REACTIONS OF PRODUCTS OF VERY RAPID PARALLEL IRREVERSIBLE FOLLOW-UP REACTIONS IN THE GALVANOSTATIC METHOD WITH CURRENT REVERSAL*

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The method of constant current reversal is applied to the case where the primary depolarization product undergoes very rapid parallel irreversible reactions of different orders and after the reversal of the current the product, P_m, of one of these reactions is consumed on the electrode. Relations for the formation of P_m and for the transition time, τ', after the current reversal are derived for several cases where the product P_m undergoes various chemical reactions. The possibilities of distinguishing these cases and the method of determining the kinetic parameters from the measured dependences of τ' on experimental parameters are discussed.

In the studies of consecutive reactions by the method of current reversal[1] usually the primary depolarization product is consumed on the electrode after the reversion of the current and the first transition time corresponds to its depletion at the electrode.

After the transfer of an electron between the depolarizer and the electrode several parallel or consecutive chemical reactions can take place, some of which can be very rapid. We shall denote as very rapid such reactions which are not measurable by the given method owing to their high rate constants. If the first chemical reactions of the depolarization product are very rapid, then the first measured transition time after the reversion of the current corresponds to exhaustion of some products of these reactions at the electrode. If these very rapid reactions are reversible they do not manifest themselves during the measurement; if they are irreversible they can be regarded from the point of view of the measuring method as a part of the electrode reaction proper, which is then irreversible, and the products of these reactions can then be considered as depolarization products due to this electrode reaction.

If the primary depolarization product undergoes very rapid parallel irreversible reactions and during the first measurable transition after the current reversal a product of only one of these reactions is consumed on the electrode, this process has the character of an electrode process with a partial production of the followed depolarization product. The fraction of this production is then given by the ratio of the rate of the reaction by which the given substance is formed to the sum of the rates of all reactions in which the primary depolarization product participates. If the very rapid parallel irreversible reactions of the primary depolarization product are of the same order, then the mentioned fraction of the production of the studied depolarization product is independent on the current. If, however, the mentioned reactions are of different orders, then
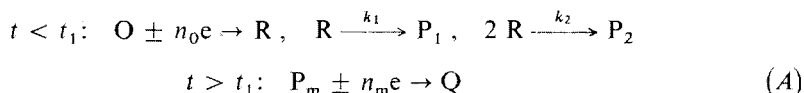
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the mentioned fraction depends on the current. This dependence is naturally reflected by the measured transition time. Since the dependence of the transition time on the current is very important for the analysis of consecutive reactions it is desirable to study in what manner is it influenced by the mentioned dependence of the production of the studied depolarization product on the current.

The dependence of the production of the followed depolarization product on the current is different according to whether the very rapid irreversible parallel reactions proceed homogeneously or in the adsorbed state and which of the reactions leads to the depolarization product under study. The latter can then also undergo different chemical reactions. Accordingly, we have to deal with a large number of different possibilities, but we shall select for the analysis only those which are most probable and typical.

FORMATION OF THE FOLLOWED DEPOLARIZATION PRODUCT

We assume that the depolarizer, O, is changed by the transfer of n_0 electrons to a substance R, which is in turn changed by very rapid parallel irreversible chemical reactions of the first and second order to substances P_1 and P_2. We assume further that one of these substances is after the reversion of the current at a time t_1 consumed on the electrode during the transfer of n_m electrons. This substance can undergo also other chemical reactions. The corresponding scheme is

$$t < t_1: \quad O \pm n_0 e \rightarrow R, \quad R \xrightarrow{k_1} P_1, \quad 2R \xrightarrow{k_2} P_2$$

$$t > t_1: \quad P_m \pm n_m e \rightarrow Q \tag{A}$$

and eventually $t > 0$: $l\, P_m \rightarrow$ products, or $l\, P_m \rightleftarrows$ products, where m is either l or 2 according to which substance is consumed after the current reversal, and l is the reaction order of P_m. The current densities before and after the reversal will be denoted as j and i, respectively, and their ratio $i/j = u$ as in the previous communications[1-6]. We shall distinguish two limiting cases: a) the reactions of R are homogeneous, b) the reactions of R proceed exclusively in the adsorbed state.

Homogeneous Reactions

The concentration of the substance R is for $t < t_1$ and a sufficient reaction rate given by[2]

$$C_R = \frac{6k_1}{k_2} \frac{M \exp\left(-x\sqrt{(k_1/D_R)}\right)}{\left(1 - M \exp\left(-x\sqrt{(k_1/D_R)}\right)\right)^2}, \tag{1}$$

$$M(1 + M)/(1 - M)^3 = b/6, \tag{2}$$

$$b = jk_2/n_0 F k_1 \sqrt{(k_1 D_R)}, \tag{3}$$

where D_R denotes diffusion coefficient of R and x distance from the electrode surface.

The reactions of **R** can be considered as sufficiently rapid within the limits of accuracy of the experimental method if[2] $k_1 t(5M + 1)/(1 - M) > 6$. If we denote the relative fraction of the substance **R** which is transformed to P_m as Φ_m, then

$$\Phi_m = \int_0^\infty k_m C_R^m \, dx \bigg/ \int_0^\infty (k_1 C_R + k_2 C_R^2) \, dx \, . \tag{4}$$

By introducing Eq. (1) and integrating we obtain

$$\Phi_1 = (1 - M)^2/(1 + M) \, , \quad \Phi_2 = M(3 - M)/(1 + M) \, . \tag{5a, b}$$

The production of the substance P_m in a time unit at a unit electrode surface area is equal to $\Phi_m j/mn_0 F$. After the reversal of the current the consumption of P_m in a time unit on a unit electrode surface area is equal to $i/n_m F$. The ratio of the consumption to the production rate, U, is therefore

$$U = u n_0 m / n_m \Phi_m = \mu/\Phi_m \, . \tag{6}$$

The dependence of Φ_m on the current j is given implicitly by Eqs (2), (3), and (5). The current is expressed preferably by the dimensionless parameter b given by Eq. (3). The dependence of Φ_1 on $\log b$, obtained by solving the mentioned equations, is shown in Fig. 1.

To simplify the numerical calculations, the dependence of Φ_m on b in the explicit form should be used. The solution of Eq. (2) by the Cardano's formula is for larger b
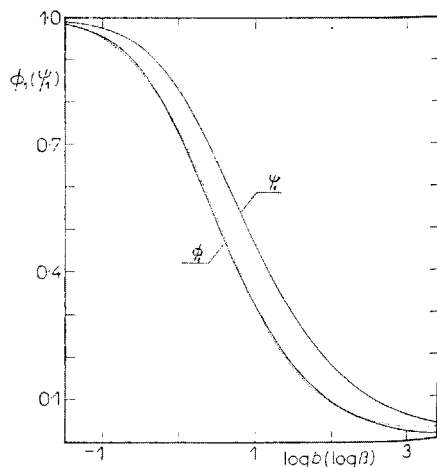

FIG. 1

Dependence of Φ_1 on $\log b$ and Ψ_1 on $\log \beta$
Dotted line according to Eq. (7a). The values of Φ_2 and Ψ_2 are equal to $1 - \Phi_1$ and $1 - \Psi_1$, respectively.

values too complicated and for small b values leads to the casus irreducibilis. The following empirical formula fits the calculated dependence of Φ_1 on b well in the range $0.04 < \Phi_1 < 0.98$:

$$\Phi_1 = 1/(1 + 0.42b^{3/4}) + 0.02 . \tag{7a}$$

Since $\Phi_1 + \Phi_2 = 1$, we have

$$\Phi_2 = 0.42b^{3/4}/(1 + 0.42b^{3/4}) - 0.02 . \tag{7b}$$

In Fig. 1 is shown the dependence of Φ_1 on b according to Eq. $(7a)$ by dotted curve.
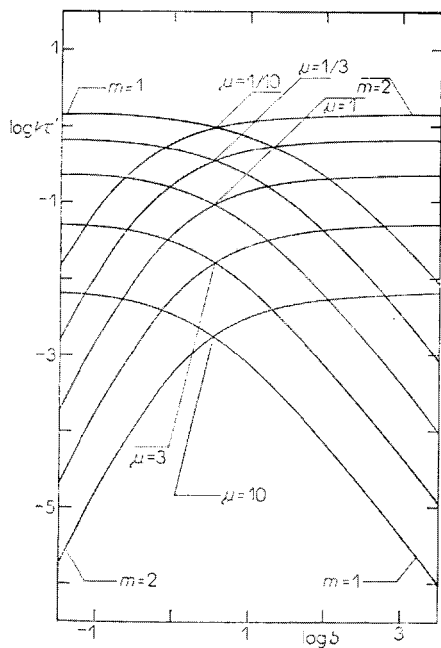

FIG. 2

Dependences of log τ' on log j for a Homogeneous m-th Order Formation Reaction of the Substance P_m Undergoing a Follow-up Homogeneous Irreversible First-Order Reaction

The curves for P_1 and P_2 at the same values of μ intersect at $\Phi_1 = \Phi_2 = 0.5$.
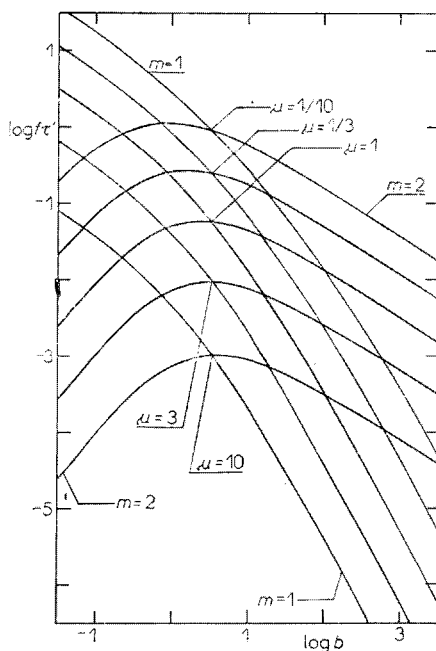
FIG. 3

Dependence of log τ' on log j for a Homogeneous Formation Reaction of the Substance P_m Undergoing a Homogeneous Irreversible Second-Order Reaction

The values given on the coordinate axes correspond to τ' and j expressed by dimensionless parameters $f\tau'$ and b; $f = (kk_1 . \sqrt{(k_1 D_R)}/k_2\sqrt{D_P})^{2/3}$.

Reaction in the Completely Adsorbed State

If the substance R is completely adsorbed on the electrode surface, then for $t < t_1$ and a sufficient rate of the reactions the following relations apply[3]

$$\Gamma_R = (k_1/2k_2)(\sqrt{(1 + \beta)} - 1), \tag{8}$$

$$\beta = 4k_2 j/n_0 F k_1^2, \tag{9}$$

where the relative error in Γ_R is of the same order as $\exp(-k_1 t(1 + \beta)^{1/2})$ so that it is negligible for such reaction rates for which $k_1 t(1 + \beta)^{1/2} > 6$.

The fraction, Ψ_m, of the substance R which is converted to P_m is given as

$$\Psi_m = k_m \Gamma_R^m/(k_1 \Gamma_R + k_2 \Gamma_R^2), \tag{10}$$

hence

$$\Psi_1 = 2/(1 + \sqrt{(1 + \beta)}), \quad \Psi_2 = \beta/(1 + \sqrt{(1 + \beta)})^2. \tag{11a, b}$$
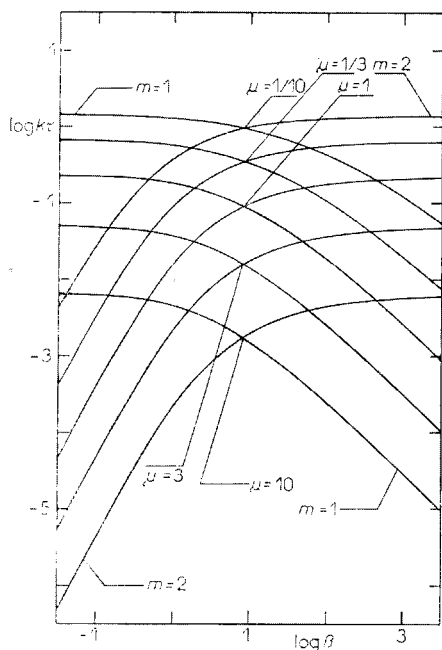

FIG. 4

Dependence of $\log \tau'$ on $\log j$ for a Formation Reaction in the Completely Adsorbed State of the Substance P_m Undergoing a Homogeneous Irreversible First-Order Reaction
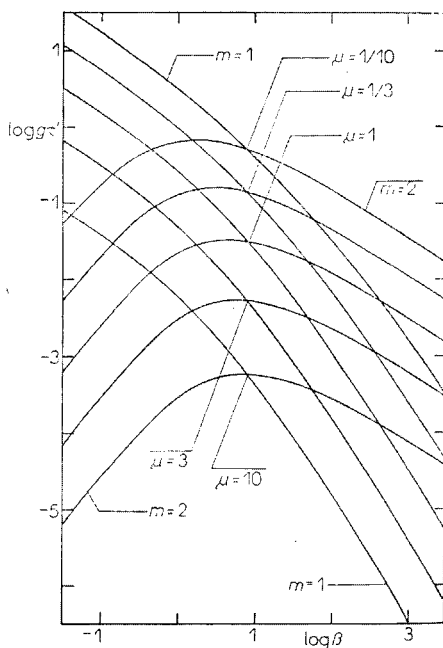
FIG. 5

Dependence of $\log \tau'$ on $\log j$ for a Formation Reaction in the Completely Adsorbed State of the Substance P_m Undergoing a Homogeneous Irreversible Second-Order Reaction $g = (kk_1^2/4k_2\sqrt{D_P})^{2/3}$.

The production of the substance P_m in a time unit on a unit surface area of the electrode is $\Psi_m j / m n_0 F$ and the ratio of its consumption to its production rate is again

$$U = u n_0 m / n_m \Psi_m = \mu / \Psi_m . \tag{12}$$

The current is purposefully expressed through the dimensionless parameter β (Eq. (9)). The dependence of Ψ_1 on $\log \beta$ is shown also in Fig. 1.

EQUATIONS FOR THE MEASURED TRANSITION TIME

The relations derived previously[1-6] can be applied to the measured transition times corresponding to the exhaustion of the substance P_m if the ratio of currents, u, is replaced by the ratio of the consumption and production rates, U, of the substance P_m (Eq.

FIG. 6

Dependence of $\log \tau'$ on $\log j$ for the Case where the Substance P_m is Formed Entirely in the Adsorbed State and Undergoes an Irreversible First-Order Reaction in the Adsorbed State
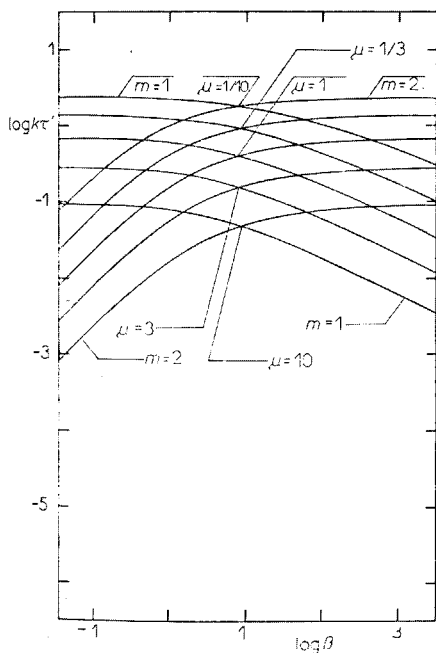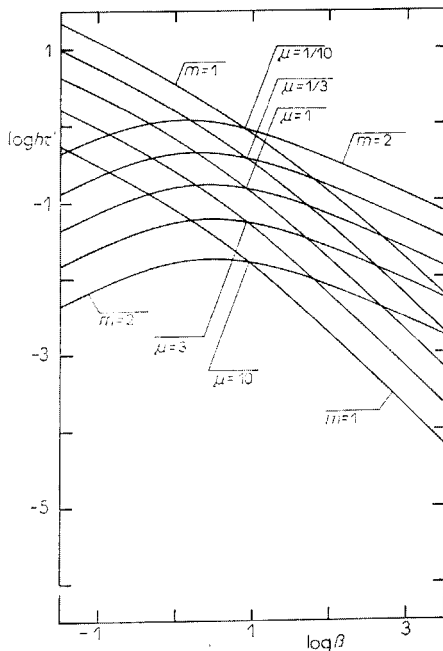
FIG. 7

Dependence of $\log \tau'$ on $\log j$ for the Case where the Substance P_m is Formed Entirely in the Adsorbed State and Undergoes an Irreversible Second-Order Reaction in the Adsorbed State
$h = (k k_1^2 / 4 k_2)^{1/2}$.

(6) or (12)). The discussion will be restricted to cases where the chemical reactions of the substance P_m are sufficiently rapid (analogously to the previous work[1-6]). We then can distinguish the characteristic cases of reversible and irreversible chemical reactions of the substance P_m. For the sake of comparison and simple discussion, we shall treat in addition the case where this substance does not react chemically.

The Substance P_m Does Not React Chemically

If the substance P_m is subject only to diffusion into the solution, then

$$\sqrt{(1 + t_1/\tau')} = U + 1 . \tag{13}$$

If, on the contrary, it is completely adsorbed on the electrode surface, then

$$t_1/\tau' = U . \tag{14}$$

Hence, it is possible to determine the U value from the measurements. From the comparison of the dependence of μ/U on $\log j$ with the dependences shown in Fig. 1 we can decide whether we have to deal with the consumption of P_1 or P_2 and eventually to decide whether the very rapid reactions of the primary depolarization product proceed homogeneously or entirely in the adsorbed state. From Fig. 1 it can be seen that the quantities Φ_1 and Ψ_1 decrease with increasing current j, whereas Φ_2 and Ψ_2 increase; this enables us to decide whether $m = 1$ or 2.

The comparison of the dependence of μ/U on $\log j$ with the curves for Φ and Ψ enables then in the favourable case to decide whether we have to deal with Eq. (6) or (12). From the factor by which the j value must be multiplied to bring the experimental dependence into coincidence with the theoretical it is possible to determine the value of $k_2/k_1\sqrt{(k_1 D_R)}$ according to Eq. (3) or the value of k_2/k_1^2 according to (9). These values characterize the ratio of the rates of parallel very rapid reactions of the primary depolarization product.

Consecutive Rapid Reactions Are Reversible

If the rapid reversible chemical reactions of the substance P_m are homogeneous, then

$$\sqrt{(1 + t_1/\tau')} = 1 + U + GU/\sqrt{\tau'} , \tag{15}$$

where the quantity G was given previously[4] for various reaction types It is seen that the dependence of $\sqrt{(1 + t_1/\tau')}$ on $1/\sqrt{\tau'}$ at constant current gives in this case a straight line which can be extrapolated to zero to give U and whose slope gives the value of G. The course of the mentioned dependence in full range was discussed in ref.[1] for a reaction of the first order; its course for other reactions is analogous.

For rapid follow-up reversible chemical reactions of a substance in the completely adsorbed state we have

$$t_1/u - \tau' = H ; \qquad (16)$$

the expression for the quantity H for various types of chemical reactions can be obtained by comparing Eq. (16) with equations given in ref.[3]. For rapid reversible chemical reactions of the substance P_m in the adsorbed state we hence obtain

$$t_1/\tau' = U + HU/\tau' , \qquad (17)$$

whence it is seen that in this case the dependence of t_1/τ' on $1/\tau'$ at constant current is linear. Its extrapolation to zero gives the value of U and its slope the value of H.

From the dependence of G or H on the current it is possible to determine the type of the reaction in which the substance P_m is involved and the parameter characterizing its rate[3,4]. The obtained quantity U can be evaluated as in the preceeding case.

Follow-up Rapid Reactions of P_m Are Irreversible

We shall restrict ourselves to rapid irreversible reactions of the substance P_m of the first and second order. If they are homogeneous, then

$$\text{1st order:} \quad k\tau' = \text{argerf}^2 \left[1/(U + 1)\right] , \qquad (18)$$

$$\text{2nd order:} \quad (jk/n_0 F \sqrt{D_p})^{2/3} \tau' = f_2(U) . \qquad (19)$$

The function $f_2(U)$ was defined in ref.[5] and tabulated in ref.[6].

If the substance P_m undergoes a rapid irreversible reaction entirely in the adsorbed state, then

$$\text{1st order:} \quad k\tau' = \ln\left(1 + 1/U\right) , \qquad (20)$$

$$\text{2nd order:} \quad (kj/n_0 F)^{1/2}\tau' = U^{-1/2} \text{arctg}\left(U^{-1/2}\right) . \qquad (21)$$

The rate constant k in Eqs $(18)-(21)$ is related to the corresponding reaction of the substance P_m.

For the evaluation of irreversible consecutive reactions, the dependence of $\log \tau'$ on $\log j$ is suitable[2,3,5]. This is in the discussed cases complicated by the fact that the value of U depends even at constant ratio of currents, u, on j according to (6) or (12). The dependence of $\log \tau'$ on $\log j$ is shown for several cases for illustration in Figs $2-7$; it is seen that the curves are always convex. If the substance P_2 undergoes a reaction of the second order, the mentioned dependence passes through a maximum (Figs 3, 5, 7), otherwise it is monotonous. The shape of the curves depends strongly on the reaction of the substance P_m as well as on m. From the shift of the curves

due to a change of the current ratio u it can be easily recognized whether the reaction of P_m proceeds homogeneously or completely in the adsorbed state (compare Figs 4 and 5, 6 and 7). In contrast, the circumstance whether the reaction of formation of P_m proceeds homogeneously or completely in the adsorbed state is little manifested in the form of the curves and their shift with the current ratio u (compare Figs 2 and 4, 3 and 5).

The rate constant of the reaction of the substance P_m and the quantity characterizing the ratio of the rates of parallel very rapid reactions of the primary depolarization product cannot be in the discussed cases obtained separately (as with reversible reactions); the evaluation requires a multiparameter optimization of fitting the experimental points with the theoretical dependence.

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