

The Journal of the American Chemical Society

VOL. 53

MARCH, 1931

No. 3

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

THE MEASUREMENT OF THE HYDROGEN-ION CONCENTRATION IN UNBUFFERED SOLUTIONS. II. APPLICATION OF THE HYDROGEN ELECTRODE

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RECEIVED JUNE 9, 1930

PUBLISHED MARCH 6, 1931

It has already been shown² that a platinized electrode in a hydrogen atmosphere adsorbs the cation or base from a salt or basic solution, thus yielding a more acid solution in the cell than before the treatment with hydrogen. All experiments described in the former paper have been repeated in a nitrogen atmosphere. There was no adsorption of cation or anion in any case. This proves definitely that the adsorbent property of platinized platinum for strong electrolytes is a function of the electrode property (hydrogen or oxygen) of the noble metal (Frumkin).

The fact that the ordinary type of platinized hydrogen electrode adsorbs cations from a solution forms a serious objection to its use for P_H measurements in unbuffered solutions. In order to overcome this change of the reaction in a slightly buffered or unbuffered solution, it is evident that the coat of platinum has to be as thin as possible.

H. T. Beans and L. P. Hammett³ in an important paper arrived at a similar conclusion. They pointed out that the bare platinum electrode is a poor catalyst for the reaction $H_2 \rightleftharpoons 2H^+ + 2e$, but that bright metallic deposits of platinum prepared electrolytically act catalytically for the hydrogen-ion reaction, and their life, while not as long as that of platinum black, is sufficient to make their use as hydrogen electrodes possible. Beans and Hammett's results were in the main confirmed by the authors, though there is one important difference between their observations of the adsorbent properties of platinized platinum and those of the authors, which can be attributed to the fact that this property of the electrode is a function of its gas charge. Acids which are adsorbed by the air electrode

¹ From the experimental part of a thesis submitted by T. Kameda to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² I. M. Kolthoff and T. Kameda, *THIS JOURNAL*, **51**, 2888 (1929).

³ H. T. Beans and L. P. Hammett, *ibid.*, **47**, 1215 (1925).

are not adsorbed by the hydrogen electrode and, therefore, can be removed from the electrode by washing out in a hydrogen atmosphere with water. This point is very important with regard to the preparation of an electrode suitable for the measurement of P_{H} in unbuffered solutions. Many attempts, a discussion of which has been given in the thesis of T. Kameda,¹ have been made to prepare such an electrode. Finally, it was decided to cover platinum or gold with a bright layer of platinum, as has been suggested already by Beans and Hammett.³ However, the procedure followed was different from that given by the authors mentioned, since it has been found that adsorbed acid can be removed easily by washing in a hydrogen atmosphere.

Materials

Chloroplatinic Acid.—Pure platinum was prepared according to the directions of Wichers.⁴ The metal was dissolved in aqua regia, evaporated several times with hydrochloric acid and then several times with water. This residue was taken up in water so that the resulting solution contained about 2% of platinum as chloroplatinic acid.

Hydrogen.—This was taken from a commercial cylinder and carefully purified by passing through a wash-bottle containing alkaline permanganate over a column of pure copper wire gauze electrically heated at 450–500° and various wash-bottles.

Water.—Conductivity water was distilled over extremely dilute sulfuric acid in order to remove traces of basic impurities, then twice without any addition and finally in a quartz apparatus with condenser. The distillate was collected in a quartz container and protected from contamination by the atmosphere. Usually the final distillate was used the same day as prepared. As will be shown in another paper, this water when made carbon dioxide free has a P_{H} of 7.0 to 7.05.

Potassium Chloride and Potassium Sulfate.—C. p. products were twice recrystallized from water and the crystals ignited for two hours in an electric furnace at 600°.

Ammonium Chloride.—A c. p. product was twice recrystallized from water and dried in a desiccator.

Zinc Sulfate.—A c. p. product was recrystallized seven times from water (for details compare next paper) and dried over deliquescent sodium bromide at a temperature below 23° until the weight was constant.

The Hydrogen Electrode Adapted for Unbuffered Solutions.—A diagram of the cell finally used is given in Fig. 1. All glass parts were made of pyrex glass. A platinum and a gold wire, both about 3 cm. long and 1 mm. thick, were used as electrodes. The wires were fused through a

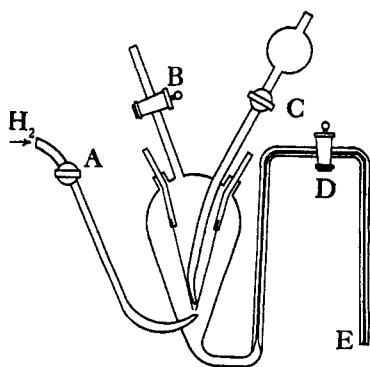


Fig. 1.

pyrex glass tube and sealed to a thin platinum wire which made the connection with a copper wire. These glass tubes were ground air tight into the upper part of the glass cell. In all cases it was found that the platinum and gold electrodes gave identical readings within 0.3 of a millivolt. It is recommended that platinum wire be used, as it is much easier to handle than the soft gold. Before platinization the electrodes are

⁴ Wichers, THIS JOURNAL, 43, 1268 (1921).

treated with a solution of potassium dichromate in strong sulfuric acid, washed with water and heated to dull redness. The plating bath contained a solution of pure chloroplatinic acid of a concentration corresponding to 2% platinum. By electrolyzing for two minutes at a current strength of 20 milliamperes, both electrodes are covered with a bright layer of platinum. The current density can be varied within wide limits. Good results are obtained at a current strength between 5 and 30 milliamperes. After the plating, the electrodes are washed well with water and then placed in the electrode cell, which is filled with conductivity water through which hydrogen has been passed for twenty minutes. The passage of hydrogen is continued for about thirty minutes, then the water is forced out of the cell in the hydrogen current. The solution to be tested is washed in hydrogen and introduced in a continuous stream which enters through A by opening stopcock C, closing D and opening B. After a few minutes the solution is again removed and the washing of the electrode in hydrogen is repeated several times. Finally the cell is partly filled with the solution so that about 2 cm. of the electrodes are covered, when the solution is not stirred. The passage of hydrogen is still continued with the stopcocks A and B open. Before taking a reading B is closed, then A, whereupon D is opened. Then the end E of the capillary tube is dipped into a saturated potassium chloride solution contained in a cell as shown in Fig. 2.



Fig. 2.

The electrodes are easily poisoned in unbuffered solutions. After each set of measurements the electrodes have to be cleaned, replated and treated as described above. Under these conditions reproducible results are obtained even in unbuffered solutions.

Results.—The most difficult problem, of course, is the P_H measurement in an unbuffered solution such as potassium chloride. A 0.05 molar solution of this salt was used.

It was not possible to obtain a constant e. m. f.; in the beginning it increased (corresponding to an increase in P_H), then it reached a maximum and remained constant for fifteen to thirty minutes, after which the values dropped slowly. Some results are given in the following table.

P_H OF 0.05 MOLAR POTASSIUM CHLORIDE WITH THE HYDROGEN ELECTRODE AT 25°

Time in minutes . . .	15	30	45	55	90
P_H	6.66	6.76	6.75	6.73	6.53
Electrodes Replatinized					
Time in minutes . . .	15	30	40	50	70
P_H	6.72	6.77	6.77	6.76	6.73

These measurements have been repeated eight times. In all cases a maximum in P_H was reached after hydrogen had been passed through for twenty to thirty minutes. If the cell was refilled with fresh potassium chloride solution after one set of measurements, no good results were obtained, the P_H indicated being much too low. Removing the film of platinum with aqua regia, igniting and replating the electrode was necessary. The P_H of the potassium chloride solution was also determined colorimetrically with brom thymol blue as indicator (for technique compare

next paper). In this way a value of 6.77 was found, the latter being in close agreement with the reading of the hydrogen electrode.

In 0.05 molar potassium sulfate solutions a P_H of 7.4 ± 0.05 was found potentiometrically.

Finally, many measurements have been made in solutions of ammonium chloride and of zinc sulfate. The e. m. f. remains constant over a much longer period of time than in the case of potassium chloride solutions and in addition the solutions can be renewed a few times before replating the electrode.

Some results are reported in the following table. The P_H values have also been determined colorimetrically with adjusted methyl red as indicator (for technique see next paper). Methyl red is of special utility here on account of its negligibly small salt error.

<i>P_H</i> IN AMMONIUM CHLORIDE AND ZINC SULFATE		
Solution used	<i>P_H</i> (H ₂ electrode)	<i>P_H</i> (color, methyl red)
0.25 Molar NH ₄ Cl	4.97	4.96
.01 Molar ZnSO ₄	6.00	6.00
.02 Molar ZnSO ₄	5.89	5.90
.05 Molar ZnSO ₄	5.76	5.77
.1 Molar ZnSO ₄	5.67	5.66

In more concentrated solutions of zinc sulfate the measurements with the hydrogen electrode were not so well reproducible. Quite generally it may be mentioned that in this tedious work irregularities occur once in a while. These may be due to inadequate platinization, but also it should be remembered that unbuffered solutions like those of neutral salts are very sensitive toward changes of their reaction.

Summary

Use is made of the fact that acid adsorbed by platinum can be removed by washing with water in a hydrogen atmosphere. Directions have been given for the preparation of an electrode coated with a bright layer of platinum, the use of which yields satisfactory results in the measurement of P_H in unbuffered or slightly buffered solutions. The electrode is easily poisoned and cleaning and replatinizing are often required, but reproducible results can be obtained even in solutions of potassium chloride.

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