CRITERIA FOR SHOWING THAT ELECTRODE PROCESSES OCCUR IN STAGES

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The appearance on the polarization curves of a discontinuity and two Tafel regions of different slopes corresponding to potential regions having different limiting stages (known as "discontinuity criteria") is one criterion for the stepwise nature of electrode processes which emerges from an analysis of the kinetic equations for an oxidation-reduction electrode process in which the consecutive electrode processes take place at finite velocities [1, 2]. For reliable observation of the discontinuity and of the Tafel regions on the polarization curves the exchange currents for the consecutive stages should not differ by more than 1.5 to 2 orders of magnitude [3-5]. Moreover, the polarization curves must be plotted up to current densities exceeding the exchange current for the overall electrode process by several orders of magnitude, which is a difficult experimental problem. If however the exchange currents for the different stages are comparable in magnitude (for example, differing by not more than a single order of magnitude) then the transitional region between the linear parts of the curve is close to the equilibrium potential q_e, and the reverse process prevents observation of the discontinuity and the two linear (Tafel) regions on the usual polarization curve. However, when the radiochemical method is used for plotting the true velocity of the electrode process (for example an anodic process i_a) distortion from the reverse process is eliminated, the discontinuity is easily seen, and furthermore is found to be close to the equilibrium potential q_e [6], a finding which significantly widens the scope of the discontinuity criterion. The application of this criterion to the results obtained by the radiochemical technique offers a means of showing that in the case of zinc and indium amalgams there is only one rate determining stage covering a wide potential range, the remaining stages being very close to equilibrium [the (q-$\log_e i_a$) curve shows no discontinuity in the region of q_e [7], whereas in the case of bismuth amalgam the consecutive electrode processes take place at similar rates and the (q $\log_e i_a$) curve exhibits a discontinuity close to q_e [8].

The object of the work reported in this article was to determine the laws governing the true anodic process and to set up appropriate kinetic equations for a wide range of potentials, on both the positive and negative sides of the equilibrium potential q_e at comparable velocities of the consecutive electrode processes, and also to test these equations experimentally.

We will consider the simplest stage type process, ionization-discharge, using the amalgams of a divalent metal as an example:

$$M \underset{k_{K_1}}{\overset{k_{a_1}}{\rightleftarrows}} M^+ + e; \quad M^+ \underset{k_{K_2}}{\overset{k_{a_2}}{\rightleftarrows}} M^{2+} + e.$$

It is assumed that the solution contains excess extraneous electrolyte, that its ionic strength is constant, and that the ψ_1 potential is insignificant and scarcely changes with the electrode potential.

In the presence of anodic polarization the velocities of the first and second stages are different, i.e.,

$$i_1 = i_{a1} - i_{K1} = k_{a1}[M]\exp(\beta_1 F\varphi/RT) - k_{K1}[M^+]\exp(-\alpha_1 F\varphi/RT), \quad (1)$$

$$i_2 = i_{a2} - i_{K2} = k_{a2}[M^+]\exp(\beta_2 F\varphi/RT) - k_{K2}[M^{2+}]\exp(-\alpha_2 F\varphi/RT). \quad (2)$$

At the equilibrium potential q_e, $i_1 = i_2 = 0$ and from Eqs. (1) and (2) we have

$$i_{01} = k_{a1}[M]\exp(\beta_1 F\varphi_p/RT) = k_{K1}[M^+]_p\exp(-\alpha_1 F\varphi_p/RT), \quad (3)$$

$$i_{02} = k_{a2}[M^+]_p\exp(\beta_2 F\varphi_p/RT) = k_{K2}[M^{2+}]\exp(-\alpha_2 F\varphi_p/RT), \quad (4)$$

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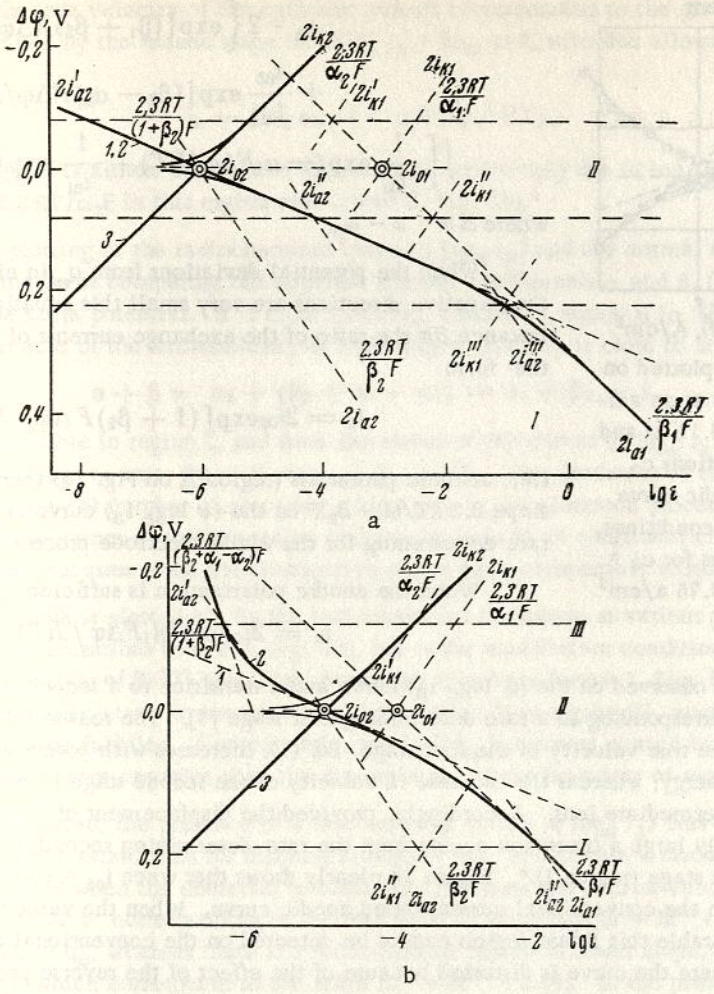


Fig. 1. Curves for the true velocities of the anodic and cathodic processes: 2, 3) curves corresponding to polarization conditions; 1) curve plotted on the basis of exchange currents with $\alpha_1 = 0.4$; $\beta_1 = 0.6$; $\alpha_2 = 0.6$; $\beta_2 = 0.4$; a) $i_{01} = 1000\, i_{02}$; b) $i_{01} = 10\, i_{02}$.

where $[M^+]_e$ is the equilibrium concentration of the intermediate regions. In the presence of polarization the $[M^+]$ can be found from the conditions for the stepwise character of the process, viz:

$$i = 2i_1 = 2i_2 = 2(i_{a1} - i_{k1}) = 2(i_{a2} - i_{k2}). \tag{5}$$

Substituting the quantities given by Eqs. (1) and (2) in Eq. (5) and rearranging it is found that

$$[M^+] = \frac{k_{a1}[M]\exp(\beta_1 F\varphi/RT) + k_{k2}[M^{2+}]\exp(-\alpha_2 F\varphi/RT)}{k_{a2}\exp(\beta_2 F\varphi/RT) + k_{k1}\exp(-\alpha_1 F\varphi/RT)}. \tag{6}$$

This expression can be used as the starting point for setting up the equation for the true anodic and cathodic curves corresponding to the various exchange currents for the different stages.

Assume for example that the exchange current for the second stage is less than for the first, i.e., $i_{02} < i_{01}$. If the process occurs in stages the anodic component of the overall current can then be expressed to a first approximation in terms of the true velocity of the slowest of the two consecutive stages:

$$i_a = 2i_{a2}, \tag{7}$$

From this equation together with Eqs. (2) and (6) and using Eqs. (3) and (4) to replace the velocity constants by the exchange currents for the various stages, an equation for the true velocity of the anodic process is produced which can be used for potentials on both the positive and negative sides of q_e, i.e.,

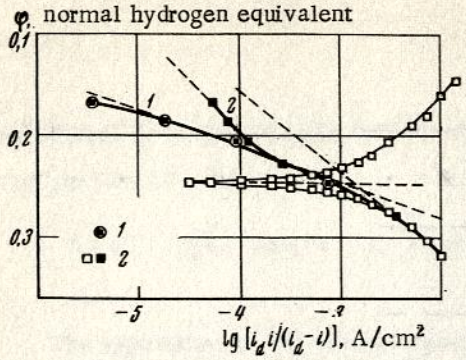


Fig. 2. 1) True anodic curve plotted on the basis of exchange currents at an amalgam concentration of c_a = 0.11 M and various equilibrium concentrations c_e ($1 \cdot 10^{-5}$-0.1 M); 2) true anodic curve corresponding to polarization conditions, and normal polarization curves for c_a = 0.11 M and c_e = 0.1 M; i_d^a = 0.76 a/cm².

$$i_a = 2\left\{\exp[(\beta_1+\beta_2)F\Delta\varphi/RT] + \frac{i_{02}}{i_{01}}\exp[(\beta_2-\alpha_2)F\Delta\varphi/RT]\right\} \Big/ \left[\frac{1}{i_{02}}\exp(-\alpha_1 F\Delta\varphi/RT)+\frac{1}{i_{01}}\exp\beta_2 F\Delta\varphi/RT\right], \quad (8)$$

where $\Delta\varphi = \varphi - \varphi_p$.

When the potential deviations from q_e in either the positive or the negative directions are very small this equation (making due allowance for the ratio of the exchange currents of the stages) takes the form

$$i_a = 2i_{02}\exp[(1+\beta_2)F\Delta\varphi/RT], \quad (9)$$

i.e., at these potentials (region II on Fig. 1a) there is a linear region of slope $2.3\,RT/(1+\beta_2)F$ on the (φ $\log_e i_a$) curve and the second stage is rate determining for the whole electrode process.

When the anodic polarization is sufficiently large, Eq. (8) gives

$$i_a = 2i_{01}\exp(\beta_1 F\Delta\varphi/RT), \quad (10)$$

i.e., a discontinuity should be observed on the (q $\log_e i_a$) curve and a transition to a second linear region having the higher slope $2.3\,RT/\beta_1 F$ corresponding to a rate determining first stage [9]. The reason for the discontinuity on the (q $\log_e i_a$) curve is that the true velocity of the first stage, Eq. (1), increases with potential only at the expense of a reduction in activation energy, whereas the increase in velocity of the second stage is also a function of the increased concentration of intermediate ions. Accordingly, provided the displacement of electrode potential in the positive direction is sufficiently large a transition occurs from the rate-determining second stage (region II on Fig. 1a) to a rate-determining first stage (region I).* Figure 1a clearly shows that when $i_{01} = 1000\ i_{02}$ a linear region of small slope is also observed on the conventional current based anodic curve. When the velocities of the consecutive electrode processes are comparable this linear region cannot be detected on the conventional anodic curve since the discontinuity is close to q_e where the curve is distorted because of the effect of the reverse process (Fig. 1b).

An analysis of Eq. (8) for the cathodic polarization region leads to important consequences. When the displacement of potential in the negative direction is sufficiently large the first term in the numerator and the second term in the denominator can be ignored so that

$$i_a = 2i_{02}\left(\frac{i_{02}}{i_{01}}\right)\exp[(\beta_2+\alpha_1-\alpha_2)F\Delta\varphi/RT]. \quad (11)$$

Consequently, when the potential deviations are in the negative direction with respect to q_e, i.e., under conditions in which the cathodic process predominates, an additional discontinuity and a third linear region having the steep slope of $2.3\,RT/(\beta_2+\alpha_1-\alpha_2)$ would be expected to appear on the (q $\log_e i_a$) curve (region III, Fig. 1b). This effect is associated with the disturbance of the reversibility of the first stage in region III whose boundary is defined by the point of intersection of the straight lines I_{k2} and i_{a1} (Fig. 1b). Moreover, as follows from Eq. (6) $[M^+]$ remains almost constant as the potential changes. Accordingly, in regions I and III both stages take place under irreversible conditions, whereas in region II only the second stage is irreversible and the conditions obtaining in the first stage are very close to equilibrium. The points of intersection of the horizontal broken lines in Fig. 1 with the curves for the true velocities of the anodic and cathodic processes, taken in conjunction with Eqs. (1) and (2), show the extent to which these stages are irreversible. Thus for example in regions I and III both stages are irreversible since at the given potential $i_{a1} \gg i_{k1}$ and $i_{a2} \gg i_{k2}$ (region I) and correspondingly $i_{a1} \ll i_{k1}$ and $i_{a2} \ll i_{k2}$ (region III). The discontinuity on the (q $\log_e i_a$) curve at the boundary of regions II and III) can be detected only by the radiochemical method, and its appearance is a certain indication that the process takes place in stages.

* The expressions for i_a for regions I and II and also the equation of the polarization curve for the stepwise process [6] can be obtained from the equations developed in Temkin's treatment of the theory of stationary reactions [10].

At all potentials the true velocity of the cathodic process corresponding to the given exchange current ratios ($i_{02} < i_{01}$) will be determined by the second stage in which $i_k = 2i_{k2}$ and, with due allowance for Eq. (2), can be expressed by the equation

$$i_к = 2i_{02} \exp(-\alpha_2 F\Delta\varphi / RT). \quad (12)$$

As is clear from Eq. (6) $[M^+]$ is almost constant in region I and accordingly the ($q \log_e i_k$) curve should retain its constant steep slope of $2.3\,RT/\alpha_2 F$ in this region also (curve 3, Fig. 1b).*

The simultaneous plotting of the radiochemical curve ($q \log_e i_a$) and the normal cathodic curve in the regions II and III offers a means of comparing the apparent transfer coefficients α and β, found from the slopes of these straight lines at the same potential. It is clear from Fig. 1b that in region II ($\alpha + \beta$) is equal to 2 as usual [6], whereas in region III, because of the irreversibility of both stages, this sum is close to unity:

$$\alpha + \beta = \alpha_2 + (\beta_2 + \alpha_1 - \alpha_2) = \alpha_1 + \beta_2 \sim 1.$$

Both stages are also irreversible in region I, and from the slopes of the curves ($q \log_e i_k$) and ($q \log_e i_a$) it can be seen that ($\alpha + \beta$) is again close to unity ($\alpha + \beta = \alpha_2 + \beta_1 \sim 1$). This deviation of the sum ($\alpha + \beta$) measured at constant potential from the total number of electrons taking part in the electrode process in regions I and III is determined by the irreversible nature of the two stages and can be used as an additional criterion for the steplike character of the electrode processes when the consecutive stages have comparable velocities.

If the true anodic curve is plotted not by the radiochemical technique at various polarizations and constant amalgam and solution concentrations (curve 2, Fig. 1b), but under equilibrium conditions by measuring the exchange current at various values of $[M^{2+}]$, then both stages are reversible (curve 1, Fig. 1b) and there should be no discontinuity on the true anodic curve in the transition from region II to region III since at equilibrium the condition $\alpha + \beta = 2$ must always be fulfilled. Consequently, the ($q \log_e i_a$) curves plotted by the above two methods should diverge at potentials more negative than the discontinuity at the boundary of regions II and III.

As has already been noted, the presence of a discontinuity on the ($q \log_e i_a$) curve in the presence of anodic polarization has already been established for bismuth amalgam [8]. In this case a discontinuity on this curve in the cathodic region was observed when the consecutive electrode processes had similar velocities (Fig. 2).† Moreover, a linear region of slope 0.074 V corresponding to the rate determining stage $Bi \rightarrow Bi^+ + e$ is observed on the anodic curve on the positive side of q_e, whereas there is a second linear region of lower slope, 0.033 V, on the ($q \log_e i_a$) curve in the region of q_e, which corresponds to the stage $Bi^+ \rightarrow Bi^{2+} + e$ [8]. In the presence of cathodic polarization an additional discontinuity and a linear region of slope 0.10 V appear on this curve (curve 2). The same curve when plotted on the basis of exchange currents (curve 1) retains the usual small slope in this potential region. At more positive potentials the curves coincide. The value of β calculated from the steep slope of the ($q \log_e i_a$) curve in the negative potential region is 0.58. In the same potential region $\alpha = 0.57$ [6] and consequently ($\alpha + \beta$) $\sim$ 1.15, i.e., this sum is significantly less than three.

Accordingly, the experimental data agree with the theoretical conclusions on the laws governing the true anodic process under conditions in which the cathodic process predominates.

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* In our previous article [6] for technical reasons some degree of inaccuracy had to be permitted in Fig. 2 (p. 1067), i.e., the ($q \log_e i_k$) should not show any discontinuities. The note appended to that figure remains true.

† An analysis of the equations for a three stage process [6] shows that under the given conditions ($i_{0.3} > i_{0.2}$) the slopes of the anodic curves for all three potential regions are the same as in the above considered two stage process.

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