

670. *Anodic Processes. Part IV.* The Anodic Generation of Calomel.*

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The initial stages of the anodic generation of calomel at the interface between mercury and dilute aqueous hydrochloric acid have been further examined in galvanostatic experiments, with oscillographic recording of the dependence of potential upon time. The influence of acid concentration and of temperature has been studied. Assessments of the current efficiency of calomel production, and the examination of open-circuit potential decay curves have been used to support and extend earlier interpretations of the interfacial phenomena which occur.

It has been shown^{1,2,3} that anodisation of mercury in dilute, aqueous hydrochloric acid is accompanied by a complex sequence of phenomena terminating in the formation of a passivating film of uniquely oriented, crystalline calomel.⁴ It was of particular interest that oscillographic records of electrode potential at constant current density showed a number of transient singularities which marked a dramatic transition between polarised and reversible states. The present paper records further observations on these phenomena, with particular reference to their dependence on temperature and acid concentration. Experiments are also recorded which make some progress towards the elucidation of the electrode processes.

The characteristics of the oscillograms taken under galvanostatic conditions⁵ may be recalled by reference to Fig. 1, which illustrates the effects of temperature at constant current density and acid concentration. It will be seen that a low temperature favours the full development of "fine structure," the features *a*, *b*, *c*, and *d*, previously assigned the trivial names "prepeak," "peak," "minimum," and "hump," being clearly visible.

* Part III, *J.*, 1953, 3988.

¹ Cousens, Ives, and Pittman, *J.*, 1953, 3972.

² *Idem, ibid.*, p. 3980.

³ *Idem, ibid.*, p. 3988.

⁴ Thirsk, *Proc. Phys. Soc.*, 1953, **66**, B, 129.

⁵ Gerischer, *Z. Elektrochem.*, 1955, **59**, 604.

The parameters of the points *a*, *b*, and *c* are reproducible within experimental error. They are characterised, for example, by overpotentials (referred to the appropriate calomel potential) which, for 0.1N-hydrochloric acid at 25°, fall upon Tafel lines with slopes of 3.2, 5.6, and 3.5 mv. The quantity of electricity required for the transition between *a* and *c* is always of the order of 90 $\mu\text{C cm}^{-2}$, independently of acid concentration, temperature, and current density, as long as the "fine structure" remains undegraded.

It is evident from Fig. 1 that rising temperature smooths out the potential changes: there is a progressive degradation, with loss of fine structure. This effect is general, and

FIG. 1. Potential-time curves for different temperatures and 0.01N-HCl at current density (*i*) 91.8 $\mu\text{A cm}^{-2}$. (Calomel potential = 0.391 v at 25°.)

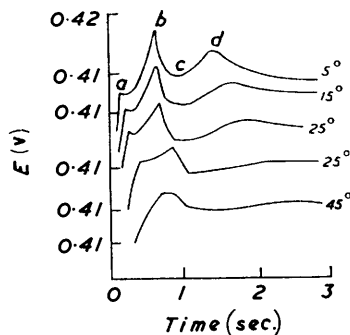
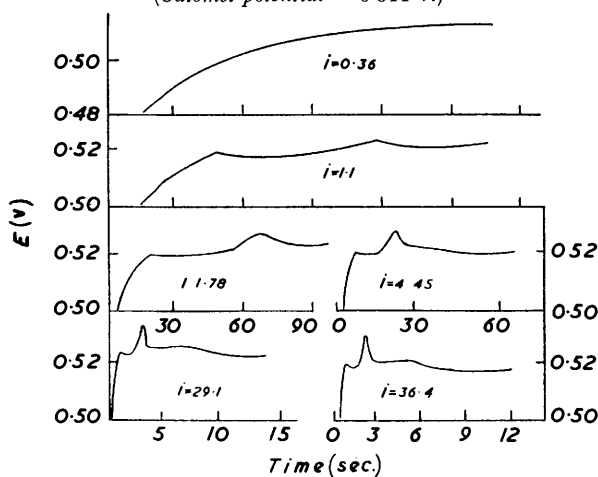


FIG. 2. Potential-time curves for different current densities (*i*, in $\mu\text{A cm}^{-2}$) in 0.01N-HCl. (Calomel potential = 0.511 v.)



can lead ultimately to loss of all special characteristics, leaving only a smoothly rising curve, very similar to those which are obtained with anodisations at very low current densities. It is noteworthy, however, that, when in a particular case this degradation has been brought about by rise in temperature, it can be reversed by an increase in current density.

The temperature effect can be described in more detail. Thus, the temperature coefficients of the points *a*, *b*, *c*, and *d*, for the conditions appertaining to Fig. 1, have the values, constant over the temperature range 5–45°, of 0.19, –0.09, 0.09, and 0.00 mv deg.⁻¹, figures which can be related, by inspection, to the changing shapes of the curves.

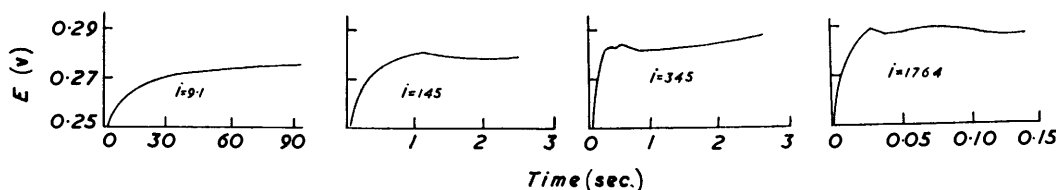
The influence of acid concentration has been studied in experiments at the additional concentrations of 0.01N and 1N. At the lower concentration, it has been found that there is an enhanced tendency for the fine structure of the potential-time record to develop; it

appears at a lower current density than for the 0.1N-acid, but is equally vulnerable to rise of temperature. The growth of the fine structure with increasing current density at a constant temperature of 25° is illustrated in Fig. 2, which is closely similar, except for the scale of current density, to Fig. 1 (relating to 0.1N-acid) in Part II.² However, the Tafel slopes relating to the potentials of the points *a*, *b*, and *c* had the somewhat higher values of 4.4, 8.4, and 5.0 mv for the more dilute solution.

For the higher acid concentration (N), the reverse tendency was outstanding; the oscillograms showed almost complete absence of fine structure, except at the lowest temperatures and relatively high current densities. This is illustrated in the sequence of oscillograms recorded in Fig. 3.

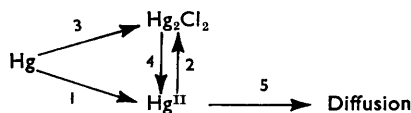
From these results a general conclusion may be drawn that the fine structure of the oscillograms tends to disappear with falling current density, with rising temperature, or with increasing acid concentration. An explanation of these trends is readily accessible.

FIG. 3. Potential-time curves for different current densities (*i*, in $\mu\text{A cm.}^{-2}$) in N-HCl at 5°.



It may be recalled¹ that a quantity of electricity 10^9 times as large as that required to saturate the whole solution phase with calomel can be passed anodically across a mercury-dilute hydrochloric acid interface without the electrode's attaining the calomel potential or achieving reversible behaviour, provided that the current density is low and that the potential-time curve during the flow of constant current is uninflected. Mercuric compounds are generated during such anodisations, and there is no evidence for the existence of calomel as an intermediate, even transiently. On the other hand, if the current density is high enough to give an inflected polarisation curve showing features *a*, *b*, and *c*, one thousandth part of the same quantity of electricity will give a reversible calomel electrode. Such an electrode, however, is not stable, but drifts away from the calomel potential and loses its reversibility after a very short time. This spontaneous decay is undoubtedly due to loss of calomel by disproportionation.

It is obvious that, whatever the conditions under which a given degree of oxidation is effected anodically, a given system must ultimately reach the same thermodynamic equilibrium state. But the route by which this state is reached varies in accordance with the reaction scheme:



where the sequence, 1, 2, occurs exclusively at very low current densities, giving place to 3, 4 at higher ones, the transition occurring suddenly. That reactions 1 and 4 should be favoured by rise in temperature, and by increase in hydrochloric acid concentration, is to be expected, and explains all of the recorded trends.

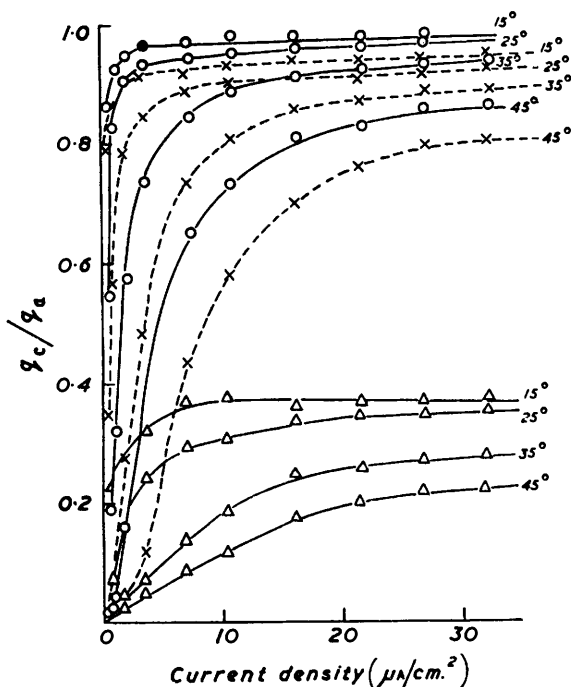
Experiments have been made to assess the current efficiency of calomel production under various conditions, and thus to trace the changing balance between the initial steps 1 and 3, as far as they can be isolated from the succeeding reactions, by passing a fixed charge, q_a , anodically at constant current density, followed by an immediate cathodic reduction at the same current density, until the electrode potential "slipped" suddenly

from its steady value close to the calomel potential. The charge passed cathodically, q_c , could then be regarded as approximately proportional to the quantity of calomel produced at the electrode surface in the preceding anodisation. Values of q_c/q_a , as a function of current density, for four temperatures and three acid concentrations, are represented graphically in Fig. 4.

All the curves are consistent with zero current efficiency of calomel production as the current density is indefinitely decreased. The very sharp rise of this quantity over a narrow range of current densities in some cases is evident, this being most marked when temperature and acid concentration are low. The rise also coincides with the transition from a featureless anodic polarisation curve to one which shows fine structure. The very great fall in yield of calomel at the highest acid concentration reflects the rapidity of the disproportionation, 4, under these conditions, as well as the greater facility of reaction 1.

FIG. 4. Plots of q_c/q_a as a function of current density (i , in $\mu\text{A cm.}^{-2}$). ($q_a = 1820 \mu\text{C cm.}^{-2}$)

Normality of HCl:
 O, 0.01; X, 0.1; Δ , 1.0.



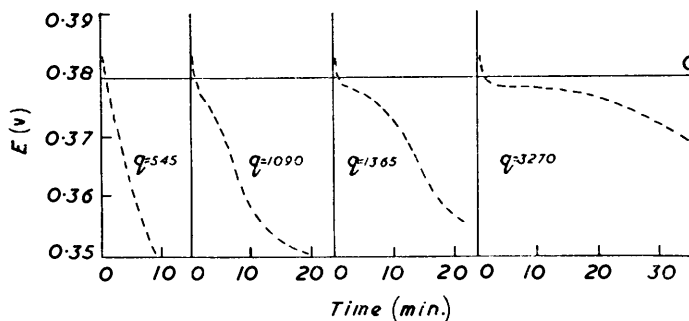
Although all the curves of Fig. 4 are affected by the continuous loss of calomel by disproportionation, both during anodisation and cathodic reduction, it is clear that a fairly comprehensive picture has been obtained of how the suggested reaction scheme responds to changing conditions. Of the two competing reaction paths, that involving calomel production (3, 4) is of immediate interest.

The states through which an electrode passes from the instant at which anodic polarisation is started are reflected in the fine structure of the potential records, and are difficult to examine because of their transience. The method previously used,² of arresting anodisation at various stages and studying the course of subsequent open-circuit potential changes has, however, been exploited with some success. It has been confirmed that the occurrence of fine structure, including *a*, *b*, and *c* (cf. Fig. 1), in the anodic polarisation curve is essential for the appearance of a well-defined arrest at the calomel potential in the post-anodisation potential decay curve. The length of the arrest increased proportionally with the time, for a given current density, that anodisation is continued after the point *c* has been traversed; that is, after the peak has been surmounted. If, on the other hand, for a similar anodic charge, conditions of temperature, concentration, and current density

are such that the anodic polarisation curve is smoothly rising, the subsequent decay curve shows no arrest or inflection, except as now discussed. This procedure can clearly distinguish between the two alternative paths of the reaction scheme, 1 or 3, 4, but to either of these should be added a step, 5, indicating the diffusion of soluble oxidation products away from the interface into the bulk of the solution. In general, the results of a large number of these "decay experiments" confirm all the conclusions, reached by other means, about the effect of the three independent variables upon electrode behaviour, and leave no doubt that the processes responsible for "the peak" are intimately associated with the appearance of calomel as a stable, potential-determining phase. It has been possible, however, to explore the fine structure of the anodic polarisation curves in greater detail than this, with the following results.

Although polarisations at low current density, with smooth potential changes, give uninflected decay curves for moderate charges, protracted anodisations under these conditions lead to slowly developing, rather ill-defined arrests somewhat below the calomel potential, as illustrated in Fig. 5. It is suggested that these represent the secondary production of calomel in the reaction sequence 1, 2. Since the interfacial zone is not in equilibrium with the bulk solution phase during, and shortly after, anodisation, this will

FIG. 5. Change of potential with time for different anodic charges (q , in $\mu\text{C cm.}^{-2}$), in 0.01N-HCl at 35° and $0.91 \mu\text{A cm.}^{-2}$. (The line C here and in Figs. 6—7 denotes the calomel potential.)



be followed by processes 4 and 5 as this equilibrium is established. This is in conformity with the observations reported in Part I,¹ and with the knowledge that a satisfactorily reversible calomel electrode, showing the proper thermodynamic potential, cannot be made by anodisation at low current density.⁶

Anodisations, of which the polarisation curves showed fine structure, were carried out with fixed, pre-determined charges at gradually increasing current densities. It is of interest that in this way a sequence of oscillograms was obtained showing abrupt termination at stages advancing in the sequence *a*, *b*, *c* (cf. Fig. 1) along the complex polarisation curve, confirming that, over quite a narrow range of current density, reaction 1 supplants reaction 3 in predominance. It has been found that the crossing of the prepeak, *a*, marks the appearance of inflections in the decay curve, but it is of great interest that if the prepeak *alone* is crossed, there are two inflections, one above the calomel potential, and one below it, with none at the calomel potential itself. As the point of termination of the anodisation moves along the "saddle" between the prepeak and the peak (*a* to *b*), the lower inflection becomes more marked and rises towards the calomel potential. This was noted in the earlier work,² in which, unfortunately, the upper inflection was missed. The attainment of the crest of the peak, *b*, marks the first appearance of an arrest at the calomel potential itself, and this arrest becomes more clear-cut and prolonged the longer the anodisation is continued beyond this point. The impression has been gained that traverse of the point *c* is marked by a "cleaner" and more rapid decay from the calomel potential.

⁶ Hills and Ives, *J.*, 1951, 311.

These statements are based upon the results of a large number of experiments. The maximum speed of manual manipulation set a rather low limit to the current density which could be used. This gave a less clear-cut separation between reactions 1 and 3 than

FIG. 6. Change of potential with time at different current densities (i , in $\mu\text{A cm.}^{-2}$) for 0.01N-HCl at 15° and $73 \mu\text{C cm.}^{-2}$.

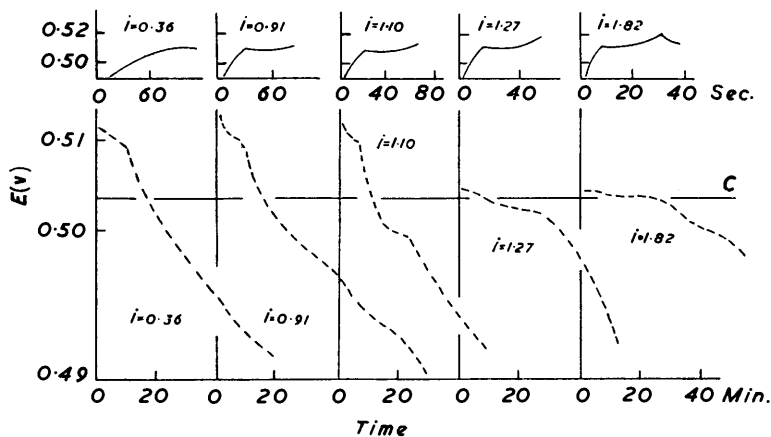


FIG. 7. Change of potential with time at different current densities (i , in $\mu\text{A cm.}^{-2}$) for 0.01N-HCl at 15° and $36.5 \mu\text{C cm.}^{-2}$.

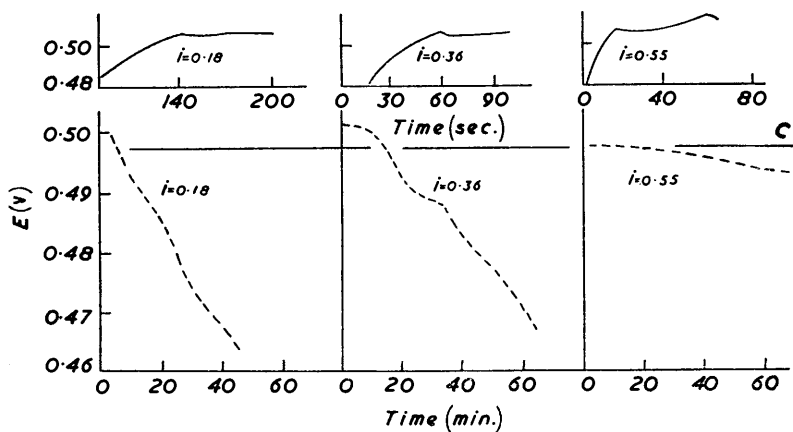
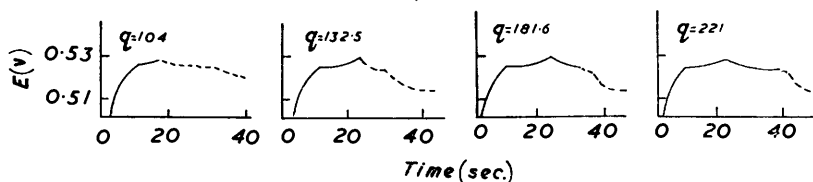


FIG. 8. Change of potential with time for different anodic charges (q , in $\mu\text{C cm.}^{-2}$) for 0.01N-HCl at 35° and $5.64 \mu\text{A cm.}^{-2}$.



could have been desired, and less than the maximum development of fine structure in the anodic polarisation curves. Typical results are illustrated in Figs. 6—8.

In the experiment recorded in Fig. 8, the alternative procedure of passing increasing anodic charges at a fixed current density was used, the early stages of potential decay being

recorded on the same oscillograph sweep as the polarisation curve. The course of the open-circuit potential is, in each case, shown by a broken line. It is of interest that no immediate fall of potential is discernible when the current-carrying circuit is broken; there is little or no overpotential. This stands in marked contrast to the polarisations at very low current density involving reaction 1 alone, where there is a considerable overpotential (cf. Part I¹). The arrest in potential decay above the calomel potential is clearly visible, and so is the arrest at the calomel potential as soon as the peak summit has been attained. The upper arrest, however, does not immediately vanish at this stage, but rapidly declines and, for slightly higher current densities or longer times than those recorded in Fig. 8, soon vanishes completely.

Discussion.—The tentative conclusions previously advanced may be extended in the light of the work now reported. It is regarded as an aphorism that a singularity, such as the prepeak, in a potential–time curve for a polarisation conducted at constant current density marks a sudden change in electrode state, or a switch in electrode process. Before the prepeak there is no evidence for the formation of any interfacial film and no trace of calomel, even though a faradaic process occurs whose only identifiable products are mercuric entities. It has been confirmed that the differential capacity of the electrode before the prepeak is surmounted is of the order of $1000 \mu\text{F cm.}^{-2}$, an order of magnitude for which there is some confirmation.⁷ In this region, far removed from the point of zero charge along the anodic branch of the electrocapillary curve, the specific adsorption of chloride ions, reinforced by Volta adsorption, must be intense. Yet the evidence is clear that no direct chloride-ion discharge occurs until the prepeak is passed, after which the evidence for it is insurmountable. It is believed that the switch of electrode process at the prepeak is in fact the onset of direct chloride-ion discharge, where none occurred before. If this is so, it becomes difficult to interpret the general view that specific adsorption partakes of the nature of covalent union. Once the switch from an adsorbed state to a covalently bound state has been unambiguously observed, it would seem to be necessary to examine again the precise significance of so-called specific adsorption.

That the first product of chloride-ion discharge at the mercury anode is a disordered monolayer of covalently bound chlorine atoms, for which the name “chloromercury” has been suggested,⁶ is supported by the appearance of the potential arrests *above* the calomel potential, corresponding with a metastable, “high-energy” form of calomel, or precursor to calomel. If the loss of this substance by disproportionation in the decay experiments is accompanied by a transformation into a trace of calomel too small to be fully potential-determining, the second arrest below the calomel potential is to be expected.

The growth in surface concentration of chloromercury should cause a rise in potential terminating when crystallisation occurs. There is clear evidence that this is the significance of the peak maximum. The decay experiments illustrated in Fig. 8 indicate that once this has happened the disordered interfacial “phase” rapidly disappears. The crystallisation, taking place in response to “intermolecular” attractions, is no doubt accompanied by a contraction, generating free space on the formerly over-populated surface; this will allow further chloride-ion discharge to take place with relatively little hindrance, and therefore with no further increase of potential. At this stage, however, the surface has become populated with “rafts” of crystalline calomel. Whether this calomel, undoubtedly extremely thin, consists initially of an *ordered* monolayer (in effect, a single {110} crystal plane) cannot be said, although the fact that it appears to have the electrochemical properties of massive calomel argues against this. Nevertheless, it is likely that the rafts will act as nuclei, building newly discharged chloride ions, and mercury ions from the substrate, into their lattices. Lateral growth of the thin islets will be favoured, and a point may be reached when the free surface again becomes restricted. If the rate of chloride-ions discharge, defined by the current density, is great enough, this may lead to

⁷ Rosental and Ershler, *J. Phys. Chem. U.S.S.R.*, 1948, **22**, 1344.

a significant hindrance which may be the basis of the hump, *d*, the least well-defined feature of the fine structure. Relief from this state is attributed to a recrystallisation process, which will be shown in Part V to play an essential rôle in the later stages of the anodisation process.

The experimental methods used in the present work were similar to those previously employed.²

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