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THE QUINHYDRONE ELECTRODE. I.

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Introduction

Ever since its discovery by Haber and Russ¹ and its early development by Granger and Nelson² and by Biilmann,³ the quinhydrone electrode has been a favorite substitute for the hydrogen electrode in the determination of the hydrogen-ion concentration of solutions. This early work indicated that, for moderate precision at least, the electrode is quickly and easily prepared, develops its potential almost instantaneously, does not require a gas bubbling through the solution continuously and can be used, therefore, for work on body fluids containing dissolved carbon dioxide, and is not affected by atmospheric pressure; moreover, it can be used in solutions in which the reducing effect of hydrogen, or of hydrogen and platinum black, prohibits the use of the usual hydrogen electrode. In view of the ease with which the electrode can be prepared, the fact that the electrodes deteriorate in a comparatively short time constitutes only a minor objection. The real limitation of the electrode lies in the fact that even for work of moderate precision the electrode cannot be used in alkaline solutions above a P_{H} of 8.5, particularly in the presence of oxygen.

Preliminary to some work on polarization which demanded a standard electrode of constant potential in acid solution, we undertook a study of the quinhydrone electrode, since it could be connected to the electromotive chain without the introduction of liquid junction potentials. Up to the time that this investigation was initiated, little work had been done from the point of view of the reproducibility of the electrode with a precision greater than 0.0001 volt; the interest of previous investigators lay primarily in the theory of the reaction producing the electrode, in the values of its potential compared to the well-known standard electrodes, in its salt error, and in the design of new forms of electrode for particular applications.

Since that time, however, the work of Biilmann and Jensen⁴ has appeared. These investigators studied the reproducibility of the electrode and its value compared to the hydrogen electrode, their measurements being reported to 0.00001 volt. However, inasmuch as our method of attack differed from theirs, and inasmuch as their work was limited to a study

¹ Haber and Russ, *Z. physik. Chem.*, **47**, 257 (1904).

² Granger and Nelson, *THIS JOURNAL*, **43**, 1401 (1921).

³ Biilmann, *Ann. chim.*, [9] **15**, 109 (1921).

⁴ Biilmann and Jensen, *Bull. soc. chim.*, **41**, 151 (1927).

with comparatively few electrodes and did not cover many of the controversial points, it seemed wise to continue the research.

We confined the first part of our work to the reproducibility of the electrode since its actual value was of no immediate interest to us. With the hope of reproducing conditions in different laboratories we selected for the base of our electrodes a variety of metals: gold, platinum, platinum-iridium alloy, platinum-rhodium alloy, old platinum which was roughened by repeated platinization and deplatinization, having been used for years as hydrogen electrodes, and new platinum purchased at different times from different companies, platinum and gold wires of different cross sections and lengths and foils of different areas. All in all we used 194 electrodes cut into different sizes from 37 different pieces of metal with the result that we had groups of four to six electrodes, the electrodes within a group being as nearly identical as we were able to make them. A total of 3299 cells were prepared by combining these electrodes in pairs and on these cells more than 8000 measurements of the potential differences were made under varying conditions. Obviously a summary of such a large number of determinations is difficult but is attempted in view of the very general usefulness of the electrode, because of the precision with which the electrode may be prepared, and in view of the fact that there are so few data given in the literature to substantiate the preferences of different investigators as to the metal to be used as a base and as to the method of preparation of the electrode and solution.

In this paper we shall report the results of our work on the method of preparation of the metal electrode, on the method of cleaning and drying the electrodes, on the method of preparation of the quinhydrone solution, and on a comparison of the reproducibility possible with electrodes of different sizes and compositions for measurements made in the presence of air. In other papers to follow we shall present results on the reproducibility possible when the air is replaced by nitrogen, on a comparison of the potentials developed in quinhydrone solutions by electrodes of different sizes and compositions, both in air and in nitrogen, on the behavior of the electrode prepared in solutions other than in 0.1 *N* hydrochloric acid, and on the electromotive force of the quinhydrone compared with other well-known half-cells. Much of the material for these papers is at hand; however, in view of the fact that some time must elapse before the data and compilations can be completed, it seems wise to make this preliminary report for the benefit of any who wish to use the electrode under the conditions described in this paper.

Preparation and Purification of Materials.—Several lots of quinhydrone, purchased from Eastman Kodak Co., and melting at 169–170° were used. The water and ethyl alcohol used were redistilled; the air for drying the electrodes was compressed by a water pump and conducted through dilute sulfuric acid, distilled water, soda lime and calcium chloride; the cleaning mixture was prepared from c. p. chemicals.

Apparatus

The electromotive force measurements, made in the usual manner with a Leeds and Northrup, Type K, potentiometer and a Type R, No. 2500 e, galvanometer, are believed to be precise to 0.000001 volt, since the usual precautions as to shielding,⁵ temperature control and thermoelectric effects have been taken.

Electrode Vessel.—A 600-cc. pyrex beaker fitted with a wood and cork stopper was used as electrode vessel. In each stopper was inserted seven lengths of glass tubing which extended about 5 cm. below the stopper and about 2.5 cm. above. Six of these tubes carried the electrodes and prevented them from touching one another in the solution; the seventh carried the motor-driven stirrer.

Electrodes.—Wires and foils were sealed, with the aid of sealing-in glass, into a piece of glass tubing. Connections with the potentiometer wires were made in some cases with mercury, in other cases, when longer wires were used, directly with a wire connector. Each electrode tube was supplied with a cork stopper fitting the glass tube in the cover of the electrode vessel. A more detailed description of the electrodes is as follows.

Small Wires.—O, Nos. 1-6; Pt, 7-12; Ir, 7-12; Rh, 7-12; Au, 7-12. (Approximately 0.38 mm. in diameter and 1.5 cm. in length.) *Series O*, six electrodes cut from same piece of new c. p. platinum. *Series Pt*, six from same piece of new c. p. platinum different from O. *Series Ir*, six from same piece new platinum-iridium, 10% alloy. *Series Rh*, six from same piece new platinum-rhodium, 10% alloy. *Series Au*, six from same piece new 24K gold.

Large Wires.—A, Nos. 1-6; B, 1-6; Pt, 1-6; Ir, 1-6; Rh, 1-6; Au, 1-6; St, 1-6. (Approximately 1 mm. diameter, 2 cm. length.) *Series A*, six pieces of old platinum of unknown composition which had been around the laboratory for years and which, just previous to this work, had been used for hydrogen electrodes. *Series B*, six electrodes of old platinum but cut from same piece of wire. History similar to A. *Series Pt*, new c. p. platinum, six from same piece. *Series Ir*, six from new piece platinum-iridium, 10% alloy. *Series Rh*, six from new piece platinum-rhodium, 10% alloy. *Series Au* and *Series St*, six electrodes in each series from each of two new pieces of 24K gold.

Special Wires (Am Pt, Nos. 1-6 and L & N, Nos. 1-4) *Series Am Pt* (0.60 mm. \times 2 cm.) six electrodes cut from the same piece of new c. p. platinum wire bought of the American Platinum Co., and recommended by Cullen.⁶

Series L & N.—Four gold electrodes bought from Leeds and Northrup and described by Parker and Greer.⁷

Aside from the short wire electrodes described, sets of electrodes, usually of six each, were made from the same pieces of metal but cut into 15-cm. lengths and the middle portion of the wire covered with glass tubing. The same length of electrode was exposed to the solution and a similar length exposed at the other end of the tubing which carried the wire connector. These electrodes are described as "long."

Foils.—D-F and I-N (old); P and G (new). *Series D-F* (approximately 1 \times 2 cm.) and *Series I-N* (approximately 2 \times 2 cm.) six pieces of each size whose age, history and compositions are unknown; had been used as hydrogen electrodes. *Series P*: Twenty platinum foil electrodes cut from the same piece of new c. p. platinum foil: 4 foils each size: P₁₁₋₁-P₁₁₋₄ (1 \times 1 cm.); P₁₂₋₁-P₁₂₋₄ (1 \times 2 cm.); P₁₃₋₁-P₁₃₋₄ (1 \times 3 cm.); P₂₂₋₁-P₂₂₋₄ (2 \times 2 cm.); P₂₃₋₁-P₂₃₋₄ (2 \times 3 cm.). *Series G*: Twenty gold foil electrodes cut from the same piece of new 24K gold foil: 4 foils each size: G₁₁₋₁-G₁₁₋₄

⁵ White, THIS JOURNAL, 36, 2011 (1914).

⁶ Cullen, *J. Biol. Chem.*, 83, 535 (1929).

⁷ Parker and Greer, *Trans. Am. Electrochem. Soc.*, 49, 451 (1926).

(1 × 1 cm.); G₁₂₋₁-G₁₂₋₄ (1 × 2 cm.); G₁₃₋₁-G₁₃₋₄ (1 × 3 cm.); G₂₂₋₁-G₂₂₋₄ (2 × 2 cm.); G₂₃₋₁-G₂₃₋₄ (2 × 3 cm.).

While the short platinum wires and long platinum and gold wires were sealed directly into the glass tube, the gold with the aid of a wax, the platinum foils and short wire gold electrodes and foils were sealed to platinum wire which was then sealed into the glass. For the gold-platinum joint borax was used as a flux. The two pieces of wire, very clean, were dipped into the flux and then placed end to end on a piece of charcoal. Fusion was brought about by playing a small flame from an air gas torch along the platinum until the platinum was red hot and then applying the torch to the gold. In sealing the metal into the glass the sealing-in glass was applied to the platinum wire just above the joining of the two metals and the seal made to cover this joint. In this way no platinum-gold couple touched the solution and no mercury the gold.

Procedure and Results

The method of procedure which we adopted to determine the reproducibility of the potential of the quinhydrone electrode involved, in the first place, the preparation of series of either four or six electrodes as nearly identical as possible. These electrodes were then immersed in 0.1 *N* hydrochloric acid containing the quinhydrone and their potential differences compared, pair by pair, under a number of varying conditions.

The Method of Preparation of the Metal Electrode.—Early in our work it became evident that by far the greatest source of error involved in the preparation of reproducible quinhydrone electrodes lay in the preparation of the metal electrode to be immersed in the quinhydrone solution. The greatest care was necessary in sealing the electrode into the glass tubing. The smallest cracks or imperfections in the seal gave rise to large variations in the voltages of the electrodes and although at times these imperfections were invisible to the eye even through a magnifying glass, inevitably sooner or later the mercury just above the seals in these troublesome electrodes became so discolored that it was obviously being attacked by the solution.

This point is well illustrated by the behavior of a cell made up of electrodes B₃ and B₄. The first day the difference in potential between the two electrodes was 0.00054 volt and became 0.00050 volt at the end of four hours. The next day, the electrodes having been cleaned and dried again, the same cell gave a difference of potential of 0.07417 volt which became 0.04695 volt at the end of one and one-half hours. Finally on a third day and after another cleaning process this combination gave a potential of 0.05577 volt which finally dropped to 0.03607 volt. When electrode B₃ was measured against one of a pair of electrodes which had been giving a low potential difference its value was still very high (0.02957 volt); B₄ on the other hand gave about the same low potential as the reference electrode. B₃, exhibiting both a crack and acid attacked mercury on being examined, was remade and when next measured against B₄ gave a potential of 0.00000 volt.

Up to this point nearly all of the cells, made up of supposedly identical electrodes, had given potential differences which varied from 0.00000 volt to about 0.000030 volt. As the latter value seemed, in view of the reproducibility reported by earlier workers, too high and could not be lowered by repeated cleansing of the electrodes, all of the electrodes then in existence were remade. During this process it became obvious that the seal, which was made in the usual manner with sealing-in glass between the platinum and soft glass used, must be heated for some time in the flame and must be carefully annealed. To test the perfection of the seal the electrodes were suspended in water which was then heated to the boiling point. The electrodes were not removed until the water had cooled, when the defective ones were either cracked or the tubes filled with water. Electrodes tested in this way gave readily reproducible potentials over long periods of time even when heated for some time in very hot cleaning mixture. Of the electrodes prepared in this way and combined over a period of three years in pairs to give 3300 cells, only 29 electrodes have had to be remade because they gave potentials which were exceedingly large or did not give constant potentials in a reasonable length of time. The results just quoted apply only to those electrodes which either were not dried or were dried by some method at room temperature. When, however, the electrodes were heated directly in the flame the mortality was much greater. These points will be discussed presently.

Our observation, namely, that these imperfections and cracks in the seals were the cause of considerable variation in potential, is not new. Biilmann and Jensen,⁸ Biilmann,⁹ and Cullen⁶ have all found difficulty with electrodes in which fissures were formed, as they were quite likely to be formed with their method of drying the electrode. However, as they give no results which indicate the magnitude of errors produced in this way, we report our results in some detail to emphasize the recommendation, originally Biilmann's,¹⁰ that several metal electrodes be immersed in the solution for a preliminary intercomparison whenever the quinhydrone electrode is used.

Because of this difficulty with electrodes made with short wires a number of investigators prefer electrodes made with longer pieces of platinum or of gold or with pieces of a base metal welded to the noble metal. While in an investigation involving the measurement of as large a number of potentials as ours, mercury as a connecting medium proved infinitely more convenient than wire connectors, nevertheless, in an attempt to determine whether the variations in potential which, though small, still remained could be obviated by dispensing with mercury, we made a number of elec-

⁸ Biilmann and Jensen, *Bull. soc. chim.*, **41**, 151 (1927).

⁹ Biilmann, *ibid.*, **41**, 213 (1927).

¹⁰ Biilmann, *Trans. Faraday Soc.*, **19**, 819 (1924).

trodes with the longer wires, but with the same surface area exposed to the solution. A rather thorough examination was made of this point with a large number of small and large platinum, gold, platinum-iridium and platinum-rhodium wires, 102 long electrodes having been made and compared with the same number of short electrodes. No difference in reproducibility was found between the two types of electrodes.

The Method of Cleaning and Drying the Electrode.—A variety of methods for cleaning and drying the electrodes were tried in the first part of this work with the idea of finding some method which would give low and consistently reproducible results. We wished to replace Biilmann's¹¹ original method, which was to wash the electrodes with distilled water and to heat them to a red heat in an alcohol flame, by a method which would avoid the heating and consequent difficulty with cracks. In the first place we attempted to dry the electrodes with filter paper but the initial potential differences were as high as 0.00054 and 0.00071 volt and the time necessary for the electrodes to come to a constant potential difference was great. We also tried a number of cleaning mixtures besides the usual chromic acid-sulfuric acid cleaning mixture. In one case the electrodes were boiled for five minutes in 6 *N* potassium hydroxide, in 6 *N* sulfuric acid, in 6 *N* nitric acid and then in distilled water, the electrodes being rinsed in hot distilled water between solutions. In another case the electrodes were cleaned in a 33% alcoholic sodium hydroxide solution and then soaked in distilled water for some time. In both cases the equilibrium potential differences were very much higher than when the chromic acid cleaning mixture made of the C. P. chemicals was used. For instance one pair of electrodes gave an equilibrium potential difference of 0.00016 volt with both the KOH-H₂SO₄-HNO₃ and alcoholic sodium hydroxide treatment and a potential difference of 0.00002 volt with the chromic acid mixture.

Our method as finally adopted for the work reported in this paper was to submerge the electrodes in cold cleaning mixture, which was then heated to about 125° and allowed to cool to room temperature. The electrodes were usually left in the mixture overnight as a matter of convenience, although the time of treatment with the cleaning mixture seemed to be of no importance. In the morning the electrodes were rinsed with a stream of tap water, then soaked for about five or ten minutes in distilled and conductivity water and finally rinsed with ethyl alcohol. They were then inserted in the cork holders already described and dried in a current of purified air. About twenty minutes sufficed to dry them thoroughly. This method was very satisfactory, being convenient, not too time consuming and without the disastrous effects upon the electrodes characteristic of the heating method. The results obtained by this method are given later for a number of series of electrodes in Table I.

¹¹ Biilmann, *Ann. chim.*, [9] 15, 109 (1921).

In that table are included results obtained when the electrodes were connected in pairs during the entire process of cleaning, drying, and between measurements, as well as results obtained when the electrodes were not short circuited in this way. We made a rather extended study of this point, since it is well known that in the preparation of silver, copper or zinc electrodes two similar electrodes reach the same potential much more readily if they are short circuited in the solutions of their salts for some time prior to use. Furthermore, in the preparation of some electrodes for the measurement of the conductance of non-aqueous solutions two of us¹² learned that much more satisfactory results could be obtained if the electrodes were short circuited during the pre-treatment and drying, and in some unpublished work done in these laboratories¹³ it was found that no equilibrium potential of any kind could be obtained when unplatinized platinum was used as a base for hydrogen electrodes unless the electrodes were short circuited.

In the case of the quinhydrone electrode, however, our work indicates that there is no difference in the results obtained when the electrodes are shorted or unshorted. Furthermore, in a series of six electrodes which had been shorted in pairs, potential differences of about the same magnitude were observed between two electrodes which were treated in this way as pairs, as between one electrode of one shorted pair and another electrode from another shorted pair. What we were not able to indicate in the table, however, was that with the shorted electrodes the potential differences decreased regularly until an equilibrium value was reached, when they became constant, whereas with the unshorted electrodes the potential differences sometimes, though not always, decreased to a minimum and then changed sign. This was particularly noticeable with the small wires. Because of this slightly greater irregularity in the potential differences of the unshorted electrodes, we shorted ours throughout most of our determinations.

It is interesting to note that when the electrodes are prepared and cleaned in this way they seem to take up fairly well defined potential differences which appear to be characteristic of the metal comprising the electrodes. For instance, in Series A, electrodes Nos. 1 and 2 could always be counted on to give an equilibrium potential of something less than 0.000010 volt, while electrodes Nos. 3 and 4 gave equilibrium potentials between 0.000010 and 0.000020 volt and Nos. 5 and 6 a value of about 0.000010 volt. These characteristic values reappeared time and time again throughout several years whenever these electrodes were coupled, although the electrodes were remade during that time, in some cases a number of times, and cleaned and used many times.

¹² Morgan and Lammert, *THIS JOURNAL*, **45**, 1692 (1923).

¹³ Travers, "Thesis," Vassar College, 1928.

To see whether this method of cleaning and drying gave results of the same order of magnitude as those obtained when the electrodes were heated, we heated a number of electrodes, selecting electrodes whose characteristic behavior was well known to us because of a large number of results available. Of the seventy-eight electrodes heated, nine cracked and gave the abnormally large results characteristic of cracked electrodes. Furthermore there was very little gain in precision when the electrodes were heated. The average potential, the range of differences and the deviations are practically the same. With the gold electrodes, however, the results were more satisfactory although the tendency of the gold electrodes to crack was greater. However, whereas the air-dried electrodes are likely to give higher initial readings, which then drop to a constant potential difference if the electrodes are short circuited, the flame heated electrodes are likely to give lower initial readings which then rise to higher values in the course of an hour. All in all there seems to be little advantage in the method of heating the electrodes over the method of air drying them and considerable disadvantage due to the readiness with which they crack.

A few determinations on the reproducibility were obtained when the electrode was not dried but was rinsed with some of the acid solution used. Our experience with conductance cells led us to believe that there would be no difficulty in obtaining at least as satisfactory a reproducibility as could be obtained with the dried electrodes but our results indicate that while the gold wires are if anything more readily reproducible with this method, the platinum electrodes are not, the averages, ranges and deviations all being higher when the electrodes are only rinsed. We varied the treatment somewhat, rinsing the electrodes one time with 0.1 *N* hydrochloric acid immediately after distilled water, another time with alcohol before the 0.1 *N* hydrochloric acid and still another time with alcohol and 0.1 *N* hydrochloric acid which was saturated with quinhydrone, but observed no striking difference in the results by different methods. Moreover, inasmuch as the quinhydrone electrode has many applications in solutions which are likely to be limited in amount, the results with the dried electrodes are the more valuable and interesting.

The Preparation of the Quinhydrone Solution.—The influence of the method of preparation of the quinhydrone and subsequent purity on the potentials of quinhydrone electrodes have been the subject of a number of investigations, reference to which is omitted in the interests of brevity. These investigations indicate very generally that the purity of the quinhydrone is of little importance in its effect upon the potential in so far as traces of iron and similar foreign substances are concerned but that methods of preparation and of drying involving raised temperatures or any other procedure which in any way alters the equimolecular proportion of

quinone and hydroquinone are to be avoided. Inasmuch as the Eastman product had been compared with other preparations by a number of investigators and inasmuch as we were interested only in the reproducibility of the electrode we used the quinhydrone furnished by the Eastman Kodak Company without further purification. Moreover, we found no difference in the potentials obtained with different lots of quinhydrone, all of which came from the same company.

The concentration of quinhydrone to be used in solution has also been the subject of investigation, the work done indicating that in accordance with the theory of the electrode the concentration of quinhydrone exerts very little influence on the potentials obtained if the concentration is not too low. Biilmann and Jensen⁸ have made perhaps the most conclusive study of this point and find that the potentials of cells made up 0.00320 *M* or more concentrated in quinhydrone agree very well with the potentials of cells prepared by saturating the solutions with quinhydrone. However, since the solutions are so readily saturated with quinhydrone we used the saturated solutions throughout the investigation. At the end of each experiment some of the excess quinhydrone remained undissolved. No difference in result was obtained when the quantity of quinhydrone was increased or decreased nor when the solution was heated slightly above 25°. However, whenever the solutions were heated to a temperature above 50°, the potential differences were larger and the solution became dark colored in a much shorter time. For this reason we did not heat the solutions before immersing the electrodes.

We made a number of determinations to discover whether there was any difference in the potential differences obtained when the solutions were stirred and when they were not stirred. We found that the average potential difference, range and deviations are of about the same magnitude, but that in the case of measurements in the unstirred solutions the potential differences varied about a mean value rather than approached an equilibrium value. Therefore, to obviate one source of variation, we stirred our solutions throughout most of our work and recommend that this be done whenever feasible, although it is recognized that to do this would frequently complicate the technique in a given application and would be impossible in others.

The Size and Composition of the Metal Electrode.—Our results on the effect of size and composition of the metal electrode on the reproducibility of the quinhydrone half-cells are summarized in Tables I and II. The voltages given are the average of a number of values taken after the electrodes had been immersed in the solution for at least an hour. The values which are averaged for the short-circuited electrodes represent the potential differences between pairs of electrodes which had been connected during cleaning and between one electrode of the series taken as a reference and

the other members of the series, one by one. Our reason for taking the averages of values after sixty minutes is that in our experience any electrodes which, under the conditions of our experiments, will come to equilibrium eventually have done so by that time, which is to say successive readings agreed with one another to within at least 0.000005 volt. To report only the equilibrium values, however, is to exclude many of the results obtained with the small wires and to do this gives an impression that the results with the small wires are better than they are in reality. These results are typical of a larger number of results obtained in the early part of this work before all of the refinements of technique had been developed. In a few cases, however, several results, which were so entirely inconsistent with the rest of the series that they appeared as accidental errors, were discarded, but when this was done the number discarded is indicated in the last column of the table and the original range indicated in parentheses beneath the other value.

TABLE I

COMPARISON OF THE POTENTIAL DIFFERENCES OBTAINED AFTER SIXTY MINUTES IN 0.1000 N HYDROCHLORIC ACID SOLUTION SATURATED WITH QUINHYDRONE BETWEEN ELECTRODES MADE OF METALS OF DIFFERENT DIMENSIONS AND COMPOSITIONS WITH DIFFERENT PRETREATMENT METHODS; SOLUTIONS STIRRED

Electrode series	Electrodes in series	Values in average	Identical cleaning and drying ops. between meas.	Av. potential difference, volt	Ranges of diff., 0.000000 to — (volt)	Av. deviation, mv.	Number results discarded in average
Small Wires							
Shorted Pt, 7-12	6	76	4	0.000008	0.000025 (.000087)	0.005	3
Shorted O, 1-6	6	101	6	.000016	.000041	.008	0
Unshorted O, 1-6	6	39	2	.000024	.000067	.015	0
Shorted Au, 7-12	6	76	4	.000066	.000330 (.000640)	.075	1
Shorted Ir, 7-12	6	40	2	.000009	.000027	.005	0
Shorted Rh, 7-12	6	22	2	.000011	.000020	.004	0
Large Wires							
Shorted A, 1-6	6	94	5	.000009	.000026	.005	0
Unshorted A, 1-6	6	51	3	.000008	.000022	.004	0
Shorted B, 1-6	6	120	6	.000004	.000025	.003	0
Unshorted B, 1-6	6	53	3	.000010	.000042 (.000054)	.009	1
Shorted Pt, 1-6	6	150	9	.000012	.000042 (.000088)	.007	2
Unshorted Pt, 1-6	6	50	3	.000011	.000037 (.000069)	.007	2
Shorted Au, 1-6	6	132	7	.000013	.000058	.011	0
Unshorted Au, 1-6	6	36	2	.000010	.000025 (.000072)	.004	2

TABLE I (Concluded)

Electrode series	Electrodes in series	Values in average	Identical cleaning and drying ops. between meas.	Average potential difference, volt	Ranges of diff. 0.000000 to - (volt)	Average deviation, mv.	Number results discarded in average
Shorted Ir, 1-6	6	84	6	0.000011	0.000034 (.000057)	0.006	2
Unshorted Ir, 1-6	6	44	2	.000006	.000024	.004	0
Shorted Rh, 1-6	6	86	6	.000005	.000014	.005	0
Unshorted Rh, 1-6	6	41	2	.000006	.000028	.004	0
Shorted St, 1-6	6	106	6	.000007	.000024 (.000064)	.004	1
Unshorted St, 1-6	6	41	2	.000007	.000020	.006	0
Special Wires							
Shorted Am. Pt, 1-6	6	74	4	.000014	.000053	.008	0
Unshorted Am. Pt, 1-6	6	39	2	.000012	.000027	.006	0
Shorted L. & N., 1-4	4	42	4	.000002	.000008	.002	0
Foil							
Shorted P ₁₁₋₁ -P ₁₁₋₄	4	54	4	.000004	.000018	.003	0
Unshorted P ₁₁₋₁ -P ₁₁₋₄	4	21	2	.000003	.000010	.003	0
Shorted G ₁₁₋₁ -G ₁₁₋₄	4	51	4	.000006	.000019 (.000064)	.003	1
Unshorted G ₁₁₋₁ -G ₁₁₋₄	4	15	2	.000002	.000007 (.000250)	.002	3
Shorted P ₁₂₋₁ -P ₁₂₋₄	4	54	5	.000004	.000009	.002	0
Unshorted P ₁₂₋₁ -P ₁₂₋₄	4	28	3	.000004	.000010	.003	0
Shorted D-F	6	85	5	.000004	.000015	.003	0
Unshorted D-F	4	9	1	.000002	.000005	.002	0
Shorted G ₁₂₋₁ -G ₁₂₋₄	4	47	5	.000004	.000013	.003	0
Unshorted G ₁₂₋₁ -G ₁₂₋₄	4	25	3	.000003	.000013 (.000055)	.003	4
Shorted P ₁₃₋₁ -P ₁₃₋₄	4	40	3	.000004	.000009	.003	0
Unshorted P ₁₃₋₁ -P ₁₃₋₄	4	23	2	.000004	.000009 (.000019)	.003	1
Shorted G ₁₃₋₁ -G ₁₃₋₄	4	50	5	.000004	.000015 (.000022)	.003	2
Unshorted G ₁₃₋₁ -G ₁₃₋₄	4	20	2	.000008	.000030 (.000039)	.006	1
Shorted P ₂₂₋₁ -P ₂₂₋₄	4	63	6	.000003	.000011	.002	0
Unshorted P ₂₂₋₁ -P ₂₂₋₄	4	26	2	.000002	.000008	.002	0
Shorted I-N	6	50	4	.000003	.000008 (.000016)	.002	2
Shorted G ₂₂₋₁ -G ₂₂₋₄	4	53	6	.000004	.000011 (.000020)	.002	1
Unshorted G ₂₂₋₁ -G ₂₂₋₄	4	26	2	.000009	.000026	.008	0
Shorted P ₂₃₋₁ -P ₂₃₋₄	4	56	6	.000003	.000009	.002	0
Shorted G ₂₃₋₁ -G ₂₃₋₂	2	8	3	.000007	.000012	.002	0

From these results it is obvious that the size of the metal electrode has a very definite effect upon the reproducibility possible with the quinhydrone

TABLE II

SUMMARY OF RESULTS SHOWING THE PERCENTAGE VARIATION IN POTENTIAL DIFFERENCES OBTAINED WHEN METALS OF DIFFERENT COMPOSITIONS AND DIMENSIONS ARE USED IN THE PREPARATION OF THE QUINHYDRONE ELECTRODE. SOLUTIONS STIRRED

Electrode	Total number measured	Percentage of total			
		<0.000010 volt	<0.000050 volt	<0.000100 volt	>0.000100 volt
Small Wires					
O, 1-6	140	27	96	100	0
Pt, 7-12	79	53	99	100	0
Ir, 7-12	40	68	100	100	0
Rh, 7-12	22	32	100	100	0
Au, 7-12	77	27	62	79	21
Large Wires					
A, 1-6	145	56	100	100	0
B, 1-6	174	82	99	100	0
Pt, 1-6	204	50	98	100	0
Ir, 1-6	130	55	98	100	0
Rh, 1-6	127	85	100	100	0
Au, 1-6	170	58	96	100	0
St, 1-6	148	72	99	100	0
Special Wires					
Am Pt, 1-6	113	40	99	100	0
L. & N., 1-4	42	100	100	100	0
Foil					
P ₁₁₋₁ -P ₁₁₋₄	75	92	100	100	0
G ₁₁₋₁ -G ₁₁₋₄	70	83	96	97	3
D-F	94	94	100	100	0
P ₁₂₋₁ -P ₁₂₋₄	82	96	100	100	0
G ₁₂₋₁ -G ₁₂₋₄	76	87	99	100	0
P ₁₃₋₁ -P ₁₃₋₄	64	98	100	100	0
G ₁₃₋₁ -G ₁₃₋₄	73	84	100	100	0
I-N	52	96	100	100	0
P ₂₃₋₁ -P ₂₃₋₄	89	98	100	100	0
G ₂₂₋₁ -G ₂₂₋₄	80	85	100	100	0
P ₂₃₋₁ -P ₂₃₋₄	56	100	100	100	0
G ₂₃₋₁ -G ₂₃₋₂	8	75	100	100	0

electrode in 0.1 hydrochloric acid. Both the average potential differences and the range of differences are greater as the size of the electrodes decreases; the larger electrodes reach a constant equilibrium value more readily than the smaller electrodes. Moreover, with the smaller wires, and particularly with the smallest gold wires, the range on the bridge wire over which there is no deflection on the galvanometer becomes greater and the results more erratic. Frequently no equilibrium value is obtained.

This would seem to indicate that when cells are made of such very small wires the capacity of the cell is so low that, even with the potentiometer

method, enough current is drawn from the cell, while determining the null point, to destroy the equilibrium and hence make the voltage vary. It is probably variations such as these, coupled with additional variations due to concentration polarization, which made it impossible for Biilmann and Lund¹⁴ to use their capillary electrode for more than one or two readings; the question naturally arises where such small electrodes are employed, as to what may be the accuracy of these initial readings. It is possible that a more fortunate form of the microelectrode would be of a type suggested by Boëz¹⁵ in which a sheet of platinum in contact with quinhydrone and two or three drops of the liquid to be examined is held between two cover glasses, since in this type a larger surface of metal could be used.

Table I also gives data on the effect of the composition of the metal on the reproducibility of the quinhydrone electrode.

Upon no point in connection with the quinhydrone electrode has there been such lack of agreement among different investigators as upon the composition of the metal to be used. One group of investigators prefers gold or gold plate, Corran and Lewis¹⁶ suggested that platinum may act as a catalyst for the oxidation of quinol; another group prefers platinum; and still another group reports equally successful reproducibility of potential for either gold or platinum.

Biilmann⁹ states that platinum which has been dulled by use should be avoided and that only new bright platinum should be employed, that platinum is preferable to gold for experiments of minute accuracy, since concentrations of quinhydrone sufficient to give exact potentials with bare platinum are not sufficient with gold but that there are some systems in which platinum may not be used.

Any comparison of our results with those of earlier investigators is extremely difficult, since in the first place, while a number of investigators state a preference, they do not always give data to substantiate their preferences, with the result that we do not know even the order of the precision which they are describing. In the second place, the size of the metal is frequently not stated and size is a factor which we find of greater importance than the composition of the electrode. It is quite probable that the entire issue is confused by the fact that some investigators are drawing conclusions as to the precision of the quinhydrone electrode in certain complex systems when they are using electrodes which are too small to give precise results in any systems.

However, in so far as measurements in 0.1 *N* hydrochloric acid are typical, our results indicate that if an electrode larger than one square centi-

¹⁴ Biilmann and Lund, *Ann. chim.*, [9] 16, 321 (1921).

¹⁵ Boëz, *Compt. rend. soc. biol.*, 101, 524 (1929).

¹⁶ Corran and Lewis, *Biochem. J.*, 18, 1358 (1924).

meter is used, different pieces of the same sample of metal give potential differences, when used as quinhydrone electrodes, which are reproducible with great precision. Table II indicates that it is extremely probable that two pieces of foil larger than one square centimeter of any composition will give potential differences, when cleaned in cleaning mixture, rinsed in water and dried in air, and measured in a solution containing dissolved air under a pressure of one atmosphere, which agree with one another to within something less than 0.00001 volt. This is true whether the metal is the purest gold or platinum obtainable and quite new or whether it is platinum whose exact composition is unknown and which is so old, dulled, roughened and battered (Series D-F and I-N) that it can scarcely be recognized. It is true that we had a few more inexplicably and quite suddenly high results with the gold foils than with the others; on the other hand, the large-surface gold electrodes (L. & N. Nos. 1-4) which we purchased from Leeds and Northrup at two different times gave us some of the best results we had. Quite contrary to Biilmann's experience we found the old platinum foils as good as if not preferable to the new.

As the size of the metal surface diminished, however, we found certain differences in reproducibility among the different metals. The old platinum gave lower averages, ranges and deviations and incidentally reproduced these same results very consistently time after time. The iridium and rhodium alloyed platinum (Series Ir Nos. 1-6, 7-12 and Rh Nos. 1-6, 7-12) gave results which indicated that the reproducibility of different pieces of these metals was of the same order as that of pure platinum (Pt Nos. 1-6, 7-12) purchased at the same time except for the larger rhodium alloyed wires, which gave results lower than either the iridium alloy or pure platinum. Furthermore, all of these electrodes improved in reproducibility as they were used. The old platinum wires (Series A Nos. 1-6 and B Nos. 1-6) gave lower averages, etc., than any of the newer metals except the rhodium alloy. The c. p. platinum from the American Platinum Company recommended by Cullen (Am. Pt Nos. 1-6) gave results intermediate between the results obtained with two samples of platinum from other companies (Pt Nos. 7-12, O Nos. 1-6) which were also smaller in diameter. These electrodes also improved with use. The largest gold wires (St Nos. 1-6), like the foils, gave results as reproducible as the other metals, but the next size of wires (Au Nos. 1-6) and particularly the smallest wires (Au Nos. 7-12) gave much larger values. In fact, so troublesome were the very small wires that time and time again we examined the electrodes for cracks, only to find no evidence of any faulty construction whatsoever.

In conclusion, then, we recommend that, from the point of view of the reproducibility of different pieces of the same sample of metal when used for the quinhydrone electrode in 0.1 *N* hydrochloric acid in the presence of

air, pieces of platinum foil, preferably old and roughened, of at least one square centimeter surface be sealed into soft glass tubing in the usual manner with sealing-in glass and carefully annealed; further, that electrodes so made be tested for leaks, by boiling in hot water, and cleaned, after the tubes are filled with mercury, by immersion in cold chromic acid cleaning mixture prepared from c. p. chemicals, which is then heated to about 125° and slowly cooled, the electrodes being short-circuited in pairs. The electrodes then should be carefully rinsed in distilled water and in alcohol and dried for about twenty minutes in a current of purified air, after which they should be immersed in the solution whose hydrogen-ion concentration is to be measured, to which has been added quinhydrone in excess of the solubility (0.4–0.6 g. per 100 cc. of 0.1 *N* hydrochloric acid). Several electrodes should be immersed for a preliminary intercomparison to eliminate the possibility of a cracked electrode being used. More consistent results are obtained if the solution can be stirred. Gold foils may be substituted for platinum foils but they are more troublesome to work with, since the metal is softer, give erratic results if accidentally contaminated with mercury, and must be welded to platinum wires to be sealed into glass.

Electrodes prepared in this way give results of great precision with ease and a reproducibility which in our experience is far more satisfactory than that possible with any of the other standard electrodes.

We are indebted to the Special Research Fund of Columbia University for a grant for this work, without which it could not have been completed.

Summary

A study has been made of the reproducibility of the quinhydrone electrode in 0.1 *N* hydrochloric acid under varying conditions and with a large number of electrodes of different sizes, ages and compositions, from which study the following conclusions may be drawn.

1. The quinhydrone electrode can be reproduced with ease and with great precision, two electrodes made from the same piece of foil consistently giving potential differences agreeing with one another to less than 0.000010 volt.

2. The greatest source of error in the quinhydrone half-cell lies in the preparation of the metal electrode, differences of almost 0.1 volt having been observed when the glass of one of the electrodes was cracked. For this reason a method of making, testing and cleansing the electrodes, which reduces the breakage to a minimum, is suggested.

3. The results which are obtained when the electrodes are heated in an alcohol flame before use do not justify the method in view of the large number of electrodes which crack.

4. Electrodes made of longer pieces of wire which can be connected directly to the potentiometer wires without the use of mercury as a con-

necting medium do not give any better results than electrodes made of short wires.

5. The size of the metal exposed to the solution determines the precision with which electrodes properly prepared may be reproduced. Very small, short wires give erratic results, larger, short wires give consistent results but larger deviations than foils or longer lengths of wire, but two foils with dimensions greater than one square centimeter give differences of potential, when measured against one another, of less than 0.000010 volt.

6. The composition and age of the metal comprising the electrode is of little importance if the electrode is large enough. However, in 0.1 *N* hydrochloric acid when the electrodes were much smaller than one square centimeter, old roughened platinum seemed to give better results than either new platinum, platinum alloyed with iridium or gold, but the platinum and platinum alloys gave better results than the gold.

Two pieces of metal, cleaned and dried by the method suggested give very nearly the same potential differences whenever they are measured against one another, which fact enables an investigator to select, from a group of electrodes, a few electrodes whose potential differences will invariably be reproduced with great precision.

Work on the effect of nitrogen and on the reproducibility and accuracy of the electrode under other conditions is in progress.

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REDUCTION POTENTIAL OF QUADRIVALENT TO TRIVALENT IRIDIUM IN HYDROCHLORIC ACID SOLUTION

BY SHO-CHOW WOO

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Introduction

It is well known that the most stable compounds of iridium in hydrochloric acid solution are the ions of hexachloriridic and hexachloriridous acids, H_2IrCl_6 and H_3IrCl_6 , in which the iridium is present in the quadrivalent and the trivalent states, respectively. Earlier investigations of these compounds were restricted to the determination of their formulas, and until very recently no studies had been made to determine their physico-chemical properties. Since this research was undertaken, however, Ogawa¹ has published measurements of the electromotive force of cells in which the sodium salts of the chloriridic and chloriridous acids were used. He observed steady changes in the electromotive force, and

¹ E. Ogawa, *J. Chem. Soc. Japan*, 50, 123 (1929).