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EFFECT OF THE SOLUBILITY¹ OF GLASS ON THE BEHAVIOR OF THE GLASS ELECTRODE

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ABSTRACT

Application of an interferometer method previously used for determining the relative solubility of optical glasses, to a glass which is commonly used for making glass electrodes, gave results leading to the following conclusions:

1. The solubility increases rapidly as the pH of most solutions increases above 8.5 or 9.

2. At all values below pH 7 for the solutions investigated (except 10 N H₂SO₄) this glass exhibits a slight swelling.

3. The rate of swelling is repressed in the acid region beyond pH 2.

4. At intermediate pH values 3.1 to 4.0 the rate of swelling is repressed by high concentrations of magnesium sulfate.

Considering these conclusions in connection with the performance of glass electrodes, these regions of marked solubility change correspond to the regions of pronounced voltage departures exhibited by electrodes made from this glass. That the anomalies of the glass electrode are definitely associated with the solubility of the glass has been further demonstrated both by the use of glasses which do not exhibit swelling in the acid range, (and hence no detectable change of swelling in the "super-acid region"), and by measurements made in alkaline solutions, such as aqueous ammonia, in which soluble silicates are not formed. Under these circumstances the voltage departures are greatly decreased or completely eliminated.

For every case investigated, voltage departures of the glass electrode have been found to be accompanied by changes in the solubility of the glass.

CONTENTS

	Page
I. Introduction.....	339
II. Experimental procedure.....	340
III. Data and results.....	340
IV. Conclusions.....	348
V. References.....	348

I. INTRODUCTION

The voltage of the glass electrode follows approximately the straight-line relation of the Nernst equation over an extended range of hydrogen ion concentrations. However, in most solutions a marked voltage departure begins at a pH of 8.5 or 9 and becomes greater with increased alkalinity. In the extreme acid range another voltage departure appears [1]² in a direction opposite to that in the alkaline region. Other voltage departures occur in salt solutions of high concentration and in ethanol solutions [2]. Since such anomalies in the voltage of any electrode suggest changes in the nature of the equilib-

¹ The term "solubility" is not used in this report in a strict sense and is not to be confused with any physicochemical interpretation of the word.

² Figures in brackets indicate the literature references at the end of this paper.

rium between the material of the electrode and its environment, a study of the solubility of the glass commonly used in electrode manufacture [3] was undertaken, employing the interferometer method previously used for estimating the rate of solution of optical glasses and comparing durability test methods [4, 5].

II. EXPERIMENTAL PROCEDURE

The interferometer method was used because it offered a rapid and convenient means of making a semiquantitative study of the relative rates of solution of the glass over an extended range of temperature and pH. Rectangular specimens (approximately 2 by 3 cm) of the glass, with surfaces sufficiently flat to show interference bands when placed under a fused-quartz optical flat, were partially immersed in the desired solution, the surface of which was covered throughout the period of test with a thin layer of liquid petrolatum to prevent evaporation. The desired temperature was maintained constant to $\pm 0.1^\circ\text{C}$ by means of an electrically heated thermostated water bath. Under these conditions very satisfactory and uniform attack of the immersed surface was obtained, beginning at the oil-solution interface. The magnitude of the attack was readily ascertained with a Pulfrich viewing apparatus, using an unfiltered helium light for illuminating the interferometer. Some determinations were made in white light without the use of the viewing apparatus, because this procedure offered an easy and rapid means of ascertaining if the exposed surface of the specimen had undergone swelling or had dissolved during the test.

All emf measurements were made with a Leeds & Northrup portable potentiometer-electrometer. Although the emf measurements of the solutions were made at room temperature, while the solubility experiments were made in most cases at higher temperatures, no account was taken of the small shift in pH of the buffer which accompanied this temperature change [6, 7]. Since all electrode measurements were made in Pyrex beakers, the solubility tests were also carried out in similar vessels, even though Pyrex is known to be attacked by the alkaline solutions [8, 9]. In no case did the pH of the buffer solutions shift as much as 0.1 from this cause, during the period of any test.

III. DATA AND RESULTS

The data plotted in figure 1 show the attack³-pH curve on Corning 015 glass by Britton universal buffer mixtures [10] over the range pH 2 to 12 for 6 hours at 80°C . At and below pH 7 the glass exhibits a slight uniform swelling, which, for convenience, is plotted as negative attack. Near pH 8 the solubility approaches zero and thereafter increases rapidly with increasing alkalinity. The region between pH 8 and 9 corresponds to the region in which voltage departures of the glass electrode just become noticeable, and as the pH increases above 9 the voltage departure increases rapidly, as does the solubility. For the pH region in which the transition from "negative" to positive attack occurs, excessive positive attack at the oil-solution interface was obtained, while below, in the main body of the solution, little or no attack was observed. For the specimen at pH 7 a marked positive

³ The term "attack" is used to express the thickness in fringes of the layer of glass removed under the conditions of the experiment. One fringe corresponds to approximately 0.29 micron.

attack appeared at the interface while swelling was exhibited below. A possible explanation for this may lie in the orientation of ions at the oil-solution interface [11, 12, 13] resulting in an increased alkalinity there. To account for the surface cuts observed, the pH at the interface would necessarily be greater than 9.

The voltage departure of the glass electrode in the alkaline region increases rapidly with increased temperature [14], and from the data plotted in figure 2 it is shown that the rate of solution of the glass approximately doubles for each 10° C rise in temperature.

That the voltage departures of the glass electrode are associated with the solubility of the glass is indicated by its behavior in aqueous-ammonia solutions in the absence of sodium ions [15] and is illustrated

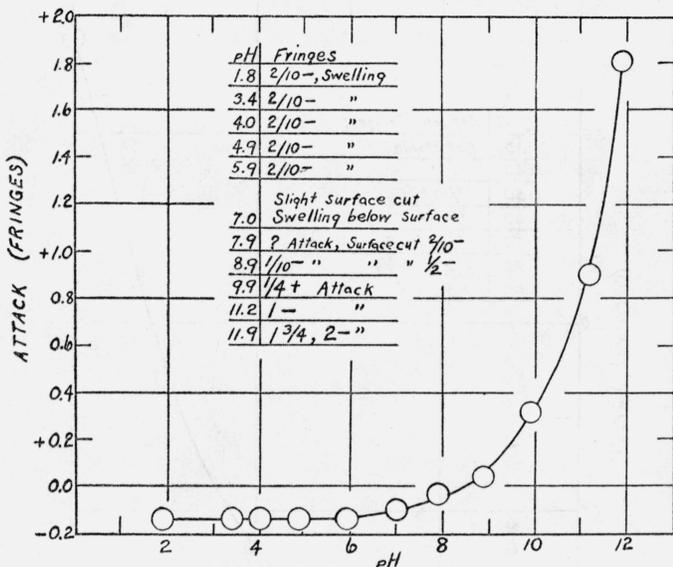


FIGURE 1.—Attack-pH curve of Corning O15 glass, exposed 6 hours at 80° C to Britton universal buffer mixtures covering the range pH 2 to 12.

The plotting of the data in this and succeeding figures is not intended to convey the idea that the attack values were determined within close limits. The size of the circles does not represent the probable error of the data presented, but merely indicates that exactness is not implied. The data, however, are known to be sufficiently reliable to justify the trends indicated by the curves.

by the data in figure 3. The interesting feature of this voltage-pH curve for ammonia buffers is that it continues as a straight line until the pH of full-strength ammonia solution is approached, at which point the voltage departs in a direction opposite to that normally encountered in alkaline solutions. This suggests that the glass is attacked less by ammonia solution at pH 13.3 than by lower concentrations, such as pH 12.5. Solubility tests in ammonia solutions at those pH values for 15 days at room temperature confirmed this, since the one at pH 12.5 produced an attack of 1/4 fringe, while the effect of the other at pH 13.3 was hardly detectable (plotted as circles, fig. 3). Comparing the voltage-pH curve for the ammonia buffer with that for the universal buffer (plotted +, fig. 3), one would expect to find the glass more resistant to attack of the NH_4^+ than of the Na^+ of the universal buffer at the same pH. This was also found

to be true. Solubility tests for 18 hours at 50° C showed an attack by the NH_3 solution at pH 12.4 to be less than 2/10 fringe, while that by the universal buffer at the same pH was greater than 1/2 fringe (plotted \times in fig. 3). From these results it seems probable that variations in magnitude of the voltage departure for different cations [1] in the alkaline range are primarily a question of differences in rate of solution of the glass in the presence of these ions. However, additional quantitative data must be obtained before such a conclusion can be substantiated.

Concerning the voltage departure in the "super-acid" region, figure 4 shows the effect produced on Corning 015 glass by hydrochloric,

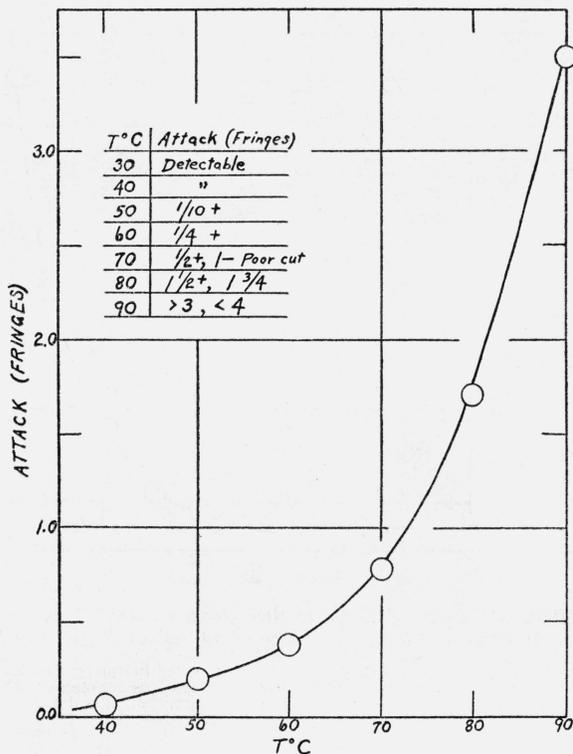


FIGURE 2.—Temperature effect on rate of solution of Corning 015 glass in 5-percent NaOH for 3 hours at 80° C.

sulfuric, and phosphoric acids. As the acidity increases the amount of swelling in 48 hours at 80° C. is repressed. Similar voltage departures are reported for high concentrations of other acids [16] and, although the solubility tests have not been made, one can predict with reasonable certainty from Donnan membrane considerations and the distribution law that repression of swelling will be exhibited in these cases also. Although the specimens exhibit less swelling in the high concentrations, it must be borne in mind that this diminished effect can be attributed to repression of the swelling of the gelatinous silica layer resulting from the change in osmosis, caused by increased

concentration of electrolyte, or to a partial solution of that silica, or to a combination of both.

TABLE 1.—Voltages for glass electrodes prepared from three commercial glasses, with reference to the saturated calomel half-cell

pH of solutions with H ₂ electrode	Emf of the glass electrodes		
	Glass A	Glass B	Glass C
HCl			
	<i>Volts</i>	<i>Volts</i>	<i>Volts</i>
2.85	-0.265	-0.157	-0.272
1.93	-.317	-.207	-.323
1.00	-.368	-.257	-.375
0.0	-.427	-.315	-.438
-1.01	-.487	-.369	-.498
H ₂ SO ₄			
2.70	-0.270	-0.165	-0.282
1.93	-.317	-.206	-.328
1.10	-.363	-.254	-.374
0.06	-.425	-.308	-----
-1.11	-.492	-.378	-.505
H ₃ PO ₄			
3.20	-----	-0.146	-0.255
2.39	-0.290	-.180	-.300
1.78	-.325	-.214	-.334
1.06	-.365	-.252	-.376
-0.01	-.429	-.315	-.441

At pH values below 7 the universal buffer produced no detectable effect on the glass in 6 hours at 80° C. Aqueous solutions of HCl, H₂SO₄, and H₃PO₄ at pH values below 3 also produced no effect under similar conditions nor was there any detectable attack or swelling in 48 hours at 80° C.

Further evidence that the voltage departures are associated with changes in solubility of the glass is shown by the fact that electrodes prepared from glasses A, B, and C (table 1) exhibited no detectable swelling or voltage departures in the super-acid region. Typical attack-pH data and the corresponding emf-pH relation for glass A⁴ are plotted in figure 5 as curves α and β , respectively. Below pH 3 the data plotted are for HCl, H₂SO₄, and H₃PO₄, while above this pH the data are for the universal buffer. Under the conditions of these determinations no voltage departure from the straight-line relation was indicated for the "super-acid" region. However, columns 2 and 3 (table 2) and figure 6 give the voltage departures from the hydrogen electrode of an electrode of Corning 015 and one of glass A in HCl solutions under more exacting conditions.

⁴ See table:

Composition (approximate)	
	<i>Percent</i>
SiO ₂	72.1
CaO	10.1
N ₂ O	13.5
MgO	3.3
R ₂ O ₃	0.7

TABLE 2.—*Electromotive force between the hydrogen electrode and glass electrodes prepared from glasses 015 and A, in HCl and H₂SO₄ solutions*

Normality of solutions (approximate)	Glass (HCl solution)		Glass (H ₂ SO ₄ solution)	
	015	A	015	A
	Volts	Volts	Volts	Volts
0.001.....	0.218	0.193	0.215	0.191
0.01.....	.218	.193	.217	.191
0.1.....	.216	.194	.217	.192
1.0.....	.213	.194	.215	.192
5.0.....	.194	.192	-----	-----
10.0.....	.175	.184	.217	.192

For these determinations the glass electrodes were compared directly with the hydrogen electrode, and the concentration of the

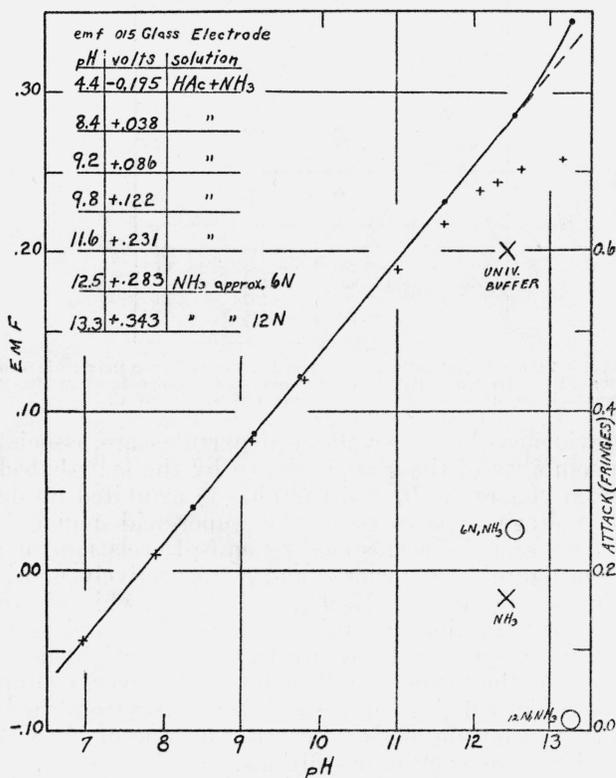


FIGURE 3.—*Comparison of the voltages of an electrode of Corning 015 glass in CH₃COOH+NH₃ solutions (•) and Britton universal buffer mixtures (+), with the solubility of the glass in these solutions.*

HCl was extended beyond pH -1.01 (approximately 5 N) used in the previous case. These departures are plotted against log 1/N

instead of pH in order to avoid the confusion of thought caused by activity coefficients for high concentrations of HCl, which indicate a degree of dissociation of 200 to 1,000 percent [17]. Although the data presented indicate that glass *A* has very desirable emf relations in the super-acid region, its resistance is so high it cannot be considered as more satisfactory than Corning 015 glass.

Since voltage departures in the super-acid region have become of theoretical concern, it is of interest to note that we have repeatedly blown electrodes of Corning 015 glass which have exhibited no definite voltage departure in H_2SO_4 solutions, while doing so in HCl. Typical data illustrating this statement are given in table 2 (columns 2 and 4)

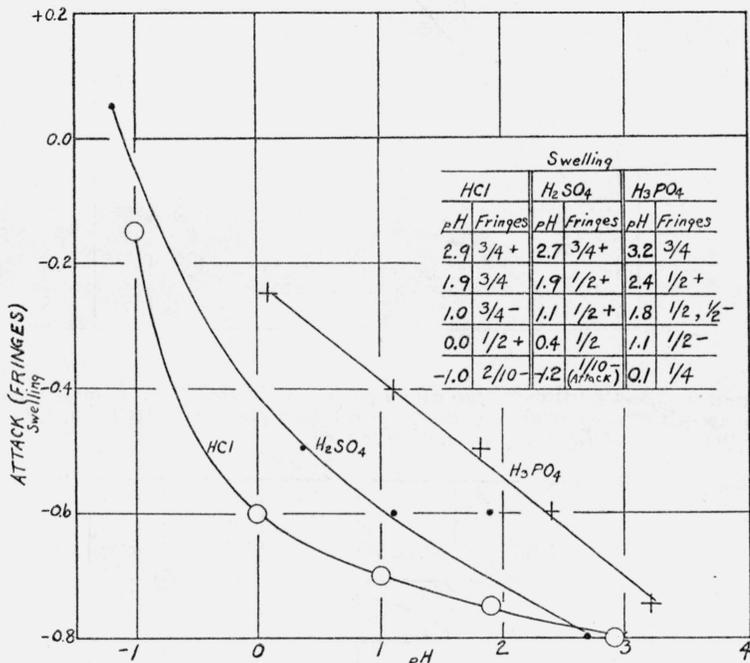


FIGURE 4.—Repression of swelling of Corning 015 glass by increasing concentrations of HCl (○), H_2SO_4 (●), and H_3PO_4 (+) for 48 hours at 80° C.

for an electrode prepared from 015 glass compared with the hydrogen electrode. Although it cannot be demonstrated, we feel this is caused by differences in solubility of the particular sample of glass under observation in these solutions. Such irregularities in the voltage departures of the glass electrode in the acid region are confusing, and it was thought that the behavior of the glass electrode toward hydrofluoric acid solutions, which attack glass relatively rapidly, might throw some light on the subject.

Table 3 gives the voltage departures from the straight-line relation when the glass electrode was compared with the hydrogen electrode in HCl, H_2SO_4 , and HF solutions of various concentrations. The voltages in HF are somewhat uncertain because of its vigorous action on the glass but, as expected, show large departures for the solutions of higher concentrations. Concentrations greater than one normal

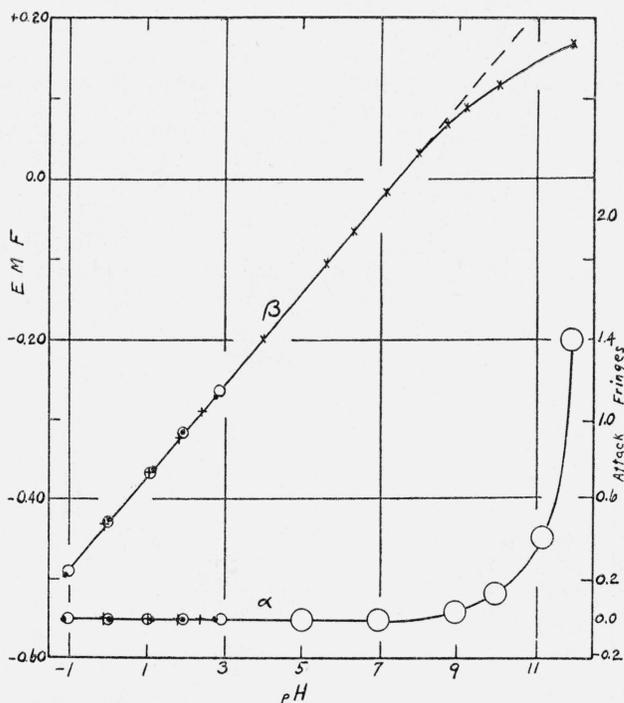


FIGURE 5.—Attack-pH curve, typical for glasses A, B, and C (○) of table 1, and the voltage-pH response of an electrode prepared from glass A in HCl (○), H₂SO₄ (●), H₃PO₄ (+), and Britton universal buffer (×).

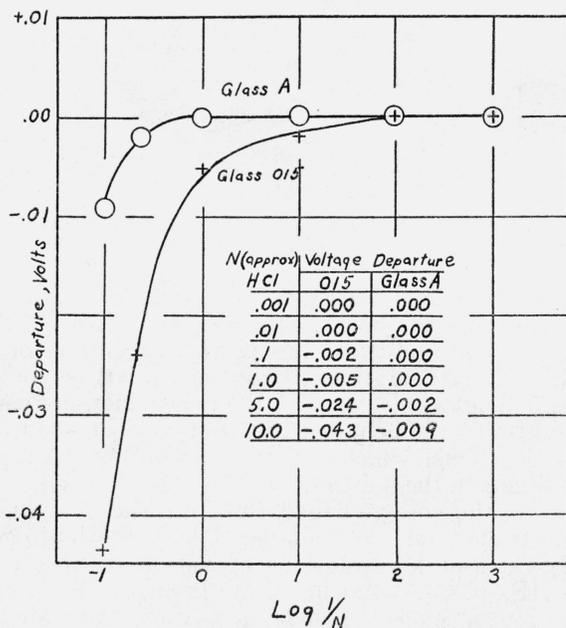


FIGURE 6.—Voltage departures from the hydrogen electrode of electrodes prepared from glasses 015, (+), and A, (○), in HCl solutions.

are not reported because the hydrofluoric acid destroyed the glass electrode.

Voltage departures similar in direction to that obtained in the super-acid region have been reported for concentrated salt solutions at intermediate pH values [2]. To determine if these departures are accompanied by repression of swelling, solubility tests in $M/20$ acid potassium phthalate solutions containing $MgSO_4$ were made. The data are plotted in figure 7 and indicate that a repression of swelling is produced by the higher concentrations of $MgSO_4$. If these data

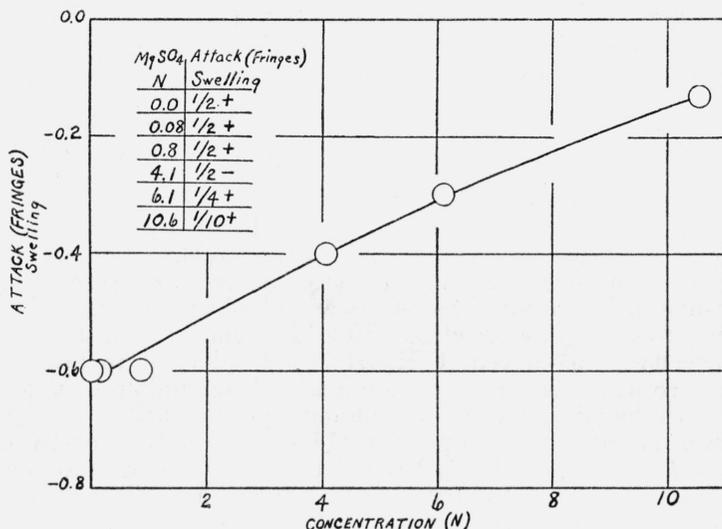


FIGURE 7.—Repression of swelling of Corning 015 glass by $MgSO_4$ solutions buffered with $M/20$ KH phthalate.

were plotted on a pMg basis, a curve similar to the solubility-pH curves for the concentrated acid solutions would be obtained.

TABLE 3.—Comparison of voltage departures of Corning 015 glass electrode in H_2SO_4 , HCl , and HF solutions, the reference voltage being that obtained in $M/20$ KH phthalate solution

N (approx.)	$H_2SO_4^1$	HCl^1	HF
	Volts	Volts	Volts
0.001	0.002	0.000	0.003
.01	.000	.000	.015
.1	.000	.002	.054
1.0	.002	.005	.188
5.0	-----	.024	-----
10.0	.000	.043	-----

¹ Based on data in table 2 for 015 glass.

TABLE 4.—pH of aqueous solutions of M/20 KH phthalate containing varying amounts of $MgSO_4$

$MgSO_4 \cdot 7H_2O$ per 100 ml of solution	pH
<i>Grams</i>	
0	4.0
1	3.9
10	3.6
50	3.2
75	3.1
5	¹ 6.2

¹ This solution contained no KH phthalate.

Although the pH of the solutions changed from 4.0 to 3.1 (see table 4) as the concentration of the $MgSO_4$ increased, it is evident from figure 1 that this pH change alone would not produce a detectable effect on the amount of swelling.

Another voltage departure of the glass electrode has been reported for solutions in which water is progressively replaced by ethanol [2], the departure being again in a direction similar to that reported for the super-acid region. Satisfactory solubility experiments were difficult to make in ethanol because of its volatility and also because the density of 95-percent C_2H_5OH is not sufficient to float the oil layer. However, it was possible to make some solubility comparisons between ethanol and water by adding equal quantities of H_2SO_4 to distilled water and to 95-percent C_2H_5OH until the density of the latter was raised sufficiently to float the oil layer. Results obtained in this manner at 70° C for 48 hours showed a swelling of less than 0.2 fringe for the water solution, while the effect on the glass by the ethanol solution was not definitely detectable.

Solubility comparisons in water-alcohol solutions buffered with M/20 KH phthalate were also attempted. Seven days at room temperature gave approximately 0.1-fringe swelling in the water solution, the 50-percent ethanol solution gave a detectable swelling, while 85- and 95-percent solutions gave no detectable effect. Although these experiments are not all that might be desired, we feel they are qualitatively correct.

IV. CONCLUSIONS

In all cases that have been studied voltage departures of the glass electrode have been found to be associated with marked changes in the solubility of the glass. This leads the authors to believe that the variations in magnitude of the voltage departures of the glass electrode in the presence of different ions are primarily caused by solubility differences of the glass produced by these ions and not by an equilibrative response of the electrode to ions other than hydrogen. From this and further investigations it may be possible to form a more satisfactory picture of the mechanism of the glass electrode and perhaps to extend its range of usefulness.

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