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New Stationary Methods for Studying the Kinetics of Redox Reactions Occurring at Inert Semiconductor/Redox Electrolyte Electrodes.
III. The »$L \cap a$« Method

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In this paper a third "intersection method" symbolized »$L \cap a$« is theoretically grounded. The method applies to multielectrodes: inert semiconductors/redox electrolyte, and is based on the simultaneously changing of both the intensity of illumination (L), and the activity (activities) of one (or more) electrochemical active species (a). A first result refers to the possibility of decomposing the »$L \cap a$« method in the two intersection methods, »$L \cap P$« and »$a \cap P$«, that have been grounded in the first two papers. This result has permitted to use the equations deduced for the »$L \cap P$« and »$a \cap P$« methods in the first two papers, in order to obtain the equations of potentiostatic, respective galvanostatic »$L \cap a$« methods. Further, these equations have been used to get the expression of the specific admittance of the multielectrode. On the basis of this expression, new methods have been grounded for studying the kinetics of electrode redox reactions occurring at inert semiconductor (inert metal)/redox electrolyte electrodes, the semiconductor operating only by one of its energetic bands. Finally, the decomposing law has been generalized to "intersection methods" in which operates an arbitrary number of factors.

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INTRODUCTION

As it has been shown in the first paper[1], in the case of a multielectrode: inert semiconductor/redox electrolyte, the current density depends on three factors: the activities of the electrochemical active species, taking part in the redox reactions:

$$\mathrm{A}_k + n_k\mathrm{e} \Leftrightarrow \mathrm{A}_k^{n_k-} \qquad (1)$$

the illumination intensity and the polarization of the multielectrode, quantities that have been symbolized by a,L and P. In the first paper, a new stationary method for studying such redox multielectrodes has been grounded, based on the simultaneously changing of the illumination and polarization; this method has been called an "intersection method", and it has been symbolized by »$L\cap P$«. In the second paper[2], an other stationary "intersection method", namely »$a\cap P$«, in which the activities and the polarization are simultaneously changed, has been grounded. It remains to develop a third "intersection method", based on the simultaneously changing of L and a. Of course, this »$L\cap a$« method may be made in *potentiostatic*, or *galvanostatic* conditions, and equations for these two particular cases are deduced. Finally, an equation expressing the relation between these three methods has been also obtained; based on this equation one arrives to a better understanding of the meanings of these intersection methods.

THE EQUATIONS OF THE POTENTIOSTATIC, RESPECTIVE GALVANOSTATIC »$L\cap a$« METHODS

Because in the first two papers we have deeply explained the meanings of the »$L\cap P$«, respective »$a\cap P$« methods in the plane (U, j) we shall pass more quickly now in giving the interpretation of the »$L\cap a$« method (see Figure 1).

In the figure is shown a magnified view of the vicinity of the point M(U,j). The polarization curves in the interior of this vicinity are practically linear and parallel. To make a choose, let's suppose that the polarization curves (L + dL,a), (L + dL,a + da) are on the same side with respect to the polarization curve (L,a). Consider first the *potentiostatic* »$L\cap a$« method. The changing of L to L + dL implies a simultaneously changing of P to P + $(\mathrm{d}P)_1$ in order to maintain U unchanged. The effects of these two simultaneous changes are represented by the segments $\overline{\mathrm{MS}}$ and $\overline{\mathrm{MQ}}$, and the resultant of

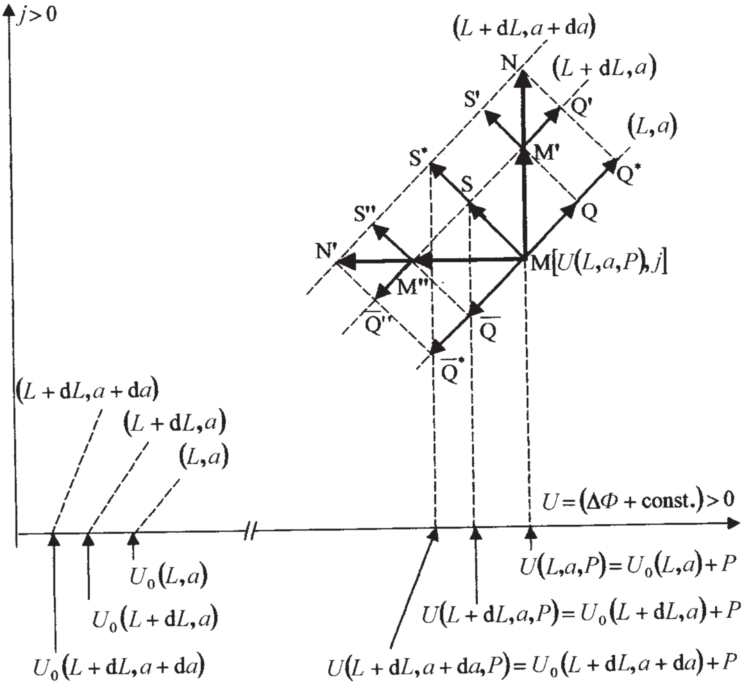

Figure 1. The interpretation of the potentiostatic and galvanostatic »$L\cap a$« methods in the plane (U,j), $\overline{\mathrm{MN}} = (\mathrm{d}_{L\cap a}j)_U$, $\overline{\mathrm{MN'}} = (\mathrm{d}_{L\cap a}U)_j$.

these effects moves the point M in M'. The length of the segment $\overline{\mathrm{MM'}}$ gives the variation of the current density j as a consequence of changing the illumination intensity with dL, in potentiostatic conditions. Therefore, $\overline{\mathrm{MM'}} = (\mathrm{d}_{L\cap P}j)_U$. But there is also a simultaneous variation of a with da, which has to be compensated by an other variation $(\mathrm{d}P)_2$ of the polarization. The segment $\overline{\mathrm{M'S'}}$ illustrates the effect of da, and the segment $\overline{\mathrm{M'Q'}}$ illustrates how this effect is compensated by a simultaneous polarization effect in order to maintain the value of U. The length of the segment $\overline{\mathrm{M'N}}$ gives the variation of j as a consequence of changing the activity with da, under an illumination L + dL, and in potentiostatic conditions. Therefore $\overline{\mathrm{M'N}} = (\mathrm{d}_{a\cap P}j)_U$.

Of course, dL, da and dP act simultaneously, and not in consecutive steps as it is shown in Figure 1. This decomposition in two consecutive steps, a »$L\cap P$« step, followed by an »$a\cap P$« step, supposes that for dL, da, dP sufficiently small (when MSM'Q and M'S'NQ' may be considered as parallelograms), one may accept that these variations act independently, *i.e.*, that they have independent effects. Therefore, because $\overline{\mathrm{MN}} = (\mathrm{d}_{L\cap a}j)_U$, one may write:

$$(\mathrm{d}_{L\cap a}j)_U = (\mathrm{d}_{L\cap P}j)_U + (\mathrm{d}_{a\cap P}j)_U \,. \tag{2}$$

Similarly, for the *galvanostatic* »$L\cap a$« method, in the first step, the segments $\overline{\mathrm{MS}}$ and $\overline{\mathrm{M}\overline{\mathrm{Q}}}$ represent the effect of dL and of a first polarization change (dP)$_1$, and their simultaneous actions move the point M in M'': further, in the second step, the simultaneous effects of da and of a second polarization change (dP)$_2$ (represented by the segments $\overline{\mathrm{M''S''}}$ and $\overline{\mathrm{M''}\overline{\mathrm{Q}}''}$) move the point M'' in N'. Therefore, one may write:

$$(\mathrm{d}_{L\cap a}U)_j = (\mathrm{d}_{L\cap P}U)_j + (\mathrm{d}_{a\cap P}U)_j \,. \tag{3}$$

From the same figure results that $\overline{\mathrm{MN}}$ may also be judged as the resultant of $\overline{\mathrm{MS}^*}$ (illustrating the effects of both dL and da) and $\overline{\mathrm{MQ}^*}$ (illustrating the effect of the total polarization dP = (dP)$_1$ + (dP)$_2$). A similar interpretation may be given to $\overline{\mathrm{MN'}}$, he only difference consisting in the fact that the total effect of the polarization action is now illustrated by the segment $\overline{\mathrm{M}\overline{\mathrm{Q}}^*}$.

Further, we must observe that in the case of the »$L\cap a$« method we have three polarization curves. Taking into account that the »$L\cap a$« method may be decomposed in a »$L\cap P$« method, followed by an »$a\cap P$« method, one sees that the first component implies the passage from the polarization curve (L,a) to the polarization curve (L + dL,a), and consequently the equations deduced in the first paper for the potentiostatic (galvanostatic) »$L\cap P$« methods remain valid. Indeed, in the »$L\cap P$« method the activity-vector a remaining constant it was not indicated, and therefore the passage (L) → (L + dL) is in fact the passage (L,a) → (L + dL,a). As for the second component »$a\cap P$«, it implies the passage from an other initial curve (*i.e.*, (L + dL,a) instead of (L,a)) to the polarization curve (L + dL,a + da), *i.e.*, a change of the activity-vector, but at an other constant value of the illumination (L + dL instead of L). For this reason, the quantities appearing in the equations deduced in the second paper must be replaced by $\Delta\Phi + \mathrm{d}_L(\Delta\Phi)$, $\Delta\Phi_\mathrm{H} + \mathrm{d}_L(\Delta\Phi_\mathrm{H})$, $j + \mathrm{d}_L j$, $j_{\mathrm{n},k} + \mathrm{d}_L j_{\mathrm{n},k}$, $j_{\mathrm{p},k} + \mathrm{d}_L j_{\mathrm{p},k}$ *etc.* But in doing this, appear infinitesimal quantities of superior orders which may be neglected, and consequently one may use also the equations deduced in the second paper for the potentiostatic and galvanostatic »$a\cap P$« methods.

Using the equations of $(\mathrm{d}_{L\cap P}j)_{\Delta\Phi}$ (first paper) and $(\mathrm{d}_{a\cap P}j)_{\Delta\Phi}$ (second paper), it results from Eq. (2):

$$(\mathrm{d}_{L\cap a}j)_{\Delta\Phi} = -f\Big\{\sum_k\big[(\beta_k-1)n_k j_{\mathrm{n},k} + \beta_k n_k j_{\mathrm{p},k}\big]\Big\}\big[\mathrm{d}_{L\cap P}(\Delta\Phi_\mathrm{H}) + \mathrm{d}_{a\cap P}(\Delta\Phi_\mathrm{H})\big]_{\Delta\Phi} + \\ + \sum_k\big\{(j^+_{\mathrm{n},k} + j^+_{\mathrm{p},k})\,\mathrm{d}\ln a_{\mathrm{red},k} - (j^-_{\mathrm{n},k} + j^-_{\mathrm{p},k})\,\mathrm{d}\ln a_{\mathrm{ox},k}\big\}. \tag{4}$$

Similarly, using the equations of $(\mathrm{d}_{L\cap P}\Delta\Phi)_j$ (first paper) and $(\mathrm{d}_{a\cap P}\Delta\Phi)_j$ (second paper), it results from Eq. (3):

$$\begin{aligned} & f\Big\{\sum_k n_k (j^-_{\mathrm{n},k} + j^+_{\mathrm{p},k})\Big\}\left[\mathrm{d}_{L\cap a}(\Delta\Phi)\right]_j = \\ & = f\Big\{\sum_k \left[(\beta_k - 1) n_k j_{\mathrm{n},k} + \beta_k n_k j_{\mathrm{p},k}\right]\Big\}\left[\mathrm{d}_{L\cap P}(\Delta\Phi_\mathrm{H}) + \mathrm{d}_{a\cap P}(\Delta\Phi_\mathrm{H})\right]_j + \\ & + \sum_k \Big\{(j^-_{\mathrm{n},k} + j^-_{\mathrm{p},k})\,\mathrm{d}\ln a_{\mathrm{ox},k} - (j^+_{\mathrm{n},k} + j^+_{\mathrm{p},k})\,\mathrm{d}\ln a_{\mathrm{red},k}\Big\}. \end{aligned} \tag{5}$$

ADDITION LAWS RELATING THE »$L\cap a$« METHOD TO ITS COMPONENTS: THE »$L\cap P$« and »$a\cap P$« METHODS

Eqs. (2) and (3) refer to a »$L\cap a$« method, and express the addition laws for the variation of the current density j in *potentiostatic* conditions, respective for the variation of the total potential difference $\Delta\Phi = \Delta\Phi_\mathrm{sc} + \Delta\Phi_\mathrm{H}$ in *galvanostatic* conditions.

If one uses the expressions of $\mathrm{d}_L j$ (obtained in the first paper) and $\mathrm{d}_a j$ (obtained in the second paper) one may get the expressions of $(\mathrm{d}_{L\cap a} j)_{\Delta\Phi}$ (by imposing the condition $\mathrm{d}_L(\Delta\Phi) + \mathrm{d}_a(\Delta\Phi) = 0$), respective of $\lfloor \mathrm{d}_{L\cap a}(\Delta\Phi)\rfloor_j$ (by imposing the condition $\mathrm{d}_L j + \mathrm{d}_a j = 0$). Here, we only mention that the expressions which result are identical to the expressions (4) and (5) if and only if:

$$\lfloor \mathrm{d}_{L\cap a}(\Delta\Phi_\mathrm{H})\rfloor_{\Delta\Phi} = \lfloor \mathrm{d}_{L\cap P}(\Delta\Phi_\mathrm{H})\rfloor_{\Delta\Phi} + \lfloor \mathrm{d}_{a\cap P}(\Delta\Phi_\mathrm{H})\rfloor_{\Delta\Phi} \tag{6}$$

and

$$\lfloor \mathrm{d}_{L\cap a}(\Delta\Phi_\mathrm{H})\rfloor_j = \lfloor \mathrm{d}_{L\cap P}(\Delta\Phi_\mathrm{H})\rfloor_j + \lfloor \mathrm{d}_{a\cap P}(\Delta\Phi_\mathrm{H})\rfloor_j\ . \tag{7}$$

Let's observe that the addition law (6) applies also to the total potential difference, but each term is equal to zero:

$$\lfloor \mathrm{d}_{L\cap a}(\Delta\Phi)\rfloor_{\Delta\Phi} = \lfloor \mathrm{d}_{L\cap P}(\Delta\Phi)\rfloor_{\Delta\Phi} + \lfloor \mathrm{d}_{a\cap P}(\Delta\Phi)\rfloor_{\Delta\Phi}\ . \tag{8}$$

By subtracting Eq. (6) from Eq. (8), one gets:

$$\lfloor \mathrm{d}_{L\cap a}(\Delta\Phi_\mathrm{sc})\rfloor_{\Delta\Phi} = \lfloor \mathrm{d}_{L\cap P}(\Delta\Phi_\mathrm{sc})\rfloor_{\Delta\Phi} + \lfloor \mathrm{d}_{a\cap P}(\Delta\Phi_\mathrm{sc})\rfloor_{\Delta\Phi} \tag{9}$$

and by subtracting Eq. (7) from Eq. (3):

$$\lfloor \mathrm{d}_{L\cap a}(\Delta\Phi_\mathrm{sc})\rfloor_j = \lfloor \mathrm{d}_{L\cap P}(\Delta\Phi_\mathrm{sc})\rfloor_j + \lfloor \mathrm{d}_{a\cap P}(\Delta\Phi_\mathrm{sc})\rfloor_j\ . \tag{10}$$

Summarizing, from the addition laws (2) and (3) result the addition laws (6) and (7), respective (9) and (10), for the two components $\Delta\Phi_\mathrm{H}$, $\Delta\Phi_\mathrm{sc}$ of the total electric tension $\Delta\Phi = \Delta\Phi_\mathrm{H} + \Delta\Phi_\mathrm{sc}$. One may conclude: the additon law $\mathrm{d}_{L\cap a}(\ ) = \mathrm{d}_{L\cap P}(\ ) + \mathrm{d}_{a\cap P}(\ )$, applies to the total electric tension $\Delta\Phi$, as well as to each of its two components $\Delta\Phi_{sc}$, $\Delta\Phi_{H}$, and this conclusion refers to both *potentiostatic* and *galvanostatic* conditions. As for the addition laws referring to the current density, they are valid too. Indeed, Eq. (2) refers to the *potentiostatic* conditions, and the addition law for the *galvanostatic* conditions is also valid *i.e.*,

$$(\mathrm{d}_{L\cap a}j)_j = (\mathrm{d}_{L\cap P}j)_j + (\mathrm{d}_{a\cap P}j)_j \tag{11}$$

because each term is equal to zero.

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

Coming back to Figure 1, and taking into account that the three polarization curves are practically parallel (in a vicinity of M), one sees that the admittance may be expressed either using the polarization curve (L + dL,a + + da), or the polarization curve (L + dL,a). Thus:

$$A_{\mathrm{sc}} = \frac{\overline{\mathrm{MN}}}{\overline{\mathrm{N'M}}} = \frac{\overline{\mathrm{MM'}}}{\overline{\mathrm{M''M}}} = -\frac{(d_{L\cap a}j)_{\Delta\Phi}}{[d_{L\cap a}(\Delta\Phi)]_j} = -\frac{(d_{L\cap P}j)_{\Delta\Phi}}{[d_{L\cap P}(\Delta\Phi)]_j}\ . \tag{12}$$

Further, because of the relations (2) and (3) it results also:

$$A_{\mathrm{sc}} = -\frac{(d_{a\cap P}j)_{\Delta\Phi}}{[d_{a\cap P}(\Delta\Phi)]_j}\ . \tag{12'}$$

The last expression (12), and the expression (12') have been used in the first two papers to express the specific admittance. It follows that the first expression (12), in which the two terms of the ratio are given by Eqs. (4) and (5), must lead to the expressions obtained in the first papers, for the specific admittance. This time, these expressions must be really identically because the »$L\cap P$« and »$a\cap P$« methods (in which the »$L\cap a$« method decomposes) refer to the same initial polarization curve (L,a); the analysis of the »$a\cap P$« method has been made in the second paper, but independent of the intensity of the illumination, which may be even equal to zero. To verify this conclusion, let's start with the metal/electrolyte case; then $\Delta\Phi_{H} = \Delta\Phi$, $j^{-}_{\mathrm{n},k} + j^{-}_{\mathrm{p},k} = j^{-}_{k}$, $j^{+}_{\mathrm{n},k} + j^{+}_{\mathrm{n},k} = j^{+}_{k}$, $j^{+}_{k} - j^{-}_{k} = j_{k}$, and performing the mathematical operations, it results:

$$A_{\mathrm{metal}} = f\sum_{k} n_k\left[(1-\beta_k)j_k + j^{-}_{k}\right]. \tag{13}$$

As for the second particular case, *i.e.*, when the polarization acts only on the component $\Delta\Phi_{sc}$, one must use the equations established in the first two papers, *i.e.*, $\lfloor \mathrm{d}_{L\cap P}(\Delta\Phi_{\mathrm{H}})\rfloor_{\Delta\Phi} = \lfloor \mathrm{d}_{L\cap P}(\Delta\Phi_{\mathrm{H}})\rfloor_{j}$, respective $\lfloor \mathrm{d}_{a\cap P}(\Delta\Phi_{\mathrm{H}})\rfloor_{\Delta\Phi} = \lfloor \mathrm{d}_{a\cap P}(\Delta\Phi_{\mathrm{H}})\rfloor_{j}$. By adding these equations, one gets $\lfloor \mathrm{d}_{L\cap a}(\Delta\Phi_{\mathrm{H}})\rfloor_{\Delta\Phi} = \lfloor \mathrm{d}_{L\cap a}(\Delta\Phi_{\mathrm{H}})\rfloor_{j}$, and after some trivial operations it results:

$$A_{\mathrm{sc}} = f\sum_{k} n_k (j^{-}_{\mathrm{n},k} + j^{+}_{\mathrm{p},k}). \tag{14}$$

THE »$L\cap a$« METHOD IN THE CASE OF AN UNIELECTRODE: INERT SEMICONDUCTOR / REDOX ELECTROLYTE

We shall consider only three particular cases.

The semiconductor operates only by its conduction band, and the polarization acts only on $\Delta\Phi_{sc}$.

In this case, $j_{\mathrm{p}} = 0$, and $j_{\mathrm{n}} = j$. From Eq. (14) one gets:

$$fnj^{-} = A_{\mathrm{sc}}\ . \tag{15}$$

The semiconductor operates only by its valence band, and the polarization acts only on $\Delta\Phi_{sc}$.

Now $j_{\mathrm{n}} = 0$, and $j_{\mathrm{p}} = j$. Consequently, Eq. (14) gives:

$$fnj^{+} = A_{\mathrm{sc}}\ . \tag{16}$$

Inert metal / redox electrolyte unielectrode.

Eq. (13) leads to:

$$A_{\mathrm{metal}} = fn\left[(1-\beta)j + j^{-}\right]. \tag{17}$$

Further, let's show how Eqs. (15)–(17) may be used in kinetic studies. Consider Eq. (15). The specific admittance may be obtained experimentally for each value j, by differentiating the experimental curve $j = j(U)$:

$$A_{\mathrm{sc}} = \left|\frac{\mathrm{d}j}{\mathrm{d}U}\right| \tag{18}$$

and, because $j = j^{+} - j^{-}$, it follows:

$$\frac{1}{j}\left|\frac{\mathrm{d}j}{\mathrm{d}U}\right| = -fn + fnj^{+}\frac{1}{j}\ . \tag{19}$$

A plot of $(1/j)\ |\mathrm{d}j/\mathrm{d}U|$ *vs.* $1/j$ will determine the product fn from the intercept, and, further, j^{+} from the slope. Once the partial curve $j^{+}(U)$ obtained, the other partial curve results as $j^{-}(U) = j^{+}(U) - j(U)$. If the linear regression analysis gives a significant correlation coefficient, one may conclude that, indeed, the semiconductor operates only by its conduction band, and the polarization acts only on $\Delta\Phi_{sc}$.

Similarly, in the case of Eq. (16) it results:

$$\frac{1}{j}\left|\frac{\mathrm{d}j}{\mathrm{d}U}\right| = fn + fnj^{-}\,\frac{1}{j} \tag{20}$$

and the linear regression analysis will decide if the semiconductor operates by its valence band, and the polarization acts only on $\Delta\Phi_{sc}$. If the answer is affirmative, by performing the experimental data, one gets an estimate of the product fn, and again a decomposition of $j(U)$ in its components $j^{+}(U)$, and $j^{-}(U)$.

In the case of Eq. (17), the equation of the regression line is:

$$\frac{1}{j}\left|\frac{\mathrm{d}j}{\mathrm{d}U}\right| = fn(1-\beta) + fnj^{-}\,\frac{1}{j} \tag{21}$$

and the regression analysis will give the products $fn(1-\beta)$ and fnj^{-}. In the cathodic Tafel domain $j \to -j^{-}$ and $(1/j)\,|\mathrm{d}j/\mathrm{d}U|$ tends to $-fn\beta$. In this way it is possible to get fn, β and j^{-}. Further, it results the two partial curves $j^{+}(U)$ and $j^{-}(U)$.

The three above methods, developed on the basis of Eqs. (15)–(21) represent new stationary methods for determining the kinetic parameters too. Indeed, suffice to observe that the exchange current density is given by $j^{0} = j^{+}(U_{eq}) = j^{-}(U_{eq})$. However, it must be underlined that, like other methods developed in our preceding papers,[3–6] these methods are important because they permit to get $j^{+}(U)$, $j^{-}(U)$, irrespective of the value U. Finally, let's particularize the expressions (15)–(21) of the admittances in the three particular cases analyzed for the equilibrium situation. Then, in equation (17), $j = 0$ and $j^{-} = j^{0}$. The expression of the exchange current density becomes: $j^{0} = (1/fn)A_{met,eq} = 1/(fnR_{ct,eq})$, where $R_{ct,eq}$ represents the specific charge transfer resistance at the equilibrium situation, expression that is identically with those given in the literature.[7,8] As for Eqs. (15) and (16), they lead to $j_{n}^{0} = 1/(fnR_{ct,eq})$, respective $j_{p}^{0} = 1/(fnR_{ct,eq})$, which again coincides to that given in the literature.[9,10]

GENERALIZATION OF THE ADDITION LAW $\mathrm{d}_{L\cap a}(\ ) = \mathrm{d}_{L\cap P}(\ ) + \mathrm{d}_{a\cap P}(\ )$

An »intersection method« supposes at least two electrochemical active factors that influence simultaneously the electric characteristics of the electrode (*i.e.*, $\Delta\Phi$, $\Delta\Phi_{H}$, $\Delta\Phi_{sc}$ and j). Let's denote these factors by C_i, because they act as electrochemical active *causes* that determine the values of the electric characteristics of the electrode. What Eqs. (2), (3) and (6)–(11) show, is the fact that the polarization P of the electrode is *a special cause* in developing »intersection methods«. Indeed, consider many electrochemical active causes $C_i \neq P$, and the intersection method »$C_1 \cap C_2 \cap \ldots = \underset{i}{\cap} C_i$«. Then, this method satisfies the addition laws:

$$\left[\mathrm{d}_{\underset{i}{\cap} C_i}(\xi)\right]_{\Delta\Phi} = [\mathrm{d}_{C_1\cap P}(\xi)]_{\Delta\Phi} + [\mathrm{d}_{C_2\cap P}(\xi)]_{\Delta\Phi} + \ldots = \sum_i [\mathrm{d}_{C_i\cap P}(\xi)]_{\Delta\Phi} \tag{22}$$

respective:

$$\left[\mathrm{d}_{\underset{i}{\cap} C_i}(\xi)\right]_j = [\mathrm{d}_{C_1\cap P}(\xi)]_j + [\mathrm{d}_{C_2\cap P}(\xi)]_j + \ldots = \sum_i [\mathrm{d}_{C_i\cap P}(\xi)]_j \tag{22'}$$

where:

$$\xi \in \{\Delta\Phi_{\mathrm{sc}},\ \Delta\Phi_{\mathrm{H}},\ \Delta\Phi,\ j\}\ . \tag{22''}$$

Therefore, an intersection method »$\underset{i}{\cap} C_i$« decomposes in the same number of intersection methods as the number of causes C_i, in each intersection method appearing two causes: the polarization P, coupled successively with one of the causes C_i.

CONCLUSIONS

By using the plane (U, j) to explain the meaning of the stationary »$L\cap a$« method, it has been shown that *there is an addition law* which permits to decompose the »$L\cap a$« method in two intersection methods, namely »$L\cap P$« and »$a\cap P$«.

This conclusion has permitted to use the equations deduced in the first two papers for the »$L\cap P$«, respective »$a\cap P$« methods, and thus to obtain the equations of *potentiostatic*, respective *galvanostatic* »$L\cap a$« methods.

Further, these equations have served to obtain the expression of the specific admittance of the electrode, and by particularizing this expression for the cases of semiconductors operating only by one of the two energetic bands, respective for the case of metal/electrolyte electrodes, it was possible to develop new methods for studying the kinetics of electrode redox reactions. These methods permit not only to determine the kinetics parameters, but also to decompose the experimental curve $j(U)$ in its two components $j^+(U)$, respective $j^-(U)$, and just because of this possibility they are superior to the standard stationary methods.

Finally, a very important conclusion has been obtained by generalizing the addition law to »intersection methods« in which operates an arbitrary number of factors.

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SAŽETAK

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

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Opisuje se teorija metode presjeka nazvane »$L \cap a$« jer se sastoji od istovremene promjene intenziteta osvjetljenja površine inertne poluvodičke multielektrode (L) i aktiviteta jedne ili više elektroaktivnih otopljenih ionskih ili molekulskih vrsta (a). Najprije je pokazano da se metoda »$L \cap a$« može smatrati jednostavnom sumom metoda »$L \cap P$« i »$a \cap P$« koje su opisane u prethodnim člancima. To omogućuje primjenu ranije izvedenih jednadžbi na opis potenciostatske i galvanostatske inačice metode »$L \cap a$« i specifične admitancije multielektrode. Na osnovi ovih razmatranja predloženi su novi postupci istraživanja kinetike redoks-reakcija na inertnoj metalnoj elektrodi i inertnoj poluvodičkoj elektrodi s jednim djelatnim energijskim pojasom. Konačno, razvijena je opća teorija metode višestrukog presjeka s istovremenom promjenom po volji velikog broja varijabli.