namic results, the divergencies exceeding the estimated error of our measurements, namely ±5 mm., only above 320°. The inferiority of their dynamic method, at least when applied to a substance like this, is apparent.

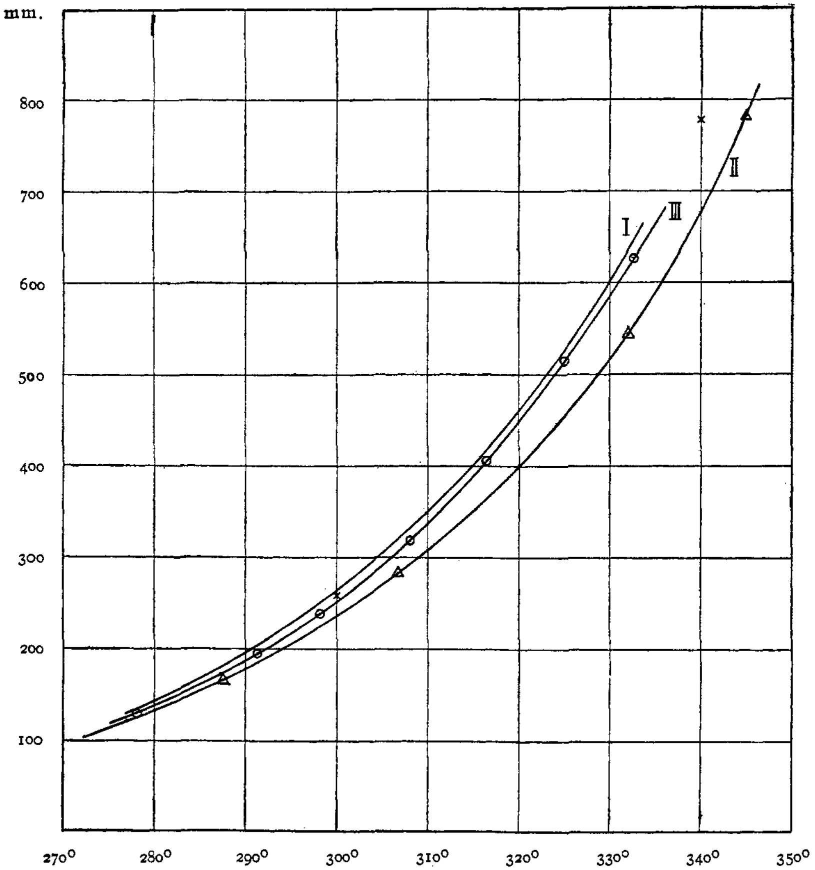

Fig. 2.

[Contributions from the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology, No. 61.]

THE POTENTIAL OF THE SODIUM ELECTRODE.

By Gilbert N. Lewis and Charles A. Kraus.

Received October 3, 1910.

The electrode potentials of a number of important groups of metals have not been measured hitherto, because their action upon water is such as to preclude the possibility of obtaining equilibrium conditions. Among these groups, those comprising the alkali metals and the metals of the alkaline earths are the most notable examples. In the present paper we shall describe a method which may be employed in the determination of electrode potentials of this kind. We shall show, moreover, that this method permits the determination of the potential of the sodium electrode with a higher degree of precision than has yet been reached in the case of any other solid electrode.

Our problem, consisting in the determination of the potential of metallic sodium against an aqueous solution of sodium ion of normal concentration, can evidently be solved only by indirect means. We have found it possible with certain precautions to measure the potential of a dilute sodium amalgam directly against an aqueous solution. It only remained, therefore, to find the difference between this potential and that of pure sodium. This difference in potential measured in any cell where the only process which accompanies the current is a transfer of sodium from the pure state to the dilute amalgam, must be independent of the nature of the electrolyte used. We succeeded in measuring this difference in potential in a cell containing sodium and sodium amalgam electrodes, and an electrolyte composed of a solution of sodium iodide in liquid ethyl amine.

The Electrode Potential of Dilute Sodium Amalgam.

The dilute sodium amalgam used throughout this investigation was prepared and preserved in the apparatus shown in Fig. 1. A bulb, E, is connected by means of a small capillary, F (having a uniform bore of about 0.2 mm.), with a straight tube, GK. While this tube is open at K, a piece of metallic sodium (Kahlbaum) is cut from a larger piece, quickly rolled into cylindrical form and placed in the tube at G. A small glass rod, H, is placed immediately above to serve as a weight in the operation about to be described. The tube is then sealed at K and the apparatus exhausted at A through the 3-way cock B, the cock J being closed and the cock I open. When the apparatus is completely exhausted I is closed and J, which communicated with a reservoir of ammonia (not shown in the figure), is opened for an instant, thus filling the tube IJ with pure ammonia gas. The tubes F and G, and the lower part of E are now surrounded by a paraffin bath and heated gradually to the melting point of sodium. When this point is reached, and the liquid sodium, pressed by the glass weight above, breaks its thin shell of oxide, the cock I is opened cautiously and the pressure of the ammonia slowly forces the molten sodium into the bulb E. The sodium is thus filtered by the small capillary from every trace of oxide or other solid impurity and appears as a bright metallic globule. The paraffin bath is now removed and the capillary is sealed off at F, the left-hand portion of the apparatus being thus removed. After the exhaustion has been continued to remove all of the ammonia gas, pure mercury is allowed to enter the bulb D at C (from an apparatus not shown in the figure) and the tube C is sealed off. B is closed. The lower part of the apparatus, comprising the bulbs E and D and the connecting tube, is then warmed in a paraffin bath to 180° centigrade. The mercury vapor passing slowly from D to E amalgamates quietly with the sodium When the latter is completely amalgamated, the apparatus is allowed to cool. It is then shaken to provide for thorough mixing of the contents and clamped in an inverted position. It may now be sealed at A to any apparatus in which the sodium amalgam is desired and the filling carried out *in vacuo*. The 3-way cock B merely serves to facilitate the cleaning of the tube A after such a filling.

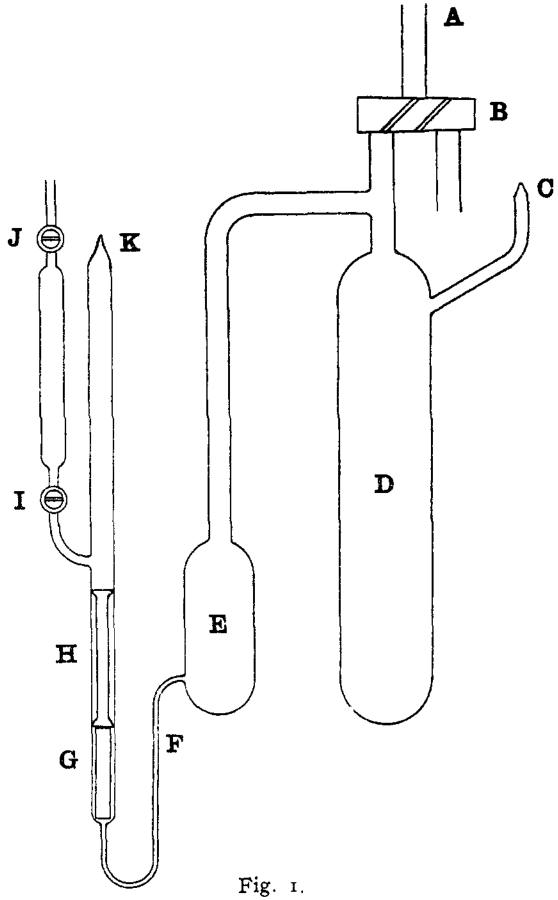

Fig. 1.

The amalgam so prepared and kept does not differ in appearance from pure mercury, and remains unchanged for years.

Two portions of the sodium amalgam were treated with standard hydrochloric acid until the sodium was removed, and the remaining acid was titrated with standard alkali. According to these two analyses (which agree within less than 0.1 per cent.) 100 grams of amalgam contained 0.2062 gram of sodium.

In determining the potential of this amalgam against fifth normal sodium hydroxide, a portion of the amalgam was introduced into the reservoir sketched in Fig. 2. This reservoir was sealed to the apparatus of Fig. 1 (at the points Q and A) and after complete exhaustion the amalgam was allowed to enter through the cock B. The reservoir was then sealed at Q. The side tube L contained phosphorus pentoxide and permelted the entrance of dry air to take the place of amalgam drawn off through M. The amalgam surface at P formed the electrode and electrical contact was provided through a platinum wire sealed in at N. The tube OP was inserted in a half-cell of the usual type, filled with 0.2 *N* NaOH, and was joined thereto by a rubber stopper, O. This half-cell dipped into another containing 0.2 *N* NaCl, which in turn communicated with 0.2 *N* KCl and finally with a normal calomel electrode. The whole system was placed in a thermostat at 25°.

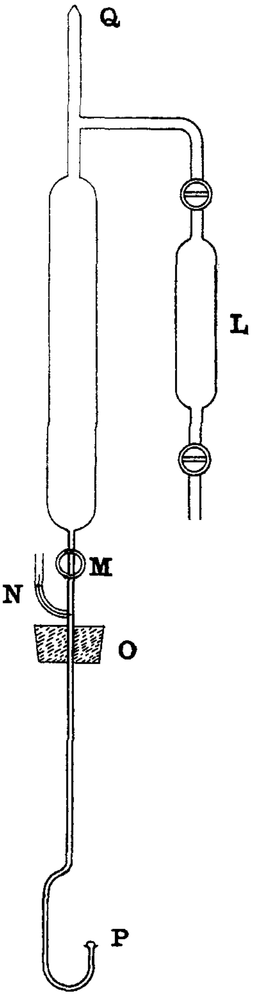

Fig. 2.

The amalgam surface at P when first placed in the sodium hydroxide evolved considerable hydrogen. The action appeared to take place at certain spots where a few extremely minute solid particles accumulated. The extraordinary influence of small amounts of catalyzers in this action of sodium amalgam upon water has already been pointed out.[1] Fortunately it was found that by opening the cock M and allowing one or two drops of amalgam to flow out at P, the minute particles that seemed responsible for the action were carried down. The new surface was acted upon less vigorously, and after this process had been repeated a number of times the surface remained clear of hydrogen for ten to twenty minutes, and showed a constant and perfectly reproducible potential within 0.1 millivolt.

The measured electromotive force was then 2.1749 volts,[2] inclusive of liquid potentials, for the combination, Na amalgam (0.206 per cent.); NaOH 0.2 *N*; NaCl 0.2 *N*; KCl 0.2 *N*; KCl *N*; normal electrode (N. E.).

The liquid potential between KCl *N* and KCl 0.2 *N* is negligible. That between NaOH 0.2 *N* and NaCl 0.2 *N* is 0.0287 v.; that between NaCl 0.2 *N* and KCl 0.2 *N* is 0.0050 v.[3]. Both these potentials oppose the main

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[1] Walker and Patterson, *Trans. Am. Electrochem. Soc.*, 3, 185 (1903); Lewis and Jackson, *Proc. Am. Acad.*, 41, 403 (1906).

[2] This experiment was repeated with the same amalgam nearly two years later and gave the electromotive force 2.1742 volts. Considering the possible change in the composition of the amalgam and the use of different electrical standards, this may be regarded as a satisfactory check.

[3] Lewis and Sargent, THIS JOURNAL, 31, 363 (1909).

e. m. f. of the cell. Adding these figures, therefore, to the measured e. m. f. we obtain for the above cell, exclusive of liquid potentials,

Na amalg. (0.206 per cent.), NaOH 0.2 N, N. E.; E. = 2.1986 v.

In order to calculate now the potential of this amalgam against sodium ion at normal concentration, it is necessary to know the degree of dissociation of fifth normal sodium hydroxide. Instead of calculating this directly from conductivities, we shall assume provisionally, for reasons that will be explained in another place, that the degree of dissociation of 0.2 N NaOH is the same as that of 0.2 N KCl, and that the latter is 82.8 per cent., as found from conductivities. If now we apply the Nernst equation, we find

Na amalg. (0.206 per cent.), Na^+N, NaOH 0.2 N, Na amalg. (0.206 per cent.); E = 0.0461 v.

Combining this equation with that given above we find

Na amalg. (0.206 per cent.), Na^+N, N. E.; E = 2.1525 v.

The Difference in Electrode Potential between Sodium and Dilute Sodium Amalgam.

The difference in electrode potential between sodium and a sodium amalgam in the same electrolyte will be independent of the nature of that electrolyte, provided it is one in which the metal and the amalgam act as completely reversible electrodes. Our problem consisted, therefore, in finding a solvent which is not attacked by sodium, and which dissolves some sodium salt to form a conducting solution. Ethyl amine was finally chosen as the solvent, and attempts were made first to use sodium chloride and sodium bromide as solutes, but neither of these substances proved to be sufficiently soluble to give the solution the desired conductivity. Sodium iodide, however, proved to be extremely soluble and its solution is an excellent conductor.

Anhydrous ethyl amine was prepared and kept for use in the following way. About 200 cc. of Kahlbaum's ethyl amine were treated for several days with metallic lithium, the solubility of which in the amine makes it especially efficient in removing water and other objectionable impurities. The liquid was then distilled into a vessel shown in Fig. 3.

The volatility of ethyl amine, and its great solvent power for such substances as are commonly used for stopcock lubricants, prevents its storage in an apparatus closed with ordinary stopcocks. For this reason a special form of valve, shown in Fig. 3, was designed. The ethyl amine is stored in tube A. In the position of the apparatus shown in the figure, its vapor may pass freely out through B, C, and the cock D. The lower part of the valve HGF contains mercury. The glass plunger I is rigidly connected with an iron rod, J, encased in a sealed glass tube. By means of a magnetic helix placed around J, this plunger may be raised or lowered. If lowered it causes the mercury on the right-hand side to rise and lift a glass float, E, which is ground to fit the conical end of the tube C. The mercury rises above this joint, tightly sealing the exit tube C. If the cock G is now closed the helix may be removed and the apparatus remains sealed until it is desired to withdraw more amine from the reservoir, when the plunger is once more raised and the valve opened. The cock D prevents the entrance of air into the reservoir when the vapor pressure of the amine falls below atmospheric pressure.

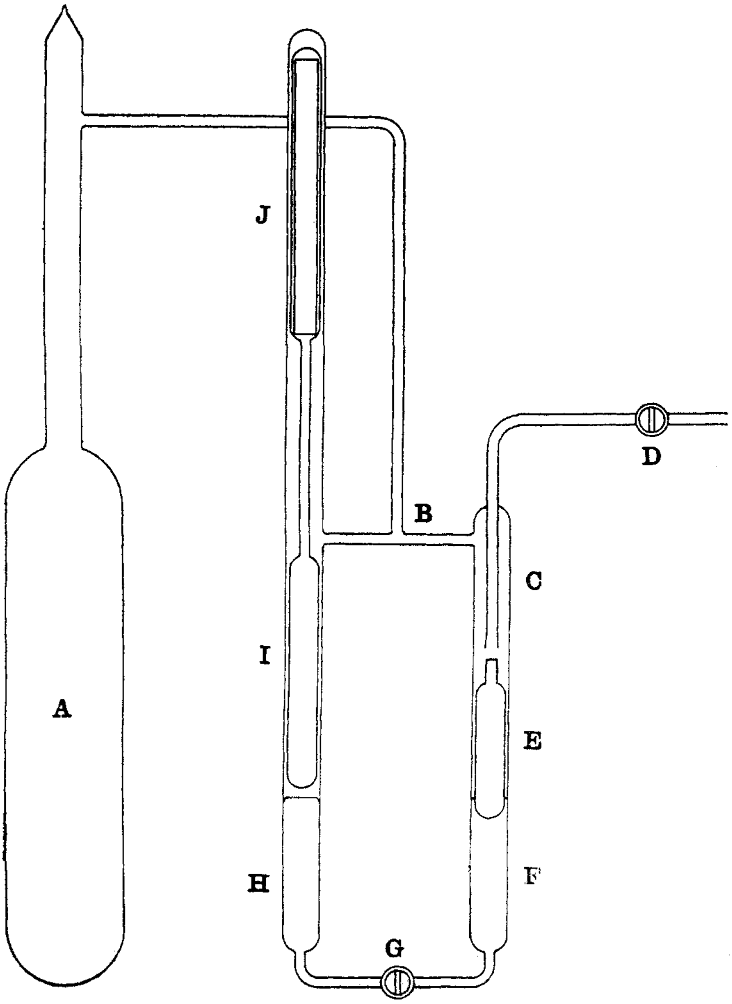

Fig. 3.

The cell in which the measurements were made is shown in Fig. 4. Two platinum wires are led to the electrodes through the tubes K and L. The capillary P is connected with the device for introducing metallic sodium, which we have already described. The tube Q is sealed to the ethyl amine reservoir, the tube S to a vacuum pump, and the tube N to the amalgam reservoir. A suitable amount of dry sodium iodide is introduced through the tube M which is then sealed off. The apparatus is thoroughly exhausted, sodium is introduced at P by the method already described, and the tube P is sealed off. The apparatus is further exhausted, the amalgam is allowed to enter through the tube N which is then sealed off. The connection to the pump is then sealed off at S. Finally the cell is cooled in ice, and the valve of the amine reservoir being opened, the amine is allowed to distil in until it rises above the connecting tube R. The tube Q being now sealed off, the cell is entirely free and its contents may be thoroughly stirred by slowly tipping from one side to the other. The bulge in the cell at O prevents any amalgam from reaching the sodium electrode in this process. The platinum terminals are completely covered, one by amalgam and the other by metallic sodium.

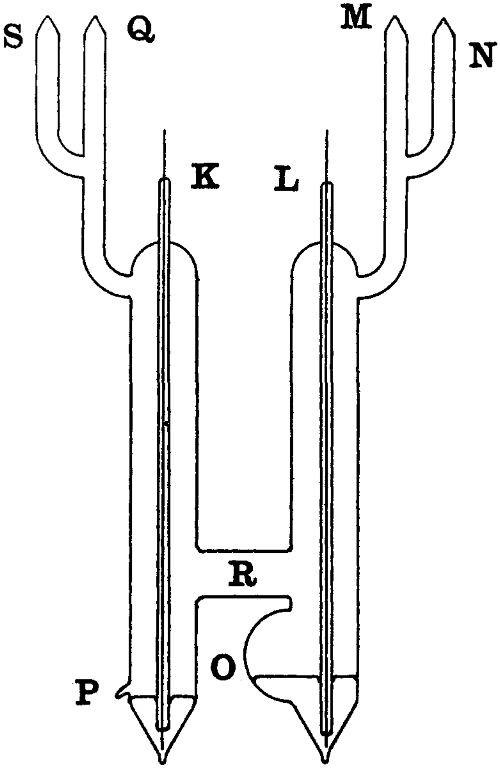

Fig. 4.

In the first cell that was set up, the sodium surface became coated with a substance that we assumed to be sodium hydroxide. The cell gave, however, a very constant electromotive force of 0.8457 v. at 25°. The coating we attributed to the presence of a trace of water in the sodium iodide, which, though it had been heated and dried, was in the form of powder and might have taken up some water while being introduced. The cell was therefore refilled, using sodium iodide which had previously been fused. This time the sodium surface was perfectly clean and remained so after the cell had stood many days.[1]

This cell gave immediately after its preparation a constant electromotive force which did not change during a number of days, in which measurements were made. Differences of 0.1 to 0.2 millivolt occasionally were found but disappeared when the contents of the cell were stirred. The electromotive force at 25° was 0.8456 v., which is only 0.1 millivolt different from that found above in the cell with the coated sodium surface. Another cell filled in the same way, containing a relatively small amount of sodium iodide, also gave 0.8456 v. A good idea of the constancy of the cell may be obtained from the following measurements made to determine the temperature coefficient of the electromotive force. The cell was changed back and forth from a thermostat at 10° to one at 35°. The electromotive force at 10° was about 1 millivolt higher than at 35°, the successive differences measured being 0.00100, 0.00093, 0.00091, 0.00100, 0.00101, 0.00102, 0.00103, 0.00103, 0.00102, the last six differences were constant within 0.00003 volt and we may take 0.00102 ÷ 25 = 0.0000408 as the diminution in electromotive force per degree rise of temperature. It is evident that the cell exhibits a higher degree of constancy and reproducibility than any cell having an electrode of solid metal which has hitherto been studied. The electromotive force of such cells usually varies very greatly, owing to surface changes in the metal. It was perhaps to be predicted that in the case of so soft a metal as sodium, such variations would not appear.

The Potential of the Sodium Electrode; the Heat of Solution of Sodium in Mercury.

In order to determine finally the electrode potential of sodium against a normal solution of sodium ion, it is only necessary to add the difference between the potentials of sodium and sodium amalgam to the electrode potential of the amalgam obtained above. This gives

$$\text{Na, Na}^{+}N\text{, N. E.; E} = 0.8456 + 2.1525 = 2.9981 \text{ v.}$$

On account of some slight uncertainty as to the electrical standards used, this final value of the potential of sodium may be in error by nearly 1 millivolt.

Wilsmore[2] in his valuable critique on electrode potentials calculated the potentials of some of the metals which decompose water from the heats of formation of their salts, according to Thomson's rule. He calculated for the sodium electrode the potential of 3.10 v. against the calomel electrode, a value differing from ours by 102 millivolts.

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[1] In the course of a few weeks a very thin black coating appeared on the metal surface and after two years' standing a considerable portion of the sodium has disappeared.

[2] *Z. physik. Chem.*, **55**, 291 (1901).

The temperature coefficient of the cell with sodium and sodium amalgam electrodes permits a remarkably accurate calculation of the heat of solution of sodium in a 0.206 per cent. sodium amalgam. We may use the equation of Helmholtz

$$E - \frac{Q}{F} = T\frac{dE}{dT},$$

where Q is the heat evolved in the solution of one equivalent of sodium in a very large quantity of 0.206 per cent. amalgam. F is the Faraday equivalent, 96580 coulombs. Substituting 0.8456 for E, and —0.0000408 for dE/dT, we find Q = 82850 joules or, if one calorie is equal to 4.186 joules, Q = 19790 calories. Were it not for some uncertainty as to the exact value of the factor to be used in passing from volts to calories, the above value of Q would be reliable within 2 or 3 calories. Berthelot found by calorimetric methods the heat of solution of sodium to form a 0.5 per cent. amalgam equal to 18800 calories. The difference between this value and ours is probably to be attributed to the heat of dilution of the amalgam from 0.5 to 0.2 per cent.

The method of handling an amalgam of an oxidizable metal, which we have described, may be of use in other lines of investigation than the present one, especially in the determination of the electromotive force of amalgam concentration cells. For this purpose the amalgams might be compared with one another in aqueous solutions by means of the apparatus of Fig. 2, but in many cases it will be preferable to work in amine solutions where the oxidation of the amalgam may be completely avoided. It is not, however, our intention to prosecute this line of research, but rather to investigate in the immediate future the electrode potential of other metals of the alkalies and alkaline earths by the method which we have found so successful in determining the potential of sodium.

In conclusion, we wish to express our indebtedness to the Bache fund of the National Academy for a grant which enabled us to carry out this investigation.

Summary.

The potential of sodium in a normal solution of sodium ion at 25° is found to be 2.9981 volts against the normal calomel electrode taken as 0.

This is the sum of two values (1) 2.1525 volts, the potential of 0.206 per cent. sodium amalgam against normal sodium ion and (2) 0.8456 volts, the difference in potential between sodium and 0.206 per cent. sodium amalgam, in a solution of sodium iodide in ethyl amine.

The temperature coefficient of the latter electromotive force is −0.0000408 volt per degree. Hence, from the Helmholtz equation, the heat evolved when one equivalent of sodium dissolves in a large quantity of 0.206 per cent. sodium amalgam is 19790 calories.

Methods are described for preparing and keeping pure sodium amalgam and anhydrous ethyl amine, and of measuring the true potential of the amalgam of an oxidizable metal in aqueous solution.

BOSTON, MASS., June 24, 1910.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

THE ELECTROLYTIC DETERMINATION OF CHLORINE IN HYDROCHLORIC ACID WITH THE USE OF A SILVER ANODE AND A MERCURY CATHODE.

BY JACOB S. GOLDBAUM AND EDGAR F. SMITH.

Received July 23, 1910.

With the introduction of the silver anode and mercury cathode, many new and interesting determinations and separations have been effected.

Much attention has been paid in this laboratory to this phase of electroanalysis, and exact and satisfactory results have been obtained.[1]

Recently there appeared an article by Gooch and Read[2] on the "Electrolytic Determination of Chlorine in Hydrochloric Acid, with the Use of the Silver Anode." From this communication it would seem that upon extending the analysis of chlorides, in neutral aqueous solution, to the determination of chlorine in free hydrochloric acid, the method as presented in previous communications from this Laboratory yields values which are "very irregular and always low." It is, therefore, proper to consider the question raised by Gooch and Read, and to submit additional evidence, together with some of the details of procedure.

Experiments were made with hydrochloric acid precisely as described by Gooch and Read, and behaviors similar to those noted by these chemists were observed; that is, the electrolysis resulted, not only in the fixation of chlorine at the anode and the liberation of hydrogen at the cathode, but also in a secondary decomposition, which gave rise to the production of hypochlorites. As a consequence, some of the silver of the anode dissolved in the electrolyte, and at times appeared at the cathode. The fixation of the oxygen at the anode was likewise observed and, indeed, when this oxygen was driven off, low and non-concordant results were obtained. Now, in these experiments a platinum cathode was employed and with the exception of a single determination, the experiments performed by Gooch and Read were with a platinum cathode, whereas, in all the work done in this laboratory on the fixation of anions, a mercury cathode has been employed. Indeed, Gooch and Read were really not using "similar means," and the criticism of the original method because of the failure of an altered arrangement is hardly fair. Hence, it is only natural that we should try the effect of a silver anode and mer-

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[1] THIS JOURNAL, 29, 447, 1445, 1455, 1460; *Ibid.*, 30, 1706.

[2] *Am. J. Sci.*, 544 (1909).