

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY
(No. 656) AND OF VASSAR COLLEGE]

THE QUINHYDRONE ELECTRODE. III.

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RECEIVED APRIL 24, 1931

PUBLISHED JUNE 8, 1931

Introduction

The first papers of this series¹ were concerned chiefly with the reproducibility in 0.1 *N* hydrochloric acid of the quinhydrone half-cell prepared under varying conditions from different pieces of the same sample of metal. While metals of different ages, sizes, and compositions were used, no intercomparisons between the different series of electrodes were reported. Therefore, except in the case of those series of electrodes which were made up of odd pieces of metal of unknown history, no conclusions could be drawn as to whether the age, size, and composition of the metal base affects the actual value of the potential difference developed or, whether as long as the electrodes are inert with respect to the solutions used, the potentials developed are the same. It is the object of this paper, then, to present the results obtained from an intercomparison not only of the electrodes of different ages, sizes, and compositions used in the first papers of this series but also of electrodes of gold, gold-plated platinum, and graphite not reported upon heretofore. Upon no point in connection with the quinhydrone electrode has there been such a divergence in opinion among earlier investigators as upon the substance to be used as the base of the electrode.

Materials and Apparatus

The materials and apparatus used have been described in the first and second papers of this series with the exception of the following new electrodes:

Gold Electrodes.—*Small Wires* (approximately 0.38 mm. in diameter and 1.5 cm. in length). *Series Au*, Nos. 7–12, six pieces of new 24K gold purchased from Baker and Co. *Series Am–Au*, Nos. 7–12, six pieces of new 24K gold purchased from American Platinum Works. *Series B–Au*, Nos. 7–12, six pieces of new 24K gold purchased from J. Bishop and Co. *Series C–Au*, Nos. 7–12 six pieces of new 24K gold purchased from Sigmund Cohen. *Large Wires* (approximately 1 mm. diameter, 2 cm. length). *Series Au*, Nos. 1–6, *Series Am–Au*, Nos. 1–6, *Series B–Au*, Nos. 1–6, *Series C–Au*, Nos. 1–6, six pieces in each series of new 24K gold purchased from Baker and Co., American Platinum Works, Bishop and Co., and Sigmund Cohen, respectively. In each case the electrodes prepared were of the type heretofore described as short electrodes.

Gold-Plated Electrodes.—*Wires* (approximately 1 mm. diameter, 2 cm. length). *Series G–P Nos. 1–12*: for this series two platinum electrodes were selected from each of the A, B, and Pt series, and six new platinum electrodes were made from a sample of new C. P. platinum wire furnished by Baker. The electrodes were plated with a potas-

¹ Morgan, Lammert and Campbell, *THIS JOURNAL*, 53, 454, 597 (1931).

sium cyanide solution, approximately 2 g. in 100 cc. water, in which some 24K gold was dissolved by electrolysis. A gold anode and three volts were used and the plating continued for some time after the platinum was covered. For one set of data the time was five minutes, for another ten, the electrode being turned during the electrolysis. The plate was perfectly adherent in all cases, although on those electrodes which were plated for the longer time the gold was somewhat darker in color.

Foils.—*Series G-P₁₁* (approximately 1 × 1 cm.) and *Series G-P₁₂* (approximately 1 × 2 cm.). For these series two of the platinum electrodes series *P₁₁* and *P₁₂* were chosen at random and plated by the method just described.

Graphite Electrodes (approximately 2.6 mm. diameter; 2 cm. length).—The lead was removed from 4B Venus pencils made by the American Pencil Company. About one cm. from one end of a three cm. length the lead was ringed with the wax-like substance "piecein" (purchased from Schroder and Ehlers) in the same manner that sealing-in-glass is used. The graphite was then pushed into a length of glass tubing of somewhat greater diameter than the lead while the piecein was still soft, until the ring of piecein was partly in the tube and partly out. More piecein completed the seal, the joint being "wiped" before the substance hardened. The glass tube was then filled with mercury through which connections were made to the potentiometer system.

Because of the sealing wax used for these electrodes the cleansing procedure was modified to some extent. In the first place while the piecein is not attacked by dilute acids, even when in contact with them for many hours, nor by dichromate cleaning mixture over a short time, it is attacked to some extent by cleaning mixture if allowed to stand in it overnight. It is only slightly soluble in cold alcohol. For this reason the graphite electrodes were short-circuited, pair by pair, and immersed in the cleaning mixture for about five minutes, after which they were rinsed hastily in alcohol and dried with purified air.

Procedure and Results

Our procedure for the measurements reported in this paper did not, in general, differ from that reported in the first two papers of this series except that in the case of the intercomparisons, rather than placing six electrodes of one series in one electrode vessel, we placed one pair of each of three series in each vessel. The potential differences between the two like electrodes were measured until the difference was constant, and then the potential differences between all possible combinations of electrodes, taken pair by pair, were measured.

Gold Electrodes.—In view of the fact that the investigators² who express a definite preference for gold or gold plate as a metal base for the quinhydrone electrode, particularly in body fluids, outnumber those³ who state a preference for platinum, and in view of the fact that of the other group⁴ who report equally successful results with either gold or

² La Mer and Parsons, *J. Biol. Chem.*, **57**, 613 (1923); Corran and Lewis, *Biochem. J.*, **18**, 1358 (1924); Mislowitzer, *Biochem. Z.*, **159**, 77 (1925); Liu, *ibid.*, **185**, 242 (1927); Watson, *Ind. Eng. Chem.*, **19**, 1272 (1927); Snyder, *J. Agr. Research*, **35**, 825 (1927); Halton and Fisher, *Cereal Chemistry*, **5**, 445 (1928).

³ Meeker and Oser, *J. Biol. Chem.*, **67**, 307 (1926); Grossmann, *Biochem. J.*, **21**, 267 (1927); Pennycuick and Best, *J. Chem. Soc.*, **131**, 551 (1928).

⁴ Haber and Russ, *Z. physik. Chem.*, **47**, 257 (1904); Biilmann, *J. Soc. Leather Trades Chem.*, **5**, 27 (1921); La Mer and Baker, *THIS JOURNAL*, **44**, 1954 (1922); Conant

platinum, La Mer and Baker make the distinction that while the potentials are the same with either gold, gold plate, or platinum, gold and gold-plated platinum give sharper readings, we did not feel satisfied to confine our investigation to the samples of gold reported in the first paper. Most of the gold electrodes reported upon in that paper were made from 24K gold supplied by Baker and Co., the small and large wires Series Au and the foils Series G₁₁, G₁₂, G₁₃, G₂₂ and G₂₃. The source and purity of the larger wires Series St was unknown and the Series L & N were gold electrodes supplied by Leeds and Northrup Co. The foils and the L & N electrodes gave excellent results, although a few inexplicably erratic results were obtained with the foils. The small gold wires were extremely erratic and unreliable and the larger wires, while fairly good, were also somewhat erratic. Therefore wires of the same size and specifications were obtained from three other companies and the electrodes already described prepared. Wires were selected rather than foils since it was among the wires that the greatest differences in reproducibility appeared. A comparison of their reproducibility in air and in nitrogen follows in Table I. Results for the Series Au are included since many beyond those reported in the first paper have been obtained.

Among the small wires (7-12) the series Am-Au and B-Au were much more readily reproducible than the Series Au which continued to be erratic, although, like the Series Au, Am-Au, B-Au and C-Au gave cells of much smaller current capacities than the platinum wires of the same size. The C-Au series, however, gave results more nearly like the Au series although neither the averages, ranges, nor average deviations were quite as large.

Among the large wires (1-6), on the other hand, the Au series gave the lowest averages, ranges and average deviations. The values for all three of the other series were not only higher than the large wires of the Au series but were higher than the small wires of the same series, although the range on the bridge wire over which there was no deflection on the galvanometer was always greater with the small wires.

All in all, then, there seems to be no doubt that, in so far as our results in 0.1 *N* hydrochloric acid are typical, wire electrodes of small surface made of 24K gold from any source are likely to be extremely erratic in their behavior and that in systems where its presence does not cause difficulty platinum is greatly to be preferred. In the first place, platinum can be sealed into the glass directly whereas gold must be welded to platinum; in the second place, the gold is easily alloyed with mercury, and Fieser, *ibid.*, 45, 2194 (1923); Clark, *Chem. Reviews*, 2, 127 (1926); Parker and Greer, *Trans. Am. Electrochem. Soc.*, 49, 451 (1926); Rosanov, *Zhurnal Exptl. Biol. Med.*, 10, 141 (1928); Gesell, *Am. J. Physiol.*, 87, 1 (1928); Meeker and Reinhold, *J. Biol. Chem.*, 77, 505 (1928); Kolthoff, *Z. physiol. Chem.*, 144, 259 (1925); Cullen, *J. Biol. Chem.*, 83, 535 (1929).

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 24K GOLD FROM DIFFERENT SOURCES. SOLUTIONS STIRRED IN AIR AND WITH NITROGEN; ELECTRODES SHORT-CIRCUITED AND DRIED IN AIR

Electrode series	Electrodes in series	Values in average	Identical cleaning and drying operations between measurements	Av. potential diff., volt	Ranges of diff., 0.000000 to volt	Av. dev., mv.	Number results discarded in average
<i>Small wires</i>							
Air Au, 7-12	6	129	9	0.000069	0.000640	0.069	0
Nitrogen Au, 7-12	6	41	5	.000068	.000410 (.004510)	.074	2
Air Am-Au, 7-12	6	63	6	.000012	.000089	.014	0
Nitrogen Am-Au, 7-12	6	58	5	.000004	.000036	.004	0
Air B-Au, 7-12	6	88	8	.000004	.000058	.008	0
Nitrogen B-Au, 7-12	6	98	10	.000006	.000130	.008	0
Air C-Au, 7-12	6	101	7	.000048	.000400	.052	0
Nitrogen C-Au, 7-12	6	120	12	.000027	.000380	.031	0
<i>Large wires</i>							
Air Au, 1-6	6	205	13	.000012	.000066	.010	0
Nitrogen Au, 1-6	6	106	11	.000005	.000041	.005	0
Air Am-Au, 1-6	6	94	8	.000020	.000150	.016	0
Nitrogen Am-Au, 1-6	6	110	9	.000015	.000210	.012	0
Air B-Au, 1-6	6	111	11	.000035	.000940 (.001880)	.040	2
Nitrogen B-Au, 1-6	6	128	9	.000015	.000580	.019	0
Air C-Au, 1-6	6	135	10	.000019	.000170	.016	0
Nitrogen C-Au, 1-6	6	139	10	.000026	.000170	.022	0

a contamination which greatly alters the potential difference of the electrode; in the third place, a cell prepared with platinum wires has a larger current capacity than a cell prepared with the same size gold wire; and in the fourth place, the gold electrodes exhibit a capriciousness in behavior which is extremely annoying. On the other hand, it is to be noted that the effect of nitrogen upon the gold electrodes is not as definite as upon the platinum electrodes. While the effect of oxidizing agents upon the electrode is a matter still under investigation and will be reported upon at some future date, it seems probable that the reproducibility of the electrode is not altered to the same extent by the presence or absence of oxidizing agents when gold is used as when platinum is used. This fact may account for the disagreement among earlier investigators as to the metal to be used.

As to the cause of the variability of the gold electrodes, we have as yet no explanation to offer. There seem to be at least two effects of the metal upon the cells constructed. One effect is upon the current capacity; cells constructed with platinum wires of a given size have greater

current capacities than those with gold of the same size; for other conditions being the same there is with the smaller electrodes a greater range on the bridge over which there is no deflection of the galvanometer of the type we are using (Leeds and Northrup Type 2500 c). With a more sensitive galvanometer of the type 2285Å, however, this range becomes much smaller.

The second effect is upon the reproducibility of the electrode potentials and may be catalytic in nature. This effect may be a combination of more than one catalytic effect, one possibly involving the quinone-hydroquinone equilibrium and the other involving some reaction with the oxygen, possibly oxidation of the quinone. Since the results with platinum are very much improved with nitrogen, it seems probable that the platinum catalyzes the reaction with oxygen more effectively than the gold. On the other hand, since the large electrodes of both kinds give much better results than the small it seems probable that the metal is instrumental in bringing the quinhydrone system to equilibrium.

We have worked for some time on the theory that gold electrodes which were contaminated with even very small amounts of mercury exhibit an erratic behavior but we can find no connection between their behavior and such contamination. Electrodes which we knew to be alloyed with mercury never improved until the mercury was removed, whereas the electrodes, which we have described as erratic, would give quite consistent results, then one or more inexplicably large potential differences, and then become quite normal. Furthermore some gold electrodes were consistently good throughout the entire research.

Gold-Plated Electrodes.—Enough investigators⁵ have used gold-plated electrodes to make it seem advisable to include some work on these in this paper.

Biilmann and Jensen⁵ found greater deviations between the potentials of quinhydrone half-cells prepared with gold-plated electrodes than with polished platinum electrodes. Biilmann⁵ states that while there are solutions in which platinum cannot be used, and in which gold plate may be used, platinum gives, when it can be used, more precise results. He states further that a concentration of quinhydrone sufficient to give exact potentials with bare platinum electrodes will not give exact potentials with gold-plated electrodes.

⁵ Biilmann, *Ann. chim.*, [9] 15, 109 (1921); *J. Soc. Leather Trades' Chem.*, 5, 27 (1921); La Mer and Baker, *THIS JOURNAL*, 44, 1954 (1922); Conant and Fieser, *ibid.*, 45, 2194 (1923); Kolthoff, *Z. physiol. Chem.*, 144, 259 (1925); Cullen and Biilmann, *J. Biol. Chem.*, 64, 727 (1925); Robinson, *ibid.*, 66, 811 (1925); Biilmann and Jensen, *Bull. soc. chim.*, 41, 151 (1927); Biilmann, *ibid.*, 41, 213 (1927); Clark, *Chem. Reviews*, 7, 127 (1926); Watson, *Ind. Eng. Chem.*, 19, 1272 (1927); Cullen and Earle, *J. Biol. Chem.*, 76, 565 (1928); Halton and Fisher, *Cereal Chem.*, 5, 445 (1928); Cullen, *J. Biol. Chem.*, 83, 535 (1929).

In our experience the gold-plated electrodes give results in air similar to the gold electrodes until they become scratched, with the exception of the foils, which do not give as good results as the gold foils. These electrodes differ from the gold electrodes, however, in that their reproducibility improves in nitrogen. As soon as the electrode is scratched it must be replaced, since a very small scratch seems to change greatly the potential developed. This seems strange in view of the fact that a platinum and a gold electrode may be connected and treated as one electrode and the potential of this combination found not to differ from a single platinum or gold electrode by any amount greater than the latter differ from each other or other platinum or gold wires. Furthermore, we find no difference in reproducibility in those gold electrodes which are prepared with some platinum exposed to the solution from those prepared in such a way that all the gold is covered, and finally, the L & N electrodes which have given such consistently good results throughout the entire investigation have more platinum exposed to the solution at the ends of the gold wire than was exposed by the scratch on a foil.

Our results for the gold-plated electrodes are collected in Table II. The results obtained from electrodes known to be scratched were not included in the average. The electrodes were deplated and tested as platinum electrodes after the results in the table were obtained. Since they were in every case normal it was evident that the results were characteristic of the gold plate and were not due to electrodes faulty in construction.

TABLE II
COMPARISON OF THE POTENTIAL DIFFERENCES OBTAINED AFTER SIXTY MINUTES IN 0.1000 *N* HYDROCHLORIC ACID SOLUTION SATURATED WITH QUINHYDRONE BETWEEN GOLD-PLATED ELECTRODES; SOLUTIONS STIRRED IN AIR AND WITH NITROGEN; ELECTRODES DRIED IN AIR; ELECTRODES SHORT-CIRCUITED

Electrode series	Electrodes in series	Values in average	Identical cleaning and drying operations between meas.	Av. potential diff., volt	Ranges of diff. 0.000000 to volt	Av. dev., mv.	Number of results discarded in average
Air G-P	12	52	4	0.000024	0.000101	0.017	0
Nitrogen G-P	12	72	4	.000011	.000079	.010	0
Air G-P ₁₁	2	10	3	.000012	.000026	.017	0
Nitrogen G-P ₁₁	2	11	4	.000003	.000009	.003	0
Air G-P ₁₂	2	13	3	.000032	.000150	.032	0
Nitrogen G-P ₁₂	2	12	4	.000002	.000016	.002	0

Unless the conditions in other solutions differ greatly from those in 0.1 *N* hydrochloric acid, we can see no advantage in using gold-plated electrodes and a number of disadvantages. In the first place, the electrodes possess most of the disadvantages of the gold electrodes to which are added the disadvantages that the plating is troublesome, that the plate is fragile, and that the electrodes are not as reproducible as the gold.

Finally, as we shall see in Table IV of this paper, the potentials of the gold-plated electrodes deviate from the potentials obtained with other metals to a far greater extent than they do with any other metals. Of course, it is possible that some special conditions of plating may give far better results but as soon as the reproducibility of an electrode depends upon a method of metal deposition, an uncertainty arises, creating a situation similar to the one which exists with respect to the hydrogen electrode, and removes one of the greatest advantages of the quinhydrone electrode, that of simplicity. Our experience very nearly corroborates that of Biilmann, who took some five or six hours to plate his electrodes. We found the gold-plated electrodes sensitive to the oxygen of the solution, however, and suspect that our more rapidly deposited plate was rougher and hence catalyzed the oxygen reaction more readily. If gold plate must be used for some reason (although we cannot foresee any condition under which gold welded to platinum would not be preferable), we suggest that it be plated very slowly.

Graphite Electrodes.—Except for the work of Flexner and Barron,⁶ we are not aware of any attempt having been made to use a carbon electrode as the base of the quinhydrone half-cell. Flexner and Barron report two results in 0.1 *N* hydrochloric acid, one (0.38835 volt) obtained when a quinhydrone half-cell prepared with carbon was measured against a saturated calomel cell, the other (0.3886 volt) when the half cell was prepared with gold plate. They state that the purity of the carbon is unimportant, the rods of a carbon arc lamp or the core of a lead pencil giving identical results.

We prepared a series of carbon electrodes using arc carbons, some carbon electrodes of different cross sections found in the laboratory, and some graphite electrodes prepared from different lead pencils. The carbons were connected directly to the potentiometer wires with binding posts; the cores of the lead pencils were sealed as already described into glass tubing with piecein.

While the lead pencil graphite cores gave promising results from the first, all of the other forms of carbons gave poor results. Moreover, it was observed that when these carbons were immersed in the same electrode vessel with a pair of platinum or gold electrodes, not only did the potentials of the carbon electrodes differ from one another, but the potentials of the platinum electrodes also differed greatly from one another even after they had given low potential differences before the carbon electrodes were introduced. This observation suggests that the carbons absorbed material from the solution, which fact affected not only the potentials of the carbon electrodes but of the others in the same vessel. Graphite not being wetted by water as is carbon and not absorbing ma-

⁶ Flexner and Barron, *THIS JOURNAL*, 52, 2773 (1930).

terial to the same extent, could be expected to yield more readily reproducible potentials.

We tried a number of pencil leads but were most successful in sealing in the 4B Venus pencil leads, possibly fortuitously, possibly because the leads were corrugated on the surface. At any rate, as we wished to examine the properties of these electrodes before we compared the lead from different sources and of different degrees of hardness, we selected from the lot those electrodes which had good seals and had given good results, which happened to be those carrying the 4B Venus leads. It is our present plan to try other forms of graphite after we have seen whether the electrode proves of enough value to justify such a research.

Our results for these electrodes are collected in Table III.

TABLE III

COMPARISON OF THE POTENTIAL DIFFERENCES OBTAINED AFTER SIXTY MINUTES IN 0.1000 *N* HYDROCHLORIC ACID SOLUTION SATURATED WITH QUINHYDRONE BETWEEN GRAPHITE ELECTRODES. SOLUTIONS STIRRED IN AIR AND WITH NITROGEN; ELECTRODES DRIED IN AIR; ELECTRODES SHORT-CIRCUITED

	Electrodes in series	Values in average	Identical cleaning and drying operations between meas.	Av. potential diff., volt	Ranges of diff. 0.000000 to ... volt	Av. dev., mv.
Air 4 B	14	86	12	0.000005	0.000033	0.005
Nitrogen 4 B	14	256	22	.000032	.000620	.038

These lead pencil electrodes have been in constant use for four or five months, and cleaned and measured many times. Prepared in the way we have described, they seem to be just as rugged as the gold or platinum electrodes and to lend themselves to the same cleaning treatments. They resemble the gold electrodes in that the results obtained in air are always as satisfactory and frequently more satisfactory than those obtained in nitrogen. This suggests that they will not be as sensitive to oxidizing agents as platinum and consequently may be more valuable in determinations in body fluids. Electrodes of the size we used give cells with a sufficiently large current capacity to be used with the Type K potentiometer and 2500 e. galvanometer; the region on the wire over which there is no current deflection is small and of about the same magnitude as that observed with the large platinum wires and much less than the gold. They are, of course, unaffected by mercury and are so readily available and so simply and cheaply constructed that they have everything to recommend them. They differ from the gold and the platinum in that the initial potential difference between two electrodes is usually higher but this large difference rapidly disappears and they soon behave in a manner quite similar to the metal electrodes.

It is our plan to try other samples of graphite. It seems quite possible

that excellent micro electrodes might be prepared with blocks of graphite, indentations in which hold the liquid-quinhydrone mixture.

Comparison of the Potential Differences Developed in the Quinhydrone Half-Cell by Different Electrode Substances.—In Table IV are collected the results of a rather extended comparison of the potentials developed by electrodes of different compositions, 24K gold, c. p. platinum, platinum-10% iridium alloy, platinum-10% rhodium alloy, gold-plated platinum, and graphite, of different sizes, ages, and sources in air and in nitrogen. While in our earlier papers we showed that the precision of the quinhydrone half-cell is very great, we hope in this table to give some idea of the probable accuracy among the results obtained in different laboratories. In this table are given only the results of the intercomparisons between electrodes of different series; for the results within any one series the reader is referred to the tables given in the first two papers of this series and to the tables given in the first part of this article. The signs of the potential differences of the cells are reported in this table, the sign being given to the first mentioned electrode. When the average deviation is of the same order of magnitude as the average potential difference, it seems probable that a sign in any direction does not represent an actual difference of potential developed but merely a deviation; when however, the average potential difference is in one direction and is larger than the average deviation, we have considered that there was an actual difference in potential developed with the two metals.

TABLE IV

COMPARISON OF THE POTENTIAL DIFFERENCES OBTAINED AFTER SIXTY MINUTES IN 0.1000 *N* HYDROCHLORIC ACID SOLUTION SATURATED WITH QUINHYDRONE BETWEEN ELECTRODES FROM DIFFERENT SERIES, MADE FROM METALS OF DIFFERENT COMPOSITIONS, SIZES AND AGES. SOLUTIONS STIRRED IN AIR AND WITH NITROGEN; ELECTRODES DRIED AND SHORT-CIRCUITED

Electrode series	Number of electrodes inter-compared	Values in average	Identical cleaning and drying operations between meas.	Average potential diff., volt	Ranges of diff. 0.000000 to volt	Average dev., mv.
Comparison of Metals						
Small Wires						
Air B-Au ₇₋₁₂ vs. Au ₇₋₁₂	12	44	3	=0.000016	0.000100	0.016
Nitrogen B-Au ₇₋₁₂ vs. Au ₇₋₁₂	12	47	3	= .000043	.000370	.058
Air C-Au ₇₋₁₂ vs. Au ₇₋₁₂	12	44	3	= .000012	.000100	.014
Nitrogen C-Au ₇₋₁₂ vs. Au ₇₋₁₂	12	46	3	= .000040	.000410	.058
Air B-Au ₇₋₁₂ vs. C-Au ₇₋₁₂	12	100	6	= .000010	.000056	.011
Nitrogen B-Au ₇₋₁₂ vs. C-Au ₇₋₁₂	12	106	6	= .000028	.000490	.037
Air Au ₇₋₁₂ vs. Pt ₇₋₁₂	12	26	2	= .000018	.000041	.010

TABLE IV (Continued)

Electrode series	Number of electrodes inter-compared	Values in average	Identical cleaning and drying operations between meas.	Average potential diff., volt	Ranges of diff. 0.000000 to volt	Average dev., mv.
Air B-Au ₇₋₁₂ vs.						
Pt ₇₋₁₂	12	56	3	±0.000025	0.000068	0.013
Nitrogen B-Au ₇₋₁₂ vs.						
Pt ₇₋₁₂	12	58	3	±.000014	.000090	.011
Air C-Au ₇₋₁₂ vs.						
Pt ₇₋₁₂	12	56	3	±.000020	.000055	.010
Nitrogen C-Au ₇₋₁₂ vs.						
Pt ₇₋₁₂	12	54	3	±.000029	.000400	.033
Large Wires						
Air Pt ₁₋₆ vs. A ₁₋₆	12	48	2	±.000007	.000024	.005
Nitrogen Pt ₁₋₆ vs. A ₁₋₆	12	48	2	— .000002	.000010	.002
Air Pt ₁₋₆ vs. B ₁₋₆	12	48	2	±.000008	.000024	.005
Nitrogen Pt ₁₋₆ vs.						
B ₁₋₆	12	48	2	±.000003	.000011	.003
Air A ₁₋₆ vs. B ₁₋₆	12	48	2	±.000006	.000023	.003
Nitrogen A ₁₋₆ vs. B ₁₋₆	12	48	2	±.000002	.000005	.002
Air Am-Au ₁₋₆ vs.						
A ₁₋₆	12	38	3	±.000039	.000087	.019
Nitrogen Am-Au ₁₋₆						
vs. A ₁₋₆	12	38	2	±.000025	.000200	.026
Air B-Au ₁₋₆ vs. Au ₁₋₆	12	44	4	±.000016	.000070	.015
Nitrogen B-Au ₁₋₆						
vs. Au ₁₋₆	12	36	2	±.000004	.000015	.002
Air C-Au ₁₋₆ vs. Au ₁₋₆	12	47	4	±.000010	.000090	.008
Nitrogen C-Au ₁₋₆						
vs. Au ₁₋₆	12	36	2	±.000009	.000100	.012
Air B-Au ₁₋₆ vs.						
C-Au ₁₋₆	12	84	7	±.000018	.000063	.013
Nitrogen B-Au ₁₋₆ vs.						
C-Au ₁₋₆	12	80	5	±.000012	.000100	.012
Air B ₁₋₆ vs. Au ₁₋₆	4	8	2	±.000006	.000014	.004
Air Pt ₁₋₆ vs. Au ₁₋₆	4	16	2	±.000015	.000030	.006
Nitrogen Pt ₁₋₆ vs.						
Au ₁₋₆	4	16	2	±.000002	.000006	.002
Air Pt ₁₋₆ vs. St ₁₋₆	12	52	2	±.000011	.000035	.006
Nitrogen Pt ₁₋₆ vs.						
St ₁₋₆	12	48	2	±.000002	.000014	.002
Air Pt ₁₋₆ vs. B-Au ₁₋₆	12	52	3	±.000030	.000110	.024
Nitrogen Pt ₁₋₆ vs.						
B-Au ₁₋₆	12	47	3	±.000012	.000038	.008
Air Pt ₁₋₆ vs. C-Au ₁₋₆	12	56	3	±.000032	.000100	.022
Nitrogen Pt ₁₋₆ vs.						
C-Au ₁₋₆	12	44	3	±.000013	.000045	.010
Air Pt ₁₋₆ vs. Rh ₁₋₆	12	52	3	— .000012	.000044	.008
Nitrogen Pt ₁₋₆ vs.						
Rh ₁₋₆	12	56	3	±.000002	.000013	.002

TABLE IV (Continued)

Electrode series	Number of electrodes inter-compared	Values in average	Identical cleaning and drying operations between meas.	Average potential diff., volt	Ranges of diff. 0.00000 to volt	Average dev., mv.
Air Pt ₁₋₆ vs. Ir ₁₋₆	12	52	3	-0.000044	0.000076	0.014
Nitrogen Pt ₁₋₆ vs. Ir ₁₋₆	12	56	3	± .000002	.000011	.002
Air Rh ₁₋₆ vs. Ir ₁₋₆	12	52	3	- .000035	.000075	.014
Nitrogen Rh ₁₋₆ vs. Ir ₁₋₆	12	56	3	± .000001	.000010	.002
Air Pt ₁₋₆ vs. G-P	4	4	1	- .000029	.000045	.014
Nitrogen Pt ₁₋₆ vs. G-P	4	1	4	- .000001	.000003	.001
Air A ₁₋₆ vs. G-P	4	8	2	- .000026	.000030	.002
Air B ₁₋₆ vs. G-P	4	8	2	- .000034	.000052	.009
Air Au ₁₋₆ vs. G-P	4	8	2	- .000033	.000049	.011
Foil and special wires						
Air D vs. P ₁₂	8	29	2	± .000002	.000005	.002
Nitrogen D vs. P ₁₂	8	32	2	± .000001	.000005	.001
Air I vs. P ₂₂	8	32	2	± .000005	.000013	.003
Nitrogen I vs. P ₂₂	8	32	2	± .000001	.000003	.001
Air D vs. G ₁₂	8	28	2	± .000004	.000012	.004
Nitrogen D vs. G ₁₂	8	32	2	± .000001	.000006	.001
					(.000014)	
Air P ₁₂ vs. G ₁₂	8	28	2	± .000003	.000008	.002
Nitrogen P ₁₂ vs. G ₁₂	8	32	2	± .000001	.000005	.001
Air L & N vs. G-P ₁₁	4	16	3	- .000047	.000108	.045
Nitrogen L & N vs. G-P ₁₁	4	6	2	± .000006	.000008	.002
Air L & N vs. G-P ₁₂	4	16	3	- .000115	.000250	.095
Nitrogen L & N vs. G-P ₁₂	4	8	2	- .000067	.000120	.046
Comparison of Metals and Graphite 4B						
Nitrogen 4B vs. Au ₁₋₆	12	64	2	- .000026	.000090	.012
Air 4B vs. Am-Au ₇₋₁₂	12	60	4	± .000012	.000090	.014
Nitrogen 4B vs. Am-Au ₇₋₁₂	12	48	2	± .000003	.000024	.004
Air 4B vs. Am-Au ₁₋₆	12	88	6	± .000016	.000110	.010
Nitrogen 4B vs. Am-Au ₁₋₆	12	78	6	± .000018	.000210	.016
Air 4B vs. St ₁₋₆	12	43	3	± .000015	.000028	.005
					(.000150)	
Nitrogen 4B vs. St ₁₋₆	12	40	3	± .000007	.000042	.006
Air 4B vs. A ₁₋₆	12	48	4	± .000045	.000071	.011
Nitrogen 4B vs. A ₁₋₆	12	56	4	± .000024	.000100	.022
Air 4B vs. Pt ₁₋₆	8	10	2	± .000028	.000060	.011
Nitrogen 4B vs. Pt ₁₋₆	12	120	8	± .000030	.000190	.023
Air 4B vs. G-P	4	6	2	± .000049	.000079	.020
Nitrogen 4B vs. G-P	4	4	1	- .000002	.000007	.002
Air 4B vs. G ₁₁	4	16	2	± .000003	.000007	.002

TABLE IV (Concluded)

Electrode series	Number of electrodes inter-compared	Values in average	Identical cleaning and drying operations between meas.	Average potential diff., volt	Ranges of diff. 0.000000 to volt	Average dev., mv.
Nitrogen 4B vs. G ₁₁	4	16	2	±0.000005	0.000012	0.005
Air 4B vs. L & N	8	34	4	±.000007	.000024	.005
Nitrogen 4B vs. L & N	8	24	2	±.000009	.000019	.006
Comparison of sizes						
Air O vs. P ₂₃	8	40	2	+ .000014	.000048	.008
Nitrogen O vs. P ₂₃	8	32	2	.000000	.000002	.000
Nitrogen Pt ₁₋₆ vs. P ₁₃	6	8	2	±.000002	.000002	.001
Air Am-Au ₇₋₁₂ vs. L & N	8	34	4	±.000010	.000090	.013
Nitrogen Am-Au ₇₋₁₂ vs. L & N	8	24	2	±.000005	.000020	.004
Air Am-Au ₇₋₁₂ vs. G ₁₁	4	16	2	-.000004	.000010	.003
Nitrogen Am-Au ₇₋₁₂ vs. G ₁₁	4	16	2	±.000001	.000002	.001
Air St ₁₋₆ vs. Au ₁₋₆	4	16	2	+ .000004	.000012	.003
Nitrogen St ₁₋₆ vs. Au ₁₋₆	4	16	2	+ .000002	.000006	.002
Air St ₁₋₆ vs. Am-Au ₁₋₆	12	44	3	±.000010	.000033	.008
Nitrogen St ₁₋₆ vs. Am-Au ₁₋₆	12	40	3	±.000009	.000032	.007
Air St ₁₋₆ vs. G ₁₂	8	32	2	±.000008	.000020	.005
Nitrogen St ₁₋₆ vs. G ₁₂	8	32	2	±.000003	.000010	.002
Nitrogen Au ₁₋₆ vs. G ₁₃	6	8	2	-.000004	.000006	.002
Air Au ₁₋₆ vs. G ₂₂	8	32	2	±.000004	.000008	.003
Nitrogen Au ₁₋₆ vs. G ₂₂	8	28	2	±.000002	.000012	.003
Air G-P ₁₁ vs. G-P ₁₂	4	16	3	±.000143	.000245	.064
Nitrogen G-P ₁₁ vs. G-P ₁₂	4	12	1	±.000013	.000025	.008
Comparison of Sizes and Metals						
Air Pt ₁₋₆ vs. G ₁₂	8	32	2	±.000011	.000023	.005
Nitrogen Pt ₁₋₆ vs. G ₁₋₂	8	32	2	±.000002	.000007	.002
Air St ₁₋₆ vs. Pt ₁₋₆	12	52	2	±.000011	.000035	.006
Nitrogen St ₁₋₆ vs. Pt ₁₋₆	12	48	2	±.000002	.000014	.002
Air L & N vs. A ₁₋₆	4	8	2	-.000012	.000014	.002
Air L & N vs. G-P	8	8	2	-.000038	.000038	.001

The following conclusions may be drawn from the results in this table. The small (Au, 7-12, Am-Au, 7-12, B-Au, 7-12, and C-Au 7-12) and large (Au, 1-6, Am-Au, 1-6, B-Au, 1-6, C-Au, 1-6 and St, 1-6) gold wires from different sources do not differ from each other to any greater extent than they differ among themselves. The reproducibility of the quin-

hydrone half-cell prepared with gold electrodes is not, in general, improved in nitrogen.

The large c. p. platinum wires (A, 1-6, B, 1-6, Pt, 1-6) give practically the same differences of potential no matter what the source or the age of the platinum. Quinhydrone electrodes prepared with these wires are reproducible with great precision, particularly when the solution is stirred with nitrogen.

When the large gold and platinum wires are compared, the average potential differences are of the same order of magnitude as the average deviations and are no larger than the differences among the gold electrodes measured by themselves, from which it may be concluded that, within the limits of experimental error, gold and platinum electrodes develop the same potential difference in the quinhydrone half-cell.

When, however, the c. p. platinum (Pt 1-6) and platinum-10% iridium (Ir 1-6) and platinum-10% rhodium (Rh 1-6) alloys are intercompared, the c. p. platinum is negative to the alloy in air and more negative to the iridium alloy than to the rhodium alloy. Quite consistently the rhodium alloy is negative to the iridium alloy. In nitrogen these differences disappear almost entirely, although there are a few more negative results than positive.

Other actual differences in potential developed appear when the large c. p. platinum (A, 1-6, B, 1-6, Pt, 1-6) or gold (Au, 1-6) wires are compared with the gold-plated wires (G-P). Here again the c. p. platinum and 24K gold are negative to the gold-plate and again the difference disappears in nitrogen.

Among the foils and longer wires (L & N) all electrodes, old and new, seem to give the same potential differences and with great precision with the exception of the gold plates. Again the gold wires, in this case L & N, are negative to the gold plate.

The potential differences obtained with the graphite electrodes (4B) deviate from those obtained with gold or platinum wires, but the deviations are both positive and negative. They give, however, with great precision, the same results as the gold foils (G_{11}) and long wires (L & N).

An intercomparison of sizes indicates that there is no difference in the potential developed, but merely the difference in range and deviation expected of the smaller wires from the previous results.

Of course, there is the possibility in an intercomparison such as this, when electrodes being compared are in the same vessel, that if the effect of the electrode substance is catalytic in nature, a small electrode, for instance, will be affected by the presence in the vessel of a large electrode. While an effect on the gold and platinum electrodes was obvious in the vessels containing the carbon electrodes, in other cases the electrodes seem to retain their own characteristics regardless of the properties of

their neighbors. Any catalytic effect seems to be upon the medium immediately surrounding the electrode.

The results given in this paper indicate that, in so far as results obtained in 0.1000 *N* hydrochloric acid are typical, an investigator in one laboratory may select either gold, platinum, or graphite for the base of a quinhydrone electrode and expect the potential of such an electrode to agree with that obtained in another laboratory with the same precision with which electrodes prepared from different samples of the same metal or graphite agree. Further work in other solutions will be reported in another paper.

We are greatly indebted to the Special Research Fund of Columbia University for a grant for this work and to Miss Margaret Campbell, who, as research assistant, made the measurements and compiled the results for this paper.

Summary

A study has been made of the comparative potential differences obtained for the quinhydrone electrode in 0.1000 *N* hydrochloric acid when prepared with metals and graphite of different sizes, ages, sources and compositions, from which study the following conclusions may be drawn.

1. Gold electrodes, from whatever source, are likely to give erratic results unless the electrode is a foil or wire as large or larger than 1 sq. cm.

2. Gold electrodes give cells of lower current capacities than do platinum electrodes of the same size under the same conditions.

3. Very satisfactory quinhydrone electrodes may be prepared from the graphite core of a lead pencil but not from lamp carbons, etc., since the latter seem to absorb the electrolyte, affecting not only their own potentials but the potentials of any metal electrodes immersed in the same solution.

4. The reproducibility of gold-plated electrodes is not as satisfactory as either gold, platinum or graphite.

5. The reproducibility of quinhydrone electrodes prepared with gold or with graphite is not in general improved in nitrogen, whereas that of electrodes prepared with c. p. platinum, platinum-iridium, platinum-rhodium alloys, or with gold-plated platinum is very decidedly improved.

6. 24K gold and c. p. platinum develop, within the limits of the reproducibilities possible with different samples of the same substance, the same potential differences, no matter what the size, age or source of the substance. Lead pencil graphite also seems to develop the same potential difference, although that from only one source has been thoroughly tested.

Platinum-10% iridium, platinum-10% rhodium alloys and gold-plated electrodes do not develop the same potentials, the c. p. platinum or 24K

gold being negative to the alloys and plate. This difference, however, disappears almost entirely if the solution is stirred with nitrogen.

Further work in other solutions and on the effect of oxidizing agents is in progress.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

MOLECULAR AND ACTIVATED ADSORPTION OF HYDROGEN ON MANGANOUS OXIDE SURFACES

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RECEIVED APRIL 28, 1931

PUBLISHED JUNE 8, 1931

In a recent communication,¹ the rapidly accumulating data relative to the variation of adsorption and heats of adsorption of gases on numerous surfaces with variation in temperature and pressure as well as data on the velocities with which adsorption and desorption equilibria are attained have been collected and analyzed. The data have been shown to be a necessary consequence of a modified theory of adsorption which differs from the classical theory in the introduction of the concept of activation energy into adsorption processes. On classical theory, the activation energy of adsorption is zero and that for desorption is λ , which is identical in magnitude with the usual heat of adsorption. The modification proposed is to require an activation energy, E , for adsorption and, consequently, an activation energy, $E + \lambda$, for desorption processes. This introduction of the activation energy concept does not change the theoretical equilibrium value for adsorption in its dependence on λ . On the other hand, the individual rates of adsorption and desorption will decrease exponentially as E increases, so the rate of attainment of equilibrium may vary within wide limits which will be dependent upon the magnitude of E .

It was shown in the earlier paper that this method of treatment could be applied to a gas whose adsorption on a given surface was of two types, one involving a low heat of adsorption and a low activation energy, the other a high heat of adsorption and a high heat of activation. It was shown that this led to two theoretical adsorption isobars, that with the high heat of adsorption involving greater amounts of adsorbed gas at a given temperature and pressure. Dependent on the magnitude of the two activation energies it was shown that, at sufficiently low temperatures, the lower adsorption would be the only type occurring, at higher temperatures the higher adsorption, while, in an intermediate temperature range, dependent on the respective magnitudes of the two activation energies, a transition region of pseudo-equilibrium adsorption values would be

¹ Taylor, *THIS JOURNAL*, **53**, 578 (1931).