FURTHER STUDIES ON THE GLASS ELECTRODE

By DUNCAN A. MACINNES AND DONALD BELCHER

In a series of papers from this Laboratory we have described a type of glass electrode which combines compactness with comparatively low resistance, its applicability to potentiometric titrations,[1] the use of the electrode for the determination of the P_H of very small volumes of solution,[2] and also a search for a glass of suitable properties to serve as electrodes.[3] In this last investigation a glass was found which has a relatively low resistance, shows small potentials in the glass membranes, and can be used over a wide P_H range to measure hydrogen-ion activities.[4] Direct comparisons between hydrogen gas electrodes and the glass electrodes were made in solutions which were given a series of P_H values. The present paper describes an extension of those measurements, using a considerably improved apparatus. The precision and reproducibility of the electrodes have also been studied by measuring the P_H of standard buffers and comparing with the results with the usual form of hydrogen electrode.

Measurements have been made of the resistance, and the "asymmetry potential" of the electrodes and of the effect of heat and drying agents. Finally, the different theories of the operation of the glass electrode are considered in the light of the new experimental work.   ·

The Construction of the Electrodes.—As explained in previous papers, the type of electrode used (G of Fig. 2) consists of a membrane of suitable glass of the order of 0.001 mm. thickness sealed over the end of a harder glass tube, of, say, 5 mm. diameter. Into this is placed 0.1 N hydrochloric acid and a silver–silver chloride electrode. Since some difficulty has been reported in following the very brief directions already published, a few additional suggestions will be given below.

A small globule is melted on the end of a tube of Corning 015 glass with a gas–air blast lamp. This globule can then be blown into a bubble thin enough to show interference colors. Such a bubble will have thicker portions, indicated by their lack of color and relative rigidity, which may be used if desired. The proper temperature for this operation can only be found by experience. A tube of ordinary soft glass on which some of this glass membrane is to be mounted is then heated on one end to low redness, and is then placed in contact with the bubble of glass. It is well

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[1] MacInnes and Dole, *Ind. and Eng. Chem. (Analytical Edition)*, 1, 57 (1929).

[2] MacInnes and Dole, *J. Gen. Physiol.*, 12, 805 (1929).

[3] MacInnes and Dole, THIS JOURNAL, 52, 29 (1930).

[4] Glass made from this formula may be obtained from the Corning Glass Co., Corning, N. Y. (their Number 015).

to cut this mounting tube with a sharp file or glass knife in order to get a flat even end. A large proportion of successful electrodes will be obtained if the mounting tube is brought into contact with the bubble with as little distortion or breakage of the latter as possible. That is to say, the mounting tube should be held as nearly as possible at right angles to, and its heated end in, the surface of the bubble. The bubble and mounting tube are separated only after the latter has had an opportunity to cool down somewhat. This separation necessarily breaks up the glass bubble. Considerable experience indicates that it is waste of time to attempt to make more than one electrode from a glass bubble, since the approximately spherical shape of the latter is necessary for the support of the membrane until it can be mounted. Loose pieces of membrane are, in general, too much disturbed by air currents to permit an effective seal onto a mounting tube.

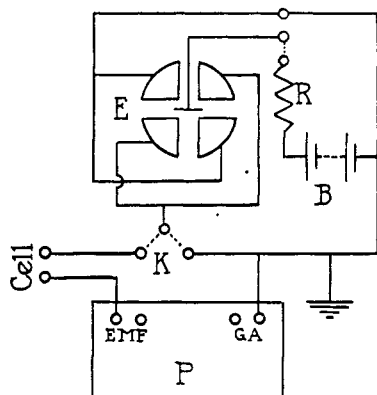The Electrical Measuring Apparatus.—A number of changes and improvements in the details of the apparatus for measuring the potentials have been made since the publication of the last paper. A diagram of the electrical connections is given in Fig. 1. We have used a Compton electrometer, E, together with a Type K Leeds and Northrup potentiometer, P.[5] Because of internal shunts in the potentiometer, the electrometer cannot be placed across the galvanometer terminals. An external circuit is, therefore, provided between the e. m. f. and galvanometer connections as is indicated in the diagram. The tapping key K of this external circuit impresses the net potential of the cell and potentiometer on two of the quadrants of the electrometer and on release automatically grounds them. To adjust the potentiometer, a galvanometer is connected to the

Fig. 1.

usual binding posts. Under these conditions the potentiometer can also be used for ordinary e. m. f. measurements without disturbing the electrometer connections. The needle of the electrometer is charged from a battery B of from 45 to 90 volts. For protection this circuit is provided with a megohm resistance R. The potentiometer P is placed in a covered box lined with grounded copper screen. An arrangement is provided by which the final setting of the wire and the potential reading can be made without opening the box. The apparatus containing the glass electrodes is placed in a large box made of 6.4 mm. wire mesh, grounded. The Compton electrometer E is placed on a Julius suspension supported by crossed tape wound springs, as recommended by Johnsrud.[6] The suspension is surrounded by a grounded galvanized iron box to protect it from air currents and to afford additional screening. This box also holds the battery B. The electrometer has a sensitivity of from 12 to 23 millimeters per millivolt at 1 meter distance. The zero is steady and shows very little drift with time. All connections, including those to the galvanometer, are made with wire armored with woven copper wire, the latter being, of course, grounded. The insulation of this wire has been measured by Dr. S. E. Hill of this Institute and found to have a resistance between the wire and metal shielding of 10^{15} ohms per linear foot. This was also found to be the minimum resistance to ground of any part of the system from the cell to the electrometer. This careful screening and insulation make it possible to study electrodes with higher resistances than those considered in our previous papers. Effective insulation is desirable because an electrical leak which tends to shunt the cell containing the glass electrode will greatly affect the measurements by producing polarization. This is especially the case when dealing with high resistance electrodes. A reversing switch in the leads between the cell and the rest of the apparatus is sometimes convenient, but must have a very high resistance between opposite leads; otherwise it may be a source of trouble. The chief difficulties we have encountered with the apparatus were located in the imperfect insulation of a reversing switch and a tapping key.

All measurements were made in a constant temperature room kept at $25 \pm 0.1°$.

The Apparatus for Comparing the Glass and Hydrogen Electrodes.— The apparatus described below, for comparing the glass and hydrogen electrodes, is an improvement on the one outlined in the previous paper in that it is possible to obtain more accurate P_H values with it and to know the pressure of the hydrogen used more accurately. It is also more convenient in use. The essential parts of the apparatus are shown in Fig. 2. The vessel A contains the solution into which are inserted the

[6] A. L. Johnsrud, *J. Optical Soc. Am.*, **10**, 609 (1925).

glass electrode G and the hydrogen electrode H. The P_H of this solution may be changed by the addition of acid or alkali from the buret B. This buret is supplied from a special flask (not shown) with solution saturated with hydrogen gas of exceptional purity. Since no oxygen is admitted with the added solution, the adjustment of the hydrogen electrode to a new P_H value is quite rapid. A stream of the purified hydrogen gas bubbles through the solution from the tube H_2, and passes out as shown through a hole in the support of the hydrogen electrode and the trap T. The P_H measurements are made with reference to a 0.1 N potassium chloride calomel electrode E. To prevent contamination of the solution in this electrode with the saturated potassium chloride solution used as a bridge, the outlet tube of the half-cell dips into the tube D which can be filled with 0.1 N potassium chloride. To make a definite liquid junction, a saturated solution from the reservoir R can then be introduced under the tenth normal solution by manipulating the stopcock S. Only the outer edges of the barrel of this stopcock are lubricated. By another adjustment of S the tube D can be drained. A definite liquid junction between the solution in A and the saturated potassium chloride solution is made by an adaptation of the method used by Clark.[7] The tubing between the stopcocks S
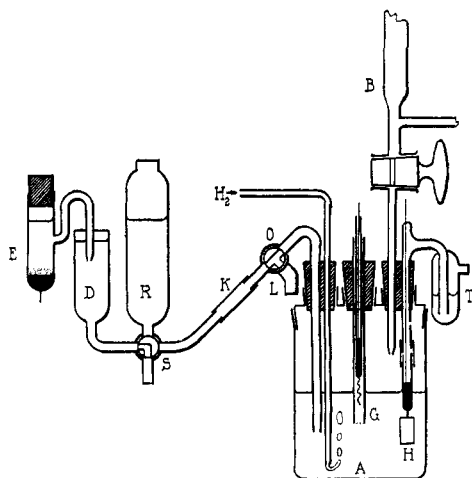

Fig. 2.

and O includes a piece of rubber tubing K. The solution in this is first swept out through the tube L by adjusting S and O. S is then closed and a screw pinchcock screwed onto the rubber tube K. The stopcock O is then turned so that solution from A can be forced through L. The flow is brought about by raising the gas pressure in A by holding a finger over the outlet of T. The stopcock O is then turned so that the solution from A and the saturated potassium chloride are in contact and the pinchcock on K is opened. A fairly sharp liquid junction then forms just below the stopcock O.

The Experimental Results

As already stated, we desired to test the glass electrode against the hydrogen electrode at a series of P_H values under conditions which would

    [7] W. Mansfield Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, 1925, p. 296.

yield a high degree of accuracy in the measurements. The P_H values were found from the e. m. f. between electrodes E and H of Fig. 2. These measurements give potentials, E_p of the cell

Hg, HgCl, 0.1 N KCl, KCl (satd.), soln. A. H_2
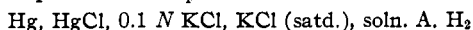
in which soln. A is the fluid in vessel A. The P_H values will be *defined* by the usual equation

$$P_H = (E - 0.3376)/0.05915$$

although there is some uncertainty as to the accuracy of the constant used, and as to the need for correction of liquid junction potentials at high and low P_H values. The efficacy of the glass electrode for determining the hydrogen-ion activities was found by determining the potentials between electrodes G and H of the same figure. Such measurements yield potentials of the cell

$$\text{H}_2, \text{soln. A} \mid \underset{a}{\text{glass}} \mid \underset{b}{\text{HCl (0.1 } N)}, \text{AgCl, Ag} \qquad (A)$$
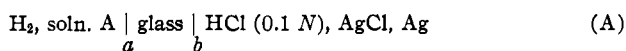
In this cell there are five sources of potential: those at the hydrogen and silver chloride electrodes, the potentials at the surfaces a and b of the glass, and an "asymmetry potential" in the glass membrane. Now if the potentials at the glass surfaces a and b change with the P_H in the same way that the potential changes at a hydrogen gas electrode, the variations of e. m. f. due to altering of the acidity or alkalinity of solution A should cancel, and the measured potential should be that of the cell

$$\text{H}_2, \text{HCl (0.1 } N), \text{AgCl, Ag} \qquad (B)$$
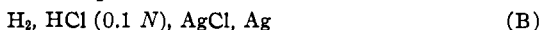
since the changes at the hydrogen electrode and at the glass surface a should be equal and in opposite directions.[8] Corrections must, however, be made for the asymmetry potential, and for the variation of the partial pressure of hydrogen from one atmosphere. On the other hand, any failure of the potential at the glass surface a to follow the changes of the hydrogen gas electrode quantitatively will result in a measurement of Cell A that differs from that of Cell B. Some quite typical results of measurements of cells of Type A are given in Table I, and indicate the nature and magnitude of the corrections which must be applied to the observed e. m. f. values. All the data in this table are taken in the P_H range in which the glass electrode functions quantitatively. It will be seen that although solution A was widely varied in composition

[8] This can be shown as follows. Neglecting the asymmetry potential, the total potential E of Cell A is

$$E = 0 + RT/F \cdot \ln (\text{H}^+)_s - (E_{0g} + RT/F \cdot \ln (\text{H}^+)_s) + (E_{0g} + RT/F \cdot \ln (\text{H}^+)_{0.1})$$
$$- [E_0' - RT/F \cdot \ln (\text{Cl})_{0.1}] = -E_0' + RT/F \cdot \ln (\text{H}^+)_{0.1} (\text{Cl}^-)_{0.1}$$

in which E_{0g} is the standard potential of hydrogen ion on the glass surface, E_0' is the corresponding potential for the Ag–AgCl electrode and the terms in parentheses are the activities of the respective ions. Thus $(\text{H}^+)_s$ is the hydrogen-ion activity in solution A, and $(\text{H}^+)_{0.1}$ that in 0.1 N HCl. E_{0g} certainly changes from one sample of glass to another but is assumed constant for the two sides of the membrane.

and P_H, and several electrodes were used in the measurements, the corrected potential of the cell was 0.3521 ± 0.0001 volt. A direct measurement of Cell B gave us 0.3521 volt. Interpolation from the recent work of Randall and Young[9] yields exactly the same result.

TABLE I

DIFFERENCE OF POTENTIAL BETWEEN HYDROGEN AND GLASS ELECTRODES

TYPICAL DATA ON E. M. F. OF CELLS

H_2, soln. A, glass, 0.1 N HCl, AgCl, Ag

Soln. A	P_H of soln. A	Electrode	Observed e. m. f.	Correction for hydrogen pressure	Asymmetry potential	Corrected potential
0.1 HAc + NaOH	4.85	D13	0.3512	0.0004	+0.0004	0.3520
0.1 HAc + NaOH	6.54	D13	.3513	.0004	.0004	.3521
HAc + LiOH	6.90	D13	.3500	.0004	.0017	.3521
HAc + Ba(OH)$_2$	7.00	D13	.3505	.0004	.0012	.3521
HCl (0.1 N)	1.02	E13	.3497	.0004	.0020	.3521
HCl (0.1 N) + NaOH	4.25	E13	.3498	.0004	.0020	.3522
HAc (0.1) + (C$_2$H$_5$)$_4$NOH	4.87	D13	.3487	.0004	.0031	.3522
H$_3$PO$_4$	3.70	F	.3481	.0004	.0036	.3521

More data of this type are given in Fig. 3, which represents the results of several series of measurements of cells of Type A in which the potential of the cell is plotted as ordinates against P_H values as abscissas. In one of these series, solution A of the cell consisted of hydrochloric acid to which sodium hydroxide was added, from buret B of Fig. 2. Due to a lack of buffer action over part of the range this combination yielded points only in the higher and lower P_H values. At the higher P_H values there are large deviations. A very similar curve (not plotted) was obtained by the addition of lithium hydroxide to hydrochloric acid. To obtain more points at intermediate P_H values, 0.1 N acetic acid was substituted for the hydrochloric acid, and to this were added solutions of a number of strong bases. Under these conditions the glass electrode follows the hydrogen gas electrode accurately up to P_H 8. The results also show that up to this P_H value the measured values of the difference between the glass and hydrogen electrodes were, when corrected for the asymmetry potential and the gas pressure, 0.3521 ± 0.0001 volt. This, it will be observed, is independent of the nature of the base and acid which made up the solution. MacInnes and Dole found agreement between the glass and hydrogen electrodes up to P_H 9. This was, however, with glass of their own manufacture. At higher P_H values deviations are observed, the values of which depend upon the nature of the base used. However, deviations when they occur are not reproducible, varying from electrode to electrode. Different deviations are found if the P_H values are decreased from those obtained on increasing the alkalinity. Due to overlapping

⁹ Randall and Young, THIS JOURNAL, **50**, 989 (1928).

parts only of some of the curves are shown. The curve for the results obtained when tetraethylammonium hydroxide was used as base is also sufficiently representative of those found when tetramethylammonium hydroxide or guanidine hydroxide was substituted as base. About the only generalizations that can be made from the observations on the deviations are that the large complicated organic ions yield smaller deviations than do the ions of the alkali metals. Also divalent ions produce smaller deviations than do monovalent ions at the same P_H values.
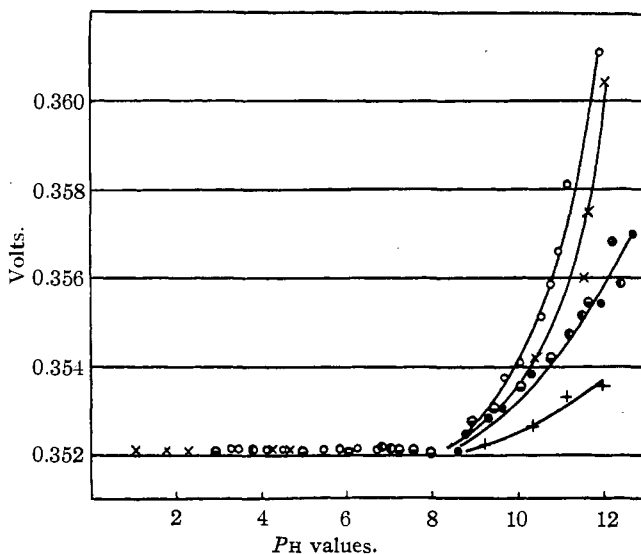

Fig. 3.—Difference between glass and hydrogen electrodes: $\times$, HCl + LiOH; $\bigcirc$, HAc + NaOH; $\ominus$, HAc + LiOH; $\mathbb{O}$, HAc + Ba(OH)$_2$; $\bullet$, HAc + (C$_2$H$_5$)$_4$ NOH; $+$, HAc + Ca(OH)$_2$.

It next became of interest to find what is the lower limit of P_H at which the glass electrode follows the hydrogen gas electrode. In these experiments a solution of about 0.01 N of the acid used was placed in vessel A of Fig. 2, and measurements of P_H and the e. m. f. between the glass and hydrogen electrodes were then made. A strong solution of the acid was next added in successive portions from buret B, thus lowering the P_H. The differences in e. m. f. between the hydrogen and glass electrodes are plotted in Fig. 4. At low P_H values there is, for all the acids tested, a deviation in the opposite direction to that observed for high P_H values. Furthermore, the deviation varies with the nature of the acid used, though as in the case of bases the variations are not very reproducible. The deviations produced by sulfuric acid are greater than those found with the monobasic acids tested, and the effect of phosphoric acid is still greater. We have not been able to find any other di- and tribasic acids, which are

otherwise suitable, by which we could make additional tests of this apparent effect of valence type on the deviations observed. Suitable acids would have to be strong and have no adverse effect on the hydrogen electrode. There is, as far as we can determine, no evidence in previous publications that other workers have observed a lower limit of P_H at which the glass electrode functions. Electrodes made of the glass used in these experiments are evidently not suitable for studying "superacid" solutions.
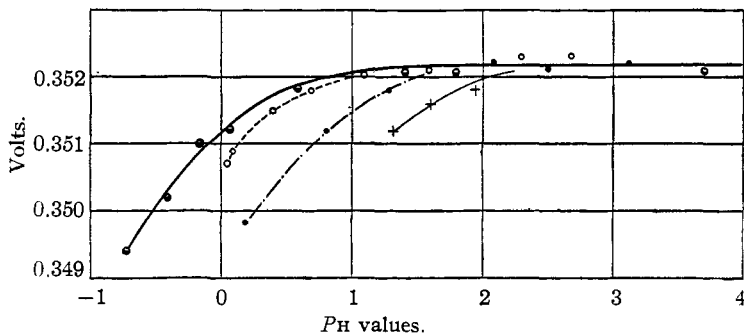

Fig. 4.—⊖, HCl; ○, HClO₄; ●, H₃SO₄; +, H₃PO₄.

Such experiments as we have just described have been designed to bring out and emphasize deviations when they occur. It should, however, be observed that these experiments indicate that the glass electrode functions quantitatively in the measurements of hydrogen-ion activity between P_H values 2 and 8 within one or two tenths of a millivolt, $i. e.$, about 0.002 to 0.003 P_H unit.

In order, however, to attain this order of accuracy, particular attention must be paid to the measurement of the asymmetry potential. Such measurements have been made by setting up the cell

$$\text{Ag, AgCl, 0.1 } N \text{ HCl} \mid \text{glass} \mid \text{0.1 } N \text{ HCl, AgCl, Ag} \qquad \text{(C)}$$
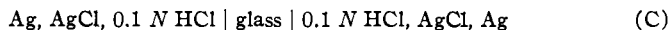
one of the acid solutions being outside and the other inside the electrode tube. We have repeatedly found that the potential of a silver–silver chloride electrode is constant only if the acid immediately on its surface is not disturbed. The measurements of Cell C were therefore made in a U-tube one arm of which held the glass electrode ensemble and the other a reference silver chloride electrode surrounded by a narrow tube which had a small opening at the bottom to allow for the passage of current.

The "Resistances" of Electrodes.—Although the opposition of the electrodes to the flow of electric current has been regarded up to the present time as ohmic resistance and has been reported in megohms, measurements by both direct and alternating current show clearly that at least the greater part of this apparent resistance is due to counter e. m. f., presumably due to polarization. Some typical measurements by both meth-

ods of a series of electrodes are given in Table II. It will be observed that the apparent resistances found by measurements using an alternating current of frequency 1200 are very much lower and roughly proportional to those obtained by d. c. determinations.

TABLE II

COMPARISON OF A. C. (1200 CYCLES) AND D. C. RESISTANCE MEASUREMENTS ON GLASS ELECTRODES

| No. of electrode | Apparent resistances | |
	A. C. megohms	D. C. megohms
1	1.28	54.5
2	1.32	51.0
3	3.96	129.0
4	1.69	52.5
5	2.84	102.0

This striking difference between the results of a. c. and d. c. measurements has long been familiar to biologists from their studies of the electrical properties of surfaces of cells.

The d. c. measurements were made using an electrometer, as described in a previous paper.[3] The a. c. determinations were kindly carried out by Dr. Theodore Shedlovsky of this Laboratory, using a Wheatstone bridge described by him in a recent paper.[10] The electrodes were shunted with a 10,000 ohm resistance to bring the measurements in the range of the bridge and the a. c. resistances computed from the bridge readings by the equation for parallel circuits. The a. c. resistances are functions of the frequency as is shown in Table III for a typical electrode.

TABLE III

APPARENT RESISTANCE OF A TYPICAL ELECTRODE AS AFFECTED BY FREQUENCY OF MEASURING CURRENT

Frequency	0	1020	1470	2050	3380
Apparent resistance, megohms	81	2.55	2.05	1.86	1.27

It will be seen that the apparent resistance decreases at first rapidly and then more slowly with increase of frequency. This change is due to the fact that the arm of the bridge, the impedance of which balances the impedance of the electrode and shunting resistance, does not imitate the latter sufficiently closely. The glass electrode has an effective capacity due to polarization in series with its ohmic resistance and, in addition, a geometric capacity in parallel due to the conducting electrolyte on each side of the glass membrane. Under these circumstances the results of resistance measurements will be a function of the frequency. However, the a. c. measurement is nearer than the d. c. determination to the true ohmic resistance.

[10] Theodore Shedlovsky, THIS JOURNAL, **52**, 1793 (1930).

Although the apparent d. c. resistance must be nearly all due to a counter e. m. f. of polarization, it is an interesting fact that such a resistance is found to be nearly constant when measured using different applied potentials. In other words, Ohm's law is approximately followed.[11] The figures given in Table IV for one electrode are typical.

TABLE IV

APPARENT RESISTANCE AS AFFECTED BY THE APPLIED E. M. F.

Applied e. m. f., volts	Current × 10⁹	Apparent resistance, megohms
0.126	1.02	123
.252	2.17	121
.377	3.12	121
.629	5.15	122
.879	7.26	·121

In view of these observations it does not appear desirable to change the current practice of reporting the apparent d. c. resistances of electrodes in megohms.

It has been our experience that it is desirable to work with electrodes with as low apparent resistances as possible in spite of the greater fragility of thin membranes. If thick electrodes are used, difficulties arise in connection with insulation and electrical screening. Obviously, accuracy can only be attained if the resistance of the path of the current through the glass membrane is small compared with all other possible paths of the current. With thick electrodes leak paths may reach the order of magnitude of the path through the active film of glass. It is a matter of observation that measurements with thick electrodes are more influenced than with thin electrodes by electrical leaks. If the cell measured is shunted by a leak resistance which is high compared with the resistance of the glass electrode, the current through the leak will be nearly constant for electrodes of varying resistances. Under these circumstances the polarization of the electrodes will increase as the resistance of the electrodes increases.

One possible source of trouble, particularly with thick electrodes, may be the supporting tube. In our work this has always been of harder glass than that forming the membrane and of a composition such that its potential does not respond accurately to change of hydrogen-ion activity. It is therefore desirable to keep the flow of current through the support-

[11] Joffé [*Ann. Physik*, **72**, 463 (1923)] has shown that for insulators the correct form of Ohm's law is $i = (E - P)/R$ in which i is the current, E the applied electromotive force, P the counter e. m. f. of polarization and R the true resistance. P is, however, a function of E. If we can assume, as a first approximation, that $P = kE$, where k is a constant, then $i = E(1-k)/R$, i. e., Ohm's law will apparently hold. Sinjelnikoff and Walther [*Z. Physik*, **40**, 786 (1927)] show that for mica the relation between P and E is approximately linear for the lower values of E.

ing tube as small as possible. This can be accomplished by using relatively thick tubing of low conductance and by employing thin membranes. The resistance of ordinary soft lime glass is about five hundred times that of Corning 015 glass. This has been shown by making several electrodes with very thin membranes (about 0.001 mm.) of the soft lime glass. Their apparent d. c. resistance was about 2500 megohms. An equivalent electrode of 015 glass has an apparent resistance of about 5 megohms. Considering that the wall of the tube is about one millimeter thick, it does not appear that any appreciable current can pass through it. Additional evidence that the supporting tube is not a source of leakage or other trouble was shown as follows. Using the technique described in the next paragraph, the P_H of a solution was determined with different immersions of the mounting tube of a glass electrode. The potential observed did not change as much as 0.1 millivolt from an immersion of one millimeter to one of eleven centimeters.

Measurements with Buffer Solutions.—It has seemed worth while to test the electrodes with standard buffers to determine their reproducibility under the conditions in which they will normally be used. The measurements were made with the aid of the electrode vessel shown in Fig. 5. The solution under observation was placed in the tube A, into which the glass electrode E could be plunged by means of a holder operated by a rack and pinion (not shown). A can be drained through tube C, and a liquid junction can be formed in tube D, with the aid of the rubber tube K. The rest of the apparatus is identical with the left-hand side of the apparatus shown

Fig. 5.

in Fig. 2. Two of the buffer solutions tested were 0.05 M potassium acid phthalate, and a sodium veronal–hydrochloric acid mixture.
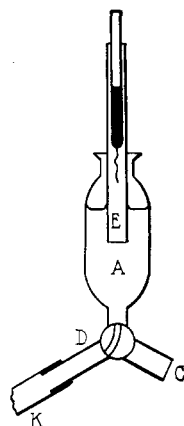
Some results with the phthalate buffer, using six different electrodes, are given in Table V. These readings were made against a saturated calomel electrode,[12] using the formula $E = -0.1063 + 0.05915 \, P_H$. As explained in the last paper in this series the constant used is the difference between Clark's "arbitrary value" of the standard potential of the saturated calomel electrode 0.2458 and the potential 0.3521 of Cell B (page 3319). A similar series made with a 0.1 N potassium chloride calomel cell as reference, using -0.0145 (*i. e.*, $0.3376 - 0.3521$) as the corresponding constant gave an average value of 3.982 for the P_H of the phthalate

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[12] The saturated calomel electrode appears to be as reproducible as the 0.1 N electrode provided that it can be kept for considerable periods at the temperature at which the measurements are made. Otherwise it shows hysteresis effects that may reach several millivolts.

TABLE V

PH VALUES OF 0.05 M POTASSIUM ACID PHTHALATE BUFFER AT 25°

Electrode	Measured e. m. f.	Asymmetry potential	P_H
R23	0.1278	+0.0013	3.980
R13	.1276	.0015	3.980
R14	.1278	.0014	3.981
R20	.1283	.0008	3.980
R22	.1284	.0008	3.981
R 8	.1309	− .0017	3.981

solution. Direct measurement with the usual Clark hydrogen electrode apparatus yielded 3.983 for the P_H value on the same basis. Clark and Lubs' original measurements[13] yield $P_H = 3.98$ at 20° if computed in the same way as for the above measurements.

The sodium veronal–hydrochloric acid mixture was prepared according to the directions of Michaelis[14] to give a P_H of 8. The results of the measurements with the glass electrode are given in Table VI.

TABLE VI

P_H VALUES OF SODIUM VERONAL BUFFER AT 25°

Electrode	Measured e. m. f.	Asymmetry potential	P_H
A5	0.4594	−0.0006	8.000
H10	.4616	− .0029	7.998
H11	.4625	− .0041	7.993
H9	.4612	− .0028	7.993
T10	.4620	− .0032	8.000
M4	.4620	− .0035	7.995
T17	.4637	− .0051	7.996
C1	.4677	− .0089	8.000

Average 7.997

A determination with the hydrogen electrode gave $P_H = 7.998$.

These examples from a number which could be given indicate that if adequate precautions are taken, especially with the asymmetry potential measurements, the glass electrode will give very accurate determinations of hydrogen-ion activity within the range in which it is applicable.
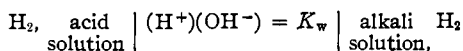
Theory of the Glass Electrode

Theories concerning the operation of the glass electrode have been proposed by several authors. The theory of Haber and Klemensiewicz[15] amounts fundamentally to the assumption that a Donnan equilibrium exists across the glass membrane with the proviso that H^+ and OH^- ions can penetrate the glass and other ions cannot. As is well known, a mem-

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[13] Clark and Lubs, *J. Biol. Chem.*, **25**, 479 (1916).

[14] Michaelis, *ibid.*, **87**, 33 (1930).

[15] Haber and Klemensiewicz, *Z. physik. Chem.*, **67**, 385 (1909).

brane at which a Donnan equilibrium exists has a potential which changes reversibly with changes of the activities of the ions that are able to pass through it.   Haber and Klemensiewicz state their assumptions in a somewhat different way.   They consider a cell of the form

$$\text{H}_2, \quad \underset{\text{solution}}{\text{acid}} \; \Big| \; (\text{H}^+)(\text{OH}^-) = K_w \; \Big| \; \underset{\text{solution,}}{\text{alkali}} \quad \text{H}_2$$

In this cell two hydrogen electrodes are in two solutions which are separated by another phase, which has the property that the ion product $(\text{H}^+)(\text{OH}^-)$ is equal to that of water.   Thermodynamically this cell should have zero potential, which would also be true if the intermediate phase were a Donnan membrane in the usual sense.   We have shown that the operation of the glass electrode is intimately related to the water in the glass by means of some simple experiments.   These experiments have shown that any process tending to dry out the electrode causes large increases in apparent resistance.   For instance, a typical electrode had an apparent (d. c.) resistance of 32 megohms.   After heating at 50° in vacuum with phosphorus pentoxide the resistance increased 40,000 megohms. The drying process can proceed even at room temperature, as is shown by the following observations.   Six electrodes were placed in a vacuum desiccator over phosphorus pentoxide for ten days at 25°.   As a control four electrodes were kept over water, but otherwise under the same conditions.   The resistance measurements are given in Table VII.

TABLE VII

CHANGES IN APPARENT RESISTANCE OF ELECTRODES WITH AND WITHOUT DRYING AT 25°

Electrode	With drying Resistance, megohms		Electrode	Over water Resistance, megohms	
	At beginning	After 10 days		At beginning	After 10 days
1	28	113	1	22	30
2	28	60	2	28	38
3	36	118	3	42	56
4	27	99	4	41	51
5	24	93			
6	41	110			

Average increase with drying, 230%   Average increase without drying, 34%

There is, it will be noted, a very much greater increase of resistance when the electrodes are kept in a dry atmosphere than when they are held in water vapor.   The increase of resistance of the electrodes kept over water may be due to a slow crystallization of the glass.   A still more marked increase of resistance due to drying took place at 39°.   After immersion in water there was a slow return to approximately the original resistance.

At room temperatures the movement of water molecules in and out of the glass must be very slow.   This is shown by the fact that a week of drying at 25° did not produce more than a small fraction of the change

of the apparent resistance found by drying at 50°. At the lower temperature the drying may have been confined to the outer layers only of the glass membrane.

That water passes very slowly through the glass was also shown by placing dehydrated copper sulfate in contact with a very thin membrane of a glass electrode, sealing off the mounting tube, and placing the outer surface of the membrane in water. Although a small amount of water would have changed the color of the copper sulfate from white to blue, there was no perceptible change of color in twenty days. More sensitive tests for the passage of water through thin glass membranes will be carried out in the near future.

That one or more of the ions of water can penetrate the glass under the influence of an electric potential is shown by the work of Quittner,[16] who found that the amount of current carried from an acidified salt solution by hydrogen ions increased rapidly with the percentage of acid present, being 100% at an acid concentration of 5×10^{-4}. Similar results were obtained in this Laboratory by L. L. Burgess, and will be presented later. He found that with very thin electrodes acid formed in accordance with Faraday's law at the glass surface. Either of these results could arise from the movement through the glass–liquid boundary of hydrion in the direction of the current or of hydroxyl ions moving in the reverse direction, although Quittner's observations make the penetration by hydroxyl ions appear quite improbable. Furthermore, we have just presented evidence that water may move in and out of the glass. It is thus possible for the theory advanced by Haber and Klemensiewicz to be correct. However, it involves the qualification that the glass must be in equilibrium with the water in the solutions with which it is in contact.

It seems to us that equilibrium of water throughout the glass is improbable because of the slowness with which water enters and leaves it. A simpler assumption, and one which accounts for all the phenomena within the P_H range in which the glass electrode functions quantitatively, is that the hydrogen ion, or proton, can pass the electrolyte–glass boundary at a lower potential than any other positive ion and that negative ions do not pass the boundary at all. This does not involve any assumptions as to the conduction in the glass. It is quite probable that other ions than hydrogen move in the body of the glass.

Hughes[17] has proposed, as an explanation of the behavior of the glass electrode, the theory that the sodium silicate and excess silicic acid in the glass act as a buffer, preventing penetration of ions from the solution from changing the hydrogen-ion concentration of the glass. The failure of the

16 Quittner, *Ann. Physik*, [IV] **85**, 745 (1928).

17 Hughes, *J. Chem. Soc.*, 491 (1928).

buffer process, according to this author, begins at P_H 9, which is about that of the first dissociation constant of silicic acid.   If it were possible to make such an assumption, it would be helpful but not sufficient.   A junction of the sort

<div align="center">soln. A | buffer</div>
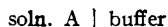
will give a potential following the hydrogen-ion activity only if the hydrogen ion is the only ion that can pass the boundary.   Further, if, as is assumed by Hughes, the glass is a buffer consisting of a mixture of an acid with a dissociation constant of 10^{-9} and its neutral salt, it has the unusual property of maintaining its P_H in contact with very strong acid, but of failing to do so in contact with solutions whose P_H values are in the region of the hypothetical P_H of the glass at its greatest "buffer value."[18] Furthermore, without additional assumptions it does not seem possible to deduce the hydrogen-ion concentration of glass from ionization constants applicable to aqueous solutions.

To account for the deviations at high and low P_H values, the assumption of ionic interchanges in the surface appears to be sufficient.   If the hydrogen-ion concentration of the solution in contact with the glass surface becomes very low, a high potential will be present between the hydrogen ion in the glass and that in the solution.   Any reaction that will reduce this potential will tend to occur.   A possible reaction from, for instance, a sodium hydroxide solution, will be

$$Na^+ + (H) = (Na) + H^+$$
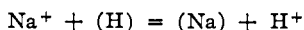
the terms in parentheses representing the material present in the glass. It is also possible that the reverse of this reaction occurs at very high hydrogen-ion activities, and accounts for the deviations at low P_H values. In this connection much light can be thrown on the observations of the behavior of glass at room temperature by a consideration of results of experiments by other workers which have been carried out at 200° and above.   At these more elevated temperatures the glass is probably largely dehydrated and some other ion (usually sodium) takes the part played by hydrogen in the colder glass.   In an important paper G. Schulze[19] showed that the reaction

$$Ag^+ + (Na) \rightleftharpoons (Ag) + Na^+$$

takes place spontaneously and quantitatively across the boundary between glass and molten silver nitrate.   In this equation Ag^+ and Na^+ represent ions in the melt and (Na) and (Ag) the corresponding constituents in the glass.   This demonstrates the reality of ionic interchanges at higher temperatures and makes them appear probable at lower ones. Furthermore Kraus and Darby[20] find that monovalent ions enter glass

[18] Van Slyke, *J. Biol. Chem.*, **52**, 525 (1922).

[19] G. Schulze, *Ann. Physik*, [IV] **40**, 335 (1913).

[20] Kraus and Darby, THIS JOURNAL, **44**, 2783 (1922).

much more readily than do divalent ions. This observation has also been made by Quittner. It will be seen that in Fig. 3 the deviations produced by sodium and lithium are much greater than those found with the divalent barium and calcium ions, which apparently do not exchange so readily, possibly because one of the latter would have to occupy the position previously taken by two hydrogen ions in the glass. The potentials at the surfaces of glass electrodes have been studied from this point of view by Horovitz and associates.[21] This investigator has recently given a formula for the potentials resulting from such exchanges.[22] His treatment, which is very briefly outlined in the reference given, includes correction for the diffusion potential which would arise from the change of composition of the glass resulting from the ionic interchange. Although his formula predicts deviations of the general form shown in Fig. 3, the computed values tend to increase more rapidly than the observed values with the PH if the necessary empirical constant is obtained from the lower PH measurements. The equation does not predict deviations in strongly acid solutions.

As a working hypothesis, then, we consider that the known facts about the glass electrode may be explained by the following assumptions. The glass contains a small amount of water which yields hydrogen ions. These can move in and out of the surface of the glass more readily than any other ions. The glass thus acts as a reservoir for hydrogen ion of constant activity. There is no need for the activity of this hydrogen ion to be the same in different samples of glass. If, however, the potential due to the difference of chemical potential of the hydrogen ion at a glass surface and that in the solution becomes too high, ionic exchanges will occur which will tend to lower this potential. When such exchanges take place the glass surface ceases to function quantitatively as a hydrogen electrode. Further experiments designed to test this hypothesis are in progress. A study is also being made of the operation of the glass electrode in solutions which are very slightly buffered.

Summary

Comparisons of glass and hydrogen electrodes have been made through wide PH ranges under conditions designed to yield high accuracy in the measurements.

From PH 2 to 8 the two electrodes agree within less than ±0.0002 millivolt, if corrections are made for "asymmetry potential." Above PH 8 deviations occur which depend upon the nature of the positive ions present. Also at very low PH values deviations of an opposite kind are

[21] Horovitz, *Z. Physik*, **15**, 368 (1923); *Sitzb. Akad. Wiss. Wien*, Abt. IIa, **134**, 335 (1925); Horovitz and Zimmermann, *ibid.*, **134**, 355 (1925).

[22] Horovitz, *Nature*, **127**, 440 (1931).

observed. These apparently depend upon the nature of the negative ions present in solution.

Resistance measurements made by a. c. methods on glass electrodes indicate that most of the apparent resistance obtained by d. c. measurements must be due to polarization.

Large increases of apparent resistance of the electrodes result from drying processes even at room temperature, indicating the importance of water, or its ions, in conduction through the glass membranes.

Theories designed to explain the operation of glass electrodes are considered in the light of these new experimental results.

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THE EQUILIBRIA AND REACTION RATES FOR THE REACTION SODIUM ARSENITE–SODIUM TELLURATE[1]

BY PHILIP T. STROUP[2] AND VILLIERS W. MELOCHE

A preliminary study of the oxidation reactions of telluric acid and the tellurates revealed some reactions which seemed to be rather significant in the chemistry of tellurium. Among these, the reaction between sodium arsenite and sodium tellurate appeared to be particularly adapted to further study. This reaction was selected for the present research because of the convenient and reliable analytical methods involved and the absence of complicating side reactions. An examination of the existing literature showed that while numerous investigations have been reported on equilibria and reaction rates involving the arsenite–arsenate half reaction, no mention has been made of any reaction of arsenite and tellurate ions.

Materials

Telluric Acid.—The telluric acid was prepared by the Staudeumaier method[3] which depends on the chromic acid oxidation of tellurium dioxide in dilute nitric acid solution. After repeated crystallization the product was dried over calcium chloride. The resulting material was shown by analysis to be exceptionally pure H_6TeO_6.

Sodium Tellurate (Na_2TeO_4).—Sodium tellurate was prepared in solution by the addition of a standard solution of telluric acid to a solution containing an equivalent amount of carbon dioxide-free sodium hydroxide. This order of combination was used since the addition of sodium hydroxide to the telluric acid solution gave the difficultly soluble sodium acid tellurate. The strength of this stock sodium tellurate solution was checked by analysis.