



ON THE CURRENT DENSITY AND OVERTENSION SIGNS IV. THE CASE OF THE TRANSFER OF TWO IONS OF THE SAME CHARGE ACROSS THE ITIES IN OPEN CIRCUIT CONDITION

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abstract: 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 physical convention for current, is made. The charge transfer through the ITIES could be treated by electrodic concepts as an electrode reaction (at single- or multi-electrode). A di-electrode of transfer of two ions having the same type of charge is investigated in open circuit conditions.

key words: entropy production; di-electrode of transfer; ITIES.

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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, η (a thermodynamic force) [2]. This dependence is caused by both the existence of the electric 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, with respect to 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. The terms cover each other in some extent, but, while the fast and slow terms refer to the rate of charge transfer step (i.e., to the kinetic viewpoint), the reversible and

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irreversible terms refer to the kinetically reversibility and kinetically irreversibility of the charge transfer step (being a thermodynamic viewpoint). The fast and the slow terms refer to the absolute size of the standard exchange current density, i^{oo} , of an electrode reaction [3-5].

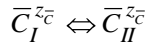
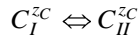
In two previous papers [6,7] we have dealt with the typical redox single-electrode reaction occurring to a single-electrode and, respectively, multi-electrode reaction occurring to a multi-electrode. In a third paper [8] we have dealt with the ionic charge transfer across the ITIES (Interface between Two Immiscible Electrolyte Solutions) and we are taking as model the case of the di-electrode of transfer across the ITIES in which two ions of opposite charge are transferred in the same direction. In this paper we are dealing with a di-electrode of transfer across the ITIES in which two ions of the same charge are transferred. Among different electrodic interface, the ITIES is of major importance especially in understanding the biological membrane electrochemistry. Even the ionic charge transfer across the ITIES may be treated as an electrode reaction [9]: obviously, the electron transfer across the ITIES resembles more with the usual electrode reaction taking place to the M/S electrodic interface. At an ITIES one could meet different cases of ionic charge transfer: single-electrode of transfer for a single ionic species, di-electrode of transfer [10-14,17,18] for two ionic species (of the same or opposite charge) or multi-electrode for at least three ionic charges transferred across the ITIES. The charge transfer across ITIES could also be seen as a "mixed potential" [15] or as two single-electrodes in series [16].

Theoretical

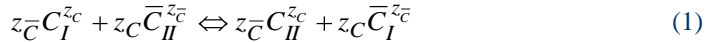
One considers a two-phase system formed by two ionically conducting phases, denoted here by S_I (in the left-side) and S_{II} (in the right-side) with an interphase region developed in between. This interphase region is the so-called electrodic interface at which an electrode reaction takes place. The electrode reaction means the transfer of some electrically charged species (usually cations and/or anions for an ITIES) between the phase S_I , whose inner (Galvani) electric potential is Φ_I , and the phase S_{II} , whose inner (Galvani) electric potential is Φ_{II} . Obviously the charge transfer itself might be seen as an electrode reaction [10-24]. Between the two phases of the system, through this special kind of electrodic interface, a flow of ionic species, positively and/or negatively charged, occurs; obviously, this charge flow is accompanied by a mass transfer too (the ions having both mass and charge). But the system as a whole is closed and, therefore, the spontaneous exchange of charge and matter inside the system is the cause of the entropy production. In its progress from the initial state to the final state of equilibrium, the system moves by a steady-state route because of the condition of open circuit (or a zero-polarization control).

Let us assume that the electrode reaction occurring at the ITIES is an ionic charge transfer of two ions of the same charge, e.g., either two cations, C^{z_c} (initially in S_I) and \bar{C}^{z_c} (initially in S_{II}) or two anions, A^{z_A} (in S_I) and \bar{A}^{z_A} (in S_{II}), which is a similar case, which cross the interphase region from the more concentrated electrolyte solution (let be S_I

for C^{z_c} and S_{II} for $\bar{C}^{z_{\bar{c}}}$) to the more diluted electrolyte solution (let be S_{II} for C^{z_c} and S_I for $\bar{C}^{z_{\bar{c}}}$). Obviously, the passage of the cation from the left to the right direction (forward direction) and the passage of the anion from the right to the left direction (backward direction) are electrically equivalent because that means a transport of a positive current from the left to the right, and *vice versa*. In fact, for this chosen interface the two different ions of the same charge pass the interface in opposite directions, each of two carrying the same quantity of electricity due to the open circuit condition. During the steady-state progress of mass and charge transfer, after the initial moment ($t=0$) the passage of each of the two ions could occur in both directions because the transfer in the initial direction becomes more and more intense while the transfer in the reverse direction becomes less and less intense (until the two processes, forward and backward, balance each other). Under open circuit condition, the two current densities associated with the two ion transfers has to fulfil the following condition $i_{C^{z_c}} + i_{\bar{C}^{z_{\bar{c}}}} = i_+ + i_- = 0$ or $i_{C^{z_c}} = -i_{\bar{C}^{z_{\bar{c}}}}$; $i_+ = -i_-$, each individual ionic charge transfer being out of its own equilibrium state (for C^{z_c} the $E_{C^{z_c},rev} = E_{+1,rev}$ value and for $\bar{C}^{z_{\bar{c}}}$ the $E_{\bar{C}^{z_{\bar{c}}},rev} = E_{+2,rev}$ value). So the equivalent electrode reactions might be written in the following form:



or in the form of a double-exchange reaction across the ITIES and considering the charge of each cation and the necessity as the open circuit condition to be fulfilled:



where the stoichiometric coefficients for the reactants $C_I^{z_c}$ and $\bar{C}_{II}^{z_{\bar{c}}}$ are negative ($\nu_i < 0$) and for the products $C_{II}^{z_c}$ and $\bar{C}_I^{z_{\bar{c}}}$ are positive ($\nu_i > 0$). Of course, the principle of charge conservation is respected being expressed by the equation (here $\nu_i = z_i$):

$$\sum_{i \neq j, i, j \in I, II}^2 z_i z_j = 0 \quad (2)$$

By introducing the degree of advancement of the electrode reaction $d\lambda$ [25], one can write the following relationships for the components in the electrode reaction:

$$d\lambda = \frac{dn_{C_I^{z_c}}}{z_{\bar{C}}} = \frac{dn_{\bar{C}_{II}^{z_{\bar{c}}}}}{z_C} = \frac{dn_{C_{II}^{z_c}}}{z_{\bar{C}}} = \frac{dn_{\bar{C}_I^{z_{\bar{c}}}}}{z_C} \quad (3)$$

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 each ion involved in the progress of di-electrode of transfer, one can write:

$$r_{C_I^{z_C}} = \frac{dn_{C_I^{z_C}}}{dt}, \quad r_{\bar{C}_{II}^{z_{\bar{C}}}} = \frac{dn_{\bar{C}_{II}^{z_{\bar{C}}}}}{dt}, \quad r_{C_{II}^{z_C}} = \frac{dn_{C_{II}^{z_C}}}{dt}, \quad r_{\bar{C}_I^{z_{\bar{C}}}} = \frac{dn_{\bar{C}_I^{z_{\bar{C}}}}}{dt} \quad (5)$$

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

$$r_{C_I^{z_C}} = z_{\bar{C}} \frac{d\lambda}{dt}, \quad r_{\bar{C}_{II}^{z_{\bar{C}}}} = z_C \frac{d\lambda}{dt}, \quad r_{C_{II}^{z_C}} = z_{\bar{C}} \frac{d\lambda}{dt}, \quad r_{\bar{C}_I^{z_{\bar{C}}}} = z_C \frac{d\lambda}{dt} \quad (6)$$

obviously, the following relationship exists between the individual rates:

$$r = \frac{r_{C_I^{z_C}}}{z_{\bar{C}}} = \frac{r_{\bar{C}_{II}^{z_{\bar{C}}}}}{z_C} = \frac{r_{C_{II}^{z_C}}}{z_{\bar{C}}} = \frac{r_{\bar{C}_I^{z_{\bar{C}}}}}{z_C} = \frac{d\lambda}{dt} \quad (7)$$

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 equation (8) one gets:

$$i_{C_I^{z_C}} = z_C z_{\bar{C}} F \frac{d\lambda}{dt} \quad i_{\bar{C}_{II}^{z_{\bar{C}}}} = z_C z_{\bar{C}} F \frac{d\lambda}{dt} \quad (8')$$

$$i_{C_{II}^{z_C}} = z_C z_{\bar{C}} F \frac{d\lambda}{dt} \quad i_{\bar{C}_I^{z_{\bar{C}}}} = z_C z_{\bar{C}} F \frac{d\lambda}{dt} \quad (8'')$$

and consequently, the elementary charge being:

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

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

$$dq_{C_I^{z_C}} = z_C z_{\bar{C}} F d\lambda \quad dq_{\bar{C}_{II}^{z_{\bar{C}}}} = z_C z_{\bar{C}} F d\lambda \quad (9')$$

$$dq_{C_{II}^{z_C}} = z_C z_{\bar{C}} F d\lambda \quad dq_{\bar{C}_I^{z_{\bar{C}}}} = z_C z_{\bar{C}} F d\lambda \quad (9'')$$

As mentioned above, the electrodic interface 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 electric 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 $C_I^{z_c}, \bar{C}_I^{z_{\bar{c}}}$ and for the products $C_{II}^{z_c}, \bar{C}_{II}^{z_{\bar{c}}}$. Therefore, by splitting the two sum symbols, one can rewrite the equation (10) as:

$$dU = TdS - pdV + \sum_i \mu_i dn_i + \sum_j \mu_j dn_j + \Phi_I \sum_i dq_i + \Phi_{II} \sum_j dq_j \quad (11)$$

where i and j counts for the cations $C_I^{z_c}$ and $\bar{C}_I^{z_{\bar{c}}}$ (they belong to the S_I electrolyte solution in which the inner (Galvani) electric potential is Φ_I), and for the cations $C_{II}^{z_c}$ and $\bar{C}_{II}^{z_{\bar{c}}}$ (they belong to the S_{II} electrolyte solution in which the inner (Galvani) electric potential is Φ_{II}). Inserting the equations (3) and (9' and 9'') into the equation (11) one gets a $d\lambda$ dependence of internal energy:

$$dU = TdS - pdV + (z_{\bar{c}}\mu_{C_I} + z_C\mu_{\bar{C}_I} + z_{\bar{c}}\mu_{C_{II}} + z_C\mu_{\bar{C}_{II}})d\lambda + (z_{\bar{c}}z_C F\Phi_I + z_C z_{\bar{c}} F\Phi_I + z_{\bar{c}}z_C F\Phi_{II} + z_C z_{\bar{c}} F\Phi_{II})d\lambda \quad (12)$$

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

$$dU = TdS - pdV + [(z_{\bar{c}}\mu_{C_I} + z_C\mu_{\bar{C}_I} + z_{\bar{c}}z_C F\Phi_I) + (z_C\mu_{C_{II}} + z_{\bar{c}}z_C F\Phi_{II}) + (z_{\bar{c}}\mu_{C_{II}} + z_C\mu_{\bar{C}_{II}} + z_{\bar{c}}z_C F\Phi_{II}) + (z_C\mu_{C_I} + z_{\bar{c}}z_C F\Phi_I)]d\lambda \quad (13)$$

Taking into account the meaning of the electrochemical potential [26], $\tilde{\mu}_k$, which consists of the chemical potential, μ_k , contribution and the electric 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:

$$dU = TdS - pdV + (z_{\bar{c}}\tilde{\mu}_{C_I} + z_C\tilde{\mu}_{\bar{C}_I} + z_{\bar{c}}\tilde{\mu}_{C_{II}} + z_C\tilde{\mu}_{\bar{C}_{II}})d\lambda \quad (14)$$

where, according to the convention, inside the parentheses the first and the second coefficients are negative and the third and the fourth coefficients are positive. So that one can write in another form by using the electrochemical Gibbs energy of the reaction describing the di-electrode of transfer:

$$dU = TdS - pdV + \Delta\tilde{G}d\lambda \quad (15)$$

from which it is possible to obtain the form in electrochemical affinity that follows:

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

The definitions of the two electrochemical amounts are given below in two forms:

$$\begin{aligned}\tilde{A} = -\Delta\tilde{G} &= -z_{\bar{C}}(\tilde{\mu}_{C^{z_C}}^{\text{II}} - \tilde{\mu}_{C^{z_C}}^{\text{I}}) - z_C(\tilde{\mu}_{\bar{C}^{z_{\bar{C}}}}^{\text{II}} - \tilde{\mu}_{\bar{C}^{z_{\bar{C}}}}^{\text{I}}) \\ &= -\Delta\tilde{G}_{C^{z_C}} - \Delta\tilde{G}_{\bar{C}^{z_{\bar{C}}}} = \tilde{A}_{C^{z_C}} + \tilde{A}_{\bar{C}^{z_{\bar{C}}}}\end{aligned}\quad (17)$$

where the coefficient are taken here all positive as they are usual used in calculations.

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

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):

$$E = \Phi_I - \Phi_{\text{II}} \quad (20)$$

$$E_{+1,rev} = (\Phi_I - \Phi_{\text{II}})_{i=0} \quad \text{when there is only } C^{z_C} \text{ transferable} \quad (20')$$

$$E_{+2,rev} = (\Phi_I - \Phi_{\text{II}})_{i=0} \quad \text{when there is only } \bar{C}^{z_{\bar{C}}} \text{ transferable} \quad (20'')$$

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:

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

(here $n = |z_C z_{\bar{C}}|$ for one occurrence of the redox reaction at ITIES).

In the stationary state ($i = 0$, $E = E_{ITIES,i=0}$) the electrochemical affinity is not zero:

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

(mixed potential condition under a zero current density through the ITIES) although the individual electrochemical affinities are different from zero:

$$0 \neq \tilde{A}_{+1,i=0} = A_{+1,i=0} - nFE_{ITIES,i=0} \quad 0 \neq \tilde{A}_{+2,i=0} = A_{+2,i=0} - nFE_{ITIES,i=0} \quad (22')$$

where $E_{ITIES,i=0}$ is the stationary state electrode potential or mixed potential under zero current density:

$$E_{ITIES,i=0} = (\Phi_I - \Phi_{\text{II}})_{i=0} \quad (20'')$$

If each electrode reaction component of the di-electrode of transfer is not at the equilibrium state ($i \neq 0$, $E_{ITIES,i=0} \neq E_{+1,rev}$, $E_{ITIES,i=0} \neq E_{+2,rev}$) the electrochemical affinity is positive for each of the two:

$$\tilde{A}_{+1,i \neq 0} = A_{+1,i \neq 0} - nFE_{ITIES,i \neq 0} \quad \tilde{A}_{+2,i \neq 0} = A_{+2,i \neq 0} - nFE_{ITIES,i \neq 0} \quad (23)$$

but, of course:

$$A_{+1,i=0} = A_{+1,i \neq 0} \quad A_{+2,i=0} = A_{+2,i \neq 0} \quad (23')$$

(because they depend only of the chemical potentials). As a result of this, the differences between the electrochemical affinity under of non-zero current density for each electrode reaction and the zero electrochemical affinity under single electrode occurrence (when only one single cation passes across the ITIES) one gets:

$$\tilde{A}_{+1,i \neq 0} = -nF(E_{ITIES,i=0} - E_{+1,rev}) \quad \tilde{A}_{+2,i \neq 0} = -nF(E_{ITIES,i=0} - E_{+2,rev}) \quad (24)$$

and then by using the polarisation notion:

$$\tilde{A}_{+1,i \neq 0} = -nFP_{+1} \quad \tilde{A}_{+2,i \neq 0} = -nFP_{+2} \quad (25)$$

which, for our discussion, shows that:

- the transfer of the cation C^{z_c} , passing spontaneously from S_I to S_{II} (\rightarrow , forward direction), occurs under negative polarisation and therefore positive electrochemical affinity. This polarisation is given by the algebraic sum of two over tensions $P_{+1} = P_{C^{z_c}} = -\eta_{c,C_I^{z_c}} + \eta_{a,C_I^{z_c}}$, namely $\eta_{c,C_I^{z_c}}$, which is cathodic in nature and controls the departure of C^{z_c} from the left side of the ITIES and, $\eta_{a,C_{II}^{z_c}}$, which is anodic in nature and controls the arrival of C^{z_c} in the right side of the ITIES;
- the transfer of the cation $\bar{C}^{z_{\bar{c}}}$, passing spontaneously from S_{II} to S_I (\leftarrow , backward direction), occurs under negative polarisation and therefore positive electrochemical affinity. This polarisation is given by the algebraic sum of two over tensions $P_{+2} = P_{\bar{C}^{z_{\bar{c}}}} = \eta_{a,\bar{C}_I^{z_{\bar{c}}}} - \eta_{c,\bar{C}_{II}^{z_{\bar{c}}}}$, namely $\eta_{c,\bar{C}_{II}^{z_{\bar{c}}}}$, which is cathodic in nature and controls the departure of $\bar{C}^{z_{\bar{c}}}$ from the right side of the ITIES and, $\eta_{a,C_{II}^{z_c}}$, which is anodic in nature and controls the arrival of $\bar{C}^{z_{\bar{c}}}$ in the left side of the ITIES.

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

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

as a sum [27] 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:

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

where the electrochemical affinity, in open circuit condition, could be written in the following manner:

$$\tilde{A}_{ITIES} = \tilde{A}_{+1,i=0} + \tilde{A}_{+2,i=0} \quad (28)$$

Taking into account the expression for $d_e S$:

$$d_e S = \frac{I}{T} dU + \frac{p}{T} dV \quad (29)$$

one gets the expression for $d_i S$ as:

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

$$d_i S = d_i S_{+1} + d_i S_{+2} = \frac{\tilde{A}_{+1}}{T} d\lambda + \frac{\tilde{A}_{+2}}{T} d\lambda = \frac{\tilde{A}_{ITIES}}{T} d\lambda \quad (30)$$

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:

$$\frac{d_i S}{dt} = \frac{\tilde{A}_{ITIES}}{T} \frac{d\lambda}{dt} \quad (31)$$

$$\frac{d_i S}{dt} = \frac{d_i S_{+1}}{dt} + \frac{d_i S_{+2}}{dt} = \frac{\tilde{A}_{+1} + \tilde{A}_{+2}}{T} \frac{d\lambda}{dt} = \frac{\tilde{A}_{ITIES}}{T} \frac{d\lambda}{dt} \quad (31)$$

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 equation (25) one obtains firstly:

$$\frac{d_i S}{dt} = \frac{d_i S_{+}}{dt} + \frac{d_i S_{-}}{dt} = \frac{-nFP_{+1}d\lambda}{Tdt} + \frac{-nFP_{+2}d\lambda}{Tdt} \quad (32)$$

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):

$$i_{+1} = -i_{e^{-}} = \frac{-nFd\lambda}{dt} \quad i_{+2} = -i_{e^{-}} = \frac{-nFd\lambda}{dt} \quad (33)$$

and then:

$$\frac{d_i S}{dt} = \frac{i_{+1} P_{+1}}{T} + \frac{i_{+2} P_{+2}}{T} > 0 \quad (34)$$

$$\begin{aligned} i_{+1} P_{+1} > 0; \quad P_{+1} > 0 \Rightarrow i_{+1} > 0 \text{ for } C^{z_c} \\ i_{+2} P_{+2} > 0; \quad P_{+2} < 0 \Rightarrow i_{+2} < 0 \text{ for } \bar{C}^{z_{\bar{c}}} \end{aligned} \quad (34')$$

an equation that offers the criterion for the current density sign for an electrode reaction occurring spontaneously at the ITIES when the two-phase system goes from the initial state to the equilibrium final state: *the current density i must be taken with the same sign as the polarisation P in an spontaneous electrode reaction*. Therefore, in such a system where the entropy production is positive, if $P > 0$ (i.e., an anodic polarisation) then $i > 0$. Consequently, if $P < 0$ (i.e., a cathodic polarisation) then $i < 0$.

On the contrary, in a driven two-phase system (an electrolysis cell) where there is no entropy production, if $\eta > 0$ (i.e., an anodic polarisation) then $i < 0$. Consequently, if $\eta < 0$ (i.e., a cathodic polarisation) then $i > 0$.

In a deeper insight, one may say that:

- the transfer of the cation C^{z_c} , in the forward direction means a reduction (negative/cathodic overpotential, negative current density) in the left side and an oxidation (positive/anodic overpotential, positive current density) in the right side of the ITIES, see the relationship $P_{+1} = P_{C^{z_c}} = -\eta_{c,C_I^{z_c}} + \eta_{a,C_I^{z_c}}$;
- the transfer of the cation $\bar{C}^{z_{\bar{c}}}$, in the backward direction means a reduction (negative/cathodic overpotential, negative current density) in the right side and an oxidation (positive/anodic overpotential, positive current density) in the left side of the ITIES, see the relationship $P_{+2} = P_{\bar{C}^{z_{\bar{c}}}} = \eta_{a,\bar{C}_I^{z_{\bar{c}}}} - \eta_{c,\bar{C}_{II}^{z_{\bar{c}}}}$.

For a multi-electrode (endowed with n different electrode reactions taking place simultaneously at the ITIES and simulating the passage across the ITIES of n different types of ions, a so called multi-electrode of transfer) a general equation [2,28,29] could be obtained:

$$\frac{d_i S}{dt} = \frac{\sum_{j=1}^n i_j P_j}{T} > 0 \quad (35)$$

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

Conclusions

The equation (34) governs the progress of an electrode reaction occurring spontaneously at an electrodic interface. This is the case of an electrode reaction taking place spontaneously

into a two-phase system containing an ITIES (a two-phase system which is not initially at equilibrium). During its occurrence, this electrode reaction has a positive entropy production. For the case when only two ions of the same type of charge pass across the ITIES either in closed or open circuit condition the electrode reaction is, in fact, a di-electrode reaction. This charge transfer of two ions was called di-electrode of transfer.

For an electrode reaction that does not take place spontaneously at an electrodic interface, there is no entropy production. So that the sum of the two ratios in the right-side of Eq. (34) may not be 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 electrodic interface belonging to a two-phase system in which a charge transfer has to be driven. For these nonspontaneous electrode reactions the product of overpotential by current density must be not positive but negative. As a consequence, for an anodic occurrence, the positive overpotential generates an anodic current that is negative, while for a cathodic occurrence the negative overpotential generates a cathodic current, which is positive.

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