

Chemistry. — *Researches on adsorption-electrodes. I. The glass-electrode.*
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It is a well-known fact that glass acts as a hydrogen-electrode. The theory of the glass-electrode has been dealt with in detail by JANSSEN; for the sake of brevity that work may here be referred to. It is also known that the deportment as a hydrogen-electrode begins to show deviations if concentrated solutions of the salts of sodium and potassium are used; the glass then acts as if it were a sodium- or potassium-electrode respectively. Since sodium, potassium, calcium and often other ions, as e.g. zinc, are component parts of the glass, it is obvious that a connection should be looked for between these ions and a specific electrode action of the glass.

The metal-ions in silicates are exchangeable by other ions; this phenomenon is very pronounced in clay, permutites and zeolites, and practically as well as theoretically it is of great importance. We now wondered whether, by exchanging as much as possible the cations present in the capillary layers of the glass by one similar ion, we might be able to make the glass function as an electrode for that ion. We were particularly interested to find whether a glass-membrane, if treated with solutions of calcium chloride, would behave as a calcium-electrode.

For that purpose we made a large number of glass-electrodes, in the manner and according to the model as described by ELEMA. We used the well-known glass of the Corning Glass Works, which has also been recommended by MAC INNES and has the composition SiO_2 72 %, CaO 6 %, Na_2O 22 %.

In the electrode we poured a solution of an electrolyte, in which then a metallic wire was put. When the electrode had been closed up by means of paraffin, an element was built up in the usual manner with a $1/10$ normal KCl-calomel-electrode, the e.m.f. of which was measured potentiometrically, amplified by vacuum-tubes. (In the table the e.m.f. of the element is always mentioned.)

For our purpose the glass-electrodes were filled with a solution of calcium chloride, which had been carefully neutralized. In this solution a silver-wire was put, on which electrolytically a thin layer of AgCl had been precipitated. This glass-electrode was placed for some days in a solution of calcium chloride of the same concentration as the solution inside the electrode. When after about five days a daily checking of the potential was started, it appeared that the latter changed until after about

ten days a constant value was attained. It also appeared that it was necessary to use new-made solutions.

Just as every glass-electrode cannot be used as a hydrogen-electrode, neither can every glass-electrode be made into a calcium-electrode. The linear relation, which must exist between the logarithm of the ion-concentration and the e.m.f., is very often not found. This relation frequently occurs with a deviation from the ideal relation, but often it also happens that there exists no linear relation at all. If there is a linear relation, but deviating from the ideal course, it signifies nevertheless that the attainment of the ideal line must be considered possible. A large number of electrodes were, therefore, systemetically examined; some of these we shall discuss more in detail.

Electrode N^o. 3 is filled with 1 normal CaCl₂ solution.
 " N^o. 4 " " " 0.5 " " "
 " N^o. 7 " " " 0.737 " " "

In the figures the dotted line shows how the ideal line would have to run if the glass-electrode behaved as an ideal calcium-electrode, starting from the same potential and with a change of 29 milli-volt after each tenfold dilution. We then see that the three electrodes between 1 normal and 1/1000 normal calcium nitrate show the desired linear relation; the deviation from the ideal course for N^o. 7 is very small.

The measured electromotive forces are found in the following table.

TABLE 1.

Conc. Ca(NO ₃) ₂ in normality	Number of the electrodes		
	3	4	7
1.0	- 100 mV	- 78 mV	- 92 mV
0.1	- 84	- 65	- 68
0.01	- 61	- 50	- 38
0.001	- 42	- 36	- 11

In the figures 1—3 the results are reproduced graphically: on the absciss the negative logarithms of the concentrations are to be seen (p_{Ca}).

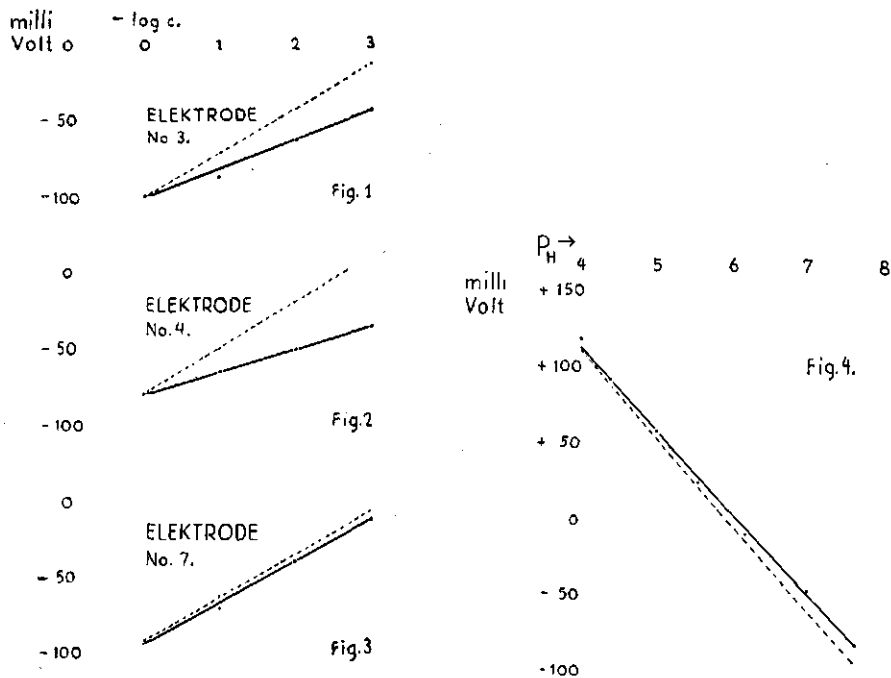
The following may be observed here.

The equilibrium was at first very slowly attained; this changed perceptibly as the electrode had exchanged more calcium-ions; ultimately the equilibrium was attained after some minutes.

The reproducibility of the separate measurements was 1—2 mV. With Ca(NO₃)₂ solutions, which had been used several times and consequently each time had been in contact with the air, larger differences were sometimes observed.

The accuracy of the measurements is 0.5 mV.

We further noticed that a glass-electrode filled with 1.0 normal KCl and AgCl-Ag-electrode, which, as appears from figure 4 and table 2,



behaved as an almost ideal hydrogen-electrode, was unfit for use as a potassium- and as a calcium-electrode.

TABLE 2.

E. M. F. of an element-glass-electrode-buffer-solution-calomel-electrode $1/10$ N.
Glass-electrode filled with 1.0 n KCl-AgCl-Ag.

P_H	E. M. F.	P_H	E. M. F.
4.0	+ 122 mV	6.2	- 7 mV
4.4	+ 97	7.0	- 45
5.0	+ 61	7.6	- 79
5.6	+ 28		

The ineffectiveness as a potassium-electrode need not surprise us, for the sodium of the glass will either not at all or very incompletely be replaced by potassium. In the light of all that has been said above, it is also evident that this electrode will certainly not be able to function as a calcium-electrode.

For the present we have the indication that a sodium-electrode may be obtained; the above-mentioned linear relation indeed exists, but the deviation from the ideal line is as yet too large.

Summary.

It appears to be possible to make a glass-membrane function as a calcium-electrode, if the exchangeable ions present in the glass are replaced by calcium-ions.

LITERATURE CITED.

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