

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

I. The » $L \cap P$ « Method

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In this first paper, a new method has been theoretically grounded, for studying the kinetics of redox reactions occurring simultaneously at multielectrodes of the type *inert semiconductor/redox electrolyte*, representing Schottky barriers. The method is based on the simultaneously changing of both the intensity of the illumination (L), and the polarization (P), of the multielectrode; for this reason, the method has been called an »intersection method«, and symbolized by » $L \cap P$ «. A kinetic model has been developed to account for the effects of these dL and dP variations, in open and closed circuit conditions, and on its basis, the equations of the *potentiostatic* and *galvanostatic* » $L \cap P$ « methods have been obtained. Further, an expression of the specific admittance has resulted, and some particular cases are given, including that of an inert metal/redox electrolyte multielectrode.

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

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INTRODUCTION

In the case of a semiconductor/electrolyte electrode, the current density is a function of: the electrode potential U^* (with respect to a reference electrode),¹ the illumination (L) of the interface, and the activities a of the electrochemical active species. Consequently, one may elaborate experimental methods based on the recording of the electric response of the electrode to *simultaneously* imposed variations of at least two of the above mentioned variables. To symbolize such methods we shall use the symbol » \cap « (from the theory of sets) and we shall call them »intersection methods«.

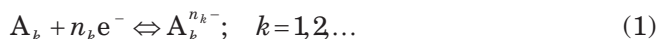
In this paper we analyze the intersection methods » $L\cap P$ « in which the two variables acting simultaneously are: the illumination L and the polarization P (*i.e.* the change of U) of the electrode.

Among the » $L\cap P$ « methods, two present a special interest, because of their theoretical and practical implications. These methods are: the *potentiostatic* » $L\cap P$ « method, in which the potential of the electrode is kept constant, and the *galvanostatic* » $L\cap P$ « method, in which the current density passing through the electrode is kept constant.

OPEN CIRCUIT CONDITIONS

The Effect of Changing the Intensity of Illumination

Let's assume that several redox reactions occur simultaneously at an inert semiconductor/redox electrolyte multielectrode:



and let $U_m(L)$ be its mixed potential at a certain illumination of the interface; because we are not interested in the intensity of this initial illumination, we simply denote it by L . We also suppose that the redox couples $A_k / A_k^{n_k^-}$ are totally independent. Further, let's change the illumination from L to $L + dL$, but keeping the mixed potential at its initial value $U_m(L)$, by using an adequate potentiostatic equipment. Then, the potentiostatic equipment compensates the change of the mixed potential due to the change of the illumination:

$$U_m(L + dL) - U_m(L) = d_L U_m \quad (2)$$

* $U = \Delta\Phi_{sc} + \Delta\Phi_H + \Delta\Phi_G + a$ constant (its value depending on the reference electrode).

by polarizing the multielectrode from the value $U_m(L + dL)$, back to the initial value $U_m(L)$. We shall denote this polarizing effect by $d_p U_m$, and the relation between the two effects is:

$$d_p U_m = - d_L U_m . \quad (2')$$

On the other hand, considering concentrated solutions (when the potential drop on the Gouy layer is zero), one has:

$$d_L U_m = d_L(\Delta\Phi_H) + d_L(\Delta\Phi_{sc}) \quad (3)$$

where $\Delta\Phi_H$, $\Delta\Phi_{sc}$ are the potential drops corresponding to the Helmholtz layer and the semiconductor, respectively.

Consider the current density j_k due to one of the reactions (1). It represents the sum of four terms:

$$j_k = j_{a,c,k} + j_{c,c,k} + j_{a,v,k} + j_{c,v,k} . \quad (4)$$

the first two expressing the contributions of the conduction band, the last two of the valence band. For the sake of simplicity we shall use the notations:

$$j_{n,k} = j_{a,c,k} + j_{c,c,k} ; j_{p,k} = j_{a,v,k} + j_{c,v,k} . \quad (4')$$

To simplify the theoretical treatment we shall assume that the reactions (1) occur only with charge transfer limitations, there are no surface states of the semiconductor, and the effect of adsorption processes of some species from the solution may be neglected. As we know^{2,3} in the case of the metal/electrolyte unielectrode, the current density has the expression:

$$j = j^{00} \{ a_{red} \exp[(1 - \beta)nf(U - U^0)] - a_{ox} \exp[-\beta nf(U - U^0)] \} \quad (5)$$

where j^{00} represents the standard density of the exchange current, a_{red} , a_{ox} , the activities of the species A^{n-} , A respectively, β the symmetry factor corresponding to the energy barrier in the solution, U^0 the Nernst standard electrode potential, U the actual electrode potential, and $f = F/(RT)$.

In the case of the semiconductor/electrolyte multielectrode the expressions of the current densities through the two bands are:⁴⁻⁶

$$j_{n,k} = j_{n,k}^{00} \{ a_{red,k} \exp[(1 - \alpha_{n,k}) n_k f(U_m - U_k^0)] - a_{ox,k} \exp[-\alpha_{n,k} n_k f(U_m - U_k^0)] \} \quad (6)$$

respective:

$$j_{p,k} = j_{p,k}^{00} \{ a_{\text{red},k} \exp[(1 - \alpha_{p,k}) n_k f(U_m - U_k^0)] - \alpha_{\text{ox},k} \exp[-\alpha_{p,k} n_k f(U_m - U_k^0)] \} \quad (6')$$

where:

$$\alpha_{n,k} = 1 - (1 - \beta_k)\beta^*; \quad \alpha_{p,k} = \beta_k\beta^* \quad (6'')$$

β^* denotes the partition coefficient of the total potential drop across the electric double layer (*i.e.*, $(\Delta\Phi)_m = \Delta\Phi_H + \Delta\Phi_{\text{sc}}$, because we consider concentrated solutions, for which the Gouy layer disappears) in the two components:

$$\Delta\Phi_H = \beta^*(\Delta\Phi)_m; \quad \Delta\Phi_{\text{sc}} = (1 - \beta^*)(\Delta\Phi)_m \quad (6''')$$

(of course, $(\Delta\Phi)_m$ is related to the mixed potential U_m by the relation $U_m = (\Delta\Phi)_m + \text{const.}$, the constant depending on the reference electrode used).

Eqs. (6)–(6''') take into account the fact that all reactions (1) occur at the same potential, namely $U_m = (\Delta\Phi)_m + \text{const.}$; as for β_k , they represent the symmetry factors of the reactions (1), associated to the energy barrier in solution.

It is easy to see, that for a metal/electrolyte unielectrode, when $\beta^* = 1$, Eqs. (6)–(6''') particularize in Eq. (5), because:

$$\alpha_{n,k} = \alpha_{p,k} = \beta, \text{ and } j_{n,k}^{00} + j_{p,k}^{00} = j^{00}. \quad (7)$$

In the following we shall refer to semiconductor/electrolyte interfaces representing Schottky barriers. For this reason we recall some of the properties of these barriers which are necessary for understanding our further developments.

The redox systems can be characterized by their potentials compared to that of the normal hydrogen electrode, considered as reference point. If instead of this electrochemical scale one uses the physical scale, having the vacuum level as reference zero point, then the redox systems will be characterized by Fermi levels $E_{F,\text{redox}}$ (introduced by Gerischer) and the relation between these levels and the redox potentials U_{redox} from the electrochemical scale is given by the equation:

$$E_{F,\text{redox}} = -(4.5 + e_0 U_{\text{redox}})$$

in which the value -4.5 eV represents the redox Fermi level corresponding to the standard redox system of the normal hydrogen electrode. The positive direction of increasing of values will be upwards for the physical scale and

downwards for the electrochemical one. Therefore, on the physical scale, in the reduction processes the electrons pass to the lower energy levels, while in the oxidation processes the holes pass to the higher energy levels, and inversely on the electrochemical scale.

Essential in a Schottky barrier is the *depletion layer* from the semiconductor which will carry a net charge of contrary sign to that of the majority of carriers and which is due either to the fixed donors (semiconductor n) or to the fixed acceptors (semiconductor p). Suppose an n type semiconductor. A Schottky barrier can be formed on condition that the Fermi level of the uncharged semiconductor E_F^0 should be higher than $E_{F,\text{redox}}$. The adjusting of E_F^0 to the value $E_{F,\text{redox}}$ implies the passing of electrons from the semiconductor to the electrolyte (*i.e.*, an *electrons depletion* in the semiconductor) and consequently the building-up of a double layer at the interface; on the other hand the Fermi level (having a thermodynamic meaning) must maintain its position as compared to the levels representing the edges of the conduction and valence bands, corresponding to the bulk of semiconductor, and, as a result, a bending of these levels appears (see Figure 1a).

Under illumination, one may speak of quasi-Fermi levels (${}_nE_F^*$) for electrons, and (${}_pE_F^*$) for holes; in the bulk of the semiconductor, the two quasi-Fermi levels are equal, while in the region which absorbs light they are different, and they complicately depend on the distance up to the interface (Figure 1b).

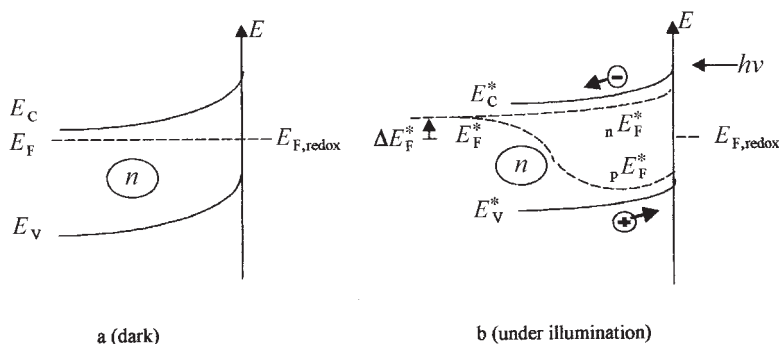


Figure 1. The effect of illuminating a Schottky barrier.

As one sees, the separation of charges induced by light absorption leads to the reduction of the bands bending and the subsequent shift of the Fermi level upwards with a value (ΔE_F^*) which corresponds to a phototension:

$$\Delta U_{\text{photo}} = U_{\text{redox}}(L) - U_{\text{redox}}(\text{dark}) = -\Delta E_F^*/e_0.$$

Let's consider now a Schottky barrier in open circuit conditions. The electron-hole pairs generated by illumination disappear by recombination in bulk or on the surface, as well as by partaking to various redox reactions occurring at the interface. The reduction of the bands bending, and thus of the electric field intensity, will favour the recombination processes and two situations may be distinguished:

In the first situation, the electron-hole pairs may not disappear by partaking to redox reactions at the interface. Then, when the stationary state is reached, the intensity of the electric field reduces to zero, there is no bands bending and the electron-hole pairs generated by illumination disappear only by recombination. Of course, such a stationary state is reached irrespective of the intensity of the illumination (*e.g.*, L or $L + dL$)

In the second situation, two or more redox reactions occur simultaneously at interface making possible the disappearance of the electron-hole pairs not only by recombination, but by partaking to these redox reactions too. Then, in the stationary state, the intensity of the electric field is reduced, but not becoming equal to zero, remains also a bands bending, and some of the reactions occur in the reduction sense (with negative current densities), the others in the oxidation sense (with positive current densities), the sum of all current densities remaining equal to zero (because of the open circuit condition). Now, the electric tension of the electrode has the meaning of a mixed potential $U_m(L)$ because some of the electrochemical active species transform from their oxidized forms into their reduced forms, and the other species inversely, of course under a total current density equal to zero, irrespective of the illumination (L or $L + dL$).

Finally, one must not forget that in this paper we assume that the reactions (1) occur with charge transfer limitations and consequently, although there are transformations $ox_i \rightarrow red_i$ and $red_j \rightarrow ox_j$, their concentrations remain practically constant (that is why one may use the Butler-Volmer type equations (6) and (6')).

Further, let's suppose that one changes the mixed potential with $d_L U_m$, remaining in open circuit conditions. From the meaning of a mixed potential, it follows:

$$\sum_k (j_{n,k} + j_{p,k})_{U=U_m} = 0 \quad (8)$$

relation that applies to both $U_m(L)$ and $U_m(L + dL)$. If $d_L U_m$ is very small, one may consider that β^* and the other quantities: β_k , U_k^0 , $j_{n,k}^{00}$, $j_{p,k}^{00}$ remain practically constant (as a consequence of the fact that at the interface, the Fermi quasilevels remain practically unchanged, if dL is very small^{7,8}). Then, writing Eq. (8), for the illuminations L , and $L + dL$, one gets (by making the difference between the obtained equations):

$$[\sum_k (\partial j_{n,k} / \partial U_m) + (\partial j_{p,k} / \partial U_m)] d_L U_m = 0 \quad (8')$$

and performing the derivatives (by using Eqs. (6) and (6')), one gets:

$$\sum_k (\alpha_{n,k} n_k j_{n,k} + \alpha_{p,k} n_k j_{p,k}) = \sum_k (n_k j_{n,k}^+ + n_k j_{p,k}^+) \quad (9)$$

where by $j_{n,k}^+$ and $j_{p,k}^+$ we have denoted the current densities:

$$j_{n,k}^+ = j_{a,c,k}; j_{p,k}^+ = j_{a,v,k} \quad (9')$$

Further, introducing the expressions (6'') of $\alpha_{n,k}$ and $\alpha_{p,k}$ it results:

$$\beta^* = \sum_k n_k (j_{n,k}^- + j_{p,k}^+) / \sum_k n_k [(\beta_k - 1)j_{n,k} + \beta_k j_{p,k}] \quad (10)$$

where the current density $j_{n,k}^-$ has the meaning:

$$j_{n,k}^- = -j_{c,c,k} \quad (10')$$

and, of course, a similar meaning has $j_{p,k}^-$, *i.e.*,

$$j_{p,k}^- = -j_{c,v,k} \quad (10'')$$

Eq. (10) is important because it expresses the partition coefficient β^* (a quantity characterizing the double layer structure) in terms of quantities characterizing the kinetics of the redox processes occurring simultaneously at the semiconductor/electrolyte multielectrode.

Further, if one multiplies both members of Eq. (10) by $d_L(\Delta\Phi)_m$, and one takes into account that:

$$\beta^* d_L(\Delta\Phi)_m = d_L(\beta^* \Delta\Phi)_m = d_L(\Delta\Phi_H), \quad (11)$$

one gets:

$$d_L(\Delta\Phi_H) = \beta^* d_L(\Delta\Phi)_m \quad (12)$$

equation equivalent to:

$$d_L(\Delta\Phi_{sc}) = (1 - \beta^*) d_L(\Delta\Phi)_m. \quad (12')$$

Eqs. (12) and (12') where β^* , is given by Eq. (10), express the effect that a variation dL of the intensity of illumination has upon the partition of $(\Delta\Phi)_m$ into its two components $(\Delta\Phi_{sc})$ and $(\Delta\Phi_H)$.

*Modeling the Effects of the Illuminating and the Polarizing Processes
on the Structure of the Electric Double Layer*

Let's consider a semiconductor/electrolyte interface representing a Schottky barrier with positive space charge in the semiconductor (when the electric field intensity \vec{E} is directed from the semiconductor to the electrolyte^{9,10}). The effect of the illumination consists in generating electron-hole pairs in the double layer of the semiconductor. With respect to the sense of \vec{E} the electrons will move in the opposite sense, and the holes in the same sense. If one passes from an illumination L to an illumination $L + dL$, dL being very small, the number of electron-hole pairs generated by the additional illumination dL will be very small too, and one may consider that the electrons and the holes are distributed in two distinct planes. Then, one may model the effect of dL as an »injection of a plane capacitor«, having the positive charge in front of the semiconductor surface, and the negative one in front of the outer Helmholtz plane of the semiconductor OHP*. Let's denote by $d\vec{E}$ the intensity of the electric field between the planes of this »injected capacitor«. Its sense is obviously opposite to that of \vec{E} , and determines a change of $\Delta\Phi_{sc}$ with:

$$d_L(\Delta\Phi_{sc}) = - \int_0^{\delta_{sc}} |d\vec{E}| dx \quad (13)$$

where δ_{sc} represents the thickness of the double layer in the semiconductor, and x increases towards OHP*. Obviously, this »injected capacitor« is not a plane capacitor homogeneously charged; indeed, such a capacitor would have an electric field only between its planes, and consequently, its effect on the potential drop $\Delta\Phi_H$ would be small, *i.e.*, $d_L(\Delta\Phi_H)$ would be equal to zero, in contradiction with Eq. (12). Nevertheless, for estimating $d_L(\Delta\Phi_{sc})$, one may consider this »injected capacitor« as an infinite plane capacitor homogeneously charged at a charge density dq , because dL has effect, especially on $\Delta\Phi_{sc}$. Therefore:

$$d_L(\Delta\Phi_{sc}) = - \frac{dq}{\varepsilon_0 \varepsilon_{sc}} \delta_{sc} \quad (13')$$

and introducing in Eq. (12)':

$$(1 - \beta^*) d_L(\Delta\Phi)_m = - \frac{dq}{\varepsilon_0 \varepsilon_{sc}} \delta_{sc} \quad (14)$$

where $\varepsilon_0 \varepsilon_{sc}$ are the vacuum permittivity, and the relative permittivity of the semiconductor.

In Figure 2a, one illustrates the »injected capacitor« by which one models the effect of changing the illumination with dL ; as one sees, this effect concerns only the semiconductor double layer.

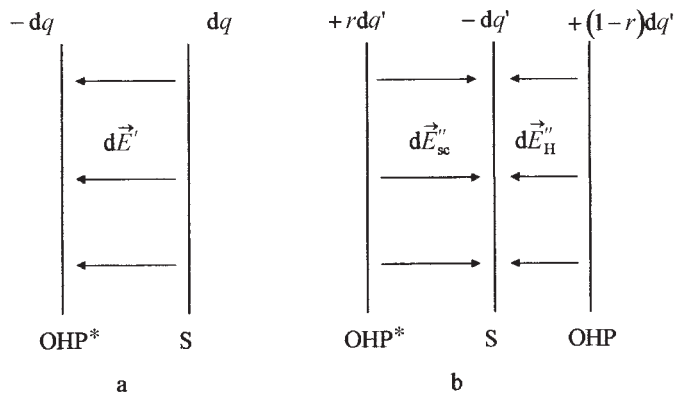


Figure 2. The effect of changing the illumination of a semiconductor with positive charge (a), and the effect of changing its polarization (b).

As for the polarizing process, it may be modeled by the »injection of three homogeneously charged planes«; one of these planes is disposed in front of the semiconductor surface and the other two ones in front of the two outer Helmholtz planes: in the solution (OHP), respective in the semiconductor (OHP*); of course, the charge densities of these three planes should respect the electroneutrality condition. This modeling of polarizing process is illustrated in Figure 2b.

As one sees, the polarizing process introduces in the semiconductor a field $d\vec{E}_{sc}''$ opposite to $d\vec{E}'$, and in the solution a field $d\vec{E}_H''$ having the same sense as $d\vec{E}'$. The charge densities on the planes are given in Figure 2b, where $0 \leq r \leq 1$; the value $r = 0$, corresponds to a metal/electrolyte interface, and the value $r = 1$ to a semiconductor/ electrolyte interface having the property that the interface polarization affects only the semiconductor layer.

To find the values $|d\vec{E}_{sc}''|$, $|d\vec{E}_H''|$, one must add the contributions of all planes. It thus results:

$$|d\vec{E}_{sc}''| = \frac{rdq'}{\varepsilon_0 \varepsilon_{sc}} \quad (15)$$

respective:

$$|d\vec{E}_H''| = \frac{(1-r)dq'}{\varepsilon_0 \varepsilon_H} \quad (16)$$

and further:

$$d_P(\Delta\Phi_{sc}) = \frac{rdq'}{\varepsilon_0 \varepsilon_{sc}} \delta_{sc}; \quad d_P(\Delta\Phi_H) = -\frac{(1-r)dq'}{\varepsilon_0 \varepsilon_H} \delta_H \quad (17, 17')$$

where ε_H , δ_H are the relative permittivity and the thickness of the Helmholtz layer.

The Potentiostatic »L∩P« Method in Open Circuit Conditions

In such a method, $(\Delta\Phi)_m$ remains constant, *i.e.*,

$$d_{L\cap P}(\Delta\Phi_H) + d_L(\Delta\Phi_{sc}) + d_P(\Delta\Phi_{sc}) = 0 \quad (18)$$

where:

$$d_{L\cap P}(\Delta\Phi_H) = d_L(\Delta\Phi_H) + d_P(\Delta\Phi_H). \quad (18')$$

Further, using Eqs. (12), (12'), (17) and (17'), equations (18) and (18') take the forms:

$$\frac{rdq'}{(\varepsilon_0\varepsilon_{sc})} \delta_{sc} = -d_{L\cap P}(\Delta\Phi_H) - (1 - \beta^*)d_L(\Delta\Phi)_m \quad (19)$$

$$\frac{(1-r)dq'}{(\varepsilon_0\varepsilon_H)} \delta_H = \beta^*d_L(\Delta\Phi)_m - d_{L\cap P}(\Delta\Phi_H) \quad (19')$$

and thus, after eliminating dq' , one gets for $d_{L\cap P}(\Delta\Phi_H)$ the expression

$$-d_{L\cap P}(\Delta\Phi_{sc}) = d_{L\cap P}(\Delta\Phi_H) = \left[(1-\beta^*)\frac{\delta_H}{\varepsilon_H} + \beta^* \frac{r}{1-r} \frac{\delta_{sc}}{\varepsilon_{sc}} \right] / \left[\frac{r}{1-r} \frac{\delta_{sc}}{\varepsilon_{sc}} - \frac{\delta_H}{\varepsilon_H} \right] d_L(\Delta\Phi)_m \quad (20)$$

where the first equality results from Eq. (18).

Eq. (20) represents the equation of the *potentiostatic L∩P* method in open circuit conditions and its importance comes from the fact that it relates quantities characterizing the double layer structure to quantities characterizing the kinetics of the redox reactions occurring simultaneously at the interface, the latter ones included in the Eq. (10) of β^* .

CLOSED CIRCUIT CONDITIONS

The Equations of the Potentiostatic (Galvanostatic) »L∩P« Methods

To understand the meaning of the *L∩P* method in closed circuit conditions, we shall consider an unielektrode redox.

In Figure 3 are shown two polarization curves, corresponding to the illuminations L and $L + dL$. They intersect the electric tension axis in the points $U_0(L)$, respective $U_0(L + dL)$, and, to make a choice, let's suppose

$$d_P U(L,P) = U(L,P + dP) - U(L,P) = dP > 0 \tag{22}$$

to which corresponds a second increase of the current density:

$$d_P j = \text{tg } \alpha_P \cdot d_P U(L,P) > 0 . \tag{22'}$$

Further, because the figure MNSQ is practically a parallelogram, it results $\alpha_L \approx \alpha_P$ and $d_L j \approx d_P j$. Thus:

$$\begin{aligned} dj &= (d_{L \cap P} j)_{U(L,P)} = d_L j + d_P j \cong \\ &\cong \text{tg } \alpha_P [d_P U(L,P) - d_L U(L,P)] \cong 2d_L j \cong 2d_P j \end{aligned} \tag{23}$$

where the potentiostatic condition $d_P U(L,P) + d_L U(L,P) = 0$ has been used.

It is easy to see that $(d_{L \cap P} j)_{U(L,P)}$ is equal to the length of the segment \overline{MN} . Of course, the illumination and the potentiostat act simultaneously, and the point M will go on the segment \overline{MN} towards the point N. One may say: the vector \overline{MN} is the resultant of the vectors \overline{MS} and \overline{MQ} . The vector \overline{MS} gives the movement of the point M when the potentiostat doesn't change its action, and only the illumination is changed, and the vector \overline{MQ} gives the movement of the point M when the illumination is kept constant, and the potentiostat acts, changing the polarization with dP . This decomposition of the resultant movement \overline{MN} into its two component movements \overline{MS} and \overline{MQ} is similar to the well known decomposition of the free fall in the gravitational field into its two components (*i.e.*, $x = v \cdot t$ and $y = 1/2 g \cdot t^2$); in this comparison the role of the gravitational field is played by the potentiostat.

To deduce the equations of the potentiostatic (galvanostatic) » $L \cap P$ « methods, we shall start with the equation:

$$\sum_k (j_{n,k} + j_{p,k})_U = j \tag{24}$$

which has for the closed circuit conditions the role that Eq. (8) had for the open circuit conditions. By changing the illumination from L to $L + dL$, the current density will change with $d_L j = j(L + dL) - j(L)$, given by:

$$d_L j = \sum_k (\partial j_{n,k} / \partial U + \partial j_{p,k} / \partial U) d_L U \tag{25}$$

where $d_L U = U(L + dL) - U(L)$.

Similarly, the changing of P to $P + dP$, will induce a changing $d_P j = j(P + dP) - j(P)$:

$$d_P j = \sum_k (\partial j_{n,k} / \partial U + \partial j_{p,k} / \partial U) d_P U \tag{25'}$$

where: $d_P U = U(P + dP) - U(P)$.

In the case of the *potentiostatic* »L∩P« method, U doesn't change and thus:

$$d_L U = -d_P U, \text{ i.e., } d_{L\cap P} U = 0 \quad (26)$$

while in a *galvanostatic* »L∩P« method, j doesn't change and thus:

$$d_L j = -d_P j, \text{ i.e., } d_{L\cap P} j = 0. \quad (26')$$

Further, we have to express $d_L j$ in function of $d_L U = d_L(\Delta\Phi)$, respectively $d_P j$ in function of $d_P U = d_P(\Delta\Phi)$. We shall use the Eqs. (6) and (6') of $j_{n,k}$, $j_{p,k}$, but with U instead of the mixed potential U_m . Maintaining the same hypothesis, i.e., β^* , β_k , U_k^0 , $j_{n,k}^{00}$ and $j_{p,k}^{00}$ remain practically constant, one gets:

$$\begin{aligned} d_L j = & -f \left[\sum_k [(\beta_k - 1)n_k j_{n,k} + \beta_k n_k j_{p,k}] \right] d_L(\Delta\Phi_H) + \\ & + f \left[\sum_k n_k (j_{n,k}^- + j_{p,k}^+) \right] d_L(\Delta\Phi) \end{aligned} \quad (27)$$

and:

$$\begin{aligned} d_P j = & -f \left[\sum_k [(\beta_k - 1)n_k j_{n,k} + \beta_k n_k j_{p,k}] \right] d_P(\Delta\Phi_H) + \\ & + f \left[\sum_k n_k (j_{n,k}^- + j_{p,k}^+) \right] d_P(\Delta\Phi). \end{aligned} \quad (27')$$

Adding Eqs. (27) and (27'):

$$\begin{aligned} d_{L\cap P} j = & -f \left[\sum_k [(\beta_k - 1)n_k j_{n,k} + \beta_k n_k j_{p,k}] \right] d_{L\cap P}(\Delta\Phi_H) + \\ & + f \left[\sum_k n_k (j_{n,k}^- + j_{p,k}^+) \right] d_{L\cap P}(\Delta\Phi). \end{aligned} \quad (27'')$$

For $d_{L\cap P}(\Delta\Phi) = 0$, Eq. (27'') particularizes in the equation of the *potentiostatic* »L∩P« method:

$$(d_{L\cap P} j)_{\Delta\Phi} = -f \left[\sum_k [(\beta_k - 1)n_k j_{n,k} + \beta_k n_k j_{p,k}] \right] [d_{L\cap P}(\Delta\Phi_H)]_{\Delta\Phi} \quad (28)$$

and for $(d_{L\cap P} j) = 0$, in the equation of the *galvanostatic* »L∩P« method:

$$\begin{aligned} \left[\sum_k n_k (j_{n,k}^- + j_{p,k}^+) \right] [d_{L\cap P}(\Delta\Phi_H)]_j = \\ = \left[\sum_k [(\beta_k - 1)n_k j_{n,k} + \beta_k n_k j_{p,k}] \right] [d_{L\cap P}(\Delta\Phi_H)]_j \end{aligned} \quad (29)$$

where the indexes $\Delta\Phi$, and j , specify that these quantities don't change.

Concerning Eq. (28) an apparent contradiction appears: from Eq. (23) it results $(d_{L \cap P})_{\Delta\Phi} \neq 0$, while for a value β^* rigorously constant, $[d_{L \cap P}(\Delta\Phi_H)]_{\Delta\Phi} = \beta^* [d_{L \cap P}(\Delta\Phi)]_{\Delta\Phi}$ should be equal to zero. In the following one shows that in general $[d_{L \cap P}(\Delta\Phi_H)]_{\Delta\Phi} \neq \beta^* [d_{L \cap P}(\Delta\Phi)]_{\Delta\Phi}$, and consequently Eq. (28) is correct and cover all possibilities (*i.e.*, including the situation when both $(d_{L \cap P})_{\Delta\Phi}$ and $[d_{L \cap P}(\Delta\Phi_H)]_{\Delta\Phi}$ are equal to zero).

First of all, one must underline that from our hypothesis: β^* remains practically constant when one passes from the point M (see Figure 3), either to the point S, or to the point Q, *i.e.*, when one changes the illumination ($L \rightarrow L + dL$), *maintaining the polarization P*, or one changes the polarization ($P \rightarrow P + dP$), *maintaining the illumination L*, doesn't result that the values β_M^* , β_S^* and β_Q^* , *must be rigorously equal*. Consequently, we have to see in what conditions $\beta_M^* = \beta_S^* = \beta_Q^*$.

Let's write the electric tension $U(L,P)$, in the form:

$$U(L,P) = U_0(L) + P = U(L,0) + P$$

where we have specified now that $U_0(L)$ corresponds to a polarization equal to zero. Passing from U to $\Delta\Phi$, the above equation writes:

$$\Delta\Phi(L,P) = \Delta\Phi(L,0) + P . \tag{a}$$

The partitions coefficient β^* , introduced by Eq. (6'''), has referred to the open circuit conditions, and with the present notations has the meaning:

$$\beta^* = \beta^*(L,0) = \frac{\Delta\Phi_H(L,0)}{\Delta\Phi(L,0)} . \tag{b}$$

Of course,

$$\beta_M^* = \beta^*(L,P) = \frac{\Delta\Phi_H(L,P)}{\Delta\Phi(L,P)} = \frac{\Delta\Phi_H(L,0) + P_H}{\Delta\Phi(L,0) + P} \tag{b'}$$

and similarly:

$$\beta_S^* = \beta^*(L + dL,P) = \frac{\Delta\Phi_H(L + dL,0) + P_H}{\Delta\Phi(L + dL,0) + P} \tag{b''}$$

respective:

$$\beta_Q^* = \beta^*(L,P + dP) = \frac{\Delta\Phi_H(L,0) + P_H + dP_H}{\Delta\Phi(L,0) + P + dP} . \tag{b'''}$$

Applying the properties of a series of equal quotients, it follows from Eqs. (b)-(b''') that the equalities:

$$\beta^*(L,0) = \beta_M^* = \beta_S^* = \beta_Q^* \quad (c)$$

hold true, if and only if:

$$\beta^*(L,0) = \frac{\Delta\Phi_H(L,0)}{\Delta\Phi(L,0)} = \frac{d_L \Delta\Phi_H(L,0)}{d_L \Delta\Phi(L,0)} = \frac{P_H}{P} = \frac{d_P P_H}{dP} \quad (c')$$

i.e., the partition coefficient $\beta^*(L,0)$, expressing the effect of illuminating the electrode (when $P = 0$), is equal to the partition coefficient $\beta^*(0,P) = P_H/P$, expressing the effect of polarizing the electrode in dark conditions. The subscripts »L« and »P« indicate that the differentials take into account only the change of L , respective P , *e.g.*, $d_L \Delta\Phi_H(L,P) = d_L \Delta\Phi_H(L,0)$.

From Eqs. (c) and (c') it follows

$$\begin{aligned} d_L \Delta\Phi_H(L,P) &= d_L \Delta\Phi_H(L,0) = \\ \beta^*(L,0) d_L \Delta\Phi(L,0) &= \beta^*(L,P) d_L \Delta\Phi(L,P) \end{aligned} \quad (d)$$

respective

$$\begin{aligned} d_P \Delta\Phi_H(L,P) &= d_P [\Delta\Phi_H(L,0) + P_H] = d_P P_H \\ &= \beta^*(L,P) d_P \Delta\Phi(L,P) \end{aligned} \quad (d')$$

and further

$$d_{L \cap P} [\Delta\Phi_H(L,P)]_{\Delta\Phi} = \beta^*(L,0) d_{L \cap P} [\Delta\Phi(L,P)]_{\Delta\Phi} = 0. \quad (d'')$$

In general, $\beta_S^* - \beta_M^*$ and $\beta_Q^* - \beta_M^*$ are *different*, because the illumination and the polarization have *different* actions upon the electrode and consequently, instead of Eqs. (d) and (d') we have:

$$d_L \Delta\Phi_H(L,P) \neq \beta^*(L,P) d_L \Delta\Phi(L,P) \quad (e)$$

$$d_P \Delta\Phi_H(L,P) \neq \beta^*(L,P) d_P \Delta\Phi(L,P). \quad (e')$$

Of course, by introducing two *different* functions $\delta_1(L,P)$ and $\delta_2(L,P)$, to account for the difference $\beta_S^* - \beta_M^* \neq \beta_Q^* - \beta_M^*$, Eqs. (e) and (e') may be transformed in two equalities:

$$d_L \Delta\Phi_H(L,P) = [\beta^*(L,P) + \delta_1(L,P)] d_L \Delta\Phi(L,P) \quad (f)$$

$$d_P \Delta\Phi_H(L,P) = [\beta^*(L,P) + \delta_2(L,P)] d_P \Delta\Phi(L,P). \quad (f')$$

Further, by adding Eqs. (f) and (f') and imposing the potentiostatic condition, one gets:

$$d_{L \cap P}[\Delta\Phi_H(L, P)]_{\Delta\Phi} = [\delta_1(L, P)d_L\Delta\Phi(L, P) + \delta_2(L, P)d_P\Delta\Phi(L, P)]_{\Delta\Phi} \neq 0. \quad (g)$$

It remains to see in what situations Eq. (d'') holds true. One situation is that of an inert metal/redox electrolyte electrode. In this case there is no difference of potential in the metal, *i.e.*, $\Delta\Phi = \Delta\Phi_H$; $P_H = P$ and thus $\beta^*(L, P) = 1$. A second situation (and the last one) is that in which $\Delta\Phi = \Delta\Phi_{sc}$; $P_{sc} = P$ and thus $\beta^*(L, P) = 0$.

Excepting these two extreme situations, which, however, don't present interest, because also $(d_{L \cap P}j)_{\Delta\Phi}$ is equal to zero, in all other situations Eq. (g) holds true. For this reason, in order to cover all possible situations, we have maintained in Eq. (28) the term $[d_{L \cap P}(\Delta\Phi_H)]_{\Delta\Phi}$.

The Specific Admittance of the Inert Semiconductor/Redox Electrolyte-Multielectrode.

Coming back to Figure 3, let's consider the polarization curve ($L + dL$). One sees that a change $-[d_{L \cap P}U]_j = -[d_{L \cap P}(\Delta\Phi)]_j$ (*i.e.*, $\overline{N'M}$) induces a change $(d_{L \cap P}j)_U = (d_{L \cap P}j)_{\Delta\Phi}$ (*i.e.*, \overline{MN}). Then, the admittance (a positive quantity) is given by:

$$A_{sc} = \overline{MN}/\overline{N'M} = -(d_{L \cap P}j)_{\Delta\Phi} / [d_{L \cap P}(\Delta\Phi)]_j \quad (30)$$

(because the two polarization curves are practically parallel, and very close, this admittance may be considered as corresponding to the point M too). Using Eqs. (28) and (29):

$$A_{sc} = f \left[\sum_k n_k (j_{n,k}^- + j_{p,k}^+) \right] [[d_{L \cap P}(\Delta\Phi_H)]_{\Delta\Phi} / [d_{L \cap P}(\Delta\Phi_H)]_j]. \quad (31)$$

Some particular cases of Eq. (31) are of interest.

*a) The polarization changes $d_P(\Delta\Phi) = d_P(\Delta\Phi_{sc}) + d_P(\Delta\Phi_H)$ are practically taken by the semiconductor, *i.e.*, $d_P(\Delta\Phi_H) = 0$.*

In such situations:

$$[d_{L \cap P}(\Delta\Phi_H)]_{\Delta\Phi} = [d_{L \cap P}(\Delta\Phi_H)]_j. \quad (32)$$

Indeed, the maintaining of the values $\Delta\Phi$, respective j , implies the arrival in the point N, respective N' (see Figure 3), by going on the polarization curve

($L + dL$) from S to N, respective from S to N'. Therefore, the effect of dL is the same, irrespective of the fact that $\Delta\Phi$, or j has to remain unchanged. In other words:

$$[d_L(\Delta\Phi_H)]_{\Delta\Phi} = [d_L(\Delta\Phi_H)]_j \quad (32')$$

which is an equation equivalent to Eq. (32), because $d_p(\Delta\Phi_H) = 0$.

Using Eq. (32) in Eq. (31):

$$A_{sc} = f \sum_k n_k (j_{n,k}^- + j_{p,k}^+). \quad (33)$$

b) The semiconductor/electrolyte is in the initial situation

$M[(\Delta\Phi)_m, j = 0]$, i.e., the point M is on the $U = \Delta\Phi + \text{const}$ axis.

Now, Eq. (20) holds true, and, because it refers to a potentiostatic method, its first member is $[d_{L \cap P}(\Delta\Phi_H)]_{(\Delta\Phi)_m}$. As regarding $d_L(\Delta\Phi)_m$, because it referred to an illumination in *open circuit conditions*, it represents in fact $[d_L(\Delta\Phi)_m]_{j=0}$. But in open circuit conditions $[d_L(\Delta\Phi)_m]_{j=0} = [d_{L \cap P}(\Delta\Phi)_m]_{j=0}$, because $[d_p(\Delta\Phi)_m]_{j=0} = 0$ (the initial mixed potential changes, but remaining all the time a mixed potential, and consequently there is no need to polarize the electrode in order to keep the value $j = 0$). This time Eq. (30) writes:

$$(A_{sc})_{(\Delta\Phi)_m, j=0} = - (d_{L \cap P} j)_{(\Delta\Phi)_m} / [d_L(\Delta\Phi)_m]_{j=0}. \quad (34)$$

Further, using Eq. (28) (to express $(d_{L \cap P} j)_{(\Delta\Phi)_m}$), and Eq. (20), one finally arrives to:

$$(A_{sc})_{(\Delta\Phi)_m, j=0} = f \left[\sum_k [(\beta_k - 1)n_k j_{n,k} + \beta_k n_k j_{p,k}] \right] \times \left[(1 - \beta^*) \frac{\delta_H}{\varepsilon_H} + \beta^* \frac{r}{1-r} \frac{\delta_{sc}}{\varepsilon_{sc}} \right] / \left[\frac{r}{1-r} \frac{\delta_{sc}}{\varepsilon_{sc}} - \frac{\delta_H}{\varepsilon_H} \right] \quad (35)$$

If $r = 1$, it means that the polarization acts only upon the semiconductor, and using the expression (10) obtained for β^* , one gets:

$$(A_{sc})_{(\Delta\Phi)_m, j=0, r=1} = f \sum_k n_k (j_{n,k}^- + j_{p,k}^+) \quad (36)$$

i.e., we have formally refound the expression (33), as it is normal. However, the two expressions are different, because $j_{n,k}^-$, $j_{p,k}^+$ are different in them; indeed, they refer to different situations, i.e., $(\Delta\Phi, j)$, respective $((\Delta\Phi)_m, j=0)$.

If $r = 0$, we are in the case of metal/ electrolyte interfaces, and Eq. (35) becomes:

$$(A_{\text{met}})_{(\Delta\Phi)_m, j=0} = f \sum_k n_k [(1-\beta_k)j_k + j_k^-]. \quad (37)$$

Formally, Eq. (37) remains valid also for the general situation:

$$(A_{\text{met}})_{\Delta\Phi, j} = f \sum_k n_k [(1-\beta_k)j_k + j_k^-] \quad (38)$$

but the values of the current densities appearing in the second members are different.

c) *Semiconductor/ electrolyte interfaces satisfying the condition*

$$\delta_H / \varepsilon_H \ll \frac{r}{1-r} \frac{\delta_{\text{sc}}}{\varepsilon_{\text{sc}}}.$$

This is a frequent case, and from Eq. (35) it follows:

$$(A_{\text{sc}})_{(\Delta\Phi)_m, j=0, C} \cong f \sum_k n_k (j_{n,k}^- + j_{p,k}^+) \quad (39)=(36)$$

where by the index C is indicated the above imposed condition.

CONCLUSIONS

The equations obtained in this paper represent basic equations which permit a more deeply understanding of the effects that the illumination and polarization have upon the structure of the electric double layers at redox multielectrodes (representing Schottky barriers) of the type inert semiconductor/redox electrolyte.

These basic equations also permit to ground a new method (experiment), based on the simultaneously changing of the illumination (L) and polarization (P), for studying the kinetics of redox reactions occurring simultaneously at such multielectrodes. The method has been called »intersection method«, and the symbol » $L \cap P$ « has been used.

A special attention has been given to the two particular cases *potentiostatic*, and *galvanostatic* » $L \cap P$ « methods, and from their basic equations, it was possible to deduce expressions for the specific admittance corresponding to some cases of interest, including the inert metal/redox electrolyte multielectrodes too.

These equations will serve in the subsequent papers to ground other intersection methods.

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SAŽETAK

Nove stacionarne metode istraživanja kinetike redoks-reakcija na inertnim poluvodičkim elektrodama.**I. Metoda »L∩P«**

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Opisana je teorijska osnova nove metode istraživanja kinetike simultanih redoks-reakcija otopljenih iona i molekula na površini inertne poluvodičke multielektrode karakterizirane Schottkyjevom barijerom. Metoda se temelji na istovremenoj promjeni intenziteta osvjetljenja (L) i polarizacije multielektrode (P) pa je zato nazvana metodom presjeka i označena simbolom »L∩P«. Predložen je kinetički model utjecaja navedenih varijabli na struju ili napon, u zatvorenom ili otvorenom strujnom krugu, s pomoću kojega su izvedene jednadžbe potenciostatske i galvanostatske inačice metode »L∩P« iz kojih slijedi izraz za specifičnu admitanciju elektrode. Diskutira se o posebnom slučaju inertne metalne multielektrode.