U. S. Department of Commerce
National Bureau of Standards

Research paper **RP1743**
Volume 37, October 1946

Part of Journal of Research of the National Bureau of Standards

Electrode Function (pH Response) of Potash-Silica Glasses

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The electrode function (pH response) of a series of potash-silica (K_2O-SiO_2) glasses was determined and a comparison made with the hygroscopicity of the glasses. All the K_2O-SiO_2 glasses investigated showed a very high hygroscopicity, with an accompanying sensitive pH response. However, between pH 2 and 4, glasses of 71.8 and 73.6 percent SiO_2 gave pH-response values higher than the 59 millivolts per pH predictable from the Nernst equation.

Electrodes prepared from all members of the series demonstrated large voltage departures from the straight-line relation with increasing alkalinity of the buffer solutions. For a glass of 75.76 percent SiO_2 content, the voltage departures were compared with the chemical durability of the glass and also with the sodium-ion concentration, [Na^+], of the Britton-Robinson universal buffer solutions used. The voltage departures correlated with the magnitude of the attack much more convincingly than with the pNa.

For several chosen pH values, the voltage departures for the electrodes of these glasses when plotted with reference to their SiO_2 content gave curves that indicated a sharp change in slope near 74 percent of silica. A corresponding change in slope was also shown by the hygroscopicity-percentage-silica curve.

I. Introduction

The suitability of a glass for use in measuring the hydrogen-ion activity of aqueous solutions in accord with the dictates of the simplified Nernst equation, $\Delta E = 0.000198 T\text{pH}$, appears to be determined largely by two properties of the glass, namely, its water sorption (hygroscopicity) and the uniformity of its chemical durability when immersed in solutions varying in pH over an extended range. The absence of adequate hygroscopicity of the glass results in electrodes of high resistance whose pH responses fall appreciably below the theoretical value [1, 2, 3],[1] whereas conditions that cause changes in the chemical

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

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durability of the glass are accompanied by voltage departures [4, 5] that are roughly proportional to the magnitude of the change in durability [6]. In addition to the above electrical characteristics, some glasses under special conditions are believed to show specific equilibrative responses to ions other than hydrogen [7; 1, p. 267].

In the present investigation, a limited series of potash-silica (K_2O-SiO_2) glasses was studied with respect to each of the above properties.

II. Experimental Procedures

The hygroscopicity values were obtained by exposing powdered samples of the glasses to the high humidity furnished by a saturated solution of $CaSO_4.2H_2O$ thermostated in an air bath at 25° C. The glass samples were prepared by repeated crushing, in a steel mortar, and sieving through a Tyler standard 150-mesh sieve. Each sample consisted of approximately 1.5 grams of glass that had passed the sieve.[2] The samples were exposed in shallow weighing bottles for 1 and 2-hour periods. The resulting hygroscopicity values for the glasses are reported in terms of known factors, namely, weight of water sorbed times the density of the glass divided by the weight of the sample.

The humidity chamber consisted of a modified glass desiccator whose base was filled with the $CaSO_4.2H_2O$ solution. To hasten equilibrium and maintain uniformity, a small fan was mounted through a lucite bearing in the top of the vessel, and the inner walls were lined with a wick made from blotting paper.

The electromotive-force measurements were made with a Beckman pH meter, Laboratory Model G. Although the sensitivity of this instrument decreases for electrodes with resistances greater than 500 megohms, this was not a contributing factor to the results obtained on the K_2O-SiO_2 series because all the electrodes from these glasses exhibited low resistance. The glass electrodes were blown as thin-walled bulbs on the end of tubing made from the experimental glasses,[3] and the inner electrical connection was obtained by filling the bulb with mercury [8].

The chemical durability measurements were made by the interferometer method [5, 6, 9]. In order to have the results directly comparable with the work reported in the previous publications, the Britton-Robinson buffer mixtures [10] were used, and the temperature was maintained at 80°C±0.2°. Durability measurements for a particular composition, and for the pH range covered were made on a single specimen of glass, which was reground and repolished after each test.

The glasses were prepared by C. A. Faick and analyzed by F. W. Glaze [11]. Glasses of SiO_2 content lower than 71.83 percent were very unstable as electrodes, and those containing over 83.07 percent were not made because of the high melting point, high viscosity, and consequent difficulty of fining.

[2] The results of a series of experiments, not reported here, indicate that reproducibility by this method of sample preparation is equal to that obtained by crushing and using a fraction passing one sieve and retained by another.

[3] Tubes of the experimental glasses were drawn by Thomas R. Tait, of the Bureau's glassblowing shop.

III. Results and Discussion

1. Hygroscopicity and pH Response

The data listed in table 1 and plotted in figure 1 give the hygroscopicity and accompanying pH response for the series of K_2O-SiO_2 glasses. To these have been added for comparison, similar data on Corning 015, an optical glass BSC 517, Pyrex, Vycor, and fused silica.[4] The last four glasses were included to complete a hygroscopicity–pH-response series [3]. For the K_2O-SiO_2 glasses the hygroscopicity was very high, and the electrodes prepared from them had a correspondingly sensitive pH response. However, the glasses, of 71.8 and 73.6 percent SiO_2, although very sensitive, showed drifting voltages which gave rise to spurious pH responses, greater than those predictable from the Nernst equation. The electrodes from other members of the K_2O-SiO_2 series gave steady readings that very closely approxi-

[4] For analyses of these glasses see reference [2].

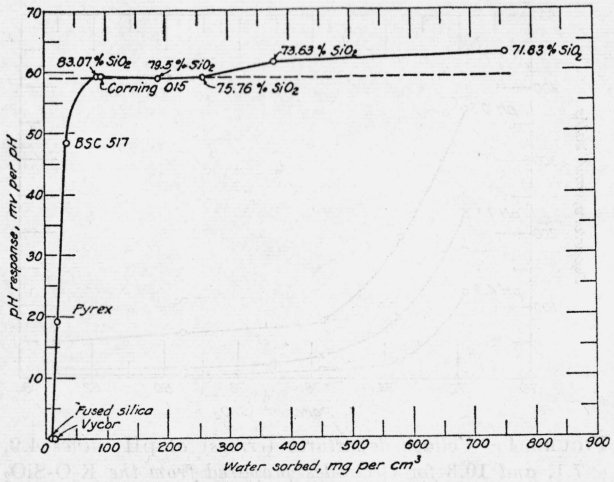


FIGURE 1.—*The water sorbed (hygroscopicity) and accompanying* pH *response of a series of* K_2O-SiO_2 *glasses, Corning 015,* BSC *517, Pyrex, Vycor, and fused silica.*

Values are plotted from columns 4 and 5 of table 1. The broken line indicates the "ideal" voltage response (59 mv) at 25° C.

mated the theoretical pH response. It should not be overlooked that the shift indicated in the pH-response—hygroscopicity curve (fig. 1) comes approximately at the same percentage composition at which breaks in the density [11] and hygroscopicity curves [2] have been reported on the same set of glasses.

TABLE 1.—*Hygroscopicity (water sorbed) and* pH *response of* K_2O-SiO_2 *glasses compared with Corning 015 and some glasses of low hygroscopicity*

[The pH-response data were obtained below pH 4.5 to avoid the voltage departures which accompany durability shifts at higher pH values. Values in italics are greater than the theoretical]

Glasses		Water sorbed after—		pH response—		Remarks
K_2O	SiO_2	1 hr	2 hr	When prepared	After 24 hr	
Percent	*Percent*	*mg/cm²*	*mg/cm²*	*mv/pH*	*mv/pH*	
28.17	71.83	240	755	*63.0*	*66.7*	Drifting.
26.37	73.63	126	375	*61.4*	*65.5*	Do.
24.24	75.76	102	259	58.9	59.3	Steady.
20.50	79.50	87	186	58.5	58.9	Do.
19.01	80.99	----------	----------	59.3	Failed	Do.
16.93	83.07	46	91	59.3	---do-----	Do.
Corning 015		54	94	59.2	59.4	Do.
BSC 517		25	36	48.3	50.4	Sluggish.
Pyrex (chemical ware)		17	22	18.8	19.1	Do.
Vycor		14	17	(1)	(1)	----------
Fused silica		11	12	(1)	(1)	----------

[1] Developed no definite pH response.

All these electrodes failed in a few days, some after standing for less than 24 hours in distilled water.

Undoubtedly K_2O-SiO_2 glasses of silica content higher than 83 percent would continue to show decreasing hygroscopicity and would follow the pH-response–hygroscopicity curve toward fused silica, the end member of the series.

2. Voltage Departures (Errors) With Increasing pH

Voltage departures were determined over an extended pH range on electrodes prepared from the K_2O-SiO_2 glasses and Corning 015, using the Beckman glass electrode as the reference electrode. If the reference electrode and the experimental electrode had similar pH response, i. e., followed the Nernst equation, the emf would remain constant over the entire pH range. Any deviations from constancy are considered due to errors in pH response of the experimental electrode and are reported in table 2 as voltage departures (errors). The measurements were taken in the buffer sequence, acid to alkaline, followed immediately by the reverse, in order to ascertain the reversibility of the electrodes and to check the effect of their immediate previous history. [12]. The

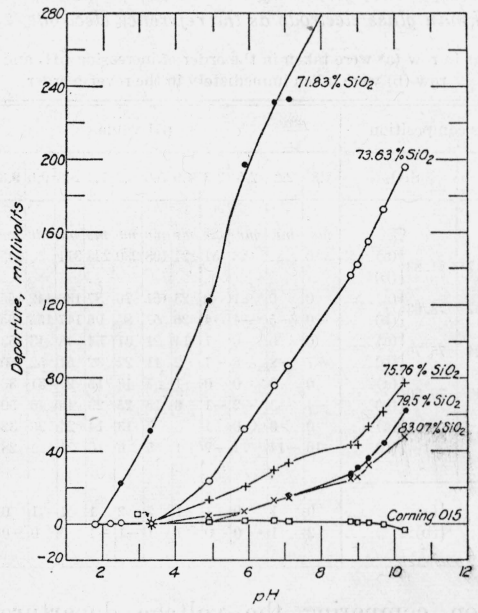


FIGURE 2.—*Voltage departures (errors) of electrodes prepared from a series of* K_2O-SiO_2 *glasses and Corning 015, using the Beckman glass electrode as the reference electrode.*

Values plotted are from table 2 and are the data obtained in the pH sequence, acid to alkaline.

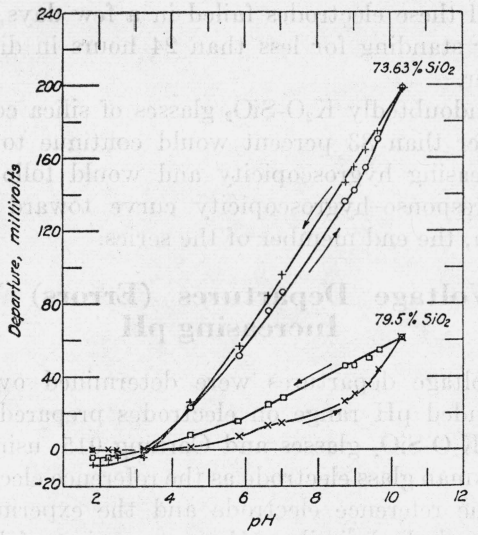


FIGURE 3.—*Voltage departures (errors) of electrodes prepared from two K_2O-SiO_2 glasses.*

These curves are typical and illustrate the irreversibility of pH measurements for the glasses investigated. The values plotted are from table 2.

voltage departures (errors) were very large (fig. 2). The reversibility was poor and greatly affected by the immediate previous environment of the electrode, as shown by the data plotted in figure 3 for glasses of 73.63 and 79.50 percent SiO_2.

TABLE 2.—*Voltage departures (errors) of electrodes prepared from K_2O-SiO_2 glasses of various compositions, using the Beckman glass electrode as the reference electrode*

Readings in row (a) were taken in the order of increasing pH, and those in row (b) were taken immediately in the reverse order

Glass composition			pH value												
K_2O	SiO_2		1.8	2.2	2.5	3.3	4.9	5.9	6.7	7.1	8.8	9.0	9.3	9.7	10.3
%	%		*mv*	*mv*	*mv*	*mv*	*mv*	*mv*	*mv*	*mv*	*mv*	*mv*	*mv*	*mv*	*mv*
28.17	71.83	(a)	0	----	23	51	121	198	230	233	311	---	345	---	375
		(b)	----	----	----	----	----	----	----	----	----	----	----	----	----
26.37	73.63	(a)	0	0	1	0	23	51	76	87	136	142	155	173	196
		(b)	−9	−5	−4	−4	26	57	85	96	147	155	165	173	196
24.24	75.76	(a)	0	0	0	1	14	21	31	34	43	43	53	62	78
		(b)	−7	−8	−8	−1	2	11	22	32	51	52	60	61	78
20.50	79.50	(a)	0	0	0	0	1	7	13	15	27	31	36	44	62
		(b)	−4	−3	−2	−1	6	16	25	29	46	46	50	55	62
16.93	83.07	(a)	0	0	0	1	5	7	13	14	24	26	32	---	48
		(b)	−16	−14	−14	−7	1	5	6	10	24	---	28	32	48
Corning 015		(a)	0	1	0	1	1	2	2	1	1	1	0	−1	−3
		(b)	2	1	0	0	1	−1	−1	−1	0	0	0	−1	−3

Upon comparing the voltage departures for this series of glasses at any chosen pH values with the percentage compositions, curves are obtained that suggest a sharp change in slope between 74 and 76 percent of SiO_2 (fig. 4). An

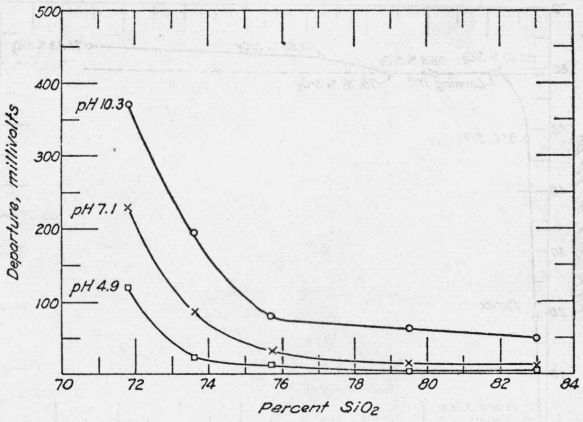


FIGURE 4.—*Voltage departures (errors) at* pH *values* 4.9, 7.1, *and* 10.3 *for electrodes prepared from the K_2O-SiO_2 glasses.*

The values plotted are from the data in table 2.

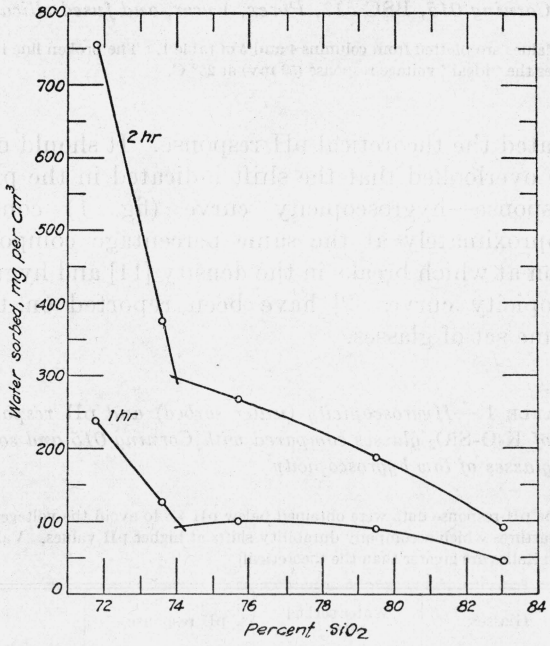


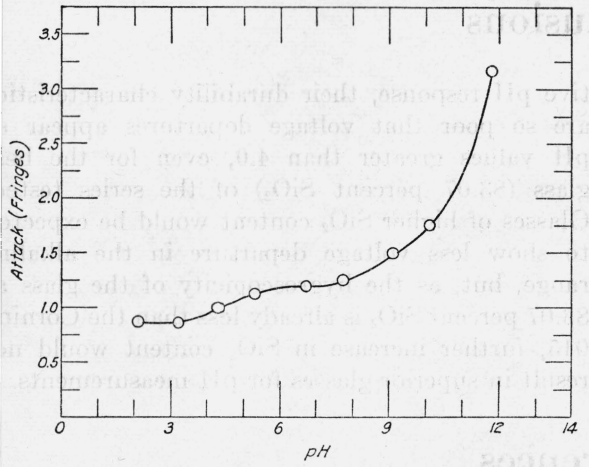
FIGURE 5.—*Water sorbed by K_2O-SiO_2 glasses (hygroscopicity) as a function of the silica content.*

Values are plotted from table 1 for water sorbed during 1-hr and 2-hr periods.

abrupt change in properties is indicated also by the hygroscopicity-percentage-silica curves shown in figure 5, and by a marked change in density [2, 11].

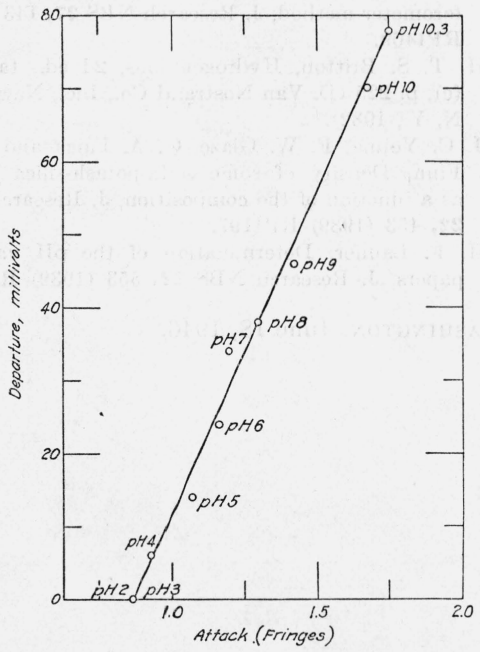
3. Voltage Departure With Reference to Chemical Durability and Sodium-Ion Concentration

Voltage departures from the straight-line relation, exhibited by glass electrodes, have generally been interpreted as an equilibrative response to



IGURE 6.—*Attack*-pH *curve of a potash-silica glass* (K_2O *24.24 percent,* SiO_2 *75.76 percent) exposed 15 minutes at 80° C to Britton-Robinson universal buffer mixtures covering the range* pH *2 to* pH *12.*

The size of the circles does not indicate the probable error of the individual ints, but does emphasize that the data must not be considered highly ecise nor accurate.



IGURE 7.—*Comparison of voltage departure with chemical attack for a potash-silica glass containing 75.76 percent of* SiO_2 *and 24.24 percent of* K_2O.

Values for voltage departure and chemical attack were obtained from fig- e 2 and figure 6, respectively.

ions other than hydrogen [7]. However, for electrodes prepared from Corning 015 and similar glasses it has been demonstrated that the regions of voltage departure have always been accompanied by a shift in the chemical durability of the glass [5, 9]. Conversely, imposed environments, such as hydrofluoric acid solutions, which induce durability shifts in the glass, have been accompanied by voltage departures [5; 1, p. 131].

In order to obtain further evidence on these two interpretations of the voltage departure of glass electrodes, the chemical durability of the glass containing 75.76 percent of SiO_2 was determined by the interferometer method [5, 9; 1, p. 83] over an extended pH range (fig. 6). The values plotted in figure 7 for attack [5] in terms of interference fringes, and the values for voltage departure were obtained by interpolation of the data in figures 6 and 2, respectively. The resulting plot indicates a straight-line relation within reasonable limits.

From the data it becomes obvious that these voltage departures are not attributable to a response to the sodium-ion concentration $[Na^+]$, at least not in accord with the dictates of the straight-line relation. From pH 3.3 to 10.3 the voltage departure was 77 mv (table 2), whereas the change in pNa was only $1.48-1.05=0.43$,[6] or 179 mv per pNa. This voltage response is much greater than the 59 mv per pNa predictable from the Nernst equation. For glasses with poorer durability, such as those of 73.63 and 71.83 percent of SiO_2, this lack of correspondence between pNa and voltage departure is even larger, and the idea of an equilibrative response to $[Na^+]$ by these glasses must be abandoned.[7]

[5] The magnitude of the attack, that is, the thickness of the glass dissolved away, was determined by observing the displacement of the interference fringes when the specimen was placed under a fused silica optical flat.

[6] The buffers of pH 3.3 and pH 10.3 were prepared by the addition of 20 ml and 80 ml of 0.2 *N* NaOH to 100 ml portions of the prepared acid mixture, yielding solutions of $[Na^+]$ equal to 0.033 and 0.088, respectively, or values for $pNa=\log 1/[Na+]$ of 1.48 and 1.05.

[7] Although the evidence strongly indicates a correspondence between the voltage departures and change in the durability of the glass, rather than a response to $[Na^+]$ of the buffers, the following observation should not be overlooked. W. J. Hamer, of this Bureau, points out that an extrapolation of the present data indicates that a glass of composition near 11% K_2O-89% SiO_2 might be expected to show a response to $[Na^+]$ approximating the theoretical 59 mv per pNa. Such a glass would be of interest, as it might serve as an indicator for a metal ion that is absent from the glass itself.

IV. Conclusions

The results of this investigation further support the belief that glasses of high hygroscopicity (water sorption) will always have sensitive pH responses and that changes in the durability of a glass will always be accompanied by voltage departures for an electrode prepared from such a glass.

The K_2O-SiO_2 glasses offer little to recommend them for glass-electrode work. Although their hygroscopicity is high, giving them a very sensitive pH response, their durability characteristi are so poor that voltage departures appear pH values greater than 4.0, even for the be glass (83.07 percent SiO_2) of the series teste Glasses of higher SiO_2 content would be expect to show less voltage departure in the alkali range, but, as the hygroscopicity of the glass 83.07 percent SiO_2 is already less than the Corni 015, further increase in SiO_2 content would n result in superior glasses for pH measurements.

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WASHINGTON, June 18, 1946.