

Atypical pH Response of Some Nonsilicate Glasses

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It is generally believed that a glass, in order to yield electrodes whose voltage characteristics serve as a satisfactory indicator of the hydrogen-ion activity of aqueous solutions in accord with the dictates of the Nernst equation, must possess at least a minimum hygroscopicity and an adequate chemical durability, uniform over an extended pH range. Three series of nonsilicate glasses, $\text{Na}_2\text{O-MgO-P}_2\text{O}_5$, $\text{Na}_2\text{O-GeO}_2$, and $\text{BaO-B}_2\text{O}_3$, were investigated for these three properties. In accord with the fact that all of the members of these series exhibited very poor chemical durability and many of them possessed very low hygroscopicity, none of them produced electrodes that had a satisfactory pH response. All of the series confirmed the generally accepted fact that hygroscopicity cannot be directly correlated with chemical durability of glasses. For example, some members of the $\text{BaO-B}_2\text{O}_3$ series possessed hygroscopic properties that compared favorably with Pyrex 7740, yet had unusually poor chemical durability.

1. Introduction

The question is often asked, "Is the presence of a silicate framework necessary in order that a glass may yield electrodes that possess satisfactory voltage response to hydrogen-ion activity of aqueous solutions?" Certainly, not all silicate glasses possess this interesting and useful characteristic. In fact, considerable evidence indicates that only those silicate glasses that have adequate hygroscopicity and uniform chemical durability over an extended pH range produce electrodes that approximate the dictates of the Nernst equation [1, 2, 3].¹ These past experiments indicate in a general way that these features of adequate hygroscopicity and satisfactory chemical durability may be of more significance than the particular chemical constituents of the electrode glass in determining the suitability for use in pH measurements. With these features in mind, the following limited series of glasses containing no SiO_2 were examined for their pH response: Soda-magnesia-phosphate ($\text{Na}_2\text{O-MgO-P}_2\text{O}_5$); soda-germania ($\text{Na}_2\text{O-GeO}_2$); and baria-boric oxide ($\text{BaO-B}_2\text{O}_3$).

2. Experimental Procedures

The experimental procedures followed in this investigation for chemical durability (surface alteration by an interferometer method [2, 4]), hygroscopicity (water sorbed, mg/cm^3 [3, 4]), and pH response (mv/pH [4]) were generally similar to those reported in earlier publications on silicate glasses. Such special alteration of procedures as were dictated by the nonsilicate glasses are mentioned in the text for those experiments in which changes were required.

As it was impossible to fuse phosphate mixtures in platinum without destruction of the crucible, the $\text{Na}_2\text{O-MgO-P}_2\text{O}_5$ glasses were prepared in a special zirconia (ZrO_2)-lined fire-clay crucible adopted for the purpose by Douglas H. Blackburn and Louis G. Cossette. The zirconia liner minimized objectionable contamination of the melts, which in turn greatly

improved the spectral transmittance of the resulting glasses to ultraviolet light.

The $\text{Na}_2\text{O-GeO}_2$ glasses were melted and fired in a platinum crucible. No glasses were obtainable for 60 percent and 70 percent of GeO_2 . Furthermore, the glasses near 85 percent and 90 percent of GeO_2 exhibited a strong tendency to devitrify, even on rapid chilling of the melts, whereas those above and below this region showed less tendency to do so.

The $\text{BaO-B}_2\text{O}_3$ series of glasses was also prepared in platinum. The compositions produced included the entire glass-making range for this binary system.

3. Results and Discussion

3.1. $\text{Na}_2\text{O-MgO-P}_2\text{O}_5$ Glasses—Chemical Durability, Hygroscopicity, and pH Response

Table 1 and figures 1, 2, 3, and 4 illustrate the chemical durability, hygroscopicity, and pH response of a series of $\text{Na}_2\text{O-MgO-P}_2\text{O}_5$ glasses compared with Corning 015 electrode glass, Pyrex 7740 (a glass of low hygroscopicity), and a P_2O_5 glass.² The chemical durabilities of these phosphate glasses (fig. 1) are markedly different in magnitude and in kind from the various series of silicate glasses previously studied. Each of the present glasses was attacked vigorously at all pH values, and none of them exhibited swelling in acid buffers, as was so characteristic of many of the silicate glasses [2, 4]. This indicates there was no preferential leaching at any pH of certain constituents of the glass, hence no leaving behind of a chemically durable, negatively charged framework [5], which in turn suggests that no satisfactory electrical equilibrium, either real, pseudo, or transient, could be set up suitably for indicating hydrogen-ion activity of aqueous solutions. Further, the hygroscopicity of these glasses (water sorbed in 1 hour), table 1 and figures 2 and 3,

² The P_2O_5 glass was prepared from ammonium dihydrogen phosphate, $\text{NH}_4\text{H}_2\text{PO}_4$, in the special fire-clay crucible with a ZrO_2 liner. The entire batch was placed in the crucible at room temperature and then heated to $1,000^\circ\text{C}$ in approximately 2 hours. This procedure was necessary, because if the batch was added to a hot crucible, the chilling effect resulting from the rapid evolution of gases invariably cracked the crucible. The resulting glass at room temperature showed such features as flexibility upon the steady application of bending forces, but shattered readily under a sharp blow. It apparently can be maintained indefinitely with adequate desiccation.

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

TABLE 1. Chemical durability, hygroscopicity, and pH response of some Na₂O-MgO-P₂O₅ glasses

Composition (batch ratio)		Surface alterations for exposures of 6 hr at 80° C and pH—						Water sorbed in—		pH response between pH 4.1 and pH 8.2
NaH ₂ PO ₄ H ₂ O	MgH ₄ (PO ₃) ₂	2.0	4.1	6.0	8.2	10.2	11.8	1 hr	2 hr	
0	10	<i>Fringes</i> 18 attack	<i>Fringes</i> 24 attack	<i>Fringes</i> 24 attack	<i>Fringes</i> 40 attack	<i>Fringes</i> 156 attack	<i>Fringes</i> 900 attack	mg/cm ³ 17	mg/cm ³ 34	mv/pH 1.
1	9	4½ attack	3 SC ^b attack	7½ attack	21 attack	27 attack	365 attack	19	37	-----
2	8	3 attack	3 attack	9 attack	12 attack	20 attack	100 attack	19	32	17.
3	7	3 attack	2½ attack	6 attack	7½ attack	11 attack	90 attack	21	37	23.
4	6	6 attack	6 attack	3 attack	3 attack	15 attack	85 attack	22	48	Devit. ^d
5	5	6 attack	6 attack	6 attack	12 attack	18 attack	270 attack	23	60	Devit.
6	4	12 attack	9 attack	10 attack	12 attack	27 attack	540 attack	29	84	10.
P ₂ O ₅ [12, 14]		WS ^e	WS	WS	WS	WS	WS	277	655	-----
Corning 015		2/10-swell	2/10-swell	2/10-swell	SC	1/4+attack	2 attack	104	168	59.
Pyrex 7740		ND ^a	ND	ND	D ^{cb}	1/4-attack	1¼ attack	17	24	12.

^a ND, not detectable; ^b SC, surface cut; ^c D, detectable; ^d Devit., devitrification; ^e WS, water soluble.

was considerably less than for most pH responsive silicate glasses [4, 6].³ Thus the second require-

³ The lower limit of hygroscopicity for a satisfactory pH responsive glass has not yet been established. For the Na₂O-CaO-SiO₂ and Na₂O-PbO-SiO₂ glasses a "sorption" value of about 30 mg/cm³ seemed to be indicated for 1 hour exposure to 98-percent relative humidity, whereas the Li₂O-SiO₂ glasses showed a somewhat lower limit. See, Donald Hubbard, Given W. Cleek, and Gerald F. Rynders, *Electrode function (pH response), hygroscopicity, and chemical durability of Na₂O-CaO-SiO₂ glasses*, J. Research NBS **44**, 247 (1950) RP2076; Donald Hubbard, Mason H. Black, and Gerald F. Rynders, *Electrode function (pH response), hygroscopicity, and chemical durability of soda-lead oxide-silica glasses*, J. Research NBS **45**, 430 (1950) RP2154; Donald Hubbard and Given W. Cleek, *Deuterium and hydrogen electrode characteristics of lithia-silica glasses*, J. Research NBS **49**, 267 (1952) RP2363.⁴

ment for satisfactory electrical response to hydrogen-ion activity is also lacking in these glasses. In accordance with the poor durability and low hygroscopicity of the available members of this series, no electrodes were obtained possessing satisfactory pH response (table 1 and fig. 4).

The chemical durabilities of these phosphate glasses are so poor that they obviously cannot be used as containers for aqueous solutions. However, their hygroscopicity is such that they might tenta-

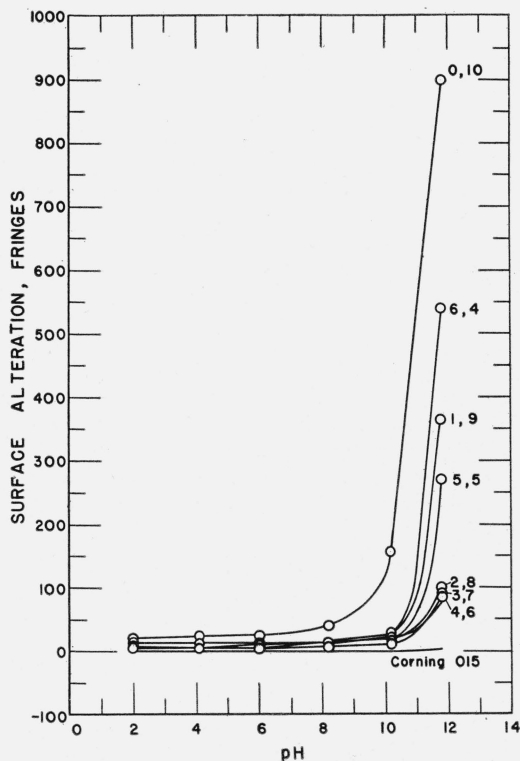


FIGURE 1. Chemical durability of Na₂O-MgO-P₂O₅ glasses.

Exposure 6 hr, 80° C. Curve designations refer to composition ratios of table I.

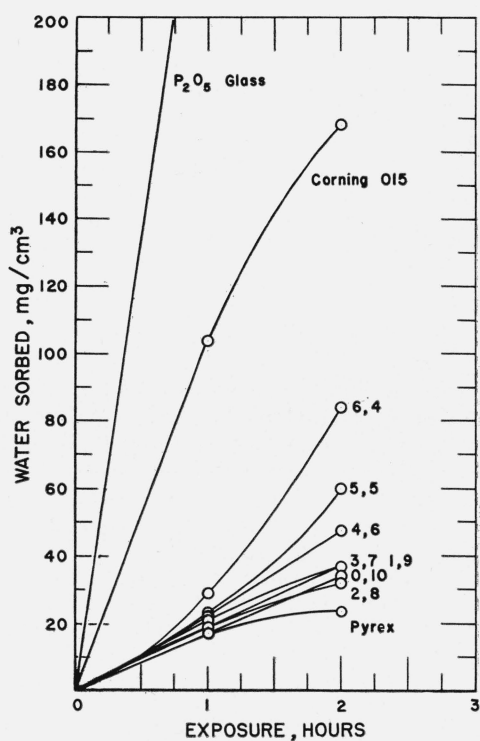


FIGURE 2. Comparison of the hygroscopicity of a series of Na₂O-MgO-P₂O₅ glasses with Pyrex 7740 and Corning 015.

Exposure to approximately 98-percent relative humidity. Experimental values for water sorbed by P₂O₅ glasses are given in table I.

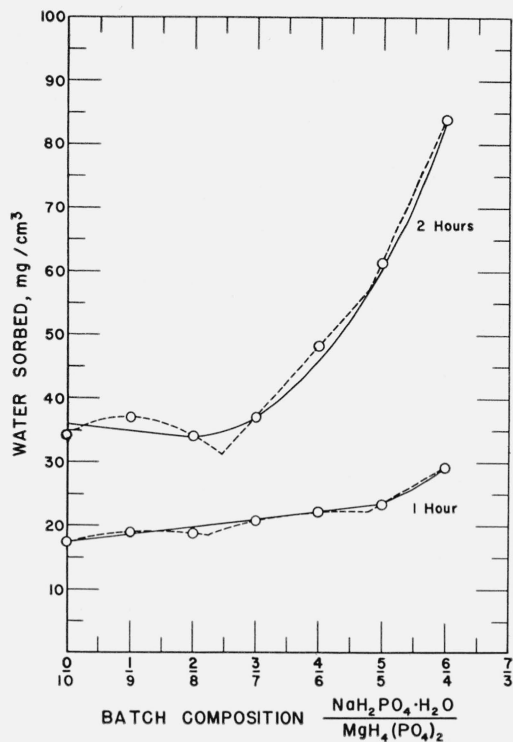


FIGURE 3. Hygroscopicity-composition curves for a series of $\text{Na}_2\text{O-MgO-P}_2\text{O}_5$ glasses.

tively be expected to maintain clear surfaces upon exposure to air.

Figure 3 shows the results of plotting the hygroscopicity against the batch composition ratios. In the absence of phase-equilibria data, and because of the uncertain composition and limited range, it is questionable if one is justified in plotting the broken lines other than to point out that the same features seem to be reflected in the chemical-durability curves and to a less and uncertain extent in the pH-response data (fig. 4). The pH response data was particularly uncertain because of pronounced devitrification while attempting to blow electrode bulbs. The procedure finally adopted was to merely seal the end of thin-walled tubes and fill them with mercury [7]. Even this simplified technique was inadequate for glasses 4:6 and 5:5.

3.2 $\text{Na}_2\text{O-GeO}_2$ Glasses—Chemical Durability-Hygroscopicity, and pH Response

Figure 5 shows the chemical durability-pH curve over the range pH 2 to pH 11.8 for a soda-germania glass containing 5 percent of Na_2O and 95 percent of GeO_2 . This glass is more vigorously attacked in the acid range below pH 4 and in the alkaline range above pH 8 than at intermediate pH values; nevertheless, it is attacked vigorously by all the buffer solutions. No comparison is readily possible with the customary pH-responsive silicate glasses, as the

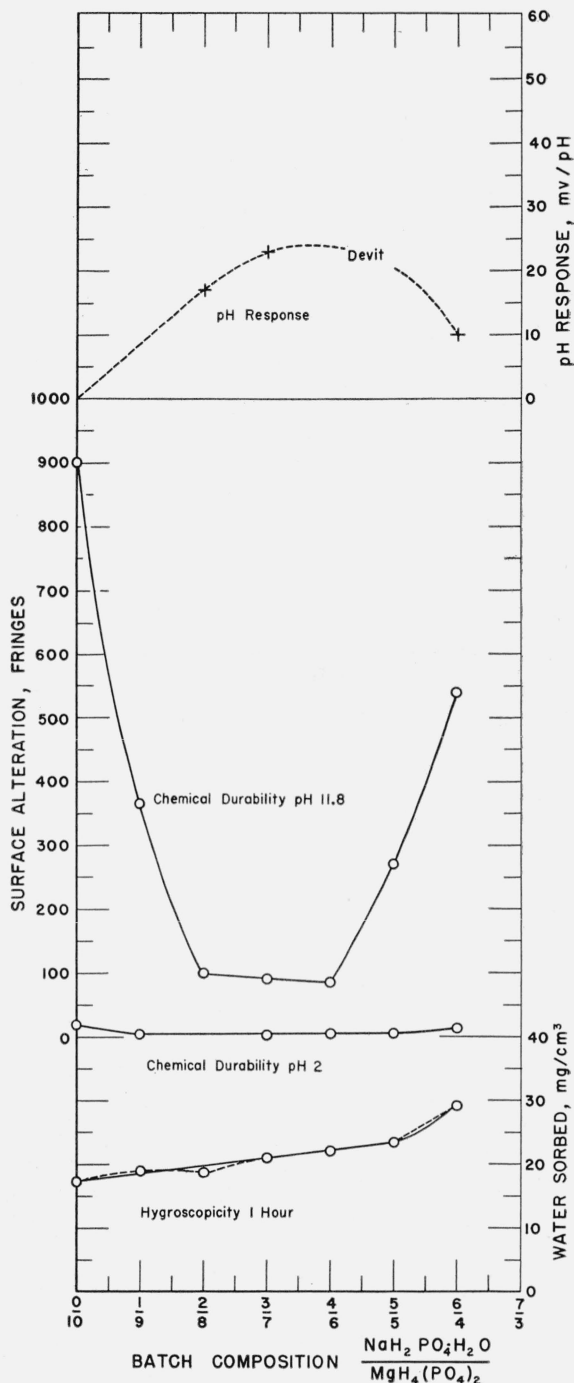


FIGURE 4. Comparison of the pH response of electrodes prepared from some $\text{Na}_2\text{O-MgO-P}_2\text{O}_5$ glasses with the chemical durability and hygroscopicity of the glasses.

surface alteration of this soda-germania glass exposed for 1 minute at 25°C is much larger than the attack or swelling exhibited by an acceptable silicate glass after 6 hours of exposure at 80°C . As the available samples of most of the germania glasses were of inadequate size for use as specimens for chemical

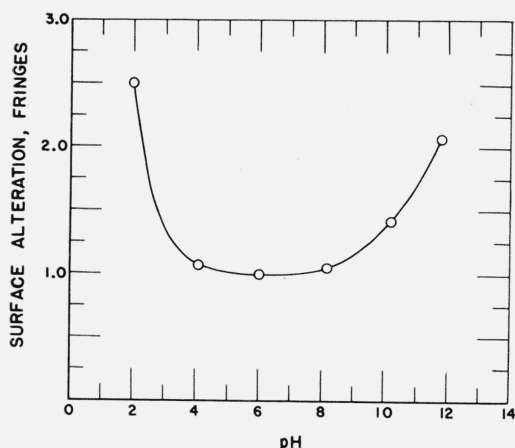


FIGURE 5. Chemical durability of a soda-germania glass, Na_2O , 5 percent; GeO_2 , 95 percent.

Exposure 1 min at 25°C .

durability by the interferometer procedure, in addition to the fact that some of the members, such as the 85 percent GeO_2 , devitrified so rapidly that clear specimens for interferometer flats could not be made even upon rapid chilling, another procedure for intercomparison of the chemical durability of the members of this series was tried. The total solids dissolved (milligrams per gram of glass) in 50 ml of distilled water in 1 hour with intermittent agitation at 25°C was determined on powders that passed a 150-mesh sieve. This procedure for determining the relative chemical durabilities of these $\text{Na}_2\text{O-GeO}_2$ glasses proved to be generally unsatisfactory, but at the same time gave interesting results (table 2 and fig. 6). The series revealed a minimum weight of total solids extracted near 85 percent GeO_2 . Further, the samples for 85 percent and 100 percent of GeO_2 gave persistent colloidal suspensions that passed through the filters. This suspended material was recorded among the total solids. The other members of the series filtered clear. Pyrex 7740 and Corning 015 were similarly treated for comparison. The Pyrex powder gave a slightly opalescent filtrate. Obviously, the chemical durabilities of these $\text{Na}_2\text{O-GeO}_2$ glasses compare very unfavorably with pH-responsive glasses.

The hygroscopicity curves for 1 and 2 hours of exposure to 98 percent relative humidity and the water retained upon heating to 110°C after the 2 hours of exposure are given in figure 6. Each of these curves passes through a minimum near 90 percent of GeO_2 .

As it was impossible to blow electrode bulbs of the usual Cremer-Haber type, an effort was made to produce glass electrodes by coating platinum wire with a thin unbroken layer of glass by dipping the wire in the molten glass, or by means of the burner to run a bead of the glass along the wire, leaving a thin glass coating [7]. If a successful continuous film of glass was established, electrodes of high resistance, as indicated by the megohm bridge, were obtained. This very high initial resistance fell

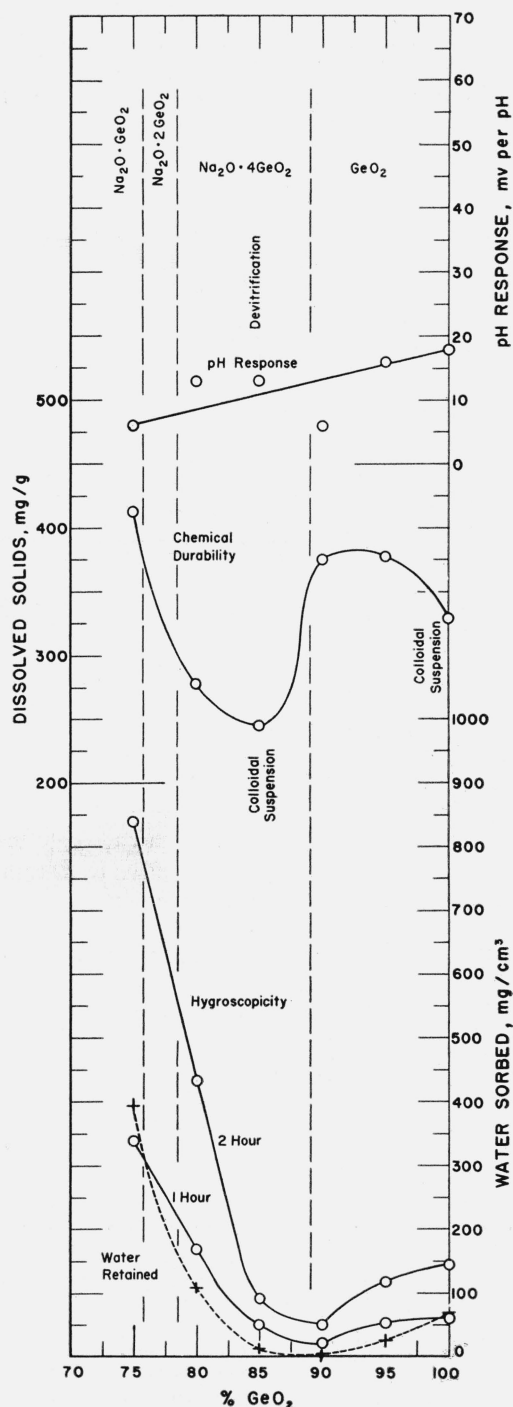


FIGURE 6. Comparison of the pH response of electrodes prepared from some $\text{Na}_2\text{O-GeO}_2$ glasses with the chemical durability and hygroscopicity of the glasses.

rapidly toward the lower limit of the instrument as the glass took on water and was dissolved in the buffers. The voltage responses obtained were transient and must be classified as superficial or even spurious. Certainly the pH-response characteristics of these electrodes were no better than the values

TABLE 2. Chemical durability, hygroscopicity, and pH response of a series of Na₂O-GeO₂ glasses

Glasses		Chemical durability in H ₂ O		Water sorbed in—		Water retained at 110° C	pH response
Na ₂ O	GeO ₂	Solids dissolved	Remarks	1 hr	2 hr		
<i>Percent</i>	<i>Percent</i>	<i>mg/g</i>		<i>mg/cm³</i>	<i>mg/cm³</i>	<i>mg/cm³</i>	<i>mv/pH</i>
25	75	412	Filtered clear.....	338	841	392	6
20	80	278	do.....	168	432	109	13
15	85	246	Coloidal suspension.....	50	91	11	13
10	90	375	Filtered clear.....	21	49	4	6
5	95	377	do.....	52	116	28	16
0	100	329	Colloidal suspension.....	60	144	67	18
Corning 015.....		81	Filtered clear.....	104	168	-----	59
Pyrex 7740.....		22	Filtrate, opalescent.....	17	24	Trace.	12

recorded. Although the hygroscopicity values for these soda-germania glasses were adequate for pH-responsive electrodes, the chemical-durability characteristics were hopelessly unsatisfactory. Under these circumstances, no physicochemical equilibria is possible, and hence no satisfactory pH response can be expected.

The same difficulties in blowing electrodes were encountered with a soda-lime-germania glass prepared by John K. Taylor⁴ for comparison with Corning 015 electrode glass of the soda-lime-silica series. Although his glass exhibited acceptable hygroscopic characteristics, no successful electrodes were obtained.

An overall picture of the interrelation of hydroscopicity, chemical durability, and pH response with the composition is given in figure 6. Also included in this figure are the approximate compositions at which new phases appear in the equilibrium diagrams (table 3) [8]. Although the data are too meager for definite conclusions, they do suggest some correspondence between the chemical and physical properties of the glasses and the critical points of the phase equilibrium diagram for this system of oxides.

TABLE 3. Known compounds and eutectics of the Na₂O-GeO₂ phase-equilibrium system [8]^a

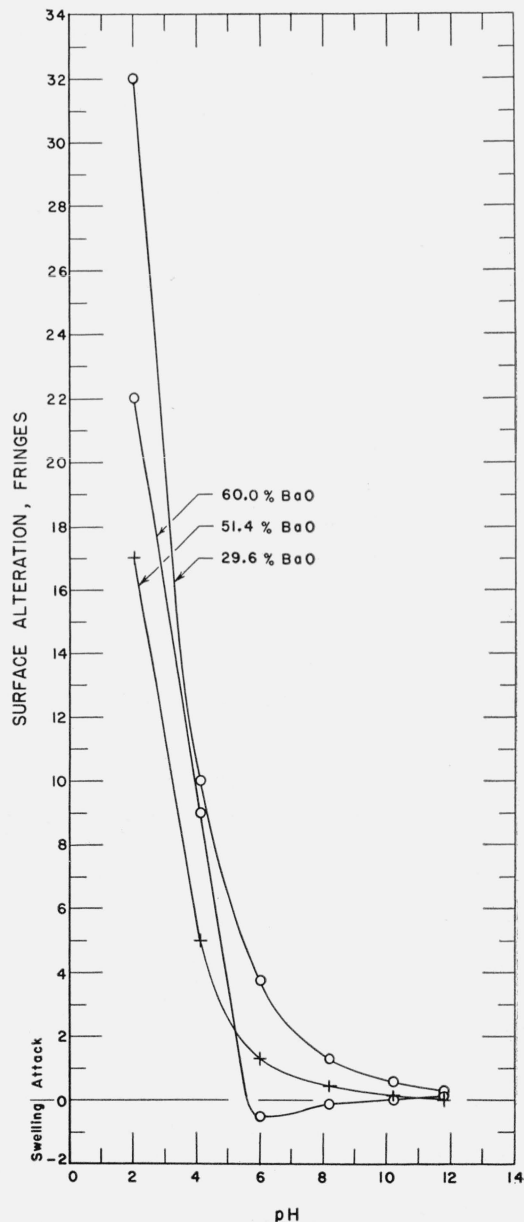
Compounds	Melting point	GeO ₂
	°C	Percent
Metagermanate (Na ₂ O·GeO ₂).....	1,083	---
Eutectic I.....	778	75.8
Digermanate (Na ₂ O·2GeO ₂).....	799	---
Eutectic II.....	789	78.5
Tetragermanate (Na ₂ O·4GeO ₂).....	1,052	---
Eutectic III.....	1,042	89.2

^a George M. Ugrinic reviewed the literature of the phase-equilibria work on germanium-oxide systems.

⁴ Personal communication.

FIGURE 7. Surface alteration (exposure 5 min, 25° C) of three BaO-B₂O₃ glasses over the range pH 2 to pH 11.8.

These glasses represent the extremes of behavior for the series. The chemical durabilities of all other members of the series fall between these limits.



3.3. BaO-B₂O₃ Glasses

a. Chemical Durability

Table 4 gives the data obtained on a series of BaO-B₂O₃ glasses for chemical durability, hygroscopicity, and pH response. This series of glasses extends over the composition range 29.6 percent of BaO, where two immiscible layers appear [9], to near 60 percent of BaO, above which devitrification limits the glass-making range. Figure 7 illustrates the extremes of chemical durability over the range pH 2 to pH 11.8 exhibited by these glasses. The chemical durability of this BaO-B₂O₃ series was so poor that the exposure time was reduced to 5 minutes and less at 25° C instead of the conventional 6 hours of exposure at 80° C previously adopted for silicate glasses. These abbreviated exposures were necessary in order to keep the surface alterations within the limitations of the interferometer method. The nature of the attack-pH curves for these glasses was markedly different from the numerous silicate glasses previously studied [2, 4], with all the members of the series being more vigorously attacked in the acid buffers than at the higher pH values. The glass of 60 percent of BaO exhibited swelling at pH 6 and pH 8.2, resulting in a conspicuous nonreflecting film on the surface of the specimens involved. This feature was so unexpected that the experiments were repeated, with the same results. A more easily understood picture of the chemical-durability characteristics of this series of glasses is given in figure 8, in which the chemical durability in the buffers at various pH values is plotted against the chemical composition (percentage of BaO). For pH 2 and pH 4.1 the surface alteration (attack) declines with increasing percentages of BaO and then increases again with further increase above 51.4 percent of BaO. The curve at pH 6 shows the same features over the composition range, except for the glass containing 60 percent of BaO. For this glass the surface alteration is one of swelling, plotted as negative attack in the figures, giving the curve a unique hook at the end. The curve for pH 8.2 exhibits this same feature, although not so conspicuously.

The question always arises as to what is the significance of the changes in chemical and physical

properties with composition. In presenting the data for chemical durability and hygroscopicity of the BaO-B₂O₃ series of glasses, lines are drawn (fig. 8) at the eutectic and compound compositions indicated by the phase-equilibrium diagram for this binary system [9]. There is little to decide as to whether the eutectic or compound compositions herald the change in direction that appears in the plotted data. The maximum and minimum composition ranges that might enter the argument are represented by vertical solid and dashed lines, respectively. Obviously, all that these data indicate is that the chemical and physical properties of glasses are influenced by the materials from which the glasses are made, and that the phase-equilibrium diagram is probably the best indicator available at present as to what compounds are melted, dissolved, or dissociated in the glassy state. The departure from randomness upon cooling the glasses from above the liquidus to room temperature, including the annealing schedule, probably contributes to emphasize the position and sharpness of the breaks as surely as does the sensitiveness or reliability of the physical and chemical indicators used. Certainly the rates of departure from randomness are very different for glasses of different composition in the same series [10].

b. Hygroscopicity

The hygroscopicity data for 1 and 2 hours of exposure to the high humidity maintained by a saturated solution of CaSO₄·2H₂O at room temperature are given in table 4 and show these glasses to be very nonhygroscopic (approximately equivalent to Pyrex 7740 [11]) at 46.9 percent BaO and greater. Below this percentage of BaO the hygroscopicity rises with increase in the percentage of B₂O₃. These glasses furnish an interesting example illustrating the distinction between a chemical-durability test (ability to withstand attacks by liquids) and one for serviceability of optical glass (the ability to maintain a polished surface upon exposure to air). These glasses obviously would be worthless as containers for most aqueous solutions over the range pH 2 to pH 12, but acceptable for optical elements, at least in their first line of defense against atmospheric moisture.

TABLE 4. Chemical durability, hygroscopicity, and pH response of a series of BaO-B₂O₃ glasses [15]

Composition		Surface alterations for exposures of 5 min at 25° C and pH—						Water sorbed in—		pH response		
BaO ^a	B ₂ O ₃	2.0	4.1	6.0	8.2	10.2	11.8	1 hr	2 hr			
<i>Percent</i>	<i>Percent</i>	<i>Fringes</i>	<i>Fringes</i>	<i>Fringes</i>	<i>Fringes</i>	<i>Fringes</i>	<i>Fringes</i>	<i>mg/cm³</i>	<i>mg/cm³</i>	<i>mV/pH</i>		
29.6	^a 70.4	32	10	3 $\frac{3}{4}$	1 $\frac{1}{4}$ +	$\frac{1}{2}$	$\frac{1}{4}$	43	109	8.....	Very short-lived.	
36.6	63.4	22	5 $\frac{1}{2}$	2 $\frac{1}{2}$	1 $\frac{1}{4}$	$\frac{1}{2}$ +	$\frac{1}{4}$ -	31	65	No electrode.....	High resistance.	
41.9	58.1	20	5	1 $\frac{1}{4}$	$\frac{1}{2}$ +	$\frac{1}{2}$	$\frac{1}{10}$ +	25	49	(54, 57)?.....	Very short-lived.	
46.9	53.1	17	5	1 $\frac{1}{4}$ +	$\frac{1}{2}$	$\frac{1}{2}$ +	$\frac{1}{10}$ +	17.3	27	No pH response.....	High resistance.	
51.4	48.6	17	5	1 $\frac{1}{4}$ +	$\frac{1}{2}$	D	D	16.7	25do.....	Do.	
53.6	46.4	19-	6-	2 $\frac{1}{4}$	$\frac{1}{2}$ -	$\frac{1}{10}$	D	16.9	25do.....	Do.	
56.1	43.9	19	6 $\frac{1}{4}$	2 $\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	D	17	24do.....	Do.	
60.0	40.0	22	9	$\frac{1}{2}$ swell ^b	$\frac{1}{10}$ swell ^b	D	$\frac{1}{10}$ +	16.5	22.6do.....	Do.	
Corning 015.....		See table 1; 6 hr of exposure at 80° C.						104	168	59.....		
Pyrex 7740.....		See table 1; 6 hr of exposure at 80° C.						17	24	12.....		

^a Analyses made by Nancy J. Tucker and Jean Rahausser Rogers.

^b Specimens showed nonreflecting films [13].

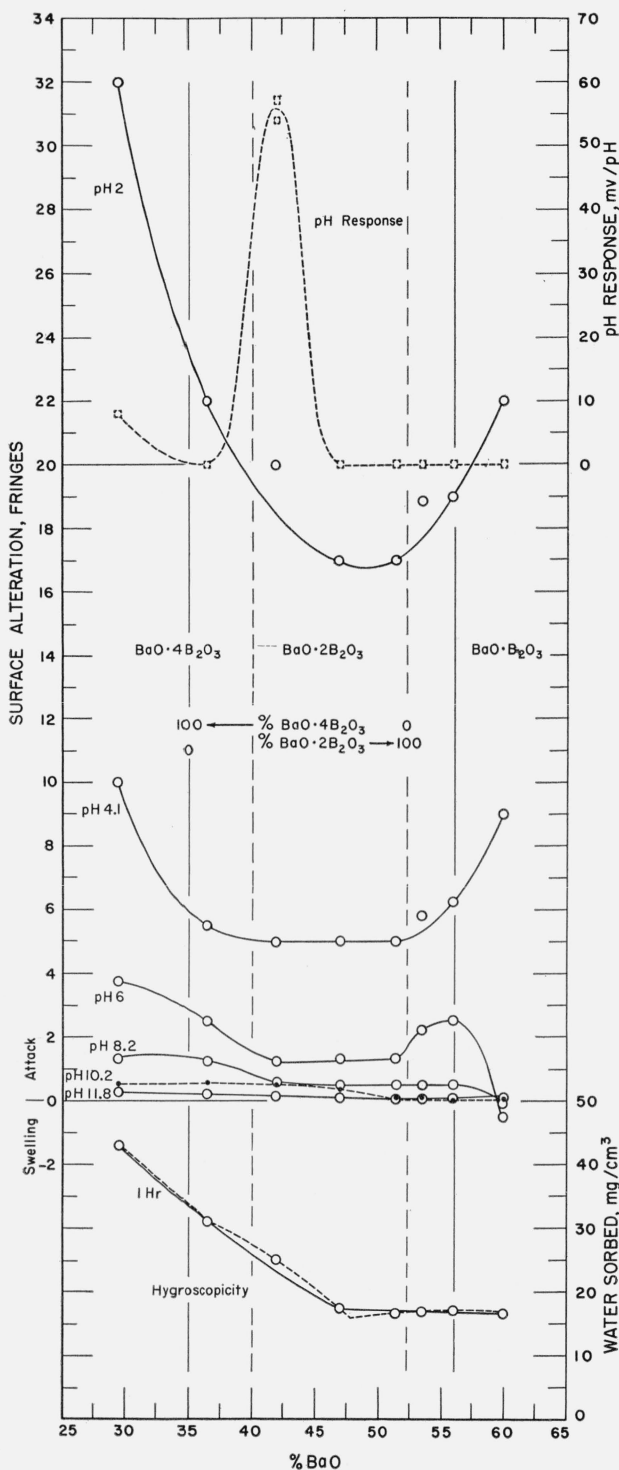


FIGURE 8. Comparison of the pH response of electrodes prepared from some BaO-B₂O₃ glasses with the chemical durability and hygroscopicity of the glasses.

(See text concerning the pH-response characteristics of these glasses.)

For this BaO-B₂O₃ series only those glasses containing less than 47 percent of BaO exhibited hygroscopicity values sufficiently high to be classified as possible pH-responsive glasses. Of these, the glass of 29.6 percent of BaO showed evidence of inhomogeneity, probably separation into two immiscible phases [9]. An electrode prepared from this glass was very short-lived and gave very indifferent pH-response values. Glasses containing 46.9 percent of BaO and greater had hygroscopicity values that correspond favorably with Pyrex 7740, and in accordance with their low hygroscopicity, electrodes prepared from them showed no evidence of voltage response to hydrogen-ion activity of the buffer solutions. The glass of 41.9 percent of BaO gave one electrode that started off with no pH response, then gave two quick values of 54 and 57 mv/pH between pH 4.1 and pH 8.2. This performance was followed in a relatively few seconds by failure of the bulb. Whether those two readings should be classified as transient or spurious is uncertain. In light of past experience of the effect of poor chemical durability on pH response of glass electrodes, it seems reasonable to classify these readings as both transient and spurious. Certainly this electrode performance could not be repeated, even after many attempts involving the consumption of several yards of tubing. The overall picture of relation of pH response (drawn as a dashed line), chemical durability, and hygroscopicity as a function of the composition is given in figure 8.

4. Conclusions

None of the Na₂O-MgO-P₂O₅, the Na₂O-GeO₂, and BaO-B₂O₃ glasses examined had sufficiently good chemical durability to produce electrodes that even approximated the theoretical voltage response dictated by the Nernst equation. In addition, many of the glasses had very low hygroscopic properties, thus ruling them out as possible sources of electrodes acting as hydrogen-ion indicators. Hence, for all practical purposes, the electrical response of all these glasses to hydrogen-ion activity of aqueous solutions must be classified as superficial or negligible.

5. References

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WASHINGTON, November 16, 1953.