MEASUREMENTS OF pH WITH LITHIUM-GLASS ELECTRODES

V. A. Zarinskii, V. A. Frolkina, and A. D. Golubev

V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry,
Academy of Sciences of the USSR
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The sensitivity gradient dE/dpH of ÉS-1 and ÉS-2 sodium-glass electrodes is not constant over a wide range of pH values; it also depends on the presence of foreign ions in the solution. Their potentials are not fully reproducible in measuring solutions with increasing and decreasing pH values [1]. This leads to errors in measuring the pH of solution, especially in the alkaline region beginning at about pH = 9.

We measured the pH of accurate buffer solutions in the range 1-12.5 by means of new electrodes (see table) made of lithium glass containing SiO_2 and Li_2O, and also La_2O_3 and Cs_2O [2 and 3].

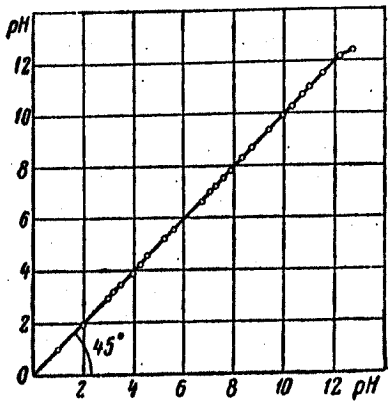

Fig. 1. Hydrogen function of electrodes 1 and 2.

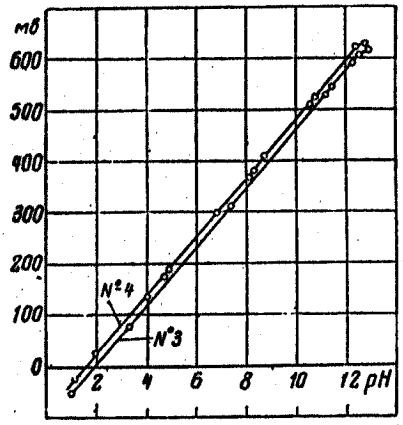

Fig. 2. Hydrogen function of electrodes 3 and 4, (ordinates represent emf values read on the millivolt scale of the instrument).

Because of their brittleness, the first two electrodes (1 and 2) are protected by glass tubes with holes; the electrodes 3 and 4 are sufficiently strong and require no protection. For plotting the curves a set of buffer solutions was prepared according to formulas published in [4-6]; accurate pH values were determined by means of hydrogen electrodes in the cell described earlier [7].

An LP-57 Moskip electronic potentiometer (1959) was used for measurements; the instrument error of this device was ± 0.5 mv which corresponds to ± 0.01 pH units. All measurements were carried out at 21.5°C; a Moskip saturated calomel electrode was used as the comparison electrode.

In working with electrodes 3 and 4, whose ohmic resistance is high, the stand with glass and calomel electrodes was protected by a sheet steel screen in order to avoid capacitance phenomena.

For electrodes 1 and 2 the readings were taken directly from the instrument scale after it had been adjusted according to operating instructions. The values found were entered on the ordinate axis of the graph; the pH values of the same solution determined by means of the hydrogen electrode were plotted on the abscissa axis (Fig. 1). The linear dependence between both values is maintained between 1 and 11.75; its slope is 45°.

Thus, the hydrogen function of these electrodes extends over a much wider range than that of electrodes made of ÉS-1, ÉS-2, and other glass grades used earlier. The minimum difference between the indications of electrodes 1 and 2 was ± 0.01 pH, which corresponds to an instrument error of the device (± 0.5 mv) and shows that both electrodes are interchangeable. In this pH range the gradient of sensitivity is constant, equalling 58.2 mv/pH (at 21.5°C).

A similar relationship for electrodes 3 and 4 is shown in Fig. 2; both investigated electrodes have hydrogen functions with a constant gradient of sensitivity dE/pH = 58.2 (at 21.5°C) for the pH range 1-12.5.

The zero points of the electrodes given in the table did not change during 15 days (their variations remained within the measurement accuracy of ± 0.01 pH, ± 0.5 mv).

Specification of Lithium Glass Electrodes

Specimen	Sphere diameter, mm	Resistance of the membrane, mohm	Internal filling	Internal electrode	Zero point pH
1	5	135	1 N H_2SO_4 saturated with $HgSO_4$	Pt(amalgamated)	7.8
2	11	120	The same	The same	7.8
3	10	280	0.1 N HCl	Ag/AgCl	1.85
4	10	275	1 N solution of $CuSO_4$, 0.2 N sol. of H_2SO_4	Cu	1.65

With electrodes 1 and 2 the potential is established practically instantaneously, while with electrodes 3 and 4 a slight delay occurs (about 2 minutes). This effect is apparently due to the high ohmic resistance of the membranes of electrodes 3 and 4; in their case the speed with which the potential is established rises rapidly with increasing temperature. The comparsion of electrochemical characteristics, with the mechanical strength of electrodes 3 and 4 taken into account, shows that they are more likely to be widely used in production inspection and research.

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DEVICE FOR THE TITRATION OF DARK SOLUTIONS

G. A. Arbuzov, A. R. Kuznetsov, and N. N. Pavlov

Moscow Technological Institute of Light Industry

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Quite often the change of color at the point of equivalence cannot be established with an adequate reliability because of the presence of brightly colored impurities, or the insufficiently sharp change of color of the indicator substance after the reaction. In these cases we use a special device shown in the figure.

A measured volume of the dark solution being investigated is poured into a circular flat dish 2 with a capacity of 250-500 ml and placed onto the electromagnetic mixer 2. The titration is accompanied by an intense mixing and, if necessary, by heating. The solution being titrated is traversed by a parallel light beam

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