Electrode Function (pH Response), Hygroscopicity, and Chemical Durability of Soda-Potash-Silica Glasses

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The pH response, hygroscopicity, and chemical durability of a series of Na_2O-K_2O-SiO_2 glasses have been investigated. The pH responses of electrodes prepared from these glasses are in accord with similar data previously reported for two other series of glasses, namely, Na_2O-CaO-SiO_2 and Na_2O-PbO-SiO_2, which showed that (1) glasses of low hygroscopicity produce electrodes whose pH response fall below the theoretical 59 millivolts per pH at 25° C predicted by the Nernst equation, and (2) electrodes prepared from glasses of poor chemical durability also fail to develop the full theoretical voltage.

Chemical durability determinations by an interferometer procedure indicate swelling of the glasses upon exposure to acid buffers and pronounced attack in alkaline solutions. During the investigation some limitations of the interferometer procedure for determining chemical durability of glass became evident. Glasses that had exhibited direct solution in the acid pH range were found to show swelling in the early stages of the exposure. This swollen layer then sloughed off giving the appearance of attack as previously interpreted.

Above 70 percent of SiO_2, glasses containing mixtures of Na_2O and K_2O have lower hygroscopicities than those having but a single one of these oxides.

The pH response-hygroscopicity curves appeared to reflect some of the critical compositions of the phase equilibrium diagram, with glasses in the composition range for alpha tridymite yielding electrodes with the optimum pH response characteristics.

I. Introduction

Previous studies of the chemical durability and hygroscopicity of optical glasses as a rapid test of their serviceability have demonstrated that these two properties are pertinent indicators of the suitability of glasses for measuring the hydrogen ion activity of aqueous solutions [1 to 5].[1] In every case studied, electrodes prepared from glasses of poor chemical durability failed to develop the theoretical voltage response indicated by the Nernst equation; $\Delta E = 0.000198\ T\Delta pH$ [1, 6, 7]. Equally obvious was the fact that glasses of very low hygroscopicity also failed to produce electrodes having satisfactory pH response [1, 6, 7]. In order to gain further information as to the universal validity of these findings, the hygroscopicity, chemical durability and pH response were studied for a series of Na_2O-K_2O-SiO_2 glasses.

II. Experimental Procedure

The pH responses of the experimental glasses were determined on electrodes of the Haber type [3] prepared by blowing thin walled bulbs on the end of tubing drawn from the molten glass. The resulting bulbs were filled with mercury for the inner electrical connection [8]. These metal filled electrodes were preferred to the conventional inner-solution filled types of glass electrodes [1], not only because of the simplicity of preparation, but also because a mercury filled electrode broken in service will not contaminate or alter the pH of the buffer solution involved. The voltage and pH measurements were made at room temperature with a Beckman pH meter, laboratory model G, using a well-conditioned glass electrode as the reference electrode.

The pH response values (mv per pH) were calculated from the electromotive force readings at pH

4.1 and 8.2. The voltage reading at pH 2 for the cell consisting of the experimental electrode and the reference electrode was taken as zero departure in every case. The values presented for the voltage departures represent in general the best performance obtained on any electrode from each glass. However, the life of electrodes varied from a few minutes to many weeks, depending upon the chemical durability of the glasses.

The procedure employed for obtaining the hygroscopicity data consisted in exposing approximately 1.5 g of powdered glass that passed a 150 mesh Tyler standard sieve, to the high humidity maintained by a saturated solution of $CaSO_4.2H_2O$ at 25° C [5, 6, 7]. All glasses were exposed for 1- and 2-hour periods and the results reported as milligrams of water sorbed per cubic centimeter of sample, that is, water sorbed times the density of the glass divided by the weight of the sample. To hasten equilibrium and uniformity throughout the humidity chamber, the walls were lined with a blotter wick and the atmosphere of the system circulated continously.

The chemical durability measurements of a semi-quantitative nature were obtained by an interferometer procedure [4, 9]. Specimens of the experimental glasses, after having been polished sufficiently flat to show interference bands when placed under a quartz optical flat, were partially immersed in Britton-Robinson universal buffer solutions at 80° C, covering the range from pH 2 to 11.8 [10]. The displacement of the bands due to surface alteration from the exposure was subsequently observed with a Pulfrich viewing apparatus. All results were reported for a 6-hour period, although some of the glasses were exposed for shorter periods of time in order to keep within the range limitations of the interferometer. In some extreme cases, the exposure time was reduced to 10 seconds and the value extra-

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

polated to 6 hours to keep the data consistent. Swelling is plotted as negative attack in the figures.

The compositions of the glasses were calculated from batch compositions and are identified in the illustrations as weight percent in the order Na_2O:K_2O:SiO_2.

III. Results and Discussion

Typical data for hygroscopicity, chemical durability, voltage departure, and pH response for the Na_2O-K_2O-SiO_2 glasses are given in table 1. For convenience of presentation and observation, the glasses are listed as five distinct series, namely, Na_2O-SiO_2, K_2O-SiO_2, Na_2O-K_2O-SiO_2 having 10 percent of K_2O, another having 10 percent of Na_2O, and a fifth set consisting of an incomplete short series of increasing percentages of SiO_2, in which the contents of Na_2O and K_2O are maintained equal on a weight percent basis. It is interesting to observe that each of these families of glasses passed through a composition range of optimum pH response (figs. 3 to 7), with a falling off on both sides of the optimum. Such a reversal does not appear for either the hygroscopicity or chemical durability values for the same families (figs. 4, 6, 7).

TABLE 1. *Hygroscopicity (water sorbed),* pH *response, and chemical durability of* Na_2O-K_2O-SiO_2 *glasses*

Glasses			Water sorbed		Voltage departure at pH—						pH response, 4.1 to 8.2	Chemical durability (attack) at pH—					
Na2O	K2O	SiO2	1 hr	2 hr	2.0	4.1	6.0	8.2	10.2	11.8		2.0	4.1	6.0	8.2	10.2	11.8
%	%	%	mg/cm³	mg/cm³	mv	mv	mv	mv	mv	mv	mv/pH	Fringes (a)	Fringes (a)	Fringes (a)	Fringes (a)	Fringes (a(	Fringes (a)
40	0	60	320	----	0	95	183	285	375	460	12	(a)	(a)	(a)	(a)	(a)	(a)
35	0	65	210	----	0	90	182	274	370	451	13	(a)	(a)	(a)	(a)	(a)	(a)
32	0	68	176	445	0	70	157	252	330	--	14	180 swell	180 swell	180 swell	180 swell	108 swell	----------
30	0	70	159	379	0	68	148	229	307	397	19	72 swell	72 swell	72 swell	72 swell	18 swell	252
28	0	72	151	346	0	17	39	68	95	138	46	36 swell	36 swell	36 swell	36 swell	1/10 swell	120
26	0	74	130	309	0	21	34	51	62	88	51	18 swell	18 swell	18 swell	18 swell	e D	36
24	0	76	127	270	0	9	24	32	49	60	53	12 swell	12 swell	12 swell	8 swell	2½ swell	20
22	0	78	112	265	0	10	18	23	39	49	55	2½ swell	6−swell	6 swell	6−swell	?	6
20	0	80	108	256	0	10	17	25	37	49	55	2 swell	2 swell	2+swell	2 swell	1 swell	3
18	0	82	96	220	G	10	18	18	26	34	57	¾ swell	¾ swell	¾ swell	½+swell	?	3+
16	0	84_1	83	178	0	3	7	7	9	11	58	¼+swell	¼+swell	¼+swell	²/10 swell	?	2½
14	0	86	61	124	0	2	4	6	8	10	58	²/10 swell	²/10−swell	²/10 swell	--------	D	2−
12	0	88	52	104	0	10	18	32	45	54	55	D swell	D swell	D swell	--------	?	2
?	0	$>88_1$	37	----	0	31	55	78	107	--	47	(b)	(b)	(b)	(b)	(b)	(b)
?	0	$>88_2$	30	----	0	36	85	133	185	-	35	(b)	(b)	(b)	(b)	(b)	(b)
?	0	$>88_3$	24	----	0	74	167	252	341	--	15	(b)	(b)	(b)	(b)	(b)	½
C	0	100	11	----	(c)	(c)	(c)	(c)	(c)	(c)	0	dND swell	ND	ND	ND	ND	½
0	36	64	446	1,146	0	96	208	304	407	503	7	(a)	(a)	(a)	(a)	(a)	(a)
0	34	66	384	956	0	89	209	310	418	500	7	(a)	(a)	(a)	(a)	(a)	(a)
0	32	68	344	835	0	85	167	257	359	431	16	(a)	(a)	(a)	(a)	(a)	(a)
0	30	60	259	636	0	77	145	220	292	370	23	270 swell	270 swell	270 swell	? swell	18 swell	Etched
0	28	72	202	406	0	43	100	170	259	332	28	126 swell	126 swell	126 swell	126 swell	Etched	¼ swell, 2 min, 1 attack, 5 min.
0	26	74	157	352	0	17	68	125	181	239	32	72 swell	72 swell	72 swell	70 swell	36 swell	90
0	24	76	122	237	0	20	48	80	142	195	44	40 swell	40 swell	40 swell	40 swell	36 swell	Etched
0	22	78	97	184	0	22	42	64	93	149	49	18 swell	20 swell	20 swell	16 swell	18 swell	24
0	20	80	80	161	0	10	21	32	54	91	54	8 swell	8 swell	8 swell	6 swell	6 swell	14
0	18	82	67	136	0	12	16	18	40	68	57.5	3½ swell	3½ swell	3 swell	3 swell	2+ swell	2½
0	16	84	57	122	0	11	13	17	21	26	57.5	½ swell	½ swell	½ swell	½ swell	½ swell	2−
0	14	86	46	100	0	4	8	12	20	31	57	1/10 swell	1/10 swell	²/10 swell	²/10 swell	1/10 swell	2−
0	12	88	37	80	0	31	93	174	220	264	23	ND	ND	ND	D	D	2+
0	10	90	29	50	(c)	(c)	(c)	(c)	(c)	(c)	0	ND	ND	ND	ND	ND	1½+
0	8	92	23	29	(c)	(c)	(c)	(c)	(c)	(c)	0	ND	ND	ND	ND	ND	1+
0	6	94	19	20	(c)	(c)	(c)	(c)	(c)	(c)	0	ND	ND	ND	ND	ND	¾
30	10	60	325	750	0	110	215	332	477	575	5	(a)	(a)	(a)	(a)	(a)	(a)
27.5	10	62.5	262	635	0	92	187	307	407	490	8	540 swell	540 swell	540 swell	540 swell	D swell	Etched
25	10	65	225	530	0	90	180	290	392	470	11	360 swell	360 swell	360 swell	Pitted	Pitted	Do.
20	10	70	159	370	0	40	85	150	207	267	32	72 swell	72 swell	72 swell	72 swell	...do...	315
17.5	10	72.5	130	275	0	17	47	86	127	185	43	27 swell	27 swell	20 swell	20 swell	20 swell	162
15	10	75	110	210	0	22	31	42	57	87	54	15 swell	15 swell	15 swell	15 swell	6 attack	120
12.5	10	77.5	85	160	0	6	11	19	32	43	56	3 swell	3 swell	3− swell	3− swell	?	15
10	10	80	60	118	0	5	14	16	22	33	57−	1¼ swell	1¼ swell	1¼ swell	1¼ swell	½+ swell	1
5	10	85	41	81	(f)	(f)	(f)	(f)	(f)	(f)	?	D swell	D swell	D swell	D swell	D	1½
0	10	90	29	50	(c)	(c)	(c)	(c)	(c)	(c)	0	ND	ND	ND	ND	ND	1½+
10	30	60	400	899	0	99	190	305	405	-----	8	1080 swell	1080 swell	1080 swell	1080 swell	500	Etched
10	25	65	262	600	0	92	182	272	365	455	14	360 swell	360 swell	360 swell	Pitted	Pitted	Do.
10	22.5	67.5	212	490	0	77	160	242	328	420	19	144 swell	144 swell	144 swell	...do...	...do...	Do.
10	20	70	172	389	0	62	137	187	255	320	28	72 swell	72 swell	72 swell	...do...	...do...	200
10	17.5	72.5	145	290	0	37	75	127	170	234	38	27 swell	27 swell	20 swell	20 swell		90
10	15	75	117	220	0	10	29	43	63	89	51	12 swell	12 swell	12 swell	12 swell	6 swell	72
10	12.5	77.5	89	160	0	16	29	34	47	63	55	3 swell	3 swell	3 swell	2 swell	D	15
10	10	80	60	118	0	5	14	16	22	33	57−	1¼ swell	1¼ swell	1¼ swell	1¼ swell	½+ swell	¾
10	5	85	45	92	0	15	30	50	67	80	50	D swell	D swell	D swell	D swell	Surface cut	¾
?	0	$>88_3$	24	--------	0	74	167	252	341	-----	15	(b)	(b)	(b)	(b)	(b)	(b)
20	20	60	345	833	0	81	172	290	425	550	9	1080 swell	1080 swell	Pitted	720 swell	270 swell	Etched
17.5	17.5	65	235	570	0	112	209		415	510	12	360 swell	Pitted	360 swell			
15	15	70	165	375	0	60	128	192	280	355	27	72 swell	72 swell	72 swell	72 swell	60 swell	315
12.5	12.5	75	110	213	0	12	21	40	78	106	52	12 swell	12 swell	12 swell	12 swell	6 swell	60
10	10	80	60	118	0	5	14	16	22	33	57−	1¼ swell	1¼ swell	1¼ swell	1¼ swell	½+ swell	1
27.5	7.5	65	210	532	0	106	212	292	420	522	14	360 swell	360 swell	Pitted	Pitted	Pitted	Etched
12.5	22.5	65	250	580	0	126	233	314	450	550	12	300 swell	Pitted	...do...			
Corning 015			59	138	0	0	0	0	0	3	59	²/10−swell	²/10−swell	²/10−swell	Surface cut	¼−attack	2

a Failed to maintain polish.
b No specimens available.
c No definite pH response.
d Not detectable.
e Detectable.
f Devitrification.

1. Na₂O-SiO₂ Glasses

(a) Voltage Departure and Chemical Durability

The voltage departures and the accompanying durability characteristics of the Na_2O-SiO_2 family of glasses over the range from pH 2 to 11.8 are shown in figure 1 and figure 2, respectively. From figure 1 it is evident that beginning with electrodes from glass 40:60 the voltage departures (errors) decrease with increasing SiO_2 content to glass 14:86. Above this composition the electrodes for glasses containing larger percentages of SiO_2 become progressively worse.[2]

Figure 2 illustrates the occurrence of swelling in the acid range and attack at the higher alkalinities. These features are characteristic of many silicate glasses [4, 6, 7, 9]. The conflict of results in figure 2 and in earlier published work [12] indicating both positive and negative attack for similar glasses exposed to equivalent solutions draws attention to an interesting feature of glass behavior and to a
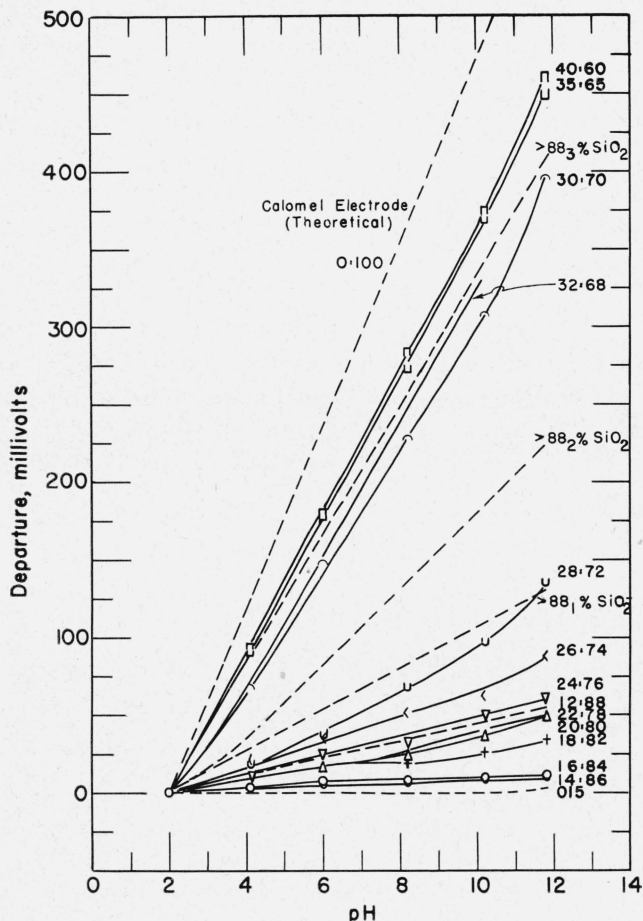
FIGURE 1.   pH-*voltage departure curves for electrodes prepared from a series of* Na_2O-SiO_2 *glasses.*

Corning 015 is included for comparison.
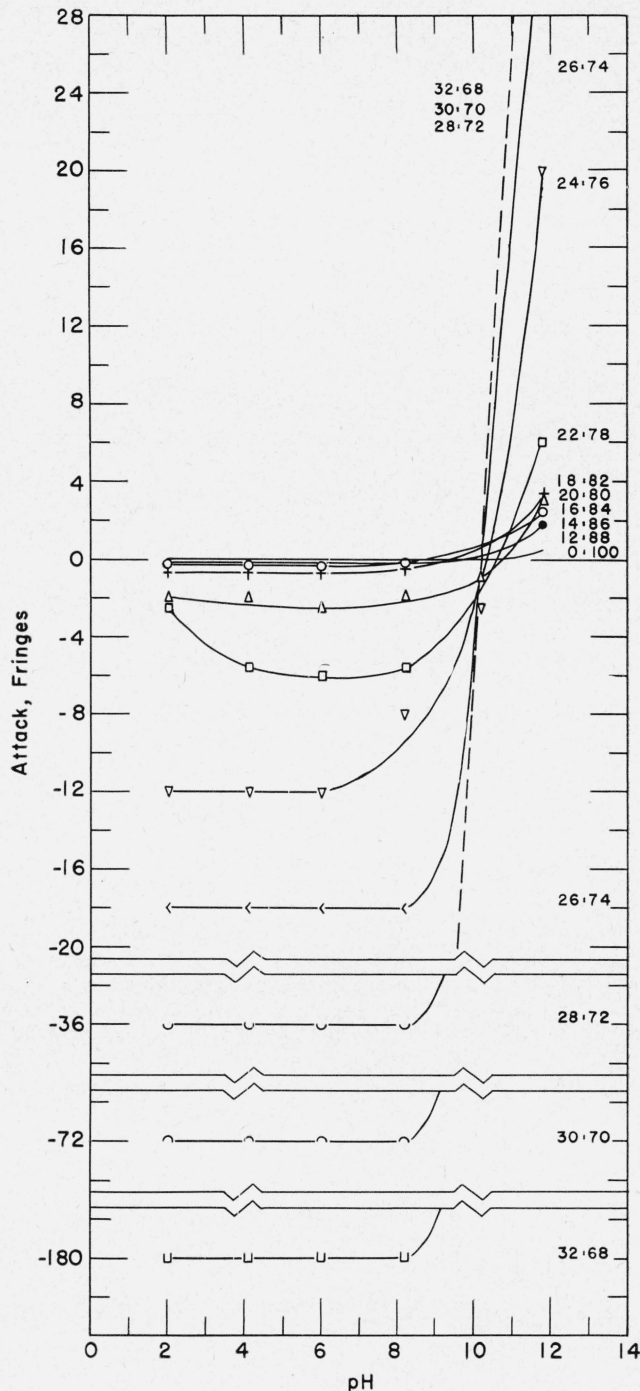
FIGURE 2.   pH-*chemical durability curves for a series of* Na_2O-SiO_2 *glasses.*

limitation of the interferometer procedure for determining the chemical durability of glasses. In some of the recent work it has become increasingly evident that the interferometer procedure can give this type of confusing result depending on the time of exposure to the attacking solution. For example, the glass 28 percent of K_2O; 72 percent of SiO_2, upon exposure to the buffer solution pH 11.8 at 80° C,
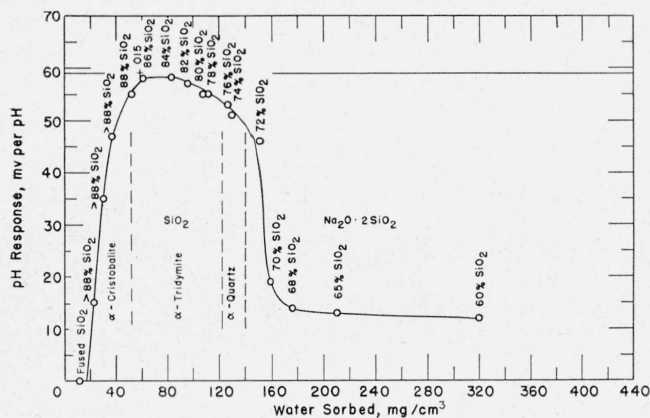
FIGURE 3. *Variation in* pH *response with increasing hygroscopicity for a series of* Na$_2$-SiO$_2$ *glasses.*

Corning 015 electrode glass included for comparison. The approximate position at which the primary phase of the equilibrium diagram changes from SiO$_2$ to Na$_2$O.2SiO$_2$ is indicated by the broken lines.

exhibited a uniform swelling of one-fourth band after 2 minutes, but at the end of 5 minutes exposure a ragged attack of over one fringe was observed (table 1). This limitation of the interferometer method for measuring surface alteration was early suspected [6, 11, p. 155] but had not been observed. Any user of the interferometer procedure should be on the alert, especially when investigating glasses of very poor chemical durability. For such glasses, only by reducing the time of exposure to a minimum can it be demonstrated that the early stages of exposure produce swelling. Furthermore, if the surface alteration is greater than two or three fringes, it becomes increasingly difficult to ascertain if the alteration of the surface is one of swelling or solution.

(b) Hygroscopicity and pH Response

Figure 3 illustrates the variation in pH response with increasing hygroscopicity for the series of Na$_2$O-SiO$_2$ glasses listed in table 1. As was found for the Na$_2$O-CaO-SiO$_2$ and the Na$_2$O-PbO-SiO$_2$ glasses [6, 7] having a long hygroscopicity range, these glasses also exhibited a region of optimum pH response. Electrodes from glasses of low hygroscopicity failed to develop the full theoretical voltage of 59 mv/pH at 25° C, while those to the right of the optimum also failed to attain the full pH response. A glance at table 1 and figure 2 shows that these latter glasses have progressively poorer chemical durabilities with increasing hygroscopicity. In figure 3 the approximate position at which the primary phase, as shown by the equilibrium diagram, changes from SiO$_2$ to Na$_2$O.2SiO$_2$ is indicated by vertical broken lines [13].

(c) Hygroscopicity, Chemical Durability and pH Response Versus Composition

A better over-all picture of the interrelation between pH response, hygroscopicity, chemical durability, and composition for the Na$_2$O-SiO$_2$ glasses can be obtained from figure 4. The chemical durability curves presented are for the extremes of

pH studied, namely pH 2 and 11.8. The divergence of these durability curves serves to emphasize the fact that swelling, plotted as negative attack, predominates in the acid range, while solution appears at high alkalinities, besides indicating the compositions at which marked durability departures appear. Further, a study of the pH response curve reveals that the hydrogen electrode function starts declining at approximately the same composition at which the chemical durability curves show a marked change [2, 4]. The approximate compositions at which a break has been reported in the specific volume curve for these glasses [14] and at which the primary phase of the equilibrium diagram changes from Na$_2$O.2SiO$_2$ to SiO$_2$ [13] are represented by
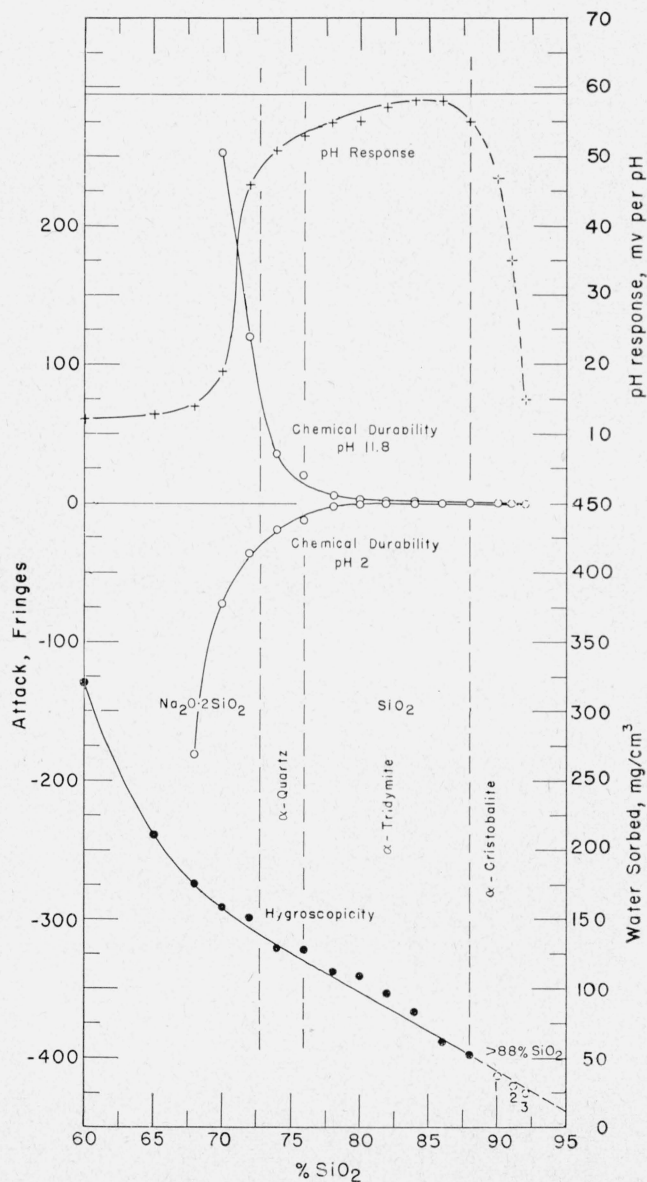
FIGURE 4. *Values for the* pH *response, hygroscopicity, and chemical durability at* pH *2 and 11.8 plotted against the percentage of* SiO$_2$ *for a series of* Na$_2$O-SiO$_2$ *glasses.*

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broken lines. In earlier work on this system [12], a pronounced change in the slopes of the respective curves for voltage departure versus percentage of SiO_2, and apparent response to sodium ions versus percentage of SiO_2 also appeared near this same composition. The failure of electrodes from glasses of low hygroscopicity to develop the full theoretical voltage is also indicated in figure 4. Figures 3 and 4 show the optimum pH response for the Na_2O-SiO_2 glasses to lie within the composition range in which α-tridymite is the primary phase.

2. K_2O-SiO_2 Glasses

(a) Voltage Departure and Chemical Durability

Table 1 shows the voltage departure over the range pH 2 to 11.8 of electrodes prepared from the K_2O-SiO_2 glasses; and gives the accompanying durability characteristics for most of these glasses over the same pH range. As was the case with the Na_2O-SiO_2 glasses, the voltage departures (errors) decrease with increasing SiO_2 content to near 86 percent of SiO_2. Near this composition the improvement ceases, and it is followed by a reversal for higher percentage of SiO_2. No definite pH response was obtained for electrodes prepared from glasses having a SiO_2 content greater than 90 percent. These glasses also follow the two general rules: (1) electrodes prepared from glasses of very poor chemical durability fail to develop the full theoretical pH reponse, and (2) glasses of low hygroscopicity likewise fall short of the 59 mv/pH at 25°C indicated by the Nernst equation.

The chemical durability data of table 1 show the familiar swelling in the acid buffers and pronounced solution at the higher alkalinities. The same limitations of the interferometer procedure pointed out for the Na_2O-SiO_2 glasses are evident for the K_2O-SiO_2 glasses, and the same precautions are necessary in order to ascertain if the attack is positive or negative, that is, solution or swelling.

(b) Hygroscopicity and pH Response

The variation in pH response with increasing hygroscopicity for the K_2O-SiO_2 glasses (table 1) is qualitatively similar to that of the Na_2O-SiO_2 glasses. Electrodes prepared from the glasses of low hygroscopicity fell below the theoretical, and the glasses of high hygroscopicity characterized by very poor chemical durability also failed to give the full 59 mv/pH at 25°C. If the position at which changes in the primary phases of the equilibrium diagram appear [15] are superimposed on this data, the indicated reduction in pH response near the change from $K_2O.2SiO_2$ to $K_2O.4SiO_2$ is possibly transient as the pH response of all the glasses of very poor chemical durability continued to decrease until the electrodes failed. Electrodes from glasses of 76 percent and 78 percent of SiO_2 survived for 24 hours, whereas electrodes from the other glasses having smaller percentages of SiO_2 failed after much shorter service.
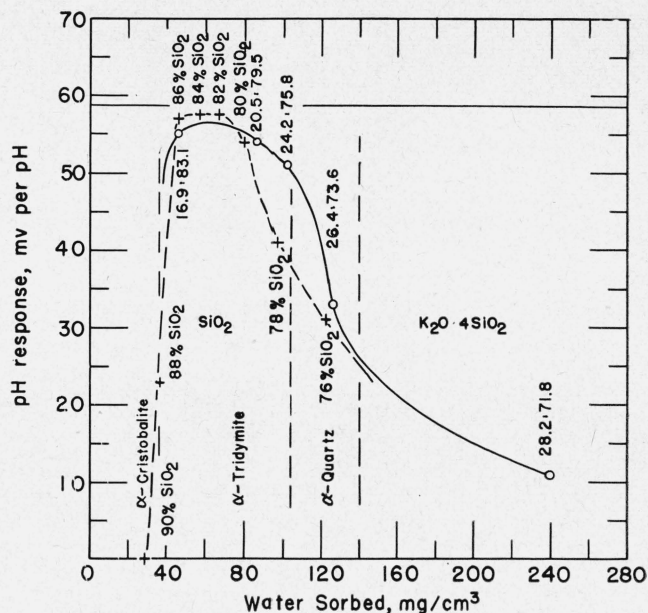
FIGURE 5. *Variation of* pH *response with increasing hygroscopicity for a limited series of* K_2O-SiO_2 *glasses previously reported.*

————, Compared with the present series; — — —, electrodes seasoned 24 hr.

In light of the present results, it seems desirable to reinterpret the pH response data previously presented for a limited series of K_2O-SiO_2 glasses [16]. Upon calculating the pH response for these "old" glasses between pH 4.1 and 8.2 (table 2), and plotting the values obtained against the hygroscopicity, the resulting curve is qualitatively similar to the curve for the present data, (fig. 5). The results as presented in the earlier publication had been calculated from the uncertain electromotive force data taken in the pH region of supposed maximum durability, giving values for pH response that appeared in contradiction to the upper voltage limits dictated by the Nerst equation. The present representation of these old data renders it in a more acceptable form. The approximate positions at which changes in the primary phase of the equilibrium diagram appear for this set of glasses [15] are inserted in this figure for the reader's inspection. Again it is apparent that the compositions of optimum pH response fall within the α-tridymite range.

TABLE 2. *Hygroscopicity and* pH *response of* K_2O-SiO_2 *glasses previously reported* [16]

Glasses		Water sorbed, 1 hr	pH response, 4.1 to 8.2
K_2O	SiO_2		
%	%	mg/cm.³	mv/pH
28.17	71.83	240	11
26.37	73.63	126	33
24.24	75.76	102	51
20.50	79.50	87	54
16.93	83.07	46	55

The differences in the performance of electrodes from the old and the new glasses may be attributed to either or both of the following factors. The old glasses were a part of a series of carefully analyzed glasses used for density determinations [14], whereas the compositions of the new series were calculated from batch composition. Electrodes of the old series were blown from tubes prepared by reworking pieces of the original glasses, while electrodes from the new glasses were prepared from tubes drawn from the melts at the time of pouring.

(c) Hygroscopicity, Chemical Durability, and pH Response Versus Composition

An over-all summary of the relationship between pH response, hygroscopicity, chemical durability, and composition for the K_2O-SiO_2 glasses can be plotted from table 1. As was the case with the Na_2O-SiO_2 glasses (fig. 4), glasses of low hygroscopicity and poor chemical durability failed to produce electrodes that developed the theoretical 59 mv/pH at 25°C. If the approximate compositions at which changes in the primary phase of the phase equilibrium diagram have been reported [15, 17] are superimposed on the K_2O-SiO_2 data of table 1, the compositions of optimum pH response fall in the range for which α-tridymite is the primary phase.

3. $Na_2O-K_2O-SiO_2$ Glasses

(a) Voltage departure and chemical durability

Three series of glasses, representing three cross sections of the $Na_2O-K_2O-SiO_2$ ternary diagram, were investigated for voltage and chemical durability characteristics. The voltage departures over the pH range 2 to 11.8 for these three series, are grouped in table 1. There is nothing unusual indicated by any of these voltage departures. The trends are qualitatively similar to the results shown by the Na_2O-SiO_2 and K_2O-SiO_2 series. The chemical durability characterized by swelling in the acid pH range and liberal solution of the glasses in the stronger alkaline buffers, improved with increased SiO_2 content.

(b) Hygroscopicity and pH Response

If the values for pH response and hygroscopicity for the $Na_2O-K_2O-SiO_2$ glasses containing 10 percent of K_2O and 10 percent of Na_2O are plotted, as was done for the Na_2O-SiO_2 glasses, curves are obtained which are similar to figure 3. Electrodes prepared from these glasses fit into the general pattern of performance, with those from glasses of low hygroscopicity failing to develop the full theoretical voltage, and those from glasses of poor chemical durability also falling well below the proper pH response. For these mixed alkali oxide glasses, those falling in the α-tridymite composition range indicated by the phase equilibrium diagram gave optimum performance [17].

(c) Hygroscopicity, Chemical Durability, and pH Response Versus Composition

The values for pH response, hygroscopicity, and chemical durability and their relation to the percentage SiO_2 are plotted in figures 6 and 7 for the two series of glasses containing 10 percent of K_2O and 10 percent of Na_2O. The approximate positions of the primary phases reported for the phase equilibrium diagram are included for inspection, and again they show that the region for α-tridymite produced electrodes which gave the optimum pH response [17].
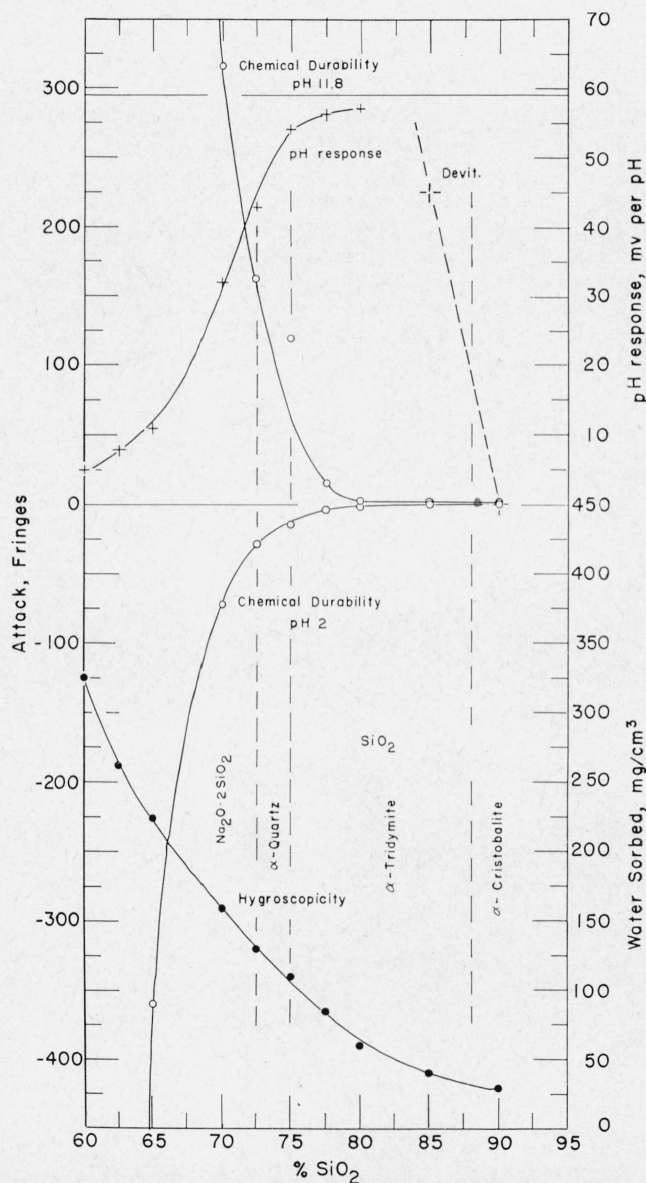

FIGURE 6. *Values for* pH *response, hygroscopicity, and chemical durability at pH 2 and 11.8 plotted against the percentage of* SiO_2, *for a series of* $Na_2O-K_2O-SiO_2$ *glasses at 10 percent* K_2O *content.*
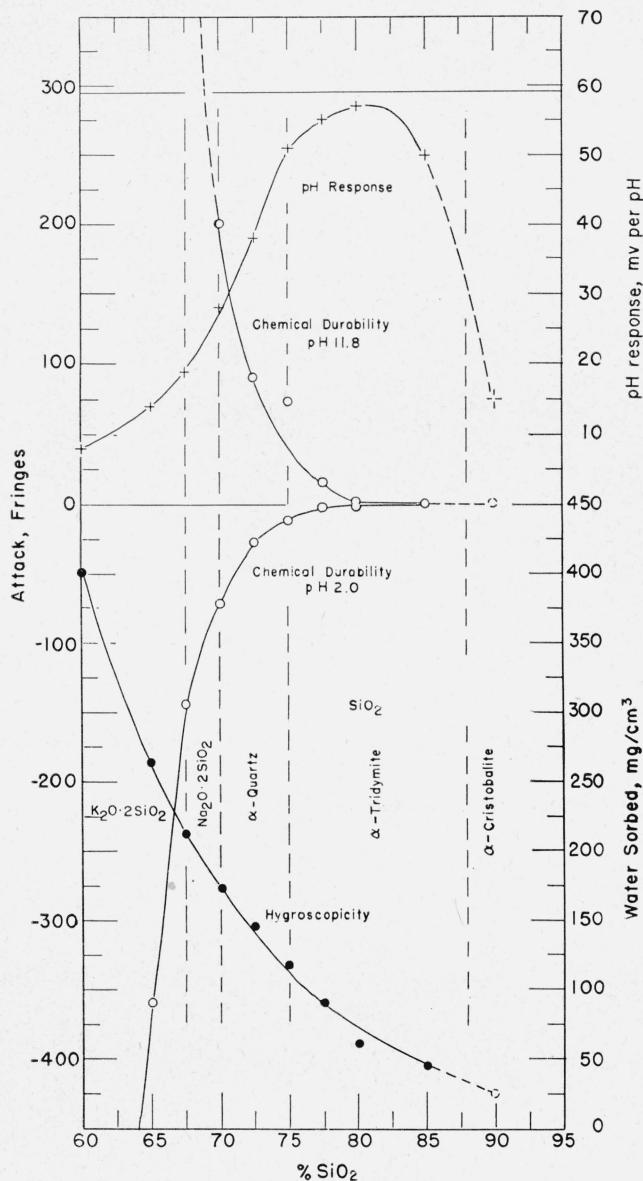
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FIGURE 7. *Values for the* pH *response, hygroscopicity, and chemical durability at* pH$_2$ *and 11.8 plotted against the percentage of* SiO$_2$ *for a series of* Na$_2$O-K$_2$O-SiO$_2$ *glasses of 10-percent* Na$_2$O *content.*

4. Summary

An over-all picture of the relation between the hygroscopicity and composition for the Na$_2$O-K$_2$O-SiO$_2$ glasses is presented in the ternary diagram, figure 8. The iso-sorbs indicate the glass compositions of equal hygroscopicity based on the water "sorbed" by powdered specimens after 1-hour exposure to approximately 98 percent relative humidity at 25° C. The glass compositions that produced electrodes having a pH response as high as 56 mv/pH are included in the shaded portion of figure 8. A glance at the chemical durability data for the glasses included in this area show that most

of these glasses have durabilities considerably inferior to Corning 015, indicating that the composition range for satisfactory electrodes is considerably more limited than the figure implies. Nevertheless, the same three groups are indicated for the Na$_2$O-K$_2$O-SiO$_2$ glasses that were found for the Na$_2$O-CaO-SiO$_2$ and Na$_2$O-PbO-SiO$_2$ glasses [6, 7] namely, group A, glasses that are too "dry" for successful electrodes; group B, glasses that produce electrodes that approach the theoretical pH response, and group C, glasses characterized by poor durability, which are too "wet."

The results obtained for the pH response, hygroscopicity, and chemical durability of the Na$_2$O-K$_2$O-SiO$_2$ glasses studied in this investigation add further evidence confirming the validity of the following generalizations: 1. Glasses of very low hygroscopicity yield electrodes whose pH responses fall appreciably below the theoretical 59 mv/pH at 25° C. 2. Electrodes prepared from glasses of poor chemical durability also fail to develop the full theoretical voltage.

The data for chemical durability gave further evidence that swelling of silicate glasses in acid buffers is more universal than generally realized. The Na$_2$O-SiO$_2$ and K$_2$O-SiO$_2$ glasses of very poor chemical durability were found to exhibit vigorous swelling in the early stages of exposure in the acid buffers. This brought out certain limitations of the interferometer procedure in differentiating between swelling and solution.

Electrodes prepared from those glasses that most nearly approximated the durability and hygroscopicity characteristics of Corning 015 approximated most nearly the theoretical pH response.

The pH response-hygroscopicity curves and the pH response-composition curves appear to reflect some
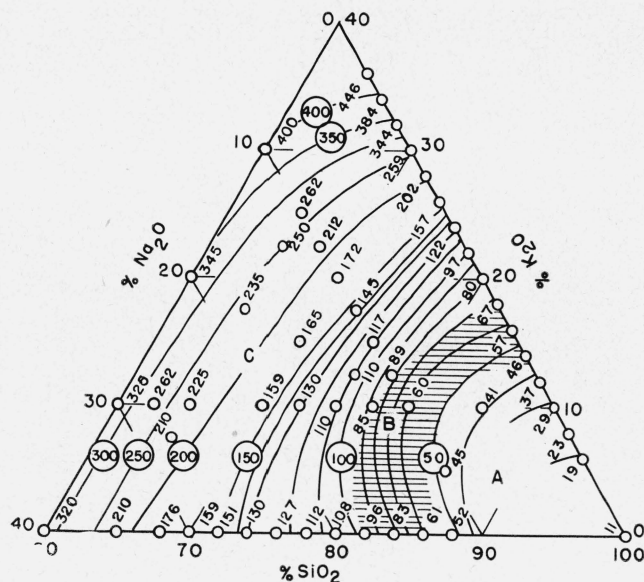

FIGURE 8. *Hygroscopicity of* Na$_2$O-K$_2$O-SiO$_2$ *glasses for 1-hr exposure, showing lines of equal hygroscopicity (iso-sorbs) and the shaded area over which electrodes prepared from these glasses developed as high as 56 mv per* pH.

of the critical compositions of the $Na_2O-K_2O-SiO_2$ phase equilibrium diagram. Perhaps the most interesting observation of the entire investigation is that the optimum pH response is shown by electrodes prepared from glasses that fall within the composition range in which α-tridymite is reported as the primary phase.

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