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Ohmic Resistance of Local Cells in the Process of the Solution of Metals in Acids

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1, Fundamental assumptions and discussion of results

The question as to the ohmic resistance of local cells has been frequently discussed in the literature, though no satisfactory computation of this resistance has hitherto been carried out.

In the present paper a calculation is made of an approximate value of the ohmic resistance for the instance in which the cathode of a local cell may be considered sufficiently polarized as is the case of the solution of metals with evolution of hydrogen. In what follows the assumptions underlying the calculation are revised and the limits of its applicability specified.

If the dimensions of the inclusions are sufficiently small (we shall subsequently restrict ourselves to this particular case) and their spacing sufficiently great, a local cell may be treated as a system consisting of an infinite metal plane surface (anode) containing an inclusion of a foreign metal (cathode), both being covered by an electrolyte layer of infinite thickness.

When the size of the inclusion is small, its shape is evidently immaterial. It may be readily seen that for a given area of inclusion the maximum ohmic resistance will correspond to an inclusion in the form of a disk, the geometric paths of the current then having a maximum length.

In this investigation we are interested in the maximum values of the ohmic resistances of local cells. We shall accordingly assume in the sequel that the inclusion is a flat disk of radius r_0. It will also be assumed that the electrode surface is free of any films of insoluble compounds.

We shall neglect anodic polarization and consider the anode surface to be an equipotential one. The potential of the anode will be taken as zero

$$\varphi_a = 0. \tag{1}$$

Our task being confined to the determination of the ohmic potential drop in the solution, we can neglect the interfacial potential between the anode and the solution in the electric double layer and assume the potential in the solution in the immediate vicinity of the anode to be also equal to zero.

The potential difference, φ_c, between the cathode and the solution is given by

$$\varphi_c = \varphi_0 - a - b \ln j_n \tag{2}$$

where φ_0 is the reversible hydrogen electrode potential in the given solution with respect to the anode, whilst the last two terms represent the hydrogen overvoltage at the cathode which is connected with the normal component of current density j_n, at the cathode—electrolyte interface by the well known Tafel relation:

$$\eta_0 = a + b \ln j_n.$$

The constant a in Tafel's formula depends upon the nature of the metal, whilst b is nearly constant for all metals and equals

$$b = \frac{2RT}{F} = 50 \times 10^{-3}\mathrm{V}$$

when natural logarithms are used.

During the operation of a local cell the current flows from the anode through the electrolyte to the cathode and from the latter directly to the metal constituting the anode. The ohmic resistance of the second part of the circuit being evidently low, the ohmic resistance of a local cell must be equal to the resistance within the electrolyte.

To determine the latter by the usual method employed for the computation of the ohmic resistance of massive conductors, it is necessary to integrate the Laplace equation for the potential with the proper boundary conditions at the anode and cathode. Knowing the potential distribution we can obtain the strength of the field

$$\mathbf{E} = -\operatorname{grad} \varphi,$$

and the corresponding current density

$$\mathbf{j} = \varkappa \mathbf{E}$$

where $\varkappa$ is the conductivity of the electrolyte.

Dividing the potential difference by the current density obtained we may find the specific ohmic resistance for the current flowing to a given point of the cathode. If this proves to vary from point to point, it is, of course, impossible to speak of the total resistance.

The boundary conditions are given by equation (1) for the anode and equation (2) for the cathode.

However, inasmuch as in boundary condition (2) the potential at the cathode depends upon the current density and this dependence is, moreover, non-linear, the solution of such a boundary problem is extremely difficult. It turns out, however, that, in the case where the cathode is sufficiently strongly polarized, an approximate solution of the problem may be suggested which proves to apply to a number of cases presenting practical interest.

From equation (2) we have

$$j_n = e^{\frac{\varphi_0 - a - \varphi_c}{b}}.$$

Let φ_{cs} denote the potential in the solution in the vicinity of the cathode. Then we may write

$$\varphi_a = \varphi_{cs} + \varphi_c = 0.$$

As the polarization of the cathode increases, the quantity φ_{cs} decreases, and φ_c tends to φ_a, *i. e.* to zero, according to our choice of zero potential. Let it be assumed that the absolute value of φ_{cs}, and hence of φ_c, is considerably smaller than the constant potential b in Tafel's formula, so that

$$e^{-\frac{\varphi_c}{b}} \simeq 1. \tag{3}$$

Then we have

$$j_n = e^{\frac{\varphi_0 - a}{b}}.$$

In this case the normal component of the current density is, as a first approximation, constant throughout the cathode.

All subsequent calculations refer to this particular case of a strongly polarized cathode.

After the solution of the problem is found, it will be shown that it is not contradictory, *i. e.* that the potential thus obtained actually satisfies inequality (3).

Assuming that conditions (3) is fulfilled and the normal component of the current density is constant throughout the cathode, we reduce our problem to the solution of the Laplace equation

$$\Delta\varphi = 0. \tag{4}$$

with the boundary conditions

$$\varphi_a = 0 \tag{1'}$$

at the anode, and

$$j_n = -\varkappa\left(\frac{\partial\varphi}{\partial n}\right) = j_0 \tag{2'}$$

at the cathode, where

$$j_0 = e^{\frac{\varphi_0 - a}{b}},$$

and the derivative with respect to the normal is taken at the cathode surface. The inward direction of the normal in the metal is considered positive and the potential at an infinite distance is taken as zero.

The solution of this boundary problem is given in a separate section (Section 2) for convenience of those readers who are not interested in the computative part of the paper. In the present section we shall only give the results obtained.

The solution yields the following expression for the potential on the cathode:

$$\varphi_{cs} = -\frac{2r_0 j_0}{\pi\varkappa}\sqrt{1-\left(\frac{r}{r_0}\right)^2} \qquad (r \leqslant r_0),$$

where r is the distance from the given point of the cathode to its centre.

The maximum negative potential will be in the centre of the cathode, where it is given by

$$\varphi_{\max} = -\frac{2r_0 j_0}{\pi\varkappa}.$$

Fig. 1 shows the potential distribution on the cathode.

The specific ohmic resistance for the current flowing from the anode to the given point of the cathode is

$$R = \frac{2r_0}{\pi\varkappa}\sqrt{1-\left(\frac{r}{r_0}\right)^2}.$$

The maximum resistance is opposed to the current flowing to the centre of the cathode:

$$R_{\max} = \frac{2r_0}{\pi\varkappa}$$

For an inclusion of the size $r_0 \sim 10^{-4}$ cm. in normal sulphuric acid ($\varkappa \sim 2\times 10^{-1}$) the maximum specific resistance equals

$$R \sim 3\times 10^{-4},$$

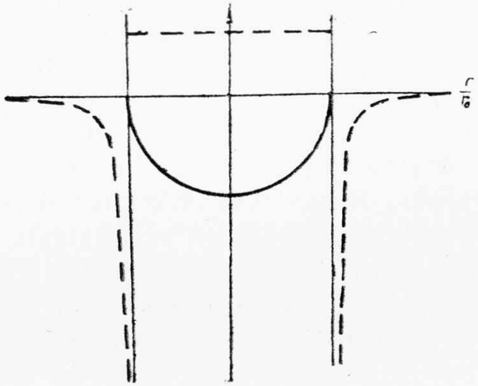

Fig. 1. Distribution of current density (dashed curve) and of potential (full curve).

and we can see that under these conditions the ohmic resistance of a local cell is extremely small.

Let us now consider the scope of application of the formulae obtained.

It is evident that our fundamental assumption as to the almost complete polarization of the cathode (3) will be fulfilled in any case, provided the following inequality is satisfied:

$$|\varphi_{\max}| \ll b,$$

or, substituting the expression for $\varphi_{\max}$,

$$\frac{2r_0 j_0}{\pi\varkappa} \ll b. \tag{5}$$

Adopting the values of r_0 and $\varkappa$ indicated above we shall readily find that the current density j_0 at the cathode should satisfy the inequality

$$j_0 \ll 160 \text{ A/cm.}^2.$$

Simple calculation shows that in most cases of practical interest the current densities at microcathodes are well below a hundred amperes.

Let us consider a few particular examples, *e. g.*, the effect of antimony inclusions in lead when the latter is being dissolved in sulphuric acid in a storage cell. According to Kolotyrkin's unpublished data, the overvoltage on pure antimony in 8 N H_2SO_4 is given by the formula: $\eta_{Sb} = 0.71 + 0.12 \lg j_n$. The potential φ_0 is in this case equal to 0.37 (*e. m. f.* of the cell: H_2, $8N\,H_2SO_4$, $PbSO_4$, Pb). It follows that $\lg j_n = -2.9$ and, inasmuch as $\varkappa = 0.74$, $|\varphi_{max}| \sim 10^{-7}$V for $r_0 \sim 10^{-4}$ cm., and 10^{-4}V for $r_0 \sim 10^{-1}$ cm. In this particular example, which is of some practical importance, the ohmic potential drop may be neglected even for large inclusions. Let us now consider another example, which has also been treated in the literature, *viz.*, the effect of nickel inclusions in zinc undergoing solution in H_2SO_4. For nickel in sulphuric acid[1] we have: $\eta_{Ni} = 0.570 + 0.114 \lg j_n$. The stationary potential established during the solution of Zn in H_2SO_4 is —0.75, *i. e.* $\varphi_0 = 0.75$, whence $\lg j_n = 1.6$. When $r_0 \sim 10^{-4}$ cm. $|\varphi_{max}|$ is, consequently, equal to 13×10^{-3}V. Somewhat larger values of $|\varphi_{max}|$ might be expected in the case of platinum inclusions, but taking into account the strong effect of adsorbed substances upon the overvoltage on platinum, it is not clear what value of overvoltage should be assumed for platinum. It is possible that in other cases too, in using overvoltage values obtained on pure metals, when discussing the conditions on local cathodes, we overestimate the cathodic current, since the overvoltage on local cathodes must be greater than that on pure metal owing to their poisoning by the products of solution of the anode.

When inequality (5) is not fulfilled, the above calculation yields potential drops which are unquestionably greater than is actually the case. In fact, the current density j_0 which occurs in the calculation has the maximum possible value.

If inequality (5) is not fulfilled, the current density at the cathode surface can no longer be considered constant, and at definite points of the cathods the current densities will be smaller than j_0, whence the potential drop under the given geometric conditions will be smaller than the value resulting from the above calculation.

Fig. 1 shows also the current density distribution for the cathodic and anodic currents. It will be seen that the anodic current density becomes infinite for $r = r_0$. Actually, however, those parts of the anode, through which a current of considerable density flows, will be polarized and the current density will remain finite throughout the anode.

It should moreover be emphasized that the condition of applicability of our calculation is at the same time the condition under which the concentration change at the cathode of a local cell may be neglected.

It has already been shown by Nernst that the problem of the diffusion of ions through an electrolyte in the presence of immobile ions of the opposite sign may be reduced to the problem of the diffusion of neutral atoms which proceeds, however, with a somewhat modified diffusion coefficient.

In estimating the rôle of diffusion and the conditions under which the concentration polarization occurs, it is therefore possible to use the expression for the diffusion current obtained in solving the problem of the diffusion of neutral particles from a plane surface to a local inclusion with the corresponding diffusion coeficient. The problem of the diffusion of neutral particles from a plane surface to a flat circular inclusion has been solved by Gröber and Erk[2].

The solution shows that the saturation value of the diffusion current density at the centre of the cathode, *i. e.* at a point where it has a minimum value, is given by

$$j_{1m} = \frac{2D^* c_0 F}{\pi r_0} \tag{6}$$

where D^* is the effective diffusion coefficient of the hydrogen ion and c_0 its concentration. Let us calculate the ratio of the minimum saturation current density of the diffusion current to the current density j_{crit} at which the above calculation ceases to hold. The latter may, evidently, be obtained if we put $|\varphi_{max}| \sim b$, so that we have

$$j_{crit} \cong \frac{\pi \varkappa b}{2 r_0} \tag{7}$$

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[1] Legran and Lewina, Acta Physicochimica URSS, 12, 246, (1940).

[2] Gröber und Erk, «Die Grundgesetze der Wärmeübertragung», J. Springer, 1933.

whence

$$\frac{j_{\mathrm{lim}}}{j_{\mathrm{crit}}} \cong \frac{4D^*c_0F}{\pi^2\varkappa b}.$$

Substituting $b = 2RT/F$ and the value of conductivity $\varkappa \sim \frac{F^2c_0D}{RT}$ we can see that the order of magnitude of this ratio is

$$\frac{j_{\mathrm{lim}}}{j_{\mathrm{crit}}} \sim \frac{D^*}{D} \sim 1$$

where D is the coefficient of diffusion of the electrolyte.

In other words, when the current density becomes comparable with the critical value j_{crit} defined by equation (7), considerable concentration gradients must appear in the solution to make up for the loss of hydrogen ions due to their discharge on the cathode. Otherwise, the diffusion current density at the centre of the cathode will be small compared with j_{lim} and relation (7) cannot be satisfied.

It is therefore inexpedient to take account of the ohmic potential drop where the concentration change is neglected as is usually done in applying Palmer's classical formula which assumes a considerable ohmic potential drop and a constant concentration of the solution.

The same conclusion results from considerations of a general nature, concerning the distribution of ions during steady diffusion in an electric field.

As is known, the concentration of immobile ions (anions at the cathode, *e. g.* SO_4'' anions) is given by Boltzmann's formula

$$c_A = (c_A)_0\, e^{\frac{n_AF\varphi}{RT}} \quad \text{or} \quad \varphi = \frac{RT}{n_AF} \ln \frac{c_A}{(c_A)_0}, \tag{8}$$

where n_A is the valency of the anion, c_A—its concentration at some point and $(c_A)_0$—its concentration at a sufficient distance from the electrode.

From this formula it follows directly that, if the potential drop is small, the concentration is nearly constant throughout the solution. If, on the contrary, a large potential drop exists in the solution, so that $|\varphi| \gg \frac{RT}{n_AF} = \frac{b}{2n_A}$, it is necessary to allow for both the change of concentration in the solution and the concentration polarization.

On applying Boltzmann's formula we at once come to the conclusion that the ohmic potential drop at the electrode surface under stationary conditions, *i. e.* φ_{cs}, equals the concentration polarization for an electrode reversible with respect to a cation whose valency would be n_A. The relation between the ohmic potential drop and the concentration polarization was derived long ago by integration of diffusion equations for the plane problem[3], but has not been taken due notice of in the electrochemical literature. Suffice it to mention that in the last, otherwise excellent, paper by Agar and Bowden on concentration polarization this relation was derived anew with an incorrect value of the prelogarithmic coefficient[4].

The above relation between the ohmic potential drop in solution and the concentration change is valid only in the absence of stirring, as has been assumed in our treatment. This condition may be considered fulfilled as long as the cathode dimensions in a local cell are small compared with the thickness of the Nernst-Brunner diffusion layer, since, as shown by experiment, the effect of stirring within this layer, whose thickness under usual conditions of stirring amounts to 5×10^{-3}—5×10^{-2} cm.[5], may be neglected. This constitutes the essential difference between local microcells and their macromodels in which, owing to stirring, beyond the limits of the diffusion layer, any potential drop may occur without a concentration gradient. It should also be borne in mind that the time required for the establishment of stationary conditions rapidly increases with an increase in the linear dimensions of the system (proportionally to the square of these dimensions).

However, ohmic potential drops without any concentration gradients may also occur in microcells, but this requires reactions other than hydrogen evolution; *viz.* this might be the case in electrocrystallization reactions owing to the rapid displacement of the points at which the deposition of metal takes place.

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[3] Baars, Handb. d. Phys. Geiger u. Scheel, **13**, 559, 1928; Eucken, Z. physik. Chem., **59**, 72 (1907).

[4] Agar and Bowden, Proc. Roy. Soc., (A) **169**, 217 (1938). Agar and Bowden calculate the ohmic potential drop in an electrolyte layer of variable resistance ignoring the fact that even in the absence of current a diffusion potential exists in such a layer.

[5] For a discussion of the theoretical value for the thickness of the diffusion layer and its dependence upon the rate of stirring *cf.* B. Levich, Acta Physicochimica, **17**, 257 (1942).

In the case of metals in acid solutions equation (8) leads to the following result. As long as the solution exhibits an acid reaction at the cathode, *i. e.* until hydroxyl ions do not appear in an appreciable amount, the ohmic potential drop in the solution can not exceed the value

$$\frac{RT}{n_A F}\ln\frac{c_s}{c_{\mathrm{Me}}+c'_s},$$

where c_s is the initial concentration of the acid, c'_s — its concentration at the surface, and c_{Me} — the concentration of the metal salt; under limiting conditions the quantity c'_s may fall to zero. For the position of the cathode and anode shown in Fig. 1, the quantity $\frac{c_s}{c_{\mathrm{Me}}+c'_s}$ will be of the order of unity, and the ohmic potential drop must be small, as it becomes obvious, if we consider the conditions of diffusion of the hydrogen ions to the cathode and of the metal ions from the anode to the cathode and into the bulk of the solution. There may, however, exist conditions, *e. g.*, when the solution of the metal occurs only at individual points rather remote from the cathode, under which higher values of $\frac{c_s}{c_{\mathrm{Me}}+c'_s}$ may arise. Finally, when the relation between the overvoltage at the cathode to the anode potential is such that the hydrogen evolution at the cathode can proceed even in an alkaline medium, the limit imposed upon the ohmic potential difference by concentration conditions drops off.

2. Solution of the boundary problem

To solve equation (4) with boundary conditions (1) and (2) it is convenient to place the origin of coordinates at the centre of the cathode and effect a transformation to elliptic coordinates (ξ, η, ζ) connected with the rectangular coordinates (x, y, z) by the relations:

$$z = r_0\xi\eta, \tag{9}$$

$$x = r_0\cos\zeta, \tag{10}$$

$$y = r_0\sin\zeta, \tag{11}$$

$$\mathbf{r} = r_0\sqrt{(1+\xi^2)(1-\eta^2)},$$

where $\mathbf{r}$ is the radius vector, and r_0 is as before the radius of the cathode.

The surfaces $\xi = \mathrm{const}$ are surfaces of revolution of co-focal ellipses having a focal length r_0 and axis $r = 0$.

At $\xi = 0$ the surface of revolution degenerates into a surface formed by both sides of the region $r \leqslant r_0$ in the plane $z = 0$.

The surfaces $\eta = \mathrm{const}$ are surfaces of revolution of co-focal hyperbolas. The surface $\eta = 0$ is the region $r > r_0$ lying in the plane $z = 0$. At $\eta = 1$ the surface $\eta = \mathrm{const}$ degenerates into the z axis.

The region $0 \leqslant \xi \leqslant \infty$; $0 \leqslant \eta \leqslant 1$; $0 \leqslant \zeta \leqslant 2\pi$ fills the region of positive values of z.

Hence it is evident that the surface $\xi = 0$ represents the cathode of a local cell, whilst the surface $\eta = 0$ constitutes its anode.

The Lamé coefficients in the principal quadratic form:

$$ds^2 = h_\xi^2 d\xi^2 + h_\eta^2 d\eta^2 + h_\zeta^2 d\zeta^2,$$

are given by

$$h_\xi = r_0\sqrt{\frac{\xi^2+\eta^2}{1+\xi^2}}, \quad h_\eta = r_0\sqrt{\frac{\xi^2+\eta^2}{1-\eta^2}},$$

$$h_\zeta = r_0\sqrt{(1+\xi^2)(1-\eta^2)}.$$

The Laplace equation for the potential $\varphi(\xi, \eta, \zeta)$ in elliptic coordinates has the form:

$$\frac{1}{r_0(\xi^2+\eta^2)}\frac{\partial}{\partial\xi}\left[(1+\xi^2)\frac{\partial\varphi}{\partial\xi}\right] + \frac{1}{r_0(\xi^2+\eta^2)}\frac{\partial}{\partial\eta}\left[(1-\eta^2)\frac{\partial\varphi}{\partial\eta}\right] + \\ + \frac{1}{r_0(1+\xi^2)(1-\eta^2)}\frac{\partial^2\varphi}{\partial\zeta^2} = 0. \tag{12}$$

The boundary conditions may be written as follows.

On the cathode $\xi = 0$:

$$-\varkappa\left(\frac{\partial\varphi}{\partial n}\right)_{\xi=0} = j_0, \tag{13}$$

the inward direction of the normal in the metal is considered positive[6].

On the anode $\eta = 0$:

$$\varphi_a = 0. \tag{14}$$

At an infinite distance the potential is zero:

$$\varphi_\infty = 0. \tag{15}$$

Let us look for a solution of equation (12) which would possess an axial symmetry and, consequently, be independent of the coordinate ζ.

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[6] The cathodic current is considered positive and the anodic one—negative.

Let us put

$$\varphi = P(\eta)\, Q(\xi).$$

Substituting this expression for φ in (12) we obtain the following equations from which $P(\eta)$ and $Q(\xi)$ may be determined:

$$\frac{d}{d\eta}\left[(1-\eta^2)\frac{dP(\eta)}{d\eta}\right] + nP(\eta) = 0, \tag{16}$$

$$\frac{d}{d\xi}\left[1+\xi^2)\frac{dQ(\xi)}{d\xi}\right] - nQ(\xi) = 0, \tag{17}$$

where n is the separation parameter.

As is known, equations (16) and (17) have no solutions unless $n = l(l+1)$ where l is any integer (including zero).

The solutions of equations (16) and (17) are Legendre functions of the first and second kinds.

The solutions of equation (17) are Legendre functions of the variable $i\xi$ and must be regular for all values lying between zero and infinity, *i. e.* throughout the imaginary axis. For the solution of equation (17) Legendre functions of the second kind should be taken since the Legendre functions of $i\xi$ of the first kind increase indefinitely with increasing ξ and do not satisfy equation (15), whereas the Legendre functions of the second kind tend to zero as ξ increases.

The general solution of equation (12) thus has the following form:

$$\varphi = \sum_l A_l P_l(\eta)\, Q_l(i\xi),$$

where $P_l(\eta)$ and $Q_l(i\xi)$ are the corresponding Legendre functions of the first order:

$$P_l(\eta) = \frac{1\cdot 3\cdot 5\ldots(2l-1)}{l!}\left[\eta^l - \frac{l(l-1)}{1\cdot(2l-1)}\eta^{l-2} + \right.$$
$$\left. + \frac{l(l-1)(l-3)}{2\cdot 4\cdot(2l-1)(2l-3)}\eta^{l-4} - \ldots\right],$$

$$Q_l(i\xi) = \frac{\sqrt{\pi}\, l!}{2^{l+1}\left(l+\frac{1}{2}\right)\Gamma\left(l+\frac{1}{2}\right)} \times \frac{1}{(\xi i)^{l+1}}\, F\left[\frac{l}{2}+\frac{1}{2};\right.$$
$$\left.\frac{l}{2}+1;\ l+\frac{3}{2};\ (i\xi)^{-2}\right],$$

where F is the hypergeometric function and Γ is the gamma-function.

Substituting the expression for φ in boundary conditions (14) we obtain

$$\sum_l A_l P_l(0)\, Q_l(i\xi) = 0.$$

This condition may be satisfied by putting $l = 2k+1$, where k is an integer.

The solution of equation (12) is therefore only expressed in terms of odd Legendre functions of the first and second kinds.

Let us now satisfy the boundary condition on the cathode.

The potential gradient $\varphi(\xi, \eta)$ in elliptic coordinates has the form:

$$\operatorname{grad}\varphi = \mathbf{e}_\xi \frac{\sqrt{1+\xi^2}}{r_0\sqrt{\xi^2+\eta^2}} \sum_k A_{2k+1} P_{2k+1}(\eta) \frac{dQ_{2k+1}(i\xi)}{d\xi} +$$
$$+ \mathbf{e}_\eta \frac{\sqrt{1-\eta^2}}{r_0\sqrt{\xi^2+\eta^2}} \sum_k A_{2k+1} Q_{2k+1}(i\xi) \frac{dP_{2k+1}(\eta)}{d\eta},$$

where $\mathbf{e}_\xi$ and $\mathbf{e}_\eta$ are unit vectors plotted along the coordinate axes in the direction of increase of the respective variables.

At the cathode surface, *i. e.* at $\xi = 0$, the unit vector $\mathbf{e}_\xi$ is directed upwards, normally to the surface $z = 0$, whilst $\mathbf{e}_\eta$ is tangential to the latter.

Therefore, with our choice of the positive direction of the normal, we have

$$\left(\frac{\partial\varphi}{\partial\eta}\right)_{\xi=0} = -\frac{1}{r_0\eta}\sum_k A_{2k+1} P_{2k+1}(\eta)\left(\frac{dQ_{2k+1}(i\xi)}{d\xi}\right)_{\xi=0}.$$

On the other hand,

$$\left(\frac{dQ_{2k+1}(i\xi)}{d\xi}\right)_{\xi=0} = iQ_{2k}(0).$$

Substituting the latter expression in equation (13) we obtain

$$\frac{i\varkappa}{r_0\eta}\sum A_{2k+1} P_{2k+1}(\eta)\, Q_{2k}(0) = j_0. \tag{18}$$

To satisfy condition (18) it is indispensable and sufficient that the left-hand side should be independent of η. This will be fulfilled if we set all coefficients A_{2k+1} except A_1 equal to zero. Then, inasmuch as $P_1(\eta) = \eta$, condition (18) will enable us to determine A_1.

Since we may write

$$Q_0(0+i0) = -\frac{i\pi}{2},$$

we have

$$\frac{\varkappa\pi}{2r_0} A_1 = j_0.$$

Therefore

$$A_1 = \frac{2r_0}{\varkappa\pi} j_0$$

whence the potential

$$\varphi = \frac{2j_0}{\pi\varkappa} P_1(\eta) Q_1(i\xi),$$

where

$$P_1(\eta) = \eta,$$

and

$$Q_1(i\xi) = \frac{i\xi}{2} \ln \frac{i\xi+1}{i\xi-1} - 1 = \xi \operatorname{arg\,ctg} \xi - 1.$$

In particular, the potential in solution at the cathode surface is given by

$$\varphi_{cs} = -\frac{2r_0 j_0}{\pi\varkappa} \eta.$$

Expressing η in terms of the radius vector r in the plane $z=0$ we obtain

$$\varphi_{cs} = -\frac{2r_0 j_0}{\pi\varkappa} \sqrt{1-\left(\frac{r}{r_0}\right)^2}. \tag{19}$$

The specific ohmic resistance for the current flowing from the anode to points on the cathode having the coordinate r is

$$R = \frac{\varphi_a - \varphi_{cs}}{j_0} = \frac{2r_0}{\pi\varkappa} \sqrt{1-\left(\frac{r}{r_0}\right)^2}. \tag{20}$$

The anodic current density is given by

$$j_a = -\varkappa \left(\frac{\partial\varphi}{\partial n}\right)_{\eta=0}.$$

On the anode surface the unit vector e_η is directed from the metal normally to the surface, whilst e_ξ is tangential to the surface of the metal.

Hence, the inward direction of the normal in the metal being taken as positive, we have

$$j_a = \frac{\varkappa}{r_0\xi} A_1 Q_1(i\xi) \left(\frac{dP_1(\eta)}{d\eta}\right)_{\eta=0} = \frac{2j_0}{\pi\xi} (\xi \operatorname{arg\,ctg} \xi - 1).$$

At the anode surface

$$\xi = \sqrt{\left(\frac{r}{r_0}\right)^2 - 1} \qquad (r \geqslant r_0).$$

Hence

$$j_a = \frac{2j_0}{\pi} \operatorname{arg\,ctg} \sqrt{\left(\frac{r}{r_0}\right)^2 - 1} - \frac{2j_0}{\pi} \frac{1}{\sqrt{\left(\frac{r}{r_0}\right)^2 - 1}}. \tag{21}$$

When r approaches r_0, j_a becomes

$$j_a \simeq -\frac{2j_0}{\pi} \frac{1}{\sqrt{\left(\frac{r}{r_0}\right)^2 - 1}}.$$

It may be readily seen that the total current at the anode is given by

$$I_a = \int h_\xi h_\zeta j_a \, d\xi \, d\zeta = -\pi r_0^2 j_0$$

as should actually be the case.

Summary

1. The conditions determining the behaviour of the cathode of a local cell are considered, the cathode being treated as an inclusion having the shape of a disk of radius r_0 embedded in the surrounding mass of the metal. The calculation is carried out assuming the anode to be non-polarizable and the cathode strongly polarized. Under these conditions the specific resistance per unit area of the cathode surface at its centre, where it is at a maximum, is $\frac{2r_0}{\pi\varkappa}$, where $\varkappa$ is the conductivity of the electrolyte.

2. A calculation carried out by this formula shows that the ohmic potential drop in the case of solution of zinc with inclusions of nickel in sulphuric acid does not exceed 13 mV if $r_0 \sim 10^{-4}$.

3. It is shown that in the cases where the ohmic potential drop in the solution cannot be neglected, the change of the electrolyte concentration at the cathode surface should simultaneously be taken into account.

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Addendum

The leading idea of this investigation was exposed by one of us in a paper presented at the Second All-Union Meeting on Metal Corrosion (Proceedings of the Second All-Union Meeting on Metal Corrosion, Moscow, 1940). The Russian text appeared in extenso in the Journ. Phys. Chem. (Russ.), **15**, 748 (1941), but the publication in Acta Physicochimica was unfortunately delayed by war time conditions.

After the publication of the Russian text, we became acquainted with the article of C. Wagner, «Chemische Reaktionen der Metalle» in «Handbuch der Metallphysik», I, Teil II, Leipzig, 1940, which contains a computation similar to ours for the case of an inclusion having the form of a long narrow strip. Wagner arrives at an expression for the ohmic drop of potential which differs from equation (19) by the value of the numeric coefficient only. Some of Wagner's other conclusions seem to us not altogether correct. On p. 199 Wagner states that the ohmic drop of potential in a local cell always remains small, whilst, as it was shown by us, under special geometric conditions or when the solution becomes alkaline through hydrogen evolution, the ohmic drop still can rise to considerable values. It is doubtful whether use can be made of Wagner's equation (74) for the computation of the ohmic drop corresponding to the limiting current, as the latter refers to the case of inclusions, which are large as compared with the dimensions of the diffusion layer. Obviously under these conditions the ohmic drop will be determined by the conditions of stirring and can be made indefinitely large by a suitable choice of these conditions. We can arrive at more definite conclusions only in calculating the value of the limiting current under the assumption that the linear dimensions of the inclusion are small when compared with the thickness of the diffusion layer as it was done in our paper [equation (6)].