting side of the membrane). Similarly, inside the membrane, species' profiles under current flow will, in general, be higher than average on the inside of the entering surface and lowered at the inner side of the exiting surface.

Application of equilibrium calculations across an interface requires use of these bulk transport determined "surface" activities. They can be found from flux balance in terms of bulk values in the steady state:

$$\text{J (left to right)} = D\left[\frac{C_{s,0} - C(0)}{\delta'}\right] = \bar{D}\left[\frac{\bar{C}(0) - \bar{C}(d)}{d}\right] = D\left[\frac{C(d) - C_{s,d}}{\delta''}\right] \tag{22}$$

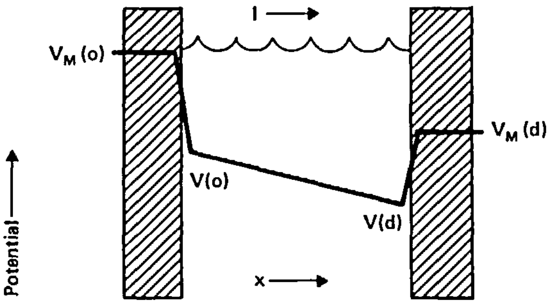

FIGURE 8. Segmented potential distribution. The conventional subdivision of the cell potential into two interfacial potentials and one internal diffusion potential is shown for negative $V_c = \Delta\varphi_m$. Space charge effects are omitted. Positive current flows when positive carriers move in the +x direction. V(0) and V(d) are computed values which can be considered extrapolations of the real bulk values through the space charge regions to x = 0,d. Interfacial potential slopes have no physical significance in the approximation. (From Buck, R. P., *J. Electroanal. Chem.*, 46, 1 (1973). With permission.)

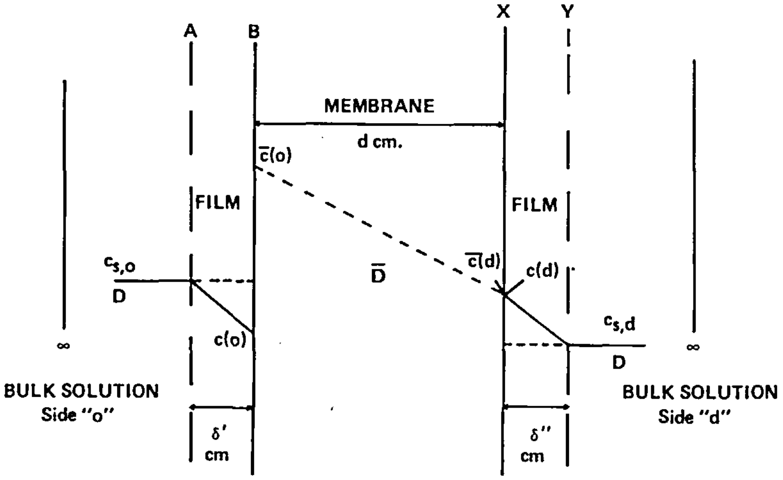

FIGURE 9. Concentration profiles of cations during transport across a liquid ion exchange membrane under applications of a positive current. As in Figure 1, anions n are restricted to the membrane, while anions x are restricted to the bathing solutions. Broken lines in "Film" indicate ideal diffusion with rapid surface equilibrium and rapid external stirring. A,B,X,Y indicate the respective boundaries: bulk solution – film, film – membranes interface at x = 0, membrane – film at x = d, and film – bulk solution. Space charge perturbations are omitted. At zero flux, the dashed internal profile is flat. δ' and δ" are Nernst diffusion layer thicknesses. This drawing also applies in the absence of current to spontaneous flow profiles of neutral molecules and salts which have preferential solubilities in the membrane phase, moving from high (left side) concentration to low (right side).

$$C_{\text{surface left}} = C(0) = C_{s,0} - J\delta'/D \tag{23}$$

$$C_{\text{surface right}} = C(d) = C_{s,d} + J\delta''/D \tag{24}$$

These equations apply for neutral species and for charged species moving in the presence of inert electrolyte. For single salt situations, D is replaced by D/(1 – t), where t is the transport number of the permeable ion. When a permeable cation species is required to obey electroneutrality in the membrane because of confined mobile sites, then

$$\bar{C}(0) + \bar{C}(d) = 2\bar{C} \tag{25}$$

and

$$\bar{C}(0) = \bar{C} + Jd/2\bar{D} \tag{26}$$

$$\bar{C}(d) = \bar{C} - Jd/2\bar{D} \tag{27}$$

Nernst diffusion layer thicknesses, δ' and δ", depend upon the stirring rate ω, i.e.,

$$\delta \propto \omega^{-1/2} \tag{28}$$

for rotating disk geometry in the steady state. For other geometries, the exponent of ω will be near −½. Prior to steady state during the transient, $\delta^2 \sim Dt$. Of course, at zero flux of each species, bulk and "surface" concentrations are the same. However, absence of current does not insure equilibrium since zero current bi-ionic diffusion (two different permeable ions diffusing in opposite directions through a membrane) is also accompanied by tipping of concentration profiles inside and outside the membrane. Analysis of film diffusion for several permeable ions, including different charges, can be worked out with some algebraic difficulty.

There is an apparent paradox in the use of "surface" concentration of ionic species. The concentrations derived from fluxes are not literally at the surface, but are extrapolated values that would occur in the absence of space charge. This distinction is nonexistent for neutral species. The "surface" concentration for a single uni-univalent salt is $\sqrt{C_+C_-}$ evaluated at x = 0. Alternatively, if the profile of salt concentration from bulk to surface is not steep (cases of low current densities so that film diffusion limitation is avoided; see below), then the "surface" concentration is approximately the value just outside the diffuse double layer region. Use of the latter "surface" value is justified because mass transport controls the "surface" concentration by continuity of flux, and depletion regions occur over a 10^{-4}- to 10^{-3}-cm distance, while the space charge region is only about 10^{-5}- to 10^{-6}-cm thick.

The local equilibrium condition for neutral species at constant temperature and pressure is simply equality of chemical potential at the interface

$$\mu_i = \overline{\mu}_i \tag{29}$$

with the usual result that the extraction coefficient K_{ext} is defined

$$K_{ext} = \overline{a}_s/a_s = \exp[(\mu^o - \overline{\mu}^o)/RT] \tag{30}$$

For species i of charge z, equality of electrochemical potential is presumed to hold locally near the interface but outside the space charge region during passage of flux or current, for rapidly exchanging, reversible species,

$$\tilde{\mu}_i = \overline{\tilde{\mu}}_i \tag{31}$$

and the single ion extraction coefficient is defined with the same form, viz.

$$K_{ext,i} = (\overline{a}_s/a_s)\exp[zF(\overline{\varphi}_s - \varphi_s)/RT]$$

$$= \exp[(\mu_i^o - \overline{\mu}_i^o)/RT] \tag{32}$$

This equation is exactly true at equilibrium, zero flux conditions where $\overline{a}_s$, a_s, $\overline{\varphi}_s$, and φ_s become bulk values $\overline{a}_b$, a_b, $\overline{\varphi}_b$, and φ_b. In the absence of flux, this equation is not limited to activities in the electroneutral region, but also applies in the space charge region. Quite generally,

$$K_{ext,i} = [\overline{a}(\overline{x})/a(x)]\exp\{zF[\overline{\varphi}(\overline{x}) - \varphi(x)]/RT\} \tag{33}$$

It is thus valid to formulate extraction in terms of activities at an interface where the local potential has a common value (in the absence of dipolar layers). Thus,

$$K_{ext,i} = \overline{a}(0)/a(0) = \exp[(\mu^o - \overline{\mu}^o)/RT] \tag{34}$$

This result follows from the general zero flux condition outside a membrane:

$$RT\ln\left(\frac{a(x)}{a_b}\right) = zF[\varphi_b - \varphi(x)] \tag{35}$$

and a corresponding expression for points within a membrane. For electroneutral salt extraction of ions of equal absolute charge from Equation 32 it follows that,

$$K_{ext,+}\,K_{ext,-} = \frac{\overline{a}_+\,\overline{a}_-}{a_+\,a_-} = (K')^2 = K_D^2\left(\frac{\overline{\gamma}_\pm}{\gamma_\pm}\right)^2 \tag{36a}$$

$$= \exp[(\mu^o_+ + \mu^o_-)/RT - (\overline{\mu}^o_+ + \overline{\mu}^o_-)/RT] \tag{36b}$$

where K′ is the thermodynamic salt extraction coefficient and K_D is the "concentration" coefficient.*

An important feature of this formulation is the fact that the interfacial potential must be satisfied by each equilibrated species according to:

$$\overline{\varphi}_s - \varphi_s = \frac{RT}{zF}\ln\left(\frac{K_{ext}\,a_s}{\overline{a}_s}\right) \tag{37a}$$

$$= \frac{RT}{zF}\ln\left(\frac{K_{ext,+}\,a_+ + \overline{a}_-}{\overline{a}_+ + K_{ext,-}\,a_-}\right) \tag{37b}$$

This equation applies at *all* points across the interface when φ's and a's are understood to be functions of position. The unusual feature of Equation 37b is that it bears a resemblance to the Goldman equation, although the former applies to interfaces and the latter applies to overall membrane potentials. When electroneutrality occurs on both sides of the interface, beyond the space charge regions, substitution of Equation 36 into 37b leads to a concentration-independent result as described below.

All of the results of charge equilibria across interfaces (Donnan Equilibria) follow from

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*I have adopted the notation of Morrison, G. H. and Freiser, H., *Solvent Extraction in Analytical Chemistry*, John Wiley & Sons, New York, 1957, 9.

Equations 37a,b as applied to each charged species, with the condition of Planck or quasi-electroneutrality at points beyond a few Debye thicknesses of the interface. In dealing with regions of electroneutrality, all charged species are included in the charge balance, not just those involved in the interfacial transfers. Thus, for ion exchangers with confined sites at concentration $\overline{X}$ charge $\overline{\omega}$,

$$\sum_i z_i \overline{C}_i + \overline{\omega} * = 0 \tag{38}$$

From this equality and Equations 37a, b, Donnan exclusion is readily derived.[21] A stronger second condition is Poisson's equation and Gauss' law rather than quasi-electroneutrality. Only in cases of very thin membranes (lipid bilayers) where quasi-electroneutrality clearly fails must Poisson's equation be used to calculate species distributions and local potentials and fields. Nevertheless, the equality of electrochemical potential still applies.

These boundary conditions based on Equation 20 are frequently used in membrane electrochemistry, although they are limited to dilute solutions where osmotic pressures can be assumed to be small or constant across an interface. A proper general formulation expresses concentrations as mole fractions and accounts for local osmotic pressure. At an equilibrium interface from Equation 21,

$$\tilde{\mu}_i + pv_i = \overline{\tilde{\mu}}_i + \overline{p}\,\overline{v}_i \tag{39}$$

Local osmotic pressures are functions of ionic strength, and therefore of distance, at least in the double layer region. Integration of flux equations then becomes especially difficult, and some compromise – such as assigning a fixed but different osmotic pressure in each phase – is an alternative; the potential difference is

$$\begin{aligned} \overline{\varphi}_s - \varphi_s &= \frac{RT}{zF} \ln\left(\frac{K_{ext}\, a_s}{\overline{a}_s}\right) + (pv - \overline{p}\overline{v})/zF \\ &= \frac{RT}{zF} \ln\left(\frac{K_{ext}\, a_s}{\overline{a}_s}\right) + \Delta pv/zF \end{aligned} \tag{40}$$

The well-known ion exchange equilibrium constant for ions of charge z follows directly for the reaction

$$a_j + \overline{a}_i \rightleftharpoons a_i + \overline{a}_j \tag{41}$$

$$\begin{aligned} K_{iexc} &= \frac{a_i\, \overline{a}_j}{\overline{a}_i\, a_j} \\ &= \left(\frac{K_{ext,j}}{K_{ext,i}}\right) \exp[\overline{p}(\overline{v}_i - \overline{v}_j)/RT - p(v_i - v_j)/RT] \end{aligned} \tag{42}$$

which can be generalized for ions of different charge.

When a membrane interface is in equilibrium with both cations and anions and quasi-electroneutrality also holds in the bulk of each phase, the interfacial potential is constant for a single salt and is a slowly varying function of concentration for two salts. Writing Equation 37a for two salts i^+x^- and j^+y^- with the conditions:

$$(i^+) + (j^+) = (x^-) + (y^-) \tag{43}$$

$$(\overline{i}^+) + (\overline{j}^+) = (\overline{x}^-) + (\overline{y}^-) \tag{44}$$

and

$$\overline{\varphi}_s - \varphi_s = \frac{RT}{F} \ln \left[\frac{K_{ext,i}\, a_i/\overline{\gamma}_i + K_{ext,j}\, a_j/\overline{\gamma}_j}{K_{ext,x}\, a_x/\overline{\gamma}_x + K_{ext,y}\, a_y/\overline{\gamma}_y}\right]^{1/2} \tag{45}$$

This equation can be generalized for complex formation. For a single salt,

$$\overline{\varphi}_s - \varphi_s = \text{const.} = \frac{RT}{F} \ln \frac{K_{ext,i}\, \gamma_i/\overline{\gamma}_i}{K_{ext,x}\, \gamma_x/\overline{\gamma}_x} \tag{46}$$

When membranes contain fixed sites at concentration $\overline{X}$, and charge $\overline{\omega}$, ions from the solution equilibrate by ion exchange across the interface. For a single 1:1 electrolyte equilibrating with fixed sites, both anions and cations will exist in the membrane unless $\overline{X}$ is very large such that

$$Q = \frac{2a_{\pm}}{\overline{\omega}\overline{X}\ \overline{\gamma}_{\pm} \exp(\Delta\, \overline{pv}/2RT)} << 1 \tag{47}$$

Single ion distributions for both ions obey Equation 37a. Beyond the space charge region, thick membranes reach electroneutrality, expressed by Equation 38. The general distributions are

$$\overline{a}_s^{+} = \frac{|\omega|\overline{X}\ \overline{\gamma}_{+}}{2} \left[\frac{-\overline{\omega}}{|\overline{\omega}|} + (1 + Q^2)^{1/2}\right] \tag{48}$$

and

$$\bar{a}_s^- = \frac{|\omega|\bar{X}\,\bar{\gamma}_-}{2}\left[\frac{\bar{\omega}}{|\omega|} + (1 + Q^2)^{1/2}\right] \tag{49}$$

For electroneutral membranes with sites exposed to 1:1 electrolytes (ignoring Δpv terms), the interfacial potential can be expressed in terms of cation activities and cation extraction coefficient,

$$\bar{\varphi}_s - \varphi_s = -\frac{RT}{F}\ln\left\{-\frac{\bar{\omega}\,\bar{X}\,\bar{\gamma}_+}{2\,K_{ext}\,a_s^+} + \left[\left(\frac{|\bar{\omega}|\,\bar{X}\,\bar{\gamma}_+}{2\,K_{ext}\,a_s^+}\right)^2 + \frac{\bar{\gamma}_+^{\,2}}{K_{ext}\,\bar{\gamma}_\pm^{\,2}}\right]^{1/2}\right\} \tag{50}$$

For high negative site concentrations, Equation 50 simplifies to

$$\bar{\varphi}_s - \varphi_s = \frac{RT}{F}\ln\left[\frac{K_{ext}\,a_s^+}{\bar{X}\,\bar{\gamma}_+}\right] \tag{51}$$

and anions are excluded. This equation is a restatement of Equation 37. An illustration of the interfacial potentials with and without current is shown in Figure 10. Equation 50 can also be cast in terms of anion activities and anion extraction coefficients.

The general procedure for reversible boundary conditions, applicable to charged and electroneutral membranes, makes use of both the electrochemical potential concept and charge balance through Gauss' law. Without regard to electroneutrality, in a membrane of thickness d at zero current, in the steady state, and ignoring osmotic pressure effects, for a two-ion problem, i^+, x^-,

$$\bar{\varphi}(0) - \varphi_s \text{ at each interface} = \frac{RT}{F}\ln\left[\frac{K_{ext,i}\,a_i}{\bar{a}_i(0)}\right] = \frac{RT}{F}\ln\left[\frac{\bar{a}_x(0)}{K_{ext,x}\,a_x}\right] \tag{52}$$

but in addition, surface displacement magnitudes are equal. Thus,

$$\epsilon\,E(0) = \bar{\epsilon}\,\bar{E}(0) \tag{53}$$

$$\epsilon\,E(d) = \bar{\epsilon}\,\bar{E}(d) \tag{54}$$

or

$$-q\,[\text{sol'n side }(0)] - q\,[\text{sol'n side }(d)] = \bar{q}_m \tag{55}$$

Equations 53 to 55 follow from application of Gauss' law. In addition, Gouy-Chapman theory permits relations between q and concentrations to be stated according to:

$$\begin{aligned} q\,[\text{sol'n }(0)] &= (4RT\,C_i\epsilon)^{1/2}\sinh\left[\frac{F}{2RT}\,(\bar{\varphi}(0) - \varphi_b)\right] \\ &= (RT\epsilon)^{1/2}\left[\sqrt{C_x(0)} - \sqrt{C_i(0)}\right] \\ &= (RT\epsilon)^{1/2}\left[\left(\frac{\bar{C}_x(0)}{K_{ext,x}}\right)^{1/2} - \left(\frac{\bar{C}_i(0)}{K_{ext,i}}\right)^{1/2}\right] \end{aligned} \tag{56}$$

and an equivalent expression for q(solution at d). The total membrane charge is specified by

$$\bar{q}_m = F\int_0^d [\bar{C}_i(x) - \bar{C}_x(x)]\,dx \tag{57}$$

and the continuity of potential at each interface is

$$\bar{\varphi}(0) = \varphi(0);\ \bar{\varphi}(d) = \varphi(d) \tag{58}$$

in the absence of a dipolar potential drop. At this point there are three independent equations (52 for each ion and 55) and four unknown surface concentrations at each interface. $\bar{C}_i(x)$ and $\bar{C}_x(x)$ are uniquely defined in terms of the field and partial currents, and a general differential equation for the field exists based on Poisson's equation. These will be stated later since they are derived from the Nernst-Planck flux equations. The final necessary relation is one between partial (ionic) currents and total current. The entire system is fully specified, but it is by no means a trivial problem to give analytical solutions. In addition there is a basic error in the formulation, viz., application of Gouy-Chapman theory requires not only zero current, but zero flux of each species. It is likely that perturbation of the space charge profiles by finite flux can be overlooked and the static theory applied. However, it is also possible to use the Nernst-Planck equations to correct concentration profiles for flux. This procedure is described below.

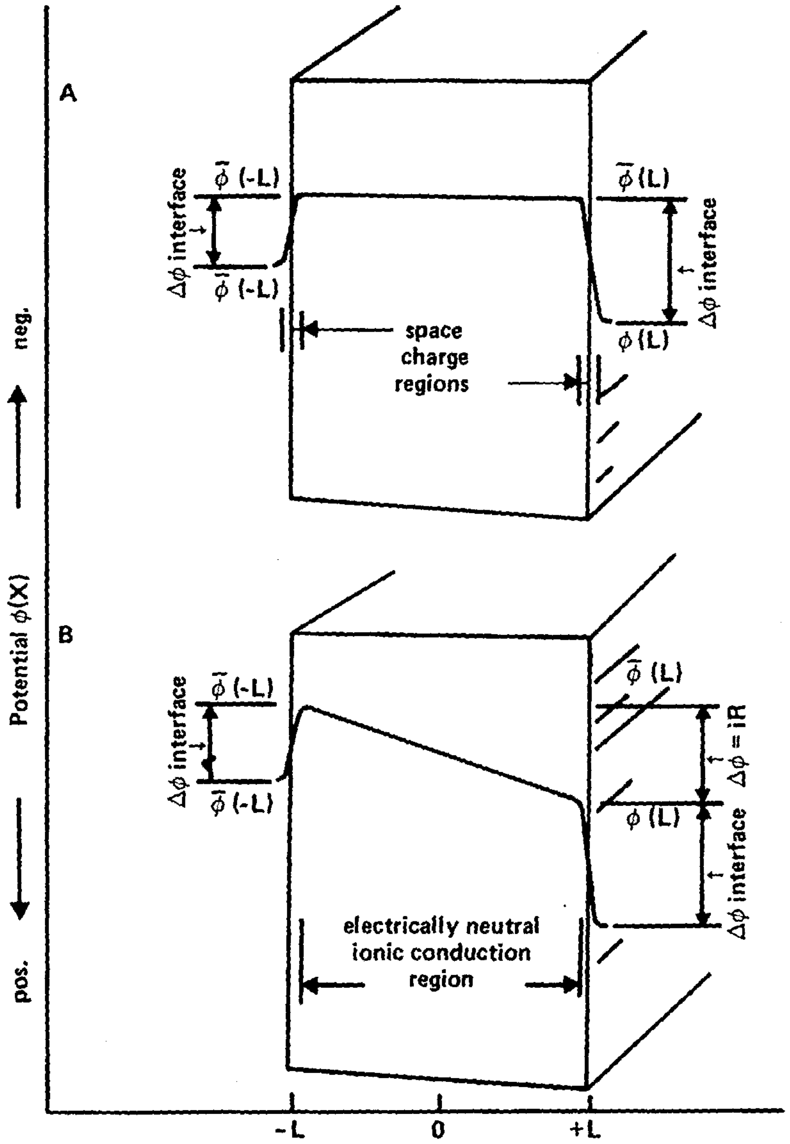

FIGURE 10. Potential distributions at reversible homogeneous cation conducting membranes. Curve A: Condition of zero current corresponding to $a_M(-L) > a_M(L)$ or $a_A(-L) < a_A(L)$. Curve B: Condition of negative current flow in the positive direction or positive current flow in the negative direction. Potential increases positive downward. The membrane thickness in this drawing is 2L. (From Buck, R. P., *Anal. Chem.*, 40, 1432 (1968). With permission.)

INTERFACIAL PROCESSES IN THE KINETIC DOMAIN

The second category of interfacial behavior admits the possibility that transport of material across an interface can be slow. Often considered theoretically, this behavior is a very well-explored topic in electrochemical kinetics. In fact, most coupled ion and electron transfers at electrolyte/metal interfaces are measurably slow and give rise to the phenomenon of overvoltage or overpotential when mass transport (via concentration gradient or electric field) is imposed on an electrochemical system. The most important single feature of slow transport at interfaces is the experimental fact that the overall rate constants for charged species (relating flux to single ion external "surface" activities) depend upon the interfacial potential difference and upon the local potential at the particular site where an electron transfers from metal to ion. In a classical way for a redox process

$$\text{Ox (charge z)} + ne^- \rightleftharpoons \text{Red (charge z')}$$

the current density is expressed as:

$$I = \vec{i} - \overleftarrow{i} = zFJ_{Ox} - z'FJ_{Red} \tag{59}$$

$$= zF\vec{k}'\, a_{Ox}(0) - z'F\overleftarrow{k}'\, a_{Red}(0)$$

$$= zF\vec{k}\, a_{Ox}(\text{“surface”}) - z'F\overleftarrow{k}\, a_{Red}(\text{“surface”}) \tag{60}$$

where $\vec{i}$ and $\overleftarrow{i}$, are forward and reverse current densities, $\vec{k}'$ and $\overleftarrow{k}'$ are interfacial, potential dependent rate constants in the forward and reverse directions, and $a_{Ox}(0)$ and $a_{Red}(0)$ are potential dependent species activities at the site where transfer occurs (presumably the OHP or between OHP and IHP). The rate constants $\vec{k}$ and $\overleftarrow{k}$ may be doubly potential dependent through intrinsic dependence and the relation of a(0) to activity a "surface." For single ion transfers, $z = z'$, and for neutral species, the flux equations alone are used, with the zF coefficient omitted. Effects of specific adsorption by the reactive species or by foreign, blocking materials are not included in the basic description.

Considering an ion in electroneutral solution at the "surface" (I), at the site of transfer (II), at the final transfer site in the membrane (III) and at the electroneutral membrane "surface" (IV), the standard energies are

$$\tilde{\mu}_I{}^o = \mu^o + zF\,\varphi_s;\ \tilde{\mu}_{II}{}^o = \mu^o + zF\,\varphi_2 \tag{61}$$

$$\overline{\tilde{\mu}}_{III}{}^o = \bar{\mu}^o + zF\bar{\varphi}_2;\ \overline{\tilde{\mu}}_{IV}{}^o = \bar{\mu}^o + zF\bar{\varphi}_s \tag{62}$$

Assume that the activation energies to react in the transition state are referred to the "surface" positions. Also introduce an activation barrier which is assumed to be a fraction α of the energy difference between states II and III. This latter assumption is one of many choices, including omission of this barrier. However, it has proved successful in electrokinetics and so is used for illustration here. The parameter α partitions the energy affecting the rates of forward and backward processes. The activation energies are written:

$$\Delta\vec{G}^o = G^* - \tilde{\mu}_I{}^o = G^* - \tilde{\mu}_{II}{}^o + (\tilde{\mu}_{II}{}^o - \tilde{\mu}_I{}^o) \tag{63}$$

$$= \Delta\vec{G}\,(\text{chemical}) + \alpha[\overline{\tilde{\mu}}_{III}{}^o - \tilde{\mu}_{II}{}^o]_e + [\tilde{\mu}_{II}{}^o - \tilde{\mu}_I{}^o]_e$$

and

$$\Delta\overleftarrow{G}^o = \tag{64}$$

$$\Delta\overleftarrow{G}\,(\text{chemical}) + (\alpha - 1)\,[\overline{\tilde{\mu}}_{III}{}^o - \tilde{\mu}_{II}{}^o]_e + [\overline{\tilde{\mu}}_{III}{}^o - \overline{\tilde{\mu}}_{IV}{}^o]_e$$

Subscript "e" means the electrical parts. Chemical parts are collected in the first term. The doubly potential dependent rate constants after collecting terms are

$$\vec{k} = \kappa\frac{kT}{h}\exp[-\Delta\vec{G}(\text{chem})/RT]\ \exp[-\alpha\, zF(\bar{\varphi}_2 - \varphi_2)/RT]\ \exp[-zF\,(\varphi_2 - \varphi_s)/RT] \tag{65}$$

and

$$\overleftarrow{k} = \kappa\frac{kT}{h}\exp[-\Delta\overleftarrow{G}(\text{chem})/RT]\ \exp[-\alpha\, zF(\bar{\varphi}_2 - \varphi_2)/RT]\ \exp[-zF\,(\varphi_2 - \bar{\varphi}_s)/RT] \tag{66}$$

The equilibrium condition $\vec{i} = \overleftarrow{i}$ gives:

$$-\Delta\vec{G}(\text{chem}) = -\Delta\overleftarrow{G}(\text{chem}) + \frac{zF}{RT}\,(\bar{\varphi}_s{}^{eq} - \varphi_s{}^{eq}) + \ln[\bar{a}_s{}^{eq}/a_s{}^{eq}] \tag{67}$$

and allows the current to be written:

$$I = \overrightarrow{i} - \overleftarrow{i} = \underbrace{i^{0} \exp\left[-\frac{\alpha zF}{RT}(\overline{\varphi}_2 - \varphi_2) - \frac{zF}{RT}\varphi_2\right]}_{i^{0}(\text{apparent})} \left\{\exp\left[\frac{zF}{RT}(\varphi_s - \varphi_s^{eq})\right] - \exp\left[\frac{zF}{RT}(\overline{\varphi}_s - \overline{\varphi}_s^{eq})\right]\right\} \quad (68)$$

$$= zF\overrightarrow{k}(eq)\, a_s \exp\left[\frac{zF}{RT}(\varphi_s - \varphi_s^{eq})\right] - zF\overleftarrow{k}(eq)\, \overline{a}_s \exp\left[\frac{zF}{RT}(\overline{\varphi}_s - \overline{\varphi}_s^{eq})\right]$$

where i^0 (apparent) is the exchange current density – that value which flows simultaneously in opposite directions at zero current. This is the experimental value affected by inert salts and, although not shown, includes activity coefficients for the transition state. By rearranging into a symmetrical form, i^0 may be written:

$$i^{0} = \kappa\frac{kT}{h}(a_{eq}\,\overline{a}_{eq})^{1/2} \exp[-(\Delta\overrightarrow{G} + \Delta\overleftarrow{G})(\text{chem})/2RT] \exp[zF(\varphi_s^{eq} + \overline{\varphi}^{eq}/2RT] \quad (69)$$

Other relations follow:

$$\overrightarrow{k}^{0}(eq) = \overleftarrow{k}^{0}(eq) = k_0 = i^{0}(app)/zF \quad (70)$$

at unit activity where $a = \overline{a} = 1$

and at other activities:

$$\overrightarrow{k}(eq) = i^{0}(app)/zFa = k_0(\overline{a}/a)^{1/2} \quad (71)$$

and

$$\overleftarrow{k}(eq) = i^{0}(app)/zF\overline{a} = k_0(a/\overline{a})^{1/2} \quad (72)$$

The rate constants depend explicitly (and implicitly) upon potential according to:

$$\overrightarrow{k} = \overrightarrow{k}(eq) \exp[zF(\varphi_s - \varphi_s^{eq})/RT] \quad (73)$$

and

$$\overleftarrow{k} = \overleftarrow{k}(eq) \exp[zF(\overline{\varphi}_s - \overline{\varphi}_s^{eq})/RT] \quad (74)$$

A number of points concerning the exchange current density are clear from this derivation. Constant interfacial potential admits many values of a and $\overline{a}$ as long as their ratio remains constant. However, i^0 depends directly on $(a\overline{a})^{1/2}$. The apparent exchange current density can also be written:

$$i^{0}(app) = \kappa\frac{kT}{h} zF \exp[-\Delta\overrightarrow{G}(\text{chem})/RT + zF\varphi_s^{eq}/RT]\, a_{eq} \times f(\varphi_2, \overline{\varphi}_2)_{eq} \quad (75)$$

$$= \kappa\frac{kT}{h} zF \exp[-\Delta\overleftarrow{G}(\text{chem})/RT + zF\overline{\varphi}_s^{eq}/RT]\, \overline{a}_{eq} \times f(\varphi_2, \overline{\varphi}_2)_{eq}$$

$$= \exp(\tilde{\mu}_I^{eq}/RT + \text{constant}) = \exp(\overline{\tilde{\tilde{\mu}}}_{IV}^{eq}/RT + \text{constant})$$

Substituting into Equation 68 and expanding exponentials, net flux is given by:

$$J = \frac{\overrightarrow{i} - \overleftarrow{i}}{zF} = (\tilde{\mu}_I - \overline{\tilde{\tilde{\mu}}}_{IV})/RT = \frac{L}{R}\Delta\left(\frac{\tilde{\mu}}{T}\right) \quad (76)$$

which is the form predicated by irreversible thermodynamics. L is an Onsager coefficient. One can therefore conclude that the usual statement of equilibrium for charged species across an interface is indeed

$$\tilde{\mu}_i = \tilde{\tilde{\mu}}_i \quad (77)$$

and it is possible to show that as $i^0 \to \infty$, the potential difference across the interface approaches the equilibrium value.

The primary consequence of slow surface transport is the creation of a surface resistance which is different from an ordinary resistance in that it can be voltage dependent. However, for $(\varphi_s - \varphi_s^{eq}) < RT/zF$, linearization gives the surface resistance R surf. as:

$$\left(\frac{\partial\varphi_s}{\partial i}\right)_{i\to 0} = R_{surf} = \frac{RT}{zF\, i^{0}(app)} \quad (78)$$

In usual electrode kinetic measurements, one can control $\Delta\varphi_s$ at an interface and measure R_{surf}. In membrane electrochemistry, the whole membrane potential is controlled, with the result that

$$\left(\frac{\partial \Delta\varphi_m}{\partial_i}\right)_{i\to 0} = R_{surf\,1} + R_{surf\,2} + R_{bulk} \tag{79}$$

By varying the membrane thickness (R_{bulk}), the surface resistance sum can be found by extrapolation.[80]

To use kinetic-domain boundary conditions in membrane systems, one must speculate, based on experience from metal/electrolyte interfaces, that the overpotentials are additive.

In the linear regime ($|i| < i^o$), the interfacial potential of each interface includes the activation overpotential (first term) and the usual activity ratio term. Thus for the side "d" interface

$$\left|\varphi_d - \bar{\varphi}(d)\right| \sim \frac{RT|i|}{zFi^o(d)} + \frac{RT}{zF}\left|\ln\left[\frac{\bar{a}_i(d)}{a_i(d)K_{ext}}\right]\right| \tag{80}$$

$$= \frac{RT}{zF} = \left|\frac{J_i}{J_i^o}\right| + \frac{RT}{zF}\left|\ln\left[\frac{\bar{a}_i(d)}{a_i(d)K_{ext}}\right]\right|$$

Now $J_i^o = i^o/zF = k^o\left[a_i(d)\bar{a}_i(d)\right]^{1/2}$ for a symmetrical barrier. If the current is small enough that the membrane interior activity profile is not perturbed, then the total membrane potential is given by

$$|\Delta\varphi_m| = |\Delta\bar{\varphi}_m\,(\text{zero flux})| \tag{81}$$

$$+ \frac{RT|i|}{(zF)^2 k_o}\left\{\frac{1}{[a_i(d)\bar{a}_i(d)]^{1/2}} + \frac{1}{[a_i(0)\bar{a}_i(0)]^{1/2}}\right\}$$

It also seems possible that the zero current potential can be perturbed in asymmetric bathing solutions where equal and opposite fluxes of different ions are passing over barriers. For symmetrical barriers a transient, non-Nernstian response might be expected. Apparently this effect has been observed.[74,74a]

IV. THEORETICAL DESCRIPTIONS OF MEMBRANE TRANSPORT

A characteristic property of chemically inert membranes is their ability to affect the transport of material from one side to another. Consequently, the thrust of theoretical descriptions is interpretation or explanation of transport processes and the measured effects resulting from transport: pressure differences, temperature differences, activity differences, and potential differences developed across membranes and currents through membranes.

A. Irreversible Thermodynamic Approach

At the most general and abstract level, without regard to the structure or chemical features of a membrane, the flux of matter and energy can be found in terms of the "forces" due to a pressure, temperature, activity, or potential difference across thin (or differential) membranes. When the gross thermodynamic "forces" are written as:

$$X_k = -T\Delta(\tilde{\mu}_k/T);\ X_u = -\Delta(1/T) \tag{82}$$

the material flux for each species i = 1 through k is

$$J_i = \sum_k L_{ik}X_k + L_{iu}X_u \tag{83}$$

and the flux of energy is

$$J_u = \Sigma_k\, L_{uk}X_k + L_{uu}X_u \tag{84}$$

The proportionality factors between each partial flux contribution and the forces are the set of Onsager coefficients, which are equivalent to system response functions and:

$$L_{ik} = L_{ki};\ L_{iu} = L_{ui} \tag{85}$$

For a symmetric set of n equations with n forces, there are only ½n(n+1) independent coefficients, rather than n^2. These forces are not arbitrarily defined but are deduced from the general expression for entropy production (rate of change of the system entropy) as the system approaches equilibrium from an initial state not far from equilibrium. The theory of fluctuations underlies this approach, known as irreversible thermodynamics, and provides proof that the coefficients form a symmetric matrix. For membranes of finite thickness, those that contain continuously varying or distributed activities, fields, pressures, etc., the same type of analysis applies by replacing Δ's by grads. The result of the treatment gives in principle no new information about membrane phenomena. However, the Onsager reciprocal relations provide rigorous connections between the friction coefficients and between system responses under reciprocal (conjugate) conditions, i.e., Saxen relations such as the pressure differences arising from current flow, the current arising from a pressure difference, etc. But more important, this analysis demands recognition of interactions among fluxes. A startling result is the indirect dependence of membrane potential on uncharged solvent flux.

As a rule, the Onsager coefficients, or quantities related to them, are known for single forces: pressure, temperature, concentration, or potential differences. However, to obtain the symmetric form above, linear combinations or transformations of simpler fluxes are invariably needed. The new Onsager coefficients then become combinations of simpler coefficients. The power of irreversible thermodynamics is the ability to interpret the Onsager coefficients relating forces and fluxes in complex systems to the simpler friction coefficients. Some basic sources on the principles of transport in the context of irreversible thermodynamics are by DeGroot,[81] Katchalsky and Curran,[82] and Caplan and Mikulecky.[83] Newer volumes by Lakshminarayanaiah[22] and the edited volume by Hanley[84] cover key papers by major contributors in this field: K. S. Spiegler, A. Katchalsky, A. J. Staverman, D. C. Mikulecky, J. G. Kirkwood, K. A. Kraus and J. S. Johnson, U. Mertens, P. Meares, O. Kedem, A. Schmid, R. P. Rastogi, P. Mazur, J. Overbeek, and others. Of more recent interest are papers by Smit and Staverman[85] and Staverman[86] which justify irreversible thermodynamic analysis of membrane processes and relate friction coefficients to extraction parameters and Onsager coefficients. Vink[87] has reviewed the foundations, while Bennion and Rhee,[88] and Singh and Shukla[89] give theory for salt-water transport in semipermeable and completely nonselective membranes, respectively. Further theoretical examinations of the flow of solute and solvent through membranes are by Srivastava and Paul,[90] Simons,[91] and Mikulecky.[92] Friedman's[93] generalization of the Nernst-Planck equations to include interactions between oppositely charged ions uses the irreversible thermodynamic approach, as does a new analysis of osmosis and electrokinetic effects[94],[95] and the relation between Staverman's reflection coefficient, σ, and solute permeability.[96]

A most comprehensive experimental and theoretical treatment of transport across membranes using the irreversible thermodynamic analysis is that by Meares, Thain, and Dawson.[97] The outstanding quality of their work, which is essentially a review, is the systematic presentation of forms for the flux equations, choices of forces and fluxes in regard to ease in relating measured responses to Onsager coefficients, and relations of relative friction and Onsager coefficients. This work is emphasized here because it is written in the context of electrochemistry by specifically considering transport of ionic species through membrances containing fixed sites. Their analysis can be simplified to cover perhaps better known studies of nonionic transport through ordinary membranes without sites.

They advocate the procedure of reversion of the phenomenological equations in the form

$$X_k = \sum_i R_{ki} J_i \tag{86a}$$

which is closely related to the usual experimentally accessible friction coefficient models where

$$X_k = \sum_{i \neq k} f_{ki}(\vec{v}_k - \vec{v}_i) \tag{86b}$$

$$= (J_k/C_k) \sum_{i \neq k} f_{ki} - \sum_{i \neq k} J_i f_{ki}/C_i$$

The relative friction coefficients f_{ki} and f_{ik} are related by $C_k f_{ki} = C_i f_{ik}$. $\vec{v}$'s are velocities in the center of mass reference frame and f_{ik}/C_k and f_{ki}/C_i are forces between 1 mol of i and 1 mol of k at unit velocity difference. The second part of Equation 86b follows from the definition of a flux of a single species as a product of a local concentration and velocity.

At constant temperature, experimental values of zero current fluxes of salt and solvent are determined for unsymmetric bathing solutions. Electroösmotic flux of solvent is determined as are tracer diffusion coefficients. There are possibly eight items of data:

(1) electrical conductance
(2) ionic transport number
(3) electroösmotic flux
(4) salt diffusion flux
(5) volume or solvent osmotic flux
(6) counter ion tracer diffusion coefficient

(7) co-ion tracer diffusion coefficient

(8) volume flow under hydrostatic pressure difference

From experimental fluxes of species under a given single gross thermodynamic force, velocity terms are computed. The resulting matrix of unknown f values are solved using reciprocal relations and assumptions such as zero friction coefficient for tracer motion among ions of its own kind, zero friction coefficient for permselective ions interacting with matrix sites, or Spiegler's assumption that friction between cations and anions in a permselective ion exchanger membrane is zero. R_{ki} values are computed from f values using Equation 86b and L_{ki} values followed by matrix manipulations. Finally, expressions for conductivity and other measurable quantities can be expressed in terms of R's and L's.

Interpretation of L_{ki} in terms of local molecular processes is not direct. Even interpretation of L_{kk} is difficult because a single gross thermodynamic force X_k producing a flux J_k simultaneously affects all other J's. Presumably these indirect interactions can be unravelled by assuming that friction coefficients represent only interactions between a pair of flows.

There are two other major contributions of irreversible thermodynamics to membrane transport and all other systems involving diffusion and migration, viz., explicit recognition that material transport by diffusion-migration involves processes which operate with respect to the center of mass coordinate system and not to the laboratory or membrane coordinates. This fact means that, in general, there are not enough flux equations to specify the time course of a system and that some other assumption, such as an equation of state or Gibbs-Duhem equation, is also required. Almost as a corollary, transport of solvent cannot be ignored except in those cases where momentum transfer from charged particles moving in opposite directions happens to cancel the net force on the solvent. Generally, the existence of a field or pressure gradient within a membrane causes motion of solvent or membrane components, and this transport should be considered experimentally and theoretically. In the dilute solution limit, where the application of Fick's Laws is permissible, it is often assumed that the center of mass and laboratory coordinate systems coincide, and therefore the solvent can be considered to be fixed in space.

Even in model systems, the basic considerations of system transport can lead to complicated mathematical descriptions. The diversity in the theoretical forms for transport phenomena, which results from simplifications made by various authors, is a particular hazard to workers in this field.

The forms of the linear phenomenological equations can be derived from basic nonequilibrium statistical mechanics beginning with the equations of molecular dynamics. Bearman and Kirkwood[98] derived, quite generally, the important macroscopic hydrodynamic equations including steady state flux equations of species and time dependences (continuity equations) from averages over molecular distribution functions. Furthermore, they were able to express transport parameters in terms of molecular variables. The latter follow from calculation of perturbations in the distribution functions arising from departures from equilibrium. When the perturbations are assumed to be linear functions of temperature gradient and diffusion velocities, the equations of motion become identical with the linearized equations of irreversible thermodynamics.

B. Chemical Engineering Approach

Closely related methods used by theoretical chemical engineers to describe membrane transport are based on turning the Nernst-Planck equations of motion inside out. These equations, known as Stefan-Maxwell equations, account for the motion of the center of mass of the membrane system and remove a source of concentration dependence that measured diffusion coefficients will otherwise show when measured in a laboratory coordinate system. For each of n mobile species in one-dimensional flow,

$$-RT\frac{d\ln a_i}{dx} - z_i F\frac{d\varphi}{dx} - (v_i - 1/C_i)\frac{dp}{dx} \tag{87}$$

$$= \sum_{j=1}^{n} (RT/\mathcal{D}_{ij}x_j)(\vec{v}_i - \vec{v}_j)$$

$$= \sum_{j=1}^{n} (RT/D_{ij}C_i)(x_jJ_i - x_iJ_j)$$

where x_i is mole fraction, C_i is concentration, in mol/cm^3, v_i is partial molar volume, $\vec{v}_i$ and $\vec{v}_j$ are observable species velocities, J's are usual fluxes in laboratory coordinates, and *D*'s are Stefan-

Maxwell diffusion coefficients. These equations apply to closed systems, i.e., total mass of a system including bathing solutions and membrane remains constant. Considering a fixed membrane with sites designated as species 4, a simplification is found. $\delta_{i4} = 1\ i = 4; \delta_{i4} = 0\ i \neq 4$.

$$-RT\, d \ln a_i/dx - z_i F\, d\varphi/dx + (\delta_{i4}/C_i - v_i)\, dp/dx \tag{88}$$

$$= \sum_{j=1}^{n} (RT/D_{ij}C_i)(x_j J_i - x_i J_j)$$

Recent examples of this approach are reported in papers by Lightfoot[99] and Cussler.[100] A characteristic feature of this method, as with the entirely consistent irreversible thermodynamic approach, is the large number of transport parameters which take into account interactions among moving and static components.

C. "Activation Barrier" Kinetic Approach

A third type of theory treats transport processes as barrier controlled kinetic events occurring sequentially in space within the membrane. Thus, for a species at concentration $\bar{C}_i$ to cross one barrier, among many, of height $\overrightarrow{\Delta G}_i$ and width λ_i, the forward flux is expressed as a rate:

$$\vec{J} = k_f \bar{C}_i \lambda_i \qquad \text{mol/cm}^2\ \text{sec} \tag{89}$$

$$k_f = \kappa \frac{kT}{h} \exp(-\Delta \vec{G}_i/RT) \tag{90}$$

and the reverse process flux is similarly:

$$\overleftarrow{J} = k_b\, \bar{C}_{i+1}\, \lambda_{i+1} \tag{91}$$

$$k_b = \kappa \frac{kT}{h} \exp(-\Delta \overleftarrow{G}_i/RT) \tag{92}$$

For a simple case where $k_f = k_b$ and $\lambda_i = \lambda_{i+1}$ the next flux is

$$J = \vec{J} - \overleftarrow{J} = k_{f \text{ or } b}\, \lambda^2\, (\bar{C}_{i+1} - \bar{C}_i)/\lambda \sim D\, \partial\bar{C}/\partial x \tag{93}$$

For a series of barriers across which a continuous flux occurs, relations can be derived to express flux in terms of concentrations just inside the membrane surfaces. For n barriers of equal height and spacing,

$$J = \frac{\lambda k}{n} (\bar{C}_1 - \bar{C}_n) \tag{94}$$

Since

$$\lambda^2 k = D \text{ and } n\lambda = d \text{ (membrane thickness)} \tag{95}$$

one obtains the trivial result:

$$J = \frac{D}{d} (\bar{C}_1 - \bar{C}_n) = P' (\bar{C}_1 - \bar{C}_n) \tag{96}$$

where P' is the internal permeability. Considering the surface processes to be determined by rate constants $\vec{k}$ and $\overleftarrow{k}$, which must be assumed to be nonzero with their ratio, $\vec{k}/\overleftarrow{k} = K_{ext}$, the extraction coefficient (without regard for possible potential dependence), then in the steady state:

$$J = \vec{k}\, C_1 - \overleftarrow{k}\, \bar{C}_1 = \overleftarrow{k}\, \bar{C}_n - \vec{k}\, C_n \tag{97}$$

and

$$J = \frac{D}{d} \left(\frac{\vec{k}}{\overleftarrow{k} + 2D/d} \right) (C_1 - C_n) \tag{98}$$

The apparent overall permeability (in terms of external bathing concentrations) varies according to:

$$P = \frac{D}{d} \left(\frac{1}{K_{ext}} + \frac{2D}{d\, \vec{k}} \right)^{-1} \tag{99}$$

For a given K_{ext}, there are an infinite number of rate constant combinations. Writing from Equation 97 for one interface:

$$J = \vec{k}\, C_1{}^{eq} \left[\frac{C_1}{C_1{}^{eq}} - \frac{\bar{C}_1}{\bar{C}_1{}^{eq}} \right] \tag{100}$$

It is clear that large values of $\vec{k}$ and $\overleftarrow{k}$, consistent with K_{ext}, demand that the interfacial concentrations be nearly at equilibrium, even though flux is passing. This point has already been made above. In this model as well, when

$$J < \vec{k}\, C^{eq} = \overleftarrow{k}\, \bar{C}^{eq} \tag{101}$$

the perturbation of interfacial equilibrium by flux can be ignored. The result is the usual reversible interface permeability:

$$P = \frac{D}{d} K_{ext} \tag{102}$$

On the other hand, when $\vec{k}$ and $\overleftarrow{k}$ are very small compared with D/d, but still consistent with K_{ext}:

$$P = \vec{k}/2 \tag{103}$$

The interesting feature of this analysis, which was later improved and generalized to include flux limitation by external concentration polarization,[22] is that the unloading rate constant, $\overleftarrow{k}$, does not affect permeability. A small $\overleftarrow{k}$ at constant $\vec{k}$ simply means that the extraction equilibrium favors the membrane. It is easy to show that the surface fluxes are compatible with very small $\overleftarrow{k}$ since $\overleftarrow{k}\bar{C}$ will be of comparable magnitude with $\vec{k}C$ because $\bar{C} >> C$.

The advantage of the so-called "kinetic" analysis of membrane transport is that it provides an overview without the introduction of specific models for forces and system functions. On the other hand, new parameters are introduced which must be related to other better known quantities.

D. Phenomenological Equation of Motion Approach

The fourth, and most widely applied transport theory is based on the Nernst-Planck (N-P) flux equation.[14,15,22,101] In its most general form, it is consistent with irreversible thermodynamic flux equations and accounts for motion of pore liquid (solvent) as well as ions. Models are introduced into the N-P equation in the sense that the coefficients relating forces and fluxes are specified in conventional terms. Irreversible thermodynamic interactions (cross-terms) are omitted by assuming, for a membrane containing dissolved neutral and charged species, that the independent motion of each species occurs under local diffusive, electric field, and pressure gradient forces. Flux for each species of charge z_i is specified as the product of concentration and velocity, where the latter is proportional to the local force. Thus, at constant temperature,

$$J_i' = \bar{C}_i \vec{v}_i = \bar{C}_i \bar{f}_i \Sigma \text{ forces} \tag{104}$$

is the flux with respect to the center of mass; f_i is a friction (proportionality) coefficient, and $\bar{C}_i$ is a local concentration. Relations with other transport coefficients are

$$RT \bar{f}_i = \bar{u}_i RT = \bar{D}_i = \bar{u}^* RT/F|z_i| \tag{105}$$

where $\bar{D}_i$ = cm^2/sec; $\bar{u}_i^*$ = cm/sec/$\underset{\approx}{V}$/cm; and $\bar{u}_i$ = cm^2/sec J/mol. The forces are grad $\bar{\mu}_i$ and $\bar{v}$ grad $\bar{p}$. By Schlögl's method[102] for transport in one direction in the laboratory coordinate system, a single ion flux may be written out as:

$$\bar{J}_i = \bar{C}_i \vec{v}_w - \bar{D}_i \left[\frac{\partial \bar{C}_i}{\partial x} + \bar{C}_i \frac{\partial \ln \bar{\gamma}}{\partial x} + z_i \frac{F}{RT} \bar{C}_i \frac{\partial \bar{\varphi}}{\partial x} + \frac{\bar{C}_i}{RT}\left(\bar{v}_i - \frac{M_i}{M_w} \bar{v}_w\right) \frac{\partial \bar{p}}{\partial x}\right] \tag{106}$$

where

$$\vec{v}_w \sim d_w \left(\bar{\omega} F \bar{X} \frac{\partial \bar{\varphi}}{\partial x} - \frac{\partial \bar{p}}{\partial x}\right) \tag{107}$$

is the solvent transport velocity for a membrane containing sites.

An alternate derivation of the ionic flux, including water transport, in the laboratory coordinate system follows from Bearman and Kirkwood[98] and Vaidhyanathan and Perkins.[103] This derivation was given by Conti and Ciani.[104]

For each ion, including mobile sites,

$$-\frac{d \tilde{\bar{\mu}}_i}{dx} - \sum_{k=1}^{n} f_{ik} \bar{C}_k \left(\frac{\bar{J}_i}{\bar{C}_i} - \frac{\bar{J}_k}{\bar{C}_k}\right) - f_{iw} \bar{C}_w \frac{\bar{J}_i}{\bar{C}_i} = 0 \tag{108}$$

where f_{ik} are the relative friction coefficients and w stands for water. The condition for water flux being zero is

$$-\frac{d \bar{\mu}_w}{dx} + \sum_{k=1}^{n} f_{wk} \bar{J}_k = 0 \tag{109}$$

The electrochemical potential does not include local pressure, but the latter is included through the equation of state (isothermal Gibbs-Duhem equation):

$$\bar{C}_w d \bar{\mu}_w + \sum_{i=1}^{n} \bar{C}_i d \bar{\mu}_i - dP = 0 \tag{110}$$

From the electroneutrality condition, they deduce that the pressure is independent of distance. By disregarding all terms not multiplied by $\bar{C}_w$, because $(\bar{C}_i/\bar{C}_w) < 1$, the results are found:

$$-\frac{d\overset{\approx}{\mu}_i}{dx} - f_{iw}\bar{C}_w\frac{\bar{J}_i}{\bar{C}_i} = 0 \tag{111}$$

and

$$-\frac{d\overset{\approx}{\mu}\,(\text{sites})}{dx} = 0 \tag{112}$$

Writing

$$\bar{u}_i RT = \bar{D}_i = \frac{1}{f_{iw}\bar{C}_w} \tag{113}$$

and

$$\bar{C}_i = \frac{\bar{x}_i}{\bar{v}_i} \tag{114}$$

the usual dilute solution form of the N-P equation is found:

$$\bar{J}_i = -\bar{u}_i RT\bar{C}_i\frac{\partial\overset{\approx}{\mu}_i}{\partial x} \tag{115}$$

To use this equation for the transport of each species in developing equations for total flux, current, and membrane potentials, simplifications are usually made:

1. Activity coefficients are assumed to be either *constant* or *simple functions of concentration*, i.e., $\bar{\gamma} = \bar{C}^{n-1}$, so that integration becomes possible.
2. Transport of solvent is ignored, as are pressure effects on the transport of other species.

Thus, the simplified N-P equation for a single ion is

$$\bar{J}_i = -\bar{D}_i\frac{\partial\bar{C}_i}{\partial x} - z_i\frac{\bar{D}F}{RT}\bar{C}_i\frac{\partial\bar{\varphi}}{\partial x} \tag{116}$$

This form is the usual starting place for calculation of concentration, field, and potential profiles within a membrane. Current densities in the absence of interactions between species, viz., ion pairing, etc. are given by:

$$I = F\sum_i z_i\bar{J}_i - \epsilon\frac{\partial^2\bar{\varphi}}{\partial x\partial t} \tag{117}$$

Time dependences follow from the continuity condition:

$$\frac{\partial\bar{C}_i}{\partial t} = -\frac{\partial\bar{J}_i}{\partial x} \tag{118}$$

The second term Equation 117 is a form of Poisson's equation,

$$\frac{d\bar{E}}{dx} = \frac{\rho}{\epsilon} = zF(\bar{C}_+ - \bar{C}_-) \tag{119}$$

which accounts for space charge build-up at the surface due to current flow. Recent papers by Macdonald[105-110] stress the importance of the latter term in accounting for short-time charging processes. Use of the N-P equations in steady state uniform (constant composition) electrolytes leads to all of the classical transport relations. These are summarized in Table 2.

Immediately after the original publications of Planck and Nernst, application of the Nernst-Planck equation was taken up by a few workers in membrane and electrolyte theory. These early results of Behn and Pleijel[20,22] are generalizations of the Planck constrained junction integration which give species fluxes in terms of interior diffusion potential difference and interior surface concentrations. The significance and limitations of the Nernst-Planck equations have only been widely recognized after many systems had been described and experimentally tested. The results of Behn and Pleijel apply not only to liquid junctions but also to site-free membranes which transport ions of both signs. However, their results do not necessarily give complete solutions for total membrane potentials since the interfacial component must be added.

Several milestones in the application of the standard form of the N-P equation and in the interpretation and modification of the N-P equation must be mentioned. The first is an integration to give membrane potentials in terms of external ionic activities, the historic Teorell-Meyer-Sievers

TABLE 2

Derived Quantities in Uniform Electrolyte Solutions of a Single Salt*

Salt $M_{|z_a|}X_{z_c}$ at concentration C_S (mol/cm^3)

Ionic concentrations

$C_+ = |z_a|C_S$ mol/cm^3

$C_- = z_cC_S$ mol/cm^3

Equivalent concentrations

$C_+' = z_c|z_a|C_S$ equiv./cm^3

$C_-' = |z_a|z_cC_S$ equiv./cm^3

Steady currents and specific conductivity σ(ohm cm)$^{-1}$

$$I = \frac{F^2}{RT}\{D_+z_c{}^2C_+ + D_-z_a{}^2C_-\}\frac{d\varphi}{dx} = \sigma\frac{d\varphi}{dx}$$

$$I = F^2[u_+z_c{}^2C_+ + u_-z_a{}^2C_-]\frac{d\varphi}{dx}$$

$$I = F[u_+{}^*z_cC_+ + u_-{}^*z_aC_-]\frac{d\varphi}{dx}$$

Conductance: $\sigma A/d$
Conductance for 1 eq/liter ($C_+' = C_-' = |z_a|z_cC_S = 10^{-3}$ mol/cm^3)

$$\sigma' = \frac{\sigma}{10^3C_+'} = \frac{\sigma}{10^3C_-'} = \frac{F^2}{10^3RT}[D_+z_c + D_-|z_a|]\ (\text{ohm cm eq/liter})^{-1}$$

Equivalent conductance Λ for a cell spacing 1 cm, area 1000 cm^2

$$\Lambda = 1000\sigma' = \lambda_+ + \lambda_- = \frac{F^2}{RT}[D_+z_c + D_-|z_a|]\ (\text{ohm eq./liter})^{-1}$$

$$\sigma = \Lambda C_+' = \Lambda C_-' = \Lambda^\circ C_+'\gamma_+ = \Lambda^\circ C_-'\gamma_-$$

Transference numbers

$$t_+ = \frac{D_+z_c{}^2C_+}{D_+z_c{}^2C_+ + D_-z_a{}^2C_-} = \frac{D_+z_c}{D_+z_c + D_-|z_a|} = \frac{\lambda_+}{\Lambda}$$

$$t_- = \frac{D-z_a{}^2C_-}{D_+z_c{}^2C_+ + D_-z_a{}^2C_-} = \frac{D_-|z_a|}{D_+z_c + D_-|z_a|} = \frac{\lambda_-}{\Lambda}$$

*In some literature a salt is described as $M_{\nu m}X_{\nu x}$ where ν_m and ν_x are dimensionless numbers. However, since $\nu_x = z_c$ and $\nu_m = |z_a|$, the extra nomenclature has been deleted. z_c and z_a should be considered dimensionless in the definition of C_+ and C_-.

Equation (69a-f), which describes the membrane potential for an ion exchanger membrane bathed in uni-univalent electrolyte of different activities. Their result includes the site concentration specifically and allows for co-ion transport. It covers the range from high site density, permselective membranes to site-free membranes. No account is taken of possible solvent transport. Subsequently, Scatchard[110a] derived an expression for the membrane potential, again for uni-univalent electrolytes, which included an integral involving transport of solvent.

The most extensive study of techniques, based on Pleijel's procedure, for integration of the standard Nernst-Planck equation system applicable to liquid junctions and ion exchange membranes is by Schlögl.[110b] His integration procedure gives the diffusion potential in terms of fluxes and interior surface concentrations, and it gives fluxes in terms of interior diffusion potential and interior surface concentrations, without consideration of solvent transport. The method, while complicated, is quite general and applicable to systems involving ions of various charges. Simplifications are possible when ions fall into monogroups, all ions have the same absolute charge. His subsequent papers are concerned with solutions for species flux, diffusion potentials, and current-voltage curves when solvent transport is included in the modified Nernst-Planck equations.[110c–g]

1. Strategy in Using Nernst-Planck Equations of Motion

The classical strategy in using these transport equations in membrane systems where the electrolyte concentration is not uniformly distributed is based on a few principles:

1. Problems are subdivided in advance according to the time domain, transient or steady state; according to flux conditions, zero species flux, finite species flux but zero total flux (zero current), or nonzero current cases; and according to the number of neutral and charge carrying species present in the membrane.

2. Flux equations for species in a membrane are integrated to express individual or total flux and current in terms of concentrations or activities just inside the space charge regions or at the inside surfaces — depending on the assumptions of quasi-electroneutrality or Poisson's equation for coupling the individual fluxes. In the steady state for ions of the same absolute charge, quasi-electroneutrality leads to the conclusion that the sum of cation concentrations (and the equal sum of anion concentrations) is linearly distributed in space for site-free membranes. For high site concentrations (permselectivity), the sum of counter ion concentrations equals site concentration. Sites, if mobile, are also linearly distributed. On the other hand, use of Poisson's equation leads to virtually intractable mathematical problems unless, as is frequently done, the electric field is taken to be constant.

3. Flux equations for species in the bathing solutions are similarly solved (usually for semi-infinite boundary conditions) in terms of bulk activities and activities at or near the surface of the membrane on the solution side of the interface.

4. Potential differences are calculated across each phase in terms of flux or current and the surface activities. Boundary conditions may be reversible (equilibrium domain), and interfacial potentials may be computed provided the calculation is done by equating the electrochemical potentials of those ions which actually equilibrate across the interface. For irreversible or slow interfacial kinetic cases (kinetic domain), interfacial potentials may be computed according to the methods above or the more recent barrier models.[74] Total membrane potentials as functions of bulk activities in the bathing solutions, flux, or current are found by summing the potentials from known points as described in Equation 18 or 19.

5. Time dependent problems including responses of membranes to changes in external or internal activities, applied voltages, pressure steps, etc. are occasionally solvable analytically depending on the linearity of the problem. Membrane transport problems involving a multiplicity of cations and anions (without considering interactions) are already intrinsically nonlinear simply because of the occurrence of terms in which $\bar{C}_i$ is multiplied by the local electric field (or pressure gradient), which is itself concentration dependent through Poisson's equation. Even steady state problems, including Poisson's equation, are not generally solvable because of cubed field terms.[53,111] Note that the steady state single ion problem is solvable because the field equation can be converted to a known form.[64]

Linearization becomes possible when individual fluxes are small enough that the forces are themselves linear in the Onsager sense. This is a more restrictive condition than requiring a small net flux or current. Thus, problems involving minimal concentration profile changes, i.e., systems not far from steady state profiles (equivalent to interior potential changes less than RT/z_iF V), can be solved for all times. Problems involving major readjustments of concentration profiles with time are not usually solvable analytically. However, certain calculations, including determination of impedance frequency spectra (responses to small, sinusoidal voltages), can be accomplished for various dc profiles corresponding to dc voltage biases.[112,113] When the dc solution is known or approximated, superposition of the ac response on the dc response in the form

$$\varphi = \varphi_{DC}(x) + \varphi(x)\exp(j\omega t) \tag{120}$$

is useful for finding the impedance, after ignoring higher order terms (harmonics). Solutions are applicable at all frequencies greater than the relaxation time for the dc processes.

Linearized problems with minimal species profile reorganization over all times can also be handled by imposing a net constant flux (current) from which membrane potentials can be calculated as functions of time via Equation 18 or 19. By ordinary Laplace transformation and the operational definition of impedance, i.e., a general Fourier transform, the frequency response of voltage and the impedance can be found. Working backwards, time responses of current for various applied voltage wave forms can be computed.

6. Coupling of homogeneous diffusion and chemical reaction is a process frequently encountered in electrodiffusion systems in solvents of low dielectric constant. These problems are handled by grouping the flux equations according to the coupling and using the chemical equilibrium constants as remaining conditions on the systems. Thus, for a cation i^+ and an anion x^-, a neutral carrier complexing agent "s" forms the species is^+ and isx with equilibrium constants

$$K_{is} = \frac{(\overline{is}^+)}{(i^+)(\bar{s})};\ K_{isx} = \frac{(\overline{isx})}{(\overline{is}^+)(\bar{x}^-)} \tag{121}$$

Individual flux equations are grouped[114]

$$J_i^* = J_i + J_{is^+} + J_{isx} \tag{122}$$

$$J_s^* = J_{is^+} + J_{isx} + J_s$$

$$J_x^* = J_x + J_{isx}$$

The time dependences follow from continuity equations which now include local sources and sinks. For example:

$$\frac{\partial \bar{C}_i}{\partial t} = -\frac{\partial \bar{J}_i}{\partial x} + \bar{k}_{is}^b \bar{C}_{is} - \bar{k}_{is}^f \bar{C}_i \bar{C}_s \tag{123}$$

$$\frac{\partial \bar{C}_{is}}{\partial t} = -\frac{\partial \bar{J}_{is}}{\partial x} + \bar{k}^f_{is} \bar{C}_i \bar{C}_s - \bar{k}^b_{is} \bar{C}_{is} \tag{124}$$

$$+ \bar{k}^f_{isx} \bar{C}_{isx} - \bar{k}^b_{isx} \bar{C}_{is} \bar{C}_x$$

One has a similar equation for the rate of change of $\bar{C}_{isx}$. Note that the divergence of the grouped fluxes leads to cancellation of the chemical rate terms. On this basis, carrier mediated transport is most readily analyzed.[32,70,114-119] This procedure is generally used for problems involving transport with chemical reactions.[120-126] For example, in dealing with liquid ion exchanger membranes containing trapped anion sites x^-, and permeable cations i^+ and j^+, both of which form neutral ion pairs ix and jx, grouping of fluxes gives

$$J_i^* = J_i + J_{ix} \tag{125a}$$

$$J_j^* = J_j + J_{jx} \tag{125b}$$

$$J_x^* = J_x + J_{ix} + J_{jx} \tag{125c}$$

At any time, the current is carried internally by i^+, j^+ and x^- so that

$$I = F(J_i + J_j - J_x) = F(J_i^* + J_j^* - J_x^*) \tag{126a}$$

However, at the surfaces, J_x^* must be zero since species containing x do not pass the interface, although none of the flux components of J_x^* need be zero. This result means that externally measured current is determined by fluxes of both cations and neutral species through the surfaces. This statement is not true inside the membrane until the steady state is reached when J_x^* is zero everywhere and

$$I = F(J_i^* + J_j^*) \tag{126b}$$

This result is similar to the polarographic case for reduction of labile complexes. Current is carried by all species containing the reducible ion, regardless of the charge on the species.

2. Observations on the Solutions of Steady State Nernst-Planck Flux Equations and the Specification of System Variables

In the steady state, assuming activity coefficients and standard chemical potentials to be independent of distance and ignoring osmotic effects, the general transport problem is specified by:

1. N-P flux equations for each ion
2. Poisson's equation
3. Charge balance q(soln 1) + q(soln 2) + $\bar{q}_m$ = 0
4. Boundary conditions relating internal surface activities to external and/or bulk solution activities (Equations 37a, 40, 45, and 50 for reversible cases)
5. I = sum over partial currents for each contributing mobile cation, anion and complex according to appropriate equations such as 117 or 126b.

For a typical problem involving two species, i^{+z} and x^{-z}, the system becomes entirely specified when given electroneutral bathing solutions where E (x→ ±∞) = 0 (no current) or constant (with current). Nevertheless, the problem is not easily solved for the field and membrane potential because of mathematical difficulties arising from the nonlinear field equations. Direct integration of an N-P equation, regardless of the field profile, and applicable at all times gives:

$$C_+(x) = \exp\left\{\frac{zF}{RT}[\varphi(0) - \varphi(x)]\right\} \left\{ C_+(0) - \int_0^x \frac{i_+}{D_+zF} \exp\left\{-\frac{zF}{RT}[\varphi(0) - \varphi(x)]\right\} dx \right\} \tag{127}$$

and

$$C_-(x) = \exp - \frac{zF}{RT}[\varphi(0) - \varphi(x)] \left\{ C_-(0) + \int_0^x \frac{i_-}{D_-zF} \exp\left\{\frac{zF}{RT}[\varphi(0) - \varphi(x)]\right\} dx \right\} \tag{128}$$

since

$$E = -\frac{d\varphi}{dx} \tag{129a}$$

$$D_+ = u_+RT \tag{129b}$$

and

$$D_- = u_-RT \tag{129c}$$

At zero current, $i_+ = i_-$, $C_+(x)$ and $C_-(x)$ are correlated by eliminating i_+ from each equation. Furthermore, when $i_+ = i_- = 0$, as in a blocked electrode situation, the general solution for cations of charge z_c and anions of charge z_a is

$$[C_+(x)]^{1/z_c}[C_-(x)]^{1/|z_a|} = \text{constant} \tag{130}$$

In general, from Equations 127 and 128 for the problem at hand,

$$C_+(x)\,C_-(x) = \text{constant} + f(i_+, i_-, \varphi(0) - \varphi(x)) \tag{131}$$

where the latter term is zero when $i_+ = i_- = 0$. Solutions to the N-P equation always admit space charge. In fact, the N-P equation for zero partial currents is a version of the Poisson-Boltzmann equation from which the Gouy-Chapman theory is derived.

The steady state flux or current for any species is expressed in surface concentrations by rearranging and writing:

$$\xi = \exp\left\{\frac{zF}{RT}[\varphi(d) - \varphi(0)]\right\} \tag{132}$$

or

$$\Delta\bar{\varphi}_m = \frac{RT}{zF}\ln\xi \tag{133}$$

$$\frac{i_+}{D_+zF} = \frac{C_+(0)/\xi - C_+(d)}{\xi^{-1}\int_0^d \exp\left\{-\frac{zF}{RT}[\varphi(0) - \varphi(x)]\right\} dx} \tag{134}$$

$$\frac{i_-}{D_-zF} = \frac{C_-(d) - C_-(0)\,\xi}{\xi\int_0^d \exp\left\{\frac{zF}{RT}[\varphi(0) - \varphi(x)]\right\} dx} \tag{135}$$

By combining Poisson's equation with the N-P equations to eliminate concentrations, the general field equation for two ions i^{+z} and x^{-z} is

$$\frac{d}{dx}\left\{\frac{\epsilon}{E}\quad\frac{d^2E}{dx^2}+\frac{(zF)^2\epsilon}{2(RT)^2}E^2 \right. \tag{136}$$

$$\left. -\frac{zF}{RT}\left(-\frac{i_+}{D_+}+\frac{i_-}{D_-}\right)x+\left(\frac{i_+}{D_+}+\frac{i_-}{D_-}\right)\frac{1}{E}\right\}=0$$

When only one ion exists in the membrane, $i_- = 0$ and $\overline{C}_- = 0$, and the derivation leads to a simpler equation:

$$\epsilon\frac{d^2E}{dx^2}-\frac{zF\epsilon}{RT}E\frac{dE}{dx}+\frac{i_+}{D_+}=0 \tag{137}$$

which integrates to:

$$\frac{dE}{dx}-\frac{zF}{2RT}E^2+\frac{i_+x}{\epsilon D_+}=\text{constant} \tag{138}$$

and is the starting point for DeLevie and Moriera.[64] Equation 136 transforms into a Painleve transcendent which can be given asymptotic solutions[53,111] but cannot be solved in general; one such asymptotic solution for low fields and finite currents is found by setting the last two terms in Equation 136 equal to a constant. Integration gives a potential $\overline{\varphi}(x)$ which is logarithmic in distance. The solution for $\Delta\overline{\varphi}_m$ contains a constant of integration as well as terms in i_+ and i_-. Solutions must be consistent with those determined from $i_+ + i_- = 0$ using Equations 127, 128, 134, and 135. This procedure has not led (and probably cannot lead) to useful results except for limiting cases.

Barry and Diamond[127] have presented an analysis of site free membranes for two permeable ions of opposite charge which takes into account all of the principles laid down above. Their treatment, however, is limited to symmetric bathing solutions in which the flux of each species is zero. Thus, instead of solving the general Equation 136, they have only the first two terms for determination of the static field. The solution is, of course, the two-sided Gouy-Chapman solution known since at least 1954.[127a] Their results are interesting and are illustrated in Figures 11 to 14 for charged membranes which prefer cations but do not exclude anions.

The approximation usually made in dealing with Equation 136 assumes a constant field within a site free membrane. This assumption is valid when no net charge resides in the membrane. However, that condition can be approximated at zero current either

1. by equal local concentrations of cations and anions, but varying total salt concentrations across the interior of a membrane for salts with equal mobility ions of both signs and same absolute charges;
2. by equal total concentration of unequal mobility ions of both signs and same absolute charges across the interior of a membrane. This case differs from Item 1 in that different ions may exist on the two sides and their individual profiles are varying, but the total salt concentrations are constant throughout;
3. or by single-ion containing membranes (or unequal concentrations of oppositely charged ions) at sufficient dilution that the membrane thickness is small compared with the Debye thickness.[25,128-136]

Ordinarily, thick, site free membranes will contain equal concentrations of ions in the bulk as in Item 1, but may not show overall constant fields because of space charge which accumulates at the surfaces due to unequal ion extraction coefficients. This point is discussed in more detail later. For membranes with fixed and mobile sites, electroneutrality will be obeyed in the bulk but the field will be only approximately constant. Again, field curvature occurs at the surfaces where space charge exists.

Constancy of field is a stronger electroneutrality condition than quasi-electroneutrality because solutions for the potential-distance profile found by inserting quasi-electroneutrality into the transport equations are logarithmic functions of distance. Calculation of fields shows they are not constant and that space charge density is nonzero but very small. This paradox of quasi-electroneutality is well known in electrochemical literature.[14,101] Although the general problem of mass transport of charged species through site free membranes (covering the entire composition range from pure space charge to electroneutral in the bulk) is difficult, a number of workers have made important contributions. In addition to References 53, 64, 111, and 127 to 136, papers by

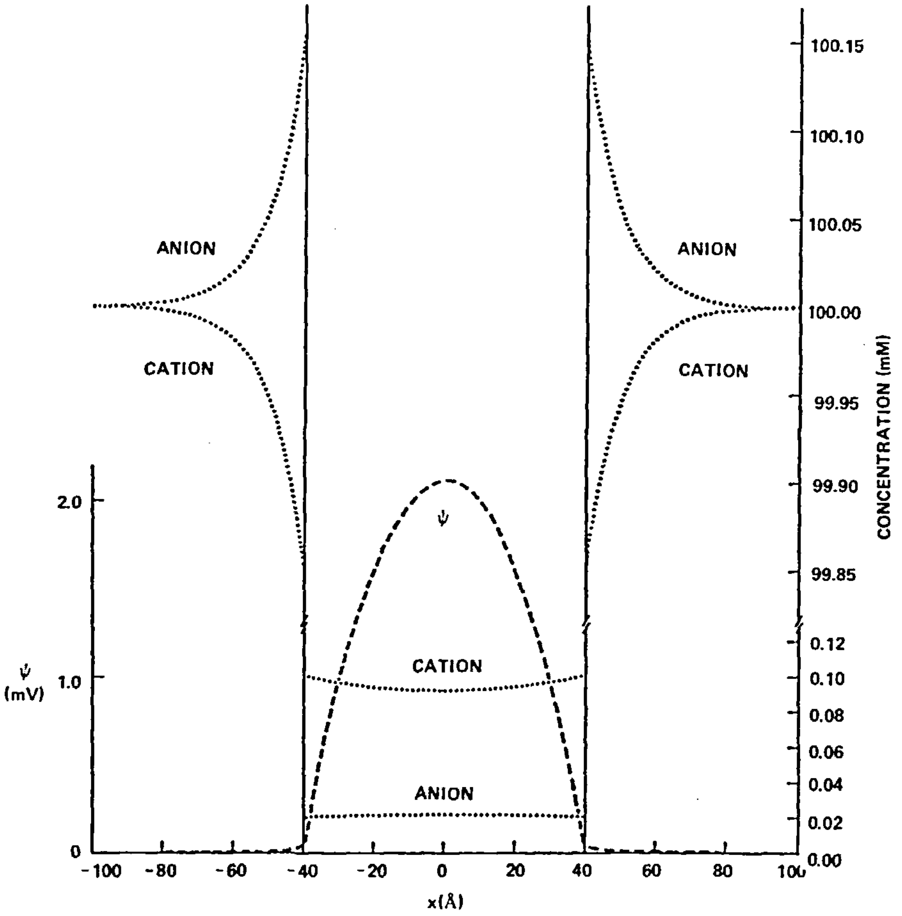

FIGURE 11. Calculated potential profile (dashed line) and concentration profiles (dotted lines) in a thin membrane charged with unequal amounts of cations and anions, as a function of x, the distance in angstroms from the center of the membrane. The membrane thickness d is 80 A, so that absolute distances greater than 40 A correspond to the bathing solutions. The cation extraction coefficient K_{ext^+} is 1×10^{-3}; the anion extraction coefficient K_{ext^-} is 2×10^{-4}. Bathing solution concentration of extracting salt is 100 m*M*, the temperature is 20°C and the dielectric constants of water and membrane are taken to be 80 and 3 times the permittivity of free space. The calculated Debye thickness is 76.1 A in the membrane and 9.6 A in aqueous solution. The figure has been condensed by interrupting the concentration axis between 0.12 and 99.85 m*M*. No boundary potential due to dipoles has been included so that the electrostatic part of the interfacial potentials is attributable to space charge. Total membrane charge is compensated within 5% by the external charge. (From Barry, P. H. and Diamond, J. M., *J. Membrane Biol.*, 4, 295 (1971). With permission.)

Tredgold[137] and Buysman and Koide[138] are significant.

Solutions for interior membrane potentials of permselective membranes with regions of internal electroneutrality take a special block logarithmic form, i.e., potential is a log ratio of the sums of the concentrations of ions just inside the space charge regions. The sums contain multiplication factors (permeabilities) for each of the membrane concentrations and the denominator contains concentrations for the opposite side. This fact has great importance in finding complete solutions for the total membrane potential and distinguishes Goldman-type solutions from Conti-Eisenman solutions. In the former, the charge balance at each interface must be used to obtain interfacial potentials. In the latter, interfacial potentials from Equation 37a can be added via Equations 18 and 19 without knowledge of the space charge. Thus, for permselective membranes, the total membrane potential is independent of the space charge on the two sides.

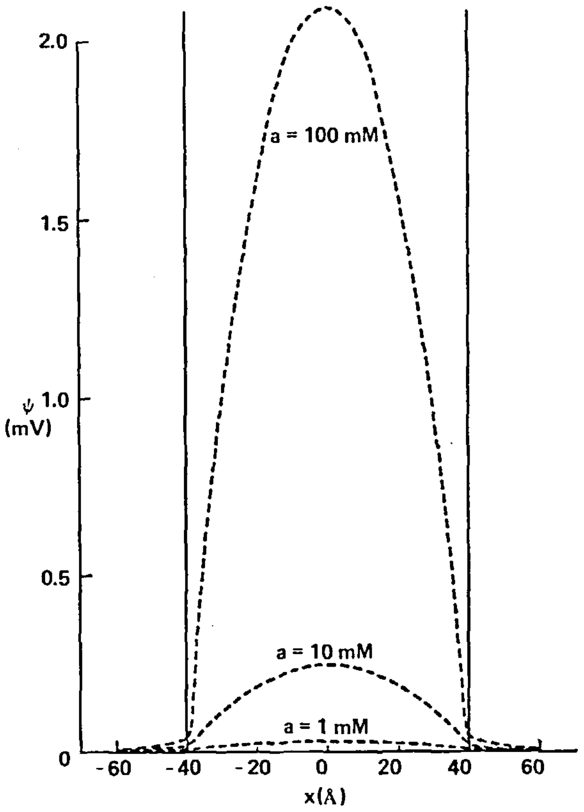

FIGURE 12. Potential profiles in a thin membrane as a function of bulk bathing solution concentration. Membrane thickness and extraction coefficients are the same as used in Figure 11. Symmetric bulk bathing solution concentrations are 1, 10, and 100 m*M*. The Debye thicknesses inside are 761.3, 240.7, and 76.1; outside values are 96.3, 30.5, and 9.6 Å for the sequence of concentrations listed. (From Barry, P. H. and Diamond, J. M., *J. Membrane Biol.*, 4, 296 (1971). With permission.)

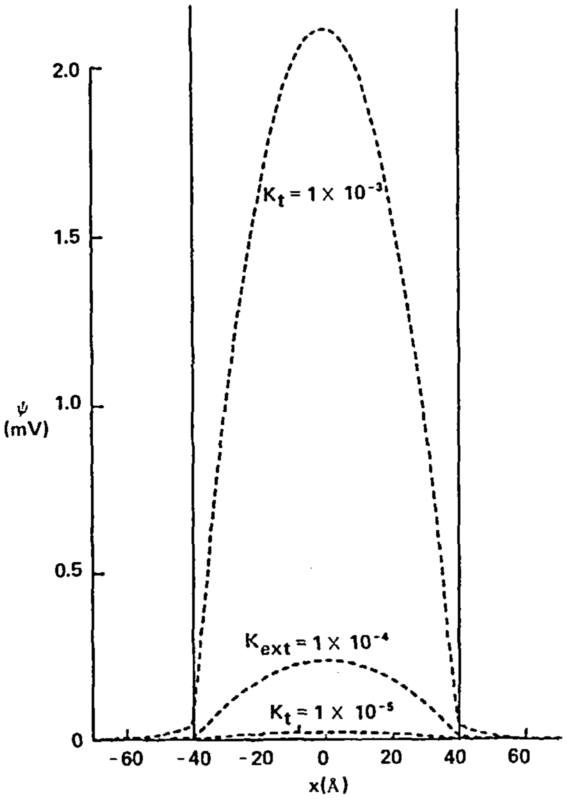

FIGURE 13. Potential profiles in a thin membrane as a function of single ion extraction coefficients. The membrane thickness is the same as in Figures 11 and 12. Bathing solution concentration of extractable ions is 100 m*M*. Cation extraction coefficients $K_{ext^+} = 1 \times 10^{-5}$, 1×10^{-4}, and 1×10^{-3} and the anion extraction coefficients are $0.2K_{ext^+}$. (From Barry, P. H. and Diamond, J. M., *J. Membrane Biol.*, 4, 295 (1971). With permission.)

V. REFERENCE CATALOGUE OF STEADY STATE SOLUTIONS TO NERNST-PLANCK EQUATIONS

Steady state, time independent solutions of the N-P equations can best be organized according to three types of membranes: Class I – site free membranes, Class II – fixed sited membranes, and Class III – mobile site membranes. These categories with major subdivisions and examples are given in Table 3. This organization is a natural consequence of the number of ions involved in the transport and the site characteristics.

A. Electrical Properties of Class I – Site Free Membranes

Homogeneous membranes containing no carriers belong to the insulator family. Conducting species normally do not exist in the membranes, and interfacial equilibrium is generally not possible. The usual conducting species are electrons and holes which can be brought into the material from external solution by redox surface reactions, by thermal generation, and by electromagnetic generation. Potential dependent surface rate parameters are usually used, and frequently only the field term in the N-P equations is considered to be the driving force. The best reference source is the book by Lampert and Mark.[39] A recent paper by Silver[140] investigates the effect of diffusion on the migration of charge in insulators (i.e., considers the whole N-P equation).

Liquid insulator membrane transport has received a great deal of attention because of the availability of lipid bilayer membranes.[141,142] These membranes permit transport of oil soluble

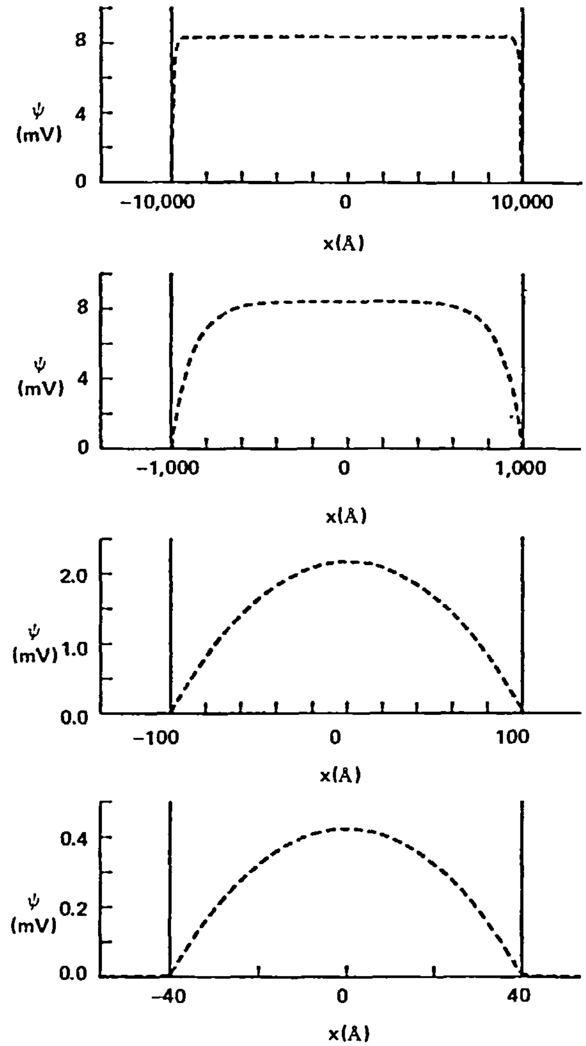

FIGURE 14. Potential profiles in a thin membrane for four thicknesses: 20,000, 2,000, 200, and 80 Å in the top, upper-middle, lower-middle, and lower curves. Cation extraction coefficient is 2×10^{-4} and the anion coefficient is 1×10^{-4}. The bathing solution concentration of salt is 150 m*M*. The calculated Debye thickness inside is 124.3 Å and outside is 7.9 Å in all cases. (From Barry, P. H. and Diamond, J. M., *J. Membrane Biol.*, 4, 295 (1971). With permission.)

ions which may be cations, anions, or both. For equilibrium extractable ions of one kind, DeLevie and co-workers[64] provide the most comprehensive treatment. N-P equations, with Poisson's equation, are solved directly for the internal field, then for potential, and finally for concentration profiles. By adding reversible interfacial potentials, the entire membrane potential has been computed. The zero current membrane potential is Nernstian, i.e.,

$$\Delta\varphi_m = \frac{RT}{zF} \ln\left[\frac{a_{left}}{a_{right}}\right] \tag{139}$$

They have also given exact solutions for steady state current-voltage characteristics,[65] concentration, and field profiles as functions of current. Reduced dimensionless parameters are used for generality, and the results prove to involve Bessel functions "J" and "I" of order 2/3, 1/3, -1/3 and -2/3. Three cases occur for (is + A) $\gtrless$ 0 because the differential equation

$$\frac{dE}{ds} + \frac{E^2}{2} = is + A \tag{140}$$

(E(s) = field, i = current, s = distance – all are reduced parameters) admits different mathematical forms depending on the sign of this quantity. "A" is an integration constant which is ultimately known in terms of external ion activities and current. For small deviations in applied potential around the potential of zero current, the current response is linear, i.e., the membrane conductance is constant. For large applied potentials, $\Delta\bar{\varphi} > RT/z.F$, the current-voltage curve remains nearly linear (constant conductance) for identical bathing solutions but are nonlinear for asymmetric external concentrations of a given permeable ion. For low concentrations such that the membrane thickness is small compared with the Debye thickness, the field is constant and approximations using constant field are applicable. Computed zero current results are illustrated in Figures 15 to 18. Finally, DeLevie and Seidah[143] have completed the N-P analysis by including film diffusion (external concentration polarization) and surface kinetics. The concentration polarization calculations were done first with the classical, quasi-electroneutral assumption and were then modified to include the increased (or decreased) surface concentrations due to natural space charge arising from fixed surface charge. Surface kinetics were treated assuming potential independent surface rate constants and an overall potential dependent rate due to the space charge perturbed surface concentrations. The fact that overall conductance is affected by external surface ionic concentrations, which are different from the bulk values, was specifically studied by McLaughlin, Eisenman, et al.[72,144,145] and Neumcke.[146]

Previously, Laüger and co-workers, who favor

TABLE 3

Passive Ion Conducting Membrane Classification

- Class I – Site free membranes
  - A. Nonporous homogeneous solids
    - Organic crystals, insulators, polymer films, uncharged lipid bilayers, bilayers containing neutral carriers,
  - B. Nonporous heterogeneous solids
    - Polyvinyl chloride and other films containing organic solvents and solvents with neutral carriers
  - C. Nonporous liquids
    - Low dielectric organic liquids, organic liquids with ion solubilizing neutral carriers such as valinomycin, actins, etc.
  - D. Porous homogeneous solids
    - Cellophane, dialysis membranes, Teflon®, and polyvinyl chloride films
  - E. Porous homogeneous liquids
    - Constrained liquid junctions
- Class II – Fixed site membranes
  - A. Nonporous homogeneous solids
    - Glass membranes, doped inorganic crystal membranes, such as AgX, LaF_3, such that only interstitials or vacancies carry current, highly cross-linked ion exchange resins, hydrophobic or oil impregnated ion exchangers
  - B. Nonporous heterogeneous solids
    - Binders (PVC, silicone rubber, etc.), supported particles of glass, AgX crystallites, ion exchange resin beads, etc.
  - C. Porous homogeneous solids
    - Loosely cross-linked ion exchange resins
  - D. Porous heterogeneous solids
    - Glass and mineral particles compacted, ion exchange resin beads
- Class III – Mobile site membranes
  - A. Homogeneous nonporous liquids
    - Liquid ion exchangers, hydrophobic cation or anion containing salts dissolved in organic liquids, including solvents that permit dissociation as well as ion pairing in the membrane
  - B. Homogenous nonporous solids, such as pore AgX, in which both vacancies and interstitial ions may carry current

activation models of transport,[146a] considered N-P equations for lipid bilayer transport in connection with calculations of the potential barrier[147,148] and derivation of current-voltage curves and conductances.[149,150] These workers were among the first to take into account the possibility of slow interfacial kinetics at finite flux and the possible, but not easily distinguishable[74] dissociation due to high fields near a membrane surface.[151] Markin, Kristalik, et al.[152] and Markin, Pastushenko, et al.[153] solved the N-P equations for the neutral carrier mediated case and introduced surface kinetic considerations. Laüger and Stark[154] also introduced surface kinetics into an Eyring formalism. Since high currents can be passed by lipid bilayers, account of external electrolyte concentration polarization is a necessity. Neumcke[155] and LeBlanc[156,157] have included this process in their theoretical work, while Haydon and Hladky[158] comment on this topic in their review. Transport through nonelectroneutral membranes has also been treated by Schlögl,[159] Vaidhyanathan,[160] Simons and Talone,[161] and Levich, the distinguished Russian electrochemist, and his colleagues.[162,163]

Solution of N-P equations for transport of single ions through membranes containing oil soluble neutral carriers is a more complicated problem. Solutions must be consistent with the trapping of carriers in the membrane or with an equilibrium distribution of carrier at the surface. Prior to 1971, the presence of carrier in the bathing solutions was discounted by the large partition coefficient, so equilibria between carriers and carrier containing species in an aqueous phase do not appear in one theory.[164] However, trinactin complexes have been detected in aqueous solutions.[165]

The first treatment using rapid, reversible interfacial conditions[70] has been extensively elaborated into an elegant, comprehensive theory which treats zero current and nonzero current transport in terms of conductance, using both "equilibrium" and "kinetic" boundary conditions.[74,74a] Two mechanisms invoking potential independent rate constants are considered as shown schematically in Figure 19.

$$K^+ (aq) + \bar{s}\,(\text{carrier}) \underset{k_i^b}{\overset{k_i^f}{\rightleftharpoons}} \overline{Ks^+} \qquad (141)$$

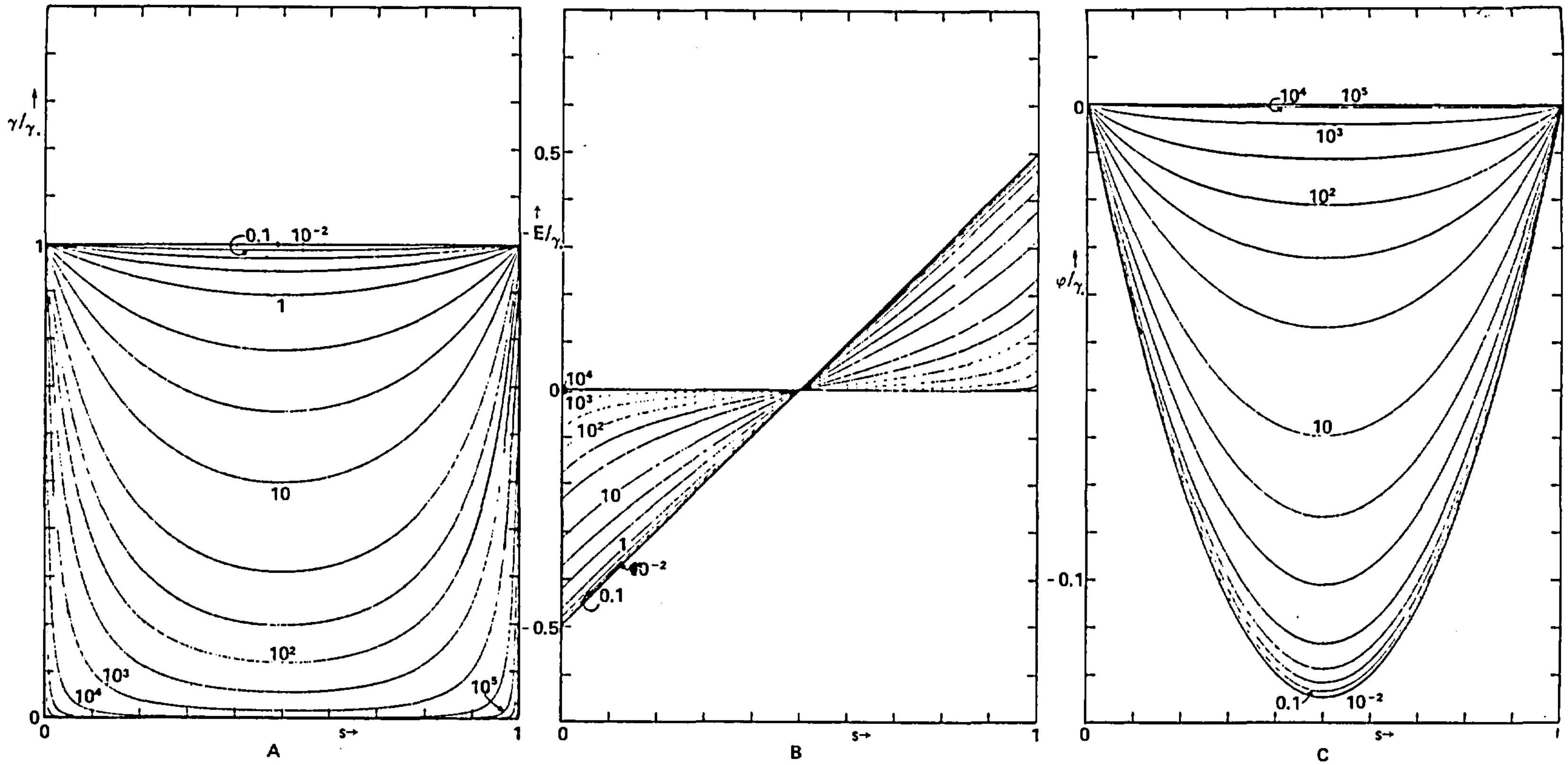

FIGURE 15. Profiles of dimensionless concentration of a single permeable ion (Figure 15A), dimensionless field (Figure 15B), and dimensionless potential (Figure 15C) for the totally symmetric case $\gamma_0 = \gamma_1 = 10^{-4}$ to 10^{-2} (identical curves), 0.1, 0.25, 0.5, 1, 2.5, 5, 10, 25, 50, 100, 250, 10^3, 10^4, 10^5, 10^6. Note that γ, E, and φ are scaled through division by γ_0, thus emphasizing the field and potential profiles at low ionic concentrations. Delevie and Moriera have defined the field and potentials with negative signs compared with normal physical usage. Thus the field in Figure 15B along the ordinate should be read without the negative sign and the potential profiles should be inverted in the reader's mind to be seen as peaks rather than valleys since the sign of it is reversed, from that used in this article. The reduced parameters are:

$s = \frac{x}{d}$

φ (in figure) $= -\frac{zF}{RT}\varphi$

E (in figure) $= +\frac{zFd}{RT}\frac{d\varphi}{dx}$

γ (reduced concentration in figure) $= \frac{4\pi z^2 F^2 d^2 \overline{C}}{\epsilon RT}$

γ_0 = reduced concentration in the left surface (x = s = 0) of the membrane

γ_1 = reduced concentration in the right surface (x = d, s = 1) of the membrane

(From De Levie, R. and Moriera, H., *J. Membrane Biol.*, 9, 241 (1972). With permission.)

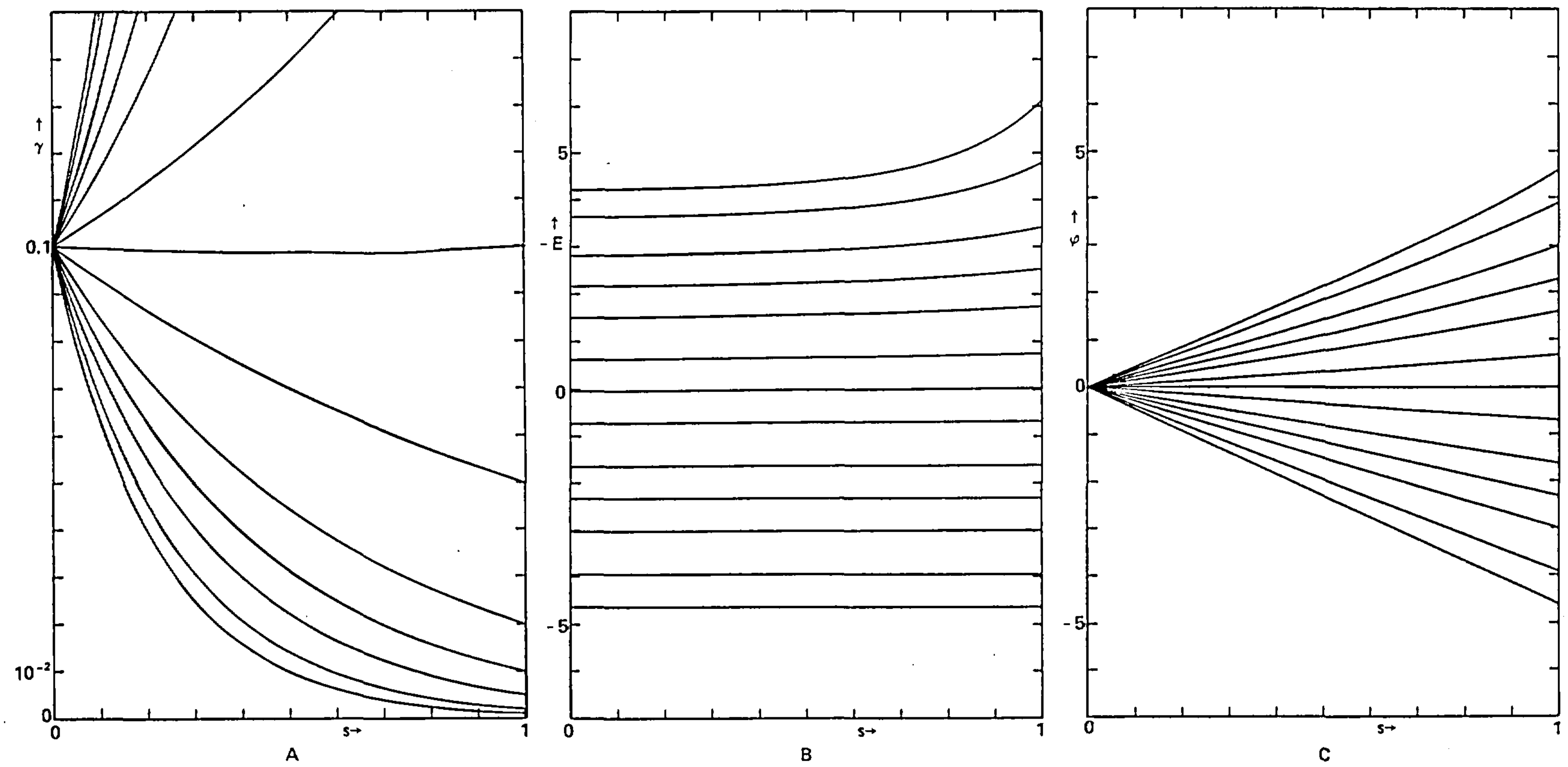

FIGURE 16. Same quantities vs. distance as in Figure 15 for membranes in asymmetric bathing solutions. $\gamma_0 = 10^{-1}$, γ_1 takes sequential values listed in Figure 15 legend. (From De Levie, R. and Moriera, H., *J. Membrane Biol.*, 9, 241 (1972). With permission.)

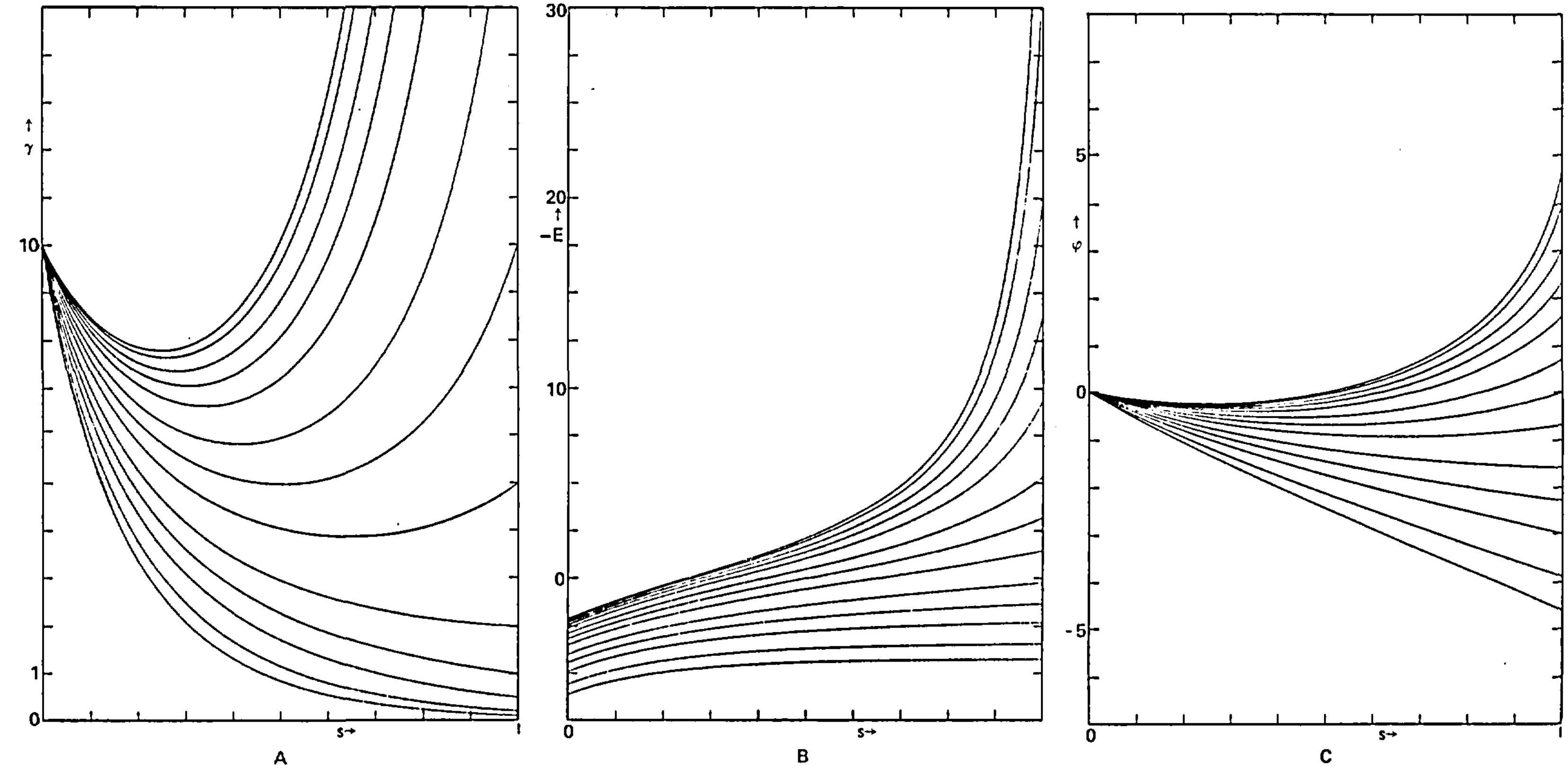

FIGURE 17. Same quantities vs distance as in Figure 15 in asymmetric bathing solutions. $\gamma_0 = 10$, γ_1 takes sequential values listed in Figure 15 legend. (From De Levie, R. and Moriera, H., *J. Membrane Biol.*, 9, 241 (1972). With permission.)

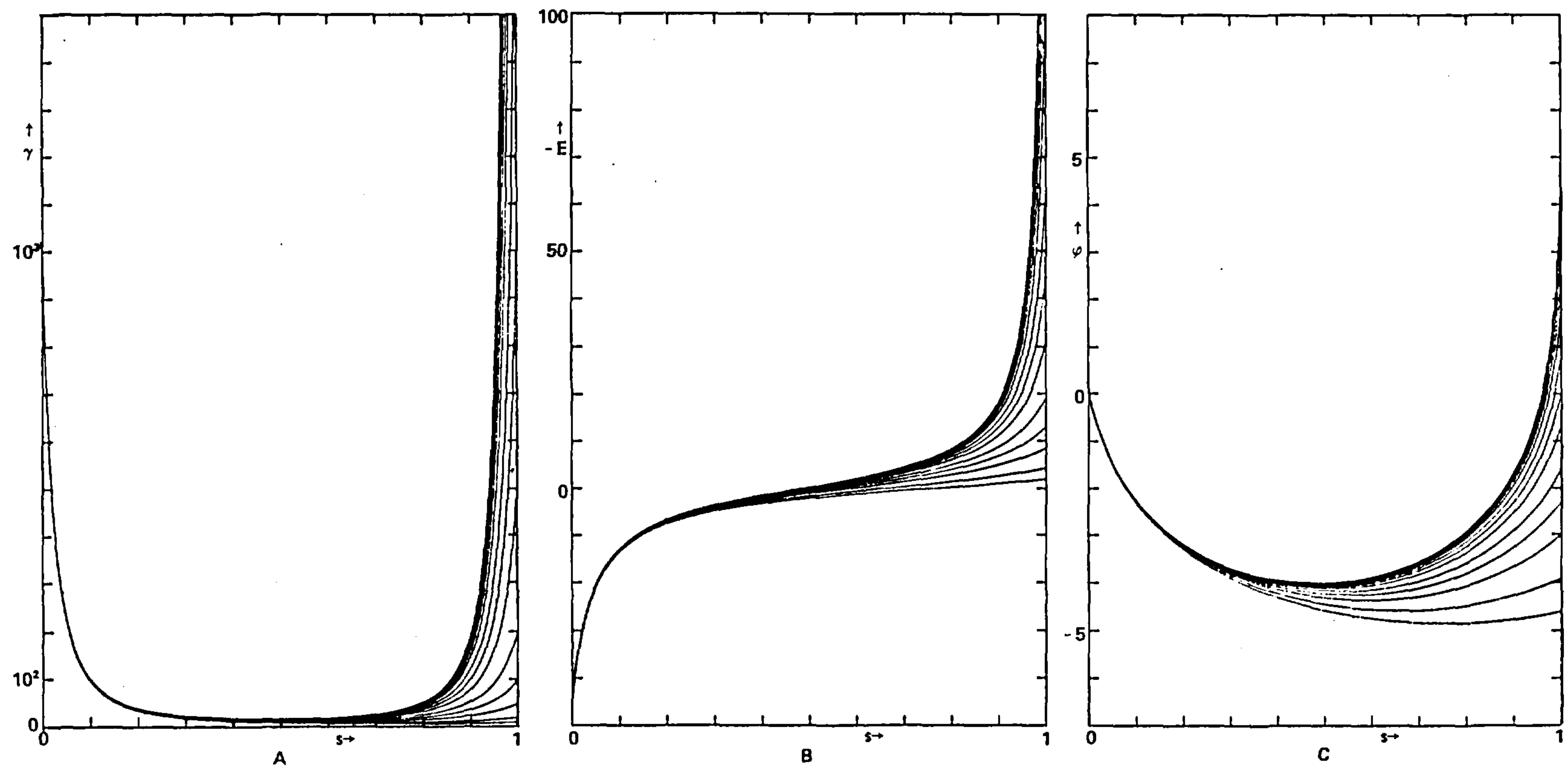

FIGURE 18. Same quantities vs. distance as in Figure 15 for membranes in asymmetric bathing solutions. $\gamma_0 = 10^3$, γ_1 takes sequential values listed in Figure 15 legend. (From De Levie, R. and Moriera, H., *J. Membrane Biol.*, 9, 241 (1972). With permission.)

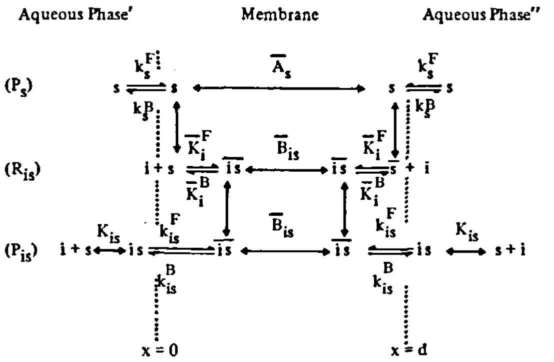

FIGURE 19. Schematic diagram of the processes by which neutral carriers mediate transport of ions through a membrane. The membrane is indicated to be interposed between two aqueous bathing solutions (') and (") with thickness d. Reactions are designated at the left. (P_s) refers to the partition process of the neutral carrier; (R_{is}) refers to the interfacial reaction process which involves the reaction at the interface between an ion in the aqueous phase and a carrier molecule already present in the membrane; (P_{is}) refers to the partition process of the complex which involves the transfer of an already formed complex from the aqueous phase into the membrane. Formal rate constants for transport across the membrane A_s and B_{is} are discussed in the text. (From Ciani, S., Laprade, R., Eisenman, G., and Szabo, G., *J. Membrane Biol.*, 11, 255 (1973). With permission.)

and

$$Ks^+ \text{ (aq)} \underset{k_{is}^{b}}{\overset{k_{is}^{f}}{\rightleftharpoons}} \overline{Ks^+} \tag{142}$$

Within the membrane, local standard chemical potentials and local electric potential are allowed to vary with position. Together, these parameters define a local energy and provide a distinctive barrier. Classically minded readers may infer that the barrier is constructed from a legitimate electrical barrier and a spatially varying activity coefficient equivalent which also bars ions from accumulating. This very interesting perspective allows solutions of the N-P equations which resemble those from the Eyring barrier models and are also formally equivalent to the classical surface rate model derived earlier. Integration of the N-P equations leads approximately to the forms below, where $\overline{A}_s$ and $\overline{B}_{is}$ are formally potential dependent rate constants. Further works needs to be done to relate the two models in a precise way. The flux of carrier is written:

$$\overline{J}_s = \overline{A}_s\,[\overline{C}_s(0) - \overline{C}_s(d)] \tag{143}$$

while the flux of ion-carrier complex is written

$$\overline{J}_{is} = \overline{B}_{is}\,[\overline{C}_{is}(0) - \overline{C}_{is}(d)] \tag{144}$$

Comparison of these equations with integrated N-P equations suggests a correspondence between $\overline{A}_s$, $\overline{B}_s$, and transport and electrochemical potentials according to

$$\frac{F\,\overline{D}_s}{\overline{A}_s} = \exp\,[F\,\overline{W}_s(0)/RT] \int_0^d \exp\,[F\,\overline{W}_s(x)/RT]\,dx \tag{145}$$

$$\frac{F\,\overline{D}_{is}}{\overline{B}_{is}} = \exp\,[\overline{\mu}_{is}{}^{o}(0)/RT] \int_0^d \exp\,[F\,\overline{W}_{is}(x)/RT]\,dx \tag{146}$$

where

$$\overline{W}_s(x) = \overline{\mu}_s{}^{o}(x)/F \tag{147}$$

and

$$\overline{W}_{is}(x) = \overline{\mu}_{is}{}^{o}(x)/F + \overline{\varphi}(x) \tag{148}$$

Hall, Mead, and Szabo[166] have developed an inversion method for extracting a barrier form from experimental I-$\Delta\phi$ curves and have computed expected I-$\Delta\phi$ curves from given barrier shapes. Triangular barriers of height $\overline{\varphi}$ V centered in the membrane give the expressions

$$I = \frac{2\,F^2\,D}{RT\,d}\,\overline{\varphi}\exp(-F\overline{\varphi}/RT)\,[\overline{C}_{left}\exp(F\Delta\varphi/2RT) - \overline{C}_{right}\exp(-F\Delta\varphi/2RT)] \tag{149}$$

and

$$I = \frac{F^2 D}{RT\,d}\,\overline{\phi}\,\exp(-F\,\overline{\phi}/RT)\,(\overline{C}_{left}\overline{C}_{right})^{1/2}\sinh\left[\frac{(\Delta\varphi - \Delta\varphi^{eq})_F}{2RT}\right] \quad (150)$$

for nonsymmetric bathing solution concentrations and

$$I = \frac{2\,F^2\,D}{RT\,d}\,\overline{\phi}\exp(-F\,\overline{\phi}/RT)\sinh\left[\frac{\Delta\varphi F}{2RT}\right] \quad (151)$$

for symmetric bathing solution. The equation is continuous through the origin and gives a constant conductivity at I = 0.

For trapezoidal barriers as shown in Figure 20, the current is given approximately (for positive and negative applied voltages separately) for symmetric bathing solutions by:

$$I = \frac{2F^2 D\overline{\phi}\exp(-F\overline{\phi}/RT)}{RTd}\,\{\exp[nF\Delta\varphi/RT] - \exp[-(1-n)F\Delta\varphi/RT]\} \quad (152)$$

$$\Delta\varphi > 0$$

or

$$I = \frac{2F^2 D\overline{\phi}\exp(-F\overline{\phi}/RT)}{RTd}\,\{\exp[(1-n)F\Delta\varphi/RT] - \exp[-nF\Delta\varphi/RT]\} \quad (153)$$

$$\Delta\varphi < 0$$

These functions, which are not symmetric about zero current except when n = 1/2, offer an explanation of the results reported by Szabo et al.[167] The nonactin-K^+ system seems to be in the equilibrium domain with n ~ 0.28. The cyclic polyether-alkali metal carrier complexes are also rapid and reversible for low salt activities.[168] Data are complicated by a high order (second and third power) dependence of conductivity on polyether concentrations and by complex formation in the aqueous phase.

Interpretations of I-$\Delta\phi$ curves for carrier systems have also been made by Laüger's group.[136-138,154,169-172a] Their chief success has been in diagnosing the K^+-valinomycin system as belonging to the kinetic domain. The interfacial surface entrance and exit rates defined by

$$\text{Rate in} = k_r(K^+)(\overline{s}); \quad (154a)$$

$$\text{Rate out} = k_d(\overline{Ks^+}) \quad (154b)$$

and transport rate constants

$$k_s = \frac{\overline{D}_s}{d^2} \text{ and } k_{Ks^+} = \frac{\overline{D}_{Ks^+}}{d^2} \quad (155)$$

have been evaluated experimentally.[172] Benz and Stark have also determined rates and partition coefficients for four macrotetrolide (monactin-trinactin) bilayer systems.[172a]

In a field which has already uncovered electrochemical effects at membrane interfaces which are comparable to those known at metal/electrolyte interfaces, at least one new result has been found in membrane electrochemistry which has no classical counterpart. This effect of ion transport through channels has been suggested before, but only recently has firm experimental evidence been accumulated. The apparent "gelling" or local organization of carriers into channels (for preferential paths) for ionic motion has been suggested experimentally in important papers by Eisenberg, Hall, and Mead,[173] Cherry,[174] Haydon et al.,[175,176] and Goodall et al.[177,178] Interpretation is based on stepwise current-time and current-voltage responses (rather than continuous responses) which imply discrete current flow.[176a] Previously, theoretical analyses of channel controlled fluxes had been provided by Bamberg and Laüger[179] and Gordon.[180,181] A review by Cherry[182] summarizes earlier work.

Theoretical electrochemists of the Levich tradition, referred to in References 115, 116, 152, 153 and 162, are making contributions to the theory of channel transport as well. Chizmadzhev et al.[182a] consider cylindrical channels lined with polar groups and inner hydration sheath. Trans-

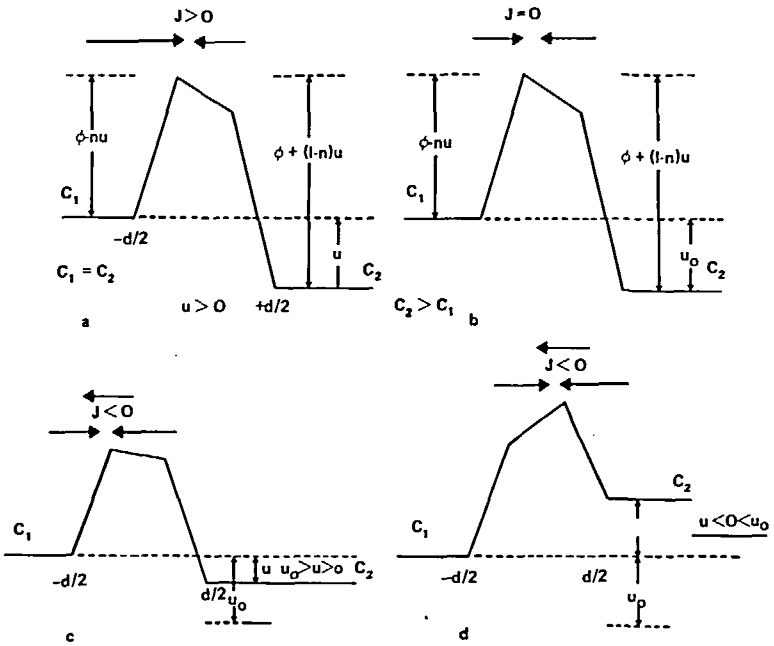

FIGURE 20. (a) A trapezoidal barrier with equal concentrations on both sides and a negative voltage applied (right side negative and left side positive). The membrane of thickness d is centered on x = 0. Net current indicated as flux is shown as the sum of forward and backward components, indicated by arrows. The barrier to flow of ions from left to right is φ-nu while the barrier to reverse flow is φ + (1 − n) u, u is the absolute value of the applied voltage. (b) A trapezoidal barrier with asymmetric bathing solution concentrations ($C_2 > C_1$). u_0 is the zero current membrane potential which is given by $\frac{RT}{F}$ ln (C_2/C_1). (c) A trapezoidal barrier with asymmetric concentrations as in Figure 20b, but with u lying between zero and u_0. The net current from right to left is still determined by the right side barrier and so the current-potential characteristic is expected to depend exponentially on φ + (1 − n)u. (d) A trapezoidal barrier with asymmetric concentrations as in Figure 20b with a positive voltage applied. The larger current component is again from right to left. However, the highest part of the barrier is now the right-hand corner. The authors assert that the current should now be determined by an exponential involving φ-nu. (From Hall, J. E., Mead, C. A., and Szabo, G., *J. Membrane Biol.*, 11, 75 (1973). With permission.).

port of sodium is modeled with the concept of successive displacement of H_2O molecules from the sheath. The energy profile is found from a series of barriers of different heights and widths as in Section IVC. above. A second paper restricts the system to three barriers.[182b] Smejtek[182c] also has explored the barrier model for cylindrical channels in which the potential energy is considered the difference between polarization energies of an ion in the channel and in the bathing solution. These authors find current-voltage characteristics with discrete conducting states.

Sign Convention: x is positive from 0 to d through a membrane of thickness d. A positive current is positive ions moving in a positive x direction.

1. Electrical Response Functions for Exceedingly Dilute Membranes Containing Ions of One Sign:[183,184]

Condition 1.

$$\text{Debye thickness} = 1/\kappa = \left(\frac{\epsilon RT}{z^2 F^2 \sum_i \bar{C}_i}\right)^{1/2} > d \qquad (156)$$

Condition 2. $\bar{\gamma}_i \neq f(x)$
Condition 3. $\bar{\mu}^0_i \neq f(x)$
Condition 4. $\bar{u}_i \neq f(x)$
Condition 5. All ions of the same charge, z
Condition 6. I = 0

The internal diffusion potential is approximately

$$\Delta\varphi_m \sim \frac{RT}{zF} \ln \left[\frac{\sum_i \bar{u}_i \bar{C}_i(0)}{\sum_i \bar{u}_i \bar{C}_i(d)} \right] \tag{157}$$

This equation should be examined by DeLevie's method to determine limits of validity with respect to Poisson's equation. Since this equation is in the block logarithmic form, interfacial potentials can be added directly without calculating surface concentrations via charge balance; result (for ions "i" on left, "k" on right) is

$$\Delta\varphi_m \sim \frac{RT}{zF} \ln \left[\frac{\Sigma_i \bar{u}_i K_{ext,i} a_i/\bar{\gamma}_i}{\Sigma_k \bar{u}_k K_{ext,k} a_k/\bar{\gamma}_k} \right] \tag{158}$$

2. *Electrical Response Functions for Exceedingly Dilute Membranes Which Contain Ions of Both Signs But Which Are Not Electroneutral and an Approximation for Higher Concentration Electroneutral Membranes (Excluding Space Charge Confined to Surface Regions)*[22,183,185]

An exact solution for electroneutral membranes with equal total salts of same absolute ion charge:

Conditions 1 through 6 apply

Condition 7. All ions have the same absolute charge

Condition 8. Nearly constant field given by:

$$\frac{d\bar{\varphi}}{dx} \sim [\bar{\varphi}(d) - \bar{\varphi}(0)]/d \tag{159}$$

$$\Delta\bar{\varphi}_m \sim \frac{RT}{zF} \ln \left[\frac{\sum_i \bar{u}_i \bar{C}_i^+(0) + \sum_i \bar{u}_i \bar{C}_i^-(d)}{\sum_i \bar{u}_i \bar{C}_i^+(d) + \sum_i \bar{u}_i C_i^-(0)} \right] \tag{160}$$

"Nearly constant field" means that there is nearly no space charge in the membrane. Similarly, there can be nearly no space charge outside the membrane at each interface. Thus $\bar{\phi}(0) - \phi_0$ and $\bar{\phi}(d) - \phi_d$ are both zero. Any potential drops through the compact layers are assumed to be the same on both sides and therefore canceling. Consequently,[186] for ion "i" on the left and "k" on the right,

$$\Delta\varphi_m \sim \frac{RT}{zF} \ln \left[\frac{\sum_i \bar{u}_i K_{ext,i} a^+_i/\bar{\gamma}^+_i + \sum_k \bar{u}_k K_{ext,k} a^-_k/\bar{\gamma}^-_k}{\sum_k \bar{u}_k K_{ext,k} a^+_k/\bar{\gamma}^+_k + \sum_i \bar{u}_i K_{ext,i} a^-_i/\bar{\gamma}^-_i} \right] \tag{161}$$

This equation can be an exact solution for the case in which the total ionic strength of the salt ions on each side of the membrane is the same. It is, in fact, a degenerate case of a Planck constrained junction, when the total inner ion concentrations $\bar{C}(0)$ and $\bar{C}(d)$ are the same even though they are comprised of different ions. When the interfacial single-ion extraction coefficients happen to be the same for each cation and another constant value for all anions, the interfacial potential contributions are the same (Equation 45) and Equation 161 becomes exact.

Frankenhaeuser[187] inserted the interfacial potentials, which are assumed to be the same on each side, to give an equation which is not very useful because the interfacial potentials are not known in terms of solution activities without a more complete charge-balance calculation:

$$\Delta\varphi_m \sim \frac{RT}{zF} \ln \left[\frac{\sum_i \bar{u}_i K_{ext,i} \exp\left(-\frac{2zF}{RT}(\bar{\varphi} - \varphi)\right) a^+_i/\bar{\gamma}^+_i + \sum_k \bar{u}_k K_{ext,k} a^-_k/\bar{\gamma}^-_k}{\sum_i \bar{u}_k K_{ext,k} \exp\left(-\frac{2zF}{RT}(\bar{\varphi} - \varphi)\right) a^+_k/\bar{\gamma}^+_k + \sum_i \bar{u}_i K_{ext,i} a^-_i/\bar{\gamma}^-_i} \right] \tag{162}$$

The corresponding single ion flux (current) for nearly constant field is

$$i_+ = -\frac{\bar{u}_i F \Delta\bar{\varphi}_m}{d} \left[\frac{\bar{C}_i(d)\,\xi - \bar{C}_i(0)}{\xi - 1} \right] = -\frac{\bar{u}_i RT}{d} \left(\frac{\ln \xi}{\xi - 1} \right) [\bar{C}_i(d)\,\xi - \bar{C}_i(0)] \tag{163}$$

for cations, and

$$i_- = -\frac{\bar{u}_i RT}{d}\left(\frac{\ln\xi}{\xi - 1}\right)[\bar{C}_i(d)\,\xi - \bar{C}_i(0)] \tag{164}$$

for anions. If both bathing solutions are identical, one can substitute for $\bar{C}_i$ using Equation 37a where $\bar{\phi}(0) - \phi_0 = \bar{\phi}(d) - \phi_d$ and $\Delta\bar{\phi}_m = \Delta\phi_m$. Except in the limit of zero space charge where $\phi(0) - \phi_0$, etc. are zero, one is left with indeterminate expressions:

$$i_+ = -\frac{\bar{u}_i RT\,K_{ext}}{d}\left(\frac{\ln\xi}{\xi - 1}\right)\left\{\frac{a_{i,d}}{\bar{\gamma}_{i,d}}\exp\left[\frac{F}{RT}\left(\varphi_d - \bar{\varphi}(d)\right)\right] - \frac{a_{i,0}}{\bar{\gamma}_{i,0}}\exp\left[\frac{F}{RT}\left(\varphi_0 - \bar{\varphi}(0)\right)\right]\right. \tag{165}$$

and similarly for i_-. If the bathing solutions are not identical, the relation between $\Delta\phi_m$ and $\Delta\bar{\phi}_m$ is specified by Equation 56 but is not readily known. Consequently, the general current-voltage curves for these systems, $I = i_+ + i_-$ vs. $\Delta\phi_m$, are not known in closed form. This indeterminacy is only apparent due to the mathematical difficulty. The system is, in fact, determined by the principles given in an earlier section of this review. Interfacial potentials could, in principle, be found from the charge balance, which is not used in the derivation of any of the above equations. Note that when the field is constant, the concentration profiles of individual ions are curved.

A number of ad hoc equations have been proposed[185,188] for single-ion currents to account empirically for the interfacial and internal diffusion potential components. If n is the fraction of the total membrane potential $\Delta\phi_m$ in the interfacial part, then according to Mullins[188]

$$i_j \sim z_j\frac{\bar{u}_j RT\,K_{ext}}{d}\left[\frac{a_{i,d}}{\bar{\gamma}_{i,d}}\exp\left(z_j(1-n)F\Delta\varphi_m/RT\right)\right.$$

$$\left.-\frac{a_{i,0}}{\bar{\gamma}_{i,0}}\exp\left(-z_j nF\Delta\varphi_m/RT\right)\right] \tag{166}$$

For the symmetrical case n = 1/2, the current obeys a sinh function of $\Delta\phi_m$. For n = 1 or 0, the current reaches limiting values at one voltage extreme or the other.

Another ad hoc hypothesis assumes (incorrectly) that a Boltzmann distribution of concentration applies with current flow[183]

$$\bar{C}_j(0) = \bar{C}_j(d)\exp[z_j\Delta\bar{\varphi}_m F/RT] \tag{167}$$

and that the interfacial potentials are equal (possibly valid for symmetrical bathing solutions); for potential independent rates:

$$i_j = z_j F\,[\vec{k}_j C_{j,0} - \overleftarrow{k}_j \bar{C}_j(0)] \tag{168}$$

$$= z_j F\,[\overleftarrow{k}_j \bar{C}_j(d) - \vec{k}_j C_{j,d}]$$

which can be written using Equation 167 as

$$i_j = -z_j k_j F\left[\frac{C_{j,d}\exp(z_j\Delta\varphi_m F/RT) - C_{j,0}}{1 + \exp(z_j\Delta\varphi_m F/RT)}\right] \tag{169}$$

This equation gives limiting currents for both large positive and negative $\Delta\phi_m$. Patlak[189] shows that this equation gives $\Delta\varphi_m$ for zero current of the same form as Equation 160, with $\vec{k}_i$ replacing each mobility u_i.

In addition to lipid bilayers and organic membranes containing neutral carriers,[80] a number of thick neutral membrane systems show potential development in membrane cell configuration. These include organic phosphates,[190-194] polyvinylchloride (PVC) plasticized with phenols, amides, and aromatic esters,[195] nitrocymene with valinomycin held in cellulose acetate,[196-198] and PVC plasticized with *o*-nitrophenyloctylether containing neutral carriers.[199,200] Transport of uranyl nitrate through PVC plasticized with various organophosphates has been measured by Vofsi et al.[201]

The growing literature in the field of neutral carrier transport has been reviewed recently by Buck.[44,45] In these reviews are found references to studies involving naturally occurring macrocyclic compounds and synthetic cyclic ether compounds. A new example of carrier transport by polyethers has recently appeared[201a] and the use of optically active, neutral, lipophilic carriers for selective transport of enantiomers has been described by Newcomb, Helgeson, and Cram.[201b]

3. Electrical Response Functions for High Concentrations of Ions of Both Signs such that Electroneutrality Exists in the Membrane Bulk

For membranes of high dielectric constant and those which take up water, such as cellophane, one has an exact analog of the classical constrained junction[22] which was treated years ago by Planck. He showed that the concentration profile of total univalent ions was linear through the membrane in the steady state, while the field was not constant:

$$E(x) = -\frac{RT \ln\xi[\bar{C}(d) - \bar{C}(0)]}{F\ \{[\bar{C}(d) - \bar{C}(0)]\ x + \bar{C}(0)d\} \ln[\bar{C}(d)/\bar{C}(0)]} \tag{170}$$

$$\frac{\xi U_d - U_0}{V_d - \xi V_0} = \frac{\ln[\bar{C}(d)/\bar{C}(0)] - \ln\xi}{\ln[\bar{C}(d)/\bar{C}(0)] + \ln\xi} \cdot \frac{\xi\bar{C}(d) - \bar{C}(0)}{\bar{C}(d) - \xi\bar{C}(0)} \tag{171}$$

$\bar{C}$'s are total concentrations, while $U = \Sigma\bar{C}_i^+\bar{u}_i$ and $V = \Sigma\bar{C}_i^-\bar{u}_i$, are evaluated at the surfaces just inside any space charge. The sum $\Sigma z_i\bar{C}_i = 0$ taken over all ions. For cations x of charge z_c and anions of charge z_a, Johnson gave a solution similar to Equation 171 (see Lakshminarayanaiah[22]). Current carried by a single cation is rigorously given by:

$$i_j^+ = \frac{-\bar{u}_j RT}{d}\left[\frac{\bar{C}(d) - \bar{C}(0)}{\bar{C}(d)\xi - \bar{C}(0)}\right]\left[\frac{\ln(\bar{C}(d)\xi/\bar{C}(0))}{\ln(\bar{C}(d)/\bar{C}(0))}\right][\bar{C}_j(d)\xi - \bar{C}_j(0)] \tag{172}$$

This form of equation applies to quasi-electroneutral membranes in which the surface salt concentrations remain constant. This situation would prevail when the interfacial exchange current is large (rapid, reversible interfacial transport). The net interfacial potential from electroneutral solution bulk to electroneutral membrane bulk is virtually constant (see Equation 45). The result means that the two space charge regions at each interface contain equal and opposite charges and that the net interfacial potentials are about equal on each side. Then,

$$\Delta\bar{\varphi}_m \simeq \Delta\varphi_m \tag{173}$$

and the entire I-$\Delta\phi_m$ curve could be constructed by summing over partial ion currents. One curious feature emerges: the individual ion flux equations for this salt system (Equation 172) and for electrostatically charged membranes (Equation 163) are in the same form when a single salt is involved at equal activities on the two sides of a membrane.

A subsequent generalization of the N-P equation integration for ions of arbitrary valence was made by Henderson.[22] He asserted that each ion concentration fraction profile was linear. While this assumption is incorrect, the errors introduced are small for systems with ions of the same absolute charge. Membrane potentials can be evaluated in closed form by this method. A detailed comparison of integration of the N-P At zero current, $\Delta\bar{\phi}_m$ is computed from (RT/F)/nξ, where ξ obeys the equation:

equations in the steady state by Henderson and by Planck has been given by Bonciocat.[201c] A catalog of cases giving the same result from both methods was provided.

B. Electrical Properties of Class II–Fixed Site Membranes

1. Electrical Response Functions for Membranes of High Fixed Site Density to Assure Permselectivity (Co-ion Exclusion)

Analysis of ion exchange membrane transport is most admirably presented by Helfferich.[20] In Chapter 8, the theoretical and experimental background known to 1962 is fully explained, and the essential modern studies of Scatchard, Kressman, Y. Kobatake, Meares, Schlögl, Spiegler, and G. Schmid are referenced. Classical early work done prior to 1950 by the pioneers Sollner, Teorell, Meyer, Marshall, and others is, of course, included. The majority of published solutions to transport problems ignore solvent transport and use the assumptions:

Conditions 1–3 above, apply.
Condition 4. $\bar{u}_i RT = \bar{D}_i$
Condition 5. I = 0
Condition 6. Inside space charge regions $\Sigma z_i\bar{C}_i + \bar{\omega}\bar{X} = 0$

The bi-ionic potential (species A, charge z_a at concentration C_a on left; species B, charge z_b at concentration C_b on right) is

$$\Delta\varphi_m = \frac{RT}{F}\left[\frac{\bar{D}_a - \bar{D}_b}{\bar{D}_a z_a - \bar{D}_b z_b}\ \ln\frac{\bar{D}_b z_b}{\bar{D}_a z_a} + \frac{1}{z_a z_b}\ \ln K_{iexc.}\frac{\bar{\gamma}_b}{\bar{\gamma}_a} + \frac{z_b - z_a}{z_b z_a}\ln\frac{\bar{X}}{C_a} + \frac{1}{z_b}\ \ln\frac{C_a}{C_b} + \ln\frac{{\gamma_a}^{1/z_a}}{{\gamma_b}^{1/z_b}}\right] \tag{174}$$

with the ion exchange constant defined as:

$$K_{iexc} = \left(\frac{\bar{a}_a}{a_a}\right)^{z_b}\left(\frac{a_b}{\bar{a}_b}\right)^{z_a} \tag{175}$$

For $z_a = z_b = z$,

$$\Delta\varphi_m = \frac{RT}{zF}\ \ln\left[\frac{\bar{D}_a\, a_a\, \bar{\gamma}_b}{\bar{D}_b\, a_b\, \bar{\gamma}_a}\ (K_{iexc})^{1/z}\right] \tag{176}$$

Because the interior surface concentrations of A and B are fixed by the site concentration $\bar{X}$ regardless of the values of C_a and C_b (except zero), fluxes are constant in the steady state, and the concentration profiles can be nonlinear:

$$z\bar{J}_a = -z\bar{J}_b = \frac{\bar{D}_a\,\bar{D}_b\,(-\bar{\omega}\bar{X})}{(\bar{D}_a - \bar{D}_b)\,d}\ \ln\frac{\bar{D}_a}{\bar{D}_b} \quad \text{for} \quad \bar{D}_a \neq \bar{D}_b \tag{177a}$$

or

$$= \frac{\bar{D}(-\omega\bar{X})}{d} \qquad \text{for } \bar{D}_a = \bar{D}_b = \bar{D} \tag{177b}$$

$$\bar{C}_a = \tag{178a}$$

$$\frac{-\bar{\omega}\bar{X}}{z}\left(\frac{\bar{D}_a}{\bar{D}_a - \bar{D}_b}\right)\left[\left(\frac{\bar{D}_b}{\bar{D}_a}\right)^{x/d} - \frac{\bar{D}_b}{\bar{D}_a}\right] \text{ for } \bar{D}_a \neq \bar{D}_b$$

or

$$= \frac{-\bar{\omega}\bar{X}}{z}\ [1 - x/d] \ \ \text{for } \bar{D}_a = \bar{D}_b \tag{178b}$$

$$\bar{C}_b = \frac{-\bar{\omega}\bar{X}}{z} - \bar{C}_a \tag{179}$$

For the multi-ionic case (i cations of charge z on the left, and k cations of charge z on the right), assuming reversible interfacial ion exchange,

$$\Delta\varphi_m = \frac{RT}{zF}\ \ln\left[\frac{\sum_i \bar{D}_i\ K_{ext,i}\, a_i/\bar{\gamma}_i}{\sum_k \bar{D}_k\ K_{ext,k}\, a_k/\bar{\gamma}_k}\right] \tag{180}$$

The interior membrane potential is an integral of an exact derivative so that the potential depends only on interior surface concentrations,

$$\Delta\bar{\varphi}_m = \frac{RT}{zF}\ \ln\left[\frac{\sum_i \bar{D}_i\,\bar{C}_i(0)}{\sum_k \bar{D}_k\,\bar{C}_k(d)}\right] \tag{181}$$

and is independent of time, i.e., independent of the adjustment of concentration profiles with time. The membrane potential-time response depends only on the time required to charge the surfaces and to establish ion exchange equilibrium.

One ion is frequently specified as "dominant," i.e., its K_{ext} exceeds all others; then dividing through numerator and denominator of Equation 180 by the coefficients of the "dominant" activities i and k, one has

$$\Delta\varphi_m = \frac{RT}{zF}\ \ln\left[\frac{a_i + \sum_i K_{ij}{}^{Pot} a_j}{a_k + \sum_\ell K_{k\ell}{}^{Pot} a_\ell}\right] \tag{182}$$

$$+ \frac{RT}{zF}\ \ln\frac{\bar{D}_i\,\bar{\gamma}_k\,K_{ext,i}}{\bar{D}_k\,\bar{\gamma}_i\,K_{ext,k}}$$

where

$$K_{ij}^{Pot} = \frac{K_{ext,j}\,\bar{D}_j\,\bar{\gamma}_i}{K_{ext,i}\,\bar{D}_i\,\bar{\gamma}_j} = (K_{iexc})^{1/z}\ \frac{\bar{D}_j\,\bar{\gamma}_i}{\bar{D}_i\,\bar{\gamma}_j} \tag{183}$$

Values are the coefficient of other activities. Super "Pot" signifies "Potentiometric Selectivity Coefficient."* Concentration profiles can be expressed and are generally nonlinear functions of distance. Fluxes can also be expressed; for example:

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*According to an IUPAC report #43 January 1975 on nomenclature for ion selective electrodes, the potentiometric selectivity coefficient should be designated k_{AB} in the future. However, the present literature uses the nomenclature above almost exclusively.

$$\overline{J}_i = \frac{\overline{D}_i(-\overline{\omega}\overline{X})(a_{i,0}B_k - a_{i,d}B_j)}{z\overline{\gamma}_i\, d\,(A_kB_j - A_jB_k)} \ln \frac{A_kB_j}{A_jB_k} \tag{184}$$

where

$$A_j = \sum_j a_j/\overline{\gamma}_j \text{ on left} \quad A_k = \sum_k a_k/\overline{\gamma}_k \text{ on right} \tag{185}$$

$$B_j = \sum_j \overline{D}_j\, a_j/\overline{\gamma}_j \text{ on left} \quad B_k = \sum_k \overline{D}_k\, a_k/\overline{\gamma}_k \text{ on right} \tag{186}$$

Conti and Eisenman[202,203] have given the most complete derivation and analysis of Equation 182 for permeable ions of the same sign through membranes containing a distribution of fixed sites, including the usual uniform distribution. The membrane potential at zero current is independent of site distribution. Conditions 2 through 4 hold, but condition 1 is expanded to include the case $\overline{\gamma}_i = \overline{C}_i^{\,n-1}$. The uninegative site distribution $\overline{X}(x)$ always occurs in the form

$$S = \int_0^d \frac{dx}{\overline{X}(x)\,\overline{u}_i(x)} \tag{187}$$

which is $d/\overline{X}\overline{u}_i$ for the uniform distribution. The steady state fluxes for two cations are

$$\overline{J}_1 = -\frac{nRT}{S}\left[\frac{\overline{C}_1(0)}{\overline{X}(0)} - \alpha\xi\frac{\overline{C}_1(d)}{\overline{X}(d)}\right]\frac{\ln\alpha\xi}{1-\alpha\xi} \tag{188}$$

and

$$\overline{J}_2 = -\frac{\overline{u}_2}{\overline{u}_1}\,\frac{nRT}{S}\left[\frac{\overline{C}_2(0)}{\overline{X}(0)} - \alpha\xi\frac{\overline{C}_2(d)}{\overline{X}(d)}\right]\frac{\ln\alpha\xi}{1-\alpha\xi} \tag{189}$$

where

$$\frac{\overline{C}_1(0)}{\overline{X}(0)} = \frac{1}{\left[1 + \left(K_{iexc}\dfrac{a_{2,0}}{a_{1,0}}\right)^{1/n}\dfrac{\overline{\gamma}_{1,0}}{\overline{\gamma}_{2,0}}\right]}\ ;\ \frac{\overline{C}_2(0)}{\overline{X}(0)} \tag{190}$$

$$= \frac{\left(K_{iexc}\dfrac{a_{2,0}}{a_{1,0}}\right)^{1/n}\dfrac{\overline{\gamma}_{1,0}}{\overline{\gamma}_{2,0}}}{\left[1 + \left(K_{iexc}\dfrac{a_{2,0}}{a_{1,0}}\right)^{1/n}\dfrac{\overline{\gamma}_{1,0}}{\overline{\gamma}_{2,0}}\right]}$$

The total current for the case where n = 1, with extraction and ion exchange constants of the same value on each side for a given ion, is

$$I = -zF\frac{RT}{S}\left[\frac{a_{1,0} + K_{1,2}^{Pot}a_{2,0}}{a_{1,0} + K_{iexc}\,a_{2,0}}\right]\frac{1-\xi}{1-\alpha\xi}\ln\alpha\xi \tag{191}$$

$$\alpha = \frac{\overline{X}(d)}{\overline{X}(0)}\left[\frac{\overline{u}_1\ \overline{C}_1(0) + \overline{u}_2C_2(0)}{\overline{u}_1\ \overline{C}_1(d) + \overline{u}_2C_2(d)}\right] \tag{192}$$

$$= \left[\frac{a_{1,0} + K_{1,2}^{Pot}a_{2,0}}{a_{1,d} + K_{1,2}^{Pot}a_{2,d}}\right]\left[\frac{a_{1,d} + K_{iexc}\,a_{2,d}\ \overline{\gamma}_{1,d}/\overline{\gamma}_{2,d}}{a_{1,0} + K_{iexc}\,a_{2,0}\ \overline{\gamma}_{1,0}/\overline{\gamma}_{2,0}}\right]$$

This equation, illustrated in Figure 21, predicts a straight line I - $\Delta\phi$ curve for symmetric electrolyte concentrations, but curves in the region of I = 0 for nonsymmetric electrolyte concentrations. At high voltage, $|\Delta\phi| > RT/zF$ straight line segments are again predicted even for asymmetric concentrations. Conductances can be easily derived.

A general expression for $\Delta\phi_m$ at zero current, using $\overline{\gamma}_i = C_i^{\,n-1}$, is

$$\Delta\varphi_m = \frac{nRT}{zF}\ln\left[\frac{a_i^{1/n} + \sum_i (K_{ij}^{Pot}a_j)^{1/n}}{a_k^{1/n} + \sum_l (K_{kl}^{Pot}a_l)^{1/n}}\right] \tag{193}$$

and flux and current can be readily generalized to include n different from 1. This equation and Equation 182 have been used to interpret the responses of synthetic ion exchanger resin and glass membranes.[31,32] More recently, Buck[204-206] has given a solution for the zero current membrane potential for solid state ion exchanger membranes with limited numbers of mobile species and more than one type of exchanger site:

$$\Delta\varphi_m = \text{const (side ``d'' activities)} \tag{194}$$

$$+\frac{RT}{F}\ln\{[a_i + K_{ij}(K_{iexc}a_ia_j)^{1/2}]\ [1 + K_{iexc}a_j/a_i]^{1/2}\}$$

where K_{ij} is formally a mobility and activity coefficient ratio, as in Equation 183, but also

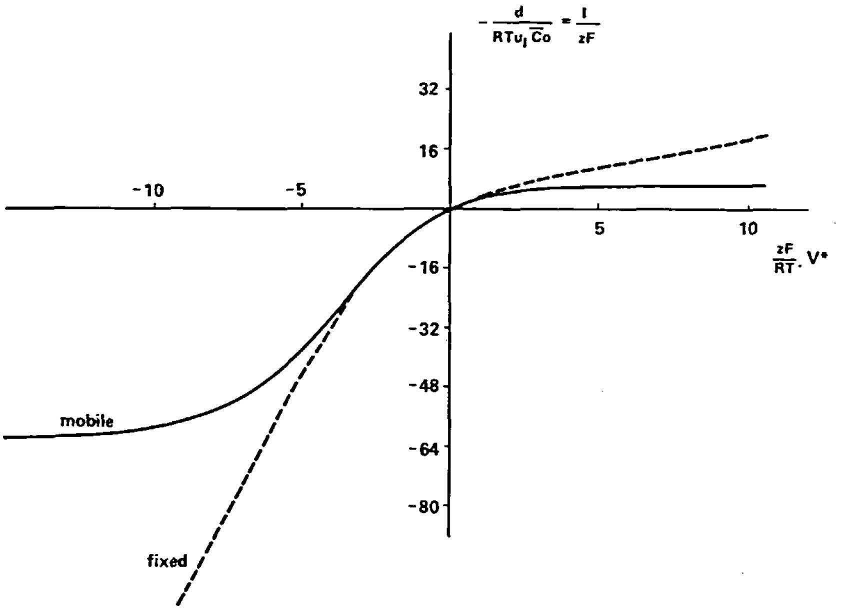

FIGURE 21. Current-voltage relationships for mobile and fixed site membranes. The reduced current is plotted as a function of reduced voltage for the values of the parameters $r = 30$, $X_1' = 0.5$, $X_1'' = 0.98$ for ion exchange membranes with mobile sites (continuous line) and with fixed sites uniformly distributed (dashed line). The two curves are not distinguishable, for these values of the parameters in the region $-3 < (zF/RT)V^* < 1$. In general, the separation of the curves is small in the region $-\ln\alpha < (zF/RT)V^* < 0$, and they are always tangent at $-\ln\alpha = (zF/RT)V^*$. Parameter r is u_2/u_1, X_1', and X_1'' are concentration ratios of permeable counter ion 1 to sites at the left and right interior surfaces of a membrane. V^* is the applied voltage relative to the voltage of zero current. α was defined in Equation 192. (From Conti, F. and Eisenman, G., *Biophys. J.*, 6, 227 (1966). With permission.)

includes the ratio of dissociation constants of the two ions i and j from a given type of site in the membrane phase.

General flux equations for two ion and water transport through a fixed site membrane have been written out in terms of Onsager coefficients by Ciani and Gliozzi.[206a] These equations contain all of the possible interaction terms among ions of different valence and solvent. Except for the assumption of a constant site concentration, the derived expression for the membrane potential is quite general and reduces to the results of Conti and Eisenman for the case of ions of the same charge and neglect of interaction cross terms.

2. *Electrical Response Functions for Membranes with Low Fixed Site Densities*

When fixed site density is not high enough to exclude co-ions, their transport becomes possible and must be considered in deriving potential and current responses. A steady state solution can be derived by the same methods used for the Planck constrained junction. This procedure is described by Lakshminarayanaiah[22] and the results are given. Potentials and currents reduce to the Planck situation when $\bar{X} = 0$. An approximate solution can also be found by using a Henderson integration. Interfacial potentials are added into the sum (Equation 18) using the complete Donnan form (Equation 50). This procedure leads to the classical Teorell and Meyer solution.[20,22]

Fixed site membranes need not control the current exclusively. If the membrane is thin, so that the resistance is comparable with bathing solution resistances, then the film diffusion limitation must be included as discussed by Helfferich.[20] Spiegler[207] has recently given a solution to this problem in general terms. At high applied voltages, current cannot continue to increase but must become limited by external concentration polarization. For a single-salt bathing solution of equal concentration C_S on each side and a cation permeable membrane,

$$\Delta\varphi_m = -(R_s + R_m)I + [(B/\Lambda) + \bar{C} - C] \ln\left[\frac{1 + I/I_{lim}}{1 - I/I_{lim}}\right] \tag{195}$$

where R_S is the solution resistance (between reference electrodes), R_m is the membrane resistance, $B = FD/(\bar{t}_+ - t_+)$, $\bar{C} = RT(\bar{t}_- - \bar{t}_+)/F$, $C = RT\ (t_- - t_+)/F$, Λ is the electrolyte equivalent conductance, and $I_{lim} = BC_s/\delta$. In excess, nonpermeable supporting electrolyte, $\bar{C}$ is the only significant multiplier of the log term. A new experimental study of concentration polarization limited membrane currents conforms well to theoretical predictions.[207a]

The extensive literature prior to 1962 on membrane potentials, current-voltage curves, and conductivities of fixed site synthetic ion exchanger membranes was considered by Helfferich.[20] Closely related tests of theory involve measurements of individual ion fluxes under self-diffusion, isotopic tracer conditions, and interdiffusion of two different ions from external bathing solutions. In addition, total salt diffusion, limited by transport of co-ion, and solvent transport have been extensively measured. Recent literature to 1972 is summarized by Riando,[18] Lakshminarayanaiah,[19,22,23] and Buck.[44,45]

Specific studies of membrane potentials include "concentration" potentials where a single salt is present at different activities on either side;[208-212] bi-ionic potentials where two different salts are present, one salt on each side;[213-220] and multi-ionic potentials where more than one salt is present on each side. Studies and applications of synthetic membrane electrodes have been a continuing program by one group of Russian researchers at Leningrad.[221,222] Considerable interest in alternating stacks of cationic and anionic membranes, with and without intentional addition of water layers, has been generated because of possible desalination applications. A number of recent theoretical and experimental studies, particularly on current-voltage behavior, have appeared on these so-called bipolar systems,[223-229a] as well as on two membrane systems of the same kind but differing in permselectivity.[230]

Studies which are of importance to theoretical basis of fixed site membrane transport verify the perturbation of internal ion concentration profiles by current;[231,231a] demonstrate the validity of the Nernst-Einstein equation relating diffusion coefficient and mobility (deduced from conductance data[232,232a]); verify the use of transference numbers in the derivation of membrane potential theory for single-salt transport by comparison with directly determined transference values;[233] and demonstrate the film diffusion limitation of current via chronopotentiometry.[234,235]

Complete analysis of ion and water transport using the Stefan-Maxwell equations has been described by Lakshminarayanaiah and co-workers.[236-238] This analysis requires measurements of water transport, conductance, self-diffusion coefficients, hydrodynamic permeability, and ion exchange constants. Likewise, Gardner and coworkers[239,240] have made measurements of the self-diffusion coefficients of monovalent cations in water swollen membranes. Their interpretation relies on the Meares-Spiegler model outlined above.[241] Certainly, when membranes contain extensive amounts of solvent, transport through aqueous pores is probable. In the limit of large pores lined with fixed sites (or no sites), one is dealing with a different kind of transport in which hydrodynamic considerations must be included.[241-248] A particularly clear presentation of the relations between diffusion in homogenous bulk and in pores can be found in Chapters 6 and 7 of Helfferich's book.[20]

3. *Electrical Response Functions for Solid, Crystalline, and Pressed Pellet Membranes*

Single-crystal Frenkel membranes, silver halides and LaF_3, for example, ordinarily behave like fixed site membranes. At room temperature, divalent anion impurities in AgX generate mobile cation interstitials (counter ions) which can move in the crystal from fixed anion to anion.[249] Similarly, divalent metal impurities in AgX generate silver ion vacancies which are also mobile. The anion lattice remains fixed. The reverse situation occurs in LaF_3, where fluoride ion interstitials and vacancies are mobile in a fixed lattice of LaF_2^+. Schottky defect crystals with mobile cations *and* anions are known at high temperatures. However, for electrochemical membrane studies and applications in the ion selective electrode field at room temperature, Frenkel defect systems (crystals and pressed pellets) have received more experimental and theoretical consideration.[6,19,23,250-253] Continuing the description using silver halides as the model system, consider an AgX membrane between two aqueous solutions saturated with AgX. Except for space charge and adsorbed ions at the membrane surfaces, crystals are electrically neutral and contain a uniform concentration of mobile species, even with current flow, assuming that generating rates are large. With the exception of intrinsic crystals, transport of either interstitials or vacancies, but not both, must be considered in deriving the internal diffusion potential. In general, it is zero even for metathetic cases where, for example, an AgCl crystal surface is partially converted to AgBr, AgI, etc. by exposure to solutions of soluble metathetic anions; it is not necessarily zero for metathetic cations such as Hg (I).

The reversible interfacial potential follows from Equations 31 and 35 and takes one of two convenient forms depending on the ion added at highest concentration in the solution:

$$\varphi - \overline{\varphi} = \frac{RT}{F} \ln \{2\overline{a}_{Ag^+}/(K_{ext,Ag^+} \times \gamma_{Ag^+} \{C_{Ag^+} + (C^2{}_{Ag^+} + 4K_{sp}/\gamma_\pm^2)^{1/2}])\} \qquad (196a)$$

for $C_{Ag^+} > K_{sp}{}^{1/2}/\gamma_\pm$

or

$$\varphi - \overline{\varphi} = \frac{RT}{F} \ln \{\overline{a}_{Ag^+} [C_{X^-} + \gamma_{X^-} (C^2{}_{X^-} + 4K_{sp}/\gamma_\pm^2)^{1/2}/2\, K_{ext,Ag^+} K_{sp}]\} \qquad (196b)$$

for $C_{Ag^+} < K_{sp}{}^{1/2}/\gamma_\pm$

When no added Ag^+ or X^- is present in a solution, these equations give the potential for the membrane in its own saturated solution since C_{Ag^+}, the added concentration, is zero. Overall membrane potentials are typically of the form:

$$\Delta\varphi_m = \frac{RT}{F} \ln \left[\frac{a_{Ag^+,o} + \gamma_{Ag^+,o} (C^2{}_{Ag^+,o} + 4K_{sp}/\gamma_\pm^2)^{1/2}}{a_{Ag^+,d} + \gamma_{Ag^+,d} (C^2{}_{Ag^+,d} + 4K_{sp}/\gamma_\pm^2)^{1/2}} \right] \qquad (197)$$

where $a_{Ag^+,O}$, $C_{Ag^+,O}$, $a_{Ag^+,d}$, and $C_{Ag^+,d}$ are quantities in the test electrolyte prior to inserting the electrode, or prior to saturation with the electrode material. This equation is illustrated in Figures 22A and 22B using folded plots. Buck gave this analysis some years ago[249] and included the effects of metathetical reagents. His general solution has the form:

$$\Delta\varphi_m = -\frac{RT}{F} \ln \left[\frac{a_{I^-,o} + \dfrac{K_{sp}\,(AgI)\,\overline{\gamma}_{X^-}}{K_{sp}\,(AgX)\,\overline{\gamma}_{I^-}} a_{X^-,o}}{1/a_{Ag^+,d}} \right] \qquad (198)$$

which is applicable when a_{Ag^+} is known and fixed on one side (the "d" side) and the solution contains I^- and the ion X^- at the "O" side. Note that the apparent selectivity coefficient, $K_{I^-,X^-}{}^{Pot}$, does not include the mobility ratio of the anions since they are not involved in the development of the diffusion potential:

$$K_{ij}^{Pot} = \frac{K_{sp}\,(Agi)\,\overline{\gamma}_j}{K_{sp}\,(Agj)\,\overline{\gamma}_i} \qquad (199)$$

Early tests of this equation suffered from the lack of consideration of film diffusion as noted by

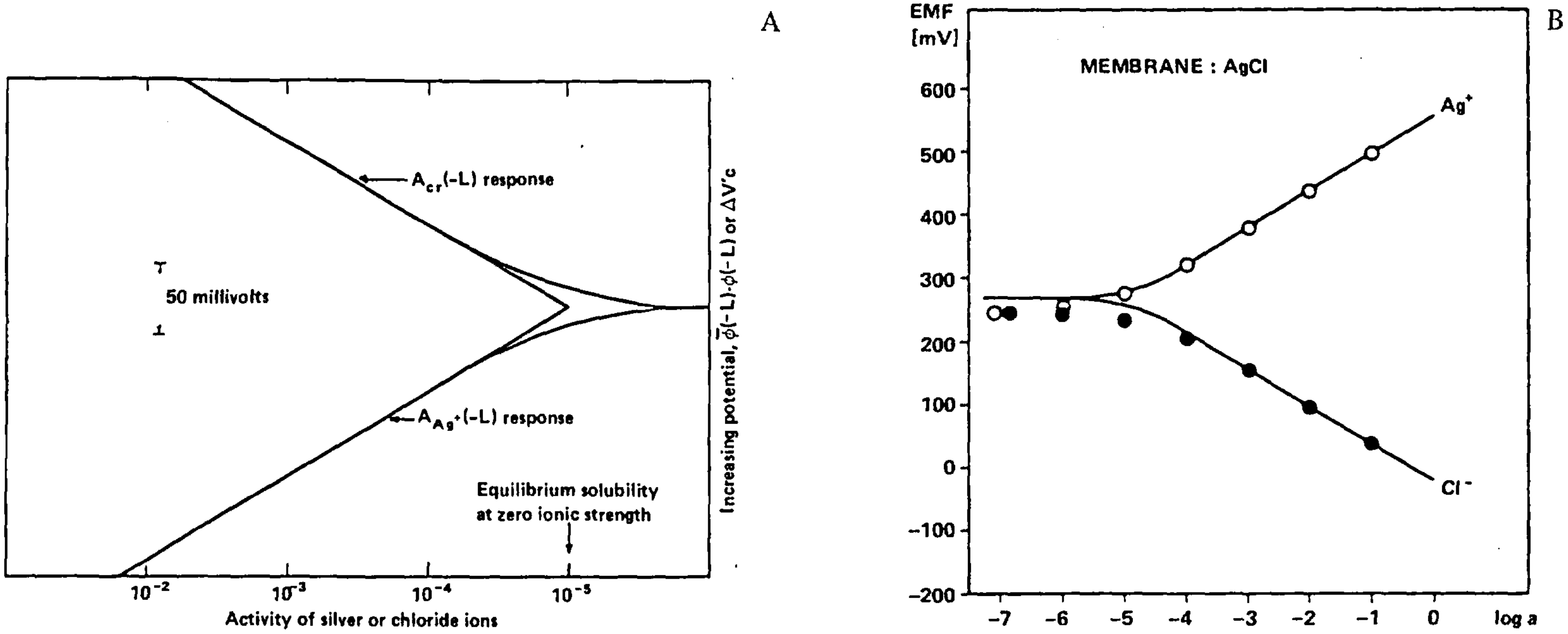

FIGURE 22. A. Test solution *interface* potential or the measured cell potential for a junction cell using a silver chloride membrane. Curves are calculated according to Equations 196a and 196b. Potential increases positive downward. Activity coefficient changes due to the presence of inert salts shift the entire curve to the left by increasing the apparent concentration-based solubility product. Reference solution contains activities of excess silver or chloride to maintain a constant interfacial potential at the reference side interface. (From Buck, R. P., *Anal. Chem.*, 40, 1432 (1968). With permission.) B. Experimental cell potential (EMF) for a silver chloride membrane electrode to activities of Ag^+ and Cl^-, for comparison with theoretical predictions shown in Figure 22A. Calculated: solid lines. Experimental points: Ag^+ (○); Cl^- (●). (From Morf, W. E., Kahr, G., and Simon, G., *Anal. Chem.*, 46, 1538 (1974). With permission.)

Koryta.[251] The two-point method yields erroneous results, while the method of mixtures[206] gives reliable data provided it is realized that the attacking anion displaces crystal anions, i.e., I^- and Br^- replace Cl^-. In the mixture method, sufficient Cl^- in solution must be used so that the increment of Cl^- released from the surface is an insignificant perturbation. Even with stirring, the film diffusion of excess Cl^- at the surface to the bulk causes significant errors. The extensive measurements of Pungor et al.[254,255] have confirmed Equation 199. Morf, Kahr, and Simon[256] rederived, extended the theory, and provided experimental tests. However, the analysis was prompted by apparent deviations from the Nernstian response which occurs in dilute sulfide solutions using Ag_2S membranes and in dilute iodide solutions using AgI membranes. These deviations are probably caused by quite different processes from that which they assumed and, while their equations are fortuitously correct, the quantities in the equations must be understood differently. Insoluble salts of soft, polarizable ions are notoriously prone to adsorption of common ion salts. Ag_2S precipitated from excess Ag^+ contains excess soluble silver salts, while precipitation from excess sulfide leads to occluded soluble sulfide salts. Electrodes made from Ag_2S are very sensitive to the method of preparation of the membrane material[256a,256b,256c] and responses range from Nernstian to virtual insensitivity to component ion activities. The best method for formation of the sulfides used in ion selective electrodes, Ag_2S, CdS, CuS, and PbS, appears to be precipitation from acidified solutions of a soluble metal salt using H_2S so that minimal excess soluble silver salt remains and yet there is no excess sulfide. Heat treatment is used to volatilize residuals.

Soluble metal ion salts are slowly leached[256d,256e] from the electrode membrane and produced by air oxidation[256f,256g] adsorbed at the outer membrane surface. Ordinarily, in activities of potential-determining cations higher than the leached surface values (and in high anion activities such that the leached-adsorbed ions are precipitated), the observed responses are Nernstian. However, at extreme dilution of either responsive anion or cation salt solutions, deviations from Nernst are observed in a direction and amount expected for excess leached cations. The appearance of this effect has led some workers to question the theory which predicts an ultimate detection level determined by the intrinsic solubility of the membrane material. However, these spurious experimental artifacts disappear when buffered test solutions are used to maintain low activities of ions via labile complex equilibria. The sensitivity to stirring and electrode washing is also consistent with leaching. If one identifies the quantity α in the equations of Morf, Kahr, and Simon with the leached cation activity (not defect interstitial ions which belong to the membrane rather than the solution phase), the theory is adequate.

An application of this effect is the monitoring of anion activities using Ag_2S electrodes involving anions which are normally weak complex formers.[256h] Since the intrinsic solubility of silver sulfide is very small, it is not possible on thermodynamic ground that pure Ag_2S membranes could respond to anions whose residual equilibrium silver ion activities are greater than that available from the membrane dissolution. Responses are observed which correspond to a relatively constant silver ion activity prior to complexation. This effect can be interpreted as leaching of silver ions from the membrane or air oxidation and suggests that purposeful addition of silver ions to solutions under test might even improve the technique.

In the presence of soluble, strong complex forming reagents, the interfacial potential is affected because one of the ionic component activities is depressed upon complex formation so that the solution is no longer saturated.[257] A variety of situations can arise depending upon complex formation constants, the sign of the complexing agent, secondary equilibria with competing ions such as H^+, rates of complexation, rates of removal of component ions from the membrane interface, and rates of mass transport of material to and from the membrane interface. Many of the possibilities have not been treated theoretically. A typical situation of CN^- attacking an AgX membrane to form X^- and $Ag(CN)_2^-$ in a rapid, reversible way can be analyzed using flux balance in the steady state. In the Nernst diffusion layer at the membrane surface,

$$J_{CN^-} + 2\,J_{Ag(CN)_2^-} = 0 \qquad (200a)$$

$$J_{X^-} + J_{CN^-} + J_{Ag(CN)_2^-} = 0 \qquad (200b)$$

and the surface concentration of X^- is approximately

$$C_{X^-}(0) \sim C_{X^-}(\text{bulk}) + \frac{D_{CN^-}\delta_{X^-}}{D_{X^-}\delta_{CN^-}} C_{CN^-}(\text{bulk}) \qquad (201)$$

for complex formation constants which are large enough to allow the principal reaction to be

$$2\,CN^- + AgX \longrightarrow Ag(CN)_2^- + X^- \qquad (202)$$

The electrode response is simply

$$\Delta\varphi_m = -\frac{RT}{F} \ln \left\{ \left[a_{X^-,o} + \frac{D_{CN^-}\delta_{X^-}}{2(D_{X^-}\delta_{CN^-})}\gamma_{X^-} C_{CN^-} \right] / a_{X^-,d} \right\} \qquad (203)$$

and the potentiometric selectivity is apparent. In stirred media, the Nernst thicknesses are nearly constant for all ions. In static diffusion cases they are proportional to the square root of the respective diffusion coefficients. In either case, the selectivity coefficient is close to 0.5.[258] Koryta[250] has extended the treatment to account for the pH effect when the complex forming anion is the salt of a weak acid. Mascini presented experimental tests.[259] Irreversible attack by complex forming or redox reagents was treated approximately by Buck.[260] The theory has also been recently extended by Morf et al.[256]

Very little is known concerning the rate of ion exchange of cations and anions at crystal/solution interfaces. The problem is twofold because the rate of dissolution and precipitation of the crystal itself is involved as well as individual rates of ion exchange at equilibrium. However, these effects are coupled because a crystal in an unsaturated or supersaturated solution must show equal fluxes of ions of both signs. Any transient space charge which develops from unequal rates creates a so-called crystallization potential which enforces equality of ionic fluxes. Of the crystals used as ion selective electrodes, LaF_3 is known to possess a slow precipitation rate presumably because La^{+3} exchange is slow. Consequently LaF_3 responds reversibly to activities of fluoride ion, but is virtually insensitive to varying activities of La^{+3}. Sulfides of transition elements, such as NiS, do not function as cation activity sensors and probably fail to do so because of slow rates of ion exchange. This interpretation is consistent with the known slow rate of metal ion reductions which results from the lack of lability of the hydrated ions. Thus it seems unlikely that simple insoluble salts containing nonhydrated ions will be found that can function as sensors for transition metal ion activities.

C. Electrical Properties of Class III – Liquid Ion Exchanger Membranes

1. Electrical Response Functions for Permselective Liquid Ion Exchanger Membranes

Condition 1. $\overline{\gamma}_i \neq f(x)$
Condition 2. $\bar{u}_i \neq f(x)$
Condition 3. $\overline{\mu}_o \neq f(x)$
Condition 4. $\bar{u}_i RT = \overline{D}_i$
Condition 5. $\int_0^d \overline{X}(x)\,dx = \overline{X}_o d$ (confinement of sites within a membrane)

The most rigorous and comprehensive of the treatments of electroneutral, dissociated liquid ion exchange electrical properties is by Conti and Eisenman.[261] Unfortunately, their derivations are cast in terms of the results deduced for distributed, fixed site membranes. They are, indeed, closely related cases, and the zero current membrane potential for permeable ions of charge z is exactly the same as that in Equation 182. However, Equation 182 applies at all times after completion of surface ion exchange for fixed site membranes, but only applies in the steady state for liquid ion exchanger membranes. The reason for this difference is that, in contrast with fixed site membranes, the inner surface concentrations of exchanging ions continue to vary in time as the sites redistribute in space and time. Only in limited cases will Equation 182 be exact at short times compared with the time required to reach steady state. The trivial case is a permselective membrane bathed by a single salt of a permeable ion and subjected to a step activity change on one side of the membrane. Another case is that involving mixtures of permeable ions, all of which have the same mobility in the membrane. In both examples, the profile of sites is flat at all times after initial double layer charging.

At zero current, the distribution of mobile sites in space is flat (zero slope) for asymmetric bathing solutions of a single electrolyte but is linear with finite slope when different permeable ions with different mobilities are present on either side. In that case, the individual ion fluxes are nonzero and can perturb the site profile. Passage of current in the steady state also creates linearly tipped site profiles. Site concentrations are higher than average at the side where permeable ions enter and lower at the exciting side. This feature is a result of the condition that the sites, while free to move, are constrained to the interior of the membrane.

For two permeable ions of charge z, sites of charge z_0,

$$z_0, \omega = |z_0/z| \tag{204}$$

one defines α as before (Equation 192) and notes that $\bar{X}$ is now a function of distance and

$$\bar{C}_1(x) + \bar{C}_2(x) = -\omega\bar{X}(x) \tag{205}$$

In the static situation with only one permeable ion,

$$\bar{C}_1(0) = \bar{C}_1(x) = \bar{C}_1(d) = -\omega\bar{X}_0 \tag{206}$$

where $\bar{X}_0$ is the flat site concentration. In general,

$$\bar{X}(x) = \tag{207}$$

$$\frac{2\bar{X}_0}{1 + (\alpha\xi)^{-\omega/1-\omega}} \left\{ 1 - \frac{x}{d}\ [1 - (\alpha\xi)^{-\omega/1-\omega}] \right\}$$

Individual ion profiles, however, are nonlinear in distance, except for the applied voltage corresponding to flat site distribution, $\xi = 1/\alpha$. These results are illustrated in Figures 23 and 24.

The current-voltage characteristic resembles a polarographic wave in that a limiting current occurs at large positive and negative values corresponding to a zero value of the site concentration at one inner surface or the other. The shape is easily compared with the fixed site case in Figure 21.

$$I = -2zFRT\bar{u}_1 \frac{(1-\omega)\bar{X}_0}{d} \left[\frac{a_{1,0} + K_{1,2}^{Pot} a_{2,0}}{a_{1,0} + K_{iexc}\, a_{2,c}} \right] \frac{1-\xi}{1-\alpha\xi} \tanh \left[\frac{-\omega}{2(1-\omega)} \ln\alpha\xi \right] \tag{208}$$

Limiting values are:

$$I(\Delta\varphi \to \infty) = -2zFRT\bar{u}_1 \frac{(1-\omega)\bar{X}_0}{d} \left[\frac{a_{1,d} + K_{1,2}^{Pot} a_{2,d}}{a_{1,d} + K_{iexc}\, a_{2,d}} \right] \tag{209}$$

and

$$I(\Delta\varphi \to -\infty) = 2zFRT\bar{u}_1 \frac{(1-\omega)\bar{X}_0}{d} \left[\frac{a_{1,0} + K_{1,2}^{Pot} a_{2,0}}{a_{1,0} + K_{iexc}\, a_{2,0}} \right] \tag{210}$$

Prior to the Conti-Eisenman treatment, a number of ad hoc equations for cation fluxes and zero current potentials were derived on the constant field assumption. Soluble anions were allowed to have +1, 0, −1, −2 charges, and no account was taken of overall chemical equilibria in the membrane, i.e., each ion combined with its own anion "carrier." In addition, kinetic boundary conditions were used.[183,189] Regardless of the inexact character of these analyses, regions of negative resistance (i.e., peak currents in the I-$\Delta\phi_m$ curve) were computed which were roughly comparable with experimental examples.[262]

Subsequently, Sandblom et al.[263] solved the algebraically difficult problem of membrane complexation for univalent permeable cations and a univalent anion liquid exchanger. The total steady state potential can be expressed as the usual log term plus an integral:

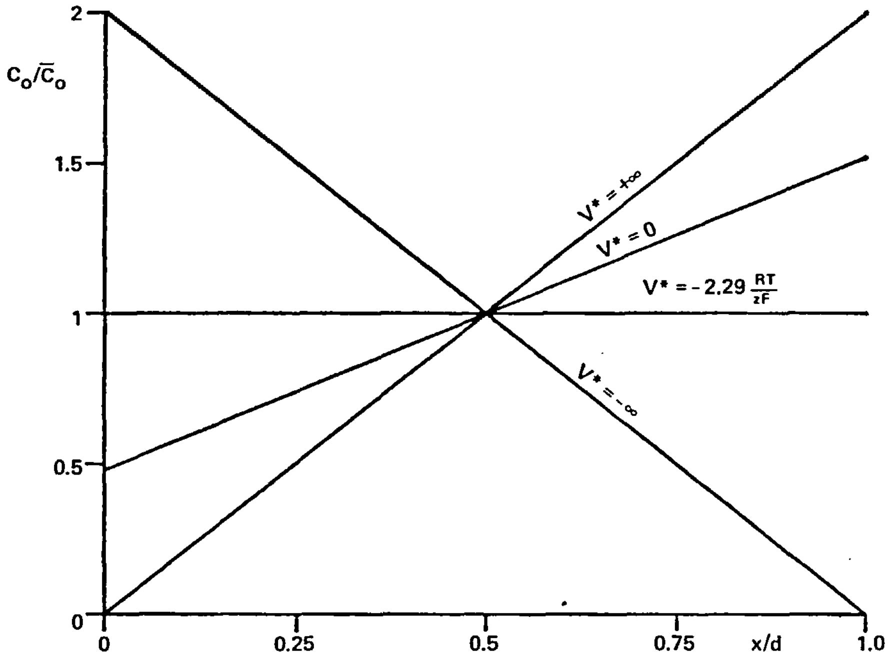

FIGURE 23. Concentration profiles of sites. $C_0/\overline{C}_0$ in the original article which is $\overline{X}(x)/\overline{X}_0$ in this text, is plotted as a function of x/d for the indicated values of the reduced voltage (zF/RT)V* for the case $z = -z_0 = 1$ and for the values of the parameters r = 30, $X_1' = 0.5$, $X_1'' - 0.98$, for which α = 9.88. Note that a uniform concentration profile occurs when ζ = 1/α, i.e., when (zF/RT)V* = −2.29. Quantities and parameters are defined in Figure 21 legend.

(From Conti, F. and Eisenman, G., *Biophys. J.*, 6, 227 (1966). With permission.)

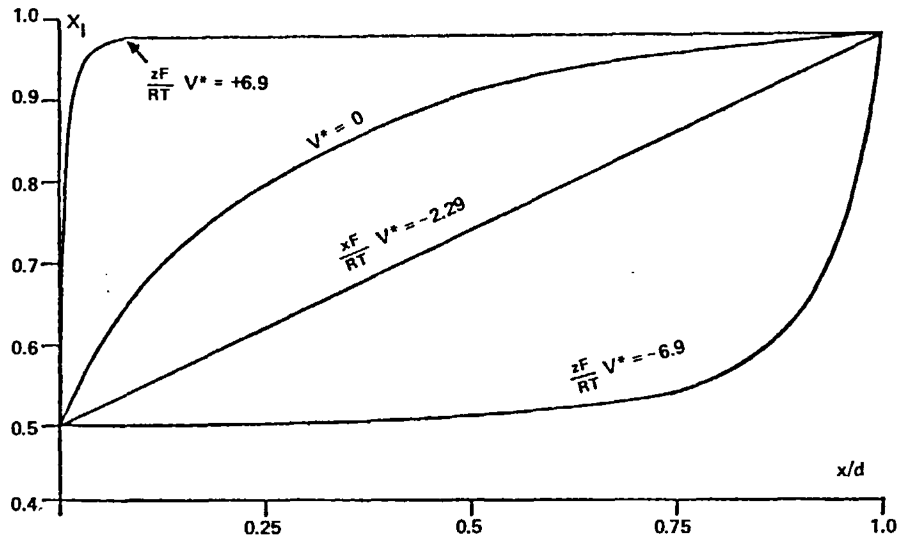

FIGURE 24. Concentration profiles for counter-ions. X_1, the mole fraction of species 1 is plotted for the case $z = -z_0 = 1$ as a function of x/d for the values of the parameters r = 30, $X_1' = 0.5$, $X_1'' = 0.98$ and for the indicated values of (zF/RT)V*. Quantities and parameters are defined in Figure 21 legend. (From Conti, F. and Eisenman, G., *Biophys. J.*, 6, 227 (1966). With permission.)

$$\Delta\varphi_m = \frac{RT}{F} \ln\left[\frac{a_n + \sum_m K^{Pot}_{n,m} a_m}{a_k + \sum_l K^{Pot}_{k,l} a_l}\right] + \int_0^d t \, d\ln\left[\frac{\sum_i \bar{u}_{is} K_{is} \bar{C}_i}{\sum_i \bar{u}_i \bar{C}_i}\right] \tag{211}$$

$$t = \frac{u_s C_s}{\left(\frac{u_s C_s}{\sum_i u_{is} C_{is}} + 1\right)\left(\sum_i u_i C_i\right) + u_s C_s} \tag{212}$$

In this statement, n and m are ions in the left bathing solution, and k and l are on the right. Superbars have been omitted; u's are again mobilities, and other quantities have been defined earlier. When the membrane is fully dissociated, $K_{is} = 0$, and only the first term remains.

For strong complexation, three cases must be noted. If only one permselective ion is involved, the response to variation in activity of this ion on one side is normal, viz., the first term in Equation 211 remains. From potentiometry alone, one cannot tell from the Nernstian response that the permeable ion is strongly complexed or not complexed at all. For a two permeable ion system, of which one is complexed but the other is not, the response again follows the logarithmic term. However, the ion forming the ion paired species is highly favored in the membrane and shows a large potentiometric selectivity coefficient since K^{Pot} is directly proportional to the product of the ion pairing formation constant and the single ion extraction coefficient. When both permeable ions are complexed strongly, Sandblom et al. evaluate the integral by further rearrangement and simplification. The responses are not necessarily Nernstian except when the bathing solution activities are widely different for the two ions.

In the second of the two papers, the current-voltage characteristic was worked out for a liquid membrane bathed in solutions of a single permeable ion with complexation in the membrane included. Evaluation of the current and the voltage are done parametrically in terms of a quantity involving an integral over sites. Limiting currents at large applied membrane voltages are readily obtained. The current-voltage characteristic is "spread out" along the usual applied voltage axis and the current shows a longer region of linearity centered on the potential of zero current. Limiting currents are reached when both free and complexed forms of the permeable ion are reduced to zero at the exiting side of the membrane. Relatively greater absolute applied voltages must be used to force the necessary current through the membrane to achieve limiting current concentration polarization.

Important derived quantities, including high frequency resistance unperturbed by concentration polarization and dc resistance are included in Table 4 together with quantities pertinent to fixed site membranes.

Sandblom[264] has worked out nonzero current I-$\Delta\phi_m$ characteristics for the more general liquid membrane permeable to many ions of the same valence with differing degrees of complexation in the membrane. These results are sufficiently complicated that the original work should be consulted. More recently, Buck[53] extended the liquid membrane potential and I-$\Delta\phi$ theory to include Poisson's equation. Space charge as a function of current could be specifically identified and field and potential profiles computed, not just in the electrolyte bulk, but up to the Outer Helmholtz Planes of the inner membrane interfaces. He also showed the exact analog between a permselective membrane and a thin-layer electrochemical cell in the steady state. Buck and Sandifer treated the zero current liquid membrane potential for mixed divalent, monovalent cations.[265]

Testing of theory, primarily of the applicability of Equation 193 (n = 1) to zero current potential-activity relations, is summarized in a number of reviews.[19,23,32,43-45,251,266] The thrust of experimental testing is the demonstration of relations between selectivity coefficients and independently measured ion exchange constants, total extraction coefficients, ion pair formation constants, ion mobilities, and concentration (loading) of the trapped liquid exchanger.[267-274] Both Eisenman and Sandblom have tested their respective theories of current-voltage curves for dissociated[275] and associated[276,277] liquid ion exchanger membranes. One cannot, however, consider the theories completely tested since it is difficult to obtain independent measurements of the various species mobilities and complex formation constants. Complex formation con-

TABLE 4

Zero Current DC and Infinite Frequency AC Resistances for Fixed and Mobile Site Liquid Ion Exchanger Membranes with Single Monovalent Counter-ions

	DC resistance R_0	Infinite frequency AC resistance R_∞
Fixed uniform site concentration X_0	$\frac{d}{F^2 u_i \overline{X}_0}$	$\frac{d}{F^2 u_i \overline{X}_0}$
Variable fixed site concentration	$\frac{1}{F^2 S}$	$\frac{1}{F^2 S}$
Mobile site general case	$\frac{(u_s + u_{is}\overline{X}K_{is})d}{F^2 u_i u_s \overline{X} + (u_i + u_s)u_{is}\overline{X}^2 K_{is}}$	$\frac{d}{F^2 (u_i + u_s)\overline{X}}$
Mobile site complete dissociation	$\frac{d}{F^2 u_i \overline{X}_0}$	$\frac{d}{F^2 (u_i + u_s)\overline{X}_0}$
Mobile site strong association	$\frac{d(K_{is})^{1/2}}{F^2 (u_i + u_s)(\overline{X}_0)^{1/2}}$	$\frac{d(K_{is})^{1/2}}{F^2 (u_i + u_s)(\overline{X}_0)^{1/2}}$

$\overline{X}$ = free site concentration
$\overline{X}_0$ = *total average site concentration*

stants obtained from ac conductivity measurements over a range of site concentrations for single permeable species systems are combined to calculate potentiometric selectivities which are then compared with directly determined values. The most extensive testing of theory is by Fabiani, Danesi, Scibona, and Scuppa.[277a]

D. Permeabilities and Selectivities

For uncharged materials penetrating a membrane barrier, simple flux equations can be written in terms of net concentration or activity differences, as in Equation 93 or 96. The quantity relating flux and activity differences is a permeability coefficient which is expressible in terms of a diffusion coefficient, extraction coefficient, and membrane thickness. When the diffusion is space and concentration independent (but not necessarily free from film diffusion control), the permeability is independent of bathing solution activities. Similarly, for pressure gradient driven transport, a concentration independent permeability, depending specifically on membrane properties, can usually be observed.

On the contrary, ion permeabilities, expressed as a proportionality with external activity differences, in general are not independent of bathing solution activities simply because the fluxes do not obey a simple equation of the form of Equation 96. More nearly constant permeabilities would be expected when they are defined for a site free membrane as the coefficient

$$P_i = \frac{RT\overline{u}_i K_{ext,i}}{Fd\,\overline{\gamma}_i} \tag{213}$$

in the second expression for $\overline{J}_i$ which follows from

$$\overline{J}_i = \frac{RT\,\overline{u}_i}{Fd}\left(\frac{F\Delta\varphi_m}{RT}\right)\left[\frac{\overline{C}_{i,d}\,\xi - \overline{C}_{i,o}}{\xi - 1}\right] \tag{214a}$$

when interfacial potentials are considered,

$$\overline{J}_i \simeq \frac{RT\,\overline{u}_i\,K_{ext,i}}{Fd\overline{\gamma}_i}\left(\frac{F\Delta\varphi_m}{RT}\right)\left[\frac{a_{i,d}\,\xi - a_{i,o}}{\xi - 1}\right] \tag{214b}$$

As pointed out before, the analytical result of Equation 214b applies rigorously only for identical bathing solutions, as in an experiment using radiotracer labeling on one side, while Equation 214b also applies for mixtures of permeable ions with the same absolute charges at the same total concentration on each side. Inasmuch as the same permeability coefficients appear in the Goldman equation for zero current potentials, it is not surprising that the permeabilities required to fit experimental data are not generally constant but depend on bathing solution compositions. Even for the few cases where Equation 214a is rigorous, the relation between $\overline{C}_i$ and a_i depends on interfacial potential and activity coefficients. Only in the unusual situation where all cation extraction coefficients have a single value (and another constant value for anions) will the interfacial potentials be identical on the two sides. Then $\overline{C}_i \propto a_i$ and Equation 214b becomes exact.

On the other hand, in electroneutral membranes with sites, the permeability coefficients are generally constant for ions of the same charge and are proportional to ion mobility and extraction coefficient,

$$P_i \propto \overline{u}_i\, K_{ext,j}/\overline{\gamma}_i \tag{215}$$

and K_{ij}^{Pot} can be expressed as:

$$K_{ij}^{Pot} = \frac{P_i}{P_j} = \frac{K_{ext,i}\,\overline{u}_i\,\overline{\gamma}_j}{K_{ext,j}\,\overline{u}_j\,\overline{\gamma}_i} = K_{iexc}\frac{\overline{u}_i\,\overline{\gamma}_j}{\overline{u}_j\,\overline{\gamma}_i} \tag{216}$$

In an elaborate and thorough analysis, Sandblom and Eisenman[278] demonstrate that permeability ratios for ions can be independent of solution compositions when the temperature is constant, no neutral species, ion pairs, or solvent transport occur, ions of only one sign are transported, and the standard chemical potentials of ions in each phase are constant. These conclusions apply to fixed site membranes at all times and to mobile site membranes in the steady state. In the appendix, they have shown that the permeabilities (coefficients of a_i, a_j, etc.) in Equation 161 are true constants when the total ionic concentraions are the same on the two sides of a site free membrane (or constrained liquid junction) and that the interfacial potentials are the same by virtue of Equation 45, when the single ion extraction coefficients are identical for all cations and have another identical value for anions.

Another general result for systems with constant permeabilities is the relation between K_{ij}^{Pot} and single-ion conductances:

$$\frac{P_i}{P_j} = \frac{K_{ext,i}\,\lambda_i\,\overline{\gamma}_j}{K_{ext,j}\,\lambda_j\,\overline{\gamma}_i} \tag{217}$$

VI. TIME DEPENDENT BEHAVIOR OF MEMBRANES

The time dependence of the electrical properties of membranes is the least well-understood topic among the fundamental characteristics. Already noted is the important distinction between linear and nonlinear perturbations. When a membrane and its bathing solutions are initially in a steady state or an equilibrium state, the system can be perturbed by applied voltage, current, or external activity change of a permeable ion (usually on one side). These perturbations are linear, when the applied voltage or resulting voltage change is less than RT/zF V. For reversible interfacial processes, a concentration step increase or decrease of 50% of the initial value (or less) is within a linear range. Total linearization implies that steady state responses obey ordinary linear differential equations (in distance), while time dependent responses obey linear partial differential equations. Linearization for calculation of time responses leads to forms in which there is a dc steady state solution plus time dependent terms. It is possible to obtain "mixed" solutions in which the time response is found by linearization, but the solution may itself be the answer to a nonlinear problem. To achieve this form, one assumes a solution for current or voltage in the form:

$$V = V_{DC} + V_n \sum_n \exp(-n_j\omega t) \tag{218}$$

For ordinary sinusoidal excitations, only the n = 1 term is retained.

Furthermore, linearized systems obey a quite general form in transform space:

$$\Delta\varphi_m(s) = Z(s)\, I(s) \tag{219}$$

where s = jω and ω = 2πf (f = frequency in Hz). Given the system response function Z(s) and the perturbation I(t) whose transform is I(s), the membrane potential can be found by inverting the transform. Conversely, a given applied voltage perturbation of any transformable type (step, pulse, sinusoid, etc.) divided by Z(s) allows current vs. time to be computed.

An exact solution for the time dependent properties of thin, site free membranes permeable to a single-sign ion has been derived by DeLevie et al.[113] under conditions of pure membrane control (exterior film diffusion limitation is ignored). The general problem of the time dependent behavior of thick, site free membranes permeable to ions of both signs has been discussed by Michaelis and

Chaplain.[111] The most extensive exact solutions for thick and thin membranes containing two ions of opposite charge and arbitrary mobilities, valences, and surface rate constants are by Macdonald.[108-110] His general theory is an extension of the uni-univalent cases previously treated.[105-107] The theory does not take into account surface adsorption, nor does it allow for generation of charge carriers from the lattice ions or recombination of charge carriers (analogous in liquid membranes to formation of ion pairs). Furthermore, it is limited to the initial state of the system without space charge at either interface (so-called flat band potential or pzc). The results are cast in the form of impedance functions Z(jω), which are thoroughly investigated by plots of parallel conductance and capacitance as functions of frequency.

A. Time Constants of Membrane Processes in the Linear Regime

In a general sense, based on accumulated theory and experiment, one can conclude that membrane systems can show at least five distinguishable time constants, although this statement does not imply that current-time response under a voltage step can be resolved into five exponentials. Not all processes occur in a given membrane situation, and there may be fortuitous overlapping of time constants. Furthermore, the slower processes involving diffusion are not precisely represented by a single time constant, but by a distribution about a central value as a result of time dependences on $t^{-1/2}$ rather than exp(−kt).

The highest frequency or smallest anticipated time constant(s) arises from the dispersion of the dielectric constants of membranes and bathing solutions causing a decrease in the dielectric constant (with increasing frequency) of the Debye, Cole-Cole, Cole-Davidson, or other types.[21] The latter two involve a distribution of time constants about a central value. The next longer time constant is that due to charging of the external [and internal by Faradaic process] surface regions coupled with the high-frequency resistance. This is also known as the Planck charging process.[279] The capacitance is geometric and is given by:

$$C_g = \frac{\epsilon A}{d} \tag{220}$$

The high frequency resistance for an electroneutral two-ion system of arbitrary charges and mobilities is

$$R_\infty = \frac{d}{F^2 (z_+^2 \, \bar{u}_+ \bar{C}_+ + z_-^2 \, \bar{u}_- \bar{C}_-)} \tag{221}$$

This time constant corresponds to the highest frequency processes determined by transport of charged species in a medium of constant dielectric. Often reported as τ_∞, it is the product $R_\infty C_g$ and corresponds to no change in the internal ionic concentration profiles. It is the usual high-frequency, space charge relaxation time in conducting systems.

The third time constant is the intermediate value due to the coupling of surface rates and the relaxed, doubly diffuse (or compact) capacitance of each interface in series. When surface rate processes are rapid and reversible, this time constant does not appear. The effective resistance at the equilibrium or steady state potential for slow surface rate control is

$$R_\theta = \frac{2RT}{zFi^0} = \frac{2RT}{z^2 \, F^2 \, k_0 \, (\bar{a}_+ \, a_+)^{1/2}} \tag{222}$$

for single cation transport, and

$$R_\theta = \frac{2RT}{F^2 \, [z_+^2 \, k_0^+ (\bar{a}_+ a_+)^{1/2} + z_-^2 \, k_0^- (\bar{a}_- \, a_-)^{1/2}]} \tag{223}$$

when ions of both signs transfer slowly with rate constants k_0^+ and k_0^- at unit activities. The appropriate relaxed capacitance $C_{0,b}$ (ignoring the compact value) is related to the doubly diffuse value given by the series combination in Equation 10, and proves to be given by

$$C_{0,b} = M \, C_g \tag{224}$$

where

$$m = d/2/\kappa \tag{225}$$

is the number of Debye lengths in half of the membrane. The theory for blocked electrodes contains the capacitance $C_{0,b} - C_g$ in series with the membrane resistance. For slow surface rates and thick membranes such that $C_{0,b} \ll C_g$, the time constant is $R_\theta C_{0,b}$. However, it should be noted that in the linearized theory, $C_{0,b}$ is independent of interfacial potential. Actually, this cannot be true over a wide bathing solution concentration range. Thus, $C_{0,b}$ is expected to vary (increase) at all potentials away from the pzc, and to reach limiting values given by the capacitance of the compact layers. This point was discussed in an earlier section.

The question of the appropriate value of $C_{0,b}$ to use in kinetically controlled membrane systems is not obvious. If the interfacial process is very slow such that charge in the capacitance is scarcely perturbed by current flow, then $C_{0,b}$ is the static, zero current (blocked) value given by the Gouy-Chapman theory. If the membrane was bathed symmetrically, one would reciprocally add the doubly diffuse values from Equation 10 to obtain the reciprocal $C_{0,b}$. If the bathing solutions were symmetric, this value is half the value for either interface. Equation 224 was derived for the case that a membrane was metal coated so that exterior charge was not diffuse. For typical large M values, Equation 224 is virtually exact because the doubly diffuse capacitance is expected to be dominated by the interior membrane portions where the dielectric constant is lower than in water and the concentration of mobile ions is generally less than in the bathing solutions.

In the low-frequency or finite Warburg region, the membrane controlled time constant is that required to adjust concentration profiles throughout the membrane. If only cations are permeable, the dc resistance R_0 is

$$R_0 = \frac{d}{F^2 z_+^2 \bar{u}_+ \bar{C}_+} = \left[1 + \frac{\bar{u}_+ z_+}{\bar{u}_- |z_-|}\right] R_\infty \tag{226}$$

for ions of charge z_+ and z_-. The dc capacitance is approximately

$$C_{0,r} = \frac{d\, F^2\, A}{2RT} (z_+^2 \bar{C}_+ + z_-^2 \bar{C}_-) = M^2 C_g \tag{227}$$

for $z_+ = z_- = z$ and potentials near the pzc, and the time constant (defined as the reciprical frequency at maximum imaginary impedance) is given by:

$$\tau_0 = \frac{1}{2.53} \left[\frac{z_+ z_-}{(z_+ + z_-)^2}\right] \frac{(\bar{u}_+ + \bar{u}_-)^2}{\bar{u}_+ \bar{u}_-} C_{0,r} R_0 \tag{228a}$$

or

$$\tau_0 = \frac{M^2}{2.53} \tau_\infty \quad \text{for } z_+ = z_-, \bar{u}_+ = \bar{u}_- \tag{228b}$$

This definition coincides with that for any true parallel network, even though the Warburg equivalent network is not a simple parallel RC, but a finite transmission line. Time constants τ_∞ and τ_0, apply to membranes in which cations and anions move within the membrane at high frequencies, but only the cations or anions pass the membrane surface and carry current at zero frequency. When both cations and anions pass the membrane surface at high *and* low frequencies, resistances are nearly the same and the finite Warburg region does not exist. Fixed site membranes permselective to ions of a given charge and lipid bilayers permeable to an ion of a single charge should not show Warburg response. It is, however, a moot point whether fixed site membranes such as glasses behave as single charge ion transporters or as two ion transporters: vacancies and interstitials. Experimentally, Warburg behavior has not been observed for glass membranes or for lipid bilayers but the possibility of some mechanism equivalent to two oppositely charged species transport cannot be ruled out for solid state systems.

Numerous cases, such as the transition from mobile anion liquid membranes to very low (including zero) mobility anions, as in fixed site membranes, are treated by Macdonald. Means are given for separating out charge carrier concentrations, charges, mobilities, and surface rate constants. Other recent studies of the Warburg region response of membranes have been done by Sandifer and Buck[48] for glass and by Sandblom[279] for fixed and mobile site membranes.

Finally, when concentration polarization (external film diffusion limitation) can occur in the bathing electrolytes, another time constant arises which is of the same form as above: δ, the Nernst thickness, replaces d, and the mobilities of ions in solution replace those for the membrane in the expression.

B. Membrane Impedance

A convenient way of expressing time dependent behavior is the impedance plot of $-Z_{quad}$ vs. Z_{real}, with frequency as a parameter. This plot is analogous to the better known Cole-Cole dielectric dispersion diagram. Macdonald's theoretical expectations[280] are best illustrated in this form, and some results showing the effects of rate constants, mobility ratios, and membrane thickness are given in Figures 25, 26, 27, and 28. Only the membrane transport controlled responses are illustrated in these figures. The most general form with well-separated time constants for a membrane containing two ions of arbitrary charges z_p and z_n

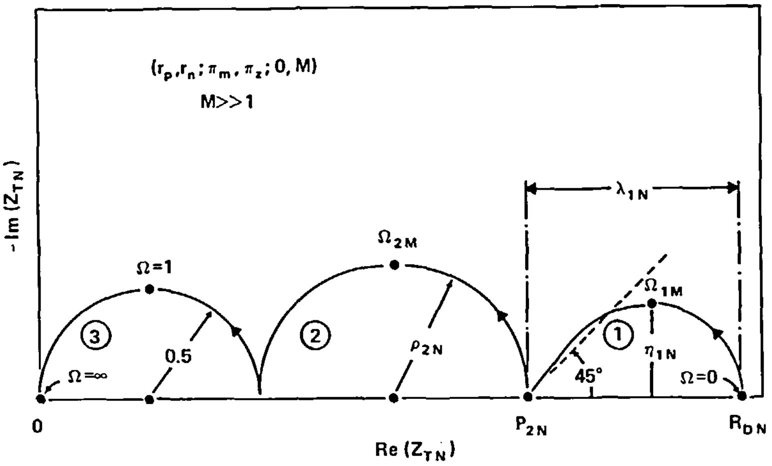

FIGURE 25. Predicted "semicircle or arc" impedance plots according to Macdonald[280] for membranes through which two ions of arbitrary charge and mobility can transport. In Macdonald's terminology, this system is designated as (r_p, r_n; π_m, π_z; O, M). r_p and r_n are Chang-Jaffe rate constants for the interfacial ion transport processes which are related to more conventional rate constants in Equations 229a and 229b. $\pi_m = u_n/u_p$; $\pi_z = z_n/z_p$; M = reduced membrane thickness defined in Equation 225. Ω is a normalized frequency given by the actual frequency $\omega \times \tau_\infty$. The ordinate is the negative imaginary part of the impedance divided by R_∞. Similarly, the abscissa is the real part of the impedance reduced by R_∞. (From Macdonald, J. R., *J. Chem. Phys.*, 61, 3977 (1974). With permission.)

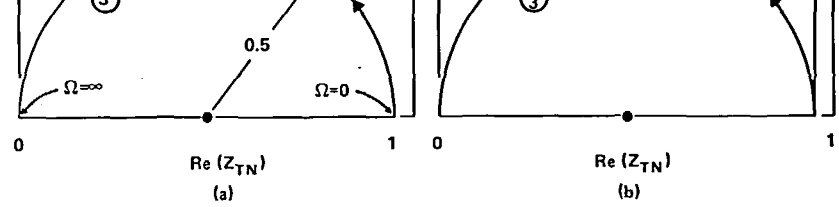

FIGURE 26. Impedance plots for (a) a completely reversible membrane in the high frequency regime (r_p, r_n) = (∞, ∞) with the corresponding equivalent circuit. C_g is the geometric capacitance and $G_\infty = 1/R_\infty$ and (b) for a completely blocked membrane (r_p, r_n) = (0, 0) with the corresponding equivalent circuit. C_{20} is the low frequency capacitance. Relationships are given in Table 5 while abscissa and ordinate are given in the Figure 25 legend. (From Macdonald, J. R., *J. Chem. Phys.*, 61, 3977 (1974). With permission.)

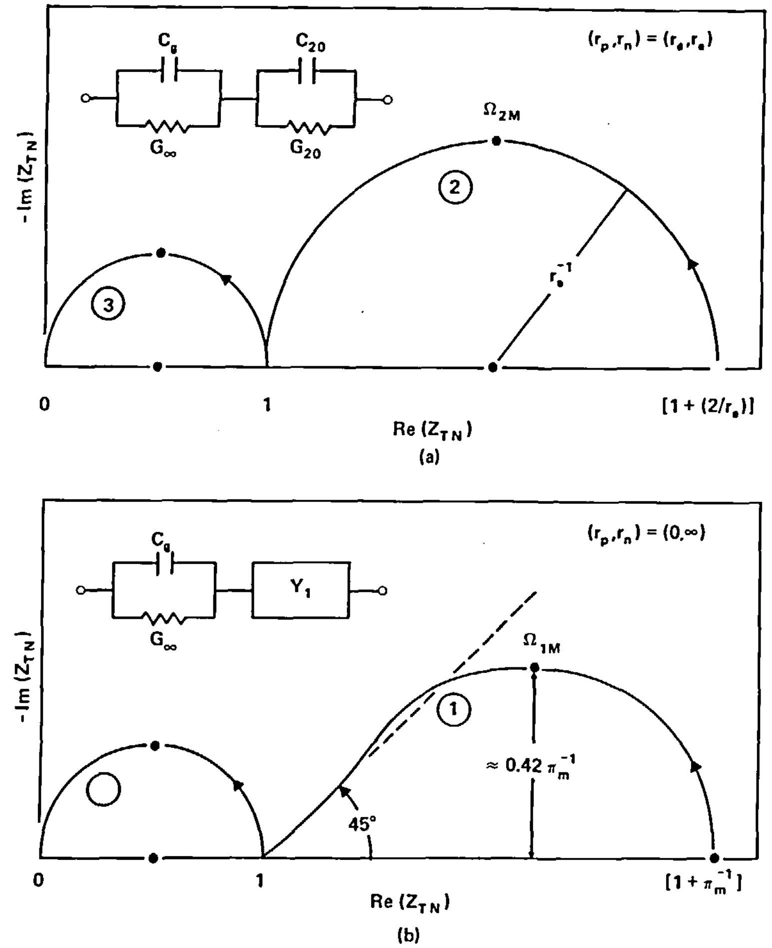

FIGURE 27. Impedance plots and equivalent circuits for membranes which transport only two ions (a) in the kinetic regime with equal discharge rates r_e and (b) in the equilibrium regime for the anion, but completely blocking for the cation. G_{2o} is the kinetically determined resistance. Relationships are described in Table 5. Abscissa and ordinate are given in the Figure 25 legend. Y_i is the finite Warburg impedance. (From Macdonald, J. R., *J. Chem. Phys.*, 61, 3977 (1974). With permission.)

and mobilities u_p and u_n is shown in Figure 25. Special symbols used by Macdonald are given with relationships in Table 5. Frequency increases around each arc from right to left, from dc to "infinite" frequency. From right to left are the finite Warburg (diffusion-migration) arc, the kinetic arc, and the high-frequency (geometrical) arc. In these figures, the Chang-Jaffe surface rate constants, r_p and r_n, are used. They are related to the more conventional rate constants, k_0^+ and k_0^-, by:

$$k_o^+ (\bar{a}_+ a_+)^{1/2} = \frac{D_+}{d\, r_p}\, \bar{a}_+ \left(\frac{\bar{u}_n}{\bar{u}_n + \bar{u}_p}\right)^2 \qquad (229a)$$

$$k_o^- (\bar{a}_- a_-)^{1/2} = \frac{D_-}{d\, r_n}\, \bar{a}_- \left(\frac{\bar{u}_p}{\bar{u}_n + \bar{u}_p}\right)^2 \qquad (229b)$$

for a general case in which both ions undergo slow surface reaction rates. Depending on the choice of data representation, equivalent, frequency dependent, parallel capacitance and resistance can be measured or computed from real and quadrature impedances or from total impedance and phase angle.

Wide-frequency range impedance measurement devices are now available for frequencies from 0.001 Hz to approximately 100 MHz. Direct reading analog pseudobridges[281] can be built

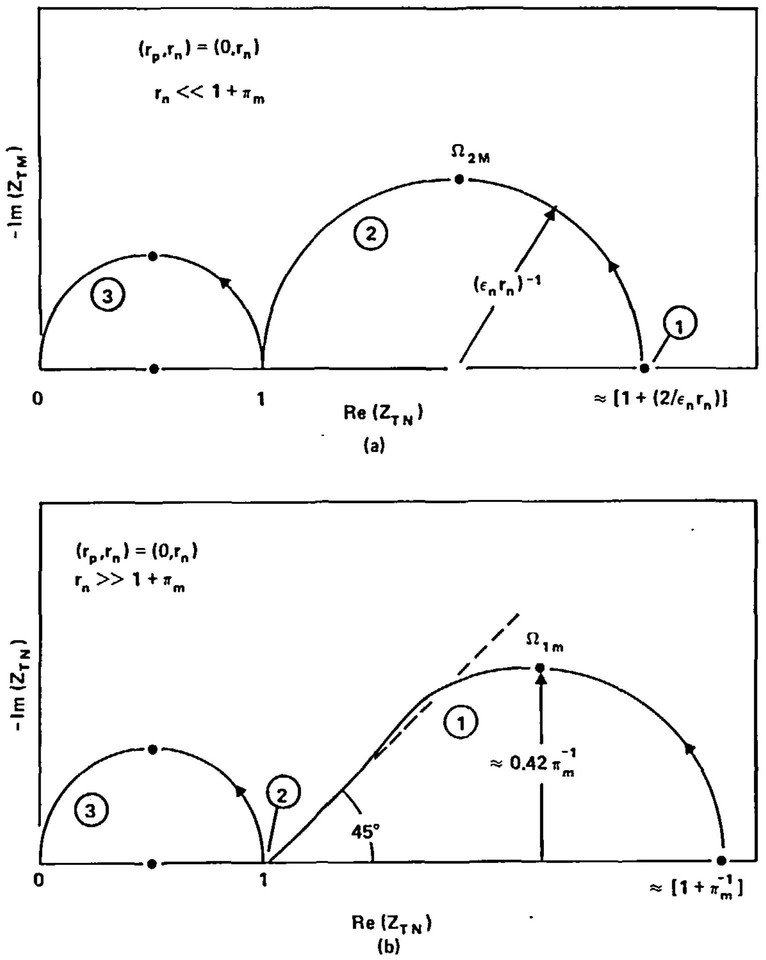

FIGURE 28. Impedance plots for membranes which transport only two ions (a) for the case that cation transport is blocked at the surface, but anion transport is kinetically limiting and (b) for the case that the cation is blocked but anion transport is limited by bulk transport rather than slow interfacial rate control. The anion interfacial rate can be considered reversible. For the calculation in (a), $r_n << 1 + \pi_m$ where $\pi_m >> 1$, $r_p \sim 1$ and in (b) $r_n >> 1 + \pi_m$ where $\pi_m \sim 1$, $r_p \geqslant 10^2$. Relationships are given in Table 5 while abscissa and ordinate are given in the Figure 25 legend. (From Macdonald, J. R., *J. Chem. Phys.*, 61, 3977 (1974). With permission.)

around commercial oscillators (i.e., Danalabs-Exact) or the high-frequency Vector Volt Meter (Hewlett-Packard). Also, impedances can be calculated digitally from computer connected fast recorders such as the Tectronix Digital Oscilloscope system or the Biomation 8100 recorder with the Hewlett-Packard Fourier Transform System. Recent examples of impedance measurements on membrane systems using impedance plots or parallel R(ω), C(ω) representations of data include those done by: DeLevie et al.[113] for lipid bilayers; Sandifer and Buck[48] for glasses, using Macdonald's interpretation; Lakshminarayanaiah and Sidiqqi[282] for collodion-polystyrene sulfonic acid membranes; Sandblom et al.[283] for HCl solutions between electrodes; Fatuzzo and Coppo[284] for AgCl between Ag or ionic contacts (see criticism by Macdonald);[285] Armstrong, Dickinson, and Willis[286] for Ag_4RbI_5 membranes between Pt (or C) and Ag electrodes; Yoshida et al.[287] for Millipore containing dioleyl phosphate; and Blue[288] for bipolar semiconductors and many one-active-electrode systems in aqueous electrolytes[289] and fused salts.[290]

TABLE 5

Expressions for Arc Points and Lengths for Various Values of r_p and r_n

	Points		Lengths	
r_p, r_n	P_{2N}	R_{DN}	ρ_{2N}	λ_{1N}
$r_p = r_n \equiv r_e$	$1 + (2/r_e)$	$1 + (2/r_e)$	r_e^{-1}	0
$0, \infty$	1	ϵ_n^{-1}	0	π_m^{-1}
$0, r_n$	$1 + (2/\epsilon_n r_n)$	$\epsilon_n^{-1}[1 + (2/r_n)]$	$(\epsilon_n r_n)^{-1}$	π_m^{-1}
r_p, ∞	1	$\left(\frac{r_p + 2}{r_p + 2\epsilon_n}\right)$	0	$\frac{\pi_m^{-1}}{1 + (r_p/2\epsilon_n)}$
r_p, r_n	$1 + \left(\frac{2}{\epsilon_n r_n + \epsilon_p r_p}\right)$	R_{DN}	$(\epsilon_n r_n + \epsilon_p r_p)^{-1}$	$(R_{DN} - P_{2N})$

$\epsilon_n = \frac{u_n}{u_n + u_p}$; $\epsilon_p = \frac{u_p}{u_n + u_p}$; $\pi_m = u_n/u_p$.

Modified from *J. Chem. Phys.*, 61, 3977 (1974).

C. Time Responses Outside the Linear Regime

Time dependences of voltages and currents out of the linear regime have often been measured despite the difficulty in interpreting the results. Rechnitz[292] used fast flow to create step activity changes in the bathing solution on one side of a membrane. The time constant for readjustment of the membrane potential corresponds well with the high-frequency, membrane controlled charging process. Without special precautions involving fast flow techniques, observed time constants from "dipping experiments" will correspond to film diffusion values since the stagnant film of initial solution changes by diffusion-migration to the new stepped value. Pungor et al. have measured the time constants of several heterogeneous membranes,[293,294] Karlberg has measured time responses of glass membranes.[295,296] Fleet, Ryan and Brand[297] and Reinsfelder and Schultz[298] report the responses of liquid membranes, and Blaedel and Dinwiddie[256f] observed the slow responses of a solid state electrode. In all of these, the time constants apparently correspond to either film diffusion on the solution side or slow surface processes. The latter may actually be the time constant for diffusion-migration through a surface film on the membrane side of the interface.

For membranes that are permselective to ions of a given sign, time responses to step changes in solution activities depend upon the slowest of three processes: surface ion exchange, bulk transport through the stagnant film "Nernst diffusion layer" outside the membrane, or bulk transport through a stagnant film on (or in) the membrane surface region. The latter may be a hydrolyzed surface film of silica on glass membranes, a very slowly encroaching water layer in the surface of liquid ion exchange membranes, or an adsorbed or occluded material surface layer on some other membranes. These are the only identified slow processes in the case of permselective membranes. Slow adjustment of concentration profiles within the bulk of a fixed site ion exchanger is not usually considered because the membrane potential is only dependent on surface activities. However, ion exchange membranes with mobile sites, neutral carrier membranes, and all ion exchanger membranes exposed to ions of different valences or subject to ion pairing can show very long time constants because the steady state concentration profiles through the entire membrane must be achieved before a steady value of membrane potential will be attained.

The simplest case is that in which an external solution film controls the time response. Crystal membranes, glasses, and liquid ion exchangers without interior surface hydrated films correspond to this case.[299,300] Diffusion of fresh electrolyte into the static Nernst layer determines the time response. This time dependent problem is analogous to the finite Warburg case at long times where concentration builds up exponentially according (approximately but adequately) to:

$$a_i(t) - a_i(0) = [a_i(\infty) - a_i(0)]\ [1 - \exp(-t/\tau)] \tag{230}$$

$$\tau \approx \delta^2/2D \tag{231}$$

where $a_i(0)$ is the concentration in the stagnant Nernst layer prior to the concentration step and $a_i(\infty)$ is the new bulk value, which slowly equilibrates by diffusion-migration throughout the layer. D is the permselective, potential determining ion diffusion coefficient in the presence of supporting electrolyte. D is replaced by the salt diffusion coefficient when a single binary electrolyte is used. The measured potential E(t) varies monotonically (except possibly during the short-time charging process) to the new equilibrium value $E(\infty)$ according to:

$$E(t) - E(\infty) = \frac{RT}{F} \ln \left\{1 - \left[1 - \frac{a_i(0)}{a_i(\infty)}\right] \exp(-t/\tau)\right\} \tag{232}$$

Even though one time constant appears, the response to a step increase is more rapid than a step to a more dilute solution. This curious effect arises from the form the equation takes. As expected, the time response depends on δ and so is sensitive to stirring.

The exponential form of Equation 230 is a long-time solution to the filling of a region of space by diffusion. At short time, the activity build-up depends on $t^{1/2}$. This fact has important consequences when two diffusion barriers are adjacent to one another. For example, filling of the external electrolyte Nernst layer with ions, some of which pass into a hydrated film on a glass or liquid membrane, requires a flux balance calculation at the surface. For high mobility ions in aqueous electrolytes, with much lower mobilities in the membrane surface film, the outer activities may be in the exponential regime, while the inner film will fill as $t^{1/2}$. Morf et al.[300] have investigated this case as a model for neutral carrier membrane responses, but it may also apply to liquid ion exchange membranes whose surfaces contain a hydrated layer and relatively low mobile site densities. In this case,

$$a_i(t) - a_i(0) \sim [a_i(\infty) - a_i(0)] \left[1 - \frac{1}{\sqrt{t/\tau} + 1}\right] \tag{233}$$

and

$$E(t) - E(\infty) \sim \frac{RT}{F} \ln \left\{1 - \left[1 - \frac{a_i(0)}{a_i(\infty)}\right] \frac{1}{\sqrt{t/\tau} + 1}\right\} \tag{234}$$

This approximation has been tested for neutral carrier electrodes and found acceptable. It is observed[297] that time constants are larger for *liquid ion exchanger membranes subject to step* changes of two ions, where one ion at lower concentration, is in fact preferred by the membrane ($K^{Pot}>1$). On the other hand, step changes of a single ion (or a mixture where the second ion is not preferred by the membrane) give shorter time constants. This topic is currently under investigation in several laboratories.

*Nothing has been said here about nonmono*tonically changing potential responses to step changes in solution activities. These are nonequilibrium effects which have not yet been sufficiently well-characterized to lead to meaningful theoretical treatment. In a study by Bagg and Robert,[301] it was found that nonmonotonic potential changes, in response to step activity changes, are *stirring sensitive* and *temperature* independent on the rising potential (shorter time overshoot portion), but are stirring insensitive and temperature dependent on the return swing. This result is predicted for the short-time (charging) time constant region where rapid surface ion exchange leads to space charge of the preferred ion during the overshoot. Slow membrane transport of the sites to compensate this charge accounts for the return to equilibrium and the temperature dependence.

D. Digital Stimulation of Time Dependent Responses

The time-course of internal, interfacial, and total membrane potentials can be acquired by a process known as digital simulation.[302] The membrane and bathing solutions are hypothetically divided into volumes by planes parallel to the membrane surfaces. Each ion's transport is described by dimensionless, finite difference Nernst-Planck equations obtained from Equation 116 using the nondimensionalizing factors:

$$J^*_{ij} = J_{ij}\, d/u_o C_o RT \tag{235a}$$

$$x^* = x/d \tag{235b}$$

$$E^*_j = E_j dF/RT \tag{235c}$$

$$I^* = Id/u_o C_o RT \tag{235d}$$

$$u^*_i = u_i/u_o \tag{235e}$$

$$C^*_{ij} = C_{ij}/C_o \tag{235f}$$

$$\varphi^* = \varphi F/RT \tag{235g}$$

$$t^* = tu_o RT/d^2 \tag{235h}$$

Thus,

$$J^*_{ij} = -u^*_i\, \Delta C^*_{ij}/\Delta x^* + z_i u^*_i\, C^*_{ij}\, E^*_j \tag{236}$$

where i stands for an ion and j for the volume element. The current equation from Equation 117 is

$$I^* = \sum_i z_i J^*_{ij} + K^*\, \Delta\, E^*_j/\Delta t^* \tag{237}$$

where

$$K^* = K\epsilon\, RT/C_o d^2 F^2 \tag{238}$$

$$= 2.35 \times 10^{-20}\ K/C_o\, d^2 \text{ (at 25°C)}$$

and K is the usual dimensionless dielectric constant of the medium. Simulations for constant current, including zero, begin with a prediction in time of E_j^* from a past value $E_j^{*\prime}$ according to:

$$E^*_j = \frac{I^* + K^*\, E^{*\prime}_j + \sum_i z_i u^*_i\, \Delta C^*_{ij}}{K^* + \sum_i z_i^2\, u^*_i\, C^*_{ij}} \tag{239}$$

and then, from a past value of concentration $C_{ij}^{*\prime}$, C_{ij}^* is found:

$$C^*_{ij} = C^{*\prime}_{ij} - (J^*_{i,\, j+1} - J^*_{i,j}) \tag{240}$$

This process is used in both the membrane and adjacent bathing solutions with reversible or irreversible boundary conditions. Furthermore, the impedance can be directly calculated and impedance plots prepared for comparison with experimental results. There are limitations on the magnitudes of reduced parameters used in explicit finite difference simulations. Reduced mobilities for multiple ion problems must be less than 0.50. For reversible interfacial processes, the interfacial potential component can be computed from Equation 37a and therefore the space charge region can be ignored and K* taken to be zero in Equation 237. If, however, potentials are computed point-by-point through the space regions by integration of local fields, K* must be large enough to avoid squeezing the space charge into too few volume elements with consequent integration errors. Digital simulation of non linear transport problems is a powerful technique and procedures are not limited to explicit formulations.

VII. MEMBRANE ELECTRODES

A. Formats for Membrane Electrodes

Applications of the membrane electrochemical principles and theory described in the preceding section are abundantly evident in the many electrodes which have been made in the last 10 years. A natural grouping of these is based on site and phase characteristics of the materials of construction:

Homogeneous fixed site ion exchange membranes
Homogeneous solid state, crystal, or pressed pellet membranes
Homogeneous glass membranes
Homogeneous liquid ion exchange membranes
Homogeneous site free membranes with or without selectivity enforcing neutral carriers
Homogeneous semiconductor membranes
Heterogeneous membranes containing homogeneous components dispersed and imbedded in hydrophobic binders
Compound electrodes using surface modification or interposed chemical reactions

Examples of these membranes, their construction features, and applications can be found in recent reviews.[22,23,32,44,45,251]

Membranes are used in electrodes in two formats: ion contacts at each interface, or ion contact at one interface and an electronic conductor contacting the second interface. The organization of membrane cells for electrode purposes is, in principle, the same as that of an ordinary membrane cell for exploratory work, as in Figure 1.

Cu;	External reference electrode: typically Mercury-calomel or silver-silver chloride in fixed activity Cl^-.	Salt bridge	External; monitored solution	Membrane; reversible and permselective to cations	Inner filling; solution containing a fixed activity of permselective cations ion and fixed Cl^- activity	AgCl;	Ag;	Cu

"Membrane" electrode [Cell I]

or a typical anion sensing electrode,

Cu;	External reference electrode typically mercury-calomel or silver-silver chloride in fixed activity Cl^-.	Salt bridge	External; monitored solution	Membrane; reversible and permselective to anions	Inner filling; solution containing a fixed activity of permselective anion and fixed Cl^- activity	AgCl;	Ag;	Cu

"Membrane" electrode [Cell II]

The commonly found organization illustrated here corresponds to a classical junction cell. The semicolons are conventional indications of interfaces involving solid-solid and solid-solution contact equilibria. The vertical lines are conventional indications of interfaces between liquids containing electrolytes. In both instances some potential difference can exist. The general form is

Cu;	External reference	Salt bridge	External monitored solution "Test solution"	Membrane; electrode	Cu

[Cell III]

The term "junction" arises because of the frequently indeterminate potentials which occur at the interfaces between contacting media containing different electrolytes, e.g., the external reference solution and the salt bridge solution, and between salt bridge solutions and the external monitored solution. Any diffusion potential within the salt bridge itself contributes to the overall sum of junction potentials. In these illustrations, the salt bridge containing an electrolyte different from that in the external reference electrode thereby constitutes a "double junction."

The reason for using junction cells is flexibility in handling a variety of external monitored solutions. Ordinarily a test solution will not contain any ions reversible at (and common to) the external reference electrode. If by plan or by chance a series of test solutions happened to contain a constant activity of Cl^-, then a Cl^--reversible external reference electrode could be dipped into the test solution. The salt bridge and fixed activity solution for the external reference electrode could be eliminated. Such a junctionless cell is shown below:

Cu;	Ag;	AgCl;	External monitored; "test" solution containing fixed activity of Cl^- (or Ag^+)	Membrane electrode; selective to cations	Cu

[Cell IV]

Membrane electrodes, patterned after glass electrodes, consist of the membrane affixed to the lower opening of a high resistance glass or plastic barrel. The latter contains the inner filling solution and a reversible internal reference electrode. The entire barrel is sealed during normal operation. Problems encountered in construction involve the quality of the membrane seal and use of barrels whose resistance to ion transport exceeds that of the membrane. The latter problem is particularly acute in fabricating miniature electrodes for biological application.[303] Low resistance pathways (compared to the membrane) offer short circuit paths and lowered membrane potential responses. Low slopes of response curves are not ideal, but they are not false responses either. Microelectrode responses can be calibrated against standard solutions to yield useful results.

Overall responses of membrane electrode cells include several terms:

$$\Delta\varphi_{\text{measured}} = \Delta\varphi_{\text{m}} + \varphi\,(\text{inner ref}) - \varphi\,(\text{ext ref}) + \varphi_{\text{Jun}} \tag{241}$$

where $\Delta\varphi_{\text{m}}$ is the membrane potential discussed at length in the earlier sections of this review. φ(inner ref) and φ(ext ref) are generally the interfacial potentials calculated from the Nernst Equation for the respective half cells in their bathing solutions and φ_{jun} is the junction potential. The junction potential (or sum of junction potentials) is the least well known quantity in the equation and chemical means for minimizing the effects of the junction are discussed later in this section. Frequently the junction potential is simply ignored when $\Delta\varphi_{\text{measured}}$ is calibrated against standard solutions of prescribed activity; or the junction potential can be avoided when $\Delta\varphi_{\text{measured}}$ is found from cells without liquid junction. The usual measured potential for cells in which a saturated calomel external electrode and an Ag; AgCl internal electrode are used, and has the form:

$$\Delta\varphi_{\text{measured}} = \frac{RT}{F} \ln\left[\frac{a_i + \sum_i K_{ij}^{\text{Pot}} a_j\,(\text{external})}{a_i\,(\text{internal})}\right] + \varphi^{\text{o}}\,\text{AgCl/Cl}^- - \frac{RT}{F} \ln a_{\text{Cl}^-}\,(\text{int})$$
$$- \varphi\begin{pmatrix}\text{sat'd calomel}\\ \text{ext ref}\end{pmatrix} + \varphi_{\text{Jun}} \tag{242}$$

For mixtures of permeable ions of different valences of the same sign, the approximation is sometimes made in the numerator of the ln term:

$$\ln\,[a_i + \sum_i K_{ij}^{\text{Pot}} a_j^{z_i/z_j}] \tag{243}$$

where a_i has charge z_i and other ions have charge z_j. The modified equation is not exact[265] and K_{ij}^{Pot} will depend on concentration a_i and a_j as well as site concentration.

Membrane electrodes which eliminate the inner filling solution and replace it with a direct metal-membrane contact are regarded as "all-solid-state" devices because the most successful examples are crystal membranes, typically silver salts, connected internally to silver wires. An extensive analysis of the interfacial potential, normally governed by reversible electron exchange between crystal and metal, was given by Buck and Shepard.[253] Their analysis makes use of the electrochemical potential equality (Equation 31) for electrons in the two phases. Results of this analysis show that the membrane potential depends on the extent of complete equilibrium between the contacting metal and crystal,

$$\Delta\varphi_{\text{m}} = \varphi^{\text{o}}{}_{\text{Ag/Ag}^+} + \frac{RT}{F} \ln\left[\frac{a_{\text{Ag}^+}}{\bar{a}(\text{Ag})^*}\right] \tag{244}$$

and the complete, measured response is

$$\Delta\varphi_{\text{measured}} = \varphi^{\text{o}}{}_{\text{Ag/Ag}^+} \tag{245}$$
$$+ \frac{RT}{F} \ln\left[\frac{a_{\text{Ag}^+}}{\bar{a}(\text{Ag})^*}\right] - \varphi(\text{ext ref}) + \varphi_{\text{Jun}}$$

for an AgX membrane with an internal Ag contact. The AgX membrane rapidly saturates with Ag metal, and $\bar{a}(Ag)^*$, the activity of metal in the salt, referred to pure metal, is unity. Consequently, all-solid-state and ionic contact electrodes using the same membrane material will, at equilibrium, show the same response. However, various other cases, e.g., membranes with ion exchange at the membrane/metal surface or membranes contacted with dissimilar metals more reactive or less reactive than the common metal, show different behavior. A large body of experimental evidence has been accumulated to demonstrate these cases and the more usual situation of a common metal contact with variable activity in the crystal where the apparent φ^o,

$$\varphi^o\,(\mathrm{app}) = \varphi^o{}_{M/M^+} - \frac{RT}{F}\ \ln\ \bar{a}(M)^* \tag{246}$$

can vary in response to purposeful variations in $\bar{a}(M)^*$.

In all cells, the external and internal reference electrodes (reference half cells) contribute part of the overall measured potential as indicated in Equations 241 and 242. Consider common reference electrodes of the second kind such as mercury-calomel and silver-silver chloride, which are reversible to anion activities. In a junctionless membrane cell using cation selective membranes for Ca^{2+} or K^+ activity measurements, the cell voltages depend upon both cation and halide activities according to

$$\Delta\varphi_{\mathrm{measured}} = \frac{RT}{2F}\ \ln\left[\frac{a_{Ca^{2+}}\,(\mathrm{test})}{a_{Ca^{2+}}\,(\mathrm{int\ ref})}\right] + \frac{RT}{F}\ \ln\left[\frac{a_{Cl^-}\,(\mathrm{test})}{a_{Cl^-}\,(\mathrm{int\ ref})}\right] \tag{247}$$

or

$$\mathrm{measured} = \frac{RT}{F}\ \ln\left[\frac{a_{K^+}\,(\mathrm{test})}{a_{K^+}\,(\mathrm{int\ ref})}\right] + \frac{RT}{F}\ \ln\left[\frac{a_{Cl^-}\,(\mathrm{test})}{a_{Cl^-}\,(\mathrm{int\ ref})}\right] \tag{248}$$

Both terms occur here because variation in salt activity not only affects the membrane potential (first term) but also the individual reference electrode potentials. Junctionless cells therefore respond to the mean salt activity and not just to the species which is membrane permeable. On the other hand, in a junction cell using reference half cells separated from the test and inner solution by salt bridges, the anion activities in the reference solutions, typically chloride, are constant. If the reference electrodes for a junction cell happen to be identical, then the right-hand terms (247) and (248) are 0. At worst, the reference electrodes in a junction cell contribute a constant value to the measured cell voltage, which creates a constant offset response.

In a junction cell the slope of cation activity response is different compared to the junctionless cells. For example, calcium chloride activity measured in a junctionless cell plotted as millivolts vs. $a_{Ca^{2+}}$ would show a slope of 3/2 × 59.14 mV/decade at 25°C and exhibit zero potential when the test solution and inner solution contain identical salt concentrations. In a junction cell, the same experiment gives a slope of 1/2 × 59.14 mV and identical solutions would yield 0 V only if the two references are identical. Note that a cell composed of an AgCl membrane and Ag/AgCl reference electrodes is independent of silver activities.

The slope magnification effect for junctionless cells is desirable, but is achievable only when strict conditions are fulfilled: (1) the composition of test solutions must be free from interfering ions which affect the reference electrode potentials; (2) reference electrodes must be reversible to ions of charge opposite to those which are membrane permeable, and (3) the solution must contain only salts in which the activities of the detected cations and anions vary in a known way. For example, if a series of unknown K^+ activities in KCl solutions were to be measured, a potassium selective membrane with Ag/AgCl external reference would suffice. However, if independently variable levels of NaCl, KI, or KNO_3 were present, the potential response could not be interpreted.

Junctionless cells can be composed of cation instead of anion selective reference electrodes. Whenever an anion responsive membrane cell is used in junctionless configuration, the reference electrode must be cation reversible. Reference electrodes reversible to a large number of anions and cations than ever before are now available. Any commercially available anion selective electrode or conveniently fabricated equivalent electrode can be suitable as a reference electrode.

Most cation selective liquid membrane and glass electrodes are possible reference electrodes. For example, if it is known that a series of fluoride samples to be measured for fluoride activity are buffered or contain either potassium ions at constant activity, or contain equal fluoride and potassium concentrations, then the following junctionless cell is possible:

Cu;	K^+ selective; electrode or pH glass electrode	test; solution	LaF_3 membrane;	Inner solution containing F^- and Cl^-	AgCl;	Ag; Cu	[Cell V]

For thermodynamic measurements, junctionless cells are mandatory, but for practical analytical work, junction cells are more generally useful and preferred. While there is a loss in accuracy from unknown junction potentials, the benefits more than outweigh this limitation. In general, junction cells allow measurements of species activities relatively unaffected by diverse counter ions which may be present. Minor problems introduced in addition to the small usually unknown junction potentials are diffusion of reference half cell components into the test solution and clogging of the junction pathway. The latter is especially prevalent when using basic aqueous test solutions or nonaqueous solutions. Many designs for the liquid junction including sleeves, controlled cracks, and porous barriers are available commercially or described in the literature.[4 3–4 5] Probably the best method is the double junction configuration in which the test solution is exposed to a compatible intermediate electrolyte in a salt bridge. This type of junction provides two diffusional barriers which is essential for use with saturated calomel references when measuring either Cl^- for K^+ with selective membranes. The double junction is commercially available and can be designated as:

$Hg; Hg_2Cl_2; KCl$(sat'd)	$Li^+Cl_3C{-}COO$, $Na^+NO_3^-$ $K^+NO_3^-$, or	test sol'n	
or			
$Ag; AgCl; NaCl(0.1M)$	$Na^+ClO_4^-$*		
or			
other external reference half cell	other salt as a bridge		[Cell VI]

B. Junction Potential Magnitudes

In contrast with interfacial potentials at membrane and reference electrode interfaces, junction or diffusion potentials denoted as φ_{Jun} arise whenever one or more phases containing electrolytes are not at uniform activity. Junction potentials arise spontaneously within a single phase when nonuniform distributions of electrolytes seek to become uniform by diffusion from regions of high activity to low. Junction potentials introduce a time dependence to overall cell potentials and an ultimate limit on the reproducibility of zero current potentiometric measurements. They also create an uncertainty in the interpretation of single ion activities.

Diffusion potentials within phases have already been considered in Section V.A.3. Integration procedures for the differential potential to give net values of φ_{Jun} are found in Reference 304 where

$$\varphi_{Jun} = \varphi_{right} - \varphi_{left} \tag{249}$$

$$= -\frac{RT}{F} \int_{left}^{right} \sum_i \left(\frac{t_i}{z_i}\right) d \ln a_i$$

If all ions in a junction situation have the same mobility, φ_{Jun} is always zero. The sign of the junction potential can be quickly found by noting

---

*Note that $NaClO_4$ as salt bridge cannot be used in contact with solutions containing potassium ions.

which side has the higher ionic activity. Then, note which ion is the most mobile. Cations and anions attempt to diffuse separately from high to low activities. The more mobile ion moves ahead at short times until a field is created which drags the slower moving species. The faster ion is slowed and the slower speeded until the salts move in an electroneutral way with an overall mean diffusion coefficient. The salt diffusion coefficient D or mobility u for a single salt is

$$D_{\text{Salt}} = \frac{D_+ D_- (z_+ - z_-)}{z_+ D_+ - z_- D_-} \tag{250}$$

$$u_{\text{Salt}} = \frac{u_+ u_- (z_+ - z_-)}{z_+ u_+ - z_- u_-} \tag{251}$$

The faster ion carries its charge sign into the lower activity side and so determines the sign of φ_{Jun}, which is the integral of field over distance. At short times, concentration profiles through the junction are nonlinear, but in the steady state, profiles are linear and this fact allows integration of Equation 249.

In practical situations, liquid junctions may be free flowing and often involve mixtures of electrolytes with no common ions. There are no equations for accurate calculation of these complicated junctions and approximate methods such as Henderson's integration[304] must be used. There are few experimental methods for independent verification of the calculations. However, junction potentials are believed to be small (less than 10 mV), unless protons or hydroxide ions are involved, or the concentrations on two sides differ by a factor of 100 or more. The junction potential between 0.1 *M* HCl and 0.01 *M* HCl is 40 mV with the dilute side positive. For KCl at the same concentrations, φ_{Jun} is only 1.0 mV with the dilute side negative since the mobility of Cl^- is slightly greater than that of K^+. A more mechanistic view of junctions is given by Buck.[305] Tables of liquid junction potentials are also given.

Elimination of liquid junction potentials is never possible, but they can be minimized. The principle of minimizing is one of "swamping" the junction with two new junctions which provide two-way diffusion from a high concentration of electrolyte, usually KCl, with nearly equal cation and anion mobilities. A given junction to be minimized is separated in space with a column of saturated KCl or $LiCl_3C_2OO$ in a salt bridge. The bridge can be a tube with fritted glass or porous carbon disks, or small holes such as cracks or asbestos fibers at the ends. Commercial reference electrodes are built with one or more surrounding salt bridges. A simple glass tube filled with agar-gelled KCl and restricted openings frequently has been used.

C. Complete Membrane Electrode Cell Response Functions

The final source of overall cell emf is that of the membrane itself. Since negligible current flows in a potentiometric measurement, there is no iR drop in the solutions on either side of the membrane. The inner potentials of the solution phases bathing the membrane are constant provided the concentrations of salts are uniform as a result of stirring. The membrane potential is found by summing the two interfacial potentials with the internal membrane diffusion potential, if any exists, according to the general segmented potential model in Equation 19. The components have already been derived and discussed in earlier sections. When all of the potential contributions in a typical cell configuration are identified, the measured cell potential often can be expressed simply for normal reversible steady state and equilibrium conditions of Nernstian response. For example, the lanthanum fluoride membrane electrode used with a saturated calomel external reference electrode can be written

$$\begin{array}{llllllllll}
\text{Cu;} & \text{Pt;} & \text{Hg;} & Hg_2Cl_2; & \text{KCl (sat'd)} & \underset{\text{Junctions}}{\|} & \underset{a_{F^-}}{\text{Test solution;}} & \underset{\text{membrane}}{LaF_3;} & \underset{0.1\,M\ \text{NaCl}}{0.1\,M\ \text{NaF;}} & \text{AgCl;}\quad \text{Ag;}\quad \text{Cu}
\end{array}$$

[Cell VII]

$$\begin{aligned}
\Delta\varphi_{\text{measured at } 25^\circ\text{C}} = {} & -0.242 && \text{(saturated calomel half cell contribution)} \\
& + \varphi_{\text{Jun}} && \text{(double junction diffusion potential contribution)} \\
& - 0.0591 \log\left(\frac{a_{F^-}}{0.1\gamma_{F^-}}\right) && \text{(membrane potential)} \\
& + 0.222 - 0.0591 \log (0.1\ \gamma_{Cl^-}) && \text{(inner reference half cell potential contribution)} \\
= {} & \text{constant} - 0.0591 \log a_{F^-}\ \text{V}
\end{aligned} \tag{252}$$

The metal/metal potentials are already accounted for in the numerical constants. The diffusion potentials are usually only a few millivolts. Activity coefficients can be computed or obtained from tables. Nevertheless, the constant term cannot be computed rigorously or exactly. Consequently, standard solutions of fluoride with calibrated activities must be used to establish the cell response $\Delta\varphi_{meas.}$ vs. log a_{F^-} in a precise way.

The equation above merely allows approximate calculation. Literature results[306,307] compiled by Butler[308] are illustrated in Figure 29.

Similarly for liquid ion exchanger membranes such as that forming a Ca^{2+} selective electrode in a test solution containing calcium at $a_{Ca^{2+}}$, when completed with a saturated calomel reference electrode, the cell has the form:

Cu;	Pt;	Hg;	Hg_2Cl_2;	KCl; sat'd	test solution; $a_{Ca^{2+}}$	Ca^{2+} sensing liquid; membrane	$CaCl_2$ 0.1 *M*;	AgCl;	Ag;	Cu

[Cell VIII]

The measured cell potential is composed of:

$$\begin{aligned}
\Delta\varphi \text{ measured at } 25^\circ\text{C} &= -0.242 && \text{(saturated calomel half cell contribution)} \\
&\quad + \varphi_{Jun} && \text{(junction potential contribution)} \\
&\quad - \frac{0.0591}{2}\log\left[\frac{a_{Ca^{2+}}\,(\text{test})}{0.1\gamma_{Ca^{2+}}}\right] && \text{(membrane potential)} \\
&\quad + 0.222 - 0.0591\log[(0.2)\gamma_{Cl^-}] && \text{(inner reference half cell contribution)} \\
&= \text{constant} + \frac{0.0591}{2}\log a_{Ca^{2+}}\,(\text{test}) - \frac{0.0591}{2}\log[(0.1)(0.2)^2\,\gamma_\pm\,3] \\
&= \text{constant} + \frac{0.0591}{2}\log a_{Ca^{2+}}\,(\text{test})
\end{aligned} \tag{253}$$

Simple halide sensitive cells such as

Cu;	Saturated calomel ext. ref.	Salt bridge	halide test; solution a_{X^-}	AgX membrane;	inner; solution	AgX;	Ag;	Cu

[Cell IX]

respond according to $\Delta\varphi$ measured at 25°C $= -0.0591\log a_{X^-} + 0.0591\log K_{sp}\,(AgX) + 0.557 + \varphi_{Jun}$ V (254)

In the "all solid state" configuration, the electrode responds in the same test solution using the same external reference electrode according to

$$\Delta\varphi \text{ measured at } 25^\circ\text{C} = -0.0591\log a_{X^-} + 0.0591\log K_{sp}\,(AgX) + 0.557 - 0.0591\log a_{Ag}\,(AgX) + \varphi_{Jun}\ \text{V} \tag{255}$$

A silver sulfide electrode in a typical configuration for direct potentiometry of Ag^+ or $S^=$ could be written:

Cu;	Saturated calomel ext. ref.	Salt bridge	test; solution a_{Ag^+}	Ag_2S; membrane	inner; solution	Ag_2S;	Ag;	Cu

[Cell X]

and responds normally according to the sum

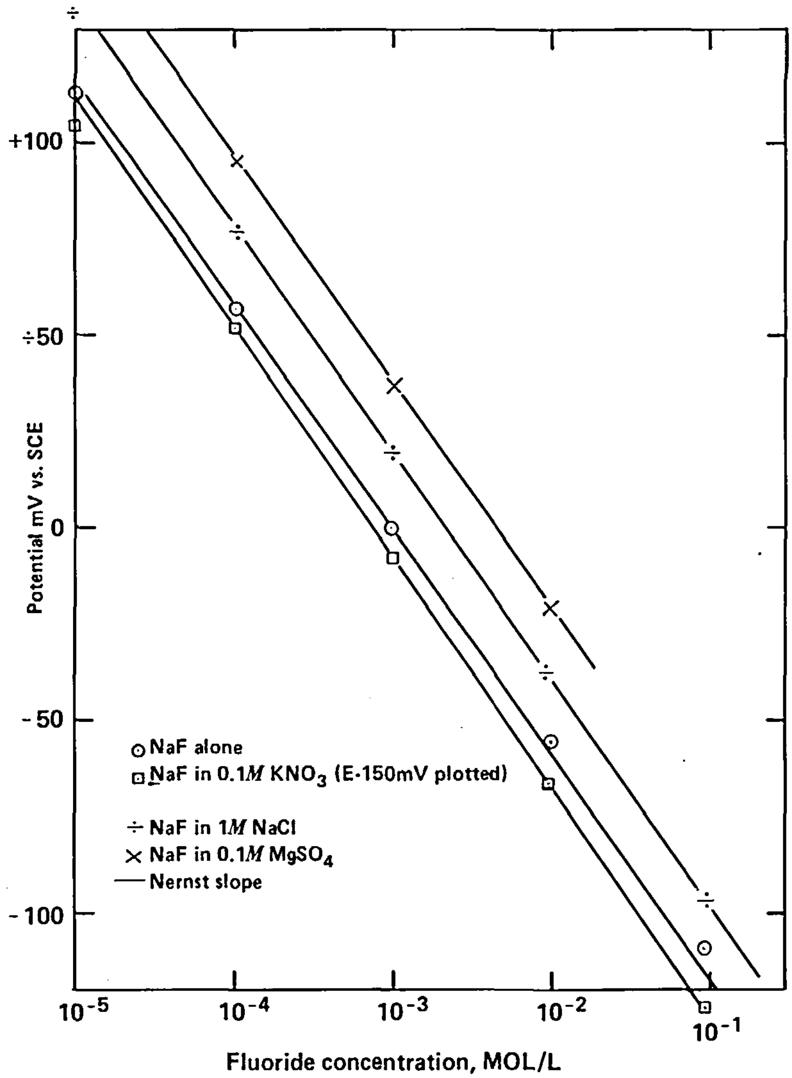

FIGURE 29. Potential of a lanthanum fluoride electrode as a function of fluoride concentration in various supporting electrolytes. Note that the zero of potential scale depends on the internal filling solution and is different for data from References 306 and 307. (From Butler, J. N., in Ion Selective Electrodes, Durst, R. A., Ed., National Bureau of Standards, Special Pub. #314, U.S. Government Printing Office, Washington, D.C., 1969, chap. 5.)

$$
\begin{aligned}
\Delta\varphi \text{ measured at } 25^\circ\text{C} &= -0.242 && \text{(saturated calomel half cell contribution)} \\
&\quad + \varphi_{\text{Jun}} \\
&\quad + 0.0591 \log a_{\text{Ag}^+}\text{(test)}/a_{\text{Ag}^+}\text{(inner)} && \text{(membrane potential)} \\
&\quad + 0.799 + 0.0591 \log a_{\text{Ag}^+}\text{(inner)} && \text{(inner reference half cell potential contribution)} \\
&= 0.557 + 0.0591 \log a_{\text{Ag}^+} + \varphi_{\text{Jun}} \text{ V}
\end{aligned}
\qquad (256)
$$

Note that the activity dependence of the inner reference and inner side of the membrane cancel out. If the test solution contains a soluble sulfide,

$$\Delta\varphi \text{ measured at } 25°\text{C} = 0.557 - \frac{0.0591}{2} \log a_{S^{2-}} + \frac{0.0591}{2} \log K_{sp}\,(Ag_2S) + \varphi_{Jun}\ \text{V} \qquad (257)$$

Using $pK_{sp} = 49.2$, the log term has a value − 1.45 V. Durst[309] and later Vesely et al.[257c] have tested Equations 256 and 257 over a wide activity range as shown in Figure 30.

These few examples are illustrative of the simple forms of the normal or Nernstian responses of ion selective membrane-based electrodes. However, ideal Nernstian response cannot be expected to hold over a wide concentration range, depending on (1) the mode of establishment of the ion activities to be detected and measured and (2) the ideality of the membrane substrate. There are potential deviations expected at both high and low activities of the sensed species, even for ideally deviations occur by one identified process: failure of Donnan exclusion. Thus, glass electrodes for pH, cation selective liquid ion exchange electrodes, and neutral carrier cation selective electrodes show sub-Nernstian deviations at high electrolyte activities because anions are no longer completely rejected from the membrane phase. Both the interfacial and diffusion components of the membrane potential are adversely affected by anion penetration.

At low activities of sensed species three cases must be distinguished: (1) low activities of a single ion from a highly diluted salt in water, (2) low activities of a single ion from a highly diluted salt in a high concentration of inert electrolyte, and (3) low activities of a single ion in a generalized buffer, e.g., low silver ion activities established by use of metal ion buffers whose components are at high concentrations typically 0.01 to 1 *M*, but the pH and complexing agent act to hold free metal ion activity at low values through labile equilibria among free and complexed metal ions species. It is commonly held that the lower limit of detectability of an ion by its selective electrode is determined by the solutility of the ideal membrane itself, or by the extent of ion exchange as permitted by competition with ions from the solvent. Thus, for salt membrane electrodes such as silver halides, response to successive dilution of $AgNO_3$ is Nernstian at high a_{Ag^+}, but deviates

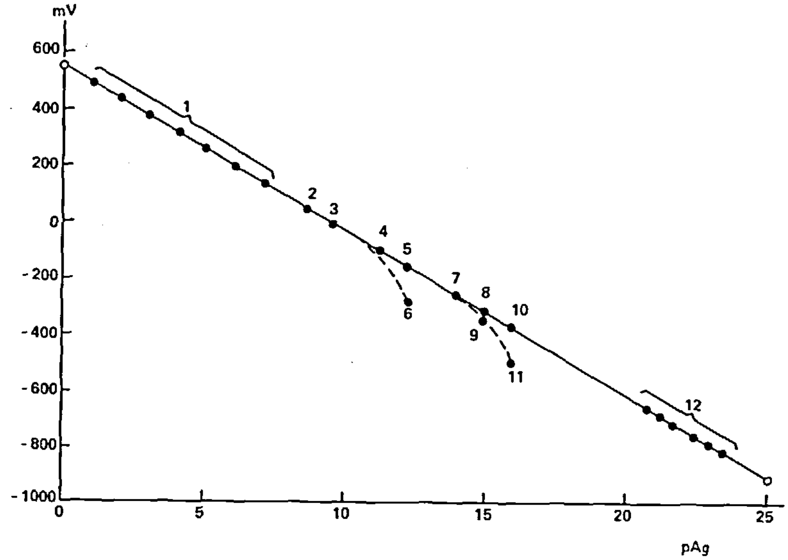

FIGURE 30. Wide range response of a silver sulfide membrane electrode; (1) solutions of $AgNO_3$ ($\mu = 0.1$), 10^{-1} to 10^{-7} *M*; (2) 0.1 *M* NaCl; (3) 1 *M* NaCl, saturated with AgCl; (4) 0.1 *M* NaBr; (5) 1 *M* NaBr, saturated with AgBr; (6) 1 *M* NaBr, unsaturated; (7) 0.01 *M* NaI; (8) 0.1 *M* NaI saturated with AgI; (9) 0.1 *M* NaI, unsaturated; (10) 1 *M* NaI saturated with AgI; (11) 1 *M* NaI, unsaturated; (12) 0.01 *M* Na_2S ($\mu = 0.11$), pH 7.0 to pH 12.0. (From Vesely, J., Jensen, O. J., and Nicolaisen, B., *Anal. Chim. Acta*, 62, 1 (1972). With permission.)

positively and becomes constant at extreme dilution since the activity of silver cannot be reduced below the intrinsic solubility of the membrane material. The same type of behavior is expected when successive dilutions are made with inert electrolytes and when activities are established with metal ion buffers. Similarly in solutions of excess anion Cl^-, Br^- and I^-, the silver activity is fixed by the common ion effect and responses are Nernstian to anion activities until extreme dilution limits the response again to the crystal solubility approached from the excess anion side.

For organic liquid ion exchanger and neutral carrier electrodes using extreme dilution of electrolyte or controlled low activities of exchangeable ions, solubility of the membrane components is again limiting in principle. However, before dissolution of the membrane becomes significant it is more likely that competitive ion exchange of protons in place of the diluted permeable cations (or OH^- for anions) will cause a leveling in the Nernstian response. The extensive, careful low level responses of calcium selective electrodes by Ruzicka et al.[310] as a function of pH suggest the validity of this interpretation.

Testing of low activity region responses can be done well with metal ion buffers and with inert electrolyte dilution.[311] Testing is not valid by use of the method of simple dilution of a single salt. The reasons are not altogether clear, but five effects have been suggested and may be pertinent: (1) interfacial exchange rates may become limiting at low dilutions, but this possible effect should occur by all three methods of testing since the theoretical rate depends on the activity of the exchanging ion at the surface; (2) failure to saturate the diluted test solutions with membrane salt so that the membrane is not in equilibrium with the solution. This problem, like the former, would cause errors in all methods. Furthermore, lack of equilibrium is indicated by stirring rate dependence of measured potentials; (3) there may not be a great enough ionic strength at extreme dilution to charge the external double layer; (4) high solution resistances at low dilutions may cause experimental measurement artifacts; (5) specific adsorption of one of the salt ions may distort the measured potential. In the author's opinion, this effect should be observable only when the interface is blocked so that the interfacial potential is no longer determined by the ion exchange process.

Probably the most important and least well-documented point concerning electrode responses at low, controlled activities is the need for preparation of stable, reversible-interface ion exchanging membrane materials. Except when using highly purified liquids and precisely stoichiometric single crystal solid membranes, the basic responses of systems are likely to be lost to a number of unreproducible surface and bulk property effects. For example, pressed pellet membranes formed from different batches of precipitates can be quite variable in their response characteristics ranging from expected ideal Nernstian behavior for component ions to general salt response without selectivity. Systematic studies of the $CuS-Ag_2S$ and $CdS-Ag_2S$ pressed pellet responses[256a,256b,312,313] show that precipitation from weakly acidic solution of soluble Cd^{2+} or Cu^{2+} and Ag^+ salts by addition of H_2S or by homogeneous precipitation leads to solids with reversible ion exchange of component cations. In contrast, precipitations made by addition of basic Na_2S presumably induce coprecipitated hydroxides such that log $a_{Cd^{2+}}$ and log $a_{Cu^{2+}}$ plots vs. potential are not Nernstian. Responses become independent of cation activities at much too high activity values and monovalent cations show significant interferences. Digestions of the precipitates in acid, and etching of pellet surfaces improve responses and decrease interferences. Air oxidation of substrate and presence of coprecipitated soluble species which are more soluble than the basic substrate have been suggested in Section V.B.3 as the source of the level response at activities high compared with the theoretical solubility of the substrate. Recent work by Vesely[256e] on iodide responses at AgI and $AgI-Ag_2S$ membranes demonstrates that responses at low a_{I^-} are sensitive to the quantity of polymorphic forms of AgI which occur together when the pressure used to make the pellets exceeds the transformation pressure and converts some β-AgI to γ-AgI.

A further complication is suggested in the work of Morf et al.[256] Although these authors speak of interstitial silver ions, their response equations follow from and correspond to an assumption of leached or reversibly adsorbed silver ions. As I have pointed out in Section V.B.3, the responses are sensitive to stirring and to use of buffer-controlled activities. The tendency of silver salt membrane components to contain coprecipitated soluble salts is enough to explain Morf's observations and to interpret applications made of the effect for sensing activities of species forming more dissociated complexes than can be accounted for from the intrinsic solubility of Ag_2S.[256h] One does not have to deny the validity of the formula for the interfacial potential component (Equation 37a) nor does one have to postulate lack of rapid ion exchange which determines the interfacial potential.

Accomplishments of the theory of membrane potentials and overall cell potentials are not restricted to predicting the idealized steady state responses of electrodes or to diagnosing and interpreting apparent failures in electrode performance. The theory presented in this review also permits cases to be identified where the transient state gives full time-independent Nernstian responses and those cases where time dependencies of potentiometric responses are expected. The forms of the latter time dependencies permit diagnosis of the sources of time responses. For example in the steady state, liquid ion exchangers in solutions of a single permselective ion (e.g. Ca^{2+} bathing solutions and a calcium organophosphonate ion exchanger) can respond rapidly to activity changes of calcium on one side and yield a fully Nernstian slope. If the membrane were inadvertently pretreated with a foreign permselective cation (e.g., H^+ or Na^+), response to $a_{Ca}2+$ is much slower due to the need to attain steady state within the membrane which requires slow removal of the foreign ion from the membrane interior. Similarly, slow responses are invariably observed in mixture of permselective ions (e.g., Na^+ and Ca^{2+} in the former example, or NO_3^- and Cl^- in an anion selective membrane case) because the entire internal distribution of permeable ions must reach the steady state profiles before a stable potential reading will be observed. Another example is the rapid response of glass or other fixed site membranes to step changes in activity of a single electrolyte or mixture of electrolytes. Here, the glass interior composition slowly changes over a period of months. Yet the response is reached rapidly and is remarkably stable. The response can be stable and Nernstian because the membrane potential is independent of the bulk membrane ionic concentration profiles and their adjustments with time.

D. Selectivity Coefficients of Ion Selective Membrane Electrodes

One of the most satisfactory results of theory is the prediction of selectivity coefficients in terms of extraction, complex formation, and transport parameters. Although the theories are not always exact and results have not been thoroughly tested, a number of published calculations for various types of membranes have been summarized in Table 6 from Eisenman,[314] Buck,[249] and Simon et al.[315]

Among these, the forms for nonassociated liquid ion exchanger, fixed site and solid state crystal, and pressed pellet membranes were derived in this text. Measured values of selectivity coefficients have been compiled in several books and papers,[32,249-251,305,316] but much data remain uncompiled at the present time. Actual testing of the theory by independent measurements of the values of mobility, extraction, and solubility parameters occurring in the expressions for selectivity coefficients in Table 6 has been done only for most convenient systems, the silver halide-based membranes for which the selectivity coefficients depend only on ratios of solubility products. A useful presentation of some results has been given by Morf et al.,[256] simply by plotting experimental log K_{ij}^{Pot} vs. calculated log K_{ij}^{Pot} and showing that a very good correlation exists. This plot is reprinted as Figure 31. Testing of the theory for liquid ion exchange and fixed site membranes is more difficult because independent single ion mobility data are required as well as the more readily accessible ion exchange constants. Recent efforts to test theory have been referenced earlier.[267-274,277a] One can legitimately conclude that there is a correlation of potentiometric selectivity and ion exchange selectivity even when mobility values are not well known. Ion exchange selectivities vary over many powers of ten while mobilities are restricted to a narrower range of values. Similar tests of the selectivity expressions for neutral carrier membranes show that the salt extraction equilibrium constants and the overall formation constants of the cation-carrier complexes correlate well with potentiometric selectivities.[317]

By general usage the expression

$$\Delta\varphi_{meas.} = \varphi^0 + \frac{RT}{F} \ln (a_i + K_{ij}^{Pot} a_j) \qquad (258)$$

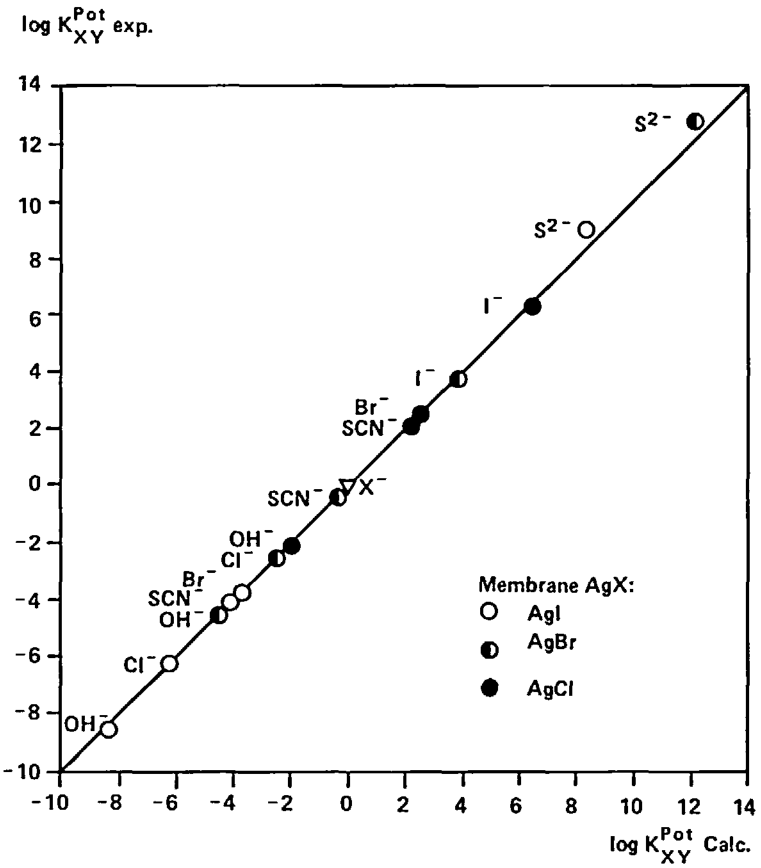

FIGURE 31. Comparison of the experimental and calculated anion selectivity coefficients of different silver halide membrane electrodes. (From Morf, W. E., Kahr, G., and Simon, W., *Anal. Chem.*, 46, 1538 (1974). With permission.)

is considered a normal form for ideal behavior of ion selective electrodes responsive to two species i and j with charge z. When, for positive ions, response is more positive for pure solutions of species i than for pure j at equal activities, then K_{ij}^{Pot} is a number less than unity and the electrode is more sensitive to i than to j. The notion that K_{ij}^{Pot} is indeed a concentration-independent constant quantity at constant temperature and pressure follows only from the most idealized models. Assumptions that ionic mobilities and activity coefficients of ions in membranes are independent of position and concentration, and that a constant fraction of membrane ions is involved in the diffusion potentials generation process are necessary to obtain a constant selectivity coefficient. Membrane systems composed of solid and concentrated liquid electrolytes can be expected to show concentration-dependent selectivity coefficients through complex formation, ion pairing, and effects of concentration and position on activity coefficients and mobilities.

Buck[206] has analyzed the forms of membrane response equations for various kinds of nonideal responses including kinetic effects. There are two distinct types of behavior expected for the dependence of K_{ij}^{Pot} (apparent) on activity: dependence on the ratio a_j/a_i and dependence on actual values of a_i and a_j. For the first case, a plot of K_{ij}^{Pot} (apparent) vs. a_j/a_i, or log–log plots of these quantities gives a single curve which describes the selectivity character of a system. For the second case, a family of curves is necessary depending on the absolute values of a_i or a_j. Reversible systems involving ion association and those with concentration-dependent activity coefficients depend on the simple first case. Some nonequilibrium, nonsteady state and possibly other as yet unrecognized sources of response belong to the second category.

TABLE 6

Selectivities for Different Types of Membrane Electrodes and Restrictions Used

Type of membrane	K_{ij}^{Pot}	Restrictions
Liquid membrane, no ligand (negligible complex formation)	$\frac{u_j k_j}{u_i k_i}$	$u_x = 0$ or $c_x(x) = 0$
	$\frac{(u_j + u_x)\,k_j}{(u_i + u_x)k_i}$	$c_x(x)$ = const. electroneutrality holds
	$\frac{k_j}{k_i}$	Zero diffusion potential $c_i(x) + c_j(x)$ = const.
Liquid membrane, electrically neutral ligand S complex formation dominant)	$\frac{u_{js}K_j}{u_{is}K_i}$	$u_x = 0$ or $c_x(x) = 0$ $c_s(x)$ = const.
	$\frac{(u_{js} + u_x)\,K_j}{(u_{is} + u_x)\,K_i}$	$c_x(x)$ = const. electroneutrality holds $c_s(x)$ = const.
	$\frac{K_j}{K_i}$	Zero diffusion potential $\alpha(x)$ = const.
Liquid membrane, electrically charged ligand S^-(complex formation dominant, flux of anions X^- negligible)	$\frac{u_j k_j}{u_i k_i}$	$u_s << u_i, u_j$
	$\frac{(u_j + u_s)\,k_j}{(u_i + u_s)\,k_i}$	$c_s(x)$ = const. electroneutrality holds
	$\frac{u_{js}\,K_j}{u_{is}\,K_i}$	$u_s >> u_i, u_j$ total flux of all ligand forms negligible
	$\frac{K_j}{K_i}$	Zero diffusion potential $\alpha(x)$ = const.
Solid ion exchangers	$\frac{u_j k_j}{u_i k_i}$	Permselective for ions of one sign and magnitude
Solid crystal membranes	$\frac{K_{sp,i}\bar{\gamma}_j}{K_{sp,j}\bar{\gamma}_i}$	Zero diffusion potential ions of same charge

Explanation:
k_i, k_j = partition coefficients of cations I^+ and J^+ between outside solution and membrane; K_i, K_j = partition coefficients of cations I^+ and J^+ between outside solution and the respective complexes in the membrane; u = mobilities in the membrane; c(x) = concentrations in the membrane; $\alpha(x)$ = degree of dissociation in the membrane, defined as the ratio of free ligand concentration to concentration of all forms of ligand; $k_i = k_{ext,i}/\bar{\gamma}_i$ $k_j = k_{ext,j}/\bar{\gamma}_j$ $k_j/k_i = K_{i,exc} \cdot \bar{\gamma}_i/\bar{\gamma}_j$, 249, 314, 315.

For diagnosis of concentration-dependent selectivity coefficients, selectivity coefficients must be computed from responses of mixture methods in the region of appreciable values of a_j/a_i such that response is not dominated by a_j or a_i alone. The two point pure solution methods[318] will not suffice because they cannot uncover composition-dependent selectivities. The advantage of the two solution method is simplicity, but even for systems where responses to pure a_i and a_j give parallel $\Delta\varphi$ meas. vs. log a_i or a_j characteristics, it can be shown that one obtains only limiting values of K_{ij}^{Pot} corresponding to high values of a_j/a_i. Using mixture methods, 3 or 4 pure solutions of a_i to establish base response, and about 15 mixtures (5 a_i levels spaced ½ decade apart at 3 levels of a_j, 1 decade apart) are sufficient. Mixture methods are quite old and were first used extensively by Lengyel and Blum[319] and later by Eisenman.[320] Srinivasan and Rechnitz[321] examined several methods for the determination of K_{ij}^{Pot} while Pungor and Toth[322,323] recognized the essental requirements for reliable measurements and strongly recommended one form of the mixture method, that version which has been outlined here. They pointed out the fact that when dealing with ion-exchanging liquid and solid electrodes (including glasses) containing the species i, responses to pure a_j are unreliable. Mixtures must be used containing a_i such that surface attack by a_j releases an insignificant activity increment of a_i at the membrane surface. A convenient form of the mixture methods is the titration procedure of Dole;[324] as modified and improved in this laboratory.[205] This method can provide extensive sets of data for determinations of K_{ij}^{Pot} (apparent). When a set of mixture responses $\Delta\varphi_{ij}$ and pure responses to a_i, $\Delta\varphi_i$, the selectivity coefficient is calculated from

$$\ln K_{ij}^{Pot}\text{ (apparent)} \qquad (259)$$

$$= \ln \{\exp[(\Delta\varphi_{ij} - \Delta\varphi_i)/S] - 1\} - \ln(a_j/a_i)$$

where S is the slope of the pure a_i response curve.

The single implication of membrane electrochemistry which proves to have the widest importance to analytical chemistry is the general conclusion that membrane potentials (interfacial and internal diffusion components) reflect the ionic composition of the bathing solutions. When a given ion is more favorably extracted into a membrane and this ion has a higher mobility (free or complexed) than others of the same sign, one can be confident that the membrane potential will respond to the bathing solution activity of this ion in preference to others. While this statement may reflect a necessary condition for selectivity, it is probably not sufficient or adequate as an operating principle for the design of new transport selective membranes and membrane electrodes because the exact relationships between transport or ion exchange preference are not well known in terms of molecular properties of membranes. Only in a phenomenological way have important selectivity-determining factors been identified. There are a number of features of membrane systems which influence and control the extractability and apparent mobility parameters of ions, viz., density of fixed and mobile sites, dielectric constant of the membrane medium (before and after equilibration with water), interactions of ions with sites to form mobile or immobile ion pairs, and possible interactions with co-ions and with complex forming reagents, including membrane solvents and additives.

The kind of theory and data that is now needed to design for specific functions is a basic, molecular level analysis from which phenomenological quantities, extraction coefficients, transport parameters, ion pair, and complex ion formation constants in membrane systems (usually of low dielectric constant values in the range 3 to 20) can be accurately predicted. We are, however, still in the era of observation, data collection, and correlation with respect to membrane functions despite the rather complete phenomenological theory base that has been outlined in this review.

Progress on molecular level theory primarily is due to the efforts by Eisenman's and Simon's groups.[315,325-327] The aim is prediction of molecular requirements for selectivity of alkali and alkaline earth ions in neutral carrier and liquid ion exchanger membranes, where extraction occurs without water of hydration. The theory attempts to interpret selectivity on the basis of specific effects on the overall extraction coefficients calculated from the free energy of transfer:

$$-RT \ln K_{ext,i} = \Delta G^{o}\text{ (transfer)} = \Delta G^{o}_{L} - \Delta G^{o}_{H} \qquad (260)$$

where

ΔG^{o}_{L} = free energy for transfer of a cation from the gas to the cavity in a ligand

ΔG^{o}_{H} = free energy for transfer of a cation from the gas to water

Each of these free energies reflects:.

a. Disengagement of the coordinating site in the ligand or water

b. Electrostatic dispersion and repulsive interactions between the cation and coordinating ligand or water
c. Polarization of the surrounding solvent medium
d. Changes in the volume of solvent
e. Corrections for relating quantities to standard states
f. Adoption of conformations suitable for cation coordination
g. Deformation of ligand to adjust the volume or size of a cavity to fit a cation
h. A statistical term depending on the number of sites in a ligand

Calculations are not precise, and small errors in differences between large numbers can have profound effects on conclusions. Yet, directional effects of ligand groups, coordination number, ligand size, steric interactions, and dielectric constant can be predicted. A particularly interesting conclusion is the fact that monovalent ions are preferred by neutral carriers in low dielectric constant media, $K < 10$, as the dielectric constant is decreased. Lipophilic ligands (which exclude many nitrogen containing compounds) containing oxygen (either ether or carbonyl) coordinating sites are preferred when five-member chelate ring formation is possible.

VIII. SUMMARY

The thrust of this review has been an accumulation of ideas, methods, and results on ionic membrane processes, membrane potentials, and current-voltage-time-activity characteristics of membrane classes. To obtain a consensus on pertinent principles, appropriate mathematical techniques and results on membrane potentials, fields and ionic profiles in the transient and steady states, a great variety of literature sources must be consulted. This literature includes references in chemical physics, physical chemistry, theoretical biology, physiology, biophysics, solid state physics, chemical engineering, desalination, and analytical chemistry. To the analytical chemist who enters the field of membrane electrochemistry for the purpose of pursuing separations based on membranes or sensor development and applications based on membranes, the message should be clear from Tables 1 and 3 that the kinds, forms, and chemical properties of membranes are very large, and the types of processes and pertinent natural and derived parameters are diverse. Yet, the principles involved in interfacial equilibria, kinetics, charge accumulation, and charge transport are relatively few. Many qualitative similarities exist in membrane electrochemical properties across a wide range of membrane materials from lipid bilayers to ion-conducting single crystals.

The reference catalog of membrane potential calculations tries to organize the results into relatively few categories, and to point out similarities and differences among categories. It is not a complete historic catalog, but rather a condensation of the "common wisdom" from recent literature. Older literature references are used only when some need for completeness arose. I have tried to point out where the theory is incomplete and it is clear that many systems have not been completely characterized. There is, however, a great deal of activity in the field of membrane electrochemistry, and problems such as transport of single ions through nonelectroneutral membranes, which was an obscure topic in solid state physics only a few years ago, are now well explored through the wide interest in lipid bilayers. In another decade there is little doubt that the catalog presented here will need expansion and revision.

If there is a single unifying concept which pervades this review and all membrane electrochemistry, it is the idea that the potential profile is continuous everywhere. Thus, it becomes the aim of theory to discover all processes which determine local potentials: charge exchange, charge motion, charge carrier profiles and field profiles, space charge distributions and adsorption of charged species. Given the potential profile one can deduce the net membrane potential by taking differences between potential values at points across a membrane where they are known. The least well-developed part of theory needed to accomplish these ends is that part required for description of blocked and nearly blocked (electrochemically irreversible) interfaces. General solutions of the Nernst-Planck equations inside and outside membranes with simultaneous satisfaction of Poisson's equations both inside and outside, with continuity of displacement and potential at the interface, have yet to be given for the entire range of surface rate processes from irreversible to reversible. As interfaces become less reversible, the role of adsorption potentials and the isotherms describing adsorbed ion activities in terms of bulk activities becomes increasingly important. Solutions of problems of the latter type are pressing as the need to interpret responses of unusual interfacial systems arises.

What, then, can be said about completely blocked interfaces, where interfacial potentials are calculated from Gouy-Chapman level theory and potentials depend upon phase charge, but only indirectly depend on ion activities in (or on) a phase through an isotherm of some sort? One does not expect blocked interfacial potentials to depend in a Nernstian fashion on ion activities. Yet, how can the observed Nernstian and near-Nernstian responses of electronic conductors, such as graphite contacting an organic liquid ion exchanger,[328] platinum coated with stearic acid,[329] and platinum coated with PVC containing liquid ion exchanger,[330] be reconciled with the need for reversible processes at the metal/organic interface? At present, there is no answer. One possibility is capacitive coupling. The second is the more probable situation that some reversible process is actually occurring between surface bound oxides and protons in the organic phase.

GLOSSARY

a_i	– Activity of an ion in exterior, bathing solution.
a_+, a_-	– Activities of cations and anions.
a_b	– Bulk activity of an ion in exterior bathing solution where electroneutrality applies.
a_s	– "Surface" activity of a species determined by mass transport, but outside the space charge region.
$a(0), a(d)$	– Activity of a species at a surface within the space charge region.
$\bar{a}_i, \bar{a}_s, \bar{a}(0), \bar{a}(d), \bar{a}_+, \bar{a}_-$	– Activities of species in a membrane phase corresponding to positions given above.
$a(x)$	– Activity of a species according to its position.
$\bar{A}_s$ and $\bar{B}_s$	– Overall rate constants defined in Equations 143 and 144.
A_j, A_k	– Sums over activities in Equation 185.
B_j, B_k	– Sums over mobility-activity products in Equation 186.
C_i	– Concentration of a species in exterior bathing solution.
C_b	– Bulk value of a species concentration, in exterior bathing solution where electroneutrality applies.
$C_{s,d}$ or $C_{s,o}$	– "Surface" concentrations of a species determined by mass transport, but outside the space charge region.
$C(0), C(d)$	– Concentration of a species at a surface within the space charge region.
$C(x)$	– Concentration of a species according to its position.
C_+, C_-	– Concentrations of a cation and an anion.
$\bar{C}_i, \bar{C}_b, \bar{C}_{s,d}, \bar{C}_{s,o}, \bar{C}(0), \bar{C}(d), \bar{C}_+, \bar{C}_-$	– Concentrations at equivalent positions to those above, but in the membrane phase.
$C_{d.l.}$	– Double layer capacitance at lowest frequencies for interfaces contacting permeable and impermeable ions, so-called "supported" electrolyte systems.
C_0	– Low frequency capacitance for binary electrolytes.
$C_{0,b}$	– Low frequency capacitance for a two blocked interface membrane system.
$C_{0,r}$	– Low frequency capacitance for a reversible membrane.
C_g	– Geometrical capacitance of membranes.
C_I, C_{II}	– Capacitances of diffuse layers of space charge.

GLOSSARY (continued)

d_v – Hydrodynamic permeability in equation 107 cm^5/joule sec.
d – Membrane thickness.
D – Diffusion coefficient in solution cm^2/sec.
$\bar{D}$ – Diffusion coefficient in a membrane cm^2/sec.
$\mathcal{D}$ – Stefan-Maxwell diffusion coefficient.
D – Electric displacement vector magnitude.
E – Electric field vector magnitude.
f – Frequency in Hertz.
f_i – Friction coefficient.
f_{ik}, f_{iw} – Relative friction coefficients.
F – Faraday constant.
G – Gibbs free energy.
G^* – Activation free energy.
ΔG – Free energy change.
ΔG – Chemical part of the free energy change.
h – Planck's constant.
I – Total current density amp/cm^2.
$i, \overrightarrow{i}, \overleftarrow{i}$ – Partial current densities carried by an ion of one type.
i^o – Equilibrium exchange current density at unit activity of species.
K – Dimensionless dielectric constant used only in the definition of ϵ.
$K_{ext}, K_{ext,i}$ – Extraction coefficient of a neutral species and the extraction coefficient for a single ion.
K' – Thermodynamic salt extraction coefficient.
K_D – Concentration ratio salt extraction coefficient.
K_{iexc} – Thermodynamic ion exchange constant.
K_{sp} – Solubility product in terms of ion activities.
K_{is} – Formation constant for an ion-carrier complex.
K_{ij}^{Pot} – Potentiometric selectivity coefficient.
k_o – Standard interfacial rate constant for unit activities of reactant and products k_o^+ for cations, k_o^- for anions.
L – Onsager coefficient.
k – Boltzmann constant in absolute rate equations.
$k, \overrightarrow{k}, \overleftarrow{k}, \overrightarrow{k}', \overleftarrow{k}'$ – Surface rate constants based on extrapolated "surface" concentrations.
$\underset{\rightarrow}{k}', \underset{\leftarrow}{k}'$ – Surface rate constants based on actual concentrations in the space charge region.
$J, \overrightarrow{J}, \overleftarrow{J}$ – Flux of material or energy in the external solution.
$\bar{J}, \overrightarrow{\bar{J}}, \overleftarrow{\bar{J}},$ – Flux of material or energy in a membrane.
j – $\sqrt{-1}$.
M – Metal or Macdonald's ratio defined in Equation 225.
M_i – Mole weight of an ion.
M_w – Mole weight of a solvent, usually water.
n – A negative ion.
$p, \bar{p}$ – Local osmotic pressure in solution and membrane, respectively.
p – A positive ion.
pzc – Potential of zero charge.
R – Gas constant.
R_{surf}, R_{bulk} – Resistances.
r_p, r_n – Chang-Jaffe rate constants for the interfacial discharge of cation p and anion n at a surface.
r_e – A common equilibrium potential value of the Change-Jaffe parameters applicable to ions of both sign.

GLOSSARY (continued)

R_θ – Apparent resistance of an activated surface process, activation resistance.
R_∞ – High frequency resistance of a phase involving motion of both blocked and non blocked ions.
R_0 – DC resistance of a membrane.
s – Reduced distance variable = x/d, Equation 140.
s – Laplace transform variable = $\sqrt{j\omega}$.
S – Integral defined in Equation 187.
s – Subscript for a neutral carrier.
T – Absolute temperature.
t, t_c, t_a – Transport number of a species, a cation and an anion.
t_s – Transport number of a solvent.
u_i, u_i^* – Mobilities of ions in solution external bathing. See Equation 105 for dimensions.
$\overline{u}_i, \overline{u}^*_i$ – Mobilities of ions in a membrane. See Equation 105 for dimensions.
$v_i, \overline{v}_i$ – Partial molar volumes of species in solution and membrane.
$\overrightarrow{v}, \overleftarrow{v}$ – Velocities of species moving under diffusion and migration.
V_c – Cell voltage.
V_{ref} – Reference electrode potential referred to a standard hydrogen electrode.
$\overline{W}_s(x)$ – Energy barrier in Equations 145 and 146.
$\overline{W}_{is}(x)$ – Energy barrier in Equations 145 and 146.
x, x_s – Volume or mole fractions.
x – Running distance variable through a parallel face membrane.
x_L – Levich thickness.
x = 0 – Left side of a membrane.
x = d – Right side of a membrane.
$\overline{X}$ or $\overline{X}_i$ – Membrane charge sites.
X_k – Generalized force, except temperature difference or gradient.
X_u – "Force" due to a temperature difference or gradient.
z or z_i – Charge of an ion with sign.

GREEK SYMBOLS*

alpha

α-Transfer coefficient in equations 65, 66 and 68. Defined quantity in equation 192. A defined quantity in Table 6.

delta

δ – Nernst diffusion layer thickness;
δ′ – applies to the left side of a membrane;
δ″ – applies to the right side of a membrane.

GREEK SYMBOLS (continued)

epsilon

ϵ – Dielectric permittivity farads/cm = KE_0.

ϵ_0 – Dielectric permittivity of space (rationalized), 8.85×10^{-14} farads/cm.

gamma

$\gamma_\pm, \bar{\gamma}_\pm$ – Mean activity coefficients in solutions and in membranes.

kappa

κ – Reciprocal Debye thickness.

κ – Transmission coefficient in absolution reaction rate Equations 65, 66 ,69, 75, 90, 92.

lambda

λ – Width of an activation barrier.

phi

$\phi, \bar{\phi}$ – Inner potential of a phase, bathing solution, and membrane.

ϕ_0 – Inner potential of a bulk phase, usually a solution, where electroneutrality applies.

ϕ_s – Inner potential of an electroneutral region near a surface (outside space charge region) during flux passage. ϕ_s is ϕ_b in the absence of flux .

$\Delta\phi_m$ – Overall membrane potential.

$\overline{\Delta\phi}_m$ – Interior diffusion potential of a membrane.

$\phi_2, \bar{\phi}_2$ – Local potential at the point where electron or ion exchange occurs.

pi

π_m – u_n/u_p: $\pi_z = z_n/z_p$.

rho

ρ – Space charge density.

sigma

σ_s – Reflection coefficient.

omega

ω – Frequency in radians.

ϖ – Charge with sign for sites in membranes.

Ω – Normalized radial frequency = $\omega\tau_\infty$.

mu

μ – Dipole moment in coulomb-cm in Equation 14 only.

$\mu, \bar{\mu}$ – Chemical potential of uncharge species (in joules/mole) in a solution and in a membrane.

$\tilde{\mu}, \tilde{\bar{\mu}}$ – Electrochemical potential of an ion in a solution and in a membrane.

$\mu^0, \bar{\mu}^0$ – Standard state chemical potentials.

tau

τ – Time constant.

τ_∞ – Time constant for the highest frequency ion transport process.

τ_0 – Low frequency Warburg time constant.

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