

STUDY OF THE KINETICS OF ELECTRODE PROCESSES BY MEANS OF ELECTROLYSIS WITH CONSTANT CURRENT. XVIII.***FOLLOW-UP REACTIONS IN A LAYER OF COMPLETELY ADSORBED SUBSTANCES**

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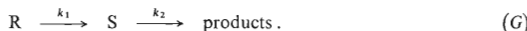
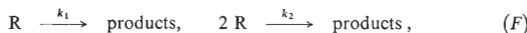
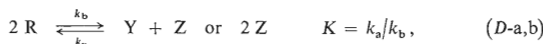
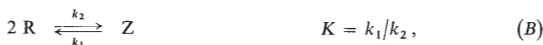
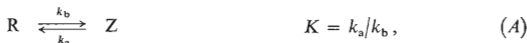
For the constant current reversal method various cases of follow-up reactions with substances completely adsorbed on electrode surface are solved. The schemes of solved cases correspond to those types of reaction which have already been solved for the same method for homogeneous reactions. The results for reactions of completely adsorbed substances are in many respects analogous to the results for homogeneous reactions; however, they differ in certain respects. For sufficiently fast irreversible reactions, the transition time after reversing the current, τ' , does not depend on the current reversal time, t_1 ; from the dependence of τ' on the current intensity, it is possible to determine the type and order of the reaction and, with the aid of the dependence of τ' on the ratio of current magnitudes after and before the current reversal, u , the reactions of completely adsorbed substances can be differentiated from homogeneous reactions. For sufficiently fast reversible reactions, the characteristic expression $t_1/u - \tau'$ has a positive non-zero value and is independent of t_1 ; from the dependence of this characteristic expression on the current intensity, it is possible to differentiate among several types of reaction. On the basis of comparison of the obtained results with the results for the corresponding homogeneous reactions, qualitative conclusions concerning the effect of adsorption on the results for homogeneous reactions are ascertained.

The method of constant current reversal, introduced for studying follow-up chemical reactions¹, has been adapted to various homogeneous chemical reactions²⁻⁶. Voorhies and Davis⁷ used this method for studying subsequent reactions in the layer of a depolarisation product completely adsorbed on a carbon electrode and derived the expression for irreversible first order reaction for this situation. During galvanostatic study of electrode processes, in which the depolarization product is strongly adsorbed on the surface of the mercury electrode⁸, it was also found that, in some cases, kinetic processes occur in the layer of adsorbed depolarization product, which can frequently be formally described as chemical reactions, whatever their actual mechanism may be.

To widen the usefulness of the constant current reversal method, it thus seems suitable to investigate what results can be obtained by this method for various following chemical reactions, during which the substances taking part in the reactions are

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practically completely adsorbed on the electrode surface, so that their diffusion into the solution and possible homogeneous reactions in solution are completely negligible. Thus we will solve for this case those types of reactions, which have been already solved for the homogeneous case¹⁻⁶. The solved reactions then proceed according to the schemes



R is always the completely adsorbed depolarization product, which is produced (and, after current reversal, consumed) in the electrode process $O \pm ne \rightleftharpoons R$, the substances Y and Z are electroinactive, the substance S is completely adsorbed and after current reversal is discharged only after the substance R is used up. The transition time after current reversal, τ' , measured from the time of reversal of the current direction, t_1 , is always obtained when the substance R has been consumed; in the case of Scheme (G), the second transition time, τ'_2 , measured from the first transition time, τ'_1 , is attained when the substance S has been consumed.

In addition we will assume that the concentration of substance R and all the other products (Y, Z, S) is zero at the beginning of the electrolysis. Identically as with the previous cases¹⁻⁶, we will represent the current before current reversal as j and after current reversal as i , their ratio as $i/j = u$, and the Faraday constant as F .

THEORETICAL

In agreement with earlier work⁸, we will indicate the concentrations of the adsorbed substances by the symbol Γ with a subscript corresponding to the substance. During the solution we will first discuss first order reactions in detail (Scheme A); then, similarly as with homogeneous reactions¹, conclusions obtained from the physical interpretation of the results of this solution enable us, to use simplifications for more complicated reactions.

In all cases solved below, the following initial condition is valid:

$$t = 0: \Gamma_R = 0, \quad \Gamma_Z = 0, \quad \Gamma_Y = 0, \quad \Gamma_S = 0 \quad (I)$$

and the relationship for the transition time is obtained from the condition:

$$t = t_1 + \tau' : \Gamma_R = 0. \quad (2)$$

To simplify writing equations we can also introduce the step function $h(t_1, j/-i)$ given by the relation

$$\begin{aligned} 0 < t < t_1: & \quad h(t_1, j/-i) = j \\ t > t_1: & \quad h(t_1, j/-i) = -i. \end{aligned} \quad (3)$$

For the individual schemes given above, description and solution of the problem is as follows:

Scheme A:

$$d\Gamma_R/dt = h(t_1, j/-i)/nF - k_b\Gamma_R + k_a\Gamma_Z, \quad (4a)$$

$$d\Gamma_Z/dt = k_b\Gamma_R - k_a\Gamma_Z, \quad (4b)$$

where condition (1) holds.

From equation (4a, b), it follows that

$$d(\Gamma_R + \Gamma_Z)/dt = h(t_1, j/-i)/nF \quad (5)$$

so that from equation (4a) we can eliminate Γ_Z and write

$$d\Gamma_R/dt = h(t_1, j/-i)/nF - (k_a + k_b)\Gamma_R + (k_a/nF) \int_0^t h(t_1, j/-i) dt. \quad (6)$$

By solution of equations (6) and (1) by a similar method as in the work¹, we obtain the relation

$$\begin{aligned} t > t_1: \quad \Gamma_R = & (jk_b/nFk^2) [(1 - e^{-kt}) + Kkt] - \\ & - [(i + j) k_b/nFk^2] [(1 - e^{-k(t-t_1)}) + Kk(t - t_1)], \end{aligned} \quad (7)$$

where

$$k = k_a + k_b, \quad (8)$$

For the transition time we obtain, after rearrangement using condition (2) and equation (7), the relation

$$\tau' = t_1/u - [u + e^{-k(t_1+\tau')} - (u+1)e^{-k\tau'}]/uKk. \quad (9)$$

If

$$e^{-k\tau'} \ll u/(u+1 - e^{-kt_1}), \quad (10)$$

relation (9) simplifies to give

$$t_1/u - \tau' = 1/Kk. \quad (11)$$

By another rearrangement we obtain from equation (7), for the transition time, the relation

$$k\tau' = \ln \{ (u+1 - e^{-kt_1})/[u - Kk(t_1 - u\tau')] \}. \quad (12)$$

As follows from the analysis of the results given below, it always holds that $\tau' \leq t_1/u$. Thus, if the following condition is valid

$$Kkt_1 \ll u. \quad (13)$$

relation (12) simplifies to give

$$k\tau' = \ln [(u+1 - e^{-kt_1})/u]. \quad (14)$$

Further, if the following condition holds

$$e^{-kt_1} \ll 1 \quad (15)$$

we obtain from equation (13) the relation

$$k\tau' = \ln[(u + 1)/u]. \quad (16)$$

Physical Interpretation of the Obtained Results

Condition (13) is, of course, fulfilled for $K \rightarrow 0$, so that relation (14) which is *de facto* identical with the relation derived by Voorhies and Davies⁷, corresponds to the case of an irreversible reaction. As with homogeneous reactions¹, the condition of sufficient irreversibility also encompasses the time of current reversal, t_1 . In practice, condition (13) may be considered as fulfilled if

$$Kkt_1/u < 10^{-2.5}. \quad (17)$$

Condition (15) will be easily fulfilled if

$$kt_1 > 6, \quad (18)$$

which is the same as the condition of sufficiently large t_1 with irreversible homogeneous reactions¹. As with homogeneous reactions, the transition time τ' is then independent of t_1 , as is given by relation (16). This situation, however, can occur — similarly as with homogeneous reactions — only with sufficiently low values of K ; conditions (17) and (18) cannot be simultaneously fulfilled if it does not hold that $K/u < 5 \cdot 10^{-4}$. From condition (18) and relation (16) can be further obtained the condition

$$t_1 > \tau' \cdot 6 / \ln[(u + 1)/u]. \quad (19)$$

Relation (11) corresponds to the case of a sufficiently fast reversible reaction. The condition of a sufficiently fast reaction (10) will, for usual values of u , be easily fulfilled in practice if, as with homogeneous reactions,

$$k\tau' > 6, \quad (20)$$

which, with relation (11) leads to the inequality

$$Kkt_1/u > 1 + 6K. \quad (21)$$

From the view point of the constant current reversal method, the reversibility or irreversibility of the reaction is therefore given by the size of the expression Kkt_1/u .

Relation (11) can, under certain conditions, be derived in an easier manner, analogous to the method of the reaction layer⁹ with homogeneous reactions. From relations (5) and (2) it may be

easily obtained that

$$t = t_1 + \tau': \quad \Gamma_Z = [j(t_1 + \tau') - (i + j) \tau'] / nF. \quad (22)$$

If we assume the attainment of a quasi-stationary state after current reversal and if we thus ignore the time derivation on the left-hand side of equation (4a), we obtain from this equation — taking into account relation (2):

$$t = t_1 + \tau': \quad \Gamma_Z = i/nFk_a. \quad (23)$$

If $K \ll 1$, i.e. if the chemical equilibrium is sufficiently shifted towards the final product of the follow-up reaction, i.e. substance Z, then $k_a = Kk$ and relation (11) follows from equations (22) and (23).

The described analysis gives us a method for solving more complicated cases for which a general and rigorous solution would be too difficult.

Schemes (B), (C), (D): These can be solved together since the approach will be the same in all cases and the solution results will be similar. The solution will be carried out by the simplified method, which we arrived at above from analysis of the results for first-order reactions for sufficiently fast reversible reactions with equilibrium shifted towards the final products of the follow-up reaction.

The problems are described by the equations

$$\text{Scheme (B):} \quad d\Gamma_R/dt = h(t_1, j| - i)/nF - k_2\Gamma_R^2 + k_1\Gamma_Z \quad (24a)$$

$$d\Gamma_Z/dt = \frac{1}{2}k_2\Gamma_R^2 - \frac{1}{2}k_1\Gamma_Z \quad (24b)$$

$$\text{Scheme (C):} \quad d\Gamma_Z/dt = h(t_1, j| - i)/nF - k_1\Gamma_R + k_2\Gamma_Z^2 \quad (25a)$$

$$d\Gamma_Z/dt = \alpha k_1\Gamma_R - \alpha k_2\Gamma_Z^2 \quad (25b)$$

for case (C-a), $\alpha = 1$, for case (C-b), $\alpha = 2$.

$$\text{Scheme (D):} \quad d\Gamma_R/dt = h(t_1, j| - i)/nF - k_b\Gamma_R^2 + k_a\Gamma_Z^2 \quad (26a)$$

$$d\Gamma_Z/dt = \alpha k_b\Gamma_R^2 - \alpha k_a\Gamma_Z^2 \quad (26b)$$

for case (D-a), $\alpha = 1/2$, for case (D-b), $\alpha = 1$, while the system of equations for each scheme is complemented with conditions (1).

From the given equations it follows that it holds in all cases that

$$d(\Gamma_R + \Gamma_Z/\alpha)/dt = h(t_1, j| - i)/nF, \quad (27)$$

where, for scheme (B), $\alpha = \frac{1}{2}$. From relation (27) and conditions (1) and (2) then follows an equation analogous to equation (22)

$$t = t_1 + \tau': \quad \Gamma_Z = \alpha(jt_1 - i\tau')/nF. \quad (28)$$

Neglecting the time derivation in equations (24a), (25a) and (26a) and substituting relation (28) and condition (2), we obtain after rearrangement the relations

$$\text{Scheme (B):} \quad t_1/u - \tau' = 2/k_1. \quad (29)$$

$$\text{Scheme (C):} \quad t_1/u - \tau' = (nF/ik_2)^{1/2}/\alpha. \quad (30)$$

$$\text{Scheme (D):} \quad t_1/u - \tau' = (nF/ik_a)^{1/2}/\alpha. \quad (31)$$

The conditions of the equilibrium being sufficiently shifted towards the end products of the reaction and of a sufficiently fast reaction can be described by inequalities in individual cases:

$$\begin{aligned} \text{Scheme (B):} \quad & Kk_1nF/i < 10^{-2}, \quad \tau' i/nFK > 6, \\ & t_1/u > (2/k_1) [1 + 3Kk_1nF/i]. \end{aligned} \quad (32)$$

$$\begin{aligned} \text{Scheme (C):} \quad & K(i/nFk_2)^{1/2} < 10^{-2}, \quad k_1\tau' > 6 \\ & t_1/u > (nF/ik_2)^{1/2} \alpha^{-1} [1 + 6\alpha K(i/nFk_2)^{1/2}] \end{aligned} \quad (33)$$

$$\begin{aligned} \text{Scheme (D):} \quad & K < 10^{-2}, \quad \tau'(ik_a/nF)^{1/2}/K > 6 \\ & t_1/u < (nF/ik_a)^{1/2} \alpha^{-1} [1 + 6\alpha K]. \end{aligned} \quad (34)$$

The numerical constants, given in these inequalities, represent, of course, only a rough estimate based on analogy with the results of the previous cases and with homogeneous reactions with the same reaction schemes. Especially the constant, 10^{-2} , in the first inequality of each scheme was estimated to within an order of magnitude. With reference to the first inequality in each scheme, the expression in square brackets in the third inequality is always close to unity, so that, considering the minimum value of the first inequalities and their approximate character, it can be replaced by the approximate value 1.1.

Scheme (E). For Scheme (E), the problem is described by the equation

$$d\Gamma_R/dt = h(t_1, j/-i)/nF - k\Gamma_R^m \quad (35)$$

and condition (1) If we analyze equation (35) and conditions (1) and (2) in a similar way as that with homogeneous reactions of the same type², we come to the conclusion that it generally applies that

$$akt' = f_m(u, akt_1), \quad (36)$$

where

$$a = (j/nFk)^{(m-1)/m} \quad (37)$$

and $f_m(u, akt_1)$ is a certain function of its argument whose form depends on the reaction order, m . If the reaction is sufficiently fast, so that

$$akt_1 \gg 1 \quad (38)$$

then the given function does not depend on t_1 , which can be described by the relation

$$akt' = f_m(u). \quad (39)$$

To obtain a concrete form of the function in equation (36) or at least (39), equation (35) with conditions (1) and (2) must be solved for each value of m individually. For $m = 1$, Scheme (E) becomes a special case of Scheme (A); in that case, equations (12) and (16) correspond to equations (36) and (39), and inequality (38) is specified by inequality (18). Below we will further derive the form of the given functions for the cases when $m = 2$ and $m = 3$. The case when $m = 2$ is important from the point of view of known reactions of the second order, the case with

$m = 3$ is notable in that the dependence of τ' on j for large values of t_1 is the same as with homogeneous reactions of the second order.

The case when $m = 2$. By integration of equation (35) in the region before current reversal with the aid of condition (I) we get

$$0 < t < t_1: \Gamma_R = a(1 - e^{-2akt})/(1 + e^{-2akt}). \quad (40)$$

By integration of equation (35) in the region after current reversal, using the condition of the continuity of the time dependence of Γ_R and equation (40), we get the relation

$$t > t_1: \Gamma_R = au^{1/2} \operatorname{tg} \{ \arctg [(1 - e^{-2akt_1})/u^{1/2}(1 + e^{-2akt_1})] - u^{1/2}ak(t - t_1) \}. \quad (41)$$

For the transition time it then follows from equation (41) and condition (2) that

$$akt' = u^{-1/2} \arctg [(1 - e^{-2akt_1})/u^{1/2}(1 + e^{-2akt_1})]. \quad (42)$$

When the inequality

$$akt_1 > 3 \quad (43)$$

holds, then relation (42) simplifies to the equation

$$akt' = u^{-1/2} \arctg (u^{-1/2}). \quad (44)$$

Relations (42) and (44) are, for the given case, concrete forms of relations (36) and (39) and inequality (43) specifies inequality (38).

From condition (43) and relation (44) follows the condition

$$t_1 > \tau' \cdot 3u^{1/2}/\arctg (u^{-1/2}) \quad (45)$$

The case when $m = 3$. For the sake of simplicity, we will, in this case, limit ourselves to determining the concrete form of equation (39) and specification of inequality (38). To simplify the notation, we will further introduce the dimensionless variable y , for which the general relation has the form

$$y = \Gamma_R/a^{1/(m-1)}. \quad (46)$$

By integration of equation (35) in the region before current reversal and with the aid of condition (I) we obtain the relation

$$\begin{aligned} 0 < t < t_1: \ln [(y-1)^2/(1+y+y^2)] - (6/\sqrt{3}) \arctg [(2y+1)/\sqrt{3}] = \\ = -6akt - \pi/\sqrt{3}. \end{aligned} \quad (47)$$

From equation (47) it follows that, if

$$akt_1 > 2.4 \quad (48)$$

then we can write

$$t = t_1: y = 1. \quad (49)$$

By integration of equation (35) in the region after current reversal and from condition (49) we obtain

$$\begin{aligned}
 t > t_1 : \ln[(u^{1/3} + y)^2/(u^{2/3} - yu^{1/3} + y^2) + (6/\sqrt{3}) \operatorname{arctg} [(2y - u^{1/3})/u^{1/3} \sqrt{3}] = \\
 = -6u^{2/3} ak(t - t_1) + \ln [(u^{1/3} + 1)^2/(u^{2/3} - u^{1/3} + 1)] + \\
 + (6/\sqrt{3}) \operatorname{arctg} [(2 - u^{1/3})/u^{1/3} \sqrt{3}]. \quad (50)
 \end{aligned}$$

For the transition time then follows from equation (50) and condition (2) that

$$\begin{aligned}
 ak\tau' = (1/6u^{2/3}) \ln [(u^{1/3} + 1)^2/(u^{2/3} - u^{1/3} + 1)] + \\
 + (1/u^{2/3} \sqrt{3}) \operatorname{arctg} [(2 - u^{1/3})/u^{1/3} \sqrt{3}] + \pi/u^{2/3} 6 \sqrt{3}. \quad (51)
 \end{aligned}$$

Equation (51) is, for the given case, a concrete form of equation (39) and inequality (38) is specified by inequality (48). From inequality (48) and relation (51) it is possible, similarly as in the preceding case, to derive an inequality between t_1 and τ' , which is the condition under which equation (51) holds.

Scheme (F). The problem is given by the equation

$$d\Gamma_R^-/dt = h(t_1, j^-)nF - k_1\Gamma_R^- - k_2\Gamma_R^{-2} \quad (52)$$

and by condition (1). For simplification of notation we introduce the symbols

$$\begin{aligned}
 b = 4k_2j/nFk_1^2, \quad \varepsilon = (1 + b)^{1/2} \\
 \sigma = (1 - bu)^{1/2}, \quad \varrho = (bu - 1)^{1/2}. \quad (53)
 \end{aligned}$$

By integration of equation (52) in the region before current reversal and with the aid of condition (1), we obtain

$$0 < t < t_1: \Gamma_R = (k_1/2k_2) \{ \varepsilon - 1 - 2\varepsilon(\varepsilon - 1)/[\varepsilon - 1 + (\varepsilon + 1) e^{k_1 t_1 \varepsilon}] \}. \quad (54)$$

Further, we introduce

$$\omega = \varepsilon - 2\varepsilon(\varepsilon - 1)/\{[\varepsilon - 1 + (\varepsilon + 1) e^{k_1 t_1 \varepsilon}]\}. \quad (55)$$

The integration of equation (52) in the region after current reversal must be carried out separately for two cases according to the value of the product bu . By carrying out the integration and with the condition of the continuity of the time dependence of Γ_R^- and from relations (54) and (55), we obtain the relations

$$\begin{aligned}
 t > t_1, bu < 1: \Gamma_R = (k_1/2k_2) \{ 2\sigma(\omega + \sigma)/[\omega + \sigma - \\
 - (\omega - \sigma) \exp(-k_1\sigma(t - t_1))] - \sigma - 1 \}, \quad (56a)
 \end{aligned}$$

$$\begin{aligned}
 t > t_1, bu > 1: \Gamma_R = (k_1/2k_2) \{ \varrho\omega/\cos^2(k_1\varrho(t - t_1)/2) \cdot \\
 \cdot [\varrho + \omega \operatorname{tg}(k_1\varrho(t - t_1)/2)] - \varrho \operatorname{tg}(k_1\varrho(t - t_1)/2) - 1 \}. \quad (56b)
 \end{aligned}$$

From relations (56a, b) we then obtain, with the aid of condition (2), for the transition time after current reversal

$$bu < 1: k_1\tau' = (1/\sigma) \ln [(1 + \sigma)(\omega - \sigma)/(\omega + \sigma)(1 - \sigma)], \quad (57a)$$

$$bu > 1: k_1\tau' = (2/\varrho) \operatorname{arctg} [\varrho(\omega - 1)/(\varrho^2 + \omega)]. \quad (57b)$$

For $bu = 1$ we obtain from both relations using the limiting transitions

$$bu = 1: k_1\tau' = 2(\omega - 1)/\omega. \quad (57c)$$

For $b \rightarrow 0$, relation (57a) is converted into relation (14) and for $b \rightarrow \infty$, relation (57b) is converted into relation (42). From relation (55) it is clear that, if the inequality

$$k_1\epsilon t_1 > 6 \quad (58)$$

holds, then practically

$$\omega = \epsilon \quad (59)$$

and thus τ' is then independent of t_1 , according to relations (57).

Scheme (G). The problem is described by the equations

$$d\Gamma_R/dt = h(t_1, j/-i)/nF - k_1\Gamma_R, \quad (60a)$$

$$d\Gamma_S/dt = h(t_1 + \tau'_1, 0/-i)/nF + k_1\Gamma_R - k_2\Gamma_S, \quad (60b)$$

$$t \geq t_1 + \tau'_1: \Gamma_R = 0 \quad (60c)$$

and condition (I). Solution of these equations in a similar manner as in Scheme (A) leads, for the region $t_1 \leq t \leq t_1 + \tau'_1$ and for $k_2 \neq k_1$, to the relation

$$\Gamma_S = [jk_1/nF(k_1 - k_2)] \left\{ (1 - e^{-k_2 t})/k_2 - (1 - e^{-k_1 t})/k_1 - (u + 1) \cdot \right. \\ \left. [(1 - e^{-k_2(t-t_1)})/k_2 - (1 - e^{-k_1(t-t_1)})/k_1] \right\}, \quad (61)$$

while τ'_1 is given by relation (14). The surface concentration of substance S at time $t + \tau'_1$ is denoted as $(\Gamma_S)_{\tau'_1}$. From equations (61) and (14) we obtain

$$(\Gamma_S)_{\tau'_1} = [jk_1/nFk_2(k_1 - k_2)] \left\{ (u + 1 - e^{-k_2 t_1}) [u/(u + 1 - e^{-k_1 t_1})]^{k_2/k_1} - u \right\}. \quad (62)$$

Solution of equation (60b) in the region $t \geq t_1 + \tau'_1$ with reference to condition (60c) leads to the relation

$$\Gamma_S = (\Gamma_S)_{\tau'_1} \cdot e^{-k_2(t-t_1-\tau'_1)} - (i/nFk_2) (1 - e^{-k_2(t-t_1-\tau'_1)}). \quad (63)$$

From the fact that, at the second transition time, $\Gamma_S = 0$, we obtain, from equations (62), (63) and (14) for τ'_1 the relation

$$\tau'_2/\tau'_1 = (k_1/k_2) \ln \left\{ 1 + [(u + 1 - e^{-k_2 t_1}) [u/(u + 1 - e^{-k_1 t_1})]^{k_2/k_1} - u] / u(1 - k_2/k_1) \right\} / \ln \left\{ (u + 1 - e^{-k_1 t_1}) / u \right\}. \quad (64)$$

If simultaneously the conditions

$$k_1 t_1 > 6, \quad k_2 t_1 > 6 \quad (65a, b)$$

hold, then equation (64) simplifies to relation

$$\tau'_2/\tau'_1 = (k_1/k_2) \ln \left\{ 1 + [(u + 1) [u/(u + 1)]^{k_2/k_1} - u] / u(1 - k_2/k_1) \right\} / \ln \left\{ (u + 1) / u \right\}. \quad (66)$$

The limiting transitions of relation (66) give

$$k_2/k_1 \rightarrow \infty: \tau'_2/\tau'_1 \rightarrow (k_1/k_2)^2 / \ln \left\{ (u + 1) / u \right\}, \quad (67a)$$

$$k_2/k_1 \rightarrow 0: \tau'_2/\tau'_1 \rightarrow k_1/k_2. \quad (67b)$$

Relations (64) and (66) are indefinite at the singular point for $k_2 = k_1 = k$. For this point we obtain, by direct solution of equations (60a, b) with condition (I), in place of relation (6I), the relation

$$\Gamma_S = (j/nFk) \{1 - e^{-kt} - kt e^{-kt} - (u+1) [1 - e^{-k(t-t_1)} - k(t-t_1) e^{-k(t-t_1)}]\} \quad (68)$$

and instead of equation (62), the relation

$$(\Gamma_S)_{t_1'} = (j/nF) [(t_1 + \tau_1') u - t_1 u(u+1)/(u+1 - e^{-kt_1})]. \quad (69)$$

Employing relation (69) instead of relation (62) in equation (63) then leads, rather than to relation (64), to the relation

$$\begin{aligned} \tau_2'/\tau_1' &= \ln \{1 + \ln [(u+1 - e^{-kt_1})/u] - \\ &- kt_1 e^{-kt_1}/(u+1 - e^{-kt_1})\} / \ln \{(u+1 - e^{-kt_1})/u\}. \end{aligned} \quad (70)$$

For

$$kt_1 > 6 \quad (71)$$

equation (70) simplifies to the relation

$$\tau_2'/\tau_1' = \ln \{1 + \ln [(u+1)/u]\} / \ln \{(u+1)/u\}. \quad (72)$$

Condition (65a) is fulfilled when inequality (I9) is valid for τ_1' . Condition (65b) may, in the region $k_2 < k_1$, be replaced by the condition

$$t_1 > (\tau_2' + \tau_1'(1 - (\tau_2'/\tau_1')_{k_2=k_1}) \cdot 6 / \ln [(u+1)/u]. \quad (73)$$

Condition (73) is equivalent to condition (65b) at the points $k_2 = k_1$ and $k_2/k_1 \rightarrow 0$; in the region, $k_2 < k_1$, fulfillment of condition (73) ensures the fulfillment of condition (65b), while the increase in the value of t_1 , required by condition (73) compared to condition (65b), is negligibly small. In the region, $k_2 > k_1$, condition (65b) is always fulfilled by condition (65a) and when inequality (I9) is valid, inequality (73) is always fulfilled. Thus, a sufficient condition for the validity of equation (66) is given by simultaneous fulfillment of inequalities (I9) and (73).

RESULTS AND DISCUSSION

The results of the solution show that, as with homogeneous following reactions, also with follow-up reactions of completely adsorbed substances we can distinguish two characteristic cases: reversible and irreversible reactions; thus we will consider each case separately below.

Reversible Reaction

For homogeneous follow-up reversible reactions, the expression⁵ $\{[(1 + t_1/\tau')^{1/2} - 1]/u - 1\} \cdot \sqrt{\tau'}$ is characteristic and for sufficiently large values of t_1 - i.e. for sufficiently fast reactions - it does not depend on t_1 and u . Similarly for the follow-up reversible reactions of completely adsorbed substances, according to analysis of results, the characteristic expression is $t_1/u - \tau'$, which for sufficiently fast reactions

attains a limiting value independent of t_1 and u . The transition of the given characteristic expression to the limiting value with increase in t_1 is shown in Fig. 1 for reaction according to Scheme (A). For other reversible reactions, this transition has a similar character and changes in the magnitude of the equilibrium constants and u affect it in the same way. In the case when, with a completely adsorbed depolarization product, no chemical reaction occurs, $\tau'_1 = t_1/u$. The value of the characteristic expression, $t_1/u - \tau'$, can then be physically interpreted as a deviation caused by a chemical reaction.

Relations for the expression, $t_1/u - \tau'$, for sufficiently fast reversible follow-up reactions of completely adsorbed substances and conditions for the validity of these relations can be summarized as follows:

Scheme (A): $k\tau' > 6$, $Kkt_1/u > 1 + 6K$:

$$t_1/u - \tau' = 1/Kk \quad (k = k_a + k_b).$$

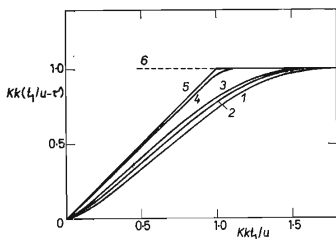


FIG. 1

The Dependence of the Characteristic Expression $t_1/u - \tau'$ on t_1 for Reversible Follow-up First Order Reaction of Completely Adsorbed Substances

1 $K = 0.1$, $u = \frac{1}{3}$; 2 $K = 0.1$, $u = 1$;
3 $K = 0.1$, $u = 3$; 4 $K = 0.01$, $u = 1$; 5
the limit for $K \rightarrow 0$; 6 the limit for $kt_1 \rightarrow \infty$.

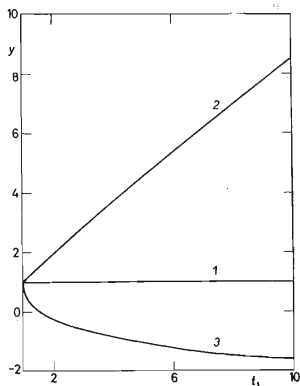


FIG. 2

The Dependence of the Characteristic Expression on t_1 , for Fast Reversible Reactions

$u = 1$, the characteristic expression corresponding to each kind of reaction follows always a straight line 1 to which values on both axes are relatively related. 2 $Y = t_1/u - \tau'$ for homogeneous reactions; 3 $Y = \{[(1 + t_1/\tau')^{1/2} - 1]/u - 1\} \sqrt{\tau'}$ for the reactions of completely adsorbed materials.

Scheme (B): $Kk_1nF/i < 10^{-2}$, $\tau'i/nFK > 6$, $k_1t_1/2u > 1.1$:

$$t_1/u - \tau' = 2/k_1.$$

Scheme (C): $K(i/nFk_2)^{1/2} < 10^{-2}$, $k_1\tau' > 6$, $(k_2i/nF)^{1/2} \alpha t_1/u > 1.1$:

$$t_1/u - \tau' = (nF/ik_2)^{1/2}/\alpha$$

for (C - a), $\alpha = 1$; for (C - b), $\alpha = 2$.

Scheme (D): $K < 10^{-2}$, $\tau'(ik_a/nF)^{1/2}/K > 6$, $(k_a i/nF)^{1/2} \alpha t_1/u > 1.1$:

$$t_1/u - \tau' = (nF/ik_a)^{1/2}/\alpha$$

for (D - a), $\alpha = 1/2$; for (D - b), $\alpha = 1$.

Similarly as with homogeneous reactions⁵ we can always interpret the condition containing t_1 as a condition of sufficient reversibility and the condition containing τ' as a condition of a sufficiently fast reaction. The first condition given with Schemes (B), (C), and (D) is always the condition of the chemical equilibrium being sufficiently shifted towards the products of the reaction.

It is further seen in the given relations that, in some cases, the characteristic expression depends on the current after reversal, i . As opposed to homogeneous reactions⁵, however, this dependence indicates only the order of the reverse reaction (*i.e.* according to the given schemes, the reaction from right to left).

A problem which still deserves attention is the question of differentiating between homogeneous reactions and reactions of completely adsorbed substances. Analysis of relations for follow-up reversible reactions shows that, in both cases, τ' increases with increasing t_1 . If we, however, use the characteristic expression which does not correspond to the case solved, then this expression depends on t_1 even with fast reactions; an example of this is given for illustration in Fig. 2.

In addition, the given illustration enables us to arrive at one more qualitative conclusion: homogeneous reactions and the reactions of completely adsorbed substances can be regarded as limiting cases and from the functions shown in Fig. 2 we can generally deduce that the effect of adsorption appears with homogeneous reactions as a decrease in the values of the characteristic expression with an increase in t_1 and the effect of diffusion on the reactions of adsorbed materials as an increase in the values of the characteristic expression with increasing t_1 .

Irreversible Reactions

With irreversible follow-up reactions of completely adsorbed depolarization products, τ' does not depend on t_1 for sufficiently fast reactions, as with homogeneous reactions. The transition of τ' to the limiting value with increasing t_1 for reactions of the first

and second order is given in Fig. 3; the analogy with the function for homogeneous reactions¹ is obvious. Analogously as with homogeneous reactions, the condition of a sufficiently fast reaction can be represented by an inequality between t_1 and τ' . Similarly as with homogeneous reactions, for first order reactions τ' is, for a given value of u , independent of the current intensity, but is dependent on it for higher order reactions. The dependence on the current intensity for higher order reactions is, however, different for completely adsorbed substances than for the corresponding homogeneous reactions.

The general relation for sufficiently fast reactions of completely adsorbed depolarization products proceeding according to Scheme (E), and the condition of a sufficiently high reaction rate have the form:

$$t_1 > \tau' \cdot g_m / f_m(u) : (j/nFk)^{(m-1)/m} k\tau' = f_m(u),$$

where $f_m(u)$ is a function of u , whose form depends on the reaction order, m , and g_m

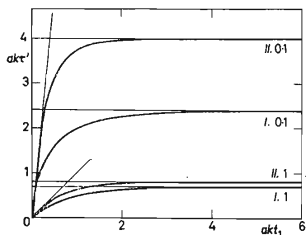


FIG. 3

The Dependence of τ' on t_1 for Irreversible Follow-up Reactions of a Completely Adsorbed Depolarization Product

Roman numerals indicate the reaction order, arabic numbers, u , and lines are asymptotes for $t_1 \rightarrow 0$ and $t \rightarrow \infty$.

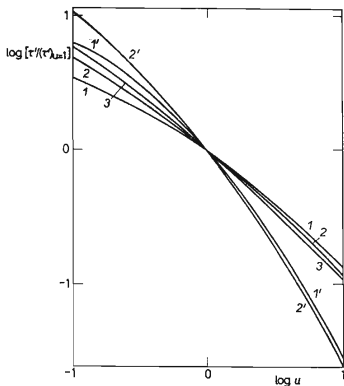


FIG. 4

The Dependence of $\tau' / (\tau')_{u=1}$ on u at Constant j for Irreversible Follow-up Reactions Plotted in log-log Co-ordinates

The numbers correspond to the reaction order, the indexed numbers correspond to homogeneous reactions, the un-indexed numbers to reactions of a completely adsorbed depolarization product.

is a constant whose value also depends on m . From the given relation it can be seen that the dependence of $\log \tau'$ on $\log j$ is a straight line, from the slope of which it is possible to determine the reaction order, m , similarly as with homogeneous reactions². The slope of this line is, however, different than with homogeneous reactions; it is worth mentioning that the slope for third-order reaction of completely adsorbed depolarization products is the same as with second order homogeneous reaction.

For the most important types of first and second order reactions, the relations for τ' and the conditions of their validity have a concrete form:

$$m = 1 : t_1 > \tau' \cdot 6/\ln [(u + 1)/u] : k\tau' = \ln [(u + 1)/u],$$

$$m = 2 : t_1 > \tau' \cdot 3u^{1/2}/\arctg(u^{-1/2}) : (kj/nF)^{1/2} \tau' = u^{-1/2} \arctg(u^{-1/2}).$$

From what has been said it is clear that, from the dependence of the transition time, τ' , on the current, j , and on the time of current reversal, t_1 , determined during the experiments, it is difficult to distinguish between homogeneous reactions, and reactions of adsorbed materials. However, it is possible to distinguish between them using the dependence of τ' on the ratio of the current intensities, u . For illustration, the dependence of $\tau' / (\tau')_{u=1}$ on u at a constant j is given in Fig. 4 for 1st and 2nd order homogeneous reactions and for 1st, 2nd, and 3rd order reactions of completely adsorbed substances. It is clear that cases with the same dependence of τ' on j (*i.e.* 1st order reactions homogeneous and in the adsorbed layer, second order homogeneous reaction and 3rd order reaction in the adsorbed layer) can easily be distinguished in this way.

Similarly as with reversible reactions, here we can also regard reactions of completely adsorbed depolarization products and homogeneous reactions as two extreme cases and draw the conclusion that the effect of adsorption in homogeneous reactions will be manifested in the dependence of τ' on u varying between the dependences for the two extreme cases. This fact was actually verified by detailed analysis of the effect of adsorption on the linear isotherm in the case of first order homogeneous reaction¹⁰.

The reaction according to Scheme (E) is a limit of reactions according to Schemes (A) to (D) for $K \rightarrow 0$; from reactions according to Schemes (A) and (C) we obtain the case when $m = 1$, from the reactions according to Schemes (B) and (D), the case with $m = 2$. The condition of sufficient irreversibility of these reactions — *i.e.* the possibility of applying the relations for an irreversible reaction — can be obtained from the conditions for sufficient reversibility given for the reverse reactions (*i.e.* conditions containing t_1) by reversing the sense of the inequality and substituting the value $10^{-2,5}$ for the right-hand side of the inequality.

For first and second order parallel reactions according to Scheme (F), the relation for τ' for a sufficiently fast reaction and the condition of its validity have the form

$$\begin{aligned}
 t_1 &> \tau' \cdot 6\varepsilon/f_{1,2}(u, b) : k_1\tau' = f_{1,2}(u, b), \\
 ub < 1 : f_{1,2}(u, b) &= (1/\sigma) \ln [(1 + \sigma)(\varepsilon - \sigma)/(\varepsilon + \sigma)(1 - \sigma)], \\
 ub = 1 : f_{1,2}(u, b) &= 2(\varepsilon - 1)/\varepsilon, \\
 ub > 1 : f_{1,2}(u, b) &= (2/\varrho) \operatorname{arctg} [\varrho(\varepsilon - 1)/(\varrho^2 + \varepsilon)], \\
 \varepsilon &= (1 + b)^{1/2}, \quad \sigma = (1 - ub)^{1/2}, \quad \varrho = (ub - 1)^{1/2}, \quad b = 4k_2j/nFk_1^2.
 \end{aligned}$$

Analysis of these relations gives results very similar to those for the parallel homogeneous reactions of various orders⁶. The dependence of $\log \tau'$ on $\log j$ is a continuous convex curve, with two asymptotes; the asymptote for $j \rightarrow 0$ corresponds to the linear dependence for a lower order reaction; the asymptote for $j \rightarrow \infty$ corresponds to the linear dependence for a higher order reaction. If we shift the curves for various values of u so that their asymptotes are superimposed, their courses are very similar. From the course of the dependence of τ' on j , the rate constants for both reactions can be determined using the given relationships. In the regions, when the effect of one reaction predominates, and the effect of the other reaction appears only as a perturbation of the relationship for a controlling reaction, the values for the predominating reaction can be obtained by extrapolating the appropriate simple dependences to zero; for predominating first-order reactions, this is the dependence of $1/\tau'$ on j , for predominating second order reactions, of $1/(\tau' \sqrt{j})$ on $1/\sqrt{j}$. The value of the quantity $6\varepsilon/f_{1,2}(u, b)$ in the condition of sufficient rate always lies between the values for similar quantities in the conditions of sufficient rate of simple 1st and 2nd order reactions, given above; thus the inequality will always be fulfilled for parallel reactions if the inequality given for first order reaction is fulfilled.

For consecutive reactions according to Scheme (G), the following relationships hold, for sufficient rates of both steps, for the consecutive transition times, τ'_1 , and τ'_2 :

$$t_1 > \tau'_1 \cdot 6/\ln [(u + 1)/u], \quad t_1 > [\tau'_2 + \tau'_1(1 - h(u))] \cdot 6/\ln [(u + 1)/u] :$$

$$k_1\tau'_1 = \ln [(u + 1)/u],$$

$$\begin{aligned}
 k_1 \neq k_2 : \tau'_2/\tau'_1 &= (k_1/k_2) \cdot \ln \{1 + [(u + 1) [u/(u + 1)]^{k_2/k_1} - \\
 &- u]/u(1 - k_2/k_1)\} / \ln \{(u + 1)/u\},
 \end{aligned}$$

$$k_1 = k_2 : \tau'_2/\tau'_1 = \ln \{1 + \ln [(u + 1)/u]\} / \ln \{(u + 1)/u\} = h(u).$$

Using the given relationships, it is possible to determine the rate constants of both reaction steps from the measured transition times. For numerical calculations, using the given equations, the fact that, as opposed to homogeneous consecutive reactions³, $k_2/k_1 < \tau'_1/\tau'_2$ always holds, is useful.

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