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## Potentials in Ion-specific Electrodes

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Ion-specific electrodes are ideal tools for studies involving ionic solutions, since no separation of the components present is necessary. Glass electrodes, typical representatives of these systems, are amenable to theoretical treatment analogous to that applied usually to ion-exchangers. Elements of the theory are given and results of experimental tests obtained in aqueous solutions and fused salts are discussed.

### INTRODUCTION

Ion-selective electrodes are revolutionizing analytical chemistry. They represent the ideal analytical tool for solutions, since no separations are needed, instantaneous and continuous results are possible, quite low concentrations can be measured, and small quantities of sample are needed. While these ideals are not easily achieved with all ion-selective electrodes that have been marketed, those for the following ions are quite satisfactory: sodium, silver, sulfide, and fluoride, as well as the standard glass electrode for hydrogen. With further development, satisfactory electrodes for many other electrodes should be possible.

The key to understanding the origin of the potential of these electrodes is ion exchange. It is the exchange of ions between the solution and the electrode material that gives rise to the potential that is related to the ionic concentration in solution. The ions in the exchanger need not be the same as those being measured; for example, the glass electrode contains sodium ions, not hydrogen; it is essential, however, that the ions being measured can exchange with those in the electrode.

The ion-exchange theory for ion-selective electrodes is based on the earlier theories of Teorell<sup>1</sup> and Meyer and Sievers<sup>2</sup> for biological and synthetic organic membranes. Eisenman applied this theory to glass electrodes, particularly to explain its changing sensitivities to monovalent cations as the glass composition is changed<sup>3</sup>. There is a good summary and discussion of this theory as applied to organic membranes in Helfferich's book<sup>4</sup>, and there is a recent book on glass electrodes<sup>5</sup>.

A number of other theories have been advanced to explain the operation of the glass electrode. These resulted from two different points of view. One was that glass does not interact with the solution; it was viewed as being an impervious dielectric. From this view resulted theories of surface adsorption for the origin of the glass electrode potential. Another view was that glass must be like a liquid junction, so that phase boundary potentials could be ignored. The good agreement between measured potentials of glass electrodes

and the ion-exchange theory shows that neither of these older pictures is correct.

Glass electrodes can be treated as conventional ion exchangers in which insoluble matrix holds fixed, charged groups, while the exchanging ions are mobile within this matrix. Silicate glasses consist of a three-dimensional lattice of silicon-oxygen tetrahedra connected at their corners. Alkali oxides break up this lattice, giving fixed oxygen anions with mobile sodium cations.

The newly developed crystalline electrodes, such as lanthanum fluoride, exchange with specific ions in the solution, in this case fluoride.

The experimental arrangement used to measure membrane potentials is shown schematically in Fig. 1. Usually the solution on one side of the membrane is held constant, for example inside the bulb of the glass electrode, while the test solution is on the other side of the membrane. The potentials of the reference electrodes must be constant with changing solution conditions.

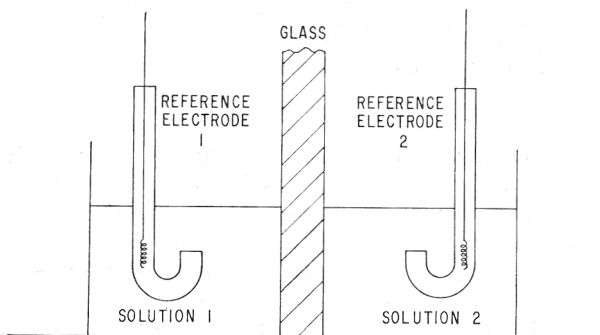


Fig. 1. Schematic diagram of a cell used to measure potentials in a membrane.

In the following paragraphs the ion-exchange theory for membrane potentials is briefly derived. Then some experimental tests of the theory are described, and factors important in determining the selectivity of the electrodes are discussed. As a summary the understanding of the conventional glass electrode for pH measurement is given.

### *Ion-Exchange Theory*

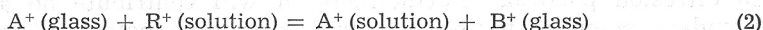
This discussion is based on my review article in Eisenman's book<sup>6</sup>. This discussion is restricted to an exchanger containing only one type of exchanging ion, a monovalent cation, with the anionic groups fixed in a rigid network. A silicate glass containing sodium ions fits these conditions; extension to other systems is straightforward.

A membrane potential can be separated into two parts, a phase boundary potential and a diffusion potential. The phase boundary potential results from the difference in thermodynamic activity between the ion in solution and in the membrane, whereas the diffusion potential results from the interdiffusion of ions of different mobilities in the exchanger. If there is only one exchanging ion in the membrane and in the contacting solution, there is no diffusion potential, and the membrane potential is equal to the phase boundary potential:

$$V = V_0 + RT/F \ln a \quad (1)$$

where  $R$  is the gas constant,  $T$  is the temperature,  $F$  the faraday, and  $a$  the thermodynamic activity of the exchanging ion in solution.  $V_0$  is independent of solution concentration, and depends upon the composition of the *internal* or constant solution and electrode potentials if they are not equal. This equation is valid for an electrode that is sensitive to only one ion; for example, the glass electrode for hydrogen ion except at highest  $pH$ , and the fluoride electrode for fluoride ion. Eq. 1 is derived by equating the electrochemical potentials of the ion in the reference solution and the membrane and solution, as shown in ref. 6.

If two exchanging ions  $A$  and  $B$  are present, their exchange can be represented in the following equation:



The relation between ionic activities  $a$  and  $b$  is

$$K = \frac{a' b''}{a'' b'} \quad (3)$$

where a single prime refers to the solution and a double prime to the glass, and  $K$  is a coefficient independent of concentration. If the exchanger is *ideal*, so that activities in it are equal to mole fractions, the phase boundary potential  $V_i$  is

$$V_i = V_0 + RT/F \ln (a' + b' K) \quad (4)$$

in terms of ionic activities in solution.

The diffusion potential results from the interdiffusion of ions of different mobilities. As interdiffusion proceeds the fast ion outruns the slow one, building up an electrical charge. This charge gives rise to a potential that slows the fast ion and speeds up the slow one until the flux of the two ions is equal and opposite, as required by electroneutrality. The resulting total membrane potential is the sum of  $V_i$  and the diffusion potential  $V_D$ :

$$V = V_i + V_D = V_0 + RT/F \ln [a + bK (u_B/u_A)] \quad (5)$$

where  $u_A$  and  $u_B$  are the mobilities of the ions in the membrane. Thus the membrane potential results from three factors: Two properties of ions in the membrane, given by the coefficient  $K$  and the activity ratio  $u_B/u_A$ , and the activities  $a'$  and  $b'$  in solution. The membrane potential does not depend upon the concentration profile in the membrane.

### Tests of the Theory

In order to test Eq. 5 three different quantities must be measured for different ratios of ionic concentrations in solution: the coefficient  $K$ , the mobility ratio  $u_B/u_A$ , and potential  $V$ .

Eisenman measured the potential of a potassium-selective glass electrode in aqueous solutions with different sodium and potassium ion concentrations, and found good agreement with the potential calculated from Eq. 5 and his values of  $K$  and  $u_B/u_A$  measured with radioactive tracers<sup>7</sup>.

Other tests of the theory have been carried out in fused nitrates. I measured the potentials of fused silica and Pyrex glass tubes in mixed sodium and silver nitrate melts, and measured  $K$  and mobility ratios with radioactive

tracer and electrolysis experiments. I found good agreement with Eq. 5 for fused silica<sup>8</sup>; agreement for Pyrex was good at high silver concentrations, but was affected by the two-phase structure of Pyrex<sup>10</sup> at lower silver concentrations. Garfinkel has found similar results for sodium-potassium exchange in Pyrex glass, including good agreement with the ion-exchange theory, recognizing the difficulties with two different ionic sites in the two phases<sup>11</sup>.

The ion-exchange theory predicts that surface adsorption should not affect the overall membrane potential, since it is the bulk properties of the membrane that are important in determining this potential. »Surface adsorption« in this sense means adsorption in a surface layer so thin that it is in equilibrium with both the solution and the membrane. If the surface adsorption layer is in equilibrium it can contain no concentration gradients, and thus contribute no diffusion potential. Furthermore, it will contribute no additional phase boundary potential to the measured membrane potential, since the electrochemical potential of ions at the membrane surface will still equal their potential in solution.

The insensitivity of membrane potential to surface adsorption was shown by experiments on fused silica membranes<sup>12</sup>. If the silica surface was treated with nitric acid its surface was highly hydrated, and it strongly adsorbed silver ions from nitrate melts containing silver ions, as shown by radioactive tracer measurements. When the silica surface was treated with dilute hydrofluoric acid the hydrated layer was removed, and the absorption of silver was negligible. However, in both of these samples the measured membrane potential was the same for the same contacting solutions, as was the coefficient *K*.

### *Factors in Ionic Selectivity*

The above discussion shows that two properties of ions in an electrode material determine the selectivity of the electrode for these ions; namely, the relative affinity of the electrode for the two ions, of which the coefficient *K* is a measure, and the mobility ratio of the competing ions in the exchanger.

Factors that influence the equilibrium affinity of the electrode for ions are shown in Table I. Eisenman<sup>3</sup> has shown that ion-site interactions can

TABLE I

#### *Factors Influencing Equilibrium Selectivity of Ion Exchangers*

1. Ion-site interactions
  - a. Effective radius or field strength of site
  - b. Size of ion (possibly solvated)
  - c. Valence of ion
  - d. Polarizability of ion
2. Structure of exchanger
  - a. Openness
  - b. Tightness of linking
3. Association and complexing in solution

explain many affinities of ion-exchangers for ions; his work emphasizes exchangers made of silicate glasses. His treatment is based on a simple electrostatic picture of ion-site interactions. He has shown that for a given group of ions, for example, alkali and hydrogen cations, the selectivity sequence is determined by the effective size or field strength of the anionic group in the

exchanger. As this site becomes effectively »larger«, or has a lower field strength, the relative affinity of the group for small ions is decreased, whereas for anionic groups with high field strength or small effective radius, small ions are preferred.

The factors affecting ionic mobility in an ion-exchanger are listed in Table II. There are two main influences on mobility. The ion must »tear

TABLE II

*Factors Influencing Ionic Mobility in Ion Exchangers*

1. Ion-site interactions
2. Resistance to motion
  - a. Size of ion (possible solvated)
  - b. Structure of exchanger
  - c. Viscosity of solvent, if present

itself away« from its site, or, for a defect model, defects must be formed. The energy for either process depends upon ion-site interactions, so that the factors influence these interactions, as listed in Table I, also influence mobilities. The stronger the ion-site interaction, the lower the mobility; thus smaller ions are hindered more than large ones by these interactions. In addition the ion must »push itself through« the exchanger; in this case the larger ion is slowed more than the smaller. Since the effect of ion size is opposite in these two factors, it is possible to have a maximum in ion mobility as the size is increased. Indeed in glass the sodium ions are the most mobile, while both hydrogen and potassium ions are much less mobile<sup>6,13</sup>.

*The Glass Electrode for pH measurement*

The above understanding can be summarized in terms of the origin of the potential in the familiar glass electrode used for pH measurements.

The electrode is a glass bulb. Inside the bulb is a buffered chloride solution and a reference electrode. The potentials inside need not be known, since the electrode is standardized with a solution of known hydrogen ion concentration; the only requirement is that they be unchanged under all conditions of use. The outside of the bulb is placed in the solution to be measured, which is connected to another reference electrode by a salt bridge. Again the potentials developed in this electrode and bridge need not be known, but must be invariant with all solution conditions used. The bulb is soaked in water to give a hydrated layer on the surface of the glass. This layer must be thick enough so that hydrogen ions do not diffuse to its inner boundary over the period of use of the electrode, since concentration changes at this boundary could lead to time variations in potential. The glass composition must be chosen so that essentially all of the sodium ions at the electrode-solution interface are exchanged for hydrogen ions; this occurs when the glass »prefers« hydrogen ions. More exactly, the product  $K_{AH}(u_H/u_A)[H+]$  where  $[H+]$  is the hydrogen ion activity in solution, must be substantially larger than the activity of all other monovalent ions A in the solution. Then the electrode potential V is:

$$V = V_0 + RT/F \ln [H+],$$

where  $V_0$  is determined by a calibrating solution. The differences in potentials

with solutions of different pH are caused by the difference between the activity of the hydrogen ion in the solution and in the surface of the glass. There is a diffusion potential in the hydrated layer caused by the interdiffusion of hydrogen and sodium ions, but its value is constant because the surface is always saturated with hydrogen ions. The »alkaline error« at high pH occurs when the product  $K_{AH}(u_H/u_A)[H^+]$  becomes of the same order of magnitude as the activity of any monovalent ion A; then both the surface and diffusion potentials in the layer can depend upon the activity of this ion, and the above simple equation no longer holds.

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## IZVOD

## Potencijali ionski-specifičnih elektroda

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Ionsko-selektivne elektrode revolucioniraju analitičku kemiju. Idealni su alat za analize otopina, jer ne zahtijevaju separacije, dobivaju se momentalni kontinuirani rezultati mjerenja, mogu se mjeriti vrlo niske koncentracije iona, a potrebne su male količine uzorka.

Staklene elektrode moguće je teoretski tretirati kao obične ionske-izmjenjivače u kojima netopiva matrica sadrži fiksne, nabijene aktivne grupe, dok su ioni koji se izmjenjuju pokretni unutar te matrice. Prikazani su elementi teorije ionskih izmjenjivača i razmotreni neki rezultati testiranja teorije u vodenim otopinama i u talinama.

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