SOME PROPERTIES OF THE GLASS ELECTRODE

Including:

The Determination of the Nature of

the Asymmetry Potential

The Determination of the Effects of

Aging in 0.1 N HCl and 0.1 N KOH

A New Approach to the Theory of the

Glass Electrode

Thesis by

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I. A GENERAL DISCUSSION ON THE GLASS ELECTRODE

A Description of the Glass Electrode

The glass electrode is a thin membrane of glass, generally in the form of a hemisphere attached to the end of a glass tube of approximately the diameter of the hemisphere. The glass tube is usually partly filled with some known solution which is, of course, in contact with the inner surface of the hemispherical membrane. Into this solution is dipped an inner reference electrode which takes up a constant potential with respect to the inner solution. This electrode is metallically connected to one lead of a potential measuring circuit. The assembly is immersed in another solution which is then, in contact with the outside surface of the glass membrane. In this outer solution there is also immersed a reference electrode which has a constant potential with respect to that solution and this last electrode is connected to the other lead of the measuring circuit. This outer reference electrode is usually referred to as "the reference electrode." The general arrangement is shown in Figure 1.

The interesting and valuable property of the glass electrode is that, if the pH of the solution in the beaker (see Fig. 1) is varied, the contact potential of that solution with the outside surface of the glass membrane varies directly as the pH. Consequently, all other potentials remaining constant, the potential measured by the potentiometer in the circuit shown, will vary directly as the pH of the solution in the beaker.
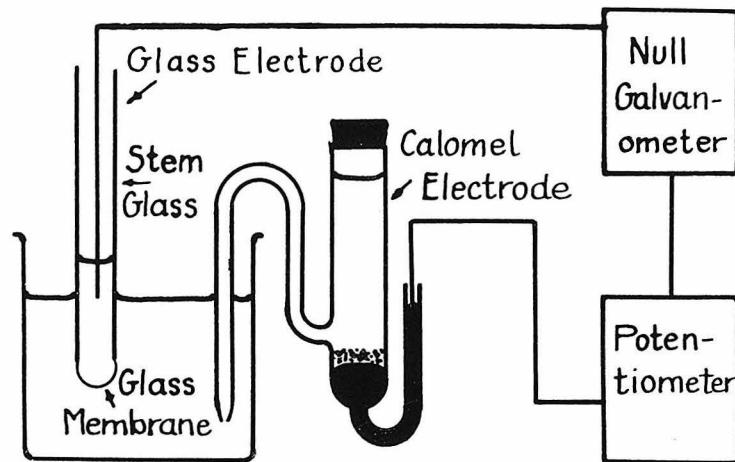
Fig. 1   The General Arrangement
            of a Glass Electrode
            Circuit.

A Brief Historical Sketch

Haber and Klemensiewicz[1] in 1909 carried out acid-base titrations with a circuit such as shown in Figure 1. For the null galvanometer they used a quadrant electrometer. The electrostatic method of measurement was necessary because of the resistance of the glass membrane. Since this resistance was of the order of 10^7 ohms, the current necessary to operate any type of current galvanometer would have produced a very large IR drop across the membrane, any variations in the current causing large errors in measurement.

Later Hughes[2] showed that the membrane potential change follows pH change through a wide range of pH values in the same manner as the potential of a cell including the usual hydrogen electrode. He also showed that the glass electrode is uninfluenced by strong oxidizing or reducing agents which seriously affect the results with any other method for obtaining pH values. Mrs. Kerridge[3] demonstrated the usefulness of the glass electrode in biological solutions which contained substances which influenced the accuracy of the usual hydrogen electrode. Highly viscous solutions could be tested with the glass electrode and even soils could be tested. Many new applications of the glass electrode appeared in places where the ordinary means for determining pH were inoperable.

Some of the Early Problems

The main limitation to the use of the glass electrode was its very high resistance. This made

measurements difficult and inaccurate. It was also
inconvenient to make measurements by means of the electro-
static galvanometer.

The measurement difficulties were vanquished by
the use of vacuum tube electrometers. For instance, the
modern Beckman pH meter contains a potential measuring
vacuum tube circuit which sends a maximum of $2X10^{-13}$
amperes through the electrode membrane. With a membrane
resistance of 10^8 ohms this produces a maximum voltage
drop of 0.02 millivolts. Since a change of unity in pH
corresponds to 59 millivolts the maximum electrical
error due to grid current variation is about 3 ten
thousandths of a pH unit. As a matter of fact, the
instrument is so constructed that even this magnitude
of variation is never allowed to occur. Therefore,
the electrical errors of this instrument are quite neglgible.

Another problem which troubled early workers
with the glass electrode, was that of electrical leakage.
On referring to Figure 1 again one can easily see how
a layer of moisture depositing from the air might make a
conducting path from the outside solution over the top
of the stem glass to the inner solution. In modern
commercial equipment this difficulty is avoided entirely
by having the internal electrode sealed in the stem
with an insulating material and the lead from the inside
surrounded by grounded shielding from the top of the
electrode into the potential measuring instrument.
The stem is made of a very high resistance glass so that

measurements made pertain only to the completely immersed membrane and depend in no way on the depth of immersion of the stem.

The optimum glass composition to use for the glass membrane was found by Mac Innes and Dole[4] in 1930 to be Na_2O, CaO, and SiO_2 in the proportions of 22, 6 and 72 per cent respectively. This glass is the lowest melting point glass possible from the three components Na_2O, CaO, and SiO_2. It is commercially available as Corning 015 glass.

Some of the Modern Problems

(The definitions of electrode function and asymmetry potential.)

A limitation of Corning 015 glass electrodes is that of pH range. In regions of pH vlaue below 1 and above 9, the glass membrane does not function well as a hydrogen electrode. In discussions on the glass electrode it is said that the "electrode function" changes in these regions. The electrode function is defined as $\frac{d\,E}{d\,pH}$ and is expressed in milivolts change per unit change in pH. In the regions of pH value from 1 to 9, $\frac{d\,E}{d\,pH}$ is constant and equal to $\frac{d\,E}{d\,pH}$ for the standard   hydrogen electrode.

The so-called acid and alkaline errors of the glass electrode have been investigated by many workers, perhaps most thoroughly by Mac Innes, Dole, and Belcher [4,5,6]. Explanations of the peculiar behaviour of the glass electrode in alkaline solutions of high pH and in extremely acid solutions have been advanced by Horovitz[7], Gross and Halpern[8], and Dole[9].

None of these theories is very satisfactory.

An important group of problems arises from a property of the glass electrode known as the asymmetry potential. It is found that if the solution inside the electrode is identical with that outside, and if the reference electrode immersed in the inside solution is made identical with that in the outside solution(by replacing the calomel electrode shown in Fig. 1 by an electrode identical with the one inside the glass electrode) there will still be a potential difference which seems to be due to the membrane itself. It seems to be the difference of the two contact potentials; solution-to-glass on one side, and solution-to-glass on the other.

This potential will vary for different electrodes and even the same electrode over periods of time. Its existence necessitates an adjustment knob on all commercial instruments to compensate for changes in its magnitude. Buffer solutions must be used to standardize the meters before use by means of the asymmetry potential compensating knob.

The nature of the asymmetry potential has been investigated by surprisingly few workers. The most interesting and exhaustive work was done by Yoshimura[10] who believed to have found correlations between asymmetry potential, **the** radii of curvature of the two membrane surfaces and the membrane thickness. The present writer believes that such correlations do not exist and that the asymmetry potential is merely due to chemical differences in the two surfaces as will be shown in the experimental section of this paper.

II. THE PURPOSE OF THE PRESENT WORK

In just the last year or two an interesting problem has arisen in connection with some possible commercial applications of the glass electrode. It was desired to use electrodes at higher than ordinary room temperatures. It was found that when used at temperatures of 80 to 100°C., the electrodes became worthless in a few days. Three major things seemed to occur: (1) the glass membrane dissolved at a high rate; (2) large asymmetry potentials developed; (3) the hydrogen electrode function changed. These effects were called summarily, "aging effects" and it was for their investigation that the present study was undertaken.

The investigation was divided into three parts: (1) preliminary experiments on asymmetry potentials and a conclusion as to the nature of asymmetry potentials; (2) preliminary experiment on aging and a conclusion as to the difference between acid and alkaline aging; (3) experiments correlating the production of asymmetry potentials and changes in the electrode function.

Finally, in attempting to make a set of simple, consistent conclusions from the experiments, some work was done on the theory of the glass electrode. The writer believes that modern knowledge of the nature of the chemical bond has been used to give the most consistent and complete explanation of the mechanism of the

glass electrode yet presented. This theory will form
the concluding part of the paper.

III. EXPERIMENTAL APPARATUS AND TECHNIQUES USED

The Glass Electrodes

The glass electrodes used were blown at the National Technical Laboratories by men who blow the Beckman pH meter electrodes and were remarkably uniform in their characteristics. They consisted of tubes of lead glass, 15 cm x 8 mm with hemispheres of Corning 015 glass put on one end. The electrical resistances of the membranes were of the order of 10^8 ohms.

The Measuring Circuit

To measure the potentials, a Leeds and Northrop potentiometer was used in conjunction with a Beckman pH meter. The Beckman pH meter contains a potentiometer, but for the purpose of these experiments it was preferable to have readings in millivolts instead of pH units. Therefore, the pH meter was used only as an amplifier and null galvanometer. The lead from the glass electrode to the amplifier was shielded.

The Measurement of Asymmetry Potentials

When asymmetry potentials were measured the glass electrode was about one fourth filled with 0.1 N HCl which contained an excess of quinhydrone, and immersed in a small beaker filled with the identical solution. Small platinum wire electrodes were inserted in the inside and in the outside solutions and the potential was measured across these electrodes.

The Cleaning of the Platinum Electrodes

Before use, the platinum electrodes were always cleaned by boiling about 2 minutes, first in concentrated

HNO_3, then in 10% Na HSO_3; then they were rinsed with distilled water. This treatment is recommended in Lange's Handbook of Chemistry[11]. It invariably gave clean electrodes which, when immersed together in a quinhydrone solution, gave zero potential with respect to each other, within 0.1 or 0.2 millivolt.

The Measurement of the Electrode Function

The hydrogen electrode function was measured by replacing the 0.1 N HCl solution outside the electrode (in the beaker) by various buffers with the desired pH values. In these measurements the reference electrode in the beaker was a saturated calomel electrode.

Precautions Against Electrical Leakage

It has been mentioned that a condensed layer of moisture on the stem glass may cause electrical leaks between the solutions inside and outside the electrode. To prevent the occurence of such leaks the precaution was taken in a few experiments of heating the stems and coating them with an insulating, non-hygroscopic wax. But due to the difficulty in cleaning the electrodes thoroughly free from wax between different aging treatments and the time consumed, this procedure was discarded as an unnecessary precaution. It was always found sufficient to wipe the stem clean and dry it in the hot air region above a Bunsen flame before making measurements. Heating of the stem near the membrane was avoided.

Accuracy of Readings

Voltage readings were reproducible to about 0.5 millivolt or much less than the experimental errors involved in the aging experiments.

Apparatus for Aging

For the aging itself, one or more electrodes were placed in a large pyrex test tube with the desired solution inside the electrode and outside in the test tube. The tube was then placed in an open water bath kept at 95-100° C. To prevent evaporation of the solution in the tube, a stopper with a fine capillary tube was inserted. This prevented the formation of pressures which might have blown off the stopper, and restricted evaporation to that very small amount which could leave the tube by diffusion through the capillary tube.

In the first experiments, the electrodes were resting on a wad of some soft substance such as "Kleenex" at the bottom of the Pyrex test tube. Later, small glass knobs were melted onto the sides of the electrodes about half way up the stem and the electrodes were hung by these knobs on glass racks placed in the test tubes, so that no part of the glass membrane was in contact with anything except the solution. The above ideas will be made clear by reference to Figure 2.

Technique of Measuring Aged Electrodes

After the desired length of time in the bath the pyrex tube was removed and allowed to cool for about half an hour. The electrodes were then removed and either rinsed with distilled water previous to measurement or,
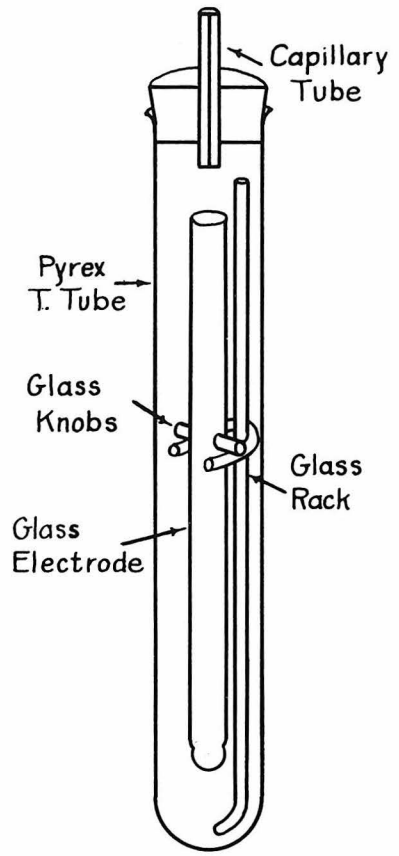
Fig. 2   The Aging Tube

in some cases, immersed directly in the measuring solution.

At all times when an electrode gave a reading of zero for its asymmetry potential, it was checked for cracks by a very simple qualitative resistance test. This test consisted merely in waving an electrified hair comb near the electrode being measured. Electrostatic pick-up produced very large deflections on the meter scale in the case of a good electrode of resistance 10 to 100 megohms, but very small or zero deflection with a cracked electrode. With this crude test the deflections obtained with a given electrode could be observed to decrease successively due to aging until zero deflection indicated aging to the point where cracks and other low resistance spots had developed in the glass.

In the measurement of potential an electrode was said to have reached equilibrium when the reading was constant over a 2 minute interval.

Convention as to the Sign of the Potential

The convention was adopted, that the potential reading was positive when the electrode immersed in the solution inside the glass electrode was positive with respect to the electrode immersed in the solution outside the glass electrode.

The Technique of Etching

In the work done on the asymmetry potential some means was sought to make both surfaces of the glass membrane chemically identical. The process decided upon was etching in 15% HF. The electrode membrane was merely immersed in the acid for the time interval chosen. The inside surface was etched by filling the electrode

about $\frac{1}{5}$ full of the acid and pouring it out after the
desired time. After the etching the surfaces were always
thoroughly rinsed with distilled water.

IV. EXPERIMENTAL WORK

Preliminary Experiments on Asymmetry Potentials

It is well known that freshly blown glass electrodes have asymmetry potentials of from 0 to 30 millivolts and that such electrodes exhibit very unsteady readings during measurements made on them. It is also well known that these initial asymmetry potentials are greatly reduced and the rate of attainment of steady readings greatly improved by soaking the fresh electrodes in water.

It was noticed by the present worker that these potentials are almost without exception of one sign, that is, all positive according to the convention stated above.

Perhaps the simplest and at the same time, one of the most important experiments performed during the course of the work was the etching by HF of both surfaces of these fresh membranes. After etching for 2 minutes, all of about 20 electrodes tried gave zero asymmetry potential and came to equilibrium rapidly. (Zero asymmetry potential in this work means zero within $\frac{1}{3}$ millivolt.) Furthermore, electrodes with these zero asymmetry potentials still gave their zero readings after soaking a month in distilled water.

As simple and obvious as this experiment seems its importance should be emphasized. Earlier investigators have measured asymmetry potentials but have not considered trying to abolish them by making both membrane surfaces.

chemically equal. For instance work done by Yoshimura[10] on the effect of curvature and thickness of the membrane on the asymmetry potential is made to appear rather meaningless by this experiment and others following. Asymmetry potentials can be repeatedly produced and destroyed chemically, on the same electrode while the thickness and curvature obviously can not be alternately increasing and decreasing. Changes observed by Yoshimura were undoubtedly due to chemical changes in the surfaces of the membranes during blowing.

In all experiments tried by the writer, no matter to what treatment an electrode had been subjected (chemical aging or drying), the asymmetry potential could be brought to zero by etching both surfaces. This could be repeated until the glass membrane became so thin that cracks and other low resistance spots developed.

Some typical data are given in Table 1. The second column shows the asymmetry potentials of some freshly blown electrodes. The third column shows the asymmetry potential after etching.

Table 1

The Effect of Etching on the Asymmetry Potentials of Some Freshly Blown Electrodes.

Electrode no.	Initial AP	AP after Etching
14	+29 mV	0 mV
15	+18 mV	0 mV
18	+14 mV	0 mV
20	+ 8 mV	0 mV

Similar data are given in Table 2 for some

electrodes not freshly blown, but possessing asymmetry
potentials due to chemical action(boiling in HCl,KOH.)

Table 2

The Effect of Etching on the Asymmetry Potential

of Some Chemically Aged Electrodes.

Electrode no.	Initial AP	AP After Etching
1	+22	0
2	+21	0
3	-11	0
4	+16	0

An interesting and simple experiment probably
first performed by Yoshimura[12] was the drying of the
outer surface of a glass electrode membrane by merely
holding the electrode filled with water about 3 inches
above a Bunsen flame for about 15 seconds. The electrode
was then filled with measuring solution and its asymmetry
potential measured. The electrodes used in the writer's
experiments were ones which had been previously etched to
zero asymmetry potential and had been soaking in water
for 5 days. A curve for a typical electrode showing
asymmetry potential as a function of time is shown in
Figure 3, curve 1. After drying, the asymmetry potential
started at a high negative value and came to zero after
a little over 5 hours immersion in the measuring solution.
Yoshimura did not perform the experiment starting with
electrodes of zero asymmetry potential and his experiment
did not demonstrate so clearly the reversibility of the
drying. The two important points to notice are: (1) the
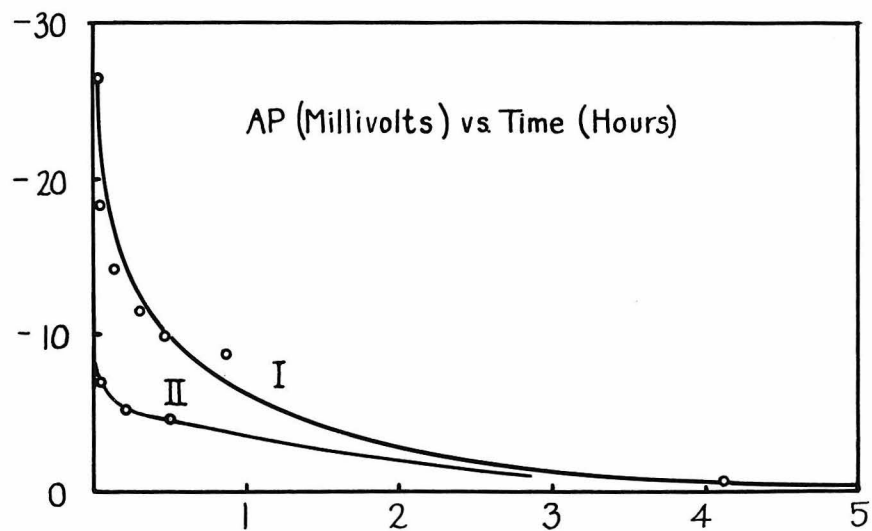reversibility of the drying and (2) the sign of the potential

Fig. 3   Asymmetry Potential Curves

I. Drying Curve

II. Etching Curve

change(the solution in contact with the dried side is positive with respect to the solution in contact with the untreated side.)

Some experiments were performed to determine the effect of etching of one surface of the membrane at a time. As has been shown above, etching made the surfaces identical but it was interesting to see what happened if one surface was left unaltered. In a typical experiment, an electrode which had been etched to zero asymmetry potential and had been subsequently soaking in water for several days was dipped in the 15% HF and the outside membrane surface etched for 1 minute. It was then rinsed off with distilled water and the asymmetry potential was measured. A curve of the asymmetry potential plotted against the time in minutes is shown in Figure 3 curve II. This curve was the same for different electrodes within a millivolt. In all cases the asymmetry potential dropped to zero in 3 to 4 hours. It is noticeable that the temporary asymmetry potential produced by etching the outside surface has the same sign as that due to drying. This may indicate that hydration of the glass surface does not proceed as rapidly as the dissolving by HF and that an etched surface is a partially dehydrated one.

An experiment which gave a little more insight into the nature of an asymmetry potential was the following. An electrode was first aged 1 $\frac{1}{2}$ hours in 0.1 N HCl. It showed an asymmetry potential of 10 millivolts. Each side was then etched for successive short periods until further etching of that side produced

significant
no change in reading. The results are shown in Table 3.

Table 3

The Gradual Disappearance of An Asymmetry

Potential due to Etching

Treatment	AP Observed
Aged in 0.1 N HCl	+10 mV
outside etched 20 seconds	+29 mV
outside etched 40 seconds	+51 mV
outside etched 60 seconds	+50 mV
inside etched 20 seconds	+15 mV
inside etched 40 seconds	0 mV
any further etching	0 mV

Now we know that had the electrode been one
that had been merely soaking in distilled water it would
have behaved in a manner given by Curve II of Figure 3.
After complete etching of the outside surface it would
have shown an asymmetry potential of -5 to -7 millivolts
in the period of 10 to 15 minutes after etching. It
actually gave an asymmetry potential of +50 millivolts
showing that the HCl had greatly altered the inside
surface. By studying the experiment we can see that
the action of HCl had caused the glass-to-solution
potential on the inside membrane surface to rise about
50 + 5 millivolts above its value for a water soaked
surface. It had caused the glass-to-solution potential
on the outside surface to rise about 40 + 5 millivolts
above the value for a water soaked surface. The differ-
ence of the two rises was 10 millivolts, the asymmetry
potential first measured. These asymmetry potentials
produced by HCl were not reduced in periods of soaking

as were the potentials due to etching and drying. The change was a definite chemical change and not a reversible dehydration.

A Conclusion as to the Nature of Asymmetry Potentials

The writer believes that the above experiments show, without the necessity of any argument, that asymmetry potentials are due to differences in the chemical composition and the state of hydration of the two membrane surfaces. The theory of the asymmetry potential will appear in the concluding section of the paper.

Preliminary Experiments on Aging

Some experiments were performed to determine the effect of aging on the asymmetry potentials of freshly blown electrodes. It was found that the measurement of the changes of the asymmetry potentials gave results which could not be correlated. For instance, two electrodes in the same aging tube, presumably had undergone the same treatment, and yet had potential changes from +3 to -18 and +16 to -43 millivolts respectively. Experiments with freshly blown electrodes were then abandoned, and electrodes whose asymmetry potentials had been reduced to zero by etching were used. It was found that these electrodes could be aged symmetrically; that is, though the potential, solution-to-glass, was changed for both surfaces of the membrane(as could be shown by etching), the two changes were equal. Therefore, for electrodes whose membrane surfaces were initially identical, asymmetry potentials of zero could be maintained during aging.

Electrodes aged in 0.1 N HCl and then measured

in the 0.1 N HCl, quinhydrone solution gave constant
readings. Electrodes aged in 0.1 N KOH gave readings
which varied in an erratic way if they were taken from
the 0.1 N KOH and immersed in the measuring solution.
For this reason the asymmetry potentials of KOH treated
electrodes were measured later in conjunction with the
hydrogen electrode function. There measurements will
be treated in the next section of this paper.

The qualitative chemical differences between
acid (0.1 N HCl) and alkaline (0.1 N KOH) aging were
indicated by some experiments in which electrodes were
aged until the membranes had developed low resistance
spots and had become worthless as electrodes. This
took from 10 to 14 days.

The membranes dissolved slightly faster in
HCl. This fact serves to emphasize the difference betweeen
Corning 015 glass and ordinary glass for which the
dissolving rate in alkaline solutions is much greater
than that in acid solutions.

Two photographs are shown. Figure 3A shows an
electrode aged in 0.1 N KOH. The visible chemical action
is the familiar action of alkaline media on glass. The
stem glass and the membrane glass are affected to approxi-
mately the same extent. Both the stem and membrane are
fairly clear; and even in the most affected parts are
translucent and smooth. On the other hand, Figure 3B
shows a distinctly different type of action, aging in
0.1 N HCl. (The very dark region in the membrane is a hole).
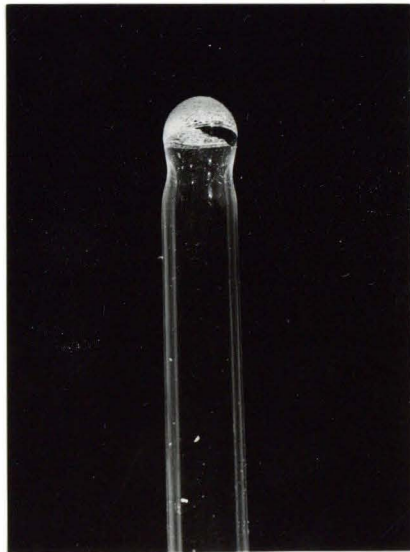
Fig. 3A   Alkaline Aging

Fig. 3B   Acid Aging

The most striking fact about this type of action is that, in contrast to alkaline aging the stem glass is hardly affected while the membrane has been more drastically affected than in the alkaline case. The membrane is densely pockmarked with small pits and instead of the smooth, translucent character of the alkaline aged sur-face, the texture is more like that of a piece of coarsely ground glass.

A Conclusion as to the Difference between Acid and

Alkaline Aging

The above results may be correlated briefly by considering that alkaline aging affects the silica in glass since the stem glass and the membrane glass both contain high percentage of Silica, the action of 0.1 N KOH on both of them is approximately the same. On the other hand the percentages of Soda and Calcium Oxide are markedly different in the two cases. The membrane glass is very high in alkali(Na_2O, 22%); CaO, 6%; SiO_2 72%) and the HCl probably attacks the glass by leaching out the soda.

This contrast of the two types of aging will be useful in the latter part of the paper in explaining the effects of the two processes on asymmetry potentials and electrode functions.

Experiments on the Electrode Function of Glass Electrodes
Aged in 0.1 N HCl.

To show the effects of aging on the electrode
function the following procedure was adopted.
The potential of a glass electrode against a saturated
calomel electrode was plotted as a function of pH before
and after aging. In order to emphasize the effects of
aging the usual changes of the electrode function above
a pH value of 9 were compensated for in the potential
measurements. This was done simply by standardizing a
set of buffers with a glass electrode (one, of course,
that had not been aged). These buffers were then used
to determine the electrode functions of the aged electrodes.
It is obvious, that in a plot of the potential of a
glass electrode against pH using these buffers, any
deviation from linearity was due to the effects of aging.

The pH values used for the buffers are shown
in table 4.

Table 4

The pH Values of the Buffers Used, as

Determined with an Unaged Electrode.

Buffer	pH
A	1.15
B	3.98
C	6.92
D	9.87

The effects of HCl aging are shown by the
following experiment. An electrode whose asymmetry

potential was zero (after etching and soaking in distilled
water) was measured against a saturated calomel electrode.
It was then aged in 0.1 N HCl and its asymmetry potential
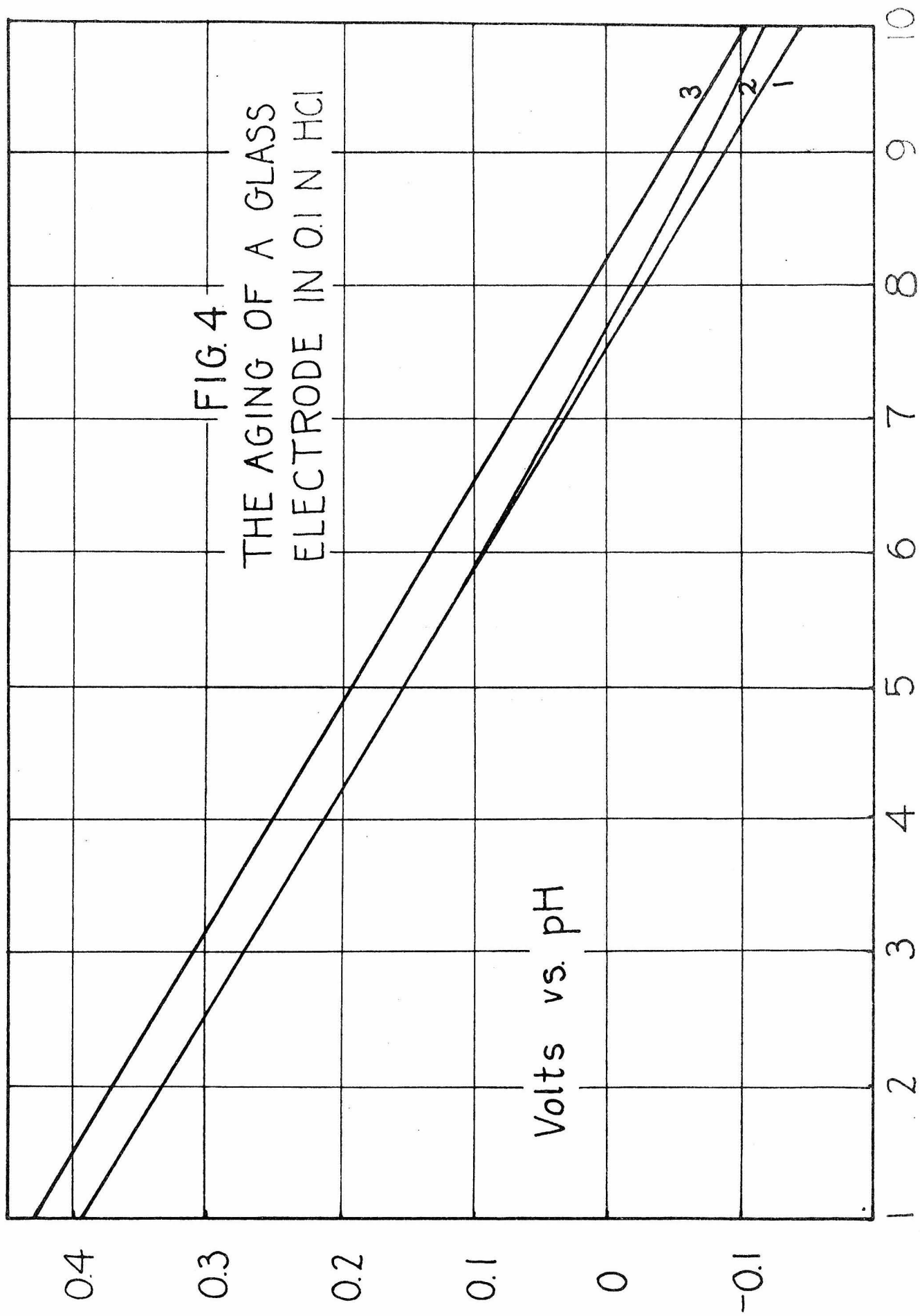and electrode function measured again. The results
are shown in Table 5.

Table 5

The Aging Effect of 0.1 N HCl

AP before aging	0 mV
AP after aging	+1 mV

Buffer	Potential Against Sat. Calomel Electrode
Before Aging	
A	0.3873
B	0.2160
C	0.0387
D	-0.1386
After Aging	
A	0.3890
B	0.2167
C	0.0447
D	-0.1110

The data of Table 5 are graphed in Figure 4.
Curve 1 shows the electrode function before aging and
Curve 2, the same after aging. (It will be remembered
that the normal amount of alkaline error is already
corrected for in all of the curves).

After the data in Table 5 were taken, the
outside surface of the electrode was etched until a
constant reading was obtained. The asymmetry potential

FIG. 4

THE AGING OF A GLASS
ELECTRODE IN 0.1 N HCl

Volts vs. pH

was then +36 millivolts. The electrode function was then

measured again and the readings are given in Table 5A.

Table 5A

Buffer	Potential Against Sat. Cal. Electrode.
A	0.4232
B	0.2538
C	0.0758
D	-0.0960

The data of Table 5A are plotted as Curve 3

of Figure 4.

From the experiments on asymmetry potentials,

if the inside surface of the membrane had been unaged,

Curve 3 would have been parallel to Curve 1, but

displaced about 5 or 7 millivolts downward. Since it

is displaced about 36 millivolts upward one can conclude

that the action of HCl on a glass surface is such as to

lower the potential, solution-to-glass. In this case,

it was lowered for each surface about 42 millivolts.

Experiments on the Electrode Function of Glass

Electrodes Aged in 0.1 N KOH.

The measurement of electrodes aged in 0.1 N KOH

could not be made as simply as in the case of 0.1 N HCl.

As mentioned above in the section on asymmetry potential

experiments, unsteady readings were obtained when electrodes

aged in 0.1 N KOH were measured directly afterward in

0.1 N HCl. After aging, the inside surface was etched

for 2 minutes and the inside of the electrode was filled

with 0.1 N HCl. The outside surface was never rinsed

free from the 0.1 N KOH during this treatment. The

electrode was then allowed to soak with 0.1 N HCl inside and 0.1 N KOH outside for 4 hours. From the experiments on asymmetry potentials, one knows that such a treatment would bring the inside glass-to-solution potential to the value for an unaged electrode.

After this soaking the potentials of the glass electrode against a calomel electrode were measured in the usual way, except that the measurements were started in buffers of high pH and successive measurements were made in buffers of successively lower pH. Each measurement took about $\frac{1}{2}$ minute. When the measurement in buffer A had been made, measurements were made going up the pH scale again. This procedure was repeated twice, so that the sequence of buffers used was in order D, C, B, A, B, C, D, C, B, A, B, C, D. The whole series of measurement took about 8 minutes. The results are shown in Table 6.

Table 6

The Aging Effect of 0.1 N KOH

Buffer	Potential Against Sat. Cal. Electrode
D	-0.1142
C	0.0430
B	0.2197
A	0.3917
B	0.2208
C	0.0440
D	-0.0193
C	0.0454
B	0.2204

FIG. 5

THE AGING OF A GLASS
ELECTRODE IN 0.1 N KOH

Volts vs. pH
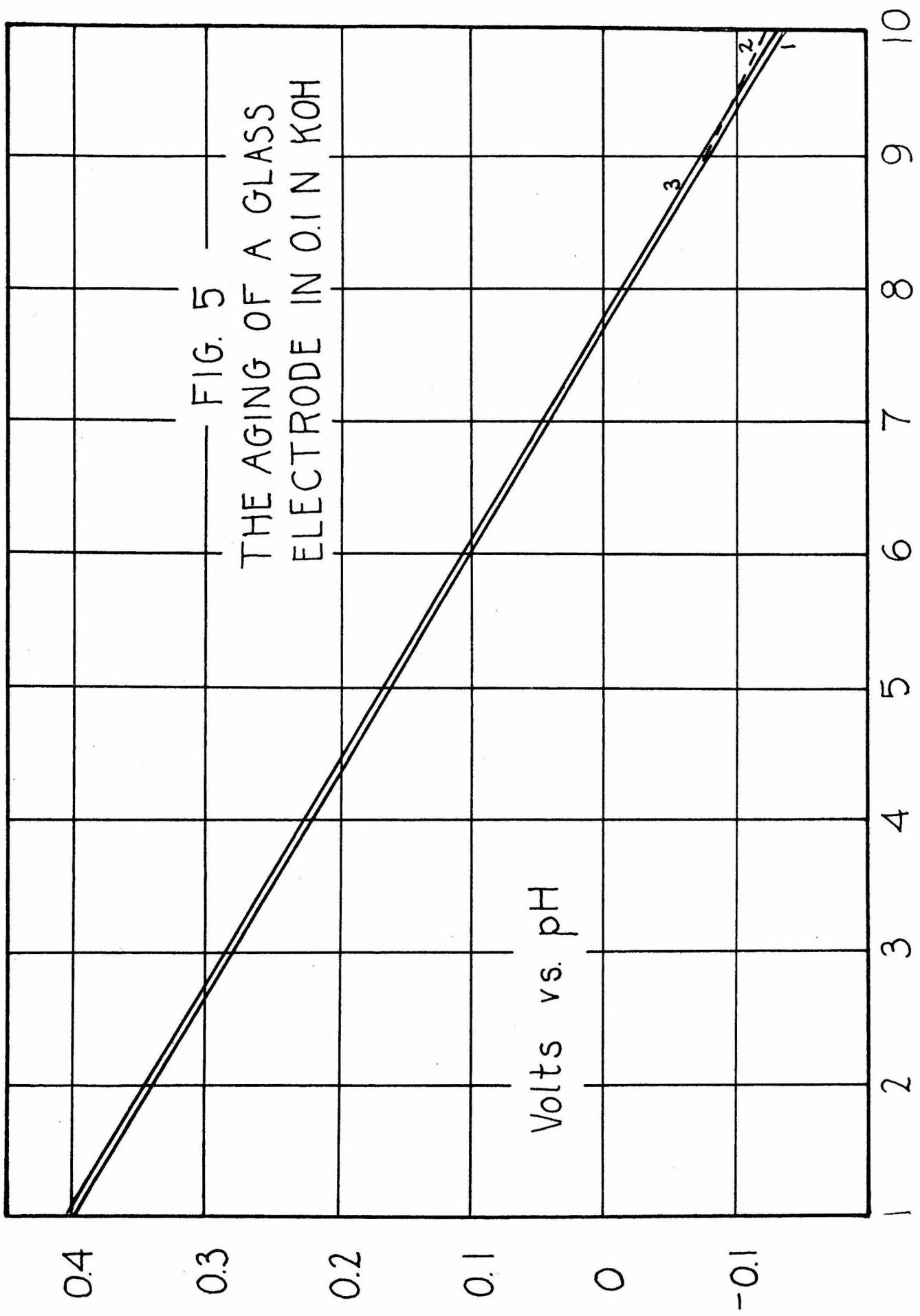
A	0.3913
B	0.2203
C	0.0424
D	-0.1223

The results of the first sequence D, C, B, A are plotted as Curve 2, Figure 5. The results of the last sequence A, B, C, D are plotted as Curve 1, Figure 5. The potentials of Curve 2 were transient and the KOH treated electrode quickly reached a state where Curve 1 could be repeated indefinitely. So it may be said that the final result is that the KOH treatment left the electrode function unaffected.

After the data for Curves 2 and 1 were obtained, the inside of the electrode was etched again, and measurements of the potential against the same calomel electrode were made about 15 minutes after etching. This curve is similar to Curve 1, but displaced about 6 millivolts upward. The data for Curve 3 are shown in Table 6A.

Table 6A

Buffer	Potential Against Sat. Cal. Electrode.
A	0.3966
B	0.2253
C	0.0472
D	-0.1270

From the experiments on asymmetry potential, the displacement of Curve 3 is just what we should expect if the outside surface after aging had possessed the same solution-to-glass potential as an unaged electrode.

Conclusion as to the Effects of Aging the Glass
Electrode in 0.1 N HCl and 0.1 N KOH.

From a study of the above experiments one can
make the following conclusions: (1) The aging of a
membrane surface in 0.1 N HCl lowers the solution-to-
glass potential throughout the whole pH range and lowers
the electrode function in the range of higher pH values
(that is, increases the usual alkaline errors). (2)
Aging is 0.1 N KOH leaves the solution-to-glass potential
and the electrode function unchanged.

These conclusions, of course, pertain only
to Corning 015 glass, the glass now in general use for
electrode membranes.

V. A NEW APPROACH TO THE THEORY OF THE GLASS ELECTRODE

(The experimental results in the preceding parts
of this paper can be used to aid in building up
and checking a concept of the mechanism of the
operation of the glass electrode.)

The Mechanism of the Formation of the Solution-to-
glass Potential

In Morey's recent monograph on glass[13], there
is a collection of the results of various workers on
the atomic arrangement in glass. The approximate
picture for the purposes of the present paper is this:
there are oxygen ion tetrahedra surrounding positive
silicon ions. In quartz, where the silicon ion is the
only positive ion, all the corners of the tetrahedra
are shared and each silicon ion is surrounded by four
oxygen ions, each oxygen being bonded to two silicon
ions. In glass, which contains alkaline and alkaline
earth oxides, there are irregularities. In general,
less than four corners of the oxygen tetrahedron will
be shared, the other corner or corners being ionically
bonded by alkali or alkaline earth ions. In general,
the alkali and alkaline earth ions are surrounded by
more than 4 oxygens, usually about 6. From these abbre-
viated conceptions of the glass interior, let us jump
to a conception of the glass surface.

For simplicity, let us consider a surface of
quartz. Since every bond in the crystal is a bond
between an oxygen and a silicon ion, when a new surface
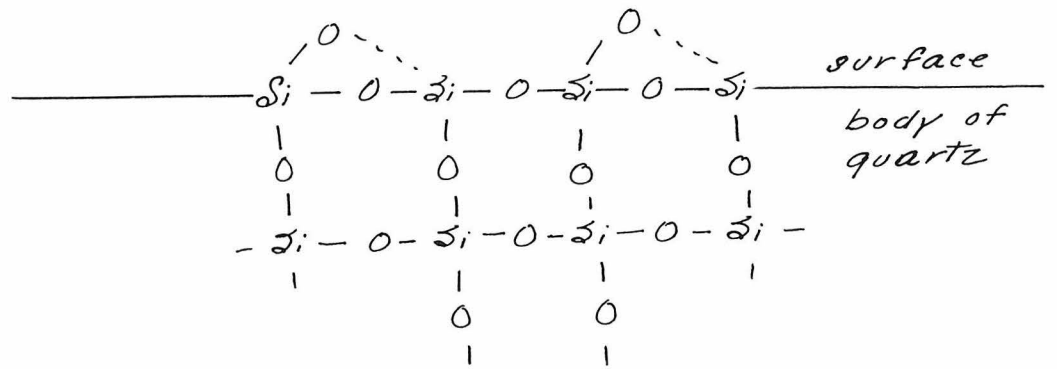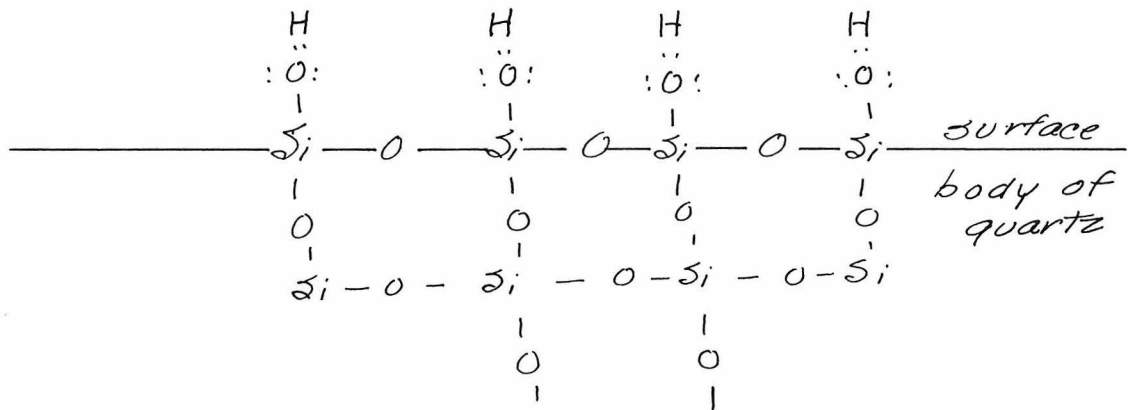is formed there will be, on the average, an equal number

Fig. 6 A

Fig. 6 B

of free silicon and oxygen valences. Strained oxygen-
silicon bonds will form on the surface. A two dimensional
representation may be made as shown in Figure 6A. If
however, any water is present near the surface, there
will be a tendency for hydrogen ions to bond to the
surface using the oxygen valences and hydroxyl ions to
bond to the surface using the silicon valences, so that
the new surface may be represented by Figure 6B. It
is experimentally known that surfaces of quartz and also
glass are hydrated, and this is the probable mechanism.
(These surface conceptions are derived from a personal
conversation with Dr. Linus Pauling.)

Let us consider the actions that may take
place on such a surface in contact with a solution con-
taining hydrogen ions. In the first place, there will
be ionization similar to the ordinary ionization of
orthosilicic acid. The protons will split off and leave
oxygen ions bonded to the glass surface. This effect
is probably quite important in alkaline solutions.
Second, there will be an exchange of protons between
the water of the solution and the glass surface in which
a proton will jump from its oxonium ion to an unshared
electron pair of a glass surface hydroxyl group.

$$H\!:\!\overset{\textstyle H}{\underset{..}{\overset{..}{O}}}\!:\!H \;+\; H\!:\!\overset{..}{\underset{..}{O}}\!:\!Si\!\!\Big\langle \;\longrightarrow\; :\!\overset{\textstyle H}{\underset{..}{O}}\!:\!H \;+\; H\!:\!\overset{\textstyle H}{\underset{..}{O}}\!:\!Si\!\!\Big\langle$$

Furthermore, because silicon is more electropositive
than hydrogen, a proton will probably have a greater
tendency to use an unshared electron pair of an oxygen

bonded to a hydrogen and a silicon than it will to use an unshared pair of an oxygen bonded to two hydrogens. The same is true of positive ions other than hydrogen, alkali ions etc. It may be supposed that when a piece of glass or quartz is dipped into water protons will attach themselves to the glass in this manner. We shall use this mechanism as the mechanism of the potential formation.

It must be noted that another extremely important effect in the case of glass is the exchange of alkali ions in the glass for hydrogen ions of the solution. This change takes place from the surface inward. However, because of the difficulty of alkali ions getting out of the glass, mainly because of size, this effect is not a very fast one and though it modifies everything we shall say about the potential formation it will not nullify anything.

This then will be the process that takes place when we dip a piece of glass into a solution: protons will jump from oxonium ions in solution to the surface of the glass. This will continue until the charge accumulated on the surface creates a potential difference between the glass and the solution that renders further proton deposition impossible. It must be borne in mind that these statements hold for other positive ions but not to such a large extent.

If the glass is a glass membrane and there is a solution on each side of it, there will occur another very important process. Except in a very rare case, the potential difference of the two solutions will

combine with the two interfacial potentials to produce an
electric field across the glass. If the glass were a
perfect insulator this field would remain. In the case
of quartz it **does** remain for a long time. But with the
better conducting glasses ionic migration soon brings
about an approximately constant potential across the
glas**s**. In the case of the very soft glass (Corning 015)
used generally for glass electrodes, this equalization
probably takes place in about one second; and in the
case of harder glasses it takes place during a period
of some seconds. This leveling off of the potential
across the glass membrane is the explanation of the
phenomena which have been grouped under the term
polarigation.

A simple calculation, taking the conductivity
ratio of glass and quartz to be about a million, shows
that months would be required for the same equalization
to occur in quartz that occurs in glass in a matter of
seconds.

A Derivation of an Equation Similar to the Dole

Equation.

Dole[14], in an attempt to explain the alkaline
errors of the glass electrode derived an equation similar
to one which we shall derive here. Here, however,
Statistical Mechanics will be avoided and only simple
Thermodynamics will be used. Through the use of a too
simple form of the Boltzmann principle, Dole introduced
an extra assumption which we shall avoid.

Let us designate some arbitrary concentration

of the ion M^+ on the glass surface as possessing unit activity. Then for the reaction

$$M^+(aq.) \text{ unit activity} \longrightarrow M^+(glass) \text{ unit activity} \qquad (1)$$

there will be a certain free energy change ΔF°. We can also write

$$-\Delta F^\circ = RT \ln\left[\frac{M^+(glass)}{M^+(aq.)}\right] \qquad (2)$$

If, however, the glass surface attains a potential V with respect to the solution, an added amount of free energy will be required for a mole of positive ions to undergo reaction (1).

This amount will be equal to ΦV where Φ stands for the Faraday. A new equation can be written

$$-\Delta F^\circ - \Phi V = RT \ln\left[\frac{M^+(glass)}{M^+(aq.)}\right] \qquad (3)$$

or

$$M^+(glass) = M^+(aq.)\, e^{-\frac{\Delta F^\circ - \Phi V}{RT}} \qquad (4)$$

A similar equation can be written for each positive ion in solution. If the terms $M^+(aq.)$ are known, then there will be for n ions, n equations in $n+1$ unknowns. However, we know also from the physical picture that the total number of ions deposited on the glass from the solution determines V, or conversely, if we pick an arbitrary voltage we have also specified the

total number of ions deposited on the glass. This
gives us one more equation and enables us to write

$$\sum_{i=1}^{n} M_i^+(glass) = \sum_{i=1}^{n} M_i^+(aq.) \, e^{\frac{-\Delta F_i^o - \Phi V}{RT}} = const. \qquad (5)$$

This equation can be solved for V

$$V = \frac{RT}{\Phi} \ln\left(\frac{1}{const.}\right) + \frac{RT}{\Phi} \ln\left[\sum_{i=1}^{n} M_i^+(aq.) \, e^{-\frac{\Delta F_i^o}{RT}}\right] \qquad (6)$$

Equation (6) is an equation in the general
form similar to the equation Dole derived for two ions
using Statistical Mechanics. Its meaning becomes clearer
if we set it up for two ions, say H^+ and Na^+

$$V = \frac{RT}{\Phi} \ln\left(\frac{1}{const.}\right) + \frac{RT}{\Phi} \ln\left[(H^+) \, e^{-\frac{\Delta F_H^o}{RT}} + (Na^+) \, e^{-\frac{\Delta F_{Na}^o}{RT}}\right] \qquad (7)$$

This equation can also be written

$$V = \frac{RT}{\Phi} \ln\left(\frac{1}{const.}\right) - \frac{\Delta F_H^o}{\Phi} + \frac{RT}{\Phi} \ln\left[(H^+) + (Na^+) \, e^{\frac{\Delta F_H^o - \Delta F_{Na}^o}{RT}}\right] \qquad (8)$$

Since V is the potential of the glass with respect
to the solution, it becomes rather clear why the glass
surface should behave as a hydrogen electrode, but it
is useful to give the complete picture for the care
of the glass electrode membrane which has two surfaces.
By writing down two such equations, one for one side
and one for the other we can obtain, if E is the
potential difference of the solutions on opposite sides

$$E = \frac{\Delta F_H^{o\prime} - \Delta F_H^o}{\Phi} + \frac{RT}{\Phi} \ln\left[(H^+) + (Na^+) \, e^{\frac{\Delta F_H^o - \Delta F_{Na}^o}{RT}}\right]$$
$$- \frac{RT}{\Phi} \ln\left[(H^+)' + (Na^+)' \, e^{\frac{\Delta F_H^{o\prime} - \Delta F_{Na}^{o\prime}}{RT}}\right] + Y \qquad (9)$$

where the primed and unprimed quantities refer to
opposite sides of the membrane. Y is a term put
in the equation to take care of any potential differ-
ence that may exist across the body of the glass. The
mechanism underlying this term and its connection with
the conductivity of the glass was discussed above.
It might be called the polarization term.

It is interesting to remark, now that we see
in equation form the importance of this polarization
term, that through knowing its connection with con-
ductivity we can predict a fact which may become
important in the commercial use of the glass electrode.
A glass with polarization characteristics which render
it impractical for use at room temperatures might
function very well at 80-100°C. where its conductivity
is greater, so that Y could rapidly approach zero.
It is an experimental fact that glass conductivities
may increase by several powers of ten in this interval
of temperature. Thus a "hard" glass which is more
chemically resistant than the ordinary Corning 015
glass might be used for a glass electrode at higher
temperatures.

An Experimentally Checked Theory of the Asymmetry
Potential.

In equation (9) we can see also the mathematical
expression of the heretofore unexplained asymmetry
potential. Let us look again at the mechanism pictured
in the first of this discussion. In glass some of the
surface oxygen ions are bonded ionically to alkali ions

as well as the silicon ions. It may be argued that since alkali ions in the glass have more oxygen neighbors than silicon ions (approximately 6 compared to 4) an alkali ion can easier shift away from an oxygen when it forms a bond with a depositing proton, ~~proton~~, consequently the oxygen ion-proton bond may be stronger than an oxygen ion-proton bond on a quartz surface. Let us pursue the argument further and predict that of two glass surfaces the one containing the least alkali will form the weaker bonds with depositing protons. From inspection of reaction (1) we can say that this surface will have the greater ΔF_H^o. Then by inspection of equation (8) we can predict that this surface will have the smaller solution-to-glass potential. We might predict, then that leaching the alkali out of a glass surface would lower the solutinn-to-glass potential. Going to the experimental part of this paper, we find that this is the case!

A Discussion of the Alkaline Errors of the

Glass Electrode

Let us go now to the discussion of the alkaline errors of the glass electrode. Dole's equation was originally derived to explain these errors. The equation does give curves which approximate the exper-imental curves in high pH regions if $-\left(\Delta F_H^o - \Delta F_{Na}^o\right)$

(for instance, in the case of sodium ion errors) is taken to be fourteen to sixteen kilo-calories per mole. Dole mentions that there is no easy theroetical way to calculate such quantities which he obtains from error

experiments.

It is quite possible, however, to justify this order of magnitude for the quantities. From the mechanism given before, it can be seen that the free energy of attachment of a mole of hydrogen ions, $-\Delta F_H^o$ would be very similar to the free energy of association of a mole of hydrogen ions with silicate ions in solution:
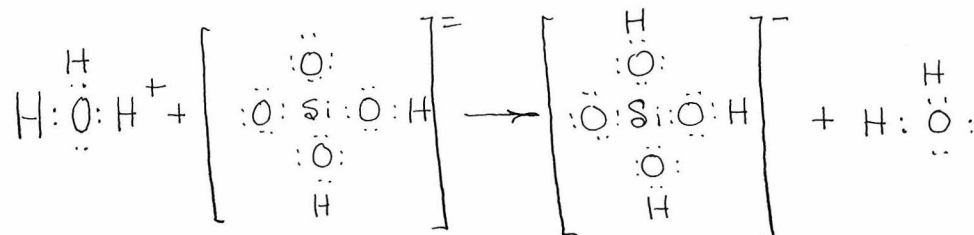
And $-\Delta F_{Na}^o$, say, would be similar to the free energy of association of a sodium ion with a silicate ion in solution:
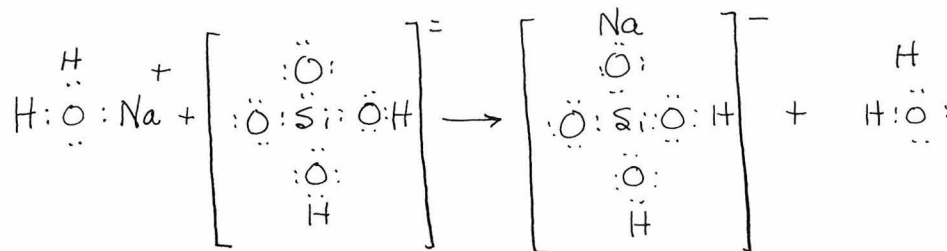
If we assume that the ionization constant for the reverse of the second reaction is about 1, knowing that the constant for the first reaction is about 10^{-12}, we can calculate for the difference in the two free energies of association approximately 16.4 kilo-calories per mole. This quantity is certainly pleasantly close to the experiment quantities obtained by Dole.

Dole ~~was~~ made some experiments, the purpose of which was to check the equation he had derived.[6]   He was disappointed to find that his experimental quantities, such as we have been discussing, varied in

most of his experiments about two kilo-calories per
mole. They seemed to vary furthermore with salt concen-
tration and even the pH itself. In the writer's opinion
however, the extreme sensitivity of the mathematical
function and the general irreproducibility of the error
experiments can be cited to show that the experiments
do not cast such a bad light on the equation.

Conclusion to the Theoretical Discussion

It is hoped that the picture of the glass
electrode mechanism suggested here and also the derivation
of Equation(9) presented may assist workers with the
glass electrode. The writer believes that the physico-
chemial picture of the mechanism presented provides a
mental working image which was badly needed. Perhaps
it may suggest further experiments which will help
to clarify the Theory of the Glass Electrode.

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