

The conclusions, drawn from the existence of the supposed hydrogen peroxide compound with regard to the reaction mechanism of the coupled oxidation of hæmochromogen and ascorbic acid, remain, however, correct. Hydrogen peroxide plays a part in this reaction, transforming porphyrin-hæmatin into oxyporphyrin-hæmatin. There is also evidence in favour of the existence of a hæm-hydrogen peroxide compound during the reaction. Whereas catalase completely prevents the formation of the oxyporphyrin-hæmatin from hæmochromogen and hydrogen peroxide, catalase inhibits the formation of this compound (and of verdohæmochochromogen) by atmospheric oxygen only partially. The most likely explanation is that the 'nascent hydrogen peroxide' is protected from the action of catalase by its combination with the molecule with which it is to react afterwards (that is, the hæm), and that the partial inhibition of the reaction by catalase is due to a partial dissociation of the hæm-hydrogen peroxide compound and catalytic destruction of the hydrogen peroxide set free by the dissociation.

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¹ NATURE, 139, 1016; 1937.

² Treibs, A., and Wiedemann, E., *Liebigs Ann.*, 466, 264 (1928).

³ Fischer, H., Halbig, P., Walach B., *Liebigs Ann.*, 453, 268 (1927).
Fischer, H., Gebhardt, H., and Rothhaas, A., *Liebigs Ann.*, 482, 1 (1930).

⁴ Fischer, H., and Lautsch, W., *Liebigs Ann.*, 528, 247 (1937).

Mechanism of the Glass Electrode

It is a well-known fact that new glass electrodes are not suitable for exact measurements until they have first been allowed to stand in water for some time. The continuous variation in potential observed with a new electrode may be connected with the property of the glass of taking up hydrogen ions. I have demonstrated¹ that hydrogen ions are exchanged for calcium and sodium ions in the glass electrode. The following experiments demonstrate the relation of the potential to the hydrogen ion uptake.

A series of bottles containing 2 gm. each of glass powder and 30 ml. of 0.1 *n* HCl were shaken at 25°. At different times bottles were removed and the liquid titrated with 0.1 *n* NaOH. From these data the amount of 0.1 *n* HCl (c_t) disappearing, equivalent to the amount of H taken up by the powder, after various lengths of time were found. The results of the titrations are given in Curve A (Fig. 1).

In order to determine whether measured potentials agree with those calculated from consideration of the chemical changes which occur, the following experiment was performed.

A spherical glass electrode was placed in each arm of a U-tube containing 30 ml. 0.1 *n* HCl and 2 mgm. glass powder in order to approximate the conditions in the experiment previously described. The inside of both electrodes and the outside of one of them had been in contact with 0.1 *n* HCl for a month, but the remaining outer surface had never been in contact with any solution. Silver wires covered with silver chloride were placed in contact with the inner liquid of both electrodes. The potentials of this system were measured periodically and the data obtained are represented by Curve B (Fig. 1).

In order to correlate the hydrogen ion uptake and the above-mentioned change in potential of new electrodes, the following assumptions have been

made. The initial hydrogen ion activity of the glass is assumed to be Pc_0 , where P is a constant, and c_0 is the number of hydrogen ions in the untreated glass per arbitrarily chosen unit of glass surface. At any time, t , after the immersion of the new electrode in hydrochloric acid, the number of hydrogen ions taken up is c_t , and the activity is now assumed to be equal

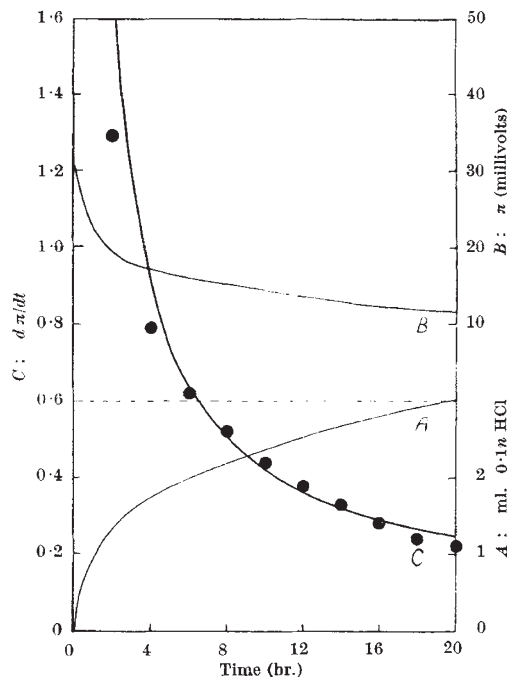


Fig. 1.

to $P(c_0 + c_t)$. Hence the variation of potential with time of the system is, when π is measured in millivolts, given by the equation:

$$\frac{d\pi}{dt} = \frac{RT}{F} \cdot 1,000 \frac{1}{c_0 + c_t} \frac{dc_t}{dt}$$

The values of $d\pi/dt$ and dc_t/dt at definite times are found graphically from Curves A and B in Fig. 1. The value 2.51 was found to be an approximation for c_0 . The details of the method of determining this value will be published elsewhere. This value means that 2 gm. of glass powder at the start of the experiment has a H ion content equivalent to 2.51 ml. 0.1 *n* HCl.

In Fig. 1, Curve C was constructed from the data obtained in the glass powder experiment and the points represent the values of $d\pi/dt$ derived from potential measurements.

From these experiments it appears that the suitability of a glass as an electrode depends upon its ability to exchange sodium and calcium ions for hydrogen ions. These experiments also confirm the hypothesis of Horowitz² published in 1923. From this point of view it should be possible to produce sodium, calcium and potassium electrodes by choosing a glass of the proper composition or a mineral of the permutit type. I am carrying out further investigations of these possibilities.

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May 12.

¹ *Tidskr. Kjemø og Bergvesen*, No. 4 (1937).

² *Z. Phys.*, 15, 369 (1923).