800. *Anodic Processes. Part V.* The Effects of Impurities on the* Hg|HCl (aq) *System: The Passivation Law, and the Properties of Passivating Calomel Films.*

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The Hg|HCl (aq) system has been found to be very sensitive to the presence of traces of surface-active impurities which are hard to eliminate except by adsorptive cleaning of solutions. This is shown by means of differential capacity measurements at mercury-pool electrodes. Studies of the passivation of mercury in hydrochloric acid solutions over a range of temperatures indicate that the impurity film is removed during the anodic growth of a calomel film. The significance of the passivation law has been re-assessed. The properties of calomel films on mercury have been studied by a variety of electrochemical methods and an explanation of their comparatively well-conducting properties is proposed.

EXTENSION of earlier studies [1-4] has been delayed by the discovery that the Hg|HCl (aq) system is highly sensitive to ubiquitous, surface-active impurities which are not eradicated by the supposedly rigorous purification methods used in connection with hydrogen overpotential measurements. The overpotential criterion of purity previously used [1] was inadequate, and the results obtained were more or less adversely affected by such impurities. Re-assessment of the earlier work has been necessary in the light of further experiments conducted under improved conditions. These have been attained by means of adsorptive cleaning of cell solutions with activated charcoal, a method for which we are greatly indebted to Dr. G. C. Barker, of A.E.R.E., Harwell. The general result of this re-assessment is that nearly all the previous results require modified description or quantitative adjustment, but none of them needs drastic revision; indeed, some of the phenomena described become, in " ultra-clean " systems, even more striking and reproducible. Others, surprisingly at first sight, become less reproducible.

The same adsorptive-cleaning process is of great assistance in dealing with an " autogenic " impurity produced by anodic oxidation, or by the disproportionation of calomel. This impurity is Hg^{II}, present as $HgCl_2$, $HgCl_3^-$, $HgCl_4^{2-}$ in equilibrium proportions determined by the prevailing Cl^- activity. Circulation of the cell solution over activated carbon (which carries a positive charge) is effective, while cathodic polarisation is ineffective, in removing these solutes, which exert profound effects upon the anodic generation of calomel.

Another difficulty, which is enhanced by the necessity of using a tranquil (as opposed to dropping or streaming) mercury electrode, is that due to penetration of solution between the mercury and its container (the wedge effect [5]). It has been countered [1-4, 6] by silicone treatment of glass surfaces and, contrary to earlier opinion,[2] this is a potential source of contamination. In experiments to be recorded, this treatment was either omitted or was carried out with specially purified Silicone fluid, and was used in conjunction with prolonged charcoal cleaning.

The existence of interface contamination was first clearly shown by measurements of differential capacities of the Hg|HCl (aq) system, by an A.C. method described in the Experimental section. Over a range of D.C. polarisations encompassing the anodic branch

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* Part IV, *J.*, 1957, 3370.

[1] Cousens, Ives, and Pittman, *J.*, 1953, 3972.
[2] Cousens, Ives, and Pittman, *J.*, 1953, 3980.
[3] Cousens, Ives, and Pittman, *J.*, 1953, 3988.
[4] Dibbs, Ives, and Pittman, *J.*, 1957, 3370.
[5] Johnson and Ubbelohde, *Proc. Roy. Soc.*, 1951, *A*, **206**, 275.
[6] Hills and Ives, *J.*, 1951, 311.

of the electrocapillary curve, the results were very much lower than those established by dropping-electrode methods;[7] they were irreproducible, decreased with time, and showed hysteresis effects. The hysteresis was subsequently shown to be due to the partial desorption of surface-active impurities by polarisations at potentials far removed from the electrocapillary maximum. Moderately satisfactory results were obtained with freshly set-up electrode systems if silicone treatment and the customary 24-hr. pre-polarisation were omitted. Progressive deterioration, however, took place in the course of a few hours, with decline of measured capacities, and disappearance of the characteristic anodic maximum. The introduction of continuous adsorptive cleaning prevented this deterioration, or even reversed it, if it had not gone too far, but the measurements still lacked reproducibility and were clearly adversely influenced by the wedge effect. The best compromise was obtained by re-introduction of silicone treatment, with use of specially purified materials, in conjunction with continuous adsorptive cleaning. Typical results of such exploratory experiments are shown in Fig. 1. They represent an improvement over some previous measurements of differential capacities at mercury pool electrodes,[8] and show that the acute difficulty of the rapid uptake of surface-active impurities by the mercury-solution interface (sometimes significant within 10 sec.[9]) had been partially overcome.

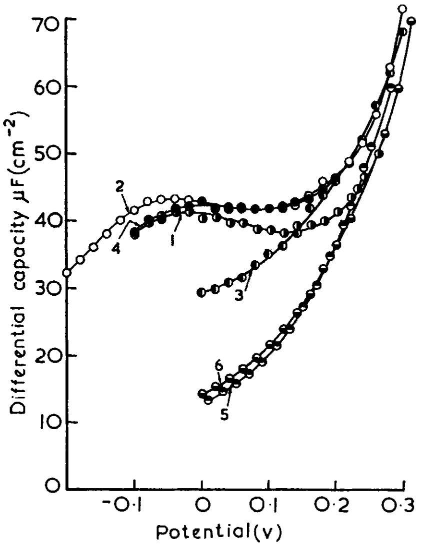

FIG. 1.

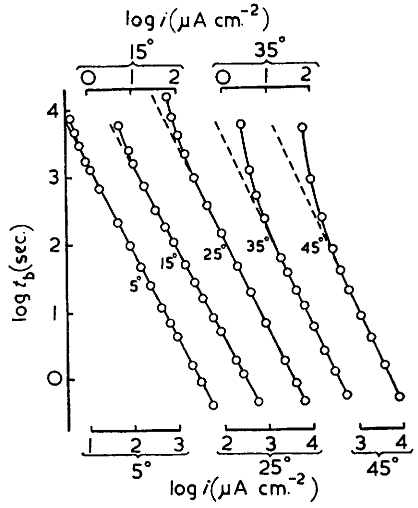

FIG. 2.

FIG. 1. Differential capacities of Hg|0·1N-HCl (aq) at 25°: (1) fresh cell, no silicone treatment; (2) the same, after 13 days' adsorptive cleaning; (3) fresh cell, treated with purified silicone; (4) the same, after 18 days' adsorptive cleaning; (5) aged cell, siliconed—increasing anodic polarisation; (6) the same, decreasing anodic polarisation. Potential is with respect to the hydrogen electrode in the same solution.

FIG. 2. The passivation law for 1·0N-aqueous hydrochloric acid.

This experience suggested that previous work, conducted with contaminated systems, should be discarded. On the other hand, such action, impartially applied, would decimate the electrochemical literature, and was unduly drastic for experiments in which conditions of purity normally considered to be rigorous had been uniformly maintained. It

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[7] Grahame, *J. Amer. Chem. Soc.*, 1949, **71**, 2975.

[8] Hansen, Minturn, and Hickson, *J. Phys. Chem.*, 1956, **60**, 1185.

[9] Grahame, Larsen, and Poth, *J. Amer. Chem. Soc.*, 1949, **71**, 2978.

is therefore justifiable to give conditional credence to such earlier results as are particularly clear-cut, especially when the effects of impurity films can be traced and reasonably interpreted. This is the case for the experiments described in the present paper.

Conformity of the anodic passivation of mercury in aqueous hydrochloric acid with the W. J. Müller passivation law has been recorded.[3] This law was deduced [10] for the special case of " protected electrodes," at which an anodic product is deposited on the electrode surface from a zone of supersaturated solution, forming an insulating barrier after a certain passivation time, which is related to the current density by the well-known double logarithmic law. The deduction has been criticised [11, 12] and the W. J. Müller mechanism cannot apply to the passivation of mercury by calomel, or to other cases in which the anodic product is highly insoluble. The fact that the law applies to the most diverse kinds of anodic passivation phenomena suggests that its real basis is either fundamental or trivial. The passivation of mercury is favourable for detailed study to settle this point, because of the unique advantages of an ideally smooth metallic substrate with reproducible properties. It differs, however, from other cases in that continued flow of current is required to maintain the high impedance state, which is not, therefore, strictly passive. The term " blocking " is therefore preferred to " passivation " and will be adopted.

It has been found that, under otherwise constant conditions, the blocking time for a given mercury electrode depends critically upon the state of the interface. In the earlier work, this appeared as an ageing effect. At a given current density, each successive blocking (with intervening cathodic stripping) required a longer period of current flow, until, eventually, a constant blocking time was asymptotically attained, together with a high degree of reproducibility in behaviour over a range of current densities embracing five orders of magnitude. This behaviour was attributed to the accumulation of Hg^{II} in solution, which could be expected to influence rates of nucleation and growth of calomel and, when at equilibrium, would permit reproducible results to be obtained. It was later shown that Hg^{II} in solution does have such effects, but they operate *in the reverse direction*, reducing, not increasing, the blocking time. The true explanation of the ageing effect was indicated by the fact that it did not occur when the cell solution was subjected to continuous adsorptive cleaning, which also largely reduced the blocking time. That the ageing was due to the slow adsorption of surface-active materials on the mercury surface was proved by differential capacity measurements, of which an example may be quoted. For two mercury electrodes in 0·1N-hydrochloric acid, differential capacities at the hydrogen electrode potential were 40 and 21 μF cm.$^{-2}$; the reproducible blocking times at 100 μA cm.$^{-2}$ were 15 and 75 sec., respectively. The first of these electrode systems was ultra-cleaned; the second was aged, as in the earlier work.

The experiments with aged (contaminated) electrodes are by no means valueless. Apart from the fact that they are more typical of mercury electrodes as normally encountered, the comparison with parallel experiments conducted with ultra-cleaned systems is particularly helpful in understanding the way in which anodic calomel films grow. The high degree of reproducibility of blocking experiments conducted with aged electrodes is illustrated by Fig. 2, which shows the results for the Hg|1·0N-HCl system at five temperatures. The deviations from the W. J. Müller law at lower current densities are seen to increase with rising temperature; they are due to the disproportionation of calomel and, concurrently, to the influence of the alternative anodic generation of mercuric chloride and its anionic derivatives, which considerably reduces the current efficiency of calomel production.[4]

The " blocking law " may be expressed in the form

$$\log t_b = A - m \log i, \qquad (1)$$

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[10] W. J. Müller, " Die Bedeckungstheorie der Passivität," Berlin, 1933; *Trans. Faraday Soc.*, 1931, **27**, 737.

[11] E. Müller and Schwabe, *Z. Elektrochem.*, 1933, **39**, 414.

[12] Halla and Weiner, *Z. Elektrochem.*, 1942, **48**, 361, 618.

where t_b is the blocking time in seconds, i is current density in μA cm.$^{-2}$, and A and m are constants. The values of these constants for all the blocking experiments conducted are assembled in Table 1.

The influence of ultra-cleaning is apparent from the results quoted for experiments with 0·1N-hydrochloric acid. They indicate, for example, that a current density of 1 mA cm.$^{-2}$ will block a mercury electrode in an ultra-cleaned system in 0·55 sec., forming a film of calomel with an average thickness of 18 Å; in an aged system, blocking under otherwise identical conditions would take 6·2 sec. and the film would be 200 Å thick. The explanation is, obviously, that the lateral growth of calomel in the plane of the mercury surface is very much faster when it is unimpeded by a film of impurity, but a more detailed interpretation can be made from the regularities of the data in Table 1. It must be noted, however, that the figures relating to 1·0N-hydrochloric acid are anomalous in that both A and m values show trends with temperature opposite to those noted for comparable experiments with the more dilute acids. This is probably due to low current efficiency (decreasing with rise of temperature) of calomel production,[4] and it must be remembered as a factor likely to confuse the issue.

TABLE 1.

Parameters of the blocking law, $\log t_b = A - m \log i$ for mercury electrodes in aqueous hydrochloric acid.

	(1)		(2)		(3)		(4)	
	0·01N-HCl		0·1N-HCl				1·0N-HCl	
	Aged		Aged		Ultra-cleaned		Aged	
Temp.	A	m	A	m	A	m	A	m
5°	5·87	1·38	4·97	1·44	3·09	1·12	4·49	1·32
15	5·50	1·27	4·87	1·38	3·13	1·10	4·51	1·30
25	5·36	1·22	4·75	1·32	3·10	1·12	4·89	1·39
35	5·29	1·22	4·57	1·27	3·20	1·07	5·12	1·45
45	4·91	1·12	—	—	3·30	1·04	5·29	1·45

It is appropriate at this stage to consider the simplest possible basis of the general passivation law. Suppose that, on 1 cm.^{2} of electrode surface, n nuclei have been established at the outset of anodisation at constant current density, i, and have developed uniformly at a time t to provide n crystals, each occupying an area, a, of the surface, and each of a thickness, or height, h. Then it is obvious that

$$hn\left(\frac{\partial a}{\partial t}\right)_i + na\left(\frac{\partial h}{\partial t}\right)_i = Ci, \tag{2}$$

where C is a constant determined by the properties of the solid anodic product. For an anodisation of finite duration,

$$n\int h\mathrm{d}a + n\int a\mathrm{d}h = \int Ci\mathrm{d}t.$$

Since i is constant, and the integration constant is clearly zero, integration (of the second term by parts) leaves

$$nah = Cit, \tag{3}$$

which, in view of the hypothetical conditions of film growth, is also self-evident. In the W. J. Müller mechanism, the crystals grow from solution uniformly along their three axes, so that $h = a^{1/2}$. Hence

$$na^{3/2} = Cit.$$

But at time $t = t_b$ (the blocking time) the unit area of surface is completely occupied, so that $a = 1/n$. Therefore,

$$n^{-1/2} = Cit_b.$$

In comparing one galvanostatic experiment with another, each conducted at a different current density, n becomes a function of i. If it is assumed that the degree of supersaturation in the zone of solution adjacent to the electrode is directly proportional to current density, this will also be the case for the number of nuclei deposited per cm.[2] of electrode surface, *i.e.*:

$$ki^{-1/2} = Cit_{\mathrm{b}}.$$

where k is a constant. Hence $t_{\mathrm{b}} = k/Ci^{3/2}$, or

$$\log t_{\mathrm{b}} = A - 1{\cdot}5 \log i, \tag{4}$$

where A is a constant. This is the passivation law, with $m = 1{\cdot}5$, a value which, ideally, is characteristic of the W. J. Müller mechanism. Values ranging from 1·4 to 1·7 have been observed for various anodic passivations.[10] If it is necessary to introduce a geometrical factor into the relation between h and a, *i.e.*, $h = ga^{1/2}$, this will modify the constant A. If the surface concentration of nuclei initially deposited is proportional to some power of current density other than the first, the value of m will vary from 1·5.

It has already been indicated that the " deposition from solution " mechanism cannot apply to the formation of highly insoluble films, for which growth in area must always be intrinsically easier than growth in thickness. The film substance, generated at the yet open metal–solution interface, must be somehow transported (activated surface diffusion) to crystal sites where final deposition will build up thickness. Whatever kind of crystal growth process may be concerned, it is clear that growth in thickness cannot be related to growth in area by any simple geometrical considerations based on ideal crystal forms. Nevertheless, if similar simplifying assumptions are retained, equation (3) may still apply. In this case, when $t = t_{\mathrm{b}}$, $na = 1$, and $h = h_{\mathrm{b}}$, where h_{b} is the supposedly uniform thickness of the passivating film. Then

$$h_{\mathrm{b}} = Cit_{\mathrm{b}}, \tag{5}$$

an obvious relation from which n has disappeared. The law becomes

$$\log t_{\mathrm{b}} = A - \log (i/h_{\mathrm{b}}), \tag{6}$$

and its final solution will depend on how h_{b} can be expressed as a function of i. There is no information about how, if at all, $(\partial h/\partial t_{\mathrm{b}})$ depends on i, but

$$h_{\mathrm{b}} = \int_0^{t_{\mathrm{b}}} \left(\frac{\partial h}{\partial t}\right)_i \mathrm{d}t$$

must do so, because the upper limit of integration decreases as i increases. If it can be assumed that h_{b} is a rational function of i, namely, $h_{\mathrm{b}} = ki^x$, where k and x are constants, then clearly equation (6) assumes the usual form (1), with m depending on the value of x. If $x = 0$, $m = 1$; if $x = -\frac{1}{2}$, $m = 1{\cdot}5$; if $x = -1$, $m = 2$; and it is clear that almost any value of m between the limits 1 and 2 can be expected. It is thus obvious that a given value of m can arise in a variety of ways and the passivation law is devoid of diagnostic value; in this respect it must be regarded as trivial. This conclusion may, however, be varied if, as in the present work, the application of the law over a range of temperatures has been studied, as can be shown by the following argument.

Equation (2) can be alternatively expressed

$$h\left(\frac{\partial \theta}{\partial t}\right)_i + \theta\left(\frac{\partial h}{\partial t}\right)_i = Ci, \tag{7}$$

where θ is the fraction of the electrode area covered by a film at time t. This is self-evidently true, irrespective of numbers of nuclei. It is obvious that the blocking time is uniquely determined by $(\partial\theta/\partial t)_i$, in whatever way it varies throughout a given anodisation, *i.e.*, $\int d\theta = 1$ when $\int dt = t_b$. In comparing one galvanostatic anodisation with another, $(\partial\theta/\partial t)_i = f(i)$, which is possible within the requirements of Faraday's law because of the complementary nature of the two contributions on the left-hand side of equation (7).

It is suggested that $f(i)$ is a rational function of the real current density at the uncovered portions of the electrode surface, *i.e.*,

$$(\partial\theta/\partial t)_i = k[i/(1-\theta)]^x, \tag{8}$$

where k and x are constants. Then

$$\int_0^1 (1-\theta)^x d\theta = k\int_0^{t_b} i^x\, dt \tag{9}$$

and, since i is not a function of t, this leads to

$$1 = k(x+1)i^x t_b.$$

Therefore,

$$\log t_b = -\log k(x+1) - x \log i, \tag{10}$$

which corresponds with equation (1) with $A = -\log k(x+1)$ and $m = x$.

It is obvious that the rate of lateral film growth is not directly controlled by current density, but, in all except ultra-clean systems, is controlled by desorption of a film of impurity. It is an activated process with an activation energy which can be identified with the desorption energy of the impurity. Insofar as the impurity is polar, this energy is likely to be linearly modified by electrode potential. Hence, an equation may be set up for the rate of lateral growth:

$$\text{Rate} = k' \exp(-\omega/\boldsymbol{R}T) \exp(\alpha\eta\boldsymbol{F}/\boldsymbol{R}T), \tag{11}$$

where k' is a constant, ω is the activation energy for zero overpotential ($\eta = 0$), α is a transfer coefficient, and the other symbols have their usual meanings. If the overpotential is determined by the current density, i, according to a Tafel law, the rate equation will become:

$$\text{Rate} = k''e^{-(\omega+\omega')/\boldsymbol{RT}} i^{\alpha b\boldsymbol{F}/\boldsymbol{RT}}, \tag{12}$$

where k'' is a constant, $(\omega + \omega')$ is a composite activation energy for desorption of impurity and ion discharge, and b is an appropriate Tafel slope. In this equation, i is the real current density, and comparison with equation (8) suggests that

$$k = k''e^{-(\omega+\omega)/\boldsymbol{RT}} \text{ and } x = \alpha b\boldsymbol{F}/\boldsymbol{R}T. \tag{13}$$

Hence the passivation law parameters become:

$$A = -\log k'' + \frac{(\omega + w')}{2{\cdot}303\boldsymbol{R}T} - \log(m+1); \tag{14}$$

$$m = \alpha b\boldsymbol{F}/\boldsymbol{R}T. \tag{15}$$

The results in Table 1 can be used in the following tests of these equations.

From equation (15), it is clear that the product, Tm should be independent of temperature. This is seen to be the case from the values (those relating to 1·0N-HCl having been excluded) shown in Table 2.

TABLE 2.

Values of the product Tm from 5° to 45°.

System	Temperature 5°	15°	25°	35°	45°	Mean	Mean deviation (%)
0·01N-HCl, aged	384	366	364	376	356	369	±2·2
0·10N-HCl, aged	401	398	394	391	—	396	±1·0
0·10N-HCl, ultra-cleaned	212	317	334	330	331	325	±2·5

The value of Tm is to be expected to vary from one electrode system to another; otherwise the constancy is well within experimental error.

Inspection of equation (14) shows that $A + \log (m + 1)$ should be linear with $1/T$ and that the slope should allow the composite activation energy to be assessed. This has been tested with the results shown in Table 3, which records the values of $(\omega + \omega')$ and $\log k''$ which give the best fit in each case, and a comparison between A values calculated from them (and unsmoothed m values) and those observed (Table 1).

The results are reasonably satisfactory. For a good fit in the last case, the ultra-cleaned system, a small negative value would be needed for $(\omega + \omega')$, but since this quantity can hardly be estimated to better than 1 kcal., this is not significant. It is, however, very interesting that, within this uncertainty, the composite activation energies are reasonable in value and fall in the order to be expected.

TABLE 3.

Parameters of equation (14); observed and calculated A values.

Temp.	5°	15°	25°	35°	40°	
(*a*) 0·01N-HCl, aged.	$(\omega + \omega') = 8{\cdot}30$ kcal.; $\log k'' = 0{\cdot}364$.					
$A_{\text{calc.}}$	5·78	5·57	5·37	5·18	5·01	
$A_{\text{obs.}}$	5·87	5·50	5·36	5·29	4·91	
Δ	+0·09	−0·07	−0·01	+0·11	−0·10	Mean ±0·08 ~±1·5%
(*b*) 0·10N-HCl, aged.	$(\omega + \omega') = 5{\cdot}52$ kcal.; $\log k'' = 1{\cdot}042$.					
$A_{\text{calc.}}$	4·99	4·85	4·72	4·60		
$A_{\text{obs.}}$	4·97	4·87	4·75	4·57		
Δ	−0·02	+0·02	+0·03	−0·03		Mean ±0·025 ~±0·5%
(*c*) 0·10N-HCl, ultra-cleaned.	$(\omega + \omega') = 0$; $\log k'' = 3{\cdot}474$.					
$A_{\text{calc.}}$	3·15	3·15	3·15	3·16	3·16	
$A_{\text{obs.}}$	3·09	3·13	3·10	3·20	3·30	
Δ	−0·06	−0·02	−0·05	+0·04	+0·14	Mean ±0·06 ~±2·0%

Finally, it may be noted that in cases where $-\log k''$ and $-\log (m + 1)$ make only a minor contribution to A, which is the case for contaminated systems, the ratio A/m should be approximately constant. This should also apply to the 1·0N-HCl system, for, in this ratio, anomalous temperature-dependences should cancel. The results of this test are shown in Table 4.

TABLE 4.

Values of A/m for contaminated electrode systems.

	Temperature					
System	5°	15°	25°	35°	45°	Mean
0·01N-HCl	4·25	4·33	4·39	4·34	4·38	4·34 ± 0·04
0·10N-HCl	3·45	3·53	3·60	3·60	—	3·54 ± 0·05
1·0N-HCl	3·40	3·47	3·52	3·53	3·65	3·51 ± 0·06

The evidence from these tests implies that the rate of lateral growth of a calomel film in aged electrode systems is determined by the stripping-away from the electrode–solution interface of adsorbed impurities. It follows that the impurities were present in the adsorbed state at all stages of the anodisations up to completion of blocking. This is in conformity with the normally irreversible nature of the ageing effect, with the trivial extent of the hysteresis observed in the differential capacity measurements, and with the magnitudes of the activation (largely desorption) energies noted above. The results of the tests also indicate that the impurities *are* desorbed in the blocking process, and this is confirmed by the fact that immediately after blocking and rapid cathodic stripping, differential capacity measurements were close to those later determined for ultra-cleaned systems.

This argument not only justifies us in recording studies of the properties of calomel films made under these conditions, but resolves an otherwise very puzzling anomaly. It has already been mentioned that maintenance of the blocked state requires continued passage of anodic current, so that, under galvanostatic conditions, the state of the system is continuously changing, because of progressive generation of calomel. Yet the properties of the blocking films were reasonably steady in time and were largely independent of the current density at which they were formed. Later work with ultra-cleaned systems not only failed to confirm this finding, but revealed complexities (to be discussed in a later paper), associated with the blocking process, that had not hitherto been observed. This apparent discrepancy can be resolved by considering that in the aged systems, in contrast to the ultra-clean ones, there was a constant factor which was of predominant importance in controlling the formation of the calomel films—the desorption of an existing foreign film. In effect, a load opposing the growth process conferred a benefit of the kind associated with reversibility so that thicker, more stable, and more reproducible films were produced. In the ultra-clean systems, free from this stabilising influence, film growth was all the more susceptible to other factors and, in any case, the films were more tenuous, vulnerable, and harder to reproduce.

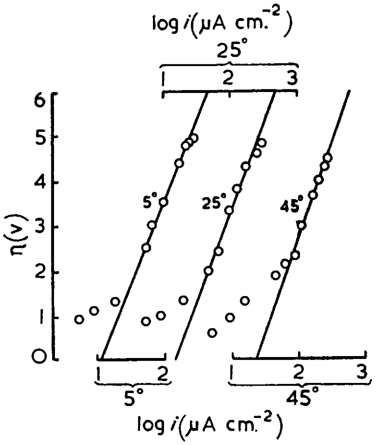

FIG. 3. Tafel plots for blocked Hg|0·1N-HCl (aq) electrodes.

For 5° plot, $b = 3{\cdot}64$ v, $i_0 = 1{\cdot}10$ μA cm.$^{-2}$; for 25° plot, $b = 3{\cdot}90$ v, $i_0 = 1{\cdot}68$ μA cm.$^{-2}$; for 45° plot, $b = 4{\cdot}16$ v, $i_0 = 2{\cdot}40$ μA cm.$^{-2}$.

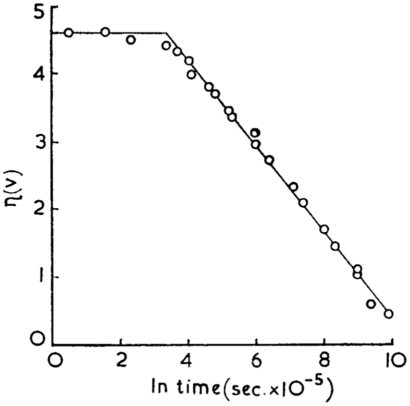

FIG. 4. Open-circuit decay of overpotential, Hg|0·1N-HCl (aq) at 25°; initial current density, 155 μA cm.$^{-2}$.

Certain properties of blocking films formed in aged systems have been studied. Overpotentials, which were not sensitive to the order in which they were measured or to the current densities at which the films were formed, are recorded in Fig. 3. Although of rather poor accuracy, they indicate the existence of two kinds of blocked state, possibly corresponding with two modes of charge transfer. A Tafel law applies reasonably well to the better-defined state of higher impedance. The lines in Fig. 3 have been drawn with slopes proportional to absolute temperature. Values of i_0, exchange current in μA cm.$^{-2}$, are shown; log i_0, plotted against $1/T$, gives a straight line with slope corresponding with an activation energy of 3·45 kcal.

When the current-carrying circuit was broken, the potential of the blocked electrode fell rapidly at first, then more slowly, finally attaining the calomel potential. No potential arrest corresponding with the presence of a solid anodic product other than calomel has been observed. The early stages of decay have been followed oscillographically and Fig. 4 contains the combined results of a number of experiments of this kind. Here the potential decay is linear with log time, and values have been calculated[13, 14] from this plot of the Tafel slope appropriate to the electrode process taking place immediately before the circuit is broken, and of the double layer capacity. Values of 1·6 v and 0·08 μF cm.$^{-2}$ were obtained for the experiment indicated. Other experiments conducted at various initial current densities gave similar results, the double-layer capacities varying on either side of 0·11 μF cm.$^{-2}$, and the Tafel slopes being about one-third of those found by the direct method.

Imposition of small A.C. signals (± 3 mv) upon D.C. polarisation allowed impedance measurements to be made, which confirmed the existence of two distinct blocked states. The transition from the low- to the high-impedance state on increase of current density, or with time at constant current density, was strikingly visible on the oscillograph screen. It involved a sudden increase in resistance from a value in the range 10^4—10^6 ohms to something exceeding 5×10^6 ohms, a region in which existing arrangements did not allow adequate measurements to be made. Maintained in the high-impedance state, the electrodes gave strictly linear plots, of slope -1, of log impedance against log frequency within the range 3—9000 sec.$^{-1}$. The differential capacity was found to be 0·45 μF cm.$^{-2}$, remarkably independent of D.C. potential and of the time for which the blocked state was maintained. When the D.C. polarisation circuit was broken, then, although the potential immediately decayed as already noted, the passivity was not quickly dissipated; the electrode passed through a sequence of changes lasting more than an hour, in which the impedance showed a complex dependence on frequency, before approaching the normal, very low impedance behaviour of the reversible calomel electrode.

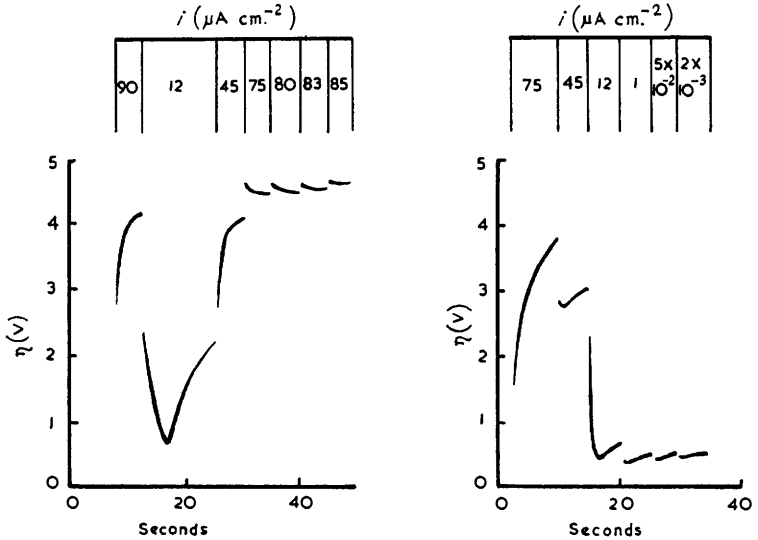

FIG. 5. Potential transients, arising from current density changes, for a blocked Hg|0·1N-HCl (aq) electrode at room temperature.

The effects of sudden " step-changes " of current density on the potentials of electrodes in the blocked state have been studied oscillographically, with results shown in Fig. 5.

The smooth rise of potential with time during the latter stages of the initial blocking process in these aged systems is seen on the left of each diagram. A sudden decrease of current density causes a fall of potential, very rapid at first, leading successively to a minimum and to a new rising section of the potential–time curve by which a re-adjusted quasi-steady state is approached. Calculation of the apparent ohmic resistance of the

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[13] Armstrong and Butler, *Trans. Faraday Soc.*, 1933, **29**, 1261.

[14] Busing and Kauzmann, *J. Chem. Phys.*, 1952, **20**, 1129.

new state shows it to be less conductive than the first. A similar effect is observed even when the step-down in current density is in the range of very low current densities so that the system is emerging, or about to emerge, from the blocked state.

A moderate increase in current density causes a potential rise similar to that for the initial passivation, if somewhat more " angular." Further increases of current density, however, produce a different effect. An almost instantaneous potential rise leads to a sharp peak or cusp, with a subsequent falling potential–time curve. Above a certain current density, at present not well defined, very small increments of current produce this effect. If the circuit supplying current to an electrode in this state was broken (*i.e.*, just after an increase of current had produced a transient potential peak), the potential drop overshot the calomel potential, falling momentarily *below* it. This can be interpreted in terms of a residual E.M.F. arising in the system; this contrasts with the consequences of the generation of any substance of higher oxidation state than calomel in the high-impedance blocked state.

Experiments in which the voltage was varied as a step-function, with potentiostatic control, provided a complementary picture. A step-up of potential caused an instant rise of current to an extremely sharp peak, followed by an initially rapid, asymptotic fall to a steady-state value. A step-down produced a sharp fall of current, immediately replaced by a climb to a lower steady-state value than before. For a given height of potential step, the steady-state currents were very reproducible. These voltage and current transients resemble phenomena reported for anodic oxide films,[15] and suggest that space charges are formed in the calomel films, and this is certainly consistent with the comparatively low resistivity of the latter. There is evidence of a very intimate relation between a calomel film and the mercury on which it is formed. This suggests the possibility of the generation of anion vacancies in the film, by anodic electrolysis in which the film acts as a solid electrolyte. Such vacancies could migrate outwards and eventually be filled at the expense of adsorbed chloride ions at the calomel–solution interface.

This hypothesis can be supported as follows. The very low differential capacity found for the blocked electrode is consistent with the establishment of an ionic double layer (with chloride ions occupying the close plane) *outside* a poorly conducting film, and thus separated by a considerable distance from the metallic phase. For the transfer of chloride ion from this layer to the mercury surface, three activation barriers might have to be traversed—the entry to the film, passage through the film, and a final barrier at the mercury–film interface. The last may be dismissed, for the ion can be discharged, combining with the mercury and falling down a potential well at least 1 ev deep. The first barrier will involve dehydration of the ion (2·9 ev), but nothing is known about the activation energy for transport across the film, for which a mechanism of field-assisted diffusion of anion vacancies has been suggested. Dewald's theory [16] also indicates that, if Tafel slopes are proportional to absolute temperature (cf. Fig. 3), it may be assumed that either the entry barrier or the transfer barrier is rate-determining. Of these, the entry barrier appears to be the more probable because of the very slight dependence of overpotential on conditions of film formation (and therefore of film thickness), and because the Tafel slopes are high and, correspondingly, the transfer coefficients are low ($\sim$0·1). This suggests that the change of field produced by change of electrode potential operates over a considerable distance in modifying activation energy.

If the entry barrier is indeed rate-determining, Dewald's theory further indicates that the concentration of current carriers in the film should increase with rising current density. This is consistent with the kind of transients observed and with the generally well-conducting nature of the systems, which never attain the very high overpotentials observed for some metal–oxide systems.[17] It is somewhat difficult to explain all the potential changes

[15] Young, *Trans. Faraday Soc.*, 1956, **52**, 502.

[16] Dewald, *J. Electrochem. Soc.*, 1955, **102**, 1.

[17] Young, *Trans. Faraday Soc.*, 1956, **52**, 515.

which follow termination of current flow and more detailed study is required. It is clear that some sort of film relaxation process sets in, which the A.C. study shows to be protracted; it takes an hour or more, and continues long after the potential has reached the calomel value. The early stages of potential decay, however, follow the " log time law " to be expected of double-layer discharge, but the concurrent changes in the nature of the film no doubt can be invoked as the basis of the discrepancies between Tafel slopes and differential capacities determined under closed- and open-circuit conditions. It is perhaps justifiable to suggest that the substance of a calomel film, during forced current flow, departs from stoicheiometry in the " mercury subchloride " direction, and the " equilibrium potential " of such an electrode would be negative to that of the calomel electrode.

Quite an important implication of these proposals is that calomel is generated at the mercury–calomel interface, *underneath* the existing film, when anodisation is continued in the blocked state. Under such conditions it might well be starved of chloride ion, and it will certainly not be so vulnerable to loss by disproportionation; the current efficiency of calomel production is indeed increased.

A brief record may be made of some potentiostatic studies of the blocking process, which gave some results of relevance in the present context. Polarisations in the range 0·5—1·4 v gave an initial current surge, limited by the maximum output of the potentiostat, followed by a gradual fall to a residual value. At 1·4 v, however, an arrest in the current–time curve appeared, and was more marked at 1·9 v. At higher potentials, up to 5 v, the initial surge was followed by a rapid fall to a minimum before a sharp climb to a maximum. This was followed by a period in which, although apparently unstable, the current generally dropped, eventually achieving a fairly constant value for each polarisation. These results give some further support to the existence of distinct low- and high-impedance blocked states, and also demonstrate the establishment, for the latter, of an abnormal, conductive, state for the film.

In galvanostatic anodisations, the initial stages of film formation occur at low potentials, no matter what the current density. This is not the case for potentiostatic experiments, and is a principal reason why this method should be exploited with more adequate equipment. The difference was strikingly demonstrated by a variation in colour of the films according to the potential at which they were formed; they were grey at 1 v, and black at potentials above 4 v. Black films of this nature have been recorded previously by Rothschild[18] and by Bockris and Parsons.[19] The latter obtained a black thread or tube by high-current-density anodisation of a dropping-mercury electrode in aqueous hydrochloric acid and were unable to detect chloride in the substance of which it was formed. The suggestion that this very odd occurrence is due to extreme concentration polarisation of chloride ion, with consequent take-over of hydroxyl-ion discharge, is not satisfactory. Mercurous oxide, hydroxide, and mercuric hydroxide are not known to exist, so there seems no reason why mercuric oxide or a basic salt should not be produced under such conditions, but none of these is black. No confirmation of such an explanation can be found in the present work, and it is believed that the black films are essentially calomel which, formed under shock conditions, is very substantially in deficit of chloride ion. The manner in which this might occur has been indicated above.

Further, purely electrochemical studies of calomel films faced great difficulties because of the complexities involved, but substantial progress was made by an entirely independent experimental approach, to be described in a later paper.

EXPERIMENTAL

The Cell (Fig. 6).—The cell was made of Pyrex glass, with ungreased, mercury-sealed, head-fitting cones and tap, and vacuum-tight electrical contact tubes,[20] and could be pumped out

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[18] Rothschild, *Proc. Roy. Soc.*, 1938, *B*, **125**, 183.

[19] Bockris and Parsons, *Nature*, 1947, **160**, 232.

[20] Ives and Janz, " Reference Electrodes," Academic Press, New York, 1961, pp. 60, 106.

to a hard vacuum; for this purpose, the cell was separated from the solution-preparation apparatus by a septum, and gas-outlets were sealed, or terminated in mercury-sealed " barometer tubes," subsequently converted into water-sealed outlet bubblers. The mercury-pool electrode (area, *ca.* 0·5 cm.^{2}, calculated with allowance for meniscus), contained in the central, internal cup, was situated above a large pre-polarisation electrode (always cathodically polarised) and just below (*ca.* 1 cm.) a lightly platinised platinum spiral electrode, used for superimposing an A.C. " signal " (*ca.* ±3 mv). Two hydrogen electrodes, contained in the right-hand compartment, were used for reference purposes, and for polarisation of the large mercury

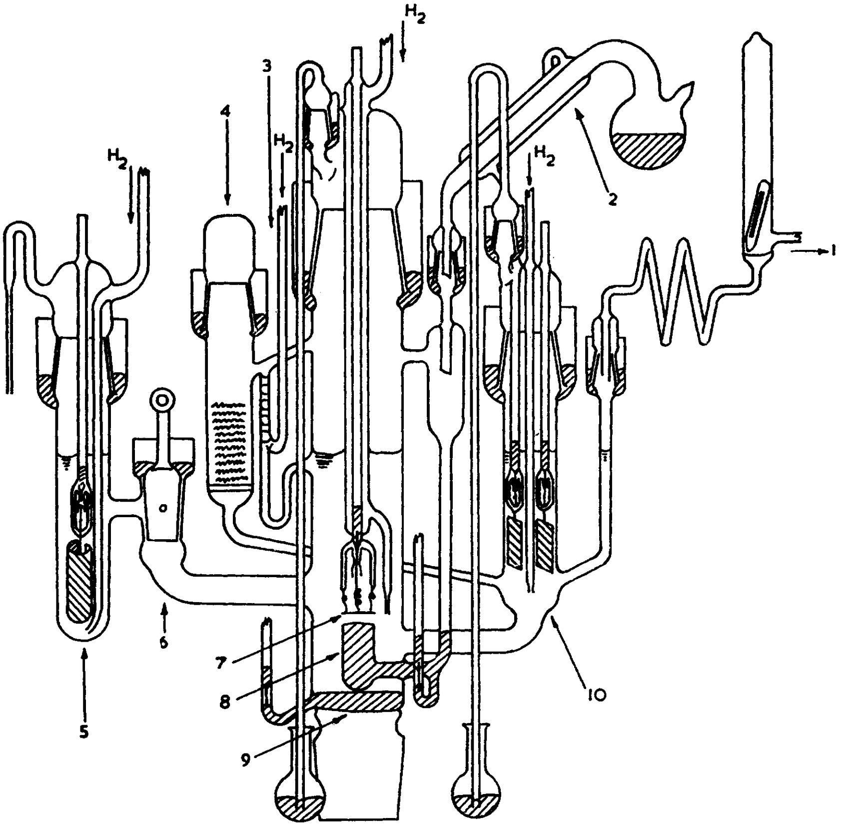

FIG. 6. The cell.

1, To solution-preparation apparatus. 2, Mercury still. 3, Hydrogen lift-pump. 4, Carbon cleaning column. 5, Working electrode. 6, Isolating tap. 7, Spiral Pt electrode. 8, Mercury-pool electrode. 9, Pre-polarising electrode. 10, Reference and polarisation electrodes.

electrode; construction of the cell was such that " *iR* drop " was negligible. The left-hand compartment contained a large, working hydrogen electrode (cathode), with an independent hydrogen supply, segregated from the main compartment by the permanently closed tap, which provided adequate electrical contact *via* a solution film. The cell incorporated its own mercury still, gas pre-saturators filled with cell solution (not shown), and a device for circulating the cell solution (by means of a hydrogen lift-pump) over a column of activated charcoal, retained by a sintered filter-disc. The cell was mounted in a bath, the temperature of which could be controlled (±0·05°) between 5° and 45°. Hydrogen (" high purity electrolytic," British Oxygen Co. Ltd.) was passed through a deoxygenating cartridge (Baker Platinum " Deoxo "), a three-way " bleeder " tap, dust filter, a column of potassium hydroxide pellets, and a silica furnace-tube containing activated, spectroscopically pure copper turnings at 550° and was distributed to the cell and solution-preparation apparatus by means of greased taps (Apiezon L). After these taps, the hydrogen was passed through traps (packed with Fenske helices) and long, narrow-bore glass spirals cooled in liquid oxygen.

Preparative Procedures.—After use, the cell was emptied (hydrogen initially displaced with nitrogen), freed from all traces of mercury (dilute nitric acid, water), and cleaned by treatment with concentrated sodium hydroxide solution (if previously treated with silicone), fuming nitric acid (24 hr. at room temperature, 6 hours' refluxing), followed by washing and standing with water (24 hr.), steaming from conductance water (2 hr.), and drying with dust-free, heated nitrogen. Silicone treatment, when appropriate, was carried out with a 2% (v/v) solution in re-distilled carbon tetrachloride of silicone fluid (Midland Silicones, Ltd., MX 200/5, fine chemical grade) that had been successively extracted with 2N-sodium hydroxide and 2N-hydrochloric acid, washed with water, dried ($CaCl_2$), filtered, and distilled under a vacuum with a nitrogen capillary leak. The dry cell was rinsed with this solution, allowed to dry, and then baked at 190° for 3 hr. After cooling, it was thoroughly extracted with re-distilled carbon tetrachloride, steamed from conductance water (6 hr.), and again dried with hot nitrogen. The carbon cleaning vessel of the cell was charged with granulated carbon (British Carbo-Norit Union, Ltd., Ultrasorb 18/25) that had been thoroughly agitated with water to remove fine particles, extracted (all-glass Soxhlet) for at least 6 weeks with constant-boiling hydrochloric acid (renewed each week), for a further 6 weeks with boiling conductance water (frequently renewed), and (immediately before use) heated to redness in a silica vessel under a stream of nitrogen, in which it was also cooled. Platinum electrodes were ignited in an alcohol flame, re-platinised by a standard method,[21] washed in water (24 hr.), steamed, and dried in warm nitrogen before being fitted into their compartments. The still attached to the cell was charged with mercury that had been passed as a spray five times through a mercurous nitrate column (10% w/v in 2N-nitric acid), dried, distilled twice under reduced pressure with an air capillary leak [22] and twice again in a high vacuum. The entire apparatus was assembled by glass-blowing *in situ* (liquid-air trap), by means of an oxy-hydrogen flame, and, after sealing of cones and outlets, was evacuated to a "dark" vacuum and left overnight. Hydrogen, purified as described above, was admitted and then pumped out, and, after two repetitions of this flushing out, the mercury in the still was refluxed gently in hydrogen for 0·5 hr. It was allowed to cool during the solution-preparation, which was carried out in a three-compartment apparatus separated from the cell by a septum and joined to it by a mercury-sealed tap and all-glass connections. This apparatus, which could be evacuated and filled with hydrogen, was charged with conductance water (10^{-7} ohm^{-1} cm.$^{-1}$) and constant-boiling hydrochloric acid, prepared from similar water and hydrogen chloride gas generated from purified potassium chloride.[23] After thorough pumping out and saturation with hydrogen, these components were distilled from their respective compartments into the main solution reservoir in an atmosphere of hydrogen. Bubbling of hydrogen through the solution was maintained during cooling.

The cell was re-evacuated and the mercury distilled without boiling, falling into the central cup, from which it overflowed to form the pre-polarisation electrode. Connections were established to keep the latter at −0·4 v and the central pool at 0 v with respect to the hydrogen-electrode potential. Hydrogen was admitted, gas outlets were opened, the septum was broken, and solution filling (including the pre-saturators) was accomplished by manipulation of hydrogen pressures. Pre-polarisation began automatically as soon as the solution circuit was completed; bubbling of hydrogen and circulation of the solution over the carbon (*ca.* 30 cm.^{3} min.$^{-1}$) were at once started and were continued as long as necessary before the commencement of measurements, during which all these operations were temporarily discontinued. The pre-polarisation electrode, however, was never allowed to become anodic to the hydrogen electrodes. An important indication of the state of the cell was given by the value of the current (arbitrarily designated i_0) required to keep the pool electrode at the hydrogen potential and by the rate of positive potential drift of the electrode on open circuit. For a freshly prepared cell, typical values were 10^{-9} A, and 0·25 mv min.$^{-1}$; both were substantially raised after the smallest anodisation of the pool electrode, but both were reduced by continuous pre-polarisation and adsorptive cleaning, particularly the latter.

[21] Hills and Ives, *J.*, 1951, 305.

[22] Hulett, *Phys. Rev.*, 1911, **33**, 307.

[23] Pinching and Bates, *J. Res. Nat. Bur. Stand.*, 1946, **37**, 311.

It is clear in the preceding text which of these experimental features (which were not uniformly adopted) apply to the various results described.

Electrical Equipment and Measurements.—Measurements of sufficiently time-invariant E.M.F.'s were made with a Tinsley type 4025 potentiometer, in conjunction with a Pye "Scalamp" galvanometer, 7094/5, of resistance 1320 ohms and sensitivity 197 mm. μA^{-1}. Rapidly changing potentials were recorded by means of a Nagard cathode-ray oscillograph, type H103, with amplifier type 103/13 and time-base type 103/1A. Slow sweeps were provided by an external mechanical time-base, supplying a linear variation of potential with time to the X amplifier of the oscillograph. Time-scale markings were obtained from 50 c./sec. mains, or from either of two calibrated clocks providing 0·5 sec. or 1—20 sec. impulses. The oscillograph, fitted with an afterglow screen, was equipped with a camera with an $f/1{\cdot}9$ bloomed lens and a manually operated shutter, giving single exposures on Kodak R55 orthochromatic 35 mm. film.

Galvanostatic experiments were carried out by means of current from 240 v batteries, stabilised by an adjustable high-resistance circuit. Currents were measured by means of either an "Avo" Mk IV or a Pye "Scalamp" galvanometer, 7093/S, resistance 382 ohms, sensitivity 98 mm. μA^{-1}, both these instruments being suitably calibrated. It was advantageous to fit the latter with a "constant-impedance switch" to avoid distortion of the suspension by long-continued deflections.

Constant-potential experiments were made by use of a potentiostat (type 1465A, A.E.R.E., Harwell) involving a difference amplifier feeding a cathode follower output stage, providing a maximum current of 20 mA.

For impedance measurements, the output of an oscillator [24] (1 c./sec. to 70 kc./sec.) was fed, *via* an isolating transformer, to the mercury-pool and platinum-spiral electrodes, and to the Y amplifier of the oscillograph. The A.C. current also passed through a selected resistance (10^3—10^7 ohms); the alternating potential across this resistance was fed to the X amplifier. In each case, D.C. polarisation was blocked by means of 0·2 μF condensers. The differential-capacity results were obtained with this arrangement in the following way.

The pool was polarised at the desired D.C. potential intervals by means of the working electrode and an ancillary potentiometer. A signal of 5 c./sec. and about 6 mv amplitude was applied in the manner indicated, and the resulting ellipse on the oscillograph screen adjusted to suitable proportions by manipulation of the X and Y gain controls. With the aid of a reference line on the screen graticule, the ellipse was displaced by its maximum vertical height by means of a backing potential supplied by a potentiometer (Tinsley 3387 B), to the second input of the Y amplifier. This potential was recorded as $2V_Y$ volts. By means of a multipole rotary switch, the backing potential was then applied to the corresponding X amplifier input, and was adjusted so as to make the ellipse just touch the screen afterglow when the backing potential was not applied. This potential, recorded as $2V_0$ volts, was proportional to the 90° out-of-phase current, and not to the total current flowing (the latter could be obtained from the projection of the ellipse on the X axis displaced by a potential $2V_X$ volts). The use of a backing potentiometer in this way, coupled with the afterglow properties of the screen, enabled rapid repetitive measurements to be made, and considerable accuracy was attained. The behaviour of the pool closely simulated that of the ideally polarised electrode, so that the electrical equivalent of the cell was very nearly that of a capacity (the double-layer capacity) in series with a resistance (the ohmic resistance of the electrolyte). The small faradaic current flowing at the more anodic potentials was negligible. The impedance was therefore

$$Z = \sqrt{R_s^2 + \frac{1}{4\pi^2 f^2 C^2}}, \tag{16}$$

where R_s is the series resistance, f the frequency, and C the double-layer capacity, and $Z = R.2V_Y/2V_0$, where R is the value of the external, standard resistance. For measurements over a range of frequencies from 5 c./sec. upwards, $\log Z$ was accurately linear with $\log f$ (slope -1), but at high frequencies tended asymptotically to a constant value equal to $\log R_s$. Impedance measurements with blocked electrodes were made and analysed by a similar method.

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[24] Sinfield, *Wireless World*, 1954, **60**, 596.

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