Chemical Studies at Ion-Selective Membrane Electrodes

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Ion-selective membrane electrodes have had an immense impact on analytical solution chemistry and have found wide application in fundamental chemical and biochemical studies.[1] There are now electrodes available for more than 20 ions, including alkali metal and alkaline earth ions, heavy metal ions, and a wide range of important anions. Satisfactory electrodes are also available for certain ions, such as F^-, NO_3^-, ClO_4^-, etc., where are difficult to measure in solution by other analytical methods.

Ion-selective membrane electrodes measure the activities of ions in solution with considerable sensitivity (often to below one part in 10^9) and, as the name implies, with selectivity. (Electrodes 5×10^4 times as responsive to Na^+ as to K^+ are common.) The selectivity of the electrodes means, of course, that they may be used without fear of interference in electrolyte solutions containing other species which may be present naturally or which may be added to control the ionic strength or pH. When these advantages are coupled with the electrodes' operational convenience and relatively fast response time, it is not surprising that ion-selective membrane electrodes are becoming such an important analytical tool.

Historically, the development of ion-selective electrodes began with the observation that thin membranes of glass develop an electrical potential related to the activity of the hydrogen ion in solutions in contact with the membrane. It may seem surprising that glass, commonly regarded as an insulator, should be able to function as an electrode. While the electrical resistance of glass indeed is very high, the glass membranes (Figure 1) used in electrodes are quite thin and, furthermore, the sophisticated and sensitive electronics currently being used to carry out the actual potentiometric measurements draw very little current so that only few charges need to be transported through the glass membrane. Hydration of the glass membrane once it comes into contact with the sample solution further lowers its resistance.

For many years it was believed that the operation of such glass membranes as electrodes required the actual transport of the ions in the sample solution through the membrane. This hypothesis delayed the development of new ion-selectivity electrodes because it was thought that only very mobile ions, like H^+, could give rise to electrode response. Later, radiotracer experiments proved that ions from solution are not transported through the membrane in normal electrode operation, and it is now known that glass electrodes function by a combination of an ion-exchange process at the glass–

solution interface and a movement of various cations in the dry and hydrated portions of the glass. Thus, it is not necessary that the ion to be measured be especially mobile nor that the ion of interest be present in the membrane. It is true, however, that electrode glasses are cation exchangers which exclude anions; thus glass electrodes respond and are selective to cations only. Furthermore, because of ion size and mobility considerations glass electrodes are primarily useful as sensors for univalent cations such as Na^+, K^+, H^+, Ag^+, Li^+, Cs^+, Rb^+, and NH_4^+.

A major step forward was taken in the later 1950's when researchers succeeded in correlating glass composition and electrode selectivity. Up to that time, selection of compositions had been made largely on a trial and error basis. These correlations and accompanying theoretical advances immediately resulted in the development of the practical cation-sensitive glass electrodes mentioned above.

It was soon realized, however, that ion-selective electrodes consisting of glass membranes would primarily be limited to electrodes responsive to univalent cations and that electrodes for other types of ion would require membranes consisting of other materials. With understanding of the processes responsible for the success of the glass membranes and the extensive information already available regarding biological membranes, choices of novel membrane materials could now be made on the basis of reason and analogy.

Two classes of new membrane materials have been found in the past few years to be highly useful—inorganic solids and organic liquids (Figure 1). The first category includes salt crystals, such as LaF_3, Ag_2S, and the silver halides, which can be used directly as membranes or in combination with some inert matrix material; the second consists largely of liquid ion exchangers which require the use of a support membrane to construct a stable electrode. In practice, the range of crystalline and other inorganic materials suitable as electrode membranes is rather limited but highly successful in the specific cases mentioned above. The liquid ion exchangers, on the other hand, offer a wide range of possibilities for almost any kind of ion but usually yield electrodes which are only moderately selective for the ion of interest, *i.e.*, they suffer interferences from chemically similar ions.

It is convenient to classify ion-selective electrodes as having either "fixed-site" or "mobile-site" membranes.[2] Electrodes of the first category, *e.g.*, glass electrodes, have anionic sites available at the membrane surface where ion exchange or ion adsorption may take place. These sites cannot move during the time scale of po-

(1) G. A. Rechnitz, *Chem. Eng. News*, **43** (25), 146 (1967).

(2) G. Eisenman, *Anal. Chem.*, **40**, 320 (1968).

GLASS ELECTRODES

GLASS MEMBRANE →

INTERNAL FILLING SOLUTION

SILVER-SILVER CHLORIDE REFERENCE ELECTRODE

LIQUID-LIQUID MEMBRANE ELECTRODES

INTERNAL AQUEOUS FILLING SOLUTION

SILVER-SILVER CHLORIDE REFERENCE ELECTRODE

ION EXCHANGER RESERVOIR

LIQUID ION EXCHANGE LAYER

POROUS MEMBRANE

SOLID-STATE MEMBRANE ELECTRODES

INTERNAL FILLING SOLUTION

SYNTHETIC SINGLE-CRYSTAL MEMBRANE
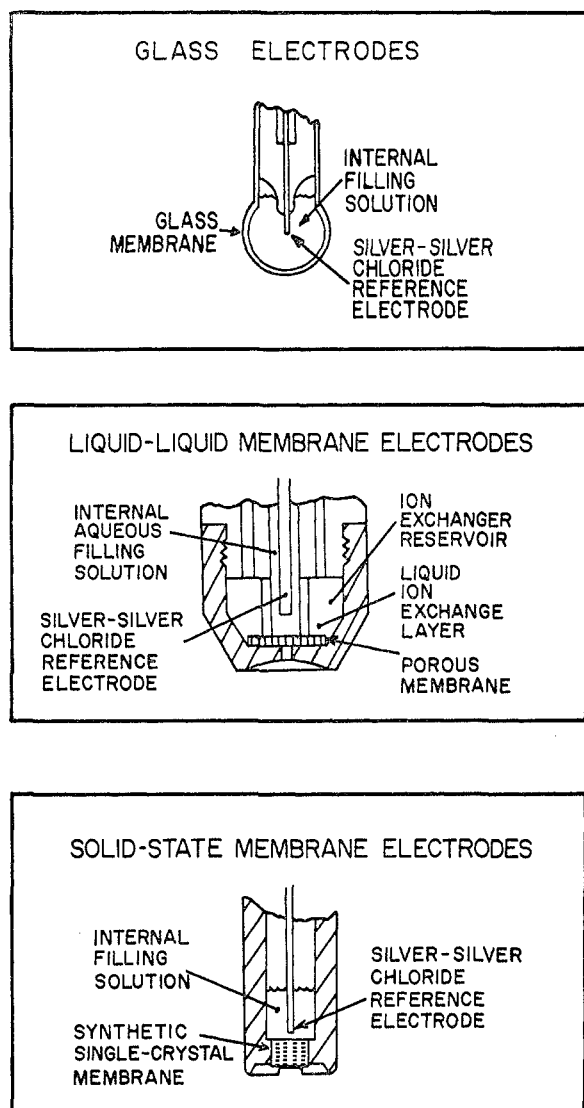
SILVER-SILVER CHLORIDE REFERENCE ELECTRODE

Figure 1. Schematic representations of ion-selective membrane electrodes.

tentiometric experiments, hence the designation "fixed site." Liquid membrane electrodes, on the other hand, belong to the "mobile-site" category in that their sites or ion-site pairs may participate in the transport of electrical charge through the membrane. It is this additional property which makes possible the creation of electrodes selective for ions not ordinarily mobile in membranes because of their size or electrical charge.

Taking as an example a typical[1] glass electrode having a membrane composition of 27% Na_2O–4% Al_2O_3–69% SiO_2, we find that this electrode has an over-all potentiometric selectivity for K^+ over Na^+ of about 8.5:1. Tracer experiments show that the surface sites of this electrode prefer K^+ over Na^+ by a factor of about 102. On the other hand, K^+ is less mobile in the electrode membrane than Na^+, with a mobility ratio of about 0.088. It is clear, then, that the over-all potentiometric selectivity of this electrode is the product of these two factors and that the favorable selectivity of the sites for K^+ outweighs the unfavorable mobility ratio.

This may be compared with a typical "mobile-site"

liquid membrane electrode selective for calcium[3] which uses calcium salts of organophosphorus compounds as the active, site-containing material. This electrode has an over-all potentiometric selectivity for Ca^{2+} over Na^+ of about 10^8. The relative contributions of the ion-exchange equilibrium constant and the mobility ratios of the ions or other charge carriers to the over-all selectivity are not known and would be difficult to measure experimentally, but it is likely that the mobility of the sites plays a key role in determining the over-all selectivity because the mobility of a divalent ion like calcium must be much lower than that of the univalent Na^+.

Transient Effects

Because the potential of ion-selective electrodes is actually composed of two or more discrete contributions arising from the various processes at the interfaces and in the bulk of the active membrane material, it follows that these several components can be separately discerned under certain experimental conditions. This is particularly true when such electrodes are used under nonsteady-state conditions, e.g., in flowing samples or in changing reaction systems. The resulting behavior can have significant consequences to the interpretation of experimental measurements carried out under dynamic conditions.

Specifically, when the potential of an ion-selective electrode is monitored as a function of time in a system of rapidly changing composition, the potential-determining processes at and in the electrode membrane may also be rate determining and result in various "transient" phenomena.

This effect has recently been demonstrated for cation-sensitive glass electrodes.[4] When such electrodes are subjected to a sudden change in activity of divalent cations such as Ca^{2+} or Sr^{2+} in the presence of a constant background concentration of univalent cations, the electrode potential undergoes a momentary (<100-msec) excursion far beyond that predicted by the equilibrium selectivity of the electrode for the ions involved (Figure 2). At slightly longer times, the potential returns to the expected value. This behavior, while initially puzzling, can now be explained on the basis of the above-mentioned two components which make up the potentiometric selectivity of the electrode, i.e., the ion-exchange equilibrium constant and the mobility ratio. In the experimental system illustrated in Figure 2 we have a situation where the ion-exchange equilibrium between Ca^{2+} or Sr^{2+} and K^+ substantially favors the uptake of the divalent ion by the electrode. This effect is momentarily dominant when the activity of the divalent ion is changed near the electrode surface and gives rise to the initial excursion of the potential. The mobility of divalent ions in the hydrated layer is vastly lower than that of univalent cations in the hydrated layer of the glass; thus, the mobility ratio

(3) G. A. Rechnitz and Z. F. Lin, Anal. Chem., **40**, 696 (1968).
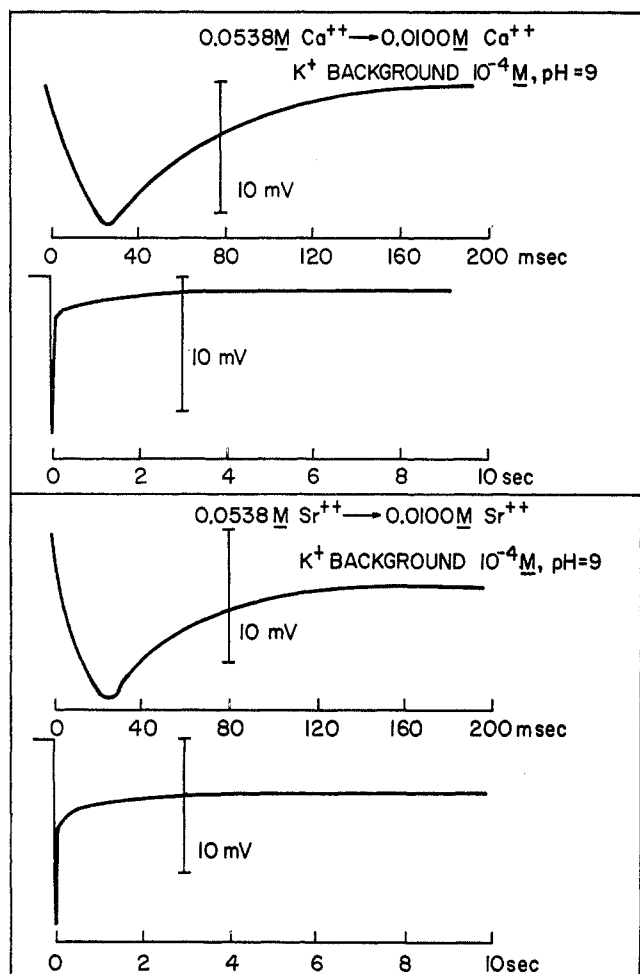(4) G. A. Rechnitz and G. C. Kugler, ibid., **39**, 1682 (1967).

Figure 2. Transient response to divalent cations of cation-sensitive glass electrodes.

(a) $[Mg^{2+}]=0 \longrightarrow 2.5 \times 10^{-4} \underline{M}$; $[Ca^{2+}] = 3.9 \times 10^{-4} \underline{M}$

(b) $[Mg^{2+}] = 2.5 \times 10^{-4} \underline{M} \longrightarrow 4.9 \times 10^{-4} \underline{M}$; $[Ca^{2+}] = 3.7 \times 10^{-4} \underline{M}$

pH = 9.63, $\mu = 0.01 \underline{M}$,   25°C

Figure 3. Transient Mg^{2+} response of Ca^{2+}-selective liquid membrane electrode.
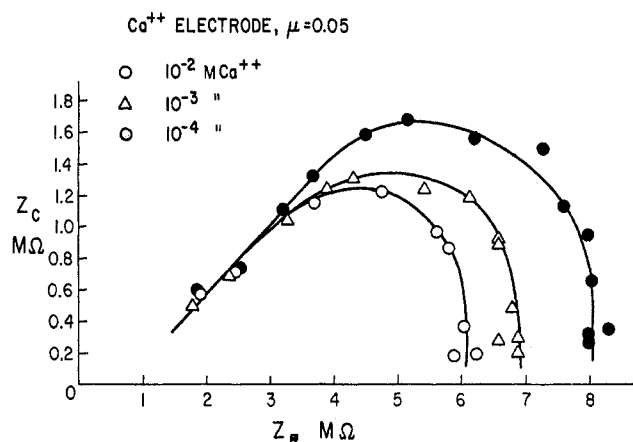
Figure 4. Impedance measurements on Ca^{2+}-selective liquid membrane electrode.

factor more than cancels the favorable ion-exchange equilibrium constant and causes the potential to return to the final steady-state value when both factors are in full effect.

Ordinarily, such phenomena would not be noticeable in experiments carried out with ion-selective electrodes on the normal laboratory time scale. In the study of fast reactions, these effects can pose a practical limitation to accurate experimentation, however. More seriously, similar effects are also observed on liquid membrane electrodes where the time scale of electrode response is very much expanded (Figure 3). As a result, the effective use of such electrodes for rate studies is difficult even for moderately rapid reactions under certain circumstances. Because the equilibrium selectivity of liquid membrane electrodes having "mobile" sites involves at least three separate components,[2] the observed transient effects cannot yet be unambiguously interpreted. Recent impedance measurements carried out in our laboratory can, however, be used to clarify the earlier potentiometric data. Figure 4 shows the results of impedance measurements for the calcium-selective liquid membrane electrode. Since this electrode corresponds to the subcategory having strong association between the ions and the mobile sites, it can be concluded that charge is transported in the membrane
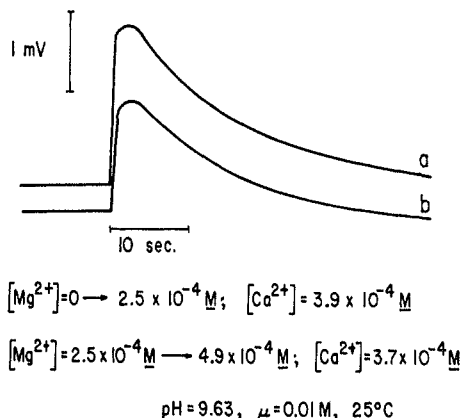
by the movement of sites or of ion-site pairs; the impedance measurements rule out the movement of electrically neutral species or the possibility of slow exchange at the membrane–solution interface as rate-determining processes. Additional studies of these processes are continuing using both impedance and charge-step techniques.

Another common and, as yet, unexplained phenomenon is the "slowing" of electrode response in the presence of interfering ions. The sodium-selective glass electrode, for example, shows (Figure 5) a more sluggish response to changes in Na^+ activity in the presence of K^+ ions than in their absence. Similarly, the calcium-selective liquid membrane electrode responds more slowly to changes in Ca^{2+} activity when magnesium ions are present than when they are not (Figure 6). A systematic investigation of these effects is currently under way but, in the meantime, it must be recognized that this slowing of response rates could be a source of error in the investigation of practical systems under dynamic conditions.

Equilibrium selectivity considerations, alone, present one of the limiting factors in the use of ion-selective electrodes for analytical studies. In this connection, it is convenient to speak in terms of accessibility "windows" for each electrode in a given system. For the LaF_3 crystal F^--selective electrode, for example, there
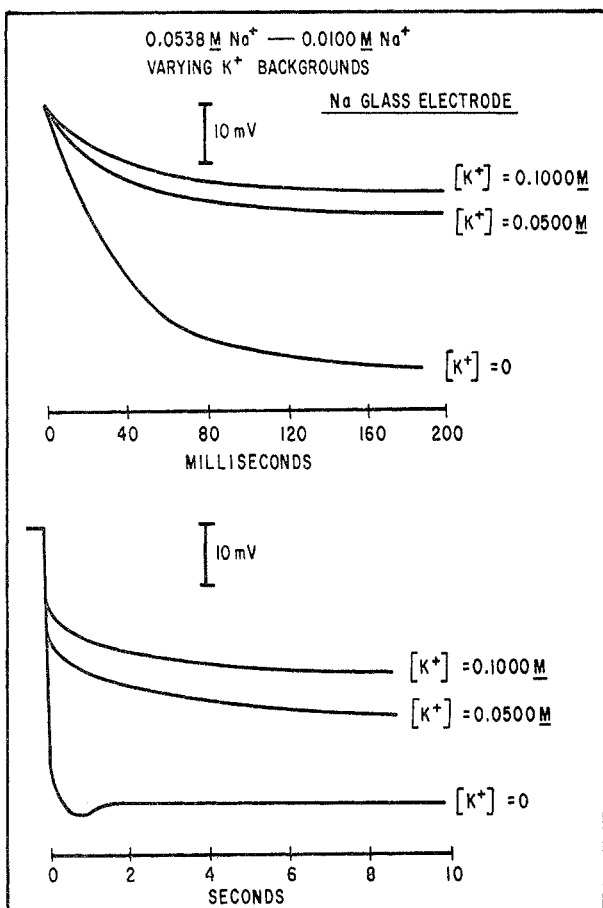
Figure 5. Effect of K$^+$ background upon dynamic response of Na$^+$-selective glass electrode to change in Na$^+$ concentration.

$[Ca^{2+}]$ = 1.0 x 10^{-4} $\underline{M}$ — 1.33 x 10^{-4} $\underline{M}$

(a)   3 x 10^{-4} $\underline{M}$ Mg^{2+}
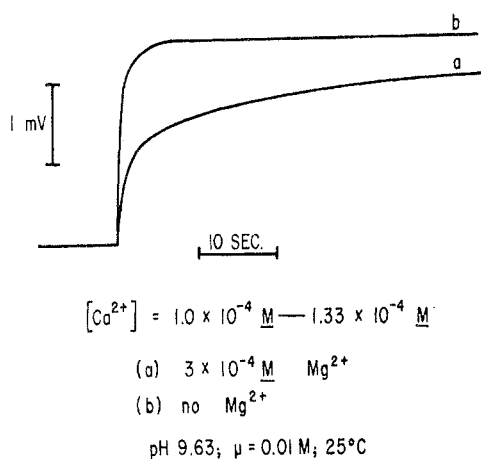
(b)   no   Mg^{2+}

pH 9.63; µ = 0.01 M; 25°C

Figure 6. Slowing effect of Mg^{2+} on response rate of Ca^{2+}-selective liquid membrane electrode.

is an accessibility window with the solution pH as the variable because the usefulness of this electrode is limited by OH$^-$ interference at high pH values and by the formation of hydrogen fluoride species at low pH values. Similarly, the liquid membrane Cu^{2+}-selective electrode has a pH window defined by its response to the hydrogen ion in acidic media and by the formation of cupric hydroxide in more alkaline media.

Such accessibility windows may be enormously large, as in the case of the pH-type glass electrode, or distressingly narrow, as in the case for some of the recently

developed liquid membrane electrodes. Naturally, the solution pH is not the only determining variable in the definition of these windows. Any interfering ion, "poisoning" material, or physical variable has an effect which can be expressed in terms of such windows for any given electrode. It has been my experience that most of the problems encountered by users, especially new users, of ion-selective electrodes can be traced to a lack of appreciation of this concept, the violation of some simple rule regarding electrode treatment and handling, or confusion about the elementary activity relationships used for the interpretation of potentiometric data. With proper handling and understanding, ion-selective electrodes become remarkably easy to use, however, and permit substantial simplification of ion activity measurements.

Ion-Association and Rate Studies

An especially attractive consequence of the fact that ion-selective electrodes measure the activity of unassociated ions is that such electrodes can be used directly and elegantly in the study of complexes and other associated chemical species. In principle, all that is necessary is to measure the activity of the ion of interest under noncomplexing solution conditions and then again in the presence of the complexing agent. From these measurements and knowledge of the initial concentrations of the reagents involved, both the stoichiometry and the formation constant of the resulting complex can be obtained by standard methods. Situations involving series of complexes, additional equilibria, kinetic complications, etc., can also be handled through proper design of experiments and use of appropriate computational techniques.

Practically every category of ion-selective electrodes has, by now, been employed for complex formation studies. The species involved have ranged from simple inorganic ion pairs to large complexes of biological interest. Table I summarizes some representative studies carried out in recent years.

There are two principal advantages to the use of ion-selective electrodes for ion-association studies aside from the convenience that the electrodes measure ion activity. First, electrodes are now available which are selective to certain ions, such as F$^-$, ClO$_4$$^-$, Ca^{2+}, etc., which are difficult to measure in solution by other analytical techniques. Second, ion electrodes have sufficient selectivity so that they may be used, without fear of interference, in electrolyte solutions containing other species necessary for control of ionic strength or pH. When these advantages are combined with the considerable sensitivity and operational convenience of ion-selective electrodes, it is not surprising that such electrodes are now becoming important tools for complex formation studies.

Similar considerations apply to reaction rate measurements and mechanistic studies in solution. In most circumstances, the response time of ion electrodes is short enough to be of no experimental consequence. Thus, such electrodes can faithfully monitor the course

Table I

Complex Formation and Reaction Rate Studies with Ion-Selective Membrane Electrodes

Species studied	Electrode	Ref
HF, HF_2^-	LaF_3 membrane	a
AlF^{2+}	LaF_3 membrane	b
FeF^{2+}, FeF_2^+	LaF_3 membrane	b
SnS_3^{2-}	Ag_2S membrane	c
Cu^{2+} complexes	Liquid membrane	d
Ca^{2+}, Mg^{2+}, EDTA, NTA complexes	Ca^{2+} electrode	e
ClO_4^- compounds	ClO_4^- electrode	f
Tetraphenylborate reactions	Cation glass electrode	g
Ag^+, Ni^{2+} reactions with EDTA	Cation glass electrode	h
FeF^{2+} + I^- reaction	LaF_3 electrode	i

^{a} K. Srinivasan and G. A. Rechnitz, *Anal. Chem.*, **40**, 509 (1968). ^{b} K. Srinivasan and G. A. Rechnitz, *ibid.*, **40**, 1818 (1968). ^{c} T. M. Hseu and G. A. Rechnitz, *ibid.*, **40**, 1054 (1968). ^{d} G. A. Rechnitz and Z. F. Lin, *Anal. Letters*, **1**, 23 (1967). ^{e} See ref 4. ^{f} T. M. Hseu and G. A. Rechnitz, *Anal. Letters*, **1**, 629 (1968). ^{g} J. E. McClure and G. A. Rechnitz, *Anal. Chem.*, **38**, 136 (1966). ^{h} G. A. Rechnitz and Z. F. Lin, *ibid.*, **39**, 1406 (1967). ^{i} K. Srinivasan and G. A. Rechnitz, *ibid.*, **40**, 1955 (1968).

of a reaction *in situ*. In the case of rapid reactions where response time might be critical, ion electrodes can be advantageously utilized in flow systems such as that shown in Figure 7 which has been employed extensively in the author's laboratory for the study of both homogeneous and heterogeneous kinetics (Table I).
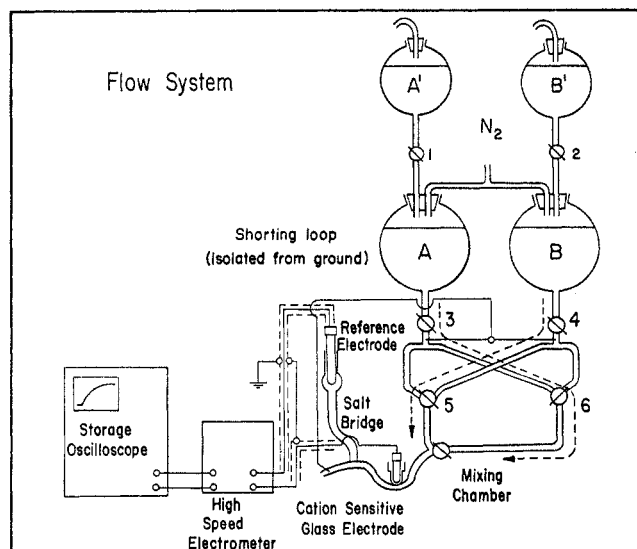

Figure 7. Schematic flow system for kinetic experiments using ion-selective electrodes.

Analysis

The impact of ion-selective electrodes on analytical solution chemistry is comparable to that of the laser on optical physics. Since solutions are part of the makeup of all living organisms and cover a majority of the earth's surface, it is not surprising that a new experimental tool capable of measuring the ionic composi-

Table II

Typical Analytical Studies with Ion-Selective Electrodes

Ion measd	Sample systems	Ref
BF_4^- (boron)	Aqueous media	a
F^-	Water, bones, minerals, metals	b
Na^+	Water, soils, sea water, blood, urine	c
ClO_4^-	Aqueous media	d
NO_3^-	Aqueous media	e
Ca^{2+}	Water, sea water	f
K^+	Water, soils, biological fluids	g
S^{2-}	Aqueous media	h
Cu^{2+}	Aqueous media	i
Mg^{2+}	Sea water	j
NH_4^+	Aqueous media	k
Cl^-, Br^-, I^-	Water, blood	l
Ag^+	Aqueous media	m

^{a} R. M. Carlson and J. L. Paul, *Anal. Chem.*, **40**, 1292 (1968). ^{b} R. A. Durst, *ibid.*, **40**, 931 (1968); E. W. Bauman, *Anal. Chim. Acta*, **42**, 127 (1968); J. J. Lingane, *Anal. Chem.*, **40**, 935 (1968); L. Singer and W. D. Armstrong, *ibid.*, **40**, 613 (1968); J. C. Van-Loon, *Anal. Letters*, **1**, 393 (1968); B. A. Raby and W. B. Sunderland, *Anal. Chem.*, **39**, 1304 (1967); M. S. Frant, *Plating*, **54**, 702 (1967); M. S. Frant and J. W. Ross, *Science*, **154**, 1553 (1966); J. B. Orenberg and M. D. Morris, *Anal. Chem.*, **39**, 1776 (1967); J. J. Lingane, *ibid.*, **39**, 881 (1967). ^{c} D. Hawthorne and N. J. Ray, *Analyst*, **93**, 158 (1968); C. A. Bower, *Soil Sci. Am. Proc.*, **23**, 19 (1959); **25**, 18 (1961); R. Siever, R. M. Garrels, J. Kanwisher, and R. A. Berner, *Science*, **134**, 1071 (1961); R. H. Jones. *Ind. Water Eng.*, **1**, March–April (1964); G. Mattock, *Anal. Chem. Proc. Intern. Symp.*, **59**, 247 (1963); T. A. Taulli, *Anal. Chem.*, **32**, 186 (1960); A. H. Truesdell, B. F. Jones, and A. S. VanDenburgh, *Geochim. Cosmochim. Acta*, **29**, 725 (1965); H. Dahms, *Clin. Chem.*, **13**, 437 (1967); J. S. Annino, *ibid.*, **13**, 227 (1967); E. W. Moore and D. W. Wilson, *J. Clin. Invest.*, **42**, 293 (1963); J. Diamond, *J. Physiol.* (London), **161**, 442 (1962); G. Ungar, *Cytologia*, **1**, 622 (1959); G. Ungar and D. V. Romano, *Fed. Proc.*, **18**, 162 (1959); J. A. Hinke, *Nature*, **184**, 1257 (1959); *J. Physiol.* (London), **156**, 314 (1961); R. N. Khuri, *et al.*, *Am. J. Physiol.*, **204**, 743 (1963); H. D. Portnoy, L. M. Thomas, and E. S. Gurdjian, *Arch. Neurol.*, **8**, 597 (1963); S. M. Friedman and F. K. Bowers, *Anal. Biochem.*, **5**, 471 (1963). ^{d} See Table I, footnote f; R. J. Baczuk and R. J. DuBois, *Anal. Chem.*, **40**, 685 (1968). ^{e} S. S. Potterton and W. D. Shults, *Anal. Letters*, **1**, 11 (1967). ^{f} See ref 4; J. W. Ross, *Science*, **156**, 1378 (1967); M. E. Thompson and J. W. Ross, *ibid.*, **154**, 1643(1966); Instruction Manual, Model 92-20 Electrode, Orion Research, Inc., Cambridge, Mass., 1966. ^{g} Z. Stefanac and W. Simon, *Microchem. J.*, **12**, 125 (1967); M. M. Mortland, *Quart. Bull. Mich. Agric. Exp. Station*, **43**, 491 (1961); H. Dahms, *Clin. Chem.*, **13**, 437 (1967); J. Diamond, *J. Physiol.* (London), **161**, 442 (1962), G. Ungar, *Cytologia*, **1**, 622-1959); G. Ungar and D. V. Romano, *Fed. Proc.*, **18**, 162 (1959); J. A. Hinke, *Nature*, **184**, 1257 (1959); *J. Physiol.* (London), **156**, 314 (1961). R. N. Khuri, *et al.*, *Am. J. Physiol.*, **204**, 743 (1963); H. D. Portnoy, L. M. Thomas, and E. S. Gurdjian, *Arch. Neurol.*, **8**, 597 (1963); S. M. Friedman and F. K. Bowers, *Anal. Biochem.*, **5**, 471 (1963); R. Geyer and H. Grank, *Z. Anal. Chem.*, **179**, 99 (1961); G. A. Rechnitz, S. B. Zamochnick, and S. A. Katz, *Anal. Chem.*, **35**, 1322 (1963). R. Geyer, K. Chojnacki, W. Erxleben, and W. Syring, *Z. Anal. Chem.*, **204**, 325 (1964). ^{h} See Table I, footnote c. ^{i} See Table I, footnote d. ^{j} M. E. Thompson, *Science*, **153**, 866 (1966). ^{k} S. A. Katz and G. A. Rechnitz, *Z. Anal. Chem.*, **196**, 248 (1963); G. A. Rechnitz and G. Kugler, *ibid.*, **210**, 174 (1965); G. A. Rechnitz, S. B. Zamochnick, and S. A. Katz, *Anal. Chem.*, **35**, 1322 (1963). ^{l} G. A. Rechnitz, M. R. Kresz, and S. B. Zamochnick, *ibid.*, **38**, 973 (1966); G. A. Rechnitz and M. R. Kresz, *ibid.*, **38**, 1786 (1966); H. Dahms, *Clin. Chem.*, **13**, 437 (1967). ^{m} A. L. Budd, *J. Electroanal. Chem.*, **5**, 35 (1963); E. Bishop and R. G. Dhaneshwar, *Analyst*, **88**, 424, 442 (1963); R. Geyer, K. Chojnacki, and C. Stief, *Z. Anal. Chem.*, **200** 326 (1964); G. A. Rechnitz, S. B. Zamochnick, and S. A. Katz, *Anal. Chem.*, **35**, 1322 (1963).

tion of solutions should be of major importance. More-over, ion-selective electrodes are most effective for the measurement of exactly those ionic species (*e.g.*, Na$^+$ K$^+$, Ca^{2+}, F$^-$, SO$_4^{2-}$, S^{2-}, NO$_3^-$, ClO$_4^-$, etc.) which are most difficult to measure by other techniques.

Ion-selective electrodes measure the activities of ions in solution and do so with considerable sensitivity and selectivity. Such measurements are rapid and non-destructive and can be carried out on a continuous, automated basis. Because of these desirable charac-teristics ion-selective electrodes are being used widely for chemical studies, biomedical measurements, pollu-tion and oceanographic monitoring, and industrial

control. About two dozen types of ion-selective elec-trodes are already available, but more are being de-veloped as the fundamentals of electrode operation and selectivity are elucidated.

At the present time, we find ourselves in the pleasant position of having suitable electrodes selective for many important ions. Table II illustrates some of the recent analytical applications of these electrodes. The state of the art has now progressed to the point where accurate analytical measurements using these electrodes are read-ily carried out and where ion-selective electrodes are being used increasingly for fundamental chemical and biochemical studies.

Photophysical Primary Steps in Solutions of Aromatic Compounds

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The electrons of molecules in nonexcited states reside in the lowest molecular orbitals. The energies of these orbitals, *i.e.*, the energies of these electrons, can be determined experimentally by photoelectron spectros-copy.[2a] For theoretical methods see, *e.g.*, Jungen.[2b]

The electrons of a ground-state molecule are often classified, for simplicity, as to the electronic systems to which they belong. For most organic molecules the electrons can be classified as follows: σ electrons which form localized σ bonds; π electrons which form π bonds, not necessarily localized; nonbonding n electrons which are localized in valence shells of atoms, and do not par-ticipate in complex formation such as hydrogen bonding, charge-transfer complexes, etc.; and δ electrons which are situated in the inner shells of atoms. In certain types of molecules, especially in molecules containing π electrons, one or more electrons can be promoted to higher orbitals without decomposing the molecule. The molecule is then said to be in an excited state and the promotion energy is called excitation energy.

In this paper we shall concern ourselves with two questions: what are the physical mechanisms by which a molecule can leave the excited state and how do these mechanisms compete with each other? All processes following absorption and leading to the first reaction product are called primary steps. The first reaction

product could for instance be an intermediate if the photochemical reaction is a multistep reaction, or it could be the original molecule in its ground state.

Theoretical approaches to the kinetics of radiationless transitions have been obtained by using time-dependent perturbation theory to obtain probabilities for Born-Oppenheimer zeroth-order excited-state transitions. However the excited states are not pure in view of con-figuration interaction between nearly degenerate zeroth-order states. The optically excited state can be de-scribed in terms of a superposition of molecular eigen-states and it can be shown that the resulting wave func-tion exhibits an exponential nonradiative decay. The line width and the radiationless lifetime can be expressed in terms of a single molecular parameter, the square of interaction energy between the zeroth-order state and the manifold of all vibronic states located within one energy unit around that state.[2c-e] "Internal conver-sion" and "radiationless intersystem crossing" are then better termed "internal mixing" and "intersystem mixing," respectively.

Luminescence spectroscopy is a useful tool to investi-gate the mechanisms of transformation of electronic excitation energy and the primary steps in photochem-istry if the latter compete with the luminescence but do not quench it beyond an experimental limit in intensity. The following quantities are measured in luminescence spectroscopy.

(1) Quantum efficiency, $Q_f \equiv n_e/n_a \leq 1$, where $n_a =$ number of quanta absorbed, $n_e =$ number of quanta emitted. The sum of the quantum yields of all compet-ing processes, fluorescence included, is unity, by defini-tion.

(2) Spectral quantum distribution $q(\bar{\nu})$, which should preferably be plotted—by international recommenda-tion—as the relative number of quanta emitted within

(1) Visiting Professor, from Iwan N. Stranski-Institut, II. Insti-tut für Physikalishe Chemie der Technischen Universität Berlin.

(2) (a) D. W. Turner, "Molecular Photoelectron Spectroscopy," John Wiley & Sons, Inc., New York, N. Y., 1969; (b) M. Jungen, H. Labhart, and G. Wagniére, *Theoret. Chim. Acta*, **4**, 305 (1966); (c) M. Kasha, *et al.*, "Radiationless Transitions in Molecules," Division of Biology and Medicine, Bulletin No. 37, U. S. Atomic Energy Com-mission (Institute of Molecular Biophysics, Florida State University, Tallahasee, 1968); (d) J. Jortner, *et al.*, *J. Chem. Phys.*, **49**, 610 (1968); **50**, 2916, 4061 (1969); (e) R. M. Hochstrasser, *et al.*, *ibid.*, **49**, 971 (1968).