Reports of the Academy of Sciences of the USSR

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1964

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1964. Volume 154, No. 2

PHYSICAL CHEMISTRY

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A GLASS ELECTRODE SENSITIVE TO CHANGES IN THE OXIDATION POTENTIAL OF A SOLUTION

Among the characteristic properties of "ordinary" glass electrodes, used in measuring pH and made from glass with purely ionic conductivity, is their insensitivity to the presence of oxidizing and reducing agents in the solution.

The discovery of glasses in which the carriers of electric current are electrons gives grounds for assuming that electrodes made from these glasses may prove sensitive to changes in the oxidation potential of a solution. Until now, for measuring such potentials, electrodes of noble metals have mainly been used. Only quite recently have reports appeared on analogous properties of electrodes made from materials of a semiconducting character: Zr/ZrO_2 ([1]), SnO_2 ([2]), and it has been found that the latter have a number of advantages over platinum electrodes.

The present work reports on features of the electronic behavior of sodium silicate glasses containing iron oxides, in which (under certain synthesis conditions) the appearance of electronic conductivity may be expected. Results are presented from a study of the behavior of electrodes made from such glasses in solutions with a varying oxidation potential. The choice of the glass system was determined by our previous work ([3], [4]), as well as by a number of reports on the presence of electronic conductivity in certain iron-containing glasses ([5], [6]).

As a result of a systematic study of the electrode properties of sodium silicate glasses containing iron, it was established ([3], [4]) that substitution of part of SiO_2 by Fe_2O_3 leads to a sharp change in the form of the E–pH curve compared with the curve for binary sodium silicate glass. Here E is the emf of the following galvanic cell:

$$\mathrm{Ag}\,|\,\mathrm{AgCl},\ \mathrm{HCl}\,(0.1\,M)\,|\,\mathrm{glass}\,|\,\mathrm{buffer\ solution}\ (C_{\mathrm{Na}^+} = \mathrm{const})\ \mathrm{pH\ variable}\,||\,\mathrm{KCl},\ \mathrm{Hg_2Cl_2\ sat.}\,|\,\mathrm{Hg}.$$

The typical E—pH curves obtained by us are presented in Fig. 1 (curves 1a, b). Curve 1a pertains to binary sodium silicate glasses containing 13-22 mole % Na_2O. They are characterized by a wide interval of the hydrogen function—a rectilinear portion of the curve with a slope coefficient equal to

$$V = \frac{RT}{F} 2.3 = 58 \text{ mV/pH}$$

at room temperature.

Curve 1b pertains to glasses in which a considerable part of SiO_2 (7-16 mole %) is replaced by an equimolecular amount of Fe_2O_3. The region of the hydrogen function is shortened, but the region of the curve corresponding to the sodium function is broadened; under the conditions of our experiment this region is parallel to the pH axis.

Sodium oxide was introduced into these glasses from sodium nitrate, and iron in the form of Fe_2O_3; melting was carried out in air, in a platinum crucible, in a silite furnace. The oxidizing conditions of glass melting here ensured the predominance of Fe(3+) in the glass.

However, in those cases where, from the melting conditions, the presence in the glass, along with Fe(3+), of an increased amount of Fe(2+) could be expected, for glasses analogous in initial composition we obtained curves

E—pH of a completely unusual form (Figs. 1, 2—4). Iron was introduced here in the form of oxalate Fe(3+) or in the form of a mixture of Fe_2O_3 and starch, and Na_2O in the form of Na_2CO_3; the specified ratio of iron to sodium, calculated as Fe_2O_3 and Na_2O, was 1 : 1 or greater. The slope coefficient of the rectilinear portion of the E—pH curves for these glasses is from one and a half to three V and often differs for electrodes made from one and the same glass, and also depends on the nature of the gas above the solution (Fig. 1). The potential values, contrary to the usual case, were unstable in this case; the curves obtained during the "forward" and "reverse" course of pH change did not coincide.

The electrical resistance of electrodes made from these glasses was about 1 Mohm, i.e., 2-3 orders of magnitude less than that of electrodes made from glasses of the same batch composition, melted under oxidizing conditions. This fact permits one to assume that the electronic component plays a significant role in the conductivity of the low-resistance glasses described.

In this case, in our opinion, the phenomena observed in studying the dependence E—pH may be explained by the fact that the glass electrode indicates the oxidation potential of the solution, and this potential is unstable, since the solution does not contain any buffer oxidation-reduction system. Under these conditions the oxidation potential of the solution depends on random impurities of oxidizing and reducing agents, especially oxygen, the content of which changes when the gas atmosphere is changed. All this may lead to an unusual course of change in the electrode potentials when the pH of the solution is changed.

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

Fig. 1. Curves E—pH for various glasses. 1 —for electrodes made from glasses with ionic conductivity: a —binary sodium glasses; b —sodium-iron-silicate glasses melted under oxidizing conditions (Fe_2O_3 concentration in the glasses above 7 mol.%); 2—4 —for electrodes made from glasses with presumed electronic conductivity: 2 —experiment in air; the pH values of the solution were increased ("forward" run); 3 —hydrogen was passed through the cell: a —forward run; b —reverse run; 4 —argon was passed through the cell: a —forward run; b —reverse run.

Fig. 2. Results of experiments in solutions of buffered oxidation-reduction systems

when the gas atmosphere is changed. The electrode potentials were measured (relative to the calomel electrode) in solutions of buffer oxidation-reduction systems, where the ratios of concentrations of the oxidized and reduced forms are specified and vary over wide limits.

The electrode potentials were measured in solutions of chlorides Fe(3+) and Fe(2+), and also in solutions of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$. The solutions were prepared in 0.1 N HCl. The constancy of pH (pH 1.1) was monitored with an "ordinary" glass electrode. The values ⋯

The change in the oxidation potential was measured with a smooth platinum electrode. The results of the experiments are shown in Fig. 2. Along the abscissa are plotted the emf values of a cell composed of platinum and calomel electrodes; along the ordinate, the emf of a glass-calomel cell, including in turn various electrodes made from the iron-containing glasses described, with unusual dependences E—pH.

At pH 1.1, for most of the electrodes, a straight line was obtained making an angle of 45° with the abscissa. This shows that the potential of our glass electrode changes in exactly the same way as that of the platinum electrode, i.e., it is the oxidation potential of the solution. It can be referred to the usual hydrogen zero by the corresponding recalculation. The normal potential of such a glass electrode depends on its internal filling.

Fig. 3

Figure 3: Fig. 3

Fig. 3. Titration of 100 ml of a 0.01 *N* solution of $Na_2C_2O_4$ with a 0.1 *N* solution of $KMnO_4$; 1 –platinum electrode, 2 –glass electrode.

The straight line for ferri-ferro solutions at pH 1.1 in Fig. 2 continues the straight line for ferri-ferrocyanide solutions. In the latter system, experiments were also carried out at pH 11 (soda was added to the aqueous solution). In this case, too, a straight line with a slope angle of 45° was obtained. The emf values were highly stable and were reproduced within ±3 mV.

The potentials of the glass electrodes were also measured in "irreversible" systems in which the platinum electrode gives unstable potential values: in acidic solutions of H_2O_2 and $KMnO_4$. For H_2O_2 at pH 1.0, we obtained a linear dependence of the emf of the glass-calomel cell on the logarithm of the H_2O_2 concentration in the concentration range 0.03-10% (0.01-$\sim 3M$); moreover, the emf values were also stable and reproducible in measurements in the "forward" and "reverse" directions. The slope coefficient approached ~ 60 mV per unit of the logarithm of concentration. For $KMnO_4$ solutions, apparently, the dependence also approaches linear in the concentration range 0.001-0.003 *M*, with a slope coefficient of ~ 52 mV.

The same electrodes were used as indicator electrodes in the titration of a sodium oxalate solution with an aqueous solution of $KMnO_4$. The equivalence point corresponded to a potential jump of ~ 400 mV (Fig. 3). As can be seen from Fig. 3, approximately the same result was obtained with a platinum electrode as well.

Thus, using iron oxides as an example, we see that, with a favorable ratio of the concentrations of oxides present in the glass in different valence states, glass electrodes can be obtained whose potentials depend on the oxidation potential of the solution in the same way as the potential of a platinum electrode. At the same time, glass oxidation electrodes have the advantage that they do not exert any noticeable catalytic decomposing action on systems such as hydrogen peroxide.

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Received
12 IX 1963

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