CHARGE TRANSFER IN CHEMISORPTION PROCESSES

PHYSICAL SIGNIFICANCE AND TERMINOLOGY

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The concept of charge transfer and its interpretation in the current literature are analyzed in the present work. The problem of partial charge transfer in adsorption phenomena is thermodynamically analyzed in the instance of the simplest reaction, of the type $O + e^- \rightleftharpoons R$, which takes place via the two adsorption steps $O + n_1 e^- \rightleftharpoons A$ and $A + n_2 e^- \rightleftharpoons R$. The physical significance of the quantities n_1 and n_2 and their connection with the partial charge transfer coefficient λ in the theory of Lorenz and with the "electrosorption valence" in the theory of Vetter and Schultze are discussed. Expressions are obtained for the formal charge transfer coefficients during adsorption of a solution ion at a reversible electrode.

The problem of charge transfer during chemisorption processes at the electrode/solution interface has been discussed in [1-13]. A consistent, general phenomenological treatment of charge transfer was given by Grafov [7, 10] on the basis of the generalized electrode-charge concept of [14] and of the ideas developed previously with reference to the platinum-group metals [15-20]. The different approach to the problem of charge transfer in adsorption phenomena as well as the different terminology employed by the authors of the papers listed above makes it necessary to summarize the results obtained in discussing the problem of charge transfer, and especially the physical significance of the charge transfer coefficients during chemisorption which can be calculated from experimental data. In the present work we shall limit ourselves to an analysis of equilibrium adsorption phenomena.

We shall discuss the simplest case of a redox system which is described by the overall equation

$$O+\bar{e}\rightleftharpoons R, \tag{1}$$

but which actually takes place via some intermediate adsorption state A, i.e., involves at least two adsorption steps:

$$O+n_1\bar{e}\rightleftharpoons A, \tag{1a}$$

$$A+n_2\bar{e}\rightleftharpoons R, \tag{1b}$$

where quantities n_1 and n_2, for reasons presented below, will be named by us the formal charge-transfer coefficients. It is obvious that $n_1 + n_2 = 1$. In the chemisorption of ions or molecules, the process can end with step (1a), for example. In this particular case one usually does not talk about a redox system, but as will be shown in the following, the relationships reported below will nevertheless prove to be correct.

We shall designate the Gibbs adsorption of O and R as Γ_O and Γ_R, respectively. By this we understand the amounts of the corresponding components which must be introduced into the system if the chemical potentials of these components in the bulk phase are to remain unchanged when, without external supply of charge, the electrode surface area is increased by 1 cm²; these quantitites are open to a direct experimental determination. It is obvious that the electrode potential in this case also retains its constant value. By definition the Gibbs adsorption of the solvent $\Gamma_S = 0$. The presence of two values of Gibbs adsorption,

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Γ_0 and Γ_R, in one adsorbed state implies that substance A can be obtained both from component O [according to Eq. (1a)] and from component R [according to Eq. (1b)]. In the case where substance A is formed only from component O or only from component R, the corresponding quantities of positive or negative charge (which we call total surface charge [14]) must be supplied to the electrode surface.

In the case of one-electron electrochemical processes, at least one of the components of the redox system must be a charged particle. To satisfy the electroneutrality condition during establishment of adsorption equilibrium it is necessary, therefore, that other cations and anions participating in the formation of the electric double layer be present in the bulk of the solution. For the sake of simplicity we shall assume at first that there is no charge transfer for these ions. It has been shown in [7, 10, 11] that under these conditions, the formal charge transfer coefficients n_1 and n_2 in steps (1a) and (1b) are determined by the relationships

$$n_1 = -\left(\frac{\partial Q'}{\partial \Gamma_\Sigma}\right)_\varphi = \left(\frac{\partial \Gamma_R}{\partial \Gamma_\Sigma}\right)_\varphi, \qquad (2a)$$

$$n_2 = \left(\frac{\partial Q''}{\partial \Gamma_\Sigma}\right)_\varphi = \left(\frac{\partial \Gamma_O}{\partial \Gamma_\Sigma}\right)_\varphi, \qquad (2b)$$

where Q' and Q" designate total surface charge [14]; $\Gamma_\Sigma = \Gamma_O + \Gamma_R$, i.e., the surface excess of substance A which is obtained by adsorption of both O and R; and φ is the electrode potential (here and in the following, all quantities are expressed in electrical units).

To explain the physical significance of relationships (2a) and (2b) we shall first of all consider the idealized case where the adsorption of O and R at the electrode does not alter the double-layer parameters. The quantity $dQ' = -d\Gamma_R$ represents the amount of charge which must be supplied to the system in order to maintain constancy of φ when the increase in the adsorption of a given substance by the amount $d\Gamma_\Sigma$ occurs at the expense of the oxidized form. In the case where the adsorption is not accompanied by external supply of charge, the oxidized form changes into the reduced form by way of donation of an amount of charge $d\Gamma_R$ to the electrode. In the case where adsorption equilibrium can be realized, without external supply of charge, by the adsorption of material wholly in the oxidized form, we have $d\Gamma_R = 0$ and $n_1 = 0$, but $n_2 = 1$. In cases where $d\Gamma_R$ is different from zero, the ratio $\partial\Gamma_R/\partial\Gamma_\Sigma$ can be regarded as a measure of charge transfer. In the case where $d\Gamma_R = d\Gamma_\Sigma$, i.e., where only substance in the reduced form is needed to realize adsorption equilibrium but substance in the oxidized form is supplied, we have $n_1 = 1$ but $n_2 = 0$.

During adsorption at the expense of the reduced form, the adsorbed substance donates to the electrode an amount of charge $-d\Gamma_O$, and the charge-transfer coefficient of the desorption process (1b) must be equated to $\partial\Gamma_O/\partial\Gamma_\Sigma$. In the case where the material is entirely in the reduced form when it goes over into the adsorbed state, we have $d\Gamma_O = 0$, $n_2 = 0$, and $n_1 = 1$. And likewise, in the case where the material is entirely in the oxidized form when it goes over into the adsorbed state but is supplied in the reduced form, we have $d\Gamma_O = d\Gamma_\Sigma$, $n_2 = 1$, and $n_1 = 0$, which corresponds to full consumption of the charge required for the transition from R to O.

For a calculation of the quantities n_1 and n_2 it is more convenient, sometimes, to start from relationships referring to given μ_O and μ_R (the chemical potentials of the O and R form) rather than to a particular value of φ. It had been shown for a particular case in [17] and in general form in [7, 10]* that

$$\left(\frac{\partial \Gamma_R}{\partial \Gamma_\Sigma}\right)_\varphi = \left[\left(\frac{\partial \Gamma_R}{\partial \mu_O}\right)_{\mu_R} + \left(\frac{\partial \Gamma_R}{\partial \mu_R}\right)_{\mu_O}\right] \Big/ \left[\left(\frac{\partial \Gamma_\Sigma}{\partial \mu_R}\right)_{\mu_O} + \left(\frac{\partial \Gamma_\Sigma}{\partial \mu_O}\right)_{\mu_R}\right], \qquad (3a)$$

$$\left(\frac{\partial \Gamma_O}{\partial \Gamma_\Sigma}\right)_\varphi = \left[\left(\frac{\partial \Gamma_O}{\partial \mu_R}\right)_{\mu_O} + \left(\frac{\partial \Gamma_O}{\partial \mu_O}\right)_{\mu_R}\right] \Big/ \left[\left(\frac{\partial \Gamma_\Sigma}{\partial \mu_R}\right)_{\mu_O} + \left(\frac{\partial \Gamma_\Sigma}{\partial \mu_O}\right)_{\mu_R}\right]. \qquad (3b)$$

In the case where the electrochemical process is an n-electron rather than a 1-electron process, the quantities n_1 and n_2 must be replaced by n_1/n and n_2/n.

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* In deducing relationships (3) one employs the equality of the derivatives $(\partial\Gamma_O/\partial\mu_R)_{\mu_O} = (\partial\Gamma_R/\partial\mu_O)_{\mu_R}$ which follows from the properties of the complete differential of the reversible surface work in the Gibbs equation or from the Onsager reciprocal relations in the thermodynamics of irreversible processes [10].

The above exposition explains why the quantities n_1 and n_2 can be called "charge transfer coefficients." It must be noted that the idea of partial charge transfer during adsorption at electrodes had been introduced by Lorenz [1-3]. In contrast to the interpretation reported above, Lorenz discusses the interface between metal and solution from a microphysical point of view. In this case, charge transfer in the adsorption process means that the electron shells of the ions or molecules which are in contact with the metal partly penetrate beyond this interface. All charge on the metal side which is beyond this microphysical boundary is regarded as true electrode charge, but the fraction of charge which has been transferred across the interface is characterized by the elementary (or microscopic, true) transfer coefficient λ. In the case where the adsorbed particles have no effect on double-layer structure, the quantities n_1 and n_2 are identical with the values of the charge transfer coefficients λ according to Lorenz.*

The above interpretation does not take into account that, generally speaking, the quantities n_1 and n_2 will not become zero when the charge of the adsorbing particle remains unchanged in the adsorption process. In fact, in cases where the adsorbing particle possesses its own dipole moment, displaces oriented water dipoles, changes the double-layer capacity, in short, somehow influences the charge distribution in the double layer, a certain quantity of charge must be expended in order to maintain constancy of φ during its adsorption, so that the thermodynamic quantities n_1 and n_2 cannot serve as a quantitative measure of charge transfer in Lorenz's sense. As a matter of fact, quantities n_1 and n_2 in the general case do not supply information about the state of the material in the adsorbed layer but indicate instead which solution components are required for forming the adsorbed layer. It will be correct, therefore, to call quantities n_1 and n_2 the "formal charge transfer coefficients" [11] (in [7], the terms "macroscopic" or "effective charge transfer coefficient" have been suggested).†

Let us introduce a surface-layer model according to which the adsorbed material consists partly of substance O and partly of substance R. Let quantities A_O and A_R represent the contributions of components O and R to the surface excess of adsorbed material. It had been shown in [14] that $\Gamma_O = A_O + \varepsilon$ and $\Gamma_R = A_R - \varepsilon$, where ε is the free surface charge of electrode. The values of A_O, A_R, and ε, in contrast to those of the Gibbs adsorption Γ_O and Γ_R, cannot be determined experimentally unless one introduces certain model-type assumptions. Thus, in work concerned with adsorption phenomena at the platinum metals [15-19] it has been suggested that the free charge ε is determined by the ionization reaction of adsorbed hydrogen $H_{ads} - e^- \rightleftharpoons H^+$, and that in presence of an excess of surface-inactive base electrolyte, all hydrogen ions (as ions lacking specific adsorbability) are removed from the surface layer, so that $A_O = 0$ and $\Gamma_O = \varepsilon$. The charge ε thus defined not only fails to account for charge transfer during the adsorption of other solution ions but also neglects the polarity of the $Pt-H_{ads}$ bond. In other words, the above definition of free charge ε does not coincide with the definition of free charge in the work of Lorenz, but it corresponds to the usual understanding of this term in the theory of the double layer and of zero-charge potentials.

From the connection between the values of Gibbs adsorption Γ_O and Γ_R and the surface excesses A_O and A_R one can obtain the following equations:

$$\nu_1 = \left(\frac{\partial A_R}{\partial (A_O + A_R)}\right)_\varphi = \left(\frac{\partial (\Gamma_R + \varepsilon)}{\partial \Gamma_\Sigma}\right)_\varphi = n_1 + \left(\frac{\partial \varepsilon}{\partial \Gamma_\Sigma}\right)_\varphi, \qquad (4a)$$

$$\nu_2 = \left(\frac{\partial A_O}{\partial (A_O + A_R)}\right)_\varphi = \left(\frac{\partial (\Gamma_O - \varepsilon)}{\partial \Gamma_\Sigma}\right)_\varphi = n_2 - \left(\frac{\partial \varepsilon}{\partial \Gamma_\Sigma}\right)_\varphi, \qquad (4b)$$

which characterize the correlation between components O and R in the adsorbed state. Expressions (4) formally are equivalent to the equations of Lorenz [1-3] linking coefficients l and λ. However, the differences in the definition of free charge between our work and the work of Lorenz which we pointed out above give rise to a different physical significance of coefficients ν and λ. These coefficients are equivalent only in the case where there are no changes whatsoever in electric double-layer structure with changing overall adsorption Γ_Σ, i.e., where $(\partial\varepsilon/\partial\Gamma_\Sigma)_\varphi = 0$. In this case $\nu = \lambda = n = l$.

Let us consider in more detail the system where the adsorbate is present in the surface layer in the R form exclusively, i.e., where $A_O = 0$. In this case, according to relationships (4), $\nu_1 = 1$ and $\nu_2 = 0$, but

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*There is the possibility, strictly speaking, that those discrepancies remain which are due to the different definition of the position of the interface; these disappear, however, in dilute solutions.

†Quantities equivalent to n_1 and n_2 are designated with the letters l and f by Lorenz.

the formal charge-transfer coefficients $n_1 \neq 1$ and $n_2 \neq 0$.* In fact, from the condition $\Gamma_O = \varepsilon$ which was adopted, one has $\Gamma_R = -\varepsilon + A_R$ and $\Gamma_\Sigma = A_\Sigma = A_R$, and therefore,†

$$n_1 = 1 - \left(\frac{\partial \varepsilon}{\partial A_R}\right)_\varphi = 1 - \left(\frac{\partial \varepsilon}{\partial A_\Sigma}\right)_\varphi, \tag{5a}$$

$$-n_2 = -\left(\frac{\partial \varepsilon}{\partial A_R}\right)_\varphi = -\left(\frac{\partial \varepsilon}{\partial A_\Sigma}\right)_\varphi. \tag{5b}$$

As mentioned above, hydrogen adsorption at the platinized platinum electrode in the presence of an excess of foreign electrolyte can serve as an example, provided that the H^+ ion does not exhibit specific adsorbability at the platinum surface and is readily displaced from the ionic side of the electric double layer by foreign, surface-inactive cations [21, 22]. Thus, $A_{H^+} = 0$, $\Gamma_\Sigma = A_H$, $\mu_O = \mu_{H^+}$, and $\mu_R = \mu_H$, whence according to Eqs. (3) and (5),

$$n_1 = 1 - \left(\frac{\partial \varepsilon}{\partial A_H}\right)_\varphi = \left(\frac{\partial A_H}{\partial \mu_H}\right)_{\mu_{H^+}} \Big/ \left[\left(\frac{\partial A_H}{\partial \mu_H}\right)_{\mu_{H^+}} + \left(\frac{\partial A_H}{\partial \mu_{H^+}}\right)_{\mu_H}\right], \tag{6a}$$

$$-n_2 = -\left(\frac{\partial \varepsilon}{\partial A_H}\right)_\varphi = -\left(\frac{\partial A_H}{\partial \mu_{H^+}}\right)_{\mu_H} \Big/ \left[\left(\frac{\partial A_H}{\partial \mu_H}\right)_{\mu_{H^+}} + \left(\frac{\partial A_H}{\partial \mu_{H^+}}\right)_{\mu_H}\right]. \tag{6b}$$

In this case quantity n_1 expresses the formal charge-transfer coefficient during transition of an H^+ ion to an adsorbed H atom, while $-n_2$ expresses the same coefficient for the transition of a dissolved H atom to an adsorbed one.‡ This last process cannot be realized experimentally, but quantity n_2 is of interest to us inasmuch as it gives an idea about the degree of polarity of the Pt–H bond and about the effect of H_{ads} on electric double-layer capacity. Values of n_1 and n_2 for H^+ ion and H atom adsorption at platinized platinum in different media and at different pH have been calculated and discussed in [7, 11].

Processes have been considered above which occurred via a single adsorbed state, in particular, via H_{ads}. It is not difficult to extend the results to the case where one must give attention to two adsorbed states, e.g., H^+_{ads} and H_{ads}. It is obvious that in this case one more formal charge transfer coefficient must be introduced, which in the example will characterize the transition of a dissolved hydrogen ion H^+_{diss} to H^+_{ads}. Within the limits of the model being proposed by us, this coefficient is close to zero.

In the case where the adsorbate in the surface layer is present wholly in the O form, we have $A_R = 0$, $\Gamma_O = \varepsilon + A_O$, $\Gamma_R = -\varepsilon$, and $\Gamma_\Sigma = A_O$. In this case

$$n_1 = -\left(\frac{\partial \varepsilon}{\partial \Gamma_O}\right)_\varphi = -\left(\frac{\partial \varepsilon}{\partial A_\Sigma}\right)_\varphi, \tag{7a}$$

$$n_2 = 1 + \left(\frac{\partial \varepsilon}{\partial \Gamma_O}\right)_\varphi = 1 + \left(\frac{\partial \varepsilon}{\partial A_\Sigma}\right)_\varphi. \tag{7b}$$

Let us now introduce the additional assumption that the material in the bulk of the solution exists practically wholly in the form in which it becomes adsorbed (as the R form in the case being described by Eq. (5b), and as the O form in the case where Eq. (7a) applies), i.e., let us pass from the general case of a redox system to the process of adsorption from a solution which contains only one of the components of the redox system, and where, moreover, it does not matter which one. Equations (5b) and (7a) can now be brought into a single form by dropping suffixes 1 and 2, and referring with n_1 to the adsorption rather than to the desorption process:

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* One must not be surprised about the result that $\nu_2 = 0$ when $n_2 \neq 0$, because under the assumptions made, free charge ε arises only as a result of reactions (1a) or (1b). Charge having its origin in the polarity of the bond of O or R with the electrode surface is not included in it.

† Minus is written in front of n_2 in Eq. (5b) because positive n_2 refers to the desorption rather than to the adsorption process (cf. Eq. (1b)).

‡ We have $-(\partial\varepsilon/\partial A_H)_\varphi = (\partial\varphi/\partial A_H)_\varepsilon/(\partial\varphi/\partial\Gamma_{H^+})_{A_H}$; therefore, as had already been shown in [15], quantity n_2 expresses the ratio of contributions of the hydrogen atom (X) and of its ionization product (Y) (i.e., of free charge and of the ion compensation it) to the generation of the potential difference.

$$n_i = -\left(\frac{\partial \varepsilon}{\partial A_\Sigma}\right)_\varphi . \tag{8}$$

According to what has been said above, Eq. (8) expresses the degree of charge exchange between the bulk of the solution and the electrode surface which will guarantee that the condition φ = const is fulfilled during the adsorption process.

Vetter and Schultze [8, 9] have suggested the name "electrosorption valence" for a quantity which is analogous to n_i and which they have labeled γ, in the chemisorption of any particle i. According to Vetter and Schultze, this quantity is defined by the relation

$$\gamma_i = -\left(\frac{\partial q}{\partial \Gamma_i}\right)_\varphi , \tag{9}$$

in the simplest case where there is an excess of foreign electrolyte present which is not specifically adsorbing. The quantity Γ_i which, in Vetter and Schultze's terminology, stands for the Gibbs adsorption of the i-th component, does not, however, correspond to our Γ_i but, rather, to our A_i [11, 12, 14], which in the case of systems being described by Eqs. (5b) and (7a) is identical with A_Σ, while the quantity q corresponds to our definition of free charge ε. A positive value of γ_i characterizes a partial oxidation of substance i when it passes into the adsorbed state. Thus, there is complete analogy between the definitions of n_i in Eq. (8) and of γ_i in Eq. (9). Vetter and Schultze have found "electrosorption valences" for a large number of adsorption processes, and have also shown into which form Eq. (9) must be cast in order to be applicable to systems not containing an excess of foreign electrolyte. The results obtained are of interest, but as has been pointed out by Vetter and Schultze themselves, and as follows from the above presentation, the quantity γ_i is not identical with Lorenz's quantity λ, inasmuch as the influence of adsorption on ε will depend not only on charge transfer but also on the effective dipole moment of the adsorbed particle, its location within the compact layer while in the adsorbed state, and on the change in compact-layer capacity caused by the adsorption. We believe, therefore, that the term "formal charge transfer coefficient" is more correct than the term "electrosorption valence." *

In conclusion let us consider the case where charge transfer takes place not only during the adsorption of O and R but also during the adsorption of other solution ions. It must be noted that it appears, with the platinum metals for instance, that charge transfer can be disregarded only in the adsorption of Li^+ and F^-, and in somewhat poorer approximation in the adsorption of Na^+ and SO_4^{2-}. Let us assume that charge transfer is observed for a single solution ion (j) only, in addition to components O and R. Using the Gibbs equation

$$d\sigma = -\Gamma_O d\mu_O - \Gamma_R d\mu_R - \Gamma_j d\mu_j \tag{10}$$

and the Nernst equation

$$d\varphi = d\mu_O - d\mu_R, \tag{11}$$

one can obtain the following relationships:

$$n_1^j = (\partial\Gamma_R/\partial\Gamma_\Sigma)_{\varphi,\mu_j} = (\partial\mu_O/\partial\varphi)_{\Gamma_\Sigma,\mu_j}, \tag{12a}$$

$$n_2^j = (\partial\Gamma_O/\partial\Gamma_\Sigma)_{\varphi,\mu_j} = -(\partial\mu_R/\partial\varphi)_{\Gamma_\Sigma,\mu_j} \tag{12b}$$

(σ is the reversible work of surface formation, Γ_j is the Gibbs adsorption of the j-th component, and $\Gamma_\Sigma = \Gamma_O + \Gamma_R$). Schultze and Vetter [13] have noted, however, that the quantities n_1^j and n_2^j as calculated by Eqs. (12) actually refer not only to the adsorption process of components O and R but also to the change in the adsorption of component j at μ_j = const which accompanies these processes. Precisely for this reason quantities n_1 and n_2 in Eqs. (12) are labeled with an index j. We note that the values of n_1 and n_2 calculated

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* The term "electrosorption valence" appears to us to be especially inappropriate for quantity γ_i when it is used in cases where practically all the influence of adsorption on electrode charge is governed by changes in electric double-layer structure, such as, e.g., in the adsorption of saturated organic compounds at the mercury/solution interface. The incorrect understanding of our interpretation of charge transfer in [9] was remedied later in [12]. In a paper just published [23], still another symbol and name, "charge coverage coefficient Z_E," is proposed for a quantity which is equivalent to n_i and γ_i. Conspicuous is the complete absence of references to the Soviet literature in [23].

previously [7, 11] for the reaction $H^+ + e^- \rightleftharpoons H_{ads}$ in chloride and bromide solutions of constant concentration actually are the coefficients n_1^j and n_2^j, because one cannot neglect the charge transfer connected with the adsorption of Cl^- and Br^- ions on the platinum metals. This had been correctly pointed out by Vetter and Schultze [12, 13].

It must be stressed, however that even in the absence of specific adsorption of a component j contained in the base electrolyte, the quantities n_1 and n_2 which are calculated by Eqs. (2) at μ_j = const still will reflect the variation in Γ_j owing to the change in diffuse-layer structure during the adsorption of O and R, if only to a smaller extent than in the presence of specific adsorption.

Making use of the properties of the complete differential one can show that

$$n_1^j = \left(\frac{\partial \Gamma_R}{\partial \Gamma_\Sigma}\right)_{\varphi, \Gamma_j} + \left(\frac{\partial \Gamma_R}{\partial \Gamma_j}\right)_{\Gamma_\Sigma, \varphi} \left(\frac{\partial \Gamma_j}{\partial \Gamma_\Sigma}\right)_{\mu_j, \varphi}; \qquad (13a)$$

$$n_2^j = \left(\frac{\partial \Gamma_O}{\partial \Gamma_\Sigma}\right)_{\varphi, \Gamma_j} + \left(\frac{\partial \Gamma_O}{\partial \Gamma_j}\right)_{\Gamma_\Sigma, \varphi} \left(\frac{\partial \Gamma_j}{\partial \Gamma_\Sigma}\right)_{\mu_j, \varphi}. \qquad (13b)$$

The derivative $(\partial \Gamma_j / \partial \Gamma_\Sigma)_{\mu_j, \varphi}$ characterizes the interaction between component j and components O and R during adsorption, and may be called the interaction coefficient. The derivatives $(\partial \Gamma_R / \partial \Gamma_j)_{\Gamma_\Sigma, \varphi}$ and $(\partial \Gamma_O / \partial \Gamma_j)_{\Gamma_\Sigma, \varphi}$ are charge-transfer coefficients during the adsorption of the j-th component under conditions where the constancy of Γ_Σ is sustained by the introduction of $d\Gamma_R$ or $d\Gamma_O$, respectively. Thus, the chemisorption of the j-th component when it occurs simultaneously with reaction (1) is characterized, not by one but by two formal charge transfer coefficients:

$$n_j' = (\partial \Gamma_R / \partial \Gamma_j)_{\Gamma_\Sigma, \varphi}, \qquad (14a)$$

$$n_j'' = (\partial \Gamma_O / \partial \Gamma_j)_{\Gamma_\Sigma, \varphi}. \qquad (14b)$$

The relationships uncovered may prove useful in the analysis of joint chemisorption phenomena in redox systems, and in particular, of the joint adsorption of hydrogen and anions on platinum metals.

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