[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

THE BEHAVIOR OF GLASS ELECTRODES OF DIFFERENT COMPOSITIONS

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In a recent article[1] the authors have described a new form of glass electrode which can be made of small size, but with sufficiently low resistance for accurate work. The design of the electrode is shown in Fig. 1. The supporting tube B (which is usually about 4 mm. in diameter) holds the thin glass diaphragm D over its lower end. The tube is partially filled with hydrochloric acid (0.1 N in our experiments) into which is inserted a silver–silver chloride electrode C. The upper part of tube B is coated, inside and outside, with paraffin.

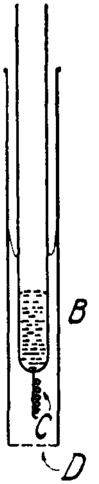

Fig. 1.

In the experiments to be described below the diaphragm D and supporting tube B were made as follows. A piece, weighing about 50 mg., of specially prepared glass for the diaphragm was first melted into the end of a pyrex tube of about 4 mm. diameter. The glass was then heated to a low red heat and blown into the form of a bubble with walls thin enough to show interference colors. The end of the tube B, which was of ordinary soft glass, was heated somewhat under red heat, and was then brought into contact with the bubble wall. If this operation is properly carried out the diaphragm will fuse onto the lower edge of the tube B. Such diaphragms are surprisingly strong. A group of tubes having these diaphragms over their lower ends held columns of nine centimeters of mercury for three weeks or more. No apparent difference in this time was observed whether the diaphragm was placed in tenth-normal acid or alkali or in water. The diaphragms are, however, easily broken by sudden jars.

The present investigation was undertaken with the purpose of finding the most suitable glass for the diaphragm.[2] The design of glass electrode just described is better than the original Haber form for comparing different samples of glass, since diaphragms of very nearly uniform and definite thickness can be selected and fused onto tubes of sufficiently uniform bore. Since commercial glasses are available with narrow ranges of composition

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[1] MacInnes and Dole, *Ind. and Eng. Chem.* (*Analytical Edition*), **1**, 57 (1929). This article contains references to the earlier work on the glass electrode. An apparatus involving the application of these electrodes to the determinaton of the hydrogen-ion concentration of very small amounts of liquids is described in *J. Gen. Physiol.*, **12**, 805 (1929).

[2] Tests of commercial glasses, using the Haber form of glass electrode, have been made by Hughes, *J. Chem. Soc.*, 491 (1928), and Elder, THIS JOURNAL, **51**, 3266 (1929).

only and contain a large number of components, some of which are definitely undesirable, it was decided to make our own samples of glass. These new glasses have, however, been compared with some commercial specimens. With the aid of Dr. Geo. W. Morey, to whom we are much indebted for assistance and suggestions, a platinum–rhodium wound furnace such as he has used in his researches on glass was constructed in the shop of the Geophysical Laboratory. The furnace is capable of reaching temperatures up to 1600°. We have also received useful suggestions from the Staff of the Bureau of Standards.

In making the glasses dry silica, calcium or magnesium carbonate and the carbonate of the alkali used were weighed out in the desired proportions and thoroughly mixed by grinding. The mixture was then melted in the furnace. It was found convenient to add the mixture a few grams at a time; otherwise the evolution of carbon dioxide causes the melt to flow over the edge of the crucible. After melting the sample it was held for an hour or so at 1200 to 1400° until all gas bubbles escaped from the melt, and to insure uniformity. The crucible and contents were then cooled, at first slowly and finally by quenching in a stream of cold water. This yielded material cracked into small pieces, some of which were suitable for making the thin diaphragms as already described.

For a first survey of the possible suitability of a glass for use as an electrode, three properties were measured, after the glass had been made into electrodes of the form shown in Fig. 1 with diaphragms of approximately 4 mm. diameter and about 0.001 mm. thickness. The properties chosen were (a) the potential existing in the diaphragm, (b) the resistance of the electrode and (c) the deviation from the theoretical potential when the electrode was placed in a buffer solution at $P_{\rm H}$ 8, and in an approximately 0.1 N sodium hydroxide solution of $P_{\rm H}$ 12.75.

(a) **The potential in the glass** was measured because, in the first place, it is a correction to the measured potential which must be made when the electrode is used for determining hydrogen-ion activities. Further, we have found by experience that if this "asymmetry potential" is large it is also likely to be varying and to require frequent determination. In addition, a glass with a large asymmetry potential is almost certainly otherwise unsuitable. The asymmetry potential was obtained by measuring the e.m.f. between the glass electrode and a silver–silver chloride electrode when both were placed in 0.1 N hydrochloric acid.

(b) **The electrical resistance of the glass** must not be too large, because a high resistance lowers the sensitivity of the measurements, and makes elaborate screening and insulation of the measuring instruments and of the cell necessary. Measurements of the resistance of the electrodes were carried out by shunting the electrometer with a 0.5 megohm resistance, after which it was connected in a circuit containing the glass electrode placed in hydrochloric acid, a silver–silver chloride electrode in the same solution and a known potential (1.2 volts). From the deflections obtained the resistances of the electrodes could be computed. With some of the harder glasses this method failed to yield quantitative measurements since the electrometer deflections were very small or zero, but in these cases the glasses were of no use for our purpose.

(c) **To measure the effectiveness of a glass when used as an electrode** for determining hydrogen-ion activity, the glass electrode was placed first in a buffer solution of P_H 8 with which a saturated calomel electrode was connected, the arrangement being

$$\text{Hg} \mid \text{HgCl, KCl (satd.)} \parallel \text{soln. A} \mid \text{glass} \mid 0.1\ N\ \text{HCl, AgCl} \mid \text{Ag}$$

If the glass surface is reversible to the hydrogen-ion activity, this combination can readily be seen to be equal in potential to the sum of the two cells

$$\text{Hg} \mid \text{HgCl, KCl (satd.)} \parallel \text{soln. A} \mid \text{H}_2 \text{ and } \text{H}_2 \mid \text{HCl } (0.1\ N)\text{, AgCl} \mid \text{Ag}$$

The potential of the first of these cells[3] is at 25°

$$E = 0.2458 - 0.05915 \log a_H$$

(in which a_H is the hydrogen-ion activity of solution A) and of the second -0.3524.[4] The relation between the e.m.f. of Cell 1 and the hydrogen-ion activity is, therefore, at 25°

$$E = -0.1066 - 0.05915 \log a_H = -0.1066 + 0.05915\ P_H$$

If, therefore, the glass surfaces are reversible to the hydrogen-ion activity Combination 1 should have a potential of 0.3663 when Solution A is at P_H 8 and of 0.6475 in the approximately 0.1 N sodium hydroxide which had a measured P_H of 12.75. Any glass at all suitable for our purpose showed no deviations in the first test but in the strong alkali large variations from the theoretical potential were always observed.

A summary of the results of the three tests just outlined made on a series of glasses is given in Table I. If the composition of a glass is given in the table it was made in this Laboratory. Most of the figures given in the table are the average of measurements on several electrodes. Though an effort was made to make the diaphragms of the electrodes of the different glasses as nearly alike as possible in diameter and thickness, it was impossible to avoid some variation. However, it will be seen that the effects of changing composition are much larger than can be accounted for by any possible uncertainty in these dimensions. An idea of the reproducibility can be gained from the measurements of resistances of five electrodes made of glass No. 6, the measurements being 11.6, 10.6, 11.1, 15.0 and 10.7 megohms. This degree of reproducibility is possible be-

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[3] W. M. Clark, "The Determination of Hydrogen Ions," The Williams and Wilkins Co., Baltimore, 3d ed., **1928**, p. 314.

[4] From the results of Scatchard, This Journal, **47**, 641 (1925), involving a slight interpolation.

cause a fair estimate of the thickness of a given portion of a glass membrane can be obtained from the interference colors present. It will be seen that the hard glasses, which are the first mentioned in the table, have large potentials present in the diaphragm, large resistances and large deviations from the theoretical potential in alkaline solutions. An improvement in all these respects is to be noted in the "soft commercial" glass (No. 4 in Table I), which showed a rather high but rapidly decreasing membrane potential. The resistance of the electrodes is lower (about 100 megohms), which makes more accurate measurement possible. This resistance, however, increased with time. The error observed in the alkali solutions is also smaller than with the harder glasses.

A great gain in each respect is found in the soft glasses (5 and 6) prepared in this Laboratory. No. 5 has the same composition as that tested by Elder and Wright[5] and is intermediate in properties between the soft commercial glass and No. 6, which has very nearly the composition corresponding to the lowest temperature found on Morey's[6] triangular melting-point diagram for the system $CaO–SiO_2–Na_2O$. This glass is, so far as our experiments have been able to determine, the best for use in determining hydrogen-ion activity. There is a low, nearly zero, potential in the membrane, the resistance is low, and the error in alkaline solution is the smallest observed. A more detailed study of the e.m.f. relations when this glass is made into electrodes is given below.[7]

Glass No. 7 made by increasing the percentage of alkali and decreasing the lime, is definitely too soft. The errors obtained in alkaline solutions are large and increase rapidly. Glasses Nos. 8 to 11 were made by systematically varying the composition of the three components by small percentages from that of glass No. 6. All these samples were inferior to that glass in the constancy of the readings in alkaline solutions, if not inferior in other qualities.

Since suitable glasses for hydrogen-ion measurements are all very soft their solubility may lead to errors if they are used with unbuffered solutions for any length of time. Direct measurements have shown that glass No. 6 will give off about 7×10^{-10} equivalent of base in twenty-four hours per square millimeter of surface. We therefore recommend that the diaphragm only be made of this glass, and that ordinary soft glass be used for the supporting tube.

It seemed possible that a "finer grained" glass might be prepared which

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[5] Elder and Wright, *Proc. Nat. Acad. Sci.*, **14**, 936 (1928). This composition is recommended by Hughes, *J. Chem. Soc.*, 491 (1928), but the glass he actually tested varied somewhat from this.

[6] Morey, *J. Soc. Glass Tech.*, **9**, 232 (1925); "International Critical Tables," McGraw-Hill Book Co., Vol. II, p. 97.

[7] The Corning Glass Co., Corning, N. Y., can usually furnish this glass (their Number 015).

TABLE I

PROPERTIES OF GLASSES AS ELECTRODES

		Composition of glasses, wt. percentage				Potential in glass, millivolts		Resistance, megohms		Initial error in 0.1 *N* NaOH millivolts
No.	Glass	SiO_2	CaO	Li_2O	Na_2O	1st day	2d day	1st day	2d day	
1	Pyrex							Very high		
2	Potassium	72	6		22^a	−52.0		High		Rapid incr.
3	Jena thermometer					−47.0	−42.7	400		Rapid incr.
4	Soft commercial					−27.9	− 6.0	72	96	Increase
5	Soda lime	72	8		20	+ 4.1	+ 6.1	47	42	Slow incr.
6	Best soda lime	72	6		22	− 3.8	0.6	12	8	−32 (const.)
7	Soda lime	72	4		24	− 2.5		5		Increase
8	Soda lime	70	6		24	− 7.5	− 1.6	7.5	5.8	−32 (very slow incr.)
9	Soda lime	74	6		20	−14.8	− 4.3	20.3	20.7	Slow incr.
10	Soda lime	74	4		22	− 3.3	0	5.4	3.4	Slow incr.
11	Soda lime	70	8		22	− 1.6	− 0.9	19.9	22.0	Slow incr.
12	Lithium	72	6	22		0	+ 1.1	1.5	0.2	Rapid incr.
13	Sodium lithium	72	6	2	20			600		Rapid incr.
14	Sodium lithium	72	6	4	18			High	700	Rapid incr.
15	Potassium lithium	72	6	11	11^a			3000	3000	Rapid incr.
16	Magnesium	64.5	10^b		25.5	−12.0	− 7.5	45	75	Rapid incr.

[a] K_2O. [b] MgO.

would show desirable properties in alkaline solution if lithium were substituted for sodium, since lithium has a much lower atomic volume. A glass was therefore made in which the sodium oxide of sample No. 6 was replaced by lithium oxide. This glass (No. 12 in the table) crystallized readily. However, by sudden chilling a workable, very low melting material was obtained which could be blown into thin bubbles. The supporting tube had, however, to be heated to a lower temperature than usual in order to avoid melting the film. The initial resistance of this glass was very low and dropped rapidly, and the e.m.f. reading at *P*H 8, which was correct on the first day, was considerably in error on the second day. The error in strong alkaline solution was initially about the same as with glass No. 6, but increased very rapidly. The glass is quite hygroscopic and becomes cloudy in a few days. Glasses Nos. 13 and 14 were prepared with the idea of discovering whether any desirable effect could be produced by replacing a part of the sodium in glass No. 6 with lithium. The unexpected result was that the electrodes had too high resistances to be of practical use. The errors in alkaline solution were also large and increasing. Electrodes with very high resistances were also obtained when they were made from a glass (No. 15) in which the sodium oxide of No. 6 was replaced by half each of potassium and lithium oxides. Sample No. 16 was made at the suggestion of Dr. Morey, who found that a melt of the composition given would not crystallize after prolonged heating. The measurements show, however, that it has no properties which recommend it for use as a glass electrode.

It next became of interest to determine the range in which measurements made with electrodes constructed of our best glass (No. 6) agree with the hydrogen electrode. An apparatus shown diagrammatically in Fig. 2 was constructed with which a hydrogen electrode H could be compared with a glass electrode G in the same solution. Connection was also made from the vessel containing this solution to a saturated calomel electrode C so that the *P*H of the solution and the constancy of the hydrogen electrode could be determined. The solution was saturated by a stream of carefully purified hydrogen entering by tube F. Arrangement was also made so that an alkaline solution could be added from the separatory funnel A to the solution in which the electrodes were dipped so that the *P*H could be progressively increased. By means of the tube D the current of hydrogen also passed through the alkaline solution in the funnel A so that, since no oxygen was introduced, the hydrogen electrodes rapidly came to a new equilibrium when the *P*H was changed. The results of such a comparison of the glass and hydrogen electrodes are given in Table II. Since the differences at low *P*H values are inappreciable, the comparison was started at *P*H 7.72, using a borax–boric acid buffer solution of approximately 0.1 *N* sodium-ion concentration.

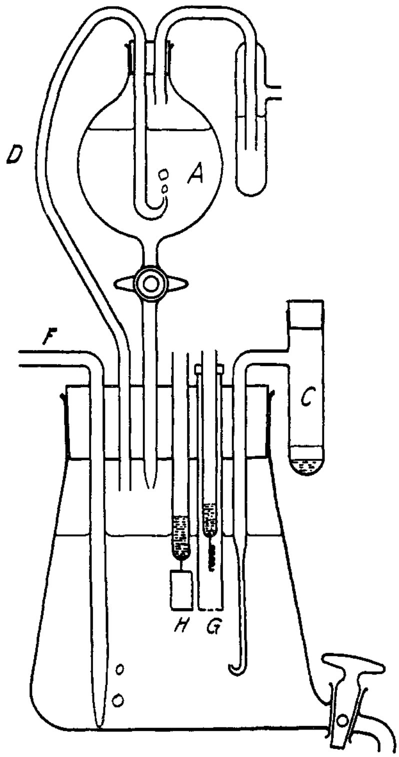

Fig. 2.

TABLE II

COMPARISON OF GLASS AND HYDROGEN ELECTRODES AT DIFFERENT *P*H VALUES

*P*H	7.72	8.20	8.73	9.23	9.83	10.47	11.64
Diff. between glass and hydrogen electrodes	0.3540	0.3540	0.3540	0.3540	0.3555	0.3577	0.3688

If the glass surface acts as a hydrogen electrode the potential of the combination

$$\mathrm{H_2} \mid \text{soln. A} \mid \text{glass} \mid 0.1\ N\ \mathrm{HCl},\ \mathrm{AgCl} \mid \mathrm{Ag}$$

should be constant and equal to that of the cell

$$\mathrm{H_2} \mid 0.1\ N\ \mathrm{HCl},\ \mathrm{AgCl} \mid \mathrm{Ag}$$

whatever the hydrogen-ion activity of solution A may be. The results illustrate the constancy of the difference (within 0.1 millivolt up to *P*H 9.2) and the deviations to be expected at higher alkalinities. The difference is within 0.0016 volt of the value given by Scatchard[4] for cell (B), the variations possibly being due to a difference in the method of preparing the silver–silver chloride electrodes, and in a lack of control, in these experiments, of the hydrogen pressure. These results are plotted on Curve A in Fig. 3, together with similar measurements (Curve B) in which the solution between the hydrogen and glass electrodes was kept saturated with sodium chloride (approximately 5.4 *N*). It will be observed that in this case the deviations from reversibility to the hydrogen activity begin at a lower *P*H value and are much greater than with the sodium-ion concentration at 0.1 *N*. The measurements were made with a potentiometer, using a Compton electrometer as a null instrument, in a constant temperature room at 25.0 ± 0.2°. Using glass No. 6 the resistance of the system is so low that ordinary care in screening is sufficient. In our work the leads were covered with a lead sheath, the cell was surrounded by a wire cage, and the necessary switches and tapping key were placed in a tin box. All these screens were, of course, grounded.

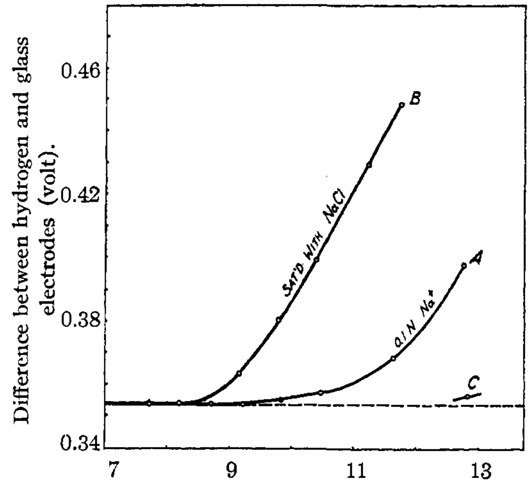

Fig. 3.

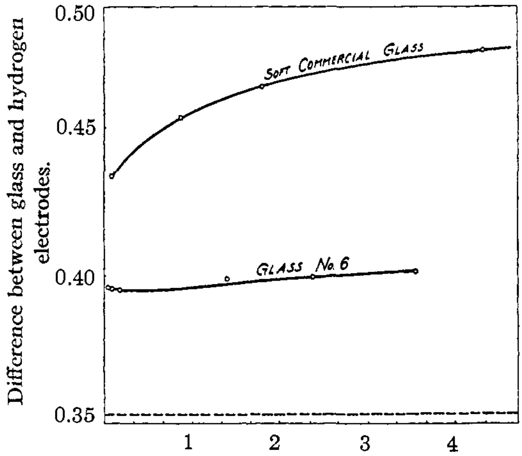

Fig. 4.

Incidentally Curve B also represents with quite sufficient accuracy the measurements of these deviations for glass No. 4 "soft commercial" of Table I, with the sodium-ion concentration at 0.1 *N*, showing that our glass No. 6 represents a decided improvement over glasses available in the market in the range of *P*H values in which the glass electrode is applicable. Furthermore we have observed that glass No. 6 shows steadier potentials in alkaline solution than any other that we have worked with. A comparison of two glasses under somewhat extreme conditions is given in the curves plotted in Fig. 4. The upper curve indicates the variation of the potential with time of the soft commercial glass, and the lower curve the corresponding variation of glass No. 6. It will be seen that the readings of the latter are roughly constant even in these strongly alkaline solutions.

Hughes[2] has shown, however, that these deviations in alkaline solutions depend upon the nature of the positive ions present. We have found, however, very small deviation at about *P*H 13 when the base present is tetramethylammonium hydroxide; this is shown in Point C of Fig. 3. We hope to be able to present in the near future a theory explaining these deviations.

Summary

Using a form of glass electrode designed by the authors, the suitability of a series of specially prepared glasses for use as electrodes has been studied, and a few comparisons have been made with samples of glass of commercial origin. The electrodes were tested for "asymmetry potential," resistance and the amount of deviation in alkaline solutions of the measured potential from the theoretically predicted potential. The best of the glasses tested has the composition SiO_2, 72, Na_2O, 22 and CaO, 6%. The potential at the surface of this glass changes quantitatively with the hydrogen-ion activity up to *P*H values of 9.5, though this limit is lowered in strong salt solutions.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

CERIC SULFATE AS A VOLUMETRIC OXIDIZING AGENT. X. THE DETERMINATION OF THALLIUM

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Introduction

A number of volumetric procedures for thallium have been proposed. Willm's method based upon the titration of thallous salt in hot hydrochloric acid solution with potassium permanganate has been the one most extensively used.[1] Hawley[1] found that if the permanganate was standardized against pure thallous sulfate in hot solution, using exactly the same

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[1] Willm, *Bull. soc. chim.*, 352 (1863); Noyes, *Z. physik. Chem.*, **9**, 603 (1892); Dennis and Doan, THIS JOURNAL, **18**, 970 (1896); Marshall, *J. Soc. Chem. Ind.*, **19**, 994 (1900); Hawley, THIS JOURNAL, **29**, 300 (1907); Müller, *Chem.-Ztg.*, **33**, 297 (1909); Berry, *J. Chem. Soc.*, **121**, 394 (1922); Bodnár and Terényi, *Z. anal. Chem.*, **69**, 29 (1926); Jílek and Lucas, *Chem. Listy*, **23**, 124 (1929).