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MATHEMATICAL STUDIES OF GALVANIC CORROSION

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PART III SEMI-INFINITE COPLANAR ELECTRODES WITH EQUAL
CONSTANT POLARIZATION PARAMETERS

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ABSTRACT

The mathematical analysis of a coplanar alternating array of long narrow electrodes has been conducted subject to the limitation that the polarization parameters for the anodes and cathodes are constant and equal. The interfacial potential and corrosion current parameters have been computed for a total of 18 values of a/L and for a/c equal to $1/2$ and $1/4$. Four perspective drawings of the distribution of potential throughout the corrodent have been made to scale to illustrate the influence of polarization. Two experimental studies were found to be in reasonably good agreement with the present theoretical analysis.

Introduction

Two important limiting cases have been discussed elsewhere^{1,2}, namely (1) that polarization was negligible and (2) that one electrode was infinitely larger than the other. It has been difficult to find experimental studies of the potential distribution or of the variation of corrosion attack which correspond to these limiting cases. However, several studies^{3,4,5,6} have been undertaken in the past to demonstrate just such distribution of corrosion and potential in the corrodent, and in these finite anode-cathode ratios were employed. Thus the distribution of corrosion attack using models similar in detail to these experimental conditions has been computed.

The most serious limitation imposed onto this investigation, largely by convenience, is the assumption that the polarization parameters of the anode and cathode are equal. This parameter, $\mathcal{L}$ as defined by Wagner⁷, has the dimensions of length and, as discussed previously^{1,2,7}, is extremely important in characterizing the behavior of a given galvanic cell. The use of equal parameters renders the case amenable to straightforward mathematical treatment whereas if the assumption were made that they are not equal, one would have to resort to the cumbersome methods available for the solution of integral equations. Solutions require, in general, iterative or trial-and-error methods.

In a previous paper², the magnitude of this parameter was calculated from various experimental data; it was found to lie in the range from one-fourth to 25 millimeters. This indicates that in many cases and particularly those cases in which extensive experimental work was done, that the assumption of equal polarization parameters would be a reasonable approximation*. This special

*That is, the electrode employed by others range from 10 to 160 cm in width and are therefore macroscopically large in comparison with $\mathcal{L}$. Even several fold variations between $\mathcal{L}^a$ or $\mathcal{L}^c$ will have a small influence on the corrosion current over much of these "large" electrodes.

case of equality will illustrate the effect of polarization and will be useful for a qualitative discussion of the more accurate and general case of unequal parameters.

This investigation was undertaken to provide numerical data which could be compared with the experimental data of Copson³ and Daniel-Bek⁴. In a separate study⁸ values of the potential were tabulated for nine widely different values of the ratio of the anode width to the polarization parameter and for each of these at over hundred locations within the electrolyte. Detailed comparison of these potential values with the experimental results will not be made here.

A comparison of the variation of the current density can be made. These data indicate that there is good agreement between the mathematical and the experimental results.

Important Limiting Cases

There are four pertinent lengths needed to characterize an alternating array of long, narrow, coplanar galvanic cells, namely the width of anode, the width of the cathode, and the anodic and cathodic polarization parameters. In agreement with the notation of the previous papers these are identified as $2a$, $2(c-a)$, $\mathcal{L}_a$ and $\mathcal{L}_c$ respectively. The behavior of a given galvanic system can be characterized by three dimensionless groups, $(a/\mathcal{L}_a)$, $(\frac{c-a}{\mathcal{L}_c})$ and a/c . If even five values of each of these groups are used to illustrate the behavior of galvanic systems, one hundred and twenty-five curves would have to be presented. The alternative is to discuss only limiting values of each ratio, and this procedure has been adopted in the present series of reports. One may distinguish four limiting conditions:

1. Negligible polarization $a \gg \mathcal{L}_a$ $(c-a) \gg \mathcal{L}_c$

This has been considered in Part I with the further

condition that $\mathcal{L}_a = \mathcal{L}_c$.

2. Strong polarization and high conductivity $a \ll L_a$ $(c-a) \ll L_c$

In this case as Wagner pointed out, IR drops within the solution represent a minor correction which can be disregarded. One may therefore use the Evans diagram of the electrode potential versus current density in order to derive the corrosion potential and the operating current density.

3. Cathodic control and protection $a \gg L_a$ $(c-a) \ll L_c$

The case of cathodic control on the dissolution of an almost pure metal has been discussed by Wagner⁹. He also adopted this assumption in his contribution to cathodic protection¹⁰. For the special condition that $L_a = L_c$, this case has been briefly discussed in Part II².

4. Anodic control $a \ll L_a$ $(c-a) \gg L_c$

This case has not been treated in general, however a portion of Part II is devoted to the analysis of the special condition that $L_a = L_c$.

In the previous reports the two limiting conditions were stated differently, namely in the first¹, L was assumed to be zero and several values of the anode-cathode ratio a/c were investigated; and in the second², L was permitted to vary over a wide range but it was assumed that one electrode was infinitely larger than the other. In the present report both these restrictions have been removed, but the requirement that $L_a = L_c$ is still imposed.

Important Experimental Studies

Electrostatic potentials have been known to exist in solution for many years and many electrochemical problems and phenomena have been explained in terms of them. However, it was apparently not until 1938 that they were shown to exist in the vicinity of corroding specimens¹⁰. Independently about this time a number

of investigations were started in Europe. The most significant contributions were made by Jaenicke and Bonhoeffer⁶ and by Daniel-Bek⁴. World War II interrupted similar work at Cambridge, and Copson³ undertook to complete the work of Agar¹² here in the United States.

Jaenicke and Bonhoeffer⁶ showed that the absolute size of the cathode, in a given medium, has a definite effect on the potentials one measures in the vicinity of the electrode surface. The ratio $(\frac{C-A}{L_c})$ has important physical significance and thus should be applied in the discussion of galvanic systems in general.

Daniel-Bek⁴ measured the variation in corrosion attack near the anode-cathode junction by measuring approximately the variation in the normal potential gradient potentiometrically. Copson obtained the variation in corrosion attack by measuring the penetration into the metal with a micrometer to indicate the changes in thickness.

MATHEMATICAL ANALYSIS AND EVALUATION

The techniques used have been well illustrated in the previous papers^{1,2} and merit little comment here.

Boundary Conditions

Inasmuch as the corrosion currents enter and leave the solution only at the electrodes, it is necessary to have the flow lines begin and end on the electrode surfaces. In order to eliminate edge effects at the boundary line of the electrode, an infinite repetition of the electrode arrangement with even symmetry has been assumed. This assumption permits us to restrict our attention to what is happening at the boundary between the anode and cathode. Mathematically we can study such an arrangement by using an even periodic function such as a Fourier cosine series which alternately takes on the potential of the anode and the cathode as a boundary condition and which

will give the potential within the corrodent. Consideration can thus be restricted to one period.

The model galvanic cell consists of two bimetallic coplanar, juxtaposed infinite strips as is indicated in Figure 1. Since current is assumed to not flow between the electrodes in different cells or periods, one can place insulators at the remote electrode boundaries as shown in Figure 1.

The unpolarized potential difference between the anode and cathode when immersed in the corrosive medium is designated as E_a . The conditions appropriate to the use of the slope of the polarization curve as though it were a linear polarization law has been discussed by Wagner⁷. This reduces our problem to the solution of a simple Sturm-Liouville problem. As in the other papers of this series, both E_a and the potential $P(x,y)$ within the solution have been measured with respect to the cathode. Clearly P is bounded in the region under consideration.

The interfacial conditions for the particular solution of this problem are:

$$P^*(\bar{x}, 0) - \mathcal{L} \left. \frac{\partial P^*}{\partial y} \right|_{y=0} = E_a S_a(x) \quad (1)$$

$$\left. \frac{\partial P^*}{\partial x} \right|_{x=0} = \left. \frac{\partial P^*}{\partial x} \right|_{x=c} = 0 \quad (2)$$

where the step function S_a is defined by

$$S_a(x) = \begin{cases} 1 \\ 0 \end{cases} \text{ for } \begin{cases} 0 \leq x \leq a-0 \\ a+0 \leq x \leq c \end{cases} \quad (3)$$

and in which $2c$ is the period of repetition. The quantity a is half of the width of the anode. The potential at the solution interface is illustrated in Figure 2.

Figure 1. Geometric Relation and
Orientation of the Electrodes.

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Figure 2. Polarized Interfacial Potential. Variation is due to the changing current density in the two electrode regions.

11 Solution of the Problem

A Fourier Series which will satisfy the two boundary conditions, satisfy Laplace's equation, and converge for infinite non-negative y is

$$P^*(x,y) = A_0^* + \sum_{n=1}^{\infty} A_n^* \exp\left(-\frac{n\pi y}{c}\right) \cos\left(\frac{n\pi x}{c}\right) \quad (4)$$

The starred coefficients may be determined by the boundary conditions (1) and (2). The asterisks indicate that polarization is being considered, in agreement with the convention adopted in earlier papers^{2,8}. Substitution of this series into equation (1) leads to

$$A_0^* + \sum_{n=1}^{\infty} A_n^* \left(1 + \frac{n\pi L}{c}\right)^{-1} \cos\left(\frac{n\pi x}{c}\right) = E_a S_a(x) \quad (5)$$

The orthogonal properties of the a cosine series can then be used to determine the coefficients. If this equation is multiplied by $\cos(m\pi x/c)$ and then integrated with respect to x, it is clear on using definition (3) that

$$\sum_{n=1}^{\infty} A_n^* \left(1 + \frac{n\pi L}{c}\right)^{-1} \left(\frac{c}{2}\right) \delta_{mn} = \frac{c E_a}{\pi m} \sin\left(\frac{m\pi a}{c}\right) \quad (6)$$

where δ_{mn} is the Kronecker delta function. The left hand side of (6) reduces to a single term of the series. The quantity A_0^* is determined in the usual way. The resulting coefficients A_m^* and A_0^* are presented in Table I, together with A_m and A_0 which were derived¹ in Part I.

TABLE I

Comparison of the Coefficients Obtained in the
Two Reports

	$L = 0$ PART I	$L \neq 0$ PART III
A_0	$E_a \left(\frac{a}{c}\right)$	$E_a \left(\frac{a}{c}\right)$
A_m	$\frac{2 E_a \sin\left(\frac{m\pi a}{c}\right)}{m\pi}$	$\frac{2 E_a \sin\left(\frac{m\pi a}{c}\right)}{\pi m \left(1 + m\pi L/c\right)}$

The resulting equation for the potential is

$$P^*(x,y) = \frac{E_a a}{c} + \frac{2E_a}{\pi} \sum_{n=1}^{\infty} \frac{\exp\left(-\frac{n\pi y}{c}\right) \cos\left(\frac{n\pi x}{c}\right) \sin\left(\frac{n\pi a}{c}\right)}{n\left(1 + \frac{n\pi L}{c}\right)} \quad (7)$$

It is clear that A_m^* reduces to A_m when L is zero as would be expected.

As long as the electrodes polarize similarly, the remote reference potential of this composite electrode is equal to A_0 or $E_a(a/c)$. This important result can be seen by setting y equal to infinity in equation (7).

To give the mathematical results more general significance and applicability, the potential function can be reduced to the dimensionless group $P^*(x,0)/E_a$. The reduced dimensionless groups x/c and a/c may also be used for the linear dimensions of the cell.

Distribution of the Interfacial Potential

The reduced interfacial potential $P^*(x,0)/E_a$ was evaluated from (7) using the Dual Coding Program on the Type 701 International Business Machine computer of this laboratory. This quantity is presented in Tables II and III as a function of various x/a , a/L and a/c values. The influence of these parameters is illustrated in Figure 3 for $a/c = 1/2$ and in Figure 4 for $a/c = 1/4$.

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TABLE II

The Reduced Interfacial Potential Function $P^*(x,0)/E_a$
Evaluated for $a/c = 1/2$ and Equal Polarization Parameters
(Part 1)

x/c					
a/L	0	0.1	0.2	0.3	0.4
0	0.50000	0.50000	0.50000	0.50000	0.50000
0.01	0.50369	0.50359	0.50328	0.50272	0.50180
0.05	0.51796	0.51748	0.51598	0.51328	0.50885
0.1	0.53477	0.53386	0.53101	0.52582	0.51728
0.5	0.63848	0.63525	0.62505	0.60603	0.57320
1.0	0.72010	0.71564	0.70132	0.67385	0.62397
5	0.90724	0.90351	0.89077	0.86270	0.79719
10	0.95110	0.94880	0.94071	0.92164	0.87036
50	0.98997	0.98946	0.98762	0.98300	0.96809
100	0.99493	0.99467	0.99373	0.99138	0.98366
∞	1.00000	1.00000	1.00000	1.00000	1.00000

TABLE II
(Part 2)

x/c						
a/L	0.5	0.6	0.7	0.8	0.9	1.0
0	0.50000	0.50000	0.50000	0.50000	0.50000	0.50000
0.01	0.50000	0.49820	0.49728	0.49672	0.49641	0.49631
0.05	0.50000	0.49115	0.48672	0.48402	0.48252	0.48204
0.1	0.50000	0.48272	0.47418	0.46899	0.46614	0.46523
0.5	0.50000	0.42680	0.39397	0.37495	0.36475	0.36152
1.0	0.50000	0.37603	0.32615	0.29868	0.28437	0.27990
5	0.50000	0.20281	0.13730	0.10923	0.096492	0.092755
10	0.50000	0.12964	0.078357	0.05929	0.051205	0.048895
50	0.50000	0.031908	0.017000	0.012383	0.010542	0.010028
100	0.50000	0.016335	0.008619	0.006266	0.005331	0.005071
∞	0.50000	0.00000	0.00000	0.00000	0.000000	0.000000

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TABLE III

Reduced Interfacial Potential Function $P^*(x,0)/E_a$ Evaluated for $a/c = 1/4$

(Part 1)

x/c						
a/L	0	0.1	0.2	0.249	0.251	0.3
0	0.25000	0.25000	0.25000	0.25000	0.25000	0.25000
0.005	0.25396	0.25371	0.25285	0.25188	0.25181	0.25082
0.05	0.28773	0.28538	0.27711	0.26777	0.26700	0.25743
0.5	0.50883	0.49384	0.43711	0.36394	0.35616	0.28189
5	0.88684	0.86980	0.77438	0.50215	0.44896	0.17618
50	0.98811	0.98574	0.96638	0.62632	0.36869	0.02862
∞	1.00000	1.00000	1.00000	1.00000	0.00000	0.00000

TABLE III

(Part 2)

x/c							
a/L	0.4	0.5	0.6	0.7	0.8	0.9	1.0
0	0.25000	0.25000	0.25000	0.25000	0.25000	0.25000	0.25000
0.005	0.24975	0.24908	0.24861	0.24828	0.24806	0.24793	0.24789
0.05	0.24731	0.24102	0.23671	0.23372	0.23173	0.23060	0.23023
0.5	0.21600	0.18076	0.15894	0.14491	0.13609	0.13121	0.12965
5	0.07588	0.04638	0.03333	0.02656	0.02288	0.02100	0.02042
50	0.008731	0.004923	0.003427	0.002690	0.002298	0.002101	0.002041
∞	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000

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Figure 3. Plot of the Reduced Interfacial
Potential $P^*(x,0)/E_a$ for Five Values
of a/L and with $2a = c$.

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Figure 4. Plot of the Reduced Interfacial
Potential $P^*(x,0)/E_a$ for Five Values of
 $a/\mathcal{L}$ and with $4a = c$.

Corrosion Current Density

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More important than the interfacial potential is the distribution of corrosion attack over the anode and the cathodic current density over the other electrode. In agreement with definition used elsewhere^{1,2}, the corrosion current parameter

$$C^*(x) = \frac{2a}{E_a} \left. \frac{\partial P^*}{\partial y} \right|_{y=0} \quad (8)$$

It is clear that the normal gradient in (8) may be calculated by means of boundary condition (1) from the interfacial potential. Thus

$$C^*(x) = -\frac{2a}{L} \left[S_a(x) - \frac{P^*(x,0)}{E_a} \right] \quad (9)$$

An additional and an important merit of calculating the interfacial potential is the facility with which the current density can subsequently be calculated. It is apparent that this equation cannot be used if the polarization parameter is negligibly small, i.e., when L is zero. The current density distribution has been discussed for zero L elsewhere¹.

The values of this dimensionless parameter $C^*(x)$ which represents the corrosion current have been computed from (9) and are presented in Tables IV and V. The dimensionless quantity employed to represent the current parameter¹ (in Part I) was $r(x)/E_a R_o h$ which is equal to $(\frac{-c}{4a})C(x)$.

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TABLE IV

CORROSION CURRENT PARAMETER EVALUATED FOR $a/c = 1/2$
(Part 1)

x/c a/L	0	0.1	0.2	0.3	0.4	0.499
0.01	-0.009926	-0.009928	-0.009934	-0.009946	-0.009964	-0.009999
0.05	-0.04820	-0.04825	-0.04840	-0.04867	-0.04912	-0.04998
0.1	-0.09304	-0.09323	-0.09380	-0.09484	-0.09654	-0.09992
0.5	-0.3615	-0.3647	-0.3749	-0.3940	-0.4268	-0.4979
1.0	-0.5598	-0.5687	-0.5974	-0.6523	-0.7521	-0.9920
5	-0.9276	-0.9649	-1.0923	-1.3730	-2.0281	-4.8454
10	-0.9779	-1.0241	-1.1859	-1.5671	-2.5928	-9.4673
50	-1.0028	-1.0542	-1.2383	-1.6999	-3.1908	-41.588
100	-1.0141	-1.0663	-1.2532	-1.7238	-3.2671	-74.236
∞	-1.0000	-1.0515	-1.2361	-1.7013	-3.2360	-318.47

TABLE IV
(Part 2)

x/c a/L	0.501	0.6	0.7	0.8	0.9	1.0
0.01	0.009999	0.009964	0.009946	0.009934	0.009928	0.009926
0.05	0.04998	0.04912	0.04867	0.04840	0.04825	0.04820
0.1	0.09992	0.09654	0.09484	0.09380	0.09323	0.09304
0.5	0.4979	0.4268	0.3940	0.3749	0.3647	0.3615
1.0	0.9920	0.7521	0.6523	0.5974	0.5687	0.5598
5	4.8454	2.0281	1.3730	1.0923	0.9649	0.9276
10	9.4673	2.5928	1.5671	1.1859	1.0241	0.9779
50	41.588	3.1908	1.6999	1.2383	1.0542	1.0028
100	74.236	3.2671	1.7238	1.2532	1.0663	1.0141
∞	318.47	3.2360	1.7013	1.2361	1.0515	1.0000

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TABLE V₁CORROSION CURRENT PARAMETER $C^*(x)$ EVALUATED FOR $a/c = 1/4$

(Part 1)

x/c a/L	0	0.1	0.2	0.249	0.251	.3
0.005	-0.007460	-0.007463	-0.007472	-0.007481	0.002518	0.002508
0.05	-0.07123	-0.07146	-0.07229	-0.07322	0.02670	0.02574
0.5	-0.4192	-0.5062	-0.5629	-0.6361	0.3561	0.2819
5	-1.1316	-1.3020	-2.2561	-4.9784	4.4896	1.7618
50	-1.1887	-1.4259	-3.3617	-37.368	36.869	2.8629
∞	-1.207	-1.4493	-3.4693	-159.26	158.54	2.9631

TABLE V

(Part 2)

x/c a/L	0.4	0.5	0.6	0.7	0.8	0.9	1.0
0.005	0.002497	0.002491	0.002486	0.002483	0.002481	0.002479	0.002479
0.05	0.02473	0.02410	0.02367	0.02337	0.02317	0.02306	0.02302
0.5	0.2160	0.1808	0.1589	0.1449	0.1361	0.1312	0.1296
5	0.7588	0.4637	0.3333	0.2657	0.2288	0.2100	0.2042
50	0.8731	0.4923	0.3428	0.2690	0.2298	0.2101	0.2041
∞	0.8881	0.5000	0.3479	0.2735	0.2332	0.2132	0.2071

Distribution of Potential in the Solution

The distribution of the potential can be obtained in the corrodent from equation (7). Because the exponential factor is present in each term of the series, the computation of the potential at a point in the solution is more rapid than equivalent computation of a value of the interfacial potential. That is, the series converges more rapidly in the former case.

As indicated above, the reduced and dimensionless polarization parameter $P^*(x,y)/E_a$ has been used to render the mathematical results applicable to the general problem. When this parameter is tabulated in terms of the reduced groups x/c , a/c and $a/\mathcal{L}$, which represent the physical dimensions of the galvanic cell, the results are independent of the actual quantities of any given galvanic cell namely, E_a , a , c , σ , etc. By calculating the several pertinent ratios, solution of a given problem can be effected.

The values of the reduced potential have been computed and presented elsewhere⁸ for a variety of $a/\mathcal{L}$ and a/c values. The effect of $\mathcal{L}$ on the distribution of potential is best illustrated by the four perspective drawings of $P^*(\frac{x}{c}, \frac{y}{c})$ which have been made to scale. In these drawings, the anodic material is assumed to be fifty percent of the total. Figure 5 was constructed for the condition that $\mathcal{L} = 0$. The cross hatching represents the portion of the interfacial potential which is hidden from view by the potential surface. Figures 6, 7 and 8 were constructed for the conditions that $a/\mathcal{L}$ was 10, 1 and 0.1 respectively. In these figures the cross hatching represents the changes in the interfacial potential from the unpolarized values 1 and 0 caused by polarization.

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Figure 5. Perspective Scale Drawing of
the Reduced Potential Function Evaluated
for $\mathcal{L} = 0$.

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Figure 6. Perspective Scale Drawing of
the Reduced Potential Function Evaluated for
 $a/\mathcal{L} = 10$.

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Figure 7. Perspective Scale Drawing of the
Reduced Potential Function Evaluated for
 $a/\mathcal{L} = 1.$

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Figure 8. Perspective Scale Drawing of the
Reduced Potential Function Evaluated for
 $a/L = 0.1.$

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Comparison Between Theory and Experiments

Adequate comparison can only be made when values of $\mathcal{L}_a$ and $\mathcal{L}_c$ have been obtained under conditions comparable to the experimental conditions that were employed. In the studies made to date, the author is not aware of any experimental study of current or potential distribution in which both $\mathcal{L}_a$ and $\mathcal{L}_c$ are available or can be computed. Any observed discrepancy revealed by comparing experiments with the present analysis will reveal mainly the degree to which $\mathcal{L}_a$ and $\mathcal{L}_c$ are dissimilar and not reveal any fundamental error in the analysis.

There is a fairly large mass of experimental data available on the distribution of potential throughout the corroding medium^{3,4,5,6,11,12}. However, comparison is complicated by the difficulty of estimating the unpolarized potential difference E_a and the subject is not as interesting, in the main, as the question of the distribution of the corrosion attack. Copson's³ and Daniel-Bek's third paper⁴ will be used for the comparison. Although only an experimental study designed for making this comparison can be adequate, these two investigations approximate the ideal conditions closely enough to merit consideration below.

Comparison with Daniel-Bek's Results

Daniel-Bek⁴ employed an approximate form of equation (8) to calculate the distribution of corrosion attack over the anode in the vicinity of the anode-cathode junction. He estimated $\left. \frac{\partial \mathcal{P}^*}{\partial y} \right|_y = 0$ by drilling tiny holes at several positions in the anode, and fitting the capillary tip of a reference electrode into them. By measuring the potential difference between these electrodes and another held a small constant distance (0.55 mm) in front of the metal surface, the normal potential gradient could be made roughly proportional to this potential difference. The assembly consisting of one anode and

one cathode was 320 cm long, so that the ratio y/c appearing in the exponential term of our series would be equal to 1.72×10^{-4} for his work, so that the difference form of the gradient $\Delta P/\Delta y$ was evaluated at approximately $y = 0$.

With this clever, approximate method he was able to show that there was a considerable variation in the amount of corrosion attack over the anode and in different strong electrolytes. Because the conductivities of the solutions were high and the anode width equal to 160 cm; one can see that $\mathcal{L}/a$ would be very small indeed.

One can estimate $\mathcal{L}$ from the data which he gives since a/c is one half. In such a case one can show that*

$$J_a(a-s) = -J_c(a+s) \quad (10)$$

Employing $s = 1/2$ cm., the largest J_c is 4.6 ma/cm^2 for 0.2 N KClO_3 , and the smallest J_c for $s = 8$ cm is 0.36 ma/cm^2 for 0.05 N KCl . One may estimate the derivative of the overvoltage curve, $\frac{\partial \Delta E_c}{\partial J_c}$, from Tafel's equation

$$\Delta E_c = a + 0.050 \ln J_c \quad (11)$$

if hydrogen evolution is the principal cathodic process. On substitution into the definition of $\mathcal{L}$ namely,

$$\mathcal{L}_i = \left| \frac{\partial \Delta E_i}{\partial J_i} \right| \sigma \quad (12)$$

it is evident that

$$\mathcal{L}_c = \frac{0.050 \sigma}{J_c} \quad (13)$$

The smallest value of the polarization parameter is 0.207 cm and the largest is 0.775 cm. These values are quite compatible with values estimated elsewhere². The largest value of $\mathcal{L}_c/c$ then would be 24×10^{-4} since in the theoretical analysis we have assumed that $\mathcal{L}_a = \mathcal{L}_c$.

Note that $J_a^(x)$, the actual current density, is equal to $(-\sigma E_a/2a)C_a^*(x)$.

The corrosion current parameter was computed from equation (9) for $\mathcal{L}/c$, namely 5×10^{-4} . When $\mathcal{L}$ is zero, equation (24) of Part I can be used to obtain the corrosion current parameter. The theoretical curves as well as the experimental data for three electrolytes are presented in Figure 9. Specifically, the ordinate is $J(160-s)/J(159.5)$ and the abscissa is $a-s$. The experimental data are well bracketed by $\mathcal{L}$ equals zero and $\mathcal{L}$ equals 1.6 mm. Therefore, the agreement would appear to be quite satisfactory considering the idealizations which have been employed.

Comparison with Copson's Results

It is not practical to compare the potentials which Copson measured in the corrodent, Bayonne tap water; however, the galvanic corrosion attack on the steel part of his steel-nickel couple can be compared with corrosion current parameter obtained in the theoretical analysis of this paper. He estimated the distribution of corrosion attack by graphically estimating the potential gradient from a map of the measured potentials. Figure 10 is his graph showing the comparison between the actual change in thickness and the calculated attack. The graphical method is clearly inadequate near the steel-nickel junction as would be expected from the tables of the corrosion current parameter presented above. Near the junction the current increases very rapidly and a linear average between two gradients is not very representative. In general, one would expect the average to be low because of the strong influence of the value taken more remotely from the junction. The estimated anodic current densities range from 0.138 ma/dm^2 or $1.38 \mu\text{a/cm}^2$ at a point one half inch from the center of the anode ($x = 1/2$) to $8.62 \mu\text{a/cm}^2$ at 3.95 inches. The cathodic current was estimated to vary from $4.32 \mu\text{a/cm}^2$ at $x = 4.00$ to $1.45 \mu\text{a/cm}^2$ at 7.80 inches. In terms of the definitions employed herein, a is 4 and c is 16 inches.

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Figure 9. Comparison of the theoretical current densities evaluated for $\mathcal{L}/c = 5 \times 10^{-4}$ and zero with Daniel-Bek's experimental results.

$$\frac{J(x)}{J(159.5)}$$

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Figure 10. Comparison between Copson's
graphical and experimental results.

Fig. Distribution of corrosion attack near the interface between the steel and the nickel (after Copson).

An estimate of the polarization parameter can be obtained from these data, using equation (13) for $\mathcal{L}_c$. It would range from 0.81 cm to 2.42 cm. If an expression such as Tafel's equation could properly be used to represent the anodic polarization, the estimated values of $\mathcal{L}_a$ would lie in the range 0.41 to 2.54 cm. The justification for making this crude estimate of $\mathcal{L}_a$ is to indicate that $\mathcal{L}_a$ and $\mathcal{L}_c$ are approximately equal, and that the present idealized analysis is pertinent.

Values of the corrosion current parameter were computed using four values of $\mathcal{L}$ namely, zero, 0.16, 0.64 and 1.0 inches. These data were plotted in Figure 11 in the form of $\frac{C_a^*(x)}{C_a^*(1/2)}$ which is equal to $J_a(x)/J(x = 1/2)$. Copson's experimental data are also plotted in Figure 11 for comparison. The agreement is fairly good considering the idealizations involved in the theoretical analysis.

Discussion

These numerical values of the polarized potential bear out the conclusions which have been deduced by others from experimental studies. The interfacial potential becomes more nearly the same for the anode and cathode as the parameter $\mathcal{L}$ increases.

This polarization parameter has the dimension of length as pointed out by Wagner⁷, and is very important in characterizing actual galvanic cells. In a given environment, irrespective of physical size, a galvanic cell may behave as though it were "macroscopic" or "microscopic" depending upon the ratio of the critical dimension to $\mathcal{L}$ is large or small. This critical dimension cannot easily be defined in a precise manner, but it is that physical dimension which affects most strongly the distribution of current over the electrodes. It thus depends on the geometry of the cell.

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Figure 11. Comparison between the distribution of Copson's experimental current densities and the theoretical variation evaluated for four $\mathcal{L}$ values.

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If the critical dimension is small in comparison to $\mathcal{L}$, that galvanic cell will behave as though it were microscopic. Since $\mathcal{L}$ is directly proportional to the conductivity of the solution, a particular system may appear to be either microscopic, or not, depending on whether the electrical resistance of the corrodent is small or large, respectively. That is, more uniform potentials over the electrodes are observed in solutions which have good conductivity as Jaenicke and Bonhoeffer⁶, among other, have shown. The "microscopic" cells are characterized by nearly uniform current distributions and hence nearly uniform interfacial potentials.

It should be emphasized here again that the present investigation is an idealization since the restriction $\mathcal{L}_a = \mathcal{L}_c$ has been imposed. However, as indicated above, the experimental values of $\mathcal{L}_c$ taken from a variety of studies range from a fraction of a millimeter to 3 centimeters. The assumption that $\mathcal{L}_a$ and $\mathcal{L}_c$ are equal is not seriously in error if either $\lambda/\mathcal{L}$ is very small or very large, since in either range fivefold changes, for instance, of this ratio do not significantly affect the interfacial potential or the current density.

Further, it is clear from the discussion that $\mathcal{L}$ is difficult to estimate from the current density and must properly be obtained from the polarization curve. For example, one chooses a value of $\mathcal{L}$ and then computes the current density. When these are taken to compute $\mathcal{L}_c$ one obtains a large range of values. This discrepancy becomes most serious when the ratio $a/\mathcal{L}$ is large, i.e., when there is small or negligible polarization.

Without going into it here, it is apparent from Wagner's analysis⁷ of $\mathcal{L}$ that it is not a fixed quantity but depends upon the curvature of the polarization curve and, therefore, will in general vary over the electrodes in a macroscopic assemblage in the same way that the current density does.

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A further feature which may not be recognized at first is that $E_{a(o)}$ is not a fixed quantity and is not necessarily the difference between the two equilibrium single electrode potentials but is somewhat dependent upon the shape of the polarization curve. It is suggested that one study Figure 2 of Wagner's paper⁷. Nevertheless, these simplifications in the treatment and accompanying increase in the tractability in mathematic analysis which is required, lead us to a more understandable picture of the influence of the various factors. The present analysis becomes increasingly accurate and pertinent if "microscopic" galvanic cells are considered.

The estimation of $\mathcal{L}_a$ depends upon a questionable technique if the anodic polarization curve is not obtained in any practical study. This is for the reason that there is no recognized expression such as Tafel's equation for relating anodic polarization to current density. A thorough analysis of the limited and scattered experimental data would be desirable.

It is clear from inspecting the perspective drawings that the variation in potential in a direction parallel to the electrode surface is greatest at the interface between the electrodes and the liquid. This variation in potential diminishes as one recedes from the interface and approaches a constant potential value at great distances. It has been shown¹³ that this constant is equal to $E_a(a/c)$ for the condition $\mathcal{L}_a = \mathcal{L}_c$. This value has been called the potential of a composite electrode¹. Therefore, it is evident that this potential which is obtained with a remote reference is dependent not only upon the potential difference E_a but also upon the relative proportions of anodic to cathodic material.

This qualitative effect of $\mathcal{L}$ is brought out in a previous paper². In the two experimental cases under consideration, the critical dimension was a , the half width of the anode. The dependence of the maximum potential

difference on a/L is clearly illustrated by the tables.

It is interesting to point out that

$$\lim_{L \rightarrow \infty} P^*(x, y) = E_a \left(\frac{a}{c} \right) \quad (14)$$

since the coefficients A_m^* become zero. Thus since the interfacial potential must converge to this value, it is clear that

$$\lim_{L \rightarrow \infty} P^*(x, 0) = P^*(x, \infty) = E_a \left(\frac{a}{c} \right) \quad (15)$$

As discussed above in connection with equation (7), the righthand side of this equation applies for all L . Thus the potential distribution within the solution must become more uniform as L increases since these potentials are being squeezed between the limiting interfacial potential and the remote potential value of the galvanic cell. That is, any potential variation in the solution is smaller than that present on the interface. This feature has not been clearly brought out in any of the previous experimental studies.

Using the definition employed in a previous paper², that the anodic region in the electrolyte is that in which the potential exceeds $1/2 E_a$, it is evident from the tables that shrinkage of the anodic region occurs as L increases and vanishes for L sufficiently large if a/c is less than $1/2$. The use of $(a/c)E_a$ is not really more satisfactory since a study of Figure 4 shows that for certain values of L/a , the liquid adjacent to the cathode is at potentials which lie between $1/2 E_a$ and $a/c E_a$. No satisfactory definition has been suggested.

The current density and the total anodic current remain finite for a given width of the anode. Consideration of tiny cathodes leads to equivalent results. This finite current density is different from calculations in which the effect of polarization is ignored. This fact justifies the present calculations in spite of the rather artificial condition of equal polarization parameters.

It is hoped that the perspective drawings presented above will be helpful and instructive to those who employ potential measurements in their corrosion studies.

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Summary

A theoretical analysis of the influence of the percentage of anodic material and of the polarization parameter on corrosion attack has been made subject to the condition that the anodic and cathodic polarization parameters are constant and equal. Two experimental studies of the distribution of corrosion attack were compared with the theoretical results and were found to be in reasonable agreement. Analysis shows that the potentials in the solution lie between the interfacial potential, as polarized, which is variable over the electrodes, and a constant value which is dependent upon the relative amounts of anodic and cathodic material. The variation in solution decreases with a/L , that is, as the galvanic system approaches "microscopic" behavior.

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