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STEPWISE REACTIONS IN ELECTROCHEMICAL KINETICS

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I. INTRODUCTION

A cathodic process is usually divided into stages — (*a*) supply of the ion to the electrode surface, (*b*) reduction of the ion, and (*c*) desorption of the reaction product or its interaction with the electrode material — and an anodic process consists correspondingly of the reverse sequence of analogous stages. The departure of the electrode potential from the equilibrium value is governed by the rate of the slowest stage.

During 1930–1933 Erdey-Grúz and Volmer[1] and also Frumkin[2] linked the polarisation accompanying the discharge and ionisation of hydrogen with the stage actually involving reduction of the ion and oxidation of a neutral atom of hydrogen.

The concept of discharge–ionisation as the slow stage proved to be extremely fruitful, and led to a theory of so-called electrochemical kinetics which in several cases provided a quantitative account of experimental results. In this theory reduction or oxidation was usually regarded as a process occurring in a single act. In other words, it was assumed that an ion undergoing reduction added on at once all the electrons required to form the final product, and that in oxidation simultaneous removal of electrons at once yielded an ion of the required valency.

Recently, however, it has become clear that this simplest form of the theory is not always consistent with the experimental data. This has led to attempts to develop

fundamental ideas, both on the lines of refining the structure of the electrical double layer and on the lines of a detailed account of the actual act of discharge or ionisation.

Following the work of Kabanov et al.[3], the act of discharge or ionisation came to be regarded quite often as a series of consecutive electrochemical reactions, the slowest of which determined the overall rate of the process.

A kinetic equation for the dependence of current density on potential is then set up on the basis of the following general principles:

(*a*) If the electrochemical stages are preceded by a rapid chemical reaction, the concentrations of the reagents are determined by means of the equilibrium constant.

(*b*) Concentrations of intermediate products formed as a result of a rapid electrochemical reaction, i.e. under equilibrium conditions, are determined by means of the Nernst equation.

(*c*) The slow electrochemical stage is described by the usual kinetic equation with the concentrations determined from (*a*) and (*b*).

(*d*) Rapid stages following the slow stage are ignored.

The present paper examines the basic assumptions of the theory of stepwise reactions and surveys critically the most characteristic cases of processes of this type.

II. FUNDAMENTALS OF THE THEORY OF THE STEPWISE OCCURRENCE OF ELECTRODE REACTIONS

Cathodic reduction, and correspondingly anodic oxidation, are inevitably accompanied by transfer of electric charges across the electrode–electrolyte boundary. There are two possibilities:

1. Charge transfer through the electrical double layer is effected by electrons. This process occurs in a pure form during electrolysis in redox systems, e.g. NO_3^-/NO_2^-, Mn^{4+}/Mn^{2+}, Fe^{3+}/Fe^{2+}, etc., in which only the valency of the reactants changes, without change in phase.

2. Charge transfer is effected by ions. This case is realised, for example, during electrolysis in metal–metal ion systems, in which the ions change phase between electrode and electrolyte.

The theory is based on the proposition that, in the discharge of multivalent ions, the transfer of n electrons in a single elementary act is far less probable than the transfer of the same electrons in n successive one-electron stages. This principle follows from views of the analogous course of redox processes at electrodes and of homogeneous oxidation–reduction reactions[4-8].

In the case of redox electrode processes, when charge is transferred through the phase boundary by electrons, the above hypothesis has a definite basis, although in Frumkin's opinion[4] "the possibility of simultaneous transfer of two electrons cannot be excluded". Bockris[7] also supposes that, in spite of the high probability of one-electron transitions in homogeneous redox reactions, it is not yet entirely clear whether spontaneous two-electron transfers are possible. A similar view is held by Basolo and Pearson[8], who regard bivalent transfers as possible when appropriate intermediate valencies are absent from the reactants.

Thus the basic assumption of one-electron transfers is not generally accepted even for the case of charge transfer by electrons. Nor is this assumption generally accepted for ionic transfers.

In the discharge–ionisation of metals, according to Grahame[6] "electrons do not leave the metallic phase, and therefore there is no theoretical necessity to postulate a one-electron transfer". Actually, the transport of charges through the phase boundary is effected in this case by charged metal ions, interaction with electrons ensuing already in the metallic phase, where, as Bockris remarks[7,9-11], the energetically most probable result is formation not of a neutral atom but of a complex of the adsorbed ion with n electrons. Thus preferential interaction with any electron in such a complex is hardly possible.

If, however, the discharge of a multivalent, e.g. an n-valent, ion takes place in stages, the transfer of such an ion must be preceded by electrochemical redox reactions accompanied by the transfer of electrons. The last stage of discharge remains, as before, transfer of the ion. Either electron transfer or ion transfer may be the slow stage in the process.

Although transfer of a univalent ion does require a lower activation energy than that of a multivalent ion, and as a result the stepwise process would appear to be the more probable, nevertheless the formation of ions of lower valency may prove to be energetically unfavourable, and transfer of electrons will not be achieved. In this case direct transfer of the n-valent ion is possible. If, however, the ion of lower valency is relatively stable in solution, occurrence of the stepwise process becomes more probable†.

III. CRITERIA OF THE STEPWISE OCCURRENCE OF ELECTRODE REACTIONS

At the present time three methods exist for establishing the stepwise occurrence of electrode reactions, and these have been termed "criteria for the stepwise occurrence of electrode reactions". One method is based on the theory of the transition state, which enables the heats of activation of all stages in the electrode reaction to be calculated; two methods involve an analysis of the fundamental equation of electrochemical kinetics.

1. Method Based on Determination of Heat of Activation of Intermediate and Final Stages in the Electrode Process

Conway and Bockris[7,9,10] have used the theory of the transition state to calculate potential-energy diagrams for the transfer of an ion from solution to the crystal lattice of the metal. By means of these diagrams it is possible to determine the free energies of the particle in each of the intermediate states, and hence to establish the stage which determines the rate of the electrode reaction.

The method has been employed by these workers to examine the conditions for the electrodeposition of Ag^+, Cu^{2+}, and Ni^{2+}. They showed that the transfer and formation of adsorbed neutral atoms requires a greater heat of

† It is interesting that the formation with anions of complexes adsorbed on the metal surface, especially of hydroxo-complexes, often facilitates the transfer of electrons and makes a stepwise occurrence of the process possible. This case will be examined in detail later.

activation than does the formation of adsorbed ions on the metal surface; in the discharge of Ag^+, Cu^{2+}, and Ni^{2+}, for example, ionic transfer is effected, with adsorption on the surface in the form of adsorbed ion + n electrons.

For bivalent ions direct transfer to any part of the metal surface (i.e. a process which does not include successive dehydration or an intermediate redox stage) must be difficult because of the higher heat of activation for the discharge of bivalent ions compared with univalent ions; furthermore, the hydration of bivalent ions requires a greater consumption of heat than does that of univalent ions. If, therefore, stable intermediate ions exist, a stepwise process of discharge will be more probable than discharge involving simultaneously two or more electrons.

In the discharge of copper, for example, the direct process $Cu^{2+} + 2e \rightarrow Cu$ requires a greater heat of activation than does the stepwise process $Cu^{2+} + e \rightarrow Cu^+$ and $Cu^+ + e \rightarrow Cu$, and the latter is therefore the more probable. In the case of the discharge of nickel, the stage $Ni^{2+} + e \rightarrow Ni^+$, if it does occur, must involve a higher activation barrier than does the corresponding stage for copper, since in the opinion of the above authors a stable univalent nickel ion does not exist in aqueous solution. Consequently the non-stepwise transfer of Ni^{2+} is possible, characterised by a high heat of activation and a low exchange current. In the opinion of Bockris low values of i_0 cannot be due to difficulties in building up the metal lattice, since $i_{0,Ni}$ is abnormally low even for deposition on liquid mercury (see also Ref. 12).

2. Method Based on Analysis of Polarisation Curves

The main theoretical regularities enabling the stepwise transfer of electrons to be established have been formulated by Parsons[13], Vetter[14-17], Losev[18-20], Mauser[21], and others. They are formally valid both for electronic and for ionic transfer of charge. Stepwise character is revealed sufficiently clearly only by the simultaneous study of cathodic and anodic polarisation.

Let us assume that the overall electrode reaction is represented by the equation

$$\text{cathodic:} \quad S_{ox} + ne \rightarrow S_{red}, \tag{1}$$

$$\text{anodic:} \quad S_{red} - ne \rightarrow S_{ox}, \tag{2}$$

where S_{ox} represents a species (ion or neutral particle) in the extreme oxidised state, and S_{red} in the extreme reduced state, the remaining subscripts denoting intermediate redox states (these symbols apply throughout the paper).

If this reaction occurs in one stage, the corresponding kinetic equations, for potentials sufficiently far from the equilibrium potential, are of the usual form

$$i_c = k_-[S_{ox}]e^{-\frac{\alpha nF\varphi}{RT}}, \tag{3}$$

$$i_a = k_+[S_{red}]e^{\frac{\beta nF\varphi}{RT}}. \tag{4}$$

If, however, reactions (1) and (2) involve n one-electron stages —

cathodic

$$\begin{gathered} S_{ox} + e \rightarrow S_{ox-1}, \\ S_{ox-1} + e \rightarrow S_{ox-2}, \\ \cdots\cdots\cdots \\ S_{ox-(n-1)} + e \rightarrow S_{red}, \end{gathered}$$

anodic

$$\begin{gathered} S_{red} - e \rightarrow S_{ox-(n-1)}, \\ \cdots\cdots\cdots \\ S_{ox-2} - e \rightarrow S_{ox-1}, \\ S_{ox-1} - e \rightarrow S_{ox}, \end{gathered}$$

the character of the kinetic curves will depend on the nature and sequence of these stages. Let us consider the following most characteristic cases.

(a) Slow stage is cathodic addition of first electron or anodic detachment of last electron. The equation will be for the cathodic process

$$i_c = k_-[S_{ox}]e^{-\frac{\alpha_1 F\varphi}{RT}}, \tag{5}$$

and for the anodic process

$$i_a = k_+[S_{ox-1}]e^{\frac{\beta_1 F\varphi}{RT}}, \tag{6}$$

where α_1 and β_1 are the transfer coefficients for the slow stage. We determine $[S_{ox-1}]$ from the Nernst equation

$$[S_{ox-1}] = k'[S_{red}]e^{\frac{(n-1)F\varphi}{RT}}. \tag{7}$$

Substitution of Eqn. (7) in (6) yields

$$i_a = k'_+[S_{red}]e^{\frac{(n-1+\beta_1)F\varphi}{RT}}. \tag{8}$$

Thus if the transfer coefficient β'

$$\beta' = n - 1 + \beta_1, \tag{9}$$

determined experimentally from the slope of the Tafel plot for the anodic process exceeds unity, while the coefficient α' has its normal value close to 0.5, a consecutive reaction with a slow first stage must be assumed.

(b) Slow stage is cathodic addition of last electron or anodic detachment of first electron. It is readily shown that in this case the relations will be the opposite of those in the previous case:

$$i_c = k_-[S_{ox}]e^{-\frac{(n-1+\alpha_n)F\varphi}{RT}}, \tag{10}$$

$$i_a = k_+[S_{red}]e^{\frac{\beta_n F\varphi}{RT}}, \tag{11}$$

and the transfer coefficient α determined from the slope of the Tafel straight line for the cathodic process will exceed unity.

(c) Slow stage is addition or abstraction of some intermediate electron. In this case the slow stage in cathodic and anodic processes is preceded by equilibrium electrochemical stages, and both transfer coefficients exceed unity. If, for example, the reaction takes place in n stages of which the mth stage is slow, we have

$$i_c = k_-[S_{ox}]e^{-\frac{(m-1+\alpha_m)F\varphi}{RT}}, \tag{12}$$

$$i_a = k_+[S_{red}]e^{\frac{(n-m+\beta_m)F\varphi}{RT}}. \tag{13}$$

It is seen from Eqns. (12) and (13) that if, for example, the reaction occurs in four stages of which the third is slow, then

$$\alpha' = 3 - 1 + \alpha_m = 2 + \alpha_m,$$

and

$$\beta' = 4 - 3 + \beta_m = 1 + \beta_m.$$

It is evident from these relationships that the experimental transfer coefficients α' and β' differ appreciably from one

another. However, in the particular case in which the middle stage of three is slow, it is impossible to establish from the experimental values of the transfer coefficients any differences between the stepwise and the direct course of the three-electron reaction.

(*d*) A two-stage process comprises a slow first stage followed by disproportionation:

$$S_{ox}+e \rightarrow S_{ox-1},$$
$$2S_{ox-1} \rightleftarrows S_{ox}+S_{red}.$$

The kinetic equation for the cathodic process is

$$i_c = k_-[S_{ox}]e^{-\frac{\alpha_1 F\varphi}{RT}}, \quad (14)$$

and that for the anodic process

$$i_a = k_+[S_{ox-1}]e^{\frac{\beta_1 F\varphi}{RT}} = k'[S_{ox}]^{\frac{1}{2}}[S_{red}]^{\frac{1}{2}}e^{\frac{\beta_1 F\varphi}{RT}}. \quad (15)$$

In this case the kinetic equations for both cathodic and anodic processes are of the form characteristic of one-electron reactions.

(*e*) The separate stages have comparable rates. Let us consider for simplicity the two-stage reaction

$$S_{ox}+e \underset{k_2}{\overset{k_1}{\rightleftarrows}} S_{ox-1} \qquad S_{ox-1}+e \underset{k_4}{\overset{k_3}{\rightleftarrows}} S_{red}.$$

The sum of the current densities i_1 and i_2 for each reaction gives the total current i, and for steady-state conditions we must have

$$i = i_1 + i_2 = 2i_1 = 2i_2 \quad (16)$$

otherwise the concentration of the intermediate product will not remain constant with time. Apart from the constancy of $[S_{ox-1}]$ with time, we must also assume the concentration of the intermediate product to be so low that its diffusion from the electrode surface can be neglected.

Let us write the kinetic equations in the form

$$i_1 = k_2[S_{ox-1}]e^{\frac{\beta_1 F\varphi}{RT}} - k_1[S_{ox}]e^{-\frac{\alpha_1 F\varphi}{RT}}, \quad (17)$$

$$i_2 = k_4[S_{red}]e^{\frac{\beta_2 F\varphi}{RT}} - k_3[S_{ox-1}]e^{-\frac{\alpha_2 F\varphi}{RT}}. \quad (18)$$

We determine the concentration of the intermediate product by Bodenstein's method of quasi-stationary concentrations:

$$\frac{d[S_{ox-1}]}{dt} = k_1[S_{ox}]e^{-\frac{\alpha_1 F\varphi}{RT}} + k_4[S_{red}]e^{\frac{\beta_2 F\varphi}{RT}} -$$
$$- k_2[S_{ox-1}]e^{\frac{\beta_1 F\varphi}{RT}} - k_3[S_{ox-1}]e^{-\frac{\alpha_2 F\varphi}{RT}} = 0,$$

whence

$$[S_{ox-1}] = \frac{k_1[S_{ox}]e^{-\frac{\alpha_1 F\varphi}{RT}} + k_4[S_{red}]e^{\frac{\beta_2 F\varphi}{RT}}}{k_2 e^{\frac{\beta_1 F\varphi}{RT}} + k_3 e^{-\frac{\alpha_2 F\varphi}{RT}}}. \quad (19)$$

On substituting for $[S_{ox-1}]$ from Eqn. (19) in (17) and (18), we obtain

$$i = 2k_1[S_{ox}]e^{-\frac{\alpha_1 F\varphi}{RT}} \frac{1-\frac{k_2k_4}{k_1k_3}\frac{[S_{red}]}{[S_{ox}]}e^{\frac{2F\varphi}{RT}}}{1+\frac{k_2}{k_3}e^{\frac{(\beta_1+\alpha_2)F\varphi}{RT}}} \equiv 2k_4[S_{red}]e^{\frac{\beta_2 F\varphi}{RT}} \frac{1-\frac{k_1k_3}{k_2k_4}\frac{[S_{ox}]}{[S_{red}]}e^{-\frac{2F\varphi}{RT}}}{1+\frac{k_3}{k_2}e^{-\frac{(\beta_1+\alpha_2)F\varphi}{RT}}}. \quad (20)$$

At sufficiently high cathodic potentials Eqn. (20) becomes

$$i_c = 2k_1[S_{red}]e^{-\frac{\alpha_1 F\varphi}{RT}} = 2i_{0,1}e^{-\frac{\alpha_1 F\Delta\varphi}{RT}}, \quad (21)$$

and at sufficiently high anodic potentials it becomes

$$i_a = 2k_4[S_{red}]e^{\frac{\beta_2 F\varphi}{RT}} = 2i_{0,2}e^{\frac{\beta_1 F\Delta\varphi}{RT}}. \quad (22)$$

Thus when the rates of the two stages are comparable, the transfer coefficients determined from Tafel straight lines for cathodic and anodic processes are not linked by the equation $\alpha + \beta = 1$, since they relate to different reactions. Furthermore, it follows from these same equations that extrapolation of these Tafel straight lines to the equilibrium potential gives different values of the exchange current for cathodic and anodic processes, since these values of i_0 correspond to different stages of the process.

On the basis of the above, the following criteria can be formulated for the stepwise occurrence of an electrode process: (1) the transfer coefficients determined from the slopes of the Tafel straight lines for anodic and cathodic processes have anomalous values; and (2) exchange currents determined from these straight lines have different values (for cases in which the separate stages occur at comparable rates).

3. Methods Based on Concentration Relations

These methods [14-17,22-27] are closely linked with the preceding methods, since they derive essentially from the same fundamental equations of electrochemical kinetics. In fact, the equations of electrochemical kinetics contain the concentrations (activities) of the reactants. Consequently the potential, overpotential, or exchange current must depend on the concentration of species taking part in the electrode reaction. The values of the partial derivatives with respect to concentration will depend on the coefficient of potential in the equation, i.e. on the number and sequence of stages and the prior occurrence of a rapid chemical reaction. Concentration criteria supplement criteria obtained from an analysis of polarisation curves. From the above equations of electrochemical kinetics we can obtain the partial derivatives

$$\left(\frac{\partial\varphi}{\partial\log[S_{ox}]}\right)_i = -\frac{2.3RT}{\alpha' F} \text{ and } \left(\frac{\partial\varphi}{\partial\log[S_{red}]}\right)_i = \frac{2.3RT}{\beta' F}.$$

Moreover, the derivative of current density with respect to the concentrations of components of the solution gives the order of reaction ν_i:

$$\left(\frac{\partial\log i}{\partial\log[S_i]}\right)_\varphi = \nu_i, \quad (23)$$

which enables us to determine which substances take part in the slow stage.

In cases in which reactions occur so rapidly that polarisation curves cannot be obtained, and only exchange currents can be measured, concentration criteria provide the sole criteria of the stepwise character of reactions, as follows from the relations

$$\left(\frac{\partial\varphi_{eq}}{\partial\log i_{ox}}\right)_{S_{ox}} = \frac{2.3RT}{\beta' F}, \quad (24)$$

$$\left(\frac{\partial\varphi_{eq}}{\partial\log i_{ox}}\right)_{S_{red}} = -\frac{2.3RT}{\alpha' F}. \quad (25)$$

IV. SOME EXAMPLES OF THE STEPWISE OCCURRENCE OF ELECTRODE REACTIONS

1. Reactions Having One Slow Stage

(*a*) Zn(Hg)/Zn^{2+} electrode. The anodic behaviour of zinc in sulphate solutions has been investigated by Losev and his coworkers [28-35]. Application of Eqns. (24) and (25)

to the concentration relations of i_0 gives the transfer coefficients $\beta' = 1.40$ and $\alpha' = 0.52$: i.e. $\beta' > 1$ and $\beta' > \alpha'$, which corresponds to a case of slow detachment of the last electron in the ionisation of zinc — see Eqns. (8) and (9).

The true transfer coefficients, corresponding to the slow stage of the process, are $\alpha_2 = \alpha' = 0.52$ and $\beta_2 = \beta' - 1 = 0.40$. The possibility of the existence of the singly charged ion Zn^+ in aqueous solution[36-38] confirms the correctness of the above mechanism. It is therefore hardly possible to justify Gerischer's view[39,40] that, although he obtained the same values of α' and β', the process was a two-electron process with α and β respectively 0.3 and 0.7.

It must be noted, however, that lack of symmetry of the potential barrier is not by itself a sufficient criterion of the stepwise occurrence of a process, since reactions of the singly charged silver ion, which occur in one stage, have values of $\alpha \simeq 0.3$ and $\beta \simeq 0.7$.[41]

(*b*) In(Hg)/In^{3+} electrode. Losev and his coworkers have investigated the anodic behaviour of indium in perchlorate solutions[42-46]. They obtained values for the transfer coefficients of $\beta' = 2.2$ from polarisation curves and concentration relations of the exchange current (24), and $\alpha' = 0.9$ from the concentration relations of the exchange current (25). Here $\beta' > 2$ and $\beta' > \alpha'$ — see Eqns. (8) and (9) — and therefore the anodic process can be regarded as occurring in stages. These workers consider that three stages are involved: $In - e \rightleftharpoons In^+$, $In^+ - e \rightleftharpoons In^{2+}$, and $In^{2+} - e \rightarrow In^{3+}$, the last stage being slow. The transfer coefficients for this stage are then $\alpha_3 = \alpha' = 0.9$ and $\beta_3 = \beta' - 2 = 0.2$. In this case an extremely unsymmetrical energy barrier is already obtained for the one-electron transfer.

Similar results have been obtained by other workers[47] in sulphate electrolytes at current densities below 0.001 A $\times$ $\times$ cm^{-2}. A more acceptable scheme is probably one involving a two-electron slow stage: $In - e \rightleftharpoons In^+$ and $In^+ - 2e \rightarrow In^{3+}$. We then have $\alpha_2 = \frac{1}{2}\alpha' = 0.45$ and $\beta_2 = \frac{1}{2}(\beta' - 1) = 0.6$.

On the basis of the results for zinc and indium, Losev and his collaborators[20,42] suggested that, with all multivalent metals, electrode processes take place in stages. They give results for transfer coefficients in the cases of copper, cadmium, iron, nickel, and cobalt. Analysis of these data shows that this hypothesis can be applied to the discharge and ionisation of copper, for example[48,49]; with cadmium there are two groups of contradictory data[50-53]; and in the case of the iron-group metals, discharge of the simple hydrated ions in a non-complexing medium, and in the absence of specific adsorption of anions, is most probably a one-stage process involving bivalent ions[7,9,10,54-58].

(*c*) Hg/$Hg(CN)_4^{2-}$ electrode. Gerischer and Perez-Fernandes[59] have investigated the reaction $Hg(CN)_4^{2-} + 2e \rightleftharpoons Hg + 4CN^-$ under conditions such that the complex $[Hg(CN)_4]^{2-}$ predominated in the solution. The slopes of the Tafel curves gave values of $\alpha' = 0.30 \pm 0.03$ and $\beta' = 1.67 \pm 0.05$. From the dependence of i_c and i_0 on the concentrations of CN^- and $Hg(CN)_4^{2-}$ it was established that the complex $[Hg(CN)_3]^-$ participates in charge transfer. Consequently the transfer reaction $Hg(CN)_3^- + 2e \rightarrow Hg + 3CN^-$ is accompanied by the chemical equilibrium $Hg(CN)_4^{2-} \rightleftharpoons Hg(CN)_3^- + CN^-$.

If, however, transfer coefficients are calculated for a simultaneous two-electron transfer, values are obtained of $\alpha < 0.2$ and $\beta > 0.8$. The possibility was therefore considered that the reaction took place in stages according to the scheme

$$Hg(CN)_3^- + e \rightleftarrows HgCN_{ads} + 2CN^-,$$
$$HgCN_{ads} + e \rightleftarrows Hg + CN^-.$$

The experimental data indicate that the first of these stages is slow. Then $\beta' = 1.67 \pm 0.05 = 1 + \beta_1$, whence $\beta_1 = 0.67 \pm 0.05$ and correspondingly $\alpha_1 = 0.30 \pm 0.03$.

The hypothesis that the transfer reaction takes place in stages has been tested by measuring the capacitance by the charging method. If the reaction occurs in stages, and the first stage is slow, a charging pulse should not only charge the double layer but also cause the establishment of a new equilibirum concentration of $HgCN_{ads}$, which is shown in an apparent increase in capacitance. The experimental relation obtained supports the accepted mechanism for the electrode reaction.

(*d*) Ni/Ni^{2+} electrode. In a study of the electrolysis of nickel in chloride electrolytes containing boric acid, Fedot'ev and Dmitreshova[60] found that at 80° discharge–ionisation takes place according to the simple scheme $Ni^{2+} + 2e \rightarrow Ni$ with transfer coefficients of $\alpha = 0.4$ and $\beta = 0.6$, whereas at 25° they found that $\alpha + \beta = 1$ only when $n = 1$. On this basis a stepwise scheme $Ni^{2+} + e \rightarrow Ni^+$ and $Ni^+ + e \rightarrow Ni$ was suggested, in which one of the stages was slow. Such a suggestion can apply if the first stage is slow in both anodic and cathodic processes. Values of $\alpha + \beta = 1$ satisfy also a one-electron transfer with subsequent disproportionation $Ni^{2+} + e \rightarrow Ni^+$ and $2Ni^+ \rightleftharpoons Ni + Ni^{2+}$.

A stepwise course for the electrode process involving the Ni^+ ion has been suggested by several workers[61-64] who have studied the polarographic behaviour of nickel. The existence of Ni^+ has been demonstrated by Khlopin[65]. Nevertheless, calculations by Conway and Bockris[7,9,10], as well as several experimental results[54-56,66], justify a simple two-electron scheme for the process. However, more detailed investigations are desirable.

A stepwise mechanism can be expected for electrode reactions with all other metals where ions of lower intermediate valencies can exist in the solution. The presence of univalent states has been detected, for example, with simple ions of the metals Mg,[37,67-69] Al,[37,67,71] Be,[37,67,71] Zn, La, Ce, Ti, U, Hg, Cu, In, and Ga,[37,67] as well as with complex ions of Cr, Mn, Co, etc.[72]

2. Reactions Having Two Slow Stages

(*a*) Quinhydrone electrode. For the quinhydrone electrode Vetter[73] has established that the electrode reaction has different mechanisms in acid and alkaline media. On the basis of experimental results he states that the two electrons of the overall reaction are transferred successively, the rates of the two stages of the reaction being comparable.

However, examination of the experimental data in Ref. 73 reveals insufficient grounds for such a conclusion in the case of results obtained in the acid region, since the anodic Tafel line has been drawn rather arbitrarily (see Fig. 1). Even with these straight lines, values of $\beta_2 = 0.46$ and $1 - \alpha_1 = 0.54$ were obtained, which are hardly sufficient for the conclusion reached by this worker.

In the alkaline region, anodic and cathodic polarisation curves have well-defined Tafel sections with different

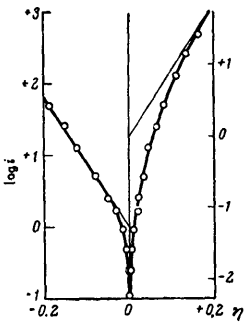


Fig. 1. Polarisation curves for the quinone–quinol system at high acidities (0.001 m quinone + 0.01 m quinol in 1 M HCl).

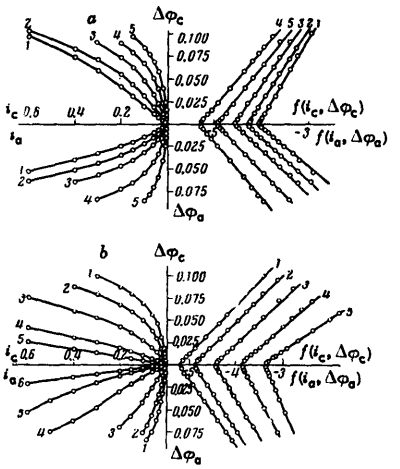


Fig. 2. Effect of pH on polarisation of cathodic and anodic processes in the quinone–quinol system in the region of:
a) high acidities (pH): 1) 0.48; 2) 1.07; 3) 1.52; 4) 2.01; 5) 3.01;
b) low acidities (pH): 1) 3.92; 2) 5.06; 3) 6.02; 4) 7.06; 5) 7.92; 6) 8.6.

slopes, of $1 - \alpha_1 = 0.37$ and $\beta_2 = 0.19$. Exchange currents determined by extrapolation of anodic and cathodic Tafel lines do not coincide. Thus the totality of experimental data not only support Vetter's theoretical conclusions, but also provide one of the very few examples of more than one slow electron transfer in the same overall reaction.

The electrochemical behaviour of the quinhydrone electrode has been investigated also by Loshkarev and his coworkers[74]. Their experimental results contradict Vetter's data, since exchange currents determined from anodic and cathodic Tafel lines coincide at all pH values (Fig. 2). According to Loshkarev and Tomilov, the slow stage is the complete electrode process involving two electrons.

Bagotskii et al.[75] have attempted to ascertain the reason for such a sharp discrepancy in the experimental data in these papers. They have shown that the results of Ref. 74 are due to the carrying out of experiments at low current densities and small polarisations, when the rate of the reverse reaction still cannot be neglected. These workers' own data are on the whole close to Vetter's results. In contrast to the latter, however, Bagotskii and his coworkers consider that the slow stage of the cathodic process in the quinone–quinol system is addition of the first electron, while that in the anodic process is abstraction of the first electron. It must be noted, however, that the experimental data obtained by Bagotskii et al. also fit a scheme in which the slow stage is addition of the first electron (and abstraction of the last) combined with rapid disproportionation. This system, too, requires further investigation.

(*b*) Tl^{3+}/Tl^{+} redox electrode. Antropov and Mizgireva[76], probably the first to investigate this system, concluded that both concentration polarisation and chemical polarisation were present. In their opinion the chemical polarisation was associated not with a slow discharge–ionisation stage but with slow desorption of secondary (reduced) ions.

Vetter and Thiemke[77] have also shown that the overpotential is determined not only by a slow electrochemical reaction but also by diffusion, and therefore curves corresponding to the experimental points have no linear sections. Curves were plotted on the basis of Eqn. (20) after allowing for diffusion. Transfer coefficients were so chosen that the curves corresponded to the experimental points (Fig. 3). The values determined in this way were $\beta_2 = 0.67$ and $\alpha_1 = 0.36$. Their sum was taken as not equalling unity, although the difference was only 0.03. By means of Eqns. (21) and (22), with the values of β_2 and α_1 substituted in them, straight lines were then plotted representing the relation between η and $\log i$ in the absence of diffusion hindrances. Exchange currents found by extrapolation of such hypothetical straight lines were also found to be rather different (Fig. 3).

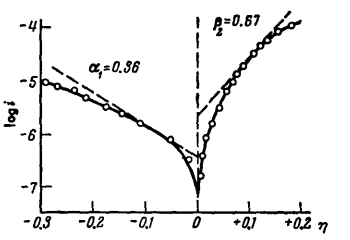


Fig. 3. Polarisation curves for the Tl^{3+}/Tl^{+} system: points represent experimental data; full curves calculated from Eqn. (20) with correction for diffusion; broken lines from Eqns. (21) and (22).

It was concluded from these results that the kinetics of the process was determined by two stages

$$Tl^{+} \rightarrow Tl^{2+} + e \text{ and } Tl^{2+} \rightarrow Tl^{3+} + e.$$

It is noted in the paper that the data were processed on the hypothesis that two electrons were transferred simultaneously, and that this hypothesis is inconsistent with the experimental results.

There is an indication in the literature that the homogeneous exchange Tl^{+}–Tl^{3+} may occur in stages with the formation of Tl^{2+}.[78] It has also been suggested that the reduction of Tl^{3+} ions on the electrode by atomic hydrogen to Tl^{+} takes place in two stages[79].

Thus the possibility of the stepwise occurrence of the electrode process is to some extent supported by hypotheses concerning the presence of Tl^{2+} ions, but the experimental data reported in Ref. 77 cannot provide adequate evidence of a stepwise mechanism.

3. Participation of Hydroxide Ions in Electrode Processes

Anions play an important part in homogeneous redox reactions between multicharged cations in the bulk of the electrolyte, by facilitating the transfer of charge from one cation to another. Thus, for example, Cl^{-} accelerates the exchange of charges between Fe^{3+} and Cr^{3+}, an activated complex of the type $[Cr-Cl-Fe]^{4+}$ being formed in which Cl^{-} acts as an "anionic bridge" for the transfer of charge[4].

Hydroxide ions have a similar effect. The participation of OH^{-} ions in electrode processes in the discharge–ionisation of metals is revealed by the fact that the rate of the electrode reaction depends on the pH of the electrolyte. Here, too, hydroxide ions have an accelerating effect, the exchange of charges between the metal surface and ions in solution through the hydroxide "bridge" being made so easy that conditions are produced for the stepwise transfer of electrons in the discharge–ionisation even of such stable bivalent aquo-ions as those of the iron-group metals.

The exchange of charges is some thousandfold more rapid between $Fe(OH)^{2+}$ and Fe^{2+} than between Fe^{3+} and Fe^{2+}. Similar results are obtained in a study of the effect of pH on the rate of exchange between chromium, cerium, plutonium, and praseodymium ions of different degrees of oxidation, as well as on the rate of oxidation of U^{4+} by Tl^{3+} and Fe^{3+} ions, and of Cr^{2+} by $[CoH_2O(NH_3)_5]^{3+}$ ions[4,80].

The kinetics of the elementary electrochemical act depends in general on the potential difference at the electrode–solution interface, the reactant concentrations at the electrode surface, and the strength of the bonds which are ruptured or formed on participation of the reactant species in the electrode process. Therefore the catalytic action of OH^{-} ions in the formation of active complexes of the reactant species with these ions can be explained by the fact that they produce changes both in the total charge on the reactant species and in its electronic structure[4].

Let us examine the effect of hydroxide ions on the electrode process with a few metal electrodes as examples.

(*a*) Fe/Fe^{2+} electrode. Study of the part played by hydroxide ions in the anodic dissolution of iron in alkaline solutions, undertaken by Kabanov and others[3,81], established that the rate of anodic dissolution is far greater in alkaline than in acid solutions, i_a being proportional to $[OH^{-}]^2$. An electrochemically active layer of adsorbed product is present on the electrode surface, and produces unusually high values for the capacitance of the double layer (of the order of 1500 $\mu F\ cm^{-2}$). The results were explained on the basis of the stepwise mechanism of the electrode process involving OH^{-} ions

$$Fe + OH^{-} \rightleftarrows FeOH_{ads} + e,$$
$$FeOH_{ads} + OH^{-} \rightarrow FeO_{ads} + H_2O + e \text{ (slow stage)},$$
$$FeO_{ads} + OH^{-} \rightleftarrows HFeO_2^{-},$$
$$HFeO_2^{-} + H_2O \rightleftarrows Fe(OH)_2 + OH^{-}.$$

The corresponding kinetic equation is

$$i_a = k_1 [FeOH]_{ads} [OH^{-}] e^{\frac{\beta F\varphi}{RT}} = k_2 [OH^{-}]^2 e^{\frac{(1+\beta)F\varphi}{RT}}. \quad (26)$$

With $\beta = 0.5$, the slope of the Tafel straight line is $2RT/3F$, as has been obtained experimentally.

Bonhoeffer and Heusler[82,83] found that the rate of anodic dissolution of very pure iron in perchloric and sulphuric acids (under conditions of constant corrosion, when φ_{eq} is independent of pH) depends on the pH, the relation being the same for acid and alkaline solutions when the process occurs under steady-state conditions. The high values obtained for the capacitance from galvanostatic charging curves could also be explained by the presence of an active layer of an intermediate product. These results indicate that hydroxide ions take part in the electrode process in acid solutions, and, because of the better adsorbability of hydroxide ions, displacement of the equilibrium $H_2O \rightleftharpoons H^{+} + OH^{-}$ in the catholyte can ensure an OH^{-} concentration sufficient to have a catalytic effect. These workers determined the orders of reaction — see Eqn. (23) — from the OH^{-} concentration for the non-stationary process ($\nu_{OH^-} = 1$) and the steady-state process ($\nu_{OH^-} = 2$, compared with an experimental value of 1.55) in the anodic dissolution of iron. Determination of the slopes of the Tafel lines gave b_a (non-stationary) = 0.063 V and b_a (stationary) = 0.030 V, which formed the basis for the following scheme for the process

$$Fe + OH^{-} \rightleftarrows FeOH_{ads} + e,$$
$$Fe + OH^{-} + FeOH_{ads} \rightarrow FeOH^{+} + FeOH_{ads} + 2e \text{ (slow stage)}.$$

The corresponding kinetic equation is written

$$i_{a,stat} = k_{+} [OH^{-}]^2 e^{\frac{(1+2\beta)F\varphi}{RT}}, \quad (27)$$

where $\beta = 0.46$ (determined from the non-stationary polarisation curve).

It was suggested that the cathodic deposition of iron takes place in a similar manner, formation of the surface catalyst being associated with the chemical equilibrium $Fe^{2+}.aq + OH^{-} \rightleftharpoons FeOH^{+} + aq$. This is followed by the discharge of $FeOH^{+}$ with formation of the catalyst: $FeOH^{+} + e \rightleftharpoons FeOH_{ads}$. The slow stage is

$$FeOH^{+} + FeOH_{ads} + 2e \rightarrow Fe + OH^{-} + FeOH_{ads},$$

which corresponds to the kinetic equation

$$i_{c,stat} = k_{-} [OH^{-}]^2 [Fe^{2+}]^2 e^{-\frac{(2\alpha+1)F\varphi}{RT}}. \quad (27a)$$

With $\alpha = 1 - \beta = 0.54$, the slope of the Tafel straight line should be ~ 0.028 V.

Similar values, of 0.027–0.030 V, were found for the slopes b_a and b_c by Hurlen and Hoar[84–87] in a study of the kinetics of the discharge–ionisation of iron in sulphate and chloride solutions, using a slow galvanostatic method with determination of current efficiencies and construction of partial polarisation curves for iron and hydrogen.

However, according to these results, the rate of the cathodic deposition and anodic dissolution of iron is proportional to the hydroxide-ion concentration to the first power, not the second as required by Eqns. (26) and (27). The cathodic reaction is of the second order with respect to $[Fe^{2+}]$. The combined effect of the data is to give a scheme for the process involving two atoms (or ions) of iron and four electrons in the rate-determining stage

$$2\,Fe + OH^- \rightarrow 2\,Fe^{2+} + OH^- + 4e.$$

Hurlen[85,86] suggested that this process can occur in stages, but his proposed reactions correspond not to successive stages of one process but to two independent modes of oxidation of iron

$$Fe + OH^- \rightleftarrows \text{active complex A} \rightleftarrows Fe^{2+} + OH^- + 2e,$$
$$Fe + H_2O \rightleftarrows \text{active complex B} \rightleftarrows Fe^{2+} + H_2O + 2e.$$

Thus if the process does occur in stages, they comprise different reactions.

Ivanov and Iofa[58] have shown that at a dropping mercury electrode the rate of reduction of iron actually depends on the relative proportions of the complexes A′ and B′, which themselves depend on the pH of the solution.

$$\underset{B'}{[Fe(H_2O)_n]^{2+}} + H_2O \rightleftarrows \underset{A'}{[FeOH(H_2O)_{n-x}]^+} + H^+ + x\,H_2O.$$

At low pH values the kinetics of the process is determined by discharge of the ion B′, whereas with rise in pH the equilibrium shifts towards the formation of A′, and the rate of the process is determined by the stage

$$[FeOH(H_2O)_{n-x}]^+ + 2e \rightarrow Fe + OH^- + (n-x)\,H_2O.$$

Unfortunately, the paper does not give results for the determination of b_c and α.

Bockris et al.[88] have put forward the hypothesis that the difference in activation energy between the different paths for the electrode reaction is extraordinarily small in the case of iron, and therefore even a slight change in the conditions of electrolysis may change the mechanism of the electrode process.

(*b*) Ni/Ni^{2+} electrode. The effect of hydroxide ions on the anodic dissolution of nickel has been studied by Hollnagel and Landsberg[89] using a non-stationary galvanostatic method at 60°. They find that the anodic potential decreases with increase in pH. These workers assume that the adsorption of hydroxide ions facilitates the escape of nickel ions through the intermediate formation of NiOH, in an analogous manner to Heusler's scheme[83] for iron.

Solov'eva and Abrarov[90] investigated the effect of solution pH on the electrodeposition of nickel and cobalt at constant current density. They noted a sharp decrease in cathodic potential within a definite narrow pH range, which was explained by the conversion of aquo-complexes of the metal ions into partly hydrolysed active complexes containing the OH^- group.

The same workers reached a similar conclusion concerning the dependence of the kinetics of discharge on changes in the composition of the species undergoing discharge on studying the effect of boric acid on the discharge of cobalt and nickel[91], as did also Kovalenko and Nadezhdina[92] from an investigation of the effect of various complexing agents on the discharge of aquo-ions of nickel and cobalt at a dropping mercury cathode.

Matulis and Slizhys[93] concluded, from a study of the effect of catholyte pH on the cathodic process in a nickel sulphate electrolyte, that the sharp decrease in cathode potential at $pH_S \simeq 4$ is due to the discharge of $NiOH^+$ ions which are formed in the bulk of the solution at pH 4 as a result of hydrolysis

$$Ni^{2+} + OH^- \rightleftarrows NiOH^+.$$

At pH ⩾ 4 a stepwise process is assumed with formation of a neutral species

$$NiOH^+ + e \rightarrow NiOH_{ads}.$$

The following stage is desorption of hydrogen evolved simultaneously on the metal surface

$$NiH_{ads} + NiOH_{ads} \rightleftarrows Ni + H_2O.$$

In the more acid region the process of discharge corresponds to the simple scheme

$$Ni^{2+} + 2e \rightarrow Ni.$$

(*c*) Co/Co^{2+} electrode. Kravtsov and his coworkers[94,95] have suggested a possible mechanism, involving hydroxide ions, for the discharge of cobalt ions at an electrode. An oscillographic method was used to obtain cathodic polarisation curves at pH 3.5 and 4.2 [95] in 1 *N* $CoSO_4 + H_3BO_3$ solutions at room temperature, as well as stationary and non-stationary anodic curves under these conditions.

The values obtained for b_a of 0.064 and 0.040 V under non-stationary and stationary conditions respectively suggest that the mechanism of the anodic dissolution of cobalt resembles that proposed by Heusler for iron[83]. It was also suggested that the two electrons involved in the anodic reaction are split off successively, not in a single act, which is consistent with the large slopes of b_c = 0.111–0.114 V obtained for the cathodic curves and the low values of b_a.

The rates of corrosion and of anodic dissolution of cobalt have been studied as a function of pH over a wide range of the latter by Iofa and Wei Pao-ming[96]. The values of b_a = 0.026 V and $\nu_{OH^-} = 2$ obtained experimentally correspond to the mechanism of the anodic dissolution of iron described in Refs. 81–83.

Heusler has investigated[97,98] the effect of the acidity of the solution on the mechanism of anodic and cathodic processes in the discharge–ionisation of cobalt from perchlorate solutions. His experimental results corresponded to the scheme which he had suggested for iron[83].

The effect of pH on the cathodic deposition of cobalt from sulphate solutions at 55° has been investigated with simultaneous measurement of the pH of the catholyte[57]. The totality of experimental data[57] obtained for the partial polarisation curves of cobalt in the pH_S range (in the catholyte) of 0.5–2.2 (b_c = -0.085 V, $\nu_{OH^-} = 0$, and $\nu_{Co^{2+}} = 1$) shows that the discharge of cobalt takes place according to the simple two-electron scheme

$$Co^{2+} + 2e \rightarrow Co.$$

In the pH_S range 2.5–4.0 an increase in b_c from 0.085 to 0.150 V is observed on a negatively charged surface, which can be explained by partial hydrolysis of the aquo-ions of cobalt according to the equation

$$Co^{2+} + H_2O \rightleftarrows CoOH^+ + H^+,$$

with simultaneous participation of the ions Co^{2+} and $CoOH^+$ in the electrode process. Increase in pH is accompanied

by displacement of the equilibrium towards formation of $CoOH^+$, and discharge takes place in the stages

$$CoOH^+ + e \rightarrow CoOH \text{ (slow stage)},$$
$$CoOH + e \rightleftarrows Co + OH^-,$$

which is consistent with Kravtsov's experimental results[95]. In this same pH range the discharge of cobalt occurs on a positively charged electrode surface (zero-charge potential about -0.45 V), where the experimental values of $b_c = -0.026$ V, $\nu_{Co^{2+}} = 2$, and $\nu_{OH^-} = 1$ correspond to an overall reaction involving four electrons, analogous to the scheme suggested by Hurlen and Hoar[84-87] for iron:

$$2Co^{3+} + OH^- + 4e \rightarrow 2Co + OH^-,$$

$$i_c = k[Co^{3+}]^{\beta}[OH^-]e^{-\frac{\alpha' F\varphi}{RT}}. \quad (28)$$

Such a process may be supposed to occur in one stage if the species transferring the charge is assumed to be the complex $[Co_2OH]^{3+}$. In this case the transfer coefficients $\alpha' = 2.5$ and $\beta' = 1.5$ [55,95] (value of β' taken from Ref. 55 is 1.4 at 60°) are regarded as $\alpha' = 4\alpha$ ($\alpha = 0.62$) and $\beta' = 4\beta$ ($\beta = 0.38$). However, the high activation energy required for the transfer of a triply charged species, and also the possibility of the transfer of electrons from the cathode surface through a hydroxyl "bridge", suggest that the process takes place in stages, with the following possibilities:

I. $$Co^{3+} + H_2O \rightleftarrows CoOH^+ + H^+, \quad (a)$$

$$CoOH^+ + e \rightleftarrows CoOH \text{ rapid}, \quad (b)$$

$$\underbrace{CoOH + Co^{3+}}_{Co_2OH^{3+}} + 3e \rightarrow 2Co + OH^- \text{ slow}. \quad (c)$$

In this case $\alpha' = 1 + 3\alpha$ ($\alpha = 0.5$) and $\beta' = 3\beta$ ($\beta = 0.5$).

II. Stages (a) and (b) remain as before, but subsequent electrons are also added on successively:

$$CoOH + Co^{3+} + e \rightleftarrows Co_2OH^+ \text{ rapid},$$
$$Co_2OH^+ + e \rightarrow Co_2OH \text{ slow},$$
$$Co_2OH + e \rightleftarrows 2Co + OH^- \text{ rapid}.$$

The experimental values of α' and β' correspond to slow addition of the third electron — see Eqn. (16). In fact, with $n = 4$ and $m = 3$, $\alpha' = \alpha_3 + 3 - 1 = \alpha_3 + 2$ ($\alpha_3 = 0.5$) and $\beta' = \beta_3 + 4 - 3 = \beta_3 + 1$ ($\beta_3 = 0.5$).

In order to choose between the possibilities suggested, it is necessary to obtain additional data on the intermediate products involved in the electrode process.

It must be noted that the reaction order with respect to hydroxide ions of $\nu_{OH^-} = 1$, which determines the mechanism of the electrode process (see, for example, Heusler's scheme[83,97], where $\nu_{OH^-} = 2$) is obtained only when the pH adjacent to the cathode is taken into account. Relations based on the pH in the bulk of the solution give values of $\nu_{OH^-} \simeq 2$. This illustrates the necessity of measuring pH in the layer adjacent to the electrode, and taking this quantity into account in investigating the mechanism of electrode reactions.

(d) In(Hg)/In^{3+} electrode. The pH dependence of the electrode process has been investigated by Losev and Molodov[44]. At $HClO_4$ concentrations below 0.1 M the rate of anodic dissolution of indium is proportional to the hydroxide-concentration to the first power, and the process is described by the equation

$$i_a = k[In][OH^-]e^{\frac{\beta' F\varphi}{RT}} \text{ (where } \beta' = 2.2).$$

The overall process is

$$In + 5H_2O + OH^- \rightleftarrows In(H_2O)_5OH^{2+} + 3e.$$

The possibility of stepwise occurrence of this process has been discussed above. Cathodic and anodic polarisation curves obtained at various pH values in this work are reproduced in Fig. 4. The unusually steep slope of the cathodic curves was explained as due to a prior chemical stage of hydrolysis, and the decrease in slope with increase in cathode potential as due to acceleration of this reaction.

However, curves of this type can be explained by a change in the charge on the cathode surface. In fact, the zero-charge potential for indium amalgam (~ 0.1 at. %) calculated by Antropov's method[99] gives a value of about -0.4 V (zero-charge potential for indium taken from Ref. 100), which corresponds to a potential region in which the polarisation curves slope steeply. Consequently the more gently sloping linear section at potentials between -0.6 and -0.8 V on the cathodic curves corresponds to the discharge of indium ions on a negatively charged surface. The slope of this section is ~0.14 V, which gives a transfer coefficient α' of around 0.4. Such kinetic parameters may correspond to a slow stage involving addition of an electron to the In^{3+} ion, while determination of the order of reaction with respect to hydroxide ions may show whether indium ions exist in the form of aquo-complexes or partly hydrolysed complexes.

4. Reactions of the Oxygen Electrode

The great practical importance of electrode reactions involving oxygen has given rise to several investigations of their mechanism. The overall four-electron process undoubtedly comprises a series of stages. In this case the presence of at least one intermediate product — hydrogen peroxide — has been firmly established experimentally both in the cathodic reduction of oxygen molecules and in the anodic oxidation of water molecules or hydroxide ions[101].

Investigation of the electrochemical reactions of oxygen is complicated by oxidation of the electrode surface, not only in the course of anodic evolution but in several cases even during the cathodic reduction of O_2 molecules[102]. As a result, the mechanism may differ on different electrodes.

Krasil'shchikov[102] established that the cathodic reduction of oxygen on silver and gold electrodes in acid medium takes place according to the scheme

$$O_2 + e \rightarrow O_2^- \text{ (slow stage)},$$
$$O_2^- + H^+ \rightleftarrows HO_2,$$
$$HO_2 + e \rightleftarrows HO_2^-,$$
$$HO_2^- + H^+ \rightleftarrows H_2O_2.$$

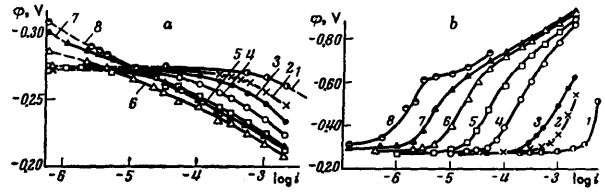


Fig. 4. Dependence of: a) anodic; b) cathodic polarisation curves for indium on acidity of electrolyte ($HClO_4$, M): 1) 0.002 (a) and 0.00095 (b); 2) 0.0077; 3) 0.016; 4) 0.05; 5) 0.1; 6) 0.5; 7) 1.3; 8) 3.3.

According to Krasil'shchikov's results, the slow stage is the same in alkaline medium as in acid solutions. Bagotskii and Yablokova [103] accept the above scheme for acid solutions, but suggest a different mechanism for alkaline solutions, at any rate on a mercury electrode, because in this case the reduction of oxygen takes place under nearly equilibrium conditions.

In the anodic evolution of oxygen all electrodes are oxidised, so that the process actually takes place on an oxidised surface. Depending on the electrode potential (current density), either chemisorbed layers can be formed in which the metal–oxygen bonding energy varies with time, or oxides of different compositions as separate phases. Their participation in the electrode process has been discussed many times in the literature (e.g. Ref. 104).

Krasil'shchikov [105] regards the following scheme

$$OH^- - e \rightleftarrows OH,$$
$$OH + OH^- \rightleftarrows H_2O + O^-,$$
$$O^- - e \rightarrow O \text{ (slow stage)},$$

as valid for oxygen evolution from alkaline solutions on nickel and cobalt. Kheifets and Rivlin [106] suggest for acid solutions a mechanism including two-electron stages. Other views have also been held on the mechanism of oxygen evolution [11]. It is significant that they all start from the assumption that the overall reaction consists of several stages.

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Examination of the above results undoubtedly shows that the concept of stepwise (consecutive) electrochemical reactions has in several cases opened up new possibilities in the theory of the slow discharge of ions and has permitted a deeper insight into the mechanism of electrode processes. However, the view that a many-electron reaction must necessarily involve a series of successive one-electron stages is not justified. Actually, non-stepwise reactions and reactions having two-electron intermediate stages are also observed.

Published data do not always provide convincing evidence of the stepwise character of processes. If we ignore papers in which the conclusions of the authors are supported neither by their own experimental results, nor by later publications, there still remain a large number of cases in which the experimental results are quite contradictory, and not always sufficient for a definite conclusion to be reached. Furthermore, the electrochemical criteria themselves are such that it is not always possible to use them to substantiate details of the mechanism of a process. However, this must not be regarded as a rejection of the whole idea of successive stages. In several cases the stepwise occurrence of electrochemical reactions has been demonstrated convincingly, as in the electrode reactions of oxygen (see above), the anodic production of peroxodisulphuric acid [101] and of the higher oxygen compounds of chlorine [107,108], a considerable number of processes involving the oxidation or reduction of organic compounds [109], the reduction of nitric acid [109], etc.

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