Chemistry. — *Researches on adsorption-electrodes* II. *Mineral-electrodes.* By H. J. C. TENDELOO. (Communicated by Prof. H. R. KRUYT).

(Communicated at the meeting of March 30, 1935.)

In the first communication [1]) researches were described on the application of glass-electrodes as calcium-electrode. These researches were continued; a number of 50 glass-electrodes, all of the glass with 72 % SiO_2, 6 % CaO, 22 % Na_2O, were examined and, by replacing the exchangeable cations by others, we occasionally succeeded in employing glass-electrodes as Ca-, Na-, or K-electrode. It appeared, however, that the reproducibility of the electrodes was very poor and that the results were totally unreliable, owing to the presence of already very low concentrations of hydrogen-ions. Moreover, the fragility of these electrodes is a very great inconvenience. Consequently the investigation was not continued in this direction.

Instead of glass other silicates were then taken, as they are found in nature in the form of minerals. Many of these minerals possess a strong exchange-capacity for other ions. The crystallographic structure and the chemical composition are factors largely influencing the exchangeability of ions. Mica (muscovite) appeared to answer the purpose; from this mineral thin plates may be easily split off. However, we also examined other minerals.

The construction of a mica-electrode may be seen from fig. 1. A thin plate was fixed on the end of a glass tube; subsequently an electrolyte solution was brought into the tube to a height of circa 1 cm, and in this solution a reversible metallic electrode was placed, conducting the potential from the mica plate to the measuring-apparatus. The construction of the element took place according to the well-known method with the aid of a 0.1 normal calomel-electrode. Potentiometrically the e.m.f. of the element was measured, amplified by means of vacuum-tubes.

The mica-electrode was filled with 0.1 normal HCl, in which chinhydrone was put; conduction was obtained by a platinum wire placed in it. Subsequently this electrode was placed during 2 days in a 0.1 normal solution of sulphuric acid. The object is that hydrogen-ions should exchange in the muscovite and thus make this mineral function as hydrogen-electrode. The electrode prepared in this manner was placed in sulphuric acid

[1]) Kon. Akad. Wet. Amsterdam, Proceedings 37. 212. 1934.

solutions of different concentration. In table I, which as the other tables indicates the measured e.m.f. of the element, the sign referring to the

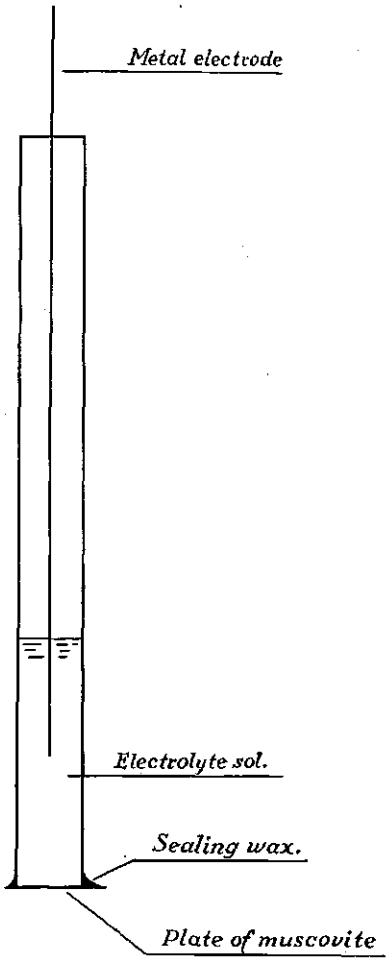

Fig. 1.

polarity of the mineral-electrode, the results may be found for mica as hydrogen-electrode.

TABLE I.

Concentration of the sulphuric acid	E.m.f.
10^{-1} normal	+ 281.6
10^{-2}	+ 249.0
10^{-3}	+ 213.0
10^{-4}	+ 176.8
10^{-5}	+ 148.5

In buffer solutions of potassium biphthalate and caustic soda the same potential was always found between $P_H 4$ and $P_H 4.8$, which points to the fact that this electrode strongly reacts to the presence of other ions.

Fig. 2 shows the graphic representation; on the ordinate the measured e.m.f. is indicated, on the absciss the negative logarithm of the concentration. The same applies to the other graphic representations.

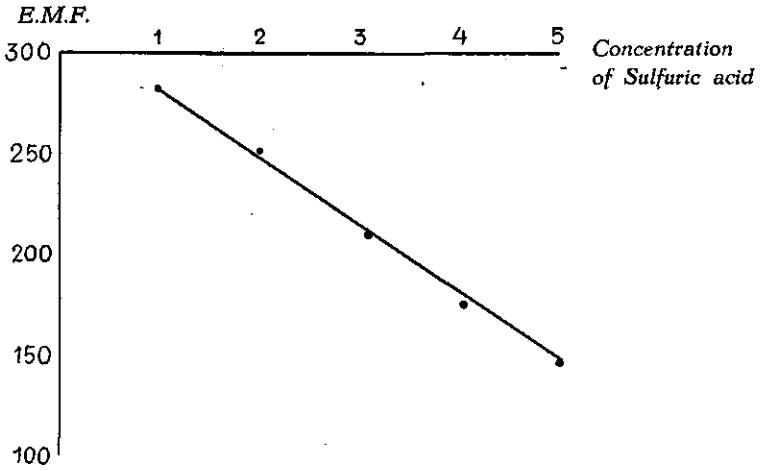

Fig. 2.

The electrode was then cleaned and placed in a weak alkaline solution of calcium chloride, containing 53 gram calcium per liter. After 2 days it was rinsed with water and filled with 1 cc calcium chloride solution, containing 14.74 gram calcium per liter. A wire of Ag Cl—Ag effected the conduction of the potential.

By means of this treatment calcium-ions are adsorbed by the mica; table II shows the measured e.m.f. in solutions of calcium nitrate, fig. 3 the graphic representation.

TABLE II.

Concentration of calcium nitrate	E.m.f.	
	Electrode No. 62	Electrode No. 63
0.902 normal	+ 97.5	+ 95.5
$0.902.10^{-1}$ „	+ 82.0	+ 81.0
$0.902.10^{-2}$ „	+ 66.5	+ 61.0
$0.902.10^{-3}$ „	+ 51.0	+ 46.0
$0.902.10^{-4}$ „	+ 38.1	+ 32.0

On repetition of the measurements several times after each other, differences occur as the result of decrease in adsorption of calcium-ions.

If however, after measuring, the electrode is left in a calcium nitrate solution, the original condition returns and practically the same results are obtained as before.

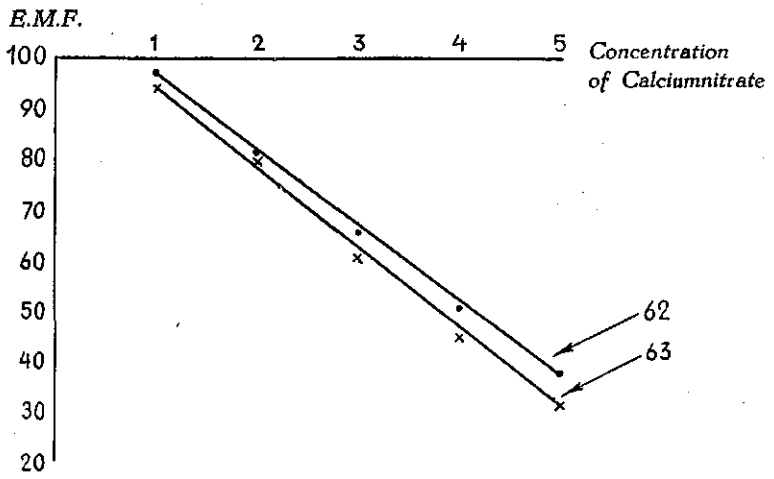

Fig. 3.

It appears, therefore, that in accordance with the expectation the same silicate reveals a relation between the potential and the electrolyte concentration down to a concentration of 0.0001 normal rounded off. At a lower concentration deviations begin to occur.

Besides mica a number of other minerals were examined, e.g. heavy spar in the following chain:

Ag-AgCl-0.1 n $BaCl_2$-$BaSO_4$-$BaCl_2$-saturated KNO_3-0.1 n calomel-electrode.

The results may be found in table III and fig. 4.

TABLE III.

Concentration of barium chloride	E. m. f.	
	Electrode No. 30	
10^{-1} normal	— 191.0	
10^{-2} „	— 165.0	
10^{-3} „	— 137.5	
10^{-4} „	— 115.0	
	No. 56	No. 54
0.5 normal	— 59.0	— 64.5
$0.5.10^{-1}$ „	— 41.2	— 49.0
$0.5.10^{-2}$ „	— 22.0	— 34.2
$0.5.10^{-3}$ „	— 4.0	— 20.0

In solutions of potassium sulphate heavy spar thus far did not yield satisfactory results.

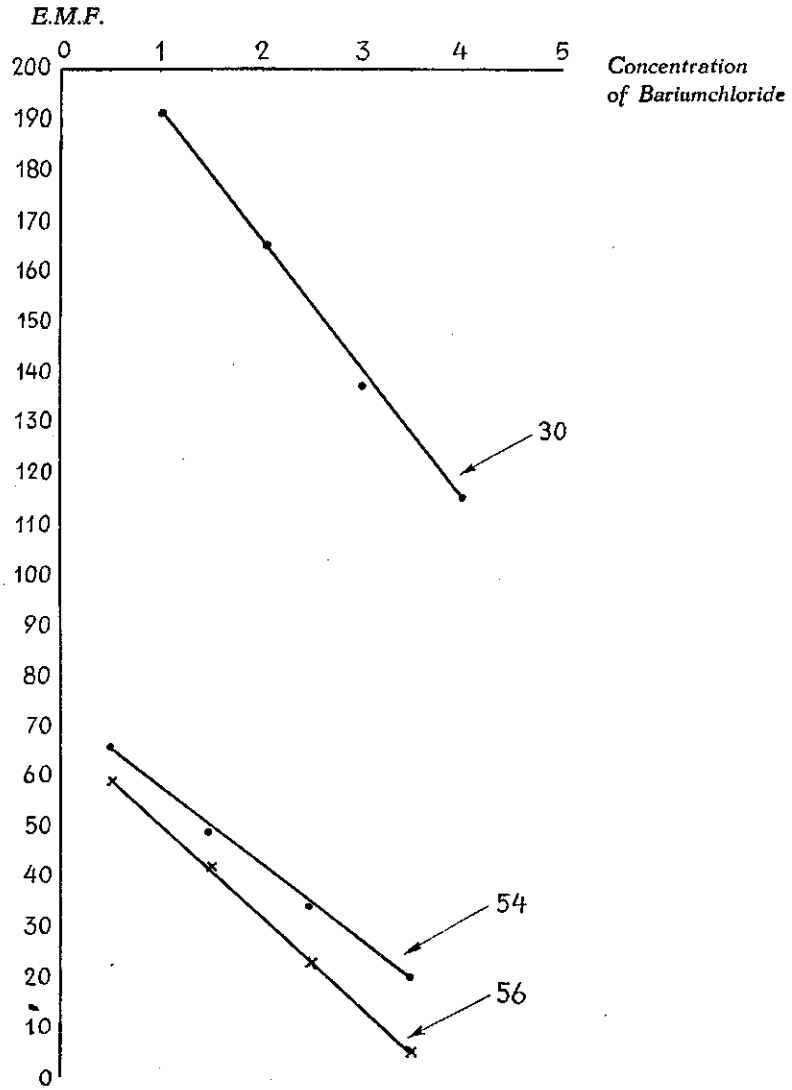

Fig. 4.

Calcium fluoride was measured in the chain:

Ag-AgCl-0.737 n $CaCl_2$-CaF_2-$Ca(NO_3)_2$-satured KNO_3-0.1 n calomel-electrode.

Table IV and fig. 5 show the results.

It should be observed here that various other CaF_2-electrodes did not answer the purpose. In future CaF_2 plates will be used in this investigation, cut according to special crystalplanes.

The calcium mineral wollastonite, $CaSiO_3$, may be used if the electrode is new. In consequence of the continual contact with water, however, it is

TABLE IV.

Concentration of calcium nitrate	E. m. f. of electrode No. 29
1.14 normal	— 72.0
$1.14.10^{-1}$ „	— 92.5
$1.14.10^{-2}$ „	— 119.0
$1.14.10^{-3}$ „	— 145.5

strongly hydrolyzed and loses its capacity to indicate a regular course of the potential in calcium nitrate solutions.

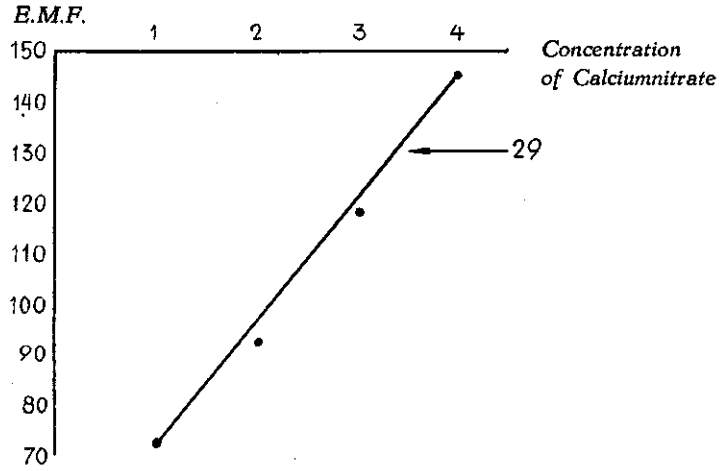

Fig. 5.

In table V and fig. 6 some results have been collected.

TABLE V.

Concentration of calcium nitrate	E. m. f.	
	Electrode No. 1	Electrode No. 39
1.14 normal	— 75.0	— 55.0
$1.14.10^{-1}$ „	— 87.0	— 63.0
$1.14.10^{-2}$ „	— 99.0	— 72.6
$1.14.10^{-3}$ „	— 111.0	— 82.5
$1.14.10^{-4}$ „	— 118.0	— 93.0
$1.14.10^{-5}$ „	— 127.0	—
$1.14.10^{-6}$ „	— 147.0	—

With the mineral colemanite, $CaHB_3O_6 . 2H_2O$, no results have as yet been obtained, neither with calcite. Plaster appeared to be too highly soluble.

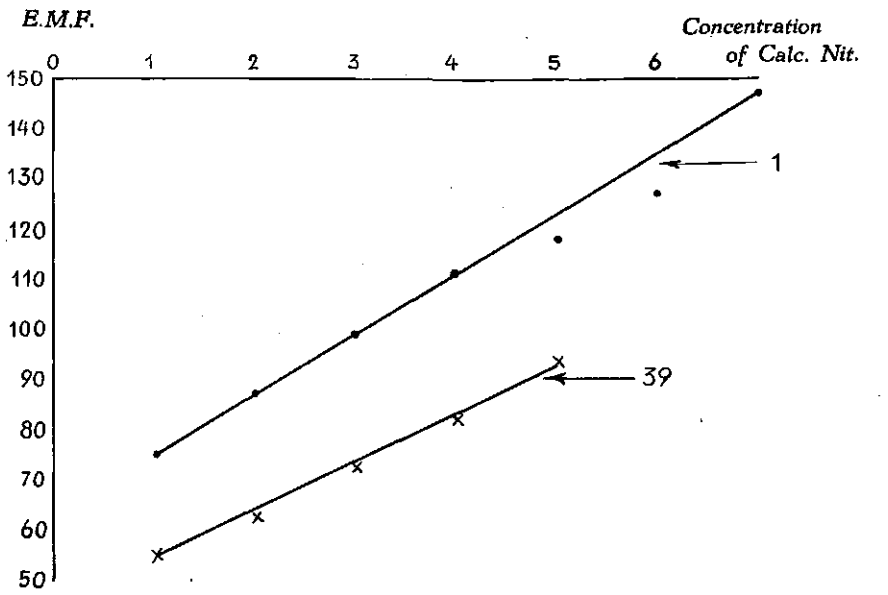

Fig. 6.

Summary.

It appeared that minerals in the form of thin plates may be used as electrodes. On further research and perfection of the methods it will probably be posible to determine electrometrically activities of ions, which thus far were not or hardly accessible for a similar investigation.

Continued research may elucidate our knowledge of the structure of the electric double layer of minerals and the exchange of ions.

Similarly as the determination of P_H has become of great value in natural scientific research, it will then appear that P_{Ca}, P_K, etc. are also of great importance, particularly in biologically important systems, where an ion-balance varying between narrow limits is essential.

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