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Author(s)	ENYO, M.
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THE COUPLED-CONTROL OF ELECTRODE PROCESSES. EXPERIMENTAL EVIDENCES AND INTERPRETATIONS

by

M. ENYO^{*)}

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Abstract

Experimental evidences are now available to demonstrate that many of the electrode processes are under coupled-control, *i.e.*, there exists no unique rate-determining step. Due to this, the mechanism of those processes readily changes with variation of the reaction affinity (overpotential). Interpretation of several experimental observations such as results of tracer experiments on the hydrogen electrode reaction, hydrogen pressure equivalent to hydrogen overpotential, and overpotential dependence of the affinity distribution to the constituent steps were presented and implications of the concept to electroreduction of organic compounds were discussed. A model was proposed to visualize the coupled-control and the mechanism change with overpotential.

Introduction

Mechanistic studies of chemical reactions should include (i) construction of the reaction route (path) from various elementary steps and (ii) determination of the rate-controlling characteristics of the steps involved. In most cases, existence of an unique rate-determining step (rds) was assumed in order to simplify the arguments and efforts were then concentrated on the identification of the rds.

However, the procedure appeared to be often an over-simplification, because many reactions were found to be consisted of the steps having the rate constants of comparable orders of magnitude. We will call below such cases as the coupled-controlled reactions. Further, as will be discussed below, the rate-controlling characteristics of individual steps should depend on the value of the reaction affinity, and hence the mechanism is subject to change with variation of the reaction conditions. The procedure based on the assumption of a unique rds without any quantitative discussion on its validity may thus often lead to an erroneous figure of the reaction. This is particularly im-

^{*)} The Research Institute for Catalysis, Hokkaido University, Sapporo, 060 Japan.

portant in the case of electrode processes in which very wide range of variations of the reaction affinity (overpotential) is frequently encountered.

The present paper is devoted to a brief survey of experimental evidences in electrode processes indicating involvement of the coupled-control and to the interpretations of various experimental data. A simple "canal model" which is convenient to visualize the mechanism change caused by changes in the reaction affinity will be proposed.

Experimental Evidences and Interpretations

(1). *The Rate-Determining Step and the Rate-Controlling Step*

The term "rate-determining step" is one of central subjects of the reaction mechanism, but its strict meaning has not gained sufficient agreement among researchers. Usual uses can be classified as:

(A). The step(s) which practically controls the overall reaction rate. We will call such a step (or steps) below in this paper tentatively as the rate-controlling step(s)".

(B). In more strict way, a unique step which alone involves a significant magnitude of the free energy change during net occurrence of the reaction; all the other steps are assumed to be in quasi-equilibrium. We will use below the term "rate-determining step (rds)" for such a step. This condition is sufficient but not necessary for (A).

Roughly speaking, (A) has been conveniently used by a larger group of chemists, usually without going into too much detailed mechanistic discussions, whereas (B) has been used by many kineticists as a base of rather strict and detailed mechanistic discussions.¹⁻³⁾ To some extent, this is only a matter of degree of strictness but, as will be discussed below, the difference plays a significant role in the mechanistic studies of the chemical kinetics and especially in the discussion of the activity of the reaction intermediates.

(2). *The Chlorine Electrode Reaction on Platinum Metals*

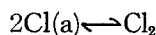
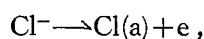
The mechanism of the chlorine electrode reaction on Pt and Ir in acidic solution was studied. The reaction orders both for the anodic and cathodic uni-directional component currents defined *e.g.* as,

$$\zeta_+(\text{Cl}^-) \equiv \left(\frac{\partial \ln i_+}{\partial \ln a_{\text{Cl}^-}} \right)_{P_{\text{Cl}_2}, \phi}$$

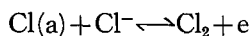
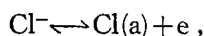
were obtained in a wide range of electrode potential covering both anodic and cathodic regions.⁴⁾ Results are plotted in Fig. 1 against the electrode

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potential, ϕ . It was found in both cases that ζ 's are dependent on ϕ and change from simple integers (or half integers) to other such values at around the reversible potential. Based on the reaction order theory,^{5,6} the following mechanisms were proposed: On Pt, it was the Volmer-Tafel route,



and on Ir, it was the Volmer-Heyrovsky route,



and in both cases the first step determined the reaction kinetics, hence the reaction orders, in the anodic region whereas the last step in the cathodic region. The mechanism change takes place with changes in the electrode potential of about 0.2 V.

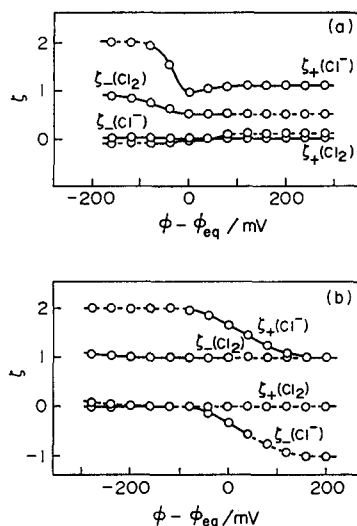
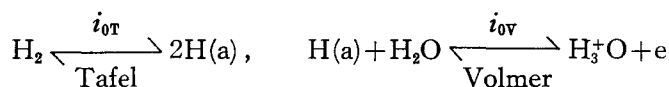


Fig. 1. Dependence of reaction orders upon electrode potential, ϕ , of the chlorine electrode reaction on (a) Pt and (b) Ir.⁴ 2N H_2SO_4 , 25°C. $P_{\text{Cl}_2} = 1 \sim 0.089$ atm, $[\text{HCl}] = 0.20 \sim 0.0060$ N. ϕ_{eq} is the reversible potential in the system, $P_{\text{Cl}_2} = 1$ atm and $[\text{HCl}] = 0.20$ N.

(3). *Tracer Experiments on the Hydrogen Electrode Reaction. The Coupled-Control*

Detailed information on the hydrogen electrode reaction (h.e.r.) on various metals have been obtained from isotope tracer experiments using deuterium.^{7,8} Both the isotope exchange rate and changes in the isotopic composition of the hydrogen gas were observed during exchange of hydrogen between H_2O and D_2 with a metal as catalyst. It was then possible on all the metals studied (Pt, Rh, Ni, Au, Ag, etc) to derive the conclusion that the reaction route is of the Tafel-Volmer type,



It was further observed that the exchange c.d's of the two steps, i_{0T} and i_{0V} , are generally of near orders of magnitude; namely, there exists no unique, overwhelming rds.

As well known, the stoichiometric number ν_{rds} of the rds, if it exists there, can be obtained from *e. g.* the exchange c. d. i_0 of the overall reaction and the polarization resistance. Naturally, in the absence of the unique rds, the stoichiometric number obtained in that way loses a simple physical meaning as the number of repetitions of the rds per unit occurrence of the overall reaction. Nevertheless, these experimental quantities are still obtainable, and we will call the "stoichiometric number" as $\bar{\nu}$, *i. e.*,

$$\bar{\nu} = \frac{2f\eta}{\ln V_+/V_-} \simeq i_0 2f \left(\frac{d\eta}{di} \right)_{\eta \rightarrow 0} \quad (1)$$

where $f \equiv F/RT$, F , R and T are in their usual meaning, V_+ and V_- are the forward and reverse uni-directional rates of the overall reaction, η is the overpotential, and i is the current.

Basic equations we have are,⁹⁾

$$2F\eta = -\Delta G = -\sum_s \nu_s \Delta g_s \quad (2)$$

$$-\Delta g_s = RT \ln v_{+s}/v_{-s} \quad (3)$$

and^{10,11)}

$$\frac{V_+}{V_-} = \prod_s \frac{v_{+s}}{v_{-s}} \quad (4)$$

where $-\Delta G$ is the overall affinity of the reaction and $-\Delta g_s$ and ν_s are the affinity and the stoichiometric number of step s , respectively. Application of these equations to eqn. (1) readily leads to

$$\bar{\nu} = \sum_s \nu_s \Delta g_s / \sum_s \Delta g_s \quad (5)$$

Therefore, $\bar{\nu}$ is an average value of ν_s 's weighted with Δg_s .

On the basis of the steady-state requirements (mass-balances) of the reaction, we have, for the net rate V of the overall reaction of the Tafel-Volmer route,

$$V = \frac{v_{+T} - v_{-T}}{\nu_T} = \frac{v_{+V} - v_{-V}}{\nu_V} \quad (6)$$

Employing eqn. (3), it is then possible to obtain,

$$m_0 \equiv i_{0V}/i_{0T} = (\Delta g_T/\Delta g_V)_{-\Delta G \rightarrow 0} \quad (7)$$

where subscript 0 indicates equilibrium of the overall reaction. Accordingly, near the equilibrium potential, we obtain by substituting eqn. (7) into (5), since $\nu_T=1$ and $\nu_V=2$,

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$$\bar{\nu}_0 = (m_0 + 2)/(m_0 + 1) \quad (8)$$

This relation was tested experimentally as reproduced in Fig. 2⁷. Experimental data are in a reasonable fit with eqn. (8). (A better fit could be obtained after introducing a parameter σ which reflects the isotope effect⁷: We will however not dwell on this matter here.) Figure 2 has the following characteristics:

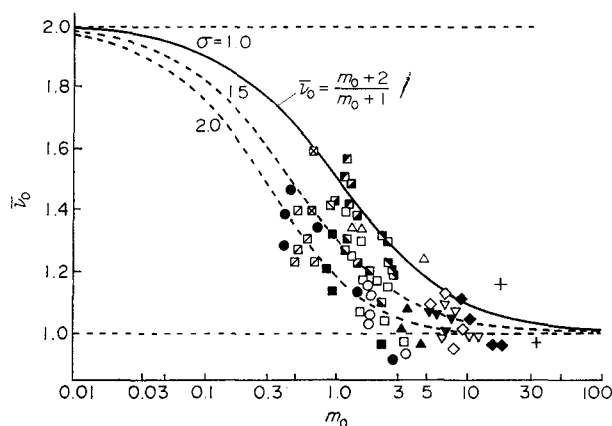


Fig. 2. The relation between $m_0 (\equiv i_{0V}/i_{0T})$ and $\bar{\nu}_0$ of the hydrogen electrode reaction obtained from deuterium exchange reaction on various metals^{7,8}. Total hydrogen pressure = 20 ± 2 cmHg, 25°C.

Ni: ● (run 1), ○ (run 2); 0.5 M NaOH
 Ag: ▲, 0.5 M H₂SO₄
 Au: ◇ (run 1), ◆ (run 2); 0.5 M H₂SO₄
 Ir: △, 0.5 M H₂SO₄
 Pt: ▼, 0.5 M NaOH; ▽, 0.5 M H₂SO₄ + H₂SO₄ (pH 1.9)
 Rh: □, 0.5 M H₂SO₄, ▤, H₂SO₄ + 0.25 M K₂SO₄ (2.0), ▥, H₂SO₄ + 0.25 M K₂SO₄ (0.9), ▦, HClO₄ (0.5), ▧, HClO₄ + 1 M NaClO₄ (0.3), ▨, HClO₄ + 1 M NaClO₄ (1.4), ▩, KOH + 0.2 M K₂SO₄ (12.3), ▪, KOH + 0.25 M K₂SO₄ (13.1), ▫, KOH + 0.25 M K₂SO₄ (13.5)

(i) $\bar{\nu}_0$ is between 1 and 2, supporting the Tafel-Volmer route. No such a variation of $\bar{\nu}_0$ may be expected for the Heyrovsky-Volmer route.

(ii) m_0 is of near orders of magnitude of unity. The reaction is therefore under a coupled-control.

The existence of a unique rds means that $m_0 \gg 1$ or $\ll 1$. In usual simplified terms m_0 is understood to be infinite (or zero), which is however certainly not very likely. The discussion of how large (small) a value of the ratio would be sufficient for allowing a simplified analysis of the reaction

kinetics assuming quasi-equilibrium of the "fast" steps need to be based on detailed analysis of the affinity distribution and of their consequences on the reaction kinetics. It will be shown below that even the ratio of $10^{\pm 2}$ should not be sufficient to approximate the rapid steps to be in quasi-equilibrium.

(4). *The Affinity Distribution. Experiments on Pd Hydrogen Electrode*

When the hydrogen electrode was under polarization, the overpotential η should be distributed to the two steps of the Tafel-Volmer route, *i. e.*,

$$\eta = \eta_T + \eta_V \quad (9)$$

where, as readily seen by referring to eqn. (2),

$$\eta_s = -(\nu_s/2F) \Delta g_s \quad (10)$$

We discuss the affinity distribution in terms of m ,

$$m \equiv \Delta g_T / \Delta g_V = 2\eta_T / \eta_V \quad (11)$$

Employing appropriate equations to various step rates in eqn. (6), we obtain⁹

$$m_0 e^{\alpha_V f \eta} \left\{ 1 - \exp \left(-\frac{2f\eta}{m+2} \right) \right\} = ZQ^{\lambda} \left\{ \exp \left(\frac{mf\eta}{m+2} \right) - \exp \left(-\frac{mf\eta}{m+2} \right) \right\} \quad (12)$$

where α_V is the (anodic) transfer coefficient of the Volmer step, $Z \equiv (1-\theta)/(1-\theta_0)$, $Q = \exp \{u(\theta-\theta_0)\}$, u is the interaction/heterogeneity factor for H(a) adsorption, θ is the surface coverage of H(a), $\Delta\lambda = \lambda_V - 2\lambda_T$, and λ 's ($0 \leq \lambda \leq 1$) are parameters related to energy levels of the critical complex of the elementary steps.⁹ Therefore, m is numerically obtained as a function of η , provided the kinetic parameters involved are known.

Variation of m with η for the h.e.r. with various parameter values have been calculated,⁹ and results for the Tafel-Volmer route are reproduced in Fig. 3 for the case of the Langmuir and the Temkin adsorption isotherm for H(a), respectively. Although the quantitative aspects of m are dependent on various kinetic parameters and the forms of the adsorption isotherm of the reaction intermediate, one can extract from the figures several common features:

(i) Curves are usually not symmetrical for the Tafel-Volmer route. They are symmetrical for the Heyrovsky-Volmer route.⁹

(ii) There is a tendency for m to approach values of the order of magnitude of unity under large values of the reaction affinity. In other words, the affinity distribution to the constituent steps even with large values

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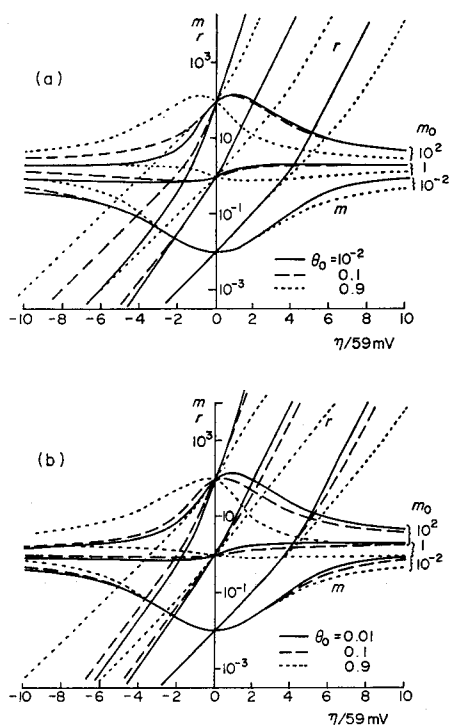


Fig. 3. Variation with overpotential of the affinity distribution to the constituent steps in the Tafel-Volmer route⁹⁾.

$m=10^2$, 1, and 10^{-2} , and $\theta_0=0.01$, 0.1, and 0.9 as indicated.

- (a) Langmuir isotherm for H(a) adsorption
- (b) Temkin isotherm with $u=5$ for H(a) adsorption

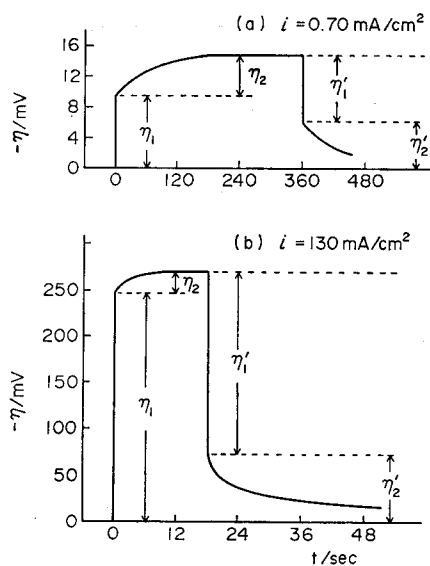


Fig. 4. Overpotential rise and decay transients of the Pd hydrogen electrode at (a) low and (b) high c.d.'s. and various overpotential components¹²⁾.

Pd foil (10 μm in thickness),
1 N H_2SO_4 , 30°C

of m_0 becomes roughly even under high overpotential values.

(iii) Accordingly, each steps eventually become irreversible at high overpotentials according to eqn. (3). It is not safe to assume quasi-equilibrium of the steps other than the slowest

step, or many of these steps will play significant roles in determining the overall kinetics and particularly the activity of the reaction intermediates.

Experimentally, the affinity of a single step is obtained if the component rates of the step are known, eqn. (3). Accordingly, the affinity distribution to the constituent steps may be obtained in principle from isotope tracer experiments, but in practice the analysis will be rather involved and be restricted to a region relatively close to the equilibrium potential (low affinity values).

Demonstration of such a variation of the affinity distribution to the

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constituent steps with change of the overpotential is directly obtainable from polarization data on the Pd h.e. Due to extensive absorption of hydrogen by Pd, the overpotential rise transient with constant current and decay transient after current interruption show characteristic shapes as exemplified in Fig. 4, in which various overpotential components are readily obtained. It has been shown elsewhere that,^{12,13}

- (i) η_1 readily gives the kinetic parameter value of the Volmer step.
- (ii) η'_2 directly represents the overpotential component for the Tafel step. Consequently, η'_1 represents that of the Volmer step.

Hence, eqn. (11) is now written as

$$m = 2\eta_T/\eta_V = 2\eta'_2/\eta'_1 \quad (13)$$

Experiments were performed using an inactive Pd electrode in order to minimize the effect of diffusion control. Results obtained are shown in Fig. 5, together with some theoretical curves. Although some parameters included in the calculations are unknown and hence are assumed, it is seen that a general shape of experimental values of m as a function of η is well reproduced by the calculations.*)

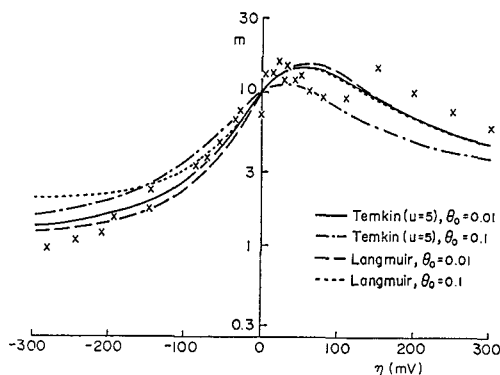


Fig. 5. Overpotential dependence of the affinity distribution to the elementary steps of the Tafel-Volmer route.

$$m \equiv \Delta g_T / \Delta g_V = 2\eta'_2 / \eta'_1$$

Experimental: Inactive Pd foil electrode, 1 N H₂SO₄, 30°C.

Theoretical: Calculated from eqn. (12) with $\lambda_V = \lambda_T = 1/2$, $m_0 = 10$, and θ_0 and u values indicated in the Figure.

*) It is interesting to note that a better fit of the theoretical line with the experimental data is obtained if θ_0 is taken to be small (e.g., $\theta_0 < 0.1$) on Pd electrode. The Pd electrode is in the β -Pd-H system and hence the atomic ratio in the bulk Pd, $(H/Pd)_{bulk} \approx 0.7$. It appears, therefore, that the ratio is lower on the surface as compared with that in the bulk Pd.

(5). *Hydrogen Pressure Equivalent to Hydrogen Overpotential*

It was often argued, in discussing *e.g.* electro-reduction of organic compounds, that the hydrogen overpotential can be converted to a equivalent hydrogen pressure $P_{\overline{H}_2}$ by the (equilibrium) Nernst equation,

$$-\eta = (1/2f) \ln P_{\overline{H}_2}/P_{\overline{H}_2,0} \quad (14)$$

This has been quoted for an interpretation of the powerful reducing ability of cathode or the nascent hydrogen, but its quantitative aspects have long been remained undiscussed.

It is easy to show that, when the h. e. r. takes place through the Tafel-Volmer route, eqn. (14) is correct only if $m_0 = \infty$ (or $i_{0V}/i_{0H} = \infty$ in the Heyrovsky-Volmer route) but otherwise the effect of η upon the hydrogen pressure during the polarization should be lower than this relation.⁹ The equivalent hydrogen pressure (the cavity hydrogen pressure) is obtained from the condition that the (hypothetical) hydrogen gas is in adsorption equilibrium with H(a). Thus,

$$\mu_{\overline{H}_2} = 2\mu_{H(a)}$$

or

$$\ln P_{\overline{H}_2}/P_{\overline{H}_2,0} = 2 \ln a_H/a_{H,0} \equiv 2 \ln \gamma_H \quad (15)$$

Hereafter, $P_{\overline{H}_2,0}$ is chosen at 1 atm. It is then possible to obtain,⁹

$$\ln P_{\overline{H}_2} = -2mf\eta/(m+2) \quad (16)$$

This deviates from eqn. (14) unless $m = \infty$.

The equivalent hydrogen pressure on Pd h.e. under polarization was experimentally evaluated by measuring hydrogen content of Pd electrode during the polarization and then combining the data with the hydrogen absorption isotherm of Pd.^{14,15} Results are reported in Fig. 6.¹² It is evident that experiments largely deviate from the Nernst relation (broken line). The solid and dotted lines in Fig. 6 are the plot of eqn. (16) for the Langmuir and Temkin adsorption isotherm, respectively, in which m was calculated from eqn. (12) with $m_0 = 10$ or 3. The theoretical

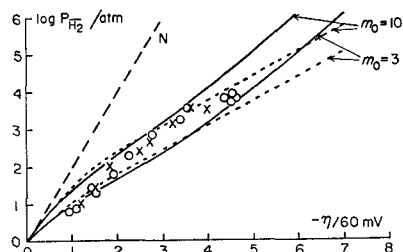


Fig. 6. Comparison of the equivalent hydrogen pressure at various cathodic overpotentials on Pd with theoretical lines calculated from eqns. (12) and (16).¹⁶

Experimental: Pd foil (10 μ m thickness), 1 N H₂SO₄, 30°C

Theoretical: Parameter values used were $\theta_0 = 0.1$, $\alpha_V = \lambda_V = \lambda_T = 1/2$, and $m_0 = 10$ or 3 as indicated. The broken line (N) indicates the Nernst eqn. (14).

lines satisfactorily interpret the experimental data.

(6). *Implication to the Electro-reduction of Organic Compounds*

Electro-reduction of organic substances would take place by picking-up either H(a) or electron followed by proton. In the former case, the reducing ability of the cathode is likely to be represented by the activity of H(a) during the polarization and it would in turn be a function of η . Although the cathodic reduction is a powerful process, it is expected from the above discussion that the reducing ability would generally be lower than that anticipated from the Nernst equation and instead be given by eqn. (16). Further, it is expected that electrode materials with slower Tafel step as compared with the Volmer step may be suited for the electro-reduction. Conversely, in the latter case, the ability is probably a direct function of η , for it is a measure of the chemical potential of electrons in the cathode. Hence, electrode materials of high hydrogen overpotential may be preferred.

The question of either H(a) or electron to be the reducing agent was the subject of several papers,¹⁷⁻¹⁹⁾ and it appears from these investigations that those substances at which electron transfer reaction readily takes place (*e.g.* *p*-benzoquinone/hydroquinone) are reduced by electron and those which are not (*e.g.* unsaturated hydrocarbons) are reduced by H(a). Some information regarding this may be obtained from the behaviours of η and η'_2 in the presence of organics to be reduced.

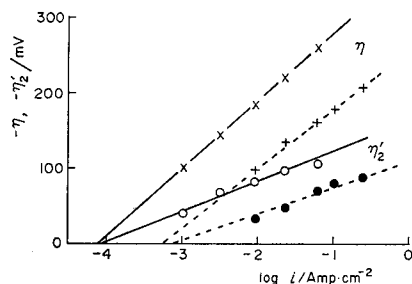


Fig. 7. Electroreduction of I_2 on Pd¹⁶⁾ Pd foil, 30°C.

Solid lines: 1 N H_2SO_4 +0.06 M KI
Broken lines: 1 N H_2SO_4 +0.06 M KI
+0.01 M I_2

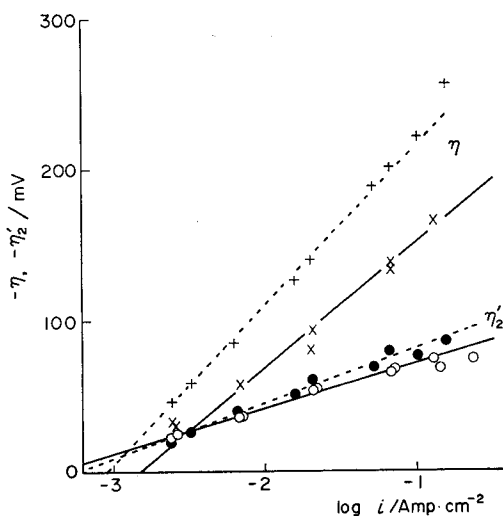


Fig. 8. Electroreduction of cis-2-butene-1,4-diol on Pd foil, 30°C¹⁶⁾.

Solid lines: 1 N H_2SO_4 +0.05 M butanediol
Broken lines: 1 N H_2SO_4 +0.05 M butanediol+0.05 M butenediol

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Figure 7 shows the polarization experiments in the system containing I^- and I_2 . It is probably doubtless that I_2 (or I_3^-) is reduced to I^- by taking up electrons.¹⁷ In support of this, by the addition of I_2 to the solution containing I^- , we found (i) the total overpotential η was considerably lowered and (ii) the relative magnitude of η'_2 as compared to η was scarcely changed. The observations could well be explained by assuming that a larger portion of the current was consumed for the I_2 reduction whereas the h.e.r. proceeded consuming the other portion of the current. The latter observation suggests that the h.e.r. takes place rather independent of the I_2 reduction and hence no significant variation of m is involved.

Figure 8 shows results of analogous experiments in the system containing cis-2-butene-1,4-diol. Considerable increase of η was observed after the addition of butenediol to the solution containing butanediol. The increase is considered to be due to a decrease of catalytic activity of the electrode, probably due to blocking of the electrode surface with butenediol as suggested by a decrease of differential capacitance of the electrode. In spite of the increase in η , it was seen that η'_2 was practically unchanged, or the relative magnitude of η'_2 as compared to η was lowered by the addition of butenediol. This may be explained in terms of consumption of H(a) by the organic substance and hence of decrease of its activity. The observations therefore indicate that the electroreduction of butenediol proceeds by picking up H(a).

(7). *Synthesis of the Overall Kinetics from the Elementary Step Rates and the Mechanism Change with Overpotential*

The overall uni-directional component rates of the Tafel-Volmer route may be related to those of the constituent steps as,²⁰

$$U_+ = \frac{u_{+T}u_{+V}}{u_{-T} + u_{+V}}, \quad U_- = \frac{u_{-T}u_{-V}}{u_{-T} + u_{+V}} \quad (16)$$

where the rates are counted by the number of hydrogen atoms transferred per unit time. Accordingly, the overall net rate U is

$$U = U_+ - U_- = \frac{u_{+T}r}{1+r} \left\{ 1 - \frac{u_{-T}u_{-V}}{u_{+T}u_{+V}} \right\} \quad (17)$$

where

$$r \equiv u_{+V}/u_{-T} \quad (18)$$

It is easy to show that r increases with increase of η in positive direction. At sufficiently high positive values of η , we obtain from eqn. (17),

$$U = u_{+T} \quad (f\eta \gg 1)$$

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and at sufficiently high negative values of η ,

$$U = -u_{-v} \quad (-f\eta \gg 1).$$

The variation of r with η for the Tafel-Volmer route is calculated and also given in Fig. 3; r is usually a strong function of η . Its variation by the factor of 10^2 which is roughly needed for the mechanism change to take place as discussed above would require the variation of η by about 0.2 V.

It has been a general observation²¹⁾ in h. e. r. kinetics that the cathodic Tafel lines on many metals are parallel with each other with the slope of 0.12 V, which is presumably attributable to the kinetic control by the Volmer reaction. On the other hand, the anodic Tafel lines on some limited number of metals on which experiments were performed always gave much a steeper slope tending to yield a limiting current. A possible cause of this behavior would be the involvement of a diffusional limit of H_2 supply in the solution, but the behavior was also seen on less active metals such as Ni.⁷⁾ It was then suggested that the Tafel step was responsible to the sharp increase of η in the anodic region. The mechanism is thus considered to be different in the cathodic and the anodic region, and the discussion presented above can provide the interpretation of the mechanism change including its direction as well.

We may summarise the situation as follows:

(i) The kinetics of the overall reaction is determined by different (rate-controlling) steps depending on the value of r and hence on the value of η . Experimentally, this means that the mechanism changes with η . In a typical case of m_0 of the order of magnitude of unity, the Tafel step should be rate-controlling under positive values of η and the Volmer step under negative values of η , with a mixed region in between around the reversible potential. With larger (smaller) values of m_0 the overpotential region in which the mechanism change takes place would be shifted to more positive (negative) overpotential values. It is to be noted that such a mechanism change takes place as a direct consequence of synthesizing the kinetics of the constituent steps; the mechanism change does not mean any change in the exchange c. d's of the steps.

(ii) The range of η which is needed to complete the mechanism change (taking changes in r from 0.1 to 10) is about 0.2 V. This is in good agreement with Fig. 1 obtained on the chlorine electrode reaction on noble metal electrodes.

(iii) At high absolute values of η , the overall kinetics is mostly or entirely

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determined by an irreversible process which exists at the upstream of the reaction flow. This is true even if the steps that follow are also irreversible.

(8). *Deuterium Separation Factor*

Variation of the electrolytic deuterium separation factor with overpotential is expected if the operative mechanism changes with overpotential. As reported elsewhere,^{8,9} the following equations are readily obtainable for the anodic (S_+) and cathodic (S_-) deuterium separation factor of the overall h. e. r.

$$S_+ = s_{+T} \frac{s_{+V}/s_{-T} + r(H)}{1 + r(H)} \quad (19)$$

$$S_- = s_{-V} \frac{1 + r(H) s_{-T}/s_{+V}}{1 + r(H)} \quad (20)$$

and

$$r(H) = r \frac{1 + Y/s_{-T}(1 - Y)}{1 + Y/s_{+V}(1 - Y)} \quad (21)$$

where Y is the deuterium atomic fraction in H(a), and the separation factors of the constituent steps are defined in terms of the individual uni-directional rate for H and D of the step and *e.g.* the deuterium atomic fraction x in the gas phase as,

$$s_{+T} = \frac{v_{+T}(H)}{1 - x} \bigg/ \frac{v_{+T}(D)}{x} \quad (22)$$

It is seen from eqn. (21) that usually $r(H)$ is close to r , and it is particularly so when s_{-T} and s_{+V} are of the same order of magnitude. Also, $r(H) \simeq r$ if electrolyses in isotopically dilute system are concerned. Since r strongly changes with overpotential, the separation factors are subject to change with η . S_+ and S_- take limiting values, when $r(H) \gg 1$,

$$S_+ \simeq s_{+T}, \quad \text{and} \quad S_- \simeq s_{-T} s_{-V}/s_{+V} \quad (23)$$

and when $r(H) \ll 1$,

$$S_+ \simeq s_{+V} s_{+T}/s_{-T} \quad \text{and} \quad S_- \simeq s_{-V} \quad (24)$$

Comparison of eqn. (20) with experimentally deduced values of m_0 with experimental data on Pt, Au, and Ni was satisfactory, as reported elsewhere.²²⁾

(9). *The Canal Model*²³⁾

The mechanism change, namely, shift of the rate-controlling step, with

the reaction affinity in the reaction under coupled-control is illustrated below with the "canal model". This model well visualizes the reaction under coupled-control and the way of mechanism change caused by the change in the reaction affinity.

Figure 9(a) illustrates the case with a unique rds. In this case, the water level h_B (chemical potential of the reaction intermediate) at the water reservoir (B) is equal either to h_A (chemical potential of the reactant group) with gate 2 (step 2) rate-determining, or h_C (chemical potential of the product group) with gate 1 (step 1) rate-determining. Accordingly, the activity change of the reaction intermediate, as referred to its value at equilibrium is readily known; it is directly given by the height h_A or h_C , namely, by an equilibrium relation such as the Nernst equation even under irreversible occurrence of the overall reaction. It is easy to realize that such is the case only when either one of the gates is fully open (quasi-equilibrium).

Figure 9(b) illustrates the case of the coupled-control; in this case, openings of both the gates are of comparable size (two steps have rate-constants of comparable magnitudes). The water level at (B) may be anywhere between h_A and h_C , and subject to change with the change in the water head (reaction affinity) and hence with the water flow rate (reaction rate).

The kinetics of the overall flow rate is of particular interest. Thus, in Fig. 9(b), the flow rate would be entirely controlled by the flow rate through gate 1, which is given by h_A measured from a definite standard level and the opening size of gate 1. In spite of this, the flow rate may also be expressed in terms of h_B and the opening size of gate 2. This would often give to the observers an erroneous impression, since the flow rate has a definite correlation with h_B , that gate 2 plays a role in controlling the overall flow rate. However, the true picture is that the steady-state

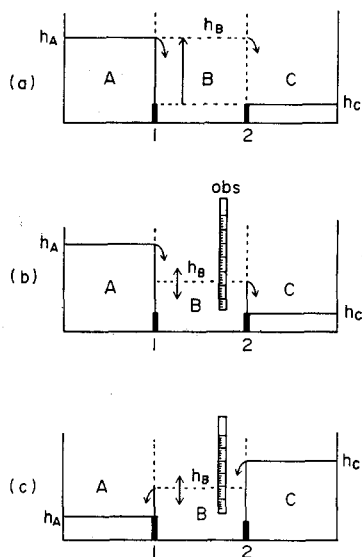


Fig. 9. The canal model of chemical reaction under coupled-control.²³⁾

- (a) Reaction with a unique rate-determining step
- (b) Reaction under coupled-control
- (c) Same as (b) with the reversed reaction affinity

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flow rate at gate 2 is equal to that at gate 1 and h_B is simply determined by the very flow rate and the size of gate 2. It is therefore concluded that the step (gate) at upstream of the canal plays the rate-controlling role.

What will happen if one exchanges h_A and h_C with each other, without changing the sizes of both the gates? One will find (Fig. 9c) that h_B again comes between h_C and h_A and the overall (now reversed) flow rate would be controlled by h_C and the size of gate 2. Namely, now gate 2 is rate-controlling instead of gate 1 in the former case of the forward water flow, or the rate-controlling step has been changed. Thus, the mechanism is changed with change in the overall affinity.

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