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Electrode Function (pH Response) of the Soda-Silica Glasses

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A series of $\text{Na}_2\text{O-SiO}_2$ glasses was studied for durability, hygroscopicity, glass electrode function, and apparent response to $[\text{Na}^+]$. These glasses show three distinct regions of durability characteristics at pH 4.6: Below 81 percent of SiO_2 , where the glass is carried into solution; between 81 and 89.5 percent of SiO_2 , where differential solution of the constituents of the glass leaves a swollen silica-rich layer; and a region in which greatly reduced attack was indicated. Glass electrodes of low silica content having poor chemical durability and high hygroscopicity exhibited large voltage departures approaching the values of a "punctured" mercury-filled electrode and a calomel half cell. The apparent response to $[\text{Na}^+]$ ranged from 9 to 339 millivolts per pNa for the glasses of 82.6 and 56.6 percent of SiO_2 , respectively.

I. Introduction

For a glass to function satisfactorily as a glass electrode, it must have uniform durability over an extended pH range as well as adequate hygroscopicity. It has been shown that where the glass is attacked excessively [1, 2, 3],¹ or where the glass has inadequate hygroscopicity [4, 5], departures from the Nernst equation occur. These departures at times have been attributed to specific equilibrative responses to ions other than hydrogen [6]. To obtain more extensive data on these subjects, a series of glasses of the soda-silica system was studied in continuation of the work done on the potash-silica glasses [5]. The portion of the latter system investigated was found to have some very hygroscopic glasses, but because of their limited durability, these glasses were unsuitable for use as glass electrodes. Accordingly, in the present investigation both durability and hygroscopicity were studied in an attempt to determine which glasses of the soda-silica system would make satisfactory electrodes.

II. Experimental Procedure

Ten glasses of the soda-silica system were prepared in a platinum crucible from raw materials

¹ Figures in brackets indicate the literature references at the end of this paper.

of the high quality used in the production of optical glass. The batches were prepared to provide a series varying in steps of about 4 percent in the range from 55 to 91 percent of silica. Glasses of higher silica content were not obtained, because the field of practical glassmaking is limited by the tendency of glasses to devitrify, their high liquidus temperatures, or their high viscosity. To insure homogeneity, the glasses were stirred with a platinum stirrer. Since volatilization of soda occurs during melting, the compositions of these glasses were determined from index of refraction measurements [7, 8].

Hygroscopicity measurements were made on samples of glass that passed through a standard 150-mesh sieve. These weighed samples (approximately 1.5 g) were subjected to the high (approximately 98%) humidity maintained by a saturated solution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ at 25°C , in accordance with a previously described method [4, 5]. The values are reported in milligrams of water sorbed per cubic centimeter of glass exposed, to compensate for differences in density of the glasses.

Durability measurements were made on the glass by partially immersing polished optical flats in Britton-Robinson Universal buffer mixture (pH 1.9 to 11.9) [9] at $80^\circ \pm 0.2^\circ \text{C}$ for 6 hr and measuring the change in thickness of the exposed

portion of the sample by an interferometer method [1, 3]. These values are reported as fringes of attack or swelling, as the case may be.

Determinations of the electrode function of the various glasses were made by measuring at room temperature the emf of a cell, consisting of an experimental glass electrode and a well-conditioned Beckman glass electrode, with a Beckman pH meter, Laboratory Model G. The experimental electrodes were made by blowing a bulb on the end of tubing² drawn from the experimental glasses and filling the bulb with mercury for the inner connection [10, 11]. The pH response of the electrodes in a solution of pH 1.9 was taken as the zero voltage departure, and the departures over the range of pH 1.9 to 11.9 were noted.

Punctured electrodes were prepared by blowing a bulb of Corning 015 glass [12, 13] on the end of

² Tubing was drawn from the experimental glasses by Leonardo Testa of the glassblowing shop at the National Bureau of Standards.

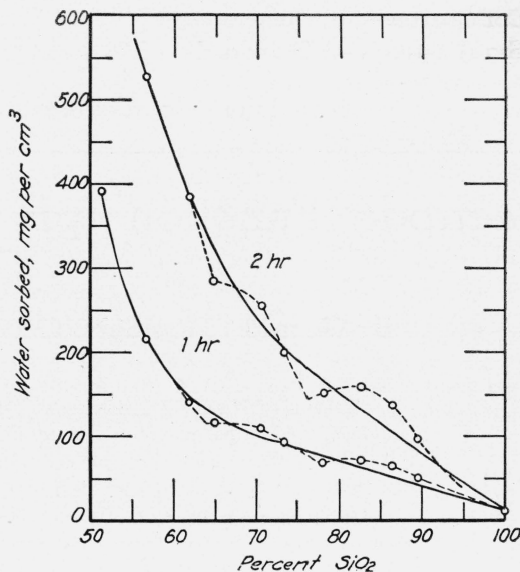


FIGURE 1. Hygroscopicity-composition curves of $\text{Na}_2\text{O-SiO}_2$ glasses for 1- and 2-hr exposures.

TABLE 1. Hygroscopicity (water sorbed), chemical durability, electrode function, and apparent response to $[\text{Na}^+]$ for a series of $\text{Na}_2\text{O-SiO}_2$ glasses compared with Corning 015 and fused silica

Glasses		Water sorbed after—		Attack (at pH) 6 hr 80° C					Voltage departures at pH values—							Apparent response to $[\text{Na}^+]^a$	
Na_2O	SiO_2	1 hr	2 hr	1.9	4.6	7.1	9.1	11.9	1.9	3.1	4.6	6.4	7.1	9.1	10.1		11.9
Percent	Percent ^b	mg/cm ³	mg/cm ³	Fringes	Fringes	Fringes	Fringes	Fringes	mv	mv	mv	mv	mv	mv	mv	mv	mv/pNa
48.7	51.3	390	1035	(e)	(e)	(e)	(e)	(e)	(d)	(d)	(d)	(d)	(d)	(d)	(d)	(d)	339
43.4	56.6	216	527	(e)	(e)	(e)	(e)	(e)	0	49	139	234	274	374	425	-----	339
38.2	61.8	139	383	(e)	(e)	(e)	(e)	(e)	0	47	126	203	235	318	369	458	294
35.2	64.8	115	283	(e)	(e)	(e)	(e)	(e)	0	34	111	189	210	283	-----	391	-----
29.4	70.6	109	253	e 60	72	Pitted	Pitted	Pitted	0	13	51	128	167	254	312	400	249
26.7	73.3	92	199	e 22	22	24	30	66	0	7	30	50	65	103	134	181	107
21.9	78.1	69	150	3.6	3.6	3.6	2	6	0	4	10	14	17	23	31	42	25
17.4	82.6	72	157	Swelling >1/2.	Swelling >1/2.	Surface cut, >1/4.	-----	3 3/4	0	4	10	10	10	10	11	4	9
13.6	86.4	65	136	Swelling >0.2.	Swelling >0.2.	Swelling 0.1.	-----	>2 1/2	(f)	-----	-----	-----	-----	-----	-----	-----	-----
10.5	89.5	50	97	Swelling, D ^g .	Swelling, D.	Swelling, D.	-----	<1 1/2	(f)	-----	-----	-----	-----	-----	-----	-----	-----
Fused silica	-----	11	12	ND	ND	ND	-----	-----	(h)	-----	-----	-----	-----	-----	-----	-----	-----
Corning 015	-----	61	140	Swelling <0.2.	Swelling <0.2.	Surface cut, D.	Surface cut, <1/2.	1 3/4 <2	0	0	0	0	0	1	1	2	-----
Corning 015 (punctured).	-----	-----	-----	-----	-----	-----	-----	-----	i 0	51	150	252	293	392	440	-----	352
Calomel reference electrode.	-----	-----	-----	-----	-----	-----	-----	-----	j 0	71	159	265	307	425	484	-----	-----

^a These data calculated from voltage departures between pH 1.9 and pH 10.1.

^b Composition computed from index of refraction data.

^c Failed to maintain polish.

^d No successful electrodes.

^e Durability data for these glasses were calculated from the attack for 15 min at 80° C.

^f No electrodes made of these glasses.

^g D, Detectable; ND, not detectable.

^h Developed no definite electrode function.

ⁱ Voltage departure values obtained for a punctured Hg filled electrode of Corning 015 glass.

^j Theoretical voltage departure of the glass electrode and calomel reference electrode.

Pyrex borosilicate tubing, with the result that hair cracks were formed on cooling due to the difference in expansion of the two glasses.

III. Results and Discussion

1. Hygroscopicity

The data for the water sorbed by this series of glasses after 1- and 2-hr exposure are given in table 1 and plotted in figure 1. Because of the limited data obtained, the results are represented by a smooth curve. However, if lines are drawn through the individual points (dashed lines, fig. 1), breaks in the slope occur near critical compositions of the phase diagram.

An interesting feature of these data is that the glass of approximately 86 percent of silica has the same hygroscopicity as Corning C15.

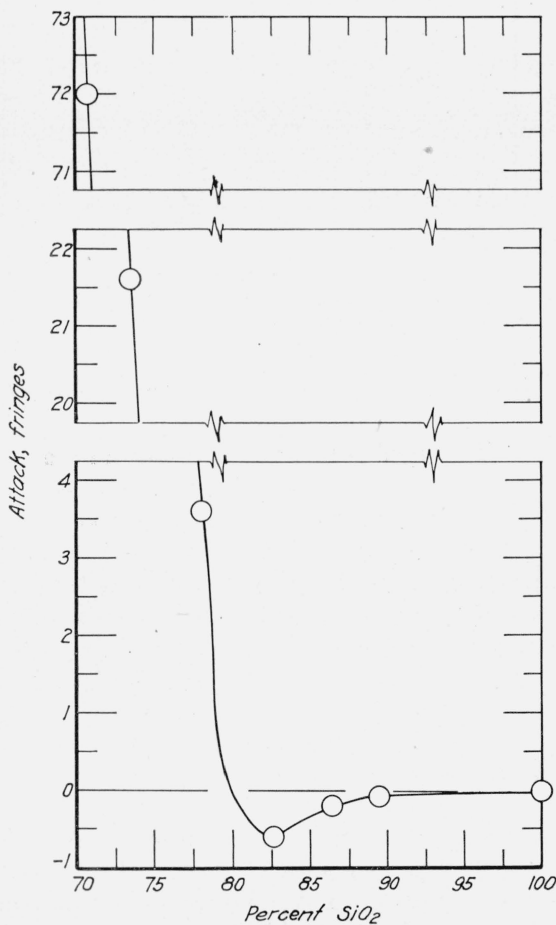


FIGURE 2. Attack on $\text{Na}_2\text{O-SiO}_2$ glasses exposed for 6 hr at 80°C to Britton-Robinson buffer mixture at pH 4.6.

2. Durability

Examination of the durability data, table 1 and figure 2, for the 6-hr exposure of the specimens in a solution of pH 4.6 indicates that the more durable glasses for this system occur in the range above 81 percent of silica. Those glasses below 64.8 percent of silica were deliquescent and failed to maintain polished surfaces when exposed to air, so that durability measurements by the interferometer method were impossible. Glasses having a composition of 70.6 and 73.3 percent of silica were less soluble, and results were calculated [1] from a 15-min exposure. Above 80 percent of

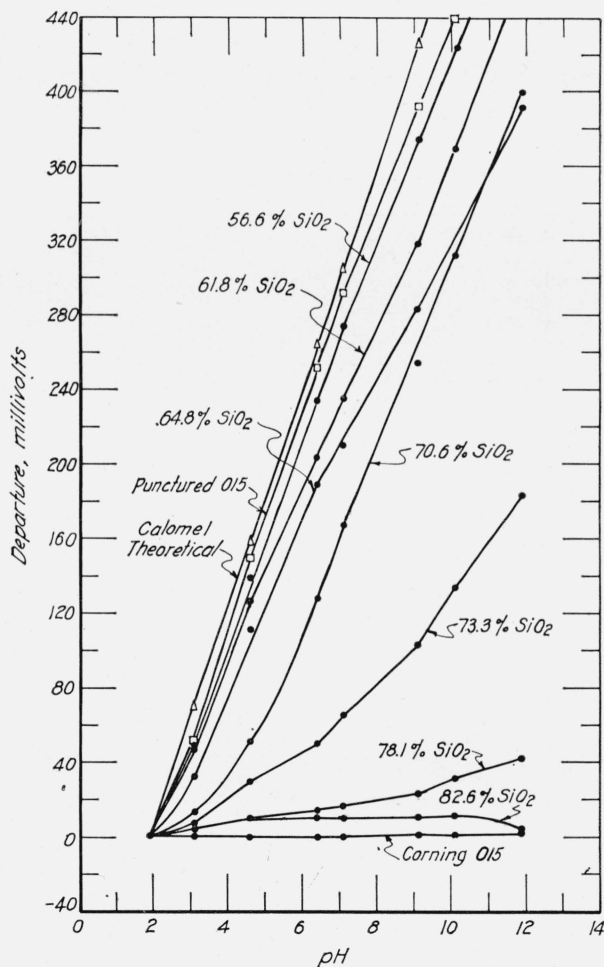


FIGURE 3. Voltage departures (errors) of electrodes prepared from a series of $\text{Na}_2\text{O-SiO}_2$ glasses and Corning 015 glass, by using the Beckman glass electrode as the reference electrode.

For comparison, the data are plotted for the theoretical voltage departure of a glass electrode from a calomel reference cell in addition to voltage departures shown by a punctured electrode of Corning 015 glass.

silica the durability of the glasses improved, and the glasses resisted solution and tended to swell. The tendency to swell decreased with increasing silica content until it became barely detectable at 89 percent of silica. It is only in the region of swelling, improved durability, and adequate hygroscopicity that one would expect to find successful electrodes. The values of hygroscopicity and durability of the glass of 86 percent of silica are similar to the values obtained on Corning 015 (see table I).

3. Electrode Function

(a) Voltage departure

The data given in table 1 and plotted in figures 3 and 4 show the trends of voltage departures in millivolts for glasses of increased silica content in solutions of various pH values. The poor durability of glasses below 82.6 percent of silica was

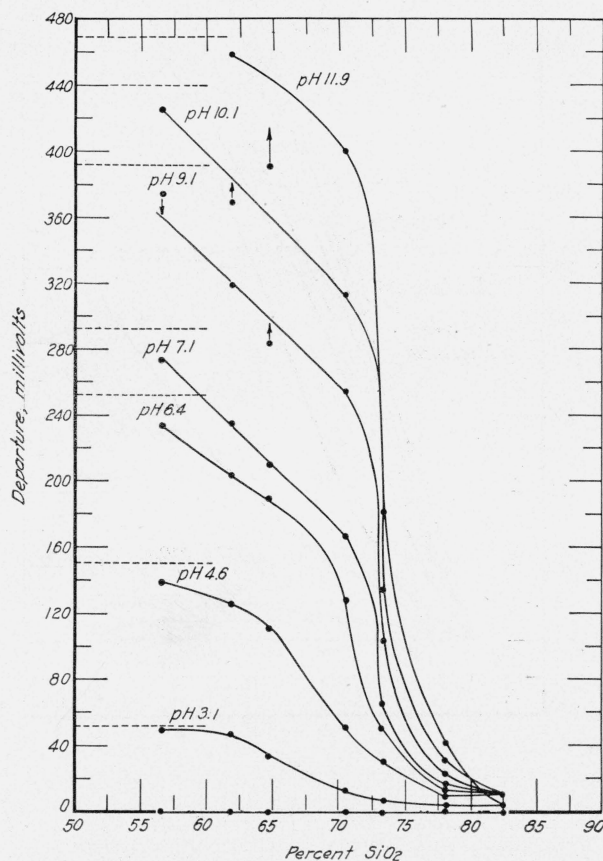


FIGURE 4. Voltage departures (errors) at various pH values for electrodes from $\text{Na}_2\text{O-SiO}_2$ glasses.

The dashed lines are the voltage departure values obtained for a "punctured" electrode.

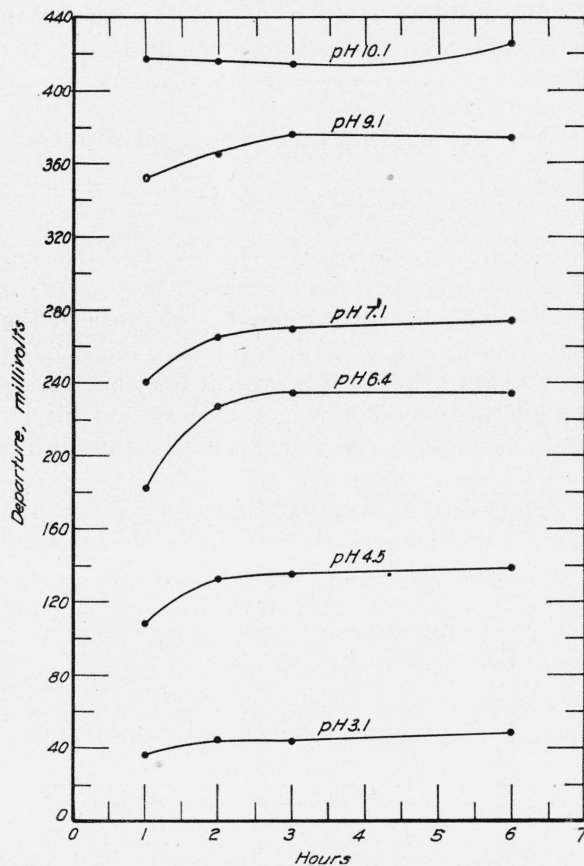


FIGURE 5. Change in voltage departure over a period of 6 hr of an electrode prepared from a glass of 43.4 percent of Na_2O and 56.6 percent of SiO_2 .

accompanied by large voltage departures, and the electrode response of these glasses was erratic. These values tended to drift, as is shown in table 2 and figure 5 for an electrode of 56.6 percent of silica. At the end of 6 hr, the electrode failed because of hydrolysis of the glass in the buffer solution. Voltage departures of electrodes from glasses of decreasing percentages of silica approached those of a punctured electrode, as shown in figure 3. These values in turn were similar to those obtained from a calomel half cell. It is obvious that an electrode prepared from a glass absorbing a sufficient amount of water would necessarily be a punctured electrode.

The response of an electrode prepared from the glass of 82.6 percent of silica approached that of the Corning 015. A maximum departure was obtained at pH 4.6, which remained constant until pH 10 and returned toward zero departure at pH 11.9. This latter effect could be attributed

either to improved durability of the glass or to deviation of the reference electrode in this pH range.

TABLE 2. Voltage departures (errors) at various time intervals for an electrode prepared from a glass containing 43.4 percent of Na₂O and 56.6 percent of SiO₂.

pH	1 hr	2 hr	3 hr	6 hr
1.9	0	0	0	0
3.1	36	44	44	49
4.5	108	132	135	139
6.4	182	227	234	234
7.1	240	265	269	274
9.1	352	365	376	374
10.1	417	416	414	425

The values of durability and hygroscopicity for some of the glasses above 82.6 percent of silica indicated that they would produce serviceable electrodes. Extrapolation of the voltage departure curves in figure 4 also indicated that this would be true. Unfortunately, these glasses have high liquidus temperatures and tend to devitrify; hence successful electrodes were not made.

4. Apparent Response to Sodium Ion Activity

Voltage departures from the straight-line relationship exhibited by glass electrodes have generally been interpreted as an equilibrative response to ions other than hydrogen [6]. The data, given in the last column of table 1 and plotted in figure 6, indicate that over the range of pH 1.9 to 10.1 for which a change of pNa of 1.25 units³ takes place, only a glass of approximately 75 percent of SiO₂ would provide the correct response of 59 mv/pNa. This glass would have poor durability. At compositions where the durability has improved, the response to pNa is too low, whereas glasses of lower silica content have ap-

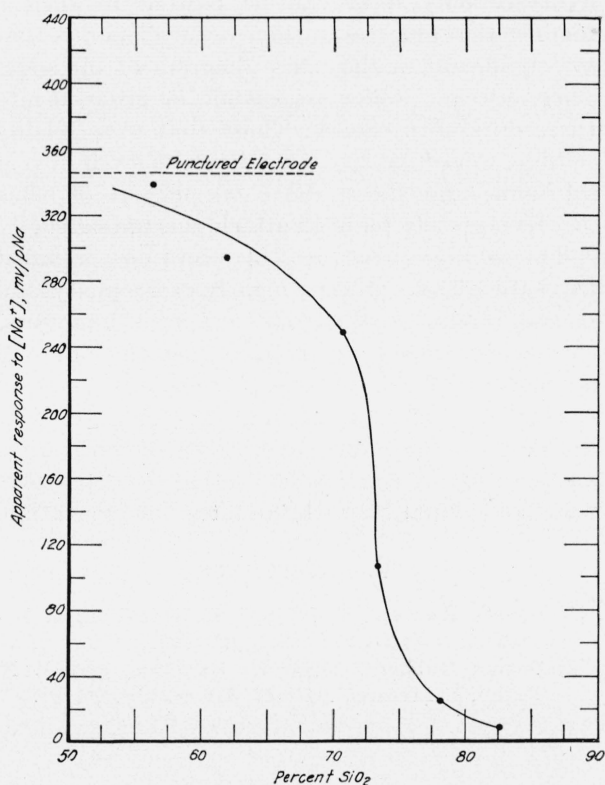


FIGURE 6. Apparent response to [Na⁺] of electrodes prepared from Na₂S-SiO₂ glasses.

The values are calculated from voltage departures and [Na⁺] for the buffer solutions at pH 1.9 and 10.1.

parent pNa responses that are too high. It is apparent that voltage departures for electrodes prepared from these soda-silica glasses cannot be attributed to response to the sodium ion activity of the buffer solutions.

IV. Summary and Conclusions

A series of glasses in the soda-silica system ranging from 51 percent to near 100 percent of silica were prepared and the durability, hygroscopicity, and electrode function studied. In accordance with the statement that the requirements for a good electrode glass were uniform durability over a long pH range and adequate hygroscopicity, it was predicted that a glass composed of 86 percent of silica and 14 percent of soda would function well as a hydrogen electrode. Unfortunately, this glass has a high liquidus temperature and tends to devitrify, so that satisfactory electrodes were not made. These glasses were hygroscopic, and it is of interest that the

pH	Britton-Robinson acid mixture volume	0.2 N NaOH volume	[Na ⁺]	pNa
1.9	ml 100	ml 2.5	0.00488	2.31
10.1	100	78.4	.0878	1.06
				ΔpNa=1.25

hygroscopicity data can be plotted in such a manner that changes in slope occur at points that are significant in the phase diagram of the soda-silica system. The glasses could be grouped into three durability classes: Those that were readily soluble, those that had a tendency to swell in acid solutions, and those above 90 percent of silica in which greatly reduced attack was indicated.

The voltage departures of electrodes prepared from the glasses of very high hygroscopicity and poor durability were similar to those of punctured electrodes, which in turn approached the values of a calomel half cell. The large departures of these electrodes could be attributed either to poor durability or to infinite hygroscopicity but not to a pNa response, as it was shown that the departures were not compatible with this latter interpretation.

V. References

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