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THE COMPLICATIONS AT THE ANODE IN THE SILVER COULOMETER (VOLTAMETER).

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In a recent paper we have emphasized anew one of the important causes of error in the silver coulometer, namely, inclusion of mother liquor in the precipitate.[1] A definite decision concerning this matter necessarily preceded the discussion of all other questions involving the weight of the cathode deposit, on account of the fact that included matter may seriously affect this weight. A brief repetition of the main conditions is perhaps in order.

(1) It was shown that the amounts of inclusion are highly variable, being dependent upon extent of surface covered by the cathode deposit and the roughness of surface of the cathode, as well as upon the presence of some kinds of impurities. The rate of deposit is doubtless also of moment; and yet other circumstances may affect the outcome.

(2) When the solution is very pure, the extent of surface limited and the surface smooth, the amount of inclusion may be very small (as little as 0.004%), but it is not safe to rely upon its constancy, unless very unusual precautions are observed. With reasonable but not excessive precautions

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[1] Richards and Anderegg, THIS JOURNAL, 37, 7 (1915).

the amount may be seven or eight times as great, even when using materials much purer than these ordinarily obtainable.

(3) Although the amounts of inclusion may thus be quite different under different conditions, sufficiently accurate results may be obtained if the volatile portion of the enclosed mother liquor is expelled by heating the deposit to dull redness. Therefore, this should always be done, applying the correction mentioned in paragraph (5) below.

(4) Part of the included mother liquor is enclosed between the crystals and the dish, and part entirely within the silver crystals.[1] The proportions thus distributed doubtless vary with the conditions. Of the former part, a portion may be evaporated at 160°, but probably not all of it.[2] For this reason satisfactory quantitative results concerning the amount of the inclusion may not be obtained from the crystals after scraping them from the dish; for some water is probably evaporated, and some silver nitrate is certainly left on the dish, when the intervening cells are opened by the abrasion.

(5) In the most accurate work correction should be made for the residual silver left by the decomposition of the enclosed mother liquor. As the amount thus left is very small, it is not necessary to know the exact concentration of the liquid; an approximation will suffice.[3]

(6) *The really essential point is to determine the true weight of pure silver deposited by the current from a sufficiently pure solution.*

(7) All these conclusions essentially confirm and amplify the Harvard

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[1] Hulett and Vinal have found in some recent interesting experiments (*Bull. Bur. Stand.*, **11**, 553 (1914)) that silver in contact with platinum is perceptibly soluble in water. That this solubility was too small to affect the question under consideration is shown by the fact that our crucibles with the adhering silver, after thorough washing, could be allowed to stand for many hours filled with pure water without imparting enough silver to that water to show in the nephelometer. Accordingly, the silver nitrate which we found upon the scraped crystals and upon the battered electrode from which they had been removed, must have been really the result of included mother liquor. Upon our other comparative results the solubility of silver in water would have no effect as all samples were treated in practically the same way.

[2] The cells are evidently, some of them, opened by the high steam pressure at 160°, the crystals having been loosened by the difference between the coefficients of expansion of silver and platinum. Water imprisoned wholly within the silver walls of cells in detached crystals requires, as has been repeatedly stated, a dull red heat for its liberation.

[3] It is clear that the evaporation of part of the included mother liquor complicates estimation of the amount of silver nitrate included, but, fortunately, the possible error is very small. The resulting surplus of silver nitrate is partly balanced by the fact that the enclosed catholyte must have been somewhat depleted. Therefore, for ordinary cases it is safe to conclude that the residual silver must weigh about 6% or 8% of the total inclusion from a 10% solution. Of course, for work of the very highest accuracy (beyond 1 part in 100,000) the exact nature of the inclusions must be determined and a more complete method must be used.

results of 1902.[1] We believe that they are also in essential accord with the heretofore published results of Hulett, making allowance for certain differences of detail already mentioned.

Before our further experiments are recounted, a few words about the history of the question may not be out of place, although a detailed discussion of the very voluminous literature would occupy too much space for the present publication.

In the early work at Harvard it had been shown that the older form of voltameter, containing filter paper as originally designed, invariably caused a deposit distinctly heavier than that in which the anode liquid is kept away from the cathode.[2] At least part of this effect was referred to a temporary surcharge of silver in the anolyte. The need of a substantial inorganic septum to separate this liquid being indicated, a porous cup was employed, and the use of filter paper entirely abandoned. More recently Rosa and his collaborators have concluded, on the basis of extended experiments, that part of the effect is due to a specific action of filter paper and not to the surcharge of silver.[3]

There has been much discussion of these conclusions, but unanimity of opinion does not seem to have been attained.[4] A study of the published experiments seems to indicate that both of the effects are probably operative at the same time; nevertheless, on account of the divergence of opinion, it seemed worth while to make further experiments concerning the nature of the anode liquid under varying circumstances. The present paper recounts the fulfilment of a portion of this program.

In studying this problem two different methods were used in the investigation to be described. In the first place, the weights of the cathode deposits in different forms of coulometers arranged in series were compared. These coulometers were so planned that the access of the anode liquid to the cathode was greatly varied, in some cases almost all of it being

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[1] Richards and Heimrod, *Proc. Am. Acad.*, 37, 415. On page 436 occur the following words: "It is evident that the amount of included mother liquor required varies according to the rate and mode of deposition;................but in applying a correction one should obviously use the value found in the particular investigation under review."

[2] Richards, Collins and Heimrod, *Proc. Am. Acad.*, 35, 144 (1899); Novak, *Proc. Roy. Bohem. Acad. Sci. Prague*, 1, 387 (1892); Rodger and Wilson, *Phil. Trans.*, 186A, 631 (1895); Kahle, *Z. f. Instruk.*, 17 (1897); *Ann. d. phys.*, 67, 1 (1899); Rodger and Wilson and Kahle had all previously shown that on repeated electrolysis solutions which had been used in such an instrument gave heavier deposits than fresh solutions.

[3] *Sc. Papers*, Bureau of Standards, Nos. 194, 195, 201, 220. Reprinted from *Bull. Bur. Stand.*, 9, pp. 151, 209, 493; 10, p. 475 (1912–1913). Many references are given in these papers, which need not be repeated here.

[4] Smith, *Phil. Trans.*, 207A, 545 (1908); Jaeger and von Steinwehr, *Z. f. Instruk.*, 28, 327, 353 (1908); *Ibid.*, 33, 321, 353 (1913); Janet, Laporte and de la Gorce, *Trav. Lab. Centr. d'Elec.*, 2, 288, 318 (1912); von Steinwehr, *Bull. soc. Int. Elec.*, 8, 178 (1911).

excluded, and in other cases much of it being admitted to the cathode. The various results thus obtained show that the anode liquid really contains an excess of silver, which it deposits with the normal crystalline precipitate, provided that the transfer is rapidly made.

Again, other experiments were instituted in which it was shown that silver plates immersed in fresh anode liquid, but not electrically connected, definitely gain in weight in that liquid. This outcome substantiates the other.

Comparison of Different Forms of Coulometers.

The modifications of coulometer which were compared in the experiments to be described were as follows: First, two standard coulometers, each precisely similar to that used by one of us with the assistance of G. W. Heimrod twelve years ago, were mounted. They consisted of large lipped crucibles, each weighing about 60 g. and containing about 120 cc., within which were suspended from glass arms small, porous, cylindrical Pukal cups which contained the anolyte, always at least 1 cm. in level below the catholyte.[1] One of these crucibles was employed in moderately roughened condition, caused by long using, and another was highly burnished. To test the effect of size, a much larger but otherwise similar porous cup coulometer, containing over 300 cc. and having twice the surface, was used; and to test the effect of the anode liquid a very permeable cup was substituted for the fine-grained one.

These instruments were not only compared with one another, but also with the older forms. In two tests the porous cup was omitted and filter paper substituted, and in many other tests we used various modifications of the Kohlrausch form (in which neither a porous cup or filter paper are employed, but a small, glass dish is placed beneath the anode), because much use has recently been made by others of this form. The object of the glass dish, as avowed by the designers, was merely to catch the so-called "anode slime" or finely powdered deposit of silver which falls from the anode during the progress of electrolysis, since they did not fear any harmful effect from the anode liquid. In preliminary experiments we tested the original form of Kohlrausch coulometer carefully and found it unsatisfactory, partly because the "anode slime" frequently floats upon the surface of the electrolyte and becomes mixed with detached crystals from the cathode. Moreover, the cathode deposit is formed only near the top of the dish, most of the surface of the platinum cathode being useless because protected by the glass cup. This unmodified form was therefore rejected.

The original Kohlrausch coulometer has been modified in various ways. The form used at the Bureau of Standards had a glass ring at the surface around the anode to prevent the dissemination of the anode slime (a

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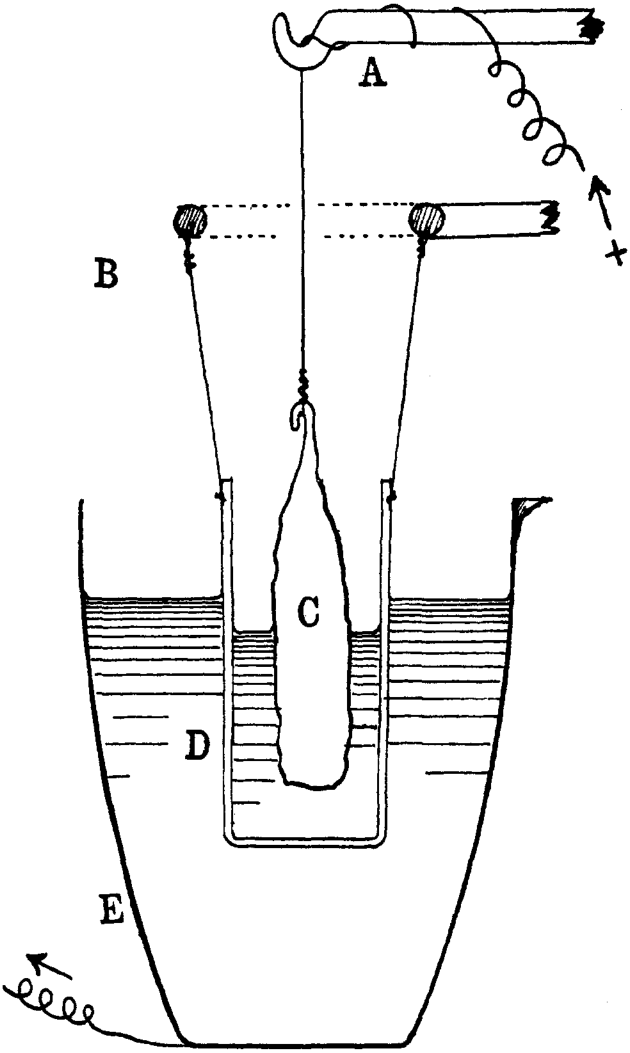
[1] For further particulars, see THIS JOURNAL, 37, 11 (1915).

phenomenon noticed by others as well as by ourselves). Moreover, the form devised by Smith has the anode placed well down in a glass cup, and has the glass ring extended into a cylinder, which at the end of the experiment may be lowered upon the cup, thus enabling the experimenter to remove the "anode slime" and anode liquid together. This, although not different in principle, is doubtless the most easily handled modification of the Kohlrausch instrument, and is perhaps as near an approach to the porous cup as one can obtain from glass apparatus; but it is neither as convenient nor as efficient for removing the anode slime as the porous cup, and, moreover, is certainly less suitable for preventing the diffusion of the anode liquid.



Standard Porous Cup Voltameter (actual size).

A, Glass hook for supporting anode.
B, Glass ring for supporting porous cup.
C, Silver anode.
D, Porous cup.
E, Platinum cathode (a large lipped crucible).

In our experiments, besides the porous cup instruments, two forms of Kohlrausch coulometer were finally used; first, one in which the anode was chiefly above a glass cup suspended in the electrolyte; and, secondly, one in which the anode was sunk entirely below the edges of a similar but deeper glass cup similarly suspended, the conducting wire to the anode being protected by a glass tube. In both forms the "anode slime" which accumulated at the surface was prevented from spreading by glass rings. The second of these two forms was essentially similar to that used by the Bureau of Standards under the name of Poggendorff coulometer, and is similar in principle to the Smith form, except that because our cup was deeper than theirs, it was probably a more efficient apparatus. In both these forms of Kohlrausch coulometer, the silver was deposited only on the upper half of the crucible which formed the cathode as before.

The first step in any such work is the careful testing of the standard of reference. This had indeed been carried out carefully by one of us with the help of G. W. Heimrod years ago; moreover, the consistency of results thus obtained with the help of the porous cup coulometer has been supported by various other experimenters, especially the Bureau of Standards, if we assume that the amounts of inclusion were fairly constant in experiments under similar conditions. The higher results obtained with large coulometers have already been shown in our previous paper to be doubtless due to greater inclusion of mother liquor in these cases, and, therefore, these results do not in the least militate against the results obtained with the porous cup instrument. Because of the great bulk of earlier work, but few new trials were necessary here; and these are recorded mainly in order to show that all was in order for the exact prosecution of the present research.

The following table shows results with the porous cup coulometer in which, first, a somewhat roughened cathode was compared with one very highly burnished, and, secondly, results in which the same coulometer was compared with the larger instrument, with about twice the surface and nearly three times the volume, but otherwise the same. The weights given below are those of the precipitates after ignition at incipient redness,[1] corrected for the small amount of silver (never exceeding 0.03 mg.) left by the mother liquor, which was driven off by the heat. This quantity, it may be remembered from our previous paper, was assumed to be 6% of the included mother liquor. The amount of included mother liquor was least in the small, smooth vessel; next in the small roughened vessel, and greatest in the large coulometers. The actual amounts of inclusion are given among the results tabulated in our last paper[2] and do not con-

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[1] This measure of temperature, rather than a more exact and elaborate one, was used because it is easily available to everyone. Carefully measured, the temperature used by us was found to be between 590° and 630°. Experiments are now in progress here testing the effects of various carefully measured temperatures on the weight of precipitate.

[2] THIS JOURNAL, 37, 16, 20 (1915).

cern us here, for here we are concerned only with the true weight of silver deposited.

TABLE I.—COMPARISON OF POROUS CUP COULOMETERS UNDER VARYING CONDITIONS.

	1st Standard. Medium porous cup coulometer. Rough.	2nd Standard. Medium porous cup coulometer. Smooth.	3rd Standard. Large porous cup coulometer.	Errors referred to 1st standard.	
				Mg.	%.
1	3.07914	3.07913	.....	—0.01	—0.0003
2	3.72682	3.72679	.....	—0.03	—0.0008
3	1.89490	.....	1.89490	0.00	0.0000
4	3.13805	.....	3.13807	+0.02	+0.0006
				Average error,	—0.0004

Evidently, the so-called "volume-effect," which has so much troubled several investigators, has been entirely vanquished. Even considerable variations in the size and condition of the cathode make no important difference in the weight of silver obtained after ignition, all of these values being within the limit of error of experimentation. Such slight variations as exist are all in the direction indicating that the residual silver from the decomposed inclusions was slightly more than 6%—a condition which must occur if some of the cells had been opened and dried at 160°, but the error never reaches 0.001%; and as the weighings could hardly be relied upon to more nearly than 0.02 of a milligram, it is safe to conclude (as one of us concluded fifteen years ago) that the porous cup coulometer is capable after ignition of giving very constant results, and, therefore, is well suited for a definite standard of comparison.

The next step in the experimental work was obviously to repeat the comparisons, so often made by others, of the weights of silver precipitated in the other forms of coulometer with those obtained from our standard instrument, bearing in mind, nevertheless, the fact that the precipitates contained varying contamination with included mother liquor, and allowing in each case for the individual amount.

With each form of Kohlrausch coulometer a series of comparisons was made with the typical standard porous cup coulometer. In order to make the results as clear as possible and to relate them directly to the recent results of others, there is given in the first table below a comparison of the weights of the precipitates not ignited, but merely carefully washed and dried at 160°, after the manner of the several National Bureaus.

The outcome is striking. Each form of Kohlrausch coulometer is seen to give almost exactly the same results as the porous cup coulometer, just as other experimenters have found. The average result shows that in nearly 16 g. of precipitate the surplus shown by the Kohlrausch coulometer was only 0.14 mg., an error of less than one part in 100,000. It is from data of this sort that so many able experimenters have concluded that there is no such thing as an anode impurity, that the porous cup is unnecessary, and that no inclusions are present in the cathode deposit.

TABLE II.—COMPARISON OF APPARENT WEIGHTS OF SILVER (DRIED AT 160°), DEPOSITED IN TWO FORMS OF COULOMETER.

	No. of expt.	Standard porous cup coulometer. G.	Kohlrausch coulometer. G.	Difference in weight of deposit. Mg.	Surplus in Kohlrausch forms. %.
First series	1	2.85028	2.85032	+0.04	+0.002
	2	3.07747	3.07746	−0.01	0.000
	3	2.29124	2.29127	+0.03	0.001
Second series	4	2.18564	2.18565	+0.01	0.000
	5	3.05583	3.05585	+0.02	+0.001
	6	2.30750	2.30755	+0.05	+0.002
		15.76796	15.76810	+0.14	Av., +0.001

Our preceding article has demonstrated, however, that the weights given in this table do not represent pure silver, but rather silver in which there is enclosed varying amounts of mother liquor in microscopic cells; hence this apparently satisfactory comparison has really little significance. The real comparison, which alone can show whether there is appreciable impurity evolved at the anode, capable of augmenting the weight of the deposit, is only to be found when the *true* weights of the silver deposited are determined by igniting the precipitates in each case, with due precautions. This had, of course, been subsequently done in each case recorded above; and Table III below presents the weights of pure silver thus found. Each of these weights is corrected for the 6 per cent. of silver assumed to be left behind by the expelled electrolyte.

TABLE III.—COMPARISON OF TRUE WEIGHTS OF PURE SILVER DEPOSITED IN TWO FORMS OF COULOMETER.

	No. of expt.	Porous cup voltameter. G.	Kohlrausch coulometer. G.	Surplus in Kohlrausch forms. Mg.	Surplus in Kohlrausch forms. %.
First series	1	2.84998	2.85017	+0.19	Av. = 0.006
	2	3.07714	3.07727	+0.13	
	3	2.29095	2.29111	+0.16	
Second series	4	2.18540	2.18554	+0.14	Av. = 0.003
	5	3.05539	3.05548	+0.09	
	6	2.30721	2.30727	+0.06	
		15.76607	15.77684	+0.77	

Evidently in every single case the Kohlrausch coulometer gave a distinctly greater deposit of *pure* silver than the porous cup coulometer. Moreover, it is very striking that in the first series (Experiments 1, 2 and 3), where the anode was above the glass cup (giving more chance for diffusion), the surplus was much more marked than in the second series

(Experiments 4, 5 and 6), where the anode was sunk well within the glass cup. The surplus is so consistent and so much beyond the limit of error that there can be no question of its real existence.

The close agreement of the figures shown in Table II is, therefore, shown to be illusory. The reason why the porous cup and Kohlrausch voltameter appeared to give the same results was simply because in the Kohlrausch form the error of a surplus of silver from the anode was hidden by the fact that in this form the inclusions were less than in the porous cup form. The reason for the smaller amount of inclusion in the Kohlrausch form has already been shown to be due primarily to the smaller surface upon which the silver was deposited, although it may perhaps be referred partly to the different form of aggregation in larger crystals, which seems to occur when small amounts of anode liquid escape into the catholyte.[1]

As has just been pointed out, the inclusions in the Kohlrausch form are less than those in the porous cup form. Evidently the amount of inclusion on the one hand and the surplus from the anode on the other hand are independent variables, and neither can be certainly predicted from a knowledge of the other.

Having thus explained the illusory agreement observed at first,' and having demonstrated that a real (if slight) surplus of silver is deposited even by the best type of Kohlrausch coulometer, we may proceed to show that under conditions where the anode liquid is allowed more freely to reach the cathode, a considerably larger surplus of silver may be obtained. This indeed had been demonstrated in the early Harvard work of 1902, but much of the evidence in that work depended on a comparison of the deposit in the coulometer containing filter paper with the porous cup form, and hence some doubt might legitimately exist, as others have pointed out, whether the surplus had not been caused by the filter paper.[2] We shall return later to this point. It is easy, however, to promote the difusion of the anode liquid to the cathode without introducing filter paper. All that it is necessary is to keep the liquid within the porous cup at a higher level than the liquid outside (instead of at a lower level in the manner always from the first maintained in the standard coulometer). This was done in some of the early Harvard experiments, and the result was published, although the experiments were not reported in detail and have been usually overlooked.[3] Buckner and Hulett also afterwards repeated a comparison of this kind and showed that, as a matter of fact, in such cases the surplus of silver is obtained upon the cathode, using a porcelain

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[1] This Journal, **37**, 16 (1915).

[2] Rosa and Vinal, *Bull. Bur. Stand.*, **9**, 206 (1912); Laird and Hulett, *Trans. Am. Electrochem. Soc.*, **22**, 345 (1912); Buckner and Hulett, *Ibid.*, **22**, 381 (1912).

[3] Richards and Heimrod, *Proc. Am. Acad.*, **37**, 419, lines 3 to 8 (1902).

porous cup.[1] Nevertheless, it seemed worth while to repeat these experiments once more.

In the trials recorded in Table IV below, the standard porous cup coulometer was placed in series with a coulometer containing a more permeable "alundum" cup, in which the liquid was kept at a higher level inside than out, promoting diffusion as mentioned above. The "alundum" cups (which had been chosen for the purpose because they were much more permeable than the Pukal cups) were carefully tested in order to be sure that they could have no reducing action on the silver nitrate. Professor Hulett has since informed us that in some cases he had detected such action, but none was found in our samples, so that the following results are significant: The "alundum" cups (like the porcelain porous cups in all our other experiments) were not only thoroughly washed with nitric acid and water, but were also soaked in silver nitrate (as recommended by the Bureau of Standards) before being used.

TABLE IV.—INFLUENCE OF ANODE LIQUID ON WEIGHT OF CATHODE.

	Dried 160°: Not ignited.		Ignited.		Extra silver.	
No. of expt.	Standard coulometer. G.	Permeable alundum cup. G.	Standard coulometer. G.	Permeable alundum cup. G.	Mg.	%.
7	2.67551	2.67597	2.67505	2.67539	0.34	0.012
8	2.41159	2.41208	2.41116	2.41155	0.39	0.016
9	2.18255	2.18288	[2.18218]	[2.18241]	[0.23]	[0.010]*
10	2.34446	2.34494	[2.34406]	[2.34441]	[0.35]	[0.015]*
11	0.94195	0.94217	[0.94179]	[0.94196]	[0.17]	[0.018]*
					Average,	0.014

* Among the five trials recorded in the table, two of the electrolyses in series were conducted in the usual way, the precipitates being ignited at incipient redness as usual. The other three were conducted under the same conditions, but the weight of ignited silver was calculated from that of the silver dried at 160°, it having been obtained under the usual conditions maintained in the first two experiments. These calculated values are enclosed in brackets in the table; although not quite as certain as the more directly obtained results, they are sufficiently accurate for the purpose in hand.

The surplus of silver evident in Table III has been markedly increased in Table IV, the average in the latter series being more than double that found in the Kohlrausch coulometer where the anode was raised above the glass cup, and nearly five times that found in the form wherein the electrode was sunk within the glass cup. Probably even the "alundum" cup is not the best apparatus for demonstrating the effect of this anode liquid, for after the electrolysis is well started, the cup is partly filled with "anode slime," and the anode liquid must penetrate through this in order to escape. Because (as will be shown) the anode liquid deposits silver upon a silver surface, it must lose some of its surcharge by depositing this upon the finely divided metal of the "slime." A yet quicker removal

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[1] Buckner and Hulett, *Trans. Am. Electrochem. Soc.*, 22, 379 (1912).

of the anode liquid from the neighborhood of the anode and its powdery environment would probably give a yet larger discrepancy as compared with the standard porous cup coulometer. In this connection it seems worth while to record two new experiments in which loosely wrapped filter paper took the place of the porous cup.

TABLE V.—COMPARISON OF STANDARD POROUS CUP COULOMETER WITH FILTER PAPER VOLTAMETER.

Standard porous cup coulometer. (Ignited silver.) G.	Filter paper voltameter. (Ignited silver.) G.	Excess of silver in filter paper voltameter. Mg.	%.
2.67503	2.67536	+0.33	0.012
2.41114	2.41152	+0.38	0.015
		Average,	0.014

There can be no question that a real excess of silver was deposited on the cathode.

Clearly, precipitates obtained in the coulometer when the anode is guarded only by filter paper are too heavy before ignition for two reasons: in the first place, mother liquor is included; in the second place, an excess of silver is precipitated. The further discussion of the action of filter paper will, however, be postponed to a subsequent paper.

Spontaneous Deposition of Silver from the Anode Liquid after Electrolysis.

In the experiments, published in 1902, made with the help of G. W. Heimrod, it was shown that the anode liquid was capable, not only of depositing an excess of silver on the cathode during electrolysis, but also of depositing silver upon a separate silver plate without any electrolytic help. In other words, it was shown that the anode liquid thus obtained had a surplus of reducible silver, which would at once crystallize on a silver surface, if it was allowed to do so before the oxygen of the air had a chance to oxidize it. Although other evidences of such behavior of the anode liquid were furnished, these results have been interpreted by others as due to the action of filter paper, and it is true that if such action existed it might account for a part of the effect, for filter paper was present. Therefore, it seemed desirable to repeat the experiment in such a way as to exclude organic matter. The problem was easily accomplished in the following fashion: The anode in a voltameter such as that used in the preceding experiments, was surrounded by a cup of easily permeable "alundum" and this in turn was surrounded by a somewhat larger, very fine-grained Pukal cup, in which the level of the electrolyte was kept below that in the inner "alundum" cell. The Pukal cup was immersed in the usual fashion in the electrolyte in the large platinum crucible-cathode, and the electrolysis was conducted as usual. During the progress of the electrolysis, however, portions of the liquid permeating from the inner "alundum" porous cup were quickly removed by means of a fine pipet from the narrow space between the two cups, and were immediately transferred to a small porcelain crucible containing a small plate of carefully weighed silver. This plate in nine successive trials was found to gain a total of 0.62 mg., an average of 0.07 mg. in each trial. The silver plate became covered, during these trials, with a curious iridescent covering, which, when examined by a powerful microscope, was seen to consist of very fine, brilliant, crystalline laminae, probably due to the deposition of silver. But whether this was silver or something else, the essential point remains, namely, that the plate had accumulated a deposit which augmented its weight.

In order to be sure that this deposition could not be due to some impurity from the "alundum" cup, four trials were made in which precisely the same procedure was conducted, taking solutions from between the two cups, except that no current of electricity was allowed to pass. The silver showed the following gains in these successive trials: +0.01, +0.01, —0.02, +0.00 mg., total change in weight, 0.00 mg.

This indicates, not only that the weighing and method were sufficiently accurate, but also that the deposit found when the current was running could not have been due to any action of the alundum cup, but must have been due to a real addition of something (probably silver) to the liquid between the cups, and this could have come only from the anode. The result, which evidently confirms the conclusion of years ago, affords convincing direct evidence of the cause of behavior of the anode liquid observed in our other experiments. As some of the anodes in the trials just described were of fused silver, whereas others were of silver deposited electrolytically, and precisely the same average gain was noted with each class of anode, it is clear that the special form of the silver at the anode is unimportant. The production of this easily reducible surplus of silver is thus a general phenomenon.

The reason why others have failed to find this effect and, therefore, have doubted its existence, is unquestionably because they have allowed too much time or too great dilution of the anode liquid to intervene before the liquid was brought into contact with a silver surface. This would give an opportunity for oxidation, which would remove the peculiar compound causing the effect, producing a slightly basic solution capable of depositing nothing upon a silver surface, at least without electrolytic help. That a negative result is thus obtained, we have found by various experiments, which need not, however, be given in detail.

It seemed a matter of interest to discover also if filter paper alone could affect the weight of a silver plate wrapped in it and immersed in silver nitrate solution, that is to say: to discover if filter paper can produce a silver compound capable of depositing silver in crystalline form upon a silver surface without electrolytic help. Accordingly, a silver plate was wrapped in purest quantitative filter paper, placed in a pure solution similar to that used in the regular electrolyses, and subjected to the same conditions as to length of time of standing and temperature as before. Eight successive trials showed a total gain of 0.01 mg. in the weight of the silver plate—a wholly negligible quantity. This shows that filter paper does not promptly produce in silver nitrate a compound like that produced at the anode, which is capable of depositing silver spontaneously upon a silver plate, and it removes entirely whatever doubt there may have been concerning the experiments of 1902 upon this subject.

A hypothetical explanation of the nature of the anode liquid was approved in 1902.[1] Although at the time this hypothesis was accepted only tentatively without insistence upon its final verity, no facts have been brought forward by others which seem to diminish the cogency of the argument. Therefore, it seems to us still the best explanation for the behavior of the anode solution. In brief, the hypothesis supposes that a complex ion, such as Ag_2^+ or Ag_3^+, containing silver in a state of lower average valency than usual, is set free at the moment of the attack on the anode; that is to say: some of the silver which is properly ionized by the current carries away with it some of the anode metal, which really ought to have been left behind. This complex, not being in equilibrium with the solution, immediately decomposes,—its rate of decomposition decreasing, of course, as its concentration decreases. Most of it must decompose in the immediate neighborhood of the anode, the presence of the silver there expediting the decomposition, just as the presence of crystals of a salt relieve its supersaturation. When, however, the anode solution which contains only a slight concentration of the complex silver ion is removed from a silver surface, it is to be supposed to be more permanent, and may remain in a metastable condition until either oxidized by the dissolved oxygen in the electrolyte or precipitated upon the silver at the cathode,—which also, of course, is able to relieve the supersaturation and reduce the metastable to a stable equilibrium. Although this explanation is avowedly hypothetical, it seems to us to cover the ground and to be entirely consistent with itself and with all the facts, explaining the existence of the anode slime as well as the peculiar behavior of the anode liquid in every detail. Whether or not a portion of the anode slime, so finely divided as to be almost colloidal, may be responsible for at least a part of the phenomena

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[1] *Loc. cit.*, p. 432. Novak seems to have been the first to propose this explanation (*Proc. Roy. Bohem. Acad. Sci.*, 1, 387 (1892)) and Rodgers and Watson offered independently a similar one [*Phil. Trans.*, 186A, 631 (1895)]. Reference may also be made to the work of Bose [*Z. Electrochem.*, 13, 477 (1907); 14, 85, 314 (1908)]; Luther [*Z. physik. Chem.*, 30, 628 (1900)]; Jellinek [*Ibid.*, 71, 513 (1910)], and Eisenreich [*Ibid.*, 76, 643 (1911)].

recounted in this paper, we have no means at present of deciding, but this explanation seems, on the whole, less adequate than the one just discussed. We shall hope for more light upon this question in the near future. Whatever explanation may be finally accepted, the desirability of keeping the anolyte away from the cathode by means of an effective diaphragm seems to be strongly indicated by the experiments described above.

The Nature of the "Anode Slime."

In the early Harvard papers it was suggested, as already remarked, that the hypothesis of the complex ion was capable of explaining the nature of the "anode slime." This point does not seem to have claimed the attention of others, but, nevertheless, it is worth reiterating because it is in accord with our explanation of the behavior of the anode liquid.[1] The anode dust was then found to be composed of extremely fine crystals of silver, as seen in the microscope; and we are to confirm this observation. Although it is conceivable that these crystals were left behind when a portion of the silver dissolved, it seems more probable that they are the result of the decomposition of most of the complex ion, which deposits its extra load in the form of this fine crystalline powder. With a large anode, the equilibrium at any one spot would be less difficult to maintain, hence the amount of the "slime" would be less, as the Bureau of Standards have found. That the total loss at the anode should nearly correspond to the gain at the cathode, as several investigators have shown, is not in the least contradictory to this theory, for when all the anode slime is collected and weighed with the anode, it is clear that the only weight lost must be due to such portion of the complex ion as escaped from the anode and became oxidized. In the siphon form employed, this amount would probably be very small, as the heavy anode liquid remained at the anode.[2] Hence, the loss at the anode and the gain at the cathode might be equal, although each might be too great. The irregular results obtained at Harvard in 1902 substantiate this explanation.[3]

No other theory seems to explain the existence of the anode slime and its peculiar finely divided nature as well as this.

The Efficacy of the Porous Cup as a Means of Retaining the Anode Liquid and "Anode Slime."

The above results make it perfectly clear that, in order to obtain an accurate result in the coulometer, the anode liquid must not be allowed to reach the cathode. Any device which effects this separation and permits the ready weighing of the cathode deposit should be adequate for the purpose. It is shown above that the Kohlrausch plan, which was intended originally only to collect the anode slime, serves also in part to

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[1] Richards and Heimrod, *Proc. Am. Acad.*, **37**, 432 (1902); *Z. physik. Chem.*, **41**, 319 (1902).

[2] Compare *Bull. Bur. Stand.*, 10, 528, 536 (1914).

[3] *Ibid.*, pp. 434 and 321, respectively.

prevent the anode liquid from reaching the cathode. But this apparatus is unsatisfactory, because even when the anode is deeply sunk within the glass cup, some excess of deposit on the cathode seems to be obtained, and in any case the anode slime is troublesome, and not always content to remain within bounds. Therefore, these forms, although better than the filter paper voltameter, do not seem to be the best.

Another device suggested by Merrill[1] places the cathode at the top and the anode at the bottom. As tested in 1902 at Harvard, it was modified by using a wire gauze as the cathode, to facilitate the escape of the depleted catholyte.[2] This arrangement, if the time of electrolysis is not too long and the vessel is not disturbed, secures a satisfactory exclusion of the anode liquid from the cathode; but it is hampered by the disadvantage of the possibility of the loss of small crystals from the cathode, which may fall upon the anode, and become mixed with the anode slime. It is useful when the experimenter desires that the resistance of the coulometer should remain nearly constant throughout the electrolysis.

The syphon voltameter, in which the anode and the cathode are in different vessels, has the disadvantage of interposing large resistance, which evolves heat and rapidly changes, even in the most advantageous form used by the Bureau of Standards, where the syphon is very wide and short. The reason why this has been found occasionally to give too large deposits can hardly be traced until the inclusions in such deposits have been determined. The excess is probably not due to the anode liquid, which, except in the shortest syphons, probably stays entirely on the anode side.

The elimination of these forms of coulometer leaves the porous cup coulometer as the only remaining form worthy of consideration. Therefore, it behooves us to discuss very carefully its virtues and its faults.

In the first place, it has the undeniable virtue that the anode slime on the one hand, and the precipitated cation on the other hand, are separated beyond the possibility of mixing; and the analytical determination of the weight of the cathode precipitate is certain and easy. For this reason alone it was first suggested by Poggendorff long ago; he had no inkling of the peculiar nature of the anolyte.

In the next place, the Harvard results of 1902, comparing this coulometer with other forms, (especially with the inverted wire-gauze form), seem to show indubitably that no important amounts of anode liquid escape from inside the cup into the catholyte. In order that the cup should thus be effective, it is important, of course, that there should be no large orifices in it, and that the level of the liquid within it should always be distinctly lower than that outside. Thus, if any diffusion takes place, it must be essentially from the outside inward. The cup must be very fine-grained

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[1] *Phys. Rev.*, 10, 169 (1900).

[2] *Loc. cit.*, Richards and Heimrod, *Proc. Am. Acad.*, 37, 420 (1902).

and the absence of large holes should be tested, both by the rate of flowing from such a cup when filled with liquid and hanging in the air, as well as by causing air to be delivered through it under water. If in the latter case considerable pressure is needed, and the air escapes in a multitude of very fine bubbles from the whole surface, the cup is suitable for the purpose. If the delivery is easy, and if one point claims most of the outflow, the cup should be rejected.[1]

It is, of course, possible that a trace of the offending complex ion, or whatever the compound may be which bears the surplus of silver, may be carried *electrolytically* through the cup, but there is good reason to believe from the quantitative results already quoted that this amount is so small as to be taken care of by the dissolved oxygen in the outside electrolyte before it can reach the cathode.

At any rate there can be no question that the porous cup coulometer gives very constant results. Even those who deny the necessity of its use grant this claim; and, indeed, the results of all three National Bureaus, as well as Hulett's (if we assume that under like conditions the inclusions are nearly constant), prove its constancy.

The chief objection which has been raised to the cup is the possibility that it may introduce impurities into the electrolyte. This it will do, of course, if it has not been properly cleaned. Neither an excess of acid nor an excess of alkali nor cyanide should remain in it. We believe, however, that if made of good insoluble porcelain it can cause no important impurity in the solution when it has been properly cleaned with nitric acid, thoroughly washed with water and soaked in silver nitrate solution. Moreover, it must be cleaned before every determination if an accurate result is desired. The glazing of the cup upon its upper portion, unless filling every pore, seems to be of doubtful efficacy because of the difficulty of washing out acid or other impurity which may penetrate upwards beneath the glaze.[2] We have found by experimental evidence that a porous cup blackened by exposure to light and dust is capable of yielding too high a deposit. In our experiments recounted above, the cups were cleaned, of course, with the greatest care, and washed until they were certainly free from acid. Ignition after such washing should not be practiced, as it alters the condition and increases the solubility of the porous silicate. Careful tests of our own—not only those described above, but also others in which the silver nitrate in cups which had been soaked were tested with permanganate—showed that our porous cups had no reducing action upon silver nitrate.

The only important difficulty which we have encountered in our own work with the porous cup is the fact that the coulometer containing such

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[1] Richards and Cox, This Journal, 26, 822 (1914).

[2] Buckner and Hulett, *loc. cit.*, pp. 371 and 380.

a cup changes its resistance somewhat as the deposit proceeds. This is more or less the case with any form of coulometer, except the inverted wire-gauze form, and in the porous cup coulometer the trouble may be minimized by keeping the levels inside and out constant by means of automatic syphons. Attention should be directed to the importance of taking the liquid from the very bottom of the anode cup, because this is where the heavy anode liquid accumulates.

Of course, nothing in this paper or the preceding paper should be construed as pretending to state the exact quantitative effect either of inclusion or of the anode liquid on any of the preceding investigations of others. So many circumstances, either already known or as yet undetermined, seem to decide the amounts of these respective effects that they can be estimated only under the special conditions present in each particular case, and cannot be exactly determined by a subsequent examination of the printed record. It may well be that some of the eminent investigators, whose work we have mentioned, have really had in their precipitates a smaller amount of inclusion, and (with the Kohlrausch instrument) a smaller anode effect than we have found in our experiments. We earnestly hope that they will determine the presence or absence of these disturbing circumstances by methods such as have been used in the present research, or by other adequate methods, so that all doubts may be removed. Especially as regards the electrochemical side of the matter this is important. Here a *constant* value for the faraday is not enough—the weights must represent the amount of pure substances chemically equivalent. The importance of this condition was seen by the Bureau of Standards as well as at Harvard in the consideration of the iodine-silver voltameter of Bates and Vinal, discussed in our previous paper.

It is to be hoped, also, that some form of precise coulometer may be found for general use, which will not involve precautions so elaborate as those recommended by some of the recent experimenters; for these are beyond the reach of many chemists and physicists. The outcome of the present research leads us to believe that results obtained by igniting the deposit in the porous cup coulometer give not only the most accurate values for electrochemical comparison, but also the safest and most easily attained standard values for the measurement of current. Perhaps when all the manifold subtle influences which determine inclusion are thoroughly known, a better way may be found; the conviction just expressed is of course based upon the actual experience up to the present time.

Because the discussion of our experiments has inevitably involved emphasis upon certain omissions in the work of other experimenters, we are especially desirous to call attention here to the real services to science rendered by them, particularly by the two series of researches which have added most to the knowledge of the subject during the last few years.

Rosa and Vinal of the Bureau of Standards have proved, in confirmation of the early tentative Harvard results, that *under perfectly constant conditions* the porous cup coulometer, even when not ignited, gives very constant deposits. This was the main question which their careful investigation sought to answer. They have further demonstrated that certain organic impurities, including filter paper, cause striated deposits, that the contamination of the electrolyte by filter paper increases the weight of the deposit dried at 160°, that acid diminishes this weight, and that large and small unignited coulometers give lower and more nearly equal results when the electrolyte is very pure. They have presented an interesting hypothesis capable of explaining, many of these varied phenomena and exhibit excellent photographs of the striations. Although they have done little concerning the anode liquid, fortunately their lack of study of this aspect of the question has had no great practical effect on their results, because for all their chief experiments they wisely used the porous cup coulometer, in which the effect of the anode liquid is nullified.

Hulett and his collaborators at Princeton have published an interesting series of carefully obtained results, which seem to us to afford valuable support for the following outcomes of the early Harvard work: First, that the inclusions are variable under varying circumstances and often important in amount, even when the electrolyte is of a high degree of purity; and, secondly, that the anode liquid, independent of organic matter, may augment unduly the weight of the cathode. They have further made careful analyses of the chemical nature of the inclusions, showing them to consist (as had been expected) chiefly of an aqueous solution of silver nitrate. Many other matters of detail were also carefully studied by them, especially the effects caused by the presence of different gases. The recent experiments of Hulett and Vinal on the solution of silver in water, when in contact with platinum, are especially interesting.

Each of these series of investigations must be carefully studied by subsequent workers, for each contains the account of well executed experimentation concerning important aspects of the subject.

As has been already pointed out, the results and conclusions recorded in our two new papers, while in no way inconsistent with the results and conclusions just mentioned in detail, have differed in other particulars from those of these eminent investigators and of several other investigators in this field. Although there has been much private correspondence between most of those concerned during the last few months, we find no reason to alter our opinions about the main points at issue. Nevertheless, we prefer at this time to forego further discussion of these differences, especially because several of the investigators (including one of us) are continuing their studies. The large number of variables which modify the precise working of the coulometer has led in the past to unfortunate confusion; but we hope that unanimity may before long be attained, and that the outcome of the present research may ultimately be of service in the attainment of this common point of view.

In conclusion, we wish once more to advocate strongly the use of the scientifically derived and logical name "coulometer" for this instrument, when it is used to determine accurately the number of coulombs of electricity in physical or chemical experimentation, in place of the vague and inaccurate term "voltameter." This latter was devised before the dimensions of electrical energy were understood, and is at present an anachronism. We feel that we are second to none in the desire to do homage to the incomparable genius of Faraday; but we cannot see how the retention of this antiquated and confusing name can, in any way, enhance his credit.

We are glad to express our indebtedness to the Carnegie Institution of Washington for much of the apparatus used in this research.

Summary.

In the previous paper we have shown in verification of the early Harvard work that the inclusion of mother liquor by a silver precipitate may vary according to circumstances from 0.004 to at least 0.03% of the weight of the precipitate, and hence should be determined in each case.

In that paper we also emphasized the importance of obtaining a definite knowledge concerning the amount of imprisoned electrolyte before conclusions are drawn from the weight of the deposit.

In the present paper it is shown experimentally, confirming our earlier results and those of Hulett, that the anode liquid may really augment the weight of the ignited cathode deposit, even when no filter paper is present. This effect is presumably due to metastably dissolved silver, in the form of an argentous ion but the mechanism of the effect is not yet fully elucidated.

The Kohlrausch coulometer, although an improvement over the filter paper form, was found in our experiments not to remove all of this trouble.

An illusory agreement between different forms of coulometer was found in some of our uncorrected experiments, because of the balanced effect of the two errors (inclusion and surcharge of silver). By comparing the weights of the ignited precipitates, this compensating effect could be detected and analyzed.

The best results were produced by the use of a small porous-cup coulometer with a highly burnished cathode and pure electrolyte, the deposit being ignited at incipient redness.

These and other questions concerning the coulometer are being yet further experimentally investigated at this Laboratory.

CAMBRIDGE, MASS., 1913-1915.