812. *Anodic Processes. Part I. Anodisation at Low Current Densities of Mercury in Hydrochloric Acid.*

By R. H. Cousens, D. J. G. Ives, and R. W. Pittman.

Experiments have been conducted on the anodisation of a mercury electrode in 0·1N-hydrochloric acid at 25°, under conditions of high purity and rigid deoxygenation. Evidence is presented that the anodic reaction results in the production of soluble mercuric compounds in excess of the concentrations defined by the disproportionation equilibrium of calomel, and that calomel is subsequently formed in a secondary, non-electrochemical reaction. Reasons for this behaviour are advanced.

Previous work (Hills and Ives, *J.*, 1951, 311) led to the suggestion that the calomel electrode possesses a specialised interfacial structure. This suggestion has been investigated by experiments on the anodisation of mercury in aqueous hydrochloric acid, with results of sufficient diversity and interest to merit an introductory survey. The experimental techniques which have been used are exacting, and simultaneous exploration of different aspects of the complex phenomena has been necessary: three of these aspects are dealt with in this and the two following papers. In these circumstances the conditions of experiment have necessarily been restricted to the single temperature of 25° and an acid concentration of approximately 0·1N, thus the effects of two main variables still await study.

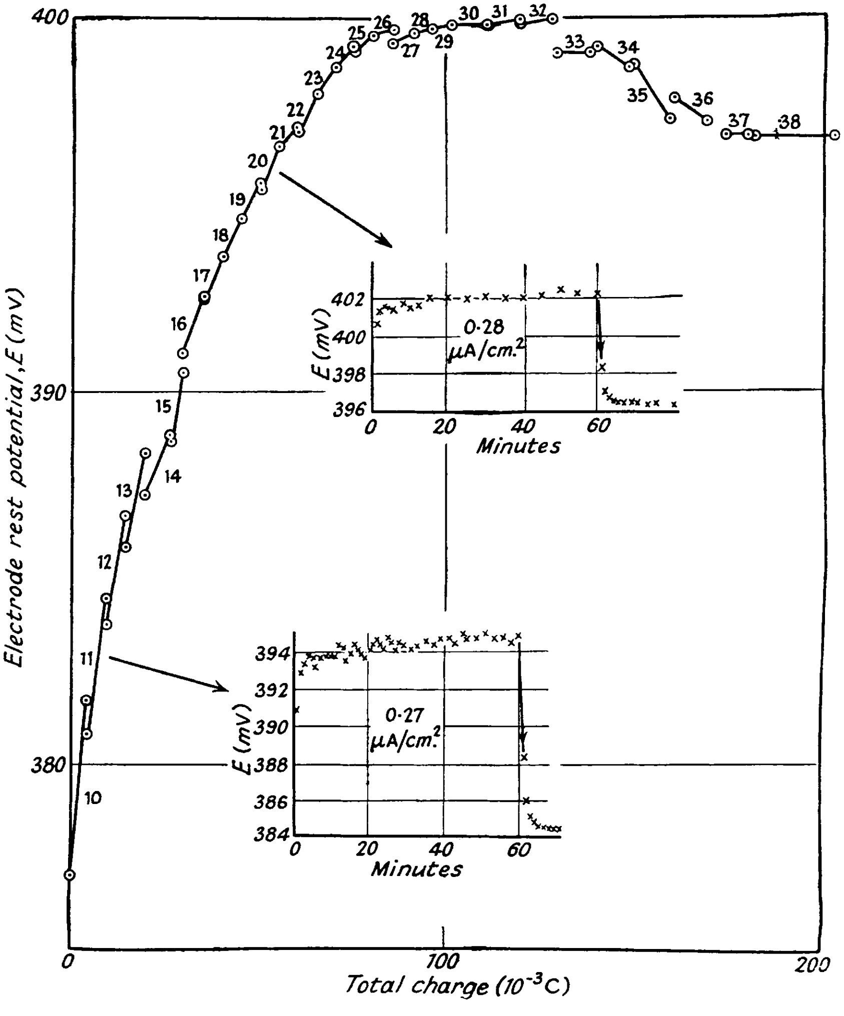
The initial system, as a polarised electrode, was very sensitive to traces of depolarising impurities, and great care was taken to exclude them. Hydrogen-overpotential measurements were made to provide a criterion of purity, and were found to conform to a Tafel equation $\eta = 1{\cdot}44 + 0{\cdot}120 \log i$, in reasonable agreement with the best available data (Jofa, *Acta Physiochim. U.R.S.S.*, 1939, **10**, 903; Bockris and Parsons, *Trans. Faraday Soc.*, 1949, **45**, 916; Hillson, *ibid.*, 1952, **48**, 462; Hiskey and Post, *J. Amer. Chem. Soc.*, 1950, **72**, 4303).

The techniques used in the anodisation investigations to be described may be broadly classified under two heads. (*a*) Those in which the potential of the mercury electrode was correlated with the quantity of electricity passed, but in which the current was not necessarily constant and was interrupted from time to time in attempts to allow the system to attain equilibrium. These will be called, loosely, "equilibrium experiments." (*b*) Those which resulted in the production of potential–time curves arising from the passage of a constant, uninterrupted current through the cell.

The present paper is concerned with experiments of the first class and these consisted of a series of anodisations performed on a mercury pool, 5 cm.^{2} in area, beneath 100 ml. of 0·1N-hydrochloric acid, through which hydrogen was continuously passed. The initial rest-potential of the electrode was some tens of mv below the calomel electrode potential appropriate to the concentration of acid (which will be implied in the term "calomel potential" throughout these papers). Each of the earlier anodisations was made at a current density of about 0·25 μA/cm.^{2} and was stopped after a total of 5000 μC had been passed. The electrode was then left to assume a steady resting state before the resumption of the step-wise anodisations. Later in the series, current density and quantity of electricity were increased, or otherwise varied, to suit immediate purposes, but a record was kept of the total charge passed anodically from the beginning of the experiment, all of the operations being accompanied by readings of current, time, and potential. Periodically, during the resting periods, "micropolarisation tests" were applied to assess the degree of electrode reversibility. These involved rapid and systematically conducted anodisations on an even smaller scale, the potentials required to establish current densities of 0·04, 0·08, 0·12, 0·16, and 0·20 μA/cm.^{2} being determined, first in rising, and then in falling sequence. These tests were diagnostic in two ways: by the extent of the hysteresis between rising and falling branches, and by the average slope, di/dE, which for an ideally reversible electrode, should approach infinity.

The first item of interest arising from this work is found in the dependence of electrode rest potential on the total charge passed anodically, shown in Fig. 1. The rest potentials before and after an anodisation are joined by a line, labelled with the ordinal number of the anodisation, and the potentials (as throughout this series of papers) are measured with respect to a hydrogen electrode in the same solution. Some eccentricities in the curve are due to the very slow final self-adjustment of rest potentials and the unavoidable variation in resting periods during this lengthy series of some fifty anodisations.

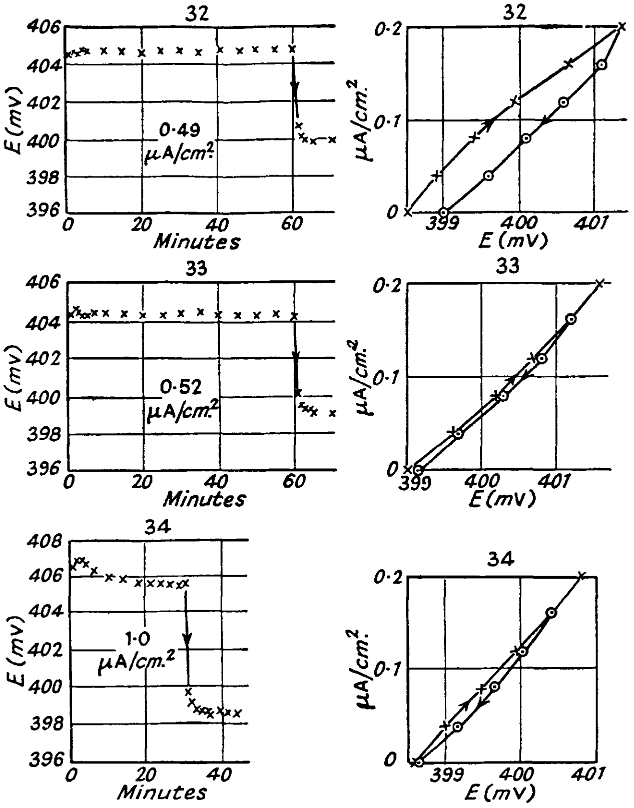
Fig. 1.



It can be seen that a charge of 60×10^{-3} coulomb was required to bring the rest potential to the calomel potential (396·8 mv) from some 20 mv below it. If calomel were the sole anodic product, about 10^{-12} coulomb should have sufficed to saturate the whole volume of the solution, but, instead, 10^{10} times this amount of electricity was required. Further anodisation on the same scale carried the rest potentials higher, over a flat maximum and finally down to the calomel potential only when visible, discrete, calomel crystals appeared, speckling the mercury surface. The fall to the calomel potential was very slow and not characteristic of removal by crystallisation of excess of solute from a normally, " physically," supersaturated solution. However, even the maximum concentration of any anodically produced solute was still only of the order of

10^{-5} equiv./l. and doubt was therefore felt whether the recorded data on the solubility (as distinct from solubility product) of calomel might not be in gross error. This would require calomel to be a weak electrolyte and, unlikely as this might be, it was a conceivable reason for the apparent low efficiency of its anodic generation. This possibility was immediately excluded by a radiochemical determination (with ^{203}Hg) of the solubility of calomel in water : although of limited accuracy, this left no doubt that calomel is esentially a strong electrolyte. The apparent solubility in hydrochloric acid, however, was very much greater and indicated the tendency of calomel to disproportionate with formation of soluble products, but it would be premature to apply this known tendency (Sillén *et al.*, *Acta Chem. Scand.*, 1947, **1**, 461, 437, 479; 1949, **3**, 539) directly to the anodisation results.

FIG. 2.

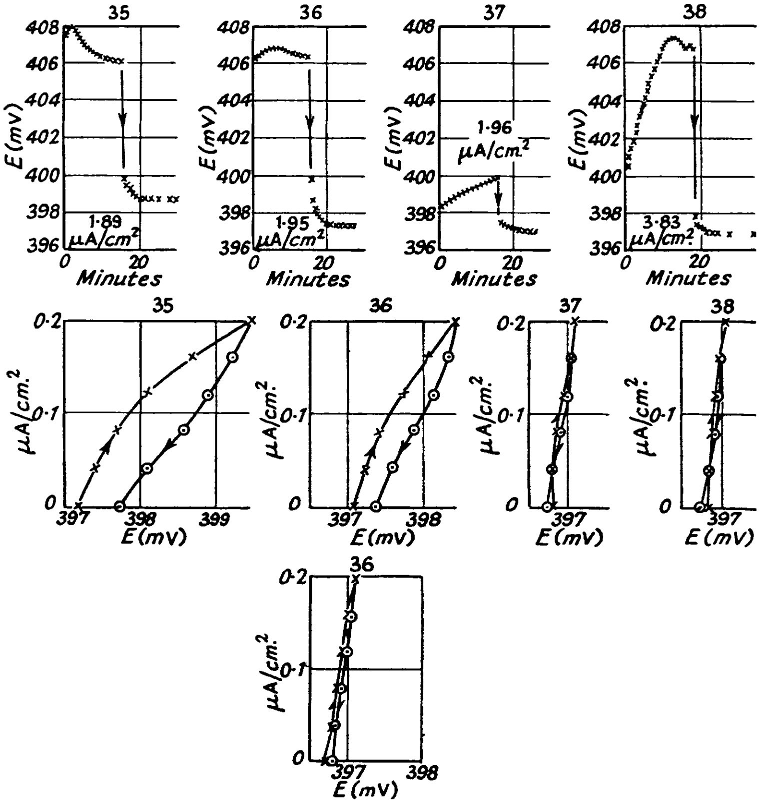


It is, however, apparent that, at least in the earlier anodisations, calomel is not the anodic product.

Attention may next be directed to the " polarisation plots " of potential against time at constant current density. Two of the earlier members (11 and 20) are shown as insets in Fig. 1, and are not remarkable. It may be noted that when the current is stopped, the potential fall is not instantaneous, but follows a course consistent with loss by diffusion from the electrode surface of a soluble, potential-determining, anodic product.

Further polarisation curves (numbered in accordance with Fig. 1), and subsequent reversibility tests, are shown in Figs. 2—5, which give a graphical representation of the main course of the anodisations and their effects. The sequence of changes which occurred can be summarised in three statements. (1) The polarisation curves developed maxima, the first appearance of which coincided with the observation of minute crystals of solid calomel upon the electrode surface [after the overnight rest following anodisation (32)]. These maxima, the traverse of which involves charges of the order of 10^{-3} c or more, are of a kind which suggests the supervention of one kind of electrode process by another, or, more conservatively, a change of dominance from one potential-determining factor to another. (2) The micro-polarisation curves, initially showing large hysteresis and low slope, underwent a series of changes coincident with the development of the peaks in the corresponding anodisation curves. After closure of the first hysteresis loop with little change of slope, a second hysteresis effect appeared, accompanied by a gradual increase in slope, followed by closure again and ultimate transition to a very steep linear plot characteristic of a truly reversible electrode. This strongly suggests a change from one electrode process to another. (3) Repeated observations were made of a very marked improvement of current-carrying ability and reversibility of the electrode on standing overnight. Thus, of the two reversibility tests following polarisation (36) (Fig. 3), the first (with hysteresis and lower slope) was taken an hour after the anodisation : the second, with no intervening operations, was taken next morning. The great improvement in reversibility is confirmed by anodisation (37), at the same current density as (36), which shows a " collapsed " polarisation curve with no peak and only a fraction of the former overpotential (measured in excess of the calomel potential). An increase of current density in the next anodisation (38), however, reinstated the higher, peaked polarisation curve. The same sequence of overnight improvement in reversibility and reinstatement of overpotential on increase of current density can be seen in anodisations (40), (41), and (42), but it will be seen that the maxima in the polarisation curves move successively to the right, whilst not increasing significantly in height.

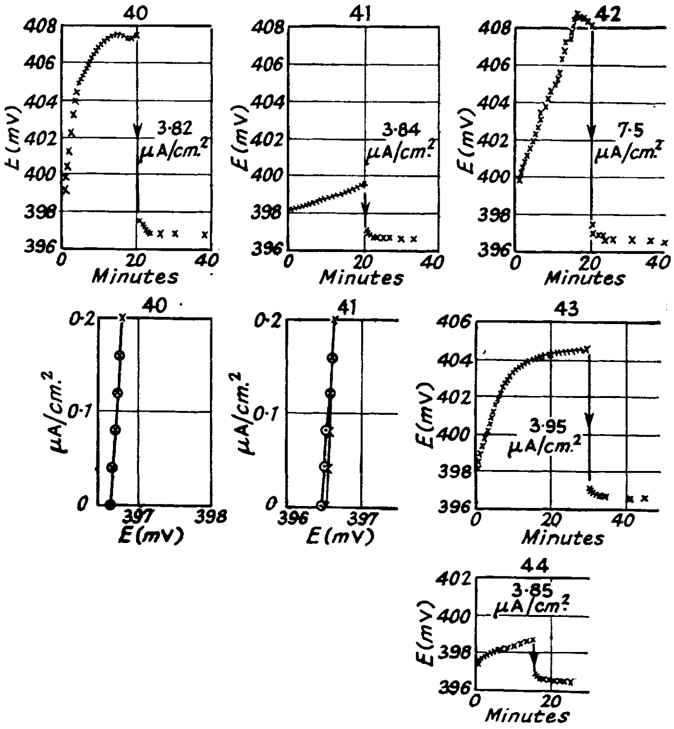
FIG. 3.



Reversions to lower current densities show, in general, the rapidly increasing depolarisation and reversibility of the electrode, but a very significant variation can be seen in anodisations (41)—(44). In the first of these, at 3·84 μA/cm.², the overpotential was low, after overnight resting: the second, following immediately, at 7·50 μA/cm.^{2}, reached the high overpotential; the third, conducted shortly afterwards, at a current density reduced to 3·95 μA/cm.^{2} (not significantly greater than the first) showed a tendency to reach much higher overpotentials than the first. The intervening anodisation at heavier current had not, apparently, effected much improvement, but rather the reverse. The benefit, however, may have been latent, for the fourth of these anodisations, at 3·85 μA/cm.^{2}, after overnight standing, showed little overpotential.

The remaining anodisations of the sequence, at current densities becoming considerable in magnitude, showed the incidence of passivation (47 and 48) and the improvement in reversibility on resting [cf. (48), (49), and (50)].

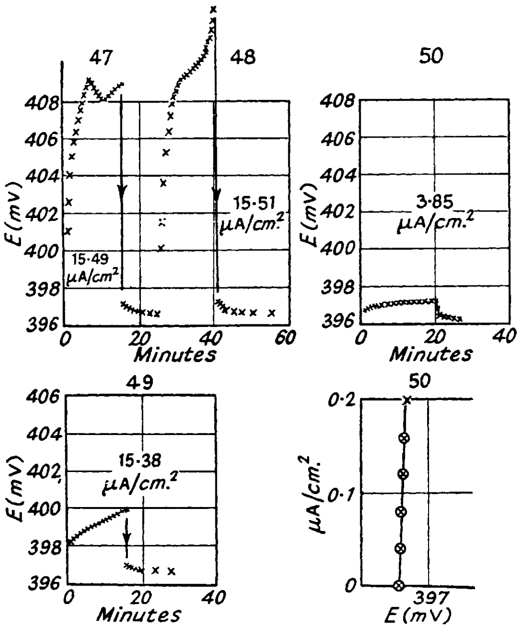
Fig. 4.



The final operation in this experiment was the attempted reversal of the effects of the series of anodisations by similar low current-density cathodisation. The calomel was rapidly stripped away, but it was found to be impossible to restore the electrode to its original state even with very prolonged polarisation involving the passage of cathodic charge much in excess of that previously passed anodically. It is notable that cathodic current continued to flow almost indefinitely at low overpotentials. There can be no doubt that a catalytic " impurity," not readily reduced at the cathode, had been formed from the system itself in the previous operations.

It seems evident that these experimental facts are consistent only with the production of a soluble anodic product which is potential-determining and is responsible for the tendency of the electrode to reach potentials and overpotentials in excess of the calomel potential. Further evidence for this has been obtained in a series of anodisations, conducted continuously, with step-wise increases of applied E.M.F. A low-resistance circuit was used, and, after the imposition of each new E.M.F., both current and potential were allowed to reach sensibly steady states. This experiment is illustrated in Fig. 6, where the upper curves indicate electrode potential and the lower current; they stand in approximately mirror-image relation to each other. It is very unlikely, at the very low currents used, that concentration polarisation could be responsible for the shapes of these curves. The effects are consistent with the generation of soluble material, positive-directing for potential, reaching a new steady-state concentration at the electrode interface (a function of rate of generation and rate of loss by diffusion) with each enhanced value of polarising E.M.F. The sudden acquisition by the electrode of new current-passing ability is very apparent, in both potential and current curves. In the inset to Fig. 6, the very approximate steady-state currents are plotted against the corresponding potentials. The steeply rising linear section of this plot, extrapolated to zero current, does not have an intercept at the calomel potential (396·5 mv), but one much in excess of it. This strengthens the view that the high and the low overpotential states, so apparent in the former experiments, have their origin in a difference of electrode process. A controlled-current anodisation at a current density of 60 μA/cm.^{2} was performed on this electrode at the conclusion of the experiment.

Fig. 5.



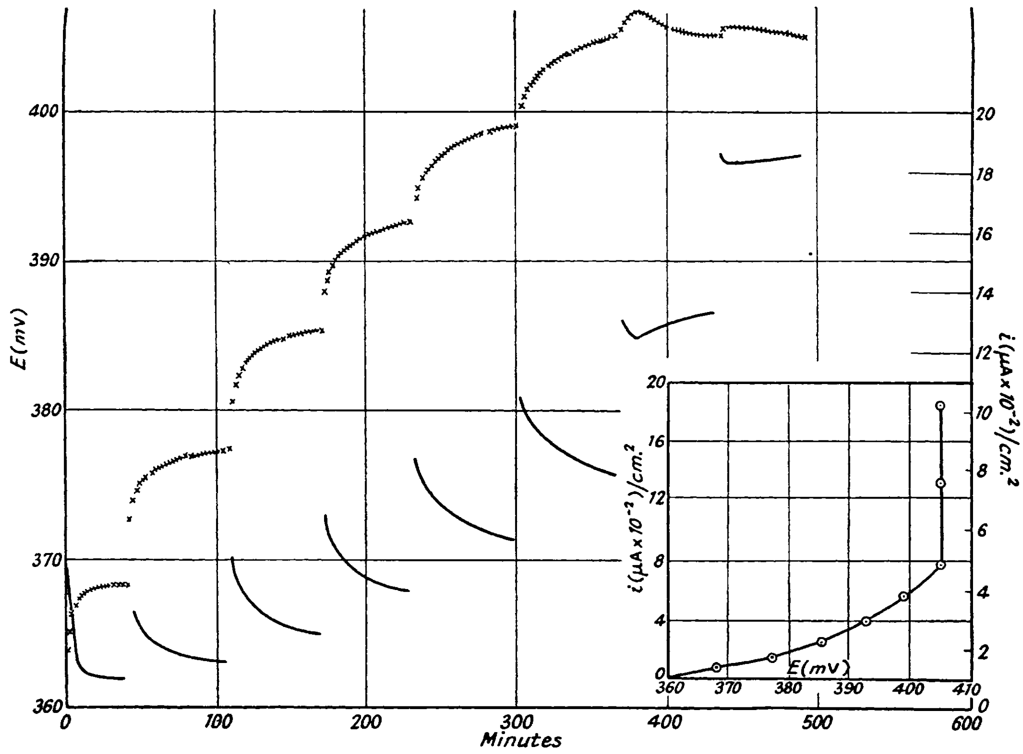
The potential–time curves, recorded oscillographically, showed a well-developed peak (see Part II).

Discussion.—There can be little doubt that in the early stages of a low-current-density anodisation of a fresh Hg/HCl electrode no calomel is produced, yet calomel is ultimately formed. There is strong evidence from the polarisation curves, from the indications of change of electrode process given by the reversibility tests and from the slow non-electrochemical reaction occurring on long standing, that the calomel is produced, partly or wholly, by a secondary process, yet, when the electrode becomes in fact a reversible calomel electrode, it is thermodynamically necessary that the reaction must be none other than the production or reduction of calomel, or species in equilibrium with it. It is, therefore, evident that, in the " equilibrium experiments," the states through which the electrode passes must really be a sequence of metastable states, very slow to reach ultimate stability. Anodisation under these conditions is therefore an inefficient way of forming a calomel electrode, and stands in very sharp contradistinction to the method of anodisation discussed in the following paper, which can generate a calomel electrode in a fraction of a second.

A provisional interpretation of these results must be attempted since the conclusions have bearing on the following papers.

The anodisation of mercury at infinitesimal current densities would be expected, by reason of negligible departure from reversibility, to generate mercuric and mercurous ions in their equilibrium concentration ratio. The presence of a large excess of chloride ions, however, must greatly disturb this ratio. It has been confirmed that mercurous chloride is a strong electrolyte: chloride ions will therefore be indifferent to mercurous ions, unless the solubility product of calomel is exceeded. However, chloride ions strongly interact with mercuric ions, forming covalent mercuric chloride and complex mercurichloride anions, so that even if solid calomel is formed in vestigial intermediate amounts, the equilibrium, in 0·1N-hydrochloric acid, will lie far over in favour of generation of mercuric compounds during the low-current-density anodisations. But, however displaced the equilibrium, there is no apparent reason why the equilibrium ratio of mercurous to mercuric compounds, proper to the given solution, should not be immediately established. Yet the "equilibrium experiments" strongly suggest that soluble mercuric compounds are generated in considerable excess even of this displaced equilibrium, and ultimately take part in a reverse reaction with mercury to generate calomel. It is suggested that the reason for this is that the generation occurs at the electrode interface, within the close Helmholtz layer, which is not representative of the bulk solution. The specific adsorption of chloride ions at mercury is generally accepted, and double-layer capacity measurements show increasingly extensive adsorption on the anodic branch of the electrocapillary curve. Such measurements are not extended as far as the calomel potential on the anodic branch without confusion due to leakage (evidence on this, however, is presented in the following paper): nevertheless, there can be no doubt that the anodic generation of mercuric ions occurs in a very high local concentration of chloride ions within the double layer. This mode of anodic generation of mercuric chloride and its derivatives will be subsequently referred to as "Mechanism I." The mercuric chloride molecules necessarily formed can

FIG. 6.



diffuse away and, as soon as they do so, the disequilibrium (with respect to the bulk solution) is frozen and must await, for its relief, either the normal processes of back-diffusion to the mercury surface, or, perhaps as well, the field-assisted diffusion of the complex mercuri-anions. It is worthy of remark that the postulation of the formation of complex mercurichloride anions provides a reasonable explanation of the ineffectiveness of cathodisation in reducing the elevated rest potential arising from anodisation.

The peaks in the polarisation curves require special comment. The rising sections of these peaks in all cases suggest the smoothly rising potential characteristic of the continuation of the former electrode process, which, however, is modified by the onset of a new process which nullifies the accumulation at the interface of the material which is positive-directing for electrode potential. The immediate explanation is that the new process is the reaction of the primary anodic product, mercuric chloride, with the mercury to form calomel, but difficulties are encountered. It is necessary to assume, for example, that this process is a delayed one in order to explain the peak, otherwise there is no reason why at this stage of the sequence of anodisations, the mercuric chloride should not play the part of an active intermediate and reach a stationary steady-state concentration. The same assumption, however, is required to account for the fact that the rest potentials can remain more positive than the calomel potential for a matter of days. Other evidence suggests that the reaction between mercuric chloride and mercury is slow, but is autocatalytic. In further sections of this exploratory work it is strongly indicated that it may be justifiable to assume, as a working hypothesis, that " nascent calomel " upon the surface of mercury has a profound effect in promoting both electrochemical and non-electrochemical reactions in which the mercury takes part.

EXPERIMENTAL

Preparation of Materials.—Mercury. A single quantity of mercury, used throughout the work (and in the previous work of Hills and Ives, *loc. cit.*), was, before each experiment, sprayed down a mercurous nitrate column, washed, dried, and distilled three times in a current of air at reduced pressure according to Hulett's method (*Phys. Review*, 1911, **33**, 307). This mercury was used for sealing taps and ground joints; the electrode mercury was in addition refluxed in pure hydrogen and finally distilled directly into the cell in a high vacuum.

Water. Water was obtained from a still of the Stuart and Wormwell design (*J.*, 1930, 85), fitted with a "Vitreosil" condenser. The steam from distilled water containing potassium hydroxide and potassium permanganate was scrubbed with phosphoric acid and admixed with a rapid stream of pure nitrogen before condensation. The distillate was not collected until its conductance fell below 10^{-7} ohm^{-1}. This water was used in the preparation of all solutions.

Hydrochloric acid. " AnalaR " potassium chloride was freed from traces of other halides by the method of Pinching and Bates (*J. Res. Nat. Bur. Standards*, 1946, **37**, 311) and twice crystallised with rejection of head and tail fractions. Hydrogen chloride generated from this with " AnalaR " sulphuric acid was passed through traps at −80°, absorbed in water, and stored at high concentration in a Vitreosil flask. The 0·1N-acid was prepared in a totally sealed, intensively cleaned apparatus, in which water was boiled repeatedly under a vacuum with intervening admissions of pure hydrogen. Water and the requisite amount of strong acid were distilled in hydrogen into the same receiver, hydrogen being passed through the distillate for some hours. This acid was transferred directly to the experimental cell, by hydrogen pressure, through all-glass connections, initially obstructed by a septum.

Hydrogen and nitrogen. Commercial gases were passed through dust filters and tubes packed with potassium hydroxide pellets and deoxygenated by reduced copper in Vitreosil furnace tubes at 450°. The gases then passed through traps cooled in liquid air, through greased, mercury-sealed control taps and then through long, narrow, glass spirals cooled in liquid air; thereafter, the apparatus contained no greased taps or joints. Either gas could be passed through the experimental cell.

Electrolysis Cell.—The mercury electrode, of 5 cm.^{2} surface area, was contained in a Pyrex electrode vessel of 100-ml. capacity. Contact was made to the electrode by means of a remote, vacuum-tight, pinch-seal of platinum foil and its potential was measured with respect to two normal hydrogen electrodes in a side vessel, communicating with the main one through a sintered-glass septum and a Luggin capillary. The other working electrode was a large hydrogen electrode in a separate compartment jointed by means of a closed, mercury-sealed tap, the barrel of which was wetted with the solution. All the fittings to the experimental cell were mounted on dry, mercury-sealed cones, and all tubes for passage of gas or solution were all-glass. The apparatus was cleaned before use by means of fuming nitric acid, washing with " equilibrium water," steaming from, and repeated washing in, conductivity water, and drying at 120°. The whole of the cell was evacuated to a "hard vacuum " and repeatedly flushed with hydrogen before the distillation of the mercury and the introduction of the solution.

Electrical Apparatus.—E.M.F. measurements were made by means of a Tinsley 4025 potentiometer. Polarising current was supplied either from an ancillary potentiometer or from commercial high-tension batteries with large, variable resistances in series when it was necessary to maintain the current at a constant value. All the electrical equipment was insulated with Polythene and screened.

The authors record their thanks to the Director, A.E.R.E., Ministry of Supply, for facilities.

BIRKBECK COLLEGE, LONDON, W.C.1.

[*Received, March 27th,* 1953.]