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Abstract

Full Text

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POTENTIOMETRIC MEASUREMENTS IN VARIOUS MEDIA

In chemical investigations, in the control of certain technological processes, and also in laboratory practice, the potentiometric method has become widespread. The essence of the method consists in measuring the emf of galvanic cells composed of a standard half-cell (calomel, mercurous sulfate, etc.), an electrolytic bridge, and a measuring electrode whose properties change in the course of the reaction under study. The potentiometric method has proved especially effective in the study of catalytic hydrogenation reactions carried out on massive or powdered catalysts. A change in the potential of the catalyst during the reaction is associated with an increase or decrease in the concentration of hydrogen on its surface, which in most cases makes it possible to judge unambiguously the mechanism of the process ([1],[2]).

A substantial shortcoming of the methods used for measuring potentials is the difficulty of employing them in studies in nonconducting media (benzene, alcohol, heptane, octane, gaseous media, etc.). Constructive modifications of potentiometric devices intended for measurements in nonelectrolytes are reduced mainly to the introduction into the gap "reference electrode—measuring electrode" of various liquid electrolytic additives. On the surface of the measuring electrode a film of electrolyte is formed, ensuring the electrical conductivity of the circuit. In this case the readings of the element are not always sufficiently stable and depend on the state of the electrically conducting film and on many other factors that are difficult to take into account and control (adsorption, properties of the solvent, etc.). These remarks are of a general nature and are valid for many electrode designs ([3]–[5]).

Fig. 1. Electrode device for potentiometric measurements in various media

In the present article a device is described that makes it possible to carry out potentiometric measurements in various media, independently of their electrical conductivity. The article was written on the basis of materials from joint-

Figure 2

Figure 2: Figure 2

Figure 3

Figure 3: Figure 3

research work of the chemistry laboratory of the Kazakh Agricultural Institute and the problem laboratories of thermophysics and organic catalysis of the Kazakh State University.

Fig. 2. Hydrogenation of *o*-nitrophenol (1) in 0.1 *N* NaOH and of dimethylacetylenylcarbinol (2) in alcohol with small additions of alkali on a nickel catalyst at 20°C. Potentiometric curves 1 and 2 were obtained by the usual method; 1′ and 2′, with the aid of the electrode described in the article.

The electrode for measuring the emf is a thin-walled glass bulb 4 (Fig. 1), whose outer surface is coated with a layer of platinum deposited from a solution of chloroplatinic acid by the ignition method until a mirror-like, translucent layer is obtained. The bulb is blown from glass having increased electrical conductivity, for example lithium glass. It should be noted that the electrode can be made from any other material possessing electrolyte properties and not chemically interacting with the medium in which the reaction is carried out. The resistance of the platinum coating in the electrode described proved to be 100–300 ohm/cm^2. A lead is made from coating 2 by means of platinum wire 5. The bulb is filled with HCl solution 3 and platinum electrode 10 is immersed in it. Leads 6 and 7 are connected through terminals 8 and 9 to a measuring instrument of sufficiently high internal resistance (for example, an EMU-3 valve electrometer). All dimensions of the electrode are given on sections 11 and 12. The electrode is immersed in solution 1, where the potentiometric investigations are carried out.

The measuring device described was used in the study of the catalytic hydrogenation of organic compounds. The procedure for carrying out the reactions is the usual one ([6]). Figure 2 presents the kinetic curves for the hydrogenation of *o*-nitrophenol in 0.1 *N* NaOH and of dimethylacetylenylcarbinol in an alcoholic medium with small additions of alkali at 20°C. Along the horizontal axis is plotted the ratio of the amount of hydrogen V, absorbed at a given moment of time, to the total amount V_m entering into the reaction. Here the curves of potential change are also compared, obtained with the aid of the measuring circuit: platinum wire–electrolytic key–standard half-cell, and with the aid of the proposed device. The catalyst is skeletal Raney nickel, the volumes are measured in ml, and the potentials in mV.

Fig. 3. Hydrogenation of dimethylacetylenylcarbinol in an alcoholic medium and in dioxane at 20°C on nickel (1, 2 –kinetic curves; 1′, 2′ –change in potential)

Fig. 4. Hydrogenation of dimethylacetylenylcarbinol in heptane on nickel (1) and in alcohol on platinum deposited on Al_2O_3 (2).

Figure 4: Fig. 4. Hydrogenation of dimethylacetylenylcarbinol in heptane on nickel (1) and in alcohol on platinum deposited on Al_2O_3 (2).

Figure 3 shows the change in potential and the kinetics of the process during hyd-

dimethylacetylenylcarbinol in alcohol and dioxane at 20°C. In this case it is not possible to measure the catalyst potential by the usual method because of the low electrical conductivity of the alcohol.

Figure 4 presents the potentiometric and kinetic curves for the hydrogenation of dimethylacetylenylcarbinol in heptane on a nickel catalyst and in alcohol on platinum deposited on aluminum oxide. With the usual method such measurements cannot be carried out. Common to all examples is the good agreement in the character of the potentiometric curves obtained with the proposed device and by the usual method.

The mechanism of operation of the electrode described is apparently as follows. The layer of platinum on the outer wall of the bead, adsorbing hydrogen, becomes a gas electrode, on the surface of which the reaction
$H_2 \rightleftarrows 2H^+ + 2e^-$
takes place, supplying electrons through the external circuit to the platinum wire inside the bead. On the surface of the latter there occurs the discharge of hydrogen ions from hydrochloric acid according to the equation
$2H^+ + 2e^- \rightarrow H_2$.
The change in the state and amount of adsorbed hydrogen on the catalyst and on the platinum film as a result of the catalytic reaction leads to a change in the emf of the entire circuit.

Fig. 4. Hydrogenation of dimethylacetylenylcarbinol in heptane on nickel (1) and in alcohol on platinum deposited on Al_2O_3 (2).

The electrode for measuring potentials may prove useful in various potentiometric measurements, both laboratory and industrial. Its essential advantage is the exclusion of the medium in which the reaction under study is carried out from the space "reference electrode–measuring electrode," and its replacement by any solid electrolyte (in the present case glass) that does not react chemically with the medium.

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Note: Figure translations are in progress. See original paper for figures.