

**EXPERIMENTAL STUDIES
ON THE
HYDROGEN ELECTRODE.
DISSERTATION**

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Experimental Studies on the Hydrogen Electrode. Dissertation by Louis P. Hammett

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LOUIS P. HAMMETT

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DISSERTATION**

UNIV. OF
CALIFORNIA

**EXPERIMENTAL STUDIES ON THE
HYDROGEN ELECTRODE**

DISSERTATION

Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy in
the Faculty of Pure Science of
Columbia University.

BY

LOUIS P. HAMMETT

II
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1922

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**EXPERIMENTAL STUDIES
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The hydrogen electrode is an instrument of such scientific importance that the lack of detailed study of its mechanism and of the conditions for precise measurements seems very remarkable. There are numerous directions for the preparation and use of the electrode¹, which in the hands of the particular investigator have given reproducible results on a given type of solution; but these are often contradictory, and there is a lack of experimental comparison of different methods. The present investigation was initiated largely by the desire to explain and eliminate the erratic and uncertain behavior of the hydrogen electrode in unbuffered solutions, but this has necessitated a general survey of the field.

Apparatus and Materials.

Electrical measurements were made with a Leeds and Northrup type K potentiometer. The Weston cell used as standard was several times compared with another cell tested by the Bureau of Standards. The hydrogen and calomel cells were kept in a Freas water thermostat regulated to .01°, all measurements being made at 25.00°. No difficulty was experienced from the use of the water bath, and careful testing of the leads and electrical system indicated no electrical leakage sufficient to cause appreciable error in the measurements.

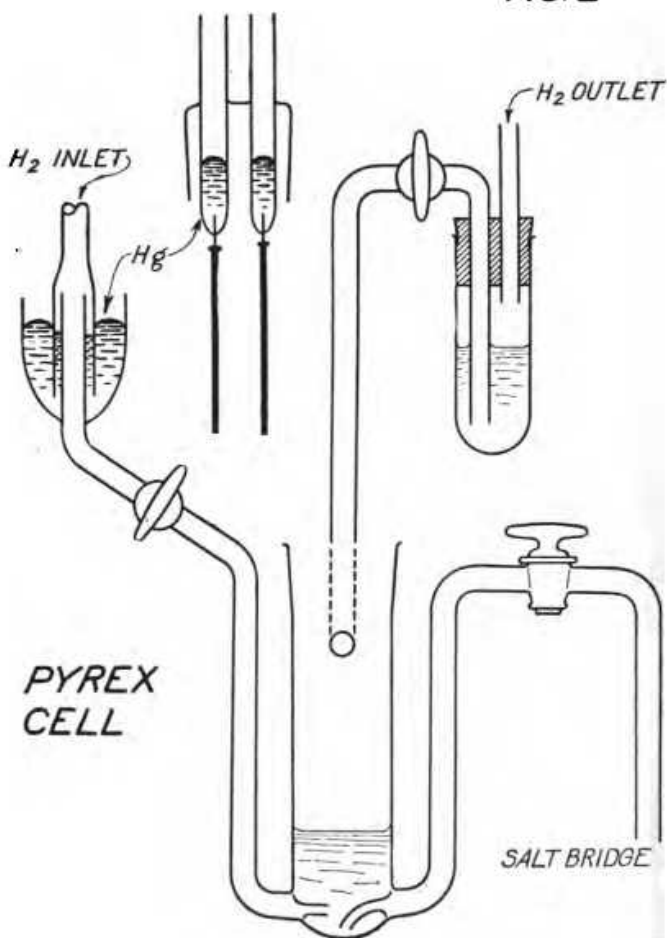
The saturated calomel cell as studied by Fales and Mudge² was used as standard electrode. Several different cells made up from different materials and at different times showed a maximum variation of 0.3 mv. Two calomel cells were always used, measurements being made against one which was frequently compared with the other. The hydrogen electrode vessel used is shown in Fig. 1.

For cleaning electrodes use was made of a scrubber designed by Mr. Walden of this laboratory, which will be described in detail by him elsewhere. In the all-glass apparatus the vapors from boiling distilled water bubble through the

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water in which the electrodes are immersed, condense in a reflux, and fall back. An intermittent syphon on the Soxhlet principle removes the condensed water at intervals of five to ten minutes and allows a fresh portion to accumulate.

FIG. 1

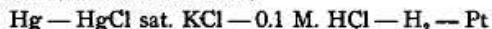


The hydrogen was generated by electrolysis of a 15% sodium hydroxide solution. It was passed successively through a column of absorbent cotton, an electrically heated quartz tube containing platinized asbestos, a bead tower through which dilute sulfuric acid was continuously circulated by the passage of the gas, and a soda-lime tower. Such few rubber connections as were used were carefully wired and shellacked. The sulfuric acid and soda lime might seem superfluous were it not that small amounts of ammonia present in the hydrogen at one time in the course of the work were traced back to a little nitrate or nitrite (diphenylamine test) in the generator electrolyte. Since the original sodium hydroxide gave no such test the only obvious source is nitrogen compounds in the nickel electrodes, the work of Fichter and Suter³ having made electrolytic oxidation or reduction of atmospheric nitrogen very unlikely.

The water used throughout this investigation was prepared in the conductivity water still in use in this laboratory, which is similar to that described by Bourdillon⁴, and was kept in a protected quartz vessel.

Some of the potassium chloride was recrystallized three times from conductivity water in platinum and heated just below the fusion point. Since it was found that other factors, particularly contamination from glass vessels, were more important than the purity of the potassium chloride; and since this research was concerned with the development of the hydrogen electrode and not with absolute measurements in pure potassium chloride solutions, the final measurements were made with potassium chloride which was only once recrystallized with centrifugal drainage and washing.

Values for the combination:



at one atmosphere total pressure have been obtained varying from 0.3080 to 0.3120 volts as compared with the 0.3100 of Fales and Mudge⁵. Since the calomel cells showed so little variation, and since the potential difference between any active hydrogen electrodes in the same solution of 0.1 M. HCl is unmeasurably small it seems reasonable to assign the variability of this cell to the contact between the two solutions.

This conclusion is supported by the fact that age of the junction, mechanical mixing, and particularly bore of tubing in which the junction is made exert a great effect upon the potential of the combination. It perhaps deserves notice that this cell, although it has a small temperature coefficient², is sensitive to sudden changes in temperature.

Electrolytic Deposition of Platinum.

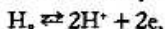
Although massive platinum can be given a temporary activity as a hydrogen electrode, all practicable electrodes are coated with electrolytically deposited metal (iridium and palladium have also been used). The usual electrode has been coated with finely divided so-called platinum black, and it has generally been assumed that a smooth, velvety, continuous coating is desirable. To obtain this the Lummer-Kurlbaum method of adding a trace of lead salt to the platinizing solution is frequently recommended and as frequently denounced as harmful³. A black deposit may often be obtained from commercial chlorplatinic acid, and Kohlrausch suspected that differences in the quality of the deposit with different samples of chlorplatinic acid are due to traces of impurities. To settle the point a solution of chlorplatinic acid was purified by three precipitations of ammonium chlorplatinite⁴. The material thus obtained gave a dull gray deposit but not a black at high current densities and with frequent reversals of the current. With a current of 2 milliamperes per sq. cm. a smooth bright deposit was obtained on a gold base. Since therefore some impurity is necessary to obtain a black deposit, there can be little objection to the conscious addition of a trace of lead ion.

For the deposition of platinum black from a solution of chlorplatinic acid containing a trace of lead ion, current density and concentration of chlorplatinic acid are of minor importance, except that with very dilute solutions stirring becomes necessary. Reversing the direction of the current at intervals seems to have little effect, but the current should always pass in the direction of cathodic polarization for some time at the end of the process if commutation is used. If the final treatment is anodic the reduction of the oxidation products formed requires so much time that the electrode is slow in coming to equilibrium.

Aside from the use of an acid solution of purified chlorplatinic acid, we have obtained bright platinum deposits by the use of alkaline solutions of the purified chlorplatinic acid. The addition of sodium hydroxide to a solution of chlorplatinic acid has no immediate apparent effect. Within the course of a few days a brown precipitate forms, which gradually increases. The platinum is not however completely precipitated after one and a half months at ordinary temperature. This precipitate does not interfere with the use of the solution for plating and is in any case easily dissolved by adding hydrochloric acid and heating. Alkaline solutions containing lead ion give, however, a black deposit. Excellent results have also been obtained with the frequently recommended alkaline citrate bath, but the bright electrodes used in this work have been plated from alkaline solutions containing no citrate, since it was felt that the decomposition products of the citrate offered an additional source of contamination of the electrode.

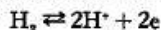
The Role of Platinum and the Effect of Oxygen.

The early workers on the gas cell discovered that more reproducible and better results with hydrogen electrodes were obtained when the electrodes were coated with platinum black than when massive platinum was used. Ostwald⁷ pointed out the role of platinum black as a catalyst for the reaction



but emphasized that all electrodes must give the same potential provided the reaction consists only in solution or deposition of hydrogen, that is that the electrodes are truly inert; and that equilibrium is obtained. There have been only few references⁸ to the marked difference in potential between bare and platinized electrodes, and no explanation. Yet previous investigators have assumed that hydrogen electrodes must be coated with finely divided platinum; varied by some by the use of palladium or iridium, and by the use of gold instead of platinum as a base.

That the essential function of the platinum black is that of a catalyst for the electrochemical reaction,



is perhaps implicit in much of the discussion of the subject,