

# Voltage Anomalies of the Glass Electrode and the Chemical Durability of the Glass

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Additional work has been done on the correspondence between voltage departures (errors) of electrodes prepared from Corning 015 glass and the change in the chemical durability of the glass. The results confirm and extend the earlier findings that voltage departures of the electrode are accompanied by durability changes of the glass. The pronounced voltage departures in the alkaline region and in hydrofluoric acid solutions are accompanied by conspicuous attack of the glass. Dilute solutions of acids that do not form soluble compounds of silica cause swelling of the glass. This swelling is repressed as the concentration of the solutions is increased. As is to be expected from the distribution law and Donnan membrane considerations, this repression of swelling was also brought about by high concentrations of organic acids and salts as well as by the so-called "strong" acids. The attack of Corning 015 glass by alkaline solutions of different ions was found to be in the order,  $\text{Na}^+ > \text{Li}^+ > \text{K}^+ > \text{Ba}^{++} > \text{NH}_4^+$ , which is the same order dictated for these ions by the voltage departure data.

## I. Introduction

The ability of a glass to function satisfactorily as an indicator of the hydrogen ion activity of aqueous solutions appears to be determined largely by two properties of the glass, namely, the hygroscopicity (water sorption) and the uniformity of the chemical durability over an extended pH range. Glasses of inadequate hygroscopicity produce electrodes of high resistance whose pH responses fall appreciably below the theoretical dictates of the Nernst equation:

$$\Delta E = 0.000198T\Delta\text{pH} \quad [1, \text{p. } 78, 2, 3].^1$$

On the other hand, solutions that cause detectable change in attack of the glass [4] also bring about voltage departures (errors) from the straight-line relation of the Nernst equation [1, 5, 6].

The glass whose hygroscopicity and durability characteristics have most nearly fulfilled the requirements for pH measurements is one of composition  $\text{SiO}_2$  72 percent,  $\text{Na}_2\text{O}$  22 percent,

$\text{CaO}$  6 percent (Corning 015) [1, 7]. Although this glass combines the two necessary properties of adequate hygroscopicity and uniform durability to a considerable degree, electrodes prepared from it exhibit voltage departures in the "super acid" range [5] and even more conspicuous errors in alkaline solutions above pH 9 [1]. Such voltage departures in alkaline solutions covering a limited range of conditions and pH values have been reported as being roughly directly proportional to the amount of attack [8, 9].

The present investigation was undertaken to ascertain if electrodes prepared from Corning 015 glass always have voltage departures accompanying changes in the chemical durability of the glass and also to determine to what extent the magnitude of these voltage departures is directly proportional to the change in the attack of the glass by the solutions.

## II. Experimental Procedure

The glass electrodes were prepared by blowing a thin bulb of Corning 015 glass on the end of

<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

soft glass tubing. The inner electrical connection was made by filling the bulb and tube with mercury [10]. Such metal-filled electrodes are simple to prepare and have the advantage that an electrode broken in service does not seriously contaminate or alter the pH of the solution under observation. All voltage and pH measurements were obtained at room temperature by means of a Beckman pH meter, laboratory model G. Unless otherwise stated, the hydrogen electrode was used as the reference electrode, and the value in 0.02 N hydrochloric acid as the zero reference voltage. This solution was chosen to avoid the uncertainty of the equilibrium between the hydrogen electrode and M/20 acid potassium phthalate [11]. Further, the acid solution served to restore the glass electrode after severe abuse to its initial condition [12].

The chemical durability (reported as attack) of the glass was determined by the interferometer method [4, 13]. This procedure offered a rapid means of determining the amount of solution or swelling of the glass over a wide range of conditions under circumstances in which the conventional analytical methods would be time-consuming, unreliable, or even impossible.<sup>2</sup> In this method the magnitude of the attack was determined by observing the displacement of the interference fringes when the specimen was placed under an optical flat. The optical flat of fused silica or other glass must have both surfaces polished "true plane" and adjusted to make an angle of 20' with each other so that interference bands will not be formed by reflection between the upper and lower surfaces.

The specimens of glass for chemical durability measurements were small rectangular strips approximately 3 cm long with one surface pitch-polished, and were sufficiently flat to show interference bands when placed under an optical flat. The exposures were made by immersing these specimens to approximately one-third of their length in the desired solution. The surface of the solution in most instances was covered throughout the test period by a thin layer of liquid petrolatum to prevent evaporation. For the experiments

<sup>2</sup> An attack of less than 0.1 of an interference fringe can be readily detected. For a glass of density 2.5, an attack of 0.1 fringe (filtered helium source) amounts to approximately:

$$0.1 \times \frac{0.587 \times 10^{-1}}{2} \times (1)^2 \times 2.5 = 0.073 \times 10^{-4} \text{g or } 0.0073 \text{ mg/cm}^2.$$

with high percentages of ethanol (C<sub>2</sub>H<sub>5</sub>OH), the density of the solutions was too low to float the oil layer. In these experiments it was necessary to make the exposures in a closed system by suspending the specimen from the cork stopper of an Erlenmeyer flask.<sup>3</sup>

The desired temperatures were maintained constant to  $\pm 0.2^\circ \text{C}$  by means of an electrically heated thermostated water bath. All chemical durability data were obtained at 80° C except for the ethanol and hydrofluoric acid solutions. For the ethanol solutions the temperature was lowered to 78° C to insure that the surface remained undisturbed by boiling during the period of exposure. In the hydrofluoric acid solutions it was necessary to make the durability exposures at room temperature because of the vigorous attack on the glass.

As the purpose of the investigation was to furnish a comparison between the voltage departure of the glass electrode and the chemical durability of the glass, the solutions were adjusted to approximate concentrations only. Whenever possible, the voltage departure of the glass electrode was observed for a given solution, followed immediately by a determination of the durability of the glass in the same solution.

### III. Voltage Departures (Errors) of the Glass Electrode and the Chemical Durability of the Glass

#### 1. Sodium Hydroxide Solutions

One of the most conspicuous voltage departures for the glass electrode occurs in the alkaline range beginning near pH 9 and increasing rapidly with increased alkalinity [1]. It has been shown that this region of voltage departure is accompanied by changing chemical durability of the electrode glass, the rate of attack increasing with increasing pH [4]. Published data covering a limited range of conditions indicate that this relation is linear [8, 9]. To check this observation further and to make as simple an experiment as possible, an aqueous solution of 1.0 N NaOH was prepared from which a series of solutions was obtained ranging in concentration from 0.015 N to 1.0 N, with each successive member of the series doubling

<sup>3</sup> The use of a closed system was tried at the suggestion of A. W. Helz, of the Portland Cement Association Fellowship. It proved very effective and greatly increases the range of usefulness of the interferometer method for durability measurements.

in concentration. No additional buffer ions were added to these solutions.

The results, listed in section A of table 1 and plotted as curve A of figure 1, indicate a linear

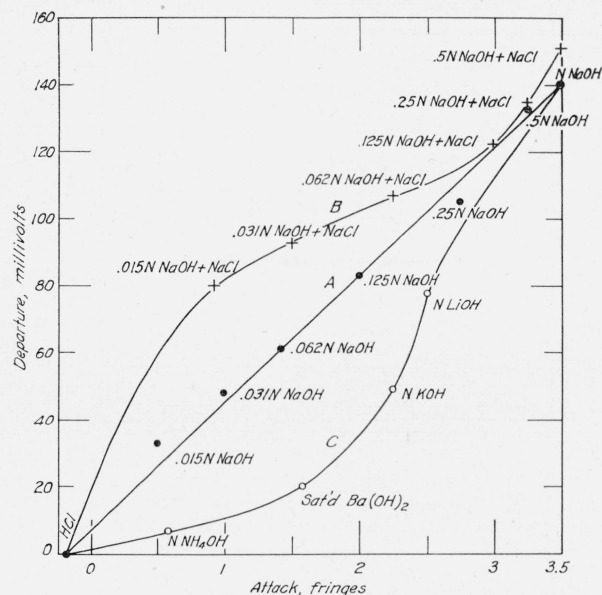


FIGURE 1.—Comparison of the voltage departures of the glass electrode with the chemical durability of the glass in different solutions.

A, NaOH solutions; B, NaOH+NaCl; C, NH<sub>4</sub>OH, Ba(OH)<sub>2</sub>, KOH, LiOH and NaOH. Durability exposure 6 hours at 80° C.

relation between voltage departure and attack within reasonable limits. The emf data were taken in order beginning with the weakest solution. The individual readings were usually steady; however, in accordance with published data, the reproducibility was found to depend greatly on the immediate previous history of the electrode

TABLE 1.—Comparison of the voltage departures (errors) of the glass electrode with the chemical durability of the glass in solution of NaOH, NaOH plus NaCl, and other hydroxides

Durability exposure 6 hours at 80° C

A			B			C		
Solution	Departure	Attack (fringes)	Solution	Departure	Attack (fringes)	Solution	Departure	Attack (fringes)
Dilute HCl	0	< 3/10 (swelling)	Dilute HCl	0	< 3/10 (swelling)	Dilute HCl	0	< 3/10 (swelling)
0.015 N NaOH	33	1/2 (attack)	0.015 N NaOH+NaCl	80	< 1 (attack)	N NH <sub>4</sub> OH	7	> 1/2 (attack)
.031 N do	48	1 do	.031 N do	93	1 1/2 do	Ba(OH) <sub>2</sub> saturated	20	> 1 1/2 do
.062 N do	61	< 1 1/2 do	.062 N do	107	2 1/4 do	N KOH	49	2 1/4 do
.125 N do	83	2 do	.125 N do	122	3 do	N LiOH	78	2 1/2 do
.25 N do	105	2 3/4 do	.25 N do	135	3 1/4 do	N NaOH	140	3 1/2 do
.50 N do	133	3 1/4 do	.50 N do	151	3 3/4 do			
1.0 N do	140	3 1/2 do						

[8, 9, 12]. Nevertheless, the data are sufficiently reliable to support the trends indicated by the curves.

## 2. Sodium Hydroxide Solutions Plus Sodium Chloride

It is known that the voltage departures of the glass electrode in alkaline solutions are increased by the addition of neutral sodium salts such as NaCl [1 p. 129, 14, 15, 16]. Chemical durability data have shown qualitatively that an increase in attack on the glass also accompanied this increased voltage departure [13]. To obtain quantitative data on this point, the same NaOH series as described in the previous section was prepared and sufficient NaCl added to make all of these solutions normal with respect to Na<sup>+</sup> ions. Once again the individual emf readings were steady. The results obtained are listed in section B of table 1 and plotted as curve B of figure 1. A pronounced increase in both voltage departure and attack was brought about by the increased [Na<sup>+</sup>]. However, the voltage departure exhibited a greater increase than did the attack, and the data do not coincide with the previous straight line A. From this it is evident that factors other than the durability shift of the glass contribute to the voltage departure of the electrode.

## 3. Solutions Containing Na<sup>+</sup>, Li<sup>+</sup>, K<sup>+</sup>, Ba<sup>++</sup>, and NH<sub>4</sub><sup>+</sup> ions

The magnitude of the voltage departure in alkaline solutions is different for different ions [1, p. 130]; for example, the departures caused by cations are in the order, Na<sup>+</sup> > Li<sup>+</sup> > K<sup>+</sup> > Ba<sup>++</sup> > NH<sub>4</sub><sup>+</sup>. Earlier work suggested that this was the order

of decreasing attack on the electrode glass by these ions [4, 13]. To check this point, normal solutions were prepared for each of these hydroxides except  $\text{Ba}(\text{OH})_2$ . For  $\text{Ba}(\text{OH})_2$  a saturated solution was used. The voltage departure of the glass electrode was determined in each of these solutions, followed by a durability test of the glass. As the concentration of saturated  $\text{Ba}(\text{OH})_2$  at room temperature is less than 1 N, and at  $80^\circ\text{C}$  is greater than 1 N, the voltage departure value obtained is probably too low and the attack value is too high. The results given in section C of table 1 and plotted as curve C in figure 1 show that the relative attack on the glass by these solutions is in the same order as for the voltage departure, but the two properties do not plot as straight line nor does the resulting curve C coincide with either curve A or curve B. These results again indicate that some factor other than durability shift of the glass contributes to the errors of the glass electrode. However, before one accepts these data as an indication of a specific equilibrative response of the glass electrode to these ions, it must be emphasized that the glass electrode gives little or no specific response to any of them except under conditions of changing durability of the glass.

#### 4. Buffer Solutions Containing $\text{NH}_4^+$ ions

The voltage departures of the glass electrodes are much less in alkaline buffer solutions containing  $\text{NH}_4^+$  ions than in basic solutions prepared with  $\text{Na}^+$  ions [17]. A typical set of data illustrating this point and making a comparison of voltage departure and chemical durability is given in table 2 and plotted in figure 2. The voltage departures were obtained on buffer solutions prepared from the Britton-Robinson universal buffer mixture [18] in which ammonia was substituted for the NaOH to obtain the desired pH range, the highest pH value being that of full strength ammonia solution.<sup>4</sup>

Most of the voltage results are qualitatively similar to those for buffers containing  $\text{Na}^+$  ions, the departure remaining nearly constant in the acid range, then increasing with increasing alkalinity beyond pH 8. However, at the higher alkalinities beyond pH 11, the rate of departure

<sup>4</sup> In the durability tests no difficulty was encountered from loss of  $\text{NH}_3$  through the oil layer except at pH 12.3 and for the full strength solution.

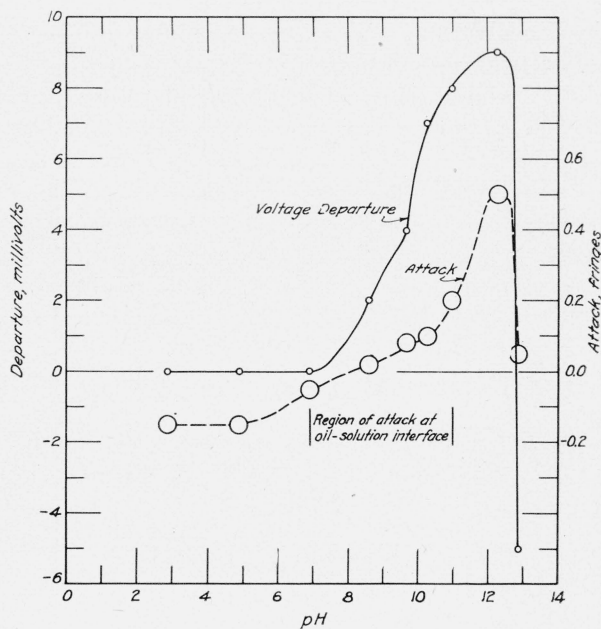


FIGURE 2.—Comparison of the voltage departures of the glass electrode with the chemical durability of the glass in buffer solutions containing  $\text{NH}_4^+$  ions.

Durability exposure 6 hours at  $80^\circ\text{C}$ . In this and other figures the size of the circles does not indicate the probable error of the individual points for durability, but merely emphasize that the data must not be considered highly precise nor accurate.

TABLE 2.—Comparison of the voltage departures (errors) of the glass electrode with the chemical durability of the glass in buffer solutions containing  $\text{NH}_4^+$  ions

[Durability exposure 6 hours at  $80^\circ\text{C}$ ]

pH	Departure	Attack (fringes)	Surface cut at oil-solution interface
2.9	0	< $\frac{1}{10}$ Swelling	None
4.9	0	< $\frac{1}{10}$ Swelling	Do.
6.9	0	?	Detectable.
8.6	2	?	$\frac{1}{10}$ .
9.7	4	< $\frac{1}{10}$ Attack	$\frac{1}{10}$ .
10.3	7	$\frac{1}{10}$ Attack	$\frac{1}{2}$ .
11.0	8	$\frac{2}{10}$ Attack	$\frac{3}{4}$ .
12.3	9	$\frac{1}{2}$ Attack <sup>1</sup>	None.
12.9 full strength $\text{NH}_3$	2-5 to 0	Detectable <sup>1</sup>	Slight.

<sup>1</sup>  $\text{NH}_3$  escaped through the oil layer during the early minutes of the attack period.

<sup>2</sup> The temperature of the full-strength  $\text{NH}_3$  fell sharply upon bubbling hydrogen through the solution.

falls off and goes through a reversal for full strength  $\text{NH}_3$ , even yielding a negative value in the latter case. This negative value for full strength  $\text{NH}_3$  has been previously reported [4] but not adequately investigated. The hydrogen stream bubbling through the full strength am-

monia causes a large drop in the temperature of the solution. When adequate precautions were taken to minimize this temperature change, the voltage departure for the glass electrode approximated zero.

The trend of the departure curve over the pH range investigated was in complete accord with the durability curve for the glass in these same buffers. In the acid range the glass exhibited a slight swelling, and between pH 6.9 and pH 11.0 excessive surface cuts appeared at the oil-solution interface, similar to the results reported for buffer solutions containing  $\text{Na}^+$  ions [4]. An increase in pH at the oil-solution interface brought about by preferential orientation of ions could account for the surface cuts in this pH range. In full-strength  $\text{NH}_3$ , the durability of the glass improved in accordance with that indicated by the voltage departure shift.

### 5. Electrode Prepared from a Glass of Low Hygroscopicity

The voltage departures for Corning 015 glass electrodes that appear under conditions of changing chemical durability of the glass [4] must not be confused with the voltage errors that are exhibited by electrodes prepared from glasses of low hygroscopicity [1, 2, 3,]. In the latter, departures appear over the entire pH range, with any departures accompanying a change in durability being merely superimposed on the general departure curve [3]. A typical example of the behavior of electrodes prepared from glasses of low and high hygroscopicity, Pyrex and Corning 015, respectively, is illustrated in table 3 and figure 3. These data were obtained in Britton-Robinson universal

TABLE 3.—Comparison of the voltage departure of an electrode prepared from a glass of low hygroscopicity, Pyrex, with the departure of an electrode of Corning 015 glass, using the hydrogen electrode as reference electrode

pH	Departure	
	Pyrex	Corning 015
	<i>mv</i>	<i>mv</i>
1.9	0	0
2.7	+27	0
5.1	+120	1
7.8	+266	1
Water sorbed, mg/cm <sup>2</sup>	1.8	1358

<sup>1</sup> Values taken from Fig. 6, RP1706 (J. Research NBS 36, 365 (1946)).

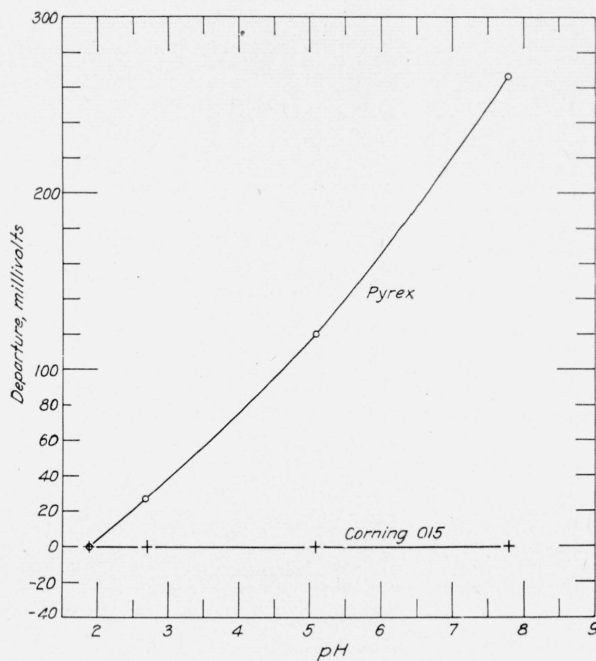


FIGURE 3.—Comparison of the voltage departure of an electrode prepared from a glass of low hygroscopicity (Pyrex) with the departure of an electrode of Corning 015 glass.

These data were taken over a pH range for which both glasses exhibit uniform durability.

buffers over a pH range in which both glasses exhibit uniform durability [13], in order to eliminate any voltage effects attributable to change in the durability of either glass.

### 6. Hydrofluoric Acid Solutions

Electrodes of Corning 015 glass exhibit very pronounced voltage departures in hydrofluoric acid (HF) solutions, the departures increasing with increased concentration [4, 16]. The data given in table 4 and plotted in figure 4 show that these increased voltage departures are accompanied by increased attack on the glass. However, the relation between voltage departure and attack is not a straight line. Although the attack on the glass was very severe, the emf readings were surprisingly steady. The attack was so rapid that to keep the durability measurements within the range of the interferometer, the time of exposure had to be reduced to 5 minutes at room temperature and further shortened to 1 minute, 30 seconds, and 10 seconds for the 2.0 N, 3.0 N and 5.0 N solutions, respectively. Hence, the results shown in figure 4 are only qualitative, but obviously the general shape of the curve will

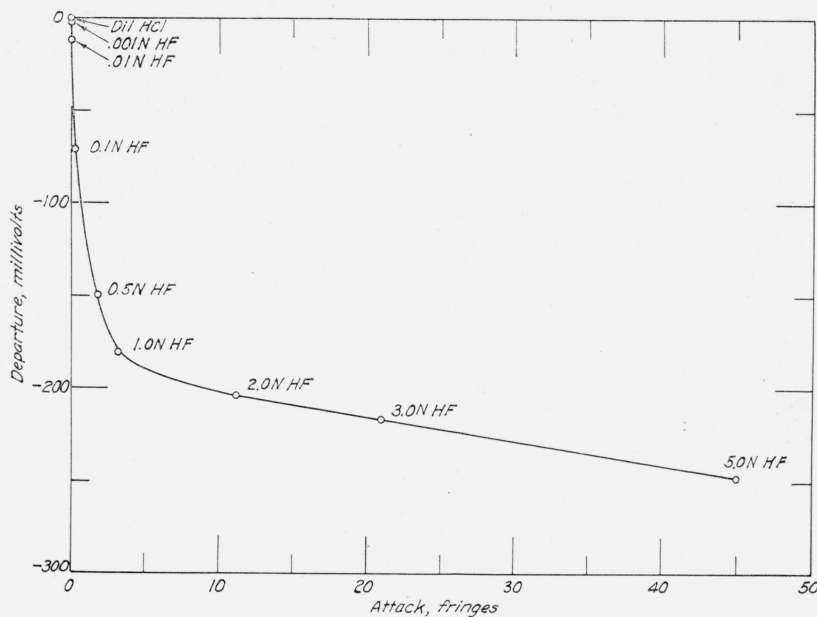


FIGURE 4.—Comparison of the voltage departures of the glass electrode with the chemical durability of the glass in aqueous solutions of hydrofluoric acid.

Durability exposure 5 minutes at room temperature.

not be altered even though the individual values may possess large cumulative errors.

TABLE 4.—Comparison of the voltage departures (errors) of the glass electrode with the chemical durability of Corning 015 glass in aqueous solutions of hydrofluoric acid

[Attack reported for 5 minutes exposure at room temperature]

Solution	Departure	Attack (fringes)
	<i>mv</i>	
Dilute HCl.....	0	Not detectable.
0.001 N HF.....	-3	Do.
.01 N HF.....	-12	Detectable.
.10 N HF.....	-71	>¼.
.5 N HF.....	-150	<2
1.0 N HF.....	-181	>¾.
2.0 N HF.....	-204	<sup>1</sup> 1¼.
3.0 N HF.....	-218	<sup>1</sup> 21.
5.0 N HF.....	-248	<sup>1</sup> 45.

<sup>1</sup> Values based on attacks observed for 1 minute, 30 seconds, and 10 seconds for concentrations 2 N, 3 N, and 5 N, respectively.

## 7. Ethanol and Acid Solutions

The voltage departures of the glass electrode that appear in nonaqueous solutions such as ethanol (C<sub>2</sub>H<sub>5</sub>OH) are often compared with the characteristic departures in strong acid solutions [1, 5, 19, 20, 21]. The increasing negative departure of the glass electrode in acid solutions

of increasing concentration is accompanied by a repression of swelling of the glass [4]. Similar durability experiments carried out for ethanol solutions indicated that a repression of swelling with increased ethanol concentration also accompanied the negative voltage departure. However, the latter data had not been convincing because of the difficulty of applying the interferometer procedure for durability, as the low density of the ethanol solutions prevented the floating of the oil layer. To obtain more conclusive data demonstrating that a durability shift of the glass does accompany the voltage departure in ethanol solutions, durability exposures were made in a closed system that eliminates the need for a layer of oil.

Table 5 and figure 5 give the results obtained for the repression of swelling of Corning 015 glass and the accompanying voltage departures of the glass electrode in water-ethanol solutions buffered at pH 4 with Britton-Robinson universal buffer mixtures [18]. The performance of this glass in ethanol appears to be similar to its performance in strong acid and salt solutions. This can be seen from inspection of table 5 and figures 6, 7, 8, and 9, which give similar data for sulfuric [5], formic, and acetic acids [21] and magnesium sulfate [22]. All of these have been plotted on a

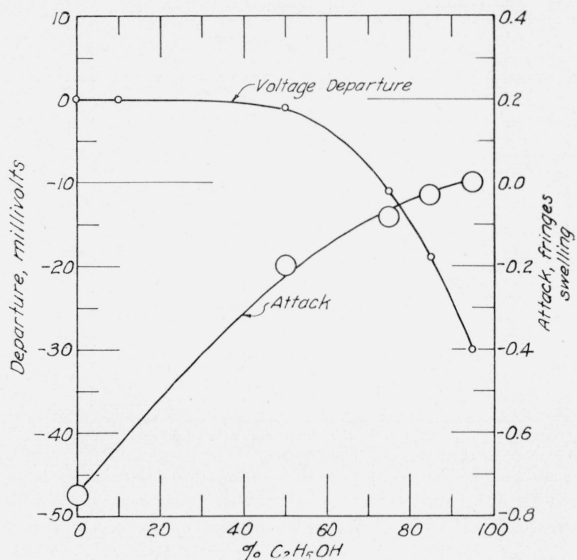


FIGURE 5.—Comparison of the voltage departures of the glass electrode with the chemical durability of the glass (repression of swelling) in acid solutions (pH 4) of increased ethanol (C<sub>2</sub>H<sub>5</sub> OH) content.

Durability exposure 48 hours at 78° C.

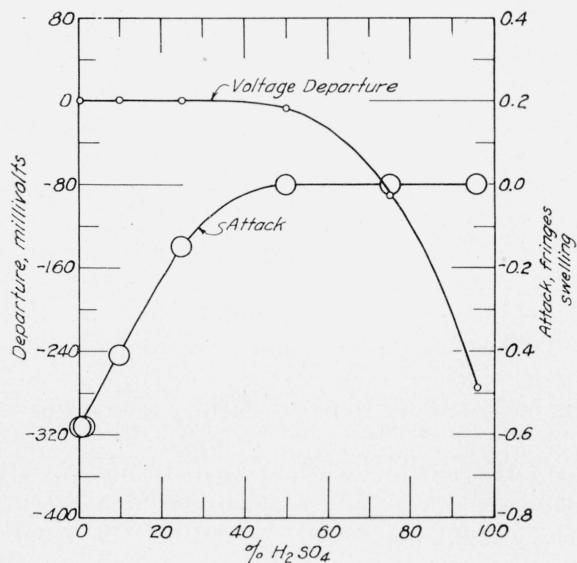


FIGURE 6.—Comparison of the voltage departures of the glass electrode with the chemical durability of the glass (repression of swelling) in acid solutions of increased H<sub>2</sub>SO<sub>4</sub> content.

Durability exposure 48 hours at 80° C.

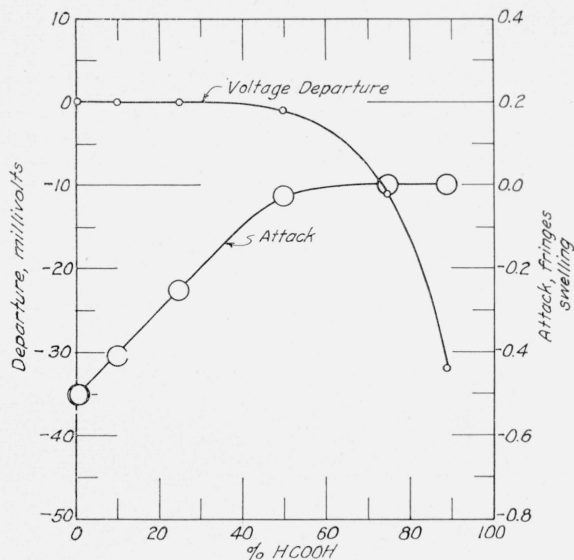


FIGURE 7.—Comparison of the voltage departures of the glass electrode with the chemical durability of the glass (repression of swelling) in acid solutions of increased HCOOH content.

Durability exposure 48 hours at 80° C.

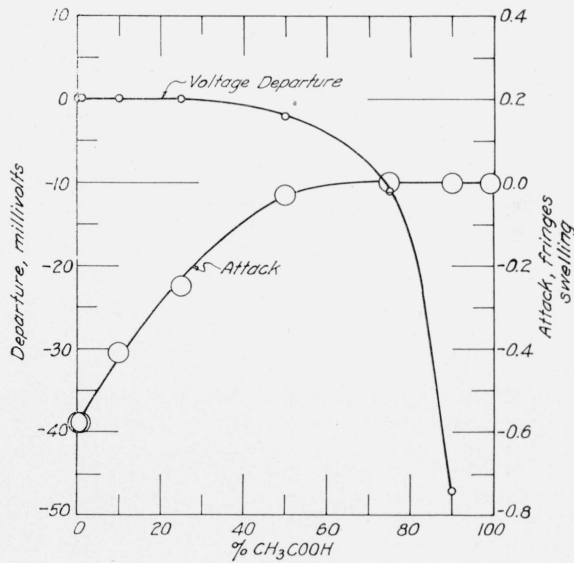


FIGURE 8.—Comparison of the voltage departures of the glass electrode with the chemical durability of the glass (repression of swelling) in acid solutions of increased CH<sub>3</sub>COOH content.

Durability exposure 48 hours at 80° C.

percentage basis in order to make an easy inter-comparison and also to avoid the confusion of thought caused by the abnormally large activities for high concentrations of strong acids [23].

TABLE 5.—Comparison of the voltage departure of the glass electrode with the chemical durability of Corning 015 glass in solutions of  $C_2H_5OH$ ,  $H_2SO_4$ ,  $HCOOH$ ,  $CH_3COOH$  and  $MgSO_4$

Solution	Departure	Attack (swelling)
$C_2H_5OH$		
Percent	<i>mc</i>	Fringes
0 pH 4	0	¾.
10	0	
50	-1	2/10.
75	-11	<1/10.
85	-19	Detectable.
95	-30	Not detectable.
$H_2SO_4$		
0.1	0	½.
1.	0	½.
10.	0	<½.
25.	-1	1/10.
50.	-7	Not detectable.
75.	-91	Do.
96.	-277 drift	Do.
$HCOOH$		
0.1	0	½.
1.	0	½.
10.	0	<½.
25.	0	¼.
50.	-1	Detectable.
75.	-11	Not detectable.
89.	-32	Do.
$CH_3COOH$		
0.1	0	>½.
1.0	0	>½.
10.	0	<½.
25.	0	¼.
50.	-2	Detectable.
75.	-11	Not detectable.
90.	-47	Do.
99.	-159	Do.
$MgSO_4$		
0.1	0	>½.
1.	0	>½.
10.	0	½.
<sup>1</sup> 27	-2	¼.
<sup>2</sup> 37	---	¼.

<sup>1</sup> Saturated at 25° C.

<sup>2</sup> Saturated at 80° C.

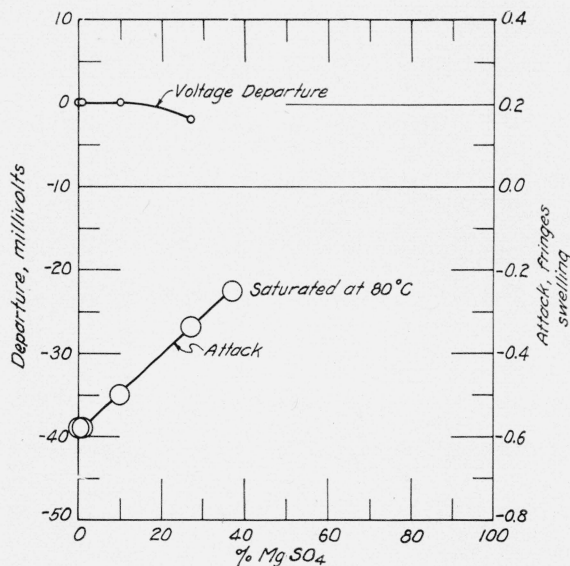


FIGURE 9.—Comparison of the voltage departure of the glass electrode with the chemical durability of the glass (repression of swelling) in acid solutions of increased  $MgSO_4$  content.

Durability exposure 48 hours at 80° C.

The repression of swelling by the higher concentrations of organic and inorganic acids, as well as for the magnesium sulphate<sup>5</sup> is readily predictable from Donnan membrane considerations and the distribution law [24]. The accompanying voltage departure can be attributed to the chemical change of the exposed glass surface [4], to a reduction of the water activity of the solution [1, 19, 20], or to a loss of electrode function because of induced decrease in water content of the glass [1, 2, 3]. Dehydration of the glass appears to be the most likely cause, as the major voltage departure is taking place over a concentration range in which no further detectable change in durability occurs.

For alkaline solutions of ethanol, the data obtained were far from satisfactory or conclusive, table 6 and [1 p. 81, 25]. Solutions of increased  $C_2H_5OH$  content, when prepared immediately before use, gave voltage departures that plotted as a straight line for 0.1 N and 0.01 N NaOH, curves A and B, figure 10. However, after the attack data, curves C and D, were obtained, the voltage-departure curves E and F for these same solutions were entirely different from curves A and B. The response of the hydrogen-glass electrode cell was sluggish, giving the impression

<sup>5</sup> A drop of  $H_2SO_4$  was added to the  $MgSO_4$  solutions to insure that they remain in the acid pH range.



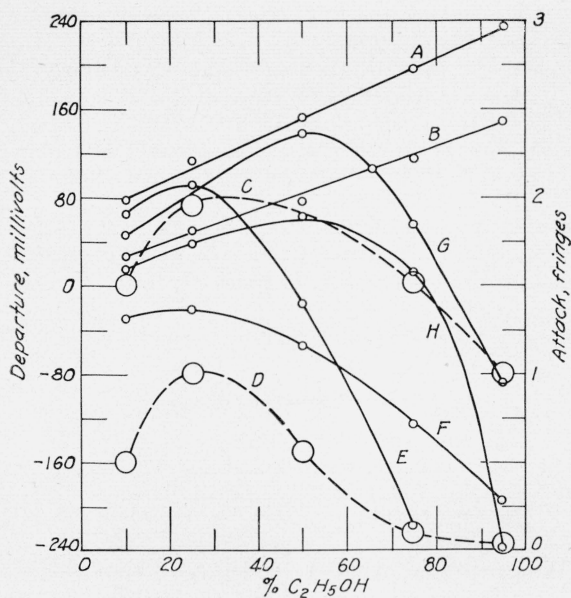


FIGURE 10.—Comparison of the voltage departures with the chemical durability of the glass for 0.1 N and 0.01 N NaOH solutions of increased ethanol content.

A, B, Voltage departure in 0.1 N and 0.01 N NaOH for freshly prepared solutions; C, D, chemical durability in solutions used for A and B 6 hours at 80° C; E, F, voltage departures in solutions A and B after the durability tests; G, H, voltage departures obtained for 0.1 N and 0.01 N NaOH prepared from stock solutions.

TABLE 6.—Comparison of the voltage departure of the glass electrode with the chemical durability of Corning 015 glass in aqueous solutions of NaOH of various C<sub>2</sub>H<sub>5</sub>OH contents

Solution	Voltage departure, millivolts, percent C <sub>2</sub> H <sub>5</sub> OH				
	10	25	50	75	95
0.1 N NaOH					
Fresh	A, +79	+113	+152	+196	+234
After 6 hr, 80° C	E, +64	+92	-16	-218	-----
Prepared from stock solution	G, +45	-----	+138	+56	-87
0.01 N NaOH					
Fresh	B, +26	+49	+77	+115	+149
After 6 hr, 80° C	F, -30	-22	-55	-125	-194
Prepared from stock solution	H, +15	+38	+61	+14	-237
	Attack, fringes				
0.1 N NaOH					
6 hr, 80° C	C, 1½	<2	-----	>1½	1
0.01 N NaOH					
6 hr, 80° C	D, ½	1	>½	¼	<sup>1</sup> D

<sup>1</sup> Detectable.

that the hydrogen electrode was poisoned. However, checking the combination in the dilute HCl solution used to establish the zero reference potential showed that the initial voltage was duplicated to within 2 mv. This indicated that the electrodes had not been affected permanently and that some alteration had taken place in the solutions during the 6-hour period at the high temperature. Further data taken on 0.1 N and 0.01 N NaOH solutions prepared from a stock solution of NaOH in C<sub>2</sub>H<sub>5</sub>OH gave the departure curves G and H, respectively. The latter curves might be rationalized as compatible with the durability curves C and D, but it seems unlikely that any of the emf values are reliable. At least, it seems improbable that all of the voltage anomalies observed can be accredited to the glass electrode. However, it must be borne in mind that the glass is being vigorously attacked by some of these solutions, so that reliable performance of the glass electrode is not to be expected.

#### IV. Conclusions

Voltage departures in alkaline solutions of electrodes prepared from Corning 015 glass are accompanied by changes in the chemical durability of the glass. The positions in a voltage departure series occupied by different metal ions are in the same order as the attack on the electrode glass by these same ions. However, the previous suggestion that the magnitude of all voltage departures might be directly proportional to the extent of the change in attack on the electrode glass is not universally true; in fact, the data obtained show that such linear relations occur for only a limited number of conditions. Furthermore, in acid solutions of high concentration (with the exception of HF), ethanol, and also salts of high ionic strength; dehydration of the glass is probably responsible for voltage departures.

#### V. References

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