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# pH Response of Nonhygroscopic Glasses

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Electrodes prepared from glasses of low hygroscopicity, high electrical resistance, and unsatisfactory pH response in aqueous solutions have been investigated in an effort to determine if their failure to develop the full pH response is due merely to a lack of sensitivity of the indicating instrument or to a real failure of these glasses to respond to hydrogen-ion activity. By increasing the sensitivity of the indicating instrument and decreasing the thickness of the electrode membrane in order to lower the electrical resistance, many of these glasses have been shown to develop the full pH response of 59 millivolts per pH at 25° C. However, theoretical and experimental evidence indicates that glasses below a limiting hygroscopicity probably do not develop full pH response regardless of the thickness of the glass membrane, the resistance of the electrode, or the sensitivity of the indicating instrument. In fact, glass electrodes for which the thickness, electric resistance, and surface are retained essentially unaltered throughout the experiments exhibit large departures from the hydrogen electrode upon the progressive removal of water.

## 1. Introduction

As is well known, any silicate glass upon immersion in an aqueous solution, develops an electromotive force, which, in the case of certain glasses, varies with pH according to the Nernst equation, $\Delta E=0.000198T\Delta \mathrm{pH}$, over an extended range of hydrogen-ion activity. The suitability of such glasses as indicators of hydrogen-ion activity of aqueous solutions seems to be largely dependent upon adequate hygroscopicity and uniform chemical durability over as long a pH range as possible [1 to 4].[1] Glasses of adequate hygroscopicity but of very poor chemical durability exhibit substantial voltage departures (errors) from the theoretical at all pH values [2, 5 to 7]; while glasses of acceptable durability but of very low hygroscopicity also fail to develop the full pH response of 59 mv/pH at 25° C as indicated by the readings of the conventional, commercial electronic pH meters [1, 2, 5 to 8]. The present investigation was undertaken to ascertain if the failure of electrodes prepared from glasses of low hygroscopicity to exhibit the full pH response is merely the result of insufficient sensitivity of the indicating instrument or is due to an actual failure of these glasses to respond to hydrogen-ion activity. The high resistance, exceeding 1,000 megohms, of the electrodes made from the nonhygroscopic glasses would be the major contributing factor in the first case, while in the second instance the determining agent would be the absence of sufficient water in the glass to give the electrode the capacity to function as a "water electrode" [2, 9, 10] or as a "protode" [11, 12].

The problem apparently resolves itself into determining whether electronic or protonic resistance limits the proper functioning of these electrodes.[2] If a parallel exists between the electronic resistance and the voltage departures of the glass electrodes, then there is reason to believe that resistance limits their functioning; whereas, if experimental evidence points toward "sorbed water" as the only related entity, then protonic resistance is the determining factor. This latter statement is merely another way of saying that protons or hydronium ions $H_3O^+$ necessarily move from water site to water site within the glass.

From a practical standpoint it would be most desirable to be able to use electrodes prepared from many of the glasses of low hygroscopicity because of their superior chemical durability. Such electrodes would better survive severe operational conditions of high-acid concentrations, temperature and alkalinity.

## 2. Experimental Procedure

The pH response and other electrical characteristics of the experimental glass electrodes were determined on specimens of the simple Cremer-Haber type [1, 2] prepared by blowing a small tin-walled bulb on the end of a section of glass tubing. Because of their convenience of preparation and the relative simplicity of interpretation of the experimental results, mercury-filled electrodes [13] were preferred over the customary inner-solution filled type [2].

All of the routine pH and voltage measurements were obtained on a Beckman pH meter, laboratory model G, using a well-conditioned glass electrode of Corning 015, the hydrogen electrode, or the saturated calomel half cell as the reference electrode, depending on the limitations dictated by the experimental conditions.

The electrometer employed, other than the Beckman pH meter, was one assembled using the General Electric GL–5740/FP–54 Pliotron tube, which, when properly installed and operated, can readily detect currents as low as $10^{-17}$ amp—about 60 electrons per second. This sensitivity being far better than was feasible to handle effectively, the simple circuit recommended for the tube in measurements of currents of the order of $10^{-15}$ amp was modified for use in these experiments.

The hygroscopicity data were obtained by observing the increase in weight of 1.5 g of powdered glass (passed by a Tyler Standard 150-mesh sieve), exposed to the high humidity maintained by a saturated solution of $CaSO_4 \cdot 2H_2O$ under controlled conditions of temperature and time, a procedure

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

[2] It is conceivable that each is equally fundamental and that these factors parallel one another and are inseparable in the case of nonhygroscopic glasses.

previously proposed for determining the serviceability of optical glasses [14, 15].

The resistance values of the glass electrode were determined with a resistance bridge, General Radio Megohm Bridge Type 544-BS8, operating with a 500-v drop across the terminals; and also with an RCA Senior Voltohmyst, Type WV-97A, which applied only 1.5 v across the resistance under measurement. Resistance readings were obtained while the electrode was immersed in the solutions in which voltage departures appeared. The circuit was completed through the mercury column of the glass electrode and a platinum wire dipped directly into the solution. This system added an unavoidable uncertainty to the resistance readings, because it constitutes a battery whose voltage is readily affected by the oxidation-reduction potential and pH of the solution. The platinum wire and the glass electrode were held a fixed distance apart during the measurements, after which the glass electrode was replaced with a second platinum wire in order to observe the resistance offered by the solution alone. In order to reduce the electric leakage from surface conductivity, the stem of the glass electrode was treated with commercial Desicote. Organic chlorosilanes, such as Desicote, for example, dimethyl dichlorosilane, $(CH_3)_2\ SiCl_2$, react with adsorbed moisture on the surface of glass evolving HCl gas, and deposit on the glass surface a water-repellent layer of dimethylsiloxane groups approximately $10^3$ molecules thick [16]. The glass electrodes were prepared from thin-walled tubing, which had a relatively low resistance per unit area. It was therefore necessary to reproduce the depth of immersion to avoid resistance variations as large as 4 megohms.

## 3. Results and Discussion

### 3.1. Instrumentation

Using the commercial Beckman pH meter, the full theoretical pH response of 59 mv/pH over the range pH 4 to 8 could be obtained with electrodes made from glasses having a hygroscopicity as low as 35 mg/cm³. The assembled General Electric Pliotron electrometer allowed the use of glasses of much lower hygroscopicity. For example, by careful attention to shielding and other details, the full theoretical pH response was observed with an electrode made from hard glass tubing having a hygroscopicity value of 19 mg/cm³. The improved sensitivity of the indicating instrument obviously effects a considerable extension of the range of usable glasses. However, instrumentation difficulties involved in obtaining adequate electric shielding and insulation became increasingly apparent. The ultimate limit to be attained by improved instrumentation, assuming perfect shielding in which all interfering charges are avoided, is the minimum noise level determined by the Brownian movement.[3] However, in the present problem the practical limit falls far short of this speculative theoretical one.

From the above evidence alone one is inclined to feel that electrodes prepared from all the glasses of very low hygroscopicity probably develop the proper pH response, but the observer is frustrated in apprehending it. In the case of electrodes made from these nonhygroscopic glasses the factors of high resistivity and low water content parallel one another, making it impossible to ascertain which one is the determining factor. Experiments designed to separate the effects of high resistance and low water content might possibly give a satisfactory answer. With the attention focused on the resistance of such electrodes, one is inclined to regard the thickness as the limiting barrier. There is some experimental evidence to support the opinion that by a sufficient reduction in the thickness, that is, by a sufficient reduction in the length of the resistive path, the full pH response of these electrodes could be realized [17, 18]. Nevertheless, the attainment of sufficiently thin films is as difficult as the other direct approaches to the problem, because of the limited strength of glass membranes thinner than 1 $\mu$ [19].

### 3.2. Water Content and pH Response

If one focuses attention on the water aspect of the problem concerning the response of the glass electrode to hydrogen ions, there appears to be a definite lower limit beyond which a glass electrode cannot be expected to function properly. If the glass electrode functions via the acid-base equilibria attainable through the dissociation constant of water, $[H^+]\cdot[OH^-]=K_w=10^{-14}$, then it is obvious that any glass in order to develop the full theoretical pH response must contain sufficient water to give one or more dissociated molecules at all times. It is certainly as difficult to measure these quantities of water as it is to obtain a direct answer from the instrumentation or thickness approach. But these considerations do lead to pertinent answers. If the thickness at which pH response failures appeared for electrodes made from four glasses previously investigated [18] is plotted against the hygroscopicity of the glass, a curve is obtained, figure 1, which, when extrapolated to zero thickness, indicates that electrodes from glasses having less than a certain limiting hygroscopicity (approximately 15 mg/cm²)[4] have no proper pH function at any thickness. These data may be open to considerable criticism, but at least they do give a definite lead for additional experiments.

That nonhygroscopic glass membranes of infinitesimal thickness do not possess a satisfactory pH function is even more strikingly supported by experiments on the thickness of inhibiting films on electrode surfaces [27]. In these experiments nonhygroscopic glass layers less than 200 A ($2\times10^{-6}$cm) thick, generated on the surface of electrodes from Corning 015 glass by acid leaching followed by heat treat-

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[3] For a discussion of this limitation, see pages 251–252 of Procedures in experimental physics by John Strong (Prentice Hall, Inc., New York, N. Y., 1938).

[4] If the suggestion is accepted that the logarithm of the hygroscopicity of glass is a linear function of the departure thickness [18] then the glass exhibiting a voltage departure at zero thickness would have a hygroscopicity not greater than 8.8 mg/cm².

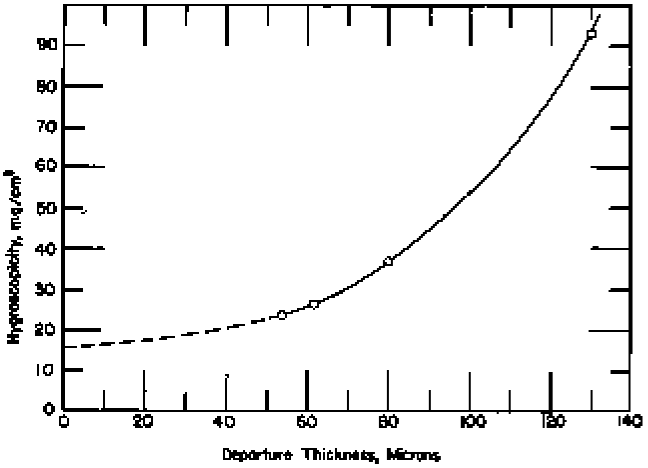

FIGURE 1. *Limiting thickness at which electrodes from glasses of various hygroscopicity values begin to show erroneous* pH *response.*

ment, caused almost complete permanent loss of pH function. Similar nonhygroscopic glass layers less than 30 A thick brought about appreciable loss of pH response.

The following experiments were designed to eliminate electric resistance as a determining factor in the observed voltage departures of the glass electrode in the "superacid" region [20, 21], and were performed in such a manner that it was hoped the only, or main, contributing variable was the progressive withdrawal of water from the electrode glass [2, 9, 10]. The voltage departures of a well-conditioned electrode of Corning 015 glass were followed well into the superacid range, using the hydrogen electrode as the reference, and any voltage departures observed were attributed to the glass electrode. This seemed a reasonable assumption because in all previous experiments in which the voltages of the glass and hydrogen electrodes have not paralleled each other, experimental evidence, such as changed chemical durability and hygroscopicity of the glass, has always indicated that the glass electrode was at fault [3 to 6]. In previous experiments in which water was withdrawn or excluded from the electrode glass by dehydration, annealing [2], and leaching followed by heat treatments [26, 27], the voltage departures introduced in each case were accompanied by variations in resistance or by surface alterations. The surface of the electrode remained unaltered throughout the present experiments, as indicated by examination of flats on Corning 015 [4] with an interferometer; at least, no alteration of the surface was detected. The usual swollen, silica-rich surface formed on this glass in acid solutions [4] was not removed, and it remained swollen over the period of the experiments in the acid solutions of high concentration. Hence, the large voltage departures cannot be attributed to any radical mechanical or chemical alteration of the electrode surface, such as is brought about by hydrofluoric acid or strongly alkaline solutions [4, 22, 23].

The data presented in table 1 and plotted in figures 2 to 6, inclusive, compare the voltage departures exhibited by a typical glass electrode with the accompanying resistance, in solutions of varying concentration for two mineral acids, $H_2SO_4$ and $H_3PO_4$, and three organic acids; HCOOH, $CH_3COOH$, and $C_2H_5COOH$. All of these voltage departures and resistance values were obtained on the same electrode, so that all the data are directly comparable. The resistance values obtained with the megohm bridge type 544–BS8 and the RCA Senior Voltohmyst are included in the plots as solid and broken lines, respectively. There is some uncertainty as to which of these instruments yields the more acceptable

TABLE 1. *Voltage departures of the glass electrode in aqueous solutions of* $H_2SO_4$, $H_3PO_4$, HCOOH, $CH_3COOH$, *and* $C_2H_5COOH$ *compared with the resistance of the electrode in each of the solutions*

| Solution | | Departure | Resistance obtained by— | |
|---|---|---|---|---|
| | | | Bridge, 500 v | Voltohmyst, 1.5 v |
| | | $H_2SO_4$ | | |
| % | pH | mv | *Megohms* | *Megohms* |
| 0.01 | 2.71 | 0 | 50 | 45 |
| .1 | 1.7 | 0 | 50 | 45 |
| 1.0 | 0.75 | 0 | 50 | 46 |
| 10 | 0 | −5 | 50 | 47 |
| 25 | −0.62 | −10 | 50 | 48 |
| 50 | −1.49 | −32 | 47 | 46 |
| 75 | −2.45 | −100 | 44 | 45 |
| 96 | −3.1 | −625 | 44 | 45 |
| | | $H_3PO_4$ | | |
| 0.01 | 2.4 | 0 | 44 | 44 |
| .1 | 2.0 | 0 | 44 | 43 |
| 1.0 | 1.4 | 0 | 44 | 44 |
| 10 | 0.7 | 0 | 44 | 44 |
| 25 | .1 | 0 | 44 | 43 |
| 50 | −.6 | −5 | 42 | 42 |
| 75 | −1.1 | −10 | 41 | 41 |
| 85 | −1.18 | −20 | 40 | 41 |
| | | HCOOH | | |
| 0.01 | 3.2 | 0 | 48 | 50 |
| .1 | 2.7 | 0 | 48 | 49 |
| 1.0 | 2.2 | 0 | 48 | 49 |
| 10 | 1.4 | 0 | 48 | 49 |
| 25 | 0.6 | 0 | 48 | 47 |
| 50 | −.6 | 0 | 47 | 46 |
| 75 | −1.6 | −10 | 47 | 45 |
| 90 | −2.3 | −32 | 46 | 45 |
| | | $CH_3COOH$ | | |
| 0.01 | 2.9 | 0 | 53 | 48 |
| .1 | 2.7 | 0 | 52 | 47 |
| 1.0 | 2.6 | 0 | 52 | 47 |
| 10 | 2.2 | 0 | 52 | 48 |
| 25 | 1.9 | 0 | 52 | 49 |
| 50 | 1.3 | −5 | 52 | 49 |
| 75 | 0.6 | −13.5 | 52 | 46 |
| 99 | −2.2 | −290 | 52 | 43 |
| | | $C_2H_5COOH$ | | |
| 0.01 | 3.2 | 0 | 51 | 42 |
| .1 | 3.0 | 0 | 51 | 43 |
| 1.0 | 2.7 | 0 | 52 | 43 |
| 10 | 2.4 | 0 | 52 | 43 |
| 25 | 2.2 | 0 | 52 | 44 |
| 50 | 1.9 | −5 | 52 | 44 |
| 75 | 1.1 | −20 | 52 | 44 |
| 99 | −0.4 | −468 | 400 | >300 |

data. Certainly the Voltohmyst[5] can be made to give spurious results because of the voltage developed by the battery consisting of the glass cell and the platinum electric contact.

A typical example of spurious data is shown in figure 5 for acetic acid. These are the apparent resistance values for the glass electrode obtained in the acetic acid solutions after the pH determinations had

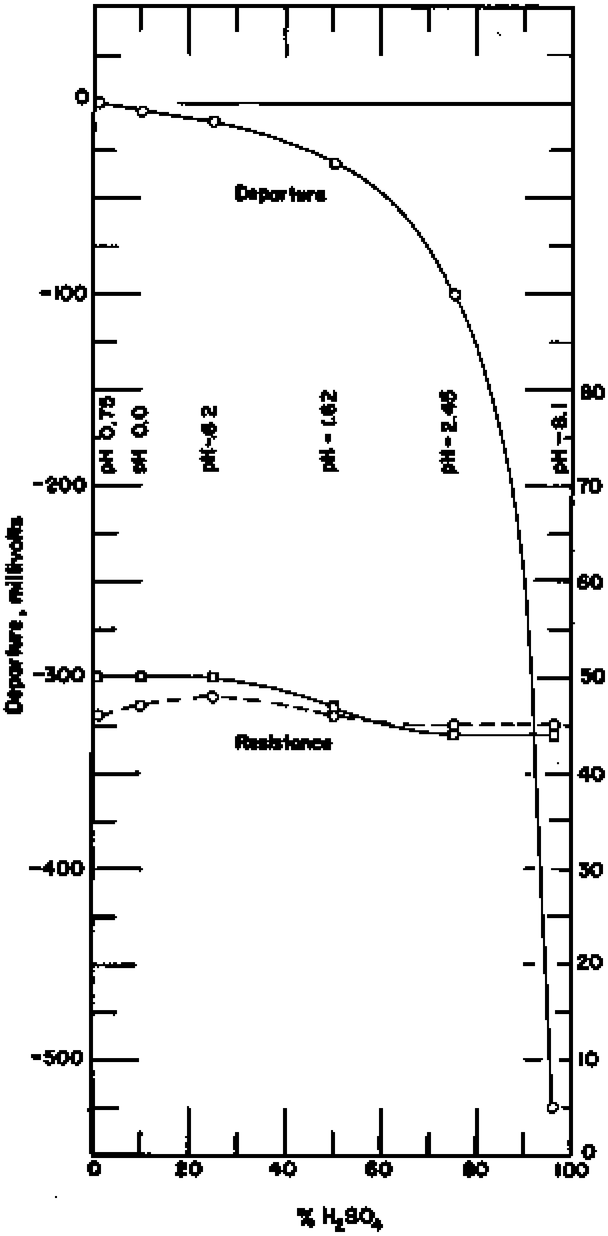

FIGURE 2. *Comparison of the voltage departure and resistance of a glass electrode (Corning 015) in various concentrations of sulfuric acid.*

——□——, Readings obtained with 500-v bridge; ——○——, readings obtained with 1.5-v voltohmyst.

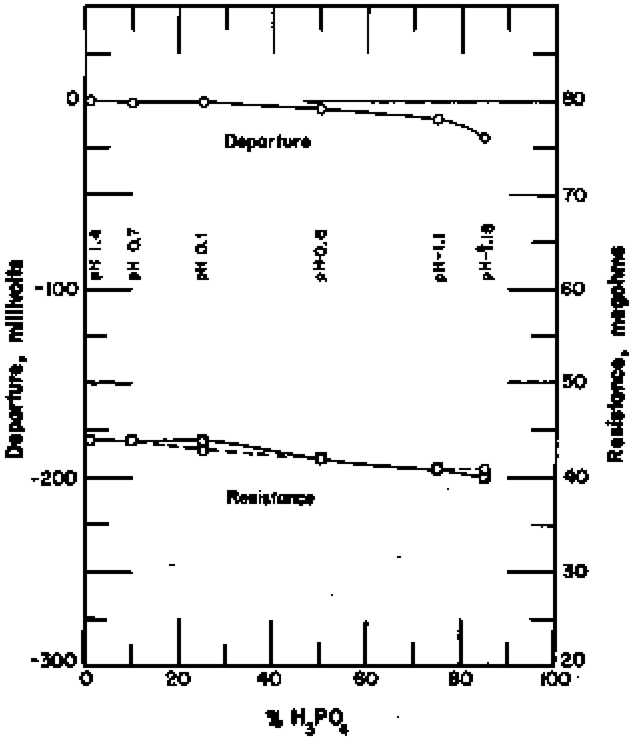

FIGURE 3. *Comparison of the voltage departure and resistance of a glass electrode (Corning 015) in various concentrations of phosphoric acid.*

——□——, Readings obtained with 500-v bridge; ——○——, readings obtained with 1.5-voltohmyst.

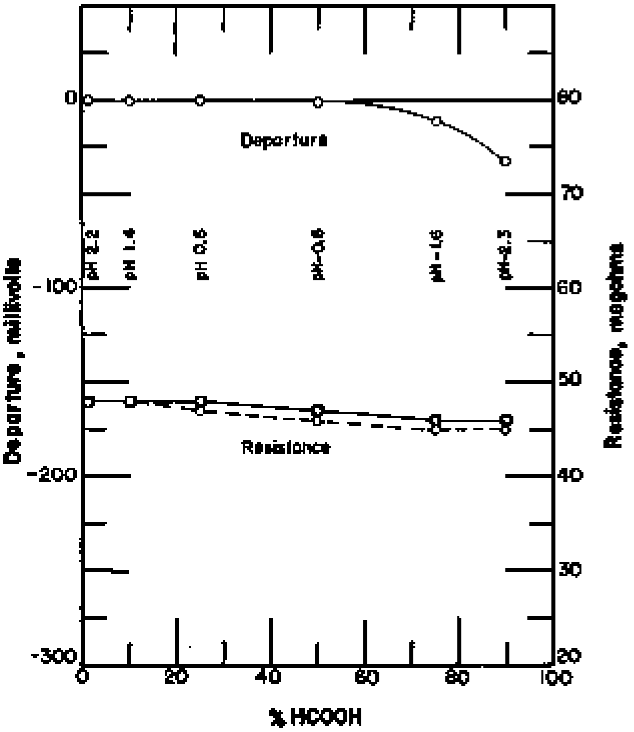

FIGURE 4. *Comparison of the voltage departure and resistance of a glass electrode (Corning 015) in various concentrations of formic acid.*

——□——, Readings obtained with 500-v bridge; ——○——, readings obtained with 1.5-v voltohmyst.

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[5] In order to obtain the information desired, that is, the resistance of the glass electrode in the solutions in which voltage departures were observed, it was necessary to operate this instrument in violation of the rules for its use, namely, that voltages shall not be present in the system whose resistance is to be measured

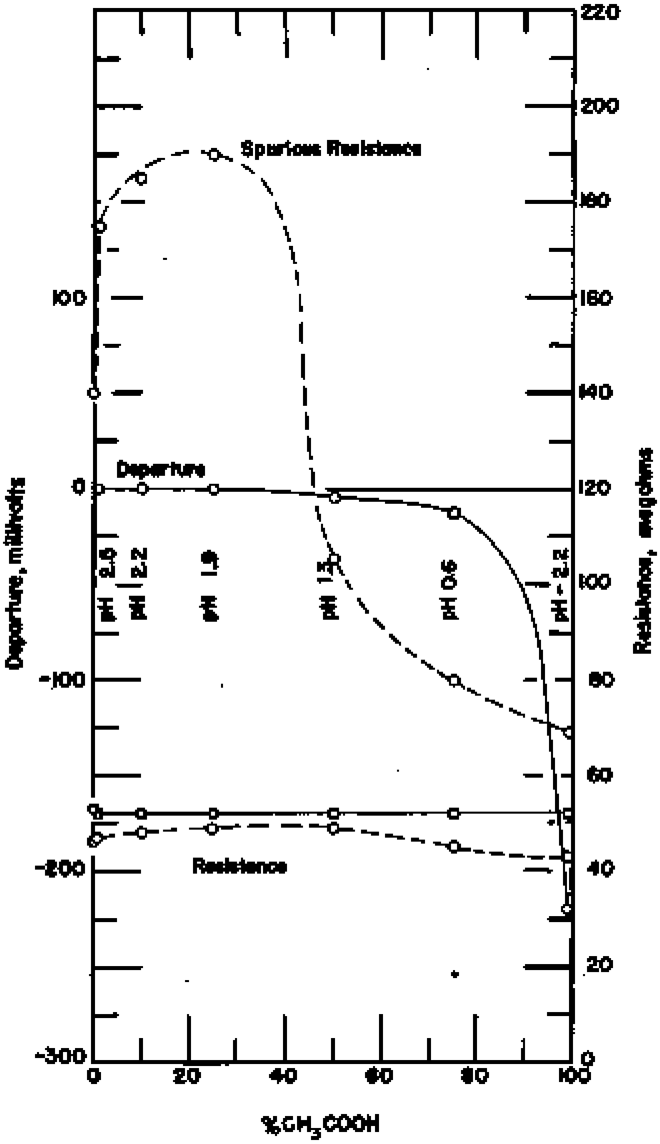

FIGURE 5. *Comparison of the voltage departure and resistance of a glass electrode (Corning 015) in various concentrations of acetic acid.*

——□——, Readings obtained with 500-v bridge; ——○——, readings obtained with 1.5-v voltohmyst.

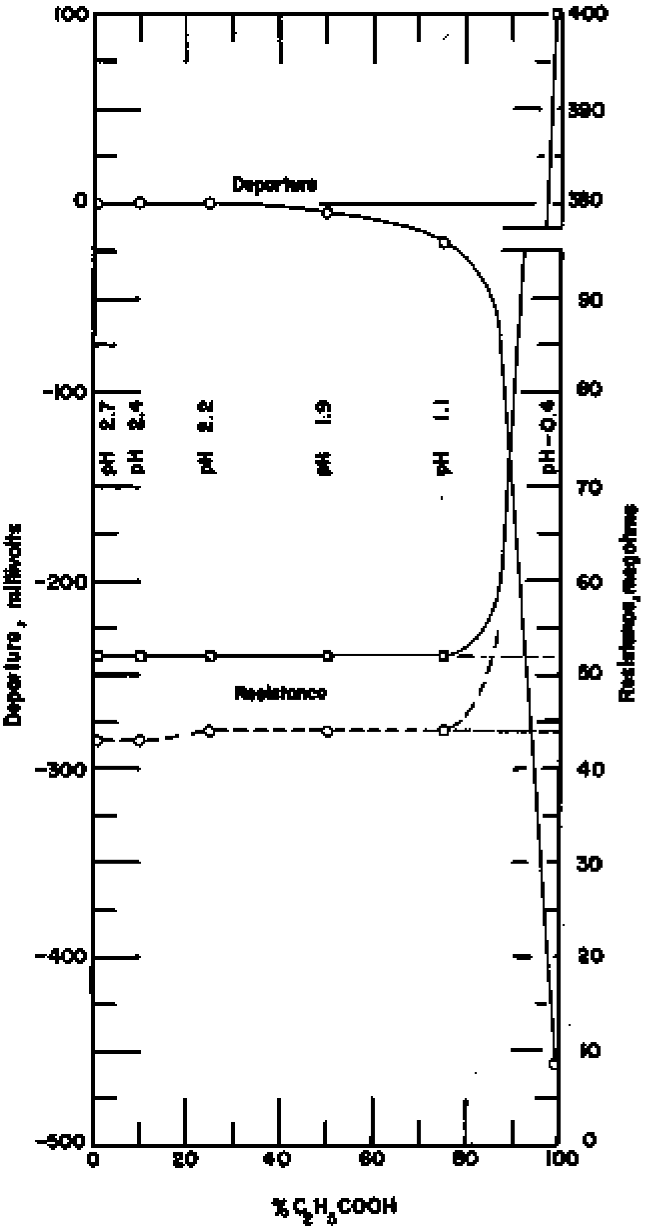

FIGURE 6. *Comparison of the voltage departure and resistance of a glass electrode (Corning 015) in various concentrations of propionic acid.*

——□——, Readings obtained with 500-v bridge; ——○——, readings obtained with 1.5-v voltohmyst.

been made, using the hydrogen electrode and the calomel half-cell. The same effect was observed after bubbling hydrogen gas through the $H_2SO_4$, but was not as pronounced. Voltage or polarization effects induced by the presence of hydrogen gas are presumably the reason for these high spurious resistances. It is interesting to note that the large drop in these apparent resistance values appears near 50 percent $CH_3COOH$, the same concentration at which marked repression in the rate of swelling had appeared in chemical-durability measurements [22]. In spite of its shortcomings, the Voltohmyst may often give more reliable readings than the resistance bridge because its low-voltage operation minimizes electrolysis and polarization. The 500 v across the terminals of the resistance bridge could conceivably cause trouble. In fact, this instrument finally terminated the resistance experiments presented in this sequence by puncturing the experimental electrode. Although the resistance bridge gave more reproducible results than did the Voltohmyst, the values obtained by the two instruments usually agreed closely, and in the cases of substantial disagreement (acetic and propionic acids) the Voltohmyst gave the lower resistance values, possibly indicating less polarization.

Figures 2 to 6 show that no general correlation exists between the voltage departures and the corresponding resistance of the electrode in the solutions. The voltage departures follow an orderly sequence as water is withdrawn, for each series of concentrations for each of the acids, whereas the resistance of the electrode remains low and essentially constant throughout the experiments. There appears to be one notable exception to this near-constancy of the resistance in the case of propionic acid. However, this apparent increase in the resistance of the electrode turns out to be merely the resistance of the full-strength propionic acid (bp 141.1°C) superimposed on the resistance of the glass electrode.

The apparent pH values indicated by the hydrogen electrode and saturated calomel half-cell were obtained and inserted in the figures to emphasize that there was no lack of hydrogen-ion activity in any of the solutions. In other words, the failure of the glass electrode to indicate hydrogen-ion activity and to behave as a hydrogen electrode is not due to any shortage of hydrogen-ion activity of the solutions. In fact, the hydrogen-ion activity of the concentrated acid solutions is anomalously high, as indicated by the hydrogen electrode. This latter phenomenon has often raised the question: does either the glass or hydrogen electrode give any acceptable information about concentrated solutions of these strong electrolytes, especially as the hydrogen-electrode readings imply activity of hydrogen ions far in excess of that available from the full dissociation of the acid molecule? However, this anomaly is one of the unsolved problems in the theory of solutions [24].

A glance at figure 7, in which the pH values indicated by the glass and hydrogen electrodes in the sulfuric acid solutions are plotted, leaves one with the impression that the glass electrode gives a more logical answer than does the hydrogen electrode. Accepting the Wynne-Jones line of reasoning that the glass electrode responds to protons [12] rather than water activity [2, 9, 10], the pH values obtained by the glass electrode tell a more comprehendible story about the dissociation of $H_2SO_4$ than does the exaggerated hydrogen-ion activity indicated by the hydrogen electrode. Certainly the hydrogen electrode must be responding to some property other than hydrogen ions.

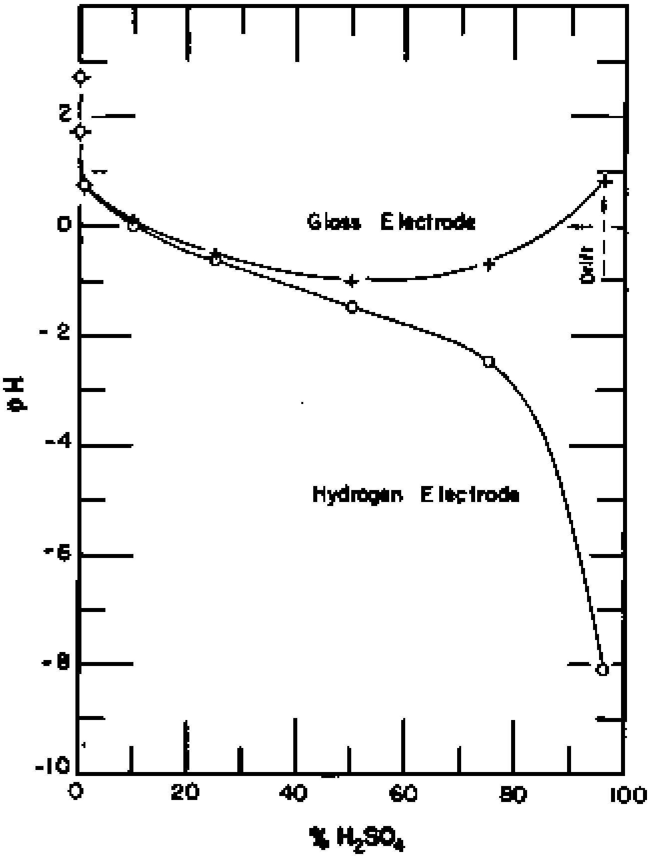

FIGURE 7. *Comparison of the pH values indicated by the hydrogen and glass electrodes for aqueous solutions of $H_2SO_4$, using the saturated calomel half-cell as the reference electrode.*

## 4. Summary

Experiments have been carried out that were designed to ascertain if electrodes prepared from glasses of low hygroscopicity and high electrical resistance fail to demonstrate full theoretical pH response because of the lack of sensitivity of the indicating instrument or because the glasses fail to respond to hydrogen-ion activity due to the absence of water. By means of an electrometer having greater sensitivity than the usual commercial electronic pH meters, electrodes prepared from glasses of hygroscopicity lying between 19 and 35 mg/cm³ were found to yield the full theoretical pH response, indicating that considerable use may be obtained from nonhygroscopic glasses by improved instrumentation. However, the increased resistance exhibited by electrodes prepared from glasses of still lower hygroscopicity appears to offer an insurmountable obstacle to the direct resolution of this problem.

Nevertheless, evidence was obtained by extrapolation of hygroscopicity-thickness data that indicated that electrodes from glasses below a limiting hygroscopicity would not have full pH response, even though their thickness were reduced to near zero. Further evidence showed that upon progressive removal of water from the glass, voltage departures appeared in electrodes, although the electric resistance remained low and essentially constant throughout the experiments, indicating that glasses of very low water content would not show full pH response to hydrogen-ion activity, regardless of the sensitivity of the indicating instrument. These data and conclusions seem to be compatible with the findings of earlier investigators [2, 3, 5, 6, 7, 9, 10, 25, 26], which indicate that water plays a vital role in the mechanism of the glass-electrode response to hydrogen-ion activity.

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