

solution. Much larger yields of the oxidizing material were easily obtained by this method. The anode solution deposits white crystals on evaporation. A solution of the crystals shows oxidizing powers but this property is destroyed on warming the solution. The compound will oxidize methyl alcohol to formaldehyde. Further investigation is being made to determine whether the oxidizing material is a percyanic acid, HO_2CN .

Summary

1. $(\text{OCN})_x$, the free oxycyanogen radical, has been isolated and some of its properties determined.
2. An explanation is offered for the oxidizing solution obtained on the electrolysis of potassium cyanate.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY. No. 685, AND OF VASSAR COLLEGE]

THE QUINHYDRONE ELECTRODE. IV

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Introduction

While a number of investigators have made determinations of the electromotive force developed between the quinhydrone and other standard half-cells in solutions other than 0.1 *M* hydrochloric acid, we have found no data which indicate that any extended study has been made of the effect of the composition and concentration of the solution on the reproducibility of the quinhydrone electrode itself.

Biilmann¹ tested the electrode in a number of dilute solutions ranging in *PH* from 1 to 9 and compared the data with results from conductance and other measurements, with which they usually agreed to about 0.1–0.003 *PH*. S. P. L. and M. Sørensen and Linderström-Lang² made a study of the inherent salt error of the quinhydrone electrode and pointed out that while the quinhydrone electrode gave the same values as the hydrogen electrode in solutions containing little or no salt it did not give the same value in solutions containing large amounts of salt or in strong acid solutions. This they explained by assuming that the electrolyte content so changed the activity ratio of quinone to hydroquinone that the potential difference measured is no longer the measure of the hydrogen-ion concentration but must be corrected by a factor other than one. Their measurements, like Kolthoff's,³ who also wrote on the reliability of the quinhydrone electrode for the measurement of hydrogen-ion concentration

¹ Biilmann, *Ann. chim.*, [9] 15, 109 (1921).

² S. P. L. Sørensen, M. Sørensen and Linderström-Lang, *ibid.*, [9] 16, 283 (1921).

³ Kolthoff, *Z. physiol. Chem.*, 144, 259 (1925).

in various solutions, were reported to only 0.0001 volt and involved the reproducibility of the hydrogen electrode as well. In view of the fact that we had found such excellent reproducibility under certain optimum conditions in 0.1 *M* hydrochloric acid⁴ and in view of the fact that no work has been done, so far as we know, on the reproducibility of the quinhydrone electrode itself in salt and in other acid solutions which would enable one to know how much of the error pointed out by Sørensen was constant, as assumed by him, and how much was due to an effect on the reproducibility of the electrode, we extended our study to solutions other than hydrochloric acid.

Procedure and Results

For this work we selected representative electrodes from those upon which we have reported previously, electrodes of c. p. platinum, 24 K gold and lead pencil graphite of different sizes. These electrodes had been used so often in 0.1 *M* hydrochloric acid that their characteristic behavior was well known and was further tested by frequent measurements in 0.1 *M* hydrochloric acid between measurements in other solutions. With the electrodes controlled in this way we felt it unnecessary to make as large a number of measurements on each electrode as we had made in the earlier part of the work or to use as many electrodes of each series, or as many series.

The solutions used are listed in the first column of the tables. In general, solutions were selected in the range of *PH* and for the concentrations at which the electrode was supposedly applicable. Recrystallized potassium chloride was used and the grade of phosphates was that sold by the LaMotte Chemical Company for buffers.

The method and apparatus have been described in the first papers of this series. We have been able to test one part of our technique which was mentioned in the third paper as a possible source of error, namely, that in intercomparisons of electrodes in the same vessel there is the possibility, if a reaction is catalytic in nature, that a small electrode will be affected by the presence in the vessel of a large electrode. Although we have made a large number of comparisons of the same electrodes in all types of combinations, we can find no effect of one upon the other except in the case of the arc carbons already mentioned. A group of electrodes of one kind and series measured in one beaker gave the same average potential differences, ranges and deviations as the same electrodes measured in several beakers containing electrodes of the widest differences in sizes, compositions and properties.

The results for the reproducibility of the different types of electrodes in different solutions stirred in air are given in Table I. The values for

⁴ Morgan, Lammert and Campbell, *THIS JOURNAL*, 53, 454, 597 (1931); Morgan and Lammert, *ibid.*, 2154 (1931).

0.1 *M* hydrochloric acid, previously reported, are included for comparison. In the first column are given the solutions used, in the second, third and fourth the values for one series of electrodes, in the fifth, sixth and seventh the values for another series. The second and fifth columns contain the values for the average potential difference in microvolts, an average obtained, as explained in the first paper of this series, from a number of values taken after the electrodes had been immersed in the solution for at least an hour. The third and sixth columns contain the values for the range of potential differences observed, also in microvolts, and the fourth and seventh columns the values for the average deviation from the average

TABLE I
COMPARISON OF THE POTENTIAL DIFFERENCES

Obtained after sixty minutes in solutions of various compositions saturated with quinhydrone between electrodes made of c. p. platinum, 24 K gold, and lead pencil graphite of different sizes. Solutions stirred in presence of air; electrodes short-circuited and dried in air.

Solutions	Electrodes: Pt, Nos. 1-4			Electrodes: Au, Nos. 1-4		
	Av. P. D., μ v.	Range, μ v.	Av. dev., μ v.	Av. P. D., μ v.	Range, μ v.	Av. dev., μ v.
0.1 <i>M</i> HCl	10	88	7	12	66	10
.01 <i>M</i> HCl and 0.09 <i>M</i> KCl	3	13	2	4	15	3
.1 <i>M</i> KCl	46	110	36	283	990	267
.34 <i>M</i> KCl	51	330	64	13824	25900	9268
.1 <i>M</i> HNO ₃	6	14	4	8	21	5
.1 <i>M</i> HC ₂ H ₃ O ₂	36	130	24	30	107	18
.1 <i>M</i> HC ₂ H ₃ O ₂ and 0.1 <i>M</i> NaC ₂ H ₃ O ₂	26	200	19	6	22	5
.1 <i>M</i> HC ₂ H ₃ O ₂ and 0.75 <i>M</i> NaC ₂ H ₃ O ₂	9	34	6	30	99	26
.05 <i>M</i> H ₂ SO ₄	17	51	10	11	64	10
.03 <i>M</i> Na ₂ HPO ₄ and 0.04 <i>M</i> KH ₂ PO ₄	40	128	25	35	125	29
.3 <i>M</i> Na ₂ HPO ₄ and 0.4 <i>M</i> KH ₂ PO ₄	8	18	5	8	21	6
	Electrodes: 4B, Nos. 1-4			Electrodes: L and N, Nos. 1-4		
0.1 <i>M</i> HCl	5	33	5	1	8	1
.01 <i>M</i> HCl and 0.09 <i>M</i> KCl	31	150	31	3	10	2
.1 <i>M</i> KCl	246	870	222	141	360	101
.34 <i>M</i> KCl	403	1200	303	165	570	155
.1 <i>M</i> HNO ₃	9	53	6	10	26	9
.1 <i>M</i> HC ₂ H ₃ O ₂	79	541	80	22	82	14
.1 <i>M</i> HC ₂ H ₃ O ₂ and 0.1 <i>M</i> NaC ₂ H ₃ O ₂	28	230	28	14	23	6
.1 <i>M</i> HC ₂ H ₃ O ₂ and 0.75 <i>M</i> NaC ₂ H ₃ O ₂	27	90	27	35	48	4
.05 <i>M</i> H ₂ SO ₄	9	34	6	20	54	15
.03 <i>M</i> Na ₂ HPO ₄ and 0.04 <i>M</i> KH ₂ PO ₄	292	926	221	44	130	40
.3 <i>M</i> Na ₂ HPO ₄ and 0.4 <i>M</i> KH ₂ PO ₄	17	63	16	15	33	11

TABLE I (Concluded)

Solutions	Electrodes: P ₁₁ , Nos. 1-4			Electrodes: G ₁₁ , Nos. 1-4		
	Av. P. D., μ v.	Range, μ v.	Av. dev., μ v.	Av. P. D., μ v.	Range, μ v.	Av. dev., μ v.
0.1 M HCl	4	18	3	6	15	4
.01 M HCl and 0.09 M KCl	1	13	2	3	5	2
.1 M KCl	31	67	17	23	67	20
.34 M KCl	16	39	13	750	2618	564
.1 M HNO ₃	2	8	2	11	25	4
.1 M HC ₂ H ₃ O ₂	6	27	4	23	80	17
.1 M HC ₂ H ₃ O ₂ and 0.1 M NaC ₂ H ₃ O ₂	4	20	4	9	17	3
.1 M HC ₂ H ₃ O ₂ and 0.75 M NaC ₂ H ₃ O ₂	3	14	3	8	26	7
.05 M H ₂ SO ₄	4	9	2	7	20	4
.03 M Na ₂ HPO ₄ and 0.04 M KH ₂ PO ₄	16	68	8	40	188	37
.3 M Na ₂ HPO ₄ and 0.4 M KH ₂ PO ₄	26	90	22	22	59	20
	Electrodes: P ₁₃ , Nos. 1-4			Electrodes: G ₁₃ , Nos. 1-4		
.01 M HCl and 0.09 M KCl	8	27	4	2	7	2

value given in the second and fifth columns. No direction of the deviation is indicated since the electrodes in any one series are supposedly identical and could not be distinguished from one another except by our arbitrary system of numbering; hence the signs are unimportant in this table.

It will be observed that for all of the electrodes except the special gold wires from Leeds and Northrup (L and N) the average potential differences are about the same for the three stronger acids, hydrochloric, nitric, and sulfuric, although the ranges and average deviations vary somewhat, and are smaller for the platinum foils (P₁₁) than for the other electrodes. The behavior of the L and N electrodes in nitric and in sulfuric acids is surprising in view of the fact that they had given such consistently low results in hydrochloric acid, but could be accounted for only as affected by the particular acids since the electrodes were frequently tested in hydrochloric acid between measurements in other acids and found to give the same characteristic low values. In acetic acid, however, the average potential differences, ranges and deviations are larger for all of the electrodes, though very little larger for the platinum foils P₁₁, which incidentally have given consistently better results throughout the measurements in all of the acids than any of the other electrodes reported upon in this paper except the L and N in hydrochloric acid. Moreover, the measurements in 0.1 M acetic acid gave rather wide ranges on the potentiometer over which there was no deflection of even our 2285 A Leeds and Northrup galvanometer. This fact suggested that the internal resistance of the cell was becoming appreciable in the case of the acetic acid and that precise measurements can no longer be made in solutions of

such high resistance unless a more sensitive galvanometer is used or the current amplified, or large platinum electrodes used. It will be recalled that in our earlier work platinum electrodes of a given size seemed to give higher current capacities than gold electrodes of the same size.

All in all, then, we are of the opinion, in view of these data and in view of other data we have in other acids and in other concentrations, data which were obtained under slightly different conditions not strictly comparable and hence not included in the table, that the quinhydrone electrode can be reproduced with great precision in solutions of all the common mineral acids, hydrochloric, nitric, sulfuric and phosphoric and in acetic acid in concentrations 0.1 *M* or less, the degree of precision being determined by the sensitiveness of the galvanometer. In a given conductance cell the resistance of the solutions we were using at the time, 0.1 *M* hydrochloric, 0.1 *M* nitric, 0.05 *M* sulfuric, 0.05 *M* hydrochloric, 0.025 *M* sulfuric, 0.033 *M* phosphoric, 0.1 *M* acetic and 0.05 *M* acetic were 39.5, 42, 62, 79, 116, 298, 3006 and 4311 ohms, respectively, and the approximate *P_H* of the solutions 1.04, 1.09, 1.22, 1.36, 1.47, 1.96, 2.88 and 2.95, respectively. That it is with the increasing resistance that the precision decreases rather than with the increasing *P_H* seems probable in view of the fact that when a moderate amount of sodium acetate (approximately 0.1 mole) is added to the 0.1 *M* acetic acid solution, decreasing the resistance to 208 ohms but increasing the *P_H* to 4.59, the average potential differences and the range of no deflection on the galvanometer both decrease. An even greater decrease is observed with the platinum electrodes when more sodium acetate (approximately 0.75 mole) is added to the same 0.1 *M* acid solution, a procedure which brings the resistance of the solution to that of the 0.1 *M* hydrochloric (39 ohms) but raises the *P_H* of the solution to 5.52. The value does not change greatly with the graphite or with the gold foil but increases with the other gold electrodes. As we shall see, this is quite consistent with the observations on the stronger salt solutions which we shall discuss presently.

The 0.01 *M* hydrochloric acid and 0.09 *M* potassium chloride mixture suggested by Veibel⁵ as a suitable solution for a standard electrode gave consistently low average potential differences and ranges for all the electrodes except the graphite.

The results with phosphoric acid have been discussed and present no special problems in reproducibility. The so-called Sørensen's phosphate mixture with a *P_H* of 6.53, approximately 0.03 *M* in Na_2HPO_4 and 0.04 *M* in KH_2PO_4 , having a resistance in our cell of 276 ohms, was used and gave average potential differences rather higher than any of the acids tested, but about the same for all of the electrodes, except graphite and platinum foils. Graphite gave exceptionally high results, platinum lower than

⁵ Veibel, *J. Chem. Soc.*, 123, 2203 (1923).

the other electrodes but higher than in the acids. When, however, the weights per liter of phosphate were increased approximately tenfold, but kept in the same proportion, with the result that the mixture had a resistance of 39 ohms, that of the 0.1 *M* hydrochloric, but a *P_H* approximately the same as the first mixture, the average potential differences decrease with all of the electrodes except the platinum foils.

The results in 0.1 and 0.34 *M* potassium chloride are by far the most interesting. Here we have unbuffered neutral solutions of resistances 122 and 39 ohms, respectively, in contrast to the other solutions which have been either acid or buffered. In the first place, in the 0.1 *M* solution all the results are higher than those in the 0.1 *M* hydrochloric acid. When the resistances of the solutions are made comparable by adding potassium chloride until the solution is 0.34 molar, the results show even greater discrepancies. In the first place, the platinum electrodes stand out as giving distinctly lower results, second, the gold electrodes and particularly the smallest gold wires give amazingly high results, and, third, the graphite gives results somewhere between the platinum and gold. Of course, these results were immediately suspected and the electrodes thoroughly examined but no reason could be found for their behavior other than the fact that unbuffered solutions in the neutral range not only give constant errors when the quinhydrone electrode is used, due to the fact that the hydrogen ion from the dissociation of hydroquinone becomes appreciable, but also that the reproducibility, particularly with the gold electrodes, is affected. All the electrodes gave rather large ranges on the potentiometer over which there was no deflection, the platinum again being better in this respect than the gold. The reproducibility for electrodes used in these solutions is so poor that the actual differences are of no value.

An intercomparison of the potential differences developed by electrodes of the series recorded in Table I was made, of which the results given in Table II are typical. As stated in a previous communication such an intercomparison gives some idea of the accuracy which can be obtained by different investigators using different electrode substances from different sources. The signs of the potential differences of the cells are reported in this table as in the third paper of the series, since, while two metals may give the same reproducibility among different pieces of the same sample, it is of course interesting to see whether the same potential difference is developed in the two cases. As stated in the third paper the sign is 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 one direction does not represent an actual difference of potential developed but merely a deviation, but when the average potential difference is in one direction and is larger than the average deviation, it seems probable that there is an actual difference developed by the two metals.

TABLE II

COMPARISON OF THE POTENTIAL DIFFERENCES

Obtained after sixty minutes in various solutions saturated with quinhydrone between electrodes from different series made from substances of different composition and sizes. Solutions stirred in air. Electrodes dried and short-circuited.

Solutions	Electrodes: Pt ₁ -4 vs. Au ₁ -4			Electrodes: Pt ₁₁ vs. G ₁₁		
	Av. P. D., μ v.	Range, μ v.	Av. dev., μ v.	Av. P. D., μ v.	Range, μ v.	Av. dev., μ v.
0.1 M HCl	±15	30	6
.01 M HCl and 0.09 M KCl	+27	42	5	± 5	14	3
.1 M KCl	±36	80	22	±86	200	58
.34 M KCl	+8726	21920	8553	±219	970	218
.1 M HNO ₃	+31	48	7	± 8	27	8
.1 M HC ₂ H ₃ O ₂	+79	177	27	±11	33	8
.1 M HC ₂ H ₃ O ₂ and 0.1 M NaC ₂ H ₃ O ₂	+47	65	9	± 5	11	3
.1 M HC ₂ H ₃ O ₂ and 0.75 M NaC ₂ H ₃ O ₂	+28	58	14	± 3	9	2
.05 M H ₂ SO ₄	+40	75	16	± 7	17	4
.03 M Na ₂ HPO ₄ and 0.04 M KH ₂ PO ₄	+64	82	12	±73	153	23
.3 M Na ₂ HPO ₄ and 0.4 M KH ₂ PO ₄	+53	70	14	+81	132	19

These results should be compared with those in Table I. In general the same solutions which gave difficulty in reproducibility when different pieces of the same metal were used gave difficulty in that high differences in potential were developed when electrodes of different kinds or sizes were coupled to form cells. In the neutral unbuffered solutions the same characteristic high values appeared whenever gold electrodes were involved. Again, in general, the larger the electrode, the smaller the differences and average deviation.

In conclusion, then, these results seem to indicate that while the quinhydrone electrode is reproducible with great precision in 0.1 M hydrochloric acid and in dilute solutions of other mineral acids, particularly if platinum foil electrodes of at least 1 × 1 sq. cm. surface are used, its reproducibility in other solutions and particularly in neutral salt solutions is largely a matter of conjecture and seems in some way to depend upon the substance used as the base of the electrode. With small gold electrodes differences in potential were observed between two pieces of the same wire immersed in the same solution, which were far greater than the salt error correction suggested by Sørensen for like concentrations of similar solutions, corrections deduced from solubility measurements and assumed to be the "constant error" of the electrode in such solutions. Saturated solutions of quinhydrone in these different electrolytes were placed in stoppered tubes and kept for some days. In all cases there was about the same amount of undissolved quinhydrone in the bottom of the tube but, while the 0.1 and 0.05 M hydrochloric, 0.1 M nitric, 0.1 and 0.05 M sulfuric acids

and the 0.1 and 0.34 *M* potassium chloride and 0.01 *M* hydrochloric acid and 0.09 *M* potassium chloride mixture all gave solutions which were only slightly darker than the original mixtures, the 0.033 *M* phosphoric and acetic acids and the strong phosphate buffer gave solutions somewhat darker. Next in intensity of color were the more dilute mixtures of phosphates and the more dilute acetate and acetic acid mixtures and then finally the more concentrated acetate-acetic acid mixtures. After three days the acetate and phosphate mixtures with quinhydrone were almost black, the acetate solutions having turned first. Apparently then there is no very obvious connection between the reproducibility of the electrode and the well-known darkening of quinhydrone solutions. As a matter of fact better reproducibility was obtained in 0.1 *M* sodium hydroxide solutions than in the potassium chloride solutions measured, although quinhydrone solutions turn black instantly when sodium hydroxide is added in excess. About the only generalization which can be made as the result of this study is that while the quinhydrone half-cell prepared in 0.1 *M* hydrochloric or solutions of other strong acids, or in the mixture suggested by Veibel, 0.01 *M* hydrochloric acid and 0.09 *M* potassium chloride, is reproducible with such precision that it recommends itself highly as a secondary standard, it must be used with great discretion as a working electrode in other solutions. Since the electrode material itself is apparently not "inert," as assumed by its early discoverers and advocates, but seems to play some role, whether catalytic or of another nature, its composition must be considered carefully with particular reference to the solution and the conditions under investigation. The use of the half-cell in any research ought to be preceded by a study of its reproducibility under the conditions demanded by the research. The simplicity of its preparation, its constancy and accuracy in some solutions and the unsubstantiated statements in the literature concerning the interchangeability of gold or platinum as electrode material make it an extremely dangerous tool in the hands of the inexperienced. While a number of explanations suggest themselves to account for these variations in application, any final conclusions will be deferred until the work in nitrogen and oxygen is completed.

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 for this paper.

Summary

The reproducibility of the quinhydrone electrode prepared with platinum, gold and graphite has been studied in 0.05 and in 0.1 *M* hydrochloric acid, in a mixture of 0.01 *M* hydrochloric acid and 0.09 *M* potassium chloride, in 0.1 *M* and in 0.34 *M* potassium chloride, in 0.1 *M* nitric acid, in 0.1 *M* acetic acid, in a mixture of 0.1 *M* acetic acid and 0.1 *M* sodium

acetate, in another 0.1 *M* acetic acid and 0.75 *M* sodium acetate, in 0.025 *M* and 0.05 *M* sulfuric acid, in 0.033 *M* phosphoric acid, in a mixture of 0.03 *M* dibasic sodium phosphate and 0.04 *M* monobasic potassium phosphate and in a mixture of 0.3 *M* dibasic sodium and 0.4 *M* monobasic potassium phosphates, and the following conclusions drawn.

1. The quinhydrone half-cell may be prepared in dilute solutions of the common mineral acids with precision comparable to that obtained in 0.1 *M* hydrochloric acid, particularly if platinum foil electrodes are used and the resistance of the solution is not too high.

2. The quinhydrone half-cell has been prepared in acetate and phosphate buffer solutions of *P_H* values approximately 4.6–5.0 and 6.1–6.5, respectively, with a fair degree of precision, the average potential differences between two like electrodes in these solutions being about ten times as large as the corresponding averages in 0.1 *M* hydrochloric acid.

3. In unbuffered salt solutions in the neutral range the quinhydrone electrode is likely to give extremely erratic results, particularly if gold or graphite electrodes are used. The error, due to lack of reproducibility, may be far greater than any constant error calculated by Sørensen and described as "salt error."

4. The role of the electrode substance in the quinhydrone half-cell cannot be overlooked and must be tested for each particular system in which the electrode is to be used.

5. The results in this paper indicate that while the quinhydrone half-cell makes an excellent secondary standard, since it gives extremely precise results when the conditions can be made optimum, it must be used with great discretion as a working electrode, its use being preceded by a study of its reproducibility in the system under investigation.

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