Studies on the Nature of the Glass Electrode Potential. III. On the Cause of the Asymmetry Potential of the Glass Electrode.

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According to the so-called Haber theory of the glass electrode, there should exist no potential, when both surfaces of a glass electrode membrane are brought into contact with one and the same solution. Actually, however, a certain potential appears, which is called the asymmetry potential. As to the cause of this potential, some experimental studies were performed by Elder(1), Buchböck(2), and Kahler and DeEds(3), though none of them can be regarded as fundamental. (The Chemical Abstracts recorded a paper by Haugaard(4). Not having read his paper, however, we must necessarily refrain from commenting upon his conclusions.) In the present investigation, this problem is examined from the point of view of current theories concerning the glass electrode. The experimental methods and the sign of the potential are the same as described in the previous report(5). Experiments were carried out at 25°C. in most cases.

(1) The Asymmetry Potential and the Difference of Hydrogen Electrode Function on Outer and Inner Surfaces of the Electrode Membrane. The hydrogen electrode functions $\Delta E/\Delta p\text{H}$ of both the inner and the outer surfaces of the electrode bulb (which serves as the electrode membrane), and its asymmetry potentials in two buffer solutions of pH 3 and 7 were determined after the electrode had been fully equilibrated with water, using many glass electrodes made of commercial soft glass, MacInnes glass, and Morton glass purchased in England. As to the meaning of $\Delta E/\Delta p\text{H}$, refer to the previous report(5). The measurement of $\Delta E/\Delta p\text{H}$ on both surfaces of the electrode membrane was performed with the two buffer solutions in a way similar to that of Kahler and DeEds(3).

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(1) Elder, *J. Am. Chem. Soc.*, **51** (1929), 3266.
(2) Buchböck, *Z. physik. Chem.*, A, **156** (1931), 232.
(3) Kahler and DeEds, *J. Am. Chem. Soc.*, **53** (1931), 2998.
(4) Haugaard, *Chem. Abstracts*, **31** (1937), 930; *Kem. Maanedsblad*, **17** (1936), 33.
(5) Yoshimura, this Bulletin, **12** (1937), 359.

On examining the data obtained, no correlation was found to exist between the asymmetry potential and the hydrogen electrode function of either side of the membrane, but there was a correlation between the asymmetry potential and the difference of $\Delta E/\Delta p\mathrm{H}$ of both surfaces, as shown in Fig. 1, where dots represent data referring to the MacInnes glass electrode, crosses those of the Morton glass electrode, and circles those of the commercial glass electrode. While these are data at 25°C., triangles represent those of commercial glass electrode determined at 18°C. The abscissa of Fig. 1 is the asymmetry potential in the solution of $p\mathrm{H}$ 3, e_3. The ordinate is the difference of the asymmetry potentials in the two solutions of $p\mathrm{H}$ 3 and $p\mathrm{H}$ 7, e_3-e_7, which is given by

$$e_3-e_7=\left\{\left(\frac{\Delta E}{\Delta p\mathrm{H}}\right)_{\mathrm{o}}-\left(\frac{\Delta E}{\Delta p\mathrm{H}}\right)_{\mathrm{i}}\right\}\Delta p\mathrm{H} \qquad (1),$$

where $\Delta p\mathrm{H}$ is the $p\mathrm{H}$ difference of the two solutions and is numerically 4. Suffixes i and o refer to the inner surface and the outer surface of the electrode membrane respectively. Thus the ordinate of the figure corresponds to the difference of $\Delta E/\Delta p\mathrm{H}$ between the two surfaces of the membrane as $\Delta p\mathrm{H}$ is constant. The plots of all the electrodes made of the three mentioned sorts of glass tend to lie on the respective straight lines which pass near the origin with a slope of about 2. This indicates that the asymmetry potential approaches zero when the hydrogen electrode functions of both surfaces of the electrode membrane approach each other. This fact suggests in turn that the electromotive nature of the membrane surface which determines the hydrogen electrode function is correlated closely with that determining the potential level of the surface, because the asymmetry potential corresponds to the difference of the potential levels of the inner and the outer surfaces. Moreover, it is suggested that this relation differs according to the chemical composition of the glass, as correlation lines of the three sorts of glass differ from one another.

(2) **The Relation between the Electromotive Effect and the Curvature of the Glass Membrane.** It is seen in Fig. 1 that the hydrogen electrode function of the outer surface of an electrode membrane is in most cases lower than that of the inner surface and the asymmetry potential is negative, that is, the potential level on the inner side of the membrane is lower than that on the outer side. This difference of the electromotive effect of the outer and the inner surfaces of the electrode bulb is supposed to be due to the difference in the curvature of these

surfaces, and therefore to the strain or atomic arrangement of the surface layer. Elder⁽¹⁾ and also Buchböck⁽²⁾ attempted to prove this supposition experimentally. The former failed in the experiment, while the latter succeeded. The present author also attempted to examine the problem. For the purpose, a bulb membrane of MacInnes glass electrode being fused into one end of a commercial glass tube, a MacInnes and Dole electrode of the diaphragm type was constructed. The convex surface of this electrode membrane is directed inside the electrode and the concave surface outside, while the relation is reverse in the electrode of bulb type. The asymmetry potential and the hydrogen electrode function of both the surfaces being estimated, data are plotted in Fig. 1 (designated with asterisks). The points tend to lie on the positive side of the correlation line of MacInnes glass electrode. It shows that the difference of the electromotive effect between the inner and the outer surfaces of the electrode membrane is caused by the difference of the curvature. This suggests that the electromotive effect of the glass membrane is closely related to the atomic arrangement of the surface layer⁽⁶⁾. Thus the asymmetry potential is supposed to be due to the difference of the atomic arrangement between the two surfaces of the electrode membrane.

(3) **The Relation between the Electromotive Effect of the Glass Membrane and its Thickness.** Kahler and DeEds⁽³⁾ pointed out that the asymmetry potential of a glass electrode approaches zero as the thickness of the electrode membrane diminishes. This can be ascertained by the data given in Fig. 2, where the asymmetry potential (e_3 at 18°C. in most cases) of various electrodes of MacInnes glass (dots) and of commercial glass (circles) are plotted against the electrical resistance of the electrodes. The plots of the electrodes made of one and the same sort of glass tend to lie vaguely on a correlation line. Though the electrical resistance depends on the size of the electrode bulb besides the thickness of its membrane, it is principally determined by the latter, the size of the bulb depending also upon the thickness of the membrane, as the bulbs are blown on capillaries of about the same bore and the same thickness. Thus it can be maintained that a correlation exists between the thickness of the membrane and the asymmetry potential.

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(6) To prove this experimentally, the effect of annealing on the glass electrode potential was examined. Unfortunately, however, the effect of heat treatment of the electrode on its potential such as the effect or drying previously reported⁽⁵⁾ covered the effect of annealing and the experiments ended in a failure. But the above suggestion as to the relation between the electromotive effect and the atomic arrangement cannot be denied on account of this failure.

This fact was ascertained further by the two following experiments: (i) A short MacInnes glass tubing of thick wall (which is about 0.4 mm. thick and serves as the electrode membrane) being connected with supports of commercial capillary tubing, an electrode of the type given in Fig. 1 in the previous report⁽⁵⁾ was constructed. After its asymmetry potential and the hydrogen electrode function had been estimated on both the inner and the outer surfaces, the thick MacInnes glass tubing was blown to make a bulb of which the thickness of the thinnest part was 10 μ or so. The effect of this blowing on its potential was examined. See an example of the results given in Table 1. On making the membrane thinner, the asymmetry potential (in the absolute value) and the difference of the hydrogen electrode function between the inner and the outer surfaces decreased.

Table 1. Effect of Blowing the Bulb.

Experiment	$\Delta E / \Delta p$H (mV. / pH)			e_3 (mV.)	Thickness of the membrane (mm.)
	Inner surface	Outer surface	Difference		
Before blowing	58.3	47.8	10.5	−110.7	ca. 0.4
After blowing	58.2	58.1	0.1	−10.5	0.01

(ii) Either the inner or the outer surface of the thick membrane of the above-mentioned electrode being soaked in a concentrated HF for 1–2 hours, and thereafter in streaming water for several days, a thin lamella of the surface was stript off. The thickness of the membrane thus being reduced, the change in its electromotive effect was examined. Examples of data are given in Table 2. It was found in most cases that the hydrogen electrode function of the corroded surface approached that of the other surface of the membrane and the asymmetry potential decreased (in absolute value), while the reverse result was found in a few cases. As HF corrodes the glass surface ununiformly, the corroded surface may not be regarded as the same as that shaven mechanically. Deducing from the results of all experiments mentioned above, however, it is concluded that the asymmetry potential (in absolute value) and the difference of the hydrogen electrode function between the inner and the outer surfaces of the electrode membrane decrease simultaneously as the thickness of the membrane decreases.

Table 2. Effect of Hydrochloric Acid Treatment.

Experiment		$\Delta E/\Delta p$H (mV./pH)			e_3 (mV.)	Resistance (Ω)
		Inner surface	Outer surface	Difference		
I	Before treatment	58.0	47.6	10.4	−108 5	1.2×10^9
	After treatment	55.9	47.6	8.3	−89.5	1.0×10^9
II	Before treatment	57.9	52.8	5.1	−71.5	1.4×10^9
	After treatment	58.5	56.7	1.8	−23.5	1.2×10^9

I. The inner surface etched with HF.
II. The outer surface etched with HF.

The above-mentioned results cannot be explained by the deviation film theory of Kahler and DeEds⁽³⁾ who maintained that the decrease of the thickness of the membrane is accompanied by increase of the hydrogen electrode function, for it is clear in Table 2 that the hydrogen electrode function on one surface has no direct correlation with the thickness of the electrode membrane. A plausible explanation is that the atomic arrangement of the inner and the outer surfaces of the membrane which are closely related with the factor determining both the hydrogen electrode function and the potential level of the surface tend to equalize with each other, as the thickness of the membrane decreases.

From data given in Table 2, it is also maintained that the glass membrane being regarded as an ensemble of many unit lamellæ, the electromotive effect of each lamella is different from the others. In the previous report⁽⁷⁾, the same fact was maintained concerning assumed unit parts of the surface of the electrode membrane. This fact suggests that the atomic arrangement of the electrode membrane is different both lengthwise and breadthwise.

(4) Dependence of the Asymmetry Potential on the *p*H of the Solution and Discussion of the Above-Mentioned Results. From the above-mentioned experimental results, it is certain that the asymmetry potential is closely correlated with the difference of $\Delta E/\Delta p$H between the inner and the outer surfaces of the electrode membrane. This fact can be explained in either of the two following ways: (i) Experiments show that a linear relationship exists between the potential of the glass electrode and the pH of the solution at least in the range of pH 2–8, even when the hydrogen electrode function of the glass electrode is lower than

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

the theoretical value. If this is correct not only roughly in the scope of experimental error, but also theoretically in the whole range of pH, the asymmetry potential e' in a solution of which the pH is higher by $\Delta p\mathrm{H}'$ than 3, is given by

$$e' = e_3 - \left\{\left(\frac{\Delta E}{\Delta p\mathrm{H}}\right)_{\mathrm{o}} - \left(\frac{\Delta E}{\Delta p\mathrm{H}}\right)_{\mathrm{i}}\right\}\Delta p\mathrm{H}' \qquad (2).$$

Thus the asymmetry potential of one and the same glass electrode is a linear function of pH. This equation has already been suggested by Kahler and DeEds⁽³⁾. If it is assumed in this equation that the asymmetry potential e' in a solution of a certain pH is kept constant among the electrodes made of one and the same sort of glass, a rectilinear relationship should exist between e_3 of the electrodes and the differences of $\Delta E/\Delta p\mathrm{H}$ between the inner and the outer surfaces of the electrode membranes. This certain pH should be ca. 11, as the slope of the correlation line experimentally found, i.e. $\Delta p\mathrm{H}'$, is ca. 2.

(ii) According to the current theories of the glass electrode, mentioned in the previous report⁽⁵⁾, $\Delta E/\Delta p\mathrm{H}$ is given by

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

R' represents 2.303 R. C_{H} and C'_{H} are the hydrogen ion concentrations of the two buffer solutions used for the determination of $\Delta E/\Delta p\mathrm{H}$, and C_{Na} and C'_{Na} their sodium ion concentrations, the cation of the salt being assumed to be sodium ion. $\Delta p\mathrm{H}$ is equal to $\log C_{\mathrm{H}}/C'_{\mathrm{H}}$. As to the constants n, X and Y, see the previous report. When the hydrogen ion concentration C_{H} is sufficiently high, the term $\frac{C_{\mathrm{Na}}}{C_{\mathrm{H}}}\frac{Y}{X}$ can be neglected, and we have

$$\frac{\Delta E}{\Delta p\mathrm{H}} = \frac{R'T}{F}\left[1 - \log\left(1+\frac{C'_{\mathrm{Na}}}{C'_{\mathrm{H}}}\frac{Y}{X}\right)^n \Big/ \Delta p\mathrm{H}\right] \qquad (4).$$

This is the equation of $\Delta E/\Delta p\mathrm{H}$ given in the previous report⁽⁸⁾. From this equation, it is clear that $\Delta E/\Delta p\mathrm{H}$ is not a constant but a function of pH and the salt concentration when $\Delta E/\Delta p\mathrm{H}$ is smaller than the

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(8) The derivation of this equation is given here as an addendum to the previous report⁽⁵⁾.

theoretical value $R'T/F$. Thus equation (2) is not valid theoretically, and the asymmetry potential e_g is given by

$$e_g = \frac{R'T}{F} \log \left\{ \frac{1 + \frac{C_{\mathrm{Na}}}{C_{\mathrm{H}}} \frac{Y_{\mathrm{o}}}{X_{\mathrm{o}}}}{1 + \frac{C_{\mathrm{Na}}}{C_{\mathrm{H}}} \frac{Y_{\mathrm{i}}}{X_{\mathrm{i}}}} \right\}^n + \frac{R'T}{F} \log \frac{X_{\mathrm{o}}}{X_{\mathrm{i}}} \qquad (5),$$

which is equal to equation (2) given in the previous report. Suffixes i and o refer to the inner and the outer surfaces of the electrode membrane respectively. When C_{H} is sufficiently large, we have

$$e_g = \frac{R'T}{F} \log \frac{X_{\mathrm{o}}}{X_{\mathrm{i}}} \qquad (6).$$

From equations (4) and (6), it is clear that, when the constant X decreases on one surface of the membrane as compared with that on the other surface, the potential level of that surface rises against that of the other surface, causing the change in the asymmetry potential, and the hydrogen electrode function on that surface decreases. Thus the fact found in the present experiments can be explained by the current theories of the glass electrode.

Now it should be decided which of explanations (i) and (ii) is correct. For this purpose, equations (2) and (5) were examined experimentally, of which the former indicates that the asymmetry potential is a linear function of the *p*H of the solution, while the latter indicates that the function is a curve which tends to transit into a plateau in the range of low *p*H, as $C_{\mathrm{Na}}/C_{\mathrm{H}}$ decreases.

Measuring the asymmetry potential of one and the same electrode in various buffer solutions of different *p*H but of 0.1 molar sodium ion concentration, data were plotted against the *p*H, of which examples obtained on a MacInnes glass electrode (dots) as well as a commercial glass electrode (circles) is given in Fig. 3. Plots did not lie on a straight line, but on a curve which showed that the asymmetry potential (not in absolute value) decreases with the decrease in *p*H but tends to attain a constant value in the range of low *p*H. Thus explanation (ii), but not (i), is to be adopted.

The above-mentioned theoretical correlation between the asymmetry potential and the difference of hydrogen electrode functions of both surfaces of the electrode membrane can be verified quantitatively to a certain extent as follows:

Putting $$\delta \equiv \frac{R'T}{F} \log \left(1 + \frac{C_{\mathrm{Na}}}{C_{\mathrm{H}}} \frac{Y}{X}\right)^n,$$

we have

$$\log \left\{ \frac{\mathrm{Antilog} \dfrac{\delta_i}{\dfrac{nR'T}{F}} - 1}{\mathrm{Antilog} \dfrac{\delta_o}{\dfrac{nR'T}{F}} - 1} \right\} = \mathrm{const.} + \log \frac{X_o}{X_i} \qquad (7),$$

the suffixes o and i referring to the outer and the inner surfaces of the membrane respectively. From equation (4),

$$\delta = \frac{R'T}{F} \Delta p\mathrm{H} - \Delta E \qquad (8),$$

and from equation (6),

$$\log \frac{X_o}{X_i} \fallingdotseq \frac{e_3}{\dfrac{R'T}{F}} \qquad (9),$$

assuming that the cation effect on the asymmetry potential is negligible in the range near pH 3. Thus equation (7) was quantitatively examined, calculating δ and $\log (X_o/X_i)$ by equations (8) and (9) from the experimental data obtained in section (1). The result is given in Fig. 4, where n in the equation (7) is taken as 1/2 according to Gross and Halpern(9). The plots lie vaguely between two parallel boundary lines of which the slope is 1. The reason why the plots do not lie on a straight line, but scattered in a zone is probably that the "const." in equation (7) is not the same among different electrodes, and moreover the assumptions made in this examination may not be completely correct. Thus it can be stated that equation (7) was verified somewhat quantitatively. Even when n is taken as 1 according to Dole(9) and Horovitz(9), the same result is obtainable. Therefore the decisive criticism of the three current theories cited in the previous report can not be deduced from the present experimental results. Moreover, it would be premature to accept any one of the current theories as completely correct only from the present experimental results.

It is interesting, however, to try to explain the experimental facts by the current theories. It was found in the above-mentioned experiments

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(9) See the discussion in the previous report(5).

that the hydrogen electrode function of the outer surface is lower than that of the inner surface and the potential level of the former which determines the asymmetry potential is higher than that of the latter. The explanation given for the fact is that the constant X in equations (4) and (6) on the outer surface is smaller than that on the inner surface. The physical meaning of this explanations is that the energy

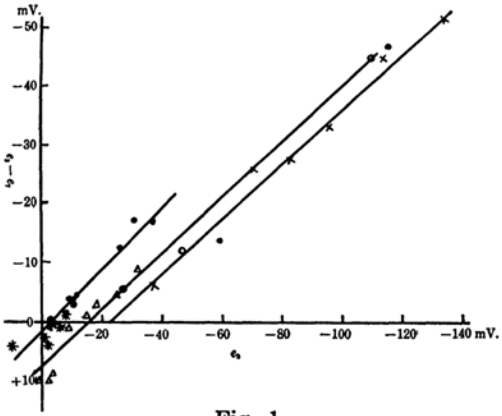

Fig. 1.

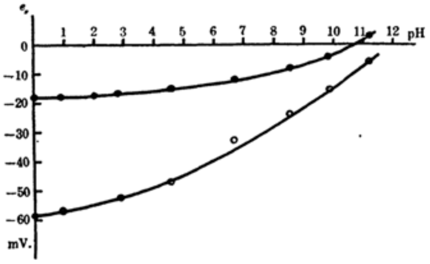

Fig. 3.

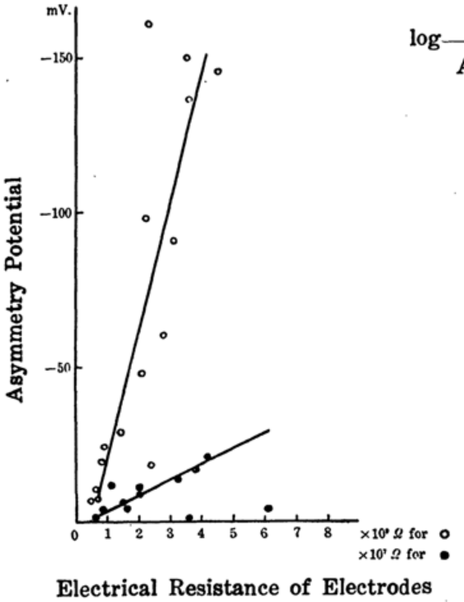

Fig. 2.

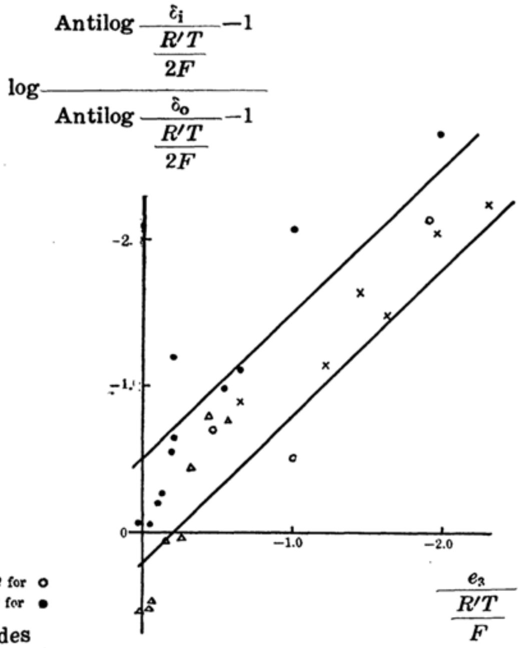

Fig. 4.

of hydrogen ion on the lowest quantum level of the glass phase according to Dole⁽⁹⁾ is greater on the convex surface than that on the concave surface, probably owing to the difference of the atomic arrangements of these surfaces. To elucidate further the interrelation between the constants in the above-mentioned theoretical equation and the atomic arrangement of the surface is a problem left for future study.

Conclusions. (1) When the difference between the hydrogen electrode functions of the inner and the outer surfaces of a glass membrane is large, a high asymmetry potential appears, and the hydrogen electrode function on the positive side of the asymmetry potential is in most cases smaller than that on the other side. Thus a correlation exists between the difference of the hydrogen electrode functions of the two surfaces and the asymmetry potential. This indicates that an intimate relationship exists between the factor which determines the potential level of the surface referring to the asymmetry potential, and that of the hydrogen electrode function. This fact can be explained qualitatively by the current theories of glass electrode.

(2) The hydrogen electrode function is, in most cases, less on the convex surface than on the concave surface of an electrode membrane, and the positive pole of the asymmetry potential is, in most cases, on the convex side. This difference between the hydrogen electrode functions of both surfaces and also the magnitude of the asymmetry potential tend to decrease as the thickness of the electrode membrane diminishes. These facts suggest that the electromotive effect of the surface of a glass membrane is closely connected with the atomic arrangement between the inner and the outer surfaces of the electrode membrane.

A glass membrane being regarded as an ensemble of many lamellæ and unit surfaces, the electromotive effects of these parts are different from one another. Therefore, the atomic arrangement of the glass membrane is probably different in each part both lengthwise and breadthwise.

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