The Effect of NaCl, KCl, Na_2SO_4, and K_2SO_4 on Glass Membrane Potentials[1]

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The errors of the glass electrode as a result of the presence of salts in the solutions in which the glass membrane is immersed have been the subject of researches, principally by Dole and his co-workers.[2] The errors caused by ions other than the hydrogen ions are most pronounced in alkaline solution. It is found that, in general, the error depends upon the nature and concentration of the positive ions present. Dole and his collaborators point out that the glass electrode deviates in behavior from the hydrogen electrode because of the fact that positive ions other than the hydrogen ion take part in the glass electrode reaction. This appears to be the result of the possible permeability of the glass membrane for positive ions other than the hydrated proton. As a result of the passage of these cations, for example sodium or potassium, through the glass membrane under the influence of a small electric current, the glass electrode will not behave as a pure hydrogen electrode but will be a so-called mixed electrode.

In the use of the glass electrode in the measurement of the hydrogen-ion concentration in the presence of sodium chloride, potassium chloride, sodium sulfate and potassium sulfate, the authors thought it advisable to determine the deviation of the glass membrane potential from the true hydrogen electrode function. The study reported in this paper shows some of the results obtained for these deviations in rather concentrated solutions of the above mentioned salts over the pH range at which the glass electrode is applicable.

Experimental

Apparatus and procedure. The potential of the following type of cell was measured to determine the effect of the salts on the potential of the glass membrane.

Quinhydrone Electrode in Buffer. pH = 3	Salt Solution under Investigation	‖	Buffer Solution	Quinhydrone Electrode in Buffer, pH = 3
		Glass Membrane		

In order to determine the effect of a given salt at a given concentration on the membrane potential at different pH values, the pH of the buffer solution on the right side of the glass membrane was varied. This procedure was carried out over the pH range 1 to 9 and for

[1] This paper is constructed from a dissertation presented by James A. Stoops to the Faculty of the Graduate School of Indiana University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] For a survey of the errors of the glass electrode see M. Dole, The Glass Electrode, John Wiley and Sons, Inc., New York, 1941.

various concentrations of sodium chloride, potassium chloride, sodium sulfate and potassium sulfate in the solution on the left side of the glass membrane.

The quinhydrone electrodes consisted of platinum electrodes immersed in buffer solutions of pH 3 which were saturated with quinhydrone. The two quinhydrone electrodes involved in each series of potential measurements were checked for equality of potential. Connection between the quinhydrone electrodes and the two solutions bathing the glass membrane was effected by means of saturated potassium chloride in agar bridges. In each experiment the pH of the buffer solution on the right of the glass membrane was determined by means of a hydrogen electrode against a saturated calomel electrode.

The glass membrane was prepared by blowing a thin bulb from Corning .015 glass. After preparation, the bulb was immersed in distilled water until diffusion equilibrium was attained. The same glass electrode was used throughout the entire series of experiments.

The potentials of the cells were measured by means of a Leeds and Northrup type K potentiometer in conjunction with a type R reflecting galvanometer. It was found that the potentials reached an equilibrium after 15 to 30 minutes and that they were reproducible to about 0.2 to 0.4 millivolts. All measurements were made in duplicate and at 25° C. in a constant temperature oil bath.

Data and Results

The data in Table I represent a summary of approximately 150 separate experiments all of which were carried out in duplicate and in many instances in triplicate. The values in the last column of the

TABLE I.—Deviations of the Potential of the Glass Membrane from that of the Hydrogen Electrode over the pH range 1 to 9 at 25° C.

Salt	Concentration of Salt Solution, Moles/liter	Average Deviation of Glass Potential from the Hydrogen Electrode over pH range 1 to 9
NaCl	0.01	0.6084 volt
"	0.10	0.6164
"	1.00	0.5490
KCl	0.01	0.5967
"	0.10	0.6800
"	1.00	0.5639
Na_2SO_4	0.01	0.5924
"	0.10	0.6109
"	1.00	0.6028
K_2SO_4	0.01	0.6025
"	0.10	0.6557
"	1.00	0.6117

table were computed in the following manner. For each series of experiments the pH of the buffer solution on one side of the glass membrane was varied over the pH range 1 to 9 while the nature and concentration of the salt solution on the other side of the membrane was kept constant. From 10 to 12 different buffer solutions were employed in each series of experiments. From the value of the glass membrane potential in each experiment, the deviation from the hydrogen electrode potential was computed as a difference. Since the deviations of the glass membrane potential from the hydrogen electrode were constant within a reasonable limit over the entire pH range studied, an average deviation was computed, the values of which for the various salts and salt concentrations are listed in the table.

In Figure 1 are plotted the potentials of the glass membrane against the pH of the buffer solution on one side of the membrane for the four series of experiments employing 0.1 *M* solutions of the four salts studied. The e.m.f.-pH relationships for the 1.0 *M* solutions of the salts are quite similar and, for this reason, the graphs for this concentration are omitted. The deviations of the glass membrane potentials for the 0.01 *M* solutions of the salts were found to be so nearly the same for all four salts that a plot of the e.m.f.-pH relationship has no conclusive significance. In the plots for all the conditions of nature and concentration of the salt solutions bathing one side of the glass membrane, the

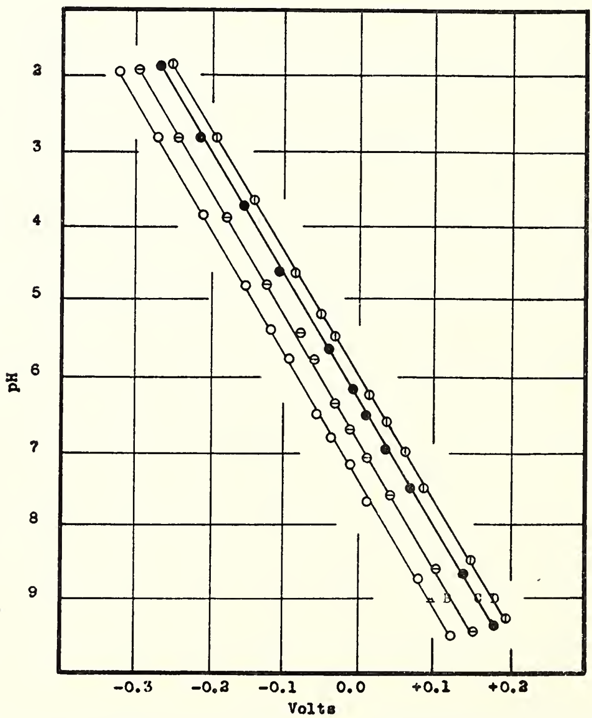

Fig. 1. Relationship of e. m. f. of the glass membrane and the pH as effected by the four salts (salt conc. $=0.1M$).(A)KCl, (B)K_2SO_4, (C)NaCl, (D) Na_2SO_4.

potential of the cell was found to be a linear function of the pH. This indicates that the glass membrane functions as a hydrogen electrode over the pH range 1 to 9 in the presence of relatively concentrated solutions of NaCl, KCl, Na_2SO_4, K_2SO_4. The deviations listed in the table represent the absolute differences in the potentials of the glass membrane and the potentials of the hydrogen electrode under similar pH conditions.

From the results of the study of the effect of the four salts at three concentrations on the potential of the glass membrane the following conclusions may be drawn. First, over the pH range 1 to 9, which is the range over which the glass electrode is applicable, the potential of the glass membrane is a linear function of the pH, and this relationship is unaffected by the nature or concentration of the salt which bathes the membrane. Second, for 0.01 *M* solutions of sodium and potassium chloride and sulfate, the glass membrane potentials are very nearly the same, within the limits of experimental error, with an average deviation from the potential of the hydrogen electrode of 0.6000 volt. In 0.10 *M* solutions of the four salts, the difference between the glass membrane potential and that of the hydrogen electrode varies with the nature of the salt. At this concentration, the order of the magnitude of the difference is $KCl > K_2SO_4 > NaCl > Na_2SO_4$. At a salt concentration of 1.0 *M*, the order is

$$K_2SO_4 > Na_2SO_4 > KCl > NaCl.$$

At the concentration of 0.10 *M*, apparently the cation is the factor responsible for the deviation, with potassium causing the greater difference between the membrane potential and the potential of the hydrogen electrode. At 1.0 *M* salt concentration, the anion seems to be the controlling factor with the sulfate ion causing the greater deviation. This change in the order of the deviations is difficult to explain, since it has been shown by many researches of Dole that the cation takes part in the electrode reaction. An explanation may be found in the effect which the different salts have on the activity of water.

Summary

The potential of the following cell was measured for 0.01 *M*, 0.10 *M*, and 1.0 *M* solutions of NaCl, KCl, Na_2SO_4, and K_2SO_4 over the pH range 1 to 9,

Quinhydrone Electrode in Buffer. pH = 3	Salt Solution under Investigation	Buffer Solution	Quinhydrone Electrode in Buffer. pH = 3

Glass Membrane

Under all conditions of the nature and concentration of the salt solution on the left side of the glass membrane, the potential of the cell was found to be a linear function of the pH of the buffer solution on the right side of the membrane over the pH range 1 to 9.

The effect of the nature and concentration of the salt solution bathing the glass membrane on the difference between the glass membrane potential and the potential of the hydrogen electrode is reported.