

## A Simple Method for the Verification of the Proton Conduction through Substances Containing Hydrogen Bonds.

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(Received 21, Dec. 1953)

### Introduction

A physical method for the direct verification of the proton conduction through the substance containing hydrogen bonds was reported by Kakiuchi, Komatsu and Kyoya in 1951, in whose experiment the electric current was made to flow through cetyl alcohol, and the evolved hydrogen gas was detected by means of the tedious spectroscopic methods.

The present author attempted to simplify the method by using a chemical detecting process instead of the physical method, and obtained the following results.

### Experimental Procedure

Zenghelis detected the fact that if hydrogen is introduced into the acidified molybdate solution in contact with platinum, molybdenum blue is produced quickly, even with as little as 0.5 C. C. of hydrogen in it. The present author used Zenghelis's principle and confirmed the advantages of the reaction in his preliminary experiments. The amount of electric current to be required to set 0.5 C. C. of hydrogen gas free will be no more than 1.1 m. A. H.

The experimental apparatus is shown in Fig. 1.

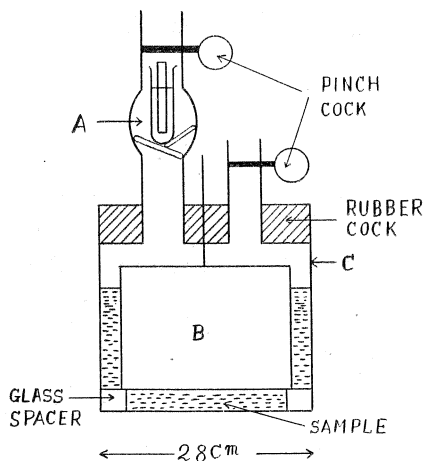


Fig. 1. Experimental apparatus

Brass vessel C and block B constitute two electrodes, which are both nickel plated. A is a small glass vessel (about 0.07 C. C.) containing a solution of ammonium molybdate and a platinum plate (15×3 mm.). The space above the sample was devised to be as narrow as possible; it was actually about 7 C.C. The air of the space was replaced by carbon dioxide gas lest the oxygen of the air should combine with hydrogen evolved through contact with platinum. Chemical purification of the carbon dioxide was made carefully. The vessel was immersed in the oil bath in which the temperature of the sample was regulated.

*Experimental results*

*Resorcin*

Commercial crude sample (m.p. 110°) was used. The conductivity curve was as in Fig. 2.

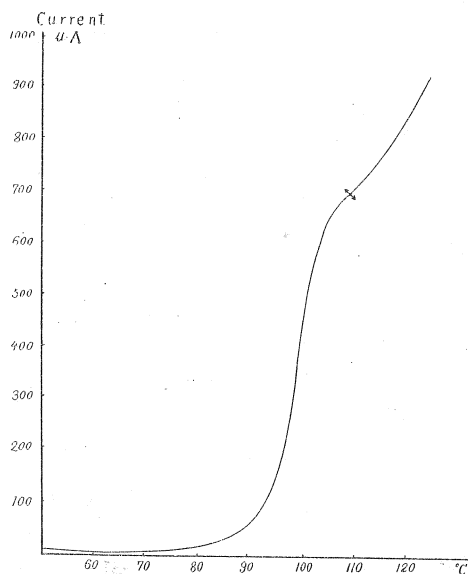


Fig. 2. Conductivity curve

The D. C. current of some 70  $\mu$ A under 135 V was made to flow for 3 hours through the sample whose temperature was kept within the range 80°—90°. 1.5 hours after, the solution turned bluish, and rich blue was observed 3 hours later. Without the current flowing, there would be no coloration. Next, A.C. current of some 200  $\mu$ A under 130 V was made to flow with the temperature within the range 80°—85°. In this

case the solution was not coloured at all even 4 hours later. In order to apply the current in liquid state the sample was kept at about 120° and the current about 3 mA under 130 V. In this case faint blue was observed after an hour. When A.C. current of some 3mA under 10 V at 115° was made to flow a faint blue was also observed.

From the results above it may be concluded that resorcin evolves hydrogen gas by D.C. current both in solid and liquid, but, A.C. current evolves the gas in liquid and not in solid state.

*Amilan*

A sample (m. p. about 210°) kindly offered by Toyo Rayon Co. was used. The contact resistance was so large that the sample was to be melted and fixed to the electrodes. Therefore it was melted between two nickel plates in vacuum and then solidified, and this was placed in a vessel instead of block B in Fig. 1. In this case the space above the sample became a little larger, but the conductivity of amilan was so large that the hydrogen evolved could be detected easily.

When D.C. current of some 1mA under 135V at 175° was made to flow for one hour faint blue was observed. In the case of A.C. current the faint blue was also observed when a current of some 1mA under 125 V at 170° was made to flow for two hours. It seemed that the amount of the hydrogen evolved was a little smaller than in the case of D.C. current.

From the results above mentioned, it may be concluded that amilan evolves hydrogen gas both in D. C. and A. C. currents in solid state. The fact that amilan evolves hydrogen gas in A. C. current in solid state is different from the case of

resorcin and cetyl alcohol which will be described later, and the softening of amilan at some  $170^{\circ}$  will be the causes of the fact. Perhaps the binding energy of the hydrogen bond will be comparable with the thermal energy at such the temperature. In the previous paper <sup>(3)</sup> the author reported that the decrease of the dielectric constant of amilan treated by D.C. or A.C. current would be caused by the decrease of hydrogen bonds in it, and this seems to have been verified by the present experiment.

#### *Cetyl alcohol*

The sample was the same as the one used in the previous experiment <sup>(3)</sup>. Its m. p. was  $48.5^{\circ}$ — $49^{\circ}$ .

Compared with resorcin and amilan, the conductivity of cetyl alcohol was so small, that the same procedure as above could not detect hydrogen, so the following device was attempted.

Two aluminum leaves ( $90 \times 2.5$  cm) and two silk ribbons immersed in cetyl alcohol liquid were rolled like a paper condenser and these were placed instead of B in the vessel in Fig. 1. By this procedure the current of some  $200 \mu$  A under 130 V could be made to flow at  $42^{\circ}$ , and the blue change of the solution was observed 3 hours after. In the case of A.C. current the change could not be found even when the current of  $400 \mu$  A was made to flow for 6 hours.

So it can be concluded that cetyl alcohol evolves hydrogen gas in solid state through D.C. current, but not through A.C. current.

This fact coincides with the explanation of the changes of dielectric properties reported in the previous paper <sup>(3)</sup>.

The author wishes to express his sincere gratitude to Professor T. Kiba and Professor H. Shoji for their kind guidance.

#### References

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- (2) Zenghelis : Z. Anal. Chem. 49 (1910), 729.
- (3) Ida : This Sci. Rep. 2 (1954), 23.