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Electrode Function (pH Response), Hygroscopicity, and Chemical Durability of Na_2O-CaO-SiO_2 Glasses

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The hydrogen electrode function (pH response), hygroscopicity (water sorbing property), and chemical durability (surface alteration in solutions of various hydrogen ion concentrations) were measured for a series of Na_2O-CaO-SiO_2 glasses. The resulting data both confirmed and extended the previous conclusion that glasses having inadequate hygroscopicity and poor chemical durability are incapable of producing satisfactory electrodes for pH measurements. Each family of glasses having equal SiO_2 content and varying Na_2O:CaO ratios was found to have a limited composition range that gave electrodes that approached the theoretical voltage. However, low hygroscopicity, poor chemical durability and devitrification limit the number of useful glasses to a small area from which the eutectic composition, 22 percent Na_2O, 6 percent CaO, 72 percent SiO_2 (Corning 015), is already known to be superior for its pH response. For the series of 70 percent SiO_2 content, the pH response and chemical durability curves appear to indicate the compositions at which changes in the primary phase are indicated by the phase diagram of the system.

I. Introduction

That the water content plays an important role in determining the suitability of glasses as indicators of the hydrogen ion activity of aqueous solutions was recognized by the early investigators of the glass electrode [1, 2, 3, 4, 5, 6, 7].[1] However, only recently have simple, semiquantitative techniques been available for readily comparing and classifying glasses for their water sorbing capacities [8, 9, 10, 11, 12, 13, 14]. Such hygroscopicity data upon comparison with the accompanying pH responses have shown in all cases investigated that glasses of very low hygroscopicity fail to develop the theoretical voltage of 59 mv per pH at 25° C predicted from the simplified Nernst equation, $\Delta E = 0.000198\ T\ \Delta\text{pH}$ [15].

Other conspicuous departures of the glass electrode from the straight-line relation of the Nernst equation appear in solutions that cause detectable changes in the chemical durability of the glass, such as hydrofluoric acid and various strong alkaline solutions [7, 16, 17, 18]. Voltage departures (errors) also occur in the "super acid" region, in nonaqueous solutions, and other solutions of a dehydrating nature [4, 18, 19, 20].

As the composition, hygroscopicity, pH response, voltage departure, and chemical durability of glasses seem to be so intimately associated, each of these properties was investigated for a series of Na_2O–CaO–SiO_2 glasses covering as great a range of compositions as the nature of the glasses and the limitations of the available glass-making equipment would permit.

II. Experimental Procedures

The procedure employed for determining hygroscopicity was that reported in previous publications [10, 11, 12], which consisted of weighing the water "sorbed" [21] upon exposing approximately 1.5 g of powdered glass that passed a 150 mesh Tyler standard sieve, to the high (approximately 98%) humidity maintained by a saturated solution of $CaSO_4 \cdot 2H_2O$. To insure speed in obtaining equilibrium and uniformity throughout the humidity chamber, the walls were lined with a blotter wick, while the atmosphere of the closed system

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

was circulated continuously. All glasses were exposed for 1- and 2-hr. periods at 25° C and the results reported as milligrams of water sorbed per cubic centimeter of sample.

The experimental electrodes were blown from tubes drawn from the melts at the time the glasses were poured. These electrodes were filled with mercury for the inner electrical connection [22], and were examined for voltage characteristics using a well-conditioned Beckman glass electrode as a reference standard. The voltage and pH observations were made at room temperature with a Beckman pH meter, model G. The pH response values (mv per pH) were calculated from the emf readings at pH 4.1 and pH 8.1. The voltage difference between the reference and experimental electrodes obtained in the buffer of pH 2 was taken as the zero voltage departure.

The durability measurements were obtained by the interferometer procedure [16, 18, 23, 24, 25] on optically flat specimens exposed to Britton-Robinson universal buffer solutions at 80° C ±0.2° C. All attack data are reported as change in thickness in fringes for 6-hr exposures, although some of the glasses were exposed for as short a period as 15 min in order to keep the attacks within the range limitations of the interferometer. Dimensional changes greater than three to five fringes are difficult to read, and the large values of swelling would be unobservable after 6 hr because of sloughing off of the swollen surface leaving a rough pitted area. As many of the glasses exhibited swelling in acid buffers, it was necessary to plot these data as "negative attack".

Throughout the paper, the glasses are identified by their composition (computed from the batch) given in weight percentage in the ratio of Na_2O:CaO:SiO_2.

III. Results and Discussion

Table 1 gives the characteristic voltage departures exhibited by electrodes prepared from typical Na_2O-CaO-SiO_2 glasses. In the same table also appear the hygroscopicity and chemical durability data for this series of glasses.

Figure 1, in which the pH response (mv per pH) between pH 4.1 and 8.1 is plotted against the hygroscopicity (water sorbed for 1-hr. exposure to 98% relative humidity), probably gives the most understandable picture of the electrode performance of this series of glasses. Electrodes prepared from glasses below a certain hygroscopicity (group A, fig. 1) failed to develop the theoretical 59 mv per pH at 25° C,[2] while those electrodes prepared from glasses that sorbed water between the approximate limits 30 to 75 mg per cm³ (group B, fig. 1)

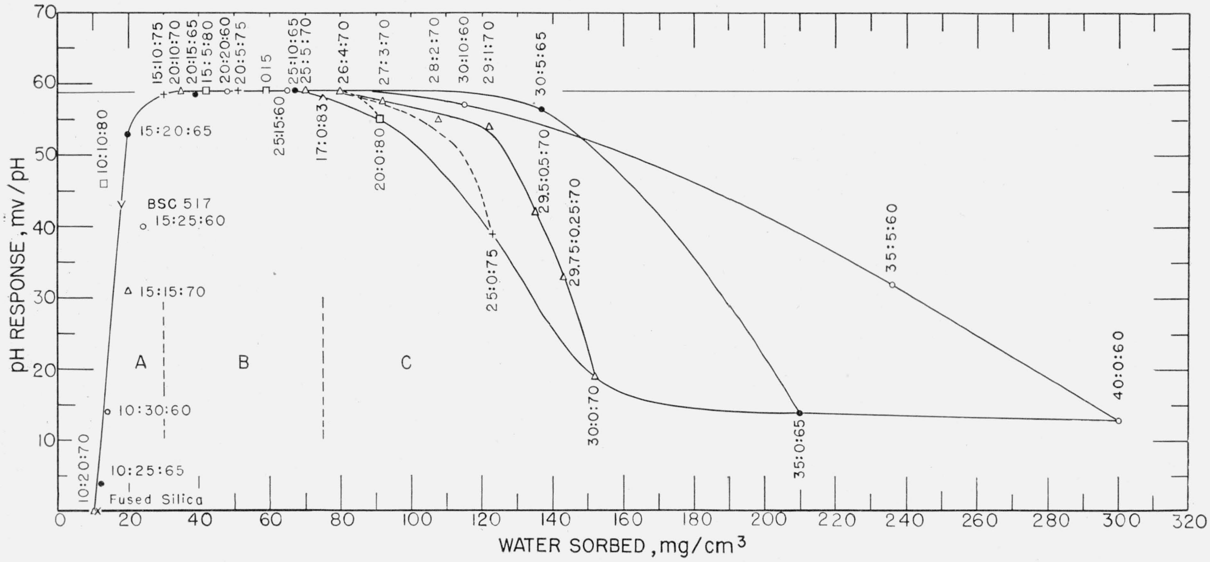

FIGURE 1. *Variation in* pH *response with increasing hygroscopicity for a series of* Na_2O-CaO-SiO_2 *glasses.*

Corning 015 electrode glass and BSC 517 optical glass are included for comparison.

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[2] Whether or not the failure of electrodes prepared from glasses of low hygroscopicity to indicate the theoretical voltage can be attributed to the limited sensitivity of the indicating instrument or to an actual failure of the glass to respond to H^+ ions is not yet certain.

TABLE 1. *Comparison of the hygroscopicity (water sorbed),* pH *response and chemical durability af some* Na_2O-CaO-SiO_2 *glasses*

No.	Glasses			Water sorbed after—		Voltage departure at pH—						pH response, pH 4.1 to pH 8.1	Chemical durability (attack) at pH					
	Na_2O	CaO	SiO_2	1 hr	2 hr	2.0	4.1	6.1	8.1	9.9	11.9		2.0	4.1	6.1	8.1	9.9	11.9
	%	%	%	*mg/cm³*	*mg/cm³*	*mv*	*mv*	*mv*	*mv*	*mv*	*mv*	*mv*/pH	*Fringes*	*Fringes*	*Fringes*	*Fringes*	*Fringes*	*Fringes*
1	10	30	60	14	20	0	57	------	238	------	486	14	⅒ swell	D swell [a]	D	1½+	2¼	16½.
2	15	25	60	24	35	0	−21	−2	53	126	234	40	D	D swell	¼	<0.2	3	19½.
3	20	20	60	48	88	0	6	1	6	47	77	59	D swell	D swell	⅒+	2¼	4½	24.
4	25	15	60	65	134	0	−10	−10	−10	14	55	59	D swell	D	2/10−	2/10 SC [b]	4½	27.
5	30	10	60	115	275	0	1	4	7	18	35	57	¼ swell	¼+ swell	⅒ SC	SC	5½	14½.
6	35	5	60	236	568	0	−22	15	86	152	269	32	36 swell	40 swell	45 swell	36 swell	SC swell	18.
7	40	0	60	300	--------	0	95	187	280	360	462	13	(c)	(c)	(c)	(c)	(c)	(c)
8	10	25	65	12	24	0	85	205	307	420	533	4	D swell	D swell	D	2½	6¼	10.
9	15	20	65	20	38	0	6	12	30	119	205	53	D swell	D swell	D swell	1¼	7½	10½.
10	20	15	65	39	85	0	0	0	2	9	14	58.5	D swell	D swell	D	3 SC, 1 attack	4½	10.
11	25	10	65	67	139	0	0	0	0	2	−7	59	D swell	⅒ swell	D swell	1¼	3¼	10.
12	30	5	65	137	270	0	−3	−3	3	17	68	57	3½ swell	4 swell	4½ swell	3¾	6¾	12.
13	35	0	65	210	--------	0	70	162	250	312	391	14	(c)	(c)	(c)	(c)	(c)	(c)
14	10	20	70	10	21	0	68	190	304	418	498	0	ND	ND	D	D SC	½	4½.
15	15	15	70	20	36	0	19	84	130	184	218	31	ND	ND	ND	D SC	½+	6.
16	20	10	70	35	88	0	0	0	0	0	−5	59	ND	ND	D	D SC	½	7.
17	25	5	70	70	160	0	0	0	0	2	9	59	½+swell	½+swell	¾ swell	½ swell	½+	7.
18	26	4	70	80	185	0	0	1	1	4	10	59−	2 swell	3 swell	3 swell	2 swell	D attack	7 attack.
19	27	3	70	92	219	0	1	5	9	14	19	57	6 swell	6 swell	7 swell	6 swell	4 swell	10 attack.
20	28	2	70	108	249	0	−2	4	14	26	34	55	18 swell	18 swell	18 swell	16 swell	6 swell	12 attack.
21	29	1	70	122	290	0	5	8	24	61	102	54	30 swell	30 swell	30 swell	30 swell	15 swell	70 attack.
22	29.5	0.5	70	135	314	0	2	15	72	136	210	42	75 swell	70 swell	70 swell	65 swell	40 swell	144 attack.
23	29.75	0.25	70	143	360	0	6	27	113	187	260	33	120 swell	108 swell	108 swell	108 swell	72 swell	288 attack.
24	30	0	70	152	379	0	45	112	205	299	400	19	60 attack [d]	70 attack [d]	------------	Pitted	Pitted	Pitted.
25	15	10	75	30	59	0	0	0	1	0	−6	58.7	ND	ND	ND	D	½+	3.
26	20	5	75	51	113	0	0	0	0	0	−1	59	⅒ swell	D swell	D swell	D swell	2/10	3−.
27	25	0	75	123	296	0	40	84	120	191	256	39	Pitted	15	15	17	------------	38.
28	10	10	80	13	32	0	25	44	75	101	155	46	ND	ND	ND	ND	D	2¾.
29	15	5	80	42	99	0	0	0	0	4	−7	59	ND	ND	ND	SC D	¼+	3−.
30	20	0	80	91	223	0	10	22	26	30	55	55	1½ swell	2 swell	2+swell	2 swell	1 swell	3 attack.
31	17	0	83	75	200	0	7	10	10	11	4	58	½+swell	½+swell	½swell	?	1½	3¾.
32	10	0	90	50	97	(e)	(e)	(e)	(e)	(e)	(e)	--------	D swell	D swell	D swell	D	------------	1½−.
33	Fused silica			11	12	(f)	(f)	(f)	(f)	(f)	(f)	0	ND	ND	ND	ND	ND	½.
34	Corning 015			59	138	0	0	0	0	0	3	59	2/10−swell	2/16−swell	2/10−swell	2/10 SC D	¼+	2−.
35	BSC 517 [9]			18	33	------	------	------	------	------	------	43	⅒	D	D	¼+	¾	1¾.

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[a] D, Detectable; ND, not detectable.

[b] SC, Surface cut.

[c] Failed to maintain polish.

[d] Durability data for this glass were calculated from the attack for 15 min at 80° C; however, it is not definitely known if the glass does or does not exhibit swelling during the earliest stages of exposure to the acid buffers.

[e] No tube.

[f] No definite pH response.

approximated the theoretical voltage over the pH range chosen for comparison. For the glasses of higher hygroscopicity (group C, fig. 1) the pH response again falls off, but, not as sharply as is the case for the glasses of very low hygroscopicity. This decrease in pH response at the higher hygroscopicities is associated with a progressive decrease in the chemical durability of successive members of the series.

It is evident from figure 1 that the previous suggestion that a low pH response might be used as a satisfactory indicator of the serviceability [3] of optical glasses [9] must be accepted with reservations. For example, a low pH response at the left end of the curve is accompanied by low hygroscopicity and satisfactory serviceability, while at the other end of the same curve a low pH response is accompanied by high hygroscopicity, poor chemical durability, and unsatisfactory serviceability.

It is interesting to note that the Na_2O–SiO_2 glasses 20:0:80, 25:0:75, 30:0:70, 35:0:65, and 40:0:60 fall into a family distinct from the Na_2O–CaO–SiO_2 glasses. Figure 2 shows how remarkably some of these glasses, chosen from the boundaries of group C, figure 1, differ among themselves in chemical durability.[4] Glasses 30:10:60, 35:5:60, and 30:5:65 containing CaO demonstrated pronounced swelling in the acid pH range while the Na_2O–SiO_2 glasses 30:0:70 and 25:0:75 were vigorously dissolved [12]. On the other hand, glass 20:0:80, which gave a much smaller voltage departure, showed swelling. A comparison of the voltage departure curves and the chemical durability curves for these six glasses shows the expected qualitative correlation. The voltage departures for electrodes from the glasses 30:0:70, 25:0:75, and 20:0:80 are in the same relative order as the durability curves for these glasses. The voltage departure curves for electrodes from the glasses containing CaO that exhibit swelling in the acid pH range also follow a durability sequence, although glass 30:5:65 possibly should not be compared with 30:10:60 and 35:5:60, as the latter are in a different family with respect to SiO_2 content. It is obvious that each series of glasses having a fixed percentage of SiO_2 falls into a distinct family (fig. 1). These

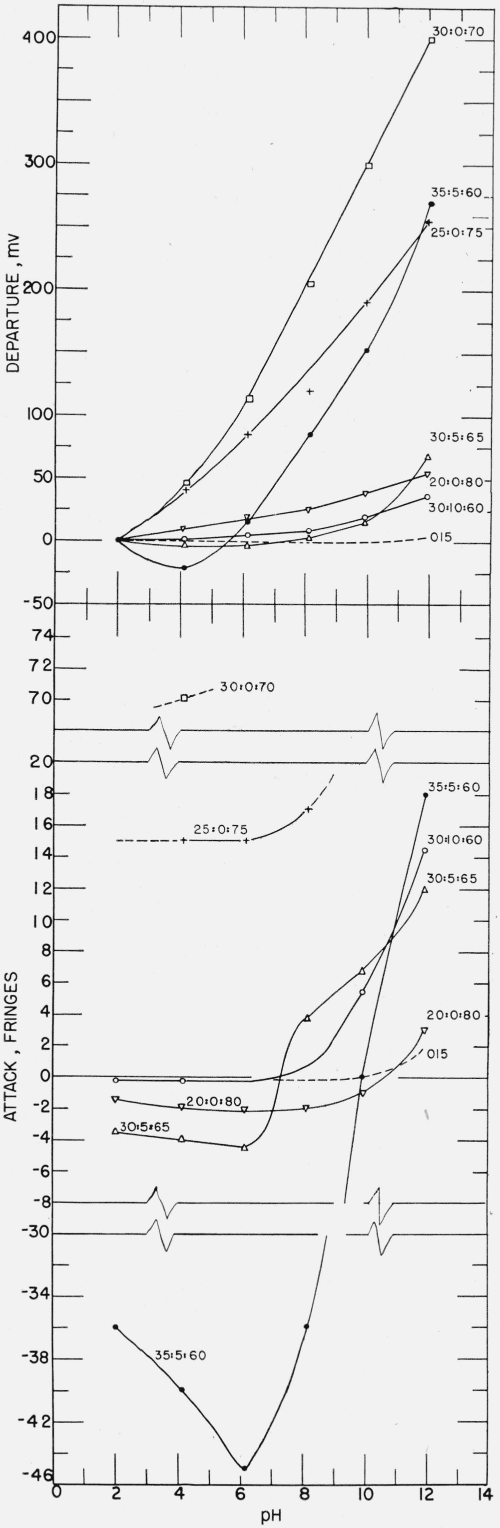

FIGURE 2. *Comparison of the chemical durability*-pH *curves with the voltage departure*-pH *curves for electrodes prepared from typical* Na_2O-CaO-SiO_2 *glasses of high hygroscopicity and poor chemical durability.*

Corning 015 electrode glass is included for comparison.

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[3] Ability to maintain a clear surface upon exposure to the atmosphere.

[4] Durability values on the Na_2O-SiO_2 glasses 40:0:60 and 35:0:65 were not obtained because the specimens did not maintain polished surfaces.

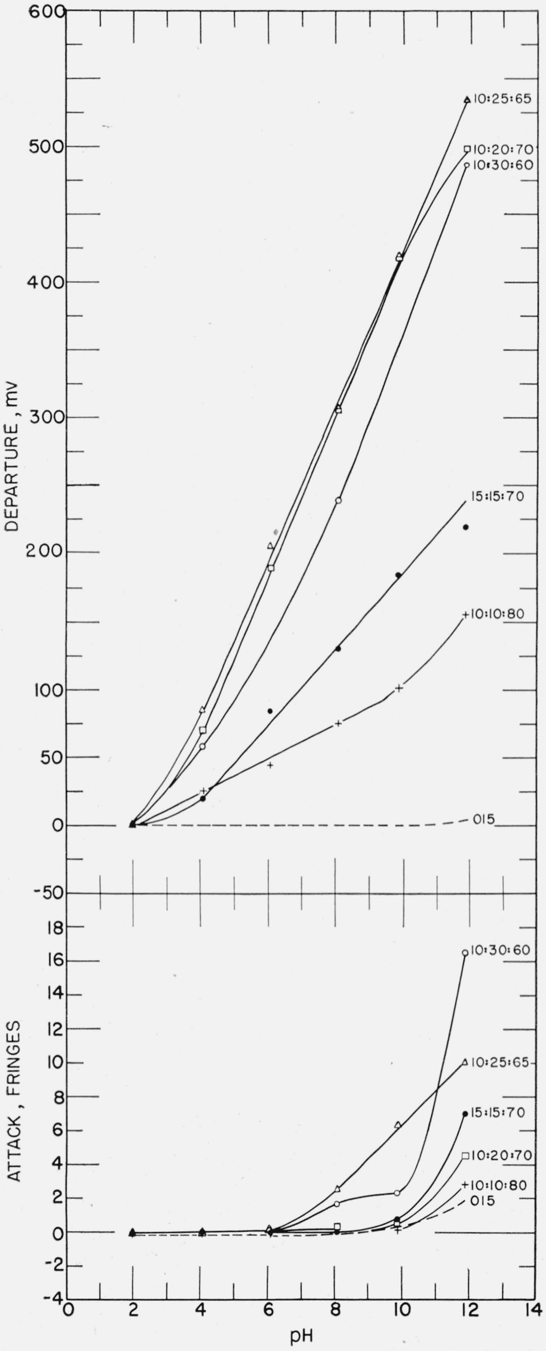

FIGURE 3. *Comparison of the chemical durability*-pH *curves with the voltage departure*-pH *curves for electrodes prepared from typical* Na_2O-CaO-SiO_2 *glasses of low hygroscopicity.*

Corning 015 electrode glass is included for comparison.

families coincide in their pH response only for those members that have adequate hygroscopicity and possess uniform chemical durability over the pH range chosen for comparison. For convenience in observing the trends within each family the pH response values in table 1 have been separated into groups. To obtain a qualitative picture of the inter-relationships between voltage departure, composition, pH response, hygroscopicity, and chemical durability of such a family of glasses (70% SiO_2) see figures 1, 6, 7, 8, and 9.

Electrodes from glasses of low hygroscopicity, group A of figure 1, show large voltage departures (fig. 3). In general the property of very low hygroscopicity seems to obscure any additional voltage departure attributable to chemical durability shifts in the alkaline range. Figure 4 shows that there are two apparent exceptions to this, viz. glasses 15:25:60 and 15:20:65. However, these two glasses are obviously not exceptions, inasmuch as their hygroscopicity is nearly adequate to yield the correct pH response, provided they possessed desirable durability characteristics.

The glasses in group B of figure 1 (i. e. those having adequate hygroscopicity and uniform chemical durability over an extended pH range and with reduced attack in the alkaline range) produced electrodes with very much decreased voltage departures (fig. 5). Also, these voltage departures are confined to the alkaline pH range of decreased chemical durability. The difference in performance of some of these electrodes in the alkaline range can possibly be rationalized. For instance, glasses 20:10:70 and 25:5:70 exhibit voltage departures in the opposite directions. Although the attack for the two glasses was the same at pH 11.9, such is not the case in the acid range. Glass 20:10:70 had no detectable attack at pH 4.1, so it is conceivable that going from no attack to an appreciable attack is not altering the surface of the glass nearly so radically as for glass 25:5:70, which passed from a swollen condition in the acid range to an over-all solution in the alkaline buffers. However it is also possible that accidental variations in blowing the electrode bulbs were responsible for such reversals.

In order to obtain some indication of the com-

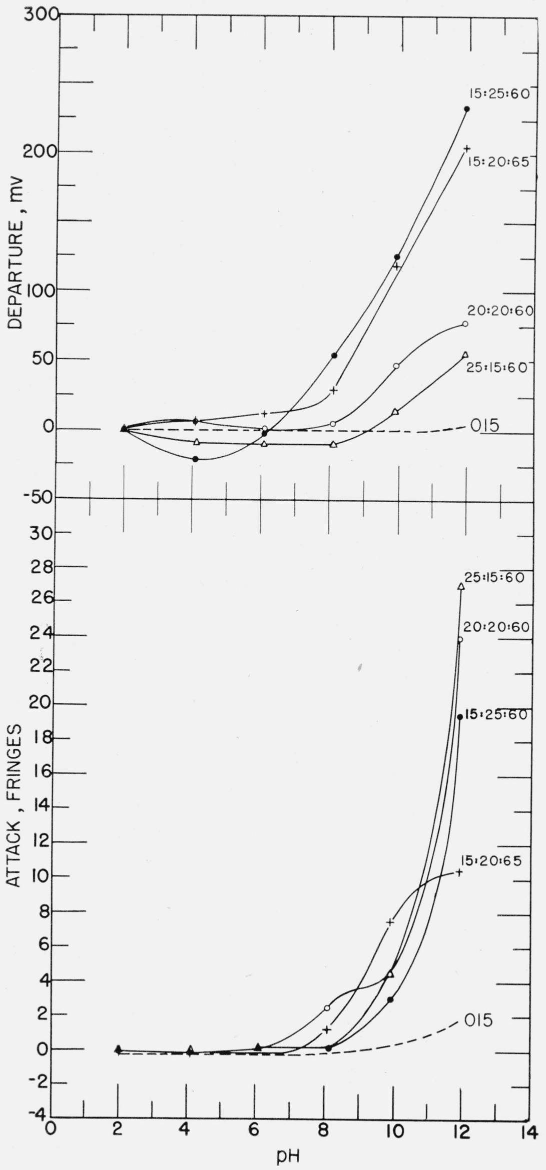

FIGURE 4. *Comparison of the chemical durability*-pH *curves with the voltage departure*-pH *curves for electrodes prepared from typical* Na_2O-CaO-SiO_2 *glasses having poor chemical durability in the alkaline range with large voltage departures appearing in this same* pH *region.*

Corning 015 electrode glass is included for comparison.

position limits within which electrodes approximating the theoretical pH response can be made, figure 6 was prepared showing composition lines of equal hygroscopicity.[5] The compositions of the experimental glasses are represented by small open circles. Those that produced electrodes that approximated the theoretical 59 mv per pH are inclosed in small hexagons, while the interpolated compositions are located as heavy dots. The lines of equal hygroscopicity (iso-sorbs) are identified by their sorption values inscribed in circles.

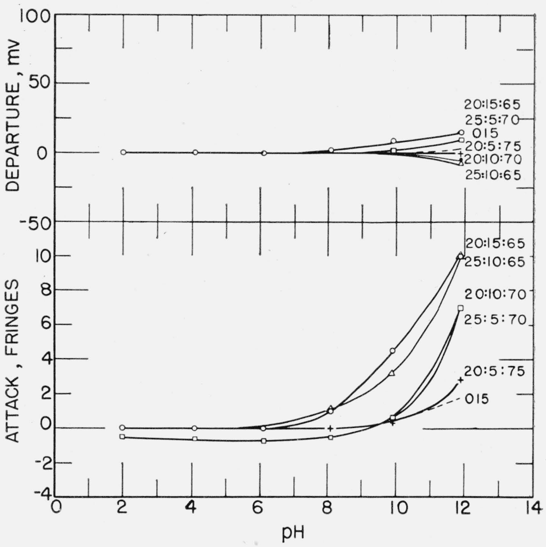

FIGURE 5. *Comparison of the chemical durability*-pH *curves with the voltage departure*-pH *curves for electrodes prepared from typical* Na_2O-CaO-SiO_2 *glasses of adequate hygroscopicity for* pH *determination.*

The resulting figure reveals that the area of promising compositions (shaded) is bounded by two hygroscopicity barriers, the one of decreasing Na_2O content, which is too "dry" and the other of increasing Na_2O, which is too "wet". The latter area is also a region of poor chemical durability. Thus figure 6 indicates the same three groupings A, B, and C that are shown in figure 1.

The glasses included in the shaded area of figure 6 are not all equally satisfactory for pH measurements. Glasses 20:20:60 and 25:15:60 (table 1) devitrified so rapidly upon reheating, that it was almost impossible to obtain unpunctured electrodes. Successful electrodes, when obtained, deteriorated so very rapidly because of the poor durability of the glasses that the erratic voltage readings obtained must be considered as superficial. Electrodes prepared from glasses 20:15:65 and 25:10:65 also deteriorated rapidly.

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[5] The position of these iso-hygroscopicity lines for the 1-hr exposures was determined by plotting the interpolated values obtained from the hygroscopicity composition data drawn as smooth curves. No effort was made to establish a correspondence between the apparent breaks in the hygroscopicity-composition curves and the critical compositions of the phase equilibrium diagram, partly because of the paucity of data, partly because of the limited capacity of the humidity chamber which necessitated the splicing of data, but more particularly because the compositions of the glasses were known only from the batch compositions.

It is obvious that these four glasses do not rightfully deserve the favorable position assigned them in figures 1 and 6. Thus the useful range of the shaded area in figure 6 is greatly reduced from left to right. The area shaded with broken lines is unexplored and is possibly too broad.

The glass compositions of optimum pH performance, (i. e. those that offer a compromise between adequate hygroscopicity and acceptable chemical durability) would probably appear in figure 6 as a line rather than an area. With all other factors involved taken into consideration, including the liquidus temperatures, the difficulty of melting, fining, drawing tubes, and tendency toward devitrification upon reworking, it is conceivable that but one composition makes the most satisfactory compromise of all these factors. The glass having the composition, 22 percent Na_2O, 6 percent CaO, 72 percent SiO_2, near the eutectic having the lowest melting temperature for this three component system [2, 3, 7], seems to be a worthy candidate for this honor for pH measurements at room temperatures. For use at elevated temperatures a glass of much better chemical durability is desirable. As the electrical resistance of glass electrodes decreases greatly with increasing temperatures [26, 27], glasses of lower hygroscopicity and much improved chemical durability can be used for pH determinations at elevated temperatures.

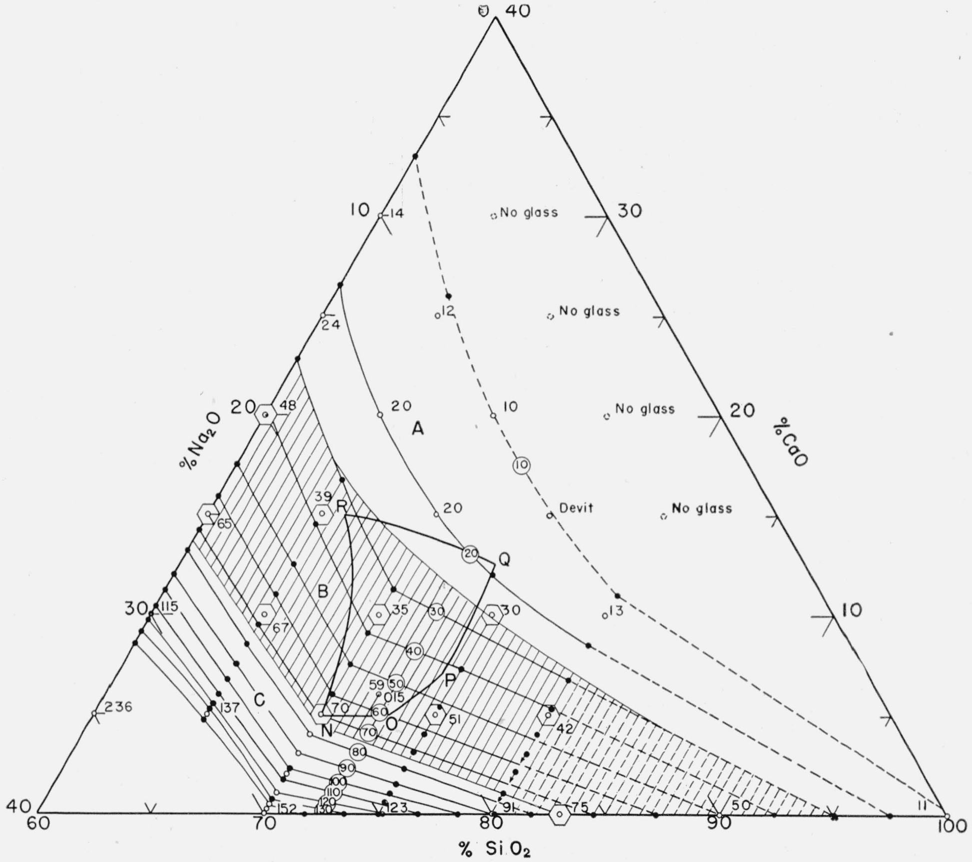

FIGURE 6. *Hygroscopicity-composition relation for glasses of the ternary system* Na_2O-CaO-SiO_2.

Shaded area indicates composition range over which electrodes were prepared approximating the theoretical pH response of 59 mv per pH.

Concerning the possibility of any glasses of the Na_2O-CaO-SiO_2 system possessing better performance in the high pH range than does this eutectic glass, a few of the experimental electrodes gave small negative departures in the buffer solution at pH 11.9. As the reference electrode was also a glass electrode normally showing a small positive departure in the alkaline range, these negative departures reported for the experimental electrodes indicate that some improvement for determinations of high pH values might be expected. Electrodes from glasses 20:10:70, 15:10:

75, and 20:5:75 (table 1) are typical examples of compositions showing this negative departure at pH 11.9.

If the region N O P Q R of the Na_2O-CaO-SiO_2 phase diagram, which includes the compositions of the best commercial glasses obtainable from this ternary system [29], is superimposed upon figure 6, most of the factors controlling the practical composition limitations for glass electrode use can be seen at a glance. This area includes the composition range in which devitrite ($Na_2O \cdot 3CaO \cdot 6SiO_2$) is the primary phase. Glasses near the boundary RN are too readily attacked by water and buffer solutions except near R where devitrification causes trouble. Below the boundary NO, excessive hygroscopicity and poor chemical durability limit the usefulness of the glasses. Above RQ, devitrification, low hygroscopicity, and high melting temperatures interfere. To the right of O P Q, the area of adequate hygroscopicity is limited by devitrification and high melting temperatures.

A fairly comprehensive picture of the nature of the Na_2O-CaO-SiO_2 glasses can be obtained by plotting the voltage departure-hygroscopicity curve for 70 percent SiO_2, and comparing it with the accompanying chemical durability-hygroscopicity curve, figure 7. The resulting two curves illustrate the subtle relationship between glass electrode performance, hygroscopicity, chemical durability and composition. For instance, voltage departures appear for electrodes from glasses of low hygroscopicity and for electrodes from glasses of high hygroscopicity and poor chemical durability. The over-all picture also suggests that these voltage departures appear at the compositions at which the phase diagram indicates a shift in the primary phase [28, 29, 30]. To emphasize this point, the approximate positions at which the primary phases $CaO \cdot SiO_2$, $Na_2O \cdot 3CaO \cdot 6SiO_2$, and Na_2O-$2SiO_2$ appear, are indicated on the graph. Perhaps the most interesting feature illustrated in figure 7 is the effect of small additions of CaO to the parent Na_2O-SiO_2 glass. The reversal from rapid solution to an even more rapid rate of swelling brought about by the addition of as little as 0.25 percent CaO suggests pertinent experiments concerning the effect of network-modifiers. [14, 27]. Any other families of glasses of constant SiO_2 content would give curves quantitatively different from, but qualitatively similar to figure 7. This is easy to visualize upon inspection of figure 1.

The performance (voltage departure), over an extended pH range of typical electrodes prepared from members of 70 percent SiO_2 series of glasses and the chemical durability of the individual glasses over the same pH range are plotted in figure 8. One point of interest in the electrode performance is the steady improvement with increasing percentages of CaO to near 10 percent, followed by a sharp reversal for percentages above this value.

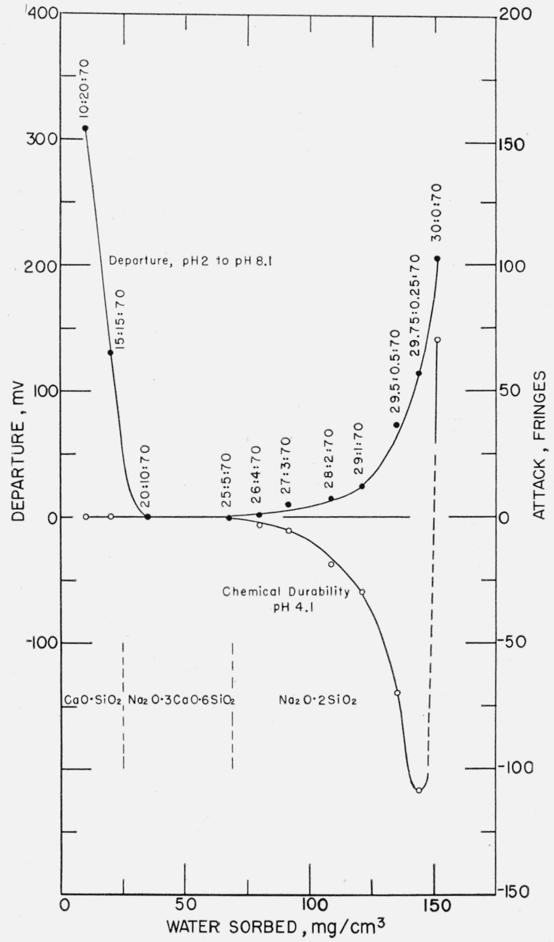

FIGURE 7. *Comparison of the chemical durability-hygroscopicity curve of* Na_2O-CaO-SiO_2 *glasses of 70%* SiO_2 *content.*

●, Voltage departure; ○, chemical durability.

The voltage departure curves for these glasses of low hydroscopicity are plotted in figure 8 as broken lines to distinguish them from the curves of glasses having poor chemical durability. The

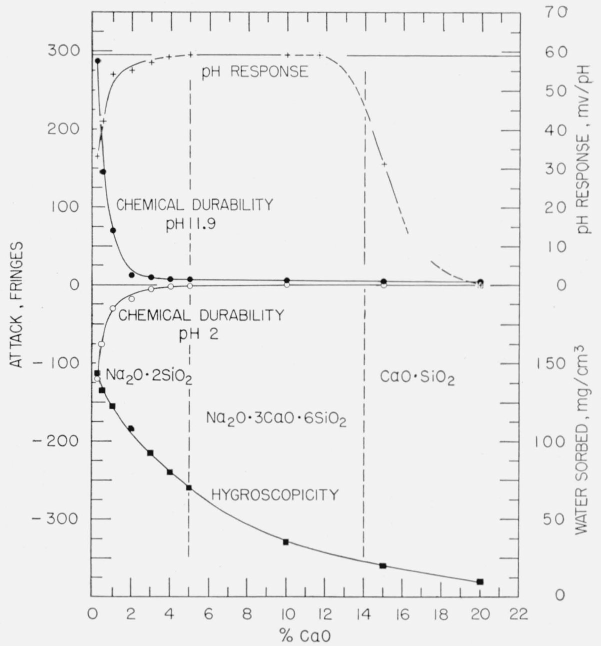

FIGURE 9. *Comparison of the* pH *response, the hygroscopicity, and chemical durability at* pH *2 and 11.9 of a series of* Na_2O-CaO-SiO_2 *glasses containing 70%* SiO_2.

The compositions at which a new primary phase appears in the equilibrium diagram are indicated by vertical dashed lines.

durability curves are of interest because of the exaggerated swelling in the acid range exhibited by members having low percentages of CaO.

The question always arises whether the chemical or physical properties of a series of glasses reflect any of the critical points of the corresponding phase equilibrium diagram [31]. To determine what evidence the present data offer on this subject, the properties of pH response, chemical durability at pH 2 and 11.9 and, hygroscopicity were plotted against the percentage of CaO for the glasses of the 70 percent SiO_2 series (fig. 9). The chemical durabilities at pH 2 and 11.9 were chosen because these curves departed in opposite directions, thereby emphasizing the composition at which a marked durability shift occurred. These chemical durability curves and the pH response curve superficially suggest the composition at which the primary phase changes from $Na_2O \cdot 2SiO_2$ to $Na_2O \cdot 3CaO \cdot 6SiO_2$. The evidence is

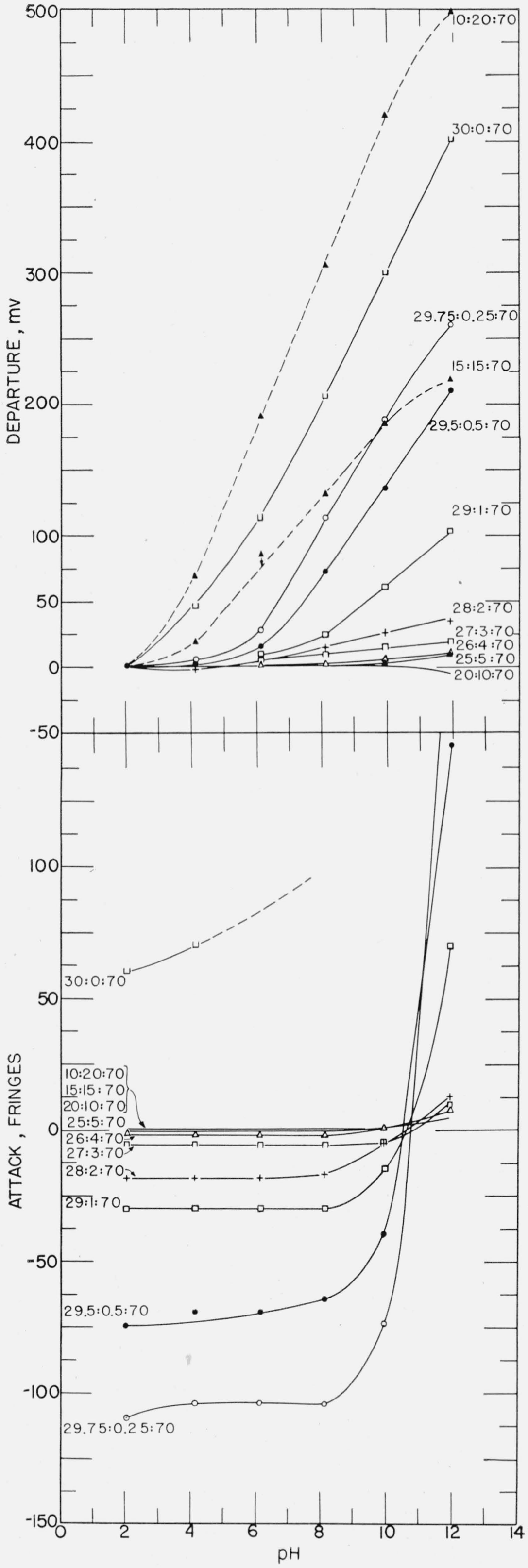

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FIGURE 8. *Comparison of the chemical durability*-pH *curves with the voltage departure*-pH *curves for electrodes prepared from* Na_2O-CaO-SiO_2 *glasses containing 70%* SiO_2 *with the* Na_2O *pregressively replaced by* CaO.

less convincing although not entirely lacking for the other boundary of the devitrite field at which $CaO \cdot SiO_2$ appears as the primary phase. The hygroscopicity curve cannot be offered as evidence, because of the experimental limitations imposed in obtaining the data.

IV. Summary

The pH response, hygroscopicity, and chemical durability of a series of Na_2O-CaO-SiO_2 glasses have been investigated. The results obtained reemphasize the fact that glasses of inadequate hygroscopicity fail to yield electrodes that perform satisfactorily as indicators of the hydrogen ion activity of aqueous solutions at room temperatures. Many of the glasses exhibited swelling in the acid buffers, and all of them showed the usual attack in the alkaline range. For any family of glasses of constant percentage of SiO_2 the extent of swelling in the acid pH range decreased progressively with the replacement of Na_2O by CaO. For such glasses the chemical durability in alkaline solutions also improved.

The glasses of the Na_2O-CaO-SiO_2 series, which produced electrodes that most nearly approximated the theoretical straight-line relation of the Nernst equation, were those whose hygroscopicity and chemical durability characteristics most nearly approached the corresponding properties of the glass of the eutectic composition, 22 percent Na_2O, 6 percent CaO, 72 percent SiO_2 (Corning 015). In accordance with previous experience, all glasses of poor chemical durability failed to yield satisfactory electrodes for pH measurements.

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