

MECHANISM OF CHARGE-TRANSFER IN THE CASE OF THE ADSORPTION OF REDOX COMPONENTS

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Received July 3rd, 1970

A model of charge-transfer in case of adsorption of the reduced and oxidized components of an electrode process is described. The reduced and oxidized components are indistinguishable in the adsorption layer. The adsorbed species has a charge value $z_r \leq z_{r,ad} = z_r + \lambda \leq z_{ox}$. Considering this adsorption, it becomes evident that the overall transfer reaction consists of partial charge transfer reactions. These can be adsorption/desorption processes or may be chemical reactions within the adsorption layer. A partial charge-transfer is possible for every partial reaction. The rate equations for the partial reactions are given. By experimental investigations on the redox system manganate/permanganate, using platinum and gold electrodes, the adsorption steps in the charge-transfer mechanism were found. These results has been discussed.

Reduced and oxidized components of a simple electrode reaction



can be adsorbed on the electrode surface. In this case the mechanism of the charge-transfer reaction can differ from the usual kinetics where no adsorption is involved. In the case of the kinetics involving no adsorption the charge-transfer occurs in one step but if adsorption is involved a stepwise charge-transfer becomes possible. The charge-transfer reaction has to be replaced by a complex charge-transfer mechanism with various intermediate reactions. Each intermediate reaction can undergo a partial charge-transfer λ where λ is a fractional number of electrons. If S_r and S_{ox} are the only substances involved in the total charge-transfer reaction than the mechanism will be subdivided as follows



The adsorbed species has a mean partial charge $z_{ad} = z_r + \lambda$. If the total charge-transfer reaction involves further substances, for example hydrogen ions, the mechanism becomes more complicated. In a general total electrode reaction

$$\sum_j \nu_j S_j + n e^- = 0, \quad (3)$$

further heterogeneous reactions with different partial charge-transfer coefficients λ' can occur. These heterogeneous reactions generally can be formulated as follows

$$\sum_k p_k S_{k,ad}^* \rightleftharpoons \sum_l p_l S_{l,ad}^* + n\lambda' e^-, \quad (4)$$

$S_{k,ad}^*$ and $S_{l,ad}^*$ are adsorbed species with partial charges, p_k and p_l are reaction numbers. The foundation and the details for this concept will be discussed in this paper.

Solvation States of Adsorbed Redox Components

The equilibrium state of adsorbed species must be discussed before the kinetics. A particle in a solution has a solvation shell which should be different for different charges. In a solution the solvation shell of a molecule can not be characterized by a definite structure because of the thermal fluctuations of the molecules. This creates a great number of various structures. Every arrangement of solvate molecules can be characterized by its solvation energy. At thermal equilibrium there is an energy distribution over the different solvation energies.

Each solvation structure is also characterized by the energy of the electron terms. For a solvated particle in solution each electron term is replaced by a distribution function. There exists a correlation between the solvation energy distribution function and the electron energy distribution function as was pointed out by Gerischer¹. The distribution functions of the electron term energies should be approximately Gaussian.

A complication arises if we consider a redox couple. Following equation (1) the reduced species can lose an electron to the electrode or the oxidized species can accept an electron from the electrode. A change in the solvation shell is accompanied with a change in charge. Therefore the exact equation (1) must be formulated

$$S_r \cdot m \text{ solv} \rightleftharpoons S_{ox} \cdot n \text{ solv} + e^- \quad (1a)$$

m and n characterize the mean solvation shells.

If a particle changes its charge the distribution functions associated with the new charge value need a relaxation time to come to the equilibrium. The time for the reorientation of the solvation shell must be at least of the order of 10^{-10} s. This is the characteristic time for a diffusion controlled reorientation. If the reaction is slow then the relaxation times will become considerably longer.

This means that, when the charge of a particle has changed by loosing or accepting an electron, the new charge state must last at least 10^{-10} s before the new solvation shell distribution is built up. In the electrolyte this is realized because charge exchange is too slow. For a particle in the adsorption layer the mean life time for a charge state can become shorter.

This mean lifetime is given by the frequency of the electron transfer between the electrode and a particle in the adsorption layer. The frequency is associated with an electron exchange bond energy (covalent bond energy). For a mean lifetime of 10^{-10} s or an exchange frequency of 10^{10} s $^{-1}$ with the equation

$$E = N_L h \nu, \quad (5)$$

an electron exchange bond energy $E = 1$ cal mol $^{-1}$ follows. In most cases much higher covalent adsorption bond energies can be assumed. The mean lifetime τ of a charge state in the adsorption layer becomes $\tau < 10^{-10}$ s.

Therefore for the reduced and oxidized components of a redox couple in the electrolyte different solvation energy distribution functions and different electron term energy distribution functions have to be used. For the adsorption layer this is nearly impossible. In the adsorption layer the solvation does not reach equilibrium for the charge states S_r and S_{ox} . The solvation shell remains in a static distribution state with a mean value of charge z_{ad} where $z_r \leq z_{ad} = z_r + \lambda \leq z_{ox}$. The adsorption of $S_r \cdot m$ solv or $S_{ox} \cdot n$ solv gives the same species S_{ad}^* with fluctuating charge but with the solvation shell of a mean charge $z_{ad} = z_r + \lambda$. A partial charge-transfer is connected with the adsorption step. Lorenz and Salié^{2,3} have introduced the concept of a partial charge and a partial charge-transfer and the value λ is called partial charge-transfer coefficient.

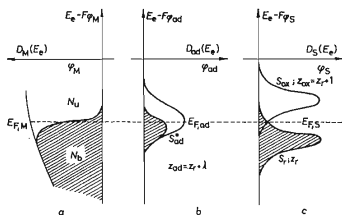


FIG. 1

Electron Term Energy Distribution Functions $D(E_e)$ for a Redox System at Equilibrium Potential ϕ_0

a) In the metal phase, b) in the adsorption layer, c) in the electrolyte.

The meaning of λ can be interpreted in different ways. First λ describes the probability of finding the transferred electron in the term system of the electrode metal. Contrary $1 - \lambda$ is the probability of locating the electron in the term system of the adsorbed substance. λ is also a measure of the dipole character of a covalent bond in a strong electric field. The dipole is the sum of the permanent dipole, when no field is present, and of the effect of electric polarization. Thirdly λ is a function of the position of the electron term energy distribution of the adsorbed species in relation to the Fermi energy level. At electronic equilibrium the Fermi-level in the metal and in the adsorption layer must have the same value.

The situation is illustrated in Fig. 1. The electron term energy distribution functions are shown. The distribution functions in the electrolyte (Fig. 1c) are compared with those in the adsorption layer (Fig. 1b) and in the metal (Fig. 1a). From Fig. 1a it can be seen there is also an electron energy distribution function in the metal. Occupied levels in the metal correspond to the charge states S_r present in the electrolyte. Unoccupied levels in the metal correspond to charge states S_{ox} present in the electrolyte. The Fermi energy level is common to the three distribution functions. Fig. 1 was first given by Plieth and Vetter⁴ where a more detailed description can be found. The situation remains unchanged if more than one electron is involved in the charge-transfer reaction (1) or (1a).

The Kinetics of the Adsorption and Desorption of the Redox Components

Now we can consider the adsorption steps which can be formulated



For a reduced or oxidized particle in a pre-electrode state the electron exchange frequency, between the metal and the outer Helmholtz plane, is smaller than the critical value 10^{10} s^{-1} . A limit of this exchange frequency can be approximately calculated in the following manner. Assume a concentration of $c_r = c_{ox} = 10^{-2} \text{ mol/l}$ (equal $2 \cdot 10^{-13} \text{ mol/cm}^2$ in a 2 \AA layer) and an exchange current density $i_0 = 1 \text{ A/cm}^2$. This gives an exchange frequency of $5 \cdot 10^7 \text{ s}^{-1}$. Much higher exchange current densities are necessary to reach the critical value 10^{10} s^{-1} .

Contrary to this behaviour the electron exchange frequency in the adsorption layer is higher than the critical value $\nu = 10^{10} \text{ s}^{-1}$. Therefore, if the reduced or oxidized particle is moving from the pre-electrode state towards the electrode surface the electron exchange frequency becomes successively higher and the covalent bond energy increases. In a first approximation the rate of the charge-transfer is determined by the equation for the tunnel effect

$$i \approx \exp(-d\sqrt{E_{\max}}/\text{const}), \quad (6)$$

where d is the distance and E_{\max} the height of the energy barrier between the particle and the electrode.

The movement of the adsorbing particle to the electrode is a part of the adsorption process. Firstly the solvation shell of the particle in the pre-electrode state orientates in such a way that the activation energy for adsorption is at a minimum. This process consists of several reorientations in the solvation shell. If the process is diffusion controlled the time constant is of the order of 10^{-10} s. Secondly the particle jumps into the new adsorption place. The time for this process is given by the oscillation frequency of the adsorbing particle (10^{-12} s). During this step electron equilibrium is established at a distance from the electrode where the electron exchange frequency is equal to the oscillation frequency of the adsorbing particle. Thirdly, the new distribution function for the solvation shell of the adsorbed specie is established. The time constant for this diffusion controlled process is 10^{-10} s.

In the transition state the energy of the system reaches a maximum. The activation energies of the reduced and oxidized components are different. The values are given in Fig. 2 (see⁵).

The question arises what happens in the reverse steps. These processes are described by the equations

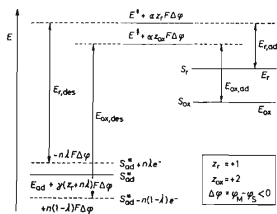
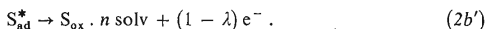
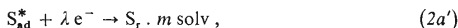


FIG. 2

Energy Levels for Substances S_r , S_{ox} and S_{ad}^* in the Adsorption Layer, the Transition State and the Electrolyte

The potential in the adsorption layer is $\varphi_{\text{ad}} - \varphi_S = \gamma(\varphi_M - \varphi_S)$; the potential in the transition state is $\varphi_{\ddagger} - \varphi_S = \alpha(\varphi_M - \varphi_S)$; the potentials are related to the potential in the electrolyte φ_S .

The same substance S_{ad}^* can desorb in two manners either by accepting λ electrons from the electrode or donating $(1 - \lambda)$ electrons to the electrode. At the beginning of the desorption of the particle S_{ad}^* the electronic equilibrium is still established. The value of λ varies with the distance of the particle from the electrode. At a critical distance the electronic equilibrium is no longer established. Desorption now occurs with the charge z_r or z_{ox} . The probability of the electron level being occupied or unoccupied at the critical distance determines the ratio of the numbers of the desorbing particles S_r and S_{ox} . After desorption separate electron term distribution functions for S_r and S_{ox} are formed.

For the desorption steps activation energies are necessary. The activation energy values for desorption as S_r or desorption as S_{ox} can be taken from Fig. 2. Details of Fig. 2 and the complete energy/distance relation can be found elsewhere⁵. From the activation energies for the adsorption and desorption steps the rate equations can be formulated. Assuming Langmuir conditions the following four equations (Vetter, Plieth⁵) are derived.

$$v_{r,ad} = k_{r,ad}a_r(1 - \Theta) \exp(-\alpha z_r F\varepsilon/RT), \quad (7a)$$

$$v_{ox,ad} = k_{ox,ad}a_{ox}(1 - \Theta) \exp(-\alpha z_{ox} F\varepsilon/RT), \quad (7b)$$

$$v_{r,des} = k_{r,des}\Theta \exp\{-[\alpha z_r - \gamma(z_r + \lambda) + \lambda] F\varepsilon/RT\}, \quad (7c)$$

$$v_{ox,des} = k_{ox,des}\Theta \exp\{-[\alpha z_{ox} - \gamma(z_r + \lambda) - (1 - \lambda)] F\varepsilon/RT\}. \quad (7d)$$

Θ is the surface coverage of S_{ad}^* , a_r and a_{ox} are the activities of S_r and S_{ox} in the pre-electrode state, α and γ the potential factors in Fig. 2 and ε a potential, relative to a constant reference electrode. Equations (7) are consistent with usual thermodynamic relations as was shown recently⁵.

For practical use Langmuir conditions are often not sufficient. By Plieth⁶ the equations (7) were extended to Frumkin-Temkin conditions. Assuming that the energy levels in the adsorption layer and in the transition state are influenced by the surface coverage Θ :

$$E_{ad} = E_{ad}^0 + g\Theta, \quad (8)$$

$$E_{\ddagger} = E_{\ddagger}^0 + \beta g\Theta, \quad (9)$$

then the following rate equations for adsorption and desorption are derived:

$$v_{r,ad} = k_{r,ad}a_r(1 - \Theta) \exp(-\beta g\Theta/RT) \exp(-\alpha z_r F\varepsilon/RT), \quad (10a)$$

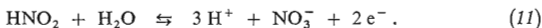
$$v_{ox,ad} = k_{ox,ad}a_{ox}(1 - \Theta) \exp(-\beta g\Theta/RT) \exp(-\alpha z_{ox} F\varepsilon/RT), \quad (10b)$$

$$v_{r,des} = k_{r,des} \Theta \exp \{ + (1 - \beta) g \Theta / RT \} \cdot \exp \{ - [\alpha z_r - \gamma(z_r + \lambda) + \lambda] F \epsilon / RT \}, \quad (10c)$$

$$v_{ox,des} = k_{ox,des} \Theta \exp \{ + (1 - \beta) g \Theta / RT \} \cdot \exp \{ - [\alpha z_{ox} - \gamma(z_r + \lambda) - (1 - \lambda)] F \epsilon / RT \}. \quad (10d)$$

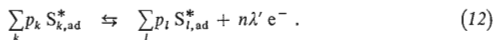
Heterogeneous Reactions in the Adsorption Layer

The previous discussion is limited to simple redox reactions (1) or (1a). The situation is different for complex redox processes, e.g. the $\text{HNO}_2/\text{HNO}_3$ -redox reaction



This has been discussed by Plieth⁷. In this paper only the results are given.

For a complicated redox system several species can be adsorbed on the electrode surface. Every adsorbed specie can have a partial charge. Reactions can be formulated between the adsorbed species



$S_{k,ad}^*$ and $S_{l,ad}^*$ are the adsorbed species, which can have partial charges, p_k and p_l are reaction numbers and $n \lambda'$ is the amount of charge-transfer (different for different heterogeneous reactions). Reaction (12) is an intermediate reaction in a general electrode process with n electrons.

In the adsorption layer, keeping in mind the discussion in the previous chapters, there is an equilibrium between the electrons in the adsorption layer and in the metal. During the reaction (12) the electronic equilibrium is shifted. Therefore the electron distribution between the metal and the adsorption layer is changed. The rate for a process in the adsorption layer is determined by the changes in chemical structure (Eq. (12)) and not by the electron transfer. Contrary to this behaviour in an ordinary charge-transfer process without adsorption steps the charge-transfer is rate determining.

For the heterogeneous reaction (12) an energy change occurs along the reaction coordinate. In the transition state the system reaches a maximum energy. The function of the energy to the reaction coordinate is described in the local cited paper⁷. Activation energies can be derived from this function. With these activation energies the rate equations for the forward and the backward reaction can be formulated (limited to Langmuir conditions and small coverages)

$$\vec{v} = \vec{k} \prod_k \Theta_k^{p_k} \exp(+\alpha(1-\gamma)n\lambda F\varepsilon/RT), \quad (13a)$$

$$\overleftarrow{v} = \overleftarrow{k} \prod_k \Theta_k^{p_k'} \exp(-(1-\alpha)(1-\gamma)n\lambda F\varepsilon/RT), \quad (13b)$$

Θ are the surface coverages, γ is the potential factor in Fig. 2, α is a factor describing charge change in transition state and ε a potential relative to a constant reference electrode. Analogous to Eq. (10) the usual thermodynamic relations are fulfilled for Eq. (13).

For practical use the Langmuir conditions have to be changed to Frumkin-Temkin conditions. Details are given elsewhere⁶. Concentrations a_k or a_1 can be inserted in Eq. (13) instead of some of the surface coverages Θ for reactions involving adsorbed and nonadsorbed species, *e.g.* hydrogen ions in the solutions.

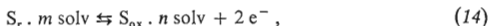
The Complex Charge-Transfer Mechanism

The previous discussion has shown that various partial reactions in an overall charge-transfer process are possible, if adsorption steps are involved. Even in a very simple overall electrode reaction, *e.g.* Eq. (1) partial reactions can occur. A charge transfer mechanism must be considered instead of one charge-transfer reaction. A partial charge-transfer is possible with every partial reaction. Therefore the single reaction steps are charge-transfer processes and remain part of the overall charge-transfer reaction.

Each partial reaction can become rate determining. Therefore it is possible that the adsorption/desorption of S_r , the adsorption/desorption of S_{ox} or a chemical reaction in the adsorption layer is the slowest step. The mathematical treatment, given by Plieth and Vetter⁵⁻⁸, shows that nearly identical types of stationary current potential relations can be derived for each of the three cases. The three cases are characterized by the possibility to obtain negative Tafel-slopes⁸, contrary to reactions involving no adsorption. It becomes difficult to determine the true nature of the charge-transfer process with stationary methods. Non-stationary methods are better for this purpose.

Charge-Transfer Reaction Involving Two Electrons

The possibility for a two electron charge-transfer reaction



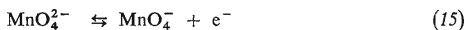
to occur has been discussed. Such a process can not occur unless adsorption steps are involved in the reaction. A transfer of a dimer electron from the outer Helmholtz plane to the metal or *vice versa* is extremely unlikely. A dimer electron is not known.

Only two separate consecutive one electron reactions can occur in an electrode process without adsorption.

If adsorption steps are involved a two electron process is possible because the electron movement is much faster than that of the atoms and the molecules. In an intermediate reaction a partial charge-transfer $\lambda > 1$ or $1 - \lambda > 1$ can be involved. Two electrons are transferred in this reaction in the limiting case $\lambda \rightarrow 2$ or $1 - \lambda \rightarrow 2$. This is followed by a second adsorption/desorption step.

Experimental Examples

Adsorption steps in an electron process have often been reported in literature. Reviews are available¹⁸ Lorenz and coworkers⁹⁻¹⁴ have found several examples of partially charged adsorbed species. In this paper experimental results are reported which indicate the existence of adsorption steps in the redox system $\text{MnO}_4^{2-}/\text{MnO}_4^-$ with the overall reaction



The experimental details are published elsewhere^{6,15}. Only a short review is given here.

Current time curves were measured with a fast potentiostat, built in our laboratory¹⁶. The potentiostat corrected for an ohmic resistance. The currents were extrapolated to $t = 0$. Diffusion effects can be eliminated and a fast charge-transfer can be

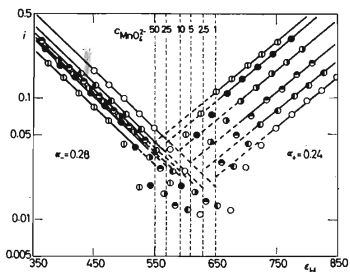


FIG. 3

The Potentiostatic Measurements of Current (i , $\text{A} \cdot \text{cm}^{-2}$)-Potential (ϵ_H , mV) Curves

$\text{MnO}_4^{2-}/\text{MnO}_4^-$ on platinum; effect of the MnO_4^{2-} -concentration; $c_{\text{MnO}_4^-} = 5 \cdot 10^{-3}$ mol/l, $c_{\text{NaOH}} = 1$ mol/l, $c_{\text{MnO}_4^{2-}}$ is indicated in the figure in 10^{-3} mol/l; temp. 25°C.

measured with this method. Current-potential curves have been plotted from the extrapolated current values. Measurements were made on platinum and gold. The results obtained using a platinum electrode are given in Fig. 3 and 4. Fig. 3 represents the effect of the MnO_4^{2-} -concentration on the current-potential curves. Fig. 4 shows the effect of the MnO_4^- -concentration on the current-potential curves.

Although Tafel-lines were found, there are characteristic difference to the normal behaviour of current-potential curves. The sum of charge-transfer coefficients α_+ and α_- does not equal 1. It is $\alpha_+ + \alpha_- < 1$. The effect of concentration is unusual. The extrapolation of Tafel-lines to $\varepsilon = \varepsilon_0$ gives different exchange current densities. Values for the polarization resistance in these solutions were determined separately. The exchange current density can also be derived from the polarisation resistance. These values differ from the extrapolated values obtained from the anodic and cathodic Tafel-lines, the same results were found for gold electrodes.

This behaviour is affected by the pretreatment of the electrode surface. The electrodes were treated with hot concentrated nitric acid and then washed with distilled water. Smaller current values and a normal Tafel behaviour were found on electrodes not treated in this manner.

The observed behaviour can be understood if adsorption steps are assumed. Then the charge-transfer reaction is formulated as follows

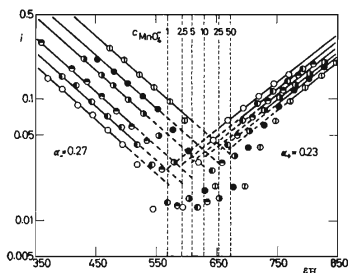
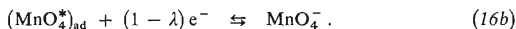
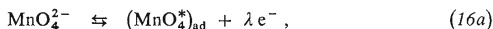


FIG. 4

The Potentiostatic Measurements of Current (i , $\text{A} \cdot \text{cm}^{-2}$)–Potential (ε_{H} , mV) Curves

$\text{MnO}_4^{2-}/\text{MnO}_4^-$ on platinum; effect of the MnO_4^- -concentration; $c_{\text{MnO}_4^{2-}} = 5 \cdot 10^{-3}$ mol/l, $c_{\text{NaOH}} = 1$ mol/l, $c_{\text{MnO}_4^-}$ is indicated in the figure in 10^{-3} mol/l, temp. 25°C .

The adsorption of the negative ions MnO_4^{2-} and MnO_4^- can occur on the positive platinum electrode. The equilibrium potential of the $\text{MnO}_4^{2-}/\text{MnO}_4^-$ redox system in $\ln \text{NaOH}$ is $\varepsilon_{0,H} = 0,610 \text{ V}$. The adsorption of the MnO_4^- ion on gold electrodes could be directly measured. The measurements indicate higher surface coverages. The fast potentiostatic measurements do not considerably change the coverage under this conditions. During the time of extrapolation it is assumed that the surface coverage is nearly equal to the equilibrium value. This assumption is confirmed by the analysis of the current time curves. If the surface coverage approaches the saturation value, despite the relative constancy of θ , the value of $1 - \theta$ in relation to $1 - \bar{\theta}$ can be remarkably changed by a potential variation. This must be considered in the interpretation of the experimental results.

A detailed discussion shows that Frumkin-Temkin conditions must be used (Eq. (10)). For the equilibrium coverage $\bar{\theta}$ the following Frumkin-Temkin isotherm can be used⁶

$$\bar{\theta} = K + [1 + \gamma(z_r + \lambda) - \lambda] \frac{RT}{g} \ln c_r - [\gamma(z_r + \lambda) - \lambda] \frac{RT}{g} \ln c_{ox}. \quad (17)$$

This equation has to be inserted for $\bar{\theta}$ into equations (10). Furthermore the effect of the potential on $1 - \theta$ must be considered. The rate determining processes can be evaluated from the resulting equations. The anodic process can be associated with the adsorption of the reduced component $v_{r,ad}$, the cathodic process can be associated with the adsorption of the oxidized component $v_{ox,ad}$.

TABLE I

Exchange Current Densities i_0 , $i_{0,+}$ and $i_{0,-}$ (mA/cm²) and the Calculated Value $i_{0,+}i_{0,-}/(i_{0,+} + i_{0,-})$ for Platinum Electrodes and Different MnO_4^{2-} Concentrations (10^{-3} mol/l); $c_{\text{MnO}_4^-} = 5 \cdot 10^{-3}$ mol/l; $c_{\text{NaOH}} = 1$ mol/l; Temp. 25°C

$c_{\text{MnO}_4^-}$	i_0	$i_{0,+}$	$i_{0,-}$	$\frac{i_{0,-}i_{0,+}}{i_{0,+} + i_{0,-}}$
1.0	9.5	22.5	18.5	9.9
2.5	10.7	25.5	18	10.6
5.0	11.7	30	21	12.4
10.0	14.6	38	22.5	14.1
25.0	18.3	44	28	17.1
50.0	18.3	44	28.5	17.3

The interpretation of experimental results is confirmed by the measured exchange current densities. If the charge-transfer occurs in two steps the polarization resistance R_p is given by the equation

$$R_p = \frac{RT}{F} \left(\frac{1}{i_{0,+}} + \frac{1}{i_{0,-}} \right), \quad (18)$$

$i_{0,+}$ and $i_{0,-}$ are the respective exchange current densities. This relationship, which was first evaluated for a two electron process^{17,18} is also valid for a one electron process involving two adsorption steps⁵. Therefore the exchange current density i_0 , which can be calculated from the experimental polarization resistance according to $i_0 = RT/FR_p$, is related to the anodic and cathodic extrapolated exchange current densities $i_{0,+}$ and $i_{0,-}$ as follows

$$i_0 = i_{0,+} i_{0,-} / (i_{0,+} + i_{0,-}). \quad (19)$$

TABLE II

Exchange Current Densities i_0 , $i_{0,+}$ and $i_{0,-}$ and Calculated Value $i_{0,+} i_{0,-} / (i_{0,+} + i_{0,-})$ for Platinum Electrodes and Different MnO_4^- Concentrations (10^{-3} mol/l); $c_{\text{MnO}_4^{2-}} = 5 \cdot 10^{-3}$ mol/l; (mA/cm²) $c_{\text{NaOH}} = 1$ mol/l; Temp. 25°C

$c_{\text{MnO}_4^-} \cdot 10^{-3}$	i_0	$i_{0,+}$	$i_{0,-}$	$i_{0,+} i_{0,-} : (i_{0,+} + i_{0,-})$
1.0	11.7	27	20	11.5
2.5	12.2	29	20	11.9
5.0	12.8	30	22	12.7
10.0	15.1	33	27.5	15
25.0	17.1	37.5	29.5	16.3
50.0	18.4	40	35	18.7

In Tables I and II the experimental and the calculated values have been compared. The result confirms strongly a mechanism of two consecutive partial reactions. For the very simple overall electrode process (15) the intermediate reactions can only be adsorption/desorption steps.

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