Influence of Structure of the Electrode Double Layer
on Electrode Processes.*

By

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The problem I am going to deal with has been restricted mostly to the influence of the potential difference in the diffuse double layer. The principal theory of Frumkin is based on two ideas.

1. The activity of the reacting particle in the outer Helmholtz plane (in the present way of speaking) differs from its value in the bulk of the solution as the energy necessary for the transfer of this particle to the outer Helmholtz plane has to be taken into account. This is expressed by the coefficient \( \exp \left( -\frac{z_A \varphi_2}{2F/R T} \right) \) where \( z_A \) is the charge of the reacting particle, and \( \varphi_2 \) the potential difference in the diffuse double layer.

2. The contribution of the difference of the electrical potential between the electrode and the solution to the activation energy of an electrode reaction is diminished by the potential difference in the diffuse double layer. Thus, the electrode reaction rate constant at the standard potential of this reaction \( k \) depends on the value of \( \varphi_2 \) in the following way:

\[
k = k^0 \exp \left[ -\frac{(z_A - n \alpha)F \varphi_2}{RT} \right]
\]

where \( n \) is the number of elementary charges transferred and \( \alpha \) the electron transfer coefficient.

With respect to this influence we have investigated in some detail the discharge of the zinc ion at the mercury electrode. The value of \( \alpha \) has been found \( \alpha \approx 0.24 \) independent of concentration of an indifferent electrolyte. This result is not in accord with the results of Hush who found a considerable dependence using the faradayic impedance method.

The dependence of \( k \) on the concentration of indifferent electrolyte is in good agreement with the above equation. The low value of \( \alpha \) suggests that there are two consecutive one electron steps, the first of them being rate-determining. The adsorption of iodide ions accelerates the electron reaction. Adsorbable cations like tetraalkylammonium ions have an inhibitive effect. In the presence of both tetraalkylammonium and iodide ions the process is accelerated at more positive potentials, but very strongly retarded at negative potentials. Perchlorate reinforces the inhibition by tetraalkylammonium ions. These effects are in connection with a composite structure of the double layer in these solutions which is still unclear.

The reduction of oxygen is an example of a consecutive electrode reaction of an uncharged particle where hydrions take part. It should also be stressed that the process takes place at potentials more positive than that of electrocapillary zero.

Reduction of oxygen at mercury electrodes was investigated by a number of authors (Vitek, Iofa and coworkers, Agar, Bagotsky and coworkers). Most of them con-

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cluded that the rate determining step in this process is the electrode reaction in which the peroxyd anion $O_2^-$ is formed. This conclusion is based on the experimental finding that the current density is independent of hydrogen ion concentration, except in very acid and alkaline media. Bagotsky was the first to observe the anodic oxidation of hydrogen peroxide at a mercury electrode, and the reversible diffusion controlled process in alkaline media. He also gave a kinetic interpretation to this phenomenon and pointed out a strong retarding effect of specifically adsorbed anions on this process.

The general case of a consecutive electrode reaction was treated by Vetter. In the present paper a somewhat different procedure has been adopted the results of which are more suitable for analysis of polarographic experiments. Furthermore the influence of the potential difference in the diffuse double layer has been taken into account.

The possible process in the two-step reduction of oxygen to hydrogen peroxide are as follows:

**First step**

\[
\begin{align*}
O_2 + e & \rightleftharpoons O_2^- \\
O_2^- + H^+ & \rightleftharpoons HO_2 \\
O_2^+ + e & \rightleftharpoons HO_2
\end{align*}
\]

**Second step**

\[
\begin{align*}
O_2^- + e & \rightleftharpoons O_2^2^- \\
HO_2 + e & \rightleftharpoons HO_2^- \\
HO_2^+ + e & \rightleftharpoons H_2O_2
\end{align*}
\]

If different protonization forms of oxygen are denoted as $A$, of peroxy radical as $B$ and of hydrogen peroxide as $C$, then the consecutive electrode reaction can be written schematically

\[
A \overset{k_1^+ + k_2^-}{\rightleftharpoons} B \overset{k_3^+}{\rightleftharpoons} C
\]

Let us suppose that oxygen takes part in the first reaction step having a charge $z_A$ (i.e. after an uptake of $z_A$ protons, $z_A$ being 0 or 1), while the reacting form of peroxy in the second reaction step is $z_B$ (it contains $z_B + 1$ protons). Considering the possible dissociation of peroxy ($K_{H\text{O}_2} \approx 10^{-7}$) and denoting the overall concentration of $A$, $B$ and $C$ as $c_A$, $c_B$ and $c_C$, respectively, we obtain the current density $j$

\[
j = \frac{k_1^+ a_{H^+} e_A}{c_A} \exp \left(\frac{-z_A F \varphi_2}{RT}\right) k_2^+-k_1^- a_{H^+ + K_{H\text{O}_2}} \exp \left[\frac{-z_A - 1}{RT}\right] c_B + k_3^+ a_{H^+ + K_{H\text{O}_2}} \exp \left[\frac{-z_B - 1}{RT}\right] c_C
\]

In this equation $\varphi_2$ is the potential difference in the diffuse double layer (between the outer Helmholtz plane and the bulk of solution), $k_1^+$, $k_1^-$, $k_2^+$ and $k_2^-$ are the potential dependent electrode reactions constants.

If the steady-state condition for the instable intermediate $B$ is introduced (i.e. $c_B = \frac{k_1^+ c_A + k_2^- c_C}{k_1^- + k_2^+}$) the resulting equation is

\[
j = \frac{2Fk_1^+ a_{H^+} e_A}{1 + k_2^- a_{H^+ + K_{H\text{O}_2}}} \exp \left(\frac{-z_A F \varphi_2}{RT}\right) \left[\frac{c_A}{k_1^- k_2^- a_{H^+ + K_{H\text{O}_2}}} \exp \left[\frac{-z_B - 1}{RT}\right] c_C\right]
\]

This may be further simplified by inserting

\[
k_1^- k_2^- = \frac{1}{k_1^+ k_2^+ a_{H^+ + K_{H\text{O}_2}}} \exp \left[\frac{2F(E - E_H^\circ)}{RT}\right]
\]

where the hydrogen ion dependent standard electrode potential $E_H$ is given by the equation
Now the exponential dependence of the electrode reaction constants will be expressed using $\alpha_1$ and $\alpha_2$ as charge transfer coefficients for the first and second electrode reaction and relating the electrode potentials to $E_R^*$:

$$E_R^* = E^* + \frac{RT}{2F} \ln [a_{H^+}(a_{H^+} + K_{H2O2})]$$

In this equation the electrode reaction constants at standard potential, $\bar{k}_1^*$ and $\bar{k}_2^*$, are given by the expressions

$$\bar{k}_1^* = k_1^* a_{H^+}^{z_{a,1/1}}(a_{H^+} + K_{H2O2})^{-z_{a,1/1}} \exp \left[ -\frac{(z_{a,1} - \alpha_1)F\varphi_2}{RT} \right]$$

$$\bar{k}_2^* = k_2^* a_{H^+}^{z_{a,2/1}}(a_{H^+} + K_{H2O2})^{-z_{a,1/2} + z_{a,1/2}} \exp \left[ -\frac{(z_{a,2} - \alpha_2)F\varphi_2}{RT} \right]$$

If the first step is rate-determining, i.e. the fraction in the denominator is smaller than unity,

$$\frac{\bar{k}_1^* \exp \left[ \frac{(1-\alpha_1)F(E-E_R^*)}{RT} \right]}{\bar{k}_2^* \exp \left[ -\frac{\alpha_2F(E-E_R^*)}{RT} \right]} < 1$$

it follows

$$j = 2Fk_1^* \left[ \exp \left[ -\frac{\alpha_1F(E-E_R^*)}{RT} \right] \right] \left[ \exp \left[ -\frac{2(1+\alpha_1)F(E-E_R^*)}{RT} \right] \right] c_1$$

For not too alkaline media, where the ionization of hydrogen peroxide may be neglected, we have

$$a_{H^+} \gg K_{H2O2}$$

$$\left( \frac{\partial \log k_1^*}{\partial pH} \right) \varphi_2 = 2 \cdot 3RT \left( \frac{\partial \log k_2^*}{\partial \varphi_2} \right) pH = \alpha_1 - z_{a,1}$$

On the other hand, if the second reaction determines the rate of the over-all electrode process the fraction in the denominator is greater than the unity

$$\frac{\bar{k}_1^* \exp \left[ \frac{(1-\alpha_1)F(E-E_R^*)}{RT} \right]}{\bar{k}_2^* \exp \left[ -\frac{\alpha_2F(E-E_R^*)}{RT} \right]} > 1$$

and we obtain

$$j = 2Fk_2^* \left[ \exp \left[ -\frac{(1+\alpha_1)F(E-E_R^*)}{RT} \right] \right] \left[ \exp \left[ -\frac{(1-\alpha_2)F(E-E_R^*)}{RT} \right] \right] c_2$$

Finally, for $a_{H^+} \gg K_{H2O2}$

$$\left( \frac{\partial \log k_2^*}{\partial pH} \right) \varphi_2 = 2 \cdot 3RT \left( \frac{\partial \log k_2^*}{\partial \varphi_2} \right) pH = \alpha_2 - z_{a,2}$$

For an irreversible process, i.e. if the backward electrode reaction may be neglected, we have in the first case

$$j = 2Fk_1^* a_{H^+}^{z_{a,1}} \exp \left[ -\frac{\alpha_1 \left[ E - E^* + \frac{z_{a,1} - 1}{\alpha_1} \varphi_2 \right]}{RT} \right] c_1$$

and in the second case
The polarographic reduction wave of oxygen is irreversible and independent of pH up to pH ≈ 8 if the concentration and kind of the anion of the electrolyte is kept constant. From this follows that either \( z_A = 0 \) in the first reaction step or \( z_B = -1 \) in the second reaction step as rate determining. In the Fig. 1 are shown the log. plots of \( \frac{i}{(i_d-i)} \) vs. electrode potential (drop time \( t_1 = 0.33 \) sec., \( T = 25^\circ C \)) for 0.1M \( \text{NH}_4\text{F} \) and 0.1M \( \text{NH}_4\text{Cl} \). The shift of the plot to more negative potential in the chloride solution is about 110 mV. If the current values are plotted vs. \( E - \varphi_2 \) instead of \( E \) a nearly identical line is obtained. This is in coincidence with the above finding. The over-all value of the charge transfer coefficient is 0.55. This means that the first step is rate-determining since otherwise the over-all value of the charge transfer coefficient had to be greater than unity.

In alkaline media the electrode reaction is no more totally irreversible and the backward reaction must be accounted for. This makes possible the direct determination of the electrode reaction rate constant at the standard potential on the basis of polarographic

\[
j = 2Fk_2^{*}a_m^{z_{*+1}} \exp \left\{ - \frac{(1-\alpha_2) \left[ E - E^\circ + \frac{z_B + 1}{\alpha_2 + 1} - 1 \right] \varphi_2}{RT} \right\} e_A
\]

![Fig. 1 Dependence of \( \log \frac{i}{(i_d-i)} \) vs. \( E \) for 0.1M \( \text{NH}_4\text{F} \) and 0.1M \( \text{NH}_4\text{Cl} \)](image1)

![Fig. 2 Dependence of \( \log k_1^0 \) vs. pH for borate and ammonia-ammonium chloride buffers](image2)
measurements. The dependence of this constant on pH is shown in the Fig. 2 for ammonium fluoride and sodium borate buffer solutions. The ionic strength was in the first case 0.1, in the second 0.2. The value of $\varepsilon - \varepsilon_s$ was 0.55 and 0.57 respectively, which is in full accord with the former results.

Much effort has been devoted by the Prague school to elucidate electrode processes influenced by adsorption of surface active, but electro-inactive substances which are strongly adsorbed at the electrode.

The initial observation was made by Wiesner. He found that the polarographic anodic wave of hydroquinone was diminished in presence of eosine. The decrease of the wave depends on the concentration of this substance. Wiesner concluded correctly that the hindrance of the electrode process was caused by adsorption of eosine. I tried to give a quantitative explanation to this effect. I assumed that eosine was so strongly adsorbed at the electrode that a concentration much lower than that present in the solution corresponded to the practically total coverage of the electrode. Thus, if the maximum concentration $I_m$ is not achieved a diffusion flux exists at the electrode. The surface concentration $I$ of the adsorbed species does not influence the electrode process unless a maximum concentration $I_m$ is reached. Then the electrode process is stopped.

Under these assumptions the surface concentration is determined by diffusion of the substance, for the dropping electrode simply

$$I' = \int_0^t \sqrt{\frac{7}{3} \frac{D}{\pi t}} dt = 2\varepsilon \sqrt{\frac{7}{3} \frac{D}{\pi t}}$$

The relative coverage $\theta$ is given by the relation

$$\theta = \frac{I'}{I_m} = \frac{t}{\bar{\theta}}$$

where $\bar{\theta}$ is the time of coverage ($I_m = 2\varepsilon \sqrt{\frac{7}{3} \frac{D\bar{\theta}}{\pi}}$).

This very simple model worked for some cases of limiting diffusion currents. A good example is the discharge reaction of cadmium ions in the presence of tribenzylammonium cation as surface active agent. The instantaneous current preserves the normal course practically to the time of coverage. Then it falls instantly to zero. The electrode process has this mechanism in a wide potential range so that on a current-voltage curve only a diminished horizontal limiting current is observed. With this experiment the sieve theory of Loshkarev and Kryukova is called in question as far as mercury electrode is concerned. These authors concluded on the basis of similar experiments that at electrodes covered by adsorbed films of surface active substances the electrode process is controlled by retarded penetration through the film. This process should be independent of potential. The real cause of the effect is that the diffusion controlled current can flow only in a fraction of the drop-time.

This treatment is restricted to limiting diffusion currents only and to some more or less exceptional cases. A more general approach was suggested by Schmidt and Reilley who assumed that during adsorption of a surface active substance the electrode may be divided in two parts, the covered and the uncovered surface. The electrode reaction takes place at both these areas with a different rate. The effective electrode reaction rate constant $k_{eff}$ is then given by the reaction

$$k_{eff} = k_o(1 - \theta ) + k_i \theta$$

where $k_o$ is the original rate constant, $k_i$ the rate constant at the covered surface. This is the principal idea of the steric inhibition of an electrode reaction. We solved this problem
together with Koutecký and Weber\textsuperscript{17} for the general case of diffusion of the electroactive substance to the electrode. As shown by Kúta and Smoler\textsuperscript{18} the experimental results coincided with this theory if uncharged surface active substances were adsorbed at the electrode. Large discrepancies were found with surface active ions. If e.g. the electroactive substance are cations and surface active ions also cations, the inhibition is much stronger than expected under assumption of the steric inhibition only. Following the lines of Frumkin’s theory\textsuperscript{19} of diffuse double layer influence on an electrode reaction Koutecký and coworkers\textsuperscript{144} tried to overcome this difficulty taking into account that the adsorbed ionic layer changes the value of the potential difference in the diffuse double layer \( \varphi_s \). This change should be a linear function of the coverage, namely,

\[
\Delta \varphi_s = \Delta \varphi_s^* \theta
\]

According to this assumption the effective rate constant could be expressed by the relation

\[
k_{\text{eff}} = k_e \exp \left[ - \frac{(z_e - \epsilon_\alpha) F \Delta \varphi_s^* \theta}{RT} (1 - \theta) + k_i \theta \right]
\]

It was possible to bring some experimental results in coincidence with this theory, however, on the other hand, the problem was elucidated by an intuitive assumption about a linear dependence of \( \Delta \varphi_s \) on the coverage \( \theta \).

Later we tried with Holub\textsuperscript{19} to work out a very simple model of the double layer for the case of adsorption of voluminous organic substances with the aim to explain the change of the electrode reaction rate with coverage of the electrode, assuming only electrostatic effects.

Thus, for the irreversible reduction of an electroactive substance, the validity of Frumkin’s formula\textsuperscript{19}

\[
i = k \exp (-\alpha n F E/RT) \exp \left[ -(z - \epsilon_\alpha) F \varphi_s^* /RT \right]
\]

is assumed where \( \varphi_s \) is the potential difference in the diffuse double layer and other symbols denote the well known quantities.

According to Grahame and Parsons\textsuperscript{19} the potential difference in the compact double layer can be approximately expressed by the equation

\[
\varphi_{\text{n-2}} = \phi^* + \psi^n
\]

where \( \psi^n \) depends only on the charge of the electrode and \( \psi^n \) only on the surface concentration of adsorbed ions. This equation may be written as follows

\[
\varphi_{\text{n-2}} = \frac{q_1}{K^s} + \frac{q}{K^o^n}
\]

where \( q_1 \) is the charge of adsorbed ions per sq. cm., \( q \) the charge of the electrode, \( K^s \) and \( K^o^n \) the corresponding integral capacities. \( K^s \) has an approximately potential independent value, \( K^o^n \) an identical potential dependence in solutions of monovalent inorganic anions (this refers to anions of the same types but the difference between halides and oxyanions does not considerably influence the results of this paper).

If large organic ions are adsorbed, water molecules are squeezed out of the interface in the area covered by the adsorbed ion and \( K^o^n \) may be expressed in the following way

\[
K^o^n = K_0^{o^n} (1 - \theta) + K_1^{o^n} \theta
\]

where \( K_0^{o^n} \) is the original value of the integral capacity corresponding to the charge of the electrode with a water layer, \( K_1^{o^n} \) the same quantity in the area covered by the organic substance which has usually a low value and is only weakly dependent on electrode potential. \( \theta \) is the coverage of the electrode.

The charge of adsorbed ions is given by the expression
where \( I_{m} \) is the maximum surface concentration and \( \zeta' \) the charge carried by the ion. For the potential difference in the diffuse double layer it follows

\[
\varphi_3 = \frac{2RT}{F} \ln \left( \frac{\theta I_{m} \zeta' F + q}{2A} \right)
\]

where \( A = 5.86 \sqrt{c} \) for aqueous solutions of a univalent electrolyte in concentration \( c \) at 25°C.

The electrode potential \( E \) (vs. S.C.E.) is given by the equation

\[
E = -0.472 + \varphi_3 + \frac{2RT}{F} \ln \left( \frac{\theta I_{m} \zeta' F + q}{2A} \right)
\]

Assuming the validity of the Frumkin equation we calculated the values of \( \varphi_3 \) as function of \( \theta \) from polarographic instantaneous current-time curves of 0.01M \( \text{VO}_2^+ \) in 0.1M \( \text{HNO}_3 \) in the presence of \( 10^{-4} \) tribenzylammonium ion for the electrode potential \(-0.917\) V where the current is controlled merely by the electrode reaction rate without interference of diffusion (Fig. 3).

The coincidence of the experimental and theoretical values is not bad for a very simple model used in the present paper. One source of discrepancy at higher coverage may be that the steric inhibition by the adsorbed substance has been entirely neglected.

Fig. 3 Comparison of the experimental and theoretical dependence for the system of 0.01M \( \text{VOSO}_4 \), 0.1M \( \text{HNO}_3 \), \( 10^{-4} \)M tribenzylammonium ion at \(-0.917\) V vs. S.C.E. Curve 1 was calculated from the experimental \( i-t \) curve; the blocking effect was neglected. Curve 2 was calculated under assumption of the blocking effect. Curves 3 and 4 are theoretical dependences for \( K^* = 15 \) and \( 21 \) \( \mu F/\text{sq.cm.} \) and \( K_{102} = 5.7 \frac{\mu F}{\text{sq.cm.}} \).

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