KINETICS OF THE EVOLUTION OF HYDROGEN AT HIGH OVERVOLTAGES

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In principle, electrode processes may proceed in the form of activationless and barrierless processes [1] as well as in the more usual form. Barrierless reactions have been studied in a series of examples but until now it has been impossible to study rapid activationless processes directly because of the diffusion limitations.

In an activationless process, when the energy of activation equals zero, the rate of reaction is equal to the value of the ideal pre-exponential factor which, for a first-order reaction, is proportional to the concentration of the discharging particles. The value of the real pre-exponential factor [2] is experimentally obtainable from the data on the temperature dependence of the rate of the electrode reaction. For the discharge of hydrogen ions this value depends substantially on the nature of the cathode and decreases sharply on transition from metals with a high overvoltage (Pb, Hg) to metals with a moderate overvoltage (Ag) [3, 4]. For this reason it was possible to assume that for metals of the silver type the rate of activationless discharge is sufficiently low to be experimentally measurable. However, the limiting currents which we found for discharge of hydrogen ions on silver from acidified sulfate and perchlorate solutions were of a purely diffusion nature even under conditions of very intense mixing. For this reason we turned to the investigation of overvoltage in concentrated buffer solutions. The high buffer concentration together with the low H^+ ion concentration, i.e., current densities which are not too high, ensured acceptable values of ohmic loss and, on the other hand, provided the possibility of removing the diffusion limitations by the buffer acting as a source of hydrogen ions.

For the investigation we chose three metals which have average hydrogen overvoltages: copper* (phosphate and butyrate buffer solutions), solid gallium (phosphate solution), and silver (acetate buffer, acidified perchlorate and sulfate solutions). An electrode with a high overvoltage was also studied for comparison: amalgamated copper (butyrate buffer).

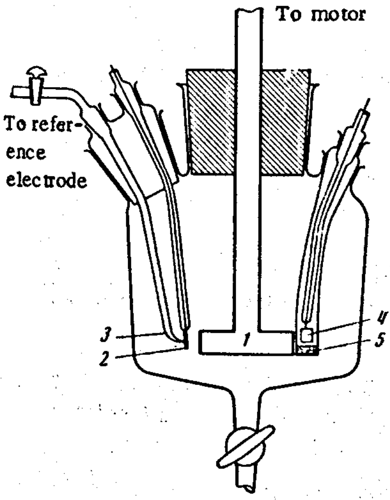

Fig. 1. Diagram of the cell.

The cell for the measurements is shown schematically in Fig. 1. The cell contained a four-bladed Teflon stirrer 1 with a blade diameter of 50 mm. The rate of rotation of the stirrer was monitored with a strobotachometer. This rate was variable from 500 to 3000

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*Nomura and Kita [5] have described the tendency for a limiting current of the order of 30 A/cm^2 to appear in the η, $\log i$ curves for the case of a Cu cathode in 1 N H_2SO_4. However, we are of the opinion that the corresponding data are not reliable, since corrections of up to 8 V for the ohmic voltage drop at a current density of 1 A/cm^2 were introduced in the measured values of overvoltage. The deviations in the corrected polarization curves in the region of current densities around 30 A/cm^2 from the Tafel curves extrapolated to this region do not exceed 0.25 V and are proportional to the current density, thus there is no real basis for the assumption that the limiting current appears in the corresponding overvoltage regions [6].

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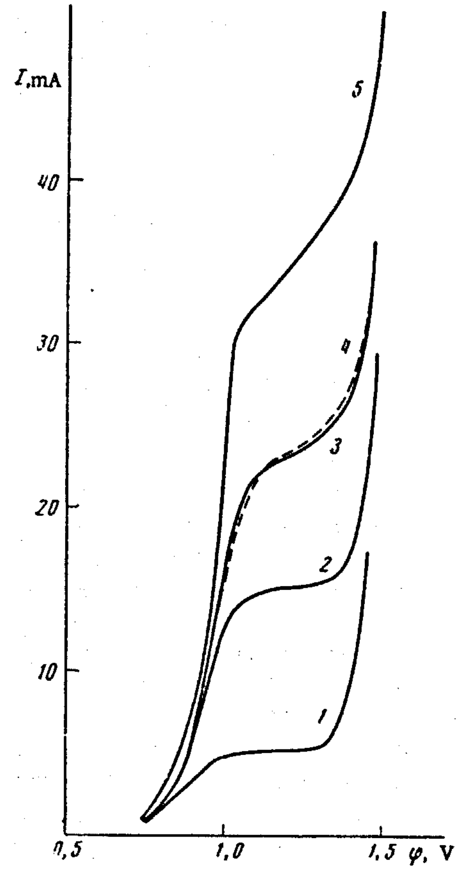

Fig. 2. I, φ relationships on a silver electrode in 5 M acetate buffer solution (potential measured relative to a saturated silver chloride electrode), pH 6.3: 1) without stirring; 2) 600; 3) 1800; 4) 2500 rpm; pH 6.03: 5) 1800 rpm.

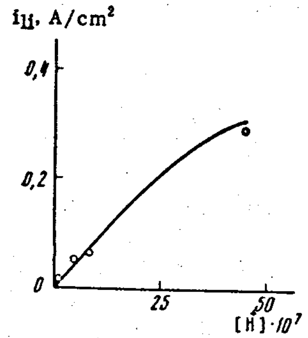

Fig. 3. Variation of the limiting current for the evolution of hydrogen i_{li} with the H^+ concentration on an amalgamated copper electrode in 1.1 M butyrate buffer solution. The solid line represents the values of the limiting kinetic currents and the dots represent the experimental data.

rpm (rate of the liquid stream 130–780 cm/sec). The test electrode 2 was in the form of a wire of diameter 0.5 mm (with a surface of around 0.1 cm^2) with a Luggin capillary 3 pressed against it at a distance of 2–3 mm from the end of the stirrer blade. A Pt anode 4 with a surface of around 2 cm^2 was placed in the tube and separated from the cathode area by a glass filter 5.

All the salts used were crystallized twice from doubly distilled water and the acids were distilled twice. The butyrate solutions were prepared from butyric acid by neutralization with tetramethylammonium hydroxide $N(CH_3)_4OH$ which was obtained by the action of freshly precipitated Ag_2O (5% excess) on twice crystallized $N(CH_3)_4I$. In the preparation of concentrated solutions the reaction was carried out with the solid iodide and a small volume of water so that the basic part of the $N(CH_3)_4OH$ was obtained in the form of a precipitate which was then dissolved in the stoichiometric quantity of butyric acid.

The overvoltage measurements were carried out in solutions which had been previously purified by electrolysis for 8–10 h on an auxiliary copper cathode with a large surface and with energetic stirring in order to ensure complete extraction of metallic impurities, in particular, silver. The solutions were also submitted to adsorption purification on platinized platinum with saturation of the solutions by hydrogen.

Preparation of the electrodes is described in [7] (Ag) and [8] (Ga); the copper electrode was dipped in HNO_3 (1:1) then washed with doubly distilled water; it was amalgamated by immersion in a solution of $Hg(NO_3)_2$.

In all the system which we studied we observed limiting currents, the values of which were investigated with variation in the rate of mixing of the solution, concentration of the buffer, and pH. The pH was varied with small additions of H_2SO_4 and the concentration of the buffer with a dilute solution of Na_2SO_4 of the same ionic strength. As an example, Fig. 2 shows typical i, φ curves for a silver electrode. It may be seen that, starting with a particular stirring rate, the current remains constant within the error limits of the experiment, which indicates the complete removal of diffusion limitations by the buffer (from now on this value will be denoted by i_{li}).

The lower branch of the i, φ curve corresponds to discharge of H^+ ions (since the electrode potential relative to the constant reference electrode falls by 120 mV for a pH drop of unity) and the upper branch of the curve (after the limiting current) corresponds to the discharge of water (the electrode potential is practically independent of pH).

Figures 3 and 4 show the variations in the limiting currents i_{li} with the concentration of hydrogen ions in the solution for an amalgamated copper electrode in butyrate and for a silver electrode in acetate buffer solutions.

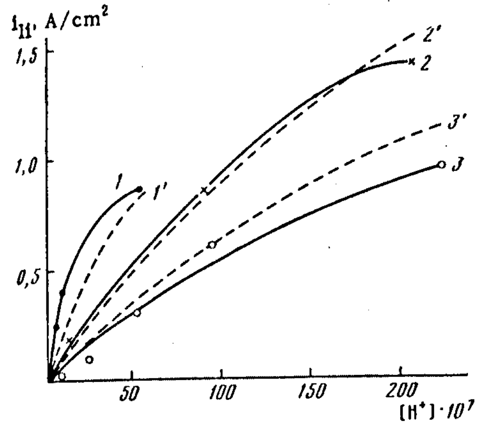

Fig. 4. Variation of i_{li} with H$^+$ concentration on a silver electrode in acetate buffer solution. Buffer concentration: 1) 5; 2) 2; 3) 1 M. The dotted lines represent the values of the limiting kinetic currents (1'-3') and the points represent the experimental data.

Similar results were also obtained for the other systems which we investigated. It turned out that i_{li} increases with increase in the buffer concentration and that the variation of i_{li} with c_{H^+} is not linear at a constant buffer concentration, i.e., the picture does not correspond to the regularities of an activationless process. For this reason the values of i_{li} were compared with the calculated values of the limiting kinetic currents i_K of the dissociation of a weak acid for the same solutions (i_K values shown dotted). The values of i_K were found from the equation [9]

$$i_{\text{к}} = F\cdot 10^{-3}\sqrt{k_d D_{\text{H}^+} c_{\text{H}^+} c_{\text{HA}}}.$$

Here k_d is the dissociation rate constant for the acid in sec^{-1} ($k_d = k_a k_r$ where k_r is the recombination rate constant and k_a is the equilibrium dissociation constant); D_{H^+} is the diffusion coefficient of the H$^+$ ions in solution in cm^2/sec (taken as equal to $3\cdot 10^{-5}$; c_{H^+} and c_{HA} are the corresponding concentrations. In the calculation the following values of parameters were used: butyric acid $k_a = 1.5\cdot 10^{-5}$; $k_r = 2\cdot 10^{10}$; acetic acid $k_a = 1.75\cdot 10^{-5}$; $k_r = 2\cdot 10^{10}$; $H_2PO_4^-$ $k_a = 3\cdot 10^{-7}$; $k_r = 3\cdot 10^{11}$. From the data presented in Figs. 3 and 4 it is seen that the nature of the change in experimental i_{li} and calculated i_K with hydrogen ion concentration and buffer concentration is the same. The absolute values of the experimental and calculated currents are also sufficiently close to one another, especially if we take into account the approximate nature of the calculation and also the divergence in the values for the rate constants determined by different methods and their dependence on the ionic strength of the solution (see, for example, [11-14]).

Thus, the limiting currents obtained in different buffer solutions on different electrodes (Cu, amalgamated Cu, Ga, Ag) are not the currents of the activationless discharge of H$^+$ ions, but are limiting kinetic currents. Consequently, the currents of activationless discharge of H$^+$ ions are greater than the i_{li} which we found. For this reason we can only estimate the lower boundary of the limiting activationless currents. Thus, for example, on silver in 5 M acetate buffer solution i_{li} is approximately (2-5) · 10^5 A/cm^2 after conversion to a 1 M concentration of H$^+$ ions (Fig. 4); this means that the activationless discharge current is greater than (2-5) · 10^5 A/cm^2 (correspondingly, the ideal pre-exponential factor K has a value greater than (2-5) · 10^5 A · liter/cm^2 · mole).

From the temperature relationship of the hydrogen overvoltage on silver (in the low η range) it is found that the real preexponent K' is around 10^0-10$^{1.2}$ liter · A/cm^2 · mole [3]. If from this we make an approximate calculation of the value of the ideal preexponential factor (taking the temperature coefficient of the change in potential of the hydrogen electrode as around 0.7 mV/deg [1b, 15]), we obtain a value for the ideal preexponent of around 10$^{1.8}$-10$^{3.0}$ A · liter/cm^2 · mole, i.e., a factor of 10^2-10^3 less than the lower limit which we found.

A similar, although not so sharply expressed, divergence is also seen in an analysis of Nürnberg's data [16]. On mercury under strongly negative potentials he observed no violation of the Tafel relationship up to 5 · 10^5 A · liter/cm^2 · mole (with a greater experimental error, up to 3 · 10^6 A · liter/cm^2 · mole). These values are also somewhat higher than the values of the preexponential factor determined from the temperature-dependence data at lower overvoltages: K' ≃ 10$^{3.3}$-10$^{4.0}$ [2, 17, 18] (estimate K = 10$^{5.1}$-10$^{5.8}$ A · liter/cm^2 · mole). The most probable explanation of this divergence is the assumption that the preexponent changes sufficiently with the potential (in an interval of around 1 V on silver it changes by not less than a factor of 10^2-10^3 times). Such an explanation is in good agreement with the fact that in acid solutions the separation factor of the hydrogen isotopes decreases with increase in potential [4]. The growth of the preexponential factor may be explained by easier tunneling of protons which is caused by attraction of the hydroxyl ion to the electrode. The easier tunneling decreases the difference in the rates of discharge of the light and heavy isotopes, i.e., decreases their separation factor.

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