813. *Anodic Processes. Part II.* Oscillographic Studies of Processes at the Mercury Anode in Hydrochloric Acid.*

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An oscillographic method has been used to study electrode potential as a function of time, when constant currents are passed anodically across the mercury/0·1N-hydrochloric acid interface at 25°. Very characteristic and reproducible sequences of potential changes have been observed, marking the incidence of electrode processes which differ from those studied in the previous paper. Evidence is adduced from various experimental tests that radical changes occur in the state of the electrode as a result of polarisations of the kind in question. Provisional interpretation of these results is given, and support is found for the previously suggested covalently bound monolayers of chlorine atoms upon the surface of mercury.

THIS Part of the series describes the results of non-equilibrium experiments in which constant and uninterrupted currents were passed across the mercury/0·1N-hydrochloric acid interface. The potential of the electrode (cf. Part I *) was measured by using a cathode-ray oscillograph with a calibrated time-base as a high-impedance, continuously recording voltmeter. A large number of potential–time curves were thus obtained which exhibited features so characteristic and reproducible as to show unmistakably that new and critical phenomena had become open to study. A selection of these curves, for increasing current densities, is shown in Figs. 1 and 2. It will be noted that only curve 452 gives a complete record of events up to passivation. Clearly, these curves describe a totally different sequence of phenomena, on different time and current scales, from these reported in Part I.

Although the curves showed variations depending on conditions, all of them obtained at current densities exceeding the lower limit (330) had certain common features. A general review of these, based upon an idealised curve (Fig. 3), would appear to be apposite as a basis of further discussion, which, at the present stage, must be very largely factual.

The idealised curve can be divided into four sections defined by abrupt changes of slope. The section from *A*, where the constant current is switched on, to *B*, where the potential has risen to the vicinity of the calomel potential (cf. Part I), may be said, as a first approximation, to correspond with the charging of a double-layer capacity, as would be expected of a polarisable electrode. The section from *C* to *D*, which indicates that the electrode remains for a considerable time at a constant potential a few mv more positive than the calomel potential, would seem to be associated with the production of calomel in excess of the minimum amount required for the mercury pool to behave as a reversible calomel electrode. The intervening section, *B*—*C*, defines a period of transition, in which the behaviour of the mercury pool changes essentially from that of a polarisable to that of a

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* Part I, preceding paper.

non-polarisable electrode. Within this section complex changes of slope may occur, the precise nature of which depends upon several factors, involving a well-marked potential peak. At *D*, a phenomenon analogous to a rapidly increasing resistance overpotential manifests itself and in a very short time the potential rises to a high value and the electrode becomes passive.

These sections undoubtedly correspond with different states of the mercury pool and will therefore be described separately in greater detail.

Section A—B : the Charging Curve.—It is generally accepted that mercury in solutions of indifferent electrolytes behaves as an almost ideally polarised electrode. This does not, however, appear to be the case for the mercury–hydrochloric acid system when subjected to positive polarisation. Evidence for this has been discussed in the previous paper and further support can be gained from a consideration of the double-layer capacities calculated from the slopes of the charging curves in the vicinity of *B* : some of these are shown in the Table.

FIG. 1.

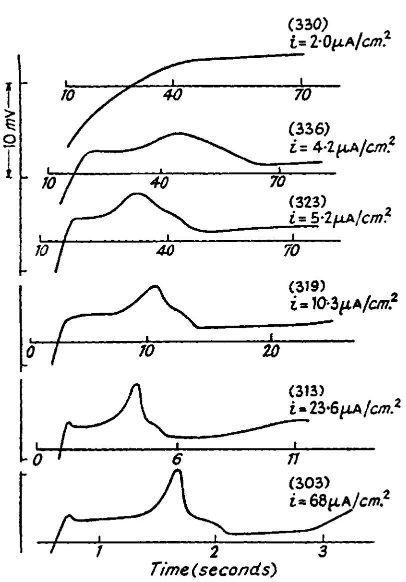
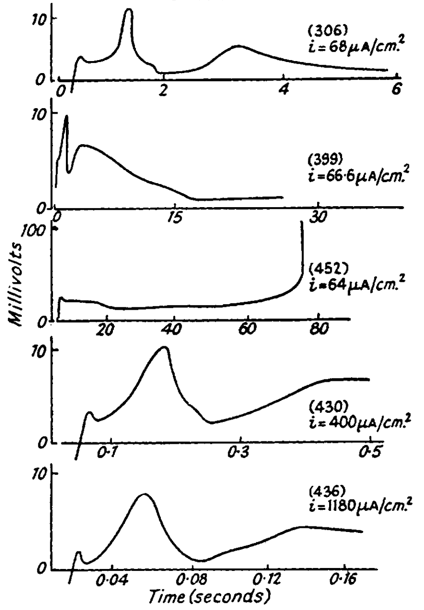


FIG. 2.



Current density (μA/cm.²)	5	10	100	400	1180
Time for 20-mv potential rise (sec.)	15	5	0·33	0·0625	0·02
dQ/dE (μF/cm.²)	3700	1750	1450	1300	1030

These apparent capacities show a dependence upon current density and asymptotically approach a value of about 1000 μF/cm.² with increasing current density. Although there seem to be no published data on the differential capacity of the mercury electrode for the potential range in which these values were obtained, it is known that this function increases rapidly as the electrode is made more positive and the value recorded, although high, is not impossible.

The usual equivalent circuit for a non-ideal polarised electrode, namely, a condenser shunted by a resistance, seems applicable here. The leakage current through the resistance (which may not necessarily be ohmic) results mainly in the formation of mercuric chloride and complex mercurichloride anions in the manner described as mechanism I in the preceding paper.

The behaviour of a system controlled by these conditions is likely to be complex. The instantaneous potential of the electrode during the passage of current will be mainly defined by the charge on the condenser, whilst the equilibrium potential, corresponding with the anodic passage of any particular quantity of electricity, will depend upon the conditions finally established at the interface. These conditions depend upon the concentrations of soluble anodic products and, together with the diffusion-controlled rate at which they are attained, will be a function of the dimensions of the apparatus.

Section B–C : the Transition Period.—When the point *B* on the charging curve, corresponding to a potential close to, but some mv in excess of, the calomel potential, is reached, a discontinuity occurs. This may show itself as a fairly abrupt decrease of slope, *e.g.*, curve 323 (Fig. 1), or as a maximum followed immediately by a minimum, curve 430 (Fig. 2) : this singularity will, for ease of reference, be called "the prepeak." After this, the curve continues upwards with diminished slope until it attains a maximum at a well-defined peak, and then descends. The descent is broken by a second discontinuity at which the curve bends abruptly to a direction parallel, or nearly parallel, to the time axis. After this second discontinuity other phenomena may appear; a second broader maximum ("the hump") curve 399 (Fig. 2) and a "collapse" to a lower, level "plateau" at a potential still significantly greater than the calomel potential. These further phenomena, however, are of a more variable nature and, as the conditions for their reproducibility have not been fully investigated, they will be left for future discussion.

FIG. 3.

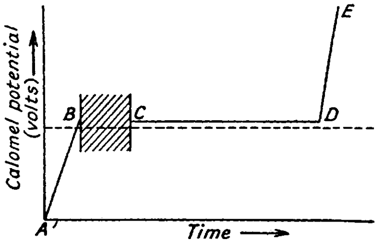


FIG. 4*a*.

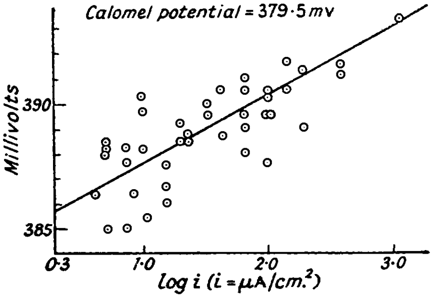


FIG. 4*b*.

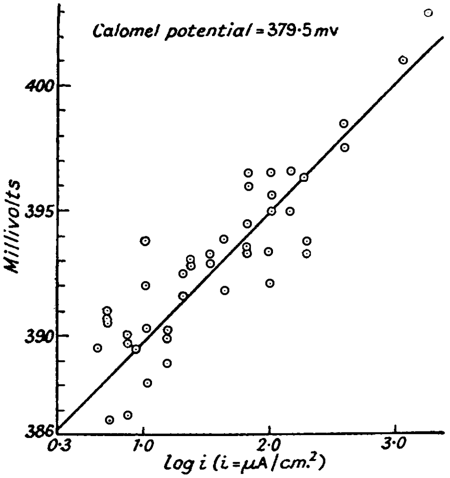
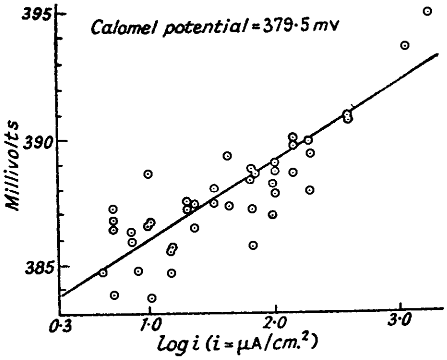


FIG. 4*c*.



The appearance of fine structure in this part of the curve seems to depend on two major factors. The first is the absence of impurities, particularly of oxygen; the use of inadequately deoxygenated solutions, or the deliberate introduction of oxygen into the gas used to sweep out the cell caused loss of structure to the peak and also a shrinkage of its dimension on the time scale. The second is the absence of an annular film of solution between the mercury and the walls of the containing vessel. The first few anodisations carried out on a freshly set up experimental system in an intensively cleaned Pyrex apparatus gave oscillographic curves with all the characteristic features fully developed, but these were soon lost, leaving a somewhat smaller peak of more rounded shape (as in Fig. 5, p. 3984), which remained, however, indicative of a radical change in the properties of the electrode (see below). This degradative effect did not occur when hydrophobic electrode vessels were used (see Experimental section): the initial behaviour was the same, and the anodisation curves preserved their reproducibility for a long period. For the results obtained under these conditions, reproducibility was not greatly inferior to that allowed by the accuracy of the oscillograph as a millivoltmeter (*ca.* ±1 mv). Data for prepeak, peak, and second discontinuity potentials are shown graphically in Figs. 4*a*, *b*, and *c*, respectively: all relate to one experimental cell, the calomel potential for which was 379·5 mv. Although the scatter of the points is rather wide, they fall randomly about straight lines with slopes of approximately 3, 5, and 3 mv, respectively, over a more than thousand-fold range of current densities. The charge involved in passing " over the peak " from the prepeak to the second discontinuity was substantially constant, from a current density of 10 μA/cm.^{2} to 1750 μA/cm.^{2}, at 95 ± 12 μC/cm.^{2}, decreasing from higher values at lower current densities. Emphasis is laid upon these results because they are sufficiently systematic to exclude any possibility that the effects in this transition region of the polarisation curves are adventitious. It is necessary to make this point because potential peaks have been observed in the initial stages of the anodisations of other electrodes, namely, lead in sulphuric acid (Kabanov, Proc. 2nd Conf. Corrosion, Moscow, 1943) and silver in hydrochloric acid (Lal, Thirsk, and Wynne-Jones, *Trans. Faraday Soc.*, 1951, **47**, 70), but these appear to be structureless and have been attributed, without investigation, to supersaturation effects.

When the second discontinuity in an anodisation has been reached, the system can be said, for convenience, to have " crossed the peak," and there is no doubt that in doing so it has undergone a profound change. Unambiguous evidence can be adduced to show this.

(1) Micropolarisation tests show that an electrode which has not crossed the peak (although it may have been subjected to prolonged anodisation at low current densities; cf. Part I) is very far from being reversible. A test on such an electrode is shown in Fig. 5*a*; the hysteresis is considerable and the test has altered the rest (zero current) potential of the electrode appreciably. When the peak has been crossed (Fig. 5*b* is an oscillographic record of this; 700 μC at a current density of 60 μA/cm.^{2}), the electrode has become much more reversible (5*c*); the hysteresis has disappeared, the slope has increased, and the test does not alter the rest potential, which is identical with the calomel potential. If left untouched, the electrode remains in this reversible state for a time, the length of which depends upon the quantity of electricity passed in the anodisation, and upon the previous history of the cell. When the solution is charged with anodic products (so that the initial rest potential is at, or even above, the calomel potential) there is long persistence (5*d*) and the electrode remains reversible (5*e* shows a peakless anodisation supporting this). If, on the other hand, the cell is fresh (with a low initial rest potential) the reversible state arising from the passage of say 1000 μC/cm.^{2} will decay in a time of the order of 12 minutes, this decay being accompanied by a potential fall which ultimately ceases at a potential approximating to the original rest potential of the electrode. The reversible state can also rapidly be abolished by cathodisation, but it is noteworthy that no matter how large the quantity of electricity passed cathodically, within the limits of these experiments, the potential of the electrode cannot be depressed permanently below its original rest potential. Obviously, at least two potential-determining substances are produced in these anodisations, one of which can be reduced cathodically and the other not. The outstanding result in this section may perhaps be restated in an alternative way. It is possible to pass, say, 1000 μC/cm.^{2}, anodically across an irreversible electrode with a rest potential equal to that of the calomel electrode without making any significant alteration in its properties, provided that the current density is such that no peak is crossed (*ca.* 1 μA/cm.^{2}). On the other hand, 100 μC/cm.^{2}, passed at a current density which involves peak crossing (5 μA/cm.^{2}), will transform the electrode into a reversible one operating at the same potential as before.

(2) The evidence collected under this head is concerned with factors causing modifications of the behaviour of the system as indicated by the shape of the oscillographic polarisation curves in the transition region *B*—*C*. It may first be stated (as already indicated)

that there is a limiting current density below which the peak does not appear (cf. Fig. 1). This limit is not fixed, but shows dependence upon the previous history of the cell, being lower for aged cells than for fresh ones.

If an anodisation, at a current density above this limit, be carried out on a mercury pool soon after a previous anodisation at the same current density, the peak and its associated fine structure are completely suppressed. Suppression of the peak remains for as long as the pool stays at the calomel potential but the peak reappears as the potential decays to the (lower) rest potential. This suppression of the peak thus appears to be another criterion of reversibility and, as such, runs parallel with the one previously quoted. The state arising from an anodisation which causes the system to " cross the peak " does not, however, correspond with ideal reversibility, for, if a second anodisation (370) be performed at a current density ten times greater than the first (369), a very " debased " peak appears (Fig. 6) and almost immediately after this the curve rises steadily as if to indicate an approach to the passive state.

Fig. 5

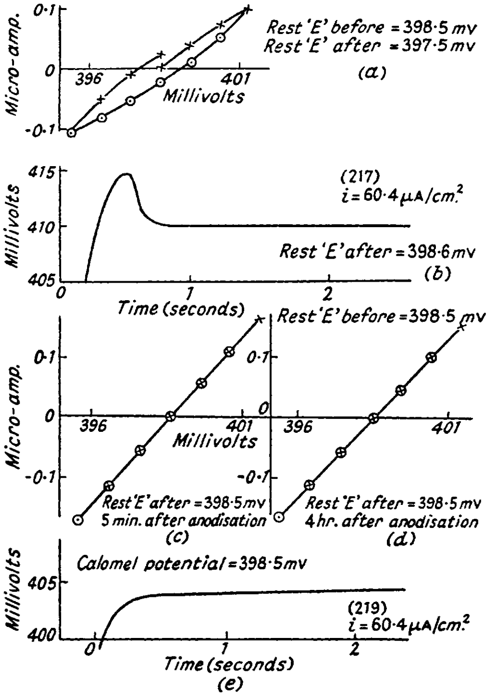
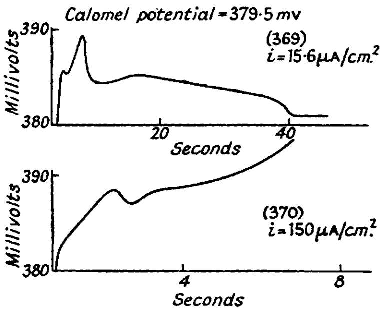


Fig. 6.



Reference might be made to a point already stressed in Part I, though with respect to experiments of a different kind, namely, that the quantity of electricity passed in any one of these anodisations should be sufficient completely to saturate with calomel the whole of the solution in the cell. Thus the decay of reversibility of the electrodes seems not to be due to physical dissolution of calomel at the interface, followed by diffusion into the bulk of the solution, but to some other non-electrochemical process : there can be little doubt that this is a disproportionation reaction.

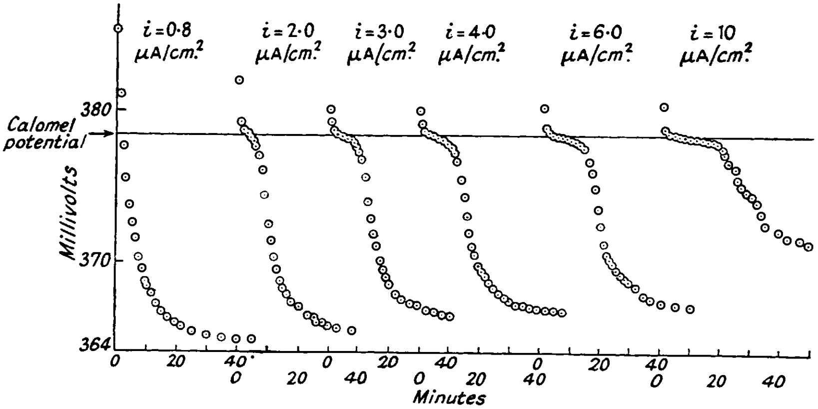
(3) A more complete examination of the decay process was accomplished by making periodic measurements of the potential of the mercury pool, starting immediately on stopping anodisation. Two kinds of experiment were performed. In one of these, fixed quantities of electricity were passed at various current densities and in the other various quantities of electricity were passed at fixed current densities : no operations were conducted upon the cell between these anodisations except the potentiometric measurement of decay.

The decay curves arising from the passage of 200 μc/cm.^{2} at different current densities are shown in Fig. 7*a*. The curve for the lowest current density (0·8 μA/cm.^{2}) is quite smooth and no peak appeared in the potential–time curve of the anodisation. At a current density of 2 μA/cm.^{2} an inflection is observable in the decay curve, with a point of minimum slope at the calomel potential, and the polarisation curve showed a peak. With higher current densities the inflections became more pronounced and tended to become almost complete arrests at the calomel potential. In this set of experiments, and in others not here recorded, the appearance of an inflection or arrest in the decay curve coincided with the appearance of a peak in the polarisation curve for the correponding anodisation. Conversely, if no peak was shown in the anodisation curve, there was no arrest in the decay curve.

The resemblance between these decay curves and cooling curves for a system undergoing a phase transition is striking, and they seem to offer definite evidence that the process of " crossing the peak " results in the formation of a new potential-determining phase, which must almost undoubtedly be solid calomel.

This suggestion is supported by the results of the other experiments, in which increasing charges were passed anodically at a fixed current density of 20 μA/cm.^{2}. The anodisations involving the smaller charges gave rise to decay curves which showed inflections, but no definite arrests, at potentials below the calomel potential. With increasing quantity of electricity passed in the anodisation, the potential at which the inflection appeared in the subsequent decay curve rose towards the calomel potential. As soon as it attained this value, the inflection became a definite arrest, the length of which increased according to the quantity of electricity passed in the preceding anodisation. Fig. 7*b* shows the potential of the decay inflection or arrest plotted against the charge passed in the previous anodisation, with an oscillographic record of a separate anodic polarisation, at the same current density, superimposed on the same abscissæ. From this it can be seen that the first inflection, for the lowest charge, seems to appear coincidentally with the prepeak. It is also clear that the second discontinuity in the oscillogram can be associated with the appearance of the new phase already mentioned.

FIG. 7*a*.



The smooth transition between inflections below the calomel potential and definite arrests at the calomel potential has special significance. It would seem to reflect the first appearance and early growth of " calomel substance " in amounts too minute to qualify as a separate phase, capable of robbing the system of a degree of freedom. Since potential is undoubtedly associated with intensive properties, it seems necessary to postulate a " dilute calomel," or a precursor to calomel. This cannot be a freely soluble substance, for, if it were, the potential decay consequent upon its loss from the interface by diffusion would be smooth and could show no inflection. It is thought that the requirement for such a substance may be met by chloromercury, an entity suggested by Hills and Ives (*J.*, 1951, 311) as participating in the functioning of the calomel electrode.

A tentative explanation of the mechanisms of the processes giving rise to the anodisation peak and its associated phenomena may be advanced at this stage.

The first discontinuity, or prepeak, marks the onset of a change of electrode process from that described in the previous paper (mechanism I) to the direct discharge of chloride ions to form chloromercury anchored to the mercury surface (mechanism II). This suggestion implies that no chloride ions were discharged before this discontinuity was traversed (observations recorded in Part I lend support to this) and that there is therefore, at the prepeak, a collapse of the electrical double layer exactly analogous to the breakdown of the dielectric of a condenser. Such a breakdown would be, it is suggested, defined solely by the properties of mercury and closely adsorbed (but not discharged) chloride ions, and this seems to be consistent with the reproducibility of the prepeak and the almost negligible dependence of its potential upon current density. The implication is also conveyed that the apparent differential capacities listed in the Table are real, and since the prepeak interrupts a rapid, almost linear potential rise, there is no sign that the double layer " condenser " is (apart from the breakdown) approaching the limit of the charge it can hold.

The peak which follows can be considered as arising from a summation of the effects of failure of the electrode as a condenser on the one hand and the gradual building up of a potential-determining chloromercury film on the other. This film will tend (supersaturation being excluded) to reach a limiting two-dimensional concentration which would be fixed by equilibrium with solid calomel, presumably attained at the second discontinuity. It may well be that the " hump " and associated phenomena could arise from supersaturation, but further speculation, in absence of decisive experimental evidence, would be only confusing at this point.

Fig. 7*b*

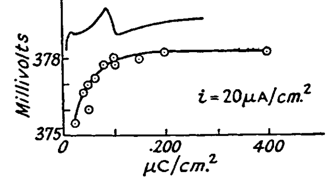
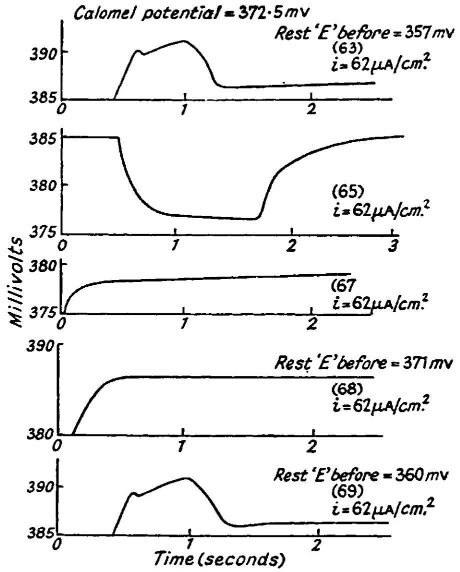


Fig. 8.



It is easy to envisage that the chloromercury entities, even although they do not possess the kinetic freedom of solute molecules, will have a tendency to " evaporate " from the mercury surface into the solution (in what form is not, at the moment, relevant), the " vapour pressure " governing this evaporation being a function of their two-dimensional concentration. If this concentration is also potential-determining, then the constant concentration arising from equilibrium with solid calomel should cause an arrest in the decay curve at the calomel potential for as long as calomel is present. If, however, insufficient chloromercury to produce an ordered calomel phase is formed in an anodisation, then a state of constant concentration will not be reached and as " evaporation " then depletes the population, no arrest, but only an inflection below the calomel potential, will be observed.

Section C—D : the Period of Non-polarisability.—This section of the curve indicates that, to a first approximation, the potential of the mercury electrode remains constant and independent of the charge passed for a long period. This is the behaviour of a reversible electrode and it is tempting to conclude that the mercury pool in this condition is acting as a calomel electrode. Although this may be so for current densities below about 5 μA/cm.^{2}, for all higher current densities the potential lies significantly above the calomel potential; there is an "overpotential" which, however, increases only by 7 mv for each ten-fold increase in current density. This slight dependence on current density seems to exclude concentration polarisation as the reason. It is found, furthermore, that when the current flow is stopped in the early part of this section the decay of the overpotential is relatively slow and consonant with the dissipation of a concentration gradient; but in the later part, where passivation is approached and concentration inequalities should be greater, the potential falls almost immediately to the calomel potential.

Other observations, bearing on the efficiency of the electrode in this state as a calomel electrode, result from successive constant current anodisations such as are illustrated in Fig. 8. The uppermost of the polarisation curves shown is the initial anodisation with a peak. The next shows the effect of breaking and restoring the current in rapid succession. The three remaining curves show anodisations performed after the first with increasing periods of rest in between. It is seen that, in the first of these (middle curve), the curve is peakless and the overpotential is reduced: in the second there is still no peak but the overpotential has risen to its original value. In the third (lowest curve), for which the resting period had been long enough for the rest potential to fall below the calomel potential, the peak has reappeared. This behaviour is strongly reminiscent of that discussed for the "equilibrium experiments" in Part I, and would seem to have the same origin. It thus appears that the potential of the mercury pool as indicated by this part of the curve arises from a composite mechanism. This is of interest in relation to the approach to passivation, and is discussed in the following paper.

EXPERIMENTAL

The apparatus, materials, and general methods were those used in the previous paper, except in two respects.

Oscillographic Equipment.—A Nagard type 103 oscillograph, fitted with a 6″ tube with an afterglow screen and an illuminated graticule for calibration, was used. This instrument was provided with a linear D.C. amplifier (of the modulated carrier-wave type) with a gain variable between 500 and 10^5 and an input impedance of 1·1 megohms. Since, with the desired sensitivity of 10 mv to 1 inch deflection on the Y axis, the instrument had an effective range of only 50 mv, the major part of the E.M.F. it was desired to measure was opposed by a Tinsley potentiometer: this had the advantage of very greatly increasing the effective input impedance. The oscillograph trace was photographed on Kodak R55 recording film, with a camera with an *f*1·9 bloomed lens. These photographs were subsequently projected by means of a standard photographic enlarger and traced on paper by hand. A second D.C. amplifier was available for the X axis and was used in conjunction with a motor-driven potentiometer to provide a time-base for the slower sweeps. Time marking was performed by means of 50 c/s mains frequency, or by one of two clocks giving either half-second or 1—20 seconds impulses as desired according to the sweep time. These time signals were recorded separately and superimposed on the potential–time records when the "enlargement" was carried out.

Silicone Treatment.—In experiments requiring the use of hydrophobic vessels, the mercury-electrode compartment only was treated with Silicone by the method described by Hills and Ives (*loc. cit.*). Very great care was taken, by prolonged extraction with "live" carbon tetrachloride vapour, and subsequent steaming, to ensure that no excess, unbonded silicone fluid was left in the vessel.

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