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A glass electrode can be made to withstand high hydrostatic pressure, up to 1500 kg/cm², by separating the inside fluid from the outside one with a layer of silicone oil acting as a liquid piston, enabling the inside and outside pressure to compensate continuously. Such a glass electrode, with two Ag-AgCl electrodes, maintains its hydrogen electrode function at high pressure. pH changes resulting from dissociation constant shifts caused by pressure in acid and buffer solutions have been measured in good agreement with theoretical expected values for HCl, acetic acid, carbonic acid, and acetate buffer. No agreement was found for bicarbonate buffer. Phosphate buffer and sea water have also been tested. An adapted version of the cell-assembly is planned to equip the French bathyscaphe for deep-sea investigations.

BATHYSCAPHES make it possible to make deep sea investigations with complex man-operated laboratory equipment. pH determinations at great ocean depth are of interest in the field of oceanography, and this work was undertaken with the aim to build a pH meter to be used on the French bathyscaphe.

In this paper, we will describe the properties of a glass electrode assembly submitted to high pressure, and give details about the laboratory test equipment.

GENERAL PRINCIPLE

The chosen electrode assembly consists in a bulb-type Corning 0.15 glass electrode with two silver-silver chloride reference electrodes. The glass electrode is partly filled with 0.1N HCl and the hydrostatic pressure inside and outside are made to compensate continuously, as shown in the simplified drawing of Fig. 1, by interposing a chemically inert, immiscible, high insulating fluid between the inner and outer aqueous solutions. The density and compressibility of this fluid must be such that its density never exceeds that of water at the highest pressure investigated, i.e., 1500 kg/cm². Silicone polymers meet all these requirements, and we have used a silicone fluid MS 200 of viscosity 1 centistoke at 25° made by Midland Silicones Ltd, London.

Figure 2 shows another arrangement better suited for laboratory work. The investigated solution is trapped in a chemically inert container and any contamination from the outer steel pressure chamber is avoided. Pressure is applied to the piston by means of a hydraulic press.

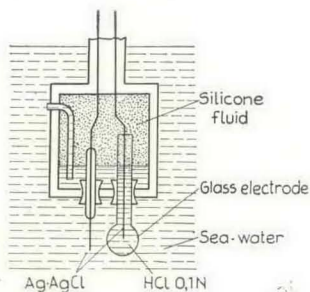


FIG. 1. Schematic drawing representing the glass-electrode assembly for measuring pH at great ocean depth.

CONSTRUCTION OF THE ELECTRODE ASSEMBLY AND PRESSURE CHAMBER

Figure 3 represents a vertical cross section through the glass electrode assembly and the pressure chamber. Electrical connections are made through a Pyrotex multilead cable (Cablerie de Clichy, France). Two of the twelve copper leads which are imbedded in an insulating mineral powder are shown. The other leads provide additional connections for temperature recordings by means of thermocouples, for detecting static electricity, and for eventual conductivity measurements.

Both ends of the cable are filled with a cold-setting potting resin, Araldite type D (Ciba, Basel, Switzerland). The outer copper shell of the cable is brazed to the steel bomb head carrying the electrode assembly.

The silver-silver chloride electrodes consist of pure silver wire (1.6-mm diam) coated with silver chloride by electrolysis. Great care should be taken to avoid any scratches, and it is recommended to use protecting sleeves on mounting. The upper rim of the glass electrode is for the same reason covered with a soft polythene ring.

The frame which supports the electrodes is made of Perspex plastic, and can easily be taken to pieces for replacement of the electrodes.

The bore through the steel base leads to a manometer and to a smaller upright cylinder (20 mm i.d.) with a piston to which pressure is applied between the plates of a ten-ton laboratory hydraulic press. The piston, terminated with a rubber cup gasket, is in contact with a lubricating

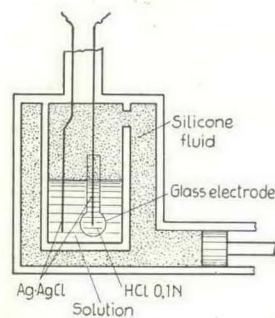


FIG. 2. Schematic drawing representing the glass-electrode assembly for measuring pH at high hydrostatic pressure with a laboratory equipment.

layer of oil which is separated from the silicone fluid, with which it is miscible, through a layer of water. Compression sends water into the main chamber, but the volumes are adjusted to avoid any contamination of the solution outside the electrode.

ELECTROMETER

The electrometer is the same as that described by Distèche and Dubuisson.¹ A d'Arsonval galvanometer is used for zero readings and the emf is measured with a precision slide wire potentiometer, the dial of which reads directly to 0.1 mv. It is calibrated with a Weston standard cell. The over-all sensitivity corresponds to 27-mm scale deflection for 1 mv.

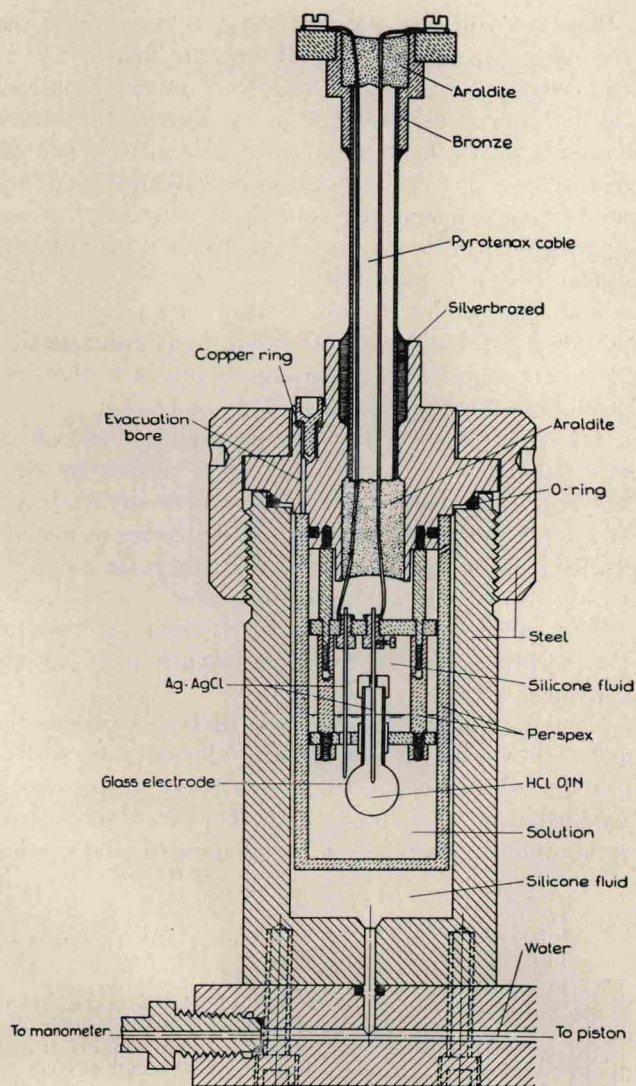


FIG. 3. Cross section through the glass-electrode assembly and pressure chamber.

¹ A. Distèche and M. Dubuisson, *Rev. Sci. Instr.* **25**, 869 (1954).

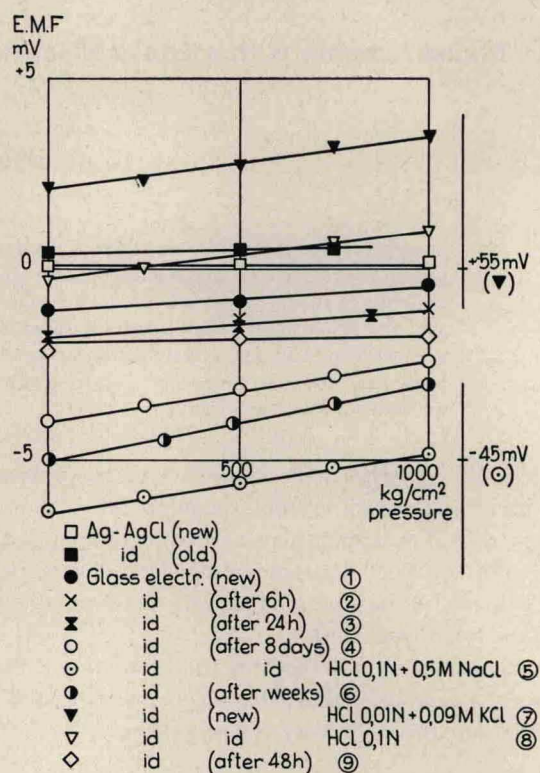


FIG. 4. Variation of the glass-electrode asymmetry potential with pressure. The scales for lines 5 and 7 are on the right.

RESULTS

Glass electrodes of the type described have been tested up to 1500 kg/cm² without damage. They maintain their hydrogen electrode function and there is no hysteresis, i.e., no zero shifts.

For all the electrolytes so far investigated the emf of the cell always varies linearly with increasing pressure as shown in Figs. 4-6.

This is true provided precautions are taken to minimize the temperature effects caused by the more or less adiabatic stepwise compression or decompression of the silicone fluid.

To evaluate these temperature effects at their maximum, sudden pressure steps of 1000 kg/cm² reached in 40 sec have been applied and the temperature changes recorded at various sites inside the electrode vessel with thermocouples (Cu-Constantan cold junction inside the potted lower end of the multilead cable).

The results indicate a quick temperature rise of 3°C in the silicone fluid followed by an exponential decay, the initial temperature being reached again after 10 min. In the water solution, the temperature rise never exceeds 1°C, the maximum being attained after 5 min, and final equilibration requiring 30 min. It appears also that the temperature changes slightly differ from place to place in the electrode vessel.

To minimize these effects which affect the emf of the cell

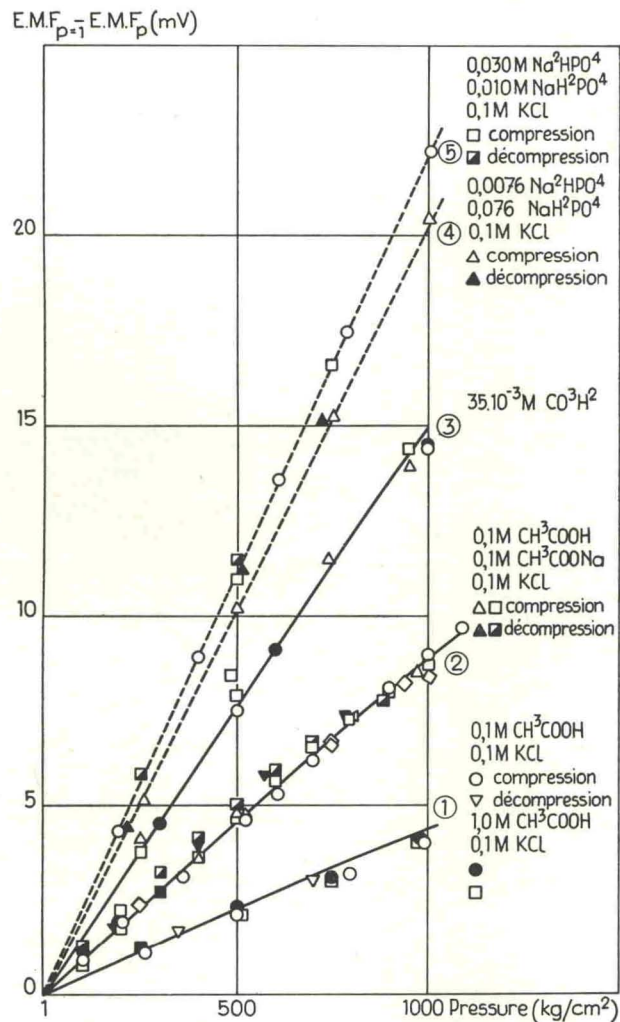


FIG. 5. Variation of the glass-electrode potential with pressure for various acid and buffer solutions. Solid lines 1, 2, and 3 are calculated from the data of Owen and Brinkley using Eqs. (4) and (5).

both directly and indirectly (through the corresponding pressure change), the following procedure was adopted to obtain the data of Figs. 4 and 5. The pressure is slowly increased to the desired value, with a final increment never exceeding 250 kg/cm². After 30 min rest, the emf is measured and the pressure read; a second reading is taken after 5 min more, and it generally agrees with the first reading; if not, further readings are taken until equilibration is attained.

All these operations are carried out in a constant temperature room at 22°C and it is estimated that the total temperature rise when a final pressure of 1000 kg/cm² is reached is probably less than 0.25°C.

The temperature coefficients of the cell for phosphate, acetate buffer, and 0.1N HCl are, respectively, 0.97, 0.60, and 0.045 mv per degree. The error introduced in this way by the estimated temperature rise is thus small. The effect

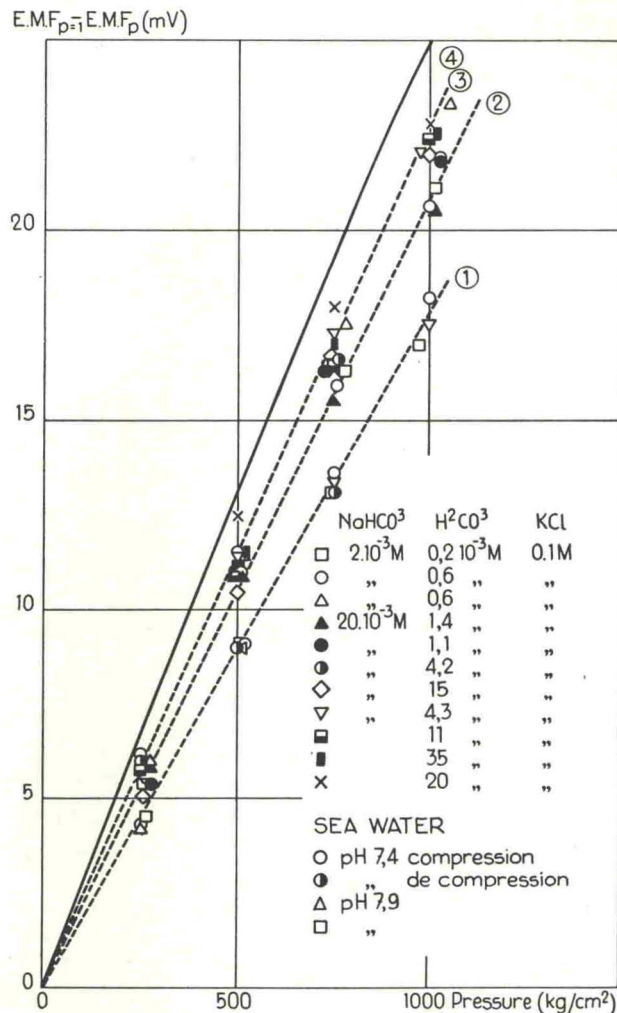


FIG. 6. Variation of the glass-electrode potential with pressure for bicarbonate buffer (2 and 3) and sea water (1). Solid line 4 is calculated from the data of Owen and Brinkley for the second dissociation step of carbonic acid [Eq. (5)].

of a temperature shift of this magnitude on the chemical equilibria in the electrolyte solutions can be neglected.

However, if more precision is required, a constant temperature (oil or water) jacket around the main pressure chamber and eventual continuous recording of the temperature inside the electrode container must be provided for.

With bicarbonate buffer (Fig. 6), especially when the concentrations are very low, additional difficulties are met with, probably caused by CO₂ diffusion causing long-range instability and also related to the fact that it is almost impossible to preserve the homogeneity of the gas solution when filling the apparatus. In this case, advantage can be taken from the observed time lag between a sudden pressure increment and the temperature rise at the electrode. Most of the emf plots of Fig. 6 for NaHCO₃ correspond to the differences between readings taken just before and

immediately after each quick pressure step. Large time intervals (30 to 60 min) separate each set of readings. When the concentration of H_2CO_3 is relatively important, the stability is sufficient to use the procedure first described.

The two methods give reproducible data and the curves can be constructed either by increasing or decreasing the pressure.

The results obtained with 0.1N HCl in and outside the electrode (Fig. 4) correspond to the asymmetry potential of the glass electrode including the eventual difference between the potentials of the two Ag-AgCl electrodes. Freshly prepared glass electrodes have a small asymmetry potential of about 1 mv or less but aged ones may show a greater value. About the same results are obtained with either acetate or phosphate buffer instead of HCl inside and outside the electrodes.

The asymmetry potential of freshly prepared Ag-AgCl electrodes is negligible and its variation with pressure is unmeasurable with our equipment. Aged Ag-AgCl electrodes, especially when scratched show a small asymmetry which varies with pressure.

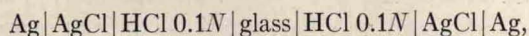
For all the glass electrodes so far investigated, the asymmetry potential was found to become more and more positive with increasing pressure (i.e., a more and more positive potential is needed to compensate the electrode potential), whereas for the buffers and weak acids investigated as outside fluid the emf of the cell always decreases. The emf values of Figs. 5 and 6 thus have been corrected at each pressure p by adding the corresponding asymmetry potential to the difference in mv between the emf measured at atmospheric pressure and the emf at pressure p .

A calomel electrode, either of the saturated type or filled with 0.1N HCl, has been tried as outside reference electrode. The emf changes with pressure fall on an exponential curve and long-range instability with zero shifts make such electrodes unsuitable in this case.

We were not able to detect any static electricity effects caused by friction even when the silicone fluid is rapidly compressed or decompressed.

INTERPRETATION

The results plotted in Fig. 4 show that the effect of pressure on the symmetrical cell,



is to modify slightly the asymmetry potential of the glass electrode. The effects on both Ag/AgCl electrodes may be assumed to cancel provided that the electrodes are freshly prepared. The asymmetry potential is often thought to arise from strains in the membrane, which may vary under the influence of pressure.²

² M. M. Dole, *The Glass Electrode* (John Wiley & Sons, Inc., New York, 1941).

The data obtained with 0.01N HCl, 0.09M KCl (Fig. 4) as outside solution are of special interest, since the hydrogen ion activity on both sides of the membrane varies so slightly with pressure in the range investigated, that it may be regarded as constant within the precision of the emf measurements. It seems clear that the glass-electrode constant (equal or nearly equal to $2.3026 RT/F$, the hydrogen electrode constant) is not modified by pressure, provided that one takes into account the asymmetry potential variations.

Let us now consider the results obtained with buffers, acetic acid, carbonic acid, and sea water.

It seems reasonable to assume that the effects of pressure on both Ag-AgCl electrodes still compensate almost completely. In most of the experiments, the Cl^- concentration is equal inside and outside the electrode and the ionic strength is kept at 0.1, except for sea water. We will further notice (Fig. 4) that the shape of the emf variation with pressure measured with 0.1N HCl outside the glass electrode is the same when 0.1N HCl is replaced by 0.1N HCl + 0.5M NaCl (approximate concentration of sea water).

The pH of an aqueous solution of a weak acid HA is given by the following equation:

$$\text{pH} = -\log[\text{H}^+]f_{\text{H}^+} = \frac{1}{2}pK_{\text{HA}} - \frac{1}{2}\log[\text{HA}] + \log\frac{f_{\text{A}^-}}{f_{\text{HA}}f_{\text{H}^+}} \quad (1)$$

When the dissociation constant K_{HA} is small, the real concentration $[\text{HA}]$ may be made equal to the stoichiometric concentration of the acid with a fair degree of accuracy.

The pH of an aqueous solution of a weak acid HA and its sodium salt NaA is represented by

$$\text{pH} = pK_{\text{HA}} + \log\frac{[\text{A}^-]}{[\text{HA}]} + \log\frac{f_{\text{A}^-}}{f_{\text{HA}}} \quad (2)$$

At pH between $pK_{\text{HA}} - 1$ and $pK_{\text{HA}} + 1$, the stoichiometric concentrations $[\text{salt}]$ and $[\text{acid}]$ may be substituted for $[\text{A}^-]$ and $[\text{HA}]$, respectively.

For dilute solutions, the activity coefficient f_{HA} of the undissociated acid is generally assumed to be unity in both equations.

Pressure is known to affect the dissociation constant and the activity coefficients according to

$$\left(\frac{\partial \ln K}{\partial p}\right)_{T,m} = \frac{-\Delta \bar{V}^0}{RT} \quad \text{and} \quad \left(\frac{\partial \ln f_i}{\partial p}\right)_{T,m} = \frac{\bar{V}_i - \bar{V}_i^0}{RT} \quad (3)$$

where $\Delta \bar{V}^0$ is the algebraic difference between the partial molal volumes of the products and the reactants of the chemical equilibrium in their standard states and \bar{V}_i the partial molal volume of the ion species i .

For weak electrolytes calculations show that K_{HA} increases with pressure and that the relative increase is the

greater the lower the temperature. Activity coefficients also increase with pressure.

If E_1 is the emf at pressure 1 of the glass-electrode cell filled with a weak acid or a buffer solution as outside fluid, and E_p the emf at pressure p , then using (1) and (2) provided $\frac{1}{2} \log [\text{HA}]$ and $\log [\text{A}^-]/[\text{HA}]$ remain constant and neglecting the potential differences arising from the Ag—AgCl electrodes, one has, after correction for the asymmetry potential, at 22°C

$$E_1 - E_p = 0.0293 \log \frac{K_p}{K_1} + 0.0293 \log \frac{f_{\text{A}_1^-} f_{\text{H}_p^+}}{f_{\text{A}_p^-} f_{\text{H}_1^+}} \quad (4)$$

$$E_1 - E_p = 0.0585 \log \frac{K_p}{K_1} + 0.0585 \log \frac{f_{\text{A}_1^-}}{f_{\text{A}_p^-}} \quad (5)$$

The contribution of the activity coefficient term in (4) and (5) is probably small as estimated from the few available data calculated from Eq. (3). A 10% increase at 1000 atmos of the activity coefficient appears to be exceptional for a 1–1 electrolyte (e.g. NaOH). This would correspond to an emf change of about 2 mv.

The values for Kp/K_1 calculated from Eq. (3) by Owen and Brinkley³ for acetic acid and for carbonic acid (first and second dissociation steps) have been used to draw the full lines of curves 1, 2, and 3 of Fig. 5, and curve 4 of Fig. 6, taking into account Eq. (4) and (5).

The experimental data, corrected for asymmetry potential but not for the activity coefficient variation, are in good agreement with the calculated values for acetic acid, carbonic acid (first dissociation step), and acetate buffer (Fig. 5). The results shown in Fig. 6 (curves 2 and 3) for the bicarbonate buffer do not fit. The observed emf difference at any pressure is only 75% of the expected calculated value which corresponds to twice the ordinate read from curve 3 of Fig. 5. It is doubtful that this is due to the experimental difficulties outlined above, since the results for carbonic acid do agree with theory. When the CO₂ con-

centration is high enough the losses caused by CO₂ escape are very small, as shown by the fact that the zero shift following compression and decompression is zero or a few tenths of a millivolt. A possible effect of carbonic acid and its salts on the potential of the outside Ag—AgCl electrode is also excluded. Exactly the same results are obtained when the outside electrode is placed in a U tube containing 0.1 M KCl and closed at one end with a filter paper stopper in contact with the buffer solution. One possible explanation would be that the dissociation of NaHCO₃ is affected by pressure, or that hydrolysis complicates the equilibrium.

There is a slight shift of the curves when the ratio [salt]/[acid] is varied. The greatest emf variation seems to be obtained when this ratio is unity.

The results with phosphate buffers indicate a similar effect. In both cases, it is clear that the emf variation is almost independent of the ratio [salt]/[acid].

The initial pH of the sea water has no effect or an extremely small effect, on the variation of the emf with pressure (Fig. 6, curve 1). The curve indicates the magnitude of the variation which should normally be found if measurements were carried out at different depths in sea water of constant composition. Any departure from the expected change will mean that other factors than pressure are involved. It is clear that the analysis of corresponding sea-water samples will be necessary for the full interpretation of the pH results at different levels. Temperature recording is also a necessary complement.

The equipment needed for all these experiments to be carried out with the French bathyscaphe F.N.R.S. III will be described in another paper.

ACKNOWLEDGMENTS

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³ B. B. Owen and S. R. Brinkley, *Chem Revs.* **29**, 461 (1941); see also H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions* (Reinhold Publishing Corporation, New York, 1943).

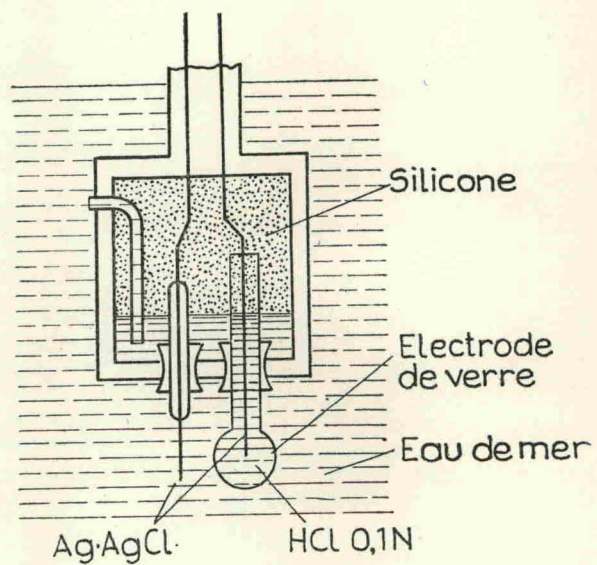


FIG. 1. — Schéma de principe de la sonde à électrode de verre (d'après DISTÈCHE [1]).