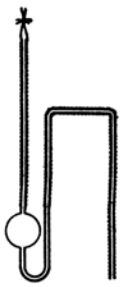
Effect of Water on the Potential of the Glass Electrode.[1]

By Hisato YOSHIMURA.

(Received July 5th, 1937.)

Since Haber and Kremensiewicz[2] set forth the hypothesis that the water absorbed by the glass membrane of a glass electrode transforms it into a hydrogen electrode, its importance has been in general implicitly recognized. No experimental studies on this point have been reported, however, except that of Laug[3], who found that, on drying the surface of one side of the electrode membrane, the hydrogen electrode function of that surface decreased and its potential level against that of the other side rose. He attributed the phenomenon to the decreased permeability of the hydrogen ion through the glass phase. The interrelation between the two facts was proved, however, neither theoretically nor experimentally. The aim of the present study is directed to these points.



The dotted line indicates the paraffin layer. The bulb part of the electrode is made either of MacInnes glass or of commercial glass, while the capillary support is always of commercial soft glass. On the details of the use of this electrode, see the previous report[4].

Fig. 1.

Experimental.

Glass electrodes made of MacInnes glass and also of commercial glass were used, the form of which is sketched in Fig. 1. The potential was measured at 25°C. with a Lindemann electrometer. The sign of the value given in this paper refers to the inside of the bulb of the electrode which serves as the electrode membrane.

(a) Experiments on the effect of submerging the glass electrode in water. After a glass electrode was prepared, it was preserved in water. Measurements of its asymmetry potential (usually in a buffer solution of *p*H 7.3), the hydrogen electrode function, the error of glass electrode

(1) Studies on the Nature of the Glass Electrode Potential. II. I: *J. Biochem.* (Japan), **23** (1936), 91.

(2) Haber and Kremensiewicz, *Z. physik. Chem.*, **67** (1909), 385.

(3) Laug, *J. Am. Chem. Soc.*, **56** (1934), 1034.

(4) Yoshimura, *J. Biochem.* (Japan), **21** (1935), 335.

(defined by Dole[5]) in an alkaline solution of pH 10.9 (its sodium ion concentration being 0.1 mol), and the degree of corrosion of the glass membrane due to water were repeated daily. The hydrogen electrode function, here stated, is the change in the potential of a glass electrode corresponding to the unit change of pH of the solution, and is expressed by $\Delta E/\Delta p$H. Estimations were made over a range of pH 2–7, where a rectilinear relationship exists between the potential and the pH. The degree of corrosion of the glass membrane due to water was examined by the following way: a 0.0001 N hydrochloric acid solution containing 0.001% methyl red was placed in the bulb of the glass electrode including a small air bubble. The electrode being rotated in a bath of 50°C., the time required for the fading of the red colour in the solution was measured. Measurements, being repeated on different days, indicate the relative degrees of corrosion by water on those days.

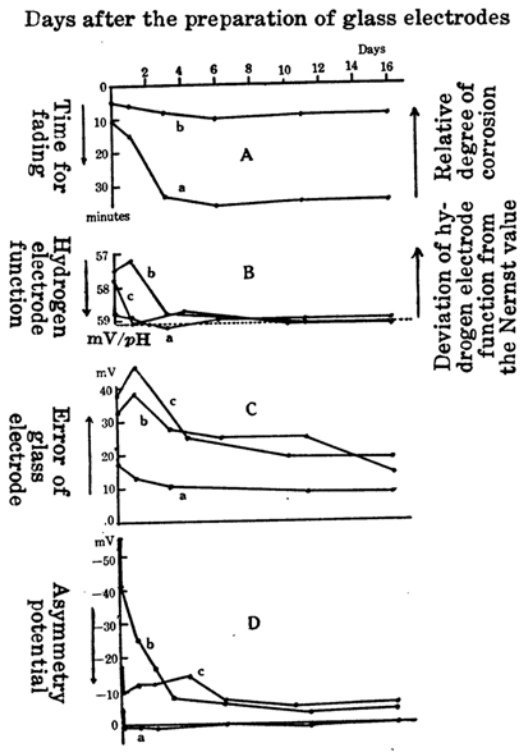


Fig. 2.

The above-mentioned examinations were carried out on a number of electrodes, examples of which are given in Fig. 2. The results of two electrodes made of MacInnes glass are given by curves a and b and those of an electrode of commercial glass by curves c. As is seen in A, the corrosion of the glass membrane decreased day by day and finally it attained a constant value after being submerged for about a week, when an equilibrium between the glass surface and the water was presumably attained. Similarly, the deviation of $\Delta E/\Delta p$H from the Nernst value (indicated by the dotted line) (B) and the error of glass electrode in the alkaline solution (C)

(5) Dole, *J. Am. Chem. Soc.*, **53** (1931), 4260.

decreased day by day and the asymmetry potential (D) approached zero from a negative value, each finally attaining a constant value.

The time required for the potential equilibration after the electrode was mounted in the solution was shortened by first submerging the electrode in water after its preparation.

(b) Experiments on the effect of drying the surface of electrode membrane. Further to clarify the relationship of water to the potential of a glass electrode, the effect of drying one surface of the electrode membrane was examined. The surface was dried either by passing through hot air (1) or by means of a desiccator (2).

(1) A commercial glass electrode which had attained the equilibrium with water was dried on one side, either inner or outer, by passing hot air of ca. 180°C. through or over it for about 6 hours, while the other side was prevented from drying by passing vapour or hot water through or over it. The asymmetry potential and $\Delta E/\Delta p$H were examined before and shortly after drying. After the examinations were completed, the electrode was preserved in water and the electromotive reactions of the electrode were observed to determine the effect of the immersion on the potential. An example of the results is given in Fig. 3, where A gives the asymmetry potential and B gives $\Delta E/\Delta p$H of the dried surface. The shadowed range represents the time of drying. The effect of drying the inner surface of an electrode is represented by continuous lines (electrode 1), while that of drying the outer surface of another electrode is shown in broken lines (electrodes 2 and 3). As is seen in the figure, drying changes the asymmetry potential by raising the potential level of the side of the dried surface, while it decreases $\Delta E/\Delta p$H on the same side. When the electrode was submerged in water after this drying experiment, this effect on the potential was reversed. Though it is doubtful whether the effect of the passage of hot air on the potential is completely due to the evaporation of water from the glass

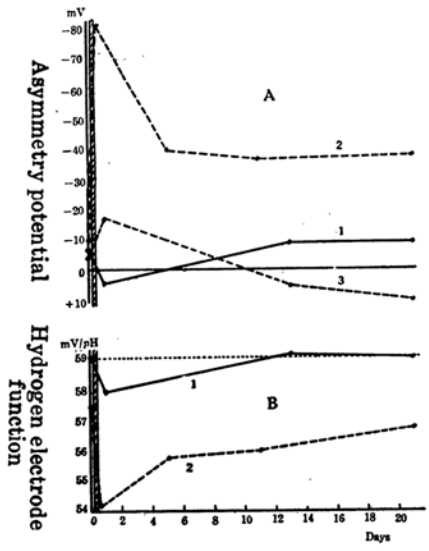


Fig. 3.

surface, drying seems to play an important rôle, as the reverse effect was produced by submerging it in water.

(2) The electrode which was equilibrated in water being connected with a sulphuric acid desiccator, its inner surface was dried for 8 days, while the outer surface was kept submerged in water. The asymmetry potential (in a buffer solution of pH 2.8) and $\Delta E/\Delta p$H before and after drying are given in Table 1, where m refers an electrode of MacInnes glass, and c that of a commercial glass electrode. The effect of drying on the asymmetry potential was similar to that found in the experiment (1), while the change in $\Delta E/\Delta p$H by drying was minute in this case.

Table 1.

			Before desiccation	After desiccation
Asymmetry potential		m	−11.5 mV	− 1.2 mV
		c	−27.4	− 5.8
$\frac{\Delta E}{\Delta p\mathrm{H}}$	Inner surface	m	58.7 $\frac{\mathrm{mV}}{p\mathrm{H}}$	58.3 $\frac{\mathrm{mV}}{p\mathrm{H}}$
		c	58.7	57.3
	Outer surface	m	57.6	58.0
		c	57.5	58.2

The attainment of the equilibrated potential after the electrode was mounted in the solution was retarded if measured shortly after the electrode was dried. But when the electrode was submerged in water for a few days, this effect disappeared.

Discussion.

From the above experimental results, it is clear that, water being removed from one surface of the electrode membrane, the $\Delta E/\Delta p$H on that surface is decreased and the potential level is raised on that side against the other, thus causing a change of the asymmetry potential. These changes in the electromotive effect of the glass membrane can be reversed by submerging the electrode in water, probably because water is absorbed in the glass surface. The asymmetry potential is created by the differences in electromotive effect between the surfaces of the electrode

membrane. Thus the change in the asymmetry potential from a negative value to zero when a freshly prepared electrode is submerged in water (refer to D of Fig. 2) is due to the fact that the effect of water on the outer surface is more severe than that on the inner surface. Thereby the electromotive effect of both surfaces is equalized by water.

While the reason for this difference between the inner and the outer surfaces is a matter for further study, the correlation between the asymmetry potential and $\Delta E/\Delta p\mathrm{H}$ can be explained qualitatively by three current important theories of the glass electrode: Dole's statistical mechanical theory[6], the partition potential theory by Gross and Halpern[7], and the ion exchange theory of Horovitz[8], all belonging to the phase boundary theory. No experimental results have yet been produced to support one against the other two, so that these three theories are taken into consideration.

In all of these theories, the phase boundary potential E is given by

$$E = -\frac{RT}{F}\ln C_{\mathrm{H}}\left\{1+\frac{C_{\mathrm{Na}}}{C_{\mathrm{H}}}\frac{Y}{X}\right\}^{n}-\frac{RT}{F}\ln X \qquad (1),$$

E being positive when the potential level of the solution is high against that of the glass phase. C_{H} is the hydrogen ion concentration (strictly the hydrogen ion activity) of the solution and C_{Na} the sodium ion concentration (the cation of the salt in the solution being assumed to be Na^{+}). n is 1 in both Dole's and Horovitz's theories, and is $\frac{1}{2}$ in Gross and Halpern's theory. X and Y are the constants which depend upon the nature of glass or, strictly speaking, upon that of the membrane surface, and are given as follows:

$$X = \beta_{\mathrm{H}}e^{\frac{Q_{\mathrm{H}}}{RT}}, \quad Y = \beta_{\mathrm{Na}}e^{\frac{Q_{\mathrm{Na}}}{RT}} \quad \text{(Dole)},$$

$$X = \frac{K_4M_4}{K_1L_4}\sqrt{\frac{L_1}{M_1}}\times\text{const.}, \quad Y = \sqrt{\frac{M_1}{L_1}}\times\text{const.}$$

(Gross and Halpern),

$$X = \frac{u_{\mathrm{H}}}{aK_{\mathrm{H}}u_{\mathrm{Na}}}, \quad Y = \frac{1}{aK_{\mathrm{Na}}} \quad \text{(Horovitz)}.$$

---

(6) Dole, *J. Chem. Phys.*, **2** (1934), 862.

(7) Gross and Halpern, *Z. physik. Chem.*, **115** (1925), 54; *J. Chem. Phys.*, **2** (1934), 136.

(8) Horovitz, *Nature*, **127** (1931), 440.

Various symbols in these equations are the constants which are independent of one another. On their physical meanings, refer to the original papers.

From the equation (1), the asymmetry potential e_g and the hydrogen electrode function $\Delta E/\Delta p\mathrm{H}$ are given as follows:

$$e_g = \frac{RT}{F} \ln \left\{ \frac{1+\frac{C_{Na}}{C_H}\frac{Y_o}{X_o}}{1+\frac{C_{Na}}{C_H}\frac{Y_i}{X_i}} \right\}^n + \frac{RT}{F} \ln \frac{X_o}{X_i} \qquad (2),$$

where the suffixes i and o refer to the inner and the outer surfaces of the electrode membrane respectively, and

$$\frac{\Delta E}{\Delta p\mathrm{H}} = \frac{R'T}{F}\left\{1-\frac{\log\left(1+\frac{C_{Na}}{C_H}\frac{Y}{X}\right)^n}{\Delta p\mathrm{H}}\right\} \qquad (3),$$

where R' represents $2.303R$.

Before using these equations to explain the experimental results, the two following points should be discussed: (i) It is noticeable that, according to these theories, the only way to explain the deviation of $\Delta E/\Delta p\mathrm{H}$ from the theoretical value $(R'T/F)$ is by the cation effect, i.e. by the term $\frac{C_{Na}}{C_H}\frac{Y}{X}$ in the equation (3). This term is generally thought to be negligible in solutions of pH lower than 8. Moreover, it is a function of C_H and C_{Na}. The deviation of the experimental values of $\Delta E/\Delta p\mathrm{H}$ from the theoretical is, however, approximately a constant at least in the range of pH 2–8. Therefore, it is a matter of question whether or not the deviation of $\Delta E/\Delta p\mathrm{H}$ from the theoretical value can be explained by the cation effect. From these points, Kahler and DeEds[9] offered the deviation film theory apart from the cation effect to explain the deviation of $\Delta E/\Delta p\mathrm{H}$. This theory has, however, already been denied by the present author[1] who maintains that the magnitude of the hydrogen electrode function is closely connected with the property of the glass surface. Then the question being left to further study, the equation (3) will be adopted provisionally in the present discussion to explain the deviation of $\Delta E/\Delta p\mathrm{H}$ from the theoretical value. (ii) All these theoretically derived equations refer to the equilibrated potential, while

(9) Kahler and DeEds, *J. Am. Chem. Soc.*, **53** (1931), 2998.

the potential observed experimentally showed the diurnal change. Regarding the observed potential be in a state of the quasi-equilibrium, these equations can be said to apply, and the diurnal change of the potential can be explained by the change in the constants in the equations.

Now, from the equations (2) and (3), it is clear that when the constant X of one surface of the electrode membrane is decreased $\Delta E/\Delta p\mathrm{H}$ on that surface decreases and the potential level on that side rises, causing the change of the asymmetry potential, and vice versa. The fact is corroborated by the experiments.

From the equation (1), the error of the glass electrode in an alkaline solution (designated by Δ) is given by the equation

$$\Delta = \frac{RT}{F} \ln \left\{1+\frac{C_{\mathrm{Na}}}{C_{\mathrm{H}}} \frac{Y}{X}\right\}^{n} \qquad (4).$$

Thus the decrease in Δ is accompanied by the increase in $\Delta E/\Delta p\mathrm{H}$. This is the fact which was found in most cases of the experiment (a).

As the level of the potential on one side of the membrane falls and $\Delta E/\Delta p\mathrm{H}$ increases when the surface of the membrane on that side is corroded with water, it must be that the constant X is increased by water corrosion, and decreased by drying. The physical meaning of this change in X can be explained separately by each of the above-mentioned three theories. For example, according to Gross and Halpern's theory, the increase of X by water corrosion can be explained by the increase in the partition coefficient of water in the glass phase; and according to Dole's theory, it is explained by the decrease in energy of the hydrogen ion on the lowest quantum level in the glass phase or by the increase in that of sodium ion.

Thus we can explain qualitatively our experimental findings by current theories of the glass electrode. It is impossible, however, to say which of the three theories is correct.

Summary.

(1) When one surface of the membrane of a glass electrode is dried, the asymmetry potential is raised on that side against the other side, and the hydrogen electrode function is decreased. This membrane being kept submerged in water, the reverse effect is observed. These facts can be explained qualitatively by any of the latest theories concerning the glass electrode.

(2) The significance of preserving the glass electrode in water after its preparation, which is a generally accepted procedure in the use of the glass electrode, can be stated as follows: (i) It makes the hydrogen electrode function approach Nernst's theoretical value, probably decreasing the cation effect on the potential of the glass electrode, (ii) it decreases the asymmetry potential, equalizing the electromotive nature of both the inner and outer surfaces of the electrode membrane, and (iii) it facilitates the equilibration of the potential after the electrode is mounted in a solution for test.

The author expresses his cordial thanks to Prof. Dr. I. Sawai of the Institute of Industrial Chemistry for his kind advices, and also to the Hattori-Hokokwai for a grant.

Institute of Physiology, Faculty of Medicine,
Imperial University of Kyoto.