A DESCRIPTION OF THE GLASS ELECTRODE AND ITS USE IN MEASURING HYDROGEN ION CONCENTRATION.

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This paper contains the description of a glass electrode and of the apparatus needed for its use. If a glass membrane is interposed between two solutions of different hydrogen ion concentration, a potential difference will be set up across the membrane. Under certain conditions this P.D. is determined by the difference in pH of the two solutions so that if the pH of one is known, that of the other can be calculated. This method of measuring pH is especially well adapted to many biological purposes. The glass electrode is as accurate as the hydrogen electrode (within the pH range of biological significance), as rapidly operated as the quinhydrone electrode, and more widely applicable than either of the other two. It is unnecessary here to discuss the theory of the potentials obtained. Nevertheless some mention of the development of the glass electrode may be of value. Cremer (1) while making a study of bioelectric phenomena was the first to observe that the magnitude of the potential at a glass membrane is affected by the difference in acidity of the two solutions on either side of the membrane. Exact measurements of this effect were made by Haber and Klemensiewicz (2) who found that the following equation expresses the relation between the hydrogen ion concentrations of the solutions and the potential at the glass membrane

$$E = RT \ln \frac{C_{H_1}}{C_{H_2}}$$

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The membrane potential may be regarded as consisting of two glass-water interfacial potentials. Under these circumstances this equation can then be derived if it is assumed that the hydrogen ion concentration of the glass phase remains constant. Recently Hughes (3) has pointed out that the hydrogen ion concentration in the glass phase may be held relatively constant by the buffer action of the glass which is a mixture of the salt of a weak acid (Na_2SiO_3) with the anhydride of that acid (excess SiO_2). At about pH 9 the divergence in values of pH between the glass and hydrogen electrodes becomes noticeable and it is here that the buffer action of the glass would be less effective since the apparent first dissociation constant of H_2SiO_3 is about 10^{-9}. The apparent second dissociation constant of H_2SiO_3 is 10^{-13} and it is at pH 13 that the divergence between the glass and hydrogen electrodes rapidly increases. Haber suggested that the glass cell could be used to measure hydrogen ion concentration. There the matter rested, however, until more than 15 years later Kerridge (4) made exact pH measurements with it. She showed that under certain conditions only the difference in hydrogen ion concentration affects the P.D. and that the measurements made with the glass electrode agree to within 0.01 pH with those made with the hydrogen electrode. The practical applications of the glass electrode begin with her contribution. The arrangement which we employ is derived directly from hers. We have made a number of changes, however, that make the construction and use of the electrode simpler.

1. The Electrode.—The electrode is made of ordinary soft soda glass. The glass we used was supplied by the Kimball Glass Company of Vineland, New Jersey. It has the following analysis:

	per cent
Silica	69.7
Alumina, iron oxide, *etc*	2.0
Zinc oxide (with small amount of manganous oxide)	1.5
Calcium oxide	6.0
Magnesia	3.8
Boric anhydride	0.8
Sodium oxide (including small amount of potassium oxide)	15.7

A borosilicate glass, such as Pyrex, cannot be used. Hughes (3) has recently tested a variety of soda glasses and finds that those of low alumina content are most suitable.

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To make the electrodes, glass tubing having walls of medium thickness and an inside diameter of $\frac{3}{8}$ inch is used. A small bulb is blown at one end with walls thick enough to be strong. By directing a fine small flame at a point on the bulb and then sucking at the open end of the tube a small cup is formed depressed below the surface of the bulb. The cup should contain about 0.5 to 1.0 cc. and should be made quickly and without annealing (3). The total length of bulb and tube is about 3 inches. The

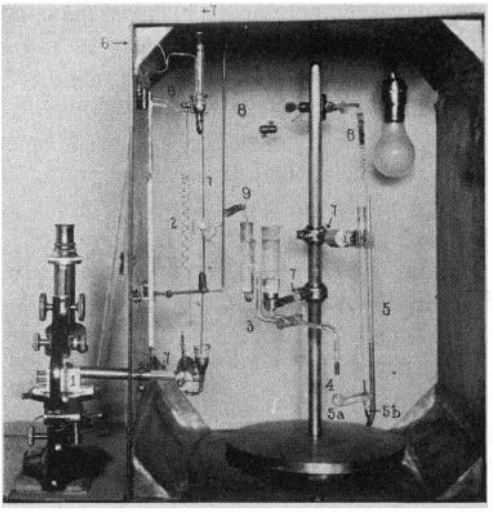

FIG. 1. 1, Lindemann electrometer; 2, switch; 3, calomel half-cell; 4, agar tip; 5, combined glass electrode and calomel half-cell; *a*, glass electrode; *b*, calomel half-cell; 6, metallic shielding; 7, quartz insulation; 8, wire to potentiometer; 9, wire to electrometer needle.

open end of the tube is joined at right angles to a longer piece of the same kind of tubing (Fig. 1). The longer tube has a length of about 10 inches. It is closed at one end and the junction with the shorter tube is made about 1 inch from the closed end. If the vertical arm of the electrode were not so long, it would be necessary before making a measurement to dry carefully the horizontal arm so as to prevent electrical leakage. The electrode is cleaned with chromic acid, carefully rinsed with tap water, and allowed to stand in water for 2 days, or more if necessary.

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The thin wall of the cup is the glass membrane. A buffer solution is placed in the large bulb, and the solution of unknown pH in the small one. The P.D. across the membrane can then be measured. Electric contact with each solution is made by means of a calomel half-cell. The system has been simplified by placing one of the calomel half-cells instead of a buffer solution inside the large bulb. The arrangement of the combined glass electrode and half-cell is shown in Fig. 1.

2. Calomel Half-Cell.—A convenient form of calomel half-cell is shown in Fig. 1. It is supported in a collar so that it can be easily moved from side to side. It can also be moved vertically by a rack and pinion. When the tip of the saturated KCl bridge dips into the cup of the glass electrode, the KCl, being heavier than water, flows down to the glass membrane where it constantly keeps changing the existing P.D. and prevents reproducible measurements from being made. This difficulty can be prevented by joining an agar-KCl tip to the end of the bridge.

3. Measurement of Potential.—The resistance of the glass membrane is so high that a galvanometer cannot be used in connection with a potentiometer to measure the P.D. across the membrane. An electrometer must therefore be used instead. The Lindemann electrometer (5) as pointed out by Kerridge, is a convenient form of this instrument, requiring no levelling and being nearly as sensitive as other electrometers. The use of the Lindemann electrometer is fully described in Kerridge's paper (4) where a description of the wiring is also to be found. The electrometer needle is earthed except when connected to the glass electrode. A convenient method for switching the needle from ground to the electrode has been devised (Fig. 2). The switch should be constructed so that when it is used the electrometer needle does not move at all if the P.D. of the glass cell is exactly balanced by the P.D. of the potentiometer system. With an ordinary switch the mere act of switching may cause the needle to jump (and then return to its zero) even at the null-point. The wire from the electrometer needle divides at 4, one part going to 5 and thence to earth, while the other goes to 7 and thence to the glass electrode. When the rod, 2, is pressed down the contact at 5 is broken and that at 7 is made, the latter being made the *instant* after (or even before) the former is broken. When the rod is released the re-

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verse contacts are made. This switch facilitates the use of the electrometer as a null-point instrument. The apparatus is shielded from electrostatic disturbances by the metal box, 9, and

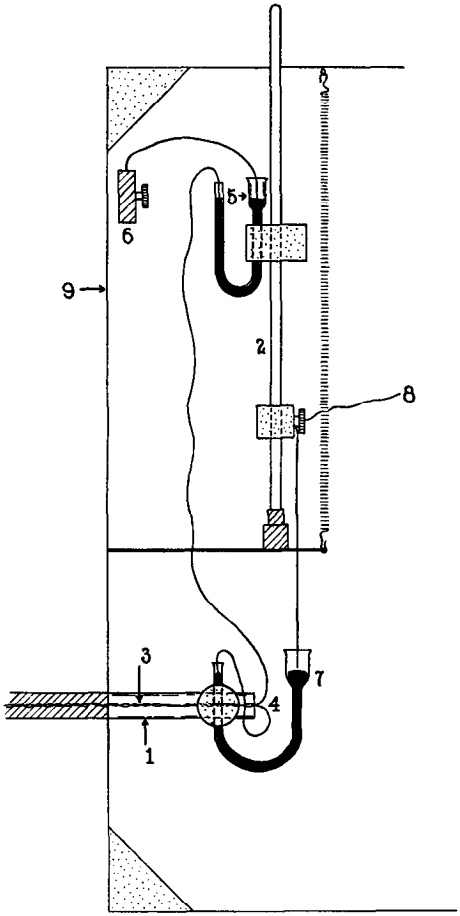

FIG. 2. The switch. 1, quartz tube; 2, quartz rod; 3, wire to electrometer; 4, wire to electrometer divides; 5, contact for earthing; 6, to earth; 7, contact to electrode; 8, to glass electrode; 9, shielding.

tube which are earthed. It has not been necessary to close the open side of the box.

4. Insulation.—As a consequence of the great resistance inter-

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posed in the circuit by the glass membrane that part of the circuit between the electrode and electrometer must be carefully insulated. Kerridge used amber for this purpose, but we find that it is accomplished just as satisfactorily and more conveniently with quartz. Insulation is necessary in each of the arms holding the electrode and calomel half-cell where there is a short length of quartz rod. For the same reason the switch leading from electrode to electrometer has certain parts made of quartz, as indicated in Fig. 2.

5. Manipulation.—When not in use the glass electrode is kept emersed in water. The water is withdrawn from the small cup by means of a small pipette furnished with a rubber nipple at one end; to the other end a piece of flexible capillary rubber tubing about 1½ inches long is attached to avoid breaking the glass membrane. To clean the electrode after a measurement has been made, all that it is usually necessary to do is to rinse the small bulb and agar tip with a stream of distilled water. It takes about 1 minute to make a measurement. The P.D. of the glass electrode is measured first when it contains a solution of known pH (*e.g.* 0.05 M potassium hydrogen phthalate). The pH is observed again when the solution of unknown pH is added to the cup of the electrode. From the two, the unknown pH can be calculated. Kerridge has shown that

$$pH_x = 3.97 + \frac{E_s - E_x}{0.000,198,37\ T}$$

E_s is the potential found when potassium hydrogen phthalate is in the electrode, E_x the potential when the unknown solution has been added, and T is the absolute temperature. Any potential due to the glass itself does not affect the final result.

It may be well to summarize the advantages of the changes which have been made from Kerridge's arrangement.

Electrode.—The present electrode is easier to make than the ones described by Kerridge; it has a greater insulation surface, and it contains in it one of the necessary calomel half-cells.

Insulation.—Quartz is stronger and easier to clean than amber.

Switch.—A switch has been described which combines speed of change of contact with ample insulation.

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KCl Contact.—The contact is made with an agar tip instead of through a ground glass joint, which is less convenient and takes more room.

SUMMARY.

The construction and use of a glass electrode for the measurement of hydrogen ion concentration is described.

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