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Abstract

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On the Calculation of Electrochemical Reactions with an Intermediate Reagent

(Presented by Academician A. N. Frumkin, 11 IV 1958)

Among the multitude of electrochemical processes there is a significant group for which it is most expedient to observe the course of the process not only by the current density, but also by the change with time in the concentration of the reacting compounds. Such cases include the electroextraction of metals, anodic oxidation and cathodic reduction of ions of variable valence, reactions of organic electrosynthesis, etc. Processes of this type can be calculated on the basis of combining the kinetics of electrode reactions with the differential equations of chemical kinetics.

For our study we chose both the special case of a direct electrode process and the more general case in which the oxidation or reduction of the selected compound (depolarizer) occurs in the presence, in the electrolyte, of an intermediate reagent. In the latter case, for example for anodic oxidation, the two parallel paths of the process may be represented by the scheme:

1) $K - e \to K^+$ (at the electrode);
2) $B - e \to B^+$ (at the electrode) and $B^+ + K \to K^+ + B$ (in the diffusion layer and in the bulk of the electrolyte).

Here K is the principal depolarizer and B is the intermediate reagent. Such systems are of great importance in electrochemical technology, and are also of interest from the standpoint of the possibility of accelerating a number of slowly proceeding electrochemical reactions.

The action of intermediate reagents or carriers was considered in papers (1–5), and especially in (6–9), and in other works on the kinetics of electrode processes in combination with chemical reactions in solution. In contrast to most of these works, we set ourselves the task, proceeding from the scheme indicated above, of giving calculation equations for the rate of the process and of checking their correctness on particular systems at solid electrodes under steady-state process conditions.

Let us suppose that the selected depolarizer is in a solution in which there is no intermediate reagent. In this case, if the volume of the diffusion layer is considerably smaller than the total volume of the electrolyte v, then the decrease in the concentration of the depolarizer with time must obey the differential equation:

$$-v\,dC = \frac{SD}{nF}\,dt, \tag{1}$$

where S is the electrode surface, n is the change in valence during electrolysis, D is the current density, C is the concentration, and t is the time in seconds.

In the general case, when the rate of the electrode process is determined both by the discharge stage and by diffusion of the depolarizer to the electrode, the dependence of the current density on the potential for stationary conditions, according to A. N. Frumkin, is given by the equation:

$$D = k_1 \exp \frac{\pm\alpha(\varphi - \psi_1)nF - \psi_1 ZF}{RT}\, C\left(1 - \frac{D}{D_{\mathrm{pr}}}\right), \tag{2}$$

where k_1 is the discharge rate constant, C and Z are the concentration and valence of the depolarizer, $D_{\mathrm{pr}} = k_d C$ is the limiting diffusion current. The signs $+$ and $-$,

standing before the first term of the exponent refer, respectively, to the anodic and cathodic processes.

Substituting the value D, determined from relation (2), into equation (1) and integrating for constant φ and T, we finally obtain

$$\ln\frac{C_0}{C} = \frac{S}{\nu nF}\left\{\frac{k\ \cdot k_1 \exp\frac{\pm\alpha(\varphi-\psi_1)nF-z\psi_1 F}{RT}}{k\ + k_1 \exp\frac{\pm\alpha(\varphi-\psi_1)nF-z\psi_1 F}{RT}}\right\} t \tag{3}$$

or

$$\ln\frac{C_0}{C} = mt, \tag{3a}$$

where C_0 is the initial concentration of the depolarizer. For purely diffusion kinetics $m = Sk\ /\nu nF$.

If, however, discharge is the slowest stage, then in equation (3a)

$$m = \frac{S}{\nu nF}\,\Phi(\varphi).$$

Here the particular value of the function $\Phi(\varphi)$, in accordance with (3), is determined by the exchange current and by the magnitudes of the φ and ψ_1 potentials. Equation (3) is readily transformed to the form:

$$\ln \frac{i_0}{i} = \frac{i_0}{\nu n F C_0}\, t, \tag{4}$$

obtained by Gilbert and Rideal (^{10}) and later by Stromberg (^{11}) in studies on polarographic coulometry. Here i_0 is the initial value of the current. It follows from equation (3) that complete oxidation or reduction is unattainable here, owing to the decrease of the current with decreasing concentration. Even the use of such a reserve as increasing the potential ultimately leads only to the appearance of limitations of a diffusion character.

The indicated shortcoming is easily removed by introducing an intermediate reagent. The general kinetic equation in this case will have the form:

$$-dC = \frac{S}{\nu n F}\,(D\ + D\ )\, dt, \tag{5}$$

where D and D are the current densities expended, respectively, on the direct electrode reaction with the depolarizer and through the intermediate reagent.

Taking into account that for constant φ and T the quantity $D = kC$, and integrating with the boundary conditions $t = 0,\ C = C_0;\ b$, we obtain

$$\ln \frac{b + a}{C + a} = \frac{i_0}{\nu n F C_0}\, t, \tag{6}$$

where $a = D\ /k$. The fraction $a/c = D\ /D$ characterizes the relative increase in the rate of the process due to the carrier. a is a function of the concentration of the intermediate reagent, the potential, the temperature, and the hydrodynamic regime. In (6), as before, the quantity $m = i_0/\nu n F C_0$ depends on the ratio of the discharge current of the depolarizer (i_0) to its concentration (C_0). Dependence (6) is an equation of fractional, variable order. It is characteristic that the larger a is in comparison with C_0, the smaller the actual order of the reaction and the greater its rate. In the general case, when the rate of both parallel reactions is determined by the potential, the values φ and ψ_1 enter both into the function under the logarithm and into the magnitude m.

Since, when the principal depolarizer and the carrier are simultaneously present in solution, the current is $I = Sk(c + a)$, then, by analogy with (4),

$$\ln \frac{I_0}{I} = \frac{i_0}{\nu n F C_0}\, t. \tag{7}$$

It is interesting that the dependences of C on t according to equations (3a) and (6) have the same form. The introduction of an intermediate oxidizer here acts equi-

Fig. 1

Figure 1: Fig. 1

is equivalent to increasing the total concentration, shifting the reaction into the initial, most favorable region. From (6) it follows that by the time

$$\tau = \frac{vnFC_0}{i_0} \ln\left(1 + \frac{b}{a}\right) \tag{8}$$

the concentration C will decrease to zero. We shall call τ the time of complete completion of electrolysis*.

From the dependence of τ on the experimental conditions one can draw a number of conclusions also concerning the features of the electrochemical behavior of the intermediate reagent. At the same time, the quantity τ should prove to be an important applied characteristic of the process.

The equations proposed above have been tested by us on a number of oxidation-reduction reactions. Fig. 1 gives data on the oxidation of $FeSO_4$ in pure H_2SO_4 solutions and in H_2SO_4 solutions containing NaCl. The experiments were carried out at 25°. The value of the anodic potential varied from 1.40 to 1.47 V.

Fig. 1. Effect of NaCl on the rate of anodic oxidation of Fe^{2+} on platinum. Electrolyte composition: 0.22 M $FeSO_4$, 1 N H_2SO_4. Temperature 25°. 1 – without NaCl, 2 –0.5 N NaCl, 3 –1 N NaCl, 4 –2 N NaCl, 5 –0.5 N NaCl

Curve 1, characterizing the dependence of the Fe^{2+} concentration on time when the reaction is carried out in the absence of an intermediate reagent, proceeds very gently. To achieve 99% oxidation of the iron in this case it is necessary to spend more than 70 hours. On the same figure are plotted the curves $C(t)$ for solutions containing sodium chloride. All of them are much steeper and have no asymptotic course with respect to the time axis. Thus, for 100% oxidation of iron during electrolysis in a solution containing 0.5 N NaCl at $\varphi = 1.47$ V, only 5.5 hours are required, i.e., almost 12 times less than in the absence of NaCl. On the same graph (curve 5) a recalculation of the experimental data according to the dependence

$$C_{Fe^{3+}} = b - c = (a + b)(1 - e^{-mt}), \tag{9}$$

obtained from equation (6), is given. The value $m = 1.73 \cdot 10^{-5}$ was taken here from experiments on anodic oxidation in the absence of NaCl in the electrolyte. The corresponding calculated value of m from the limiting current ($m = i_0/vnFC_0$) under the same conditions is $1.86 \cdot 10^{-5}$.

As can be seen, in the coordinates $C_{Fe^{3+}}/(1 - e^{-mt})$ a straight line is obtained with a slope coefficient equal to 0.85. The value of the sum $a+b$ calculated on the basis of the current ratio was 0.80. The results of recalculating the experimental data on the oxidation of iron ions under different conditions are given in Table 1. The values were calculated from the magnitudes of the currents. In all cases good agreement with equation (6) was observed, as follows from the constancy of the coefficient m.

In Fig. 2 are presented the curves for the reduction of Fe^{3+} in pure H_2SO_4 solutions and in the presence, as an intermediate reagent, of tetravalent titanium sulfate. The experiments were carried out at $\varphi = -0.6$ V, which corresponded to attainment of the limiting diffusion currents both for Fe^{3+} ions and for Ti^{4+}. The values of a were calculated from the magnitudes of the currents. In co-

Table 1

Anodic oxidation of Fe^{2+}. Electrolyte volume 100 cm^3. Anode –smooth platinum ($S = 10$ cm^2), temperature 25°. Electrolysis with a diaphragm, without stirring. Values of the constants in the equation $\ln \frac{b+a}{c+a} = mt$

No.	Electrolyte composition, mol/l	Electrolyte composition, mol/l	Electrolyte composition, mol/l	φ, V	Constants	Constants	Constants
No.	Fe^{++}	NaCl	1/2 H_2SO_4	φ, V	a	$b+a$	$m \cdot 10^{-5}$
1	0.22	0.0	1.0	1.435	0.0	0.22	1.80
2	0.1	0.0	1.0	1.435	0.0	0.1	1.81
3	0.05	0.0	1.0	1.435	0.0	0.05	1.86
4	0.22	0.5	2.0	1.435	0.198	0.418	1.83
5	0.22	0.5	1.0	1.435	0.156	0.376	1.75
6	0.22	2.0	1.0	1.435	0.427	0.647	1.83
7	0.1	0.5	1.0	1.435	0.198	0.298	1.83
8	0.05	0.5	1.0	1.435	0.220	0.270	1.83
9	0.22	0.5	1.0	1.400	0.088	0.308	1.83
10	0.22	0.5	1.0	1.470	0.574	0.794	1.73

In coordinates $\lg \frac{b+a}{c+a} - t$, straight lines were obtained with slopes $2.25 \cdot 10^{-5}$ (without stirring) and $14.2 \cdot 10^{-5}$ (with stirring), which agreed well with the calculated values of m.

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* In reality, the reaction between the carrier and the depolarizer will end somewhat later because of its finite rate. This, however, will naturally not affect the required amount of electricity

$$Q = \int_0^{\tau} I\,dt.$$

Fig. 2. Effect of Ti^{4+} ions on the cathodic reduction of $Fe_2(SO_4)_3$ on lead. Electrolyte composition: 0.1 M $Fe_2(SO_4)_3$, 1 N H_2SO_4, temperature 20°. 1 – without stirring, 2 –with stirring.

The influence of intermediate reactants has been studied by us in the deposition of metal hydroxides, the recharge of titanium ions, and individual reactions of the electrosynthesis of organic compounds. In all cases, good agreement with the derived equations was obtained. Especially noteworthy is the use of intermediate reactants in organic electrosynthesis, where, along with acceleration of the reaction, it becomes possible to use homogeneous catalysts and to regulate the "rigidity" of oxidation and/or reduction by selecting the corresponding carrier. The use of intermediate reactants makes it possible to avoid spatial difficulties characteristic of heterogeneous processes. Finally, in the presence of considerable kinetic difficulties in the direct electrode reaction of the depolarizer, the carrier may act as a catalyst of the process.

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