162. *The Electrolytic Properties of Hydrogen. Part I. Hydrogen as an Anodic Depolariser. Part II. Effect of Anodic Polarisation of the Platinum Electrodes.*

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Part I. *Hydrogen as an Anodic Depolariser.*

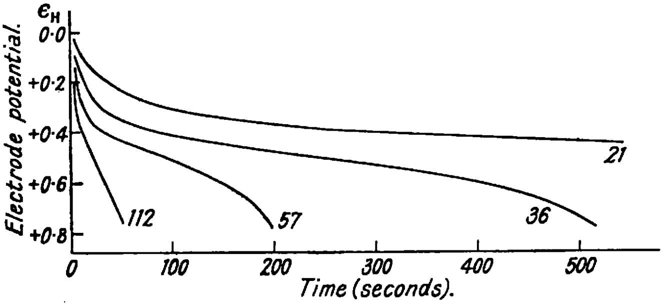
The liberation of hydrogen at the cathode in the electrolysis of aqueous solutions has been extensively studied in recent years both experimentally and theoretically. According to Gurney's theory (*Proc. Roy. Soc.*, 1931, *A*, **137**, 132), the rate of the process is primarily determined by the conditions necessary for the transfer of electrons from the cathode to hydrogen ions in the solution, *i.e.*, by the process $\varepsilon + H^+ = H$, the subsequent combination of hydrogen atoms to form molecules having no influence on the rate. It has been pointed out by one of us (Butler, *Trans. Faraday Soc.*, 1932, **28**, 379; cf. Hammett, *ibid.*, 1933, **29**, 770; Erdey-Grúsz and Volmer, *Z. physikal. Chem.*, *A*, 1930, **150**, 203) that the occurrence of the reversible hydrogen potential at platinised electrodes requires that the reverse process, which may be represented provisionally as $H_2 = 2H^+ + 2\varepsilon$, may also take place. There is, however, much uncertainty as to the conditions under which such a process may occur. Gurney (*Trans. Faraday Soc.*, 1932, **28**, 447) suggested that the transfer of electrons from molecular (or atomic) hydrogen in the solution to metal electrodes at any appreciable rate is prohibited by the quantum-mechanical conditions of the process, and that any reverse action which may be observed is due to the ionisation of hydrogen which has been adsorbed on or dissolved in the metal. This is supported by the fact that, although there is no difficulty in realising the reversible hydrogen potential at platinised platinum electrodes, yet a bright platinum electrode placed in a hydrogen-saturated solution usually takes up a potential about 0·3 volt more positive than the reversible value and shows no sign of approaching the latter even after a considerable time. Also, if such an electrode is anodically polarised, only a small amount of depolarisation which could be ascribed to such a reverse process is observed. However, in a general survey of the behaviour of hydrogen and oxygen at platinum electrodes (*Proc. Roy. Soc.*, 1932, *A*, **137**, 604), we observed that, if a platinum electrode is first polarised cathodically so as to liberate hydrogen and is then polarised anodically, a depolarisation process is observed at about $\varepsilon_H = +0{\cdot}5$ volt. The object of these experiments was to examine this process in greater detail and to determine whether it is due to the transfer of electrons to the electrode from the hydrogen present in the solution, or to the transfer of hydrogen ions to the solution from hydrogen which has been adsorbed or dissolved in the metal during the cathodic polarisation.

EXPERIMENTAL.

The electrodes were of bright platinum having an apparent area of 1 cm.^{2}. Their real area, as established by measuring the quantity of electricity required to set up the hydrogen or oxygen over-voltage (Bowden and Rideal, *Proc. Roy. Soc.*, 1928, *A*, **120**, 59), was 2—3 cm.^{2}. The electrolyte was $M/10$-sulphuric acid prepared from conductivity water and As.T. sulphuric acid, twice distilled in a Pyrex apparatus. The electrode vessel consisted of two cylindrical tubes of glass, containing severally the electrodes under examination and an auxiliary electrode, connected by a glass tube which was fitted with a tap that was normally kept closed. The solution was freed from oxygen by prolonged boiling at reduced pressure in a stream of pure hydrogen, and was then introduced into the electrode vessel, which had previously been freed from oxygen. The electrode potentials were measured with reference to a mercurous sulphate electrode in sulphuric acid of the same concentration. The potential of this electrode with reference to a reversible hydrogen electrode in the same solution is + 0·7372 volt. The potential of the electrode on the absolute hydrogen scale is thus $\varepsilon_H = +\ 0{\cdot}668$ volt, and the ε_H values were obtained by adding this value to the observed *E.M.F.*

FIG. 1.

Anodic curves with various currents (*amp.* × 10^{-7}) *after cathodic polarisation with* 112 × 10^{-7} *amp. for* 5 *minutes.*



Behaviour of Electrodes after Cathodic Polarisation with Small Currents.—In the first experiments the electrode was cathodically polarised for a definite time, and after as short an interval as possible a suitable anodic current was passed. Some typical curves obtained after 5 minutes' cathodic polarisation with 112 × 10^{-7} amp. are shown in Fig. 1. No depolarisation occurs in the vicinity of the reversible hydrogen potential, but a well-defined depolarisation appears between + 0·3 and + 0·5 volt. For the purpose of this discussion the length of this process is taken as the total time to reach + 0·67 volt (0·0 on the experimental scale). The anodic current was stopped when the potential had reached + 0·7 in order to avoid the liberation of oxygen which occurs at a more positive potential.

It is difficult to reproduce the curves thus obtained, the behaviour of the electrodes being markedly influenced by their previous treatment; *e.g.*, in a series of exactly similar experiments in which the cathodic polarisation was 740 × 10^{-7} amp. for 5 mins., and the anodic current 110 × 10^{-7} amp., the times to + 0·67 volt were 108, 126, 146, 170, 185, 190, 197 secs. The effect of the cathodic polarisations is thus to some extent cumulative. On the other hand, if the electrode is originally given first a long and then a series of short cathodic polarisations, the length of the cathodic curve gradually falls. The length of the anodic process is thus partly determined by the treatment received by the electrode prior to the immediately preceding cathodic polarisation. It is therefore necessary to interpret a single or short series of experiments with caution.

Table I shows a series of experiments in which the anodic current was varied. The electrode had previously been used for determining a cathodic current–voltage curve and the first anodic time was exceptionally long, but after a few repetitions slowly increasing times were obtained which are reasonably comparable.

TABLE I.

Electrode polarised cathodically with 112 × 10^{-7} amp. for 5 mins. (3·4 × 10^{-3} coulomb). Anodic current started immediately.

Anodic current (i), amps. × 10^{-7}.	Anodic time (t) to +0·67 volt.	it (mean), coulombs × 10^{-3}.
112	(120), (63), 47, 42, 42, 44	0·5
57	167, 179, 202	1·0
36	518, 530, 468,* 506*	1·8
21	1270, 1050	2·2

* Obtained after the measurements with 21 × 10^{-7} amp.

Similar series of experiments were carried out in which the conditions were varied in various ways and the following observations were made.

(1) The length of the anodic process is increased by increasing either the time of the cathodic polarisation with a given current, or the cathodic current for a given time. It is difficult to obtain any quantitative relation on account of the cumulative effect of successive cathodic polarisations, but it is clear that the efficiency of the cathodic process, regarded as the ratio of the amount of anodic to the amount of the previous cathodic polarisation, is, under comparable conditions, greater for small than for large cathodic currents. For instance, in a series of cathodic polarisations with 750 × 10^{-7} amp. for 5 mins. (22·5 × 10^{-3} coulomb), made after the observations of Table I, it was found that successive anodic times with 112 × 10^{-7} amp. were 108, 126, 145, 170, 185, 190, 197 secs., giving it (mean) = 1·8 × 10^{-3} coulomb. This is greater than the corresponding value of Table I, but not in proportion to the increased cathodic polarisation. Similar results were obtained with other anodic currents.

(2) The anodic time is reduced by allowing an interval between the cathodic and the subsequent anodic polarisation; but it is increased somewhat by stirring by bubbling hydrogen through the solution during the anodic polarisation.

(3) After the anodic polarisation, the electrode potential rises in a few minutes to near the reversible hydrogen potential. If it is now polarised anodically again without a preliminary cathodic polarisation, an appreciable amount of depolarisation occurs, though considerably less than after the cathodic treatment. This amount increases only slowly as the interval between the first anodic polarisation and the second is increased; but when an electrode has been standing at open circuit in the hydrogen-saturated solution for a considerable time, the amount of depolarisation is of the same order as after cathodic treatment. This may be illustrated by the following series of observations. Initial cathodic polarisation, 750 × 10^{-7} amp. for 5 mins.; anodic current, 56 × 10^{-7} amp., time to + 0·67, 170 secs. Subsequent anodic without previous cathodic polarisation, 43, 37, 26 secs. After standing 16 hours at open circuit, 248 secs.; after 5 mins., 7 secs.; after 1 hr., 20 secs.; after 5 mins. with stirring, 4 secs.

DISCUSSION.

No depolarisation has been observed near the reversible hydrogen potential, and it may therefore be concluded that hydrogen cannot be ionised in this region by anodic polarisation under the conditions of these experiments. The well-defined process which occurs at + 0·3 to + 0·6 volt may be due to (1) a metallic impurity which has been deposited on the electrode during the cathodic polarisation, (2) the ionisation of hydrogen which is either present in the solution or adsorbed on or dissolved in the electrode. The quantity of electricity passed during the anodic process is frequently 20—50% of that passed cathodically, and although the deposition of minute quantities of metals might occur at the appropriate potential, it is impossible for the current efficiency of such a process, in highly purified solutions, to approach such values. We avoided the use of large cathodic currents, with which the results might be ambiguous in this respect. The depolarisation is thus due to hydrogen in some form or other.

That the hydrogen present in the solution is inactive in this respect may be inferred from the facts that (1) although appreciable depolarisation may be observed with an electrode which has been standing in the hydrogen-saturated solution for some hours, yet this cannot be repeated until after a similar interval, suggesting that some slow process such as the solution of hydrogen in the platinum must occur before it can act as depolariser; (2) stirring the solution during the anodic process somewhat increases the length of the anodic curve, but to a much smaller extent than has been observed in known cases of depolarisation by a dissolved substance, *e.g.*, in the cathodic depolarisation by dissolved oxygen (Armstrong, Himsworth, and Butler, *Proc. Roy. Soc.*, 1933, *A*, **143**, 89).

It is therefore reasonable to conclude that the depolariser is hydrogen either adsorbed on or dissolved in the metal. If the depolariser were a definite amount of adsorbed hydrogen, the quantity of electricity (*it*) required to effect the depolarisation would be independent of the anodic current employed, but if hydrogen is also present in the interior of the metal this quantity will depend also on the amount of hydrogen which can reach the surface by diffusion during the depolarisation. It will therefore be greater the longer the depolarisation time, *i.e.*, the smaller the current. The comparable data of Table I show that the second alternative is in accordance with the facts.

If this view is correct, it follows that with a small cathodic current a considerable part of the hydrogen liberated passes into the platinum, and the experiments indicate that the proportion increases as the cathodic current is decreased. In these circumstances the difficulty of obtaining constant anodic times is easily understood. The length of the anodic curve will depend on the amount of hydrogen which can reach the surface of the electrode during the anodic polarisation, and this will be determined not only by the amount deposited by the previous cathodic treatment, but also by the amount and distribution of the hydrogen originally present in the electrode, and by the interval between the cathodic and the anodic treatment, during which the hydrogen deposited near the surface can diffuse into the interior of the platinum. That a single anodic polarisation does not remove all the hydrogen in the electrode is shown by the appreciable amounts of depolarisation observed in successive anodic polarisations, without intervening cathodic treatment. These experiments also show that the hydrogen of the solution passes into the platinum and becomes available as a depolariser at a very slow rate, and a considerable amount of depolarisation is observed without the preliminary cathodic treatment only when the electrode has been standing in the solution for a long time.

PART II. *Effect of Anodic Polarisation of the Platinum Electrodes.*

BEANS and HAMMETT (*J. Amer. Chem. Soc.*, 1925, **47**, 1215) observed that the " catalytic activity " of a bright platinum electrode was much increased by anodic polarisation or by treatment with oxidising agents followed by cathodic polarisation. Bowden (*Proc. Roy. Soc.*, 1929, *A*; **125**, 446) found that when an electrode had been successively polarised anodically and cathodically in solutions containing hydrogen, a lengthy arrest appeared in the subsequent anodic polarisations, in the anodic curve near the reversible hydrogen potential. He attributed this to an increase in the catalytic activity of the platinum surface, caused by the successive formation and reduction of a superficial layer of oxide, whereby it is brought into a state in which it " readily catalyses the formation of active hydrogen from gaseous hydrogen." In order to elucidate this phenomenon we carried out series of successive anodic polarisations in hydrogen-saturated solutions in which the potential was progressively taken to more positive values.

EXPERIMENTAL.

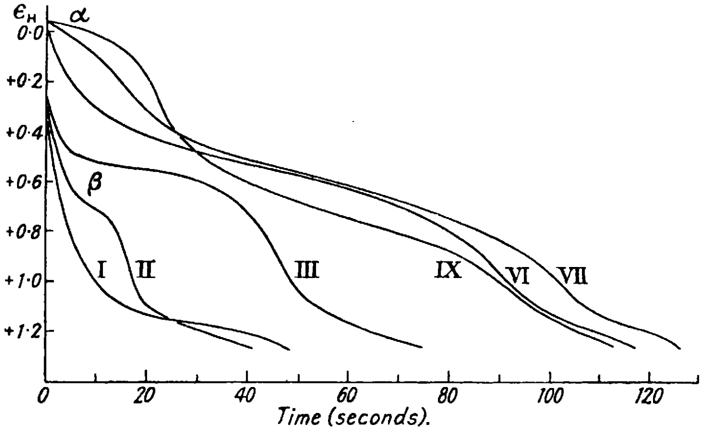
When a platinum electrode is polarised anodically and the current is not stopped at + 0·7 volt, a second depolarisation stage is observed which begins at about + 1·1 volts. This stage has been studied in some detail (Armstrong, Himsworth, and Butler, *loc. cit.*) and shown probably to be due to the formation of adsorbed oxygen at the surface of the electrode. It has been shown above (p. 745) that if the potential is allowed to reach + 0·7 volt only, the times of successive anodic polarisations steadily diminish; this holds until the second depolarisation stage is reached. For example, an electrode which was initially at + 0·3 volt was polarised anodically several times to + 1·07 volts with 219×10^{-7} amp. The length of the anodic curve gradually diminished, until after several such treatments an approximately constant time (8 secs.) was required to reach this value. The potential in each polarisation was now allowed to reach + 1·17 volts, bringing it just within the region in which adsorbed oxygen is formed. The amount of depolarisation at about + 0·5 volt steadily increased in successive experiments, until after the eighth curve it remained approximately constant.

A similar series of experiments was now performed in which the anodic polarisation was carried 0·1 volt further to + 1·26 volts. The effect of the successive anodic polarisations is much greater than in the previous series. The potential at open circuit between the experiments rises to near the reversible value. At first the process β (Fig. 2) at + 0·5 volt increases in length, then the shape of the curve begins to change, and finally a well-marked stage (α) appears near the reversible hydrogen potential.

The potential in each experiment was now allowed to reach + 1·7 volt, the current being increased to 725 × 10^{-7} amp., since with smaller currents characteristic periodicities appeared which will be described later. In the first place, a series of anodic polarisations to + 1·26 volts was made (curves 1—7, Fig. 3). When no further marked changes occurred in successive curves, the potential was allowed to reach 1·7 volt in each experiment (curves I—VI). The length of the stage α was considerably increased in the next anodic curve, and it continued to grow until about 12 × 10^{-3} coulomb was required in curve VI to bring the potential to + 0·15 volt. This was the maximum extension of the curve in this series, and somewhat shorter curves were obtained in succeeding polarisations.

FIG. 2.

Successive anodic polarisation to +1·26 *volts* (i = 219 × 10^{-7} *amp.*).



Reversibility of the Electrode after the Anodic Process.—The length of the depolarisation process which appears near the reversible hydrogen potential after this anodic treatment is greatly influenced by stirring the solution. In one experiment about 25 secs. were required in a number of successive anodic polarisations with a current of 1990 × 10^{-7} amp. for the potential to reach + 0·07 volt, whereas when the solution was stirred in a stream of hydrogen, the potential had reached only −0·04 volt in 900 secs. (*i.e.*, after the passage of 0·18 coulomb). On stopping the stirring, it fell to + 0·07 in 13 secs. In another experiment the stirring was started without any interruption of the current when the potential had reached + 0·07. The potential rose again to − 0·05 and remained nearly constant, but on cessation of the stirring it fell in a short time to more positive values. The depolariser is therefore brought up to the surface of the electrode by stirring the solution, and can hardly be other than the hydrogen of the solution.

Nevertheless, even when the solution is stirred the anodic process does not continue indefinitely. A series of experiments was carried out in which the electrode was repeatedly anodically polarised to + 0·07 volt, with 1 min. intervals while the solution was stirred. The following are the successive times taken to reach + 0·07 volt: 60, 77, 54, 51, 49, 43, 40, 48, 40, 37, 24, 22, 13, 11, 9, 7, 4 secs. The gradual decrease in the length of the process must be due to the loss of activity of the electrode rather than a failure of the supply of hydrogen, for long stirring after the last curve did not increase the time.

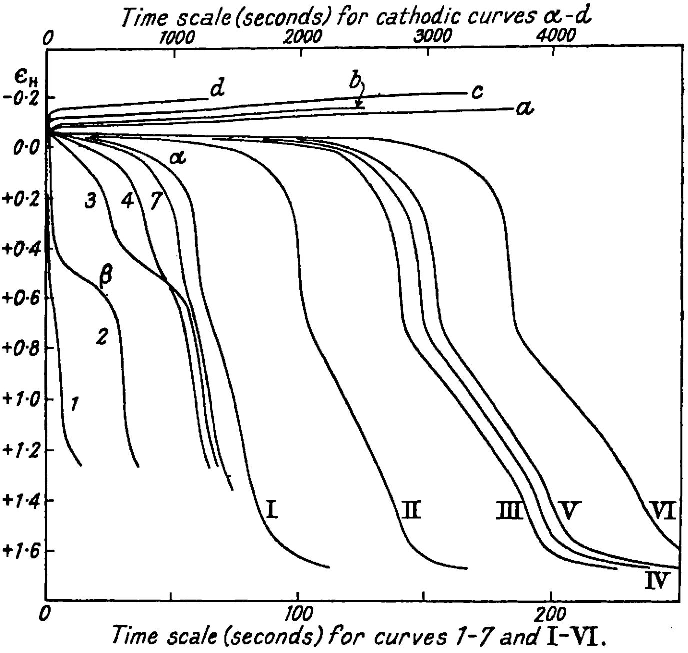
The hydrogen (cathodic) over-voltage of the "activated" electrodes is also extremely low. Some cathodic curves for electrodes which have been previously polarised to + 1·7 are shown in Fig. 3, curves (*a*)—(*d*). The potential remains nearly constant a few centivolts above the reversible hydrogen potential for a considerable time. It is thus evident that an electrode which has been anodically treated behaves as a reversible hydrogen electrode, anodic and cathodic currents causing only a small displacement of the potential from the reversible value. In this active state the electrode responds very readily to changes in the p_H of the solution, and has been used in this laboratory for performing electrometric acid–alkali titrations. Good titration curves can be obtained with the Hildebrand type of electrode holder, using a bright platinum electrode which is occasionally " activated " by anodic polarisation.

The electrode loses its activity after standing in the solution for some hours at open circuit. The activity is also destroyed by long-continued cathodic polarisation, for, as can be seen from curves (*a*)—(*d*), Fig. 3, the hydrogen over-voltage gradually rises towards its normal value.

Fig. 4 shows some cathodic current–potential curves obtained with an electrode which had been " activated " by anodic polarisation. Curve I was obtained immediately after the recovery from the anodic polarisation. The potentials shown are those reached after 100 secs.' cathodic polarisation with the various currents, a very nearly constant potential being reached in this time. A linear relation is obtained between the potential and currents from 0 to 2000 × 10^{-7} amp. With larger currents, the potential rises continuously and no nearly constant value can be given.

FIG. 3.

Successive anodic polarisations to +1·67 *volts.*



Curves 1–7 : *Successive anodics to* +1·27 *volts.*
Curves I–VI : *Successive anodics to* +1·67 *volts.*
Curves a–d : *Cathodic curves after anodic polarisation to* +1·67 *volts.* a, 710; b, 1470; c, 3018; d, 5480 × 10^{-7} *amp.*

In order partly to deactivate the electrode, it was now polarised anodically for a time with a small current, and the cathodic current–potential curve then redetermined. By successive treatments in this way Curves II—V were obtained. (Two similar curves were obtained between curves I and II, after the anodic passage of 1 × 10^{-3} and 1·8 × 10^{-3} coulomb respectively.) These are also linear within 0·04 volt of the reversible potential, but the slope di/dV decreases as the electrode loses its activity. The great effect of the anodic treatment can be seen by comparison with curve VI, which was obtained with an electrode which had previously received only a short cathodic polarisation.

A similar set of curves was obtained when the deactivation of the electrode was brought about by cathodic polarisation with a large current between the individual curves.

DISCUSSION.

The linear relation between the cathodic current and the potential of the "active" electrodes can easily be shown to be a consequence of their reversibility. If i' is the rate of transfer of electrons from the metal to the solution, and i'' the rate of the reverse process by which electrons are returned to the metal, the total current at the potential v is given (Butler, *Trans. Faraday Soc.*, 1932, **28**, 379) by

$$i = i' - i'' = k'e^{-b'(V-V_0)} - k'e^{+b''(V-V_0)} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

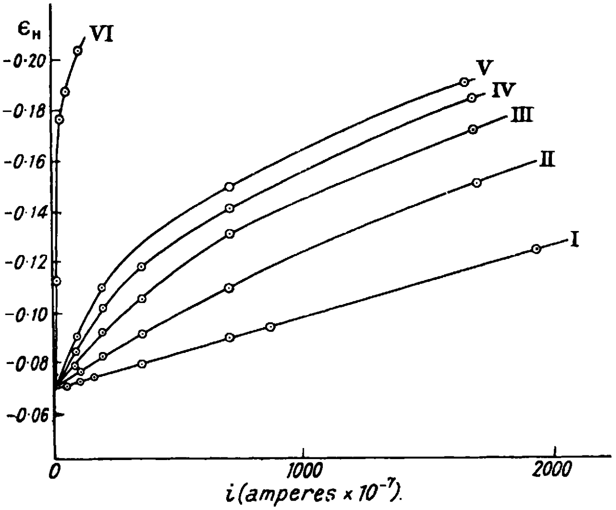
where V_0 is the reversible potential, or for small values of $V - V_0$,

$$i = -k'(b' + b'')(V - V_0) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

i.e., the displacement of the potential difference is proportional to the current. This approximation holds only within a few centivolts of the reversible potential, but the range of *currents* over which it holds increases with the value of k'.

FIG. 4.

Cathodic current–voltage curves of platinum electrodes after anodic treatment.



I. *Immediately after activation by anodic treatment.*
II–V. *After anodic polarisation with small currents. Total previous anodic polarisation,* II, 6·4; III, 10·0; IV, 16·0; V, 20·0 × 10^{-3} *coulomb.*
VI. *Normal curve of unactivated electrode.*

The slope di/dV of the linear part of the curve is proportional to k'. The effect produced by the anodic treatment, as compared with a normal electrode, is thus a great increase in k', *i.e.*, in the rate of transfer of electrons from the metal to the solution at a given potential difference. At the same time the electrode becomes reversible, *i.e.*, there is a reverse process which has the same magnitude at the reversible potential.

According to Gurney's theory k' is proportional to $e^{-\phi/2RT}$, where ϕ is the thermionic work function of the metal. The increase in k' produced by the anodic treatment might therefore be due to a decrease in the thermionic work function of the metal. This is, however, by itself insufficient to account for the simultaneous increase of the rate of the reverse process. Since it has been shown that the depolarisation process α is caused by the hydrogen of the solution, there are two possible mechanisms : (1) the direct transfer of electrons from hydrogen molecules in the solution as $H_2 = 2H^+ + 2\varepsilon$; (2) the preliminary adsorption or solution of hydrogen in the metal, followed by its ionisation, as H (metal) = ε(metal) + H^+. Now, the rate of transfer of electrons from a substance in the solution to the metal will be influenced by the thermionic work function of the metal in the opposite sense to a transfer from the metal to the solution. A lowering of this function, which is required by the reduced hydrogen over-voltage, will therefore not account for the increased rate of the reverse process, so the mechanism (1) is not adequate. If, however, the rate of adsorption is great, hydrogen being replaced at the surface as fast as it is ionised as in scheme (2), the observed effects due to depletion of the hydrogen near the electrode might be obtained. The observations might thus be accounted for if the anodic treatment produces a change wherein (1) the thermionic work function of the metal is reduced, (2) the adsorption of hydrogen and its ionisation are facilitated.

We must now consider the nature of the change brought about by the anodic polarisation. In the first place, it might be thought that the anodic polarisation removes a layer of some metallic impurity which has been deposited on the electrode while standing in the solution, or during the cathodic polarisation, leaving a clean surface of platinum. If this were the case, however, the solution of the metallic impurity would appear as a stage in the anodic curve, and it would, in fact, be necessary to identify it with the depolarisation process observed at about + 0·5 volt. Arguments against this supposition have already been given (Part I). In addition, it would be expected that the electrode would become active at the end of this stage, *i.e.*, as soon as the removal of the impurity is completed. Actually the activation process begins at the lower depolarisation stage, which has been ascribed to the formation of adsorbed oxygen. It is therefore reasonable to suppose that the activation is brought about in some way by the adsorbed oxygen. Since it is almost certain that the adsorbed layer of oxygen is reduced during the spontaneous recovery of the electrode potential in hydrogen, it is necessary to look for some change in the surface brought about by the deposition of adsorbed oxygen and its subsequent reduction.

It has frequently been observed that the catalytic activity of metals is increased by alternate oxidation and reduction. In such cases, however, a considerable amount of oxidation usually takes place, and there is no difficulty in postulating a considerable rearrangement of the surface layers. In this case the extent of the " oxidation " certainly does not exceed a single layer of adsorbed oxygen atoms, for it has been shown that the electrode is activated by anodic polarisation several times to + 1·26 volt, which is near the beginning of the stage in which the deposition of adsorbed oxygen occurs. It follows that the change brought about by the anodic polarisation is not deep-seated. That comparatively small differences of spacing in the surface layer might have a considerable influence on the ease of adsorption and dissociation of hydrogen is shown by the calculations of Sherman and Eyring (*J. Amer. Chem. Soc.*, 1932, **54**, 2661), who found that the energy required for the chemi-adsorption of hydrogen by carbon has a minimum value for a carbon–carbon spacing of 3·6 Å., which is considerably greater than the usual (1·58 Å.).

SUMMARY.

1. The anodic polarisation of bright platinum electrodes in hydrogen-saturated solutions has been investigated. After cathodic polarisation with small currents, and after contact with the solution for a considerable time, a process is observed at $\varepsilon_H = + 0{\cdot}5$ volt, which is attributed to the ionic solution of hydrogen dissolved in the metal. No depolarisation has been observed under these conditions which can be ascribed to the direct action of the hydrogen of the solution.

2. Experiments have been made to elucidate the remarkable effect of anodic polarisation on the behaviour of the electrodes. After several anodic polarisations to or beyond the point at which oxygen is first liberated in an adsorbed state, depolarisation by the hydrogen of the solution takes place near the reversible hydrogen potential with great ease. In this state the cathodic current–voltage curve is linear with the current over a considerable range, and in this and other respects the behaviour is that of a completely reversible electrode. These effects may be accounted for if the anodic treatment causes a change in which (1) the thermionic work function of the metal is reduced; (2) the adsorption of hydrogen at the surface of the electrode and its subsequent passage into solution as hydrogen ions are facilitated. A possible cause of such changes is suggested.

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