

A QUICK-ACTING HYDROGEN ELECTRODE

BY P. J. MOLONEY

When the hydrogen electrode is used for determining the acidity (hydrogen-ion concentration) of solutions, it is assumed that the platinum is in equilibrium with hydrogen at atmospheric pressure; the absorption of hydrogen by platinum, however, is far from instantaneous, and if the electrolyte contains dissolved oxygen or an oxidizing agent, the concentration of hydrogen in the platinum will be lower than that assumed, and the conclusions drawn from the E. M. F. measurement will be erroneous. When working with synthetic solutions this source of error can be avoided by using pure chemicals and working in the absence of air; with blood, sera, etc., the method adopted is to reduce the oxidizing substances, if any are present, by the continued action of the hydrogen and the platinum of the electrode. In the cells of Hasselbalch, Clark, Hildebrand,¹ etc., this result is brought about by shaking the liquid with hydrogen gas and a fairly large electrode of platinized platinum sheet. In the cell known as Michaelis', shaking must be avoided altogether, and the electrode previously saturated with hydrogen is allowed merely to touch the surface of the liquid; there is here no attempt to remove oxidizing agents from the bulk of the solution, only a small film immediately surrounding the electrode is reduced and if the apparatus be jarred, fresh solution is brought in contact with the platinum, and the E. M. F. changes at once.

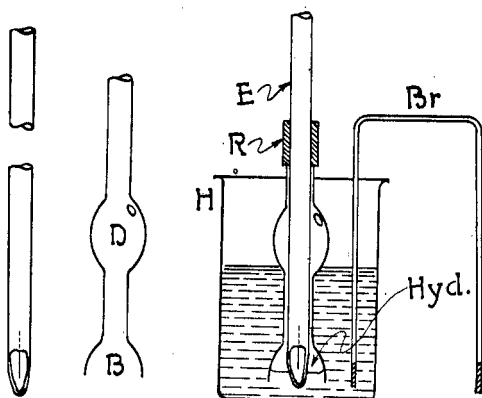
During the past year I have had occasion to make hundreds of these determinations, and after much experience with the usual forms, have devised a hydrogen electrode which combines the advantages of both types referred to above. In this new apparatus, the platinized platinum wire is surrounded

¹ Illustrations of the common forms are given in W. M. Clark: "The Determination of Hydrogen Ions," 138 (1920).

by a drop of the liquid to be measured which is held in position by capillarity and is surrounded by an atmosphere of hydrogen. Oxidizing agents are thus removed from only a small quantity of liquid, and as in Michaelis' form equilibrium is rapidly attained; on the other hand, as all the liquid that can come in contact with the platinum is reduced, jarring is without effect, and the advantages of Clark's form are retained.

This electrode has been in constant use for several months for determining the acidity of broths used in the culture of bacteria; as the results agree with those obtained from a cell of the Clark form, while the manipulation is simpler and very much quicker, I thought that a description of the apparatus might prove of general interest.

Electrode and Loop.—The electrode (see Fig. 1) consists of a platinum wire sealed into a glass tube of 4 mm diameter; 4 mm of the end of the wire is exposed, contact is made through



Figs. 1-3

mercury in the usual way. On either side of the wire there is sealed to the glass tube a small piece of glass rod, 1 mm in diameter; these two are joined at the bottom to form a loop, as shown in the figure; the length of this loop should be 9 to 10 mm, it is to hold the drop of liquid in which the platinum is immersed. The glass rods should be sealed well towards the edge of the tubing, but should not extend beyond the sides,

so that there may remain a gap of at least one-half millimeter between the platinum wire and each side of the loop. When the glass-blowing is finished, the wire is platinized in the usual way.

Bell-Tube.—The electrode has been used with several types of holders, a convenient form is shown in Fig. 2; it is made from a piece of tubing just large enough to slip over the electrode tube without binding. A bulb D is blown near the lower end of the tube, and a small hole about three-quarters way up the bulb; a bell B is then blown at the bottom of the tube; the distance from the bottom of the bulb to the top of the bell should be about one centimeter.

Operation.—The electrode tube E is slipped into the bell tube H, and a piece of rubber tube R fitted over the joint so that the relative position of electrode and bell can be easily adjusted. The electrode is pulled up until wire and loop are within the bulb, and the whole is immersed in the liquid to be measured (which may be in an open vessel) until the tube connecting bulb and bell is filled. The apparatus is held in this position by means of a clamp, and the electrode is pushed down until wire and loop are in the bell; hydrogen is then introduced under the bell, and the electrode adjusted until the wire is surrounded by hydrogen, while the lower end of the loop dips into the main body of liquid in the bell (see Fig. 3). Connection between the main body of the liquid and the calomel electrode is made by a bridge Br, consisting of a capillary filled with saturated potassium chloride solution, both ends being plugged with cotton wool; when not in use, both ends of this bridge tube are left standing in tubes filled with the potassium chloride solution.

In making duplicate readings, when the solution to be measured is exposed to the air in an open vessel, it is safer not to renew the liquid in the loop (at least not more than once or twice) by merely lowering and raising the electrode; the electrode should be pulled up into the bulb, and the hydrogen renewed, as in the first instance.

Summary

(1) A new form of hydrogen electrode has been described in which the electrolyte is held by capillarity in a glass loop surrounding a platinized platinum wire, and surrounded in turn by an atmosphere of hydrogen.

(2) Equilibrium, as indicated by constant E. M. F., is reached very rapidly, usually in less than one minute; and the readings agree with those of a Clark electrode to within one millivolt.

(3) The electrode can be rapidly washed and sterilized.

(4) The liquid to be measured can be contained in an open vessel; but if it is proposed to measure electrolytes whose acidity depends on the presence of dissolved carbon dioxide, a closed vessel must be employed, such as a Michaelis' V tube, or a modification of Walpole's or Barendrecht's apparatus. With the open vessel it is obvious that the carbon dioxide would rapidly pass from the drop into the surrounding hydrogen, and the acidity as measured would be less than that of the original liquid.

I am glad of this opportunity to express my thanks to Professor J. G. Fitzgerald for the facilities he has placed at my disposal, and the continued interest he has taken in the progress of the work.

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