

Existence of Two Sets of Kinetic Parameters in the Correlation of the Hydrogen Electrode Reaction

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It has been demonstrated that the dependence of the current density on overpotential for the hydrogen electrode reaction described through the Volmer-Heyrovský-Tafel mechanism can be correlated by two different sets of the kinetic parameters. Such sets lead to two different dependences of the surface coverage on overpotential, while a unique dependence of the corresponding pseudocapacitance of adsorption is obtained. The expressions that relate both sets of kinetic parameters have been established and analyzed for the simultaneous occurrence of the three steps and for the different kinetic routes.
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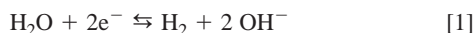
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The existence of two sets of kinetic parameters that produce the same dependence of the current density (j) on overpotential (η) for the Volmer-Heyrovský route was found by Lasia and Rami,¹ studying the kinetics of the hydrogen evolution reaction on nickel electrodes. They have shown that, when the symmetry factor of the Volmer and Heyrovský steps are equal ($\alpha_V = \alpha_H$), the simultaneous permutation of the kinetic constants $k_{+V} \leftrightarrow k_{+H}$ and $k_{-V} \leftrightarrow k_{-H}$ does not alter the dependence $j(\eta)$, but transforms the dependence of the surface coverage on overpotential $\theta(\eta)$ into $[1-\theta(\eta)]$. This statement was extended for different values of the symmetry factor^{2,3} and was also mentioned by Cheong *et al.*⁴ Furthermore Berthier *et al.*,⁵ analyzing the application of the Volmer-Heyrovský route to the oxidation of metals and considering both steps irreversible, also concluded that the permutations $k_{+V} \leftrightarrow k_{+H}$ and $\alpha_V \leftrightarrow \alpha_H$ do not alter the dependence $j(\eta)$.

The property pointed out by these reports is very important for its consequence on the correlation of experimental j vs. η data and deserves a more detailed study. Therefore, the present work extends the analysis to the simultaneous occurrence of the three steps of the Volmer-Heyrovský-Tafel mechanism, solved without kinetic approximations for the case of a Langmuir-type adsorption. The relations obtained are applied to the simulation of the dependence of the surface coverage on overpotential from one set of experimental kinetic parameters. Furthermore, the conditions leading to a particular kinetic route are indicated.

Theoretical Analysis

Basic equations.—The hydrogen electrode reaction in alkaline media can be written as



The corresponding elementary steps for the Volmer-Heyrovský-Tafel mechanism are



The kinetics of the hydrogen electrode reaction for the simultaneous occurrence of the Volmer-Heyrovský and the Volmer-Tafel routes in a steady state can be described on terms of the reaction rate of the elementary steps by the following equalities⁶

$$2v = v_V + v_H = 2(v_H + v_T) = 2(v_V - v_T) \quad [3]$$

where v is the overall reaction rate and v_s is the reaction rate of the step s , being positive for the reduction process and negative for the

oxidation one. The rate of the elementary steps, when a Langmuir-type adsorption is considered for the adsorbed hydrogen, in the absence of mass-transfer limitations, can be written as

$$v_V = v_V^e \frac{(1-\theta)}{(1-\theta^e)} \exp[-(1-\alpha_V)f\eta] - v_V^e \frac{\theta}{\theta^e} \exp(\alpha_V f\eta) \quad [4]$$

$$v_H = v_H^e \frac{\theta}{\theta^e} \exp[-(1-\alpha_H)f\eta] - v_H^e \frac{(1-\theta)}{(1-\theta^e)} \exp(\alpha_H f\eta) \quad [5]$$

$$v_T = v_T^e \frac{\theta^2}{\theta^{e2}} - v_T^e \frac{(1-\theta)^2}{(1-\theta^e)^2} \quad [6]$$

where the superscript e indicates equilibrium, $f = F/RT$, and η is negative for reduction and positive for oxidation. The following implicit Eq. $f(\theta, \eta) = 0$ can be obtained from the second or third equality of Eq. 3

$$a\theta^2 + b\theta + c = 0 \quad [7]$$

where

$$a = \frac{2v_T^e(1-2\theta^e)}{\theta^{e2}(1-\theta^e)^2} \quad [7\text{a}]$$

$$b = \frac{4v_T^e}{(1-\theta^e)^2} + \exp(\alpha_V f\eta) \left[\frac{v_V^e \exp(-f\eta) + v_H^e \exp[(\alpha_H - \alpha_V)f\eta]}{(1-\theta^e)} + \frac{v_V^e + v_H^e \exp[-(1-\alpha_H + \alpha_V)f\eta]}{\theta^e} \right] \quad [7\text{b}]$$

$$c = -\frac{2v_T^e}{(1-\theta^e)^2} - \exp(\alpha_V f\eta) \left[\frac{v_V^e \exp(-f\eta) + v_H^e \exp[(\alpha_H - \alpha_V)f\eta]}{(1-\theta^e)} \right] \quad [7\text{c}]$$

Starting from Eq. 7-7c, it can be demonstrated that $\theta(\eta)$ reaches a limiting value (θ^*) for both anodic and cathodic potentials. The expressions of θ^* , according to the relative values of α_V and α_H , for $\eta \gg 0$ (θ_a^*) are

$$\theta_a^* = 1 \quad (\alpha_V < \alpha_H) \quad [8\text{a}]$$

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$$\theta_a^* = \frac{\theta^e v_H^e}{(1 - \theta^e)v_V^e + \theta^e v_H^e} \quad (\alpha_V = \alpha_H) \quad [8b]$$

$$\theta_a^* = 0 \quad (\alpha_V > \alpha_H) \quad [8c]$$

The corresponding expressions for $\eta < 0$ (θ_c^*)

$$\theta_c^* = 0 \quad (\alpha_V < \alpha_H) \quad [9a]$$

$$\theta_c^* = \frac{\theta^e v_V^e}{(1 - \theta^e)v_H^e + \theta^e v_V^e} \quad (\alpha_V = \alpha_H) \quad [9b]$$

$$\theta_c^* = 1 \quad (\alpha_V > \alpha_H) \quad [9c]$$

Furthermore, the dependence $j(\eta)$ can also be obtained from Eq. 3 taking into account that $j = 2Fv$

$$j(\eta) = \frac{2F \exp(\alpha_V f \eta)}{(1 - \theta^e)} \left\{ v_V^e \exp(-f \eta) - v_H^e \exp[(\alpha_H - \alpha_V) f \eta] \right. \\ \left. - \left[v_V^e \exp(-f \eta) - v_H^e \exp[(\alpha_H - \alpha_V) f \eta] \right] \right. \\ \left. + \frac{(1 - \theta^e)}{\theta^e} \left\{ v_V^e - v_H^e \exp[-(1 - \alpha_H + \alpha_V) f \eta] \right\} \theta(\eta) \right\} \quad [10]$$

It should be noticed that Eq. 7a-c and 10, are reduced to those previously derived by the authors by making $\alpha_V = \alpha_H$.⁶

Analysis of the dependence $\theta(\eta)$.—For a given set of kinetic parameters θ^e , v_V^e , v_H^e , and v_T^e , a unique dependence $\theta(\eta)$ is obtained, corresponding to the following solution of Eq. 7

$$\theta(\eta) = \frac{-b + \sqrt{b^2 - 4ac}}{2a} \quad [11]$$

because the second analytic solution corresponding to the minus sign does not verify the condition $0 \leq \theta(\eta) \leq 1$. Under these conditions, the dependence of the surface coverage on overpotential is studied for the following two sets of parameters (S_j)

$$S_1(\theta_1^e, v_{V1}^e, v_{H1}^e, v_{T1}^e, \alpha_{V1}, \alpha_{H1}) \quad [12a]$$

$$S_2(\theta_2^e, v_{V2}^e, v_{H2}^e, v_{T2}^e, \alpha_{V2}, \alpha_{H2}) \quad [12b]$$

The corresponding expressions for a_j , b_j , and c_j ($j = 1, 2$) can be obtained from Eq. 7a-c. Then, considering the following relationships between the parameters of the two sets

$$\theta_2^e = (1 - \theta_1^e) \quad [13a]$$

$$v_{V2}^e = v_{H1}^e \quad [13b]$$

$$v_{H2}^e = v_{V1}^e \quad [13c]$$

$$v_{T2}^e = v_{T1}^e \quad [13d]$$

$$\alpha_{V2} = \alpha_{H1} \quad [13e]$$

$$\alpha_{H2} = \alpha_{V1} \quad [13f]$$

The relationships between the constants are straightforwardly obtained

$$a_2 = -a_1 \quad [14a]$$

$$b_2 = b_1 + 2a_1 \quad [14b]$$

$$c_2 = -(c_1 + b_1 + a_1) \quad [14c]$$

Consequently, if θ_1 is the solution of the equation $a_1 \theta_1^2 + b_1 \theta_1 + c_1 = 0$, it can be verified from Eq. 14a-c that

$$\theta_2(\eta) = 1 - \theta_1(\eta) \quad [15]$$

is the solution of the equation $a_2 \theta_2^2 + b_2 \theta_2 + c_2 = 0$. Therefore, the dependence $\theta(\eta)$ can be transformed into the dependence $[1 - \theta(\eta)]$ by replacing the kinetic parameters θ^e , v_V^e , v_H^e , v_T^e , α_V , and α_H according to Eq. 13a-f. The first consequence of such replacement is related to the behavior of the steady-state pseudocapacitance, which is defined as

$$C_\phi = q_m \left| \frac{d\theta}{d\eta} \right| \quad [16]$$

where q_m is the charge needed to complete one monolayer of adsorbed hydrogen. If $C_{\phi 1}(\eta)$ and $C_{\phi 2}(\eta)$ correspond to the set of kinetic parameters S_1 and S_2 , respectively, then

$$C_{\phi 1}(\eta) = C_{\phi 2}(\eta) \quad [17]$$

Analysis of the dependence j vs. η .—The expressions of the current density can be obtained by replacing the two sets of kinetic parameters given in Eq. 12a and 12b, respectively, in Eq. 10

$$j_1(\eta) = j(\eta, S_1) \quad [18a]$$

$$j_2(\eta) = j(\eta, S_2) \quad [18b]$$

Taking into account Eq. 13a-f and that the dependence of the surface coverage on overpotential for the two sets of parameters verifies Eq. 15, it can be demonstrated from Eq. 18a-b that

$$j_1(\eta) = j_2(\eta) \quad [19]$$

Equation 19 indicates that there are two sets of kinetic parameters that can reproduce a given dependence $j(\eta)$. The relevance of this result can be immediately appreciated if it is intended to determine the kinetic parameters of the hydrogen electrode reaction through a nonlinear regression of the experimental dependence j vs. η . In this case, if a set of kinetic parameters θ_1^e , v_{V1}^e , v_{H1}^e , α_{V1} , and α_{H1} is found, which gives a $j_1(\eta)$ dependence, there is another set of kinetic parameters θ_2^e , v_{V2}^e , v_{H2}^e , α_{V2} , and α_{H2} , related to the first one by Eq. 13a-f, which also fits the experimental dependence.

It can also be inferred from Eq. 19 that the polarization resistance (R_p) is invariant to the permutation of the two sets of the kinetic parameters. This fact can be verified taking into account that R_p for the hydrogen electrode reaction described by the Volmer-Heyrovský-Tafel mechanism is given by⁶

$$R_p = \frac{RT}{4F^2} \left[\frac{4v_T^e + v_H^e + v_V^e}{v_H^e v_V^e + v_T^e v_V^e + v_H^e v_T^e} \right] \quad [20]$$

Considering the two sets of kinetic parameters as in the previous item and taking into account Eq. 13a-f, it can be verified that $R_{p1} = R_{p2}$, a result that derives directly from Eq. 19. Furthermore, the exchange current density for the Volmer-Heyrovský-Tafel mechanism is given by⁶

$$j^o = 2F \frac{v_V^e v_H^e + v_V^e v_T^e + v_H^e v_T^e}{v_V^e + v_H^e + 2v_T^e} \quad [21]$$

and is also invariant to the permutation of the two sets of kinetic parameters.

Another form for expressing the kinetic parameters.—The reaction rates are usually expressed in terms of the kinetic constant $k_{\pm s}$. Their corresponding relationships with the equilibrium reaction rates v_s^e are⁶

$$(1 - \theta^e)k_{+V} = \theta^e k_{-V} = v_V^e \quad [22]$$

$$\theta^e k_{+H} = (1 - \theta^e)k_{-H} = v_H^e \quad [23]$$

$$\theta^e k_{+T} = (1 - \theta^e)k_{-T} = v_T^e \quad [24]$$

Besides, the following equalities are accomplished⁷

$$\frac{k_{+V}k_{+H}}{k_{-V}k_{-H}} = \frac{k_{+H}k_{-T}}{k_{-H}k_{+T}} = \frac{k_{+V}k_{+T}}{k_{-V}k_{-T}} = 1 \quad [25]$$

Table I. Kinetic parameters obtained from Bai⁸ (set S_1) and calculated (set S_2) from Eq. 26a-f.

Parameter (mol cm ⁻² s ⁻¹)	Set S_1	Set S_2
k_{+V}	4.4×10^{-8}	2.4×10^{-9}
k_{-V}	4.4×10^{-7}	2.4×10^{-10}
k_{+H}	2.4×10^{-9}	4.4×10^{-8}
k_{-H}	2.4×10^{-10}	4.4×10^{-7}
k_{+T}	8.8×10^{-8}	8.8×10^{-8}
k_{-T}	8.8×10^{-10}	8.8×10^{-10}
α_V^a	0.5	0.5
α_H^a	0.5	0.5

^a Dimensionless.

Table II. Kinetic parameters calculated from Table I and Eq. 22-24, 8b, and 9b.

Parameter	Set S_1	Set S_2
θ^e	0.0909	0.90909
θ_a^*	5.45×10^{-4}	0.99945
θ_c^*	0.9483	0.0517
v_V^e (mol cm ⁻² s ⁻¹)	4.0×10^{-8}	2.182×10^{-10}
v_H^e (mol cm ⁻² s ⁻¹)	2.182×10^{-10}	4.0×10^{-8}
v_T^e (mol cm ⁻² s ⁻¹)	7.272×10^{-10}	7.272×10^{-10}

Given a set of kinetic parameter $k_{\pm s1}$, a second set $k_{\pm s2}$ can be derived from Eq. 13a-f and Eq. 22-24

$$k_{+V2} = k_{+H1} \quad [26]$$

$$k_{-V2} = k_{-H1} \quad [27]$$

$$k_{+H2} = k_{+V1} \quad [28]$$

$$k_{-H2} = k_{-V1} \quad [29]$$

$$k_{+T2} = k_{-T1} \quad [30]$$

$$k_{-T2} = k_{+T1} \quad [31]$$

Consequently, due to the existence of these two solutions, other experimental procedures or theoretical arguments are necessary in order to elucidate the correct one.

Application to the simulation of experimental data.—In order to illustrate the relationships derived above, the values reported by Bai⁸ for the HER on platinum in 0.5 M NaOH at 296 K were used as the first parameter set (see Table I, set S_1). The alternative forms of the kinetic parameters, used in this work, were evaluated and are shown in Table II (set S_1). The second set of the kinetic parameters obtained applying the corresponding transformation equations (set S_2) is also shown in Table I (Eq. 26a-f) and II (Eq. 13a-f), respectively.

The kinetic parameters given in Table II allowed simulation (from Eq. 7-7c and Eq. 10) of the dependence of the $\ln j$ vs. η for sets S_1 and S_2 in the whole range of overpotentials, which is shown in Fig. 1. The corresponding two dependences of the surface coverage $\theta_1(\eta)$ and $\theta_2(\eta)$ are shown in Fig. 2. They were evaluated from Eq. 7-7c and verify the relationship given in Eq. 15. The experimental evidence^{9,10} would indicate that S_1 is the correct set for this case. If the equilibrium surface coverage lies between $0.3 \leq \theta^e \leq 0.7$, the elucidation of the correct parameter set will need strong experimental or theoretical evidence.

Discussion

The present study demonstrates the existence of two sets of kinetic parameters that fit the same j vs. η dependence of the hydrogen

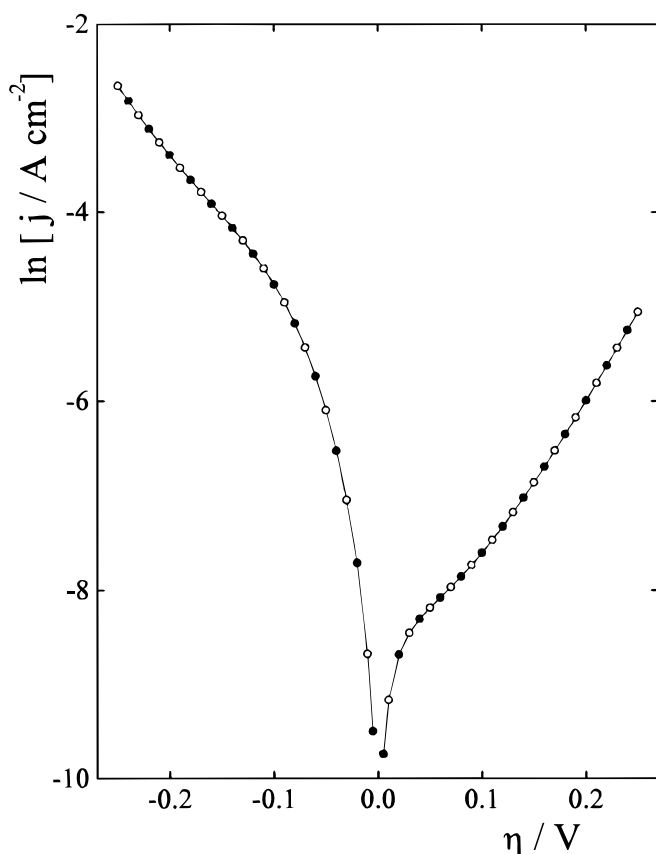


Figure 1. $\ln j$ vs. η dependence for the hydrogen electrode reaction on platinum. Kinetic parameters (Table II): (○) set S_1 ; (●) set S_2 .

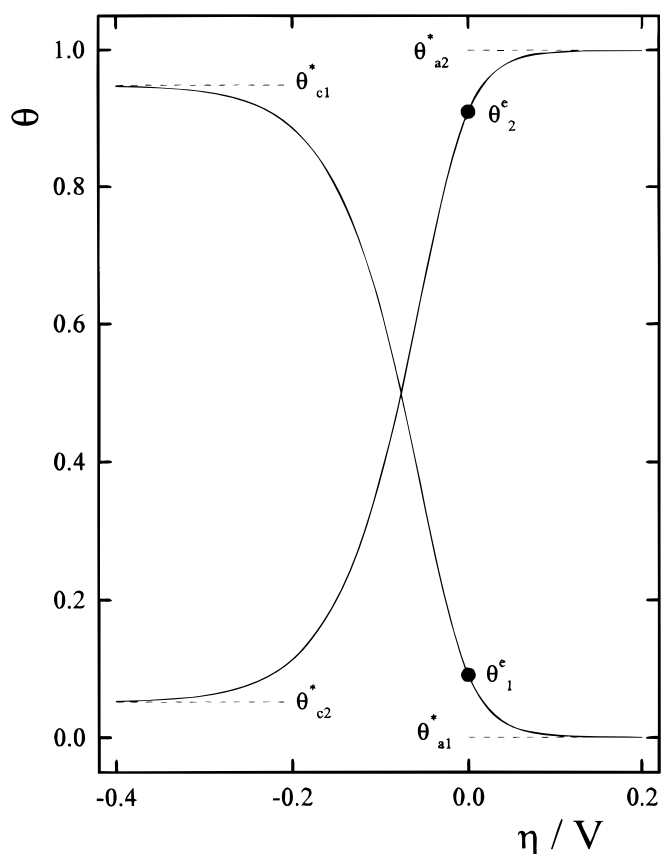


Figure 2. θ vs. η dependences corresponding to the $\ln j$ vs. η dependence shown in Fig. 1.

electrode reaction through the Volmer-Heyrovský-Tafel mechanism and establishes the equations that relate both sets. In this context, it should be interesting to discuss two particular cases, which can be derived from Eq. 13a-f.

1. The equilibrium reaction rate for the Tafel step equal to zero in S_1 . Taking into account Eq. 13d, it follows that in this case both sets of parameters characterize the reaction through the Volmer-Heyrovský route. It can be observed that for $\alpha_V = \alpha_H$, this case is reduced to that originally found by Lasia and Rami.¹

2. The equilibrium reaction rates for the Heyrovský step equal to zero in S_1 . Taking into account Eq. 13b, it follows that in this case set S_1 defines the route of Volmer-Tafel. The dependence $\theta_1(\eta)$ increases with the displacement of the overpotential toward negative values, as is well known.^{8,11} Nevertheless, when set S_2 is analyzed, the same dependence $j(\eta)$ is described by the less known Tafel-Heyrovský route.¹² The dependence of $\theta_2(\eta)$ in this case is opposite that of $\theta_1(\eta)$. This result is important, as it demonstrates that Tafel slopes of $2.3026 RT/2 F V \text{ dec}^{-1}$ are a necessary but not sufficient condition for the diagnostic of the Volmer-Tafel route.¹² On the other hand, if the equilibrium reaction rate for the Volmer step is equal to zero in S_1 , according to Eq. 13c, S_1 defines the Tafel-Heyrovský route, and S_2 the Volmer-Tafel route, respectively.

Finally, the distinction between the two sets of kinetic parameters should be of interest. An alternative that could give some evidence should be the study of the HER on membrane electrodes, where the hydrogen absorption reaction (HAR) takes place. For example, recent results should indicate that, on iron electrodes, only one set of kinetic parameters should be compatible with the HER/HAR.^{13,14}

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