CXIX.—*Overvoltage. Part I. A Comparison of the Methods of Determination, especially as Applied to the Mercury Cathode.*

By SYDNEY DUNNILL.

THERE are two main difficulties which stand in the way of a quantitative theory of overvoltage.

(1) Metallic surfaces cannot be reproduced exactly, and their properties change during the passage of the current.

(2) There is still a considerable difference of opinion as to which of the methods of determination gives the true value, namely, the "commutator method," by which the potential of the electrode is measured at a small interval, say 0.012 second, after the main

P P 2

current has been cut off, or the "direct method," by which the potential is taken while the current is flowing. The first difficulty, however, does not arise in the case of the mercury cathode, and hence that was the electrode with which the present investigation was begun.

The most complete studies of the mercury cathode are those of Tafel (*Zeitsch. physikal. Chem.*, 1905, **50**, 641), Lewis and Jackson (*ibid.*, 1906, **56**, 193), and Newbery (T., 1914, **105**, 2419; 1916, **109**, 1051).

Tafel employed the direct method upon a mercury surface of 25 sq. cm. The results from overvoltages of 1.0 volt to 1.2 volts could be represented by the equation $E = a + b \log I$, where E is the overvoltage, I is the current, and a and b are constants. Lewis and Jackson, also using the direct method, measured the overvoltage at a mercury cathode contained in a tube of 0.2 cm. diameter. The same form of equation was found to hold from overvoltages of 0.3 volt, but at about 0.7 volt the readings became unsteady and the measurements were not carried further. At this point also, bubbles began to appear down the side of the tube to a distance of 1 cm. below the mercury surface. Newbery, using the commutator method, with the mercury in a tube of 1 sq. cm. cross-section, found exceedingly erratic overvoltages with a general tendency to decrease as the current was increased. At the highest current densities, zero and even negative readings were recorded.

The difference between the results given by the two methods is strikingly shown in the following table of overvoltages at a mercury cathode in *N*-sulphuric acid. The current density is given in milliamperes per square centimetre.

Current density.	Tafel.	Newbery.
1	1.07	—
10	1.18	0.54
40	1.24	—
100	—	0.30
1000	—	-0.01
2000	—	-0.05

EXPERIMENTAL.

With the object of using a definite volume of mercury, the first experiments were made with the mercury in a small cup blown on the end of a capillary tube. Progress, however, was found to be impossible, since the current could not be passed for more than a few minutes without the breaking of the mercury thread in the capillary owing to the formation of a bubble of gas.

Experiments were then made in which the mercury covered the

bottom of a crystallising dish and at the edge was connected with the source of current by a platinum wire sealed into glass. The anode was a platinum wire suspended in the centre of the dish about 0.5 cm. above the mercury. *N*-Sulphuric acid was the first electrolyte used, in a dish of 11 cm. diameter.

Bubbles form quite smoothly over the surface until the current exceeds about 50 milliamperes. There now appears below the anode a circular patch quite free from bubbles. The diameter of the patch increases with increasing current and at 100 milliamperes is about 7 cm. By the observation of moles it can be seen that the mercury surface is flowing rapidly outwards from the centre. Thus the mercury, after receiving current, travels outwards for some distance before visible bubbles have time to form, the hydrogen being either in the mercury or in the solution near the surface. About 0.5 cm. within the circumference of the bare space there is a slight discontinuity, similar in appearance to the bevel on a mirror. Possibly this marks the limit of the actual movement of the mercury while the stream of solution clears away the bubbles for a short distance further.

The phenomenon is readily accounted for by a consideration of the electrocapillary curve. In *N*-sulphuric acid the potential of mercury at which hydrogen is being liberated is higher than the potential of mercury of maximum surface tension. Hence, the mercury in the centre, which is receiving most current, being at a higher potential, has a lower surface tension than that nearer the circumference, and because of this the mercury at the centre is being continuously dragged outwards. This view is confirmed by the following observations :

(1) The same phenomenon occurs, but more readily, when the mercury is acting as anode, that is, on the other branch of the curve. This can best be seen by removing the platinum connexion from the mercury and suspending it in the solution a short distance above the surface. The discontinuity is seen in this case also.

(2) With the mercury as cathode in mercurous nitrate solution, the surface tends to draw towards the centre. Here the potential is on the same branch of the curve as in (1), but the mercury is being polarised in the opposite sense, so that the mercury at the centre now has the higher surface tension.

(3) In alkaline solution, where the surface tension decreases rapidly with increasing cathodic polarisation, the ring is especially large. A normal solution of ammonium hydroxide containing in addition 66 grams of ammonium sulphate per litre was used as electrolyte in a 14 cm. dish arranged as before. With a current

of 100 milliamperes no gas appeared for several minutes and the whole surface of the mercury seemed to be travelling out to the edge. The flow continued underneath the mercury and small bubbles, together with some of the solution, were seen between the mercury and the bottom of the dish, moving towards the centre, where, no doubt, the ammonium amalgam was accumulating. The solution and the gas bubbles would collect together in places and occasionally burst through the mercury, leaving an effervescing patch which immediately floated on the mercury to the side of the dish. Apart from this, the surface remained quite blank. On opening the circuit the surface moved in a direction opposite to that previously observed and large areas of effervescing amalgam were drawn round the edges on to the upper surface of the mercury. In this case, in addition to the purely electrical effect, there will, of course, be some change of surface tension due to formation of the amalgam, although whether this produces an increase or a decrease is unknown.

Potential measurements were now made in order to determine the effect of this phenomenon on the overvoltage as given by the commutator method, since the motion of the mercury would be likely to cause a very rapid fall of potential when the current ceased to flow. The general arrangement of the apparatus was similar to that described by Newbery (T., 1914, **105**, 2419). The rotating commutator used was of the type known as the MacGregor drum. It was driven by an electric motor which could be set at three speeds, giving approximately 0.020 sec., 0.013 sec., and 0.010 sec. respectively as the mean interval between the interruption of the main current and the reading of the potential. When the commutator was applied, the mercury was thrown into stationary vibrations, which removed the bubbles from the surface except at the nodes, which were several millimetres apart. At higher speeds the distance between the nodes became less.

The mercury cathode filled a small, shallow, glass dish, connexion being made by a platinum wire sealed into a glass tube. The surface area of the mercury was approximately 10 sq. cm. The anode was of platinum foil contained in part of a test-tube drawn out to a point, leaving an opening of 0.1 cm. diameter. This was supported a few millimetres above the surface of the mercury.

The electrolyte was *N*-sulphuric acid and the potential was measured with reference to a mercurous sulphate electrode in the same solution. A capillary electrometer was used as zero instrument. The syphon connecting the main solution with the reference electrode terminated in a capillary of about 0.01 cm. internal diameter, which could be adjusted exactly to any point on the

mercury surface. Except where otherwise stated, the capillary touched the mercury immediately below the anode.

All the experiments were made at room temperature, that is, at about 12°.

In the following table a few of the results are shown. The current is given in milliamperes. The figures are the overvoltages measured directly and with the three speeds of the commutator, assuming the combination $H_2 | N-H_2SO_4, Hg_2SO_4 | Hg$ to have an *E.M.F.* of 0.70 volt.

Current.	Overvoltage.			
	Direct.	0.010 sec.	0.013 sec.	0.020 sec.
36	1.14	0.85	0.82	0.75
68	1.23	0.83	0.79	0.71
68	1.22	0.73	0.67	0.51

The last series gives the results obtained when the solution was stirred by means of a stirrer with vanes driven at 250 revolutions per minute. It is seen that stirring had very little influence on the potential while the current was passing, as would be expected, since the mercury surface was already in rapid motion. The rate of decay, however, was considerably increased.

The overvoltage values obtained by the direct method were quite steady and after an initial rise were fairly accurately reproducible, a slight increase with time being most likely due to concentration changes. The following figures were obtained by means of the same apparatus as before, with the opening into the anode compartment 0.25 cm. above the centre of the cathode. The solution was stirred for a short time after each change in the applied *E.M.F.*, but was allowed to come to rest before the reading was taken.

On first passing a current of 11 milliamperes the centre of the cathode had an overvoltage of 0.85 volt, which became 0.87 volt at 22 milliamperes. Up till then no ring had appeared, but when the current was interrupted for a few seconds and applied again, a ring was formed, which still remained when the current was reduced to 11 milliamperes. Readings were then taken, the current being gradually increased to 78 and then brought back to lower values.

Current.	Overvoltage.	
	increasing.	decreasing.
11	0.93	0.94
20	1.02	1.02
35	1.11	1.12
50	1.18	
78	1.26	

The bare space becomes larger with increasing current, but the circumference does not remain at a constant potential. At 20 milliamperes, the diameter was about 1.8 cm. and the overvoltage at the boundary of the space was 1.00 volt, whilst at 78 milliamperes, with a ring of about 2.5 cm. diameter, the overvoltage at the circumference was 1.12 volts.

The overvoltages given above are similar to those of Tafel, although in his experiments a ring was most likely not formed owing to the more equal distribution of the current.

Since the mobility of the mercury surface introduces complications, experiments were made with a cathode of amalgamated lead. This consisted of a small rod of lead fixed into a glass tube with sealing wax and covered with paraffin wax except over an area of about 1 sq. cm. at the end, which was amalgamated. Mercury contained in a crystallising dish formed the anode. The electrolyte was *N*-hydrochloric acid. The potential was measured against a calomel electrode, also in *N*-hydrochloric acid, and connected as before with a fine capillary touching the cathode.

The solution was contained in a wide-mouthed bottle provided with a cork, through which passed the connexions and the sleeve of the stirrer. Hydrogen was bubbled through the solution for two days before readings were taken. The results were similar to those obtained for mercury, as is shown by the following example. The combination $H_2 | N-HCl, Hg_2Cl_2 | Hg$ is taken as having an *E.M.F.* of 0.28 volt.

Current.	Overvoltage.			
	Direct.	0.010 sec.	0.013 sec.	0.020 sec.
5	1.20	0.91	0.89	0.86
5	1.19	0.77	0.74	0.62

In the second series the solution was stirred.

Obviously the overvoltage decays too rapidly for any decision to be made as to the true value.

The same apparatus was used in the next experiments, except that the electrolyte was *N*-sodium hydroxide, with a reference electrode of mercuric oxide. A current of 1.2 milliamperes was maintained throughout the whole series. The overvoltage diminished while the current was passing to the extent of 0.2 volt in forty-five minutes and the cathode became dull owing to deposition of sodium. The following is a typical set of consecutive readings

$(H_2 | N-NaOH, HgO | Hg = 0.930 \text{ volt}).$

Direct.		0.020 sec.	0.013 sec.	0.010 sec.	Direct.
0.875	0.878	0.852	0.855	0.856	0.870

It seems scarcely justifiable to compare the results when a direct

current is used with those obtained by means of the intermittent current. The second drum of the commutator enabled the potential to be taken during the latter half of the period in which the current was passing, leaving the electrometer circuit open during the remainder of the time. This potential is given in the second column above.

Discussion of Results.

The earlier experiments with the mercury cathode provide an explanation of several previous observations. A mercury cathode in a narrow tube where the sides are wet with the solution but are receiving very little current is in a similar condition to that of a pool of mercury with the current concentrated at one point on the surface. The outward flow of the mercury, bringing with it a layer of solution supersaturated with hydrogen and perhaps itself containing hydrogen in some form, is quite sufficient to account for the appearance of bubbles down the side of the tube. As the current is increased, the movement will become more rapid and the potential will fall more quickly should the current be interrupted. This is shown by the decreasing values obtained by the commutator method. The fall of potential is so rapid that small changes in the motion of the mercury, by changing the rate of decay, would produce erratic variations in the potential readings at a given interval of time.

The stationary waves produced by the commutator are in themselves sufficient to show that changes of surface tension, denoting changes of potential, take place during the interval in which no current is flowing.

Results previously obtained by the direct method have shown for all metals an increase of hydrogen overvoltage with the current, whereas the commutator method shows an increase in alkaline solution, but in acid solution there appears to be always a slight decrease. This is most likely owing to the stirring of the solution round the cathode by the bubbles of hydrogen, since, as is shown above, stirring considerably increases the rate of decay of the polarisation. At higher current densities more hydrogen is evolved and hence the stirring is more vigorous.

According to Newbery, the results obtained by the direct method are inaccurate owing to the electrical resistance of a film of gas which is said to be present on the electrode. It would be difficult to give a direct proof of the presence of this film. The paper by Newbery on "The Electrical Resistance of an Electrolytic Cell" (*Trans. Faraday Soc.*, 1919, **15**, Part I) contributes nothing to this discussion, since it is assumed at the outset that the difference

between the overvoltages determined by the two methods is due to "transfer resistance," whereas a rapid fall of potential during the first one-hundredth of a second would have exactly the same effect. The "transfer resistance" was found to be very high at low current densities, but became much smaller when the current density was increased. This is owing to the fact that the fall of potential varies much less rapidly than the current, so that at higher current densities the hypothetical resistance necessary to account for the loss of *E.M.F.* becomes smaller.

However, the experiments with an alkaline solution show that, in this case at least, the resistance film, if it exists at all, does not produce an error of more than 20 millivolts. Oscillograph measurements would most likely prove that the possible error was much smaller than this, as the rate of decay in the first one-hundredth of a second is usually greater than that found afterwards. It is improbable that there is any considerable variation in the mechanism of bubble formation at different electrodes. Further, we should not expect the overvoltage to vary very much on changing the electrolyte, and the overvoltage values obtained by the commutator method with a freshly-amalgamated electrode in alkaline solution approximate to those given by the direct method in acid solution.

We may thus conclude that in all cases the direct method gives very nearly the true value of the overvoltage. The commutator method is incapable of giving accurate results, the error amounting to several tenths of a volt for cathodes with acid electrolyte and being especially large for the mercury cathode in acids.

Summary.

(1) A description is given of a remarkable phenomenon depending on the change of surface tension with potential at a mercury electrode.

(2) The overvoltages at cathodes of mercury and amalgamated lead have been measured by the direct method and by the commutator method.

(3) These experiments show that the direct method gives the more accurate results.

The author's thanks are due to Professor Sir James Walker for helpful advice in the presentation of this paper.

CHEMISTRY DEPARTMENT,
UNIVERSITY OF EDINBURGH.

[Received, May 6th, 1921.]