

and ethyl bromide are used to calculate the moments which might be expected in the molecules. The observed values are lowered by proximity of the two bromide dipoles, which also gives rise to the temperature variation of the moment. In decamethylene bromide the two dipoles are so far apart that the observed and calculated moments agree satisfactorily and the moment shows no variation with temperature.

Rotation around the C-C bonds probably causes some bending of the carbon chain, but there is no evidence of pronounced bending of the supposedly rod-like structures of the long chains, even in the external electric fields used in the measurement of the dielectric constants.

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[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF HEALTH]

## THE GLASS ELECTRODE. THE STUDY OF VARIOUS CHARACTERISTICS

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### Introduction

The theory of the glass cell which so far is the most widely accepted is that of Haber.<sup>1</sup> He derived several expressions for the potential difference across a glass membrane when the two surfaces are in contact with solutions whose hydrogen-ion concentrations (activities) are  $1a$  and  $1b$ . All of these expressions may be summarized into the equation  $E = RT \log (1a/1b) - F(G)$ , where by  $F(G)$  is meant a function of the glass, when immersed in different solutions.

The difference between the equations of Haber as well as between different hypotheses which have since been stated, arises from differences assumed for  $F(G)$ . When  $F(G)$  is a small constant the glass is said to be "good," since it then has the theoretical slope for the calibration curve and also a small zero correction. Haber made the hypothesis that the glass is hydrated at its surfaces, this hydrated layer having the product  $[H^+][OH^-]$  constant. In his paper, under certain conditions,  $F(G) = RT \log (IIa/IIb)$ , where  $IIa$  and  $IIb$  are the hydrogen-ion concentrations (activities) in the two hydrated layers.  $F(G)$  then is small only when  $IIa$  is nearly equal to  $IIb$ , which occurs when the hydrated layer is uninfluenced by the successive solutions coming in contact with the glass, or  $[H^+]$  and  $[OH^-]$  are constant. Hughes<sup>2</sup> pointed out that this constancy could be attributed to the sodium silicate buffer system in the hydrated layer at the phase boundary. It is also evident that any increase in the buffer capacity of the hydrated layer improves the electrode performance.

<sup>1</sup> Haber and Klemensiewicz, *Z. physik. Chem.*, **67**, 385 (1909).

<sup>2</sup> Hughes, *J. Chem. Soc.*, 491 (1928).

Horovitz and collaborators<sup>3</sup> showed that certain glasses exhibited metal electrode functions for ions other than  $H^+$  and  $OH^-$  when the glasses contained the metal whose ion was being measured in solution.

It has been observed by nearly every worker that thin glass electrodes give better results than thick glasses, though no one has shown any good reason for this. MacInnes<sup>4</sup> has gone so far as to use glasses only 1 micron thick, the membranes exhibiting interference colors. It is obvious from a practical standpoint that thick glasses having great mechanical strength would possess advantages in most applications.

We discuss thickness, resistance, zero correction, deviation and temperature coefficient, following the experimental technique generally employed by others as described in the literature. Following this, we show how some of these results may be greatly modified by using the methods outlined in this paper.

**Chemical Composition of Glass.**—On the basis of the work of Hughes and of MacInnes and Dole, the glasses we selected were those whose composition approached Corning Glass 015. Four such glasses are shown in Table I. The first glass to be used is unknown in origin and it has been designated "A." A second glass designated as 015 (Al) was obtained from the Corning Glass Company, and its designation is given the suffix Al because analysis showed the presence of aluminum. A third batch of glass called 015 is a sample of Corning soda lime glass and differs from 015 (Al) in that it yields electrodes having a calibration curve very close to the theoretical. Glass "M" is a sample prepared by Dr. G. W. Morey of the Geophysical Laboratory from c. p. ingredients.

TABLE I  
RESULTS OF EXPERIMENTS

Designation	SiO <sub>2</sub> , %	CaO, %	Na <sub>2</sub> O, %	(Al, Fe) <sub>2</sub> O <sub>3</sub> , %	Al <sub>2</sub> O <sub>3</sub> , %	Other constituents, %	Analyst
"M"	72	6	22				G. W. Morey
015	72	6	22				Corning Glass Works
015(Al)	69.8	6.1	21.6	2.2		PbO 0.3	W. Taylor
"A"	70	4.5	22.7		0.3	Fe <sub>2</sub> O <sub>3</sub> 0.3 Mn <sub>2</sub> O <sub>3</sub> 0.2 MgO 1.7	E. Wherry

**Resistance and Thickness Measurements.**—Glass bulbs whose thickness was 10 microns and over were measured by Dr. W. R. Earle with a microscope having a vertical adjustment calibrated in microns.<sup>5</sup> In measuring the thickness of the glass its thickness was determined at four different places. When the glass was not sufficiently uniform, the

<sup>3</sup> Horovitz, *Z. Physik*, **15**, 369 (1923).

<sup>4</sup> MacInnes and Dole, *THIS JOURNAL*, **52**, 29 (1930).

<sup>5</sup> Gage, "The Microscope," **1925**; Chamot and Mason, "Handbook of Chemical Microscopy," John Wiley and Sons, Inc., New York, **1930**, Vol. I, p. 407.

sum of the reciprocal thicknesses was made  $1/T = 1/t_1 + 1/t_2 + 1/t_3 + 1/t_4$  in order to compare with the resistance of several parallel resistances  $1/R = 1/r_1 + 1/r_2 + 1/r_3 + 1/r_4$ . On measuring the area of the bulb and its total resistance the specific resistance  $\rho$  could be obtained. The total resistance  $R$  was measured by an electrometer-capacity method as follows (Fig. 1).

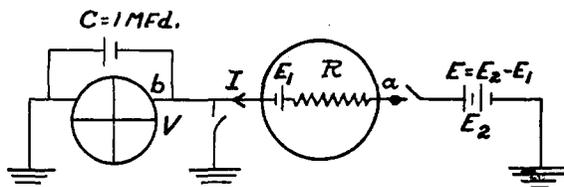


Fig. 1.—Resistance measurement:  $V$ , voltage of electrometer;  $E_1$ , potential difference across glass cell for zero current;  $E_2$ , voltage applied by potentiometer;  $E$ , excess potentiometer voltage for zero current;  $I$ , current;  $R$ , glass cell resistance.

The cell being first balanced by the null method, at a given time let the earth connection of  $b$  be broken and the excess potential  $R$  from the potentiometer applied so that the electrometer charges up at a certain time rate. This rate is observed and the resistance computed according to the equation

$$R = - \frac{t}{2.3C \log (E - V)/E}$$

$R$  is the resistance,  $t$  is seconds where  $C$  is the capacity of the shunt condenser;  $E$  is the applied voltage,  $V$  is the electrometer voltage. This method has the great advantage that low applied voltages may be used and small currents flow, thus causing a minimum polarization.

As a result of such experiments the glass 015 Al gave a specific resistance of  $2.0 \times 10^{+10}$  ohms/cm. cube, while glass "A" gave a specific resistance of  $6.5 + 10^{+10}$  ohms/cm. cube. We estimate from the data of MacInnes and Dole for glass 015 that they would get about  $1.2 \times 10^{10}$ . For 015 we find  $\rho = 3.6 \times 10^{10}$  at  $22.3^\circ$ . Horovitz obtained for various German glasses  $10^7$  to  $10^{+10}$  for the specific resistance, the former of which seems remarkably low.

In some cases the glass electrode was provided with a guard ring and connected as in the well-known method. A check on the work is the graphs obtained for different cells of the same glass. These show that the resistance is proportional to the thickness of the glass. In passing it may be remarked that the guard ring is necessary for a short shanked glass electrode or a damp glass surface but for a well dried glass insulating surface in a fairly dry atmosphere and a length of shank of 10 cm. there is little need of the guard ring except in measurements of high precision or when the cell membrane has a very high resistance.

It can readily be seen that the leakage is related to the ratio of the surface resistance to the resistance of the glass membrane for electrolytic currents. If the latter be taken at  $10^8$  ohms, then the shank should be long enough so that the former would have a resistance of  $10^{11}$  ohms with a humidity of 60%. The measurements were made at a measured humidity of 55%, the room being provided with an air dryer.

**Resistance and Temperature.**—The variation of resistance over the temperature range from 5 to 55° was ascertained. At 55° the resistance is only a fraction of the value obtained at 5°. Thus a cell which at 5° showed a resistance of over 1200 megohms at 55° had a resistance of only 12 megohms.

**Potential Measurements.**—In measuring potential differences across the glass membrane, the solution on each side of the membrane is electrically connected to a saturated calomel half cell by means of an agar-potassium chloride bridge. In the ensuing experiments a potentiometer and Compton type electrometer were used interchangeably with vacuum tube voltmeters. Three vacuum tube amplifiers were used. The first is of the previously described<sup>6</sup> type, using a 201-A tube critically balanced in the first stage for a minimum grid current, followed by a two-stage resistance coupled amplifier with a microammeter in the output of the last stage. The second amplifier was used with the FP-54 General Electric tube in the first stage followed by 222 and 212 tubes in successive stages. A third amplifier used the German Osram double grid (E series) tube with the control grid inserted in the tube through an amber plug, followed by 222 and 212 tubes.

In an electrometer-potentiometer system of small electrostatic capacity and small leakage the sensitivity of the system is independent of resistance in the circuit so long as a sufficient current flows to charge up the quadrant, since in the final steady state the current approaches zero. However, when leaks occur on the electrometer side of the potentiometer, the sensitivity of the equipment drops. The chief effect of increase in resistance is to increase the time necessary to get the final steady reading.

Similar considerations with regard to the glass cell, keeping the Haber theory in mind, might indicate that the resistance or thickness of the cell as such could play no part other than the time factor in the potential measured since, at the time of the final reading, there is no current flowing except that due to unavoidable insulation leakage.

However, experiments now to be described, as well as those previously reported in the literature, show that this is not the case, *viz.*, resistance (thickness) appears to affect the performance of the glass cell indirectly, at least under some conditions.

In measuring the hydrogen-ion activities of solutions, one of the first

<sup>6</sup> Kahler, DeEds, Rosenthal and Voegtlin, *Am. J. Phys.*, 91, 225 (1930).

steps is to measure the potential when the same solution is on both sides of the glass. This gives the zero correction, also called the strain value by some writers, and the asymmetry value by other writers. By changing the solution simultaneously on both sides, a relation between the observed potential and the  $P_H$  value of the solutions was obtained. This curve is shown in Fig. 2. This particular graph illustrates the manner in which a very poor cell may show a large change in zero correction with  $P_H$ . The interpretation of this is that the slopes of the calibration curves on the two sides differ since the difference in slopes  $S_2 - S_1 = Z_2 - Z_1$  the difference of zero corrections at two  $P_H$  levels.

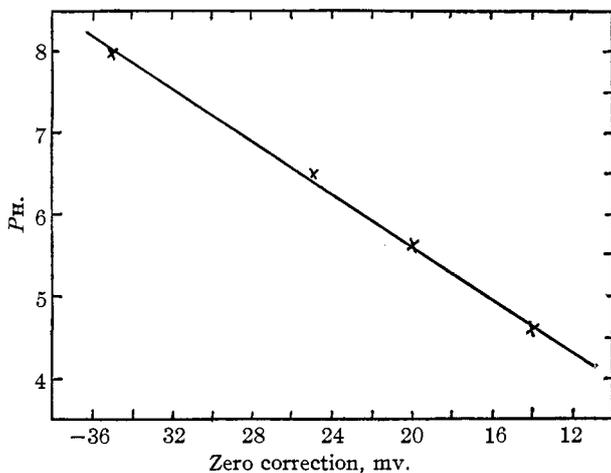


Fig. 2.—Glass "A," thick bulb.

#### Relation between Resistance (Thickness) and Zero Correction.—

By taking a large number of cells of the Haber bulb type of the same kind of glass but differing in thickness and total resistance, it was shown that usually the higher resistant (thicker) cells have the larger zero corrections when using a liquid of  $P_H$  4 on each side if the outside surface is only immersed to the top of the bulb.

**Deviation and Resistance (Thickness).**—By keeping the fluid on the inside of the glass cell constant and varying the  $P_H$  of the solution on the outside, a calibration curve for the cell outer surface may be obtained. It is found that as the resistance of the glass cell increases for the same glass composition, the curve for the glass cell markedly deviates from the theoretical relationship. In order to have a definite criterion for this effect, we take as a convenient measure of the deviation from the theoretical the difference between the hydrogen electrode and glass electrode reading for unit  $P_H$  change:  $E_H - E_G = \Delta(\text{H.G.})$ . A perfect electrode has a difference of 0. MacInnes and Dole,<sup>4</sup> using thin membranes, were

able to get a difference of zero over a range  $P_H$  1 to 9.8. At  $P_H$  values for which the glass is attacked all glasses deviate markedly from the theoretical, as has been shown by many workers including Horovitz, Hughes, MacInnes and Dole.

The relation between  $\Delta(H.G.)$  and thickness for different glasses on their outer surfaces is shown in Fig. 3. As can be seen, the "A" glass containing no aluminum is quite similar to 015(Al).

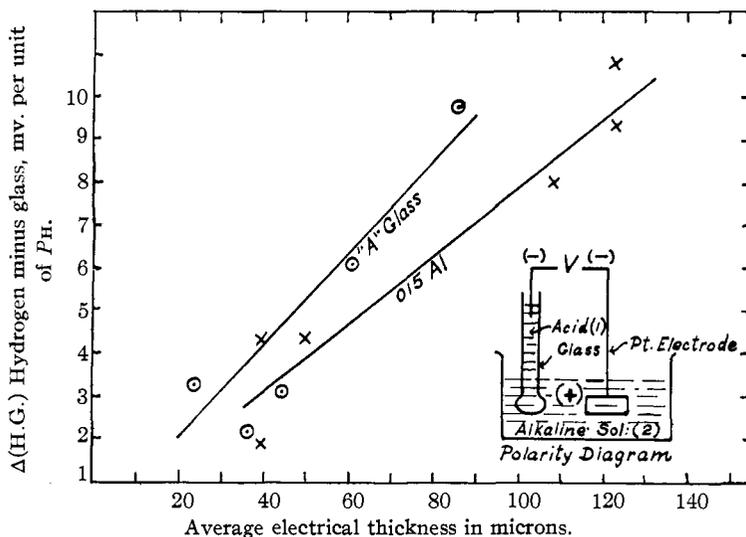


Fig. 3.—Polarity: when inside solution in glass cell is acid with respect to the outside—inside is negative. (Both calomel half cells are omitted in the diagram.)

For reasons to be pointed out later, it should be here stated that these measurements were all made when the outer glass surface was immersed only about 1 cm. below the surface of the solution.

**Effect of Hydrofluoric Acid Treatment.**—If the surfaces of the glass bulbs are etched with hydrofluoric acid, the thickness may be reduced at will. Experiments were performed with the idea of testing whether the zero correction and deviation from the theoretical would follow the thickness (resistance) deviation curves. The results for several glass cells are shown in Table II.

At this point it is well to make clear that all the above-mentioned experiments were made with a large area of wetted glass on one side of the membrane and a small area on the other side. The shank and bulb were of the same glass and the statement refers to the total combined areas. It seems likely that most of the work reported in the literature was done under somewhat comparable conditions.

TABLE II  
HYDROFLUORIC ACID TREATMENT

Electrode	Thickness, microns	$P_{H\ 4}$ zero correction	$\Delta(H.G.)$	Time in hydrofluoric acid, minutes
"A" 21	233	0.078	0.028	0
	146	.011	.011	15
	116	.009	.008	12
"A" 38	121	.031	.015	0
	83	.009	.006	4
	70	.009	.003	15
015A1 12	225	.063	.052	0
	220	.020	.026	5
	110	-.003	.003	28
"A" 34	71	.047	?	0
	68	.011	?	3
	67	.011	.001	3

**Temperature.**—Literature describing the use of the glass electrode for the measurement of  $H^+$  has contained little discussion of the influence of temperature changes upon the observed potential. In making these measurements both the electrometer and a vacuum tube voltmeter were

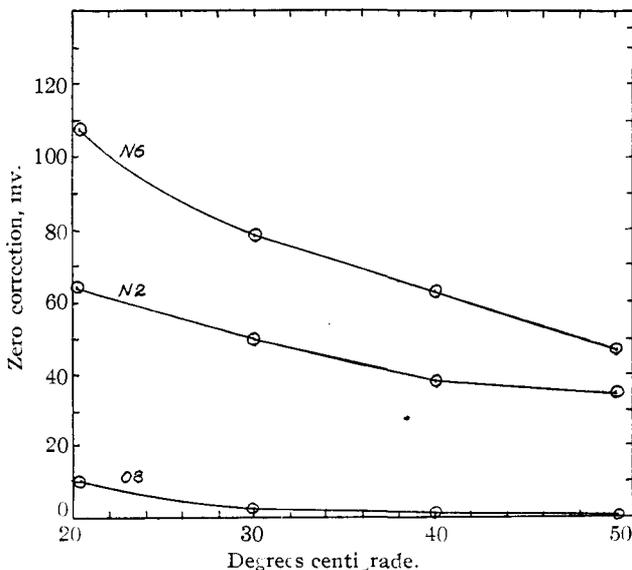


Fig. 4.

used. Curves showing the relationship between zero correction and temperature are shown in Fig. 4, these measurements being made with the electrometer. In Fig. 4, O8 is a thin electrode; N2 and N6 are thicker electrodes. Additional measurements on a good electrode in a buffer

system at three different temperatures showed that as the temperature was elevated the slope of the calibration deviated a little more from the theoretical.

**Effects of Surfaces upon Potential Measurements.**—Experiments were performed to see if a given glass electrode gave the same calibration curve on the two sides of the bulb when the outside immersed surface was only a fraction of the inside wetted area. Although a difference in calibration on the two sides, without exception, was found on twenty electrodes, to conserve space we give the data on only a single electrode in the form of a matrix (Table III).

TABLE III

THICK ELECTRODE C 60. VOLTS MEASURED ON VACUUM TUBE VOLTMETER

		3.97	PH Inside	748		
		Reading in volts				
PH outside 7.48 3.97		0.1842		-0.020	0.2042	Inside diff.
		.300		.096	.2040	
		.1158		.1160	Theor. diff. =	
	Outside diff.			0.2046 volt		

This evidence shows clearly that an electrode may have different calibration curves on the two sides. A large number of experiments testing the importance of such factors as method of blowing the bulb, hydrostatic pressure at time of measurement and surface curvature gave negative results.

The important factor in determining the electrode characteristic was finally found to be the detailed conditions connected with the geometry of the wetted surfaces. Before discussing these details, however, it is first necessary to determine whether these phenomena are connected with states of non-equilibrium or equilibrium.

**Time Required to Reach Equilibrium.**—Most electrodes giving a poor performance show time lag in reaching a steady value. To study this, fourteen similar tube type electrodes were made, by sealing one end of 30-cm. lengths of 7-mm. diameter tubing of 1 mm. wall, and tested in buffer solutions. It was found that under similar experimental conditions all behaved alike. In going from one buffer to another, on the side of small immersion, the initial value was poor, improving on standing for the first and subsequent days (Table IV). This leaves little doubt that the de-

TABLE IV

TUBE TYPE ELECTRODE. PH 3.97 INSIDE. INSIDE LENGTH WETTED 21 CM.; OUTSIDE LENGTH IMMERSSED 4 CM. (VOLTS MEASURED ON ELECTROMETER)

	3.97	PH outside volts	8.24	Outside Δ	Theor.
Time of immersion before reading					
Immediately	0.909		0.800	0.109	
24 hours	.980		.760	.220	0.252

viation effects are transient phenomena, disappearing when the system ultimately reaches equilibrium.

**Potential Dependence on the Geometry of the Two Wetted Surfaces.—**

It was first established that in the tube type of electrode the larger surface gives the theoretical slope or something near thereto, and the smaller surface gives a calibration considerably under the theoretical. This effect is roughly proportional to the thickness. In the case where a glass tube electrode is partially immersed in a fluid so that the height is the same on both sides, the electrode also gives a good value (Table V).

TABLE V  
EXPERIMENTAL DATA

Height inside, cm.	Height outside, cm.	$\Delta$ outside	Theoretical
5.5	5.5	246.5 <sup>a</sup>	246.3
8.75	5.5	201	
8.75	8.75	245.9 <sup>a</sup>	
19.00	8.75	240.7	
19.00	5.50	217.8	
19.00	19.00	246.5 <sup>a</sup>	
30.00	4.50	191.5; 152.9; 176.5 <sup>b</sup>	

<sup>a</sup> Close agreement with theoretical value when levels are equal. <sup>b</sup> Erratic value when levels are markedly different.

The most careful checks were made to test the influence of instrument leakage and it was definitely settled that the relations mentioned in the preceding paragraph were a function of the glass electrode itself and could not result from any deficiency of the measuring equipment.

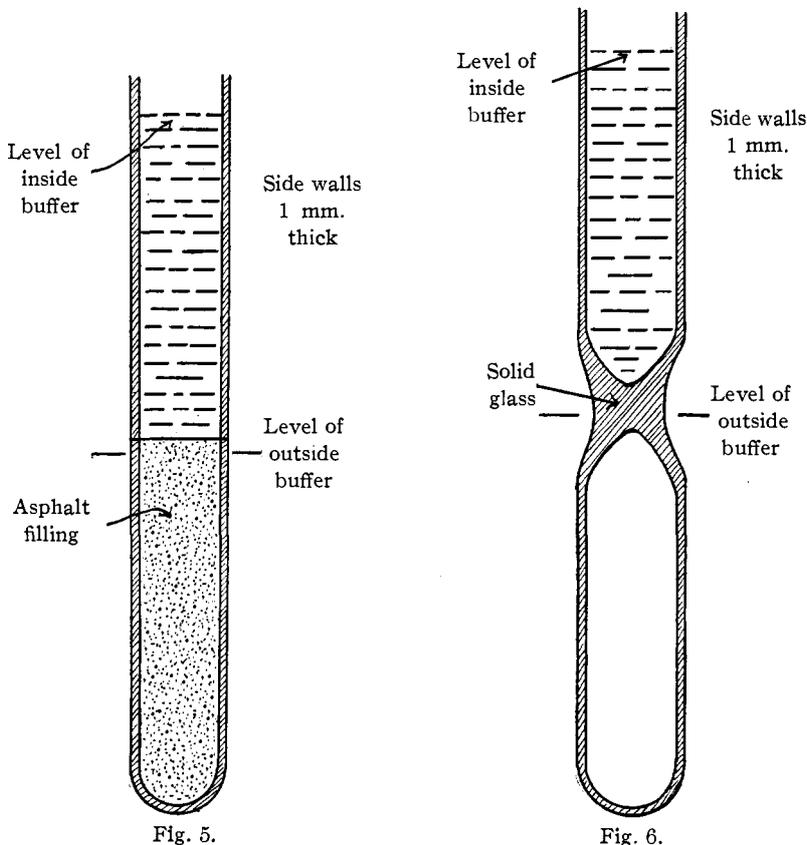
The electrical capacity of the electrode was also eliminated as a factor in the deviations of the measurement from the theoretical value.

Next, tubes were made with equal areas on the two sides of the glass wall but in such a relationship to each other that no immersed surfaces would be directly opposite each other. Changing the solution inside gives the correct slope but changing the solution outside has practically no influence on the potential measured. Now an inspection of Figs. 5 and 6 showed that the current which flows through such an electrode must pass up a film on the surface of the glass, since the resistance through the glass would be several times the actually measured value. This indicates the existence of an aqueous conducting film on the glass above the solution line which we simply call the deviation film, since we attribute most of the deviations to it.

Between this film and the glass there must be a phase boundary potential and between the film and main body of the solution a small diffusion potential. The deviation film through the process of diffusion gradually takes a  $P_H$  value depending in part at least on the  $P_H$  of the solution.

The measured potential difference is therefore the result of the parallel

electromotive forces existing at the phase boundaries between the solution and glass and between the deviation film and glass, to the latter of which is added a small diffusion potential. In the simplest case of two parallel e. m. f.s, the measured potential, neglecting the diffusion potential, is  $(Er + eR)/(R + r)$ , where  $E$ ,  $e$  and  $R$ ,  $r$  are the potential differences and resistances in the two regions, respectively. Thus the higher the relative resistance of the submerged part of the electrode, the greater is the effect



of the deviation film above the solution surface and hence the greater the deviation. This explains the resistance effects experimentally given in preceding paragraphs. A thick glass may therefore be used providing a large immersed area is used to lower the resistance.

Two further tests of the deviation film hypothesis were (1) a tube which had stood in a solution for a week with a fixed level on the outside was found to give the theoretical difference for the solutions measured. The solution on the outside had been  $P_{\text{H}}$  8.24. The tube was held horizontally and painted above the immersion line with a hydrochloric acid solution,

care being taken to keep well above the line of top immersion. The tube was now wiped off with a towel and put back in the original position. The e. m. f. was now too low by 70 mv., showing the importance of the film above the liquid line. The value slowly recovered in the course of a day.

(2) If the deviations ordinarily found are to be attributed to films above the line, then by painting on a dry tube a layer of insulating paint, asphalt or paraffin, and just immersing to the edge of the coat, it should be possible to eliminate the spurious effects. A tube was so painted and it then gave the theoretical slope with only one-sixth the outside area immersed. This was verified in perhaps thirty cases.

**Glass Cells with Solid Poorly Conducting Coats.**—A few tests on the response of poorly conducting coats to change in  $P_H$  of the solution were made. The coating should have two properties. (1) By simply adding resistance to the region covered it would give protection as pointed out in the preceding paragraphs. (2) If the coating itself does not respond to  $P_H$  changes, it should give protection irrespective of resistance. In order to study the response of the coats to  $P_H$  the entire bulb of a Haber-Klemensiewicz type electrode was coated with the material in question. Thin films of paraffin about  $5\mu$  thick, collodion, flexible collodion, oleic acid and stearic acid were put on the outer wall of the glass bulb as in Fig. 7.

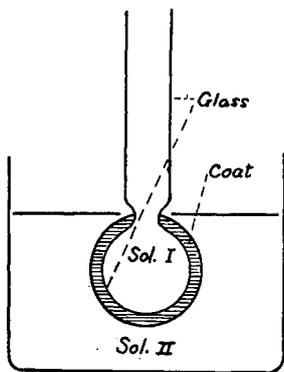


Fig. 7.

Shellac, DeKhotinsky cement and asphalt were also tried.

It was found that varying the  $P_H$  of solution I in contact with the bare glass gave the usual calibration curve for a good electrode. The bulbs used in these tests were of large area and were quite thin ( $20\mu$ ). The resistance of the combination was usually measured. It was found that changing the  $P_H$  of solution II in contact with these coatings had little effect on the potential of the chain, but changing the salt concentration in solution II had a marked influence on the readings. Table VI shows some typical experiments. The case of electrode A-81 shows that readings can be duplicated from day to day.

An inspection of the table shows that for the coatings mentioned change of  $P_H$  of the solution in contact with the coated side of the glass has little effect on the potentials measured. It is reasonable therefore to use such coatings in an attempt to cut out the change in potentials occurring above the level of immersion of the glass.

Practically we find that most paints are worthless after a few hours of immersion due to the fact that water penetrates between the paint and the soft alkaline glass.

TABLE VI

ELECTRODE NO. A-81. PARAFFIN COAT.		RES. = 150 MGS.		Temp., °C.
Date	PH inside	PH outside	Volts measured	
4- 8-30	3.97	7.94	0.364	19
4-10-30	3.97	10.3	.365	
	7.94	10.3	.135	
4-12-30	3.97	7.94	.361	
4-14-30	3.97	3.97	.363	23
	3.97	7.94	.363	
	7.94	7.94	.130	
	7.94	7.94 + NaCl	.069	
Electrode No. A-83. Collodion Coat				
4	7.94		0.155	
4	4		.156	
Electrode No. A-31. Stearic Acid Coat				
3.97	3.97		0.200	
3.97	7.94		.200	
Electrode No. A-32. Stearic Acid Coat				
3.97	7.94		0.200	
3.97	7.94 + NaCl		.150	
			.120	5 minutes later
3.97	7.94		.200	In 20 minutes
Electrode C-20 + Paraffin Wax Coating				
3.97	7.94		0.406	0.046
3.97	7.94 + NaCl		.360	
3.97	7.94		.401	
Electrode N-17. Collodion Coating				
3.97	7.96		0.334	0.058
3.97	7.96 + NaCl		.276	
Electrode A-61. Paraffin Coating				
	Mg. added KCl		M. v.	
			0.165	
	100		.170	
	100		.164	
	100		.159	
	100		.155	

**Influence of Ions Other than Hydrogen and Hydroxyl.**—There are statements in the literature to the effect that at least certain glasses, when made into thin membranes, are capable of measuring potential changes due to alterations in the concentration of ions other than hydrogen and hydroxyl. Horovitz and Schiller, in their widely known papers, showed for the special glasses they examined that sodium, potassium, silver and zinc electrode functions were exhibited. This is a matter of considerable significance, and we have, therefore, studied this phenomenon

especially with reference to the sodium electrode function of the glasses in our possession.

For the purpose of studying the sodium electrode function, Horovitz in one case used a sodium acetate buffer. To this buffer varying amounts of sodium chloride were added. It was observed by him that the potential changes, indicated by the glass electrode, upon the addition of successive amounts of sodium chloride, could be accounted for by assuming that the glass membrane had a sodium electrode function.

In our work we found large sodium electrode effects, if we assumed that the  $P_H$  of the buffer remained constant. On the basis of a consideration of ionic activities, such an assumption was not justified, and we therefore modified the experimental procedure as follows. A 50-cc. bottle was provided with a rubber stopper having holes to permit insertion of a hydrogen electrode, a glass electrode, an agar-potassium chloride bridge, an inlet for purified hydrogen gas and an escape for the gas. This arrangement made it possible to measure the potential of either the hydrogen electrode or the glass electrode in conjunction with a saturated calomel half-cell. Using this technique, the potentials were obtained on 25 cc. of a buffer solution, after all traces of oxygen had been eliminated as

TABLE VII  
EXPERIMENTAL DATA

Solution used	NaCl added, %	$\Delta Eh^a$	$\Delta Eg^a$	$P_H^b$	$\Delta Eg - \Delta Eh$
M/20 acid potassium phthalate	5	0.0355	0.036	3.97	+0.0005
Phosphate buffer <sup>c</sup>	5	.0335	.0305	7.48	- .0030
Phosphate buffer	5	.0320	.0335	8.24	+ .0015
Phosphate buffer <sup>d</sup>	5	.0545	.0570	10.77	+ .0025
Phosphate buffer	5	.0545	.0565	10.77	+ .0025
Phosphate buffer	5	.0545	.0590	11.19	+ .0045
Phosphate buffer	10	.0790	.0785	11.19	- .0005
Phosphate buffer	5	.0525	.0555	11.4	+ .0030
Phosphate buffer	10	.0735	.0765	11.4	+ .0030
Phosphate buffer	10	.0470	.064	11.94	+ .0170
Glycine buffer	5	.0220	.0370	11.97	+ .0150
Glycine buffer	10	.0375	.0630	11.97	+ .0255
Glycine buffer	1	.0055	.0180	12.26	+ .0125
Glycine buffer	5	.0205	.0460	12.26	+ .0255
Glycine buffer	1	.0045	.0190	12.55	+ .0145

<sup>a</sup>  $\Delta Eh$  and  $\Delta Eg$  are the changes in potential of the hydrogen and glass electrodes, respectively, due to the addition of the salt. <sup>b</sup> The  $P_H$  column refers to the values before addition of the salt. <sup>c</sup> Buffer system composed of varying ratios of monosodium phosphate and disodium phosphate. <sup>d</sup> Buffer system composed of varying ratios of disodium phosphate and trisodium phosphate. These mixtures and the glycine series yield buffer mixtures having buffer capacities characteristic for each series; hence the difference in magnitude of salt effect noted on the hydrogen electrode.

judged by the constancy of the hydrogen electrode reading. A weighed amount of sodium chloride was then introduced and the potentials again observed. The data of a series of such experiments covering a  $PH$  range from 3.97 to 12.55 are given in Table VII.

Similar effects were obtained when electrodes were constructed so that equal areas were used on both wetted sides.

It is seen that the change in voltage at the glass electrode unaccounted for by the change in hydrogen-ion activity is definite but very small in the lower  $PH$  range. Only in alkaline solutions does the glass 015 show a significant sodium electrode function and even then it is far below the hypothetical magnitude. Similar experiments showed an even smaller effect produced by potassium.

The fact, here brought out, that the sodium effect becomes important only when the glass buffer properties begin to break down favors the idea that the salt is simply interfering with the hydrogen-ion measuring system.

Referring back to the introductory paragraph, it now appears that so far as Haber's theory is concerned, in the equation  $E = RT \log (Ia/Ib) - F(G)$ ,  $F(G)$  is probably the term involved in the deviation of the electrode calibration at extreme  $PH$  values, while the deviations at intermediate  $PH$  levels are due to the deviation film and have no special relation to the Haber hypothesis.

### Conclusions and Summary

1. The specific resistances of several glasses were determined as well as decrease of resistance with rise of temperature.

2. It was shown that without waiting for the system to come to complete equilibrium, glasses give deviations from the theoretical calibration curve (volts against  $PH$ ) which are roughly proportional to the thickness on the side of smaller fluid immersion. On the larger side the calibration is close to the theoretical.

3. This effect was shown to be caused by the formation of a hygroscopic deviation film on the glass surface above the water line. It is suggested that the potential measured is the value of the spurious film potential and the true value of the immersed glass connected in parallel.

4. By changing the character of the film above the line, the values given by the electrode could be changed.

5. By suppressing the film through coats of dielectric paints, the deleterious effect could be practically eliminated as long as no water penetrated under the coating.

6. Potentials were measured through various thin semi-conducting coatings on glass bulbs. The potential on the coated side of the glass shows only a slight dependence on the  $PH$  of the solution and large salt effects. The opposite side of the glass wall, however, shows its usual calibration.

7. The change in salt effects for a  $P_H$  range from 3.97 to 12.55 was determined. Specific salt effects over the secondary hydrogen ion change only become important in the extreme range of  $P_H$  values.

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### NOTES

**The Atomic Weight of Chlorine. The Solubility of Silver Chloride.**— I am grateful to Messrs. Scott and Johnson<sup>1</sup> for calling my attention to an erroneous statement in the paper by Hönigschmid and Chan<sup>2</sup> on the atomic weight of chlorine.

Our reason for deciding that it was unnecessary to apply a correction for the silver chloride removed in making the nephelometric tests, when the precipitate was subsequently to be weighed, was that we had assumed its solubility under the conditions of the analysis at 0° to be 0.05 mg. per liter. At that time we had not determined this value ourselves but, through an error in reading, had taken from the paper by Richards and Willard<sup>3</sup> this value instead of the true one, 0.5 mg. per liter. After reading the communication of Scott and Johnson, we determined this solubility in analyses both of sodium and potassium chlorides at the equivalence point, after the usual shaking and cooling in ice for several days. Portions of the perfectly clear solution were pipetted into nephelometer tubes and, after addition of silver and chloride ion, respectively, showed the same opalescence as a standard containing 0.53 mg. of silver chloride per liter, thus completely confirming the work of Richards and Willard. When an excess of 0.3 mg. of silver was added, the solubility was 0.42 mg. or only 80% as much. This common ion effect makes the correction uncertain.

The nature of the precipitate obtained by us was probably different from that obtained by Scott and Johnson, and this doubtless accounts for the lower solubility found by us. In making the correction we prefer to use our own value because we consider it more applicable.

A calculation of the correction to be applied was easily made by referring to the laboratory notebook which contained all the data. Usually only two or three tests were necessary, because the proper amount of silver was carefully weighed to within 0.1 or 0.2 mg. It was assumed that 100 cc. of the solution contained 0.05 mg. of silver chloride, as already determined, because although it may have been less in the first test, when an excess of one ion was present, this value is certainly a maximum. Each nephelometer tube contained 22 cc. The corrections are shown in Table I.

<sup>1</sup> Scott and Johnson, *THIS JOURNAL*, **52**, 3586 (1930).

<sup>2</sup> Hönigschmid and Chan, *Z. anorg. allgem. Chem.*, **163**, 315 (1927).

<sup>3</sup> Richards and Willard, *THIS JOURNAL*, **32**, 4 (1910).