Theory of Concentration Polarization. III

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Transition regime

In Parts I and II[1] of this series only the steady state of current flow through a solution has been discussed. We shall now turn to processes occurring on closing the circuit. When the potential difference V applied to the electrodes is gradually increased, the current first reaches its limiting value; later, at large enough values of V, a new electrochemical process sets in, for instance, the evolution of hydrogen. If a current, equal to the limiting current, were passed through the solution, the potential should rise indefinitely. Actually the potential cannot, of course, become infinite, and some new electrochemical process sets in on the electrode. When a current, exceeding the limiting current, is passed through the solution, the electrode potential does not begin to rise immediately after the circuit is closed, but only after a certain lapse of time called the transition time. The latter is obviously the time required for the current in the solution to reach its limiting value. It is of interest to determine the transition time τ.

We shall calculate it in the case of an electrode in form of a large rotating disc, assuming a considerable amount of indifferent electrolyte to be present in the soluton.

At the initial moment, $t=0$, there begins to pass through the electrode a definite current, the density j of which exceeds that of the limiting current j_{lim} in the given solution under the given stirring conditions.

Prior to switching-on the current, the concentration of the solution is constant and equal to c^l. With $t>0$ the concentration will

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[1] Part I, Acta Phys. Chim. URSS, **17**, 257 (1942).
Part II, Acta Phys. Chim. URSS, **19**, 117 (1944).

for c is found:

$$\frac{\partial c}{\partial t} - D\frac{\partial^2 c}{\partial z^2} = -\frac{v_z c^l}{2\sqrt{\pi D t}}\left[\int\limits_0^\infty e^{-\frac{(\xi-z)^2}{4Dt}}\frac{(\xi-z)}{2Dt}\,d\xi - \int\limits_0^\infty\left(1-\frac{2j\xi}{FD}\right)\left(\frac{\xi+z}{2Dt}\right)e^{-\frac{(\xi+z)^2}{4Dt}}\,d\xi\right]. \tag{7}$$

We are seeking the solution of (7) for small values of z or, more exactly, small $z/\sqrt{Dt}$, for which the value v_z obtained from formula (7) Part I, Section 3, may be used.

At large values of z far from the disc, v_z is constant, and correspondingly c is constant. At small values of z we may write

$$\frac{\partial c}{\partial t} - D\frac{\partial^2 c}{\partial z^2} = 0.17\frac{\omega^{3/2}}{\nu^{1/2}}\frac{jz}{D}\,. \tag{8}$$

The solution of equation (8) satisfying the initial and boundary condition at the electrode, is

$$c = c^l - \frac{j}{F}\sqrt{\frac{t}{\pi D}}\,e^{-\frac{z^2}{4Dt}} - \frac{2jz}{FD\sqrt{\pi}}\int\limits_{z/2\sqrt{Dt}}^\infty e^{-y^2}\,dy + 0.17\,\frac{\omega^{3/2} j z^2 t}{\nu^{1/2} D} + 0.08\,jt^2\,\frac{\omega^{3/2}}{\nu^{1/2}}\,. \tag{9}$$

Expression (9) for c obviously does not satisfy the condition at infinity. This is related with the fact that the value for v_z was taken from formula (7), Part I, Section 3, which is certainly valid only for small values of z. With $z \sim \delta'$, where δ' is the diffusion layer thickness, our solution should adjusted to that corresponding to large values of z. Since we are interested only in the value of c at $z=0$ and for small time intervals, this adjusting is of small interest to our end, although it can be carried out without much trouble.

For the concentration at the electrode surface there is found from (9).

$$c = c^l - \frac{j}{F}\sqrt{\frac{t}{\pi D}} + 0.08\,\frac{\omega^{3/2} j t^2}{\nu^{1/2}}\,. \tag{10}$$

Expressions (9) and (10) hold only for such values of t for which the latter terms, depending upon convection, represent a small corchange on account of the diffusion and the convective ion transfer to the electrode. At the electrode surface, at $z=0$, the condition

$$j = DF\left(\frac{\partial c}{\partial z}\right)_{z=0} = \text{const} \tag{1}$$

is satisfied.

On the electrode itself the velocity of the liquid becomes zero and there is no convective flow. In this case the equation of convective diffusion is

$$\frac{\partial c}{\partial t} + v_z \frac{\partial c}{\partial z} = D\frac{\partial^2 c}{\partial z^2}\,, \tag{2}$$

where v_z is a given function of z but not a function of time since the rotation of the electrode is stationary[2]. At small values of t, immediately after the current is switched on, ions from adjacent zones of the solution, where the flow velocity v_z is low, will move towards the electrode. Therefore at small values of t the substance will be transported to the electrode mainly on account of molecular diffusion from the adjacent zones of the solution and the convection term in equation (2) will be small compared with the diffusion one.

Thus, for small time intervals the transfer equation may be simplified by omitting the convection term, so that

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2}\,. \tag{3}$$

The solution of equation (3) satisfying the boundary condition (1) and initial condition $c = c^l$, when $t=0$, may be found by the general method of solving the equation of heat transfer in limited bodies[3].

Let us write the solution in the form

$$c = \frac{1}{2\sqrt{\pi D t}}\left\{c^l \int\limits_0^\infty e^{-\frac{(\xi - z)^2}{4Dt}}\, d\xi + \int\limits_0^\infty f(-\xi)\, e^{-\frac{(\xi+z)^2}{4Dt}}\, d\xi\right\},$$

which obviously satisfies the initial condition. The function $f(-\xi)$ is chosen so as to satisfy the boundary condition (1). This yields

$$f(-\xi) = c^l - \frac{2c^l j\xi}{FD}\,,$$

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[2] Frank und Mises, «Die Differential- und Integralgleichungen der Mechanik u. Physik», 2. Teil, Braunschweig, 1935.

[3] See formulae (7) and (15), Part I, Section 3.

whence, after simple transformations, we obtain

$$c = c^l - \frac{j}{F}\sqrt{\frac{t}{\pi D}}\, e^{-\frac{z^2}{4Dt}} - \frac{2jz}{DF\sqrt{\pi}} \int\limits_{z/2\sqrt{Dt}}^{\infty} e^{-y^2}\, dy . \qquad (4)$$

In particular, the concentration at the electrode itself in the plane $z = 0$ is obviously

$$c = c_0 - \frac{j}{F}\sqrt{\frac{t}{\pi D}} . \qquad (5)$$

Formula (5), first obtained by Sand[3] (see lower), shows that the concentration at the electrode surface decreases with time, and becomes zero after an interval of time

$$\tau = \frac{\pi D c_0^2}{j^2} . \qquad (6)$$

On the other hand, a zero concentration of ions at the electrode surface is the condition for the passage of the limiting current through the solution.

Since the concentration is related to the electrode potential by Nernst's equation

$$\varphi_k = \frac{RT}{F} \lg (c)_{z=0} + \varphi_0 ,$$

the electrode potential will rapidly rise when $t \cong \tau$.

Thus τ is nothing else than the transition time.

The expressions obtained for concentration c and transition time τ are the solutions of the problem in the zero approximation and are valid for small values of τ. The curve j as a function of $1/\sqrt{\tau}$ is, obviously, linear at large values of $1/\sqrt{\tau}$.

In the first approximation, at somewhat greater values of t, the convective term in equation (2) can no longer be omitted.

However, since this term is small, its value taken from the zero approximation from (4) may be substituted for $\frac{\partial c}{\partial z}$. Taking the derivative of (4) and substituting $\frac{\partial c}{\partial z}$ into (2) the following equation

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[4] Sand, Phil. Mag., 1, 45 (1900).

rection for the first terms, depending upon molecular diffusion, *i. e.* for

$$\frac{\nu^{1/2}}{0.08\,F\sqrt{\pi D}} \gg t^{3/2}\,.$$

With t equal to τ the concentration at the electrode surface becomes zero and equation (10) results in the following dependence of transition time upon the density of the current passed through the solution:

$$j=\frac{c^l F}{\sqrt{\frac{\tau}{\pi D}}}\;\frac{1}{(1-0.08\,\omega^{3/2}(\pi D)^{1/2}\,\nu^{-1/2}\,\tau^{3/2})}\,. \tag{11}$$

It may be seen from this expression that τ increases somewhat owing to stirring, and the curve $j=j\left(\frac{1}{\sqrt{\tau}}\right)$ departs from a straight line. For still greater values of τ, when the convective term in (2) becomes of the same order of magnitude as the diffusion term, the solution of the equation for c could not be found.

Formula (5) was first derived by Sand[4], but his derivation is erroneous.

Formula (5) for the zero approximation of c is in fair agreement with Sand's experiments[4, 5], as well as with those of other authors[6]. Butler and Armstrong[7] have, however, disclosed an essential departure from it at large transition times (small $1/\tau$). They suggested the following empirical formula relating j and τ

$$(j-j_0)=\frac{\alpha}{\tau} \tag{12}$$

where j_0 and α are constants depending upon the stirring of the solution.

This dependence seems very strange, since it follows therefore that with small enough values of j the stationary passage of a limiting current through the solution is not attained even in an infinite time interval τ. The experiments of Butler and Armstrong were carried out under conditions of natural stirring, so that our computations cannot be directly compared with the results of their measurements.

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[5] Sand, Z. physik. Chem., **35**, **641** (1900).

[6] Karnoglanoff, Z. Elektochem., **12**, 5 (1906).

[7] Butler and Armstrong, Proc. Roy. Soc., **139**, 406 (1933).

Qualitatively, however, such a comparison may be attempted. In Fig. 1 the data of Butler and Armstrong are plotted j/A *viz.* $1/\sqrt{\tau}$. It is seen that with large values of $1/\sqrt{\tau}$ a linear course of $j = f\left(\frac{1}{\sqrt{\tau}}\right)$ is observed, but with smaller values of $1/\sqrt{\tau}$ the decrease in j becomes slower. This is no full qualitative agreement with the formula. (It should be reminded that formula (11) cannot be used for very small values of $1/\sqrt{\tau}$.) A quantitative comparison is difficult, since the thickness of the diffusion layer in the experiments of Butler and Armstrong is unknown.

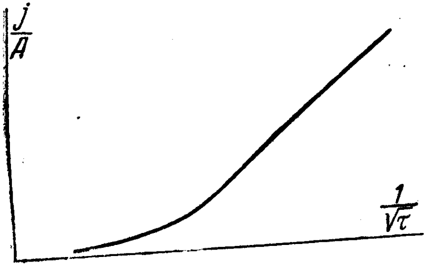

Fig. 1.

Thus on our opinion, it is quite likely that the departure observed by these authors from formula (6) is related to the discussed effect, and that the empirical formula (11) results from unjustified extrapolation.

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