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METALS IN ACIDS by Ya. V. Durdin (USSR)

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PROBLEMS ENCOUNTERED IN THE ELECTROCHEMICAL THEORY
GOVERNING THE DISSOLUTION OF METALS IN ACIDS. IV

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At present many works indicate that the speed of dissolution of metals (assuming that the speed is not markedly influenced by the diffusion of reagents) may be studied according laws which govern the speed of the electrode processes, i.e., the cathodic process of hydrogen liberation and the anodic process with the escape of metal ions into the solution (1-9). We find direct verification of this supposition in experiments of Wagner and Traud (2) on the determination of the speed of dissolution of zinc amalgams and the hydrogen overvoltage on these amalgams, and also in the work of Kolotyркиn and A. N. Frumkin on the speed of dissolution of lead and the hydrogen overvoltage on lead (5).

The theoretical basis of this supposition rests to a considerable degree upon the work of B. G. Levich and A. N. Frumkin (7) and also upon the conclusions obtained in our previous reports (9).

We should emphasize that these laws hold not only for the case of metals dissolving in acids (which is studied in our works) but also for the general theory of metal corrosion, since this type of laws corresponds to the special case of the Evans and Khor diagrams (cathode-anode control) (10, 11).

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In G. B. Akimov's recently published monograph "Theory and Methods of Investigating Corrosion in Metals" (12), this type of laws in metal corrosion is also considered as a real possibility.

Thus, special interest is attached to the laws governing the speed in the cathodic process of hydrogen liberation and the anodic process releasing metal ions into the solution.

In principle, one can generally solve this problem by simultaneously solving the equations describing the speed of the cathodic and anodic processes and by deriving the corresponding general equation. An attempt to derive such an equation was made by A. I. Shul'tin, (8) by a method involving great difficulties as is apparent from his works. These difficulties arise partially from the complexity of the expression obtained, and also from the dependence of this equation upon quantities not easily determined. In addition, the general equation will naturally depend upon the correctness of both individual equations describing the speeds in the cathodic and anodic processes, and upon which equation should be used to express the speed of the anodic process.

Taking these facts into consideration, one should represent more concretely the problem of how much each of these processes influences the kinetics of dissolution of metals.

Any concrete presentation of this problem should treat quantitatively the laws governing the dissolution of metals.

At first glance, the laws governing the speed in cathodic and anodic processes in some cases can be treated in a substantially simplified manner because the kinetic weight (degree of influence) of the cathodic process may so sharply predominate over the kinetic weight of the anodic process that one may neglect the influence of the latter. Actually, one could quite naturally assume that the kinetic weights of the cathodic and anodic processes

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should correspond, although roughly, to the amount of polarization in each of these processes. Moreover, the overvoltage corresponding to the cathodic process is generally high, while anodic (chemical) polarization is relatively weak for most metals. Thus, Pol'ner includes liberation and discharge of Zn, Cd, Sn, Pb, Cu, Hg ions among electrode processes which begin immediately after attainment of equilibrium potentials (more precisely, for very low polarization).

Thus one naturally assumes that in the dissolution of many metals the anodic polarization may be of the order of hundredths of a volt and the cathodic, tenths of a volt; i.e. cathodic polarization may be ten times greater than anodic polarization. At first glance, with this ratio between these quantities, we should rightly consider that the cathodic process practically determines the kinetics of the system. This should simplify considerably the treatment of the laws determining the speed of dissolution of metals. Unfortunately, such evaluations of the kinetic weight of these processes are purely intuitive and therefore might lead to incorrect conclusions.

In this work, we attempt, using the method which we developed previously for evaluating the kinetic weight of processes, to present more concretely the general picture of the possible relations between the kinetic weights of the cathodic and anodic processes, and at the same time to clarify the significance to be attached to the relations between the values of cathodic and anodic polarization.

1. Concerning the Coefficients: J^0 , η^0 and η in The System of Cathode and Anode Processes.

In the works entitled "Concerning the Kinetic Weight of a Process", [14] we introduced three coefficients that characterize the kinetic weight of a process: namely, the coefficient (J^0) governing the disturbance of equilibrium in the process, the coefficient (η^0) governing the decrease in the process speed and the coefficient (η) governing the influence of the parameters in the equation for the process' speed.

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In order to clarify the meaning of these coefficients in a given system, we at first accept conditionally that the speed of the cathodic process of hydrogen liberation and the speed of the anodic process releasing metal ions into the solution are proportional to the polarization corresponding to these processes.

Adopting at first this very simple assumption, we hope to show graphically how completely the whole picture of kinetic weight in the cathodic and anodic processes changes when we shift to more realistic assumptions concerning the functional relations between speed and polarization.

We adopt, consequently:

$$v_k = k_k \Delta \varphi_k = k_k (\varphi - \varphi_k^0) \quad (1a)$$

$$v = k_A \Delta \varphi_A = k_A (\varphi_A^0 - \varphi) \quad (1b)$$

In these equations φ is a potential identical for both electrode processes for a stationary state, relative to any standard electrode, for example, a normal hydrogen electrode, but taken with the reverse sign.

$\Delta \varphi_k$ is the overvoltage for the cathodic process of hydrogen liberation; φ_k^0 is the equilibrium potential corresponding to this process under the given conditions; φ_A^0 is the corresponding equilibrium potential for metal ions; $\Delta \varphi_A$ is the polarization corresponding to the anodic process releasing metal ions into the solution. We assume:

$$\Delta \varphi_k = (\varphi - \varphi_k^0) \quad \text{and} \quad \Delta \varphi_A = (\varphi_A^0 - \varphi) \quad (P.347a)$$

v_k and v_A , here as later, denote the resulting speed of the corresponding processes; i.e., v_k is the difference between the speed of the direct reaction discharging hydrogen ions and the ionization speed, and is the difference between the speed of release of metals ions into the

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solution and the speed of their discharge. We consider both speeds measured by the corresponding values of current density or by the number of gram-equivalents of hydrogen (in the case of v_k) or metal (in the case of v_A) released or dissolved per unit time per unit geometrical surface of the metal. (We also consider the current density measured relative to unit geometrical surface of the metal dissolved). Under these conditions, for the stationary state we have the equality $v_k = v_A$.

Figure 1 (Figures appended) shows graphically speeds v_k and v_A versus ϕ , according to equations (1a) and (1b). The point α describes the stationary state. This point is equivalent to the unique speed $v = v_k = v_A$ and the unique potential ϕ . This diagram corresponds to Evan's diagram for cathodic-anodic control. At the same time we easily see that in the system of the cathodic and anodic processes the potential plays the part of a regulating parameter, which we denote in the general case by Z ; therefore, from the standpoint of the principles developed in our work entitled "Concerning the Kinetic Weight of a Process", [14] this diagram is a particular case of the speed diagram - that is, a regulating parameter. Making use of this, we may easily clarify the meaning of the coefficients J^0 , η^0 and η for the given system of processes.

Recalling this, according to the definition given in our second report entitled "Concerning the Kinetic Weight of a Process", we set the coefficients J^0 equal to, respectively,

$$J_A^0 = \Delta Z_A^0 / \Delta Z_{AB}^0 \quad (2a)$$

$$J_B^0 = \Delta Z_B^0 / \Delta Z_{AB}^0 \quad (2b)$$

In the expressions (2), ΔZ^0 is a conditional measure of the disturbance of equilibrium corresponding to the processes A or B. ΔZ^0 is equal

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to the variation of the regulating parameter (Z) which is necessary in order to drive the given process from a given stationary state to a state of equilibrium, when all remaining parameters in its speed equation remain constant.

ΔZ_{AB}° is a conditional measure of the disturbance of equilibrium of the system:

$$\Delta Z_{AB}^{\circ} = \Delta Z_A^{\circ} + \Delta Z_B^{\circ}.$$

In the given system of processes $Z = \varphi$; therefore $\Delta Z_K^{\circ} = \Delta \varphi_K^{\circ}$; $\Delta Z_A^{\circ} = \Delta \varphi_A^{\circ}$ and $\Delta Z_{AK}^{\circ} = \Delta \varphi_A^{\circ} + \Delta \varphi_K^{\circ} = \varphi_A^{\circ} - \varphi_K^{\circ} = \Delta \varphi^{\circ}$.

Therefore, according to equation (2a), the coefficient of equilibrium disturbance of the cathodic process is equal to:

$$J_K^{\circ} = \frac{\Delta \varphi_K^{\circ}}{\Delta \varphi^{\circ}} \quad (3a)$$

and the coefficient of equilibrium disturbance in the anodic process J_A° is equal to

$$J_A^{\circ} = \frac{\Delta \varphi_A^{\circ}}{\Delta \varphi^{\circ}} \quad (3b)$$

Thus, in the system of cathodic and anodic processes, the quantity $\Delta \varphi^{\circ}$ which we took as a measure of equilibrium disturbance of the system is equal to the difference between the equilibrium potentials φ_A° and φ_K° , while the coefficient of equilibrium disturbance of each of these processes is equal to that fraction of this quantity which is due to polarization in the corresponding process. The meaning of the coefficients η° for the given system of processes can be clarified in the following manner:

If we assume that in figure 1 the straight line V_K occupies its same position, while the straight line V_A coincides with the normal N_A , then the stationary state is determined by the point $V_{K \max}$. In this case, the coefficient of equilibrium disturbance of the anodic process is equal to zero,

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while that of the cathodic process is equal to unity. The cathodic process in this case is the process determining the kinetics of the system, and the kinetic weight of the anodic process is equal to zero. The speed corresponding to this stationary state is equal to the maximum speed $V_{k \max}$, which the cathode process can have for the given straight line V_k and the given difference of potential $\Delta \varphi^0$. In all cases where the straight line V_A deviates from the normal N_A and $J_A^0 > 0$, the stationary state for the same straight line V_k will correspond to a speed less than $V_{k \max}$, for example, as the speed corresponding to point a in figure 1. We can consider this decrease in the cathodic process' speed compared with the speed $V_{k \max}$ as a result of the superposition of the influence of the anodic process. Therefore, as a measure of this influence, we can take the coefficient of reduction in the cathodic process' speed equal to

$$\eta_{k/A}^0 = (V_{k \max} - v_a) / V_{k \max} = 1 - v_a / V_{k \max} \quad (1a)$$

We can write a similar expression for the coefficient of reduction in the anodic process' speed

$$\eta_{A/K}^0 = 1 - v_a / V_{A \max} \quad (1b)$$

Here $V_{A \max}$ is the speed corresponding to the stationary state for $J_K^0 = 0$ which (i.e. states) corresponds to the straight line V_k coinciding with the normal N_k , and to the same straight line V_A corresponding to state described at the point a.

Since

$$\frac{v_a}{V_{k \max}} = \frac{\Delta \varphi_k}{\Delta \varphi^0} \quad (P.318, b)$$

we have

$$\eta_{k/A}^0 = J_A^0 = 1 - \frac{\Delta \varphi_k}{\Delta \varphi^0} = \frac{\Delta \varphi_A}{\Delta \varphi^0} \quad (5a)$$

and similarly

$$\eta_{A/K}^0 = \frac{\Delta \varphi_k}{\Delta \varphi^0} = J_k^0 \quad (5b)$$

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The differential coefficient characterizing the influence of the process parameters η , adopted by us as a third characteristic of the kinetic weight of a process, was considered at length in the work entitled "Concerning the Kinetic Weight of a Process", [14] and used in a latter work entitled "The Problem of the Electro-Chemical Mechanism".(9). Therefore, we simply mention that this coefficient is equal to the differential quotient of the inertia of the corresponding process

$$\eta_A = \frac{i_A}{i_A + i_B} = \frac{1}{1 + v_A^*/v_B^*} \quad (6a)$$

$$\eta_B = \frac{i_B}{i_A + i_B} = \frac{1}{1 + v_B^*/v_A^*} \quad (6b)$$

where η_A and η_B are the differential coefficients of influence of the parameters, respectively, of the processes A and B; i_A and i_B are the differential inertias of these processes corresponding to the given stationary state.

v_A^* and v_B^* are the absolute values of the partial derivatives of the speeds of the processes A and B with respect to the general regulating parameter Z for the same stationary state; whereupon $i_A = 1/v_A^*$ and $i_B = 1/v_B^*$.

In the case under consideration $Z = \varphi$; therefore because of the linear relation between the speeds v_k and v_A and phi φ , as is immediately apparent from Figure 1, we have:

$$\frac{v_k^*}{v_A^*} = \frac{\Delta \varphi_A}{\Delta \varphi_k} \quad (P.349, a)$$

from which we get

$$\eta_k = (1 + \Delta \varphi_A / \Delta \varphi_k)^{-1} = J_k^0 \quad (7a) \text{ and}$$

$$\eta_A = (1 + \Delta \varphi_k / \Delta \varphi_A)^{-1} = J_A^0 \quad (7b)$$

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According to expressions (5) and (7), we have:

$$\eta_k = \eta_{A/k}^{\circ} = j_k^{\circ} \text{ and } \eta_A = \eta_{K/A}^{\circ} = j_A^{\circ} \quad (8)$$

As was shown in our second report on the kinetic weight of a process [14 pp. 1379-1380], this equality of all three coefficients holds in all cases in which the speeds of both processes are linear functions of the regulating parameter. Moreover, according to the same report (p. 1387), if the speeds of both processes are linear functions of the regulating parameter, then the speed corresponding to the stationary state can be expressed by an equation similar to Ohm's law, in which the value ΔZ_{AB}° , adopted by us as a measure of equilibrium disturbance in the system, replaces the difference of potentials, while the resistance of the conductors is replaced by the inertias i_A and i_B . Then in the general case we have $V = \frac{\Delta Z_{AB}^{\circ}}{i_A + i_B}$. In the case under consideration, ΔZ_{BA}° is equal as in Ohm's Law to the difference in potentials

$$\varphi_A^{\circ} - \varphi_k^{\circ}; \text{ the inertias } i_A \text{ and } i_B \text{ are equal to } i_A = \frac{1}{k_A}, \text{ and } i_B = \frac{1}{k_B}.$$

Therefore in the given case we have

$$V = (\varphi_A^{\circ} - \varphi_k^{\circ}) / (i_A + i_k) = (\varphi_A^{\circ} - \varphi_k^{\circ}) k_A k_k / (k_A + k_k). \quad (\text{P. 350, a})$$

Assuming linear dependency of the speeds of the cathodic and anodic processes upon the polarizations corresponding to these processes, G. B. Akimov derived a general equation for current strength in a local cell. The expression which we obtained is essentially similar to the particular expression obtained by G. B. Akimov for the case of cathodic-anodic control. (See [12], p.84) We should also note that the equation $V = \frac{\Delta Z_{AB}^{\circ}}{i_A + i_B}$ may be retained even in nonlinear functions $V_A(Z)$ and $V_B(Z)$, if one understands the inertias i_A and i_B to be the "average inertias of the processes for the stationary state," as discussed by us in the aforementioned second report on the kinetic weight

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of a process (p.1377). We should remember, however, that in these cases the inertia is a considerably more complex function than in the case of linear functions $V_A(z)$ and $V_B(z)$ and ohmic resistance in conductors. For linear dependence of the velocities V_A and V_B upon z , each of the processes correspond to a specific value of inertia i which is determined by the slope of the corresponding straight line. But in the case of the nonlinear functions $V_A(z)$ and $V_B(z)$, the value of the "average inertias of the process for the given stationary state" will be determined not only by the behavior of the curve $V(z)$ of this process, but also by the behavior of the curve $V(z)$ of the second process.

Equations (8) show that if the speeds of the cathodic and anodic processes were proportional to the polarizations corresponding to these processes, the kinetic weight of the cathodic and anodic processes would actually be wholly determined by the ratio of the values $\Delta\phi_k$ and $\Delta\phi_A$. For a given value of $\Delta\phi^0$, the coefficients characterizing the kinetic weight of the process will vary directly with the polarization corresponding to this process. Thus, this dependence is shown graphically by straight lines, as in Figure 2. In this drawing, the values of anodic polarization are placed from left to right on the abscissa, and the values of cathodic polarization are placed from right to left. $\Delta\phi^0$ is taken equal to 0.75V. According to equations (8) and Figure 2, for $\Delta\phi_A = 0$

$$\begin{aligned} \text{we have } J_A^0 &= \eta_A = \eta_{k/A}^0 = \eta_A = 0, \\ J_k^0 &= \eta_k = \eta_{A/k}^0 = 1. \end{aligned} \quad (\text{P.350,b})$$

In this case the cathodic process is determining the kinetics of the system, and the kinetic weight of the anodic process is equal to zero. From the absolute point of view, in all cases where $\Delta\phi_A > 0$ and consequently $J_A^0 = \eta_A = \eta_{k/A}^0 > 0$ and $J_k^0 = \eta_k = \eta_{A/k}^0 < 1$, the cathodic process no longer determines the kinetics of the system. However, taking

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the error in the experiment into consideration, we can consider the cathodic process as practically determining the kinetics of the system for values of J_A^0 slightly greater than zero and J_K^0 slightly less than unity. Let us suppose that $\Delta\varphi^0 = 0.75$ V and $\Delta\varphi_A = 0.05$ V; then from the equation $J_A^0 = \Delta\varphi_A / \Delta\varphi^0 = 1 - \Delta\varphi_A / \Delta\varphi^0$ it is easy to find that for these values of $\Delta\varphi_A$ and $\Delta\varphi^0$ the deviation of J_K^0 from unity must be about 6-7%. Hence, we might conclude that for the case of dissolving zinc in acids, for example, in which the anode polarization may apparently be even less than 0.05 V, we may within the limits of probable error in the experiment, about 10%, actually disregard the effect of anodic polarization. We disturb the simple relations between the kinetic weight of the cathodic and anodic processes and the values $\Delta\varphi$ that we have considered, however, as soon as we negate the assumption which we made concerning the linear type of polarization curves for both processes.

2. Equations Determining the Polarization Curves of the Cathodic and Anodic Process.

One of the most important problems is which equation should be used in the electrochemical theory of dissolving metals to describe the speeds of the cathodic and anodic processes. The problem itself is not sufficiently clear at this time. This problem will be simplified for the purposes of this work if we interest ourselves only in the dependence of the speeds of the cathodic and anodic processes upon a limiting change of potential, that is, the equations of the polarization curves corresponding to these processes. However, even in this case we do not have equations, whose correctness can be considered fully proven; the equation for the anodic process speed is more indefinite. Therefore, keeping in mind that the aim of this work is only to make more concrete the general picture of the possible relations among the kinetic weights of the cathodic and anodic processes and their dependence upon the polarizations corresponding to these processes, we proceed in the following manner.

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The basic equation for the cathodic process speed is taken to be the expression:

$$v_k = B \cdot \exp(\Delta\phi_k/b) \quad (9)$$

where

$$b = 2RT/F = 50 \text{ mv.}$$

Moreover, in some cases it will be convenient to use the more complete expression:

$$v_k = B \left[\exp\left(\frac{\Delta\phi_k}{b}\right) - \exp\left(-\frac{\Delta\phi_k}{b}\right) \right] \quad (10)$$

The first of these equations corresponds essentially to Tafel's equation and, consequently, we may consider that it reflects quite well the dependence of the cathodic process speed upon overvoltage for most cases of hydrogen liberation at cathodes during electrolysis. Assuming that this equation also holds for hydrogen liberation at the surface of a dissolving metal, we make the previous assumption. Equation (10) corresponds to the theory of delayed discharging. In this equation, $B \cdot \exp(\Delta\phi_k/b)$ describes the speed of direct discharge of hydrogen ions, and $B \cdot \exp(-\Delta\phi_k/b)$ is the speed of the reverse process of hydrogen ionization. As was shown before by Fol'ner, for values of $\Delta\phi_k$ approx. equal to 0.05 - 0.1 V (depending upon the accuracy of calculation), the last term of equation (10) may be disregarded, whereupon equation (10) becomes equation (9),

In these and further expressions, we will consider the velocity V measured in the units stipulated above in equations (1).

The problem of selecting an equation for the anodic process' speed is considerably more difficult. Several authors [2, 3, 4, 6, 8] have surmised that an equation, corresponding to the theory of delayed discharge could be used for the speed of this process. In this case, we might write:

$$v_A = A \left[\exp\left(\frac{\Delta\phi_A}{a_1}\right) - \exp\left(-\frac{\Delta\phi_A}{a_2}\right) \right] \quad (11)$$

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where $a_1 = \frac{RT}{nF\alpha_1}$ and $a_2 = \frac{RT}{nF\alpha_2}$.

If we assume further, by analogy with the cathodic process of hydrogen liberation, that $\alpha_1 = \alpha_2 = 1/2$ and take the valence of the metal's ions $n = 2$, then we have:

$$a_1 = a_2 = RT/F = \frac{1}{2} b.$$

With increase of anode polarization, the second term in equation (11) must become small in comparison with the first; then this equation is simplified as was equation (10):

$$v_A = A \cdot \exp \frac{\Delta\phi_A}{a} \quad (12)$$

It is easily seen that for the condition $a = \frac{1}{2} b$ this simplification may be adopted, depending on the desired accuracy of calculation, for values of $\Delta\phi_A$ of the order of 0.025-0.05 V.

The employment of the theory of delayed discharge for the anodic process in dissolving metals was based, to a considerable degree, on the works of V. A. Royter, V. A. Yuza, Ye. S. Poluyan [15], and also on those of V. A. Yuza and L. D. Kopyl [16], in which these authors showed that the data obtained from oscillograph studies of the polarization of metallic electrodes from iron, zinc, nickel and copper could be reconciled with the equations stemming from the theory of delayed discharge. At the same time, however, as these authors show, this correspondence with the theory of delayed discharge is obtained only with the oscillograph method of investigating polarization. If the usual methods are used, however, other dependencies are obtained. Thus, V. A. Royter and V. A. Yuza found that the speed of the anodic process in dissolving iron could be best expressed by an equation corresponding in form to Langmuir's isothermal curve:

$$\Delta\phi_A = \frac{\alpha \cdot \beta v_A}{1 + \beta v_A} \quad \text{or} \quad v_A = \frac{\Delta\phi_A}{\beta(\alpha - \Delta\phi_A)} \quad (13)$$

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In equation (13) α and β are constants, while α naturally is of a different value from the α in Folmer's equation. In the same work, it is shown that Shokl's data on the anodic polarization of nickel can be expressed by the equation:

$$v_A = k \Delta \varphi_A^n \quad (11)$$

These authors assumed that these deviations from logarithmic dependence are determined by changes of the electrode surface when loaded by current. These changes depend upon the current density and, consequently, on the value of $\Delta \varphi$. In dissolving metals, the speed corresponding to the stationary regime, which is established a certain time interval after the test begins, is usually investigated; therefore, in this case, it is more correct to proceed from the polarization curves obtained for the anodic process in metal electrodes by the usual method. The introduction of a coefficient which allows for the surface changes (as was done, for example, in the works of A. I. Shul'tin [8]) fails in its purpose, since we do not know the dependence of this coefficient upon current density.

Nevertheless, it is expedient to consider from the start those relationships which are obtained on the basis of equation (11), since in the first place in some cases (as, for example, in the dissolution of amalgams), distortions of the polarization curves caused by surface changes may not possibly occur; in the second place the laws obtained in this case are quite representative and the basic characteristics of these laws can be shown to be dependent only upon whether the anodic process's speed is in agreement with equation (12), whereupon a may not be equal to $\frac{1}{2}b$. The last equation, for an arbitrary value of a , can be considered independent of the theory of delayed discharge.

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Since the values $\Delta\phi_K$ and $\Delta\phi_A$ are connected by the relations $\Delta\phi_K = \phi - \phi^0$, $\Delta\phi_A = \phi^0 - \phi$ and $\Delta\phi_K = \Delta\phi^0 - \Delta\phi_A$, we can by making the proper substitutions in the equations for the speeds of the cathodic and anodic processes always express both of these speeds as functions of ϕ , $\Delta\phi_K$ or $\Delta\phi_A$; whereupon one of the latter will act as the regulating parameter in the given system of equations. However, in the search for expressions for the partial derivatives v_K' and v_A' such a substitution is superfluous, since we can find these values directly by differentiating equations (10) and (11) respectively with respect to $\Delta\phi_K$ and $\Delta\phi_A$, where the quantity ϕ^0 under these circumstances must be considered a constant, and v_K' and v_A' are equal to the absolute values of the corresponding partial derivatives. Let us assume from the beginning that in equation (11) $a_1 = a_2 = \frac{1}{2}b$, where $n = 2$. For the sake of convenience we introduce the designations: $\exp \frac{\Delta\phi_K}{b} = h_1$, $\exp -\frac{\Delta\phi_K}{b} = h_2$; $\exp \frac{2\Delta\phi_A}{b} = m_1$, $\exp -\frac{2\Delta\phi_A}{b} = m_2$. (P.353(a))

Equations (10) and (11) may then be written in the form:

$$V_K = B(h_1 - h_2) \text{ and} \quad (15a)$$

$$V_A = A(m_1 - m_2), \quad (15b)$$

Hence $v_K' = \frac{B}{b} (h_1 + h_2) \quad (16a)$

$$v_A' = \frac{2A}{b} (m_1 + m_2). \quad (16b)$$

The ratio of these derivatives in equation (6) is equal to:

$$\frac{v_K'}{v_A'} = \frac{B}{2A} \left(\frac{h_1 + h_2}{m_1 + m_2} \right). \quad (17)$$

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For the stationary state, V_k and V_A are equal so that according to equations (15a) and (15b), we have

$$\frac{B}{A} = \frac{m_1 - m_2}{h_1 - h_2} \quad (18)$$

and thus on the basis of equations (17) and (6) we obtain

$$\frac{1}{\eta_v} = 1 + \frac{1}{2} \cdot \frac{(h_1 + h_2)(m_1 - m_2)}{(h_1 - h_2)(m_1 + m_2)} \quad (19)$$

We do not have to write the corresponding expression for η_A , since we have the relationship $\eta_A = 1 - \eta_k$.

In equation (19), η_k is completely determined by the values of anodic and cathodic polarization.

Figure 3 shows the curves corresponding to this equation, which express the dependence of the coefficients η_k and η_A upon the values of anodic and cathodic polarization. In this figure, the same quantities as in Figure 2 are used for the coordinate axes; $\Delta\phi^0$ is taken equal to 0.5 V for convenience.

By comparing the curves shown in Figures 2 and 3, we see that for exponential dependency of the speeds of the cathodic and anodic processes upon polarization, we have an entirely different type of curve $\eta(\Delta\phi)$ than for a linear dependence.

Actually in Figure 3 and Figure 2, we have $\eta_A = 0$ and $\eta_k = 1$ in the limiting case $\Delta\phi_A = 0, J_A^0 = 0$, and we have $\eta_k = 0$ and $\eta_A = 1$ in the case $\Delta\phi_k = 0, J_k^0 = 0$. But for finite values of cathodic and anodic polarization, the curves in Figure 3 give an entirely different picture than the straight lines in Figure 2. The most representative conclusion to be obtained from the curves in Figure 3 is that in the given case the coefficients of influence in the parameters in both processes acquire a certain constant value $\eta_k = 2/3$ and $\eta_A = 1/3$, which we will call characteristic.

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This characteristic value is acquired by both coefficients from the moment that the cathodic and anodic polarization achieve a certain small value.

From Figure 3, we see that we can consider that the coefficients acquire the characteristic value approximately even for cathodic polarization ≥ 0.05 V and anodic ≥ 0.025 V, and accurately for cathodic polarization ≥ 0.1 V and anodic ≥ 0.05 V. One is easily convinced that these values of anodic and cathodic polarization are precisely those values for which we may disregard the second terms namely, h_2 and m_2 in the equations of speeds V_A and V_K and derivatives V_A' and V_K' ; hence, those values of cathodic and anodic polarization for which the speed of the reverse processes (that is, the process of hydrogen ionization and the process of discharging metal ions) become sufficiently small in comparison with the speeds of the corresponding direct processes.

According to this, we have a right to expect that for existence of the characteristic values of the coefficients η , it is sufficient that the speeds of the cathodic and anodic process conform to equations (9) and (12).

Actually, the derivatives V_K' and V_A' in the given case are equal to

$$v_k' = \frac{B}{b} \cdot \exp \frac{\Delta \phi_k}{b} \quad (20a)$$

$$v_A' = \frac{A}{a_1} \cdot \exp \frac{\Delta \phi_A}{a_1} \quad (20b)$$

It is important that the derivatives in the given case be proportional to the speeds; that is, we write:

$$v_k' = v_k / b \quad (21a)$$

$$v_A' = v_A / a_1 \quad (21b)$$

and since for the stationary state $v_A = v_k$, then we have

$$v_k' / v_A' = a_1 / b = \text{constant} \quad (22)$$

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This constancy of the ratio of the derivatives, obviously, is the reason for the existence of characteristic values for the coefficients η . By substituting the expression which we obtained for the ratio of derivatives into equation (6), we have:

$$\eta_k = \frac{1}{1+a_1/b} = \text{constant.} \quad (29)$$

In the special case where $a_1 = \frac{1}{2}b$ we have:

$$\eta_k = \frac{1}{1+1/2} = 2/3. \quad (\text{P.355,a})$$

On the basis of the above, we make the following conclusions:

characteristic values for the coefficients η will be present when the speeds of the cathodic and anodic processes can be expressed by equations (9) and (12).

The characteristic value of the coefficients η is determined, according to equation (22), by the ratio of a_1 and b . If $a_1 = b$, then the characteristic values of these coefficients are equal: $\eta_k = \eta_A = 1/2$; if $a_1 < b$, then $\eta_k > \eta_A$; if $a_1 > b$, then $\eta_k < \eta_A$. In the special case where $a_1 = \frac{1}{2}b$, then the coefficient of influence in the cathodic process parameters is twice as large as that of the anode. If the equality $a_1 = \frac{1}{2}b$ is defined so that $b = \frac{2RT}{nF}$ and $a_1 = \frac{2RT}{nF}$ where $n = 2$, then the twice greater value for the coefficient of influence in the cathode process's parameters is the result of a twice greater charge of the metal ions. For $n = 3$, we would have $a_1 = \frac{1}{3}b$ and correspondingly: $\eta_k = \frac{3}{4}$ and $\eta_A = \frac{1}{4}$.

Further, we observe that if the speeds of the cathodic and anodic processes conform to equations (9) and (12), then the general type of curves

$\eta(\Delta\phi)$ should correspond to the type of curves shown in Figure 3, since the correctness of these equations as we have seen is determined by the existence of horizontal sections in these curves; moreover, the end points of these curves must always satisfy these conditions:

$$\begin{cases} \text{for } \Delta\phi_A = 0, \text{ then } \eta_k = 1 \text{ and } \eta_A = 0; \\ \text{for } \Delta\phi_k = 0, \text{ then } \eta_k = 0 \text{ and } \eta_A = 1. \end{cases} \quad (\text{P.356a})$$

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CONFIDENTIAL4. The Speed of the Anodic Process As Expressed by Equation (14).

We now assume that the speed of the cathodic process is expressed by equation (9) and the speed of the anodic process by equation (14). The derivative v_k' in this case as formerly is expressed by equation (20a). The derivative of v_A in this case is equal to

$$v_A' = nk \Delta \phi_A^{n-1} \quad (24)$$

from which, by a derivation similar to that discussed in the preceding cases, we have:

$$\gamma_k = \frac{1}{1 + \Delta \phi_A / nb} \quad (25)$$

In the special case $n = 1$, we have

$$\gamma_k = (1 + \Delta \phi_A / b)^{-1} \quad (26)$$

Curves corresponding to these equations will be considered later.

We note that expression (26) is quite similar to the expression for the coefficient γ_k which we obtained in one of the preceding reports for this coefficient in the system: cathodic process — electroconductivity process; the only difference is that in equation (26) we have the anodic polarization instead of the ohmic potential drop in the microcell.

5. The Speed of the Anodic Process as Expressed by Equation (13)

We now assume that the speed of the anodic process is expressed by equation (13) and the cathodic speed, as before, by equation (9).

Then the derivative v_A' is equal to:

$$v_A' = \frac{1}{\beta(\alpha - \Delta \phi_A)} + \frac{\Delta \phi_A}{\beta(\alpha - \Delta \phi_A)^2} = \frac{\alpha}{\beta(\alpha - \Delta \phi_A)} \quad (27)$$

According to equations (13) and (21a) we have, accordingly:

$$\frac{v_A}{\Delta \phi_A} = \frac{1}{\beta(\alpha - \Delta \phi_A)} \quad \text{and} \quad v_k = b v_k' \quad (P. 356, b)$$

and thus for a stationary state $v_k = v_A$ we have:

$$\frac{1}{\beta(\alpha - \Delta \phi_A)} = \frac{b v_k'}{\Delta \phi_A} \quad (P. 356, c)$$

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By making the proper substitution in equation (27), we obtain

$$v_A = \frac{v_i \alpha b}{\Delta \phi_A (\alpha - \Delta \phi_A)} \quad (\text{p. 356, d})$$

Hence

$$v_k / v_A = \Delta \phi_A (\alpha - \Delta \phi_A) / \alpha b, \quad (28)$$

and

$$1/k = \frac{1}{1 + \Delta \phi_A (\alpha - \Delta \phi_A) / \alpha b} \quad (29)$$

In order to draw the actual curve $\eta_k(\Delta \phi_A)$ corresponding to equation (29) we must know not only the coefficient b , but also the coefficient α . The value of this coefficient can be found by an experimental determination of the anodic polarization curve, but we should think that the value of α may change substantially in the changeover from one concrete case to another.

In this work, we can limit ourselves in any consideration of the curve $\eta_k(\Delta \phi_A)$ to some arbitrarily assigned but plausible values of α . For this purpose, we may consider that the polarization curves $v_A(\Delta \phi_A)$ corresponding to equation (13) must be of the saturation curve type, with the limiting value $\Delta \phi_A = \alpha$. Let us assume that this limiting value of $\Delta \phi_A$ is of the order 0.2 V. This is of the same order of magnitude as the experimental curves for anodic polarization obtained by V. Royter and V. Yuza for technical iron.

Setting $\alpha = 200$ mV and $b = 50$ mV in equation (29), we obtain the curve $\eta_k(\Delta \phi_A)$ shown as curve I in Figure 4. For graphic illustration of the effect of changing α upon this curve's characteristic, the curve $\eta_k(\Delta \phi_A)$ for $\alpha = 100$ mV. (curve II) is also shown in this figure.

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CONFIDENTIAL**6. The Coefficient of Reduction in the Cathodic Process Speed**

For brevity we will limit ourselves to the derivation of an expression for the coefficient of reduction in the cathodic process speed, which is more interesting and definite than the corresponding coefficient for the anodic process. For the cathodic process speed we shall take equation (9), in which we replace the quantity $\Delta \phi_k$ with its equivalent $(\Delta \phi^0 - \Delta \phi_A)$; then we have:

$$v_k = B \cdot \exp \frac{\Delta \phi^0 - \Delta \phi_A}{b} \quad (30)$$

If $\Delta \phi_A = 0$, we have:

$$v_k = v_{k, \max} = B \cdot \exp \frac{\Delta \phi^0}{b} \quad (31)$$

On the basis of the general expression for the coefficient of reduction of process speed (11a) and equations (30) and (31) we have:

$$\eta_{k/A}^0 = 1 - \exp \left(-\frac{\Delta \phi_A}{b} \right) \quad (32)$$

According to equation (32), the coefficient of reduction in the cathodic process speed is completely determined by the amount of anodic polarization and the value of the coefficient b in the equation for the cathodic process speed.

(Note: We also note that, in the general case, when there is not only a marked amount of anode polarization, but also an ohmic potential drop, the coefficient of reduction in the cathodic process speed may be expressed as

$$\eta_{k/AE}^0 = 1 - \exp \left(-\frac{\Delta \phi_A + \Delta \phi_E}{b} \right) \quad (\text{P. 358, c})$$

where $\Delta \phi_E$ is the ohmic potential drop in the microcell. When $\Delta \phi_E = 0$ we obtain equation (32); with $\Delta \phi_A = 0$, we shall obtain a similar expression for the system: cathodic process-electroconductivity).

CONFIDENTIAL**7. Interpretation of the Results**

Let us try now to use the equations we have obtained in order to evaluate the degree to which the kinetic weight of the cathodic process is reduced because of the presence of the anodic process in the system. For this purpose, it is convenient to rely on the equation for the cathodic process speed and try to find to what degree this equation becomes invalid because of the increased kinetic weight of the anodic process.

We will use equation (30) here to describe the speed of the cathodic process.

In those cases where anodic polarization equals zero, we have the conditions:

$$\begin{aligned} J_A^0 &= \eta_A = \eta_{A,0} = 0, \\ \text{and } J_k^0 &= \eta_k = \eta_{k,0} = 1. \end{aligned} \quad (\text{P. 358, a})$$

Moreover, in this case, equation (30) may be written in the form:

$$v_k = v_{k, \text{max}} = B \cdot \exp \frac{\Delta \phi^c}{b}. \quad (31)$$

In this case, the cathodic process is determining the kinetics, and equation (31) is a valid expression of speed in the system of cathodic and anodic processes.

When $\Delta \phi_A > 0$, we have the inequalities:

$$\begin{aligned} J_A^0 &> 0, \eta_A > 0, \eta_{A,0} > 0; \\ \text{and } J_k^0 &< 1, \eta_k < 1, \eta_{k,0} < 1. \end{aligned} \quad (\text{P. 358, b})$$

The cathodic process in this case, generally speaking, no longer determines the kinetics of the system; because of this, equation (31) does not determine the speed of the system of cathodic and anodic processes. Equation (30) remains correct, but is not completely valid, since the regulating parameter $\Delta \phi_A$ varies the anodic process speed, the result of which is a reduction of the coefficient of influence in the parameters in the equation for the cathodic process speed; that is, the inequality becomes $\eta_k < 1$. For

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the nature of the degree of influence of the anodic process, we find it convenient not to examine the value η_k itself, but rather the value $1-\eta_k$ or the value $(1-\eta_k) \cdot 100$. The last quantity characterizes the reduction of the value of η_k , expressed in percents, which is determined by the influence of the anodic process (we recall, also, that $1-\eta_k = \eta_A$).

Besides reducing the value of the coefficient η_k , the influence of the anodic process is also reflected in the fact that the speed corresponding to the stationary state becomes less than the speed $V_{k_{max}}$.

The coefficient $\eta_{k/A}^0$ characterizes the amount of this reduction of speed V_k , which also we find convenient to express in percents, thus taking the value to be $100 \cdot \eta_{k/A}^0$. Moreover, at $\Delta \phi_A > 0$, the coefficient J_A^0 naturally becomes greater than zero and the coefficient J_k^0 less than unity. Now, we use the equations obtained to try to imagine what values we might expect for the quantities $(1-\eta_k) \cdot 100$ and $\eta_{k/A}^0 \cdot 100$ for various values of $\Delta \phi_A$ and $\Delta \phi_k$. With this in mind, we will first consider the system of curves shown in Figure 5.

In this drawing, the anodic polarization is placed along the abscissa and the quantities $\eta_{k/A}^0 \cdot 100$ and $(1-\eta_k) \cdot 100$ are placed along the ordinate.

Curves 1 and 2 correspond to values of η_k , calculated from equation (29). These curves correspond, consequently, to curves 1 and 2 in Figure 4, with the difference that in Figure 4 we had the dependency of η_k upon $\Delta \phi_A$, while here we have the dependency of $(1-\eta_k) \cdot 100$ upon $\Delta \phi_A$.

Curve 3 corresponds to values of η_k calculated from equation (19); curve 4 corresponds to values of η_k calculated from equation (26); curve 5 is from equation (25) (with $n = 3$). The straight line 6 shows values of η_k calculated from equation (7a); that is, for the case where the speeds of both the cathodic and anodic processes are linear functions of the respective polarization $\Delta \phi_k$ and $\Delta \phi_A$. Here straight line 6 expresses

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simultaneously the dependence upon $\Delta \varphi_A$ of all three quantities, $(1-\eta_c) \cdot 100$, $\eta_{k/A}^0 \cdot 100$, and $V_A^0 \cdot 100$ for $\Delta \varphi^0 = 0.5V$. Finally, curve 7 expresses the dependence upon $\Delta \varphi_A$ of the coefficient of reduction in the cathodic process speed $\eta_{k/A}^0 \cdot 100$, according to equation (32).

(a) With regard to the system of curves shown in Figure 5, we note first of all the following situation: Those parts of the curves which correspond to the condition $\Delta \varphi_k > 0.1 V$ are shown by solid lines in this drawing. Obviously, these solid sectors of the respective curves 1, 2, 4, and 5 correspond exactly to equations (29), (26), and (25), since this condition justifies the simplified expression for the cathodic process speed (9) which we adopted in the derivation of these equations. The dotted portions of curves 4 and 5 were drawn in approximately. As is immediately apparent from equations (25), (26), and (29), the solid portions of the respective curves corresponding to values of the quantity $(1-\eta_c) \cdot 100$ are determined by one value of anodic polarization and do not depend on values of cathodic polarization or, consequently, upon the ratio $\Delta \varphi_k / \Delta \varphi_A$ and the quantity $\Delta \varphi^0$. The same principle holds for the solid portion of curve 3, since for $\Delta \varphi_k > 0.1 V$, the terms h_1 and h_2 in equation (19) drop out. In this relationship, we have the essential difference of the curves 1-5 from the straight line 6, whose slope will vary with $\Delta \varphi^0$. This characteristic of the curves 1-5 is due to the fact that the continuous sections of these curves correspond to the same initial equation for the cathodic process speed (9) and, consequently, to the proportionality of the quantities V_k and V_A , for which as was shown above the coefficients become independent of the value of $\Delta \varphi$ corresponding to the given process. Thus, we can conclude that whenever equation (9) holds for the cathodic process speed, the reduction of the coefficient of influence in the cathodic process parameters is determined by the amount of anodic polarization

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and does not depend upon the amount of cathodic polarization or, consequently, upon the value of $\Delta\phi^0$. We have a similar situation, according to equation (32), for the coefficient of reduction in the cathodic process speed (curve 7 in Figure 5). This does not mean, however, that cathodic polarization is of less importance than anodic polarization. We must take into consideration that in the beginning the influence of cathodic polarization was very sharply felt in the value of the coefficients η (the dotted section of the curves in Figure 5), reaching a somewhat definite limiting value for $\Delta\phi/k \gg 0.1$ V. Moreover, the coefficient of reduction in the anodic process speed, as is easily seen, will be determined by the amount of cathodic polarization, and since the latter is usually high the value $\eta_{A/k}^0$ must generally be close to unity.

(b) The second thesis, based directly upon considerations of the system of curves shown in figure 5, is that the dependence of the quantity $(1-\eta_k) \cdot 100$ upon the amount of anodic polarization varies not only quantitatively, but also qualitatively, with a change in the equations determining the polarization curves of the cathodic and anodic processes, or even the polarization curves of one of these processes — the anodic as is seen from a comparison of curves 1-5.

Comparison of curves 1-5 and 7 with the straight line 6 shows directly that knowledge of the coefficient of disturbance of equilibrium I^0 is still not enough to evaluate the relations between the kinetic weights of the cathodic and anodic processes.

(c) From Figure 5 we also see that, in the region of small values of anodic polarization from zero up to about 0.02 V, curves 1-3 in the first approximation may be considered as coinciding with curve 4. This obviously results from the fact that curve 4 corresponds to a linear dependency of the anodic process speed upon $\Delta\phi_A$ (equation 14) with $n = 1$); and for small

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values of anodic polarization equations (13) and (11) also give a linear dependence of the anodic process speed upon $\Delta \varphi_A$. Finally, in this region of values for $\Delta \varphi_A$, curve 7 for the coefficient of reduction in the cathodic process speed also coincides quite closely with curve 4.

Curve 4 corresponds to values of η_k calculated from equation (26):

$$\eta_k = \frac{1}{1 + \Delta \varphi_A / b} \quad \text{or} \quad (1 - \eta_k) \cdot 100 = \frac{\Delta \varphi_A \cdot 100}{\Delta \varphi_A + b} \quad (33)$$

Thus, we can conclude that, with the anodic process speed linearly dependent upon $\Delta \varphi_A$ in the region of small values of $\Delta \varphi_A$, the reduction of the coefficient of influence in the cathodic process parameters will approximately equal the coefficient of reduction in the cathodic process speed; whereupon both values can be approximately expressed by equation (33). This thesis is an important one for us, since generally the dependence of the anodic process speed upon $\Delta \varphi_A$ for small $\Delta \varphi_A$ is quite likely linear and the correctness of equation (33) leads to the conclusion that the kinetic weight of the anodic process must become noticeable even for very small values of $\Delta \varphi_A$. Actually, let us assume for purposes of approximate calculation that the experimental error in determining the speed of dissolving metals is about 10% and that, after taking this error into consideration we may take the equation for the cathodic process speed as valid until the quantities $(1 - \eta_k) \cdot 100$ and $\eta_k^0 \cdot 100$ reaches 10%.

According to equation (33), the quantities $(1 - \eta_k) \cdot 100$ and $\eta_k^0 \cdot 100$ reach 10% with an anodic polarization $\Delta \varphi_A = 0.005$ V, that is, less than 0.01 V. For anodic polarization of 0.02 V, the value of these quantities has already reached about 30%. Thus according to equation (33) the error in using equation (31) will exceed the limits of error permitted by us in the experiment even for anodic polarization $\Delta \varphi_A < 0.01$ V; and for an anodic polarization of 0.02 V, this error has really become substantial.

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As we note, using for an example the dissolution of zinc and assuming $\Delta\phi^0 = 0.75$ V; we should obtain, for the coefficients of disturbance of equilibrium J_K^0 and J_A^0 with $\Delta\phi_A = 0.02$ V, the values $J_K^0 \cdot 100 = 97\%$ and $J_A^0 \cdot 100 = 3\%$ and, for the ratio of these values, $J_K^0/J_A^0 = \Delta\phi_K/\Delta\phi_A \approx 35$.

Thus according to equation (33) we must attribute a noticeable kinetic weight to the anodic process, notwithstanding the fact that in the given case the overvoltage due to the cathodic process is approximately thirty times greater than the anodic polarization.

By assuming linear polarization curves for both processes, we should have in this case $(1-\eta_k) \cdot 100 = \eta_{k/A}^0 \cdot 100 = J_A^0 \cdot 100 = 3\%$ and should be able to consider the equation for the cathodic process speed valid within the limits of the accepted error and the kinetic weight of the anodic process practically equal to zero.

We have in these relations an example of the situation discussed in our second report on the kinetic weight of a process according to which a small, but not infinitely small, value for the coefficient of disturbance of equilibrium in the given process, for example process A (that is, the condition $J_A^0 \ll J_B^0$), still does not necessarily determine process A as a practically inert process, or process B as the process which determines the kinetics of the system.

(d) For values of anodic polarization above 0.02-0.03 V, all the curves in Figure 5 have begun to diverge. Nevertheless, as an approximate evaluation, one should expect a higher value for the coefficient of influence in the cathodic process parameters, that is $\eta_k > \eta_A$, for all values of $\Delta\phi_A < 0.05$ V.

In addition, the coefficient of reduction of cathodic process speed in this region must still be less than about 50%, while the coefficient of reduction of the anodic process speed must as a general rule be close to 100% in these cases.

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In other words, for anodic polarization up to 0.05 V, the predominant kinetic weight must still belong to the cathode process. For values of anode polarization $0.05 \text{ V} < \Delta \phi_A < 0.1 \text{ V}$ then close values for the coefficients η_k and η_A can be expected; and for $\Delta \phi_A$ equal approximately to 0.1 V, the coefficient of reduction in the cathodic process speed increases to about 90%. For anodic polarization greater than 0.1 V, the amount the coefficient of influence in the cathodic process parameters is reduced may be entirely different for different anodic polarization curves. We have the most characteristic dependence, obviously, in the case of curves 1, 2, and 3. Curve 3 has already been considered above. Curves of the type 1 and 2 may be of real interest; therefore we will consider this case in greater detail.

In discussing the dependence of $(1-\eta_k) \cdot 100$ upon $\Delta \phi_A$ described by curves 1 and 2 in Figure 5, we must take into account that this dependence corresponds to constant α in equation (29). This type of dependence $\eta(\Delta \phi_A)$ can be conveniently represented by one's considering a series of stationary states corresponding to the points of intersection of one polarization curve V_A with the series of curves V_k , which have progressively increasing slope. The diagrammatic representation of this system of curves is given in Figure 6.

With an increase in the slope of the curve V_k the amount of anodic polarization will increase continuously, while the coefficient η_k will at first decrease. At $\Delta \phi_A = \frac{1}{2} \alpha$, this coefficient will reach some minimum value (the maximum for the quantities $(1-\eta_k) \cdot 100$ in curves 1 and 2, Figure 5). When $\Delta \phi_A$ becomes close to the value α , then $\eta_k \cdot 100$ will become practically equal to 100, while the quantity $(1-\eta_k) \cdot 100$ approaches 0 (in Figure 6 this condition is described by the states corresponding to the points γ_1 , and γ_2).

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The stationary states corresponding to these conditions are interesting. In fact, when they are present we have what appears to be a return to the case of very low anodic polarization; i.e., to states corresponding to the points γ_1' and γ_2' in Figure 6. There actually is an essential similarity between the stationary states corresponding to the points γ and γ' , since in both cases η_k approaches 1; in both cases, moreover, the potential of the dissolving metal may remain constant although the speed of dissolution of the metal may vary widely. The common reason is apparently that the curves V_A are practically vertical in both cases. (For the case of states γ_1' and γ_2' , where $\Delta \phi_A$ approaches 0, the curve V_A in the limit coincides with the ordinate; and for the case of states γ_1 and γ_2 where $\Delta \phi_A$ approaches α , the curve V_A coincides with the normal N_A in the limit).

As should be emphasized, this similarity occurs despite the fact that for the case of states γ' the coefficient J_A^0 approaches 0 while J_k^0 approaches 1, while for the case of the states γ even the condition $J_A^0 > J_k^0$ may hold.

Of course, both conditions are not identical. For example, the coefficient of reduction in the cathodic process speed when $\Delta \phi_A$ approaches zero equals zero; but when $\Delta \phi_A$ approaches α , it may be close to unity.

The situations we have considered permit us to make some general conclusions. Obviously we can consider it quite likely that the influence of the anodic process on the speed of dissolving metals must become noticeable even for very small values of anodic polarization (of the order of 0.01 V and possibly even smaller) and moreover become independent of the overvoltage corresponding to the cathodic process of hydrogen liberation. Accordingly, we can consider improbable cases of ^{metals} dissolving

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metals in which the influence of the anodic process can possibly be completely disregarded (quantitatively). For anodic polarization of the order of several hundredths of a volt and more, the coefficients η_k and η_A may already be of the same order of magnitude. At the same time, despite this, the predominant influence upon the speed of dissolution in metals should, in general, be ascribed to the cathodic process. In the first place, one may consider actually possible cases of dissolving metals in which the anodic polarization is low, i.e., $\Delta \phi_A \leq 0.05$ V. Here the predominant kinetic weight must be ascribed to the cathodic process, both from the standpoint of the coefficients of influence in the parameters and even more so from the standpoint of the coefficients of speed reduction. In addition, even for considerable anodic polarization, the kinetic weight of the cathodic process, as we have seen, may be predominant in the system. Thus, in the realization of curves 1-2, we can expect for sufficient anodic polarization an apparent return to the regularities corresponding to very small values of anodic polarization. Further, in the realization of curve 3 the coefficient η_k until the condition $\Delta \phi_k \gg 0.05-0.01$ V is observed, which condition is practically always fulfilled in metals dissolving in acids. At the same time, on the basis of the study, we naturally must ascribe to the anodic process a very substantial influence upon the kinetics of dissolving metals. The kinetic weight of the anodic process is considerably greater and its relationship with the kinetic weight of the cathodic process is much more complex than might have been expected from assuming linear polarization curves for both processes or from the ratio of polarization $\Delta \phi_k$ and $\Delta \phi_A$ or the coefficients of equilibrium disturbance J_k^0 and J_A^0 . From this standpoint, we must acknowledge that more detailed studies of anodic polarization curves, and also measurements of the potentials of dissolving metals are very important for the theory

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of interaction of metals with solutions. In principle, the measurement of potential of dissolving metals may be considered as an experimental method for determining the magnitude and variations of the regulating parameter in the system of cathodic and anodic processes, which theoretically could compensate for the inadequacy of the formula for the cathodic process speed caused (i.e. inadequacy) by the superposition of the influence of the anodic process.

Conclusions

An attempt has been made in this work to evaluate to what extent the cathodic process in hydrogen liberation and the anodic process releasing metal ions into the solution influence on the kinetics of interaction between metals and acids. In this study we assumed that diffusion and conductivity had no marked effect upon the speed of this reaction. With this purpose, we employed the method for the evaluation of kinetic weights which was developed in the author's previous works (14). It turned out that the relationship between the kinetic weights of the cathodic and anodic processes could vary quantitatively, depending upon what types of polarization curves correspond to these processes. Accordingly one arrives at completely inaccurate ideas by attempts to evaluate the relation between the kinetic weight of the cathodic process and that of the anodic process which assume for simplification that linear polarization curves describe these processes.

The relationship between the kinetic weights of the cathodic and anodic processes cannot be evaluated, in general, from knowledge of the amounts of cathodic and anodic polarization.

The influence of anodic processes on the kinetics of dissolving metals may become noticeable even for small values of anodic polarization of the

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order of 0.01 V or even less, and is independent of the amount of polarization corresponding to the cathodic process. Thus, cases where one may completely and quantitatively influence the anodic process in dissolving metals are not considered likely. At the same time, however, there may be cases where one observes an apparent return to regularities corresponding to very small values of anodic polarization for sufficient increase in anodic polarization.

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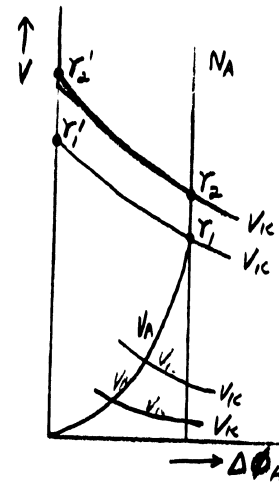
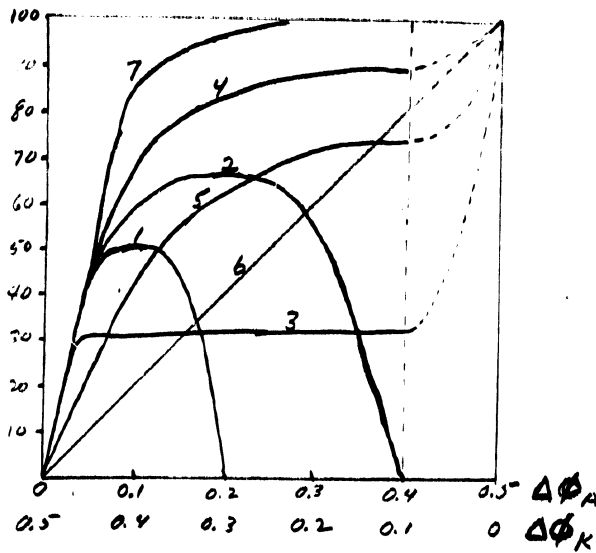
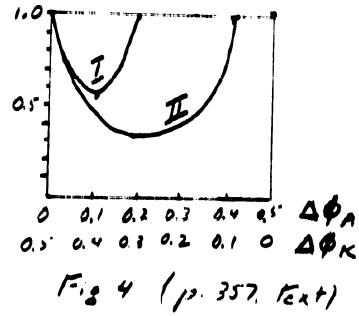
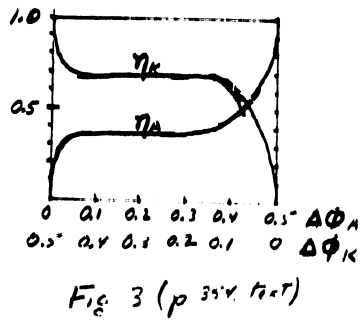
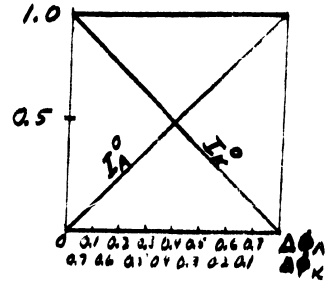
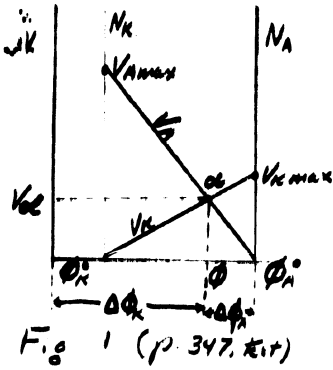
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pp 345-363

(Figures follow)

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Figures CONFIDENTIAL



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