VII. A SIMPLE HYDROGEN ELECTRODE.

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For methods to estimate the true reaction of a liquid biologists are indebted to a series of investigators, of whom only Sørensen [1909], Hasselbalch [1911, 1913], Michaelis [1909, 1912] and Walpole [1913] may be mentioned. The last of these has succeeded in constructing hydrogen electrodes, which allow very rapid and easy estimations.

Fig. 1.

However, the apparatus, which Walpole used, is not simple and strong enough for continuous use and does not give all the security which is obtainable.

In the accompanying Figure 1 a modified arrangement is represented; which has proved still more serviceable for everyday work on the open bench without a constant temperature bath.

The hydrogen electrode is here simply a bent piece of glass tube (Jena glass), with a platinum wire sealed in its wall. The form of this glass tube, as will be shown further on, is carefully devised to meet all the requirements brought out by previous investigations. By means of a piece of rubber tubing it is connected to a perforated brass or copper syringe.

In carrying out an estimation, the hydrogen is first admitted through the tap, while the piston is still pushed home. After shutting the tap, the gas is nearly all contained in the electrode tube itself. By drawing the piston out and in several times, equilibrium between the enclosed hydrogen and the

Fig. 2.

carbonic acid, which the liquid may contain, is better secured with this arrangement than with the apparatus of Walpole, where there is a considerable dead space behind the electrode tube. The sample, which is at last drawn up into the tube, when the gas-equilibrium is established, is evidently a fresh one.

Michaelis found, that a definite potential was much sooner attained, if the electrode only just dipped into the liquid. Konikoff [1913] drew attention to the fact, that dissolved oxygen might combine with the hydrogen of the electrode, which explained the fact observed by Michaelis. By submerging only a small point of the electrode a lasting saturation with hydrogen is sooner and better secured.

As the liquids to be examined in a biological laboratory often contain carbonic acid and oxygen, dissolved or loosely bound, it is important to take account of both of them.

As long as the liquid near the electrode contains some oxygen, this combines readily under the influence of the platinum black with the hydrogen of the electrode, thereby lowering its solution tension, i.e. its potential.

To secure a quick and automatic removal of the oxygen from the actual sample in the electrode tube I first tried to bring into this tube a second piece of blacked platinum wire, not connected with the electrode.

Figure 2 illustrates the experiments, made with this arrangement. Only the hydrogen electrode and the stretched wire *AB*, which served as potentiometer, are represented here. *A* is the point where the slide, connected with the gas cell, compensates the current from the accumulator. If now, before repeating the experiment with the same liquid, we bring inside the electrometer tube a platinum or gold wire with some platinum black on it, the other end of the wire coming out free into the air, the electrometer shows a large current, if the slide is pressed down in point *A*. Generally the slide has to be moved a considerable distance to the left (positive side), seldom to the right. If, however, we press the free end of the second wire, insulating it from the fingers with a piece of rubber tubing, on the potentiometer wire to the left of *A*, a point *B* can be found, at which the influence of the second wire is eliminated. This equilibrium does not last long. To maintain it we must gradually move the point *B* further to the left.

The interpretation of these facts is as follows. Ionised hydrogen can pass freely from the one blacked wire to the other. The hydrogen in the platinum black of the second wire will soon be oxidised by the oxygen, dissolved in the liquid, to which it is on all sides exposed; its solution tension will be lowered and it will therefore take more and more hydrogen out of the electrode. This transport of hydrogen is stopped, if we bring the second wire to a potential so much higher than that of the electrode, that the difference in solution tension of the hydrogen in the two wires is just compensated. The progressive oxidation of the hydrogen in the second wire will require a gradually increasing potential difference to do this.

If we pass hydrogen again through the electrode tube, while the second wire is inside it, both blacked wires will be saturated with hydrogen and therefore show no potential difference. This was observed repeatedly. Shortly after a renewed passage of hydrogen the point *B* came very near to *A* and then had gradually to be moved again to the left.

After saturating the liquid in the beaker (Sørensen's phosphate mixtures were mostly used in these experiments) with oxygen, *B* must be moved still more quickly away from *A*.

A blank platinum wire, introduced into the electrode tube, gives no effect at all, if its other end comes out free into the air. Neither does a gold or copper wire. If the other end is pressed on the potentiometer wire, very irregular effects are obtained by polarisation.

By these experiments it became clear, that the necessary removal of the oxygen from the liquid near the electrode wire had to be performed by the blacked platinum electrode itself.

I therefore placed the electrode as indicated in Fig. 1 with its point near the narrow part of the tube. If now, after securing the carbonic acid equilibrium as described in the beginning, the surface of the actual sample of liquid to be examined is several times drawn up and down the blacked wire (not higher and not lower), it is quickly reduced by the hydrogen in the relatively large surface of blacked platinum wire. The diameter of the platinum wire is about 0.6 mm., the inside diameter of the tube around it about 4 mm. By then pushing the reduced liquid down the long narrow end of the electrode tube until its surface is near the platinum point, we prevent original, not reduced, liquid from diffusing into the neighbourhood of the electrode.

With this arrangement it did not prove absolutely necessary to make the liquid just touch the electrode, though it is quite as simple and safer to observe this precaution.

These operations for securing the equilibrium of the carbonic acid and the removal of the oxygen take only a very short time, less than a minute.

Before this improvement was worked out, an increase of a few millivolts was generally noticed in the potential during the first minutes. The fact, that freshly boiled liquids did not show this phenomenon, drew attention to the marked influence, above described, of oxygen, often even of some dissolved air.

The glass bead on the electrode tube serves to fasten the thin copper wire, which is soldered to the outer end of the platinum wire.

The other half of the galvanic cell, represented in Fig. 1, has also proved to be very useful. A bottle of some 150 cc., filled with saturated KCl, is closed by a rubber stopper, through which three tubes pass. The wider one is the mercury-calomel-saturated KCl electrode proper, a tube, closed at the bottom, but with two openings in its side. The second is a capillary tube

with a tap and connected by a small piece of rubber tubing to a capillary, filled with cotton wool. The third tube serves simply to prevent air-pressure in the top of the bottle from causing inconvenience. This electrode bottle has been in use for months without needing any refilling or cleaning. The tap, which is not greased, remains always closed. There proved to be sufficient conductivity and even some capillary transport of KCl solution down the open cotton wool tube, purifying automatically the open end of it, which has dipped in the examined liquid; usually, in the morning, some KCl was found to have precipitated round the opening. Both glass tubes, dipping in the titrated liquid, may of course have smaller dimensions if the available volume is very small. The usual capacity of my electrode tube was about 0.3 cc.

SUMMARY.

A simple arrangement for the estimation of the true reaction of liquids, which remains always ready for use, is described and explained. It is in some points an improvement on Walpole's electrometric titrating apparatus for the open bench, special provision being made for allowing instantaneous and accurate estimations even in liquids, which contain carbonic acid and oxygen.

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