at the changes for the better that have taken place within my life time. Chemical research is in a healthy condition in our country and the signs of future growth are most promising. May I add in conclusion that, though circumstances have kept me out of the field of chemical work for some years past, I now see my way clear to entering that field again, and I can think of nothing that could give me greater pleasure than the prospect of taking up the work in chemistry that I had to abandon thirteen years ago. It is a little late for me to begin again, but I believe that I shall yet be able to experience some of the joys that came to me so abundantly in the past while struggling with my old, inanimate laboratory friends. The transformation from university president to chemist is complete, and I rejoice.

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

# THE INCLUSION OF ELECTROLYTE BY THE DEPOSIT IN THE SILVER VOLTAMETER.

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## I. Introduction.

The silver voltameter (or better, coulometer) is an instrument of such great importance in the exact measurement of the electrical quantity that its study by many investigators is highly desirable; therefore, the widespread attention which it has received during recent years is gratifying.

Since the classical researches of Lord Rayleigh and Mrs. Sidgwick[1] and F. and W. Kohlrausch,[2] carried out between 1880 and 1883, the subject has been studied in may places and from many points of view. The earlier of these investigations are mentioned in detail in the description of a protracted research carried out at Harvard University, and published years ago by one of the present authors in conjunction with two assistants.[3] More recently the National Bureau of Standards, at Washington, the National Physical Laboratory, at Teddington, near London, England, and the Physikalisch-Technische Reichsanstalt, at Charlottenburg, Berlin, as well as other independent physical chemists, have conducted elaborate investigations concerning the nature of several irregularities in this instrument.

The most careful of these researches have verified the main calculations

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

[2] *Wied. Ann.*, *N. F.*, **27**, 1 (1886).

[3] Richards, Collins and Heimrod, *Proc. Am. Acad.*, **35**, 123 (1899); Richards and Heimrod, *Ibid.*, **37**, 415 (1902); also *Z. physik. Chem.*, **32**, 321 (1900); **41**, 302 (1902).

brought forward in the earlier research conducted at Harvard; but unanimity has not yet been attained with regard to all the details.

Much time has been spent upon the question as to the purity of the electrolyte and the cleanliness of the apparatus, especially the porous cup recommended in the Harvard researches. These investigations were important perhaps from the standpoint of the average chemist, or especially that of the physicist unused to working with pure material, but there seems to be no important point (except perhaps the precise effect of acidification) in all this part of the recent work which was not appreciated at Harvard, fifteen years ago. Any one who has worked much upon atomic weights dealing with silver nitrate solutions would think of contaminating such a solution with organic matérial of any kind, especially filter paper; and there is no question that the silver nitrate used in the early Harvard work satisfied all the necessary requirements of the more recent critics. Moreover, it is obvious that a porous cup (if one is used) must be thoroughly washed free from either acid or alkali immediately before use. These patent facts might perhaps have been more emphasized instead of having been assumed almost as a matter of course, in the early Harvard papers; and if this had been done, time and trouble on the part of others might have been spared; the essential precautions were recognized long ago.

About the importance of pure materials, chemically clean apparatus, and electrically perfect insulation, there can thus be no doubt that all authorities are now agreed, the very recent work having emphasized the earlier conclusions; but concerning certain other irregularities of the silver voltameter, as has been said, there seems to be a real difference of opinion. Some of the investigators seem to think that organic impurity in the electrolyte is the *only* cause of excessive deposits on the cathode. That it is one of the causes there is no doubt; but it is equally clear to us that there are others. It is with regard to these points, especially, that the present work was undertaken.

The points in dispute concern in the first place the existence or nonexistence of included mother liquor in the crystals deposited upon the cathode; secondly, the nature of the mother liquor (if any) thus included; thirdly, the existence or nonexistence of a surplus of silver in the liquid flowing from the anode; and fourthly, the efficacy of a porous cup as a means of promoting exact coulometric work through the separation of the anode and the cathode.

The present paper considers the first two of these points, *viz.*, those which concern the included mother liquor. It was necessary to settle these before any conclusive evidence concerning the other two could be obtained; for the decision depends largely upon small differences in weight of the precipitated silver crystals, and these differences might either be caused or be masked by differences in the amount of mother liquor included.

The experiments in the three national physical laboratories seem to have underrated the importance of this point, while exerting very praiseworthy care in other directions.

The first investigators to call attention to this very important source of error caused by inclusion of electrolyte were Lord Rayleigh and Mrs. Sidgwick. They determined the extent of the inclusion chiefly by heating the crystallized silver just short of redness. Their results showed that in many cases the inclusion of mother liquor unquestionably takes place; moreover, there could be no question that its amount varied according to circumstances. New solutions yielded less inclusion in the crystals than the old ones, and large crystals less than small ones.

These results were entirely verified by the Harvard work carried out many years afterwards.[1] The magnitude of the inclusion was found to vary from 0.003 to 0.03% from loss of weight on heating, and an average case was verified by analysis. The experience with silver crystals has been supported by plentiful experience with other kinds of crystals in the course of the Harvard work upon the atomic weights. Indeed, it is not too much to say that we have never been able to obtain crystals of any kind free from traces of mother liquor, although, of course, the amount included varies greatly according to the details of crystallization.[2]

In spite of this experience, Gray[3] and van Dijk[4] denied the existence of such included mother liquor, and Smith, Mather and Lowry have supported these doubters,[5] as well as Jaeger and von Steinwehr.[6] A study of these papers, however, shows that either the accuracy of the work was not adequate, or else the heating was not carried far enough to prove the point. Unquestionably, van Dijk and Smith, Mather and Lowry in most cases failed to use a temperature sufficiently high to drive off the inclusions and probably this was the case also with Jaeger and von Steinwehr. Attention has already been called to the need of heating the silver to so high a point that the metal has become somewhat softened.[7] The mother liquor is then set free by a series of small explosions or decrepitations, and the temperature needed is over 550°. It is quite possible, indeed, that the last traces of included matter are not expelled until the silver is completely fused,[8] but very nearly all of it is driven out at dull redness,

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[1] Richards, Collins and Heimrod, *Proc. Am. Acad.*, **35**, 123 (1899).

[2] Richards and Heimrod, *Ibid.*, **37**, 415 (1902); Richards, "The Inclusion and Occlusion of Solvents in Crystals," *Proc. Am. Phil. Soc.*, **42**, 28 (1903); *Z. physik. Chem.*, **46**, 189 (1903).

[3] *Phil. Mag.*, [5] **22**, 389 (1886).

[4] *Ann. d. Phys.*, **14**, 569 (1904); **19**, 249 (1906).

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

[6] Jaeger and von Steinwehr, *Z. f. Instrumentenk*, **28**, 327, 353 (1908).

[7] Richards, *Proc. Am. Acad.*, **44**, 91 (1908).

[8] Richards, *Proc. Am. Phil. Soc.*, **42**, 28 (1903); *Z. physik. Chem.*, **46**, 189 (1903). Hulett has confirmed this inference.

as we have repeatedly shown. In discussing their experiments on this point, Jaeger and von Steinwehr make a somewhat incomprehensible correction for loss of weight of the crucible during heating. A clean platinum crucible, in our experience, heated to a temperature below redness, does not usually lose an important amount in weight, although they applied such a correction. If this doubtful correction were omitted, their results tend to confirm ours.

The recent work carried out by the Bureau of Standards seems not to have heeded sufficiently the inclusion of mother liquor, in spite of the arguments previously presented concerning it. More recently results which have been obtained by Hulett in careful collaboration with Duschak and with Laird[1] have entirely confirmed the conclusions of Lord Rayleigh, which had indeed been thoroughly verified at Harvard long before the Princeton work was begun. Hulett and his collaborators adopted van Dijk's somewhat questionable preliminary operation of scraping the crystals from the platinum dish. This is necessary, if the crystals are to be heated in a tube, but it has one important disadvantage, namely, that this forcible treatment of the crystals might very well open cells containing mother liquor which would otherwise remain closed, especially cells between the crystals and the platinum cathode. In his later work with Laird, Hulett used melted tin as a solvent for the silver; but one cannot help thinking, especially because of the large amount of carbon dioxide which he found, that dust had, during some stage of the operation, found its way into the tube. Neither of these methods (although each gives interesting results) seems to provide exactly the information desired, namely, the weight of the inclusions actually held by the deposit as weighed.

The attempt to determine the inclusions by attacking the silver deposit with mercury, as practised by the Bureau of Standards,[2] is likewise of uncertain value, because the solubility of silver in mercury is very slight (as we have found by careful experiment[3]) and the metal is merely converted into a solid amalgam which might withhold some of the included impurities.

For these reasons it is not necessary to discuss more fully here the interesting details of all this recent work. The very careful researches of Hulett and his collaborators substantiate that previously carried out at Harvard in showing, first, that the inclusions are often important in amount, and secondly, that they vary considerably according to the details of experimentation. Thus, for an accurate determination of the weight of

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[1] Hulett and collaborators, *Trans. Am. Electrochem. Soc.*, **12**, 257 (1907); **22**, 345 (1912).

[2] Bur. Standards, *Bull.* **10**, 520 (1914).

[3] See also Reinders, *Z. physik. Chem.*, **54**, 609 (1906). A saturated liquid amalgam at 20° contains only 0.04% of silver.

metallic silver deposited by the current the amount of inclusion must be determined in each experiment.

Nevertheless, it seemed desirable to institute new experiments touching the more essential points involved. In the course of these experiments, the weight of silver chloride obtained from the coulometric deposits was compared with the weight of silver chloride obtained from perfectly pure silver. This gives theoretically the most conclusive method of determining the amount of the impurity, but is, of course, difficult of execution. Again, crystals were ignited at high temperatures and care was taken to find the point at which constancy of weight was attained, and also the point at which appreciable volatilization of the silver began to invalidate the result. Yet further, a number of deposits were scraped from their cathodes à la van Dijk and Hulett. Both crystals and cathode were washed with pure water before ignition, and it was thus found that cells containing silver nitrate solution had really been opened up by the scraping. The analyses of these crystals pointed to the same conclusion. Finally, methods for determining the amounts of inclusion having been settled, comparisons were made of the extent of inclusion involved in the various forms of the coulometer. These experiments are set forth in detail below. One does not see how any candid or unprejudiced reader, however he may have felt with regard to previous contributions on this subject, can escape the inference that inclusions in silver crystals are really important and that no coulometric work is complete until the amount which pertains to the particular method employed is discovered by actual analysis.

## II. Details Concerning the Apparatus.

The porous cup coulometer as used consistently throughout this research as a standard instrument was precisely similar to that recommended by one of us in connection with G. W. Heimrod, twelve years ago.[1]

A large platinum crucible with a lip, weighing about 60 g. and containing about 120 cc. was used to contain the catholyte. In it was suspended from a glass arm a small porous cylindrical Pukal cup which contained the anolyte, always kept at least 1 cm. in level below the catholyte. Everything was thoroughly insulated by glass and paraffin, and the whole was arranged under a bell-jar to protect from dust or outside impurity. The inner level was maintained constant either by a constant level siphon or by a pipet. The anodes consisted of metal carefully prepared in a pure state according to the usual method,[2] fused in hydrogen on lime in the electric furnace. They were scraped with pure sea-sand and etched with pure dilute nitric acid. In a few cases they were plated with additional silver electrolytically. The porous cups were, of course,

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[1] *Proc. Am. Acad.*, 37, 415 (1902); *Z. physik. Chem.*, 41, 302 (1902).

[2] See Richards and Wells, THIS JOURNAL, 27, 481 (1905).

thoroughly digested with nitric acid and then boiled with repeated portions of the purest water until every trace of acid had been washed from their pores. In the crucial portion of the work this was done after every experiment.

The nitric acid used throughout the work was always the middle third, carefully redistilled, of an acid already very pure.

The silver nitrate used as electrolyte was prepared either from silver made according to the method of Stas, or in the later experiments from silver precipitated by acidified ammonium formate. The salt was always crystallized twice, the first time from a slight excess of nitric acid and the second time from pure water, a trace of acid remaining in the mother liquor from the previous crystals. This method provides, as the work of the Bureau of Standards has shown, a solution which is free from basic salt. In some cases also solutions which had already been used in the coulometer were filtered through asbestos and then recrystallized three times, the first two times from 10% acid and the final time as before without adding any acid. Each batch of crystals was centrifuged as usual. All the water used in the important parts of this research was purified by redistilling first from alkaline permanganate solution, and again from a trace of sulfuric acid.

For convenience in regulating the current, an ampere meter was included in the circuit. Unless otherwise stated a current of about 0.25 ampere was used in the work. After the electrolysis was completed, the porous cup was removed and the catholyte was siphoned into a small labelled crystallizing dish, leaving a few cubic centimeters of the solution in the bottom of the large crucible. The occasional loose crystals of silver which either remain at the bottom or float on the surface of the electrolyte are thus kept in the original vessel. The cathode vessel was then filled with pure water, which was immediately siphoned into a large labelled dish; and this process of washing was repeated several times at even greater intervals until evening, when the crucible filled with the purest water was allowed to stand over night. On the next morning this wash-water was tested in the nephelometer with sodium chloride against pure water, to see if all the accessible silver nitrate had been washed from the pores of the crystals. In all cases, except two, this wash-water was found to be free from silver nitrate, and in these two cases another change of water left till noon showed no traces of this salt. Finally the deposit was rinsed with very pure water, a few milliliters of which were left in the crucible. Any minute crystals of silver that may have passed over were recovered with a small platinum spatula. Our experience agrees with Hulett's, that a particle smaller than 0.01 mg. may be seen and recovered. The crucibles were heated two hours at 160°, after the water had been evaporated, in electric ovens, cooled and weighed as before with all the precautions for exact weighings.

A building with its temperature regulated by thermostats, a balance very free from vibration, and favorable conditions of every kind, were of great assistance in making accurate weighings of the cathode. The weighings were regularly duplicated to within 0.02 mg.

### III. Inclusions Determined by Analysis.[1]

After a regular double electrolysis (with two coulometers in series) had been made, the crucibles containing the weighed deposits were placed in large covered beakers nearly filled with warm water, and a slight excess of redistilled nitric acid was added. When the silver had been completely dissolved, the solution was quantitatively transferred to a two-liter precipitating flask. To the large bulk of solution an excess of very pure hydrochloric acid was gradually added—enough to precipitate all the silver—leaving dissolved an excess of ionized chlorine, in hundredth normal concentration.[2]

The precipitate was agitated till it had thoroughly coagulated, and allowed to stand in a dark room for twenty-four hours with occasional shaking; the filtering was done through a tared Gooch-Monroe crucible. The precipitate was washed ten times with wash water containing hundredth normal hydrochloric acid, being transferred to the crucible with the same wash water, and finally dried for five hours at 180–190°, cooled and weighed. The bulk of precipitate was then placed in a previously ignited porcelain crucible; and after weighing, the silver chloride was fused in a porcelain air bath. The fused mass was nearly colorless in all cases. Except silver chloride, the only substances present in this analysis are volatile, hence the process is an unusually precise one. A trace of silver chloride remaining in the precipitating flask was dissolved in a little ammonia, determined in the nephelometer, and added to the main weight.

The vacuum corrections for metal and halide are respectively, —0.031 mg. and +0.071 mg. per g. These were duly applied, and the calculation was carried out on the assumption that the atomic weights of the two elements are respectively, 107.880 and 35.459. The results are given in

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[1] This method was tried once before at Harvard, the analyses having been made by Mr. E. Collins near the beginning of his part in the research (*Proc. Am. Acad.*, **35**, 139 (1899)). No claim was then made for great accuracy, but the outcome was in favor of a slight inclusion. The cause of the errors in Expts. 35 and 36 noted by Rosa (Bur. Standards, *Bull.* 10, 518 (1914)) cannot now be traced, as the original notes are no longer accessible. In any case, the older analyses do not compare in authority with those given below.

[2] Forbes (THIS JOURNAL, 33, 1937–1911) has shown that silver chloride is least soluble in such a concentration of chloride ions. Calculating from the solubility product ($2 \times 10^{-10}$) it would take five liters of solution to dissolve 0.01 mg. of silver chloride, and hence no correction need be applied.

Table I; the table is easily comprehensible. For each of the last two analyses the products of the two coulometers were united for analysis. The calculated figures in the last column make allowance for the fact that the included mother liquor must have contained about 8 or 10% of silver nitrate, the silver in which must have been precipitated as chloride and weighed with that coming from the electrolytic metal.

TABLE I.—ANALYSIS OF ELECTROLYTIC SILVER DRIED AT 160°.

| No. of Expt. | Corrected wt. Ag. Grams. | Corrected wt. AgCl. Grams. | Calculated AgCl. Grams. | Diff. Mg. | Diff. in %. | Inclusions corrected for Ag as $AgNO_3$. Per cent. |
|---|---|---|---|---|---|---|
| 20 | 2.79247 | 3.70988 | 3.71033 | 0.45 | 0.0121 | 0.0128 |
| 21 | 3.25640 | 4.32631 | 4.32674 | 0.43 | 0.0100 | 0.0106 |
| | 3.25644 | 4.32637 | 4.32680 | 0.43 | 0.0100 | 0.0106 |
| 22 | 2.66857 | 3.54521 | 3.54570 | 0.49 | 0.0138 | 0.0144 |
| | 2.66859 | 3.54531 | 3.54573 | 0.42 | 0.0118 | 0.0125 |
| 23 | 5.92000 | 7.86453 | 7.86585 | 1.32 | 0.0167 | 0.0176 |
| 24 | 5.72318 | 7.60322 | 7.604335 | 1.115 | 0.0147 | 0.0155 |
| Total | 26.28565 | 34.92083 | 34.925485 | 4.655 | 0.0133 | 0.0141[1] |

Evidently the actual weight of silver chloride found was always less than the theoretical weight. Hence the silver contained included impurity.

The quantity of inclusion thus found by direct analysis (0.014%) is close to that found by Richards and Heimrod, 0.018.[2] The present series of analyses determines this quantity by a method quite different from the old way.

In order to forestall the criticism that the deficiency thus found might simply be due to loss of silver during the analysis, very pure fused silver was prepared and analyzed with exactly the same precautions.

TABLE II.—ANALYSIS OF PURE FUSED SILVER.

| Corrected wt. Ag. Grams. | Corrected wt. AgCl found. Grams. | Calculated wt. AgCl. Grams. | Diff. Mg. | Diff. in %. |
|---|---|---|---|---|
| 6.22211 | 8.26738 | 8.26725 | +0.13 | +0.002 |
| 5.16568 | 6.86361 | 6.86359 | +0.02 | +0.000 |
| 5.18476 | 6.88876 | 6.88893 | —0.17 | —0.002 |
| 16.57255 | 22.01975 | 22.01977 | —0.02 | 0.000 |

This result is very different from that previously found in the case of the crystallized electrolytic silver, and corresponds exactly with the value 35.459 for chlorine. The international value 35.460, also, is within the limit of experimental error. The evidence is very strong, therefore, that the analytical procedure was correct, and hence that the electrolytic silver prepared as we had prepared it, contains more than one part in ten thousand of included mother liquor.

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[1] If Cl = 35.460, this value would be 0.0148%.

[2] *Loc. cit.*, p. 435.

## III. Inclusions Determined by Heating the Deposits in the Cathode Crucible.

The ignition of the deposit for the purpose of determining the inclusions by loss of weight has been often used in the past, first by Lord Rayleigh and Mrs. Sidgwick, and later by many others. Some, trying to use it, have failed to heat the silver hot enough, as already stated.

In our experiments, after the crucible with its deposit had been washed, dried and weighed as usual, it was placed on a quartz triangle in a dark room. A clean porcelain crucible was inserted into the mouth to protect the material from dust and to cool and catch traces of silver vapor. The platinum was heated very carefully, with a burner held in the hand, until it attained dull redness, just barely perceptible in the dark. Great care was used to not exceed this temperature, and to heat the crucibles all over, as evenly as possible. The crucible was then cooled, and weighed once more.

Such heating slightly alloys the two metals; on dissolving the silver in nitric acid a perceptible amount of platinum remained. In preparation for a new trial, the inner surface was afterwards scrubbed, washing finally with acid and water. The crucibles lost a few tenths of a milligram each time, due to the removal of the platinum. Burnished crucibles suffered much less than those roughened by continuous use. This complication, of course, had not the slightest effect upon the quantitative experiment.

To settle the question raised by Jaeger and von Steinwehr, as to whether a platinum crucible alone loses weight when heated, one of ours was heated five times, just as if it had contained silver. The total loss was only 0.05 mg., or 0.01 mg. for each heating. This is negligible, but the corresponding correction was applied to each result for the sake of completeness.

The results concerning the amounts of included electrolyte found by heating the precipitated silver are summarized in Table III. Each figure is calculated from the actual loss on heating by adding to that quantity 6% of its value, to allow for the silver which must have remained from the included nitrate decomposed by heat. This will be explained more fully later. The first column records the amount of inclusion in silver precipitated on a crucible which had been somewhat scratched and roughened by van Dijk's process of mechanical removal of previous precipitates; the second column records the result for freshly burnished crucibles (both used as porous-cup coulometers); the third column gives the amount in an instrument according to Kohlrausch (the first four results coming from burnished crucibles and the last three from rough ones); the fourth column shows the increased inclusion when some of the anolyte is permitted to come into contact with the cathode deposit, and the last column shows the greatly increased effect when a large surface receives the silver crystals. The deposit varied in weight from 1.9 to 3.1 g. In order to be sure that no silver volatilized during the ignition, the porcelain crucible which had been used as a cover during all the heatings was warmed with nitric acid; but no silver was found in this liquid on testing in the nephelometer.

TABLE III.—INCLUSIONS IN PRECIPITATED SILVER, FOUND BY HEATING.

(Expressed in fractions of per cent of weight of silver.)

| Porous cup roughened crucible. | Porous cup burnished crucible. | Kohlrausch form. | Cathode less protected from anode. | Porous cup, large cathode vessel (roughened). |
|---|---|---|---|---|
| 0.0155 | 0.0076 | 0.0072 | 0.0218 | 0.0352 |
| 0.0134 | 0.0108 | 0.0061 | 0.0224 | 0.0311 |
| 0.0174 | 0.0097 | 0.0039 | .... | .... |
| 0.0194 | 0.0100 | 0.0115 | .... | .... |
| 0.0171 | 0.0100 | 0.0045 | .... | .... |
| 0.0174 | 0.0119 | 0.0055 | .... | .... |
| 0.0178 | .... | 0.0115 | .... | .... |
| 0.0125 | .... | .... | .... | .... |
| 0.0107 | .... | .... | .... | .... |
| 0.0139 | .... | .... | .... | .... |
| Av., 0.0155 | 0.0100 | 0.0083 | 0.0221 | 0.0332 |

These results are worthy of careful study.

In the first place, one notes that the average of the first column, including all the results obtained with the ordinary somewhat roughened porous cup voltameter, is 0.015—a figure close to that found by the actual analysis of the silver, 0.014, recorded in the last section, as well as to the earlier results found at Harvard and the still earlier work of Lord Rayleigh.

In the next place, it is clear that a roughened crucible considerably increases the inclusion, its figure being 0.015 instead of 0.010 found in the case of a burnished crucible.

Again, it is apparent from Column 5 that other things being equal, the inclusion is approximately proportional to the surface on which the silver is deposited—for the large platinum beaker-crucible used in this series had about twice the surface of the smaller vessel used for the experiments in Column 1, and the inclusion was about double. This surface effect is doubtless the real cause of the so-called "volume effect" noticed by various other experimenters,[1] for they failed to observe and correct for this greater occlusion which occurs on a larger surface. These figures give striking evidence of the importance of determining the amount of inclusion in each case, and by their final consistency strongly support the other work.

The surface-effect, producing greater inclusion, is doubtless also the reason why the Kohlrausch form of voltameter gave a lesser deposit; for in this form the receptacle placed under the anode to receive the "anode slime" cuts off nearly half of the cathode from usefulness, and the silver is actually deposited upon only a part of the platinum surface which would

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[1] See for example Rosa, *Bull. Bur. Standards*, **9**, 514 (1913).

be available in the porous-cup voltameter. This, of course, by increasing the current density, diminishes the practical maximum current strength which the instrument can safely endure, and makes a large crucible no more efficient than a small one would be with the porous cup.

Finally, it is evident from Column 4 that the anode impurities promote the inclusion, in confirmation of the Harvard work of 1900–1902 and of Hulett's later results.

Because, also, as the work at the Bureau of Standards has shown, by very extended experiments, both current density and temperature affect the size and distribution of the crystals, these factors also must affect the inclusion.

Evidently it is impossible to apply a correction so variable to any work upon this subject, either one's own or that of others, without an intimate knowledge of every detail. The only satisfactory method is *to determine with due precaution the amount of included electrolyte in every crystalline precipitate;* and no work in which this has not been done can possess final authority, at least as regards the exact weight of the precipitate.

## IV. The Nature and Distribution of the Inclusion.

It is, of course, possible that the mother liquor included in the crystals is not of exactly the same composition as the original electrolyte. Around the cathode during active electrolysis the solution of silver nitrate is necessarily diluted; and the solution may be caught and imprisoned in this diluted condition.

A moment's thought will show, however, that the exact concentration of the imprisoned mother liquor is not a serious question. For example, if the total inclusion is 0.015%, a knowledge of the composition of the mother liquor within 7% would correspond to an accuracy of 1 part in 100,000 of the crystallized silver. This is a high degree of accuracy, which rarely needs to be exceeded. Supposing, therefore, that one starts with a 10% solution of silver nitrate, more than half of the dissolved substance might be eliminated without causing a serious effect upon the result. The error from any possible change of concentration is, therefore, less than the possible error which might be caused by scraping the crystals from the dish; for this process (as will be shown) allows water to evaporate from cells opened by abrasion. *The really important point, as usual, is to determine the amount of included water.*

On this account we have made no search as to the exact composition of the included mother liquor. The analyses made by Hulett seem to be more than sufficient for the purpose. Although variable, they indicate that the enclosed liquid under the conditions involved does not lose anything like as much as half of its dissolved salt.

As already stated, the presence of carbon dioxide, found by Hulett in the gases obtained from the silver, is probably to be ascribed to dust, which doubtless furthers occlusion of mother liquor. No other reasonable source is assignable. At a high temperature this dust, even if protected from air, would burn in the oxygen of the nitric acid and be expelled. Obviously, therefore, the carbon would be eliminated from the final result, whether its weight were calculated from the amount found as a gas, or simply from the loss of weight of the heated silver. It is almost impossible to exclude such minute traces of dust under ordinary conditions; therefore, it is comforting to feel that in this case, at least, their influence is negligible.

One milligram of the original 10% electrolyte leaves 0.063 mg. of silver on ignition; and 8% solution would leave 0.051 mg. The cathode occlusions are probably between these limits, which are close enough for the purpose. Hence, to obtain the exact weight of the silver deposited electrolytically as metal, one must subtract from the weight of the precipitate ignited at a dull red heat about 6% of the loss on heating, as has been done above. As already stated, this is quite accurate enough. Incidentally, it may be stated, that a similar correction was thus applied in the early Harvard investigations.[1] For most purposes, where the weighings are not carried beyond 0.1 mg. the correction may be neglected altogether; the weight of the silver crystals heated to incipient redness may be taken directly as the weight of the metallic silver precipitated by the electrolysis.

The question concerning the distribution of the inclusion in the deposit is of more importance. Is the imprisoned liquid wholly in the body of the crystals, or is part of it held between the crystals and the platinum cathode? If the latter is the case, van Dijk's and Hulett's method of removing the crystals from the dish may open a part of the cells, allowing some of the liquid to evaporate; thus both the weight and concentration of the included solution may be wrongly estimated. This is a matter easily susceptible of experimental decision; and our study of it is recounted below.

In the first place, a number of deposits were prepared with the purest electrolyte and all the precautions already described. After most carefully washing, weighing and drying the deposit, each deposit was removed as far as possible from the platinum cathode with a platinum spatula. Both dish and spatula suffered somewhat, and the detached crystals of silver contained some platinum; but this did not affect the main point in question. The crystals were placed in a test tube and washed with a little water, which was then filtered through a Gooch crucible provided with quantitative asbestos. The cathode crucible was similarly washed, and its wash water similarly filtered. These wash waters were tested in the nephelometer by comparison with standard silver nitrate solution with every precaution.

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[1] *Proc. Am. Acad.*, 37, 421 (1902); *Z. physik. Chem.*, 41, 308 (1902).

Table IV summarizes the results obtained with crystals deposited on cathodes somewhat roughened by this drastic treatment.

TABLE IV.—SILVER NITRATE CONTAINED IN THE WASH WATER FROM THE CRUCIBLES AND CRYSTALS.

| No. of Expt. | Deposit Ag in gms. | On crucible. mg. | On crystals. mg. | Total mg. | $AgNO_3$. %. |
|---|---|---|---|---|---|
| 13 | 2.91711 | 0.025 | 0.037 | 0.062 | 0.0021 |
| | 3.00918 | 0.023 | 0.031 | 0.054 | 0.0018 |
| 14 | 2.73102 | 0.025 | 0.030 | 0.055 | 0.0020 |
| | 2.73097 | 0.028 | 0.024 | 0.052 | 0.0019 |
| 15 | 2.43529 | 0.011 | 0.018 | 0.029 | 0.0012 |
| | 2.43523 | 0.017 | 0.014 | 0.031 | 0.0013 |
| 16 | 3.19442 | 0.014 | 0.016 | 0.030 | 0.0009 |
| | 3.19439 | 0.026 | 0.012 | 0.038 | 0.0012 |
| Total, | 22.64761 | 0.169 | 0.182 | 0.351 | 0.00155 |

Thus, on the average, every gram of silver precipitated in this way enclosed 0.015 mg. of silver nitrate between the crystals and the dish. It remained to discover the amount of mother liquor imprisoned within the crystals themselves.

After drying these washed crystals for at least an hour at 160°, they were placed in a quartz crucible provided with a cover of the same material. When carefully weighed, they were heated in the flame of a Bunsen burner to dull redness. This heating was usually accompanied by a crackling sound, as the inclosed substances made their escape. The cooled crucible was weighed, and again heated, cooled and weighed as before until constant weight had been obtained.

The values obtained by this method gave a measure of the volatile matter in the crystals, which must be corrected for residual silver as before. In four determinations, 7.22 g. of silver lost 1.23 mg., or 0.017%. Corrected for residual silver from the enclosed nitrate, this becomes 0.018%.

Because of a fear lest some silver might have been lost by volatilization from the quartz crucible, the test was repeated, with a quartz test tube, fifteen centimeters long, in place of the crucible. In this test tube there were heated two portions of crystals which had been accumulated from several electrolyses, scraped from the crucibles and afterwards washed as before. To insure precision in weighing, a tare was used, consisting of a similar amount of silver which had already been heated in the crucible. A small tube of radioactive substance was kept in the balance case to remove any electrostatic charges from the tubes, and every precaution was taken to insure accuracy. During the ignition a thin-walled, cone-shaped glass tube was inserted well down into the top of the quartz tube, which was then inclined at an angle of 30–45° with the horizontal, and heated in a Bunsen flame. From this arrangement no trace of silver vapor could escape during the ignition. The inner glass tube was duly tested for volatilized silver by treatment with nitric acid. In one case a trace was found, and due correction applied. In the second trial none was found.

When the silver had reached constant weight on successive treatings, the tube was evacuated with a water pump and again heated to see what effect the absence of most of the oxygen would have. Von Wartenburg[1] suggests the formation of silver oxide at high temperatures to explain the fact that silver is more volatile in oxygen than in an atmosphere of nitrogen or in a vacuum. The heating in the partial vacuum produced no perceptible effect on the weight. Two trials were made, using 10.1 and 9.8 g. of crystallized silver, respectively. The corrected losses of weight were 1.37 mg. and 1.12 mg. (or 0.0135 and 0.0115%), respectively. Averaging the results, we see that these specimens of washed silver contained 0.0125% of mother liquor. To this must be added the amount of silver nitrate which had been washed from their abraded surfaces, namely 0.00155 (see Table IV), making 0.014% in all. This is somewhat less than the loss of weight found in similar deposits when the crystals have not been removed from the dish (see Table III); hence it would appear that the removal of the crystals opens some cells which otherwise would remain closed at 160°, and allows the water to evaporate from the previously imprisoned silver nitrate. Hence it is clear that the method of van Dijk and Hulett is probably not an adequate way of determining the actual total amount of included mother liquor which is weighed with the crystals while the latter are still adhering to the dish.

Another very strong piece of evidence in support of these conclusions about the included mother liquor is to be found in the comparison of the final weights, after ignition, of deposits upon large and small coulometers in the same circuit. Whereas before heating the two gave very different results, after heating they were almost identical.

Table V.—Weight of Deposits in Large and Small Porous-cup Coulometers.

| 1st Expt. | Weight after drying at 160°. | Weight after ignition at dull redness. | Final weight after cor. for residual Ag from $AgNO_3$. | Weight of included electrolyte. |
|---|---|---|---|---|
| Large coulometer..... | 1.89559 | 1.89494 | 1.89490 | 0.00069 |
| Small coulometer..... | 1.89525 | 1.89492 | 1.89490 | 0.00035 |
| Difference........... | 0.00034 | 0.00002 | 0.00000 | 0.00034 |
| 2nd Expt. | | | | |
| Large coulometer..... | 3.13902 | 3.13812 | 3.13807 | 0.00095 |
| Small coulometer..... | 3.13868 | 3.13808 | 3.13805 | 0.00063 |
| Difference........... | 0.00034 | 0.00004 | 0.00002 | 0.00032 |

The second and third columns of figures show how nearly alike the results are after the ignition: that is to say, the apparently large difference

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[1] *Z. Elektrochem.*, **19**, 482 (1913).

between the results of the two sizes of coulometers (which would have been left unexplained as a "volume effect" if the methods of the three national bureaus had been used) is annihilated by the simple device of heating the crystals to a temperature high enough to drive off the included water.

In a recent able article by Bates and Vinal[1] appears the following statement: "The whole question of inclusions has been critically discussed by Rosa, Vinal and McDaniel.[2] Their opinion is that the deposits so perfectly crystalline as those formed from the purest silver nitrate do not contain significant inclusions." To us it seems that any such superficial evidence is far from convincing. One of us has shown repeatedly[3] that no matter how beautiful a crystal, or how perfectly crystalline and transparent its structure may be, yet when it is crystallized from aqueous solution it is almost, if not quite, certain to contain some of the mother liquor, either in accidental submicroscopic cells or in "solid solution." Indeed, a careful review of this latest published comment, in the light of the foregoing experiments, fails to reveal any adequate argument against our conclusion.

### V. The Purity of the Ignited Deposit.

Only one final question remained: is crystallized silver, which has been thus heated at a dull red heat, really pure silver? Upon this point the validity of the whole coulometric process depends. From the fact that the amount of inclusion as found by analysis agreed closely with that found by heating the silver, it is clear that the heated crystals must have been very nearly pure; but the matter was clinched by actual analyses of two of the specimens remaining from the work described on p. 20. On solution in nitric acid, each preparation was filtered through a Gooch-Munroe crucible with every quantitative precaution, and the residual platinum derived from the cathode was carefully weighed. The analysis of the solution was conducted by precipitation with pure hydrochloric acid exactly as on page 13.

TABLE VI.—ANALYSES OF IGNITED CRYSTALLIZED SILVER.

| Weight Ag + Pt vac. | Weight Pt. | Weight Ag. | Cor. weight fused AgCl vac. | AgCl calc. | Deficiency. mg. |
|---|---|---|---|---|---|
| 5.94112 | 0.01833 | 5.92279 | 7.86933 | 7.86938 | 0.05 |
| 5.01726 | 0.01020 | 5.00706 | 6.65256 | 6.65262 | 0.06 |
| | | Total, | 14.52189 | 14.52200 | 0.11 |

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[1] THIS JOURNAL, 36, 932 (1914).

[2] Bur. Standards, *Bull.* 10, 516 (1914). The main quantitative evidence depended upon a single experiment (p. 522), in the interpretation of which the erroneous assumption was tacitly made that inclusion does not exist in the porous cup voltameter, and is the only error in the filter-paper voltameter. The fallacy will be explained more clearly in the next paper upon this topic, to appear shortly.

[3] *Proc. Am. Phil. Soc.*, 42, 28 (1903); THIS JOURNAL, 33, 885 (1911).

The conclusion is, therefore, that such finely crystallized electrolyzed silver, which has been ignited at a dull red heat, contains less than 0.001% of impurity. Except for the difficulty of removing the silver from the cathode, and from the clinging contamination of platinum therefrom, this would be a good method of making very pure metal. Possibly the fine crystals precipitated in an electrolytic silver-tree, or by formate, would, on gentle ignition, show equal purity; if so, either of these very obvious processes would be extremely convenient for the preparation of this substance for many quantitative purposes.

In a recent paper Bates and Vinal[1] have compared in a very interesting way the iodine coulometer of Washburn with the silver coulometer. Deviations among the results were noticed, but no satisfactory explanation of them was given. When, however, it is remembered that the investigations made no allowance whatever for included mother liquor, and when one studies the tables on the foregoing pages in this paper, the reasons for the deviations become manifest. With the porous cup voltameter the inclusion is greatest on the largest surface; hence such deposits were the heaviest, as they found. The Kohlrausch form,[2] because it restricted the surface of the large vessel, would be expected to yield a result between the two; moreover, the error due to anolyte, to be discussed in a subsequent paper, may enter into its results, as well as into those from very diminutive coulometers. The exact correction of these results for inclusions is unfortunately impossible, because the inclusion varies with the extent and roughness of the surface of the cathode. But an approximation may be made if we assume the 120 cc. porous-cup voltameter (which gives the lowest results) as a standard, and then correct its indications by applying the average correction which we have found in this present work (0.015%). This would, of course, raise the calculated atomic weight of iodine by this percentage, if silver is assumed as the standard. Taking silver as 107.88, iodine was found to be 126.898 by Vinal and Bates with the small porous-cup instrument; but corrected for inclusions in the silver this becomes 126.917. This corrected value is in much better agreement with Baxter's best result, 126.932, than before. The remainder of the difference may perhaps be ascribed either to the need of a larger correction for inclusions, or possibly to the existence of a trace of chloride of iodine in the iodine used by Bates and Vinal for standardization. The latter's result is almost identical with Baxter's preliminary value, 126.916.[3]

The assumed international value of the Faraday is also, of course, affected to an equal extent by inclusion. If, as we cannot but believe,

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[1] THIS JOURNAL, 36, 916 (1914).

[2] Smith's large new form is a modification of the Kohlrausch arrangement.

[3] Bates and Vinal took great pains in the purification, but not so much as Baxter. See Baxter, THIS JOURNAL, 32, 1591 (1910); also *Proc. Am. Acad.*, 40, 419 (1904).

the 1.11800 mg. of silver supposed to be deposited by a coulomb contained inclusions, the true value may well be nearer 1.1179. It is profoundly to be regretted that all the able recent experimenters on this absolute value seem to have entirely overlooked the importance of this matter.

We are much indebted to the Carnegie Institution of Washington for apparatus used in this research.

## Summary.

In confirmation of earlier work by Lord Rayleigh and that at Harvard, as well as of the subsequent work of Hulett, the presence of included electrolyte in the crystallized silver deposited in a silver coulometer (voltameter) has been shown in the following ways:

First, by quantitative analysis of the crystals after drying to constant weight at 160°.

Secondly, by ignition of the crystals on the cathode at a dull red heat.

Thirdly, by ignition of the crystals, separated from the cathode, in a quartz test tube, arranged so as to prevent evaporation of silver.

Fourthly, by showing that simultaneous deposits which were unequal in weight before ignition had attained equality after ignition.

The included mother liquor was shown by quantitative experiments to be partly within the crystals, and partly between the crystals and the walls of the cathode.

The quantity of the inclusion varies, increasing (as would be expected from the immediately foregoing statement) with increasing surface and with increasing roughness of the cathode. It may vary from 0.004 to 0.035% of the weight of the silver. The silver remaining after the ignition was shown to possess a very high degree of purity, and at incipient redness it was shown to be essentially nonvolatile during brief treatment.

The experiments of the three national bureaus of America, England and Germany, while illuminating in many respects, failed to throw light on the matter, because of incomplete experimentation. Either the temperature of ignition was inadequate, or some other oversight intervened—as, for example, in the attempt to dissolve the precipitated metal in 50 times its weight of mercury when 2500 times its weight are really needed for complete solution.

Because of the variation of the amount of inclusion according to circumstances, it is unfortunately impossible to correct older results. But there seems to be no question that correction is necessary, especially in the case of the large dishes used by Smith, Mather and Lowry. Hence, much of the work should be repeated. The correction affects the value of the electrochemical equivalent, the Faraday, the value assigned to the Standard Weston cell, and all ratios of atomic weights determined electrically; hence, it is a question of importance.

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