

Effect of Temperature on the Electrical Resistance and Voltage Departures (Errors) of Glass Electrodes, and Upon the Hygroscopicity of Glass

Donald Hubbard

The effect of temperature upon the electrical resistance and pH response has been studied on electrodes prepared from three types of glasses: Pyrex 7740, commercial soft-glass tubing, and Corning 015; glasses of low, intermediate, and high hygroscopicity, respectively. The results show that electrical resistance is not the determinant in most cases of voltage departure from the theoretical, and in the inherent failure of many glasses to act as satisfactory indicators of hydrogen-ion activity of aqueous solutions. For example, the electrodes prepared from Pyrex glass gave no significant pH response even when the resistance was as low as 12 megohms. The results of electrodes from glasses of intermediate hygroscopicity gave a pseudo-correspondence of pH response with resistance, whereas electrodes of Corning 015 gave voltage departures that could in no way be attributed to the electrical resistance of the electrode.

1. Introduction

Considerable confusion exists in the general concept as to what part the electrical resistance of a glass electrode plays in its voltage response to hydrogen-ion activity of aqueous solutions, the voltage departures (errors) that appear at high alkalinities and in the "superacid" region, and particularly in the failure of electrodes from many glasses to follow the simple dictates of the Nernst equation, $\Delta E = 0.000198 T \Delta \text{pH}$. For example, the difference in performance shown between electrodes from Pyrex 7740 and a satisfactory pH-responsive glass (fig. 1) is presumed to be related somehow to a difference in resistance of the glass membranes forming the effective portion of the electrode. With the electrometer tubes available requiring grid currents of only 10^{-12} to 10^{-15} amp, a glass electrode having a resistance as great as 1,000 megohms would exhibit an IR drop (error) ranging from 10^{-3} to 10^{-6} v [1, pages 47 and 89 to 92].¹ Such errors are small, and for most practical pH measurements can be disregarded. It is obvious that glass electrodes exhibiting large voltage departures, pH errors, but having resistances less than 1,000 megohms, are failing to show full pH response not because of their high electrical resistance nor because of a lack of sensitivity of the available indicating electrometers.

The present investigation was undertaken to ascertain what individual parts the hygroscopicity (water sorption) of the glass and the electrical resistance of the glass membrane play in the over-all picture of the ability, or lack of ability, of electrodes from various glasses to act as indicators of hydrogen-ion activity of aqueous solutions over the temperature range 20°C to near the boiling point of water.

2. Experimental Procedures

The hygroscopicity values were obtained in the apparatus described in previous publications [2].

The experiments at elevated temperatures were carried out by immersing the humidity chamber in a thermostated water bath. Although no mechanical difficulties were encountered, this procedure for obtaining hygroscopicity was not entirely satisfactory, because of excessive condensation on the walls of the chamber at the elevated temperatures for the high humidity (approximately 98 percent) required for the experiments. However, the results appeared to be qualitatively acceptable. The hygroscopicity values reported are those obtained for 1-hour exposures.

The voltage performance of any experimental electrode was determined by the voltage change that appeared when the cell consisting of the experimental electrode and a reference electrode was transferred from a buffer solution at pH 4.1 to a buffer at pH 8.2. The reference electrode employed was either a hydrogen electrode or a glass electrode calibrated at the elevated temperatures. Thus if the experimental electrode gave full pH response, no change in voltage appeared in the two buffers at any temperatures. Typical examples of the data obtained by this procedure are illustrated in figure 1 for a commercial electrode and one prepared from Pyrex glass 7740. The above pH interval was chosen because it is a region of uniform chemical durability of the glasses studied [3]. Thus, voltage shifts are eliminated or minimized, which might be credited to a change in chemical durability [2]. The calibrated mercury-filled glass electrode [4] was preferred over the hydrogen electrode as a reference electrode because of operational simplicity and ease of temperature control by eliminating the hydrogen-gas chain. Furthermore, with both the reference and experimental electrodes filled with mercury, any small thermoelectric voltages generated at the Pt-Hg junction would be compensated by the symmetry of the system. All electromotive-force measurements were made with a Beckman pH meter, laboratory model G.

The resistance values for the experimental glass electrodes were followed at the different tempera-

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

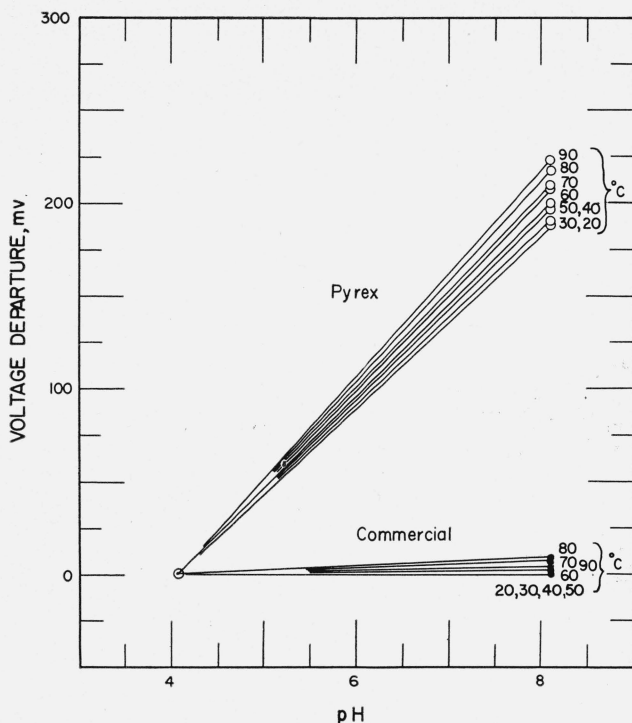


FIGURE 1. Voltage departures at various temperatures observed over the interval pH 4.1 to pH 8.2 for two glass electrodes, one of which was a commercial glass-electrode and the other prepared from Pyrex glass 7740.

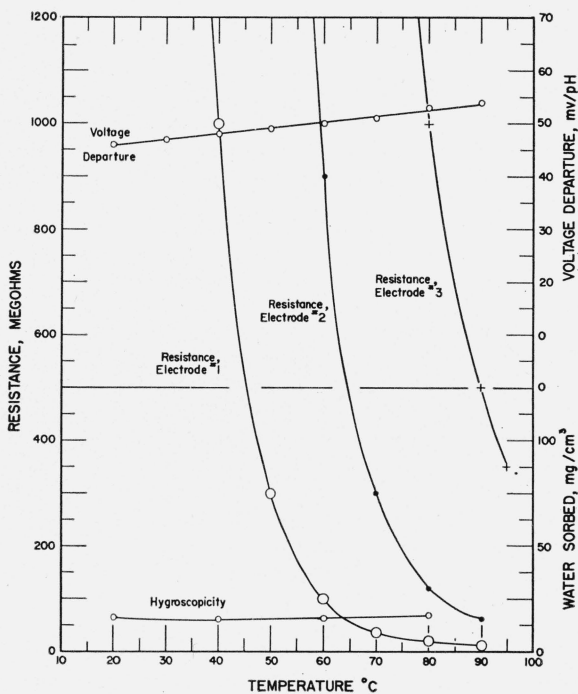


FIGURE 2. Effect of temperature upon the resistance, hygroscopicity, and pH response of electrodes prepared from Pyrex glass 7740, a glass of low hygroscopicity.

tures with an RCA Senior Voltohmyst TWV-97 A, which imposes 1.5 v across the glass membrane, while the bulb of the electrode was immersed in Britton universal buffer at pH 4.1. The electrical connections for these measurements were established by means of platinum leads, one of which was dipped into the buffer solution and the other into the mercury filling the glass electrode bulb. A number of parallel observations were made with a General Radio type 544-B88 megohm bridge operating with 100-v drop across the terminals, to make sure that neither polarization nor the voltage generated by the battery, consisting of the two cells, glass electrode, and platinum wire, was causing spurious resistance values to be reported [5]. The higher voltage of the megohm bridge might cause polarization resistance at the glass surface or even puncture the glass membrane, whereas the low operation voltage of the Voltohmyst might be seriously affected by counter voltage generated by the battery consisting of the glass electrode and the external platinum-wire connection. Because the two instruments indicated approximately the same resistance, it seemed reasonably sure that the effects of polarization and interfering voltages were not large.

3. Results and Discussions

3.1. Electrodes Prepared from Pyrex Glass 7740; A Glass of Low Hygroscopicity

Figure 2 and table 1 show the effect of temperature upon the electrical resistance and pH response of electrodes prepared from the sample of Pyrex 7740, chemical-ware glass, and the hygroscopicity of this glass over the same temperature range. The resistance curves for these three electrodes are in accord with the long known fact that the electrical resistivity of glass decreases rapidly as the temperature is increased and follows in a general way the exponential equation

$$R = Be^{A/T},$$

where

R = the resistivity,

B = a constant,

A = a constant involving the activation energies,

T = temperature,

$e = 2.71828$, the limit of the series $(1 + 1/n)^n$ as $n \rightarrow \infty$ [6].

At times the resistance curve obtained experimentally may depart conspicuously from this shape; typical examples obtained on an electrode are illustrated by A and B in figure 3. Such S curves can be readily accounted for qualitatively by electrical surface leakage under conditions in which the resistance of the electrode bulb becomes increasingly great in comparison to the surface resistance of the glass tube. The total resistance, R , of the two con-

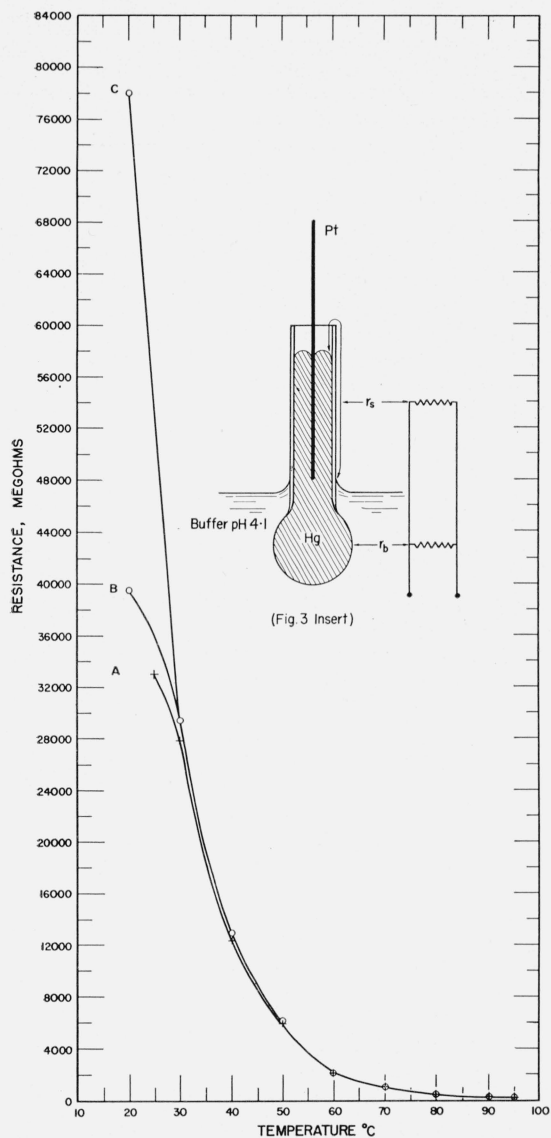


FIGURE 3. Resistance values obtained on a single glass electrode illustrating the effect of surface conductivity upon the shape of the resistance-temperature curves.

Curves A and B were obtained before surface treatment; C, after cleaning and drying. Insert is a schematic diagram illustrating the resistances involved. r_s = surface resistance, r_b = resistance of the glass electrode

ductors, electrode bulb and glass surface in parallel (fig. 3 insert), whose separate resistances are r_b and r_s , is given by the relation

$$1/R = 1/r_b + 1/r_s, \text{ or } R = \frac{r_b r_s}{r_b + r_s}$$

As r_b becomes so very large as to approximate the resistance of an open circuit, R approaches r_s as a limiting value

$$1/R = 1/\infty + 1/r_s, \text{ or } R = r_s.$$

These S curves are readily brought back into conformity by cleaning, drying, or treating the surface

TABLE 1. Characteristic resistance, voltage departure, and hygroscopicity values observed at different temperatures for electrodes prepared from glasses of high, intermediate, and low hygroscopicity

Corning 015 electrode					
No.	Temperature	Water sorbed	Voltage departure	Electrical resistance	
	°C	mg/cm ³	mV/pH	Megohms	
1	20	105	0	115	
	30	---	0	48	
	40	112	0	19	
	50	---	0	9.3	
	60	131	0	4.8	
	70	---	0	2.5	
	80	144	0	1.1	
	90	---	0	0.59	
	2	20	105	5	495
30		---	4	225	
40		112	3	120	
50		---	2	59	
60		131	1	33	
70		---	0	17	
80		144	0	9.3	
90		---	0	5.8	
3		20	105	42	950
	30	---	32	500	
	40	112	19	250	
	50	---	12	110	
	60	131	8	45	
	70	---	8.5	21	
	80	144	8.5	10	
	90	---	9.5	5.2	
	Soft-glass electrode				
1	20	26	0	8,300	
	30	---	0	3,800	
	40	36	0	1,800	
	50	---	0	950	
	60	53	0	350	
	70	---	0	120	
	80	87	0	41	
	90	---	0	16	
	2	20	26	---	31,000
30		---	52	12,000	
40		36	36	5,390	
50		---	15	2,490	
60		53	1	1,110	
70		---	0	455	
80		87	0	207	
90		---	0	---	
Pyrex 7740 electrode					
1	20	17	46	5,800	
	30	---	47	2,300	
	40	15	48	1,000	
	50	---	49	300	
	60	16	50	99	
	70	---	51	35	
	80	17.5	53	19	
	90	---	54	12	
	2	20	17	---	---
40		15	---	---	
60		16	---	900	
70		---	---	300	
80		17.5	---	120	
90		---	---	61	
3		20	17	---	---
		40	15	---	---
		60	16	---	---
	80	17.5	---	1,000	
	90	---	---	500	
	95	---	---	350	

of the glass stem with appropriate water repellants, such as paraffin, organic chlorosilanes, or commercial Desicote [6].

The voltage-departure characteristics of electrode 1 as affected by temperature are also plotted in figure 2. From this curve it is evident that there was no improvement in the pH response of this Pyrex electrode, although the resistance fell to such low values as 99, 35, 19, and 12 megohms. In other words, the low resistance was not accompanied by a correspond-

ing improvement in pH response. Electrodes 2 and 3 were checked at 30° and 90° C and were also found to be unresponsive to the pH of the buffer solutions. Obviously, if electrical resistance were the major determinant in pH response of this glass, the three Pyrex electrodes would be expected to develop improved response at different temperatures in accord with their resistance curves. However, they are all useless as indicators of hydrogen-ion activity. Only upon a study of the hygroscopicity curve obtained on Pyrex glass does one get a plausible reason for the complete indifference of these electrodes to the lowered resistance at the elevated temperatures (fig. 2). The water sorbed by the glass has not changed appreciably with the increase in temperature and does not at any temperature approach a value commensurate with an effective electrode glass. [5, 7] Certainly the lowered resistance can not be attributed to water penetrating the glass. As a result, the voltage departure of the electrode in mv/pH becomes greater with increased temperature. This increased departure is largely the result of the temperature effects inherent in the derivation of the Nernst equation. Based on previous evidence, the electrodes prepared from this nonhygroscopic glass probably would have no satisfactory pH response, regardless of how thin the glass membranes were blown [5, 8, 9].

3.2. Electrodes Prepared from a Glass of Intermediate Hygroscopicity

Figure 4 shows the effect of temperature on the resistance and pH characteristics of two glass electrodes prepared from a commercial soft glass of intermediate hygroscopicity. The performance of these

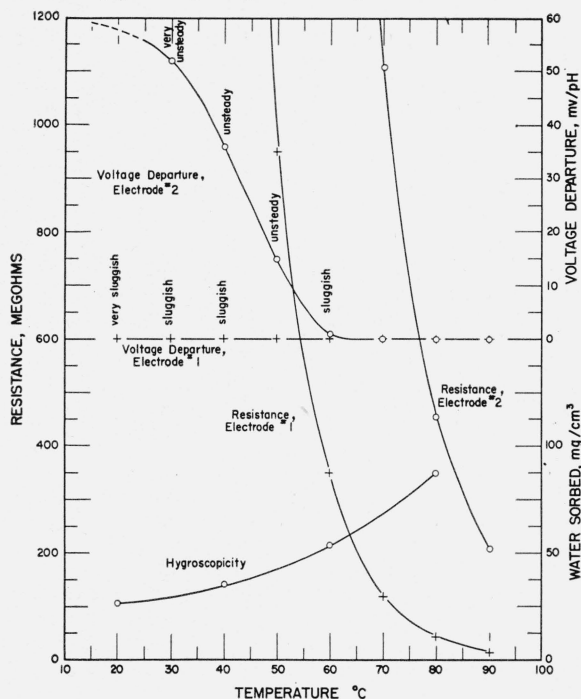


FIGURE 4. Effect of temperature upon the electrical resistance, hygroscopicity, and pH response of electrodes prepared from a glass of intermediate hygroscopicity.

electrodes more nearly follows the general conception of the part that resistance should play in determining the suitability of a glass for pH measurements. Electrode 1 at 20° C was very sluggish in drifting toward a steady voltage, whereas at 30° and 40° C the performance was still sluggish, but markedly improved. Above 50° C the resistance of the bulb fell rapidly below 1,000 megohms, and the electrode performed in an acceptable manner for high-temperature pH measurements. As the chemical durability of this glass is far superior to that of Corning 015, the life expectancy of electrodes prepared from it when used for high-temperature pH measurements would be correspondingly greater [1, 10, 11]. Electrode 2 was blown with a bulb considerably thicker than electrode 1. At 30° C the voltage departure was large and very unsteady. This electrode showed marked improvement, but was still unserviceable at 40° and 50° C. The voltage departures were small at 60° and 70° C, but the electrode performance was still sluggish. Beyond 80° C, the resistance of the bulb had fallen well below 1,000 megohms, and the over-all performance of the electrode was acceptable. As the pH response of these electrodes improved with decrease in resistance, a correlation of the pH response with the resistance values would apparently be acceptable, but not entirely adequate, as will be seen from the discussion and evaluation of the data in figure 7. However, the shape of the hygroscopicity-temperature curve is entirely different from that of Pyrex and probably is equally satisfactory in accounting for the improved performance of the glass electrode. (Compare the hygroscopicity curves in fig. 2 and 4.)

3.3. Electrodes from Corning 015

Figure 5 shows the electrical resistance and voltage performance of three electrodes prepared from a single sample of Corning 015 glass. Electrode 1 had low resistance values at all temperatures, ranging from 115 megohms at 20° C to 0.59 megohm at 90° C. Having been prepared from a glass of relatively high hygroscopicity and of uniform chemical durability over the pH interval chosen, this thin-walled electrode gave satisfactory performance (approximating the theoretical) over the temperature range from 20° to 90° C. Electrode 2 was blown from the same length of glass tubing as electrode 1, but with much heavier wall thickness. The resistance curve for this electrode fell below 500 megohms at 20° C and showed the usual rapid decline with increased temperature. However, this thicker electrode exhibited appreciable voltage departure at all temperatures up to 70° C, beyond which temperature it paralleled the performance of the reference electrode. Electrode 3, with a wall thickness in excess of 1 mm, still had resistance values lower than many satisfactory electrodes, but gave voltage departures over the entire temperature range from 20° to 90° C. This performance is in accord with the general knowledge that every glass has a critical thickness at which voltage departures appear [8]. Such failures of an electrode to respond to hydrogen-ion activity certainly cannot be attributed to electrical resistance

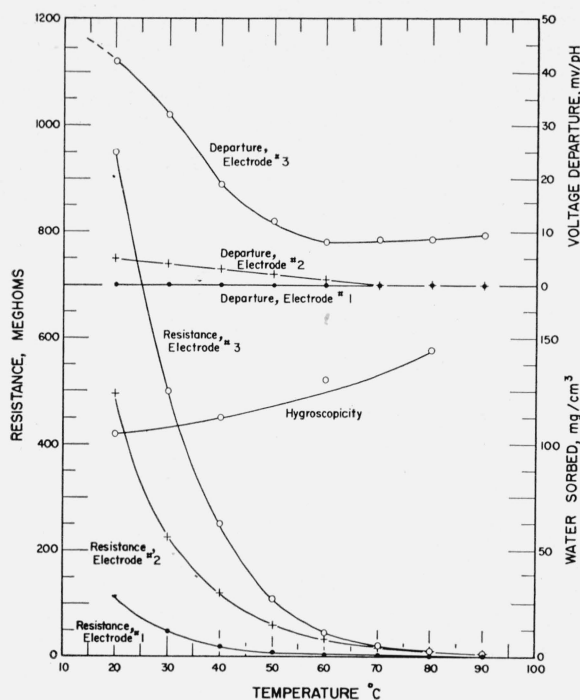


FIGURE 5. Effect of temperature upon the electrical resistance, hygroscopicity, and pH response of electrodes prepared from Corning 015, a glass of high hygroscopicity.

of the electrode, because at all temperatures the resistance is at values far below that at which the IR drop across the membrane would be as great as 1 mv. Possibly proton or H_3O^+ resistance due to the thickness of the membrane, lack of water penetration of the glass, or a combination of both, give a more acceptable concept. It seems probable that the glass-water-hydrogen-ion-activity equilibrium does not become established throughout the glass, even though the inherent hygroscopicity of the glass is high (fig. 5).

In order to further emphasize the lack of universal correspondence between voltage departures of glass electrodes and electrical resistance of the glass membrane, resistance values were determined for an electrode of Corning 015 over an extended pH range (conc. H_2SO_4 to pH 12) for temperatures from 20° to 90° C, and the results considered in relation to a conventional voltage departure curve obtained at room temperature over the same pH range (table 2,

fig. 6). These results show that the voltage departures in the high alkaline and superacid ranges are not attributable to excessively high electrical resistances, nor are they associated with marked changes in electrical resistance. Their causes have been discussed elsewhere in connection with the water activity of the solutions [1], chemical durability of the glass [2], heterogeneous equilibria at the glass electrode solution interface [15], and equilibrative response to ions other than hydrogen [1, 16].

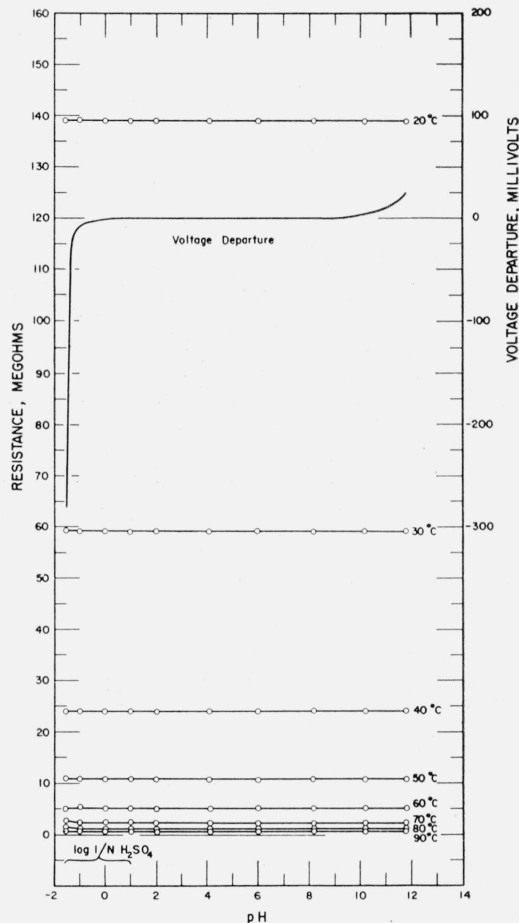


FIGURE 6. The pH-resistance curves obtained on an electrode of Corning 015 over an extended pH range (conc. H_2SO_4 to pH 12) for temperatures from 20° to 90° C, compared with a typical voltage departure (error) curve over the same pH range.

TABLE 2. Resistance values obtained for an electrode of Corning 015 over an extended pH range for temperatures from 20° to 90° C

Temperature	Resistance in—									
	H_2SO_4				Britton buffers at pH—					
	36N	10N	1N	0.1N	2	4.1	6.0	8.2	10.2	11.8
°C	Megohms	Megohms	Megohms	Megohms	Megohms	Megohms	Megohms	Megohms	Megohms	Megohms
20	138	139	139	139	139	139	139	139	139	139
30	59.4	59.2	59	59	59.2	59.2	59.2	59.1	59.2	59.2
40	24	24	24	24	23.9	24	24	24	24	24
50	10.8	10.7	10.7	10.7	10.7	10.7	10.7	10.6	10.7	10.7
60	5 to 5.3	5.1	5	5	5	5	5	5	5	5
70	2.39 to 2.7	2.3	2.3	2.29	2.29	2.27	2.29	2.3	2.27	2.27
80	1.21 to 1.42	1.19	1.19	1.20	1.19	1.19	1.19	1.19	1.19	1.19
90	.60 to .72	.59	.57	.57	.57	.58	.57	.57	.57	.57

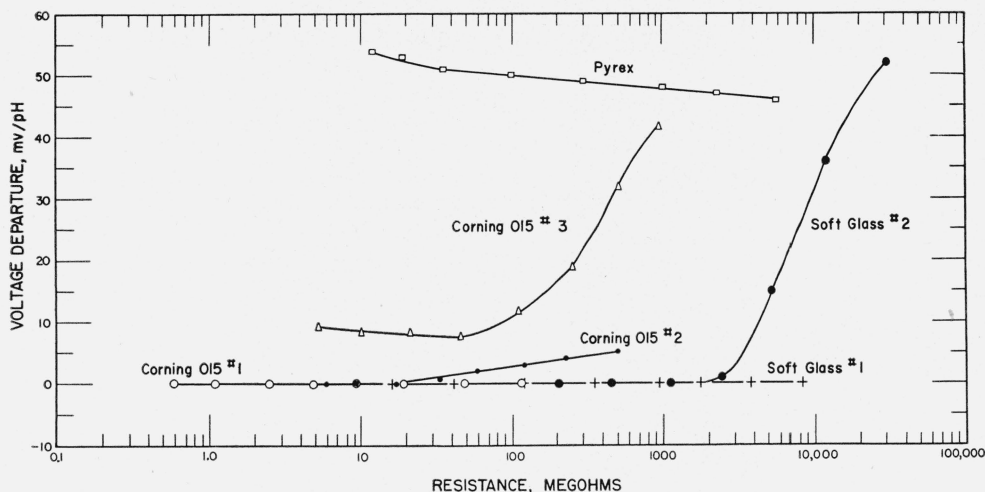


FIGURE 7. Comparison of the voltage departure and electrical resistance values of electrodes prepared from Corning O15, a commercial soft-glass tubing, and Pyrex glass 7740.

The resistance sequence for each of the electrodes was produced by varying the temperature.

3.4. Hygroscopicity versus Temperature

Although the hygroscopicity curves for the three glasses reported must be classified as being of uncertain reliability, they do warrant a brief evaluation. If adsorption were the major factor contributing to the water sorbed, the hygroscopicity curves should decrease with increased temperature [12]. As the curves for two of the glasses, figures 4 and 5, show a liberal increase with temperature, it is obvious that absorption and reaction are predominating factors.

4. Summary

Figure 7, in which the voltage departures (errors) are plotted as the dependent variable and resistance as the determinant, illustrates the incongruous part played by electrical resistance in the over-all picture of the pH response of glass electrodes. Not only do the pH response-resistance curves for electrodes from different glasses not coincide, but curves for electrodes from the same length of tubing (Corning O15 and soft-glass tubing) fail to exhibit similar characteristics. From the present investigation the part played by electrical resistance in determining the effectiveness of a glass for use as glass electrodes seems to be largely superficial. For example, electrodes prepared from glasses of low hygroscopicity, such as Pyrex, do not develop a satisfactory pH function even at very low resistance values. Furthermore, electrodes from glasses of high hygroscopicity and low resistance, such as Corning O15, fail to give full response to hydrogen-ion activity if the membrane thickness is excessive. From the data on the above two glasses, plus the results obtained on a glass of intermediate hygroscopicity, it appears that resistance values below 1,000 megohms are desirable, but certainly not sufficient to bring about satisfactory pH response.

Voltage departures from the theoretical pH response can appear for glass electrodes of low electrical resistance for the following reasons:

1. Low hygroscopicity of the glass from which the electrode is prepared [2, 7].

2. Membrane walls greater than a limiting thickness value, which differs for every glass [8].

3. Poor chemical durability of the glass [2].

4. High concentration of electrolytes [13, 14, 15].

5. Inhibiting films [9].

5. References

- [1] Malcolm Dole, *The glass electrode* (John Wiley & Sons, Inc., New York, N. Y., 1951).
- [2] Donald Hubbard, Mason H. Black, Sylvanus F. Holley, and Gerald F. Rynders, Electrode function (pH response), hygroscopicity, and chemical durability of soda-potash-silica glasses, *J. Research NBS* **46**, 168 (1951) RP2189.
- [3] Donald Hubbard and Edgar H. Hamilton, Studies of the chemical durability of glass by an interferometer method, *J. Research NBS* **27**, 143 (1941) RP1409.
- [4] M. R. Thompson, A metal-connected glass electrode, *BS J Research* **9**, 833 (1932) RP511.
- [5] Richard G. Goldman and Donald Hubbard, pH response of nonhygroscopic glasses, *J. Research NBS* **48**, 370 (1952) RP2324.
- [6] J. E. Stanworth, *Physical properties of glass* (Oxford University Press, Oxford, England, 1950).
- [7] Donald Hubbard, Hygroscopicity and electrode function (pH response) of glasses as a measure of serviceability, *J. Research NBS* **36**, 511 (1946) RP1719.
- [8] J. J. Diamond and Donald Hubbard, Thickness of glass electrodes, *J. Research NBS* **47**, 443 (1951) RP2270.
- [9] Donald Hubbard and Gerald F. Rynders, Thickness of inhibiting films on glass electrode surfaces, *J. Research NBS* **41**, 163 (1948) RP1915.
- [10] Henry H. Cary and Warren P. Baxter, U. S. Patent 2383709 (1945).
- [11] George A. Perley, Composition of pH-responsive glasses, *Anal. Chem.* **21**, 391 (1949).
- [12] Herbert Freundlich, *Colloid and capillary chemistry* (E. P. Dutton & Co., Inc., New York, N. Y.).
- [13] D. A. MacInnes and D. Belcher, Further studies on the glass electrode, *J. Am. Chem. Soc.* **53**, 3315 (1931).
- [14] Donald Hubbard and Gerald F. Rynders, Voltage anomalies of the glass electrode and the chemical durability of the glass, *J. Research NBS* **39**, 561 (1947) RP1848.
- [15] Donald Hubbard and Richard G. Goldman, Heterogeneous equilibria at the glass electrode-solution interface, *J. Research NBS* **48**, 428 (1952) RP2333.
- [16] B. Lengyel and E. Blum, The behavior of the glass electrode in connection with its chemical composition, *Trans. Faraday Soc.* **30**, 461 (1934).

WASHINGTON, April 9, 1953.