[CONTRIBUTION FROM THE DEPARTMENT OF PHYSIOLOGY, SCHOOL OF MEDICINE, UNIVERSITY OF PENNSYLVANIA]

Studies on the Glass Electrode[1]

BY EDWIN P. LAUG

The MacInnes type[2] glass electrode, made by fusing a thin membrane of Corning 015 glass over the end of a 4-mm. soft glass tube, has been found to give generally satisfactory results. Nevertheless, more information concerning, (a) the seasoning of freshly prepared membranes and their stability, (b) their behavior under a variety of experimental conditions, seemed desirable.

For the purpose of this investigation three factors were used as criteria of reliability for glass membranes: (1) asymmetry potential, (2) hydrogen electrode function, (3) d. c. resistance.

Measurements of asymmetry potential and *P*H were made by the following system

$$\mathrm{Hg} \mid \mathrm{Hg_2Cl_2},\ \text{satd. KCl} \parallel \text{soln. A} \mid \text{Glass} \mid \mathrm{PO_4}\ \text{Buffer}\ P\mathrm{H}\ 6.5 \parallel \text{satd. KCl},\ \mathrm{Hg_2Cl_2} \mid \mathrm{Hg}$$

Careful construction of the calomel cells and adjustment of the liquid junctions made potentials originating from these sources negligible. The sign of the e. m. f. developed by the system was given by the following convention: minus, when solution A was more alkaline; plus, when solution A was more acid than the reference solution of *P*H 6.5. Asymmetry potentials (designated henceforth as A. P.) were determined by taking the difference between the e. m. f. observed in the system without the glass membrane, and the e. m. f. observed with the glass membrane, phosphate buffer of *P*H 6.5 being used on both sides.

The hydrogen electrode function (designated henceforth as $\Delta E/\Delta P\mathrm{H}$) of the glass membranes was determined by plotting through several points *P*H of buffers as determined by the hydrogen electrode against e. m. f. as observed with the glass electrode. The slope of the straight line $\Delta E/\Delta P\mathrm{H}$ equaled 0.0617 at 38° if the electrode functioned as a perfect hydrogen electrode.

The d. c. resistance of the system was determined by impressing known potentials across the glass membrane with isohydric solutions on both sides, and measuring the deflection of a galvanometer having a sensitivity of 5.0×10^{-10} amp. per mm. scale division at one meter. While it is admitted that the flow of this current through the glass membrane may be enough to cause polarization of the membrane, yet repeated observations indicated that this did not affect the potential of the chain when used for determining *P*H.

The e. m. f. developed across the high resistance of the glass membrane was measured by means of a vacuum tube electrometer developed by Stadie *et al.*[3] All determinations reported in this paper were made at 38°. To this end the glass electrode and calomel cells were enclosed in a stirred air-bath electrically maintained at 38°.

Experimental

Many different methods for sealing the fragile glass membrane to the soft glass shank were tried.

Practically 80 to 85% of these electrodes showed gross leaks when filled with water or exhibited erratic behavior when set up in the apparatus. By accident it was discovered that if the electrodes were filled with water as soon as they were cool, the percentage of failures was very much reduced. It appeared that strains which occurred where the thin glass was sealed to the soft glass shank caused minute cracks to form along the seal and this was prevented if they were moistened.

New membranes required aging for at least four to five hours in water. Without this treatment their behavior was very erratic, being characterized chiefly by large fluctuations in A. P. and low values for $\Delta E/\Delta P\mathrm{H}$. During this period there was also a rapid decrease in membrane resistance of the order of 100%, presumably conditioned by the penetration of ions into the glass phase, since resistance measurements with mercury in contact with dry membranes did not show such rapid changes.

Daily observations over periods of one month or more on a series of membranes which had been aged showed that the A. P. was quite constant, ranging in value from -0.5 to $+0.5$ mv. The slope $\Delta E/\Delta P\mathrm{H}$ was also very constant; calculated standard deviation from the mean value for each electrode was 0.0005, which was within the error of the method.

---

[1] Aided in part by a grant from the Special Faculty Research Fund of this University.

[2] D. A. MacInnes and M. Dole, *Ind. Eng. Chem., Anal. Ed.*, **1**, 57 (1929).

[3] W. C. Stadie, H. O'Brien and E. P. Laug, *J. Biol. Chem.*, **91**, 243 (1931).

Observations of membrane resistance over considerable periods of time showed that there was also a slow drop in d. c. resistance which undoubtedly was caused by gradual solution of the glass. It is well known that water takes up alkali from soft glass, and it was observed during attempts to measure P_H in unbuffered solutions with the glass electrode that rapid drifts toward more alkaline values occurred. This solution of the glass membrane was more rapid at 38°. Table I presents comparative data showing how the resistance of membranes decreased at room temperature and at 38° while in contact with water or a slightly acid buffer. Taking for example membranes 12 and 27 with almost equal initial resistances, it can be seen that during five days at 38° the resistance of No. 27 decreased from 44.5 to 10 megohms, while within a period of almost a month at room temperature, that of No. 12 only decreased from 50 to 40 megohms. This change in resistance, however, whether slow or rapid, did not cause any significant changes either in A. P. or $\Delta E/\Delta P_\mathrm{H}$. This observation of the comparatively rapid solution of glass membranes at 38° proved useful in reducing the resistance of thick membranes. The process was also speeded up if, in addition to the elevated temperature, the membranes were placed in mildly alkaline buffer solutions.

TABLE I

RESISTANCE CHANGES IN GLASS MEMBRANES

Date, 1933	Resistance, meg.	A. P., mv.	$\Delta E/\Delta P_\mathrm{H}$
	At 38°		
	Membrane 27		
3/2	44.5	+0.7	0.0618
3/7	10.0	− .4	.0626
	Membrane 20		
3/12	106	−0.2	.0587
3/21	86	− .5	.0593
	Membrane 10		
2/26	114	−0.2	.0607
3/1	100	− .3	.0610
	At room temperature		
	Membrane 14		
1/21	33	0.0	.0614
2/16	27	.0	.0617
	Membrane 8		
1/22	100	+0.5	.0617
2/18	89	+ .3	.0615
	Membrane 12		
1/22	50	0.0	.0612
2/17	40	+ .3	.0613

Drying.—Drying the outer surface of a previously stabilized glass membrane, while keeping the inside moist with 6.5 phosphate buffer, usually made the A. P. more negative. This increase in A. P. was roughly correlated with the length of the drying period, as can be seen in Table II.

TABLE II

THE EFFECT OF DRYING ONE SIDE OF THE GLASS MEMBRANE

Membrane	Resistance, meg.	Length of time dried hrs.	Length of time dried mins.	Before A. P. mv.	Before $\Delta E/\Delta P_\mathrm{H}$	After A. P. mv.	After $\Delta E/\Delta P_\mathrm{H}$
5	100	17		−0.3	0.0617	−15.2	0.0598
5	100		16	− .3	.0617	− 3.8	.0616
7	8.5		18	− .2	.0617	− 0.8	
7	2.5		15	− .2	.0616	− .2	.0616
7	2.5		50	− .2	.0616	− .2	.0617
7	2.35	21		− .2	.0616	− .3	.0616
6	70.7		21	− .2	.0613	− 3.2	.0613
1	53.5		16	− .6	.0618	− 3.2	.0618
14	33.0	4		− .2		−13.1	
17	21.0	16		− .2	.0614	− 9.3	.0595

The effect on the A. P. was, however, also modified by the resistance of the membrane. For example, in the case of No. 7 with resistance of 2.35 megohms, even twenty-one hours produced no effect, while No. 5, with resistance of 100 megohms, increased its A. P. roughly ten-fold by only sixteen minutes of drying. $\Delta E/\Delta P_\mathrm{H}$ seemed not to be affected by short drying periods although prolonged periods did cause a lowering. Although MacInnes and Belcher[4] have shown that ten days of drying produced on an average a 230% increase in the resistance of membranes, there is no evidence of any increase from these comparatively

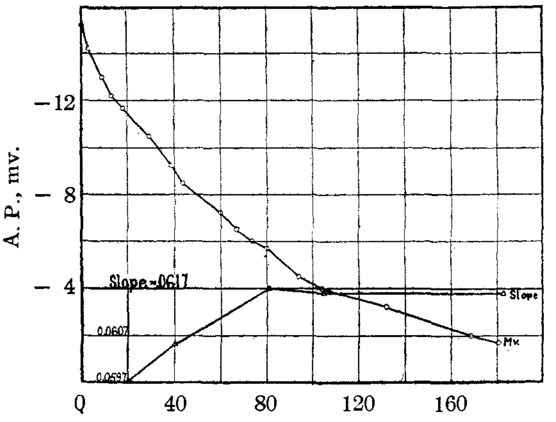

Fig. 1.—Changes in asymmetry potential (A. P.) and slope ($\Delta E/\Delta P_\mathrm{H}$) with time after the outer surface of the glass membrane had been dried for seventeen hours.

---

[4] D. A. MacInnes and D. Belcher, THIS JOURNAL, 53, 3315 (1931).

short drying periods. How rapidly the A. P. fell and the $\Delta E/\Delta P_H$ rose when an average resistance membrane was moistened after prolonged drying of the outside can be seen from Fig. 1. From this it appears that at least three to four hours are required to recondition the membrane.

There is no longer any doubt that water is very intimately associated with the ability of the glass membrane to function as a hydrogen electrode. It is believed from these experiments on drying one side of the membrane that the state of hydration of the layer of glass immediately in contact with the outer solution is of prime importance. If the water content is reduced, then the ease with which the hydrogen ions could cross this phase would presumably be reduced, the net effect being an apparent reduction in hydrogen activity of the outer solution. This condition actually obtains, since the A. P. after drying is always more negative. Moreover, if the membrane is thin enough, as has fortunately been so in one case, then presumably the inside solution will maintain a sufficient state of hydration, even on the outer layers of the membrane, to prevent a rise in the A. P.

Saturated Potassium Chloride.—It has been shown by MacInnes and Belcher[4] and Dole[5] that the readings of the glass electrode deviate from those of the hydrogen electrode in solution more alkaline than P_H 8, and that these deviations are influenced by the kind and concentration of the cation present. Thus MacInnes and Dole[6] have shown these deviations to be many times greater when the solution to be measured was saturated with sodium chloride than when the salt was only present in 0.1 N concentration. MacInnes and Belcher[4] conclude that to account for these deviations in alkaline solution and also in acid solution the assumption of ionic interchange in the surface of the glass membrane may be sufficient. This is also in accord with the theory advanced by Horovitz.[7] Besides influencing the ability of the glass membrane to function as a true hydrogen electrode, it is conceivable that contact with saturated solutions may produce temporary changes in the A P. of the membrane due to unequal distribution of ions on the two surfaces of the membrane. This should in effect result in a difference in the rate at which hydrogen ions passed through the two surfaces. The experiment was tried by placing the outer side of the glass membrane in contact with saturated potassium chloride for varying lengths of time, carefully washing away all traces of potassium chloride and then determining A. P. and $\Delta E/\Delta P_H$. The results are given in Table III. The effect on the A. P., while not as marked, was very similar to that produced by drying one side of the membrane. Here again the degree to which the A. P. became more negative was influenced by the length of exposure to potassium chloride and the resistance of the membrane. It must be pointed out that if the assumption that the disturbance to the A. P. is caused by the same factors which produce deviations of the glass electrode readings from the hydrogen electrode, then $\Delta E/\Delta P_H$ should also have been affected. This was not the case. One reason for this may be that the determinations were not made in a sufficiently alkaline range (P_H 7.0–7.5).

TABLE III

EFFECT OF CONTACT OF SATURATED POTASSIUM CHLORIDE WITH ONE SIDE OF THE GLASS MEMBRANE

Membrane	Resistance, meg.	Time of contact, mins.	Before A. P. mv.	Before $\Delta E/\Delta P_H$	After A. P. mv.	After $\Delta E/\Delta P_H$
6	70.7	5	0.0	0.0615	0.0	0.0615
		15	− .3	.0613	− .7	.0613
		20	− .0	.0615	− .8	.0615
		30	− .1	.0614	− .6	.0613
7	2.5	40	− .2	.0617	− .2	.0617
5	100	20	+ .2	.0618	− .0	.0626
8	71	20	− .3	.0616	−1.2	.0614
1	47	5	− .3	.0613	−0.2	.0614
		60	− .2	.0614	−1.0	.0612

Summary

Using the MacInnes form of glass electrode, membranes were studied with respect to their hydrogen electrode function, asymmetry potential and d. c. resistance. It was found that these three factors offered convenient means of checking their reliability from day to day, as well as following their behavior when subjected to conditions such as drying and exposure to potassium chloride.

PHILADELPHIA, PA. RECEIVED JANUARY 8, 1934

---

(5) M. Dole, THIS JOURNAL, **53**, 4260 (1931).

(6) D. A. MacInnes and M. Dole, *ibid.*, **52**, 29 (1930).

(7) K. Horovitz, *Ann. Physik*, **15**, 369 (1923).