participate. The adsorption of iodide will change the rate of this reaction on account of a strength of the Me–OH bond; however, it does not affect the isotopic effect, since the distance between adsorption centers is inconstant.

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MECHANISM OF THE FORMATION OF AN ANODIC FILM OF $Fe(OH)_2$ ON IRON IN ALKALINE SOLUTIONS

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During the first anodic process on an iron electrode in solutions of alkali, the basic reaction product is $Fe(OH)_2$, deposited in the form of a film on the electrode [1, 2]. The increase in the film thickness at constant potential obeys a parabolic law, which can be explained by the occurrence of a process of slow nonsteady-state diffusion of Fe^{2+} ions through the film to its boundary with its solution. A consequence of the parabolic law of growth is a direct proportionality of the limiting current of the reaction to the reciprocal of the square root of the time ($i = kt^{-1/2}$). The slope of the i versus $t^{-1/2}$ straight lines characterizes the value of the ionic conductivity of the $Fe(OH)_2$ film formed [3].

In [4] it was suggested that the main factor in the process is the overcoming of the energy barrier by the Fe^{2+} ion under the action of the applied potential and the escape of these ions from the lattice of $Fe(OH)_2$ into the interstices, followed by their movement under the action of the established potential and concentration gradients along the vacancies and defects to the boundary of the film with the solution [5]. From this picture it follows that the presence of additions of certain anions in alkali, as well as an increase in the alkali concentration, lead to adsorption of anions and OH^- ions at the lattice points. The supplementary negative charge created by them, surrounding the Fe^{2+} ion in the lattice, facilitates the escape of the latter into interstices, leading to an increase in the ionic conductivity of the film and the limiting current of the anodic reaction. Additions of Ca^{2+}, Mg^{2+}, and other cations act in the opposite direction, lowering the ionic conductivity of the $Fe(OH)_2$ film.

In this work we studied the influence of temperature on the limiting currents of the formation of $Fe(OH)_2$ on the time at a constant potential of -0.86 V (HgO) on a smooth electrode of zone-melted iron. The electrolytes were freshly prepared solutions of KOH, purified by cathodic polarization on a platinum mesh for 2 h. The salts used for the additives were subjected to double recrystallization. Before the experiment the electrodes were thoroughly freed of oxide films by polishing with fine glass powder, etching in 1N H_2SO_4, and cathodic polarization with a current of 10^{-2} A/cm^2 in the working solution. Thermostatic control of the cell was performed with an accuracy of ± 1°C with an ultrathermostat. The experiements were conducted in an atmosphere of argon. The potentials at various experimental temperatures were measured relative to a mercury oxide reference electrode, with the same KOH concentration as the investigated solution, and kept at a constant temperature of 17°C. The values of the limiting currents on various samples of electrodes under the same conditions might differ substantially; however, on each individual electrode the reproducibility of the experiments at all the investigated temperatures was about 5%.

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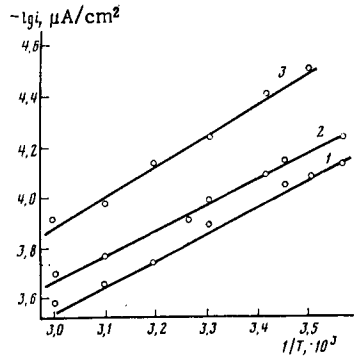

Fig. 1

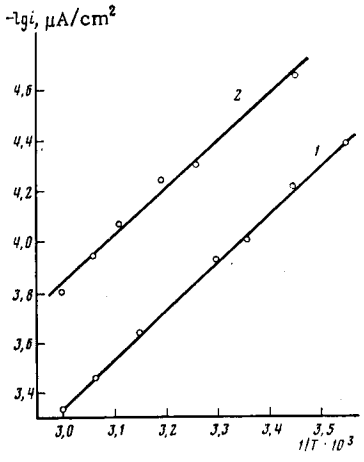

Fig. 2

Fig. 1. Dependence of −log i on 1/T in solutions of KOH: 1) 10; 2) 5; 3) 1N.

Fig. 2. Dependence of −log i on 1/T in a solution of 1N KOH with additives: 1) $Mg(OH)_2$ (sat.); 2) 0.01N CsCl.

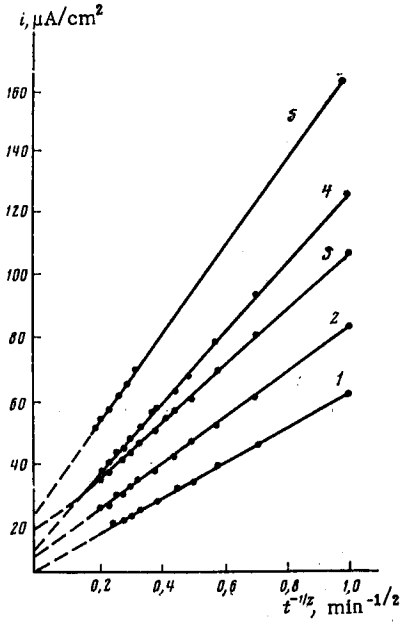

Fig. 3

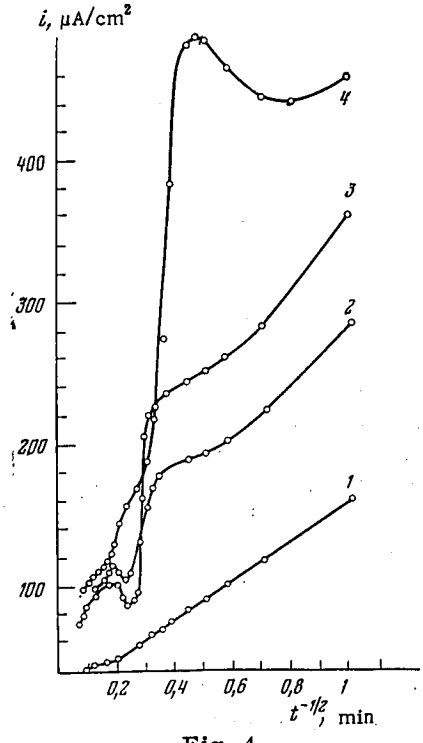

Fig. 4

Fig. 3. Dependences of i versus $t^{-1/2}$ in 1N KOH + 10^{-3}M Na_2SiO_3 at temperatures (°C): 1) 20; 2) 30; 3) 40; 4) 50; 5) 63.

Fig. 4. Dependences of i versus $t^{-1/2}$ in 1N KOH + 10^{-4}M $Na_2S_2O_3$ at temperatures (°C): 1) 17; 2) 30; 3) 40; 4) 50.

In pure solutions of KOH, as was shown in [4], the dependences of i on $t^{-1/2}$, calculated from the experimental data, are expressed by straight lines leading to the origin when extrapolated to $t \to \infty$. The same dependence is observed at all temperatures from 7 to 70°C in solutions of 1.5 and 10N KOH. Figure 1 presents the dependences of the logarithms of the slopes of these straight lines, corresponding to the values of the cur-

rent density at t = 1 min, on the receiprocal of the absolute temperature. From these dependences, the values of the apparent activation energies (A) were calculated according to the Arrhenius equation log i = B + (A/2.3 RT); they were equal to 5.7 kcal/mole in 1N KOH and 5.0 kcal/mole in 5 and 10 N KOH.

The introduction of an addition of $Mg(OH)_2$, saturated at 17°C, or 0.01N CsCl into a 1N solution of KOH led to a decrease in the slope of the i versus $t^{-1/2}$ straight lines at the temperature 17°C, 14 and 25 $\mu A/cm^2$, respectively. The activation energies of the growth of the film, calculated with the aid of Fig. 2, are 8.5 kcal/mole in the presence of the Mg^{2+} cation and 9.0 kcal/mole in the presence of Cs^+. The influence of the Cl^- ion, present in a solution of 1N KOH + 0.01 N CsCl, was verified in individual experiments in a solution of 1N KOH + 0.01N KCl. The deviations in the values of the limiting currents in this solution and in a solution of pure alkali, 1N KOH, were within the limits of reproducibility of the experiments.

Figure 3 presents the dependences of i on $t^{-1/2}$ for a solution of 1N KOH + 10^{-3}M Na_2SiO_3. The presence of certain anions, as was shown in [4], somewhat changes the nature of the dependence of i on $t^{-1/2}$. The changes consist in the fact that the straight lines i versus $t^{-1/2}$ do not lead upon extrapolation to the origin, intercepting a certain segment on the y axis, probably corresponding to the oxidation current, not associated with diffusion of Fe^{2+} ions through the $Fe(OH)_2$ film. Increasing the experimental temperature increases this current. From the dependences of the logarithms of the slope $\Delta i/\Delta t^{-1/2}$ on 1/t we determined the activation energy of the process in 1N KOH, containing 10^{-3}M $NaSiO_3$, equal to 4.5 kcal/mole.

The appearance of a "nondiffusion" current in the presence of additions of SiO_3^{2-} and S^{2-} anions is probably associated with the formation of a more defective $Fe(OH)_2$ film, as a result of their adsorption on the electrode surface. With increased experimental temperature in a solution of 1 N KOH + 10^{-4}M $Na_2S_2O_3$ (Fig. 4), the smooth decrease in the current with time is disrupted, which is evidently associated with partial peeling off of the film and the flow of solution between the film and electrode.

The values of the calculated activation energies of the formation of a $Fe(OH)_2$ film in the presence of additions of anions and cations confirm the mechanism of the process suggested above. The introduction of cations into the electrolyte leads to their adsorption at the lattice points. During growth of the film, they are incorporated into the film structure. By creating a relative excess of positive charge, surrounding the Fe^{2+} ion in the lattice, the impurity cations inhibit the transfer of the Fe^{2+} ion to the interstices, increasing the activation energy of the process. The concentration of current carriers of the Fe^{2+} in the interstices is lowered which leads to a decrease in the ionic conductivity of the film and a decrease in the limiting anodic current. In the case of an addition of anions, their adsorption decreases the activation energy of the escape of Fe^{2+} ions from the lattice as a result of the appearance of a supplementary negative electric field around the Fe^{2+} cations in the lattice. This increases the concentration of Fe^{2+} in the interstices and, consequently, the current in the anodic reaction.

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