

APPLICATION OF QUANTUM MECHANICS METHODS TO THE STUDY OF  
OXIDATION-REDUCTION ELECTROCHEMICAL REACTIONS OF  
METALS AND SEMICONDUCTORS

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16. Abstract After a discussion of oxidation-reduction reactions and the tunneling effect in general, the author discusses the distribution of quantum states as a function of their energy in terms of quantum state density, exchange equilibrium conditions, anodic and cathodic polarization, limiting currents and overvoltage-current relationships. The intrinsic properties of the semiconductor and the electrolyte's oxidation-reduction voltage determine whether the transfer occurs predominantly at the valency band or at the conduction band. The article concludes with a discussion of the experimental results of many authors which best confirm the theoretical expectations.		13. Type of Report and Period Covered  Translation
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## Symbols

$\theta$	Electron
$\oplus$	Hole
$a$	Width of rectangular energy barrier
$A$	$2.3 kT/e$
$b_a$	Anodic Tafel slope
$b_c$	Cathodic Tafel slope
$c_O$	Concentration of oxidized species
$c_R$	Concentration of reduced species
$D(E)$	Quantum state density
$D_{Ez}(E)$	Quantum state density of an oxidation-reduction system
$D_M(E)$	Quantum state density of a semiconductor
$e$	Absolute value of the electron charge
$E$	Energy of an energy level
$E_a$	Height of a rectangular energy barrier
$E_C$	Energy level at the edge of a conduction band of a semiconductor
$E_V$	Energy level at the edge of a valency band of a semiconductor
$E_F$	Fermi energy level
$E_{F,Ez}$	Energy of the Fermi level of an oxidation-reduction system
${}^0E_{F,Ez}$	Energy of the Fermi level of an oxidation-reduction system at unit concentrations
$E_{F,M}$	Energy of the Fermi level of a metal
$E_{F,S}$	Energy of the Fermi level of a semiconductor
$iE_{F,S}$	Energy of the Fermi level of an intrinsic semiconductor
$E_0$	Energy of a particle

$E_0$	Energy level of the process $O + \theta_{\infty} \rightarrow R^*$ , where O has an equilibrium configuration and $R^*$ has the same atomic configuration as O.
$E_R$	Energy level of the process $R \rightarrow O^* + \theta_{\infty}$ , where R has an equilibrium configuration and $O^*$ has the same atomic configuration as R.
$f(E)$	Fermi function
$h$	Planck's constant
$I$	Current density
$i$	Total current
$i_0$	Exchange current for a metal
$i_{n,0}$	Exchange current for electrons for a semiconductor
$i_{p,0}$	Exchange current for holes for a semiconductor
$i_+$	Partial anodic current for a metal
$i_-$	Partial cathodic current for a metal
$i_n^+$	Partial anodic current due to electron transfer in the conduction band of a semiconductor
$i_n^-$	Partial cathodic current due to electron transfer from the conduction band of a semiconductor
$i_p^+$	Partial anodic current due to hole transfer from the valency band of a semiconductor
$i_p^-$	Partial cathodic current due to transfer of holes in a semiconductor's valency band
$i_{n,sat}^-$	Cathodic saturation current due to electron transfer from the conduction band of a semiconductor
$i_{p,sat}^+$	Anodic saturation current due to hole transfer from the valency band of a semiconductor
$k$	Boltzmann's constant
$m$	Mass of a particle
$O$	Oxidized species of an oxidation-reduction system
$R$	Reduced species of an oxidation-reduction system

$T$	Absolute temperature
$\alpha$	Transfer coefficient for a metal
$\beta$	See text
$\gamma$	See text
$\epsilon$	Electrode voltage
$\epsilon_0$	Electrode voltage at equilibrium
$\eta$	Electrode overvoltage
$\eta_C$	Overvoltage in the region of space charge of a semiconductor
$\eta_C^0$	Overvoltage in the region of space charge of a semiconductor less the transport overvoltage (of electrons or holes)
$\eta_H$	Overvoltage in the Helmholtz double layer
$\eta_{T,n}$	Electron transport overvoltage in a semiconductor
$\eta_{T,p}$	Hole transport overvoltage in a semiconductor
$\phi$	Galvani potential relative to uncharged vacuum and at infinity
$\Delta\phi$	Galvani voltage
$\Delta\phi_C$	Galvani voltage in the space charge region of a semiconductor
$\Delta\phi_C^0$	Galvani voltage in the space charge region of a semiconductor at equilibrium
$\Delta\phi_H$	Galvani voltage in the Helmholtz double layer
$\Delta\phi_{H,0}$	Galvani voltage in the Helmholtz double layer at equilibrium

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Introduction

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The study of reactions taking place at the electrode-electrolyte interface is part of the more general problem of the influence of a solid's electronic structure on the course of a reaction; this problem is also of basic interest in the field of catalysis. It is obvious that if such influence exists, it will be stronger for reactions in which electrons are directly participating, such as electrode reactions. In this review, we propose to examine and discuss especially the charge transfer reactions taking place under near-equilibrium conditions and those far from equilibrium in a solid, metal or semiconductor in contact with an electrolyte containing an oxidation-reduction system in solution; we will also observe the influence of the solid's electronic structure on the electrode reaction and compare the results anticipated by the theoretical analysis with those obtained from experimental determinations. This subject is currently of great interest also due to the increasing importance of semiconductor electrodes; this importance has long been recognized through numerous applications: on this subject, it is difficult to remember that, in many types of batteries, electrodes made of semiconductor oxides are used, and that the passivity phenomena, which are so important in the field of corrosion, are due to semiconductor surface layers.

The preparation of solids of high purity or containing strictly controlled impurities has recently made it possible to

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\* Numbers in the margin indicate pagination in the foreign text.

undertake a series of very pertinent investigations on the electrochemical behavior of semiconductors, following the original observation in 1955 by Brattain and Garrett [1] that germanium's electronic structure exerted a direct effect on electrode reactions. Theoretical research has been carried out concurrently with experimental work for the interpretation of these results, at first by Green [2] and Dewald [3], and then by Dewald [4] again, but mainly by Gerischer [5-9]. Other authors who have made basic contributions in this field are Marcus [10], Dogonadze [11] and Levich [12]. Gerischer is the first researcher to adequately study, i.e., using quantum mechanics methods, the electrochemical oxidation-reduction reactions [5] in metals [6] and in semiconductors [7]. We shall refer often to these works, which were published in 1960 and 1961.

#### Oxidation-Reduction Reactions and the Tunnel Effect

As is known, during an anodic electrochemical oxidation-reduction reaction:



or, during a cathodic reaction:



(where R indicates the reduced species and O the oxidized species of an oxidation-reduction system, and  $\theta$  indicates the electron), the transfer of electrons takes place through the double layer at the interface between the electrode (metal or semiconductor) and the electrolyte.

This requires that a potential barrier be surmounted. Gurney [13] has shown that electrons, having a relatively small mass, through the quantum mechanics tunnel effect are able to surmount the potential barrier with a much higher probability than

that of the transfer between different energy levels, i.e. by excitation of the electron at energy levels high enough to overcome the barrier.

This is due to the fact that the probability that a particle of mass  $m$  and energy  $E_0$  is able to overcome a rectangular energy barrier with height  $E_0$  and width  $a$  is given (if it occurs by the tunneling effect) by the expression:

$$\exp \left[ -\frac{4\pi a}{h} \sqrt{2m(E_a - E_0)} \right]$$

(where  $h$  is Planck's constant) [14], while, if it occurs through excitation, it is given by Boltzmann's exponential: /440

$$\exp (-E_a/kT)$$

(where  $k$  is Boltzmann's constant and  $T$  is the absolute temperature).

It can be seen from these formulas that for particles with small mass, such as the electron, the tunnel effect is favored (for example, if  $E_a = 1$  eV,  $a = 5 \text{ \AA}$ , we have  $6 \cdot 10^{-3}$  and  $5 \cdot 10^{-12}$ , respectively, and with  $E_a = 4$  eV we have  $4 \cdot 10^{-5}$  and  $6 \cdot 10^{-46}$  at  $25^\circ\text{C}$ ); for heavy particles such as metal ions with a mass larger than that of the electron by a factor of  $10^5$ , the tunnel effect becomes negligible.

As is known, the overcoming of an energy barrier by the tunnel effect occurs between two quantum states, initial and final, with the same energy value, and, precisely in the cases considered here, during the anodic process there will be a transfer of the electron from a quantum state occupied in the electrolyte to an unoccupied one in the electrode with the same energy, while during the cathodic process, the reverse will occur.



It is thus indispensable to briefly recall some concepts of the distribution of quantum states as a function of their energy, and the manner in which they are occupied by electrons in metals, semiconductors and electrolytes.

### Density of Quantum States

According to the band model, in solids there is a succession of quantum states that can be grouped in bands: these quantum states are occupied by electrons in order of increasing energy and according to the exclusion principle (not more than one electron per quantum state).

In the case of metals, the bands are partially filled. The probability that an energy level (i.e. the whole of the corresponding quantum states) is occupied by the electrons as a function of the energy  $E$  of that level is determined with Fermi-Dirac statistics and is expressed by Fermi's function:

$$f(E) = \frac{1}{\exp(E - E_{F,M})/kT + 1}$$

where  $E_{F,M}$  represents the energy of the so-called Fermi level.

Fig. 1 shows the course of Fermi's function as a function of energy: the dotted curve refers to the case in which the temperature is  $0^\circ\text{K}$ , and the solid curve refers to the case in which the temperature is higher than  $0^\circ\text{K}$ . As the figure and the above equation show, at absolute zero all energy levels below Fermi's level are occupied by electrons, while those above are not occupied; because of thermal agitation at temperatures higher than absolute zero, some levels with lower energy than that of Fermi's level are not completely occupied and some with higher energy are not completely unoccupied. In addition, when  $E = E_{F,M}$ ,  $f(E) = 1/2$ ;

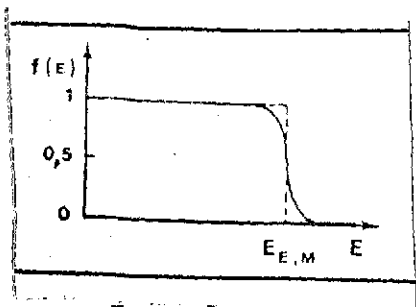


Fig. 1. Course of Fermi's function as a function of energy for a metal at  $0^\circ\text{K}$  (dashed line) and at  $T > 0$  (solid line).

this means that Fermi's level represents the energy level whose occupation probability is 50% when the temperature is different from absolute zero.

In order to know the number of electrons occupying the different energy levels as a function of the energy of those levels, it is necessary to multiply the probability of occupation of an energy level that we have just

seen by the number of quantum states corresponding to each level, i.e., by the density of quantum states  $D_M(E)$ :  $f(E) D_M(E)$ . Since the resulting function is rather complex, we shall only look at its course: Fig. 2 gives the density of quantum states  $D_M$ , and the ordinates give the energy  $E$ ;  $D_M(E)$  is represented by the solid line and the occupation of the various levels by the dotted line. Fermi's level  $E_{F,M}$  corresponds to a 50% occupation, as can be seen in the figure. In the example, the first band is almost completely filled, the second almost completely empty, and the two bands overlap: we thus have a conductor.

In the case of a semiconductor, the band theory anticipates forbidden bands (i.e., energy value intervals in which the quantum state's density is annulled), alternating with permitted bands.

In particular, if a nondegenerated semiconductor is considered, the valency band will be almost completely filled and the conduction band almost completely empty, and Fermi's level will be within the two bands, in the area of the forbidden band. This means that the following inequalities will be verified simultaneously

$$\left| E_{F,S} - E_V > 2kT \right| \quad \text{and} \quad \left| E_C - E_{F,S} > 2kT \right|$$

(where  $E_{F,S}$  indicates Fermi's level and  $E_V$  and  $E_C$  the energy levels corresponding to the edges of the valency and conduction bands, respectively); thus Fermi's function become approximately equal to Boltzmann's exponential:

$$f(E) = \frac{1}{\exp(E - E_{F,S})/kT + 1} \rightarrow \exp[-(E - E_{F,S})/kT]$$

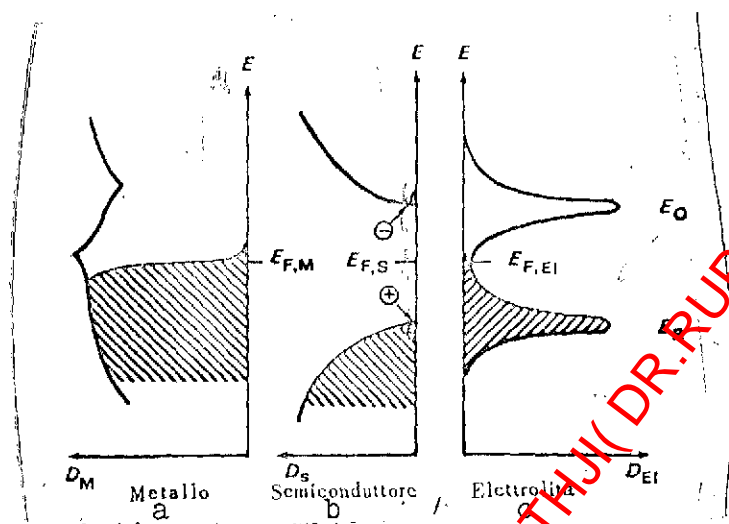


Fig. 2. Distribution of energy levels and their occupation by electrons for a metal, a semiconductor and an electrolyte containing an oxidation-reduction system as a function of their energy, at equilibrium (from Gerischer [8]).

Key: a. Metal; b. Semiconductor; c. Electrolyte

Fig. 2 represents, in a manner similar to that previously seen for metals, the course of the quantum state density  $D_S(E)$  as a function of energy for a nondegenerated semiconductor, and, as usual, the regions of the bands occupied by the electrons have been crosshatched.

When the semiconductor becomes degenerate, its behavior approaches that of a metal, either because the valency band has numerous unoccupied levels or

because the conduction band has numerous occupied levels, due to failure of either the first or second inequalities consider above. Boltzmann's approximation is also no longer verified, and the probability of occupation of the energy levels is expressed by Fermi's function; in addition, as we shall see later, the

Galvani voltage between the electrode and the electrolyte is almost completely localized in the Helmholtz double layer, as is the case for metals. This case is thus less interesting, and it will not be discussed (except when explicitly mentioned), because it is considered to be included in the considerations relating to metals.

In order to determine the course of the quantum state density as a function of the energy of an electrolyte containing an oxidation-reduction system in solution, it is necessary to keep in mind that the reduced species R represents the occupied electron states, and the oxidized species O, the unoccupied electron states.

The energy of the occupied electron states is, in fact, equal to the energy exchanged when an electron located in a quantum state of the reduced species is brought from the solution to infinity (vacuum) without any variations in the solvation structure,<sup>1</sup> i.e., it corresponds to the energy of the reaction:



On the contrary, the energy of the unoccupied electron states is equal to the energy exchanged when an electron coming from infinity (vacuum) is accepted by the oxidized species without changes in the solvation structure of the latter.

The energy of the electron states will thus be a function of the various solvation configurations of R and O, configurations which keep changing due to thermal motion (for instance, due to vibrations and rotations of the solvated ions), but which, according to the Franck-Condon principle, must remain the same when electron transfer takes place.

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<sup>1</sup> This is due, as we shall soon see, to the existence of the Franck-Condon principle.

The various configurations are present in the solution at completely different concentrations, depending on their energy, and it is actually their distribution as a function of energy that determines the density of the quantum states of the oxidation-reduction system contained in the electrolytes  $D_{EL}(E)$ . This latter function is represented in Fig. 2 as a function of energy  $E$ : it has two maxima (as has been shown by Gerischer [5]), corresponding respectively to the energy levels  $E_R$  and  $E_O$  for which the number of existing configurations is maximum. This happens when the species  $R$  or  $O$  assume their own equilibrium configuration, i.e., the most probable one. The first of the two maxima has lower energy than the second one, because it is related to the equilibrium configuration of the occupied electron state; the second one has higher energy than the first one because it relates to the equilibrium configuration of the unoccupied electron state; in addition, the values of the density of the corresponding quantum states  $D_{EL}(E_R)$  and  $D_{EL}(E_O)$  are proportional to the concentration of the reduced and oxidized species, respectively.

Gerischer has shown that Fermi's function relating to the probability of occupation is valid also in this case: Fermi's level, which must represent the energy level occupied to an extent of 50%, will thus have a value depending on the concentration ratio.

In conclusion, as is also seen in the figures, where Fermi's level  $E_{F,EL}$  is also indicated, the electrolyte has a structure with two superimposed bands, of which the band of lower energy concerns the occupied energy levels (crosshatched area) and the other concerns unoccupied levels.

#### Exchange Equilibrium Condition

When the electrode is placed in contact with the solution and the equilibrium conditions has been reached, i.e., the

electrode voltage  $\epsilon$  is equal to the equilibrium voltage  $\epsilon_0$  and a Galvani voltage is established between the electrode and electrolyte for which the corresponding Fermi levels become equal to (see Figs. 3b and 4b):

$$E_{F,M} = E_{F,E1}$$

and, respectively:

$$E_{F,S} = E_{F,E1}.$$

Since the electrons' Fermi level corresponds to the electrochemical potential of the electrons in the phase under study, the above relationship expresses the electrochemical equilibrium as the equality of the electrochemical potential of the electrons in the electrode and in the electrolyte.

The Galvani voltage that has been established between the two phases in contact is almost completely localized, for metals, in the Helmholtz double layer or, in the case of dilute solutions, which are not considered here, partially also in the diffuse double layer in the interior of the solution<sup>2</sup>, while, on the other hand, for nondegenerated semiconductors, it is almost completely localized in the diffuse double layer inside the semiconductor itself.

This happens because, as we have seen, the concentration of holes in the valency band is rather low in nondegenerated semiconductors<sup>3</sup>, as is the concentration of electrons in the conduction

<sup>2</sup> As is known, the double layer at the electrode-electrolyte interface is formed by the Helmholtz double layer, in which chemical forces with short action range are acting, and of the diffuse double layer in which Coulombian forces with long range are acting.

<sup>3</sup> Since the vacancy of an electron (i.e., a quantum state not occupied by the electron) in the valency band behaves like a moving carrier of positive charge, it is handled as a second type of charge carrier called a hole or gap.

band, so that next to the electrode surface in contact with the electrolyte a region forms, called the region of space charge, wherein the values of the holes and electron concentration also differ substantially from the value that it takes inside the electrode.

Thus the energy levels corresponding to the surface of a semiconductor in contact with the electrolytic solution are displaced very slightly relative to the case when the semiconductor was isolated, while the occupation of the quantum states near the surface may be substantially changed, according to the value of the Galvani voltage localized within the space charge region.

In a metal (or in a degenerate semiconductor) in contact with the electrolyte, the opposite takes place: the energy levels are substantially displaced, because almost the whole Galvani voltage is localized within the Helmholtz double layer, while the electron distribution near the electrode's surface changes very little. /442

As we pointed out at the beginning of this review, during an anodic process, tunneling of electrons occurs from an occupied quantum state in the electrolyte to an unoccupied one, having the same energy, in the electrode. Thus, the partial anode current  $i_+$  will be proportional to the density of the occupied quantum states in the electrolyte and of the unoccupied quantum states in the electrode, with the same energy. The proportionality coefficient will be closely bound to the frequency with which the electrons make the transitions. For the partial cathodic current  $i_-$ , the reverse is true: it will be proportional to the density of the occupied quantum states in the electrode and of the unoccupied quantum states in the electrolytes, with the same energy.

Under equilibrium conditions, the partial anodic and cathodic current are, as is known, equal to each other and to the exchange current.

In the case of a metal, we have:

$$i_+ = i_- = i_0.$$

Concerning a metal, in Fig. 3b (diagram on the right side; abscissa: current intensity; ordinate: energy), the product of the density of quantum states and of the quantum mechanics frequency factor for tunneling corresponding to each energy value are given. The integral of these products relative to energy, i.e., the area under the curve, corresponds to the exchange energy.

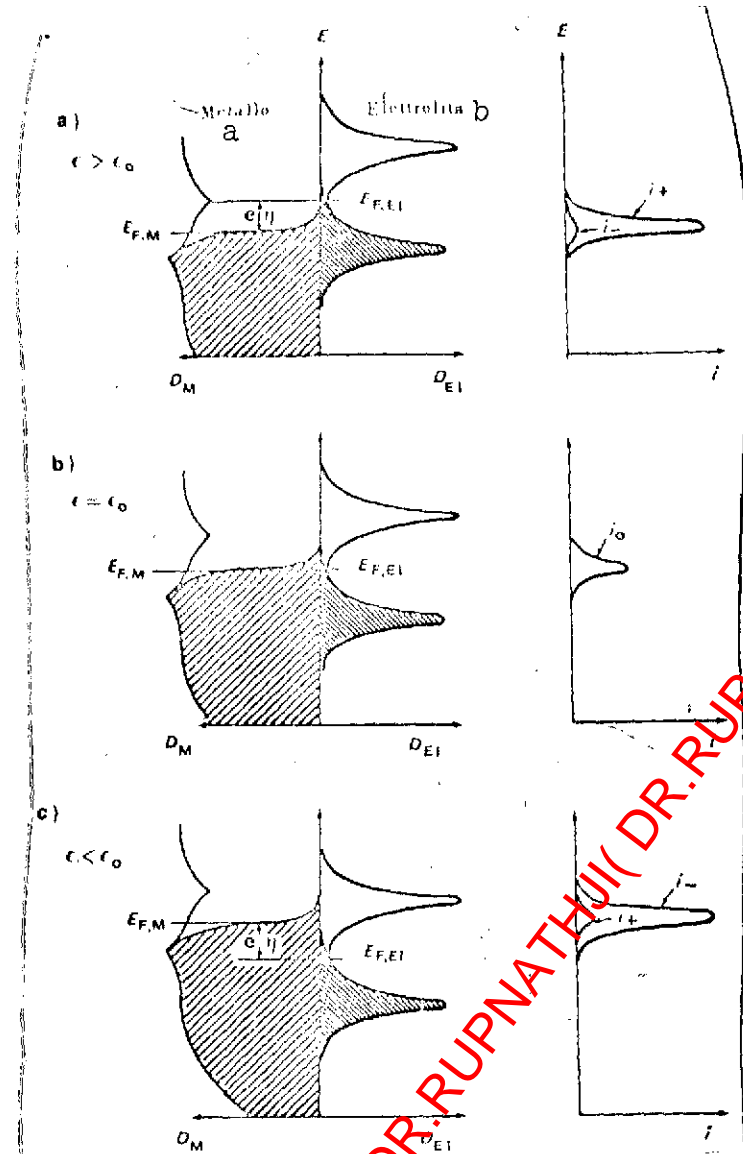


Fig. 3. Distribution of energy levels and their occupation by electrons for a metal in contact with an electrolyte containing an oxidation-reduction system and anodic and cathodic currents as a function of energy, when the electrode voltage is higher (anodic polarization) (a), equal to (b), and lower (cathodic polarization) (c) than the equilibrium voltage (from Gerischer [5,6]).

Key: a. Metal; b. Electrolyte

As Gerischer [8] has deduced, based on simple considerations, the exchange currents for the oxidation-reduction reactions are much higher for metals than for semiconductors. This is essentially due to the fact that in semiconductors the Fermi



level is within the forbidden energy band (Fig. 2), so that no electron exchanges can take place around this energy value, while, on the other hand, in metals the exchange occurs just in an interval of energy values centered around the Fermi level, where the density of quantum states is high.

The exchange reaction thus occurs in a semiconductor only under the edge of the valency band and above the edge of the conduction band; therefore, two exchange currents are observed for it; the one relating to the valency band may also be described as being due to the exchange of holes.

In the formulation of the oxidation-reduction process, it is in fact possible to distinguish two mechanisms involving holes and electrons, respectively [3, 7], i.e., the mechanism with hole transfer:



(where  $\ominus$  indicates a hole) and the mechanism with electron transfer already examined:



It follows that for a semiconductor in general, two exchange currents may be distinguished (Fig. 4b):

$$i_{p,o} = i_p^+ = i_p^-$$

$$i_{n,o} = i_n^+ = i_n^-$$

the first of which relates to the exchange of holes with the valency band (and precisely the anode current corresponds to the transfer from the valency band to the electrolyte, and the cathodic current to the transfer from the electrolyte to the valency band), and the second to the exchange of electrons with the

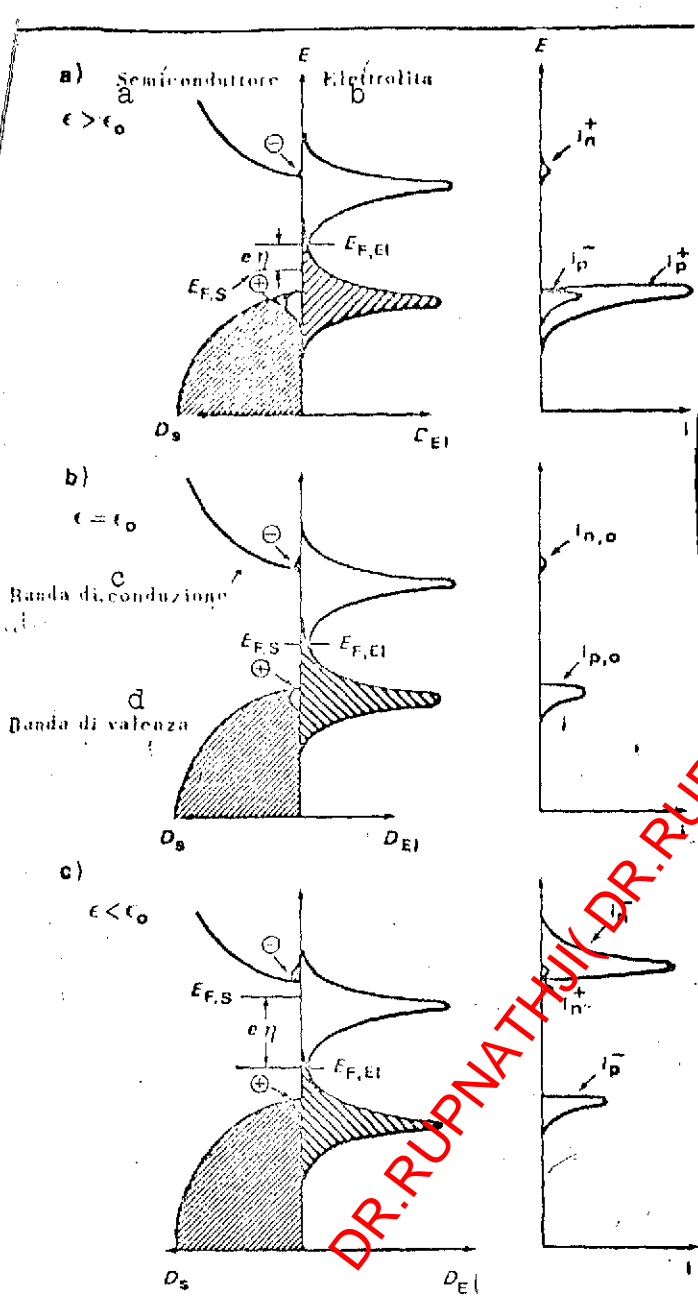


Fig. 4. Distribution of energy levels and their occupation by electrons for a semiconductor in contact with an electrolyte containing an oxidation-reduction system and anodic and cathodic partial currents as a function of energy, when the electrode voltage is higher (anodic polarization) (a), equal to (b) and lower than (c) the equilibrium voltage (from Gerischer [5,6]).

Key: a. Semiconductor; b. Electrolyte; c. Valency band; d. conduction band

conduction band (the anode current corresponds to the transfer into the conduction band and the cathode current from the conduction band).

The total exchange current is the sum of the exchange currents of holes and electrons.<sup>4</sup>

Gerischer has determined that the deciding factor, capable of controlling the

<sup>4</sup>If the forbidden band at the semiconductor's surface is sufficiently broad (more than about 0.5 eV) either only one of the two exchange currents is practically observed, or none. There is however the possibility of existence of a third exchange current, when the presence within the forbidden band of energy levels due to foreign substances (additives) or to surface effects causes an electron exchange at the energy level of these levels. In this case, it is possible that the surface layers may be the only ones giving a non-negligible exchange current.

predominant exchange mechanism type at equilibrium conditions, is given by the following difference

$$E_{F,EZ} - (iE_{F,S} - e\Delta\phi_{H,O})$$

i.e., by the difference between the Fermi level of the oxidation-reduction system and the Fermi level of the isolated semiconductor, assumed to be intrinsic<sup>5</sup>.  $iE_{F,S}$  is displaced by the amount  $-e\Delta\phi_{H,O}$ , where  $e$  represents the absolute value of the electron charge and  $\Delta\phi_{H,O}$  represents the Galvani voltage localized in the Helmholtz double layer under equilibrium conditions. The last term takes into account the displacement of the energy levels corresponding to the semiconductor's surface as a consequence of the establishment of the Galvani voltage in the Helmholtz double layer, and, due to the reasons already cited, is very small if the semiconductor is not degenerate. /443

Let us now assume that we are considering a similar semiconductor in contact with two different oxidation-reduction systems (Figs. 5 and 6). From the above relationship, it can be deduced that when the electrolyte's Fermi level is very low, so that  $E_{F,EZ} < iE_{F,S} - e\Delta\phi_{H,O}$ , under equilibrium conditions, the exchange of holes with the valency band (Fig. 5) is predominant, while when the Fermi level in the electrolyte is very high, so that  $E_{F,EZ} > iE_{F,S} - e\Delta\phi_{H,O}$  under equilibrium conditions, the exchange of holes within the conduction band predominates (Fig. 6).

If the two oxidation-reduction systems just considered are compared with each other, it is immediately seen that the first is more oxidizing than the second. In fact, since the Fermi level of the first system is lower than that of the second one, the average energy required to remove the electrons from the occupied states

<sup>5</sup> As is known, an intrinsic semiconductor (isolated and pure) has the same number of holes in the valency band of electrons in the conduction band.

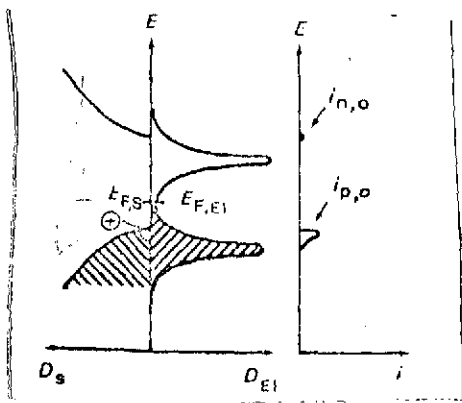


Fig. 5. Charge transfer process at equilibrium between a semiconductor and a strongly oxidizing oxidation-reduction system (from Gerischer [8]).

and to bring them into vacuum, at infinity is higher in the first case than in the second one, i.e., the course of the anodic process is more difficult in the first system than in the second one, and thus the first system is more oxidizing.

In addition, since the Fermi level of the electrolyte depends on the concentration of the reduced species ( $c_R$ ) and of the oxidized species ( $c_O$ ), according to the following relationship:

$$E_{F,EI} = E_{F,EI}^0 + kT \log c_R/c_O,$$

an increase in the concentration of the reduced species relative to that of the oxidized species favors the exchanges in the conduction band.

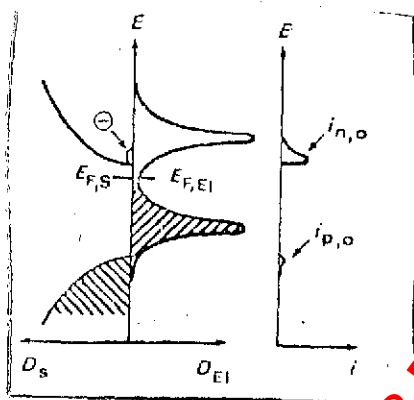


Fig. 6. Charge transfer process at equilibrium between a semiconductor and a strongly reducing oxidation-reduction system (from Gerischer [8]).

On the other hand, a variation of the doping does not change the predominating type of exchange mechanism (even though the position of the Fermi level can vary substantially), since it does not play an essential role in the position of energy levels corresponding to the electrode surface, which are the determining ones in exchanges with one band or the other.<sup>6</sup>

<sup>6</sup> Indeed, the exchange current is also independent of the semiconductor's doping.

## Anodic and Cathodic Polarization

When the electrode is polarized, for example, anodically, the electrode voltage becomes greater than the equilibrium voltage, i.e.,  $\epsilon > \epsilon_0$ , and there is an accumulation of positive charges, i.e., of holes, in the electrode relative to the electrolyte, and thus the Fermi level of the metal or of the semiconductor, which is by definition equal to the 50% filled energy level, becomes less than the electrolyte's Fermi level by an amount proportional to the overvoltage  $\eta = \epsilon - \epsilon_0$ , i.e.

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$$E_{F,M} = E_{F,E} - e\eta$$

and, respectively,

$$E_{F,S} = E_{F,E} + e\eta$$

This formula is valid also in the case when the electrode is cathodically polarized, since in this case the value of the overvoltage is negative: the Fermi level of the electrode will then be higher than that of the electrolyte.

Let us now consider Fig. 3 again, relating to a metal: in Fig. 3b, the case which we have already seen is considered, in which the electrode voltage is equal to the equilibrium voltage; in Fig. 3a the case is considered in which the electrode has been anodically polarized, and in Fig. 3c, the case in which it has been cathodically polarized. In these two latter cases, it is seen that the entire band is displaced by the same amount and in the same direction as the Fermi level, i.e., downward after anodic polarization and upward after cathodic polarization.

This also occurs because, as we have said, in the Galvani voltage of the metal, and thus the overvoltage, is almost entirely localized in the Helmholtz double layer, so that:

$$\eta \simeq \eta_H = \Delta\phi_H - \Delta\phi_{H,0}$$

(where  $\Delta\phi_H$  and  $\Delta\phi_{H,0}$  represent the Galvani voltage localized in the Helmholtz double layer in conditions respectively far from and near equilibrium), and, since the establishment of a Galvani potential  $\phi$  in a phase uncharged and at infinity, relative to vacuum, involves displacement by  $-\epsilon\phi$ <sup>7</sup> of the electrons' energy levels.

The displacement of the energy levels of the metal phase relative to those of the electrolytic solution, when going from case  $\epsilon = \epsilon_0$  to case  $\epsilon \neq \epsilon_0$ , must thus be equal to the variation of the metal-electrolyte Galvani potential difference, when going from the equilibrium condition to the nonequilibrium condition, i.e., equal to  $\Delta\phi_H - \Delta\phi_{H,0} = \eta$ .

In conclusion, there will be a displacement of energy levels of the metal relative to those of the electrolyte equal to a  $-\epsilon\eta$ .

Once again, the behavior of a nondegenerate semiconductor is different (Figs. 4a and c): while the Fermi level is displaced after polarization by an amount  $-\epsilon\eta$  (as in metals), the energy levels (and thus the edges of the valency and conduction bands) corresponding to the semiconductor's surface are displaced relative to those of the electrolyte, only by  $-\epsilon\eta_H$ .

If we indicate by  $\eta_H$  the overvoltage localized in the Helmholtz double layer and by  $\eta_C$  that overvoltage in the space charge region, we have

$$\eta = \eta_H + \eta_C = \Delta\phi_H - \Delta\phi_{H,0} + \Delta\phi_C - \Delta\phi_{C,0}$$

<sup>7</sup> The minus sign appears because if, for example, the phase becomes positive, more work must be done to extract the electrons; i.e., the corresponding energy levels have been displaced downward.

and

$$|\eta_c| \gg |\eta_a|$$

Thus the greatest effect brought about by a polarization, anodic for instance, consists of increasing the concentration of holes in the valency band at the surface of the semiconductor and of decreasing that of the electrons in the conduction band, while the relative position of the energy levels (electrode-electrolyte) is changed very little (Fig. 4a).

The opposite takes place after cathodic polarization (Fig. 4c).

In Figs. 3 and 4 the partial anodic and cathodic currents as a function of the energy values are also given. Since, as we have stated several times, the partial anodic current is proportional to the density of quantum states with the same energy occupied in the electrolyte and empty in the solid, while the opposite holds true for the partial cathodic current, when the overvoltage is positive, the partial anodic current is greater, and when it is negative, the cathodic partial current is greater. For a metal, two partial currents can be distinguished, corresponding to each overvoltage value: anodic  $i_+$  and cathodic  $i_-$ ; for a semiconductor, four can be distinguished: two partial anodic,  $i_p^+$  and  $i_n^+$ , and two partial cathodic,  $i_p^-$  and  $i_n^-$ .

For a semiconductor, it is further possible to change the predominant transfer mechanism by polarizing it adequately, as has been shown by Gerischer [7, 8] in his mathematical treatment. This can be very well visualized with the examples given by Gerischer, examples which are now commonly used, since they are often quoted by many authors (for instance by Boddy [16]).

Let us consider the semiconductor-electrolyte system, depicted in Fig. 6, for which, at equilibrium conditions, the electron exchange with the conduction band predominantly takes place, and let

us polarize it anodically. When the voltage change is small, the transfer of electrons into the conduction band still predominates, although the partial cathodic transfer current  $i_n^-$  is strongly decreased relative to its value at equilibrium, due to the decrease of surface concentration of electrons brought about by displacement of the Fermi level. When the voltage is further increased, a change of the main transfer mechanism is observed, because, as is seen in Fig. 7, the transfer of holes from the

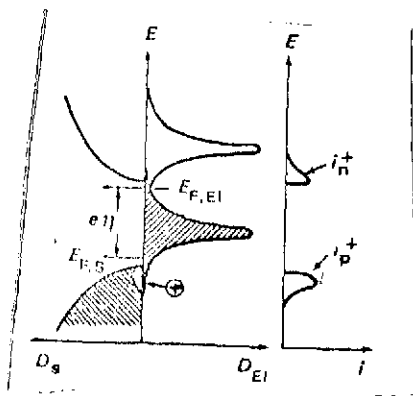


Fig. 7. Charge transfer process between the semiconductor and the strongly reducing oxidation-reduction system, represented at equilibrium conditions in Fig. 6, due to high anodic polarization (from Gerischer [8]).

valency band to the electrolyte  $i_p^+$  becomes predominant. When the voltage increase is high enough to cause degeneration of the semiconductor at its surface (Fig. 8), an increasing part of the voltage is localized in the Helmholtz double layer, and the energy levels are displaced toward values that are so negative that the valency band falls in a region of energy values where there are no energy levels of the electrolyte. The transfer of electrons into the conduction band then becomes predominant, in spite of the high number of holes in the valency band.

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When the semiconductor is cathodically polarized, for small voltage variations (Fig. 9) we have electron transfer from the conduction band to the electrolyte still predominating, with a gradual increase of  $i_n^-$ ; for large variations (Fig. 10), for which the semiconductor becomes degenerate at its surface, the displacement of the semiconductor's energy levels toward less negative values is so large that the transfer of holes in the valency band becomes predominant, since there is no longer an overlapping of the energy levels of the conduction band with those of the electrolyte.



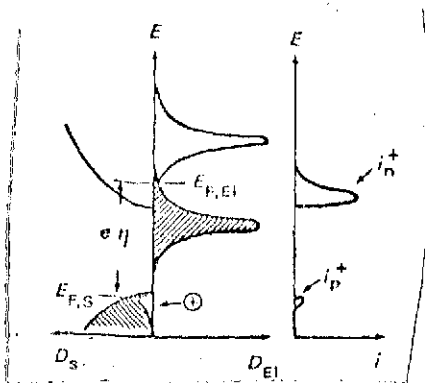


Fig. 8. Charge transfer process between the semiconductor and the strongly reducing oxidation-reduction system, represented under equilibrium conditions in Fig. 6, due to a very high anodic polarization (from Gerischer [8]).

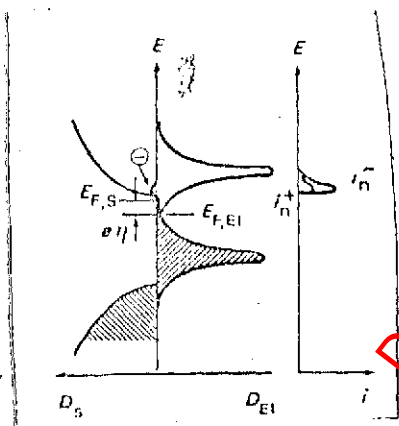


Fig. 9. Charge transfer process between the semiconductor and the strongly reducing oxidation-reduction system, represented at equilibrium in Fig. 6, due to a small cathodic polarization (from Gerischer [8]).

These results may thus be summarized and extended to the case of a semiconductor which at equilibrium conditions exchanges holes predominantly with the valency band: near equilibrium, the transfer takes place, when the current is circulating, at the band for which the exchange current is higher; a further polarization (without reaching surface degeneration conditions) favors, relatively, the transfer of holes from the valency band, if it is anodic, or the transfer of electrons from the conduction band, if it is cathodic; a high polarization with strong degeneration, on the other hand, leads to transfer of electrons in the conduction band, if it is anodic, and to transfer of holes in the valency band, if it is cathodic.

### Limiting Currents

In the course of the above considerations, we have assumed that the partition of the carriers in the semiconductor can be treated as if it were at equilibrium, in spite of current circulation. This means that the supply or elimination of the carriers from the surface takes place so fast that current circulation does not cause a change of their concentration in the surface layer. However, this does not

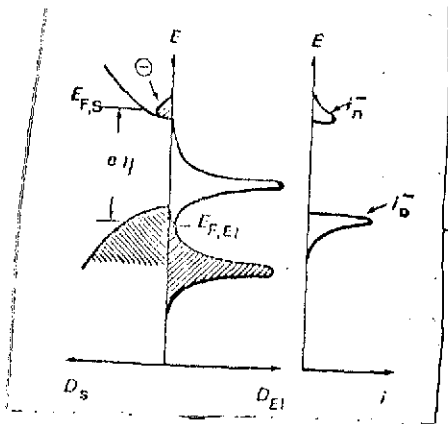


Fig. 10. Charge transfer process between the semiconductor and the strongly reducing oxidation-reduction system, represented at equilibrium in Fig. 6, due to a very high cathodic polarization (from Gerischer [8]).

occur in every case. For instance, if a semiconductor of type n is anodically polarized, when the oxidation process takes place predominantly with transfer of holes from the valency band to the electrolytes, the limited supply of holes from the interior may lead to circulation of a limiting current, the so-called saturation current [8], which cannot be further increased without increasing the concentration of the holes, for example, by exposing the sample to light. Indeed, electron transport out of the space charge area takes place by electric transport, while that of holes, minority carriers, is mainly controlled by diffusion, and

thus the flow of holes from the inside of the semiconductor toward the space charge area will depend on their concentration difference, so that a limiting anodic current is anticipated when the hole concentration becomes zero at the boundary plane of the space charge area toward the inside of the semiconductor. It will thus be possible to define a hole transport overvoltage,  $\eta_{T,p}$ , representing the contribution of the hole transport to the overvoltage localized in the space charge area:

$$\eta_c = \eta_c^0 + \eta_{T,p}$$

where<sup>8</sup>

$$\eta_{T,p} = A \lg \left( 1 - i_p^+ / i_{p,sat}^+ \right)$$

It can be deduced from this latter formula that when  $i_p^+ = i_{p,sat}^+$ , the overvoltage becomes infinite.

<sup>8</sup> For typographic reasons,  $2.3 kT/e$  has been indicated by A.

A similar situation occurs for a semiconductor of type p cathodically polarized, when the reduction process takes place predominantly with transfer of electrons from the electrolyte's conduction band. The limited supply, in this case of electrons, from the interior to the surface may lead to a cathodic saturation current  $i_{n,sat}^-$ . Analogously with the previous case, we can then define an electron transport overvoltage  $\eta_{T,n}$ .

Both in metals and in semiconductors it is further possible to observe an overvoltage due to transport by diffusion in the electrolyte of the species taking part in the reaction,<sup>9</sup> i.e., due to transport in the liquid layer located near the electrode's surface and practically still even when the electrolyte is stirred. It will thus be possible to reach a limiting current when, at the electrode surface, the concentration of the reduced species will become zero during an anodic process (limiting anodic current) and that of an oxidized species during a cathodic process (cathodic limiting current).<sup>10</sup>

### Overvoltage-Current Curves

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Fig. 11 (curves  $i_+$  and  $i_-$ ) depicts the course of the overvoltage as a function of the decimal logarithm of the partial anodic and cathodic currents for a metal. At the value  $\eta = 0$ , there is equilibrium, where the two partial currents become equal to the exchange current. The course is linear, and the two curves are symmetrical, this being a consequence of the choice of the value of  $\alpha$ , as well shall now see.

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<sup>9</sup> It is of no interest for the present purposes, and we shall assume that it is negligible in the cases considered.

<sup>10</sup> In the case of a semiconductor, this limiting current is easily distinguishable from the saturation currents, since it does not increase when the sample is exposed to light.

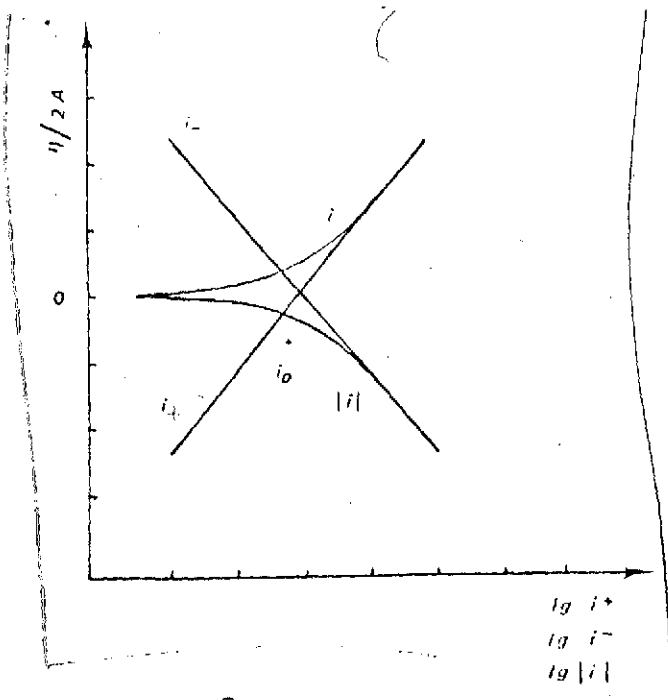


Fig. 11. Dependence of overvoltage from partial currents: anodic ( $i_+$ ) and cathodic ( $i_-$ ) and from the resulting currents ( $i$ ) for a charge transfer process between a metal and an oxidation-reduction system ( $\alpha = 0.5$ ).

Gerischer [6] has indeed calculated that, with some approximations concerning the density of quantum states of the metal and the electrolyte and the frequency with which the electrons make the transitions, the slopes of the curve are equal to:

$$\frac{d\eta}{d \lg i_+} = A/\alpha \quad ; \quad \frac{d\eta}{d \lg i_-} = -A/(1 - \alpha)$$

where  $\alpha$  represents the transfer coefficient for the partial anodic reaction: it has an approximately constant value when the overvoltage

varies; between 0 and 1, it is equally equal to 0.5.<sup>11</sup>

The same result might have been reached by the usual nonquantum-mechanics kinetic and electrochemical methods (see, for example, the textbooks by Vetter [7] and Bockris [18]).

These methods assume that the reaction rate (partial current) depends on the activation energy of the process,<sup>12</sup> i.e., on the energy difference between the initial energy level and the energy level corresponding to the maximum of the energy barrier, located

<sup>11</sup> In Fig. 11 it has been assumed that  $\alpha = 0.5$ .

<sup>12</sup> More precisely, the electrochemical free activation enthalpy.

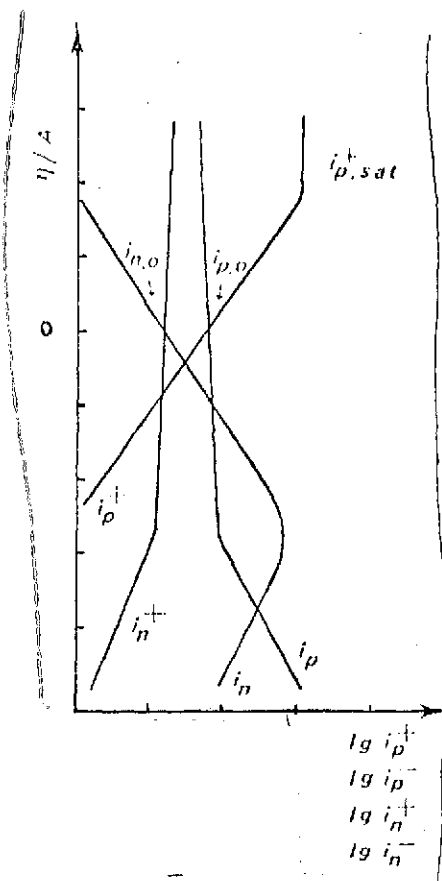


Fig. 12. Dependence of overvoltage from the transfer current of holes ( $i_p^+$ ,  $i_p^-$ ) and of electrons ( $i_n^+$ ,  $i_n^-$ ) for a charge transfer process between a type n semiconductor and an oxidation-reduction system which, at equilibrium, exchanges predominantly holes with the valency band (from Gerischer [8]).

/logarithmic unit at 25°C, when  $\alpha = 0.5$ ), only at overvoltage values for which the contribution of the anodic, or, respectively, cathodic, process is negligible. The slope of this straight line

in the Helmholtz double layer, which the electron must overcome in order that the products may be formed. The activation energy depends in its turn on the overvoltage, since the transfer, for example, of an electron from the electrolyte to the metal, as happens during an anodic process, intuitively is faster when the metal is more positive relative to the electrolyte. The variation of reaction rate with changes of overvoltage must thus be attributed to the variation of activation energy of the barrier, and  $\alpha$ , the symmetry factor of the barrier (when it is equal to 0.5, the barrier is symmetrical) takes into account the shape of the potential barrier, i.e., of the distribution of the contribution of overvoltage between the anodic and cathodic processes.

Fig. 11 also depicts the law of dependence of overvoltage from the resulting current  $i$  (equal to the difference between the anodic and cathodic partial currents), the only one that is observed experimentally. The course is linear<sup>13</sup>, with a slope equal to  $A/\alpha$  and to  $-A/(1 - \alpha)$  (i.e.  $\pm 118$  mV/

<sup>13</sup> That is, Tafel's law is valid.

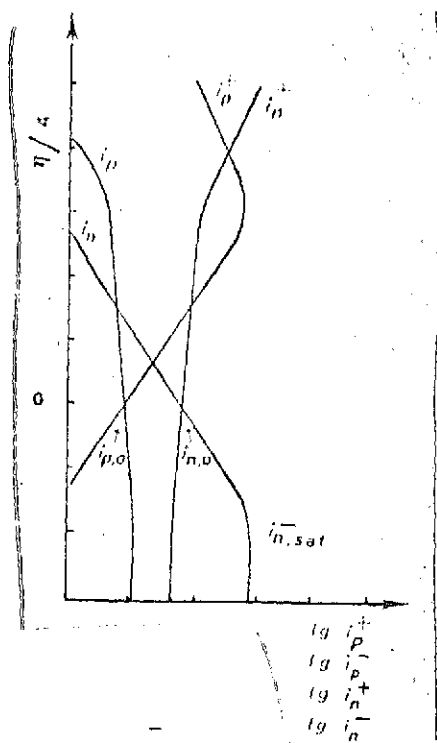


Fig. 13. Dependence of overvoltage from the hole transfer currents ( $i_p^+$ ,  $i_p^-$ ) and electron transfer currents ( $i_n^+$ ,  $i_n^-$ ) for a charge transfer process between a semiconductor of type p and an oxidation-reduction system which, at equilibrium, exchanges predominantly electrons with the conduction band (from Gerischer [8]).

and its intersection with the straight line  $\eta = 0$  permit us to obtain, respectively, the value of the transfer coefficient and of the exchange current.

Let us now look at the results concerning a semiconductor.

Fig. 12 depicts the overvoltage curves as a function of the decimal logarithm of the partial currents for a semiconductor of type n, which, at equilibrium conditions, exchanges predominantly holes with the valency band. Fig. 13 illustrates the behavior of a semiconductor of type p, which, at equilibrium conditions, exchanges predominantly electrons with the conduction band.

As can be seen from the figures, which are Gerischer's [8], the course is usually linear, as we have seen for metals, but the slope changes and the saturation currents are possible.<sup>14</sup>

Gerischer [7] has determined the expressions of overvoltage as a function of the partial currents when the

<sup>14</sup> Examination of Figs. 12 and 13 permits us to find the results already obtained on the manner in which the predominant transfer mechanism varies with polarization. For instance, when  $i_{p,0} > i_{n,0}$  (Fig. 12) with anodic polarization, the transfer of holes keeps predominating, while with cathodic polarization the hole transfer predominates at first, and eventually electron transfer will predominate.

semiconductor is not degenerate and when the distribution of the carriers inside the semiconductor itself may be considered to be at equilibrium. In particular, for the slopes he found that:

$$\left. \begin{aligned} \frac{d\eta}{d \lg i_p^+} &= A/(1 - \beta) & ; & & \frac{d\eta}{d \lg i_p^-} &= -A/\beta \\ \frac{d\eta}{d \lg i_n^-} &= -A(1 - \gamma) & ; & & \frac{d\eta}{d \lg i_n^+} &= A/\gamma \end{aligned} \right\}$$

where  $\beta$  and  $\gamma$  are very complex expressions, equal to the product of two factors, one of which is the derivative  $d\eta_H/d\eta$ .

As long as the semiconductor is not degenerate, the variation of overvoltage in the Helmholtz double layer with the variation of the total overvoltage is negligible, as we have seen: consequently, the above derivation becomes very small and thus  $\beta$  and  $\gamma$  become much less than 1. As a consequence of this (see Figs. 12 and 13), the slopes of the curves  $\eta(i_p^+)$  and  $\eta(i_n^-)$  become respectively equal to  $A$  and  $-A$  (i.e., to  $\pm 59$  mV/logarithmic unit, at  $25^\circ\text{C}$ ), while those of curves  $\eta(i_p^-)$  and  $\eta(i_n^+)$  are much larger (in absolute values). The result is again reached that when the overvoltage is changed, the rates of the partial anodic processes in the valency band ( $i_p^+$ ) and cathodic processes in the conduction band ( $i_n^-$ ) vary much more than the rates of the opposite processes.

In Figs. 14 and 15, the curves of overvoltage vs. current relative to the resulting exchange of holes in the valency band and of electrons in the conduction band are given by the solid line, respectively, in the case where  $i_{p,0} > i_{n,0}$  and  $i_{p,0} < i_{n,0}$ , evidencing doping of the semiconductor with the letters  $p$  and  $n$ . The dashed line represents the course of the resulting current and corresponds to the curve that should be observed experimentally in the hypothesis that the diffusion overvoltage is negligible.

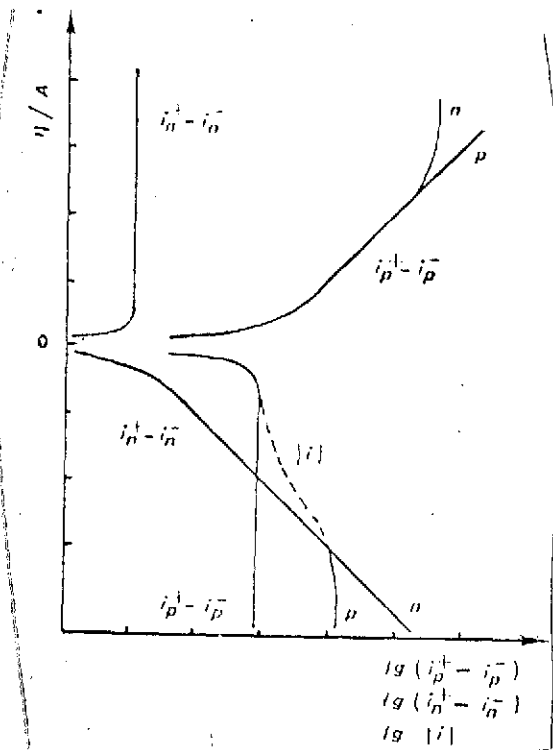


Fig. 14. Dependence of overvoltage from the currents in relation to the resulting hole transfer ( $i_p^+ - i_p^-$ ) and electron transfer ( $i_n^+ - i_n^-$ ) (solid lines) and from the resulting current ( $i$ ) (dashed line) for a charge transfer process between a type p or n semiconductor and an oxidation-reduction system that, at equilibrium, exchanges predominantly holes with the valency band (from Gerischer [9]).

The figures are self-explanatory on the basis of what we have already seen. It is only appropriate to observe here that if, near the equilibrium voltage,  $b_a < b_c$  (or  $b_c < b_a$ ), where  $b_a$  and  $b_c$  represent the absolute value of the slope of the linear portion (Tafel slope), respectively, anodic and cathodic, of the resulting curve, the transfer under equilibrium conditions takes place predominantly in the valency band (or in the conduction band).<sup>15</sup> In addition, when a high value cannot be reached, which would make it possible to observe the saturation currents, if the portion of the curve far from equilibrium voltage (where both bands contribute)  $b_a < b_c$ , the semiconductor is of type p; otherwise, it is type n.

#### Interpretation of Experimental Results

In the preceding parts of this review, we have discussed the theory by means of which the oxidation-reduction reactions taking place on metals and semiconductors are studied. Let us now

<sup>15</sup> This result follows from neglecting the contribution of one of the two bands.



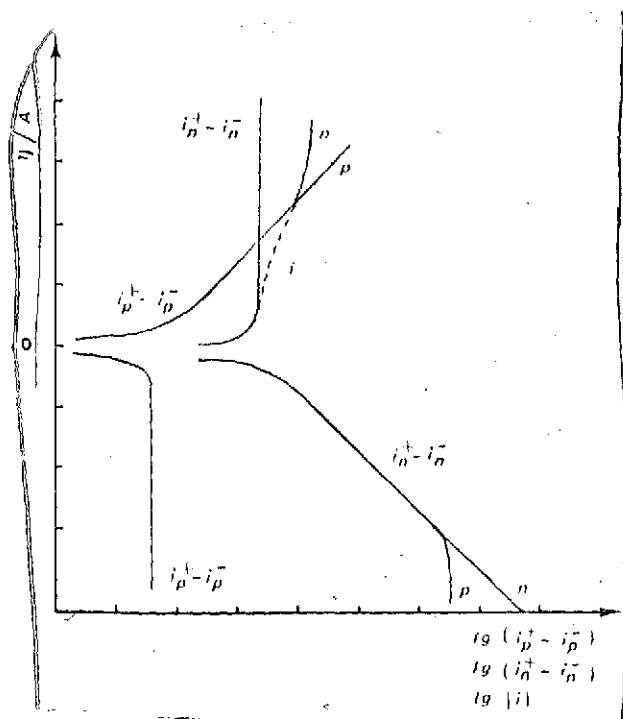


Fig. 15. Dependence of overvoltage from the currents relating to the resulting hole transfer ( $i_p^+ - i_p^-$ ) and electron transfer ( $i_n^+ - i_n^-$ ) (solid lines) and from the resulting current ( $i$ ) (dashed line) for a charge transfer process between a type p or n semiconductor and an oxidation-reduction system which, at equilibrium, exchanges predominantly electrons with the conduction band (from Gerischer [9]).

examine the more important experimental results obtained by various authors, which best confirm the theoretical predictions.

First of all, while the results relating to oxidation-reduction reactions in metals are very numerous [17] (even if their interpretation is often complicated by superposition of diffusion phenomena in solution [19-23]), those

on semiconductors are rather scarce [9]. In practice, most of the determinations have been made with germanium, in which, however, the processes of anodic solution and cathodic hydrogen evolution are superposed on the reaction studied, or with semiconductors having a broad band of forbidden energy, for which practically

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only one of the two processes can be observed, the anodic one when they are type p, such as nickel oxide, and the cathodic one when they are type n, such as zinc oxide, cadmium sulfate and potassium tantalate.<sup>16</sup>

<sup>16</sup> Recently, some semiconductors with broad bands have been obtained, such as SiC and GaP, which may be either type p or n.

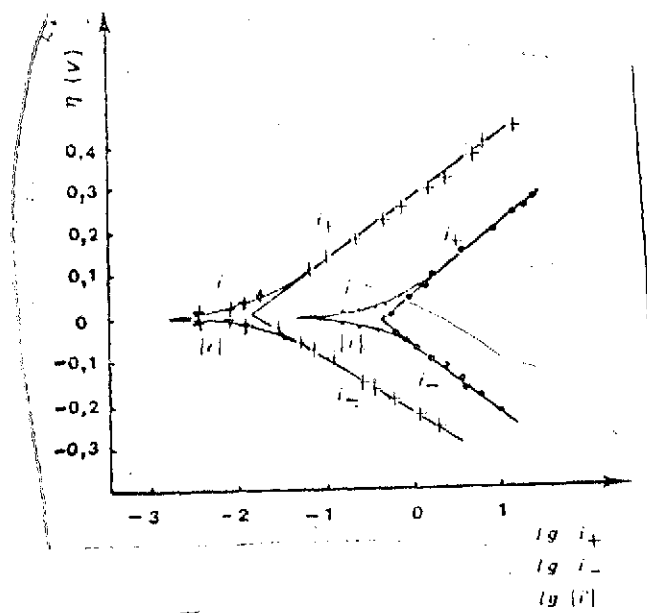


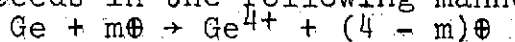
Fig. 16. Dependence of overvoltage from anodic ( $i_+$ ) and cathodic ( $i_-$ ) partial currents and from the resulting current ( $i$ ) for the oxidation-reduction reaction  $Ti^{4+}/Ti^{3+}$  on mercury at  $25^\circ C$ . Composition of solutions (●)  $Ti^{4+}$  0.21 M +  $Ti^{3+}$  0.017 M +  $H_2SO_4$  1 M. (+)  $Ti^{4+}$  0.17 M +  $Ti^{3+}$  0.03 M +  $H_2SO_4$  1 M (from Essin [24]).

Fig. 16 gives the results obtained by Essin [24] on the law of dependence of overvoltage from the partial currents and from the resulting current for the oxidation-reduction reaction  $Ti^{4+}/Ti^{3+}$  on a mercury electrode. There is satisfactory, although not perfect, agreement with the deductions from the above theoretical analysis (Fig. 11), since the absolute value of the observed slopes is between 134 and 155 mV/logarithmic unit<sup>17</sup> (instead of being equal to 118 mV/logarithmic unit) for anodic straight lines, and between 113 and 144 mV for the cathodic ones.

Beck and Gerischer [25] have utilized the limiting current which is observed during anodic dissolution of germanium in acid solution<sup>18</sup> of type  $n$  semiconductors as an index of the mechanism of a superimposed oxidation-reduction reaction. Indeed, when the reduction of an oxidized system with transfer of holes from the electrolyte to the valency bands, as in the case of the reduction reaction of the  $Ce^{4+}$  ion to  $Ce^{3+}$  (Fig. 17), is superposed on the solution reaction, an increase of the limiting current is

<sup>17</sup> Determinations have been made at  $25^\circ C$ .

<sup>18</sup> That reaction proceeds in the following manner:



where  $2 < m < 4$ , i.e., it consumes holes and produces electrons.

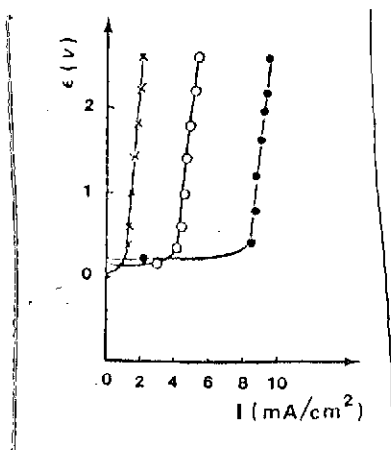


Fig. 17. Dependence of voltage vs. a calomel electrode from the current density for germanium of type n in  $\text{H}_2\text{SO}_4$  0.5 M (x), in  $\text{H}_2\text{SO}_4$  0.5 M +  $\text{Ce}(\text{SO}_4)_2$  0.02 M (o) and  $\text{H}_2\text{SO}_4$  0.5 M +  $\text{Ce}(\text{SO}_4)_2$  0.2 M (•) at  $25^\circ\text{C}$  (from Beck and Gerischer [25]).

observed<sup>19</sup>; on the other hand, when a concurrent reaction, also consuming holes, as in the case of the oxidation of ferrocyanide ions to ferricyanide, is superimposed, a decrease of the limiting current is observed (Fig. 18). In both cases, since the oxidation-reduction systems are strongly oxidizing, the reaction takes place in the valency bands<sup>20</sup>, while for poorly oxidizing systems, such as  $\text{V}^{3+}/\text{V}^{2+}$ , it takes place in the conduction band (see Fig. 19) where it is seen that the oxidation of the  $\text{V}^{2+}$  ion to  $\text{V}^{3+}$  brings about a strong increase of the limiting current (for type n germanium).

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In addition, these authors have been able to verify that the exchange currents of the oxidation-reduction reactions are higher for metal electrodes than for semiconductor electrodes.

For semiconductors having a very broad forbidden band, the experimental results are also in agreement with theory [4, 29-33].

In Fig. 20 the course of the voltage-current density curve for the cathodic reduction of ferricyanide ions to ferrocyanide at  $25^\circ\text{C}$  on a zinc oxide crystal is given as an example. The law is linear, with a slope equal to  $-59 \text{ mV}/\text{logarithmic unit}$ , in perfect agreement with theory, in the hypothesis that a variation

<sup>19</sup> The same results are obtained by studying the reaction of  $\text{Fe}^{3+}$  reduction on gallium arsenide of type n [26].

<sup>20</sup> Tomashov and co-workers [27] and Plěškov [28] have observed that strongly oxidizing systems such as  $\text{H}_2\text{O}_2/\text{H}_2\text{O}$  and  $\text{Fe}^{3+}/\text{Fe}^{2+}$  instead exchange electrons with the conduction band when the cathodic polarization is very high, in agreement with Gerischer's theory.

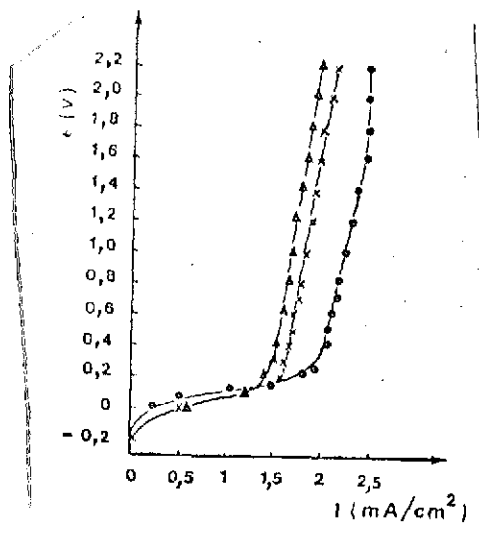


Fig. 18. Dependence of voltage vs. calomel electrode from the current density for type n germanium in  $\text{H}_2\text{SO}_4$  0.05 M (●),  $\text{H}_2\text{SO}_4$  0.05 M +  $\text{K}_4\text{Fe}(\text{CN})_6$  0.085 M (x) and  $\text{H}_2\text{SO}_4$  0.025 M +  $\text{K}_4\text{Fe}(\text{CN})_6$  0.140 M (▲) at  $25^\circ\text{C}$  (from Beck and Gerischer [25]).

of the Helmholtz double layer is negligible when the total voltage change ( $\beta = \gamma = 0$ ).

It has recently been found by Bianchi and colleagues [34] that oxide films<sup>21</sup> on stainless steel are semiconductors for which both oxidation and reduction processes may be observed.

Fig. 21 gives the overvoltage curves of the anodic and cathodic processes as a function of the current density for the oxidation-reduction reaction ferrocyanide-ferrocyanide, taking place on oxides formed at two different temperatures, representing the limiting current observed on platinum electrodes.<sup>22</sup>

The course of the curves is very similar to that pictured in Fig. 14, regarding a semiconductor of types p and n, which, at equilibrium conditions, exchanges predominantly holes with the valency band. Indeed, near the equilibrium voltage, it is possible, in both cases, to identify in the anodic branch a linear portion with slope about 60 mV/logarithmic unit, while for the cathodic branch, this slope is (in absolute values) much higher. This is in agreement with the theoretical predictions for a strongly

<sup>21</sup> These films are transparent, invisible to the naked eye, but of significant thickness, and have been found to be promoters of pitting corrosion [35]; their nature is poorly understood [31].

<sup>22</sup> For platinum, the exchange current density of the oxidation-reduction process is much higher than for semiconductor oxides, by a factor of about  $10^4$ - $10^5$  [21, 36], in agreement with theory.

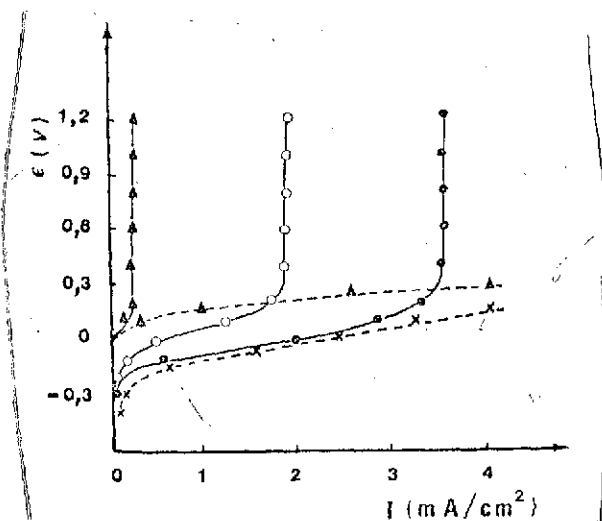


Fig. 19. Dependence of voltage vs. calomel electrode from the current density for type p germanium (dashed lines) and type n germanium (solid lines) in H<sub>2</sub>SO<sub>4</sub> 1 M (▲), in H<sub>2</sub>SO<sub>4</sub> 1 M + VSO<sub>4</sub> 0.017 M (○), and in H<sub>2</sub>SO<sub>4</sub> 1 M + VSO<sub>4</sub> 0.033 M (x and ●), at 25°C (from Beck and Gerischer [25]).

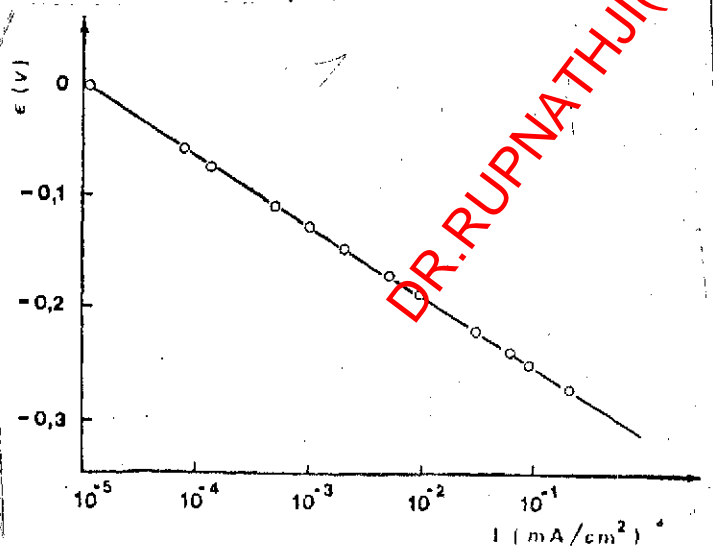


Fig. 20. Dependence of voltage vs. calomel electrode from current density for the oxidation-reduction reaction  $[\text{Fe}(\text{CH}_6)]^{3-7}/[\text{Fe}(\text{CH}_6)]^{4-}$  on zinc oxide at 25°C (from Dewald [4]).

oxidizing oxidation-reduction system, such as the one under consideration, when the contribution of the conduction band can be neglected. At higher current densities, where both bands contribute, a sharp differentiation is observed between the values of the anodic and cathodic slopes relating to the two films. Indeed, for the film formed at 300°C, the cathodic slope is (in absolute value) less than the anodic slope<sup>2,3</sup>, while for the one formed at 150°C, the opposite occurs, and the tendency to a cathodic

saturation current is less marked. If we keep in mind the previous treatment, there is no doubt that the conduction properties of the oxide films can be deduced from these results: the first of type n and the second of type p, respectively.

<sup>2,3</sup> In order not to compromise the integrity of the oxide film, it is not possible to reach very high absolute values of overvoltage.

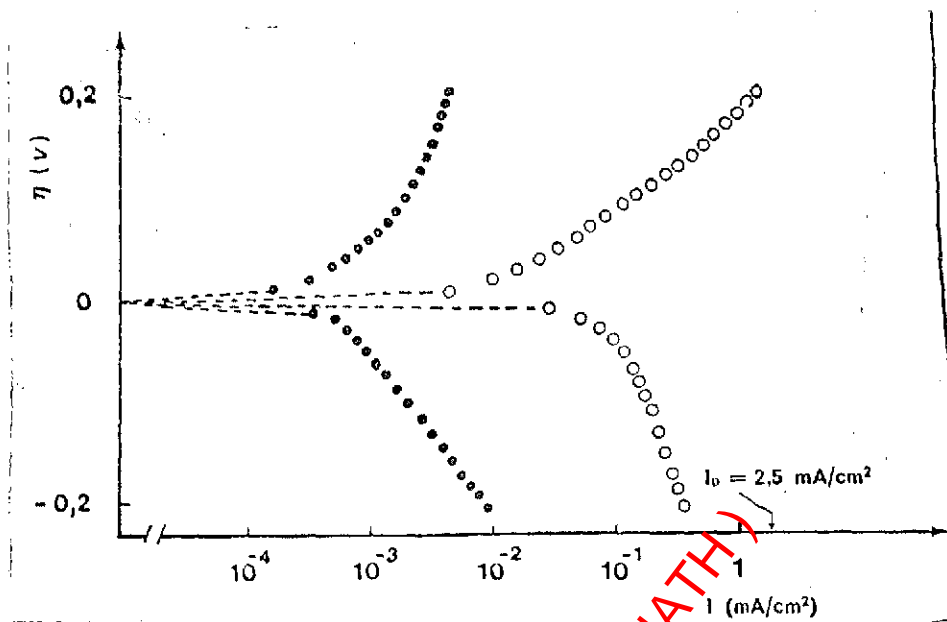


Fig. 21. Dependence of overvoltage from current density for the oxidation-reduction reaction  $[\text{Fe}(\text{CH})_6]^{3-} / [\text{Fe}(\text{CN})_6]^{4-}$  on an oxide film obtained by oxidation in dry air respectively at 300°C (●) and at 150°C (○) of a sample of austenitic stainless steel AISI 304 L. Temperature 25°C. Composition of the solution:  $\text{K}_3\text{Fe}(\text{CN})_6$  0.1 M +  $\text{K}_4\text{Fe}(\text{CN})_6$  0.1 M +  $\text{Na}_2\text{SO}_4$  0.5 M (from Bianchi [14]).

Bianchi and co-workers [34, 37-39] have further been able to establish a phenomenological correlation between conduction properties of oxide films and susceptibility to pitting attack: the type p film is the least susceptible; the type n film is the most susceptible to this type of corrosion. This has been interpreted to be due to the lack of stoichiometry of the film, i.e., to the existence in the type p film of metallic vacancies, and of anionic vacancies in the type n films<sup>24</sup>; these latter were the conditions for penetration of the chloride ions of the attacking solution into the film itself, and therefore for seeding the pittings.

<sup>24</sup> As is known, when the metallic vacancies are ionized, holes are injected into the valency band; when anionic vacancies are ionized, electrons are injected into the conduction band.

It has recently been found that copper oxide films are also poorly susceptible to pitting corrosion, contrary to those of type n [40].

### Conclusions

We have described in this review the manner in which it is possible to study the oxidation-reduction electrochemical reactions according to quantum-mechanics methods, when the electrodes on which these reactions take place are metals or semiconductors.

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After explaining that the charge transfer of an electron at the electrode-electrolyte interface occurs via a tunneling process between two quantum states of the same energy, we have reviewed the fundamental concepts relating to quantum state density and their occupation by electrons in metals, semiconductors and electrolytes containing an oxidation-reduction system in solution. For these latter types, the occupied electron states are represented by the reduced species, and the unoccupied states by the oxidized species.

When the electrode is immersed in the measuring solution and the electrode voltage is equal to the equilibrium voltage, the partial anodic and cathodic currents are equal to each other and to the exchange current; when the electrode voltage is higher than the equilibrium voltage, i.e., the overvoltage is positive, the anodic partial current is greater, and when the overvoltage is negative, the cathodic partial current is greater.

During the anodic process, transfer of electrons takes place from an unoccupied quantum state in the electrolyte to an unoccupied one, with the same energy value, in the electrode: the anodic partial current will thus be proportional to the density of the quantum state occupied in the electrolyte and of the unoccupied

quantum states, with the same energy, in the electrode. The opposite is true for the partial cathodic current.

In the case of a semiconductor, the existence of the forbidden band should be kept in mind, and, if it is not degenerate, the existence of a small concentration of holes in the valency band and of electrons in the conduction band, so that two anodic partial currents are possible, due respectively to the transfer of holes from the valency band of the electrolyte and the transfer of electrons from the electrolyte to the conduction band, and two corresponding cathodic partial currents. The intrinsic properties of the semiconductor and the electrolyte's oxidation-reduction voltage (and thus the relative concentrations of the oxidized and reduced species) determine whether, at equilibrium conditions, the transfer occurs predominantly at the valency band or at the conduction band. By polarizing the semiconductor, it is obviously possible to change the main transfer mechanism, since polarization favors (without reaching surface regeneration conditions) the transfer of holes from the valency band if it is anodic and, relatively, that of electrons from the conduction band, if it is cathodic.

When the oxidation-reduction process takes place with extraction of minority carrier, i.e., holes from a type n semiconductor or electrons from a type p semiconductor, it is possible to observe saturation currents, anodic and cathodic respectively. This is a method for obtaining information on the doping of the semiconductors.

The law of dependence of the overvoltage from the logarithm of partial currents is linear for metals, while this happens only within limited ranges of current values for semiconductors. In any case, the overvoltage curves as a function of the logarithm of the absolute value of the resulting current are obtained experimentally, and this makes their interpretation more difficult.



In the case of metals, however, the resulting current is identical with the partial currents in the regions where the contribution of one of the two partial pressures is negligible, i.e., for high absolute overvoltage values. In that case, Tafel's law is valid, which enables us to obtain the values of the kinetic parameters: exchange current and transfer coefficient.

The analysis is more complex in the case of semiconductors. From the relative slopes of the anodic and cathodic branches in the region near the equilibrium voltage (where the contribution of the band with lower exchange current is negligible), it is possible to deduce which of the two transfer mechanisms takes place predominantly under equilibrium conditions, while from the relative slopes in the area far from the equilibrium voltage (where it is indispensable to take into account the contribution of both bands), it is possible to deduce whether the semiconductor is type p or n, even if the saturation currents are not taken into account.

As we have seen, the experimental results are in agreement with the theoretical predictions. There are many more results available for metals (which also have a higher value of the exchange currents) than for semiconductors. A semiconductor satisfying simultaneously both the following conditions has not yet been found: (1) not to give parasitic reactions superimposing on and masking the oxidation-reduction processes, such as anodic solution of the semiconductor itself or cathodic hydrogen development, and (2) not to have too broad a band of forbidden energy, so as to enable us to observe both the anodic and cathodic process. The films formed by air oxidation of austenitic stainless steels probably do satisfy these conditions, but, as we have pointed out, they are still little known and not well-defined.

It would thus be very useful to find new stable semiconductors, with well-defined and reproducible properties, which might be of

type p or n. They would also permit us to check into the small further details of the theory reported in this review, which we have been obliged to pass over due to reasons of space.

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