

shorter than the ordinary one, it has been established that the height equivalent to one theoretical plate was approximately 1 cm for the given packing. These results, as well as those represented in Fig. 3, show that the number of theoretical plates of the column exceeds one hundred.

LITERATURE CITED

- [1] Distillation, Foreign Literature Press, 255 (1954).
- [2] M. I. Rozengart, The Technique of Laboratory Distillation and Rectification 79, 106 (1951).
- [3] W. M. Langdon, Ind. Eng. Chem. 17, 590 (1945).
- [4] Methods and Processes of Chemical Technology, Symposium I, Academy of Sciences USSR, 46 (1955).

A STABLE GLASS ELECTRODE FOR pH MEASUREMENTS AT TEMPERATURES UP TO 100°C

N. A. Fedotov

(L. Ia. Karpova Scientific Research Physico-Chemical Institute)

The thin-walled glass electrodes of sodium electrode-glass of types ES-1 and ES-2 have insufficient stability and low chemical resistance, which limits the possibility of using them at temperatures above 40°C, and they also have a low sensitivity in the region $\text{pH} > 9$ (particularly in media with a substantial concentration of salts).

The indicator portion of the electrode (the bulb) was made of lithium glass containing, in addition to lithium, silica and rare-earth elements (lanthanum and cesium). The electrode properties of these glasses have already been described in detail [1]. Lithium glass has a relatively high chemical stability and a fairly low specific resistance. It crystallizes quickly upon cooling from a fused mass, becomes cloudy and fuses poorly to the tube; it fuses best with No. 23 glass or the so called "chemical" glass from the Klin factory

In making the electrodes one must see to it that the drop of molten lithium glass (with a diameter of 3-4 mm) placed on the heated end of the tube is not only fluid but also clear, and that the heating is done carefully (in a flame with oxygen added). The bulb is blown through narrow rubber tubing with a length of 60-70 cm and an inside diameter of 1.5-2.0 mm. After the bulb is made it is annealed in a muffle furnace at $500 \pm 10^\circ\text{C}$ for an hour.

Fig. 1. Electrodes with a bulb of lithium glass;

- 1) bulb of lithium glass;
- 2) tube of No. 23 glass with a diameter of 10 mm; 3) lead of silver with a diameter of 1 mm and length of 15 mm; 4) lead of platinum with a diameter of 0.3 mm; 5) "platinite" with a diameter of 0.5 mm; 6) glass tube with a diameter of 3.5 mm;
- 7) ebonite cap; 8) cement.

Figure 1 shows the external view of two varieties (a and b) of the stable glass electrodes prepared from tubes with outside diameters of 10 and 12 mm respectively. The second variety (b) completely eliminates the effect of nonelectrode glass walls on the results of measurements in the region $\text{pH} > 9$, an effect which manifests itself as decrease of ~ 0.1 pH units in the electrode readings upon immersion of the electrode to a large depth. In both varieties, the bulb of the glass electrode has a diameter of 9-10 mm and a glass wall thickness of 0.2-0.3 mm. The inner tube has an outside diameter of 3.0-3.5 mm and a wall thickness of about 0.5-0.7 mm.

Chlorination of the silver electrode is carried out by anodic polarization in 0.1 N HCl with a current of 3 ma for 2 hours; then the electrode

is reduced cathodically to full brightness and is again polarized with the same current for 3 hours. The electrodes are filled with a 0.1 N solution of C.P. hydrochloric acid.

The use of "platinite", which fuses well into glass, assures hermetic sealing of the electrode without using cements so that vaporization of the liquid inside the electrode is completely prevented.

In the upper portion of the electrode is a cap (of ebonite) with a hollow metal pin to which a "platinite" lead is soldered with tin. The cap is made fast to the electrode with BF-2 cement (heating at 60-70°C for 3 hours) or with dental phosphate cement.

The characteristic behavior of the glass electrode is shown in Fig. 2. Values of the hydrogen electrode potential with reference to a saturated calomel reference electrode are plotted along the abscissa axis; while the emf values with a glass electrode in the same solutions at temperatures of 25, 60, and 95°C are plotted along the ordinate axis.

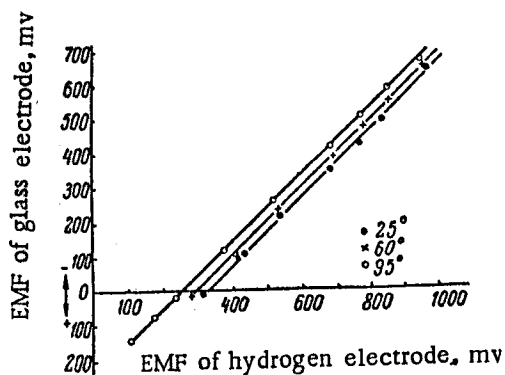


Fig. 2. Characteristic behavior of glass electrode.

The linear behavior of the function, with a slope of 45°, at all the noted temperatures indicates that the potential of the glass electrode and of the hydrogen electrode vary to the same extent for the measurement of the pH of the solutions, i.e., that the behavior of the glass electrode is analogous to that of the hydrogen electrode in the pH range of 0.5 to 12.5.

At 80-95°C the range of the straight-line portion of the electrode behavior extends to low pH values (up to 10 N), which indicates the possibility of using the glass electrode in many cases for an evaluation of the acidity of solutions.

The electrodes withstand extended heating in acid and base solutions without having their characteristics disturbed. The reproducibility of the described electrodes in the indicated pH range at temperatures about 50°C is about 0.05 pH units.

A material characteristic of the electrodes is their interchangeability, which lies within the limits of ± 0.05 pH units at temperatures above 50°C. At temperatures below 50°C, in acid solutions, the interchangeability lies within the limits of ± 0.1 pH units. The constancy of the electrode characteristics and the interchangeability of the electrodes is evidently connected not only with the relatively good chemical stability of lithium glass, but also with the constancy of the asymmetry potential of the electrodes, the absolute value of which does not exceed 5-10 mv in the temperature range of 25-95°C. For a temperature change of 60 to 95°C the asymmetry potential remains constant within the limits of ± 2 mv.

The so-called "zero point" of the electrodes, i.e., the pH value at which the emf of the circuit (with a saturated calomel reference electrode) is equal to zero, lies at a pH of 1.85 ± 0.05 when the temperature is 25°C.

The resistance of the electrodes is about 200 ± 50 megohms at 25°C and decreases to 3 and 0.5 megohms when the temperature of the solution increases to 80 and 95°C respectively. The low resistance values of the stable glass electrodes, particularly at temperatures above 40-50°C, make it possible to use them for measuring the e.m.f. of cathode devices with a low output resistance. However, even at room temperature the type LP-5 domestic potentiometers can be used successfully.

The electrodes have good mechanical strength and withstand rapid temperature fluctuations. Industrial tests of the operating electrodes in apparatus at 90-95°C and at pressures up to 8 atm showed their applicability for the control of technological processes involving elevated temperatures and pressures. Laboratory tests showed that the electrodes also withstand extended heating at a temperature of 120-130°C.

The geometrical dimensions of the electrodes as well as the manner in which the contact is let out can, if it is so desired, be different, depending on the design of the unit, the manner of bracing the electrode, etc.

LITERATURE CITED

- [1] G. Perley, Anal. Chem. 21, 394 (1949).