

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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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* » $a \cap P$ « 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.

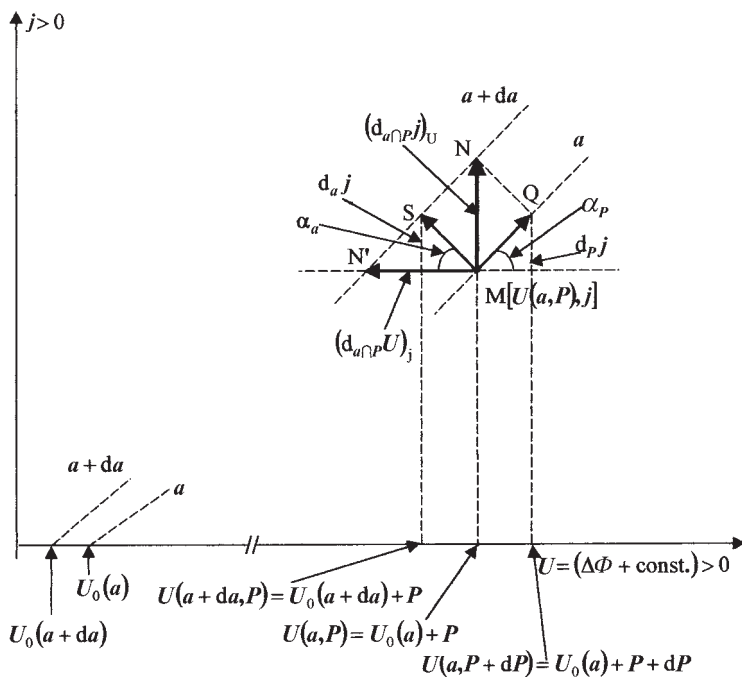


Figure 1. The meaning of the » $a \cap P$ « method in the plane (U, j) .

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 $a = (\alpha_{ox}, \alpha_{red})$. Like in the first paper, the vicinity of the point M is magnified, and two small parts of the polarization curves (α) and $(\alpha + da)$ that may be practically considered as two parallel line segments are shown.

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

$$d_a U(a, P) = U(a + da, P) - U(a, P) = U_0(a + da) - U_0(a) < 0 \quad (1)$$

while the current density increases with:

$$d_a j = -\operatorname{tg} \alpha_a \cdot d_a U(a, P) > 0. \quad (1')$$

If we want to maintain the electric tension at its initial value $U(a, P)$, the potentiostat must compensate the decrease $d_a U(a, P)$ by an increase:

$$d_P U(a, P) = U(a, P+dP) - U(a, P) = dP > 0 \quad (2)$$

to which corresponds a second increase of the current density:

$$d_P j = \operatorname{tg} \alpha_P \cdot d_P U(a, P) > 0 \quad (2')$$

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

$$(d_{a\cap P} j)_U = d_a j + d_P j = \overline{MN}. \quad (3)$$

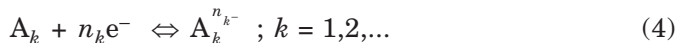
As one sees, although the change of the activity-vector and the action of the potentiostat occur simultaneously, one may consider that they act independently, *i.e.*, although the real movement of the point M is on the segment \overline{MN} , one may consider a decomposed movement, *e.g.*, first on the segment \overline{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:

$$(d_{a\cap P} U)_j = -\overline{N'M} \quad (3')$$

where the length $\overline{N'M}$ is positive. By explicating the lengths \overline{MN} and $\overline{N'M}$ 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∩P« METHODS, IN THE CASE OF INERT SEMICONDUCTOR/REDOX ELECTROLYTE ELECTRODES

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



(the redox couples $A_k / A_k^{n_k^-}$ being totally independent), and let

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

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

$$j_{n,k} = j_{n,k}^+ - j_{n,k}^- = j_{n,k}^{00} \left\{ \alpha_{\text{red},k} \exp[(1 - \alpha_{n,k}) n_k f(U - U_k^0)] - \alpha_{\text{ox},k} \exp[-\alpha_{n,k} n_k f(U - U_k^0)] \right\} \quad (5')$$

$$j_{p,k} = j_{p,k}^+ - j_{p,k}^- = j_{p,k}^{00} \left\{ \alpha_{\text{red},k} \exp[(1 - \alpha_{p,k}) n_k f(U - U_k^0)] - \alpha_{\text{ox},k} \exp[-\alpha_{p,k} n_k f(U - U_k^0)] \right\} \quad (5'')$$

where:

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

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., $\Delta\Phi = \Delta\Phi_{\text{sc}} + \Delta\Phi_{\text{H}}$; $\Delta\Phi_{\text{H}} = \beta^* \Delta\Phi$), $U_k^0 =$ the Nernst standard potential of reaction k , and $j_{n,k}^{00}, j_{p,k}^{00}$ 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:

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

and

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

But

$$d_a j_{n,k} = \frac{\partial j_{n,k}}{\partial \alpha_{\text{ox},k}} d\alpha_{\text{ox},k} + \frac{\partial j_{n,k}}{\partial \alpha_{\text{red},k}} d\alpha_{\text{red},k} + \frac{\partial j_{n,k}}{\partial U} d_a U + \frac{\partial j_{n,k}}{\partial \beta^*} d_a \beta^* \quad (7)$$

respective:

$$d_a j_{p,k} = \frac{\partial j_{p,k}}{\partial \alpha_{\text{ox},k}} d\alpha_{\text{ox},k} + \frac{\partial j_{p,k}}{\partial \alpha_{\text{red},k}} d\alpha_{\text{red},k} + \frac{\partial j_{p,k}}{\partial U} d_a U + \frac{\partial j_{p,k}}{\partial \beta^*} d_a \beta^* \quad (7')$$

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

In the expression of $j_{n,k}$ enters (in addition to $a_{ox,k}$, $a_{red,k}$) 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, $U(a,0) = \Delta\Phi(a,0) + \text{const}$ depends on the activities of all electrochemical active species participating to the electrode reactions, because $\Delta\Phi_H(a,0)$ 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., $d_a U(a,P) = d_a U(a,0)$. This is the meaning of $d_a U$ in Eqs. (7) and (7'), and is obvious that in finding the expression of $d_a j_{n,k}$ one must take into account not only the activities $a_{ox,k}$, $a_{red,k}$ appearing explicitly, but also the effect of the change of U with $d_a U = d_a U(a,0)$.

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

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

$$d_a j = \sum_k [(j_{n,k}^+ + j_{p,k}^+) d \ln a_{red,k} - (j_{n,k}^- + j_{p,k}^-) d \ln a_{ox,k}] + f \left[\sum_k n_k (j_{n,k}^- + j_{p,k}^+) \right] d_a (\Delta\Phi) - f \left[\sum_k [n_k (\beta_k - 1) j_{n,k} + n_k \beta_k j_{p,k}] \right] d_a (\Delta\Phi_H) \quad (8)$$

where it has been taken into account that:

$$d_a U = d_a (\Delta\Phi); \beta^* d_a (\Delta\Phi) = d_a [\beta^* (\Delta\Phi)] = d_a (\Delta\Phi_H). \quad (8')$$

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

$$d_P j = f \left[\sum_k n_k (j_{n,k}^- + j_{p,k}^+) \right] d_P (\Delta\Phi) - f \left[\sum_k [n_k (\beta_k - 1) j_{n,k} + n_k \beta_k j_{p,k}] \right] d_P (\Delta\Phi_H). \quad (9)$$

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 $d_a j$ and $d_L j$ (first paper), they are essentially different, in expression of $d_a j$ appearing additional terms. This explains why the »L∩P« and »a∩P« methods must be separately founded.

Further, the *potentiostatic* »a∩P« method is defined by:

$$d_a (\Delta\Phi) + d_P (\Delta\Phi) = 0 \quad (I)$$

and its equation is:

$$\begin{aligned} (d_{a \cap P} j)_{\Delta \Phi} = & \sum_k [(j_{n,k}^+ + j_{p,k}^+) d \ln a_{\text{red},k} - (j_{n,k}^- + j_{p,k}^-) d \ln a_{\text{ox},k}] - \\ & - f \left[\sum_k [n_k (\beta_k - 1) j_{n,k} + n_k \beta_k j_{p,k}] \right] [d_{a \cap P} (\Delta \Phi_H)]_{\Delta \Phi} \end{aligned} \quad (10)$$

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

$$d_a j + d_P j = 0 \quad (II)$$

and its equation is:

$$\begin{aligned} f \left[\sum_k n_k (j_{n,k}^- + j_{p,k}^+) \right] [d_{a \cap P} (\Delta \Phi)]_j = \\ - \sum_k [(j_{n,k}^+ + j_{p,k}^+) d \ln a_{\text{red},k} - (j_{n,k}^- + j_{p,k}^-) d \ln a_{\text{ox},k}] + \\ + f \left[\sum_k [n_k (\beta_k - 1) j_{n,k} + n_k \beta_k j_{p,k}] \right] [d_{a \cap P} (\Delta \Phi_H)]_j . \end{aligned} \quad (11)$$

As one sees, we have maintained in the equation of the potentiostatic » $a \cap P$ « method the term containing the factor $[d_{a \cap P} (\Delta \Phi_H)]_{\Delta \Phi}$. The explanation is simple: this factor is equal to zero if and only if the partition coefficient β^* is *rigorously* constant on both ways $\overline{\text{MS}}$, respective $\overline{\text{MQ}}$ (see Figure 1), *i.e.*, $\beta_{\text{M}}^* = \beta_{\text{S}}^* = \beta_{\text{Q}}^*$. In reality, $\beta_{\text{S}}^* - \beta_{\text{M}}^*$ and $\beta_{\text{Q}}^* - \beta_{\text{M}}^*$ 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 $\overline{\text{MS}}$, *i.e.*, when one gets the expression $d_a j$, and an other mean value β_{MQ}^* for the way $\overline{\text{MQ}}$, *i.e.*, when one gets the expression of $d_P j$. Then, $d_a (\Delta \Phi_H)$ in Eq. (8) will be $\beta_{\text{MS}}^* d_a (\Delta \Phi)$, while $d_P (\Delta \Phi_H)$ in Eq. (9) will be $\beta_{\text{MQ}}^* d_P (\Delta \Phi)$, and consequently, when $d_a (\Delta \Phi) + d_P (\Delta \Phi)$ is equal to zero, the sum $\beta_{\text{MS}}^* d_a (\Delta \Phi) + \beta_{\text{MQ}}^* d_P (\Delta \Phi)$ is no more equal to zero. In the first paper, an analysis of the factor $[d_{L \cap P} (\Delta \Phi_H)]_{\Delta \Phi}$, 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 $[d_{L \cap P} (\Delta \Phi_H)]_{\Delta \Phi} = 0$, in all other cases $[d_{L \cap P} (\Delta \Phi_H)]_{\Delta \Phi} \neq 0$. All the developments made in that analysis remain valid for $[d_{a \cap P} (\Delta \Phi_H)]_{\Delta \Phi}$, 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 $[d_{a \cap P} (\Delta \Phi_H)]_{\Delta \Phi} = 0$, the current density $(d_{a \cap P} j)_{\Delta \Phi}$ 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∩P« METHOD IN THE CASE OF INERT METAL/REDOX ELECTROLYTE ELECTRODES

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

$$(d_{a\cap P}j)_{\Delta\Phi} = \sum_k (j_k^+ d \ln a_{\text{red},k} - j_k^- d \ln a_{\text{ox},k}) \quad (12)$$

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

Eq. (12) describes the *potentiostatic* »a∩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:

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

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

$$j^+ = \frac{a_{\text{red}}}{da_{\text{red}}} (d_{a_{\text{red}}\cap P}j)_{\Delta\Phi} \quad (13')$$

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

$$j^- = -\frac{a_{\text{ox}}}{da_{\text{ox}}} (d_{a_{\text{ox}}\cap P}j)_{\Delta\Phi}. \quad (13'')$$

It follows:

$$j = j^+ - j^- = \frac{a_{\text{ox}}}{da_{\text{ox}}} (d_{a_{\text{ox}}\cap P}j)_{\Delta\Phi} + \frac{a_{\text{red}}}{da_{\text{red}}} (d_{a_{\text{red}}\cap P}j)_{\Delta\Phi}. \quad (14)$$

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

$$j^0 = \frac{a_{\text{red}}}{da_{\text{red}}} (d_{a_{\text{red}}\cap P}j)_{(\Delta\Phi)_{\text{eq}}} = -\frac{a_{\text{ox}}}{da_{\text{ox}}} (d_{a_{\text{ox}}\cap P}j)_{(\Delta\Phi)_{\text{eq}}}. \quad (14')$$

Kinetic Applications

Suppose that for a given $\Delta\Phi$ (*i.e.*, for a given $U = \Delta\Phi + \text{const.}$) one changes only the value of a_{red} with da_{red} , maintaining potentiostatically the value $\Delta\Phi$. Then, the current density j will change with $(d_{a_{\text{red}}\cap P}j)_{\Delta\Phi}$, 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_{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 $j_{\text{th}}(U)$. If the experimental curve $j_{\text{ex}}(U)$ is compatibly with $j_{\text{th}}(U)$, one may conclude that at the electrode occurs only one reaction $A + ne^- \leftrightarrow A^{n-}$ (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 $A + ne^- \leftrightarrow A^{n-}$.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 $da_{\text{ox}} = da_{\text{red}} = \Delta$, Eq. (14) writes:

$$\frac{1}{\Delta} [a_{\text{ox}} (d_{a_{\text{ox}} \cap P} j)_U + a_{\text{red}} (d_{a_{\text{red}} \cap P} j)_U] = j \quad (15)$$

and for the equilibrium situation:

$$a_{\text{ox}} (d_{a_{\text{ox}} \cap P} j)_{U_{\text{eq}}} + a_{\text{red}} (d_{a_{\text{red}} \cap P} j)_{U_{\text{eq}}} = 0. \quad (15')$$

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

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

In this case:

$$[d_{a \cap P}(\Delta \Phi_H)]_j = [d_{a \cap P}(\Delta \Phi)]_j \quad (16)$$

and Eq. (11) particularizes to:

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

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

In the case of unielectrodes:

$$f[n(j^+ - \beta j)] [d_{a \cap P}(\Delta \Phi)]_j = j^- d \ln a_{\text{ox}} - j^+ d \ln a_{\text{red}} \quad (18)$$

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

$$\frac{[d_{a_{\text{ox}} \cap P}(\Delta\Phi)]_j}{[d_{a_{\text{red}} \cap P}(\Delta\Phi)]_j} = -\frac{j^- a_{\text{red}}}{j^+ a_{\text{ox}}} \quad (19)$$

if one uses equal concentration variations, *i.e.*, $da_{\text{ox}} = da_{\text{red}} = \Delta$.

Kinetic Applications

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

$$\frac{[d_{a_{\text{ox}} \cap P}(\Delta\Phi)]_{j=0}}{[d_{a_{\text{red}} \cap P}(\Delta\Phi)]_{j=0}} = -\frac{a_{\text{red}}}{a_{\text{ox}}} \quad (20)$$

From the Butler-Volmer equation¹⁰ it follows:

$$j^- / j^+ = \exp(-nf\eta) \quad (21)$$

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

$$nf\eta = \ln \frac{[d_{a_{\text{ox}} \cap P}(\Delta\Phi)]_{j=0}}{[d_{a_{\text{ox}} \cap P}(\Delta\Phi)]_j} + \ln \frac{[d_{a_{\text{red}} \cap P}(\Delta\Phi)]_{j=0}}{[d_{a_{\text{red}} \cap P}(\Delta\Phi)]_j} \quad (22)$$

which permits to verify if the electrode is an unielektrode with respect to the redox reaction $A + ne^- \leftrightarrow A^{n-}$. Indeed, the experimental values $\eta_{\text{exp}} = U_{\text{exp}} - U_{\text{eq}}$ 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 unielektrode. In this case,

$$j_{\text{exp}} = j = j^+ - j^- \quad (23)$$

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 $U \rightarrow U_{\text{eq}}$, one gets $j^0 = j^+(U_{\text{eq}}) = j^-(U_{\text{eq}})$.

Electroanalytic Application

As we have seen, the *potentiostatic* »a∩P« method, permits to determine $a_{\text{ox}}, a_{\text{red}}$, 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), be-

cause Eq. (19), corresponding to the application of the method for $j \neq 0$, is an equation with the same variable: $a_{\text{red}} / a_{\text{ox}}$. 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 $a_{\text{ox}}, a_{\text{red}}$, in order to determine the other activity.

The best way to demonstrate the importance of the kinetic and electroanalytical 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 *cathodic 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 unielektrode or a multielektrode, because the functions $j^+(U), j^-(U)$ once obtained, their difference $j^+(U) - j^-(U)$ may be compared with the experimental function $j_{\text{exp}}(U)$.

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 $U \rightarrow U_{\text{eq}}$. 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 $a_{\text{ox}}, a_{\text{red}}$ in a very simple way, based on the applying of the method at only two electric tensions: the equilibrium tension U_{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:

$$A_{sc} = \frac{\overline{MN}}{\overline{N^1M}} = - \frac{[d_{a\cap P} j]_{\Delta\Phi}}{[d_{a\cap P}(\Delta\Phi)]_j} . \quad (24)$$

Adding Eqs. (10) and (11), and afterwards dividing both members with $[d_{a\cap P}(\Delta\Phi)]_j$, one finally gets:

$$A_{sc} = f \sum_k n_k (j_{n,k}^- + j_{p,k}^+) - f \left[\sum_k [n_k (\beta_k - 1) j_{n,k} + n_k \beta_k j_{p,k}] \right] \frac{[d_{a\cap P}(\Delta\Phi_H)]_j - [d_{a\cap P}(\Delta\Phi_H)]_{\Delta\Phi}}{[d_{a\cap P}(\Delta\Phi)]_j} . \quad (25)$$

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

The Polarization Acts Only upon $\Delta\Phi_{sc}$ (i.e., $d_P(\Delta\Phi_H) = 0$)

In the first paper¹ we have shown that in such a situation $[d_{L\cap P}(\Delta\Phi_H)]_{(\Delta\Phi)} = [d_{L\cap P}(\Delta\Phi_H)]_j$. It is easy to understand that the arguments used, remain valid for the »a∩P« method too, and from Eq. (25) results:

$$A_{sc} = f \sum_k n_k (j_{n,k}^- + j_{p,k}^+) \quad (26)$$

which is identically from the point of view formal with the expression obtained in the first paper for the same case, i.e., $d_P(\Delta\Phi_H)$. 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∩P« method, or of the »a∩P« method; of course the value $j_{n,k}^-$, $j_{p,k}^+$ depend on the fact that the interface is in dark or illuminating conditions.

The Inert Semiconductor is Replaced by an Inert Metal

Then:

$$[d_{a\cap P}(\Delta\Phi_H)]_{\Delta\Phi} = [d_{a\cap P}(\Delta\Phi)]_{\Delta\Phi} = 0 \quad (27)$$

and

$$[d_{a \cap P}(\Delta\Phi_H)]_j = [d_{a \cap P}(\Delta\Phi)]_j . \quad (27')$$

Introducing in Eq. (25):

$$A_{\text{met}} = f \sum_k n_k [(1 - \beta_k) j_k + j_k^-] \quad (28)$$

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:

$$[d_{a_{\text{ox}} \cap P} j]_{\Delta\Phi} [d_{a_{\text{red}} \cap P}(\Delta\Phi)]_j = [d_{a_{\text{red}} \cap P} j]_{\Delta\Phi} [d_{a_{\text{ox}} \cap P}(\Delta\Phi)]_j \quad (29)$$

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 unielec-trodes. 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^0 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 unielec-trode or a multi-electrode, 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 multielec-trode inert semiconductor/redox electrolyte has been obtained; by particu-

larizing it for the inert metal/redox electrolyte case, respective inert semiconductor/redox electrolyte multielectrodes for which $\Delta_P(\Delta\Phi_H) = 0$, 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 principally 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.

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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 » $a \cap P$ «.