xylene. These aromatic isomers thus show much greater differences than was encountered in the aliphatic octane series.

If the value of Fischer and Wrede for sugar be accepted (1 gram = 16.545 kilojoules) the heat of combustion of 1 gram of ethylbenzene (weighed in vacuum) is 42.63 kilojoules. The heat of combustion of 1 gram mole (106.023 grams) is 4520 kilojoules. If a large calorie be considered equivalent to 4.179 kj. a gram-mole of ethylbenzene has a heat of combustion of 1081.5 Calories. On the other hand, if the value of the Bureau of Standards (1 gram sugar *in vacuo* = 3943 calories) be accepted, the heat of combustion of a gram-mole of ethylbenzene is 1077.3 Calories. This is the first determination of this constant.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF ILLINOIS.]

THE IODINE COULOMETER AND THE VALUE OF THE FARADAY.[1]

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PART I.—REVIEW OF PREVIOUS COULOMETER INVESTIGATIONS.

1. Introduction.

Although Faraday's law of electrochemical change has been universally accepted for many years, there still exists a considerable degree of uncertainty regarding the exact value of the Faraday. Theoretically, any chemical reaction which can be brought about by means of the electric current, might be employed for the determination of the value of the Faraday, but as a matter of fact, very few reactions have been studied in this connection and the value at present accepted for this constant is practically based upon measurements with a single electrochemical reaction, the deposition of silver from an aqueous solution of one of its salts. When we consider the amount of care and labor expended and the variety of reactions which it is deemed necessary to employ in order to fix the atomic weight of a single element, it is certainly remarkable that, in the case of such an important and universal a constant as the Faraday, scarcely any serious consideration has ever been given to any electrochemical reaction except that which occurs in the silver coulometer. And when we add to this the fact that this particular reaction is known to be affected by numerous sources of error and uncertainty which have not been entirely removed by years of laborious investigation participated in by many chemists and physicists, it must be apparent to all that serious

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[1] Presented before the Eighth International Congress of Applied Chemistry at New York, Sept. 9, 1912. Abstract of a thesis presented by Mr. Bates to the Graduate School of the University of Illinois in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

consideration should be directed to the problem of discovering some other electrochemical reaction which will fulfil the exacting requirements necessary for a successful determination of the Faraday, at least as well and preferably more perfectly than does the process which occurs within the silver coulometer.

In addition to the silver coulometer, the copper, the iodine, and the oxyhydrogen coulometers have received some attention from investigators, but none of them seems to have been considered seriously by the scientific world, either as a rival to or even as a valuable check upon the silver coulometer. Before taking up the description of the present investigation it will be advantageous to review briefly the results of previous investigations with the above coulometers[1] and especially the present state of affairs with reference to the silver coulometer.

2. The Silver Coulometer.

The large amount of study which this coulometer has received from so many investigators has naturally arisen from the fact that the international ampere is at present defined in terms of the mass of silver deposited per second from a solution of silver nitrate under more or less definit physical and chemical conditions. The silver coulometer is apparently the only one receiving serious consideration at the present time, being in fact within the last five years the subject of extensive investigation by the national physical laboratories of the leading nations of the world. Of these investigations the following have been completed: (1) that of Smith, Mather and Lowry[2] at the National Physical Laboratory of England; (2) that of Laporte and de la Gorce[3] at the Laboratoire Centrale d'Electricité of France; (3) that of Jaeger and von Steinwehr[4] at the Physikalisch-Technische-Reichsanstalt of Germany; and (4) that of Rosa, Vinal and McDaniel[5] at the National Bureau of Standards at Washington.

These investigations together with that of Duschak and Hulett[6] and that of Foerster and Eisenreich[7] have added considerably to our knowledge of the behavior of the silver coulometer under various conditions. Foerster[7] has reviewed at length the work on this coulometer up to the end of

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[1] The lead and the mercury coulometers have also been studied to some extent but will not be considered in the present discussion as an accuracy greater than 0.1 per cent is not claimed for them. See Mathers and Germann, *Ind. Univ. Studies*, **8**, 41 (1910); Betts and Kern, *Trans. Amer. Electrochem. Soc.*, 6, 67 (1904); Wright. *Lond. Electrician*, **60**, 297, 319.

[2] *Phil. Trans.*, (*A*) **207**, 545 (1908).

[3] *Bull. soc. internat. Electriciens*, **10**, II, 157 (1910).

[4] *Z. Instrumentenkunde*, 28, 327, 353 (1908).

[5] This work has not been published in extenso but the final result is given in the paper of Rosa, Dorsey and Miller. Bur. of Standards, *Bull.* **8**, 367 (1911).

[6] *Trans. Amer. Electrochem. Soc.*, 12, 257 (1907).

[7] *Z. physik. Chem.*, **76**, 643 (1911).

1909, and Professor Hulett has announced a paper upon the subject to be presented to this Congress. It would, therefore, be superfluous to attempt anything like an exhaustive discussion of this coulometer in the present paper. In order to understand some of the results obtained in this investigation, however, it will be necessary to review very briefly the present state of our knowledge respecting several of the factors which influence the accuracy and precision of the silver coulometer.

The Influence of the Anode Products.—The investigations of Smith, Mather and Lowry have shown that the differences heretofore observed between the filter paper type of coulometer and the porous cup type can be eliminated by using very pure silver nitrate and by employing a large bulk of solution with the filter paper arranged in the form of a cup around the anode. Their conclusion upon this point has been confirmed by the results obtained by the German and the French investigators.

Smith, Mather and Lowry found as a mean of all their results, the value 1.11827 mg. per coulomb, for the electrochemical equivalent of silver. Laporte and de la Gorce obtained the value 1.11829. Jaeger and von Steinwehr's investigation was a comparison of the silver coulometer with the Weston cell and the International ohm. If we adapt the value 1.01820 for the electromotive force of the Weston normal cell, their results give the value 1.11815 for the electrochemical equivalent of silver. The American observers found the value 1.11804, using only porous cup and non-septum types of coulometers.

The results obtained by the English and French investigators justify the conclusion that with sufficiently pure silver nitrate, the errors due to the products formed at the anode may be eliminated *equally well* either by using a sufficiently large volume of solution *or* by placing the anode in a clean porous cup. Whether the error from this source is entirely eliminated (or compensated) by *either* procedure is as yet rather uncertain. In fact some experiments of Eisenreich[1] suggest the possibility that *neither* type is perfectly efficient in preventing the anode products from reaching the cathode. Eisenreich found that both the filter paper and the porous cup coulometers gave too high results at 90°, the latter type giving deposits too high by as much as 0.1% at this temperature. Hence it is not impossible that the deposit obtained at ordinary temperatures may still be slightly but appreciably too great owing to the diffusion of some of the anode solution through the porous cup during the electrolysis. The evidence offered[2] by Smith, Mather and Lowry would seem to indicate, however, that in their experiments the error from this source is probably less than 0.003%.

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[1] *Loc. cit.*, p. 680.

[2] *Loc. cit.*, see page 566.

The Purity of the Silver Deposit.—If the silver deposit after drying to constant weight still contains water or silver nitrate, it should undergo a loss in weight on heating to a sufficiently high temperature. Various estimations of this loss in different cases show such poor agreement that the amount and character of the included material is evidently subject to considerable variation with the conditions. Rayleigh and Sidgwick[1] found that well washed deposits showed a loss of 0.01–0.02% on heating to the verge of redness. Richards and Heimrod[2] dried their deposits to constant weight at 160° and then heated them over an alcohol flame to the verge of fusion. In twelve experiments the loss of weight varied from 0.003 to 0.030% the mean value being 0.018 ± 0.002%.[3] Van Dijk[4] found that after washing and drying the deposit at 150° there was no further loss of weight on reheating to 500–600°. Smith, Mather and Lowry heated their silver deposits to constant weight at 160° and in eight instances they were afterward heated to 240° and in three to 400°, without any loss in weight being observed. Laporte and de la Gorce apparently did not heat their deposits above 160° in any instance. In six instances after drying the deposit at 160–200°, Jaeger and von Steinwehr heated it to the verge of redness (not higher) and observed no loss in weight.

Both the English and the German investigators conclude that appreciable amounts of included material are *not present* in the silver deposit. This conclusion has been justly criticized by Richards[5] who points out that the temperatures employed were not sufficient to soften the silver and release the included material. The admirable experiments of Duschak and Hulett upon this point have demonstrated beyond question that the silver deposit contains *both* water and silver nitrate and that these impurities cannot be *completely* removed without fusion. In their experiments the total quantity of included material amounted to 0.014% of the deposit, for deposits in air and 0.0084% for deposits *in vacuo.* These results are for a coulometer of the porous cup type. The amount of this inclusion doubtless varies considerably with the type of the coulometer and the conditions of the experiment and should therefore be determined for each experiment (a tedious procedure) if an accuracy of 0.001% is aimed at. The value 1.11827 may therefore be in error from this cause by at least 0.01% and possibly by much more, as the amount

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[1] *Phil. Trans.*, 175, 411 (1884).

[2] *Proc. Amer. Acad.*, 38, 435 (1902).

[3] Throughout this discussion, unless otherwise stated, the quantity, a. d./$\sqrt{n}$, where a. d. is the average deviation of the individual observations from the mean and n is the number of observations, will be employed as the precision measure of the observed quantity. This precision is $^3/_2$ of the "probable error."

[4] *Arch. neerl.*, 10, 287 (1905).

[5] *Proc. Amer. Acad.*, 44, 91 (1908).

of inclusion in the coulometers used by Smith, Mather and Lowry is not known.

The Effect of Filter Paper.—Smith, Mather and Lowry do not seem to have made any direct experiments to determin whether or not the mere presence of filter paper in the silver nitrate solution produced any appreciable influence upon the deposit. Laporte and de la Gorce sought to answer this question by employing in one coulometer double the quantity of filter paper ordinarily used. In one experiment the coulometer with the double filter paper gave a deposit only 0.001% heavier than their ordinary coulometer but in a second experiment the difference amounted to 0.012% in the same direction. A third experiment was made using a filter paper which had been previously soaked in the silver nitrate solution for 7 hours and then washed and dried before using. The coulometer in which this paper was employed gave a deposit 0.005% lighter than their ordinary filter paper coulometer.

These three experiments all point to an appreciable though small influence of the filter paper upon the mass of the deposit. This conclusion is substantiated by the recent work at the National Bureau of Standards where the use of two or three thicknesses of filter paper was found to materially increase the weight of the silver deposit.[1] This effect is ascribed to the presence of oxycellulose on the surface of the filter paper which reduces silver nitrate to colloidal silver. This colloidal silver is then carried to the cathode, where it is deposited and by breaking up the crystallin silver causes a greater inclusion of solution than would otherwise be the case.[2]

The Effect of Oxygen.—Smith, Mather and Lowry found that their coulometer gave the same result *in vacuo* as in air. Jaeger and von Steinwehr employed atmospheres of nitrogen and of hydrogen in different experiments, but the mass of silver obtained under these conditions was not appreciably different from that obtained in contact with the atmosphere.

In direct contradiction to these results, the experiments of Duschak and Hulett show that "the deposit from a water solution of pure silver nitrate, free from air and *in vacuo*, is distinctly *lighter* (nearly 0.01% in some cases) than one formed in air. This fact, supported as it is by two different, but concordant pieces of evidence, namely, the directly determined difference in the mass of the deposits and their different impurity content, seems indisputable. Results further indicate that saturating the solution with nitrogen produces the same effect as simply removing the air." The evidence upon this question seems, therefore, to be contradictory and further investigation is needed.[3]

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[1] Vinal, *Science*, N. S. **34**, 31 (1911).

[2] McDaniel, *Science*, N. S. **34**, 160 (1911).

[3] Foerster suggests that the results of Duschak and Hulett may be due to a dif-

Summary.—The results of the above considerations may be summed up as follows: If very pure materials are employed, the silver coulometer in the hands of a careful and experienced worker is reproducible to one or two thousandths of 1% under a given set of conditions. The mass of the deposit even under the most favorable conditions does not, however, correspond exactly to the reaction, $Ag^+ + (-) = Ag$, but is greater than this reaction requires, owing chiefly to the inclusion of solution. The above considerations indicate that a *minimum value for the Faraday* can be obtained from the silver coulometer operated under the following conditions: (1) A large volume of solution of very pure silver nitrate free from dissolved oxygen; (2) an electroplated anode surrounded preferably by *two* perfectly clean porous cups provided with suitable syphons for maintaining the proper level; (3) electrolysis *in vacuo*; (4) determination of and correction for included material by the method of Duschak and Hulett.

Up to the present time no investigation in which all of these conditions have been simultaneously observed, has been published. The value of the Faraday which is generally accepted at the present time is that calculated from the work of Smith, Mather and Lowry, that is,

$$F = \frac{107.880}{1.11827} = 96{,}470 \text{ coulombs.}^1$$

For the reasons stated above it seems probable that this number is too small by at least 0.01% and possibly by as much as 0.05% as every one of the four factors discussed above tend to produce too heavy a deposit.

3. The Copper Coulometer.

The copper coulometer has been the subject of a number of investigations but the work of Richards, Collins and Heimrod[2] may be considered as superseding that of earlier investigators. They found that the two most important sources of error influenced the result in opposit directions. (1) "Metallic copper slowly dissolves in an

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fusion of some of the anode solution through the porous cup during the five hours time consumed in the electrolysis. This seems rather improbable, however, since the surface of the solution within the porous cup was kept one centimeter lower than that of the solution outside. Moreover, as Duschak and Hulett point out, the nature and amount of the included material was decidedly different in the two cases. Foerster's suggestion may, however, possibly explain the difference of "0.002 to 0.003 per cent, unaccounted for" which Duschak and Hulett found between the masses of their deposits in the two cases (*loc. cit.*, p. 291).

[1] The value 1.11804 obtained by Rosa, Vinal and McDaniel gives 96,500 coulombs as the value of the faraday, a result higher by 0.03 per cent than that of the English observers. In a private communication to one of us, Dr. Rosa states that no determination of, or corrections for, included material were made in these experiments. Hence it is probable that the value, 1.11804, is still too large.

[2] *Proc. Am. Acad.*, **35**, 123 (1899).

acid solution of cupric sulfate.... The losses of weight of the plates were found to be roughly proportional to their respective areas if the volume of solution was large." (2) "Plates of copper immersed in *neutral* solutions of cupric sulfate always *gain* in weight, becoming coated with a film of cuprous oxide."

The second source of error was eliminated by using a slightly acid solution, while the influence of the former was reduced by employing a low temperature and working in an atmosphere of hydrogen. Assuming then that the rate of solution of the metallic copper varies directly as the area of the plate, it was possible by using plates of different areas as cathodes in two coulometers in series, to extrapolate to the increase in weight of a plate of zero area, *i. e.*, to calculate what would have been the gain in weight of the cathode if none of it had dissolved.

A series of seventeen experiments was made with two copper coulometers having different sized plates in series with two coulometers of the Rayleigh filter paper type. In each experiment the mass of copper was corrected to correspond to a plate of zero area as explained above. In most of the cases recorded the larger plate always showed the smaller deposit of copper, so that the "corrected copper" was larger than the amount deposited upon either plate. In three experiments, however (Nos. 9, 10, and 11) the larger plate showed the *greater* deposit, so that the "corrected" value was *smaller* than either of the observed values. These irregularities decrease somewhat the reliance which can be placed upon the results of the copper coulometer. The mean value for the atomic weight of copper obtained from this series of experiments was 63.563 ± 0.0044, a precision of 0.0069%.[1]

In order to correct this value for the errors in the Rayleigh filter paper coulometer, Richards and Heimrod made a series of 18 experiments in which their filter paper coulometers were compared with the porous cup type and were found to give on the average a deposit, 0.041 ± 0.0040% heavier than that of the latter type. In addition to this correction, a correction for included material (0.018 ± 0.0019%)[2] was also made

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[1] This precision measure is not taken from the original paper but has been computed as explained in the footnote, p. 1344 of this paper. In a private communication, Professor Richards, to whom this portion of the manuscript was submitted, informs us that Collin's notebook contains an entry indicating that the copper solution employed in Experiments 9, 10 and 11. referred to above, was slightly impure, without stating the nature of the impurity, which must, however, have caused the solutions to be somewhat basic and hence produced the abnormally heavy deposits obtained in these experiments. If, however, the results of these three experiments be rejected, practically the same mean value (65.564) is obtained as when they are included. The average deviation from the mean is 0.025% and the maximum 0.081%, which shows that even under the best conditions the copper coulometer does not give very reproducible results.

[2] See page 1344.

which brought the value for the atomic weight of copper up to 63.601. This would have a precision of $\sqrt{(0.0069)^2 + (0.0040)^2 + (0.0019)^2}$ or 0.0082%. This value is based upon the value 107.93 for silver. Assuming 107.88 for silver, we obtain finally the atomic weight 63.572 ± 0.0082% for copper which is in very close agreement with the value (63.575) obtained by chemical means.

If the assumption were justified that the mean value of the "corrected" copper obtained by Richards, Collins, and Heimrod, represented only the reaction,

$$Cu^{++} + 2(--) = Cu$$

then we would be justified in concluding that the "corrected" silver deposit obtained in the Richards porous cup coulometer could be relied upon to give the value of the Faraday with an accuracy of 0.008%. In view, however, of the rather irregular behavior of the copper coulometer already referred to, it is on the whole of rather doubtful value as a check on the silver coulometer.

Richards, Collins and Heimrod make the statement[1] that, "The last six determinations were consecutive; and in these the conditions of experiment were much more satisfactory than in the earlier ones, for much practice was naturally acquired in the course of the work." If we consider only the results obtained in these six experiments, we obtain for the atomic weight of copper the value, 63.575 ± 0.017%. It would seem, therefore, reasonably safe to conclude that the corrected silver deposit from the porous cup coulometer used by Richards was not in error by more than 0.02%.

4. The Iodine Coulometer.

The iodine coulometer has been studied by a number of investigators;[2] but for the present purpose the results of Kreider and of Gallo alone need be considered; the earlier investigators did not claim an accuracy greater then 0.5%.

In Kreider's coulometer the cathode was surrounded with a solution of hydrochloric acid and the platinum anode with a solution of potassium iodide. The iodine formed at the anode was titrated with sodium thiosulfate. The amount of iodine liberated in two or three coulometers in series agreed within 0.01 or 0.02%. In *two* experiments the iodine coulometer was compared with a silver coulometer of the filter paper type and the iodine liberated is stated to be from 0.06 to 0.09% *more* than that calculated from the silver coulometer. The atomic weights which were employed in this calculation are not given, neither are there any data from which they may be inferred. The atomic weights for 1904 were

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[1] *Loc. cit.*, p. 134.

[2] Herroun, *Phil. Mag.*, [5] 60, 91 (1895); Danneel, *Z. Electrochem.*, **4**, 154 (1897); Kreider, *Am. J. Sci.*, [4] **20**, 1 (1905); Gino Gallo, *Gazz. chim. Ital.*, **36**, II, 116 (1906).

Ag = 107.93, I = 126.85; for 1905, Ag = 107.93, I = 126.97. The paper is dated June, 1905, hence it is quite possible that the atomic weights for 1904 were employed. If this is the case, the amount of iodine formed, when calculated on the basis of the atomic weights for 1912 is from 0.01 to 0.04% *less* than that which corresponded to the silver deposited. This is in agreement with the well known fact that the Rayleigh filter paper coulometer gives too heavy a deposit of silver. Kreider's experiments were too few to justify any further conclusion from his results.

Gallo's investigation was undertaken in the hope that the results might throw some light upon the iodine-tellurium anomaly in the periodic system. In the apparatus employed by him the platinum electrodes (4 square millimeters in area) were placed in separate limbs; the cathode at the bottom of one tube, the anode somewhat more than half way up the other. Before filling the apparatus with the potassium iodide solution, the cathode was surrounded with solid iodine. During the passage of the current considerable hydrogen was evolved at the cathode but the hydroxyl ion formed was neutralized by the iodine. In order to prevent diffusion of the iodine from cathode to anode, the two limbs were connected by two small tubes (4 mm. diameter) both of which dipped into a wide mouthed bottle. At the completion of a run a stopcock at the bottom of the anode limb was opened and the anode solution received in a flask for titration with sodium thiosulfate. A current density of 0.1 ampere per sq. cm. was employed, the amount of iodine produced being only 0.3 gram in each run.

Assuming that the theoretical quantity of each element was freed from the ionic state by the passage of the current, Gallo found the atomic weight of iodine to be 126.89 (Ag = 107.93) as the result of 24 determinations. The maximum deviation was 0.075%, the average deviation 0.021%. Calculated on the basis of the present value for silver (107.88), iodine becomes 126.83, a difference of 0.07% from the accepted value, 126.92.

On the other hand we may assume that the current frees the theoretical amount of iodine in the iodine coulometer, and consider that the silver coulometer measures the amount of electricity which has passed. Gallo used porous cup coulometers and following Richards and Heimrod, made a 0.018% correction for included material. The effect of this correction was to lessen the discrepancy between the silver and iodine coulometers, and hence if we compare his results with those of Smith, Mather and Lowry who made no correction for included material, a difference of 0.09% appears. On this basis the iodine coulometer gives the value 96,560 coulombs for the faraday. The uncertainty in this figure due to the difficulty in reproducing the exacting conditions in connection with the silver coulometer alone is at least 0.02%.

5. The Oxyhydrogen Coulometer.

Lehfeldt[1] measured the combined volumes of hydrogen and oxygen evolved when a known current was passed through an aqueous solution of an electrolyte and from these data calculated the value of the faraday. The current was determined by means of the Weston Standard Cell and standard resistances; the author estimated that the quantity of electricity which passed through the coulometer was known to be within 0.01%.[2] In the coulometer, solutions of some twelve different electrolytes were tried. It was found that with a given current, solutions of sodium sulfate and of potassium bichromate gave practically the same volume of gas, while solutions of the other electrolytes gave a *smaller* quantity. The mean of 16 determinations with solutions of these two electrolytes was 0.17349 cc. of gas evolved per coulomb. The average deviation was 0.027%, and the maximum, 0.058%. The value of the faraday calculated on the assumption that the theoretical quantity of gas is evolved from these solutions is 96,590 coulombs. This value should be considered as an upper limit, however, because no attempt was made to prove the assumption, that the theoretical volume of gas was liberated from the sodium sulfate and potassium bichromate solutions.

6. Summary.

To facilitate comparison, the results obtained with all of the above coulometers are brought together in Table I. It is evident from this table that the results obtained with the copper, the iodine, and the oxyhydrogen coulometers, in so far as they can be relied upon, all agree in supporting the conclusion that the silver coulometer gives too low a value for the faraday. In reproducibility, however, the silver coulometer when properly handled, greatly excels all of the other types hitherto employed.

TABLE I.

Coulometer.	Observer.	Date.	Faraday.	Precision[3] in %.
Silver	Smith, Mather, and Lowry	1908	96,473	0.0003
Silver	Jaeger and von Steinwehr	1908	96,481	0.002
Silver	Laporte and de la Gorce	1910	96,471	<0.001
Silver	Rosa, Vinal and McDaniel	1911	96,500	<0.001
Copper,	Richards, Collins and Heimrod	1902	96,535	0.008
Iodine	Gallo	1906	96,560	0.006
Oxyhydrogen	Lehfeldt	1908	96,590	0.006

PART II.—THE IODINE COULOMETER.

1. Purpose and Outline of the Investigation.

This investigation was undertaken for the purpose of perfecting an iodine coulometer which should equal the silver coulometer in reproduci-

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[1] *Phil. Mag.*, [6] 15, 614 (1908).

[2] *Loc. cit.*, p. 621.

[3] *i. e.*, a. d./$\sqrt{n}$.

bility and which should be entirely free from all sources of error amounting to more than 0.001%, since it is desirable to determin the value of the faraday with approximately this degree of accuracy.

An aqueous solution of potassium iodide to which iodine has been added contains both iodide and tri-iodide ions. When a current of electricity is passed through such a solution the reaction

$$I_3^- + 2(-) = 3I^- \qquad (1)$$

takes place in the direction from left to right at the cathode and in the reverse direction at the anode. Hence a cell in which the electrodes are surrounded by such a solution should contain the same total amount of "free iodine" before and after the passage of an electric current. By separating the electrodes and the solutions surrounding them by a conducting solution of an iodide, the changes in the amounts of "free iodine" at the two electrodes can be separately determined, and if the reaction is a perfectly clean cut one, free from all disturbing side reactions, the results at the two electrodes should check each other. The iodine coulometer, therefore, contains within itself the proof of its own correctness, for if it can be shown that identical amounts of iodine are involved in the reactions at *both* electrodes under varying conditions of concentration and current density it will establish beyond question the fact that *the only reaction*, involving electricity, which occurs at the anode is that expressed by the equation,[1]

$$3I^- = I_3^- + 2(-). \qquad (2)$$

In this particular the iodine coulometer possesses an enormous advantage over the silver coulometer, for, as is well known, no such quantitative proof of the nature of the reaction is possible with the latter coulometer.

It is clear, therefore, that the problem of perfecting an iodine coulometer which will fulfil the above requirements consists chiefly in the satisfactory solution of the following questions:

(1) The discovery of an analytical method for determining "free iodine" in an aqueous solution of an iodide with an accuracy of 0.001%.

(2) The perfection of the mechanical features and arrangement of the apparatus; the nature, form, size, and position of the electrodes, etc.

(3) The measurement of the reproducibility of the anode reaction, for it is this reaction alone which would be ultimately employed in the coulometer, since it involves less manipulation and consequently possesses greater freedom from accidental errors from mechanical sources than does the cathode reaction.

(4) The proof of the reversibility of the reaction as indicated above, by

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[1] Or some reaction or set of reactions which are ultimately equivalent to this in the final analysis, which is, of course, just as satisfactory, for the value of the faraday does not depend upon the mechanism of the reaction but only upon the final result.

comparing the amount of free iodine formed at the anode with that which disappears at the cathode.

2. Determination of the Iodine.

The Analytical Method.—The iodine formed or used up during the electrolysis was determined by titration with a standard solution of arsenious acid. The reaction involved in this titration is the following:

$$H_3AsO_3 + I_3^- + H_2O = H_3AsO_4 + 2H^+ + 3I^- \qquad (3)$$

By making the hydrogen ion concentration sufficiently small this reaction can be driven towards the right as completely as desired. If it is made too small, however, an error will be produced owing to the occurrence of the following reactions:

$$OH^- + I_3^- = HIO + 2I^- \qquad (4)$$

and

$$6OH^- + 3I_3^- = IO_3^- + 8I^- + 3H_2O. \qquad (5)$$

The success of the method depends, therefore, upon the control of the hydrogen ion concentration in the solution at the end of the titration. The method of effecting this control has been described in a previous paper,[1] where the theory and practice of this analytical method when an accuracy of 0.001% is required have been discussed in detail. The details need not be repeated here.

In all of the titrations performed in connection with this investigation the solution at the end of the titration contained a mixture of Na_2HPO_4 and NaH_2PO_4 in such proportions as to insure a hydrogen ion concentration of 10^{-7} moles per liter.[2] The method is easily capable of an accuracy of 0.001 to 0.002% and since a definit equilibrium is reached, the end-point is permanent for an indefinit time.[3]

3. Purification of Materials.

Water.—The water from which the various chemicals were recrystallized and which was used in making up all of the solutions was conductivity water obtained by distillation from alkalin permanganate.

Iodine.—The iodine employed was Kahlbaum's "Resublimed" which

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[1] Washburn, THIS JOURNAL, 30, 31 (1908).

[2] The calculations carried out in the paper referred to indicated that this value is the most favorable for the titration. As the concentrations of the various substances involved were somewhat different in the present investigation from those employed in the previous calculation, it was thought best to repeat the calculation for the new conditions. This was the more desirable because some of the equilibrium constants involved have been redetermined since the publication of the previous paper. The new values for the equilibrium constants are $5 . 10^{-2}$ for reaction (3) above (recently determined in this laboratory by Mr. E. K. Strachan) and $3 . 10^{-13}$ for reaction (4) [Bray and Connolly, THIS JOURNAL, 33, 1486 (1911)]. The result of the new calculation was practically identical with that of the previous one, however, so that no changes in the conditions previously described were necessary.

[3] THIS JOURNAL, 30, 43 (1908).

was freed from possible traces of chlorine, bromine, etc., either by subliming from a concentrated solution of potassium iodide, or by precipitation from such a solution by means of potassium permanganate and sulfuric acid. The iodine was thoroughly dried in a desiccator over sulfuric acid and sublimed in a current of dry air.

Potassium Iodide.—The potassium iodide used was, except where otherwise specified, obtained by recrystallizing J. T. Baker's "Special" until it was no longer alkalin to phenolphthalein. The product was pure white and when dry remained so indefinitly. When protected from strong light, a saturated solution of the iodide remained colorless for at least twenty-four hours.

Arsenious Oxide.—The arsenious oxide was obtained by recrystallizing Merck's product from conductivity water.

Sodium Hydroxide.—The sodium hydroxide employed in preparing the standard arsenious acid solution was Kahlbaum's "mit Alkohol gereinigt in Stücken."

Starch Solution.—The starch solution used as an indicator in titrating the iodine was prepared by grinding 6–7 grams of corn starch with a little cold water and adding it to a liter of boiling water. After settling in a tall cylinder over night, the upper half of the solution was drawn off into test tubes, stoppered with cotton wool and then sterilized in an autoclave. Starch solutions thus prepared keep well for six weeks or two months and give an end point of the proper shade.[1]

4. Preparation of the Standard Solutions.

The Sodium Phosphate Solution.—This solution was prepared by dissolving J. T. Baker's C. P. disodium phosphate ($Na_2HPO_4.12H_2O$) in about five times its weight of water. The solution was kept in a ten-liter stock bottle from which the required amount was siphoned off and poured into the flask in which the titration was performed.

The Standard Iodine Solution.—The standard iodine solution used at the cathode in the coulometer was prepared by dissolving about 680 grams of iodine and 840 grams of potassium iodide in 700 grams of water. This solution was kept protected from the light in a stock bottle into the neck of which was ground a delivery tube which reached to the bottom of the bottle. Air previously bubbled through a wash bottle containing some of the same solution was used to force the solution out of the stock bottle. To prevent loss of iodine or water vapor the end of the delivery tube and that of the tube through which pressure was applied were protected by means of glass caps. The solution was made up eight months before it was used for the experiments recorded below.

The Dilute Iodine Solution.—This solution, which was used only when the end point was overstepped with the arsenious acid, was 0.005 normal.

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[1] See Washburn, THIS JOURNAL, **30**, 42 (1908).

It was prepared by weight from the above solution and was kept in a bottle into whose neck was ground a glass stopper which carried a Göckel automatic buret.

The Standard Arsenious Acid Solution.—The standard arsenious acid solution was prepared by dissolving 530 grams of arsenic trioxide in a solution containing about 650 grams of sodium hydroxide (3 moles). When all the trioxide had dissolved, the solution was filtered through asbestos and diluted until it was approximately 0.9 weight normal.

5. Standardization and Behavior of the Standard Solutions.

Treatment of the Standard Iodine Solution.—Since this solution was employed at the cathode in the coulometer, it was deemed best to duplicate, in standardizing it, the same conditions to which it was subjected during use in the coulometer. Hence the proper amount of the solution was weighed out, transferred to the coulometer and allowed to stand over night in contact with the electrode. The following day it was withdrawn and received in a flask containing a weighed amount of the standard arsenious acid solution and the titration completed as described below. The method of procedure employed in handling the iodine solution duplicated exactly that employed during the regular runs with the coulometer and is fully described in the next section (p. 1359).

Weighing out the Arsenious Acid Solution.—The standard arsenious acid solution was kept in a 15-liter bottle which stood beside the balance case in a constant temperature room in the basement of the building. The stock bottle was provided with a rubber stopper carrying a delivery tube which could be swung directly over the mouth of a flask upon the pan of the balance. This arrangement permitted any desired amount of the solution to be weighed out into the flask very exactly. The air or gas which entered the stock bottle was bubbled through a wash bottle containing some of the same solution. Liter Erlenmeyer flasks of white glass were employed for weighing out the arsenious acid solution, a similar flask being used as a counterpoise. The quantity of solution weighed out each time was always from 0.05 to 0.1 gram less than the exact amount required to react with the iodine solution in the titration.

Completion of the Titration.—After the flask containing the arsenious acid solution had assumed constant weight, the necessary amount of the disodium phosphate solution was added, the flask was connected to the coulometer and the iodine solution drawn over into it as described in the next section. The solution was then thoroughly mixed and the titration completed with a dilute solution of arsenious acid. This solution was prepared by diluting about 5 grams of the concentrated solution to exactly 100 times its weight. The buret from which the dilute solution was delivered was calibrated by the use of this dilute solution. On account of the possibility of an error due to the oxidation of the dilute solution a fresh lot was prepared every two or three weeks; the maximum change in strength due to oxidation was estimated to be 0.5%. Practically never was it found necessary to use more than 10 cc. of this solution to complete a titration, and since 1 cc. corresponded to about 0.02% of the total arsenious acid used in the titration, the error due to the change in strength of the dilute solution was never greater than 0.001%.

Under the conditions employed it was found that equilibrium between the iodine and the arsenious acid was attained almost immediately. The reaction between the starch and the triiodide ion is, however, much slower. Hence in the titrations, the dilute arsenious acid solution was added until the solution was colorless; in a good light and with a flask of water as a standard, the disappearance of the yellow iodine color could be judged to about 0.10 cc. of the dilute arsenious acid solution, *i. e.*, to about 0.002%. As a check, however, 5 cc. of the starch solution were then introduced, and the dilute iodine solution (0.005 normal) added, until on standing for a few moments, the proper pink colored end point remained. This end point is a little more sensitive than the other. About 0.4 cc. of the 0.005 normal iodine solution was required to change from one end point to the other.

Temperature has but a slight effect upon the end point. After finishing one of the titrations, the solution was warmed to 35° and the pink colored end point reached. On cooling to 15°, only 0.15 cc. of the 0.01 normal arsenious acid solution was required to give the same colored end point. This represents a change of 0.003% for the 20°, and hence no attempt was made to regulate the temperature of the solutions during titration.

Oxidation of the Arsenious Acid Solution.—When the stock solution of arsenious acid was first made up it was fitted with a Göckel buret for delivering approximately the desired quantity of the solution into the flasks to be weighed. With this arrangement irregular results were obtained. It was noticed, however, that in general the solution tended to become weaker with time, indicating oxidation.[1] When this was noticed, the solution was protected from the light and kept under hydrogen. The hydrogen was generated from C. P. zinc and sulfuric acid. It was washed by bubbling through solutions of lead nitrate and alkalin pemanganate and then through a wash bottle containing some of the arsenious acid solution. To free the solution from air, the pressure upon it was three times reduced as far as possible with a filter pump and then increased to

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[1] The irregularity of the results may be explained by the fact that the buret was in general filled to the top before each titration, but was usually only a little more than half emptied. The other half of the solution which had become pretty well saturated with air, then lay for an indefinite period in the lower part of the buret until the next portion was drawn off. This portion of the standard solution then oxidized more rapidly than that in the stock bottle, and thus irregular results were obtained. The rate of oxidation of the stock solution was estimated to be about 0.02% per day.

that of the atmosphere by slowly bubbling hydrogen through the liquid. The stock bottle remained attached to the hydrogen generator so that as the solution was withdrawn it could be replaced by hydrogen.

This procedure did not, of course, remove the last traces of dissolved oxygen from the solution nor is hydrogen prepared in the above manner entirely free from oxygen. It was expected, however, that the partial pressure of the oxygen would be sufficiently reduced to materially decrease the rate of oxidation. This was found to be the case, the rate of oxidation being reduced from 0.02% to less than 0.003% per day. This rate was, moreover, perfectly constant, as is evident from the data in Table II which represent the results of comparisons of the arsenious acid solution with the standard iodine solution extending over a period of 47 days. In the first column is given the number of the comparison, in the second the date on which the arsenious acid solution was drawn from the stock bottle for immediate titration. The third and fourth columns give the weights of the iodine and arsenious acid solutions, respectively, which were used. The number of grams of arsenious acid solution required to titrate one gram of the iodine solution is given in the fifth column. In the sixth column is given this value as "calculated" for the day in question (see below). The seventh column contains the percentage difference between these values as found and as calculated. When these results are plotted on cross-section paper, the slope of the curve corresponds to a rate of oxidation of 0.00273% per day. The "calculated" value of the ratio of the two solutions at any given time (see column six, Table II) as read off from the curve is known to 0.001%.

TABLE II.—RATIO OF THE ARSENIOUS ACID AND IODINE SOLUTIONS.

No.	Date.	Grams of iodine solution.	Grams of arsenious acid solution.	Ratio.		Difference. Per cent.
				Found.	Calculated.	
1	Mar. 6	20.3883	51.1787	2.51020	2.51017	0.0012
2	9	23.0459	57.8530	2.51038	2.51038	0.0000
3	11	19.1883	48.1824	2.51105	2.51051	(0.02)
4	19	21.9252	55.0486	2.51080	2.51105	(0.01)
5	26	26.0033	65.3085	2.51160	2.51154	0.0024
6	26	23.0414	57.8686	2.51150	2.51154	0.0016
7	28	27.0322	67.8960	2.51167	2.51167	0.0000
8	Apr. 22	24.6357	61.9202	2.51342	2.51339	0.0012
					Average deviation,	0.00106

In calculating the average deviation from the mean for this column of the table, the results of standardizations 3 and 4 were rejected; the former because it was subsequently found that the potassium iodide used in making up the solutions for the coulometer, already contained some iodine. The result of standardization 4 was rejected because the deviation from the mean was more than four times as large as the average of the deviations of the other results. All of the results of the investigation of the behavior of the iodine coulometer which are recorded in the following pages were obtained within the period covered by Table II and this table and the corresponding graph were employed in computing the strength of the arsenious acid solution for any desired date.

From the value of the equilibrium constant[1] for the reaction between oxygen and arsenious acid in solution it was found on calculation that in order to prevent entirely the further oxidation of the stock solution, it would be necessary to reduce the partial pressure of oxygen to 10^{-60} atmospheres. While it is quite possible to obtain hydrogen of this degree of purity or sufficiently free from oxygen to prevent any appreciable oxidation of the arsenious acid, it was not deemed necessary to do this at this stage of the investigation, as no error of any importance was introduced in correcting for the oxidation as explained above.

6. The Iodine Coulometer and the Method of Procedure.

The Coulometer.—The iodine coulometer as finally perfected is shown in Fig. 1. It consists essentially of two upright limbs connected by a V tube. At the bottom of each limb is placed an electrode. The caps (I) are ground into the upper parts of the limbs. Two short tubes are sealed into the top of each cap; through one runs a glass tube (K) which carries the electrode connection, and through the other a capillary tube (J) which passes through a hole in the center of the electrode to the lowest point of the limb. A short sleeve of rubber tubing (H) is fitted over these tubes, thus making an air tight joint with the cap, and yet permitting the capillary tube, or this and the cap together, to be withdrawn without disturbing the electrode. The side tube (N) with which a leveling bulb may be connected serves for filling the apparatus and for adjusting the level of the solution in the capillary tubes.

The coulometer was supported in a battery jar which was filled with water to the level of the V tube. No attempt was made to keep the temperature of the bath constant, but the arrangement eliminated convection currents and stirring due to sudden temperature changes. A white plate placed behind the coulometer served to detect any diffusion of the iodine solutions.

The Electrodes.—The electrodes were of platinum-iridium foil. They were cut (see Fig. 1) so that they would fold up while being introduced into the limb of the coulometer and then when in position, spread out so as to fill the bulb (M) at the bottom of the limb. To assist in removing the electrode when necessary a small hole was made in each of the leaflets

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[1] The value of this constant was computed from the electromotive force of the normal iodine electrode, the electromotive force of the oxygen-hydrogen cell, and the electromotive force of the normal arsenious-arsenic electrode, the latter quantity having been determined in this laboratory recently by Mr. E. K. Strachan.

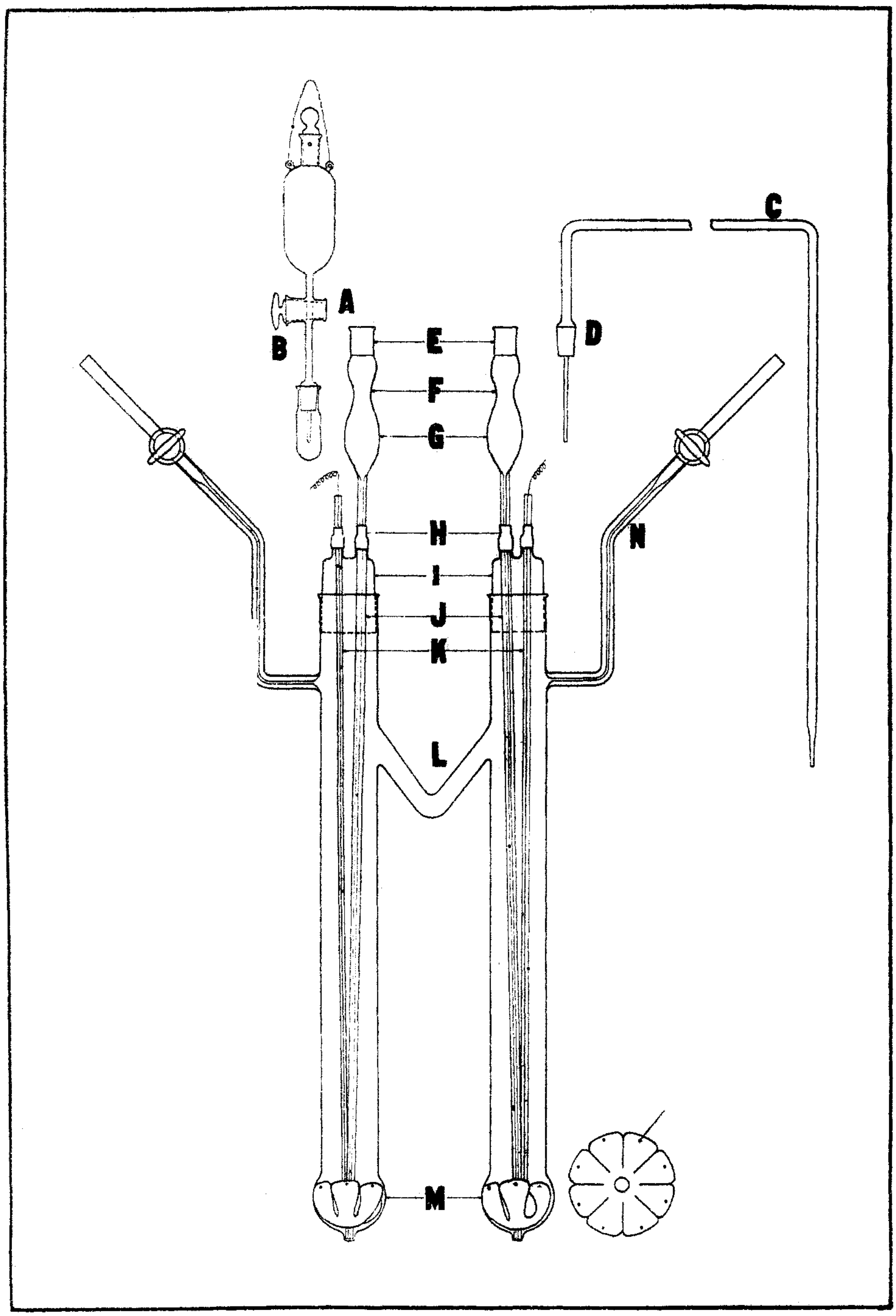

Fig. 1.

into which a wire could be hooked. A hole of 0.7 cm. diameter was cut in the center of the electrode, and through this the tip of the capillary tube passed. The effective area of each electrode was about 50 sq. cm.

The electrical connections were made by means of a wire welded on to one of the leaflets of the electrode and sealed into a glass tube which passed out through the cap at the top. In the case of one of the electrodes the connecting wire was woven through slits in one of the leaflets instead of being welded onto it. This gave greater flexibility and ease of manipulation in introducing the electrode as well as eliminating the danger of breaking the connection. A little paraffin was melted and run down the tube carrying the electrical connections; this served to hold in place the mercury, which formed part of the circuit.

Filling the Coulometer.—After the electrodes are in place, the whole coulometer is first filled by means of the side tube (N) to a little above the level of the V tube (L) with a 10% solution of potassium iodide. Care is taken that no air is entrapped around the electrodes and that no bubbles adhere to their surfaces. The leveling bulb which is attached to the side tube (N) is then raised until the solution rises to the top of the capillary tube (J), which opens rather abruptly into the bulb (G).

(*a*) *The Anode Limb.*—At the anode side, about 25 cc. of a concentrated solution of potassium iodide (one gram of salt to one gram of water), previously freed from air by boiling, is next run into the bulb (G) and allowed to cover the electrode to a depth of about 5 cm. During the electrolysis the opening E is protected by means of an inverted test tube.

(*b*) *The Cathode Limb.*—In a similar manner 6 to 8 cc. of the same concentrated potassium iodide solution are then introduced below the solution in the cathode limb. This solution is immediately followed by about 45 grams (20 cc.) of the standard solution of iodine in potassium iodide. This is run in from the weight buret, (see below) and care is taken that no air is drawn down the capillary. The ground glass joint (B) between the buret and its cap, just fits into the bulb on the capillary at F, the tip of the buret extending well below this point. As soon as the buret is empty it is withdrawn and the tip protected by means of the glass cap. Loss of iodine from the bulb (G) is prevented by immediately placing the delivery tube (C) in position. The ground joint between (D) and (E) is lubricated with a little phosphoric acid.[1]

The leveling bulb attached to the side tube N serves to regulate the flow of solution down the capillary tube and makes it possible to surround the electrodes with a dense solution without causing any appreciable mixing with the dilute solution above.

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[1] In rinsing out the bulb after a run this phosphoric acid is washed into the bulb (G) and then sucked over into the flask in which the titration is performed. The presence of this acid does not affect the titration; in fact, it was found that the addition of 5 cc. of the acid employed did not affect the result by 0.001%.

(c) *The Weight Buret.*—The weight buret employed in introducing the standard solution into the cathode limb is shown in Fig. 1. It is filled by suspending it in such a way that the tip of the delivery tube of the stock bottle containing the iodine solution is well within the neck of the buret. The solution is then forced over by air pressure. After filling, the buret is transferred to the balance case and carefully weighed, using a similar buret as a counterpoise.

The stopcock (A) of the buret is lubricated with a drop or two of vaselin. This vaselin had been shaken up with a strong solution of iodine in potassium iodide, allowed to stand during the summer, washed with a dilute sodium thiosulfate solution until it was free from iodine, and finally distilled under reduced pressure.

Removal and Analysis of the Electrode Portions.—The current was passed through two iodine coulometers, a silver coulometer and a milliammeter in series. The silver coulometer was not handled with any particular care, as it was employed merely for the purpose of calculating the approximate amounts of the arsenious acid solution required for titrating the electrode portions. The time required for a run varied from about 15 to 65 hours. During this time little mixing of the iodine solution at either electrode with the dilute solution above it, occurred. At the anode side no iodine could be detected higher than one-fourth of the distance up the limb. At the cathode side the iodine was rarely visible one-half of the way and usually not more than one-third of the way up the limb. The few cubic centimeters of the concentrated potassium iodide solution which were introduced through the capillary at the cathode side were found to diminish materially the migration in this limb. This is due to the fact that the layer of strong potassium iodide solution greatly diminishes the potential gradient and hence also the migration velocity of the tri-iodide ions.

When about 0.05 faraday of electricity has passed, the circuit is broken. The approximate amount of electricity which has passed through the system is calculated from the weight of silver deposited in the silver coulometer, and thus are found the approximate amounts of standard arsenious acid solution necessary to titrate the cathode and anode portions, respectively. About 0.05 gram less than the required amount of the arsenious solution is then weighed out into a liter Erlenmeyer flask as described above and the flask is fitted to the delivery tube (C) in such a way that the tip of the delivery tube is well below the level of the liquid in the flask. On applying a gentle suction to the flask the electrode portion is sucked over through the capillary tube and the delivery tube. The dilute solution of potassium iodide in the upper part of the limb completely washes the iodine from around the electrode and the latter half of the solution sucked over into the flask shows no color. The solution in the flask is thoroughly mixed and the titration completed in the manner already described.

7. Precision of the Anode Reaction.

Table III shows the agreement obtained between two iodine coulometers in series. All of the data obtained with reference to this point are included in the table. On account of an accident, one of the anode portions in runs 6, 10 and 11, was not titrated. In the calculation of the average deviation from the mean, the results of runs 5, 7 and 8 were not employed. The first was rejected because the deviation was more than four times as great as the average of the others; the results of runs 7 and 8 were not used for the reason explained below. The average deviation from the mean as calculated from the results given in this table is just equal to the uncertainty in judging the end point (see p. 1355).

Table III.—Reproducibility of the Anode Reaction.

No.	Date.	Current (milli-amperes).	Grams of arsenious acid solution.			Deviation from the mean, (per cent).
			Anode No. 1.	Anode No. 2.	Mean.	
1	Mar. 4	37	58.6584	58.6598	58.6591	0.0012
2	6	40	52.6863	52.6841	52.6852	0.0021
3	9	20	57.2657[1]	57.2622	57.2640	0.0030
4	11	40	55.1379	55.1404	55.1391	0.0023
5	16	40	60.7797	60.7682	60.7740	(0.0095)
7	21	43	65.5012	65.4968	65.4990	(0.0034)
8	23	68	63.3568	63.3517	63.3542	(0.0041)
9	Apr. 7	45	65.2055	65.2100	65.2077	0.0035
12	20	70	62.2437	62.2415	62.2426	0.0018
13	27	80	59.8340	59.8345	59.8342	0.0004
					Average deviation from the mean,	0.0020

Permissible Current Density.—The object of runs 7 and 8 was to make certain that the current densities employed were not too large. In one coulometer an anode of the usual size (50 sq. cm. total area) was employed while the total surface of the second was but 8 sq. cm. In these two experiments the larger electrode gave the greater amount of iodine. The difference is, however, but slightly greater than the average of the other experiments, and the result obtained from but two runs cannot be regarded as conclusive. It will be seen, however, that a current density of 0.005 amperes per sq. cm. is allowable; in all the runs except these two, the current density was between 0.0004 and 0.0015 ampere per sq. cm. and hence well below this possibly limiting value.

8. Comparison of the Reactions at Anode and Cathode.

For the purpose of comparing the amount of iodine formed at the anode with the amount which disappears at the cathode, a series of runs were made in which the current was passed through two iodine coulometers

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[1] Baker's "Special" potassium iodide, without further purification, was used in preparing the solutions for anode No. 1.

connected in series. The anode portions from both coulometers were then titrated as was also the cathode portion from one of them, that from the other being rejected.[1]

In Table IV are given the results of these comparisons. In the first column is given the number of the run, in the second column the day on which the arsenious acid solution was withdrawn from the stock bottle for the titration, and in the third column, the current in milliamperes. The next column gives the weight of the concentrated standard iodine solution which was introduced from the weight buret into the cathode limb. The fifth column gives the mean weight of arsenious acid solution used to titrate the two anode solutions (see Table III). For Experiment No. 5, however, the data for both anode solutions are given separately, since as pointed out above (Table III and discussion) the difference between them is too large to be the result of chance and one value is probably correct and the other one incorrect. The weight of arsenious acid solution required for the cathode portion is given in column six. The next column gives the total amount of arsenious acid solution used in titrating both the cathode and the anode portions. The eighth column gives the quantity of this solution which should be required for the titration of the amount of the standard iodine solution used, as calculated from its weight and from the ratio of the two standard solutions as read off from the curve for the day in question (see p. 1357).

Table IV.—Comparison of Anode and Cathode Reactions.

				Grams of arsenious acid solution.				
No.	Date.	Current (milliamperes).	Grams of iodine solution.	Anode.	Cathode.	Total found.	Total calc.	Deviation. (per cent).
2	Mar. 6	40	47.0374	52.6852	65.4103	118.0955	118.0719	(+0.020[2])
4	11	40	45.6123	55.1391	59.3737	114.5128	114.5100	+0.0024
5*a*	16	40	45.4523	60.7795	53.3585	114.1382	114.1238	(+0.013[2])
5*b*	16	40	45.4523	60.7682	53.3585	114.1267	114.1238	+0.0025
6	19	20	44.6216	48.3080	63.7373	112.0453	112.0471	—0.0016
7	21	43	45.6662	65.4990	49.1721	114.6711	114.6763	—0.0045

Average deviation, 0.0028

The results show that, within the limit of error of the analysis the same amount of iodine is formed *from* iodide ions at the anode as is converted into iodide ions at the cathode.

The iodine coulometer is, therefore, certainly free from any constant source of error amounting to more than 0.002%. The reproducibility of the reaction at the anode is all that could be desired and fulfils all of the requirements necessary for a trustworthy determination of the value of the faraday within 0.005%.

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[1] This was necessary because only three suitable electrodes were available at the time these comparison runs were made.

[2] Rejected in computing the average deviation.

9. Summary and Conclusions.

The results of the foregoing study of the iodine coulometer as a precision instrument may be summed up by comparing its advantages and disadvantages with those of the silver coulometer.

1. *Reproducibility.*—Practically the same for both coulometers, 0.001 to 0.002%.

2. *Purity of Materials.*—(*a*) For the silver coulometer the silver nitrate requires special purification and must be very carefully protected from dust or organic matter of any kind. (*b*) A filtered solution of commercial C. P. potassium iodide is satisfactory for the iodine coulometer. It needs only to be protected from a strong light.

3. *Electrochemical Equivalent.*—The number of grams per coulomb is about the same for both coulometers with the advantage in favor of the iodine coulometer.

4. *Influence of Electrode Products.*—(*a*) The anode products constitute an annoying source of error in the case of the silver coulometer, the employment of porous cups being necessary in order to diminish it. These cups require very careful treatment and are possibly not entirely effective, especially if the electrolysis is a prolonged one. (*b*) The iodine coulometer is not subject to this source of error.

5. *Included Material.*—(*a*) The silver deposit contains included material which must be separately estimated and corrected for by a rather tedious process.[1] An appreciable degree of uncertainty is also involved in making this correction due to the fact that the included material contains both water and silver nitrate. (*b*) This source of error and uncertainty does not affect the iodine coulometer, since no deposit is obtained in that instrument. A quantity of very pure and dry iodine must, however, be prepared for standarization purposes. This is fully as tedious a process as the determination of the correction for inclusion in the case of the silver coulometer, but it involves no element of uncertainty and does not need to be performed in connection with every electrolysis. In fact, 25 grams of pure iodine can be easily made to suffice for the measurement of a quantity of electricity which would give four or five hundred deposits of silver of 5 grams each, if measured with a single silver coulometer.

6. *Reversibility.*—(*a*) The reaction in the silver coulometer is not reversible. The reaction at the anode is complicated by the formation of complex ions which not only make it impossible to employ this electrode as a check on the cathode but also constitute a source of error at the latter electrode, as explained above. There is no means of knowing certainly under what conditions (if any) the process at the cathode deposits pure silver, by the reaction $Ag^- + (-) = Ag$, only. (*b*) The reaction in the iodine coulometer is perfectly reversible, the same result being obtained

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[1] Cf. Duschak and Hulett, *Loc. cit.*

from both electrodes, which may be regarded as conclusive proof of the purity of the reaction, $3\text{I}^- = \text{I}_3^- + 2(—)$, occurring at the anode. Certainty upon this point is of the utmost importance in determining the value of the faraday.

7. *Apparatus.*—The silver coulometer and auxiliary apparatus is simpler but somewhat more expensive than the iodine coulometer. For the same degree of accuracy there is not much advantage either way as far as manipulation and time required are concerned.

PART III.—COMPARISON OF THE IODINE AND SILVER COULOMETERS AND DETERMINATION OF THE VALUE OF THE FARADAY.

(PRELIMINARY RESULTS.)

1. Introduction.

Owing to lack of time no attempt was made in connection with the present work to undertake the final determination of the value of the faraday by means of the iodine coulometer, as this would have involved the preparation of new and more stable standard solutions and the preparation of perfectly pure, dry iodine as well as considerable preparatory work in connection with the silver coulometers. It is our intention to proceed with this more extensive investigation during the coming year.

A provisional comparison of the iodine and silver coulometers employing material already at hand was, however, undertaken and although an accuracy of more than 0.01 or 0.02% was not aimed at, the results obtained seem worth recording, as they have an important bearing upon the silver coulometer.

2. Purity of Materials and Standardization of Solutions.

Iodine.—The iodine employed in standardizing the arsenious acid solution was prepared as already described (Part II, p. 1353). For the present purpose it was necessary to dry it thoroughly. A portion of that employed for the standardizations had been standing over sulfuric acid for eight months. A second sample was similarly dried for one month. The weighing bottle was filled by subliming the iodine into it in a current of dry air, in an apparatus especially constructed for this purpose by Dr. Grinnell Jones of this laboratory. In some instances this sublimation was repeated. The air was dried by passing it through a number of towers filled with glass beads moistened with sulfuric acid containing potassium bichromate. It is improbable that the iodine thus obtained could have contained 0.01% of moisture.

Silver Nitrate.—The silver nitrate for use in the silver coulometers was prepared by several recrystallizations of Kahlbaum's product, from conductivity water containing an excess of pure nitric acid. The crystals were drained by suction each time on a Büchner funnel without employing any filter paper. In order to remove the excess of nitric acid the crystals were fused in a porcelain casserole. As soon as the last trace of nitric acid had been driven out (which was readily noted by an immediate quieting and clearing of the surface), the fused silver nitrate was poured into a platinum crucible floating in water. The product thus obtained was perfectly white and gave a perfectly neutral solution.

Standardization of the Arsenious Acid Solution.—Two slightly different methods were employed in standardizing the arsenious acid solution against iodine. In the first of these methods, the weighing bottle containing the dry iodine (about 5 grams) was introduced into a flask containing approximately the required amount of the standard arsenious acid solution and was opened below the surface of the solution. In order to duplicate the conditions employed in analyzing the electrode portions, and also to hasten the solution of the iodine, about 20 grams of potassium iodide were then added. When the iodine had completely dissolved, the required amount of disodium phosphate solution was poured into the flask and the titration completed with the dilute arsenious acid solution.

In the second method, seven or eight grams of potassium iodide were placed in the weighing bottle and not quite enough water to dissolve this salt was then added. The stoppered bottle was left in the balance case for two or three hours and then weighed. Five or six grams of iodine were then quickly added and the bottle again weighed.[1] It was next introduced into the flask containing the arsenious acid and opened under the solution.

Both methods gave practically the same results. The results of all the standardizations made are shown in Table V. Those of April 24 and 26

TABLE V.—STANDARDIZATION OF ARSENIOUS ACID SOLUTION.

Date.	Grams of iodine.	Grams of arsenious acid solution.	Grams arsenious acid soln. per gram iodine.		Deviation from mean, per cent.
			Found.	Calc. to Apr. 14.	
Apr. 9	4.73000	42.6330	9.0133	9.0146	—0.012
9	6.08660	54.8667	9.0143	9.0156	—0.001
10	5.03120	45.3625	9.0162	9.0172	+0.017
10	4.19525	37.8086	9.0122	9.0132	—0.028
16	8.17150	73.6790	9.0166	9.0161	+0.004
24	5.28225	47.6270	9.0164	9.0139	—0.020
26	6.88315	62.0797	9.0191	9.0161	+0.004
26	4.66625	42.0788	9.0177	9.0148	—0.010
29	7.05620	63.6516	9.0208	9.0171	+0.015
29	6.13420	55.3434	9.0221	9.0184	+0.030

Mean, 9.01570

Average deviation from mean, 0.014%

Precision $= 0.014/\sqrt{10} = 0.0044\%$

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[1] The weight of water lost by evaporation from this concentrated solution during the introduction of the iodine was very small; blank experiments showed that it was not over 0.3 mg. and a correction for this loss was applied.

were made by the second method and the others by the first. The figures in the fifth column were calculated to April 14th by correcting for the rate of oxidation (0.00273 per cent per day) of the arsenious acid solution as explained in Part II. A standardization of the arsenious acid solution was made in connection with *each* of the comparison runs with the iodine and silver coulometers.

3. The Silver Coulometers.

The quantity of electricity which passed through the system was determined by means of two silver coulometers. These were practically the same type as those employed by Smith, Mather and Lowry, and the various conditions and methods of procedure employed by them were duplicated as closely as possible.

The anodes were of pure mint silver. They were surrounded by filter paper cups, suspended by means of insulated platinum wire. A 15% solution of silver nitrate was employed in the coulometers. At the end of every second run the solution was rejected and a fresh lot employed for the next experiment.

Each of the bowl-shaped platinum vessels, which served as cathodes, weighed about 50 grams and was 10 cm. in diameter at the top. Bowl A was 4.5 cm. in depth and held when full 275 cc.; bowl B was 5.5 cm. in depth and held 350 cc. The volumes of silver nitrate solution which were used in the coulometers during a run were about 150 cc. and 200 cc., respectively. Before using, the bowls were thoroughly washed with nitric acid and water and dried in an electric oven at 160°. A third bowl, which was of practically the same dimensions and weight and which was used for a counterpoise was similarly treated. On the completion of a run the electrolyte was removed from the bowls by means of a pipet. They were rinsed five or six times with water and finally filled with water and allowed to stand over night. Three or four more rinsings with water followed, after which they were heated in an electric oven at 160° for one hour. After cooling in a desiccator for several hours they were placed on the balance pan and allowed to come to constant weight. The silver deposit was removed from the bowls by means of nitric acid. The bowls were then thoroughly washed and heated in the oven in preparation for the next experiment.

Weights and Balances.—The gold plated brass weights which were used in this investigation were calibrated and standardized by the National Bureau of Standards. The arsenious acid solution was weighed into liter flasks on a Rueprecht balance, sensitive to 0.1 milligram with this load. All the other weighings were made on a Becker balance sensitive to 0.05 milligram. The weights of iodine and silver were reduced to *vacuo* by subtracting 0.0099 and 0.0031%, respectively, from the apparent weights of these elements.

4. Comparison of the Iodine and Silver Coulometers and the Determination of the Faraday. Results and Conclusions.

In this series of experiments a current of electricity was passed through two iodine coulometers and two silver coulometers connected in series. The results are shown in Table VI. The amount of electricity which passed through the system (column 7) was calculated by dividing the mass of silver (column 6) by 0.00111827, which Smith, Mather and Lowry found to be the increase in weight of the cathode bowls per coulomb, under similar conditions. In order to calculate the amount of iodine formed, the amount of arsenious acid solution which was required for the titration was calculated to April 14th, by correcting for the rate of oxidation. The result is given in column 9. The number of grams of iodine formed (column 10) was then obtained by dividing these values by 1.01565, the number of grams of arsenious acid solution corresponding to one gram of iodine (see Table V). The electrochemical equivalent as given in the twelfth column was found by dividing the number of milligrams of iodine formed, by the number of coulombs of electricity which had passed. The corresponding values for the faraday were obtained by dividing the results in column 12 into the atomic weight of iodine, 126.913.[1]

TABLE VI.—THE ELECTROCHEMICAL EQUIVALENT OF IODINE AND THE VALUE OF THE FARADAY.

I. No.	II. Date.	III. Current (milli-amperes).	IV.	V. Silver deposited in coulometer.	VI.	VII. Coulombs.
			Bowl A.	Bowl B.	Mean, corr. to *vacuo*.	
9	Apr. 7	45	6.15330[2]	6.15285[2]	6.15289	5502.17
10	10	50	6.50800	.....	6.50779	5819.52
11	14	40	5.94555	5.94500	5.94510	5316.35
13	27	80	.....	5.64250	5.64232	5045.75

I. No.	VIII. Grams arsenious acid solution.	IX.	X. Iodine, grams.	XI. Ratio, Ag : I.	XII. Electrochemical equiv. of iodine. mg. per coulomb.	XIII. Faraday I = 126.913.
	Used.	Calc. to Apr. 14.				
9	65.2077	65.2201	7.2341	0.85054	1.31477	96,529
10	68.9599	68.9674	7.6497	0.85072	1.31450	96,549
11	63.0049	63.0049	6.9884	0.85071	1.31452	96,548
13	59.8342	59.8119	6.6342	0.85052	1.31482	96,526
			Mean,	0.85062	Mean,	96,538
					Average deviation,	0.010%
					Precision,	0.005%
			(Baxter)	0.849906		

If I = 126.92, F = 96,543

The following facts with reference to the results shown in Table VI should be noted:

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[1] Baxter, THIS JOURNAL, **32,** 1602 (1910).

[2] The silver nitrate employed in this run was Kahlbaum's product once recrystallized from conductivity water and not dried.

(1) The mean value for the faraday, 96,538 coulombs, given in column XIII has a precision of 0.005%. The average deviation of the individual results from the mean is 0.010% and the maximum is only 0.012%. These deviations are caused by the silver coulometer, not by the iodine coulometer.

(2) The value 96,538 agrees astonishingly well with the value, 96,535, obtained by Richards with his copper coulometer (see Table I).

(3) The results with the iodine coulometer confirm the conclusion, already reached, that the silver deposit obtained in the silver coulometer, even under the best conditions, is greater than that required by the reaction, $Ag^+ + (-) = Ag$.

(4) The value 96,538 coulombs per equivalent corresponds to the value 1.1174 milligrams per coulomb for the *true* electrochemical equivalent of silver. This is 0.08% lower than the value obtained by Smith, Mather and Lowry and 0.05% lower than the recent result of Rosa, Vinal and McDaniel (see Table I).

(5) Although we have no reason to believe that our results are affected by any source of error amounting to 0.03%, they are, perhaps, too few in number to justify the conclusion that the value, 96,538 coulombs, is correct within this limit. We believe, however, that the evidence presented in the foregoing pages justifies the statement that the value of the faraday is certainly *greater than* 96,500 coulombs and that the *true* electrochemical of silver is certainly *less than* 1.1180 milligrams per coulomb. We hope to be in a position to make a more definit statement during the coming year.

URBANA, ILL., June 27, 1912.

PASSIVITY OF IRON UNDER BOILER CONDITIONS.

BY HORACE G. BYERS AND FLOYD T. VORIS.

Received August 10, 1912.

Introduction.

The use of substances which inhibit the rusting of iron in order to protect it from the action of corrosive agents was suggested by Cushman,[1] who says that "small quantities of inhibitive substances in boilers should be highly efficacious in preventing pitting." Wyatt[2] suggests the use of sodium bichromate in boilers to precipitate the scale-forming materials and states that the chromic acid formed does not attack the iron. On the other hand, Schoch and Randolph[3] state that "the corrosive character of an aqueous solution cannot be extensively lessened by additions of certain electrolytes such as chromates, hydroxides, etc." Also it was shown by one of us[4] that in many solutions, in which iron as an anode is

[1] Office Public Roads, U. S. Dept. Agric., *Bull.* 30, 29.

[2] *Eng. Min. J.*, 60, 220.

[3] *J. Physic. Chem.*, 14, 719.

[4] Byers, THIS JOURNAL, 30, 1718.