THE MECHANISM OF THE REACTION Fe(II) ⇌ Fe(III) IN KOH SOLUTIONS

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Measurements made using direct current [1] showed that the electrochemical reaction

$$Fe(OH)_2 + OH^- \rightleftarrows Fe(OH)_3 + e^- \tag{I}$$

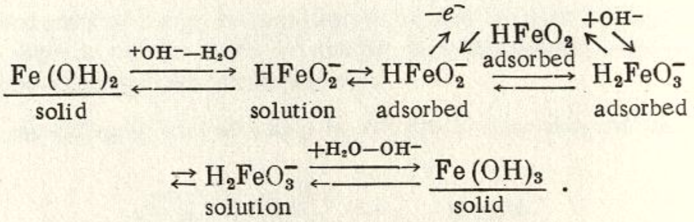
takes place without significant overvoltage, but is complicated by spontaneous processes of dehydration and crystallization of Fe(III), as a result of which the electrode potential is displaced towards more negative values, and the process

$$Fe(OH)_2 + OH^- \rightleftarrows \delta\text{-}FeOOH + H_2O + e^-, \tag{II}$$

which also takes place without significant overvoltage, begins.

In order to investigate further the mechanism of the reaction Fe(II) ⇌ Fe(III) in alkaline solutions, measurements were made of the impedance of an iron electrode–alkali solution boundary at alternating current frequencies from 10 kHz to 0.11 kHz under conditions in which the reaction Fe(II) ⇌ Fe(III) takes place at the electrode. In order to select an electrical scheme equivalent to the electrochemical system being studied, the experimentally determined frequency dependence of the components of the impedance of the iron electrode was compared with the calculated frequency dependence of probable electrical schemes.

Reaction (I) can be represented as taking place, for example, in the following stages:



$$\underset{\text{solid}}{\underline{Fe(OH)_2}} \underset{\longleftarrow}{\xrightarrow{+OH^- - H_2O}} \underset{\text{solution}}{HFeO_2^-} \rightleftarrows \underset{\text{adsorbed}}{HFeO_2^-} \underset{\longleftarrow}{\xrightarrow{\text{adsorbed}}} \underset{\text{adsorbed}}{H_2FeO_3^-}$$

$$\overset{-e^-}{\nearrow\swarrow}\ HFeO_2\ \overset{+OH^-}{\nwarrow\searrow}$$

$$\rightleftarrows \underset{\text{solution}}{H_2FeO_3^-} \underset{\longleftarrow}{\xrightarrow{+H_2O - OH^-}} \underset{\text{solid}}{\underline{Fe(OH)_3}}\ .$$

A possible electrical equivalent of the electrode–electrolyte boundary under the conditions of this process is Scheme A (Fig. 1),* where C_{dl} is the capacity of the double layer, R_{dis} a resistance characterizing the rate of electrochemical discharge, R_k and C_k are the active and reactive components of the input impedance $\dot{Z}$ and the semi-infinite RC-line characterizing diffusion processes [2] ($\dot{Z} = A/\sqrt{\omega} - jA/\sqrt{\omega}$, where A is a constant whose value depends on the diffusion coefficient and the concentration of diffusing species), C_a is a capacity characterizing the adsorption of ions or intermediate products on the electrode, and R_{des} is the resistance of desorption. Since graphical analysis of this complex scheme is difficult, we analyzed simpler schemes, which should be equivalent to the electrochemical system being studied in different frequency ranges, if Scheme A is an electrical equivalent throughout the entire range.

We analyzed Schemes B, C, D, E, F, and G, and showed by graphical analysis (Fig. 2) [3] that in 2 N KOH the resistance R_{dis} is negligibly small and that the resistance R_{des} at frequencies greater than 1 kHz can be neglected compared with the impedance of the element C_a, so that Scheme F is applicable in this range of frequencies. At lower frequencies the resistance R_{des} cannot be neglected, and in the range of frequencies from 0.8 to 0.21 kHz,

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*A resistance equivalent to the resistance of the solution is not indicated in the schemes.

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TABLE 1. Elements of the Equivalent Scheme for Reaction (I)

t, °C	KOH concentration, N	Range of equivalence of scheme F, kHz	Constant A, $\Omega\cdot cm^2/sec^{1/2}$ from the relationship		C_a from relationship $1/C' - \Omega^{1/2}$, $\mu F/cm^2$	Range of equivalence of scheme G, kHz	C_a and R_{des}, calculated for a number of frequency pairs			Value of the diffusion impedance and adsorption impedance, $\Omega\cdot cm^2$		
			$R' - \omega^{1/2}$	$1/C' - \omega^{1/2}$			Frequency pair, kHz	C_a, $\mu F/cm^2$	R_{des}, $\Omega\cdot cm^2$	Frequency, kHz	$\frac{1}{\omega C_a}$	Diffusion impedance
1	2	3	4	5	6	7	8	9	10	11	12	13
20	2	7 to 1	240	230	150	0,8 to 0,21	0,41 - 0,8	166	17	7	0,14	1,6
							0,31 - 0,61	159	14	0,8	1,2	4,6
							0,21 - 0,41	162	15	0,41	2,4	6,5
							Means	162	15	0,21	4,7	9
	10	7 to 0,61	110	110	290	0,61 to 0,11	0,31 - 0,61	272	15	7	0,08	0,7
							0,16 – 0,41	280	18	0,61	0,9	2,5
							0,11 - 0,31	280	17	0,41	1,35	3,0
							Means	277	17	0,11	5	5,8
80	2	10 to 0,21	22	24	—	—	—	—	—	10	—	0,13
										2		0,29
										0,61		0,52
										0,21		0,89
	10	10 to 0,8	8	9	2000	—	—	—	—	10	0,008	0,05
										2	0,04	0,1
										0,8	0,1	0,17

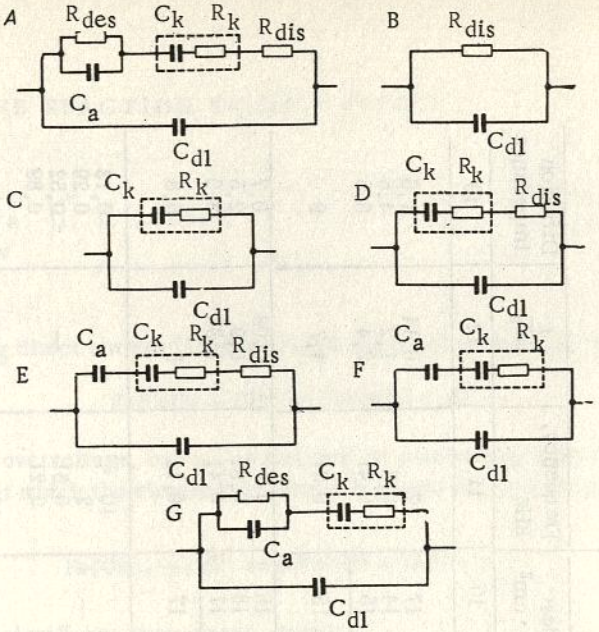

Fig. 1. Possible electrical equivalent schemes for the iron–alkali boundary while the process Fe (II) ⇌ Fe (III) is taking place at the boundary.

Scheme G is an electrical equivalent. This was demonstrated analytically, as in [3]. An important feature is that the analytically determined value of C_a in the range of frequencies from 0.8 kHz to 0.21 kHz, in which Scheme G is applicable, coincides with the graphically determined value of C_a in the range of frequencies from 7 kHz to 1 kHz, in which Scheme F is applicable, with an accuracy of 7-8%, confirming the applicability of Schemes F and G.

The values of A, C_a, and R_{des}, determined in typical experiments for 2 N and 10 N KOH at temperatures of 20 and 80°C are given in Table 1. It can be seen from the table that R_{des} and C_a are independent of frequency (columns 8, 9, and 10 in Table 1). These values can be calculated while the value of R_{des} is comparable with the impedance of adsorption $1/\omega C_a$ (column 12 in Table 1). At a frequency of 0.8 kHz the impedance of adsorption becomes smaller than the value of R_{des} by a factor of approximately 13, as a result of which, in the range of higher frequencies, the process being studied should be equivalent to the simpler Scheme F, as confirmed experimentally. This is in agreement with the fact that the linear dependence of R' on $1/\sqrt{\omega}$, characteristic of Scheme F, is broken down and the curve bends towards the axis of ordinates (Fig. 2a) as soon as the impedance of adsorption ($1/\omega C_a$), with decrease in frequency, becomes comparable with R_{des}. In this range of frequencies the electrical equivalent of the boundary being studied, as noted above, is Scheme G. It has thus been shown that the process $Fe(OH)_2 \rightleftharpoons Fe(OH)_3$ is accompanied by adsorption of the reaction product on the electrode, and the adsorption capacity (150 $\mu F/cm^2$ in 2 N KOH and 300 $\mu F/cm^2$ in 10 N KOH) and the rate of adsorption–desorption (15 $\Omega \cdot cm^2$) have been determined.

The suggestion put forward earlier [1] regarding the low overvoltage of Reaction (I) has been confirmed, since the resistance characterizing the rate of discharge (R_{dis}) in Scheme A is negligibly small in all cases; for example, for 2 N KOH R_{dis} is less than $5 \cdot 10^{-2}\ \Omega \cdot cm^2$, i.e., the exchange current is greater than $5 \cdot 10^{-2}\ A/cm^2$, calculated on the true surface area.

Moreover, it follows from the data given in Table 1 that the kinetics of process (I) in concentrated alkalies (2 N and above) is determined by the diffusion of iron ions in the solution. This conclusion was reached on the basis of an analysis of the dependence of the coefficient A on the concentration of diffusion ions and their diffusion coefficients. The constant A for the redox reaction close to equilibrium is given by the formula [4]:

$$A = \frac{RT}{n^2F^2\sqrt{2}}\left(\frac{1}{c_O\sqrt{D_O}} + \frac{1}{c_R\sqrt{D_R}}\right). \tag{1}$$

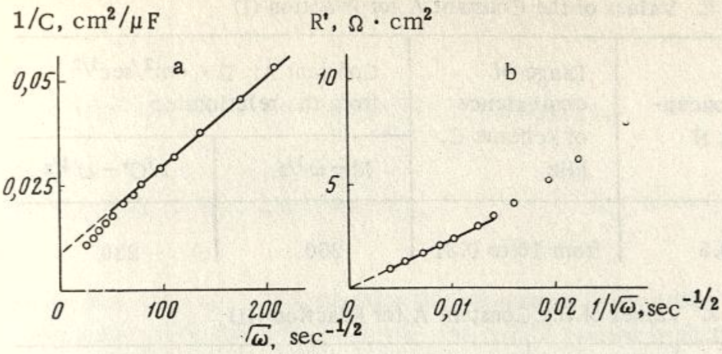

Fig. 2. Components of the impedance of the process $Fe(OH)_2 \rightleftharpoons Fe(OH)_3$ in 2 N KOH at temperature of 20°C.

It may be assumed that with change in the concentration of alkali the diffusion coefficients of the Fe (II) and Fe (III) ions undergo identical changes. If it is assumed that the solubility of $Fe(OH)_3$, and that of $Fe(OH)_2$, are proportional to the concentration of alkali [5], it follows that with change in the concentration of alkali the two quantities $c_0\sqrt{D_0}$ and $c_R\sqrt{D_R}$ in the saturated solution undergo equal changes. Thus in order to prove that the slow stage of Reaction (I) is diffusion in the solution, it is sufficient to show that A changes with change in the concentration of alkali and temperature in accordance with the change in the variables of one of the terms of Eq. (1) with change in the same parameters.

In concentrated solutions the chief factor bringing about a change in the diffusion coefficient D is the change in viscosity. The viscosity of 10 N KOH solution at 20° is greater than the viscosity of 2 N KOH solution by a factor of approximately 3.25,* i.e., the value of $\sqrt{D}$ in 10 N KOH is smaller than that in 2 N KOH by a factor of 1.8. Since the solubility of iron oxides in alkali is directly proportional to its concentration, their solubility in 10 N KOH is greater than that in 2 N KOH by a factor of 5. If it is assumed that the concentration of oxides is proportional to their solubility, it follows that on going from 2 N KOH to 10 N KOH the coefficient A, according to (1), should change by a factor of approximately 2.5, as is observed experimentally. The dependence of A on the concentration of dissolved oxides is equally satisfactory in 10 N KOH at temperatures of 20°C [5] and 80°C [8] with allowance for the change in the viscosity of the alkali with change in temperature.

On the basis of our data, it is possible to calculate approximately the diffusion coefficient of the $H_2FeO_3^-$ ion in 2 N KOH at 20°C. It can be seen from the curves given in [1] that the limiting current for the anodic process is several times greater than the limiting current for the cathodic process, indicating that divalent iron has a higher solubility than trivalent iron. Moreover, under the conditions of the cathodic process, when divalent iron is formed, it can give a supersaturated solution, and this further increases the concentration of divalent iron relative to trivalent iron. Thus in Formula (1) we can neglect one term and write the following expression for A:

$$A = \frac{RT}{n^2F^2\sqrt{2}\sqrt{D}} \cdot \frac{1}{c_0}, \tag{2}$$

where c_0 is the concentration of $H_2FeO_3^-$ in solution. The limiting current for the cathodic process is known [1], so that we can express c_0 in terms of the limiting current,

$$c_0 = \frac{\delta \cdot i_d}{nFD}$$

and use Eq. (2) to calculate the diffusion coefficient of the $H_2FeO_3^-$ ion:†

$$D = \left(\frac{A \cdot \delta \cdot i_d\sqrt{2}}{RT/nF}\right)^2 = \left(\frac{235 \cdot 3 \cdot 10^{-2} \cdot 6 \cdot 10^{-6}\sqrt{2}}{0.025}\right) \simeq 6 \cdot 10^{-6}\ \text{cm}^2/\text{sec}.$$

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* The data on the viscosity of KOH solutions were taken from [6, 7].

† The value of δ was taken as $3 \cdot 10^{-2}$ cm, with the assumption that under the conditions of our experiments there is practically no mechanical mixing and that natural convection takes place.

TABLE 2. Values of the Constant A for Reaction (I)

KOH concentration, N	Range of equivalence of Scheme C, kHz	Constant A, $\Omega \cdot cm^2/sec^{1/2}$ from the relationship	
		$R' - \omega^{1/2}$	$1/C' - \omega^{1/2}$
0.5	from 10 to 0.31	260	230

TABLE 3. Values of the Constant A for Reaction (II)

Temp., deg C	KOH concentration, N	Range of equivalence of Scheme C, kHz	Constant A, $\Omega \cdot cm^2/sec^{1/2}$ from the relationship	
			$R' - \omega^{1/2}$	$1/C' - \omega^{1/2}$
20	2	from 10 to 0.41	140	130
	10	from 20 to 0.21	70	65
80	2	from 7 to 0.41	23	24

The value obtained for the diffusion coefficient is close to the value of the diffusion coefficient of zinc ions in 2 N alkali [9]. Experiments carried out in more dilute alkali solutions (0.5 N KOH) at 20°C showed that under these conditions the simplest Scheme C is applicable, the coefficient A in the concentration range 2-0.5 N being now practically independent of the alkali concentration (Tables 1 and 2). From this it follows that in alkalies with concentrations less than 2 N, in which the solubility of iron oxides is smaller, the rate of the process $Fe(OH)_2 \rightleftharpoons Fe(OH)_3$ is possibly determined by the diffusion of the components of the reaction through the solid oxides.

For Process (II), analysis of the frequency dependence of the impedance of the electrode again gives as electrical equivalent the simplest Scheme C, since the coefficient A depends on the concentration of iron ions in the solution, but its increase with decrease in temperature and alkali concentration is less than that for Process (I) (Table 3).

This indicates that for Reaction (II) the rate of the process is again limited by the diffusion of $HFeO_2^-$ ions in the solution, but at the same time Process (II) is possible in the solid phase, as suggested in [10, 11], for the chemical oxidation of $Fe(OH)_2$ to δ-FeOOH. It should be noted that the authors of [10, 11], unlike us, were unable, because of the conditions of the method, to detect the primary formation of $Fe(OH)_3$ in the oxidation of $Fe(OH)_2$.

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