

NEW METHOD FOR THE DESCRIPTION OF MIGRATION CURRENTS
AND A CRITICAL ANALYSIS OF THE HEYROVSKY METHOD

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For a detailed description of complex, multicomponent, current systems, it is necessary to solve a system of nonlinear equations, taking into account the diffusion i^{dif} and migration i^{migr} current components in the diffusion layer:

$$D_k z_k \frac{dc_k}{dx} + z_k^2 D_k c_k \frac{d\psi}{dx} = \frac{i_k}{F}, \quad (1)$$

where D_k , c_k , z_k , and i_k are the coefficients of diffusion, concentration, charge, and current, corresponding to the k^{th} component of the solution, and $\psi = F\varphi/RT$ is the dimensionless potential. System (1) supplements the condition of electrical neutrality $\sum_i c_i z_i = 0$ and the boundary conditions $c_k(L) = c_k^0$, $\psi(L) = 0$ where L is the thickness of the diffusion layer.

Since the production of a solution for system (1), in explicit form, could be found only in the simplest cases, Heyrovsky, in 1934, proposed an approximate method for calculating the migration currents [1, 2] (see also [3]), assuming a linear relation:

$$i_k^{\text{migr}} = t_k i, \quad i = \sum_k i_k, \quad (2)$$

where $t_k = z_k^2 D_k c_k^0 / \sum_i D_i c_i^0 z_i^2$ is the number of transpositions of the k -th component. (In his original paper

Heyrovsky considered the case when ions of only one sort were discharged.) The simple linear relation (2) makes it possible, in the general case, to link the diffusion current of the k -th component with the full current

of any component: $i_k^{\text{dif}} = i_k - t_k \sum_i i_i$. The relationship (2) could also be registered in the form: $i_k^{\text{migr}} = \alpha_{kl} i_l$

where $\alpha_{kl} = z_k^2 D_k c_k^0 / \sum_m D_m c_m^0 z_m^2$.

In the general case it is not difficult to see that the relationship between i_k^{migr} and i_l resulting from the nonlinear system (1), must itself be nonlinear. However, if the current in the system is small, as compared with the limiting currents, this relationship must transform into a linear one, and this will be derived below. From (1), with allowance for the condition of electrical neutrality, it is easy to derive:

$$\frac{d\psi}{dx} = \left[\sum_i (i_i / D_i F) \right] / \left(\sum_m z_m^2 c_m \right). \quad (3)$$

With currents which are small, compared with the limiting currents, we may write approximately, in (3) and in the expression for i^{migr} , that $c_m \sim c_m^0$. Then, for i^{migr} we have

$$i_k^{\text{migr}} = z_k^2 D_k c_k^0 \left[\sum_i (i_i / D_i) \right] / \left(\sum_m z_m^2 c_m^0 \right) = \beta_{kl} i_l, \quad (4)$$

where

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$$\beta_{kl} = z_k^2 D_k c_k^0 / \left(D_l \sum_m z_m^2 c_m^0 \right). \quad (5)$$

A comparison of the matrices α and β shows that, even with a linear approximation, the Heyrovsky method is incorrect. The matrix elements β_{kl} , as distinct from the elements α_{kl} , depend on the index l . The diagonal elements β are relative ionic forces, while the diagonal elements α are transport numbers.

Since correct linear relationships of the type (4) and (5) are valid only for small currents, an estimate of the limiting currents based on them, as in the case of the Heyrovsky method, is very imprecise. The following example illustrates the improvement of the method: We will consider a 1-component system ($i_1 = 1$, $i_k > 1 = 0$) in (1), and (3) $c_m = c_m^0$ ($2 \leq m \leq 1$) and $c_1 = c_1(x)$. Then, integrating (1), we obtain at $c_1(0) = 0$:

$$i_{\max} = \frac{z_1 F D c_1^0}{L} \left\{ 1 + c_1^0 z_1^2 / \left[2 \left(\sum_{m=2} c_m^0 z_m^2 \right) \right] \right\}. \quad (6)$$

Comparison of (6), and of the result based on (4), (5), with the precisely solved Eucken problem, shows the proximity of the limiting current (6) to Eucken's result, over a wide range of the ratio of the concentration of the discharging cation to the concentration of the supporting electrolyte.

A detailed analysis of the consequences of the proposed method and consideration of concrete problems will be given in a more detailed publication.

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POLAROGRAPHIC ELECTROREDUCTION OF METAL IONS WITH CATALYSIS BY THE LIGAND PRODUCT OF A PARALLEL ELECTRODE REACTION

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Catalytic electrode processes of reduction or oxidation of metal ions, with participation of a ligand catalyst, are normally investigated by introduction into the solution of the corresponding ligand [1]. At the same time, there are a very few examples [2, 3], in which analogous processes are observed, under the conditions that the ligand catalyst is produced at an electrode, as the result of a parallel electrode reaction. Similar modeling of electrocatalytic processes is very important for an understanding of their nature.

In the present contribution, we introduce a new example of the electroreduction of metal ions (Ge(IV) ions) in the presence of a ligand catalyst (I^- ions), formed at an electrode as the result of a parallel electrode reaction (electroreduction of IO_3^- ions). The mechanism of the catalytic process of reduction of Ge(IV) in strongly acid solutions, containing I^- ions (in the absence of IO_3^-), was studied by us previously [4]. If, in a supporting electrolyte of 7 to 8 M $HClO_4$, the I^- ions were replaced by IO_3^- ions, which are reduced at more positive potentials than Ge(IV) to form I^- ions [5], the same catalytic wave was produced as for the reduction of Ge(IV) ($E_{1/2} = -0.51$ V relative to sce), which enabled us, with allowance for the data of [4], to propose the following scheme for the electrode catalytic process:

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