

# ON THE CURRENT DENSITY AND OVERTENSION SIGNS

## I. THE CASE OF METAL/ELECTROLYTE SOLUTION INTERFACE

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For a spontaneous electrode reaction the entropy production and the current density across the electrodic interface and the overpotential under which the electrode reaction occurs are intimately linked. From this relationship, considering only the sign convention for the anodic and cathodic overpotential, the signs of the anodic and cathodic current densities, in a galvanic cell and in an electrolysis cell, could be deduced. No other convention, except the completely accepted overpotential convention and the well-known physical convention for the current, is made.

### Introduction

It is well known that the entropy production for a chemical reaction depends on the chemical rate and of the chemical affinity [1]. One knows that for an electrode reaction the entropy production also depends on the rate of the electrode reaction that is the current density,  $i$  (a thermodynamic flux) and of the overpotential under which the electrode reaction occurs,  $\eta$  (a thermodynamic force) [2]. This dependence is caused by both the existence of the electrical field across the electrodic interface and the chemical changes that occur in at least one of the two phases of the two-phase system. Usually, the electrode reactions are considered, in respect with the rate of the charge transfer step, as fast (reversible) or slow (irreversible). Between the terms fast and reversible, on one hand, and slow and irreversible, on the other hand, there is some superposition but they are not at all identical. In some extent, the terms cover each other, but, while the fast and slow terms refer to the rate of charge transfer step (i.e., to the kinetic viewpoint), the reversible and irreversible terms refer to the kinetic reversibility and kinetic irreversibility of the charge transfer step (being in some extent a thermodynamic viewpoint). The fast and the slow terms refer to the absolute size of the standard exchange current density,  $i^{00}$ , of an electrode reaction [3÷5].

An electrode reaction is kinetically reversible if the partial anodic and cathodic current densities are much greater than the net current density (these partial current densities are comparable in size). For this reason (i.e., fast charge transfer in both anodic and cathodic directions) the fast electrode reaction reaches the equilibrium state being thermodynamically reversible. An electrode reaction is kinetically irreversible if at least one of the two partial anodic and cathodic current densities is much slower than the net

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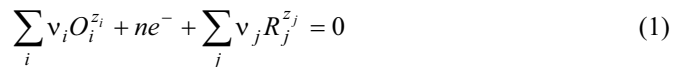
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current density. For this reason (i.e., a rate in a direction is much slower than the rate in the opposite direction, the both being in fact slow) the slow electrode reaction does not reach the equilibrium state.

## Theoretical

On considers the electrode as a two-phase system (an electronically conducting phase, denoted here by *Me*, and an ionically conducting phase, denoted here by *Sol*) with an interphase region developed between (having different special properties from the two phases in direct contact but determined by these two phases), called electrodic interface at which an electrode reaction takes place [6]. The electrode reaction means the transfer of some electrically charged species (electron, cation, anion etc) between the phase *Me*, where the inner (Galvani) electrical potential is  $\Phi_{Me}$ , and the phase *Sol* where the inner (Galvani) electrical potential is  $\Phi_{Sol}$ . If this charge transfer, between the two phases of well-defined electrical potential, is accompanied by a change in the chemical composition of at least one of the two phases, then at the electrodic interface an electrode reaction takes place. The charge transfer itself with no chemical reaction could be seen as an electrode reaction [7÷12]. Between the two phases of the system, through the electrodic interface, a flow of charge only (for the case of the electron and of the hole) or a flow of charge and matter (for the others transferable species) occurs. But the system as a whole is closed and, therefore, the spontaneous exchange of charge or charge and matter inside the system, is the cause of the entropy production.

Let us assume that the electrode reaction occurring at the electrodic interface is a redox electrode reaction written in the cathodic direction as follows:



where the stoichiometric coefficients for the reactants  $O_i$  and  $e^-$  are negative ( $\nu_i < 0$ ,  $n < 0$ ) and for the products  $R_j$  are positive ( $\nu_j > 0$ ). Of course, the principle of charge conservation is respected being expressed by the equation:

$$\sum_i \nu_i z_i + \sum_j \nu_j z_j = n \quad (2)$$

By introducing the degree of advancement of the electrode reaction  $d\lambda$  [13,14], one can write the following relationships for the components in the electrode reaction:

$$d\lambda = -\frac{dn_{O_i}}{\nu_i} = -\frac{dn_{e^-}}{n} = \frac{dn_{R_j}}{\nu_j} \quad (3)$$

describing the connection with the stoichiometric coefficient and the mole number of each consumed (for  $O_i$  and  $e^-$ ) or produced ( $R_j$ ) species. As it is known, the electrode reaction

rate is given by the ratio between the increment of the degree of advancement,  $d\lambda$ , and the interval of the time,  $dt$ , in which this increment occurs:

$$r = \frac{d\lambda}{dt} \quad (4)$$

Expressing the rates in respect with  $O_i$ ,  $e^-$  and  $R_j$  one can write:

$$r_{O_i} = -\frac{dn_{O_i}}{dt}, \quad r_{e^-} = -\frac{dn_{e^-}}{dt}, \quad r_{R_j} = +\frac{dn_{R_j}}{dt} \quad (5)$$

or, if one takes account to the equation (4), one obtain:

$$r_{O_i} = -\nu_i \frac{d\lambda}{dt}, \quad r_{e^-} = -n \frac{d\lambda}{dt}, \quad r_{R_j} = \nu_j \frac{d\lambda}{dt} \quad (6)$$

obviously, the following relationship exists between the individual rates:

$$r = -\frac{r_{O_i}}{\nu_i} = -\frac{r_{e^-}}{n} = +\frac{r_{R_j}}{\nu_j} \quad (7)$$

In the electrode kinetics the rate of the electrode reaction is expressed as current density:

$$i_k = z_k F r_k \quad (8)$$

therefore, inserting, in turn, each individual equation from the equation (6) into the equation (8) one gets:

$$i_{O_i} = -z_i \nu_i F \frac{d\lambda}{dt} \quad (8')$$

$$i_{e^-} = n F \frac{d\lambda}{dt} \quad (8'')$$

$$i_{R_j} = z_j \nu_j F \frac{d\lambda}{dt} \quad (8''')$$

and consequently, the elementary charge being:

$$dq_k = i_k dt \quad (9)$$

the elementary charges associated with each current density are given by:

$$dq_{O_i} = -z_i \nu_i F d\lambda \quad (9')$$

$$dq_{e^-} = n F d\lambda \quad (9'')$$

$$dq_{R_j} = z_j \nu_j F d\lambda \quad (9''')$$

As mentioned above, the electrode endowed with an electrode reaction could be seen as a two-phase system and a charge transfer between the two phases which determines chemical composition changes at least in one of the two phases. From a thermodynamic viewpoint,

one can assume that the internal energy equation (the so-called Gibbs equation) extended with the electrical term:

$$dU = TdS - pdV + \sum_k \mu_k dn_k + \sum_k \Phi_k dq_k \quad (10)$$

is still valid, where  $k$  counts both for the reactants ( $O_i$  and  $e^-$ ) and for the products ( $R_j$ ). Therefore, by splitting the sum signs, one can rewrite the equation (10) in the following form:

$$dU = TdS - pdV + \sum_i \mu_{O_i} dn_{O_i} + \mu_{e^-} dn_{e^-} + \sum_j \mu_{R_j} dn_{R_j} + \Phi_{Sol} \sum_i dq_{O_i} + \Phi_{Me} dq_{e^-} + \Phi_{Sol} \sum_j dq_{R_j} \quad (11)$$

where it was considered that all  $O_i$  and  $e^-$  and  $R_j$  being dissolved into the same electrolytic solution have the same inner (Galvani) electrical potential (i.e.,  $\Phi_i = \Phi_j = \Phi_{Sol}$  and  $\Phi_{e^-} = \Phi_{Me}$ ). Inserting the equations (3) and (9', 9'' and 9''') into the equation (11) one gets a  $d\lambda$  dependence of internal energy:

$$dU = TdS - pdV - \left( \sum_i \nu_i \mu_{O_i} + n \mu_{e^-} - \sum_j \nu_j \mu_{R_j} \right) d\lambda - F\Phi_{Sol} \left( \sum_i \nu_i z_i - \sum_j \nu_j z_j \right) d\lambda + nF\Phi_{Me} d\lambda \quad (12)$$

Rewriting the equation (12), by gathering all the terms referring to the same species, one gets:

$$dU = TdS - pdV - \sum_i \nu_i (\mu_{O_i} + z_i F\Phi_{Sol}) d\lambda - n(\mu_{e^-} - F\Phi_{Me}) d\lambda + \sum_j \nu_j (\mu_{R_j} + z_j F\Phi_{Sol}) d\lambda \quad (13)$$

Taking into account the meaning of the electrochemical potential [15],  $\tilde{\mu}_k$ , which consists of the chemical potential,  $\mu_k$ , contribution and the electrical work,  $z_k F\Phi_k$ , contribution ( $\tilde{\mu}_k = \mu_k + z_k F\Phi_k$ ) the equation (13) can be written in a shorter form:

$$dU = TdS - pdV - \sum_i \nu_i \tilde{\mu}_{O_i} d\lambda - n \tilde{\mu}_{e^-} d\lambda + \sum_j \nu_j \tilde{\mu}_{R_j} d\lambda \quad (14)$$

or in another form:

$$dU = TdS - pdV - \left( \sum_i \nu_i \tilde{\mu}_{O_i} + n \tilde{\mu}_{e^-} - \sum_j \nu_j \tilde{\mu}_{R_j} \right) d\lambda \quad (15)$$

from which it is possible to obtain the shortest form that follows:

$$dU = TdS - pdV - \tilde{A}d\lambda \quad (16)$$

in electrochemical affinity term  $\tilde{A}$  :

$$\tilde{A} = -\Delta\tilde{G} = \sum_i \nu_i \tilde{\mu}_{O_i} + n\tilde{\mu}_{e^-} - \sum_j \nu_j \tilde{\mu}_{R_j} \quad (17)$$

The electrochemical affinity is defined as follows (i.e., in the same manner as the chemical affinity is defined):

$$\tilde{A} = -\Delta\tilde{G} = -\left(\frac{\partial\tilde{G}}{\partial\lambda}\right)_{p,T} \quad A = -\Delta G = -\left(\frac{\partial G}{\partial\lambda}\right)_{p,T} \quad (18)$$

(as concerns the others quantities theirs meanings are the usual ones:

$$\Delta\tilde{G} = \sum_j \nu_j \tilde{\mu}_j - \left(\sum_i \nu_i \tilde{\mu}_i + n\tilde{\mu}_{e^-}\right), \quad \Delta G = \sum_j \nu_j \mu_j - \left(\sum_i \nu_i \mu_i + n\mu_{e^-}\right).$$

One knows the relationship between electrochemical Gibbs energy and chemical Gibbs energy:

$$\Delta\tilde{G} = \Delta G + nFE \quad (19)$$

where  $E$  is the electrode potential of the electrode endowed with the electrode reaction (1):

$$E = \Phi_{Me} - \Phi_{Sol} \quad (20)$$

Using the corresponding meanings in affinity terms of Gibbs energies, given in the equations (18), the equation (19) can be written in the form that governs the progress of the electrode reaction:

$$\tilde{A} = A - nFE \quad (21)$$

In the electrochemical equilibrium state ( $i = 0$ ,  $E = E_{rev}$ ) the electrochemical affinity is zero:

$$0 = \tilde{A}_{i=0} = A_{i=0} - nFE_{rev} \quad (22)$$

where  $E_{rev}$  is the reversible (equilibrium) electrode potential:

$$E_{rev} = (\Phi_{Me} - \Phi_{Sol})_{i=0} \quad (20')$$

If the electrode reaction is not at the equilibrium state ( $i \neq 0$ ,  $E \neq E_{rev}$ ) the electrochemical affinity is positive:

$$0 < \tilde{A}_{i \neq 0} = A_{i \neq 0} - nFE \quad (22')$$

Combining the equations (22) and (22') and taking into account that:

$$A_{i=0} = A_{i \neq 0} \quad (23)$$

(because they depend on the same chemical potentials) one gets:

$$\tilde{A}_{i \neq 0} = -nF(E - E_{rev}) \quad (24)$$

and then by using the overpotential notion:

$$\tilde{A}_{i \neq 0} = -nF\eta \quad (25)$$

which, for our discussion, shows that the reduction (cathodic) electrode reaction ( $\rightarrow$ ) is spontaneously having negative overpotential and therefore positive electrochemical affinity.

From equation (16) one gets the total entropy change:

$$dS = \frac{1}{T}dU - \frac{p}{T}dV + \frac{\tilde{A}}{T}d\lambda \quad (26)$$

as a sum [16] of the entropy change  $d_e S$  with the exterior and the entropy change  $d_i S$  due to the spontaneous electrode reaction occurring at the electrode interface:

$$dS = d_e S + d_i S \quad (27)$$

Taking into account the expression for  $d_e S$  :

$$d_e S = \frac{1}{T}dU - \frac{p}{T}dV \quad (28)$$

one gets the expression for  $d_i S$  as:

$$d_i S = \frac{\tilde{A}}{T}d\lambda \quad (29)$$

showing that the electrochemical affinity of the spontaneous electrode reaction is responsible for the entropy production in the two-phase system. The rate of entropy change/increase is given by the equation:

$$\frac{d_i S}{dt} = \frac{\tilde{A}}{T} \frac{d\lambda}{dt} \quad (30)$$

where  $\tilde{A}$  plays the role of a thermodynamic force closely related to the electrode reaction rate. The electrochemical affinity and the electrode reaction rate must have the same sign.

Combining the equation (30) with the equation (25) one obtains firstly:

$$\frac{d_i S}{dt} = \frac{-nF\eta d\lambda}{T dt} \quad (31)$$

because one can write (considering the physical convention on the current, the direction of  $i$  is the same as that of the moving positive charge):

$$i = -i_e = \frac{-nFd\lambda}{dt} \quad (32)$$

and then:

$$\frac{d_i S}{dt} = \frac{i\eta}{T} > 0 \quad (33)$$

an equation that offers the criterion for the current density sign for an electrode reaction occurring at the electrodes into a galvanic cell: *the current density  $i$  must be taken with the same sign as the overpotential  $\eta$  in a spontaneous electrode reaction.* Therefore, in a galvanic cell where the entropy production is positive, if  $\eta > 0$  (i.e., an anodic overpotential) then  $i > 0$  (i.e., the partial anodic current density is also positive). Consequently, if  $\eta < 0$  (i.e., a cathodic overpotential) then  $i < 0$  (i.e., the partial cathodic current density is also negative).

On the contrary, in an electrolysis cell where the entropy production is not positive, if  $\eta > 0$  (i.e., an anodic overpotential) then  $i < 0$  (i.e., the partial anodic current density is negative). Consequently, if  $\eta < 0$  (i.e., a cathodic overpotential) then  $i > 0$  (i.e., the partial cathodic current density is positive).

For a multielectrode (where at least two different electrode reactions take place simultaneously and spontaneously) a general equation [2,17,18] may be obtained:

$$\frac{d_i S}{dt} = \frac{\sum_{k=1}^n i_k \eta_k}{T} > 0 \quad (34)$$

describing the spontaneous entropy production as a sum of entropy changes of each electrode reaction component of the multielectrode.

## Conclusions

The equation (33) governs the progress of an electrode reaction occurring spontaneously at an electrode interface. This is the case of an electrode reaction taking place into a galvanic cell, the so-called electrical energy producer. During its occurrence, this electrode reaction has a positive entropy production. Therefore, for an anodic occurrence, the positive overpotential generates an anodic current that is positive too, while for a cathodic occurrence the negative overpotential generates a cathodic current that is also negative.

For an electrode reaction that does not take place spontaneously at an electrode interface, the entropy production is not positive. To take place, the electrode reaction needs to be helped by an external energy contribution. This is the case of an electrode reaction occurring at an electrode interface into an electrolysis cell, or the so-called substance producer. For these nonspontaneous electrode reactions the product of overpotential by current density is always negative. As a consequence, for an anodic occurrence, the positive

overtension generates an anodic current that is negative, while for a cathodic occurrence the negative overtension generates a cathodic current, which is positive.

Therefore, the usual classification of electrode reactions as reversible (fast) and irreversible (slow), whose criterion is the charge transfer rate, has nothing to do with the terms of reversible and irreversible processes considered by thermodynamics. Such fast and/or slow electrode reactions can occur at the electrode interface into a self-driven cell as spontaneous electrode reaction (having a positive entropy production) as well as into an externally driven cell as nonspontaneous electrode reaction (for which the entropy production is not positive).

Concluding, the anodic current is positive for a galvanic cell and negative for an electrolysis cell and, conversely, the cathodic current is negative for a galvanic cell and positive for an electrolysis cell.

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