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Abstract

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ON THE DIFFERENCE OF POTENTIALS AND THE ACCUMULATION OF THE CONSTITUENTS OF A SOLUTION IN THE DIFFUSION LAYER UNDER STATIONARY ELECTROLYSIS

The purpose of the present communication is to draw attention to certain features of the distribution of concentration and potential in the diffusion layer under stationary electrolysis. Although, for the special case of a solution containing univalent ions at a dilution allowing the laws of ideal systems to be applied, the correct treatment was given by Eucken as early as 50 years ago (^{1}), subsequently insufficient attention has been paid to these questions. Let us first consider the case of stationary electrolysis of a binary electrolyte of arbitrary concentration, consisting of a discharging cation with charge number n_1 and a non-discharging anion with charge number n_2. The activities of the one and the other ion in the bulk of the solution outside the diffusion layer, which we shall assume to be the same at all points of the solution, will be denoted by a_1' and a_2', and the activities in the diffusion layer directly at the electrode surface by a_1'' and a_2''. Since under stationary conditions the non-discharging anion is immobile, according to Boltzmann' s formula

$$\Phi = \frac{RT}{n_2 F} \ln \frac{a_2''}{a_2'}, \tag{1}$$

where Φ is the potential difference between a point at the electrode surface and the middle of the solution.

At first sight it appears that equation (1) permits determination of the quantity a_2''/a_2' and, consequently, comparison of the values of the activity of an individual ion at any concentrations. Such a conclusion, however, would be erroneous, since what is directly accessible to measurement is not the quantity Φ, but the sum $\Phi + \Delta\varphi$, where $\Delta\varphi$ is the change in the electrode-solution potential difference φ

owing to the change in concentration in the near-electrode layer (concentration polarization in the usual sense of the word).* If it is assumed that the electrode is reversible with respect to the discharging cation, then

$$\Delta\varphi = \frac{RT}{n_1 F} \ln \frac{a_1''}{a_1'},$$

whence

$$\Phi + \Delta\varphi = \frac{RT}{F} \ln \left(\frac{a_1''}{a_1'}\right)^{\frac{1}{n_1}} \left(\frac{a_2''}{a_2'}\right)^{\frac{1}{n_2}} = \frac{1}{n_1 n_2} \frac{RT}{F} \ln \frac{a''}{a'} = \frac{n_1 + n_2}{n_1 n_2} \frac{RT}{F} \ln \frac{a_\pm''}{a_\pm'}. \tag{2}$$

where a is the activity of the electrolyte molecule, $a_\pm$ is the mean activity of its ions; the primes $'$ and $''$ retain their previous meaning. It follows from equation (2), that the measurable quantity $\Phi + \Delta\varphi$ is expressed in terms of mean activities, and not in terms of the individual activities of separate ions. As far as the author knows, equation (2) has not yet been subjected to experimental verification, even for the simplest case of a dilute solution.* Of great interest would be the application of equation (2) to concentrated solutions, for example acids. In this case, combining the determination of the quantity $\Phi + \Delta\varphi$, using as the cathode a reversible hydrogen electrode, with direct measurement of the distribution of the electrolyte concentration in the diffusion layer, which could be carried out, for example, by an interferometric method, would make it possible to determine activities in concentrated solutions.

Let us now consider the case of a dilute solution containing a cation 1, discharged at the cathode, with charge n_1, at concentration c_1 (in equivalents per cm^3), and a non-discharging anion 2 and cation 3 with charges n_2 and n_3, at concentrations c_2 and c_3. According to the condition of electroneutrality,

$$c_1 + c_3 = c_2. \tag{3}$$

Between the concentrations of the non-discharging ions at the electrode surface (c_2'', c_3'') and in the bulk of the solution outside the double layer (c_2', c_3'), under stationary electrolysis there exist the relations

$$c_2'' = c_2' \exp\left(\frac{n_2 \Phi F}{RT}\right), \tag{4}$$

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* In this connection, the ohmic potential drop in the bulk of the solution outside the diffusion layer is assumed to have been eliminated by calculation or direct measurement, which in principle is always possible.

$$c_3'' = c_3' \exp\left(-\frac{n_3 \Phi F}{RT}\right), \tag{4a}$$

whence

$$c_1'' = c_2' \exp\left(\frac{n_2 \Phi F}{RT}\right) - c_3' \exp\left(-\frac{n_3 \Phi F}{RT}\right), \tag{5}$$

where c_1'' is the value of c_1 at the electrode surface.

When the limiting current is reached, $c_1' = 0$, and, consequently,

$$\Phi = \frac{RT}{(n_2 + n_3)F} \ln \frac{c_3'}{c_2'}, \tag{6}$$

$$c_3'' = c_3' \left(\frac{c_2'}{c_3'}\right)^{\frac{n_3}{n_2+n_3}} = (c_3')^{\frac{n_2}{n_2+n_3}} (c_2')^{\frac{n_3}{n_2+n_3}}. \tag{7}$$

Of particular interest is the case when $c_3' \ll c_1', c_2'$ and, consequently, $c_1' \simeq c_2'$,

$$\frac{c_3''}{c_3'} = \left(\frac{c_1'}{c_3'}\right)^{\frac{n_3}{n_2+n_3}}. \tag{8}$$

For $c_1'/c_3' = 10^4$, $n_3 = 3$, and $n_2 = 1$, the degree of enrichment of the non-discharging cation, expressed by the right-hand side of equation (8), is 10^3. Practi-

the practical applicability of such a method of enrichment is limited by the increase in the time τ necessary for the establishment of a stationary distribution of concentrations in the diffusion layer as its thickness l increases. Since, in order of magnitude,

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* In a solution of a univalent electrolyte ($n_1 = n_2 = 1$), the coefficient before the logarithm becomes 2. It follows from this that the slope of the $\varphi, \ln \frac{I_d - I}{I}$ curve, where I is the current and I_d is the limiting diffusion current, in the case of the process of cathodic reversible formation of an amalgam, must have twice the value compared with that observed in the presence of an excess of indifferent electrolyte. The difficulties of experimental verification are associated with the relatively large ohmic potential drops in the bulk of the solution outside the diffusion layer in the absence of a supporting electrolyte; however, as calculation shows, they are surmountable if the cathode diameter is sufficiently small (for example, $\sim 5 \cdot 10^{-3}$ cm) and the thickness of the diffusion layer is sufficiently large ($\sim 10^{-1}$ cm), which can readily be realized by using a mercury meniscus in a capillary as the cathode.

$$\tau \approx \frac{l^2}{D},$$

then for $l = 0.1$, $\tau \approx 10^3$ sec., while for $l = 1$ cm, $\tau \approx 10^5$ sec. However, analytical applications of such enrichment seem quite real. Thus, for example, if a cation present as an impurity, which is not discharged at the potential at which stationary electrolysis is carried out, can be discharged at a more negative potential, then its accumulation in the diffusion layer during deposition of the principal metal can be used for subsequent oscillographic polarography. The accumulation of a surface-active organic cation at the surface of a hanging mercury drop during cathodic discharge of the background cation could be detected by subsequent measurement of the interfacial tension at the mercury—solution boundary.

The quantity Φ in equation (6) is usually called the ohmic drop of potential in the diffusion layer. It should be remembered, however, that it is not equal to the potential drop calculated by Ohm' s law from the specific resistance and current density in a column of electrolyte of variable concentration, which is the diffusion layer, but differs from it by an extraneous electromotive force equal to the diffusion potential arising in the same column in the absence of current because of the difference in ion mobilities. This was shown earlier for the case of a binary electrolyte ([2]).

However, since the theory of this question is often presented incorrectly, it is useful to illustrate the relation between the total and "ohmic" potential drops in the diffusion layer by the example of an electrolyte with three ions. In doing so, for simplicity of calculation we shall take all n equal to unity and assume, in contrast to the example just considered, that the concentration of the discharging ion c_1 is small in comparison with the concentrations of the non-discharging anion and cation c_2 and c_3. It follows hence that $c_2 \approx c_3 \approx c$, where c denotes the background concentration. From (6) and (3) it follows for the case considered that

$$\Phi = \frac{RT}{2F} \ln \frac{c_2' - c_1'}{c_2} = -\frac{RT}{2F} \frac{c_1'}{c_2'} = -\frac{RT}{2F} \cdot \frac{c_1'}{c'}. \tag{9}$$

Let us compare this quantity with the potential drop in the diffusion layer Φ_{ohm}, calculated according to Ohm's law from the current density j and the electrolyte resistance per 1 cm^2 of surface r. The quantity j is equal to $\frac{FD_1c_1'}{l}$, where D_1 is the diffusion coefficient of cation 1, and l is the thickness of the diffusion layer. Replacing D_1 by the mobility U_1 according to the Nernst formula, we obtain

$$j = RT\frac{U_1 c_1'}{l}. \tag{10}$$

Since the concentration c_1 at all points of the layer is small in comparison with c, r is approximately equal to $l : c'(U_2+U_3)F$, where U_2 and U_3 are the mobilities of anion 2 and cation 3. Hence we obtain

$$\Phi_{\text{ohm}} = -rj = -\frac{RT}{F}\frac{c_1'}{c'}\frac{U_1}{U_2+U_3}. \tag{11}$$

From comparison of (9) and (11) it is evident that $\Phi \neq \Phi_{\text{ohm}}$. From equations (7) and (9), in the case $n_2 = n_3 = 1$ and $c_1/c_3 \ll 1$, it follows that

$$c_3'' \approx c_2'' \approx c_3' + \tfrac{1}{2}c_1' = c_2' - \tfrac{1}{2}c_1'. \tag{12}$$

Since the concentration difference in the diffusion layer in the case under consideration is small, the magnitude of the diffusion potential Φ_{d} arising in this layer can be calculated by Henderson' s formula (^{3}) from the values of the concentrations and mobilities at its boundaries, without considering the distribution of concentrations within the layer. For a small concentration difference, according to Henderson' s formula, equation (12), and the conditions $c_1'' = 0,\ c_1' \ll c',\ c_2' \approx c_3' \approx c'$, we find:

$$\Phi_{\text{d}} = -\frac{RT}{F}\frac{U_1(c_1''-c_1') - U_2(c_2''-c_2') + U_3(c_3''-c_3')}{U_1c_1' + U_2c_2' + U_3c_3'} = \frac{RT}{F}\frac{c_1'}{c'}\left(\frac{U_1}{U_2+U_3} - \frac{1}{2}\right). \tag{13}$$

From (9), (11), and (13) we obtain, as was to be expected, $\Phi = \Phi_{\text{ohm}} + \Phi_{\text{d}}$.

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REFERENCES CITED

[1] A. Eucken, *Zs. phys. Chem.*, **59**, 72 (1907); E. Baars, "Elektrolyse," in H. Geiger, K. Scheel, *Handb. d. Phys.*, **13**, 517 (1928).

[2] V. G. Levich, A. N. Frumkin, *ZhFKh*, **15**, 748 (1941); *Acta Physicochim. URSS*, **16**, 325 (1943).

[3] See, for example, S. Glasstone, *Introduction to Electrochemistry*, IL, 1951, p. 282.

Note: Figure translations are in progress. See original paper for figures.

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