ON ELECTRICAL PHENOMENA OF PALLADIUM FILAMENT OCCLUDING HYDROGEN

Investigation of Hirota and Horiuti's Results

By

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Results of HIROTA and HORIUTI's experiments on electric behavior of a palladium filament occluding hydrogen were reexamined, but not reproduced.

Introduction

The state of hydrogen dissolved in palladium has long been a subject of a number of investigations. SIEVERTS and his co-laborators[1] have studied isothermal absorption of hydrogen by palladium, and found a linear relation between the amount of absorbed hydrogen and the square root of its pressure at equilibrium. This relation suggests that hydrogen molecule dissociates into atoms in palladium metal. COEHN and his co-laborators[2] have shown the migration of hydrogen through a palladium wire along the potential drop. This phenomenon suggests the presence of cationic hydrogen, or proton. DUHM[3] has extended the latter work and calculated an effective charge of proton by means of the NERNST-EINSTEIN relation from measured diffusion coefficient and mobility as twenty fifth of an elementary charge. FRANCK[4], HELZFELD and GOEPPERT-MAYER[5] and ISENBERG[6] have discussed the cause of ionization of hydrogen atom in palladium metal into proton and electron, concluding that proton existed in an energetically stable state surrounded by electron cloud.

HIROTA and HORIUTI[7] have investigated electrical phenomena of a palladium filament occluding hydrogen. They have preliminarily balanced with a steady current a WHEATSTONE bridge comprizing in one of its arms a palladium filament sealed in a glass cell immersed in a thermostat at 100°C, and observed, on closing the circuit through the bridge, a current decaying exponentially by a galvanometer inserted in the bridge until it was steadily balanced or on opening the circuit after steadily balanced. They have also observed the resistance of the palladium filament to vary gradually on continuous evacuation at 100°C from an initial value 13.18 Ω to a practically constant one 25.77 Ω via

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a minimum 11.35 Ω at 864 hours after the start of the evacuation. They have interpreted these phenomena as a migration of dissolved proton through the potential gradient along the filament.

These experimental results differ from those of other authors in following points.

1. The migration of proton attributed to the exponentially decaying current must have occurred far quicker than that observed by COEHN and SPECHT[2] to attain a "sedimentation equilibrium"*) within *ca.* 5 minutes.
2. Their result leads, in accordance with the assumption of the co-conduction of proton attributed to the exponentially decaying current, to a value of transference number of proton in palladium metal, *i. e.* the ratio of the current carried by the proton to the total current carried by proton and electron, which is much larger than that extraporated at 100°C from the results by WAGNER and HELLER[8] at 182° and 240°C.
3. Resistances of palladium wires measured by other authors[9] were shown to vary monotonously with hydrogen content in distinction from the HIROTA and HORIUTI's result.

Following experiments were conducted in the present work in order to elucidate the causes of the above discrepancies.

Experiment and Result

I. Control of WAGNER and HELLER's experiment.

WAGNER and HELLER have observed the transmission of hydrogen from a compartment to the other one through a palladium wire of 0.1 mm diameter, which was polarized between both ends respectively projected into the compartments and determined the transference number of proton as the fraction of transmission rate of hydrogen atoms from the anodic to the cathodic compartment multiplied by an elementary charge over the total current through the wire. Under the condition of the above experiment, hydrogen has first to dissolve into the bulk of palladium metal through the surface of the anodic end, migrate through the bulk of metal toward the cathodic end, and there evaporate through the surface.

It has been investigated by the following experiments whether the observed rate of the WAGNER and HELLER's experiment was controlled by the dissolution (or evaporation) through the surface or by the migration through the bulk of the wire.

*) It is meant by these words that the migration under the applied potential is balanced by diffusion caused by inhomogeneous distribution of protons.

The present author[10] has observed the permeation of hydrogen at different pressures through palladium wire of 0.3 mm diameter along *ca.* 1～2 cm of its length toward a vacuum space at different temperatures ranging from 170° to 290°C by following the pressure increase in the vacuum space. It has thus been found that the rate of permeation V_p was proportional to the square root of hydrogen pressure P_{H_2}, as shown in Fig. 1, and inversely proportional to

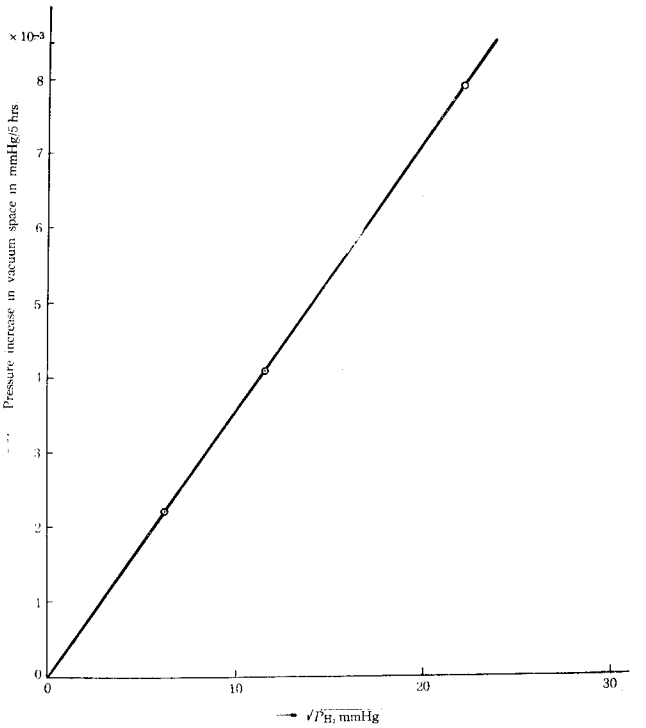

Fig. 1. Dependency of permeation rate on hydrogen pressure.

the length of permeation path d of the wire fused to a glass, as shown in Fig. 2. It follows from the result that the rate of the permeation is governed by diffusion but not by dissolution (or evaporation) at the surface, *i.e.* the unidirectional rate of dissolution or evaporation must be much larger than the observed rate of permeation, which is about ten times as large as the rate of migration of proton through the same cross section of palladium wire as observed by WAGNER and HELLER. It follows that the dissolution (or evaporation) of hydrogen through the surface is far from being rate-controlling but practically in equilibrium as postulated by WAGNER and HELLER.

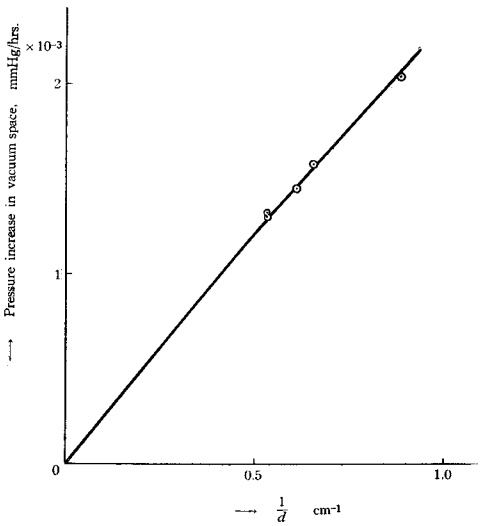

Fig. 2. Dependency of permeation rate on permeation path, $P_{H_2} = 67.6$ cm Hg.

II. Reproducibility of HIROTA and HORIUTI's Experiments.

(A) Exponential Decay of Currents.

The exponential decay of currents observed by HIROTA and HORIUTI, as described above, were reexamined by experiments carried out under a similar condition.

Palladium filaments of 10 μ diameter were prepared by the following two methods[11] from a silver coated palladium WOLLASTON wire.

(1) An integumentary silver layer were dissolved by warming the WOLLASTON wire moderately in a solution of 50% nitric acid. The palladium core obtained was washed repeatedly by distilled water.

(2) The silver layer were removed by anodic electrolysis of the wire in a solution of 10% KCN against a platinum cathode. The core obtained was repeatedly washed by distilled water.

The palladium filament of the respective preparation will be denoted by (1) or (2).

Cracks and slags were found by microscope on the surface of the filament (1) but not on (2) in agreement with the observation of WAETZMAN, GNIELINSKI, and HEISIG[11] on a platinum WOLLASTON wire.

This palladium filament of *ca.* 1 cm length was cramped at both ends by copper or nickel wires sealed in a glass cell, which was connected to a vacuum

line through a trap immersed in liquid nitrogen. After evacuation of the cell at 350°C for one day by diffusion pump, hydrogen of 1 cm Hg pressure was introduced into the cell at the same temperature. After several hours, the cell was evacuated again at the same temperature, then, was immersed in a thermostat at 100°C, and, thereafter, was filled with hydrogen of 10^{-2}mmHg pressure.

The palladium filament was inserted to one arm of a WHEATSTONE bridge, as shown in Fig. 3 (figures in parentheses show the resistance values in the experiment of HIROTA and HORIUTI).

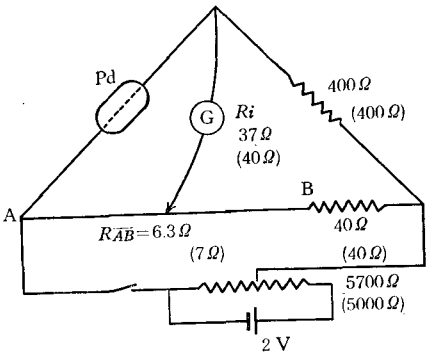

Fig. 3. WHEATSTONE bridge.
Galvanometer
internal resistance 37 Ω
period 7 sec
sensitivity 2.7×10^{-8} A/mm in scale
Pd, *Pd* filament
dia. 10 μ length *ca.* 1 cm

Observations were carried out as follows. The bridge were balanced at first by closing the circuit with a steady current of 2×10^{-4}A through the cell for a quarter of an hour, then left for one hour with the circuit open. The circuit were again closed, but any detectable current passing through the galvanomenter was not observed. After the circuit were closed for ten minutes, the circuit were again opened, but no detectable current was observed on the galvanometer. The same results were obtained when the current through the cell was raised to 2×10^{-3}A or the hydrogen pressure in the cell was increased to 10 cm Hg. All the above results were commonly observed by filament either (1) or (2).

The "sedimentation equilibrium" in the filament described by HIROTA and HORIUTI should be established much quicker than evaporation of hydrogen. It took now 5 minutes for the current attributed to the migration toward the "sedimentation equilibrium" to die away in the case of HIROTA and HORIUTI's experiment. The equilibrium of evaporation or dissolution should hence be attained sufficiently slower than 5 minutes for the current to be observed at all. Measurements have been made on this ground on the evaporation into vacuum of hydrogen from the palladium filament saturated with hydrogen at *ca.* 20 cm Hg*), by following the hydrogen content of the filament by its resistance. The result is that the evaporation is practically completed within 8 minutes or 5 minutes

*) This is the pressure of hydrogen far higher than that in HIROTA and HORIUTI's experiment, which is supposed to be in equilibrium with dissolved hydrogen polarized at one end of palladium filament in the latter experiment.

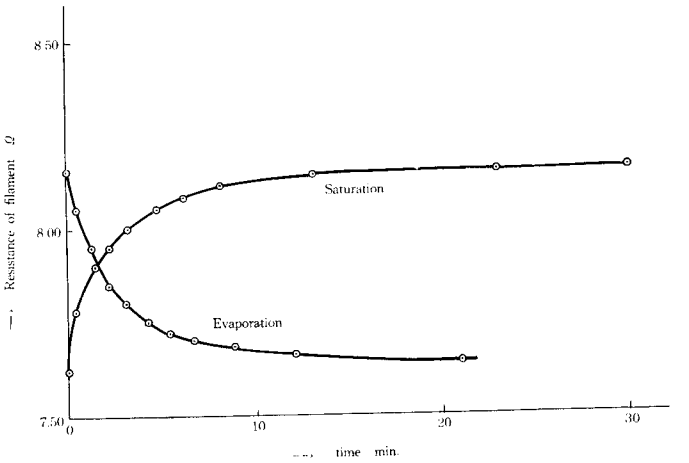

Fig. 4. (A). Rate of dissolution and evaporation of H_2 [*Pd* filament (1)].
Saturation pressure : 16.6 cm Hg.

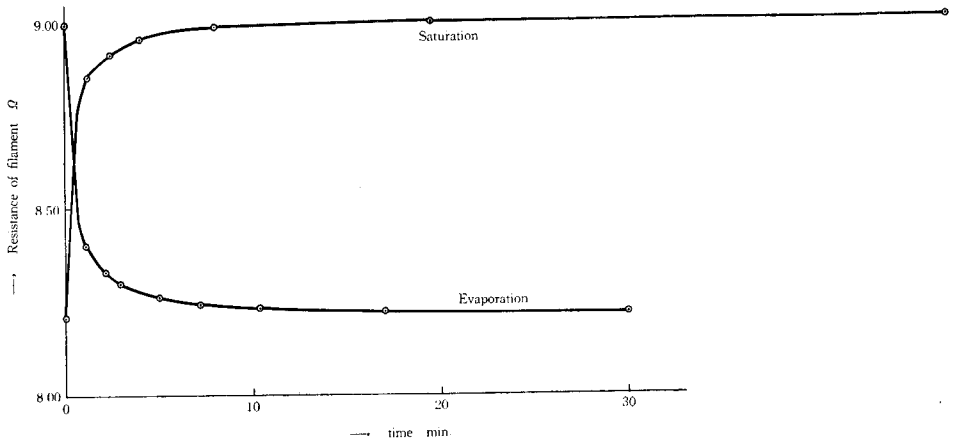

Fig. 4. (B). Rate of dissolution and evaporation of H_2 on *Pd* filament
[*Pd* filament (2)].
Saturation pressure : 24.9 cm Hg.

as shown in Fig. 4 respectively with the filament (1) or (2), indicating that the "sedimentation equilibrium" as described by HIROTA and HORIUTI could hardly be established in our experiments.

The dissloution of hydrogen is retarded as found by ONO[12] by a previous exposure of palladium to carbon monoxide. This result was confirmed by using the palladium filament together with the retardation of evaporation as shown in Fig. 5. It was found that mercury vapor retarded the dissolution and

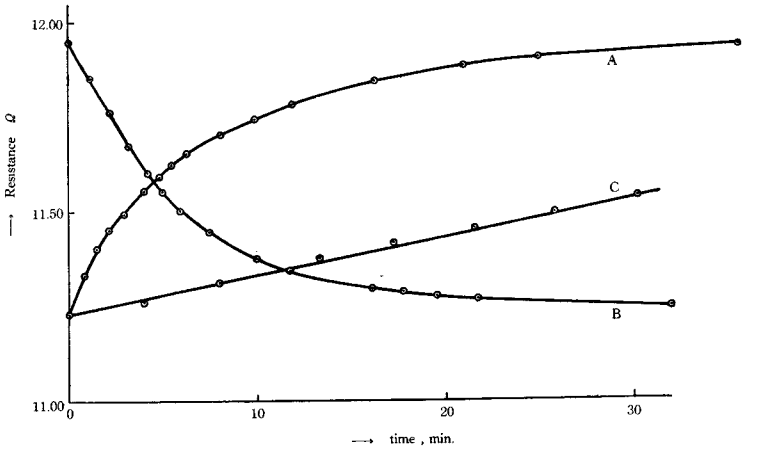

Fig. 5. (A). Retardation by CO of H_2 dissolution into *Pd* filament (1).
A, dissolution of H_2 at 17.0 cm Hg.
B, evaporation of H_2 after saturation at 17.0 cm Hg.
C, dissolution of H_2 at 16.0 cm Hg.
preliminarily exposed to CO of 3.8 mm Hg. pressure.

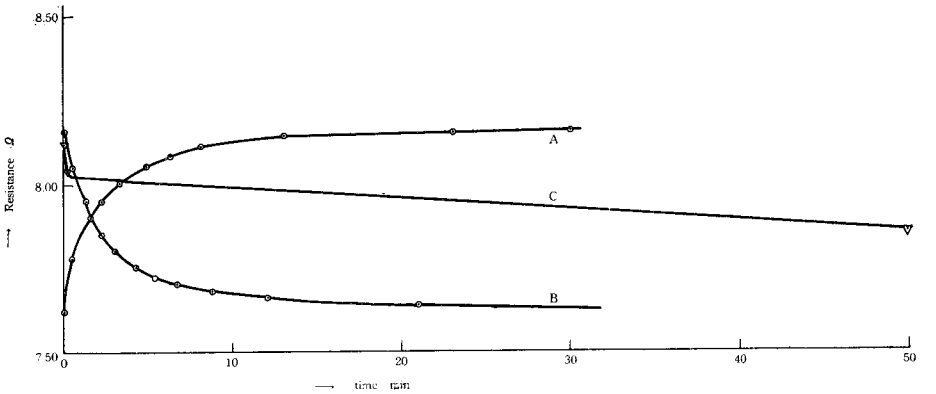

Fig. 5. (B). Retardation by CO of H_2 evaporation from *Pd* filament (1).
A, dissolution of H_2 at 16.6 cm Hg.
B, evaporation of H_2 after saturation at 16.6 cm Hg.
C, evaporation of H_2 in the pesence of 11 cm Hg CO
(H_2 replaced by CO after saturatio).

evaporation as shown in Fig. 6. The exponential decay of current was not however observed neither in the case of the evaporation of hydrogen from the filament retarded by carbon monoxide or by mercury vapor.

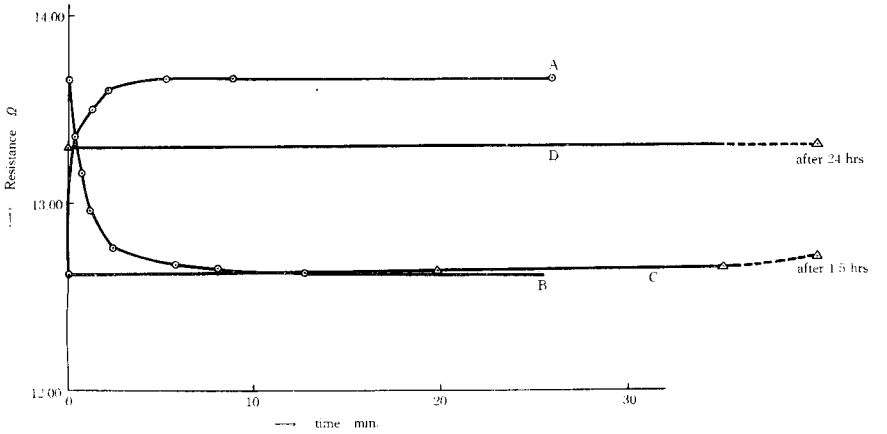

Fig. 6. Retardation of H_2 dissolution and evaporation by Hg vapor [*Pd* filament (2)].
A, dissolution of H_2 at 21.6 cm Hg.
B, evaporation of H_2 after saturation at 21.6 cm Hg.
C, dissolution of H_2 at 18.4 cm Hg preliminarily exposed to Hg vapor.
D, evaporation of H_2 exposed to Hg vapor after the experiment C for 10 days.

(B) Variation of the Resistance.

HIROTA and HORIUTI have observed the resistance of the palladium filament to shift gradually from an initial value 13.18 Ω to a practically constant value 25.77 Ω *via* a minimum 11.35 Ω by continuous evacuation at 100°C. This result was not however reproduced, the resistance of palladium filament of either preparation being found to keep constant for a few weeks after a few hours from the begining of evacuation.

Conclusion

The results described above show that the phenomena reported by HIROTA and HORIUTI are not reproduced, and that their results were quite different from those reported by others. It requires further investigation to elucidate the discrepancy.

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References

1) A. SIEVERTS and W. DANZ, Z. Phys. Chem. (B) **38**, 46 (1938); A. SIEVERTS and G. ZAPF, Z. Phys. Chem. (A) **174**, 359 (1935).
2) A. COEHN and W. SPECHT, Z. Phys. **62**, 1 (1930); A. COEHN and H. JÜRGENS, Z. Phys. **71**, 179, (1931); A. COEHN and K. SPERLING, Z. Phys. **83**, 291 (1933).
3) B. DUHM, Z. Phys. **94**, 434 (1935); **95**, 801 (1935).
4) J. FRANCK, Nachr. Ges. Wiss. Göttingen. Math.-Phys. KI. Fachgruppe II, Nr. 44.
5) K. F. HERZFELD and M. GOEPPERT-Mayer, Z. Phys. Chem. (B) **26**, 203 (1934).
6) I. ISENBERG, Phys. Rev. **79**, 736 (1950).
7) K. HIROTA and HORITUI, Ōyō Butsuri (Applied Physics) 8, 266 (1939); Proc. Imp. Acad. XV 10 (1939).
8) C. WAGNER and G. HELLER, Z. Phys. Chem. (B) **46**, 242 (1940).
9) D. P. SMITH and G. DERGE, Trans. Electrochem. Soc. **66**, 253 (1934); A. R. UBBELHODE, Trans. Faraday Soc., **28**, 275 (1932); Proc. Roy. Soc. (London) A **159**, 295 (1937).
10) G. TODA, this Journal **6**, 13 (1958).
11) E. WAETZMANN, M. GNIELINSKI and H. HEISIG, Z. Phys. **58**, 449 (1929).
12) S. ONO, Rev. Phys. Chem. of Japan **17**, 115 (1943).