

RESEARCHES ON ADSORPTION ELECTRODES V. GLASS ELECTRODE. ION EXCHANGE AND ELECTRODE PROPERTIES ¹⁾

BY

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The incorporation of Al_2O_3 in a network of SiO_4 tetrahedra has a marked influence on the electrode properties of a glass.

From theoretical considerations it follows, as could be proved experimentally in this paper, that the exchange capacity and the hydration is less for a glass containing Al_2O_3 , than for Corning glass 015, which does not contain Al_2O_3 .

As was stated in the previous communication ²⁾ the behaviour of glass electrodes can be explained by the adsorption of ions on the surface of the electrode. We assume, qualitatively for the present, that the action of the glass electrode is as follows:

Let us consider the Corning glass 015 electrode.

• According to Zachariassen ³⁾ the structure of this glass may be described as a network of SiO_4 tetrahedra which are arranged with their points together in such a way that closed chains containing varying numbers of Si-atoms are formed. The interstices in this network, which must be imagined in three dimensions, offer room for the metal ions, for example Na and Ca. When the surface of the glass is brought into contact with water, or more especially with acid, Na and Ca dissolve in the water or acid and H takes their place. Each H-ion brings at least one H_2O -molecule with it, so that a swollen, water-containing layer is formed on the surface which is free, or for the greater part free, of other cations, and consists exclusively of silicic acid. In the case of Corning glass 015, as will appear, this layer must be relatively thick, and a reservoir of constant H-ion concentration is thus formed. The electrode must now function as a hydrogen electrode according to Nernst's formula

$$E = \frac{RT}{F} \ln \frac{c_e}{c_w} + \text{const.},$$

where c_w is the concentration of an ion in the electrode wall and c_e that in the solution, as long as c_w is really constant. This quantity may change when H-ions from the active layer are for instance replaced by Na-ions from the solution. This will take place to an increasing degree with rising p_H and the electrode will assume the character of a mixed electrode. At still higher p_H , when all or almost all of the H-ions are replaced by Na-ions and a reservoir of constant Na-ion concentration has thus been formed, the electrode will have become a Na-electrode. The firmer the bond of the H-ions to the glass surface, the higher the p_H to which the hydrogen function is retained. Apparently in the case of Corning glass 015 this bond is very strong — silicic acid is a very weak acid — as the electrode behaves as a practically ideal

¹⁾ See also A. J. Zwart Voorspuj, *Onderzoekingen over Glaselectroden*. Diss. Utrecht 1943.

²⁾ H. J. C. Tendeloo and A. J. Zwart Voorspuj, *Rec. trav. Chim.* 61, 531 (1942).

³⁾ *J. Am. Chem. Soc.* 54, 3841

hydrogen electrode up to high p_{H} values. It is also clear that an alteration in the proportion of Na, K or Ca in the original glass causes no fundamental change in the electrode properties. No matter what that proportion is, after the treatment with water or acid a silicic acid surface will always be formed with approximately the same structure, to which H-ions are firmly bound. This gives the electrode the properties of a hydrogen electrode.

In this respect the position is different in the case of the glass electrodes which we have investigated. Al_2O_3 is included in the silica skeleton itself and forms more positive spots among the negative Si-atoms. In this way one obtains on the surface a checker-board distribution of negative and more positive spots, as a consequence of which the interchange with H-ions becomes more difficult and can now only take place superficially. In this case therefore a considerably less thick layer will be involved in the interchange, less water will penetrate into the surface and only relatively few H-ions will be found on the active surface. Moreover these few H-ions — and this will determine the electrode properties — will be much less firmly bound and will be able to approach this checker-board surface much less closely than a surface consisting exclusively of negative Si spots. The H-ions are thus more easily replaced by other cations present in the solution, which causes the appearance of mixed electrode or Na-electrode functions already at a lower p_{H} value.

Although the number of H-ions which are bound to the glass surface does not determine the electrode function — the quartz electrode, where few H-ions are involved, behaves as a H-electrode⁴⁾ up to a high p_{H} value — nevertheless the stability of the potential will be promoted by a large number of ions, thus by a well filled reservoir. It is perhaps in this respect that Corning glass 015 is favourably distinguished from other kinds of glass for the construction of hydrogen electrodes.

If the above assumptions are correct, our glasses must differ in three respects from Corning glass 015:

1. The hydration must be less.
2. The exchange-capacity must be less.
3. The bond of the H-ions to glass surface must be weaker, i.e. the "dissociation constant" of the "glass acid" must be higher.

By means of a simple experiment we have proved the correctness of the conclusion mentioned under 1.

Glass of composition 5⁵⁾ was pulverized, and from the powder the fraction from 100 to 200 μ was separated out by means of suitable sieves. The same was done with Corning glass 015. 1 g of each kind of glass was now weighed out in weighing bottles of about the same diameter, 2 cm³ of water added and the two bottles were placed open in a desiccator filled with CaCl_2 . From time to time the bottles were weighed and the results, shown in table 1, recorded.

From this it may clearly be seen that Corning glass 015 binds the water considerably more firmly than glass of composition 2.

⁴⁾ B. v. Lengyel, Z. phys. Chem. A 153, 425 (1931); 159, 145 (1932).

⁵⁾ H. J. C. Tendeloo and A. J. Zwart Voorspuij, loc. cit. Table III. p. 535 (6% CaO — 14% Li_2O — 10% Al_2O_3 — 70% SiO_2).

Table I. Hydration determined by drying.

	Composition II	Corning glass 015
Wt. bottle + glass + water. . .	44.1261 g	59.2220 g
Wt. bottle + glass	42.1531 ..	57.2722 ..
Wt. bottle empty	41.1531 ..	56.2722 ..
After 4 days	42.1531 ..	57.2767 ..
After 5 days	42.1531 ..	57.2767 ..

With respect to the smaller ion-exchange capacity of our kinds of glass compared with Corning glass 015 — the conclusion stated under 2 — it may be noted that some information on this point must be obtainable from titration-curves of suspensions of the powdered glass.

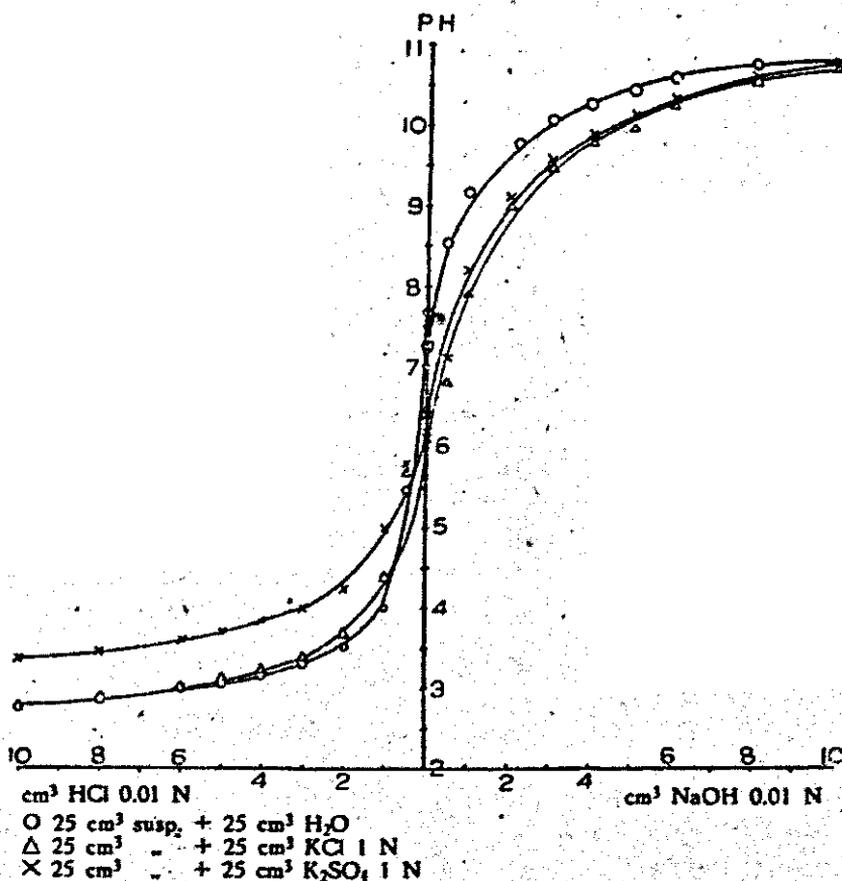


Fig. 1.

If we take the view that the H-ions which are initially stored in the hydrated layer of the glass particles — we are first considering Corning glass 015 —, do not contribute to the p_{H} of the glass suspension, or do so only to a very

limited extent, then upon the addition of a neutral salt, for instance KCl, a lowering of the p_H must occur. The K-ions will for some part occupy the places where originally H-ions were situated, and the latter are thus driven into the solution and there cause a lowering of the p_H .

The effect will appear most clearly in the alkaline region. In that region, due to the low H-ion concentration of the external solution, the tendency for the H-ions on the wall to dissociate will be the strongest. It may be expected that the effect will not be noticeable in the acid region.

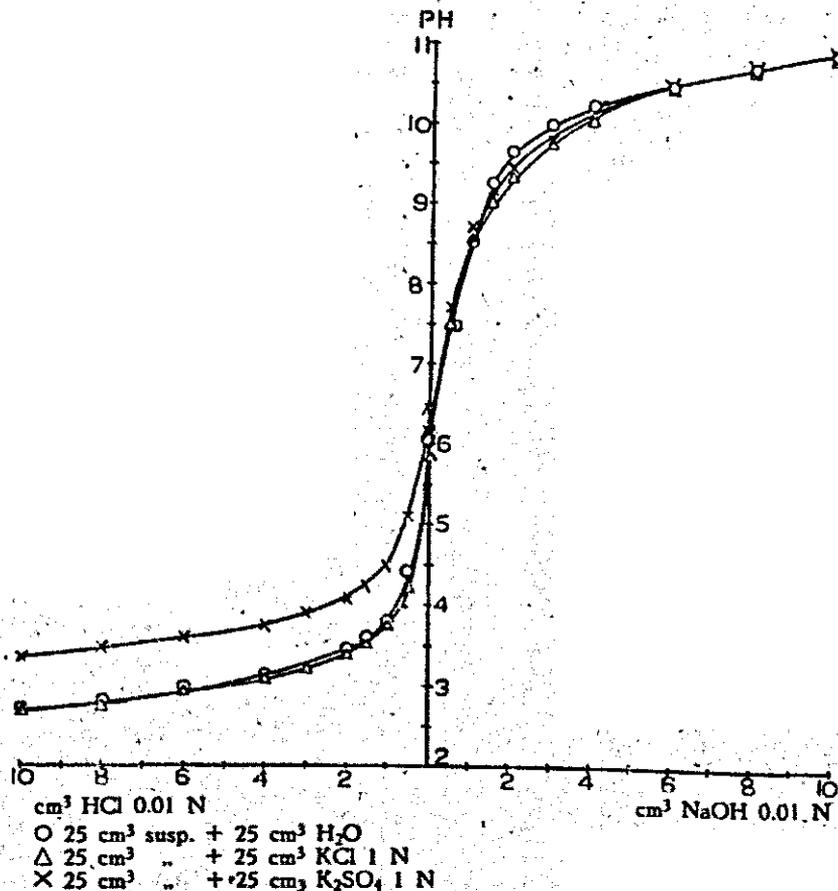


Fig. 2.

On the other hand the glasses investigated by us should not exhibit the phenomenon at all or to a much smaller extent, because the number of ions taking part in the process is so much smaller.

The suspensions with which these experiments were performed were prepared as follows. The glass was pulverized⁶⁾, first in a mortar, then in

⁶⁾ Prof. Dr. C. J. van Nieuwenburg of Delft was kind enough to fuse a larger quantity of glass for this purpose, for which we are glad to express our gratitude at this place.

Table II.
Corning glass 015. Conc. of the suspension 29.3 mg/25 cm³.

cm ³ NaOH 0.01 N	pH	cm ³ HCl 0.01 N	pH
25 cm ³ suspension + 25 cm ³ water.			
0.00	7.25	0.00	7.65
0.51	8.52	0.50	5.45
1.00	9.18	1.00	3.98
2.20	9.77	2.00	3.52
3.00	10.07	3.00	3.30
3.97	10.30	4.00	3.16
5.00	10.47	5.00	3.06
6.00	10.62	6.00	2.97
8.01	10.82	8.00	2.85
10.03	10.94	10.00	2.75
25 cm ³ s		25 cm ³ KCl 1 N	
0.00		0.00	6.10
0.50		0.50	5.70
1.00		1.00	4.40
2.00		2.00	3.70
3.00		3.00	3.43
4.00		4.00	3.25
5.00		5.00	3.14
6.00		6.00	3.03
8.00		8.00	2.90
10.00		10.00	2.80
25 cm ³ suspension + 25 cm ³ K ₂ SO ₄ 1 N			
0.00	6.39	0.00	6.20
0.51	7.10	0.50	5.80
1.00	8.20	1.00	4.88
2.00	9.12	2.00	4.25
3.00	9.61	3.00	4.02
4.00	9.92	4.00	3.84
5.00	10.17	5.00	3.71
6.00	10.36	6.00	3.62
8.00	10.65	8.00	3.48
10.00	10.85	10.00	3.37

a ball mill, and allowed to stand overnight with 0.05 *n* HCl. The following day it was filtered over cyclostyl paper, which according to the experience of our laboratory is an excellent method of ultrafiltration¹⁾, and washed with distilled water until the chlorine reaction had disappeared. By the application of sedimentation analysis in *Atterberg's* apparatus, a suspension containing the fraction < 2 μ could be isolated from the coarser components. Finally, after settling, the solid material was rinsed into a measuring flask of 250 cm³ which was filled to the calibration mark.

With suspensions containing larger particles (2—25 μ) it is difficult to obtain reproducible results, and for that reason we always used the fraction < 2 μ in our later experiments.

The p_H of the suspension was measured with a hydrogen electrode, which was also done after the addition of increasing quantities of NaOH or HCl.

¹⁾ H. J. C. Tendeloo, *Chem. Weekblad* 33, 294 (1936).

Table III.
Corning glass 015. Conc. of the suspension 68.9 mg/25 cm³.

cm ³ NaOH 0.01 N	pH	cm ³ HCl 0.01 N	pH
25 cm ³ suspension + 25 cm ³ water.			
0.00	6.11	0.00	5.90
1.00	8.07	1.00	3.77
2.00	8.91	2.00	3.27
3.00	9.42	3.00	3.11
4.00	9.70	4.00	3.04
5.00	9.94	5.00	2.86
6.00	10.13	6.00	2.80
7.00	10.23	7.00	2.73
8.00	10.43	8.00	2.69
9.00	10.53		
11.00	10.71		
25 cm ³ suspension + 25 cm ³ KCl 1 N			
0.00	5.48	0.00	4.17
1.00	6.28	1.00	3.60
2.00	6.75	2.00	3.33
3.00	7.28	3.00	3.28
4.00	8.05	4.00	3.17
5.00	8.46	5.00	2.96
6.00	8.72	6.00	2.89
7.00	9.01	7.00	2.83
8.00	9.27	8.00	2.78
10.00	9.50		
12.00	9.81		
15.00	10.10		
20.00	10.56		

In this way a curve can be obtained which gives the relation between the number of cm³ of NaOH or HCl added and the p_H. The same experiment can be repeated after a neutral electrolyte, for instance KCl, has been previously added to the suspension. In this way an idea is obtained of the ion exchange occurring over a wide p_H range.

The apparatus with which the measurements were made consisted of a cell built up in the ordinary way. A 100 cm³ beaker containing the suspension could be closed by means of a three-holed rubber stopper. The first hole was for the hydrogen electrode, the second for the microburette containing NaOH or HCl and the third for the KCl-agar siphon. The latter was only brought into contact with the suspension for the performance of the measurements in order, as far as possible, to prevent KCl from the siphon from entering the solution to be measured. The other end of the siphon was placed in a container with a saturated solution of KCl in which also a saturated calomel electrode was placed. The hydrogen, which was passed through, served also to keep the suspension homogeneous, although the rate of settling of the particles was already slight, due to their small dimensions. For the measurements we used a Lautenschläger ionometer. In tables II to V inclusive some of the results obtained in this way are given.

▲ The values given in tables II and IV are plotted graphically in figs. 1 and 2.

Table IV.
Glass composition II. Conc. of the suspension 90.9 mg/25 cm³.

cm ³ NaOH 0.01 N	pH	cm ³ HCl 0.01 N	pH
25 cm ³ suspension + 25 cm ³ water.			
0.00	6.07	0.00	6.52
0.60	7.48	0.50	4.42
1.00	8.53	1.00	3.80
1.50	9.26	1.50	3.59
2.00	9.65	2.00	3.43
3.00	10.03	4.00	3.13
4.00	10.25	6.00	2.97
6.00	10.53	8.00	2.80
8.00	10.82	10.00	2.68
10.00	10.94		
25 cm ³ suspension + 25 cm ³ KCl 1. N.			
0.00	5.84	0.00	5.85
0.50	7.51	0.50	4.24
1.00	8.56	1.00	3.76
1.50	9.06	1.50	3.53
2.00	9.34	2.00	3.41
3.00	9.77	3.00	3.22
4.00	10.05	4.00	3.10
6.00	10.49	6.00	2.92
8.00	10.75	8.00	2.78
10.00	10.91	10.00	2.67
25 cm ³ suspension + 25 cm ³ K ₂ SO ₄ 1 N.			
0.00	6.45	0.00	6.15
0.50	7.74	0.50	5.10
1.00	8.69	1.00	4.51
1.50	9.18	1.50	4.25
2.00	9.46	2.00	4.11
3.00	9.83	3.00	3.91
4.00	10.15	4.00	3.77
6.00	10.57	6.00	3.59
8.00	10.81	8.00	3.46
10.00	10.96	10.00	3.36

The following may be noted in connection with these results. It is found that in the case of Corning glass 015 in the alkaline region there is actually a clear lowering of the p_H upon the addition of KCl. In the case of suspensions of glass of composition II this lowering is not observed. In fig. 2 a slight lowering is visible, but this certainly falls within the experimental error, as indeed may be seen from table V, where a slight rise in p_H is even measured. Furthermore in comparing figs. 1 and 2 it must be taken into account that the concentration of the suspension was only 29.3 mg in the first case and in the second case 90.9 mg/25 cm³. As will be seen from a comparison of tables II and III, an increase in the concentration of the suspension strongly reinforces the influence of the added electrolyte toward lowering the p_H .

The p_H as measured in the suspension without the addition of acid or base is not very reproducible, because the system is not or only very weakly buffered.

Table V.
Glass composition II. Conc. of the suspension 68.1 mg/25 cm³.

cm ³ NaOH 0.01 N	pH	cm ³ HCl 0.01 N	pH
25 cm ³ suspension + 25 cm ³ water.			
0.00	7.28	0.00	7.52
0.50	8.45	0.50	6.64
1.00	9.01	1.00	4.58
1.50	9.30	1.50	3.83
2.00	9.52	2.00	3.57
3.00	9.82	3.00	3.29
4.00	10.06	4.00	3.10
6.00	10.40	6.00	2.91
7.00	10.54	8.00	2.78
8.00	10.63	10.00	2.66
10.00	10.78		
25 cm ³ suspension + 25 cm ³ KCl 1 N.			
0.00	7.02	0.00	7.10
0.50	8.55	0.50	6.12
1.00	8.99	1.00	4.45
1.50	9.28	1.50	3.80
2.00	9.53	2.00	3.60
3.00	9.88	3.00	3.30
4.00	10.14	4.00	3.15
6.00	10.56	6.00	2.95
8.00	10.81	8.00	2.80
10.00	10.95	10.00	2.71
25 cm ³ suspension + 25 cm ³ K ₂ SO ₄ 1 N.			
0.00	7.12	0.00	6.98
0.50	8.42	0.50	6.21
1.00	8.96	1.00	5.41
1.50	9.38	1.50	4.55
2.00	9.62	2.00	4.31
4.00	10.21	3.00	4.01
6.00	10.61	4.00	3.85
8.00	10.84	6.00	3.60
10.00	11.00	8.00	3.47
		10.00	3.36

As to the results with K₂SO₄, as far as the alkaline region is concerned, they may be compared with those with KCl. There is a general tendency to cause a slightly smaller decrease in the p_H, which must probably be ascribed to the smaller activity of the K-ions.

In the acid region the situation is however different. In all the cases investigated an increase in the p_H is here observed, and it is reasonable to assume here a removal of OH-ions, which might be exchanged by the bivalent SO₄-ions to a larger extent than by the monovalent Cl-ion. In the case of KCl also a small increase in p_H can in most cases be observed in this region. The explanation of the phenomenon must however be sought in quite a different direction. It is found that the increase in p_H is not connected with the presence of suspension material, but that it is also observed in the ordinary aqueous solution.

In table VI the results of some measurements are given ⁶⁾.

Apparently the HSO_4^- must not be considered as completely dissociated, so that in collaboration with added sulphate buffer action occurs. In the case of $\text{KCl} + \text{HCl}$ also this is apparently the case, although to a much smaller degree.

In the case of Corning glass 015 therefore an interchange of H^+ and K^+ -ions takes place in the alkaline region and the H -ions liberated cause a clear lowering of the pH . Without any doubt such an interchange also takes place somewhere on the curve of the suspension of composition 2, but the number of ions taking part in this process is so small that it is not noticeable in this way.

The large number of H -ions which disappear from the boundary layer in the case of Corning glass 015 is only a small part of the total, because the deviations of the H -electrode function are still very slight. In the case of composition II the small number of H -ions not observable in this manner which disappear from the wall in neutral and alkaline region is apparently such a large percentage of the total that the hydrogen function is, as we shall see, entirely destroyed.

Table VI.
Influence of the addition of electrolyte on the pH of an aqueous solution.

50 cm ³ H ₂ O		25 cm ³ H ₂ O + 25 cm ³ Na ₂ SO ₄ 1 M	
cm ³ H ₂ SO ₄ 0.01 N	pH	cm ³ H ₂ SO ₄ 0.01 N	pH
0.00	4.00	0.00	4.37
0.50	3.79	0.50	4.25
1.00	3.60	1.00	4.14
1.50	3.49	1.50	4.05
2.50	3.28	2.50	3.89
3.50	3.15	3.50	3.81
4.50	3.05	4.50	3.71
5.50	2.98	5.50	3.63

The assumptions which we have made about the exchange capacity of our kinds of glass compared with Corning glass 015 are thus proved convincingly by the experiments here described.

In the following publication we shall be concerned in detail with the conclusion stated under 3 and shall also give a quantitative treatment of the glass electrode.

We wish also to thank Mr. P. Tiersma, cand. li., for his collaboration in the performance of the potentiometric titrations.

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⁶⁾ These measurements were carried out in our laboratory by Messrs. D. W. Stolp and D. v. d. Woerd.