CROATICA CHEMICA ACTA CCACAA **73** (2) 471–484 (2000)

ISSN-0011-1643
CCA-2659
Original Scientific Paper

New Stationary Methods for Studying the Kinetics of Redox Reactions Occurring at Inert Semiconductor/Redox Electrolyte Electrodes.

II. The »$a \cap P$« Method

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Received June 1, 1998; revised October 25, 1999; accepted December 7, 1999

In this second paper an other »intersection« method is theoretically grounded. The method is symbolized »$a \cap P$«, and it is based on the simultaneously changing of both the activity (activities) of one (or more) electrochemical active species (a), and the polarization (P), of the multielectrode: *inert semiconductor / redox electrolyte.* Equations for the *potentiostatic*, respective *galvanostatic* »a∩P« methods have been deduced, and some important kinetic and electroanalytic applications, especially those referring to the *inert metal / redox electrolyte* unielectrodes are given. These methods permit not only to determine the kinetic parameters, but also to separate the total current density $j(U)$ into the two partial current densities $j^{+}(U)$, $j^{-}(U)$, irrespective of the electrode potential U. Finally, the expression resulted for the specific admittance is equivalent to that obtained in the first paper by using the theory of the »$L \cap P$« method; this demonstrates the correctness of both »$L \cap P$«, and »$a \cap P$« theories.

Key words: kinetics of redox reactions, multielectrodes, activities, polarization, inert semiconductor/redox electrolyte

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INTRODUCTION

In this »intersection method«, one modifies simultaneously, the electrode polarization, and the activity of at least one electrochemical active species. Like in the case of the »$L \cap P$« method, we shall use the plane (U, j) for explaining the meaning of this method.

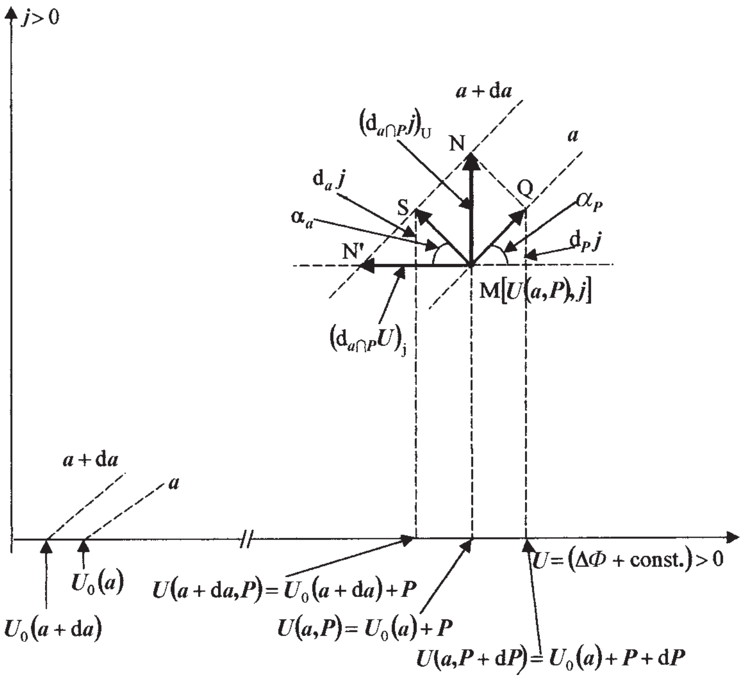

Figure 1. The meaning of the »$a \cap P$« method in the plane (U, j).

The initial state of the system is represented by the point M$[U(a, P), j]$. By a we denote the activity-vector having as components the activities of active species, *e.g.*, in the simplest case $a = (a_{\text{ox}}, a_{\text{red}})$. Like in the first paper, the vicinity of the point M is magnified, and two small parts of the polarization curves (a) and $(a+\mathrm{d}a)$ that may be practically considered as two parallel line segments are shown.

At P = const., when the activity-vector changes from a to $a+\mathrm{d}a$, the point M moves in the point S, and the electric tension U decreases with:

$$\mathrm{d}_a U(a,P) = U(a+\mathrm{d}a,P) - U(a,P) = U_0(a+\mathrm{d}a) - U_0(a) < 0 \tag{1}$$

while the current density increases with:

$$\mathrm{d}_a j = -\mathrm{tg}\ \alpha_a \cdot \mathrm{d}_a U(a,P) > 0. \tag{1'}$$

If we want to maintain the electric tension at its initial value $U(a,P)$, the potentiostat must compensate the decrease $\mathrm{d}_a U(a,P)$ by an increase:

$$\mathrm{d}_P U(a,P) = U(a,P+\mathrm{d}P) - U(a,P) = \mathrm{d}P > 0 \tag{2}$$

to which corresponds a second increase of the current density:

$$\mathrm{d}_P j = \mathrm{tg}\ \alpha_P \cdot \mathrm{d}_P U(a,P) > 0 \tag{2'}$$

and thus a total increase equal to the length of the segment $\overline{\mathrm{MN}}$:

$$(\mathrm{d}_{a\cap P} j)_U = \mathrm{d}_\mathrm{a} j + \mathrm{d}_P j = \overline{\mathrm{MN}}\ . \tag{3}$$

As one sees, although the change of the activity-vector and the action of the potentiostat occur simultaneously, one may consider that they act independently, *i.e.*, although the real movement of the point M is on the segment $\overline{\mathrm{MN}}$, one may consider a decomposed movement, *e.g.*, first on the segment $\overline{\mathrm{MS}}$, and afterwards on the polarization curve (a+da) from S to N. Let's apply this procedure to the case when one wants to maintain the current density at its initial value j. Then the two movements of the point M will be from M to S, and afterwards on the same polarization curve (a+da) from S to N', resulting a decrease of electric tension:

$$(\mathrm{d}_{a\cap P} U)_j = -\,\overline{\mathrm{N'M}} \tag{3'}$$

where the length $\overline{\mathrm{N'M}}$ is positive. By explicitating the lengths $\overline{\mathrm{MN}}$ and $\overline{\mathrm{N'M}}$ will result the equations of the two variants »potentiostatic« and »galvanostatic« of the »a∩P« methods, and this is done in the next paragraph.

THE EQUATIONS OF THE POTENTIOSTATIC AND GALVANOSTATIC »$a\cap P$« METHODS, IN THE CASE OF INERT SEMICONDUCTOR/REDOX ELECTROLYTE ELECTRODES

Consider again an inert semiconductor/redox electrolyte multielectrode, with the reactions:

$$\mathrm{A}_k + n_k\mathrm{e}^- \Leftrightarrow \mathrm{A}_k^{n_k-}\ ;\ k = 1,2,... \tag{4}$$

(the redox couples $\mathrm{A}_k / \mathrm{A}_k^{n_k-}$ being totally independent), and let

$$j = \sum_k (j_{n,k} + j_{p,k}) \tag{5}$$

be the current density; the expression of $j_{n,k}+j_{p,k}$ (the current densities through the two bands) are those given in the first paper,[1] and we just reproduce them

$$j_{n,k} = j^+_{n,k} - j^-_{n,k} = j^{00}_{n,k}\{a_{red,k}\exp[(1-\alpha_{n,k})n_k f(U-U^0_k)] - \\ - a_{ox,k}\exp[-\alpha_{n,k} n_k f(U-U^0_k)]\} \tag{5'}$$

$$j_{p,k} = j^+_{p,k} - j^-_{p,k} = j^{00}_{p,k}\{a_{red,k}\exp[(1-\alpha_{p,k})n_k f(U-U^0_k)] - \\ - a_{ox,k}\exp[-\alpha_{p,k} n_k f(U-U^0_k)]\} \tag{5''}$$

where:

$$f = F/(RT);\ \alpha_{n,k} = 1-(1-\beta_k)\beta^*;\ \alpha_{p,k} = \beta_k\beta^*;\ \mathrm{A}_k = \mathrm{ox},k;\ \mathrm{A}_k^{n_k-} = \mathrm{red},k \tag{5'''}$$

β_k being the symmetry factors of the reactions (4), associated to the energy barrier in the solution, β^* the partition coefficient of the total potential drop $\Delta\Phi$ across the electric double layer (*i.e.*, $\Delta\Phi = \Delta\Phi_{sc} + \Delta\Phi_H$; $\Delta\Phi_H = \beta^*\Delta\Phi$), U^0_k = the Nernst standard potential of reaction k, and $j^{00}_{n,k}, j^{00}_{p,k}$ the standard exchange current densities through the two bands.

By changing the activities, respective the polarization, the current density j will change with $d_a j, d_p j$ respectively, given by:

$$d_a j = \sum_k (d_a j_{n,k} + d_a j_{p,k}) \tag{6}$$

and

$$d_P j = \sum_k (d_P j_{n,k} + d_P j_{p,k}). \tag{6'}$$

But

$$d_a j_{n,k} = \frac{\partial j_{n,k}}{\partial a_{ox,k}} da_{ox,k} + \frac{\partial j_{n,k}}{\partial a_{red,k}} da_{red,k} + \frac{\partial j_{n,k}}{\partial U} d_a U + \frac{\partial j_{n,k}}{\partial \beta^*} d_a \beta^* \tag{7}$$

respective:

$$d_a j_{p,k} = \frac{\partial j_{p,k}}{\partial a_{ox,k}} da_{ox,k} + \frac{\partial j_{p,k}}{\partial a_{red,k}} da_{red,k} + \frac{\partial j_{p,k}}{\partial U} d_a U + \frac{\partial j_{p,k}}{\partial \beta^*} d_a \beta^* . \tag{7'}$$

A few words have to be said about the meaning of Eqs. (7) and (7').

In the expression of $j_{\mathrm{n},k}$ enters (in addition to $a_{\mathrm{ox},k}$, $a_{\mathrm{red},k}$) the electric tension U, which in fact is $U(a,P) = U(a,0)+P$ (see Figure 1) because $U_0(a)$ represents the electric tension when $P = 0$. Of course, $U(a,0) = \Delta\Phi(a,0)$+const depends on the activities of all electrochemical active species participating to the electrode reactions, because $\Delta\Phi_{\mathrm{H}}(a,0)$ is strongly influenced by the values of these activities in the bulk of the solution.

Further, Eqs. (7) and (7') suppose that the potentiostat doesn't act, and thus the change of $U(a,P)$ is determined only by the change of $U(a,0)$, *i.e.*, $\mathrm{d}_a U(a,P) = \mathrm{d}_a U(a,0)$. This is the meaning of $\mathrm{d}_a U$ in Eqs. (7) and (7'), and is obvious that in finding the expression of $\mathrm{d}_a j_{\mathrm{n},k}$ one must take into account not only the activities $a_{\mathrm{ox},k}$, $a_{\mathrm{red},k}$ appearing explicitly, but also the effect of the change of U with $\mathrm{d}_a U = \mathrm{d}_a U(a,0)$.

Of course these considerations apply to all terms $j_{\mathrm{n},k}$, $j_{\mathrm{p},k}$.

If da is very small, one may accept that β^* changes very little, *i.e.*, $\mathrm{d}_a\beta^* \cong 0$, and one may neglect the contributions of the last terms in Eqs. (7) and (7'). Consequently, Eqs. (6), (7) and (7') lead to:

$$\mathrm{d}_a j = \sum_k \left[\left(j^+_{\mathrm{n},k} + j^+_{\mathrm{p},k}\right) \mathrm{d}\ln a_{\mathrm{red},k} - \left(j^-_{\mathrm{n},k} + j^-_{\mathrm{p},k}\right) \mathrm{d}\ln a_{\mathrm{ox},k} \right] +$$
$$f\left[\sum_k n_k \left(j^-_{\mathrm{n},k} + j^+_{\mathrm{p},k}\right)\right] \mathrm{d}_a(\Delta\Phi) - f\left[\sum_k \left[n_k(\beta_k - 1) j_{n,k} + n_k \beta_k j_{\mathrm{p},k}\right]\right] \mathrm{d}_a(\Delta\Phi_{\mathrm{H}}) \qquad (8)$$

where it has been taken into account that:

$$\mathrm{d}_a U = \mathrm{d}_a(\Delta\Phi);\ \beta^* \mathrm{d}_a(\Delta\Phi) = \mathrm{d}_a[\beta^*(\Delta\Phi)] = \mathrm{d}_a(\Delta\Phi_{\mathrm{H}})\ . \qquad (8')$$

By a similar procedure, based on Eq. (6'), where $\mathrm{d}_P j_{\mathrm{n},k} = \dfrac{\partial j_{\mathrm{n},k}}{\partial U} \mathrm{d}_P U$ and $\mathrm{d}_P j_{\mathrm{p},k} = \dfrac{\partial j_{\mathrm{p},k}}{\partial U} \mathrm{d}_P U$ one may get the relation between $\mathrm{d}_P j$ and $\mathrm{d}_P(\Delta\Phi)$:

$$\mathrm{d}_P j = f\left[\sum_k n_k \left(j^-_{\mathrm{n},k} + j^+_{\mathrm{p},k}\right)\right] \mathrm{d}_P(\Delta\Phi) - f\left[\sum_k \left[n_k(\beta_k - 1) j_{n,k} + n_k \beta_k j_{\mathrm{p},k}\right]\right] \mathrm{d}_P(\Delta\Phi_{\mathrm{H}})\ . \qquad (9)$$

Formally, this equation is identically with that derived in the first paper; in fact they are different, because they refer to different polarization curves. As for the expression of $\mathrm{d}_a j$ and $\mathrm{d}_L j$ (first paper), they are essentially different, in expression of $\mathrm{d}_a j$ appearing additional terms. This explains why the »$L\cap P$« and »$a\cap P$« methods must be separately founded.

Further, the *potentiostatic* »$a\cap P$« method is defined by:

$$\mathrm{d}_a(\Delta\Phi) + \mathrm{d}_P(\Delta\Phi) = 0 \qquad \text{(I)}$$

and its equation is:

$$\begin{aligned}(\mathrm{d}_{a\cap P}\,j)_{\Delta\Phi} = &\sum_k\Big[\big(j^{+}_{\mathrm{n},k}+j^{+}_{\mathrm{p},k}\big)\mathrm{d}\ln a_{\mathrm{red},k}-\big(j^{-}_{\mathrm{n},k}+j^{-}_{\mathrm{p},k}\big)\mathrm{d}\ln a_{\mathrm{ox},k}\Big]-\\ &-f\Big[\sum_k\big[n_k(\beta_k-1)j_{n,k}+n_k\beta_k j_{\mathrm{p},k}\big]\Big]\big[\mathrm{d}_{a\cap P}(\Delta\Phi_{\mathrm{H}})\big]_{\Delta\Phi}\end{aligned} \tag{10}$$

while the *galvanostatic* »$a\cap P$« method is defined by:

$$\mathrm{d}_a j + \mathrm{d}_P j = 0 \tag{II}$$

and its equation is:

$$\begin{aligned}&f\Big[\sum_k n_k\big(j^{-}_{\mathrm{n},k}+j^{+}_{\mathrm{p},k}\big)\Big]\big[\mathrm{d}_{a\cap P}(\Delta\Phi)\big]_j =\\ &-\sum_k\Big[\big(j^{+}_{\mathrm{n},k}+j^{+}_{\mathrm{p},k}\big)\mathrm{d}\ln a_{\mathrm{red},k}-\big(j^{-}_{\mathrm{n},k}+j^{-}_{\mathrm{p},k}\big)\mathrm{d}\ln a_{\mathrm{ox},k}\Big]+\\ &+f\Big[\sum_k\big[n_k(\beta_k-1)j_{n,k}+n_k\beta_k j_{\mathrm{p},k}\big]\Big]\big[\mathrm{d}_{a\cap P}(\Delta\Phi_{\mathrm{H}})\big]_j\ .\end{aligned} \tag{11}$$

As one sees, we have maintained in the equation of the potentiostatic »$a\cap P$« method the term containing the factor $\big[\mathrm{d}_{a\cap P}(\Delta\Phi_{\mathrm{H}})\big]_{\Delta\Phi}$. The explanation is simple: this factor is equal to zero if and only if the partition coefficient β^* is *rigorously* constant on both ways $\overline{\mathrm{MS}}$, respective $\overline{\mathrm{MQ}}$ (see Figure 1), *i.e.*, $\beta^*_{\mathrm{M}}=\beta^*_{\mathrm{S}}=\beta^*_{\mathrm{Q}}$. In reality, $\beta^*_{\mathrm{S}}-\beta^*_{\mathrm{M}}$ and $\beta^*_{\mathrm{Q}}-\beta^*_{\mathrm{M}}$ are not rigorously equal to zero, and in addition their values are different. Consequently, if we want to use a *constant* value of the partition coefficient, one must use a mean value β^*_{MS} for the way $\overline{\mathrm{MS}}$, *i.e.*, when one gets the expression $\mathrm{d}_a j$, and an other mean value β^*_{MQ} for the way $\overline{\mathrm{MQ}}$, *i.e.*, when one gets the expression of $\mathrm{d}_P j$. Then, $\mathrm{d}_a(\Delta\Phi_{\mathrm{H}})$ in Eq. (8) will be $\beta^*_{\mathrm{MS}}\,\mathrm{d}_a(\Delta\Phi)$, while $\mathrm{d}_P(\Delta\Phi_{\mathrm{H}})$ in Eq. (9) will be $\beta^*_{\mathrm{MQ}}\,\mathrm{d}_P(\Delta\Phi)$, and consequently, when $\mathrm{d}_a(\Delta\Phi) + \mathrm{d}_P(\Delta\Phi)$ is equal to zero, the sum $\beta^*_{\mathrm{MS}}\,\mathrm{d}_a(\Delta\Phi) + \beta^*_{\mathrm{MQ}}\,\mathrm{d}_P(\Delta\Phi)$ is no more equal to zero. In the first paper, an analysis of the factor $[\mathrm{d}_{L\cap P}(\Delta\Phi_{\mathrm{H}})]_{\Delta\Phi}$, appearing in the equation of the potentiostatic »$L\cap P$« method, has been carried out, showing that excepting the cases $\beta^* = 0$ and $\beta^* = 1$, when $[\mathrm{d}_{L\cap P}(\Delta\Phi_{\mathrm{H}})]_{\Delta\Phi} = 0$, in all other cases $[\mathrm{d}_{L\cap P}(\Delta\Phi_{\mathrm{H}})]_{\Delta\Phi} \neq 0$. All the developments made in that analysis remain valid for $[\mathrm{d}_{a\cap P}(\Delta\Phi_{\mathrm{H}})]_{\Delta\Phi}$, by simply changing in them L by a; consequently, also the above mentioned conclusions hold true, with a difference in the favour of the potentiostatic »$a\cap P$« method, namely, in the particular case of the inert metal/ redox electrolyte electrodes, when $\beta^* = 1$, although $[\mathrm{d}_{a\cap P}(\Delta\Phi_{\mathrm{H}})]_{\Delta\Phi} = 0$, the current density $(\mathrm{d}_{a\cap P}j)_{\Delta\Phi}$ is different of zero, and this fact will be used in the next section to extend the area of the kinetic and electroanalytic applications of the »$a\cap P$« method.

THE EQUATION OF THE POTENTIOSTATIC »$a \cap P$« METHOD IN THE CASE OF INERT METAL/REDOX ELECTROLYTE ELECTRODES

For these electrodes, $\Delta\Phi = \Delta\Phi_{\mathrm{H}}$ and thus $\beta^* = 1$, *i.e.*, the hypothesis $\beta^* =$ const., used in deriving Eq. (10), is now a correct assertion. Therefore, the equation obtained by particularizing Eq. (10) will give a correct equation, namely:

$$(\mathrm{d}_{a \cap P} j)_{\Delta\Phi} = \sum_k \left(j_k^+ \mathrm{d} \ln a_{\mathrm{red},k} - j_k^- \mathrm{d} \ln a_{\mathrm{ox},k} \right) \tag{12}$$

because: $[\mathrm{d}_{a \cap P}(\Delta\Phi_{\mathrm{H}})]_{\Delta\Phi} = [\mathrm{d}_{a \cap P}(\Delta\Phi)]_{\Delta\Phi} = 0$, and $j_{\mathrm{n},k}^+ + j_{\mathrm{p},k}^+ = j_k^+, j_{\mathrm{n},k}^- + j_{\mathrm{p},k}^- = j_k^-$.

Eq. (12) describes the *potentiostatic* »$a \cap P$« method for inert metal/redox electrolyte-multielectrodes. A special interest presents the case of an inert metal/redox electrolyte unielectrode, when Eq. (12) particularizes to:

$$(\mathrm{d}_{a \cap P} j)_{\Delta\Phi} = j^+ \mathrm{d} \ln a_{\mathrm{red}} - j^- \mathrm{d} \ln a_{\mathrm{ox}}. \tag{13}$$

If $a_{\mathrm{ox}} =$ const.:

$$j^+ = \frac{a_{\mathrm{red}}}{\mathrm{d}a_{\mathrm{red}}} \left(d_{a_{\mathrm{red}} \cap P} j \right)_{\Delta\Phi} \tag{13'}$$

and if $a_{\mathrm{red}} =$ const.:

$$j^- = -\frac{a_{\mathrm{ox}}}{\mathrm{d}a_{\mathrm{ox}}} \left(d_{a_{\mathrm{ox}} \cap P} j \right)_{\Delta\Phi}. \tag{13''}$$

It follows:

$$j = j^+ - j^- = \frac{a_{\mathrm{ox}}}{\mathrm{d}a_{\mathrm{ox}}} \left(d_{a_{\mathrm{ox}} \cap P} j \right)_{\Delta\Phi} + \frac{a_{\mathrm{red}}}{\mathrm{d}a_{\mathrm{red}}} \left(d_{a_{\mathrm{red}} \cap P} j \right)_{\Delta\Phi}. \tag{14}$$

Of course, for the equilibrium situation, $j = 0$, and $j^+ = j^- = j^0$ (the exchange current density). Thus

$$j^0 = \frac{a_{\mathrm{red}}}{\mathrm{d}a_{\mathrm{red}}} \left(d_{a_{\mathrm{red}} \cap P} j \right)_{(\Delta\Phi)_{\mathrm{eq.}}} = -\frac{a_{\mathrm{ox}}}{\mathrm{d}a_{\mathrm{ox}}} \left(d_{a_{\mathrm{ox}} \cap P} j \right)_{(\Delta\Phi)_{\mathrm{eq.}}}. \tag{14'}$$

Kinetic Applications

Suppose that for a given $\Delta\Phi$ (*i.e.*, for a given $U = \Delta\Phi +$ const.) one changes only the value of a_{red} with $\mathrm{d}a_{\mathrm{red}}$, maintaining potentiostatically the value $\Delta\Phi$. Then, the current density j will change with $(\mathrm{d}_{a_{\mathrm{red}} \cap P} j)_{\Delta\Phi}$,, a quantity that can be measured, and therefore Eq. (13') will give the value of j^+, corresponding to the electrode potential U. Similarly, changing only the value of

$a_{\rm ox}$, one gets the value of j^- (by means of Eq. (13'')), and further, of $j = j^+ - j^-$. Repeating the procedure for other values of U, one gets the *theoretical* polarization curve $j_{\rm th}(U)$. If the experimental curve $j_{\rm ex}(U)$ is compatibly with $j_{\rm th}(U)$, one may conclude that at the electrode occurs only one reaction $\mathrm{A} + n\mathrm{e}^- \Leftrightarrow \mathrm{A}^{\rm n-}$ (*i.e.,* the electrode is an unielectrode), and secondly, one may divide $j(U)$ in its two parts $j^+(U)$, respective $j^-(U)$, *i.e.*, one may get the two partial polarization curves. These two possibilities demonstrate the *superiority* of the potentiostatic »$a \cap P$« method as compared with all stationary standard methods used to study the redox reaction $\mathrm{A} + n\mathrm{e}^- \Leftrightarrow \mathrm{A}^{n-}$.[2–5] This important conclusion has been also obtained recently, but using an other approach, more limited in generality.[6–9]

Electroanalytic Applications

If one uses equal changes $\mathrm{d}a_{\rm ox} = \mathrm{d}a_{\rm red} = \Delta$, Eq. (14) writes:

$$\frac{1}{\Delta}\left[a_{\rm ox}\left(\mathrm{d}_{a_{\rm ox}\cap P}\, j\right)_U + a_{\rm red}\left(\mathrm{d}_{a_{\rm red}\cap P}\, j\right)_U\right] = j \tag{15}$$

and for the equilibrium situation:

$$a_{\rm ox}\left(\mathrm{d}_{a_{\rm ox}\cap P}\, j\right)_{U_{\rm eq.}} + a_{\rm red}\left(\mathrm{d}_{a_{\rm red}\cap P}\, j\right)_{U_{\rm eq.}} = 0\,. \tag{15'}$$

The system of equations has two unknowns: $a_{\rm ox}$, $a_{\rm red}$. Therefore, the method permits to determine the activities $a_{\rm ox}$, respective $a_{\rm red}$.

THE EQUATION OF THE GALVANOSTATIC »$a \cap P$« METHOD IN THE CASE OF INERT METAL/REDOX ELECTROLYTE ELECTRODES

In this case:

$$\left[\mathrm{d}_{a\cap P}(\Delta\Phi_{\rm H})\right]_j = \left[\mathrm{d}_{a\cap P}(\Delta\Phi)\right]_j \tag{16}$$

and Eq. (11) particularizes to:

$$f\left[\sum_k n_k\left(j_k^+ - \beta_k j_k\right)\right]\left[\mathrm{d}_{a\cap P}(\Delta\Phi)\right]_j = \sum_k \left(j_k^- \mathrm{d}\ln a_{{\rm ox},k} - j_k^+ \mathrm{d}\ln a_{{\rm red},k}\right). \tag{17}$$

Eq. (17) describes the *galvanostatic* »$a \cap P$« method for inert metal/redox electrolyte-multielectrodes.

In the case of unielectrodes:

$$f\left[n\left(j^+ - \beta j\right)\right]\left[\mathrm{d}_{a\cap P}(\Delta\Phi)\right]_j = j^- \mathrm{d}\ln a_{\rm ox} - j^+ \mathrm{d}\ln a_{\rm red} \tag{18}$$

which, applied twice (*i.e.*, for $a = a_{\mathrm{ox}}$, $a = a_{\mathrm{red}}$) leads to:

$$\frac{\left[\mathrm{d}_{a_{\mathrm{ox}}\cap P}(\Delta\Phi)\right]_j}{\left[\mathrm{d}_{a_{\mathrm{red}}\cap P}(\Delta\Phi)\right]_j} = -\frac{j^- a_{\mathrm{red}}}{j^+ a_{\mathrm{ox}}} \tag{19}$$

if one uses equal concentration variations, *i.e.*, $\mathrm{d}a_{\mathrm{ox}} = \mathrm{d}a_{\mathrm{red}} = \Delta$.

Kinetic Applications

Let's apply Eq. (19) for the equilibrium situation (*i.e.*, when $j^- = j^+ = j^0$, and $j = 0$). One gets:

$$\frac{\left[\mathrm{d}_{a_{\mathrm{ox}}\cap P}(\Delta\Phi)\right]_{j=0}}{\left[\mathrm{d}_{a_{\mathrm{red}}\cap P}(\Delta\Phi)\right]_{j=0}} = -\frac{a_{\mathrm{red}}}{a_{\mathrm{ox}}} \; . \tag{20}$$

From the Butler-Volmer equation[10] it follows:

$$j^- / j^+ = \exp(-nf\eta) \tag{21}$$

and thus Eqs. (19)–(21) lead to a very important equation:

$$nf\eta = \ln\frac{\left[\mathrm{d}_{a_{\mathrm{ox}}\cap P}(\Delta\Phi)\right]_{j=0}}{\left[\mathrm{d}_{a_{\mathrm{ox}}\cap P}(\Delta\Phi)\right]_j} + \ln\frac{\left[\mathrm{d}_{a_{\mathrm{red}}\cap P}(\Delta\Phi)\right]_{j=0}}{\left[\mathrm{d}_{a_{\mathrm{red}}\cap P}(\Delta\Phi)\right]_j} \tag{22}$$

which permits to verify if the electrode is an unielectrode with respect to the redox reaction $\mathrm{A} + n\mathrm{e}^- \Leftrightarrow \mathrm{A}^{n-}$. Indeed, the experimental values $\eta_{\mathrm{exp}} = U_{\mathrm{exp}} - U_{\mathrm{eq.}}$ are known, and may be compared with the values given by Eq. (22). If the two sets of values are mutually compatible, the electrode is an unielectrode. In this case,

$$j_{\mathrm{exp}} = j = j^+ - j^- \tag{23}$$

and Eqs. (21)–(23) permit to determine the two partial components $j^+(U)$,$j^-(U)$ of the total current density $j(U)$. Further, by extrapolating $j^+(U)$, or $j^-(U)$ for $U \to U_{\mathrm{eq.}}$, one gets $j^0 = j^+(U_{\mathrm{eq.}}) = j^-(U_{\mathrm{eq.}})$.

Electroanalytic Application

As we have seen, the *potentiostatic* »*a*∩*P*« method, permits to determine a_{ox},a_{red}, by solving the system of equations (15) and (15'). In the case of *galvanostatic* »*a*∩*P*« method, we have only one equation, namely Eq. (20), because Eq. (19), corresponding to the application of the method for $j \neq 0$, is an equation with the same variable: $a_{\mathrm{red}} / a_{\mathrm{ox}}$. Therefore, the electroanalytical performances of the *galvanostatic* »$a \cap P$« method are inferior to those of the *potentiostatic* »$a \cap P$« method. Indeed, the galvanostatic variant necessitates the knowledge of one of the two activities $a_{\mathrm{ox}}, a_{\mathrm{red}}$, in order to determine the other activity.

The best way to demonstrate the importance of the kinetic and electroanalytic potentialities of the »$a \cap P$« method is to show by making a comparison with the corresponding potentialities of the classical polarization experiment, what are the advantages of the »$a \cap P$« methods. It thus results:

1. Both *potentiostatic* and *galvanostatic* »$a \cap P$« methods permit to separate the total current density $j(U)$ into the two partial current densities $j^{+}(U), j^{-}(U)$ irrespective of the value of U. How this separation may be made is shown in the *potentiostatic* variant (Eqs. (13') and (13'')), and in the *galvanostatic* variant (Eqs. (21)–(23)).

1'. The classical polarization experiment doesn't permit such a separation of $j(U)$ into $j^{+}(U)$ and $j^{-}(U)$. This experiment is useful in determining the kinetic parameters j^{0} and β but in doing this one must make the measurements either in the *anodic Tafel region* (when $j \cong j^{+}$), or in the *catodic Tafel region* (when $j \cong -j^{-}$); in-between these Tafel regions, the classical polarization experiment doesn't permit to get experimentally the components $j^{+}(U), j^{-}(U)$.

2. Both *potentiostatic* and *galvanostatic* »$a \cap P$« methods offer a way of testing if the electrode is an unielectrode or a multielectrode, because the functions $j^{+}(U), j^{-}(U)$ once obtained, their difference $j^{+}(U) - j^{-}(U)$ may be compared with the experimental function $j_{\mathrm{exp}}(U)$.

2'. It is obvious that the classical polarization experiment has not such a possibility.

3. Both *potentiostatic* and *galvanostatic* »$a \cap P$« methods permit to determine the exchange current density, by extrapolating either the values, $j^{+}(U)$ or $j^{-}(U)$, for $U \to U_{\mathrm{eq.}}$. In addition, the *potentiostatic* variant permits to determine the value of j^{0} from a single measurement (see Eq. (14')).

3'. The classical polarization method necessitates many measurements, either in the anodic Tafel region, or in the cathodic Tafel region.

4. The *potentiostatic* »$a \cap P$« method permits to determine the activities $a_{\mathrm{ox}}, a_{\mathrm{red}}$ *in* a very simple way, based on the applying of the method at only two electric tensions: the equilibrium tension $U_{\mathrm{eq.}}$, and an arbitrary electric tension U (see Eqs. (15) and (15')).

4'. Of course, the classical polarization method has not such a possibility.

THE SPECIFIC ADMITTANCE OF THE MULTIELECTRODE: INERT SEMICONDUCTOR/REDOX ELECTROLYTE

Consider the polarization curve (a+da) in Figure 1. Then, the specific admittance is given by:

$$A_{sc} = \frac{\overline{\mathrm{MN}}}{\overline{\mathrm{N'M}}} = -\frac{\left[\mathrm{d}_{a\cap P}\, j\right]_{\Delta\Phi}}{\left[\mathrm{d}_{a\cap P}(\Delta\Phi)\right]_{j}} \ . \tag{24}$$

Adding Eqs. (10) and (11), and afterwards dividing both members with $\left[\mathrm{d}_{a\cap P}(\Delta\Phi)\right]_{j}$, one finally gets:

$$A_{\mathrm{sc}} = f\sum_{k} n_k\left(j^{-}_{\mathrm{n},k} + j^{+}_{\mathrm{p},k}\right) -$$

$$f\Big[\sum_{k}\left[n_k(\beta_k - 1)j_{n,k} + n_k\beta_k j_{\mathrm{p},k}\right]\Big]\frac{\left[\mathrm{d}_{a\cap P}(\Delta\Phi_H)\right]_j - \left[\mathrm{d}_{a\cap P}(\Delta\Phi_{\mathrm{H}})\right]_{\Delta\Phi}}{\left[\mathrm{d}_{a\cap P}(\Delta\Phi)\right]_j} \ . \tag{25}$$

The expression is difficult to analyze in the general case, and consequently, we shall analyze only two particular cases.

The Polarization Acts Only upon $\Delta\Phi_{\mathrm{sc}}$ *(i.e.,* $\mathrm{d}_P(\Delta\Phi_{\mathrm{H}}) = 0$)

In the first paper[1] we have shown that in such a situation $\left[\mathrm{d}_{L\cap P}(\Delta\Phi_{\mathrm{H}})\right]_{(\Delta\Phi)}$ = $\left[\mathrm{d}_{L\cap P}(\Delta\Phi_{\mathrm{H}})\right]_{j}$. It is easy to understand that the arguments used, remain valid for the »$a\cap P$« method too, and from Eq. (25) results:

$$A_{\mathrm{sc}} = f\sum_{k} n_k\left(j^{-}_{\mathrm{n},k} + j^{+}_{\mathrm{p},k}\right) \tag{26}$$

which is identically from the point of view formal with the expression obtained in the first paper for the same case, *i.e.*, $\mathrm{d}_P(\Delta\Phi_{\mathrm{H}})$. This is a normal conclusion, because the expression of A_{sc} must not depend on the theory used to deduce it, *i.e.*, the theory of the »$L\cap P$« method, or of the »$a\cap P$« method; of course the value $j^{-}_{\mathrm{n},k}$, $j^{+}_{\mathrm{p},k}$ depend on the fact that the interface is in dark or illuminating conditions.

The Inert Semiconductor is Replaced by an Inert Metal

Then:

$$\left[\mathrm{d}_{a\cap P}(\Delta\Phi_{\mathrm{H}})\right]_{\Delta\Phi} = \left[\mathrm{d}_{a\cap P}(\Delta\Phi)\right]_{\Delta\Phi} = 0 \tag{27}$$

and

$$\left[\mathrm{d}_{a\cap P}(\Delta\Phi_{\mathrm{H}})\right]_j = \left[\mathrm{d}_{a\cap P}(\Delta\Phi)\right]_j \ . \tag{27'}$$

Introducing in Eq. (25):

$$A_{\mathrm{met}} = f\sum_k n_k\left[(1-\beta_k)j_k + j_k^-\right] \tag{28}$$

which, again, formally is identically with the expression obtained in the first paper by using the theory of the »$L\cap P$« method.

Finally, let's observe that Eq. (24) applies also when only a_{ox}, or only a_{red}, is changed. It then results the following invariant:

$$\left[\mathrm{d}_{a_{\mathrm{ox}}\cap P}\, j)\right]_{\Delta\Phi}\left[\mathrm{d}_{a_{\mathrm{red}}\cap P}(\Delta\Phi)\right]_j = \left[\mathrm{d}_{a_{\mathrm{red}}\cap P}\, j\right]_{\Delta\Phi}\left[\mathrm{d}_{a_{\mathrm{ox}}\cap P}(\Delta\Phi)\right]_j \tag{29}$$

which expresses the relation between the responds, in current, respective tension, of the potentiostatic (galvanostatic) »$a\cap P$« methods.

CONCLUSIONS

The »$a\cap P$« intersection method theoretically developed in this paper is superior to the »$L\cap P$« intersection method developed in the first paper, because it may be applied to study both the inert semiconductor/redox electrolyte, respective inert metal/redox electrolyte, multielectrodes.

The equations obtained for the two very important cases, namely the potentiostatic, respective galvanostatic »$a\cap P$« methods, are important not only by themselves, but also by their important kinetic and electroanalytic applications, especially those referring to the inert metal/redox electrolyte unielectrodes. Indeed, both *potentiostatic* and *galvanostatic* methods, are superior to all standard stationary method used to study the electrode redox reaction, because they permit not only to determine the kinetic parameters (j^{00} and β), but also to separate the total current density $j(U)$ into the two partial current densities $j^+(U), j^-(U)$, irrespective of the value of U. This possibility offers a way of testing if the electrode is an unielectrode or a multielectrode, because the functions $j^+(U), j^-(U)$, once obtained, their difference $j^+(U) - j^-(U)$ may be compared with the experimental function $j(U)$.

Finally, using the equations of the potentiostatic and the galvanostatic »$a\cap P$« methods, the expression of the specific admittance of the multielectrode inert semiconductor/redox electrolyte has been obtained; by particularizing it for the inert metal/redox electrolyte case, respective inert semiconductor/redox electrolyte multielectrodes for which $\Delta_P(\Delta\Phi_{\mathrm{H}}) = 0$, have resulted, formally, the same expressions as those obtained in the first paper (*i.e.*, by using the theory of the »$L \cap P$« method). Of course, this demonstrates that both the »$L \cap P$«, and »$a \cap P$« theories are correct.

It is very important to understand that, the »$L \cap P$«, respective »$a \cap P$« theories, are principially different, and for this reason they must be separately grounded. Indeed, by illuminating a semiconductor one acts upon the Fermi level *(cvasi Fermi levels)* of the semiconductor, while by changing the activities of the electrochemical active species in the bulk of solution one acts upon the Fermi level of the redox electrolyte. Thus in the »$L \cap P$«, respective »$a \cap P$« methods, one acts upon the solid , respective liquid parts of the electrode, and the potentiostat may control these actions.

REFERENCES

1. N. Bonciocat, S. Borca, L. Oniciu, and I. O. Marian, *Croat. Chem. Acta* **73** (2000) 451–469.
2. A. J. Bard and L. R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, Wiley & Sons, New York, 1980, pp. 100–110.
3. I. M. Kolthoff and J. J. Lingane, *Polarography*, 2nd ed., Interscience, New York, 1952, Vol. 1, Chap. 7.
4. W. Vielstich, *Z. Electrochem.* **57** (1953) 646–655.
5. N. Ibl, *Chemie-Ingeneur-Technik* **35** (1963) 353–356.
6. N. Bonciocat, M. Borda, S. Borca, R. Ivanov, C. Mihailciuc, and S. Moldovan, *Proceedings of the 37th Meeting of the ISE*, Vilnius, USSR, August 1986, Vol. 3, pp. 487–510.
7. N. Bonciocat, M. Borda, S. Borca, R. Ivanov, and C. Mihailciuc, *Proceedings of the 2nd Symposium of the Applied Electrochemistry*, Timisoara, 4–5 October 1985, pp. 67–75.
8. N. Bonciocat, M. Borda, S. Borca, R. Ivanov, C. Mihailciuc, and S. Moldovan, *Proceedings of the 2nd Symposium of the Applied Electrochemistry*, Timisoara, 4–5 October 1985, pp. 76–84.
9. N. Bonciocat, *Electrochimie si aplicatii*, Ed. Europa Dacia Nova, Timisoara, 1996, pp. 222–225.
10. L. Oniciu, P. Ilea, and I. C. Popescu, *Electrochimie Tehnologica*, Casa cartii de stiinta, Cluj-Napoca, 1995, sect. 2.1.5.

SAŽETAK

Nove stacionarne metode istraživanja kinetike redoks-reakcija na inertnim poluvodičkim elektrodama.
II. Metoda »$a \cap P$«

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Postavljeni su teorijski temelji druge metode presjeka obilježene simbolom »$a \cap P$«. Metoda se zasniva na istovremenim promjenama aktiviteta jednog ili više elektroaktivnih reaktanata otopljenih u elektrolitu (a) i polarizacije inertne poluvodičke multielektrode (P). Dane su jednadžbe potenciostatske i galvanostatske varijante metode »$a \cap P$« i prikazana je njihova kinetička i elektroanalitička primjena. Posebno je obrađen slučaj inertne metalne elektrode homogene površine. Opisne metode omogućuju određivanje kinetičkih parametara redoks-reakcije i razdvajanje ukupne gustoće struje $j(U)$ na redukcijsku i oksidacijsku komponentu $j^{-}(U)$ i $j^{+}(U)$ pri bilo kojem potencijalu elektrode, U. Konačno, izveden je izraz za specifičnu admitanciju elektrode koji je identičan izrazu izvedenom u prvom članku. Time je dokazana ispravnost teorija metoda »$L \cap P$« i »$a \cap P$«.