reaction. An attempt is being made to isolate and identify an intermediate at liquid-air temperatures.

## Summary

1. The velocity of the reaction between nitric oxide and oxygen has been studied at 0° and 30°. The reaction was found to be one of the third order at the higher temperature; while the acceleration in the velocity constants at 0° may be due to the formation of $N_2O_3$ or to the imperfect state of $N_2O_4$.

2. A large increase in surface-to-volume ratio by the introduction of glass wool into the reaction chamber caused a marked acceleration in the velocity constants in the latter half of the reaction at 30°; the acceleration was less marked at the lower temperature.

3. No evidence of autocatalysis was obtained.

4. The negative temperature coefficient of the reaction has been ascribed to intermediate compound formation.

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[Contribution from the Department of Chemistry, Columbia University, No. 468]

# EXPERIMENTAL STUDIES ON THE HYDROGEN ELECTRODE[1]

By H. T. Beans and L. P. Hammett

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Two or more hydrogen electrodes in the same solution must agree in potential and their common potential will be the true hydrogen electrode potential of the solution, provided the system is at equilibrium. The present investigation is an attempt to classify some of the conditions which give rise to variable potentials of hydrogen electrodes with platinum catalysts and to show how the variability may be eliminated.

**Apparatus and Materials.**—Electrical measurements were made with a Leeds and Northrup Type K potentiometer, using a carefully standardized Weston cell. The constant temperature bath was a Freas water thermostat, set at 25.00°. The electrical system was carefully tested for leakage. The saturated calomel half-cell[2] was used as reference electrode. Several cells prepared at different times and from different materials showed a maximum variation of 0.3 mv. The hydrogen electrode vessel is shown in Fig. 1. An apparatus on the Soxhlet principle designed by Dr. Walden of this Laboratory was used for cleaning electrodes.

Hydrogen was prepared by electrolysis of 15% sodium hydroxide solution. It was passed successively through a column of cotton, an electrically-heated silica tube containing platinized asbestos, a bead tower through which dil. sulfuric acid was continu-

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[1] The material of this article is taken from a dissertation submitted by L. P. Hammett to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Fales and Mudge, This Journal, 42, 2434 (1920).

ously circulated,[3] and a tube of soda lime. The water used was prepared in the conductivity water still in use in this Laboratory, which is similar to that described by Bourdillon[4] and was kept in a closed silica container. Potassium chloride was once crystallized with centrifugal drainage. Hydrochloric acid was redistilled through a silica condenser. Potassium hydroxide was prepared by the decomposition of electrolytically prepared potassium amalgam in a protected vessel.

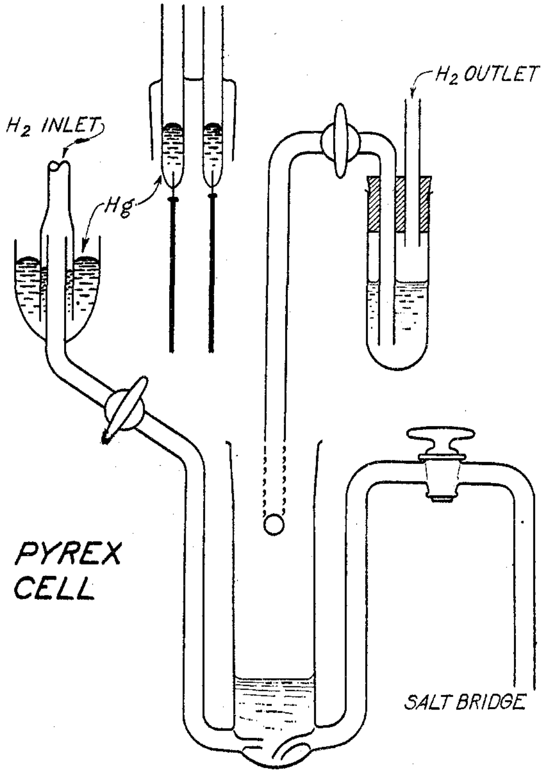

Fig. 1.

**Catalytic Activity of Electrodes.**—An extreme case of variability due to the nature of the electrodes is offered by the behavior of an unplatinized platinum foil. If a bare platinum foil and a platinized one be placed in the same solution of 0.1 *N* hydrochloric acid saturated with hydrogen, a potential, which in the present work has been anything up to 0.3 volts, will exist between the electrodes. This phenomenon has been mentioned previously, notably by Plzák,[5] but deserves further consideration.

A pair of platinum electrodes, one bare and one platinized, were sealed into a cell which, after saturation with hydrogen, was completely closed

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[3] This was similar to the tower described by Kraus and Parker, THIS JOURNAL, **44,** 2432 (1922).

[4] Bourdillon, *J. Chem. Soc.*, **103,** 791 (1913).

[5] Plzák, *Z. anorg. allgem. Chem.*, **32,** 385 (1902).

by fusing off inlet and outlet. Under these conditions the potential, although variable, showed no tendency to diminish materially during the periods, up to one month, of observation. When the electrodes were connected a small current flowed, that is, energy may be drawn from the system; but when the electrodes were short-circuited for as much as a week, the original potential difference was soon reëstablished, when the circuit was opened.

It is obvious that such a withdrawal of energy cannot continue indefinitely; the system must be one out of equilibrium, but one whose progress toward equilibrium is so slow as to be imperceptible. Such a slow process might be, for instance, saturation of the bare electrode with hydrogen, and the possibility of obtaining electrical energy is analogous to the production of electrical energy by the solution of zinc in acid when connected with another electrode of lower overvoltage.

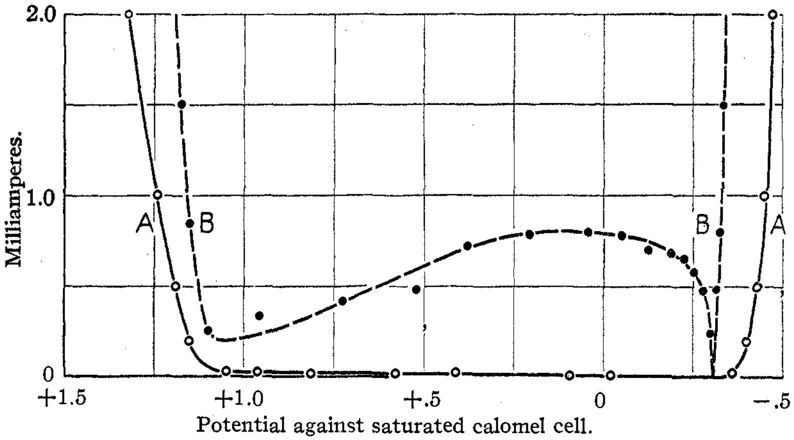

Fig. 2.

The essential difference between bare and platinized electrodes may be seen by a comparison of the polarization curves on bare and platinized electrodes given as Curves A and B, respectively, in Figs. 2 and 3. These were taken on 1-cm. square foils separated by 1 cm. in 0.1 *N* hydrochloric acid saturated with hydrogen and stirred by a hydrogen stream. Potentials were measured against a saturated calomel cell, the tube making the connection leaving the hydrogen cell about halfway between the two electrodes. The potential drop due to the resistance of the solution was neglected. The platinized electrode is an excellent catalyst for the reaction, $H_2 \rightleftharpoons 2H^+ + 2e$, that is, it increases the velocity in both directions; the bare electrode is a poor catalyst.

It has frequently been argued that an electrode formed by coating gold or gold-plated platinum with platinum black should come to equilibrium more quickly than one with a platinum base, because of the time required to saturate the massive platinum. Actually, the current required to polarize a bare electrode to the potential of a platinized one is too small to produce a measurable polarization of the latter; and it has been found experimentally that a short-circuited combination of bare and platinized electrodes takes up immediately a potential equal, within the error of measurement, to that of the platinized electrode alone. Massive platinum is not prejudicial to speed in the attainment of equilibrium, since it need not be saturated with hydrogen.

The necessary catalytic activity is not confined to electrodes coated with finely divided metals of the platinum group. When a smooth platinum foil is subjected to the oxidizing action of an electric current in various electrolytes or of such oxidizing agents as chloroplatinic acid, *aqua regia*, or chromic acid, and then reduced by more or less prolonged action of hydrogen or by cathodic electrolysis, it has at first a considerable catalytic activity. Curve C in Fig. 3 shows the anodic polarization of such an electrode in hydrochloric acid saturated with hydrogen. Curve D for a platinized electrode anodically polarized and then reduced compared with Curve B for the same electrode before this treatment shows the same effect of increased activity. This effect appears even when long periods have elapsed between the oxidation and the reduction. With a bare electrode the activity disappears rapidly after the reduction has taken place, so rapidly that such an electrode is of no practical use for the measurement of hydrogen-electrode potentials. The close correspondence between these results and the effects of oxidation upon platinum catalysts for the combination of hydrogen and oxygen, first noticed by Faraday,[6] is striking and suggestive.

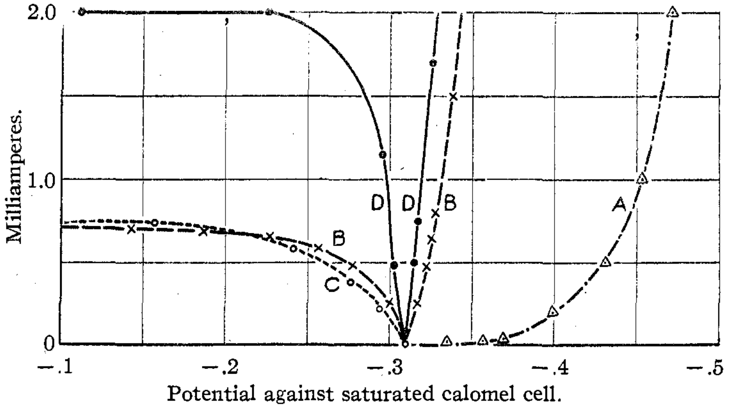

Fig. 3.

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[6] Faraday, "Experimental Researches," (Everyman's Library), p. 84.

Bright metallic deposits of platinum prepared electrolytically are catalytically active for the hydrogen-hydrogen ion reaction, and their life, while not as long as that of platinum black, is sufficient to make their use as hydrogen electrodes possible. Such deposits were easily obtained from a solution of chloroplatinic acid purified by the method of Wichers.[7] Over a wide range of concentration and current density such solutions gave brilliant metallic deposits on electrolysis; and, most important, bright deposits were obtained when the plating bath was strongly alkaline with sodium hydroxide. It would be interesting to determine what chance impurity makes it possible to obtain platinum black from some samples of commercial chloroplatinic acid, and to compare its effect upon catalytic activity with that of lead which is often added to platinizing solutions. Contrary to some statements in the literature, we have had no difficulty in preparing platinized electrodes of high activity from platinizing solutions containing lead.

Consideration of these various methods for obtaining catalytic activity suggests that it is not extent of surface but quality of surface that determines activity, and that freshly prepared surfaces are the active ones. If, as seems likely, platinum becomes covered with a layer of combined oxygen atoms or molecules when oxidized, it is to be expected that the removal of this layer will leave a highly unsaturated, active surface. The decay in activity may be attributed to a saturation by rearrangement of the surface layer, or to accumulation of poisons which may be removed by renewed oxidation.

**Effect of Oxygen.**—That hydrogen electrode measurements cannot be made in the presence of oxidizing agents which react with hydrogen on the active platinum of the electrode is well known. At the start of any measurement the solution contains oxygen, which is such a substance. The well-known difficulty of completely removing one gas from a solution by bubbling another gas through the liquid shows that the removal of this oxygen must depend upon a combination with the hydrogen. A study was therefore made of the effect upon the potential of known percentages of oxygen in the hydrogen stream supplying the electrode vessel. An auxiliary generator fed a mixture of oxygen and hydrogen into the main hydrogen stream, the proportion of oxygen being determined by the ratio of the currents in the two generators. The rate of gas flow was 2.5 liters per hour. In Table I are given representative values of the change in potential from that of the electrode in pure hydrogen produced by the given percentage of oxygen.

The main variables are seen to be type of electrode, life in a reduced condition, and hydrogen-ion concentration of the solution. In respect to the two latter factors, and particularly to the great effect of oxygen in

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[7] Wichers, This Journal, **43,** 1268 (1921).

alkaline solutions, this work is in agreement with that of Hofmann and collaborators[8] on the velocity of combination of oxygen and hydrogen on platinum catalysts.

TABLE I

EFFECT OF OXYGEN ON HYDROGEN POTENTIAL

| Electrode | Time in $H_2$ Hours | Solution | % $O_2$ | Mv. | % $O_2$ | Mv. | % $O_2$ | Mv. |
|---|---|---|---|---|---|---|---|---|
| Bright deposit | 1 | Phosphate buffer, *P*H 6.5 | 0.009 | 0.02 | 0.043 | 0.16 | | |
| Same | 44 | Phosphate buffer, *P*H 6.5 | .010 | 1.4 | .048 | 7.0 | | |
| Black | 1 | Phosphate buffer, *P*H 6.5 | .009 | 0.00 | .045 | 0.02 | 0.90 | 1.6 |
| Same | 47 | Phosphate buffer, *P*H 6.5 | | | .047 | 2.5 | | |
| Same | 117 | Phosphate buffer, *P*H 6.5 | | | .047 | 4.5 | | |
| Black (new) | 1.5 | 0.1 *M* HCl | | | .046 | 0.00 | .91 | 0.12 |
| Black (new) | 1.5 | 0.1 *M* KOH | .009 | 2.9 | .046 | 19.0 | | |

From the practical point of view, these results indicate the importance of freshly prepared electrodes; they show why very little attention to exclusion of oxygen is necessary with strongly acid or even with neutral solutions; and they demonstrate the necessity for the most rigid exclusion of oxygen when measurements are to be made in strongly alkaline solution.

It has been noted by various investigators that the speed with which a hydrogen electrode attains equilibrium is markedly dependent upon the shape and size of the cell, that is, upon efficiency of saturation and speed of destruction of oxygen in the solution.[9] This has been notably recognized in the design of the Clark "shaking" electrode. Our experience has been that such questions as this are at least as important as the nature of the electrode in respect to rapid attainment of equilibrium.

**Measurements in Unbuffered Solutions.**—The measurement of hydrogen-electrode potentials in inorganic solutions which are strongly acid, strongly alkaline, or well buffered meets with little difficulty. In a neutral salt solution, however, our experience using the ordinary technique of the bubbling electrode has given a picture of absolute uncertainty—potentials changing rapidly up and down and over wide ranges; large differences in the potential of two electrodes in the same solution; and even differences in the direction of drift. This, moreover, was the case with electrodes which agreed to within 0.02 mv. in 0.1 *M* hydrochloric acid.

Lorenz and Mohn[10] quote Nernst as saying that measurements in neutral salt solutions would give only "undefinierbare Potentiale;" and other authorities have doubted the possibility and even the value of such measurements. There should, nevertheless, be a difference in degree only between a measurement in 0.1 *M* hydrochloric acid and one in millionth molar

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[8] Hofmann and others, *Ber.*, **49,** 2369 (1916); **53B,** 298 (1920); **55B,** 573, 1265 (1922); **56B,** 1165 (1923).

[9] See Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, **1922,** p. 181.

[10] Lorenz and Mohn, *Z. physik. Chem.*, **60,** 422 (1907).

hydrochloric acid, or in pure water, or in potassium chloride solution. As to the theoretical importance and value of such measurements there can be very little question. The electrical properties of pure water are, for instance, fundamental to the electrical properties of aqueous solutions.

The properties of platinum black are such that contamination by the electrode of solutions to be measured was to be expected, and the conclusion has been reached in this work that it is futile to attempt measurements with the platinized electrode on unbuffered solutions in the neutral range. The active, bright-plated electrode already described was therefore developed, and with this it soon became apparent that the greatest single source of difficulty was the overwhelming tendency of platinum to occlude substances of an acid nature and to give up the occluded acid slowly but continuously. This property of platinum was observed by Faraday[11] but deserves further emphasis. Aside from the universal tendency of electrodes prepared in an acid solution to exhibit a potential drifting toward the acid side, the following experiment may show the nature of the phenomenon.

Two electrodes plated in alkaline solution on a platinum foil base which had been cleaned by treatment with fused sodium hydroxide were thoroughly washed in the scrubber mentioned in the section on apparatus. In 0.1 *M* potassium chloride solution they gave potentials after 28 hours of 0.7290 and 0.7285 volt, respectively, constant for 1.5 hours. Used for a measurement in 0.1 *M* hydrochloric acid lasting 26 hours they gave a potential, of 0.3101 v., with variations from time to time of 0.1 mv.; the electrodes always, however, agreed with one another within the precision of measurement. After four hours' washing in the scrubber, they were placed in a fresh portion of the same potassium chloride solution as before and gave the following values: after 23.5 hours, 0.6571, 0.6472 v.; after 26.5 hours, 0.6407, 0.6342 v.

The only absolutely reliable method of removing this occluded acid seems to be treatment with fused sodium hydroxide. It is then the slow release of acid from the electrodes which accounts for the drift toward the acid side; for the failure of electrodes to agree, because electrodes in a solution of rapidly changing hydrogen-ion concentration rarely agree; and for the sudden rapid changes in potential when the hydrogen flow is shut off, because the composition of the layer immediately next to the electrode, and hence the potential, is a function of the rate of stirring.

Gold-wire electrodes coated with bright platinum from an alkaline solution were therefore used, and electrodes were obtained whose agreement with one another and the steadiness of whose final potential left little to be desired. Two possible objections remained. The time required to reach a steady potential varied from eight to twelve hours,

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[11] Ref. 6, p. 228.

whereas a steady value is attained in buffered solutions in the same range in 15 to 30 minutes. The final, steady potential was in the neighborhood of 0.75–0.77 volt, well on the alkaline side. These facts might be used to argue that there is contamination of the solution with alkali by the electrode in spite of the steadiness of the final equilibrum value and of the fact that successive runs on separate portions of solution with intermediate thorough scrubbing of the electrodes showed no tendency to produce a less alkaline value in the second run.

The possibility that the slowness of attainment of equilibrium was due to the removal of carbon dioxide from the solution by the hydrogen stream was next investigated. It was found that immersion of the electrodes in the potassium chloride solution in the closed cell for 15 hours before starting the hydrogen had no marked effect upon the time required to come to equilibrium; but that bubbling hydrogen through the solution in the cell for several hours before introducing the electrodes had a very marked effect, as may be seen from the curves in Fig. 4, where A is the curve of potential against time for a fresh solution, and B is for a solution previously thoroughly saturated with hydrogen.

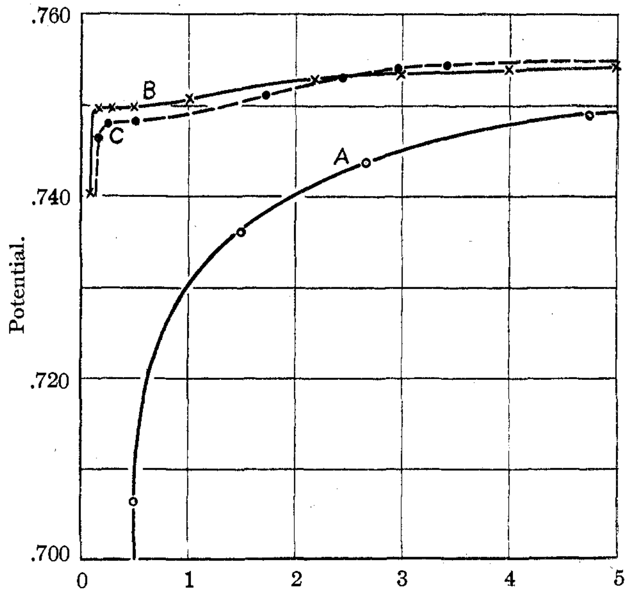

Fig. 4.

There still remained a drift of 8 to 10 mv. toward the alkaline side during the course of eight to ten hours after the first half hour, which was considered to establish equilibrium as regards saturation and oxygen removal. That even this was due to atmospheric contamination was established by the following experiment. A pair of electrodes which had come approximately to equilibrium was removed from the cell into the atmosphere for 30 seconds and then replaced. In Fig. 4, Curve B shows the potential time curve of the electrodes when removed directly from scrubber to the solution which had previously been thoroughly saturated with hydrogen; Curve C is the corresponding curve after removal of the electrodes into the atmosphere for 30 seconds and replacement in the cell.

For a large part of the development work and for the final measurements a stock solution of potassium chloride in conductivity water of a concentration of 0.0863 *M* was used. This was kept in a well-steamed Non-sol bottle. The alkalinity of the solution is accounted for by the following experiment. To 200 cc. of the solution described above was added 0.5 cc. of 0.001 *M* hydrochloric acid and the potential was found to be 610 mv. against the saturated calomel cell. After nine days' standing in a well-steamed Non-sol bottle the potential was found to be 704 mv.

Contamination of solutions with alkali even by resistance glass is thus seen to be a serious matter. In the Pyrex cell used in these measurements, which had been in constant use over a period of four months, being steamed out on an average two to three times a week, such contamination of a solution which is already slightly alkaline seems to be negligible, and in the Non-sol bottles the rate of drift slows down materially as the solution becomes more alkaline.

TABLE II

1. Solution not previously saturated with hydrogen. Date, 7/26.

| | | | | | |
|---|---|---|---|---|---|
| Time (hours: minutes) | 14:47 | 16:00 | 18:33 | 19:37 | 20:56 |
| Electrode I | 0.7507 | 0.7512 | 0.7506 | 0.7514 | 0.7510 |
| Electrode II | .7510 | .7512 | .7506 | .7513 | .7511 |
| | 24:15 | 38:46 | 39:55 | 41:00 | |
| | 0.7514 | 0.7527 | 0.7519 | 0.7518 | |
| | .7514 | .7523 | .7519 | .7514 | |

2. Freshly plated electrodes scrubbed for four hours; solution treated with hydrogen for 16 hours. Date, 8/22.

| | | | | | | |
|---|---|---|---|---|---|---|
| Time (hours: minutes) | 0:10 | 0:32 | 0:56 | 2:00 | 4:26 | 6:23 |
| Electrode I | 0.7552 | 0.7558 | 0.7568 | 0.7588 | 0.7617 | 0.7631 |
| Electrode II | .7552 | .7556 | .7568 | .7588 | .7617 | .7631 |
| | 7:27 | 8:28 | 9:38 | 10:43 | 23:03 | 23:43 |
| | 0.7637 | 0.7638 | 0.7636 | 0.7635 | 0.7636 | 0.7634 |
| | .7637 | .7638 | .7636 | .7635 | .7636 | .7633 |

3. The same electrodes scrubbed for four hours; a fresh portion of the same solution treated with hydrogen for 23 hours. Date, 8/24.

| | | | | | |
|---|---|---|---|---|---|
| Time (hours: minutes) | 0:10 | 0:31 | 1:14 | 3:08 | 4:00 |
| Electrode I | 0.7564 | 0.7595 | 0.7616 | 0.7644 | 0.7652 |
| Electrode II | .7564 | .7595 | .7616 | .7644 | .7652 |
| | 6:02 | 8:48 | 10:46 | 11:46 | |
| | 0.7668 | 0.7685 | 0.7685 | 0.7688 | |
| | .7668 | .7685 | .7688 | .7691 | |

The preceding series of measurements may serve as examples of the sort of results that may be obtained.

It should be noted in these typical measurements that the maximum variation between duplicate electrodes is 0.4 mv., and that only with old electrodes which are particularly sensitive to traces of oxygen and more exposed to the chance of having become contaminated; that in Run 1 the maximum variation from the 15th to the 41st hour is 1.9 mv.; that while successive runs with the same electrodes in different portions of the same solution leave considerable to be desired in agreement, there is certainly no tendency for further scrubbing of the electrodes to reduce the alkalinity of the final potential.

Measurements have also been made on solutions prepared by adding small amounts of very dilute hydrochloric acid to the stock potassium chloride solution. Such a run is given in Table III.

TABLE III

Fresh electrodes. Solution previously saturated with hydrogen.

| Time (hours: minutes) | 0:22 | 0:37 | 0:53 | 1:07 | 1:22 | 1:52 | 2:22 | 2:54 | 3:22 | 3:54 | 4:22 | 5:12 | 6:17 | 20:27 | 20:54 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Electrode I | 0.6075 | 0.6073 | 0.6063 | 0.6057 | 0.6053 | 0.6044 | 0.6040 | 0.6042 | 0.6042 | 0.6044 | 0.6046 | 0.6050 | 0.6057 | 0.6304 | 0.6315 |
| Electrode II | .6075 | .6071 | .6061 | .6056 | .6053 | .6042 | .6039 | .6038 | .6040 | .6041 | .6044 | .6049 | .6057 | .6303 | .6314 |

These results show that even as near the neutral point as this, close agreement between duplicate electrodes may be obtained; that in slightly acid solutions the carbon dioxide effect is of much less importance; that in such solutions the potential reaches a maximum rapidly, then drops a few millivolts (this seems to be very general); and that this drop is followed by a slow but steady drift toward higher potentials. As for the drop from the maximum, which is in any case small, it should be noted that the electrode is transferred directly to the solution from the scrubber in which the water is, if anything, alkaline from the action on the glass and that adjustment to a new solution may well be slow. The increase in alkalinity which follows may very well be due to the glass of the cell. Such contamination, it is evident, is unmeasurable with solutions already slightly alkaline, but by analogy with the Non-sol bottles might well be much more serious in a neutral solution where, in the volume used, a change of 1 mv. requires only $4 \times 10^{-11}$ moles of hydrogen or hydroxyl ion. The results show, it is felt, that measurements in this range may certainly be relied upon to within a few millivolts. The whole behavior of these electrodes as contrasted with those prepared in acid solution indicates that there is no such occlusion of alkali by the platinum as there is of acid, but a final proof that there is absolutely no contamination by the electrodes will call for silica apparatus and redistillation in a closed system protected from atmospheric contamination. This will, of course, also be necessary for the accurate determination of the hydrogen electrode potential of pure water and of pure potassium chloride solutions.

The method which has been found satisfactory for measurements in such solutions as these, together with the necessary precautions, is as follows. The electrodes, two of which were always used, were of gold wire 1.25 mm. in diameter, of which about 1 cm. was immersed in the solution. About 3 cm. above the level of the solution these were fused to platinum leads which were fused through the mercury cups on the cap of the cell. The platinum was thus kept well away from the solution. The electrodes when new were cleaned with hot chromic acid mixture, heated to low red heat, then treated for one-half to one hour with fused sodium hydroxide. They were then plated in an alkaline solution of purified sodium chloroplatinate with a current of about 20 ma. for 5 minutes, the electrolyte being stirred mechanically. The thickness of the platinum deposit seems to have little effect upon the life of the electrode. When not in use the electrodes were kept immersed in about 0.1 *M* sodium hydroxide solution. Immediately before use they were washed in the scrubber for one hour or more, the water in the scrubber having been previously well boiled, and then transferred as quickly as possible, to avoid contamination, to the cell which contained the solution to be measured and through which hydrogen was already bubbling. As already mentioned these electrodes are comparatively sensitive to oxygen; the ground joint in the cell cap must, therefore, be kept moistened with conductivity water and all stopcocks through which hydrogen passes must be well greased. Electrical leakage between hydrogen and calomel cells, too small to affect the accuracy of the potential measurement may, nevertheless, allow enough current to flow to produce a perceptible increase in the acidity of the solution.

It is hardly safe to rely upon such electrodes for more than 24 hours' continuous service in a hydrogen atmosphere, and deposition of new platinum on top of the old seems to give uncertain results. The old deposit may be removed with some loss of gold by treatment with hot *aqua regia,* after which the electrodes should be heated to incipient fusion, then treated with fused sodium hydroxide and replated as before.

The criteria for satisfactory measurements in solutions of this nature are as follows: agreement of two electrodes in the same solution; steadiness of potential over considerable periods of time; and potentials which are unaffected by variations in the rate of hydrogen flow or even its complete cessation. It cannot be emphasized too strongly that almost any ill to which hydrogen electrodes are subject affects two electrodes differently and that two electrodes in the same solution offer a most potent means of separating errors due to the hydrogen electrodes from errors due to other parts of the cell. When the electrodes are contaminating the solutions or when there are leaks which allow oxygen to enter the system, stopping the hydrogen flow and sealing the cell produces a sudden sharp change in potential, so that this is also a very valuable criterion.

## Summary

The formation of platinum black demands the presence of some impurity, since purified chloroplatinic acid solutions give only bright electrodeposits.

Catalytic activity for the hydrogen-electrode reaction may be obtained with bright electrodeposits, or evanescently with massive platinum. The prerequisite is a freshly prepared or exposed surface.

Speed of attainment of equilibrium of hydrogen electrodes depends upon removal of oxygen, which is determined by cell design, and by catalytic properties of the electrode. Catalysis by electrodes decreases with exposure to hydrogen, is increased by oxidation, and is much less in alkaline solutions than in acid ones.

Hydrogen-electrode measurements are possible in unbuffered solutions in the neutral range, provided the electrodes are clean. This implies that the platinum has not been deposited in acid solution, that it has not been in contact with acid, and that it is in suitable physical condition.

NEW YORK, N. Y.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WASHINGTON]

# THE INSTABILITY OF PHTHALATE SOLUTIONS TOWARD THE HYDROGEN ELECTRODE

BY CARL Z. DRAVES AND HERMAN V. TARTAR

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A difference of opinion has appeared in the literature concerning the stability of phthalate solutions toward the hydrogen electrode. As a result, the confidence of many has been shaken in the use of the phthalate buffer solutions recommended by Clark and Lubs[1] as working standards of hydrogen-ion concentration for the hydrogen electrode. Because of the ease of preparation of pure standard buffer solutions of potassium hydrogen phthalate, a further investigation of this reported instability was undertaken.

Drifting potentials of the hydrogen electrode in phthalate solutions have been observed by Merrill[2] and by Oakes and Salisbury.[3] Indicators were used by the latter to prove that the phthalate buffers actually changed in hydrogen-ion concentration by an amount equivalent to more than one Sörensen unit when they were in contact with the hydrogen electrode for about 48 hours.

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[1] (a) Clark and Lubs, *J. Biol. Chem.*, **25,** 479 (1916). (b) Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, 1923, p. 273.

[2] Merrill, THIS JOURNAL, **43,** 2690 (1921).

[3] Oakes and Salisbury, *ibid.*, **44,** 948 (1922).