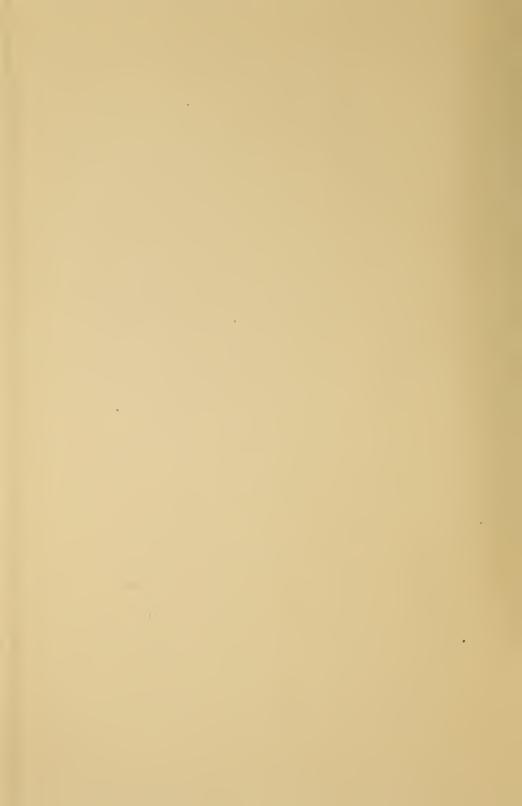
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REPORT TO THE INTERNATIONAL COMMITTEE ON ELECTRICAL UNITS AND STANDARDS OF A SPECIAL TECHNICAL COMMITTEE APPOINTED TO INVESTIGATE AND REPORT ON THE CONCRETE STANDARDS OF THE INTERNATIONAL ELECTRICAL UNITS AND TO RECOMMEND A VALUE FOR THE WESTON NORMAL CELL

**JANUARY 1, 1912** 



WASHINGTON
GOVERNMENT PRINTING OFFICE
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# REPORT ON THE CONCRETE STANDARDS OF THE INTERNATIONAL ELECTRICAL UNITS

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#### I. INTRODUCTION

The International Conference at London in 1908 adopted specifications for the mercury ohm, the silver voltameter and the Weston Normal Cell, and fixed a provisional value (1.0184 international volts at 20° C) for the latter. The specifications for the mercury ohm and the Weston cell were more or less complete, but for the silver voltameter the specifications were very inadequate, and since the value to be assigned to the Weston cell necessarily depends upon the specifications for the silver voltameter, and the results of different investigators were not in close agreement, the conference selected an approximate value which it adopted as provisional only, until further experiments could be made and more precise values determined.

In order that such experiments might be encouraged, and that different countries might cooperate in fixing and maintaining uniform throughout the world the values of the electrical units, the London Conference established an International Committee on Electrical Units and Standards, charged with the duty of promoting investigations in electrical standards and electrical measurements, and of securing the intercomparison of the standards of different countries.<sup>1</sup>

The first and most important undertaking for this committee was to ascertain more definitely the value which should be assigned to the Weston cell in accordance with the definitions of the London Conference. This involved completion of the specifications and a series of careful experiments with the silver voltameter, whereby the electromotive force of the cell would be determined from the amount of silver deposited, the resistance and the time, the electrochemical equivalent of the silver being taken as 1.11800 mg per coulomb. Many investigations of the silver voltameter were made between Rayleigh's work of 1884 and the London Conference of 1908, but at that conference principal weight was given to several investigations, then only recently completed, at the national laboratories of England, Germany, and France.

¹ In specifying the duties of the International Committee, the London Conference uses these words:

"\* \* \* to formulate a plan for and to direct such work as may be necessary in connection with the
maintenance of standards, fixing of values (this will include the reconsideration from time to time of the
emf of the Weston Normal Cell) intercomparison of standards, and to complete the work of the conference."

An extended investigation at the National Physical Laboratory had been carried out in 1906–7, in which the silver voltameter had been studied, and the electrochemical equivalent of silver determined to be 1.11827 mg per coulomb in terms of the absolute ampere, as measured by the current balance of that institution. The electromotive force of the Weston Normal Cell was given as 1.01819 at 20°, using the international ohm as given by their own mercury units. The Rayleigh form of voltameter was most used in these experiments, but the Richards form with porous cups was also used, as well as the siphon and other forms. All forms were found to give substantially the same results.

In 1907–8 an extended series of experiments was carried out at the Physikalisch-Technische Reichsanstalt to determine the electromotive force of the Weston Normal Cell, in terms of the electrochemical equivalent of silver taken as 1.11800 mg per coulomb, the value adopted at the Chicago Congress of 1893 and later adopted by Germany, and by the London Conference of 1908. The results gave a mean of 1.01834 (for cells with new mercurous sulphate) which was in fairly good agreement with the results of the National Physical Laboratory. The provisional value adopted at the London Conference of 1908 (1.0184 volts at 20°), was a mean between the results of the NPL (1.01843) and the PTR (1.01834), although the latter value was not yet published.

At the Laboratoire Central d'Électricité experiments were made in 1908 with the Rayleigh form of voltameter, in which taking the value of the Weston cell as 1.01869 volts at 20° (value found by current balance and resistance differing by 1/10000 from that used at the NPL and PTR) they found for the electrochemical equivalent of silver 1.11821. This gave for the Weston cell 1.01879 when referred to silver as 1.11800 after correcting  $\frac{1}{100}$  per cent for the difference in the resistance.

At the Bureau of Standards an extended series of experiments was made in 1907, 1908, and the early part of 1909, with the Rayleigh form of voltameter, and some experiments with the Richards. The results with the Richards form were 1.01837 volts at 20° for the Weston Normal Cell, as the mean of six deposits made December 22, 1908, and February 11 and 27, 1909, taking 1.11800 as the electrochemical equivalent of silver, and with the

Rayleigh form about 1.01863, as the average of 28 deposits in 1908 and February, 1909. Fifty-four deposits in the Rayleigh voltameter in 1907 had given a slightly higher value for the value of the standard cell. With two sheets of filter paper still higher values were obtained. The above results obtained at the Bureau of Standards are, however, still unpublished.

Summing up the figures given above we have:

# Taking 1.11800 Mg Per Coulomb-

	Volts at 20°.
At Nat. Phys. Lab., using filter paper	1.01843
At PhysTech. Reichs., using silk and porous cups	
At Bureau of Standards, using porous cups	1.01837
At Bureau of Standards, using filter paper	1.01863
At Lab. Cen. d'Élec., using filter paper	1.01879

This is the way the figures appeared on the first of March, 1909, at the Bureau of Standards. In view of the fact that so large differences had been found at the Bureau between the Richards and Rayleigh forms, whereas at the National Physical Laboratory they were found to be alike, it seemed difficult to come to an agreement without further investigations, and in order to reach such agreement as speedily as possible, it appeared desirable that the men who had made the several investigations referred to above might come together in the same laboratory and work out together the solution of their differences.

It had been suggested at the London Conference of 1908 that delegates from the several national standardizing laboratories might come together under the auspices of the International Committee for cooperative work on standards whenever that seemed necessary, and this was a case where it did seem necessary.

Accordingly, it was suggested to the president and vice president of the International Committee by Drs. S. W. Stratton and E. B. Rosa jointly in letters dated March 15, 1909, that such an investigation be carried out at Washington, in the laboratories of the Bureau of Standards. It was suggested in this letter that if the representatives of the several laboratories spent "a month or two setting up cells and working with the silver voltameter, that we might perhaps come to complete agreement, not simply as to numerical values, but as to specifications and procedure." This proposal met with a very cordial approval, and accordingly the

following circular letter was sent out to the International Committee in June:

Dr. Stratton and Dr. Rosa have made the proposal that a member of the scientific staff of each of the two institutions, the National Physical Laboratory and the Physikalisch-Technische Reichsanstalt, shall be sent to Washington in October, 1909, for a period of one or two months, for the purpose of carrying on joint experiments with the Bureau of Standards upon the standard cell and the silver voltameter. An attempt would be made in these investigations to come to an agreement upon numerical values and specifications. The treasurer of the committee, Dr. Stratton, stands ready to procure the necessary funds for covering the traveling expenses. The work would be regarded as undertaken by the International Committee, to which a report of the results would be submitted.

The undersigned hereby move the acceptance of this plan, and respectfully request that you send an expression of your opinion to the president.

The proposal to have only two representatives was due to the desire to limit the expenses, as no funds are provided for the work of the committee, and it was necessary for the treasurer to solicit money to defray the expenses. Later it was arranged that a third delegate from Europe be sent, to represent the Laboratoire Central d'Électricité.

The traveling expenses of the delegates were defrayed from a fund provided by the following American societies, each of which contributed \$500: The American Institute of Electrical Engineers, National Electric Light Association, Association of Edison Illuminating Companies, and Illuminating Engineering Society.

The generosity of these societies in this matter is greatly appreciated by the treasurer and the International Technical Committee.

Ample laboratory facilities for the work and a considerable number of scientific assistants were provided by Dr. S. W. Stratton, the Director of the Bureau of Standards, who took a deep personal interest in the work of the delegates from the several institutions, and did everything possible to make the work successful.

# II. CONCLUSIONS AND RECOMMENDATIONS OF THE INTERNATIONAL TECHNICAL COMMITTEE

The International Technical Committee assembled at Washington April 4, 1910, under the presidency of Dr. S. W. Stratton, Director of the Bureau of Standards, and treasurer of the International Committee on Electrical Units and Standards.

The committee unanimously elected as chairman Dr. E. B. Rosa, Physicist of the Bureau of Standards, and secretary of the International Committee.

The International Technical Committee consisted of the following persons:

Dr. E. B. Rosa, Chairman.

Dr. W. JAEGER, Geheimer Regierungsrat, Mitglied der Physikalisch-Technischen Reichsanstalt.

Prof. F. LAPORTE, Sous-Directeur du Laboratoire Central d'Électricité.

Mr. F. E. Smith, Principal Assistant, National Physical Laboratory.

Dr. F. A. Wolff, Associate Physicist, Bureau of Standards.

The committee unanimously appointed Dr. F. W. Grover secretary for the preparation of the minutes and records.

From April 4 to May 25, 1910, the committee has held 19 meetings, has made or has had made 17 series of experiments on the silver voltameter, besides numerous comparisons of resistances, of standard cells and of weights.

The apparatus and installations which were used in carrying out these experiments and these comparisons were those which are in use at the Bureau of Standards, except such of the voltameters, resistances, standard cells, weights and chemical materials as were brought by the delegates.

The committee appointed several subcommittees charged with conducting experiments and preparing reports.

After examination of the results obtained and discussion of the reports, the International Technical Committee decides to present to the permanent International Committee the following resoutions adopted unanimously:

- (1) The committee decides to choose as the value of the Weston Normal Cell the mean value of the cells presented by the delegates of the four laboratories. This mean was determined in the following way: There was first determined the mean value of the normal cells presented by each delegate, then the mean was taken of the four numbers thus found.
- (2) The committee decides to choose, for the present and until there are other mercury ohms prepared, as the value of the international ohm, to be recommended to all countries for general use, the mean of the values of the units realized at the Physikalisch-Technische Reichsanstalt and at the National Physical Laboratory. Although the international ohm as defined by the London Conference has not yet been

strictly realized, the committee believes that its value has been attained in two laboratories independently with a good degree of precision, and that future work is not likely to change it by more than 2 or 3 parts in 100 000.

(3) In view of the fact that the mean of the results with the silver voltameter obtained by this committee will probably not be changed by more than a few parts in 100 000 when the specifications are finally completed, the committee decides to recommend to the International Committee on Electrical Units and Standards the following value for the electromotive force of the Weston Normal Cell:

#### E=1.0183 INTERNATIONAL VOLTS AT 20°C

On the subject of the standard cells, the committee is of the opinion that new experiments are necessary before completing or changing the specifications of the London Conference.

On the subject of the ohm, the committee expresses the hope that new international ohms, fulfilling all the specifications of the London Conference, may be realized soon in different laboratories.

On the subject of the silver voltameter, the committee is of the opinion that the specifications for the silver voltameter should not be completed until further experiments shall be made by the members of the committee in their respective laboratories on subjects which are not considered settled at the present time, and that after these experiments, the committee shall complete the general specifications.

The committee decides that no publication shall be made of the results obtained or of any details of the work without the permission of the International Committee on Electrical Units and Standards.

The committee decides that a complete copy of the report shall be sent to the president of the International Committee on Electrical Units and Standards, and to each of the national laboratories represented on the Technical Committee, and that it make no recommendation with respect to its publication.

WASHINGTON, May 25, 1910.

# III. MINUTES OF THE MEETINGS

#### FIRST MEETING, APRIL 4, 1910

The first meeting of the delegates from the Physikalisch-Technische Reichsanstalt, the National Physical Laboratory, the Laboratoire Central d'Électricité and the Bureau of Standards, constituting a special Technical Committee, acting under the auspices of the International Committee on Electrical Units and Standards, to carry on a joint investigation on electrical standards, was called to order by Dr. S. W. Stratton, Director of the Bureau of Standards, at 3.30 p. m., Monday, April 4, 1910.

The delegates present were the following:

From the Physikalisch-Technische Reichsanstalt	Dr. W. Jaeger
From the National Physical Laboratory	
From the Laboratoire Central d'Électricité	Prof. F. Laporte
From the Bureau of Standards	Dr. E. B. Rosa
	Dr. F. A. Wolff

The Director welcomed the delegates to the Bureau, and made some appropriate remarks respecting the work to be undertaken. In reply, the several European delegates expressed their appreciation of the manner in which they had been received, and particularly of their entertainment in New York, where Dr. C. H. Sharp had acted as representative of the Bureau, as well as representative of the electrical interests of New York City.

Director Stratton then stated that while he intended to keep in touch with the work of the committee, he could not be present at its meetings regularly, and therefore invited the delegates to elect one of their own number as chairman. Mr. Smith nominated Dr. Rosa as chairman. This nomination was seconded by Dr. Jaeger and M. Laporte, and the Director declared Dr. Rosa elected chairman.

Dr. Rosa then took the chair, and after expressing his appreciation of the honor accorded him, asked whether the committee would prefer to elect one of their own number as secretary, or would have some one not a delegate. A general preference was expressed for the latter, and Dr. F. W. Grover was suggested by the chairman for the position of secretary to the committee. By unanimous consent Dr. Grover was appointed secretary.

Some discussion followed as to the form of the report which should be presented by this committee to the International Committee on Electrical Units and Standards, and the chairman asked Mr. Smith to draw up a resolution embodying some suggestions he had made for consideration at the next meeting.

After some further informal discussion concerning the work to be done, the committee adjourned to meet at 10 a. m., April 5.

# SECOND MEETING, APRIL 5, 1910

The meeting was called to order at 10.25 a. m., Tuesday, April 5, 1910, all members present. The minutes of the preceding meeting were read and approved.

The chairman then called upon Mr. Smith to present his resolution (postponed from the preceding day), on the form in which the report of the committee shall be published:

That since it is highly desirable to have a unanimous report, the experiments be made, so far as is practicable, in an impersonal manner, and in compiling the report references be made to laboratories and samples and methods, and not to individuals.

Mr. Smith explained that the motion was not fully descriptive of his desires, but he thought that the committee would see his reasons for such a proposal, and he hoped that some agreement might be reached. After some discussion the motion was withdrawn, although it was understood that the committee were unanimously of the opinion that the idea embodied in the motion should be carried out.

The suggestion of the chairman that a list of all the standard cells, resistances, weights and other apparatus intended to be used by the committee be handed to the secretary, was agreed to.

It was also agreed that the delegates hand to the secretary a list of such apparatus and chemicals as they might wish to place at the disposal of the committee.

The following subcommittees, proposed by the chairman to take especial charge of these intercomparisons, were approved:

Dr. Wolff and Mr. Smith, subcommittee on resistances.

Dr. Wolff and Dr. Jaeger, subcommittee on standard cells.

Dr. Rosa and M. Laporte, subcommittee on weights.

It was decided that the subcommittee on standard cells should report to the committee as soon as possible a list of standard cells, the mean value of the electromotive force of which shall be taken as representing provisionally the value of the Weston Normal Cell, to be used by the committee in its work; this report to be a recommendation subject to action by the committee. Similarly, it was agreed that the subcommittee on comparisons of the standards of resistance should recommend to this committee a provisional value for the international ohm, to be used by the committee in its work.

A list of suggestions and papers already received from the different members was read and declared to be correct. The meeting was adjourned at 11.15 a. m.

# THIRD MEETING, APRIL 7, 1910

The committee was called to order at 10.25 a. m., all members being present. The minutes of the last meeting were read and approved.

Dr. Rosa for the subcommittee on weights, and Dr. Wolff for the subcommittees on resistance and standard cells, reported progress, and stated it would probably be possible to make a formal report by Saturday, April 9.

Some discussion followed, relating to points which should be treated in these reports.

The chairman then made a formal announcement to the effect that the first experiments on the silver voltameter would take place on April 8, in which the current should be passed through 10 voltameters in series, two cups belonging to each of the delegates (except in the case of the Bureau of Standards, which would include two large voltameters and two of smaller size), each voltameter being set up and manipulated according to the practice of the country to which it belongs.

It was moved by Mr. Smith, and approved by the committee, that a meeting be held every day, if only for a few minutes, whereupon the meeting adjourned at 11.15 a.m.

# FOURTH MEETING, APRIL 8, 1910

The meeting was called to order at 10 a. m., and immediately adjourned in order that the members could attend to experimental work in progress.

## FIFTH MEETING, APRIL 9, 1910

The meeting was called to order at 10 a. m., and immediately adjourned in order that the members could attend to experimental work in progress.

## SIXTH MEETING, APRIL 12, 1910

The meeting was called to order at 10.50 a. m., all members being present.

The chairman made a statement to the effect that, owing probably to some contamination of the electrolyte used in the Bureau of Standards voltameters, the deposits obtained therein in the experiments on the preceding Saturday were abnormal, being not only discordant in weight but showing a dark band along the upper edge of the deposit. Examination under the microscope showed that a dark substance had deposited along with the normal silver crystals and this foreign substance was supposed to be colloidal silver. The same substance was also seen in the deposit in the voltameters of the National Physical Laboratory.

Accidents were also met in one of the voltameters of the Physikalisch-Technische Reichsanstalt and of the Laboratoire Central d'Électricité. The first experiment was therefore regarded as preparatory merely.

The following program for the week was agreed upon: First, a second comparison run of 10 voltameters in series, a repetition of the experiment of April 9, with the single difference that in two of the voltameters of the Bureau of Standards silk shall be used for a septum; second, the Bureau of Standards was authorized to make some side experiments with the different samples of silver nitrate brought by the delegates. For this purpose, it was agreed to make up the electrolytes for Friday's experiment on Thursday, and that portions of these be taken, diluted when necessary to 10 per cent concentration, and used in four of the Bureau of Standards porous cup voltameters.

It was planned to devote the rest of the day in finishing the weighings of the first experiment, and in a microscopic examination of the various deposits.

On motion of Dr. Wolff it was resolved that the meetings take place on call of the chairman or whenever requested by any member.

Adjourned at 12.20 p. m.

## SEVENTH MEETING, APRIL 22, 1910

The meeting was called to order at 10.10 a.m., all members being present. The minutes of the third, fourth, fifth, and sixth meetings were read and approved.

A preliminary report of the subcommittee on standard cells was presented by Dr. Wolff. This report showed that the mean values of the cells of the four laboratories are in close agreement, and the average deviations of the individual cells are quite small. The somewhat higher values of the French cells are in agreement with those of cells made at the National Physical Laboratory and the Bureau of Standards, from a sample of mercurous sulphate from the Laboratoire Central d'Électricité, made by the alternating current electrolysis method. The report recommended that in view of the constancy of the mean differences of each lot from the Bureau of Standards reference cells, the voltameter measure-

ments should be referred to the latter as heretofore, and that appropriate corrections be applied to the results at the completion of the work on the silver voltameter, and after agreement has been reached as to the cells to be taken as defining the Weston Normal Cell.

A preliminary report of the subcommittee on resistances was also submitted by Dr. Wolff, in which it was shown that although the open resistance coils have shown changes with respect to the sealed coils since their arrival, the standards of the Physikalisch-Technische Reichsanstalt, the National Physical Laboratory, and the Bureau of Standards, do not differ among themselves probably by more than 2 in 100 000.

The chairman next suggested that the committee agree to some program for the experiments on the standard cell. It was moved by Mr. Smith, and seconded by M. Laporte, that each delegate receive samples of  $\mathrm{Hg_2SO_4}$  from each of the other delegates, and that with this material and his own he make up 12 cells, 3 from each of the samples, using the method of preparation which he chooses. After some discussion, the motion was unanimously carried.

It was also moved by Mr. Smith, and seconded by M. Laporte, that 3 cells be made by each delegate, using a single sample of  $\mathrm{Hg_2SO_4}$ , but washing it in four different ways. This motion was also carried unanimously.<sup>2</sup>

The question of a program for the special experiments on the silver voltameter was next brought up by the chairman, who discussed the results of experiments already done on the different electrolytes. The experiments showed that the four electrolytes of the delegates give substantially the same value as used in the small porous cup voltameters. The chairman then outlined a number of experiments to settle differences in the behavior of the different types, and to throw light on the question as to what agreement can be reached when different observers use the same type of voltameter. After a good deal of discussion, it was decided to defer agreement on a program until another international experiment like the two previous had been completed.

Adjourned at 12.15 p. m.

<sup>&</sup>lt;sup>2</sup> These last cells were not set up as proposed.

## EIGHTH MEETING, APRIL 29, 1910

The meeting was called to order at 10.10 a.m., Friday, April 29, all members being present. The minutes of the last meeting were read and approved as corrected. The tabulated results of the experiments to date were presented and examined.

Mr. Smith suggested that an estimate of the possible error in the current be made after each experiment, before making the weighings. This was agreed to.

Dr. Jaeger called attention to the fact that since trouble had been met in some of the previous experiments from uncertain contacts, a blank experiment should be carried out before the next regular experiment to locate possible troubles of this kind. This was also agreed to.

A discussion followed as to whether further experiments should be made using filter paper. Mr. Smith and M. Laporte expressed themselves as satisfied that filter paper increased the deposit and should be avoided in precision work with the voltameter. Dr. Taeger expressed himself as not satisfied that the filter paper effect had been demonstrated, as the experiments at the Reichsanstalt on this subject were not yet finished, and he wished that further experiments might be made. The chairman expressed the hope that as little time as possible be expended on the investigation of filter paper if it was agreed that it should not be allowed in the official specifications which are to be agreed to and recommended to the International Committee. Dr. Jaeger stated that, according to his views, it was not the task of the committee to propose a single type for the voltameter, but that different types be permitted, and that the principal task of the committee was to compare the different types as used in the countries represented, and to deduce from the results a value for the Weston Normal Cell. This value should be given to 1 part in 10 000.

The chairman expressed the view that this committee should undertake to agree upon uniform specifications for the silver voltameter, as had in large measure been done for the standard cell and the mercury ohm, and that in so doing as great liberty be allowed as to details, as the committee can justify by its own experiments taken in connection with previous work. It will,

therefore, in his opinion, be necessary to investigate further several important features of the voltameter. For example, (1) the volume effect, or the reason why large voltameters give heavier deposits than small ones. This seems probably due to impure electrolyte, and if found to be due to this alone, it will prove to be a valuable criterion by which to test the purity of an electrolyte: that is, if large and small voltameters agree in the weight of the deposit, the electrolyte will probably be pure. If they disagree, the smaller voltameter giving the lighter deposit, the latter will be more nearly the proper weight. (2) The effect of silk should be carefully studied to see if it can be used without increasing the weight of the deposit. It appears that even pure raw silk increases the weight of the deposit unless thoroughly washed, and even then it may do so. This should be very thoroughly tested before silk is permitted. (3) The larger weight of silver, using large siphons, may be due to impure electrolyte, but this also should be tested. (4) The size of anode and effect of anode slime on the weight of the deposit when no septum is employed between anode and cathode should be tried. Other experiments of this kind will probably be suggested as the work proceeds.

As no motion was made respecting the carrying on of such experiments, the chairman, after considerable discussion had taken place, asked whether the committee would permit Mr. Smith and himself, as a subcommittee of two, to carry on a series of side experiments to test the various questions suggested. This was unanimously agreed to by the committee. Dr. Jaeger emphasized that such experiments should not interfere with one or two further comparisons made with the voltameters as used in the four separate countries.

On motion of Mr. Smith, seconded by M. Laporte, it was voted to have two more 10-cup experiments, in the first of which filter paper should be used in some of the voltameters, and in the second such changes should be made in the electrolyte, size, etc., as were suggested after the results of the first experiment were obtained.

The meeting adjourned at 3.20 p. m., a recess for lunch having been taken between 12.30 and 2.00 p. m.

## NINTH MEETING, MAY 16, 1910

The meeting was called to order at 2.15 p. m., all members except Dr. Wolff being present. The minutes of the preceding meeting were read and approved.

The chairman announced that the report of the subcommittee of two, under whose auspices the special experiments on the silver voltameter had been conducted, was not quite ready, but would be presented in the near future. He asked for suggestions for experiments to be done in the current week, and none being advanced proposed that another experiment be made to confirm the important effects observed in the preceding two experiments, when acid or alkali were added to the electrolyte. Such an experiment could be carried out on the following day during the absence of the delegates in New York.

It was decided that although further experiments could not be regarded as the work of the committee, the results of such experiments might be taken into account in the same way as other work of the Bureau of Standards, before the meeting of the committee, has been presented for the information of the delegates.

The proposal of Dr. Jaeger that each delegate should tabulate and discuss the results of the experiments to aid in their interpretation was accepted.

It was then proposed by the chairman that certain points relative to the framing of general specifications for the silver voltameter be selected, to be considered by each delegate for himself and discussed at the following meeting. After a good deal of discussion the following general subjects were agreed upon to be considered in outlining the specifications:

- 1. Methods for purifying the electrolyte, and the criterion for determining when a sufficient degree of purity has been reached.
- 2. The extent to which the solution may depart from neutrality at the beginning of the experiment, and the allowable change during the deposit.
  - 3. The limits of concentration of the electrolyte.
- 4. Whether silk can be recommended as a septum, and if so, how it shall be prepared and used.
- 5. Whether a porous pot can be recommended as a septum, and if so, how shall it be prepared and used.
- 6. Whether use of filter paper can be recommended as a septum or in the preparation of the silver nitrate.

- 7. Under what conditions the voltameter may be used for purposes of highest precision, without any septum.
  - 8. The size and method of preparation of the anode.
  - 9. The allowable limits of the current density.
  - 10. The best values of current to be employed.

The meeting adjourned at 4.20 p. m.

#### TENTH MEETING, MAY 18, 1910

The meeting was called to order at 11 a.m., all members being present.

Dr. Jaeger proposed that the report to be submitted to the International Committee should give full details of the manner of making the experiments, the apparatus used, methods of calculation of results, and the like. It was agreed that the value of the Weston cell at 20°, in terms of the group mean of the cells of the four countries, be the only value tabulated in the report, the difference from the observed value at 25° to the value at 20° being stated. The chairman asked that the subcommittee on standard cells should submit a report on the following day, showing the relation between the standard cell used in the voltameter experiments and the mean of those cells which are to be used in defining the Weston cell. This led to the discussion of the method to be adopted in combining the results on the cells of the four countries. In this connection Dr. Jaeger moved that the method of calculating the mean value of the standard cells submitted by the four different laboratories which shall be employed at this time, should not be considered a precedent for the future. After some discussion this was agreed to. With this understanding, M. Laporte moved that the arithmetical mean of all the cells, excepting those which in the judgment of the maker are to be regarded as abnormal, be taken. This was seconded by Mr. Smith. Dr. Jaeger moved as an amendment that the arithmetical mean be taken of the mean values of the four groups of cells of the four countries. The motion, as amended, was seconded by Dr. Wolff, and was carried unanimously.

M. Laporte called attention to the fact that the Laboratoire Central d'Électricité had found itself in a different position from the other laboratories with regard to the preparation and selection of cells for the experiments, since it had had only three weeks at its disposal for this purpose.

The next question, as to what unit of resistance the results of the voltameter experiments should be referred, was after some discussion reserved for further consideration until after the noon recess.

The meeting was again called to order at 1.45 p. m., after a recess of an hour and a half, all members being present except Dr. Wolff.

It was suggested by the chairman that some of the Bureau of Standards coils be carried back to Europe and compared with the standards of the Physikalisch-Technische Reichsanstalt, National Physical Laboratory, and the Laboratoire Central d'Électricité, the results to be incorporated in an appendix to the report to the committee. Mr. Smith preferred that the comparisons should be made as near as possible at the same time as comparisons of the wire standards with the mercury ohm were made. The chairman and Mr. Smith emphasized the distinction between the comparison of the mercury ohms of the different laboratories, and intercomparisons of their wire standards alone. According to the London Conference, the relation between the units of the various laboratories ought to be determined by comparison of their mercury ohms, the wire standards simply serving as intermediaries. The chairman proposed as a recommendation to the committee that at some stated time, say April of next year, intercomparisons of the mercury and wire standards of each laboratory be made, the traveling comparison coils being carefully selected for constancy, inasmuch as they must be assumed to remain constant during the comparison.

# ELEVENTH MEETING, MAY 19, 1910

The committee was called to order at 2.25 p. m. In the temporary absence of the chairman, Dr. Wolff took the chair. The minutes of the ninth and tenth meetings were read and approved after correction.

M. Laporte brought up the question of what data should be included in the report of the experiments, and the following pro-

visional form for the presentation of the results of the voltameter experiments was drawn up:

Date

							on	
							iean agreed upon	
Limit within which the current is supposed to be known								
Labora- tory	Cup	Cup Type	Anode			Weight (to o.or mg)	Weston cell at 20° (reduced to group mean)	Remarks
				Kind	Volume		mean)	

General remarks.

No of experiment

It was agreed that one of the experiments should be tabulated in this manner and submitted to the committee for approval or revision.

(Dr. Rosa then took the chair.)

Dr. Wolff reported for the subcommittee on standard cells, that the group mean of the cells submitted by the delegates as normal, and combined as was voted in the preceding meeting, was 26 microvolts higher than the reference cells of the Bureau of Standards.

The consideration of those headings, which it was proposed at the ninth meeting to treat in forming the general specifications of the voltameter, was next taken up. Mr. Smith asked that those points which after discussion remained in doubt should be dismissed until the end.

The chairman asked that in order to promote discussion he be permitted to read what seemed to him were the general points which might be specified regarding the electrolyte:

The electrolyte shall consist of a solution of silver nitrate in distilled water, having from 10 to 20 g of silver nitrate in 100 cc of the solution. The electrolyte must be free from organic or other reducing substances, as shown (1) by a suitable chemical test, (2) by giving a crystalline deposit free from striations, (3) by giving the same weight of deposit in a large and in a small voltameter. The silver nitrate is purified by crystallization, and if the chemical test for purity be omitted it should be recrystallized until further crystallization does not change the weight of the deposit.

The voltameter should contain not less than 75 cc in the cathode chamber, and the deposit should not continue long enough to reduce the mean concentration of the electrolyte in the cathode chamber below 5 per cent. If no septum is used, no greater weight of silver should be deposited in a single experiment than is contained in the electrolyte at the start.

The electrolyte when ready for use must be neutral or very slightly acid, as tested by iodeosine. As one part in a million of alkali may increase the deposit appreciably, it is better to have a slight acidity (say one part in a million) than to take the risk of slight alkalinity in attempting to make it strictly neutral. The electrolyte must be neutral or slightly acid at the end of the experiment, no alkalinity and not more than a trace of acid being permissible. Any septum or other substance which produces appreciable alkalinity or acidity must be avoided.

It was decided to discuss these points one at a time, distinguishing between what has been found in experiments of the committee and the results of previous work. With regard to the limits of concentration, the following were agreed upon:

No special experiments have been made by the committee to investigate the effect of varying concentration, although concentrations between 10 and 20 per cent have been used in the experiments without evidences of differences due to this cause being detected.

Previous experiments in two of the laboratories have shown no certain differences when the concentration was varied between the limits 1 per cent and 50 per cent, and 5 per cent and 25 per cent, respectively, so that 10 per cent to 20 per cent would appear to be safe limits.

The limit below which the concentration of the electrolyte in the cathode chamber, if this be distinct from the anode chamber, should not be allowed to fall during an experiment, was next considered. The chairman expressed the opinion that although his suggestion of a limit of 5 per cent was to some extent arbitrary, it had the advantage of being a round number and was sufficiently large to be safe. After some discussion it was agreed "that the average concentration of the electrolyte in the cathode chamber (if it is distinct from the anode chamber) during an experiment should not be allowed to fall below 5 per cent."

The detection of impurities in the electrolyte.—The chairman in his draft proposed "that the electrolyte should be free from organic matter and reducing agents as shown by chemical tests, or, in lieu of these, as shown by its giving a crystalline deposit free from striation, of the same weight in large as in small voltameters, and which is not changed after recrystallization." It was agreed to discuss the separate points of these proposals one at a time.

Mr. Smith expressed the opinion that there is no suitable chemical test known for some of the impurities which may be present.

A discussion of the permanganate test for reducing substances followed, and it was pointed out that this test is not a sure indication of the presence of all kinds of organic material. The chairman stated that there is evidence that on fusion of the silver nitrate, organic substances present in the salt are often put into condition to be acted on more readily by permanganate, and may thus be detected although not found in the test of the crystallized salt before fusion. With respect to the absence of striation as a criterion for the purity of the electrolyte, the chairman stated that although an impure solution might give a deposit free from striae, he had never seen a striated deposit from an electrolyte which was shown by chemical tests to be pure. Dr. Jaeger remarked that the silver deposits in his cups, in the opinion of the chairman, often showed striations, although the weight of silver was normal, and that, therefore, the striations can not be a sufficient criterion for abnormal deposits. The chairman replied that it was on account of the difficulty of reaching a certain result from any one test alone that he had proposed three criteria to be taken in conjunction with one another.

With respect to the volume effect, Dr. Jaeger said that there might be such an effect, but that he did not think the experiments were conclusive.

Mr. Smith expressed the opinion that the experiments had shown a volume effect to be present in some of the electrolytes, and that he could not conceive of such an effect being present with a pure electrolyte.

It was decided to postpone action on these points until the report of the subcommittee on the special experiments should have been presented.

Adjourned at 5.30 p. m.

# TWELFTH MEETING, MAY 20, 1910

The meeting was called to order at 10.30 a.m., all members being present.

Dr. Jaeger asked if the report of the subcommittee on side experiments was ready. The subcommittee reported that it had

not been possible to finish it as yet. Dr. Jaeger suggested that the meeting adjourn until this report was at hand, as nothing else for the moment required action.

Adjourned at 10.40 a.m.

## THIRTEENTH MEETING, MAY 21, 1910

The meeting was called to order at 10.15 a.m. by the chairman (Dr. Burgess being elected secretary pro tem in the absence of Dr. Grover). All members present.

The chairman called for reports of the subcommittees on standard cells and resistances.

Dr. Wolff gave a summary of the report on standard cells, which showed that in terms of the unit agreed upon by the committee, namely, the mean of the group means on a basis of eight comparisons, the NBS reference cell No. 109 was 23 microvolts low.

Messrs. Wolff and Jaeger submitted a form of report that they had agreed on as a subcommittee on the comparison of standard cells, as follows:

# Comparison of Standard Cells

Object.—Direct comparison of standards of emf of different laboratories; accuracy of reproduction; and basis of expressing results of yoltameter experiments.

The cells.-PTR, NPL, LCE, and NBS cells.

Give table for each and supplementary table of additional cells for NPL, LCE, and NBS.

Table or footnote should give information concerning materials, Hg, Cd, CdSO<sub>4</sub>, Hg<sub>o</sub>SO<sub>4</sub>.

Method of washing and such other details as may have a bearing on the subject.

The comparison baths.

Electrical measurements.

The results.

Reference cells of NBS.

Cells of each country in separate tables.

Additional cells of each country in separate tables.

Values of exchange cells at NBS (English and miscellaneous).

Table of present values of cells previously tested abroad or belonging to same set.

The above was accepted.

It was also decided to put the results on abnormal cells in a separate table if they were found by the committee to be useful,

and that the relative values of all cells as found at the Bureau of Standards and in the home laboratories could be added as an appendix.

Messrs. Smith, Jaeger, and Laporte presented a draft of a form that the final report to the International Committee on Electrical Units and Standards should take. This form was agreed upon in principle, as follows:

The report of the International Technical Committee consists of the following portions:

- 1. The conclusions and recommendations of the International Technical Committee.
  - 2. Minutes of meetings.
  - 3. Appendixes:
    - (a) Reports, papers and suggestions of the delegates already in the hands of the secretary of the committee (10 papers).
    - (b) List of apparatus, standard cells and materials brought by the delegates for the work of that committee.
    - (c) Description of experiments.
    - (d) Data of experiments.
    - (e) Reports of subcommittees on weights, resistances, standard cells, voltameters.

After considerable discussion as to the publishing, printing and distribution of the report, it was voted, on motion of Mr. Smith, and seconded by M. Laporte, that one copy of the complete report be sent to the president of the International Committee on Electrical Units and Standards, and to each of the national laboratories represented at Washington, and that this Technical Committee could make further recommendations later regarding the other matters.

Dr. Wolff presented a further report from the subcommittee on resistances which, after reading and discussion, was referred to the subcommittee for completion and incorporation in a complete report from that committee.

On motion of Mr. Smith, seconded by Dr. Wolff, Messrs. Jaeger and Laporte were made a subcommittee to draw up in more detail the form of the final report to the International Committee on Electrical Units and Standards. After some discussion regarding future meetings and program, it was agreed to adjourn at 11.35 a. m. until 1.30 p. m. in order to give time for the subcommittees to complete their reports.

#### FOURTEENTH MEETING, MAY 21, 1910

The fourteenth meeting was called to order at 2.15 p. m., all members being present. After inspection of the tabulated results of an experiment arranged according to the form agreed upon in the eleventh meeting, this form was approved.

The minutes of the preceding meeting were examined and approved after correction. The chairman asked for the report of the subcommittee on resistance comparisons. This was presented by Dr. Wolff, who indicated briefly the following relations. The intercomparisons of the resistance standards indicate the following values for the difference in the values of a given coil when measured in terms of the Physikalisch-Technischen Reichsanstalt unit and the Bureau of Standards provisional unit:

PTR-NBS using—	Millionths.
First measurement	6
Last three measurements	
Last measurement	+9
All the measurements	+2

The difference between the value of a given coil when measured in terms of the mean of the units of the Physikalisch-Technische Reichsanstalt and National Physical Laboratory, and when measured in terms of the provisional unit of the Bureau of Standards is (omitting L87, which is only a current standard):

Mean of PTR and NPL-NBS using—	Millionths	
First measurement	+2	2
Last measurement	+	9
All measurements	+	7

The measurements on the PTR 1000-ohm coil, using the values found at the Physikalisch-Technische Reichsanstalt by Dr. Lindeck, give the value—

#### PTR-NBS=+8 millionths.

The subcommittee suggested in conclusion that the results of the voltameter experiments should be referred to the mean of the units of resistance maintained at the Physikalisch-Technische Reichsanstalt and the National Physical Laboratory, and that in accordance with the above data the value of the resistance of a coil measured in terms of this unit is to be regarded as 7 millionths higher than the value found in terms of the basis of reference o the

Bureau of Standards. This is equivalent to the statement that the mean of the values of the mercury ohms of the Physikalisch-Technischen Reichsanstalt and the National Physical Laboratory is 7 millionths *smaller* than the value of the ohm maintained by the Bureau of Standards wire coils.

Taking this value in conjunction with the difference between the group mean of the cells of the four laboratories and the mean of the reference cells of the Bureau of Standards, the values of the Weston Normal Cell found by voltameter measurements on cell No. 109 (whose value is 3 millionths higher than the mean of the Bureau of Standards reference cells) should be corrected by

26-3+7=30 millionths.

These suggestions were adopted.

The consideration of the report of the subcommittee on the special voltameter experiments was next taken up. In order to be better able to take part in the discussion Dr. Rosa asked Dr. Wolff to take the chair.

I. Mr. Smith wished to especially emphasize the clause which states that this report has been presented in a form convenient for discussion, and recommended that the points be considered in the order in which they appear in the report. Since, however, the report had been in the possession of the members for only half an hour before the meeting, he would suggest deferring action on the report until the members had had more opportunity to examine it. He would amend the first line on page 164 to read "by recrystallizing three times and fusing. It is then neutral, etc." This was agreed to.

The first line of the second paragraph on page 164 was amended as suggested by M. Laporte to read "Table XLVIII gives the difference on three electrolytes, etc.," and on suggestion of Dr. Jaeger the next to the last line of the second paragraph on page 164 to read "required before fusion, as used by the Laboratoire Central d'Électricité, 0.5, and after fusion 5 or 6 cc," etc.

A discussion followed, introduced by Dr. Jaeger, on the behavior of the French salt which gave no test with the permanganate before fusion but showed the test for reducing agents after fusion. M. Laporte asked the subcommittee if the permanganate test made

on a salt after fusion gave any indication of the purity of the salt before fusion. Has it been shown that the same deposit will be obtained from a given salt unfused and showing no permanganate reaction as is obtained with the same salt fused and giving a reaction with permanganate? The subcommittee stated in reply that this experiment had not yet been tried either by the subcommittee or by either individually. In the case of the French salt only one fusion had been made, and it could not be definitely stated that it was impure. In general, it was their opinion that a salt which showed the volume effect and was always observed to give a reaction with permanganate, should be regarded as impure. There are samples of AgNO, which show no permanganate reaction either before or after fusion. The subcommittee wished again to emphasize their belief that the permanganate test alone is a useful but has not yet been shown to be an absolute test, for certain impurities of the salt.

Dr. Jaeger, referring to the fact that a permanganate test of 5 cc corresponds to only two in a million of furfural, asked if tests had been made to show that this quantity of impurity should be avoided. In reply Dr. Rosa stated that it can be regarded as established from the heavy deposits obtained with such salts, that such an amount of impurity is appreciable.

Dr. Jaeger called attention to three deposits obtained in the French cups which, with the other experiments, seemed to indicate a negative volume effect. Prof. Rosa explained that since the individual three deposits referred to were made in medium-sized cups only, and not some in large and some in small voltameters, they could not, in his opinion, be regarded as conclusive evidence against the volume effect.

M. Laporte inquired if Mr. Smith had in previous work found the volume effect with his new form of voltameter. Mr. Smith stated that he had always used salt in this form which other tests had shown to be pure. With an electrolyte proven by other tests to be impure he had observed three years ago an effect as great as 8 in 10 000. It was not, however, tested by means of potassium permanganate.

2. The committee next considered the section on the siphon voltameter. The suggestion of Dr. Jaeger that the relative values

of the deposits in the experiment, using siphon voltameters (14th), should be referred to the mean of all the deposits, was adopted, as was also the proposal that the differences between the siphons in large and small voltameters should be given.

Dr. Rosa gave it as the experience at the Bureau of Standards that the siphon form of voltameter, although theoretically reliable, had in practice always given higher results than with the porous pot or with no septum. If a porous pot is placed over the cathode end of the siphon, the deposit is the same as that found in the same cup with a porous pot. If a porous pot is placed over the anode end of the siphon, the deposit is larger. He attributed this to the volume effect, the effect being increased, due to the added volume of the electrolyte in the siphon.

Mr. Smith stated that he had always taken the siphon form as the standard by which to judge other forms, and to test whether the anode was producing any disturbance, and had always obtained identical values with electrolytes believed to be pure.

Dr. Rosa replied that the siphon form had never been used at the Bureau of Standards with electrolyte in which the deposit was the same in both large and small cups. With a solution in which the deposit was larger in the large cups by only 3 or 4 in 100 000, the volume effect was larger using the siphon and still larger with two siphons in parallel. He supposed that Mr. Smith's salt had been pure, and regarded the siphon as a very severe test on the purity of the electrolyte. In practice it is a very awkward form to use, and has little to recommend it.

Dr. Jaeger called attention to the slightly larger values with siphons in the NPL electrolyte over those with the new form. M. Laporte pointed out that the values with the siphons in this case were the same with two sizes of cups, a result not to be expected if the solution were impure.

3. Effect of silk. Mr. Smith suggested that the first sentence be amended to read "silk unless thoroughly washed can greatly increase the deposit." Dr. Jaeger expressed the opinion that those values indicating a light deposit with well-washed silk might be explained as due to accidental errors.

The discussion of the chemical report submitted as a part of the report of the subcommittee was postponed until the next day. Dr. Jaeger brought up the question of the method in which the experiments on the voltameter should be combined in obtaining the value of the standard cell. Leaving out of account all deposits where the impurities were purposely introduced into the electrolyte he found

including results with filter paper 1.01833 not including results with filter paper 1.01832

with a maximum deviation of 8 in 100 000.

Taking only the deposits in his own cup, he found

including results with filter paper 1.01833 not including results with filter paper 1.01829

Dr. Rosa suggested that in finding the mean only those deposits should be included in which the voltameters conformed to our own specifications. If it was agreed that those deposits where acid was purposely added to the electrolyte should not be included in taking the mean, then why should not those deposits be excluded also where the electrolyte was shown to have become acid during the experiment?

M. Laporte expressed the opinion that the importance of the work of the committee would be very much lessened if the members should go home without being able to connect their former practice with voltameters conforming to the new specifications. His results with filter paper here had agreed with those in Paris, but he was not sure that in using a new kind of voltameter his results would agree with those of other observers. Dr. Rosa called attention to the fact that the use of the voltameter rests on the assumption that different observers will obtain the same results with voltameters conforming to the same specifications. Dr. Jaeger expressed himself as not in favor of specifying the voltameter. Mr. Smith read the following extracts of letters from Dr. Warburg (to Dr. Stratton, Feb. 4, 1910) upon the specifications of the voltameter: "It is, however, of importance to indicate the factors which must be avoided or observed in making up the chemicals, etc.," and he then refers to the Report of the London Conference, page 21, and appendix, page 3. The last-named reference reads as follows: "In this appendix certain institutions

have described in more detail methods which are believed to fall within the general international specifications. When international cooperation in standardizing work has been further developed, mutual agreements on methods of procedure will no doubt be secured with a corresponding degree of accuracy. At the present time the international comparisons which have been made indicate that the various methods of procedure give very nearly identical results." Mr. Smith believed from this that one of the main objects was to agree upon methods of procedure.

Dr. Rosa emphasized that he did not wish to specify one form of voltameter but merely that the committee should rule out what, in their opinion, must be regarded as sources of error. He would suggest that each member of the committee write out a draft of those points which he believed it well to specify, and that these drafts be compared and discussed on Monday. This was not agreed to, and the discussion of the report of the subcommittee was continued.

Dr. Jaeger moved "the committee is of the opinion that from the information at hand the existence of a volume effect can not with certainty be deduced." Under this motion he stated that he would include only those electrolytes in the report of the subcommittee. Prof. Rosa wished to substitute "with a high degree of probability" in place of "with certainty." Mr. Smith suggested that the motion be amended to read: "The committee is of the opinion that the information at hand does not indicate with probability the existence of a volume effect in any electrolyte in the experiments of the subcommittee." He could then vote against the motion. Neither the motion nor the amendment was seconded.

Dr. Jaeger moved also "that the relation between the volume effect and the test with permanganate has not been established, and it appears doubtful that the impurity indicated by the permanganate (two or three in a million) is of importance." This motion was not seconded. Mr. Smith emphasized that the subcommittee had nowhere claimed the *certainty* of the relation between the permanganate test and the volume effect.

M. Laporte believed that it would be well to remember after this long discussion that a very satisfactory series of experiments have showed the concordance of results given by the four electrolytes in voltameters of small dimensions. He regretted that these experiments, favorable for an agreement, had not appeared in the report of the subcommittee.

Adjourned at 6.05 p. m. to meet at 10 a. m. May 22.

### FIFTEENTH MEETING, MAY 22, 1910

The committee met at 10 a.m., all members being present, Dr. Wolff in the chair and Dr. Burgess acting as secretary.

After informal discussion of the form of final specifications, the committee proceeded to consider further the report of the subcommittee on the special voltameter experiments.

Dr. Jaeger called attention to paragraph 5, page 166, of this report, and asked if the accompanying report of the chemist, Dr. McDaniel, expressed the views of the subcommittee. Messrs. Smith and Rosa stated that the chemist's report was transmitted to the Technical Committee for its information, but that the subcommittee was not responsible for its contents.

A long discussion ensued concerning the experiments carried out by the subcommittee, particularly with reference to the tests for acid and organic impurity in the electrolyte, and the effect of acid and silk upon the weight of the silver deposited. It was held by Messrs. Jaeger and Laporte that the information contained in the report of the subcommittee, together with the report of the assisting chemist, Dr. McDaniel, was not sufficient to justify the committee in excluding silk from use in the silver voltameter, or in requiring that the electrolyte be strictly neutral, or contain only a trace of acid.

Dr. Rosa, remarking that agreement on uniform specifications was apparently impossible at present in all subjects, such as silk, acidity, purity, etc., he would defer such matters for future settlement by correspondence, and he therefore moved:

It is the sense of the committee that the specifications for the silver voltameter should not be completed until further experiments shall be made by the members of the committee in their respective laboratories on subjects which are not considered settled at the present time, and that after these experiments, the committee shall complete the general specifications.

The motion as amended was carried unanimously.

Dr. Wolff retired, and Dr. Rosa took the chair. After informal discussion of the significant figures to represent the value of the Weston cell from the work here, the committee adjourned at 12.55 p. m. to meet at 10 a. m. the day following.

## SIXTEENTH MEETING, MAY 23, 1910

The meeting was called to order at 10.30 a. m., Monday, all members being present.

The typewritten minutes of the fifteenth, fourteenth, and the tenth meetings of the committee were examined in turn and corrected.

It was agreed that it would be instructive and interesting for each delegate to group and average the results of the experiments, and an informal discussion followed on the different ways of grouping.

M. Laporte suggested that it would be well for each delegate to present in the report all the results found, using his own type to show the agreement with previous work which had been obtained.

A recess was taken from 12.40 to 3.15 p. m.

The chairman asked that the first and third reports of the Bureau of Standards on the voltameter be included in the list of papers of the committee. This was agreed to.

Mr. Smith and Dr. Jaeger submitted tables of the results of the experiments with the different forms of voltameter, subject to possible later correction and modification.

The chairman proposed that each member should add signed comments to either or both of the tables.

Mr. Smith moved "that we recommend to the International Committee the value 1.0183 international volts for the value of the Weston cell at 20°." This was seconded by Dr. Jaeger.

M. Laporte wished to amend this to read "for the value, at the present, of the Weston cell at 20°." He called attention to the fact that no work on the mercury ohm has been carried out in accordance with the specifications of the London Conference, and that, therefore, any value assigned at present to the Weston cell is subject to revision.

Mr. Smith stated in reply that provision had been made by the London Conference for the revision from time to time of the value of the Weston Normal Cell in international volts, and referred to Schedule D of the London Conference.

It was suggested by the chairman that the recommendation for the value of the Weston cell be introduced by preamble, explaining that the international ohm is at present not as specified by the London Conference. This was agreed to. The motion, modified to embody the suggestions of the various members, was as follows:

Although the international ohm, as defined by the London Conference, has not yet been strictly realized, we believe that its value has been attained in two laboratories independently with a good degree of precision, and that future work is not likely to change it by more than 2 or 3 parts in 100 000, and, further,

In view of the fact that the mean of the results with the silver voltameter obtained by this committee will probably not be changed by more than a few parts in 100 000 when the specifications are finally completed,

Resolved, That we recommend to the International Committee the value 1.0183 international volts (instead of the provisional value 1.0184) as the electromotive force of the Weston Normal Cell at 20°.

This was seconded by Dr. Jaeger and carried unanimously.

The chairman then asked the committee if it would allow the incorporation of one more experiment in the report of the committee. Within a few days Dr. McDaniel had prepared a salt which answered all the tests for purity which had been suggested, and four deposits had been made in large and small cups, using an electrolyte prepared from this salt. On account of the interest pertaining to the salt, he would like to see these four deposits which could not appreciably change the mean found from the previous experiments, included with the other deposits. This was agreed to.

The chairman then stated that he would be glad if the committee would make out a list of the experiments in continuance of the work of this committee which should be done by the members after their departure from Washington.

The following list was compiled from suggestions of the various members:

- T. The effect of acid and alkali, and the limits of acidity and alkalinity which can be allowed. Tests for acidity and alkalinity should be made at the beginning and end of the experiment.
  - 2. Methods for purifying silver nitrate and testing for organic impurity.
  - 3. Effects of added impurities, organic and inorganic.

- 4. Limits of current density that can be allowed at anode and cathode.
- 5. Is the deposit independent of the volume of the electrolyte; if not, what are the causes of any observed variation? Find the quantitative relation between impurity and excess of deposit.
- 6. Study the relation between the degree of electrolysis and the excess of the deposit with an impure electrolyte.
  - 7. Influence of organic septa, especially silk.
  - 8. The best treatment of porous cups as septa.
  - 9. Under what circumstances may one use the voltameter without any septum?
  - 10. Can an electrolyte be safely used more than once?

The chairman instructed the secretary to make a list of all formal resolutions of the committee.

With respect to the transmission of the report after it shall be finished, the chairman suggested that a copy be sent first to each of the delegates, and that any necessary changes be made by correspondence, after which the reports will be turned over to the directors of the various laboratories.

Mr. Smith moved "in the opinion of this committee, that there is no complex anode ion." The chairman suggested that this be qualified to read "that in a pure neutral electrolyte within proper limits of current density, we believe that Faraday's law is undisturbed by side reactions or the formation of complex ions." No action was taken.

Adjourned at 5 p. m.

## SEVENTEENTH MEETING, MAY 24, 1910

The meeting was called to order at 10.15 a.m., all members being present.

Dr. Jaeger recommended making a list of what should be attempted in the time remaining, and the following list was suggested by the different members:

- 1. Formal consideration of the tables presented by Dr. Jaeger and Mr. Smith.
- 2. To connect results obtained by the committee with the work of the delegates before coming to Washington.

The chairman proposed that Mr. Smith, whose suggestion this was, should, with the collaboration of the other delegates, undertake the preparation of such a report. This was agreed to.

- 3. The maintenance of the international ohm.
- 4. The maintenance of a concrete international average Weston Normal Cell.
- 5. Exchange of Hg<sub>2</sub>SO<sub>4</sub> samples.
- 6. Revision of the minutes and examination of reports.
- 7. Exchange of samples of silk.

Mr. Smith next brought up the question of preparing provisional specifications for the voltameter, in order to indicate where there is a difference of opinion on this subject. The chairman pointed out that this should be done to make it easily possible for the International Committee to check up the value of the cell found by this committee, as it is likely to wish to do. Prof. Egoroff has suggested that the results obtained by this committee should be confirmed by experiments made by other members of the International Committee. The chairman suggested that the points where there was disagreement could be printed in italics and alternative specifications could be prepared to cover these points.

M. Laporte believed that in those cases where experimental data is not at hand, the specifications should comprise the limits of actual practice in these experiments.

Dr. Rosa asked Dr. Wolff to take the chair that he might be free to make the following motion:

That some member of the committee shall prepare provisional specifications for the voltameter and submit them to each member, and that before or after leaving Washington each member shall underline that which he thinks should be omitted or shall replace such passages by something else, or substitute an entirely new set of specifications, or shall make any comments he shall see fit over his signature, and that such provisional specifications be added to the report.

Vote: Yes; except Dr. Jaeger, who did not vote.

Dr. Rosa recommended that the members should do this either before leaving Washington or after their return home, and in the former case they should be free to make revisions later.

Mr. Smith moved that Dr. Rosa should be requested to draw up such provisional specifications. This motion was seconded and agreed to by the committee.

Mr. Smith moved two alternatives "that in the specification of cadmium amalgam either the percentage composition be changed or else the temperature limits be changed."

Dr. Jaeger believed this to be of less importance than other matters, and wished to consider something else.

It was moved by Prof. Rosa, and seconded by Mr. Smith, that the amalgam be considered. Vote: All yes; except Dr. Jaeger, who did not vote. Dr. Jaeger rose to a point of order, but the motion was ruled to be in order by the chairman.

Mr. Smith moved "that in all cases for which the Weston cell is used for purposes of precision between 0° and 12° C, the percentage of the cadmium amalgam be reduced to 10 per cent, and that between 12° and 40° a 12½ per cent amalgam may be used." This was not seconded, and was withdrawn.

Dr. Rosa moved that, in order to use the time advantageously, the points already suggested for consideration might be considered in the following order:

- 1. Cooperative work:
  - (a) Plan for maintenance of a concrete ohm.
  - (b) Comparison of cells.
  - (c) Outline for future work on the silver voltameter.
- 2. Report of Mr. Smith connecting results of previous work with that of this committee.
  - 3. Final review of resolutions and minutes.
- 4. Receiving report of committee on standard cells, and consideration of specifications.
  - 5. Report of subcommittee on weights.
  - 6. Final report of subcommittee on resistances.
  - 7. Report of subcommittee on the form of the report to the International Committee.
  - 8. Consideration of the results on the silver voltameter.
  - 9. Provisional specifications for the voltameter.

This was seconded by Mr. Smith.

Dr. Jaeger wished to put No. 8 first. This was agreed to, and the motion thus amended was carried unanimously.

Dr. Rosa asked that a subcommittee be appointed to bring in resolutions on heading No. 1 on the next day. This was seconded by M. Laporte, and agreed to unanimously. By general agreement, Dr. Wolff and M. Laporte were selected to serve.

Adjourned at 12 o'clock m.

## EIGHTEENTH MEETING, MAY 24, 1910

The meeting was called to order at 3.25 p. m., with all members present, and Dr. Wolff in the chair.

The first matter under consideration was the voltameter experiments. Mr. Smith suggested that each member write out a statement of what conclusions he would draw from the voltameter experiments, and read those comments which he had written concerning the table he had already presented.

Dr. Rosa moved that those comments on the tables may be revised or added to by the delegates after their return to their laboratories, so that each member may have opportunity to make changes after having seen the comments and tables of the other delegates. This was seconded by Mr. Smith.

M. Laporte thought it very important that a draft of all these comments and conclusions be prepared before leaving Washington in order that possible agreement on some of the points may be reached at the present time.

The motion of Dr. Rosa was unanimously carried.

The report of the subcommittee on the subject of cooperative experiments was deferred until the next day.

Mr. Smith stated that the statements of the concordance between the present experiments and earlier work of the delegates had already been prepared, and moved that they be accepted without discussion as being mere statements of the facts. This was agreed to. In this connection, M. Laporte suggested that Mr. Smith prepare a short note on the conclusions which may be drawn from an inspection of these statements. This was agreed to.

Mr. Smith submitted the following note after the adjournment of the committee:

I have made an examination of the four reports which connect the past and present work on the silver voltameter of members of this committee. The main results are conveniently tabulated thus:

Laboratory	Form of voltameter used	Value found in own country for emf of cell at 20°	Value found in Washington for emf of cell at 20°	Difference
LCE	Rayleigh  Porous pot, small voltameter(mean)  With silk and with porous pots(mean)  New form, no septum	1.01845 1.01827 1.01834 1.01827±2	1.01844 3 1.01828 4 1.01829 1.01829	1×10 <sup>-5</sup> 1×10 <sup>-5</sup> 5×10 <sup>-5</sup> 2×10 <sup>-6</sup>

<sup>&</sup>lt;sup>3</sup> With larger voltameters higher values were obtained, but since Dr. Rosa has found, that with impure electrolytes the larger the voltameter, the larger is the mass of the deposit, he considers the results with the small voltameters to be the most reliable.

The results are certainly most gratifying, and should help pave the way for an agreement on a type of voltameter which all may use with satisfaction.

<sup>&</sup>lt;sup>4</sup> In this case the value obtained at Washington is that with the cups of the Reichsanstalt excluding filter paper. Silk was used as a septum, except in one case where no septum was used.

M. Laporte thought it would be well to prepare in concise form a draft of all the conclusions adopted and recommendations made to the International Committee, and agreed to draw up such a draft for action by the committee on the following day.

Dr. Wolff gave an informal statement concerning the new cells set up by the delegates, and promised to report more at length on this subject at the next meeting.

The question of the further specification of the Weston Normal Cell was next brought up and discussed. Dr. Rosa wished that the opinion of the committee might be expressed as to whether an attempt should be made to agree on more uniform procedure or not. Mr. Smith believed that on account of the relatively good agreement of the cells with great differences in the mode of construction, it was a very difficult matter to draw up specifications. M. Laporte believed after a trial of other methods that it was difficult to choose between them, although he preferred his method of alternating current electrolysis.

Dr. Rosa wished that a series of questions might be formulated to aid in deciding what points in the present methods of procedure required further study. It was agreed that a study of the methods of washing the  $\mathrm{Hg}_2\mathrm{SO}_4$  was, perhaps, the most important single subject. The chairman called attention to those subjects which he had recommended for further study in his report submitted to the members at the beginning of this work.

Dr. Jaeger thought that there was not time to discuss these subjects, and that the committee ought to proceed to decide which cells are to be interchanged.

Dr. Rosa wished to learn the opinion of the committee as to whether the members could not agree to cooperate in the future to the bringing about of uniformity in procedure with the standard cell, and moved "that although the Weston cells brought here by the several delegates are in good agreement, there is still room for improvement with respect (a) to the cells taking up their values quickly, (b) to holding their values constant, and (c) showing small hysteresis, and, therefore, that it is the sense of this meeting that the four laboratories should cooperate in the future to improve the specifications of the Weston Normal Cell, if possible, and to adopt a uniform practice." This was seconded by Dr. Jaeger, and carried unanimously.

The report of the committee on weights was deferred until the following meeting. The report of the committee on resistances was unanimously adopted.

Dr. Rosa stated that the provisional specifications for the voltameter, which he had drawn up as requested by the committee, and which had been submitted before the meeting, were to be accompanied by explanatory notes, as indicated, and asked that he be allowed to submit these later but before the final report be prepared, and that the specifications be inserted with the statement that they are for the guidance and information of the International Committee.

Mr. Smith suggested that as these questions have been so thoroughly discussed already, that these specifications be voted upon section by section in order that the opinion of the different members on the various points might go on record. A decision on this point was deferred until the meeting of the following day.

Dr. Rosa submitted the report on the results with four electrolytes in the small cups, and read the report of the experiments of Dr. McDaniel on silk. It was moved by Dr. Jaeger and agreed to, that these reports be included in the papers of the committee.

The order of business for the next meeting was next discussed. The secretary was instructed to prepare a list of all tables, papers, etc., and to number them consecutively.

Adjourned at 5 p. m.

## NINETEENTH MEETING, MAY 25, 1910

The meeting was called to order at 10.40 a. m., all members being present, and with Dr. Wolff in the chair.

The report of the subcommittee on weights was submitted and adopted. The chairman suggested that all reports adopted should be subject to correction of clerical errors.

As requested in the previous meeting, M. Laporte submitted the draft of the conclusions and recommendations of the International Technical Committee, which summarized the work and proceedings of the committee. This report contained several proposals not already acted on by the committee, namely:

(a) The committee decides to accept as the international ohm the mean of the units of the Physikalisch-Technische Reichsanstalt and the National Physical Laboratory.

It was agreed to amend this, as suggested by Dr. Rosa, to read "decides to accept for the present and until mercury ohms are prepared in other laboratories the mean of the units, etc."

- (b) The committee is of the opinion that new experiments are necessary before changing the specifications of the standard cell given in the appendix to the London Conference.
- (c) The committee expresses the desire that the new mercury ohm as specified by the London Conference shall be realized as soon as possible in the various laboratories.
- (d) The committee decides that no publication shall be made of the results obtained or the details of the experiments without the permission of the International Committee.
  - Mr. Smith seconded this motion, and it was carried unanimously.
- Dr. Jaeger suggested that the wording of the decision of the International Committee, appointing this committee, should stand at the head of this report, and any possible inconsistencies with this could be modified.

Mr. Smith moved the adoption of this report, which was done unanimously.

The report of the subcommittee to draw up the form for the final report was submitted by Dr. Jaeger, and adopted.

The report of Mr. Smith on the connection of the present work with former experiments was adopted.

(Dr. Rosa in the chair.)

The minutes of the seventeenth and eighteenth meetings of the committee were next examined and accepted.

It was agreed to have the report of M. Laporte on the "conclusions and recommendations of the committee" translated and presented in final form to the members before their departure.

The provisional specifications of the silver voltameter were next considered. Dr. Jaeger objected to the clause which specified that the surface of the cathode should be bright, that it had nothing to do with the precision of the measurements. The chairman stated that if Dr. Jaeger would agree to the rest of the specifications he was willing to have this clause canceled.

Mr. Smith suggested that the specification of the current should be amended to read "the current during a deposit is preferably not more than I ampere."

Mr. Smith then asked that the committee vote on the different sections of the provisional specifications section by section in order to show for the guidance of the International Committee just what are the points on which the members of this committee are in agreement, and where they have a difference of opinion.

Dr. Jaeger believed there was not time for this. Mr. Smith thought that it need not consume more than ten minutes. In case any member had not made up his mind on any point he could go on record as not voting on this point. Dr. Jaeger expressed his opinion that these specifications touched on points that it was not necessary to specify. Mr. Smith thought they were, on the contrary, very general. M. Laporte had not had time to study the specifications sufficiently, and had not arrived at an opinion on all the points. He preferred, therefore, not to express an opinion, even provisionally, before having made up his mind with regard to the whole.

It was finally agreed that Dr. Rosa and Mr. Smith should go on record as adopting provisionally these provisional specifications, that Dr. Jaeger did not agree with some of the conclusions, it being his opinion that a number of points in the proposal would indicate that the past experiments on the voltameter at the Physikalisch-Technische Reichsanstalt, as well as the work here, would have to be considered of minor value, and that M. Laporte preferred to defer expressing his opinion until he had reached a more definite opinion on some of the points.

Dr. Wolff next submitted two reports, one on the resistance intercomparisons, and the other on the standard cells. These were accepted after revising on page 92 of the report on resistances, the statement regarding the National Physical Laboratory standard of resistance.

Dr. S. W. Stratton, Director of the Bureau of Standards, who had opened the meetings of the committee on April 4, was now informed that the committee had completed its deliberations and was prepared to report to him upon its work. Upon his appearance with the committee, the chairman, speaking for the committee, said that the members of the committee had all taken a deep interest in the work, and had endeavored to come to an agreement on as many of the questions at issue as possible. Some of the questions were, however, difficult to settle in a short time,

and many points of importance had been deferred for further consideration. It was the sense of all the members of the committee that further experimental work was necessary, and that it should be carried out during the next ten months, if possible, so that by April 1, 1911, agreement could be reached concerning the completion of the specifications of the silver voltameter and the standard cell. The chairman added that if it appeared that the committee had not made as much progress as was expected, it should be remembered that much time is often required to clear up seemingly minor difficulties.

Dr. Stratton then expressed the hope that the work of the committee would not be regarded as complete until the members could come to a definite agreement on the principal points. He stated that he would be satisfied with the final decision when it shall have been reached, and, although he had hoped that the report could be finished before the departure of the delegates, he thought that, considering the largeness of the subject, it was hardly to have been expected that this should be accomplished. In expressing his appreciation of the work of the committee he dwelt upon the urgent need of uniformity in all units, and hoped that this meeting would serve as a precedent for others in the future for bringing about this desired end. In conclusion, he thanked the delegates for their patience in putting up with all inconveniences or insufficiencies of the equipment, which in the nature of things he supposed had not been absent.

Dr. Jaeger expressed his appreciation of the kindly reception tendered the delegates on their arrival in New York and elsewhere. He thought that on the whole the committee should be satisfied with the results and believed that after calmly looking over the results rather than the differences, the reasons for satisfaction would be better appreciated. He had found it a great advantage to become acquainted personally with other workers in the same line as his own, and to exchange views on these subjects.

Mr. Smith wished to thank Prof. Stratton and all members of the Bureau for the kindnesses accorded to the committee, and was very glad to have had the opportunity of being here.

M. Laporte, in concurring with what had already been said, wished particularly to congratulate Prof. Stratton on having inaugurated this, the first meeting of its kind.

Mr. Smith wished also to move a vote of thanks to Dr. Rosa for having acted as chairman, and M. Laporte asked that this vote be extended to include Dr. Burgess and Dr. Grover for their connection with the work.

Dr. Rosa, in acknowledgment, expressed the hope that the work begun may go on as successfully in the future.

The meeting was declared adjourned by Prof. Stratton at 12.50 p. m.

### IV. APPENDIXES

# APPENDIX A. REPORTS, PAPERS, AND SUGGESTIONS TENDERED TO THE COMMITTEE BY THE DELEGATES AT THE BEGINNING OF THE WORK

- 1. First report of the Bureau of Standards on preliminary investigations of the silver voltameter. (See p. 44.)
- 2. Second report of the Bureau of Standards on the silver voltameter.
- 3. Third report on the work of the Bureau of Standards on the silver voltameter.
- 4. Suggestions of the Bureau of Standards respecting cooperative work in Washington. (See p. 55.)
- 5. Notes on the Weston Normal Cell (from Bureau of Standards). (See p. 59.)
- 6. Instructions for the German delegate taking part in the joint experiments at Washington, April, 1910. (See p. 61.)
- 7. Report of experiments on the silver voltameter (from Physikalisch-Technische Reichsanstalt). (See p. 63.)
- 8. The last intercomparison of the new cadmium standard cells of the Physikalisch-Technische Reichsanstalt, etc. (See p. 65.)
- 9. Report of work on standard cells and the silver voltameter at the National Physical Laboratory. (See p. 67.)
- 10. Suggestions of Mr. F. E. Smith for the experimental work to be done at Washington. (See p. 78.)
- 11. Recherches effectués au Laboratoire Central d'Électricité sur l'équivalent électrochimique de l'argent par MM. Laporte et P. de la Gorce (Bull. Soc. Int. Elect., vol. x, p. 157, 1910).
- 12. Recherches faits au Laboratoire Central d'Électricité sur l'étalon de résistance et l'étalon de force électromotrice par M. R. Jouaust (Bull. Soc. Int. Elect., vol. x, p. 187, 1910).
- 13. Suggestions of M. F. Laporte for the experimental work to be done at Washington. (See p. 79.)

Nine of the thirteen papers are reproduced here in full. Of the other four, Nos. 2 and 3 (second and third reports of the Bureau of Standards) are to be included substantially as presented in a paper shortly to be published in the Bulletin of the Bureau of Standards as part of the researches of the Bureau on the silver voltameter. The other two, Nos. 11 and 12, are researches by the Laboratoire Central d'Électricité which have been published in full in the Bulletin de la Société Internationale des Électriciens. It is therefore unnecessary to reprint them here.

The numbering of the tables and footnotes in these papers has been left as when the papers were originally presented and are therefore not consecutive with those in the main body of the report.

1. FIRST REPORT OF THE BUREAU OF STANDARDS ON PRELIMINARY INVESTIGATIONS OF THE SILVER VOLTAMETER.

Introduction.—The International Electrical Conference, which met in London in October, 1908, adopted the following definition of the International Ampere:

The International Ampere is the unvarying electric current which, when passed through a solution of nitrate of silver in water, in accordance with the Specification B, attached to these resolutions, deposits silver at the rate of o.ooiii800 of a gram per second.

Specification B as adopted by the conference is as follows:

Specification relating to the Deposition of Silver.—The electrolyte should consist of a solution of from 15 to 20 parts by weight of silver nitrate in 100 parts of distilled water. The solution may only be used once, and only for so long that not more than 30 per cent of the silver in the solution is deposited.

The anode shall be of silver, and the cathode of platinum. The current density at the anode shall not exceed one-fifth ampere per square centimeter, and at the cathode one-fiftieth ampere per square centimeter.

Not less than 100 cubic centimeters of electrolyte shall be used in a voltameter.

Care must be taken that no particles which may become mechanically detached from the anode shall reach the cathode.

Before weighing, any traces of solution adhering to the cathode must be removed and the cathode dried.

The means which are to be employed to insure "that no particles which may become mechanically detached from the anode shall reach the cathode" were not specified. These and other particulars of the preparation of the materials used in the silver voltameter, as well as particulars of the manipulation of the voltameter, were left to be agreed upon and formulated by the International Scientific Committee which was appointed by the conference.

To aid in coming to such an agreement, it has been arranged to have a joint investigation by representatives of some of the National Standardizing Laboratories, to take place in the laboratories of the Bureau of Standards, Washington, beginning April 1, 1910. As a preparation for such investigation we have been carrying out in the Bureau of Standards a careful study of different forms of voltameters, and we present herewith a brief report on one phase of this research. We invite a critical examination of our observations and conclusions, and after such time as is required for any necessary verification, an expression of opinion respecting our proposal (p. 53).

Apparatus Employed and Procedure Followed.—1. In our work on the silver voltameter, we have used ten platinum cups and two gold cups. Four platinum cups were 10 cm diameter by 7 cm deep; four were 8 cm diameter by 5 cm deep; two platinum cups and two gold cups were 6 cm diameter and 7 cm deep. Their capacities were 350 cc, 175 cc, and 125 cc, respectively. The four large cups were adjusted to the same weight, 80.277 g; three were used as cathodes, and one was reserved as a tare. Similarly, one of the four medium-sized cups (each weighing 55.098 g) was used as a tare. The small cups weighed 39.113 g and were counterpoised by platinum. Generally the deposit was timed to weigh about 4.100 g, and gold-plated silver weights of 4.100 g were used as counterpoises in the weighing, the small difference being made up with platinum weights or riders. In most cases the cups after being weighed against the tare were also balanced against each other as a check.

2. Three balances were employed. One by Rueprecht, capacity 200 g; one by Oertling, capacity 100 g, similar to the one used by Smith at the National Physical Laboratory; one by Stückrath, capacity 200 g, similar to the one used by Jaeger and von Steinwehr at the Physikalisch-Technische Reichsanstalt.

The large cups were weighed on the Oertling balance, the medium cups on the Rueprecht, the small ones on the Stückrath. On the latter, the cups are interchanged and the riders manipulated at a distance by means of rods and levers.

3. The weighings were made in a balance room built in the basement especially for the purpose. One-half of this basement room, which has massive concrete walls, was lined on sides and ceiling with hollow tile, an additional air space being left between the tile and the concrete wall and the tile plastered inside. A tile partition separated the balance room from the other end of the basement room, in the partition being double doors (with vestibule between) and two double windows.

Weighings were made from outside the balance room by means of telescopes extending through the windows. The cups were placed on the balance pans (often using all three balances at once) and allowed to swing for half an hour before taking readings.

The temperature and humidity of the atmosphere in the balance room were very constant, changing but little in 24 hours; they were recorded on a thermograph and hydrograph. Means were provided for reducing the humidity when necessary, but this was seldom required. The precision of the weighings is very satisfactory.

- 4. The voltameters were mounted upon substantial supports, each under a bell jar, and ample electrical insulation insured. The electrolyte was always carefully prepared (15 g of AgNO<sub>3</sub> to 85 g of water), and handled in Jena glass vessels. A set of numbered beakers was reserved for each voltameter with which to handle the solution and perform the washings of the cups at the end of the runs. Everything was arranged systematically to avoid confusion or accident.
- 5. The current was derived from a storage battery of 120 volts and 25 amperes (normal charging current) capacity. The current was measured by means of Weston normal cells, standard resistances, and potentiometers. In some cases two observers, each with a complete equipment, observed at once, one keeping the current as constant as possible and the other observing the slight fluctuations of the current.

The Weston cells were in an oil bath, the temperature being regulated by a thermostat.

The time was measured by means of a chronograph and a Riefler standard clock. The current has usually been either one ampere for one hour, or one-half an ampere for two hours.

- 6. The deposits have been examined by means of a microscope, and in some cases qualitative runs have been made in a small voltameter in the field of a microscope. Many qualitative runs have also been made in smaller platinum cups, using the same current density as in large platinum cups. Microphotographs have been made of many deposits, and samples of the deposits prepared as slides suitable for microscopic examination.
- 7. The silver nitrate employed has been purchased as pure from the J. T. Baker Chemical Company, Phillipsburg, N. J., and the Gold- und Silber-Scheide-Anstalt, Frankfurt; some of it has been recrystallized, but more has been used as purchased. The anodes have been of pure silver, generally electrolytically deposited, as described by Smith.
- 8. The washing, drying, and weighing have been done with the utmost care, the drying being in an electric oven at 150° C.

Ample chemical facilities have been available for the work.

The Observations.—9. We have made many quantitative determinations, as well as numerous qualitative runs, under very many conditions. In our present report we do not wish to discuss the actual values found, more than to say that with the Richards and Kohlrausch forms we nearly agree with the values found by Jaeger and Von Steinwehr when using the porous cup (being a few parts in 100 000 less), and hence still more under Smith's value, which is about 12 parts in 100 000 larger than the latter. With the Rayleigh form we get widely different results, according to the procedure followed, always getting a heavier deposit than with the others, the larger differences and the greater striations being associated together. If we always follow exactly the same procedure, we get substantially the same results. But, having become convinced that any use of filter paper in a voltameter is very undesirable, we deem it necessary, in view of the considerable use of the Rayleigh voltameter and the strong preference for it at the National Physical Laboratory, to give very fully the grounds for our objections.

10. Remembering that the heavier deposit found by various investigators in the Rayleigh voltameter, as compared with the Richards, had been attributed to the imperfect separation by the filter paper of the heavy anode liquid from the cathode solution,

<sup>22451°—12——4</sup> 

we tried the effect of using two, or even three, thicknesses of filter paper instead of one. Instead of agreeing better with the result obtained with the porous cup, the deposits were still heavier, two sheets of filter paper giving an excess about double, and three an excess about treble that due to one sheet. That is, the excess in weight was proportional to the quantity of filter paper, and was therefore not due to the filter paper being an imperfect filtering medium. This result also followed when the finest grades of filter paper were used, the excess weight above the normal weight in a Richards voltameter being practically the same for all filter paper tried if the weight of filter paper submerged in the electrolyte was the same. The excess weight  $\Delta$  of silver, with a relatively large amount of filter paper, may be as much as 0.1 per cent.

II. Striations are more marked as the quantity of filter paper is greater, so that one can predict a heavy deposit (large value of  $\Delta$ ) by its appearance. It is not necessary to use filter paper during the run to obtain striations and an excess of weight. If a sheet of filter paper is allowed to stand for some time in the solution of silver nitrate before putting the latter into the voltameter, the deposit will be striated and too heavy, even though no filter paper was present during the run. If several sheets are used, and it stands several hours, the deposit is very strongly striated, and is large. If the filter paper is allowed to stand in distilled water for some time, and the latter is then poured off and used in preparing the electrolyte, the deposit is striated and the weight excessive, the filter paper itself not coming into contact with the silver nitrate. The conductivity of pure distilled water is immediately increased when filter paper is added to it.

Filtering silver nitrate solution through filter paper will contaminate it, and enough to be very evident both in the appearance and the weight of the deposit if the solution is hot, even though the quantity of filter paper is small.

These remarks apply to all grades of filter paper, including the finest of quantitative papers. Heavy papers produce a greater effect because of their greater mass.

12. If both porous cup and filter paper are used in the same voltameter, the deposit is striated and heavy if the filter paper sur-

rounds the porous cup. If the filter paper is inside the porous cup, the deposit is normal in appearance and weight, provided the external electrolyte be pure and not have been brought into contact with filter paper.

- 13. Cotton, linen, and silk textiles used as separators instead of filter paper, produce similar effects, but cotton less than linen. Rag paper, blotting paper, wood-fiber paper and pine wood all produce the same effects, the last named giving greatly exaggerated effects. Glucose, gelatine, and some other organic substances produce striations. Cane sugar and starch do not, except after long contact with the electrolyte.
- 14. Striations are closely spaced with large current density, and widely spaced with small current density. When fine and not very pronounced, they disappear, if the current runs long enough; that is, where the silver deposit is relatively thick. For this reason an impure electrolyte may give a nonstriated deposit. In a 7 g deposit the striations will be less marked than in a 4 g deposit for the same reason.
- 15. But although the appearance to the eye of the deposit may change with the depth of deposit, the appearance of the deposit under the microscope indicates whether it has come down from an electrolyte containing filter paper, or the products of filter paper or other organic impurity, or whether it has come down from a pure electrolyte of AgNO<sub>3</sub> and water, uncontaminated by such foreign substances. In the first case the deposit is noncrystalline or imperfectly crystalline, according to the quantity of the impurity. It may resemble molten metal that has been dropped on a cold plate and spattered, or lava having a rough, irregular surface, and the deposit more or less massed together; or it may be in needleshaped crystals, or imperfectly crystalline when the impurity is slight. The color may be grayish or tarnished when considerable quantities of impurities are present. The pure electrolyte in a Richards or Kohlrausch voltameter gives a beautiful crystalline deposit, the crystals having well-defined planes and angles, and looking much like glass or diamonds under the microscope, and, by reflected light, are generally without a metallic luster. Sometimes, however, there is a metallic luster, with some planes and angles.

and the appearance is more like nuggets of metal. In the larger cups (with one-half ampere for two hours) the crystals are well separated, the clean platinum surface showing between them, and they are approximately equiaxial. In the smallest cups, where the quantity of silver is twice as much per unit of area, the crystals are elongated, but otherwise similar.

- 16. We discover no difference in size or appearance between the crystals given in the Richards and Kohlrausch voltameters, nor in those deposited on gold from those on platinum for the same current density and quantity of silver per unit of area. The presence of a small quantity of acid reduces the size of the crystals; that is, the deposit starts at a larger number of points, and therefore there is a larger number of crystals of a smaller size. The presence of a small quantity of organic matter affects the appearance of the crystals, and in larger quantity destroys the crystalline character entirely.
- 17. The porous cups may be so thoroughly cleansed that they can stand for hours in distilled water without greatly increasing its conductivity. Filter paper increases it instantly, and the increase goes on gradually with time.
- 18. When a large quantity of filter paper is allowed to stand some hours in a solution of silver nitrate before it is placed in the voltameter, the deposit on the bottom of the cup grows up in stiff rods like trees. If a hot solution is filtered through filter paper, the deposit is wooly. In some cases of striated deposit, the striæ are tenacious and the deposit comes off in strips. Under the microscope the silver looks something like slag.
- 19. Richards, Smith, and others have attributed the striæ to the heavy anode liquid, in connection with the upward currents of weak electrolyte along the surface of the cathode. That the direction of the striæ is determined by these convection currents of the electrolyte seems demonstrated by the inclination of their direction produced by rotation, and by the further fact that they disappear when the silver is deposited on the under surface of a horizontal cathode plate. But, we do not find reasons for thinking that the striæ are produced by the heavy anode liquid. Indeed, if the filter paper around the anode be removed (all other circumstances remaining the same) the striæ disappear. The heavy

anode liquid would then flow down as before, or even more freely. Moreover, we always obtain striæ when filter paper is used provided the quantity of silver deposited is not great enough to cover them up, even though percautions are taken to keep the heavy anode liquid from the cathode. With the small current density the striæ are farther apart and easily seen; with larger current density they are nearer together and not so conspicuous. Also, when very little filter paper is used, they are less conspicuous and the deposit might be considered nonstriated even if the quantity of silver is not large. In short, we believe striæ are always produced by filter paper; and, according to quantity of filter paper, current density, and quantity of silver deposited per square centimeter, they are more or less distinct, between the extreme limits of heavy ridges and barely perceptible striæ.

20. The reason why striations are never seen in the Richards and Kohlrausch voltameters (when pure electrolyte is employed) is not because the heavy anode liquid is kept from the cathode, but merely because the organic impurity due to the filter paper is absent. If filter paper has been employed in the preparation of the silver nitrate, however, striations may appear in these voltameters, unless the salt has subsequently been sufficiently purified by recrystallization. Silk, cotton, linen, and all organic matter, as well as filter paper, should therefore be scrupulously avoided.

Glucose, furfuraldehyde, formaldehyde, and many similar strong reducing agents when added in minute quantities to a pure solution of silver nitrate produce striations and render the deposit less crystalline. Milder reducing agents do not produce these results. Since furfuraldehyde is always produced in greater or less amounts by the hydrolysis (often by water alone) of all kinds of vegetable and animal textile fibers, it seems probable that this substance, partially at least, accounts for the observed effects produced by filter paper, silk, etc. This possibility is being investigated and will be reported upon later.

That the action of filter paper is due to the products formed by the action of water or electrolyte alone upon the cellulose fibers, and not to the presence of soluble impurities in the filter paper, is shown by the fact that filter paper which has been repeatedly extracted with hot water is still capable of producing strong striations. In a particular case, filter paper which had been extracted with water for six hours in a Soxhlet apparatus was immersed in the silver nitrate electrolyte for ten minutes, and the liquid filtered off through purified asbestos and electrolyzed under usual conditions. Very pronounced striations were formed.

- 21. With relatively large anodes of pure silver, the "heavy anode liquid" is not appreciably abnormal. We have used the solution saved from the *inside* of the porous cups on previous runs, and obtained a deposit normal both in appearance and weight. The used solution from the *cathode* space of a Richards voltameter also, as might be expected, gives normal deposits. With the Rayleigh voltameter, used solutions generally give heavy deposits. We do not mean to say that used solutions from the Richards voltameter give absolutely normal deposits, as we have not made runs enough to establish that fact. But as far as we have tried them, they give substantially normal deposits; that is, within a very few parts in 100 000. We think the rôle of the "heavy anode liquid" has been greatly exaggerated. On the other hand, the evil effects of organic matter have not been fully appreciated.
- 22. It was pointed out by the Reichsanstalt in 1902 that filter paper reacted on silver nitrate, and might be a source of error in the voltameter. Others have warned against it without having investigated it. F. E. Smith, in his elaborate investigation of the subject recently published, repeatedly cautions us against the evil effect of filter paper. He found it increased the weight of the deposit when the silver nitrate was filtered hot, and when there was a large quantity of filter paper. He does not say that a single sheet used in a large voltameter produces no effect, but only claims that in the *voltameter as he used it*, the effect was negligible, and the voltameter was accurately reproducible. Although Smith's work was extremely well done, we doubt whether the effect of filter paper in his work was really entirely negligible.
- 23. We think that we have shown that the effect of filter paper is more serious than has been supposed, and that to permit its use in any degree is unwise. Because a voltameter is accurately reproducible when used with a large cup and a large quantity of electrolyte, and a heavy deposit with a single sheet of a particular

kind of filter paper, is not sufficient. A source of contamination so serious should be utterly avoided, and if possible a voltameter should be specified which is consistent with itself throughout a considerable range of dimensions and deposits.

24. We have recently employed a new form of voltameter in which an asbestos mat in a perforated glazed cup is used instead of the filter paper or porous cup. The purified asbestos is renewed each time, and of course the glazed porcelain is easily cleaned. This avoids the troublesome cleaning of the porous cups and perfectly separates the anode chamber from the cathode, without any reaction whatever on the electrolyte. In practice this form of voltameter is very satisfactory, provided there are very many fine holes in the glazed porcelain cups, so that the resistance is not excessive. The deposit has exactly the same appearance as in the Richards and Kohlrausch forms. We shall give more details of this form after we have had a larger experience with it.

Proposals and Suggestions of the Bureau of Standards.—I. That neither filter paper nor any other organic substance or impurity be used in the silver voltameter, and that the use of filter paper be entirely avoided in the preparation of the silver nitrate salt and the solution of the salt.

- 2. That when a porous cup is used it should be a thin fine-grained cup such as made by the Königliche Porzellan Manufaktur, Berlin, and the method employed of freeing it from acid or alkali should be controlled by noting whether the washed cup increases the conductivity of very pure distilled water on standing in it for some time.
- 3. That when a porous cup is not used to separate the anode and cathode, but a glass cup is used after the manner of Kohlrausch, that the anode should have as large an area as practicable, and be placed down in the bottom of the cup, so that the current flows up and over the edge of the cup. It is also well to have a glass guard ring in the surface of the solution to prevent particles brought up from the anode by bubbles of gas floating away and dropping down into the cathode deposit. The cup and guard ring should be so mounted that at the end of the run they and the anode can all be lifted out together.

- 4. That whatever form of voltameter be used, the deposit should never be considered normal unless free from striations, and appearing under the microscope as a mass of separate crystals, some of which have well-marked planes and angles. These crystals appear in the microscope more like glass or diamonds than a metal, except that in some illuminations they may have a metallic luster. Their appearance is a valuable check on the purity of the electrolyte.
- 5. That our observations respecting the effects of filter paper and other organic substances (cotton, linen, silk, wood, etc.) be verified by the other laboratories.
- 6. That our observations concerning the appearance of the deposit when examined under a low-power microscope and the criterion which it offers respecting the presence of impurities be verified.
- 7. That our experience with porous cups be checked, and any laboratory having a different experience should report to us, and if possible exchange cups with us, that we may aid in locating the cause of the difference.
- 8. That very careful comparisons be made between large cups and small cups, the electrolyte and the separator being the same, to see if a difference in the weight of deposit is found, and if so, to try to determine the reason.
- 9. That careful comparison be made between the Richards and Kohlrausch forms of voltameters (the electrolyte and size of cups being the same) to see whether any difference in weight occurs.
- 10. That the electrolyte employed in these investigations be prepared from the purest of silver nitrate and very pure distilled water, and that if any solution be used more than once, the record shall indicate its past history very carefully.
- 11. That in the use of the Richards form of voltameter special attention be given to determining whether there is any difference between a new porous cup and one that has been used before, and in the use of the Kohlrausch form attention be directed to devising a form of glass cup and mounting for the same that is convenient and satisfactory in practice.
- 12. Since the side reactions at the anode, and the size of crystals and adherence of deposit on the cathode, depend on the

current density and total mass of silver dissolved, or deposited per square centimeter, respectively, that attention be given in the investigation to ascertain what are the best values of these quantities for work of highest precision. The specifications adopted in London only set upper limits.

## 4. SUGGESTIONS OF THE BUREAU OF STANDARDS RESPECTING COOPERATIVE WORK IN WASHINGTON ON STANDARD CELLS

A new room has been especially fitted up for the cell comparisons, and ample space will be provided in the automatically regulated petroleum tanks for any number of cells which the representative of your institution may desire to bring here. In view of our experience with sealing wax and other sealing compounds, it is, however, urgently recommended that all cells be hermetically sealed. We have besides found this far simpler than the use of wax seals.

To make our arrangements complete, and to avoid delay in beginning the comparisons, we would be pleased to have you indicate in advance the approximate number of cells you propose to bring, and also their dimensions, diameter of limbs, distance between limbs, etc., so that we can have prepared any special mountings which might be necessary.

The necessary facilities will also be provided for setting up cells at the Bureau, and for such chemical work as may be found desirable.

With reference to the materials, we understand that you will bring with you sufficient quantities of all the chemicals employed in setting up your cells, so that if necessary check cells may be set up at the Bureau to determine the cause of any differences which might be found on comparison of the cells set up at the different laboratories. On our part, we shall have on hand an ample supply of all the materials, so that it will be possible to undertake any further investigations which might suggest themselves after conferring with each other.

With reference to the details in the specifications for the Weston cell, it may be advisable for each laboratory to indicate, after looking over the preliminary specifications submitted to the London Conference, any special points which might seem to call for further investigation.

Our own views may be put as follows:

A. Mercury.—In regard to the mercury, it will be readily agreed that it would be well to specify a preliminary treatment for the removal of accidental impurities, which might have a large influence on the electromotive force, with a subsequent distillation in a vacuum still, or under reduced pressure in a Hulett still.

In the opinion of the Bureau, the most effective method for the preliminary treatment is method b, page 4, Appendix to Report of London Conference. If facilities are available for the electrolytic preparation of mercurous sulphate, the same apparatus, with slight modification, can be used, making the method the simplest as well. This method has been subjected to a rigorous investigation at the Bureau, where it has been found that mercury, even contaminated with large quantities of zinc and cadmium, when subjected to the anode purification gave the same electromotive force to within several microvolts as mercury purified by Hulett's method. The differences were so small that they may have been due to slight differences in manipulation in setting up the cells employed to test the electromotive properties.

This result is readily accounted for since the impurities having a higher electrolytic solution tension than mercury will leave the mercury until their solution pressure is diminished by dilution to the solution tension of mercury. In addition, it appears from some recent work of Hulett's on the electromotive force of dilute amalgams that pure mercury in contact with cadmium sulphate solution reacts with the latter to form an extremely dilute cadmium amalgam, an equivalent amount of mercury going into solution in accordance with the principle of chemical equilibrium.

As a special precaution it is recommended that mercury thus purified be subjected to distillation in an ordinary vacuum still, or by Hulett's method, at greatly diminished pressure with a current of air passing through the mercury, by which bumping is practically eliminated. The additional function of the air in Hulett's method, of oxidizing impurities vaporized with the mercury, is no longer of importance since all the oxidizable impurities have practically been removed.

b. Mercurous Sulphate.—It is evident that the method of preparation should be selected which gives the best results as judged

from the rapidity with which the cells attain their normal values, their constancy under the most favorable conditions (when maintained at constant temperature) as well as the rapidity with which they adjust themselves to temperature changes.

In the opinion of the Bureau, it is desirable to have mercury distributed throughout the paste, and this can not be satisfactorily accomplished with white samples, without grinding them, by which a "size of grain" effect would be introduced. The best way, therefore, of introducing it is in its manufacture. Samples prepared by methods a, c, and d of the preliminary specifications, all contain finely divided mercury, so that by specifying one of these methods for the preparation of the mercurous sulphate, one step, the mixing of the mercury in the paste, can be omitted.

- c. Cadmium Sulphate.—Apparently the preliminary treatment of the commercial  $CdSO_4$  for the removal of iron by heating the solution to which an excess of basic cadmium sulphate<sup>a</sup> and a small quantity of  $H_2O_2$  have been added, filtering, precipitating by evaporating the water and finally slowly recrystallizing at room temperature from a solution either neutral or very slightly acid, will give a product answering all purposes.
- d. Cadmium Amalgam.—It will be necessary to specify either a method for the preparation of pure metallic cadmium, or a method for the preparation of cadmium amalgam by electrolysis of a cadmium sulphate solution made from previously recrystallized CdSO<sub>4</sub>. In the opinion of the Bureau, it would be simplest to specify the second method, as the preparation of pure cadmium is a much more difficult operation.

With regard to the composition of the amalgam, no difficulty should be found in coming to an agreement, since the two phases persist over a relatively wide range of composition and temperature.

In this connection, the question is raised as to whether it might not be regarded as a proper function for the national laboratories

a The basic cadmium sulphate is prepared as follows: To a concentrated solution of cadmium sulphate add enough strong ammonia to dissolve the precipitate which is first formed. Filter into a large volume of distilled water, filter off the precipitated basic sulphate and wash thoroughly with distilled water. Dry in an air bath and finally ignite, with frequent stirring, in a porcelain dish over a Bunsen burner to remove ammonium salts. The product is probably a mixture of oxide and sulphate, or basic sulphate. It is better to use this product than to attempt to prepare cadmium oxide by precipitation with fixed alkali, on account of the difficulty of completely removing the latter.

to furnish, to investigators and others, specially prepared or purified materials for use in standard cells. It appears to us that in this way the highest accuracy of reproduction would be obtained. Such materials, prepared at the different institutions, could be interchanged, and cells set up at each institution would bring to light any electromotive differences which might exist before their distribution is undertaken.

e. The Paste.—Especial attention is directed to the desirability of further investigating the cause of abnormal values sometimes found. In the work done at the Bureau on the temperature coefficient of the Weston cell, it was found that in most cases cells exhibiting abnormal initial values, as well as those falling to abnormally low values, showed considerable hysteresis when subjected to temperature changes. In some cases this was undoubtedly due to an improper mixture of the ingredients of the paste. This subject is regarded as of the greatest importance in the specifications, and will receive further attention at this laboratory.

In view of this, the Bureau desires to propose that all cells used for reference work be tested for hysteresis by transferring them from a bath maintained at 20° or 25° to another 5° or 10° lower, in which they should be kept at least 48 hours and then raised to the original temperature. Measurements should be made soon after the temperature changes, and at intervals, to determine the magnitude of the hysteresis, and any cells which do not come to normal values, within certain limits to be agreed upon and stated in the final specifications, should be rejected as untrustworthy.

Some success has been found with mercurous sulphate, prepared in acid solution by several different methods, and washed with absolute alcohol and anhydrous ether. It is hoped that in this way it may be possible to obtain dried mercurous sulphate which can be kept without suffering change, and which can be used without further treatment in making up the paste.

It is suggested that cells set up in connection with the international cooperative work be tested to determine whether they exhibit any appreciable hysteresis. In the temperature coefficient work it was found that much more marked hysteresis was exhibited on lowering the temperature than on raising it.

With regard to the setting up of cells, we wish to inquire whether any new cells have been set up and, if so, whether we could obtain a preliminary report of their behavior and their values in terms of the Bureau cells which may be in your possession. On our part we will shortly be prepared to set up a considerable number of cells in strict accordance with any special directions you may desire to submit. We would be greatly obliged for a sample of mercurous sulphate made by you, and in return we are sending you a sample of electrolytic mercurous sulphate recently made here. In this connection we would point out that in setting up cells, a better estimation of the accuracy of reproduction will be obtained if a separate lot of paste be made up for each cell or for, at most, two cells at a time.

### 5. NOTES ON THE WESTON NORMAL CELL

#### From the Bureau of Standards

### OUTLINE OF MATTERS TO BE SUBMITTED FOR DISCUSSION

- A. Revision of definition of Weston Normal Cell.
- B. Purification and preparation of materials.
  - (a) Mercury.
  - (b) Mercurous sulphate.
  - (c) Cadmium sulphate.
  - (d) Cadmium sulphate solution.
  - (e) Cadmium amalgam; cadmium; composition of amalgam.
- C. Setting up the cell.
  - (a) Washing mercurous sulphate; use of material already washed and dried.
  - (b) Composition of paste; Hg<sub>2</sub>SO<sub>4</sub>; CdSO<sub>4</sub>; solution; mercury in paste.
  - (c) Amalgamation of platinum terminals.
  - (d) Purity of platinum.
  - (e) Sealing.
- D. Hysteresis test.
- E. Proposal for distribution of purified materials for standard cells by National Laboratories under the auspices of the International Scientific Committee.
- F. Value to be adopted for Weston Normal Cell.
- G. Should value be changed to correspond to voltameter measurements made from time to time if apparent changes are within limits of accuracy with which the Weston Normal Cell can be produced.
- H. Best method of maintaining international agreement of values of Weston cell.

### DETAILED

- A. Schedule C should be replaced by a definition of the Weston Normal Cell and separate specifications and notes to the specifications.
- B. It is preferable to specify a single method unless a number of different methods have been shown to lead to identical results.

Methods should be selected which give minimum hysteresis and prompt attainment of normal values.

(a) Mercury-

Preliminary purification.

Alternative methods may be indicated. Bureau of Standards recommends anode purification.

Final purification.

Either in vacuum still or Hulett still.

(b) Mercurous sulphate.

Electrolytic method advocated on account of uniformity of product, ease of specification, absence of other materials than sulphuric acid, water, and mercury (with exception of platinum terminals and glass).

(c) Cadmium sulphate.

Purification by method in use here recommended.

(d) Preferable to have cadmium sulphate solution saturated to avoid possibility of leaching the CdSO<sub>4</sub>+8/3H<sub>2</sub>O crystals out of the paste.

(e) Preparation of metallic cadmium advocated if distribution by National Laboratories is decided upon. Amalgam to be prepared by heating together appropriate quantities of the ingredients.

Otherwise, electrolytic method of preparing the amalgam is recommended. Compositions may be changed to 10 per cent. Temperature limits of two-phase amalgam to be specified.

C. (a) Washing mercurous sulphate.

Washing with acid, alcohol, and ether, and drying in vacuo, and preservation in vacuo, recommended if distribution is to be undertaken by National Laboratories.

Otherwise, washing with saturated CdSO<sub>4</sub> solution is simplest to specify. First method would involve specifications for purification of the alcohol and ether.

(b) Composition of paste.

 $Hg_2SO: CdSO_4 + 8/3H_2O = 4: 1$  by volume.

 $CdSO_4+8/3H_2O$  to be very finely ground.

Sufficient CdSO<sub>4</sub> solution to make paste flow easily through filling tube.

- (c) Amalgamation of platinum terminals recommended as a special precaution.
- (d) Purest Heraeus platinum might be specified.
- (e) Hermetical sealing recommended.

D. Hysteresis.

Test should be made to determine amount of hysteresis of each cell. All cells having abnormal hysteresis should be rejected.

E. Strongly advocated by Bureau of Standards.

F. Must be decided after voltameter measurements.

G. Bureau would advocate retaining same value under the conditions stated in same way as has been done at the Reichsanstalt.

H. By periodic interchange of materials and cells and setting up new cells. Each laboratory to base its results on the mean value of a considerable number of cells. Values to be assigned to mean from results of international intercomparisons.

6. INSTRUCTIONS FOR THE GERMAN DELEGATE TAKING PART IN THE JOINT EXPERIMENTS IN WASHINGTON, APRIL, 1910

[Translation.]

Principal Aim of the Work.—At the London Conference in 1908 the value 1.0184 volts at 20° was provisionally adopted for the electromotive force of the Weston Standard Cell, but up to this time has been adopted in England only. Furthermore, a decision of the International Committee (circular of June 1, 1909) states:

It appears advantageous that a definite value for the Weston Standard Cell be adopted in the different countries simultaneously. For this purpose the values for the cell obtained by different observers from measurements with the silver voltameter should be in such agreement that the deviations of the different values from their mean value are less than 0.0001 volt. It was decided to postpone the adoption of a definite value for the standard cell until in the opinion of the committee such an accuracy has been obtained.

It is therefore to be regarded as the primary purpose of the projected joint work at Washington to lay the foundation for such a decision of the committee, in order that, by international acceptance of the value found, the long-striven-for uniformity in electrical units may be attained as soon as possible.

Plan of the Work.—(a) In order to fix with all the certainty possible the standard to which the measurements are referred, a more frequent comparison of the standards belonging to the different countries—resistances, standard cells, weights, etc.—will have to be made. It will be advantageous that a comparison of standard cells shall take place on every convenient occasion; the comparison of the other standards is necessary less frequently. The measurements will themselves show best upon what, in this connection, the greatest attention is to be laid.

(b) With the principal measurements it will be best so to carry out the work that, first of all, a sufficient number of measurements shall be undertaken in which all the cups shall be connected in series and in which the cup of each delegate shall be set up and manipulated according to the manner customary in his country. The value of the current, which flows through all the cups in common, and likewise the quantity of silver to be deposited must be agreed upon by the delegates. It appears to be unnecessary to hold the current by regulation at a constant value in the experi-

ments. It is sufficient if it is measured at suitable intervals. The measurements on the silver voltameter give simultaneously with the absolute values of the standard cell a relative comparison of the different silver voltameter methods.

(c) Special questions respecting the silver voltameter, such as, for example, the influence of the filter paper, weight of cup, etc., will best not be included in these measurements, but be reserved for further purely relative measurements. How far these shall be extended can not previously be estimated and must be left open to the later decision of the assembled delegates. The same is true with respect to questions having to do with the standard cell, preparation of the mercurous sulphate, etc. The extent of these special investigations will depend on how much time remains for them.

Order of Business.—In order to organize the joint work efficiently and to submit the results of the experiments in a form free from objection, it is to be recommended that an agreement may be reached on the following points. These individual points are to be regarded as proposals, which may be laid before a conference of the delegates in Washington.

- (a) First of all a council of the delegates with Director Stratton as chairman (or a substitute appointed by him) shall be held to discuss a plan for the work to be undertaken, the distribution of the various parts of the work among the participants, the allotment of the apparatus, etc., the minutes of which meeting, signed by the delegates, shall be prepared for the proceedings of the International Committee. This shall be done in the case of all other general discussions on the work. Copies of the minutes shall be given to each delegate.
- (b) The original notes of the observations (numerical data) of each observer shall be delivered to the secretary of the International Committee and kept sealed for the proceedings of the committee. Each delegate shall receive copies of these minutes, upon which the calculation of the results shall be made to rest.

A common record of the arrangement of each experiment is to be prepared and signed, of which the individual delegates shall each, in like manner, receive a copy. (c) At the close of the work a report to the International Committee shall be prepared by the delegates in common, which shall contain the essential results of their investigations. In this it will be well to submit those points upon which all the participants are agreed as being the common opinion of the delegates, but to expressly state the dissenting opinions of the single delegates on those points on which there remains a difference of opinion.

The report shall then be sent, printed in three languages (German, English, French) and with such numerical data as shall seem requisite to the delegates, to all the members of the committee, for their information and consideration.

(Signed) E. WARBURG.

# 7. REPORT OF EXPERIMENTS ON THE SILVER VOLTAMETER

From the Reichsanstalt

[Translation.]

In the following are communicated the results of experiments carried out by Dr. Feustel at the Physikalisch-Technische Reichsanstalt as a result of the stimulation of the Bureau of Standards to the investigation of the effect of organic substances on the silver equivalent.

First of all were considered relative measurements in which part of the silver anodes were wrapped in silk and part were without covering. In all of the experiments little glass cups were placed under the anodes.

The silver nitrate which was obtained from the gold and silver refining institution at Frankfurt was washed before being dissolved to remove any organic substance possibly adhering to it and was used unfiltered.

The treatment of the cups was the same as described in the work of Jaeger and von Steinwehr.

The silk was kept for a week in distilled water, daily renewed, and was carefully freed from the adhering anode slime after every experiment. The silk wrapping was attached with threads of the same piece of silk.

The current was 0.3 ampere in all the experiments; the length of the electrolysis varied between 1 hour and  $3\frac{1}{3}$  hours. The

quantity of silver deposited amounted, accordingly, to from 1.2 grams to 4 grams. No effect of the length of the electrolysis, and therefore of the weight deposited, on the relative weights was detected.

In Table I are contained the results of the relative comparisons with and without silk. From Table II it can be seen that a difference between the experiments with and without silk could not be established.

Further, other experiments on the influence of filter paper were carried out, which, however, are not yet finished. They indicate no effect on the amount of the deposit when small quantities of filter paper are present. Using larger quantities of filter paper, especially when finely divided, larger deposits were obtained. In particular, there seems to be present an influence working in the same direction, due to the illumination of the silver nitrate solution containing the filter paper.

The maximum increase of the silver deposits in the experiments, due to the use of filter paper, amounted to 20 parts in 100 000 of the whole value.

TABLE I
Results of Experiments

Number of experiment	Number of cup	Quantity of silver	Difference Δ	Меап	Δ in parts in 100 000
		g	mg	mg	
1	III IV *	1.2	$   \left\{     \begin{array}{r}     +0.127 \\     -0.127   \end{array}   \right. $	1199.912	$   \left\{ \begin{array}{c}     +10.6 \\     -10.6   \end{array} \right. $
2	III *	1.2	+0.165 -0.166	1193.977	{ +13.8 −13.8
	I		+0.162	)	+ 6.7
3	IV*	4 2.4	-0.181 +0.020	2413.482	$\begin{cases} -7.5 \\ +0.8 \end{cases}$
	I .	,	-0.031	ĺ	- 1.1
4	IV *	2.8	-0.088 +0.118	2780.919	- 3.2 + 4.2
	I II*		+0.261 -0.184		+ 6.5 - 4.6
5	III	4.0	+0.163	3994.800	+ 4.1
	( IV*		-0.241	}	- 6.0

The cups marked with an \* had anodes with silk wrapping.

TABLE II

With	silk	Withou	ıt silk
Number of experiment	Deviation in parts in 100 000	Number of experiment	Deviation in parts in 100 000
1	-10.6	1	+10.6
2	+13.8	2	-13.8
3	+ 0.8	3	+ 6.7 - 7.5
4	- 1.1 + 4.2	4	- 3.2
5	- 4.6	5	+ 6.5
	— 6.0 ——		+ 4.1
Mean	- 3.5	Mean	+ 3.4

CHARLOTTENBURG, GERMANY, March 21, 1910.

8. THE LAST INTERCOMPARISON OF THE NEW CADMIUM STANDARD CELLS OF SEC-TION I OF THE PHYSIKALISCH-TECHNISCHE REICHSANSTALT AND A FEW CELLS OF THE BUREAU OF STANDARDS AND NATIONAL PHYSICAL LABORATORY

German Cells

Cell	Emf	Cell	Emf	Cell	Emf	Cell	Emf	Cell	Emf
xm1	1.01866	$ym_1$	1.01867	zm <sub>1</sub>	1.01867	$a\mathbf{m}_1$	1.01871	$\beta$ m <sub>1</sub>	1.01867
$\mathbf{D}_1$	8675	$\mathbf{E}_1$	869	zm <sub>2</sub>	867	G <sub>1</sub>	873	$H_1$	869
$\mathbf{D}_2$	8675	$\mathbf{E}_2$	867	F <sub>1</sub>	870	$G_2$	872	$\mathbf{H}_2$	869 <sub>5</sub>
$\mathbf{D}_3$	867	$\mathbf{E}_3$	868	$\mathbf{F}_2$	869	G <sub>3</sub>	873	$H_3$	869
$\mathbf{D}_4$	8685	E4	868	$\mathbf{F}_3$	869	G,	873	$\mathbf{H}_{4}$	869
$\mathbf{D}_5$	8675	$\mathbf{E}_5$	867	.F4	869	G <sub>5</sub>	872	$H_5$	869
$\mathbf{D}_6$	871	E <sub>6</sub>	868	$\mathbf{F}_{5}$	8695	G <sub>6</sub>	873	$\mathbf{H}_{6}$	8695
$\mathbf{D}_{7}$	867	E7	866	$\mathbf{F}_6$	872	G <sub>7</sub>	871	H <sub>7</sub>	868 <sub>5</sub>
$\mathbf{D}_8$	867	$\mathbf{E}_8$	8665	$\mathbf{F}_{7}$	869	G <sub>8</sub>	872	$H_8$	867
$\mathbf{D}_{9}$	868	$\mathbf{E}_{9}$	867	$\mathbf{F}_8$	870	G <sub>9</sub>	873	$H_9$	869
$\mathbf{D}_{10}$	867₅	E10	8675	$\mathbf{F}_{9}$	870	G10	8735	$\mathbf{H}_{10}$	871
$\mathbf{D}_{11}$	867	E11	866	F <sub>10</sub>	869	G:1	874	$\mathbf{H}_{11}$	8705
$\mathbf{D}_{12}$	865	$\mathbf{E}_{12}$	867	F <sub>11</sub>	8675	G12	874	$\mathbf{H}_{12}$	8695
		E <sub>13</sub>	867	$\mathbf{F}_{12}$	867				
	1.018672		1.018672		1.018690		1.018727		1.018690

The sample of mercurous sulphate for each series of cells is designated by the same letters as for the first cell of the series; that is,  $xm_1$ ,  $ym_1$ , etc.

The cells taken to America were  $D_1$ ,  $D_2$ ,  $D_3$ ,  $D_4$ ,  $E_{10}$ ,  $E_{11}$ ,  $E_{12}$ ,  $E_{13}$ ,  $F_7$ ,  $F_8$ ,  $F_9$ ,  $F_{10}$ ,  $H_1$ ,  $H_2$ ,  $H_3$ .

Other Cells

	e		rman			An	ıerican	E	nglish
Cell	Emf	Cell	Emf	Cell	Emf	Cell	Emf	Cell	Emf
im <sub>1</sub> im <sub>2</sub> im <sub>3</sub> im <sub>4</sub>	1.01868 869 868 868 <sub>5</sub> 868	mmı mm"ı mm'ı	1.01871 870 <sub>5</sub> 871	nm <sub>1</sub> qm <sub>1</sub> rm <sub>1</sub> rm <sub>1</sub> rm <sub>1</sub> rm <sub>1</sub> rm <sub>1</sub> rm <sub>1</sub> sm <sub>1</sub> vm <sub>1</sub> wm <sub>1</sub> am <sub>1</sub> bm <sub>1</sub> bm <sub>2</sub> ap <sub>3</sub> ap <sub>4</sub>	1.01874 872 872 873 871 875 876 875 876 853 861 869 871 872 868	W183 W184 PW8	1.01866 865 <sub>5</sub> 865	NC <sub>1</sub> CB <sub>1</sub> AH <sub>6</sub>	1.01867 866 815
	1.018683		1.01870 <sub>8</sub>				1.018656		

As an arbitrary unit the electromotive force of a cell of the Weston Company was taken as 1.01896 volts. The measurements were made on March 14, 1910, between noon and 1 o'clock at 18°.8 °C. The values are not reduced.

Measurements in Section II on March 9 and 11, 1910

	American cells			English cells	
Cell	Mar. 9	Mar. 11	Cell	Mar. 9	Mar. 11
W 213	1.01860	1.01860	NPL 08	1.01862	1.01863
215	860	860	HA <sub>6</sub>	811	811
216	858	859	CB <sub>1</sub>	863	864
217	858	859	NC <sub>1</sub>	864	864
105	859	860	H 29	828	828
188	860	861	P 55	766	767
193	860	860	C 117	837	836
PW 8	860	859	C 12	858	858
W 184	862	863	NPL 05	857	857
W 183	863	863	L <sub>1</sub>	864	864
			$\mathbf{L}_2$	864	864
			$L_3$	865	864
			$Z_1$	864	864
			$\mathbf{Z}_2$	865	864
			$\mathbf{Z}_3$	865	864

Values are in terms of W 213, which was arbitrarily taken as 1.01860. Observations on March 9, 1910, were at 17.8 C, and on March 11, 1910, at 18.5 C. PW 8 had a high resistance.

# 9. REPORT ON RECENT WORK ON THE WESTON NORMAL CELL AND THE SILVER VOLTAMETER BY THE NATIONAL PHYSICAL LABORATORY

In 1907 three papers dealing with electrical standards were published by the National Physical Laboratory. These are:

- (1) "A New Current Weigher and a Determination of the emf of the Normal Weston Cadmium Cell." (Ayrton, Mather, and Smith.)
  - (2) "The Normal Weston Cadmium Cell." (Smith.)
  - (3) "The Silver Voltameter." (Smith, Mather, and Lowry.)

Since 1907 we have made many experiments with standard cells and with the silver voltameter; from time to time we have also determined the emf of the Weston Normal Cell by the aid of the Ayrton-Jones current balance and a standard resistance. The last of such emf determinations was made during the present month (March, 1910), and it is now of interest to compare the emf's of cells measured in 1905–1907 and 1910. The results of experiments with the silver voltameter are also given in this report, and these serve to show what defects in the voltameter remained undiscovered in 1906–7. In conjunction with the international ohm, the determinations also helped to fix the emf of the Weston Normal Cell in international volts.

In order to make the results of general interest and to enable them to be confirmed or otherwise, we have chosen May, 1907, as the date from which changes are most conveniently reckoned. The reason for this choice is that in that month 24 English and American (United States) cells were compared at the NPL and afterwards distributed among the following laboratories: Laboratoire Central of Paris, the Reichsanstalt, the Bureau of Standards, and the National Physical Laboratory. It is possible to state the emf in 1907 of all these cells and the present emf of two of the cells which were left at Teddington. At first we will limit our attention to the latter two cells, which are numbered W 181 and W 182.

These two cells were made at Washington in April, 1907, and the emf of either of these did not differ by so much as 1 part in 100 000 from the emf of any one of 21 of the other cells. The

remaining cell (W 105) was I part in 100 000 lower in emf than W 181 and W 182. We may safely assume therefore that in 1907 the four previously mentioned laboratories were in possession of cells of identical emf.

The emf of W 181 and W 182 can be obtained from papers (1) and (2). Referring to page 403 of the paper on the Weston Cell, we find the statement:

The mean emf of the 12 National Bureau of Standards' cells is less than the mean emf of the 12 NPL, cells by 3 microvolts. Also the mean emf of the 12 NPL, cells is not quite the mean of all the NPL, cadium cells which are believed to be normal; the latter cells have the higher mean by about 2 parts in 100 000.

Table I of the same paper gives the emf of 60 cells. The first 50 of these are regarded as normal and their mean emf is 1.01829<sub>3</sub> at 17° C, agreeing almost exactly (as it should do) with the value 1.01829<sub>7</sub> (or in round figures 1.01830) obtained with the aid of the current balance and the international ohm. (See p. 536).

We conclude, therefore, that the mean emf at 17 $^{\circ}$  C of the 24 cells was

$$1.01829_3 - 0.00002_2 = 1.01827$$
 very nearly,

this value being in terms of the ampere as realized by the current balance and the international ohm as realized at the NPL.

Further determinations of emf by means of the balance and a standard resistance were made in January, 1908; March and April, 1909; and in March, 1910. From intercomparisons of the cells W 181 and W 182 with others, the emf's of which were directly determined, we obtain the following results:

Date	Emf of W 181 at 17° C	Emf of W 182 at 17° C
May, 1907	1.01827	1.01827
January, 1908	26	27
March-April, 1909	24	25
March, 1910.	24	25
Apparent change in 3 years.	0.00003 v	0.00002 v

TABLE I

Cells W 181 and W 182 were set up 10 days before being sent to the NPL, during which time there was a fall in the emf of 1.3 parts in 100 000.

Having indicated the manner in which we have endeavored to determine the change in emf of standard cells, it will be sufficient to give the emf's of certain cells of general interest.

In 1904 Prof. Carhart gave to Dr. Glazebrook the two cells referred to in the paper by Carhart and Hulett as D 1 and D 2. The probable emf's of these cells on various dates are as follows:

TABLE II

Date .	D 1 at 17°	<b>D</b> 2 at 17°		
October, 1904.	1.01827	1.01826		
May, 1905	26	24		
October, 1905	26	23		
February, 1906.	24	22		
October, 1906	20	17		
May, 1907	10	05		
May, 1908.	04	00		
September, 1908	03	1.01798		
May, 1909	1.01796	93		
September, 1909	91	89		
March, 1910.	82	82		

Both cells contain electrolytic Hg2SO4.

In October, 1908, Dr. Rosa brought a number of cells to Teddington, which were set up by Dr. Wolff and Dr. Waters at the Bureau of Standards. Four of these cells were left in our possession, and we conclude that the emf's have changed as shown in Table III. The values given are at 17° C.

TABLE III

Date	W 206	W 208	W 211	<b>W</b> 212
October, 1908.	1.01825	1.01825	1.01825	1.01825
March-April, 1909	25	24	23	25
March, 1910	25	24	23	24

All of the cells in Table III contain electrolytic mercurous sulphate.

From Prof. Janet we have received six cells. In June, 1909, we received also a sample of electrolytic mercurous sulphate and some of it was used in setting up six cells. Three of these we sent

to Paris, but they were hopelessly damaged in transit; the remaining three are at Teddington and we have numbered them JAN 1, 2, and 3, respectively.

The electromotive force of all the French cells are given in Table IV. Values at 17° C.

TABLE IV

Cell	Hg₂SO₄	June, 1908	September, 1908	February, 1909	June, 1909	August, 1909	March, 1910
E 10	El. A. C	1.01839	1.01841			1.01833	1.01833
E 8	do	38	38			32	32
v	Chemical (acid).	14	15			15	15
J 6	El. D. C			1.01826		15	05
J7	do			24		1.01792	1.01793
S 6	do			33		1.01819	1.01820
	do				1.01830	31	31
JAN 2	do				30	31	31
JAN 3	do				30	31	. 31

We have not received any cells from Berlin, but in July, 1908, Dr. Warburg very kindly forwarded a dry sample of mercurous sulphate which had been washed with water. The salt was quite white. In September, 1908, we used this salt in the preparation of 17 cells. At the same time we prepared some mercurous sulphate and washed part of it with water and part with saturated cadmium sulphate solution. The results of our observations are given in Table V.

TABLE V Values at 17° C

Cell	Hg <sub>2</sub> SO <sub>4</sub>	September, 1908	December,	September, 1909	December, 1909	March, 1910
T 1 T 2 T 3 T 4 T 5 T 6 T 7 T 8 T 9	PTR, mixed with cadmium sulphate crystals and made into paste  PTR, washed with 2 lots of water for 30 minutes before making into paste	1.01828 28 28 28 28 30 30 31 30 30	1.01830 29 29 28 26 28 28 28 28 28	1.01829 29 29 29 29 18 21 27 26 26	1.01829 29 28 28 14 17 28 27 27	1.01828 29 29 28 09 13 27 26 27
T 10 T 11 T 12 V 1	NPL, washed as T 1 to 4	30 28 28 28	29 29 29	22 28 28 26	22 28 28 25	21 28 28 24
V 2 V 3 V 4 V 5 V 9	PTR, in contact with 150 cc of water for 3 days; water changed 6 times  NPL, washed with cadmium sulphate solution only	28 28 28 28 28 26 26	24 28 28 27 24 25	24 27 23 25 25 25	22 24 21 25 24 24	22 23 21 25 24

We have now to report on the cells made at the NPL, and we think it desirable, in the first place, to indicate the changes which have resulted in the cells reported on in the paper on the Weston Normal Cell. The values are given for December of each year. Temperature, 17° C.

TABLE VI

С _	ell	Hg <sub>2</sub> SO <sub>4</sub>	Decem- ber, 1904	December, 1905	December, 1906	December, 1907	December, 1908	Decem- ber, 1909
В	41	Chem. pptd			1.01829	1.01829	1.01827	1.01826
	42	do			29	28	27	27
	43	do			29	29	28	28
1	.49	do			28	27	24	25
1	.51	do			28	27	27	27
CH	10	Chem	1.01830	1.01830	29	27	26	27
	11	do	29	28	28	28	28	27
	16	do	31	30	28	28	28	2
	25	do	32	31	30	31	31	. 32
	26	do	30	32	31	31	29	29
	27	do	32	32	31	30	27	25
	12	do	30	29	29	27	27	2'
	51		31	32	28	26	25	24
		do	30	30	32	30	26	2.
		do	33	31	30	28	26	2.
		do	31	29	28	20	19	16
		do	29	26	26	Broken		
		do		34	33	Broken		
		do		33	31	1.01831	30	30
							5.	29
		do		33	31	30	29	
		do		30	34	30	29	30
		do		28	27	28	28	28
		do		28	24	23	22	20
		do	•••••	28	26	26	26	26
	23			29	31	30	30	30
		do		30	32	31	30	3:
		do		32	31	31	30	3:
	26	do		31	32	31	30	3:
		do		32	30	30	31	30
HA	1	Chem. pptd			30	26	1.01794	1.01723
	2	do			30	28	1.01817	1.01807
	3	do			32	24	00	1.01796
	4	do			31	30	24	1.01816
	5	do			30	27	24	22
	6	do			30	27	25	20
R	1	Recryst			32	31	31	31
	2	do			32	31	30	30
	3	do			32	31	. 31	30
E	80				29	Broken open		
	81	do			29	Broken open		
		do			31	Broken open		
		do			27	Broken open		
	7				31	1.01830	30	29
		do			30	30	30	29
		do			30	30	29	29
		do			28	28	27	27
P 4	10				. 20	29	25	22
		do				29	27	26
		do				30	. 26	24

TABLE VI—Continued

c	ell	Hg <sub>2</sub> SO <sub>4</sub>	December, 1904	December, 1905	December, 1906	December, 1907	Decem- ber, 1908	December, 1909
AB	1	Nord		22	21	21	21	20
	2	do		20	19	18	17	17
D	1	Electrolytic		22	07	1.01792	1.01741	1.01705
	2	do		17	10	Broken open		
	3	do		15	07	Broken open		
	4	Nord		26	23	1.01819	1.01810	1.01806
	5	do		26	20	16	00	1.01789
M	6	)						
	7	}		Broken open				
	8	J						
		<u> </u>			1			

Note.—The last ten are given as examples of abnormal cells.

It is of interest to note that of the cells which in 1907 appeared to be quite normal, the cells HA I to 6 have since changed considerably. These cells were used to obtain the recovery curves after short circuiting, shown on pages 412-413 of the paper on the Weston Normal Cell.

Since 1907 very many cells have been made. These contain many different samples of mercurous sulphate. On December 10, 1909, 210 cells were intercompared. The emf's at 17° C were as follows:

TABLE VII

No.	No. Remarks		Mean
5	Emf's greater than	1.01830	
6	Emt's equal to	30	
8	do	28	
25	do	27	
26	do	26	
53	do	25	1.01825
66	do	24	
9	do	23	
8	do	22	
	do	21	
3		1.01820	

Observations on cadmium amalgams have been published in full and are not referred to in this report.

The silver voltameter.—In determining the electrochemical equivalent of silver we have measured the current by a combina-

tion of a number of cells in parallel and a standard resistance, the combination being frequently standardized by means of the current balance.

Our solutions contained either 10 or 15 per cent of silver nitrate, the latter being obtained from a number of sources. At times the salt was fused in a platinum crucible in an electric oven, the crucible being covered over with glass so as to exclude all dust, etc.

The form of voltameter termed "New Form" is not described here, but four such voltameters will be brought to Washington.

With regard to the deposits, close inspection showed that those in the Rayleigh form of voltameter were always slightly striated and those in other forms were either free from striæ or only slightly striated.

In no instance (except on January 30, 1910, and observations previous to November 8, 1909) were the solutions filtered through filter paper before using; purified asbestos was, however, used.

The results are given in Table VIII.

TABLE VIII

					Rayleigh greater than—		
Date	Silver nitrate	Voltameter	Deposit	E. C. E.	Syphon	New Form	Rich- ards
1909							
Feb. 11	Recryst. F. E. S	Rayleigh	6,99962	1.118262			
	Do	do	6.99942	8231		<b>-</b>	
18	Harrington (1)	do	6.99874	8250			
	Harrington (2)	do	6.99842	8200			
23	Recryst. F. E. S	do	7.00122	8282		<b></b>	
	Harrington (2)	do	7.00060	8185		<b></b>	
	Do	do	7.00051	8171			
	Recryst. F. E. S	do	7.00115	8271			
Mar. 11	Recryst. Barr	do	7.19855	8227			
	Harn. (2) Recryst	do	7.19860	8236			
	Recryst. F. E. S	do	7.19876	8260			• • • • • • •
30	Harn. (3)	do	6.99959	8445		<b></b> .	
	Harn. (3) Recryst	do	6.99868	8302		<b></b> .	
Apr. 5	Recryst. Barr	do	6.99900	8271		<b></b>	
19	Recryst. Barr	do	7.00083	8302		<b></b>	
Nov. 8	Merck's	do	7.00554		5		
	Do	Syphon	7.00518				
16	Harrington (1)	Rayleigh	7.00138		-4		
		Syphon	7.00166		ll		

# TABLE VIII-Continued

					Rayleig	h greate:	than—
Date	Silver nitrate	Voltameter	Deposit	E. C. E.	Syphon	New Form	Rich- ards
1910							
Jan. 13	Recryst. F. E. S	Rayleigh	7.00711		10		
		Do	7.00716				
		Syphon	7.00642				
17	Recryst. F. E. S	Rayleigh	7.00349		5		12
		Do	7.00355				
		Syphon	7.00315				
		Richards	7.00263				
20	Recryst. B. & T. (fused)	Rayleigh	7.01432		1		
		Syphon	7.01438				
	Recryst. F. E. S.	Rayleigh	7.01441		12		
	Do	Syphon	7.01354				
27	Recryst. B. & T. (fused)	Rayleigh	7.02488		11		
		Syphon	7.02408				
	(Filter paper)	Rayleigh b	7.02617				
30	Recryst. F. E. S	do	7.00625		_		
	(Filtered through paper)	Syphon	7.00618				
		Richards	7.00606				3
		Do	7.00596				4
Feb. 16	Recryst. F. E. S	Rayleigh	7.00090				13
	Do	Richards	7.00000				13
	Do	Rayleigh	7.00092				
	Do	Syphon	7.00071	4 4100	3		
28	Recryst. F. E. S	Rayleigh	6.99832	1.118274		12	
25- 4	Description of	New Form	6.99749	8144		9	
Mar. 4	Recryst. F. E. S	Rayleigh	6.99879	8252		9	
		New Form	6.99815	8150			10
7	Harn. (1)	Richards	6.99808 7.00040	814 <sub>0</sub> 828 <sub>0</sub>			10
'	Hain. (1)	New Form	6.99979	8184			
9	L. C. E	Rayleigh	6.99980	8304		1	
,	Recryst. F. E. S.	do	6.99952	8260			1
	Do	New Form	6.99876	8140		14	
11	Recryst. F. E. S.		7.00032	8240			
11	Recryst. B. & T.		7.00052	8268			
	Merck's	do	7.00036	8231			
	Do	New Form	6.99966	8135			
14			7.00078	8259			
- 1	Do		7.00078	8171			
		do	7.00001	8135		1	
			1100001	1			

 $<sup>^</sup>b$  In this case 4 large filter papers were inserted in 500 cc of the solution and the latter put on one side for 7 days. The solution was then used in the Rayleigh form.

The values for the electrochemical equivalent as obtained from the Rayleigh form with electrolyte believed to be pure are:

1.118261	1.118227	1.118302	1.118260
231	235	274	240
250	260	252	268
282	$3O_2$	280	231
271	271	304	259

Mean =  $1.11826_3$ , a value agreeing within less than 1 part in 100 000 with that of 1905-7.

The values for the electrochemical equivalent as obtained with the New Form are:

1.118144	1.118135
I 5 <sub>0</sub>	171
184	135
I40	

Mean = 1.11815<sub>1</sub>, which is 10 parts in 100 000 less than with the Rayleigh form as we have used it. We have found this New Form to be very convenient in practice.

We think it best to now state the emf of the standard cells which we propose to bring to Washington. Of the cells already reported on we have chosen a number of abnormal ones, as an examination of them may be profitable. In addition we are bringing 34 cells, of which 33 have been set up since October, 1909. These 33 cells are in nine groups, and no two groups contain mercurous sulphate from the same sample. The amalgams in the 33 cells contain 10 per cent of cadmium. Without exception all of the cells have fallen in emf by 1 to 2 parts in 100 000 since the day on which they were set up.

S 35 was made in March, 1909, and during the whole of last summer it was exposed to the action of direct sunlight. The exposed surface of the paste is now coal black.

The emf's are given in international volts at 20° C, the international ohm being taken as equal to the ohm realized from the NPL mercury standards of resistance, and the international ampere that realized when the New Form of voltameter is used with a pure electrolyte.

TABLE IX  $\label{eq:Values} \mbox{Values in International Volts at } 20^{\circ}\,\mbox{C}$ 

Value	Cell	Value
1.01833	(T 1	1.01829
1.01816	T 2	1.01830
1.01821	\T 5	1.01810
1.01832	T 6 ·	1.01814
1.01783	V 3	1.01824
1.01783	181	1.01825
	1.01833 1.01816 1.01821 1.01832 1.01783	1.01833

## New Cells

Cells	Paste	Set up—	Mean emf Febru- ary, 1910
A. 1. 2. 3. 4. 5.	A	October, 1909	1.01825-6
B. 1. 2. 3.	В	Do.	26-7
C. 1. 2.	С	Do.	26-7
D. 1. 2. 3.	D	November, 1909	27-8
E. 1. 2. 3. 4.	E	Do.	27–8
F. 1. 2. 3. 4.	F	Do.	27-8
G. 1. 2. 3. 4. 5.	G	January, 1910	28-9
H. 1. 2. 3. 4. 5.	H	Do.	28-9
K. 1. 2. 3.	K	February, 1910	27-8
S. 35	s	March, 1909	27
			Mean c 1.01826-7

c If made with 121/2 per cent amalgam probable value=1.01828-0.

It is now desirable to state the results of our observations on normal and abnormal cells. It has been previously shown that the presence of free acid in a cell results in a lowering of the emf and Hulett has suggested that the fall of emf of his cells (such as D I and D 2) is due to hydrolysis of the mercurous sulphate by cadmium sulphate solution in the absence of acid. Cells containing free acid, although lower in emf, are quite stable—in fact they appear to be more stable than cells believed to be acid free.

Examination of Table V suggests that if part of some freshly precipitated mercurous sulphate is washed in the usual way with

cadmium sulphate solution until apparently free from acid, and a second part is washed with water, cells containing the two samples will differ in emf by about 4 to 5 parts in 100 000, the cells with water-washed mercurous sulphate having the higher voltage. If the washing with water is not prolonged the cells containing the water-washed salt appear to remain stable—at least for several years. On the other hand prolonged washing appears to result in the cells remaining stable for a considerable time, such as 12 months, but afterwards irregularities become very marked.

Most of our cells which we regard as stable vary in emf from 1.01825 to 1.01830 international volts at 20° C. Very few are lower than 1.01825. It appears to us to be probable that in many cases the mercurous sulphate has retained a small quantity of acid which has been slowly liberated after the cell has been set up and as a result there has been a gradual fall in emf to a steady value approximating to 1.01826. The presence of this small quantity of acid appears also to be favorable to the stability of the cell. In a few cases the washing has been very thorough—in some cases the process being conducted a second time after an interval of some months. These cells have been slightly higher in emf and in some cases have become unstable after a number of years. At present we have a number of cells under observation which contain paste washed in different ways, but two or three years must elapse before decisive evidence is obtained.

From all the observations recorded in this report we conclude that the emf of the Western Normal Cell is

# 1.01827±0.00002 International Volts at 20° C.

The best value stated to 1 part in 10 000 appears to be 1.0183, the international ohm being obtained from the NPL mercury standards of resistance and the international ampere from a form of silver voltameter in which the electrolyte is uncontaminated with filter paper either before or during electrolysis.

# 10. SUGGESTIONS FOR EXPERIMENTAL WORK AT WASHINGTON, D. C. By F. E. Smith

1. Consideration of reports and suggestions handed in by the four delegates.

- 2. Consideration of the form of the report to be prepared by the delegates.
  - 3. Comparison of resistance coils, standard cells, weights.
- 4. Decision as to the limits within which the emf of the cell shall be stated.
- 5. Examination of the voltameter circuit, especially as regards insulation of parts, etc.
- 6. Choice of some cells to temporarily represent the Weston Normal Cell.
- 7. Choice of one or more forms of voltameter to be experimented with.
- 8. Comparison of the different samples of silver nitrate. Decision to be arrived at as to the best mode of preparation.
- 9. Decision as to effects of temperature, pressure, anodic impurities, organic matter.
  - 10. Comparison of the different forms of voltameters.
  - 11. Determination of the emf of some cells.
- 12. Decision as to: (a) Depolariser, i. e., its preparation and washing; (b) the amalgam, its preparation and composition; (c) the range of temperature.
- 13. Comparison of results at Washington with previous results at Washington, Berlin, Paris, and Teddington, and decision as to value of the emf of the cell.

#### 13. SUGGESTIONS FOR EXPERIMENTAL WORK

#### By M. F. Laporte

#### [Translation]

Before the value of the electromotive force of the Weston Normal Cell in international volts can be fixed, it is necessary to carry out first the following preparatory work:

- 1. To determine the best procedure in assembling the voltameter and for purifying the electrolyte to assure the constancy of the deposit.
- 2. To determine the method of making and purifying the chemicals and the construction best suited to yield cells of the same electromotive force.

3. A comparison of values obtained for the ohm by the indirect means of comparing the metallic copies.

The work might be carried out as follows:

- 1. The Silver Voltameter.
  - (1) A comparison of weights of deposit in several voltameters in series.

(2) A determination of satisfactory forms.

- (3) A determination of a satisfactory process of purifying the silver nitrate.
- (4) The limits observed in previous experiments for the current density, the concentration, the temperature, and the pressure should be indicated as provisional limits of precision to be verified later on. In the course of the work the verification of the method of microscopic examination (of the deposits) should find its place.
- 2. Standard Cell.
  - (1) A comparison of cells made in different laboratories.
  - (2) A comparison of cells made at the Bureau of Standards from materials prepared by different methods in different laboratories.

(A further study in case of differences arising.)

- (3) A determination of how the mercurous sulphate should be washed to yield a cell that will at once assume its normal electromotive force.
- 3. The Ohm.
  - A comparison of metallic copies and a determination of the relative values of the ohm.

This work can be only partially done (the ohms of M. Benoît not being finished, but their comparison in the future with the metallic resistances expressed in terms of the present LCE ohm will permit them to be connected with the other values). The differences between the ohms will moreover be certainly less than I part in 10 000. Thus it seems that agreement can be reached for the electromotive force of the Weston element if one is content with four decimal places.

If this program can be carried out then the value resulting from new experiments will show directly the value of the electromotive force of the Weston Cell under the most favorable circumstances, and, if possible, without a correction factor.

This determination will be made in terms of a provisional value of the ohm pending the final value, which can not be obtained until the termination of the researches now in progress.

# APPENDIX B. LIST OF APPARATUS, STANDARD CELLS, AND MATERIALS BROUGHT BY THE DELEGATES FOR THE WORK OF THIS COMMITTEE

## 1. FROM THE PHYSIKALISCH-TECHNISCHE REICHSANSTALT

- (a) Resistances, Standard Cells, Weights, etc.—Two 1-ohm coils of manganin, O. Wolff, No. 2836, 2838; 1000-ohm coil in paraffin oil, O. Wolff, No. 4089; brass weights (3, 2, 1, 1 g); platinum and aluminum weights (400, 300, 200, 100, 40, 30, 20, 10, 4, 3, 2, 1 mg, and fractions of 1 mg); two platinum ballast weights of about 10 g and 50 g; 15 standard cells, viz ( $D_1$ ,  $D_2$ ,  $D_3$ ,  $D_4$  of the xm<sub>1</sub>" series;  $E_{10}$ ,  $E_{11}$ ,  $E_{12}$ ,  $E_{13}$  of the ym<sub>1</sub>" series;  $F_7$ ,  $F_8$ ,  $F_9$ ,  $F_{10}$  of the zm<sub>1</sub>" series;  $F_1$ ,  $F_2$ ,  $F_3$  of the \$\frac{\pi}{2}m\frac{\pi}{2}\$ series.
- (b) Other Apparatus and Chemicals.—Two platinum cups marked I and III, with accessory apparatus; 10 silver anodes, platinum tongs, etc.; 1 kg silver nitrate (fused) from the Gold-und Silber-Scheide-Anstalt, Frankfurt a. M.; two samples of mercurous sulphate in cadmium sulphate solution; one bottle saturated solution of cadmium sulphate, 12½ per cent cadmium amalgam; 10 cmpty tubes for making standard cells; mercury.

### 2. FROM THE NATIONAL PHYSICAL LABORATORY

- (a) Resistances, Standard Cells, Weights, etc.—One sealed manganin coil L 17; one open strip manganin coil L 87; two weights (5 g and 2 g); 34 standard cells (NPL cells, 1909–10), viz: A<sub>1</sub>, A<sub>2</sub>, A<sub>3</sub>, A<sub>4</sub>, A<sub>5</sub>; B<sub>1</sub>, B<sub>2</sub>, B<sub>3</sub>; C<sub>1</sub>, C<sub>2</sub>; D<sub>1</sub>, D<sub>2</sub>, D<sub>3</sub>; E<sub>1</sub>, E<sub>2</sub>, E<sub>3</sub>, E<sub>4</sub>; F<sub>1</sub>, F<sub>2</sub>, F<sub>3</sub>, F<sub>4</sub>; G<sub>1</sub>, G<sub>2</sub>, G<sub>3</sub>, G<sub>4</sub>, G<sub>5</sub>; H<sub>1</sub>, H<sub>2</sub>, H<sub>3</sub>, H<sub>4</sub>, H<sub>5</sub>; K<sub>1</sub>, K<sub>2</sub>, K<sub>3</sub>).
- (b) Other Apparatus and Chemicals.—Four platinum bowls, spatula and tongs; 4 voltameter stands, with parts for the Rayleigh form and the new form; 6 silver anodes; 200 filter papers (as purchased); 2 porous cups; 36 H-vessels for standard cells; two 4-limb vessels; 8-oz cadmium; 1 bottle of mercury (about 2 kg); 2 bottles of cadmium sulphate solution sufficient for 200 cells; 2 bottles of cadmium sulphate crystals sufficient for 200 cells; 5 samples of mercurous sulphate sufficient for 200 cells; 7 lbs silver nitrate (3 lbs recrystallized by F. E. S., 2 lbs from Baird and Tatlock and 2 lbs from Merck); 2 glass siphons.

## 3. FROM THE LABORATOIRE CENTRAL D'ÉLECTRICITÉ

- (a) Resistances, Standard Cells.—One box of five 1-ohm coils, J. Carpentier, 1417-K; one 1-ohm coil, Otto Wolff, No. 3961; 15 standard cells, viz (E<sub>8</sub>, E<sub>12</sub>, E<sub>13</sub>, E<sub>14</sub>; D<sub>2</sub>, D<sub>3</sub>; P<sub>1</sub>, P<sub>2</sub>, P<sub>3</sub>; S<sub>2</sub>, S<sub>4</sub>, S<sub>5</sub>, S<sub>7</sub>, S<sub>8</sub>; Z<sub>2</sub>).
- (b) Other Apparatus, Chemicals, etc.—Two voltameter stands; 2 platinum cups for cathodes; 2 silver cups for anodes; 4 silver anodes (two hemispherical, two disks); 2 siphons; 1 glass spoon; 2 kg of pure silver nitrate (commercial) from the Maison Poulene frères; 400 to 500 g silver nitrate crystallized twice in a vacuum at less than 50°; 12 H-shaped tubes for standard cells; 1 bottle of purified cadmium sulphate; 1 bottle of mercurous sulphate, obtained by electrolysis with alternating current; 1 bottle of cadmium amalgam; filter paper "free from chlorine," No. 595, from Schleicher and Schüll; congo paper.

#### 4. FROM THE BUREAU OF STANDARDS

(a) Resistances, Standard Cells, Weights, etc.—Resistances used in the comparisons, Nos. 3, 7, 8, 3939, 3940. (For list of standard cells selected for the intercomparisons, see Appendix C, 2, Table VI.) Special weights,  $\dot{S}$ ,  $\ddot{S}$ ,  $\Sigma$  and a box, NBS 6550.

(b) Other Apparatus, Chemicals, etc.—Eight platinum cups; 2 gold cups; 10 mountings for voltameters; 2 kg silver nitrate from the Gold-und Silber-Scheide-Anstalt in Frankfurt (unfused); a collection of anodes for different forms of voltameters; a collection of porous cups of different sizes for the Richards voltameter; 3 siphons for the siphon voltameter; 4 special glass vessels for the Kohlrausch form; pure silk thoroughly washed for use in the Kohlrausch form; filter paper and filter tubes for the Rayleigh form, besides apparatus and chemicals for investigations with the voltameters; materials for standard cells.

## APPENDIX C. DESCRIPTION OF THE EXPERIMENTS

## 1. RESISTANCE MEASUREMENTS

Each delegate brought with him one or more resistance standards with the object of furnishing additional data on the relative values of the unit of resistance employed in the four laboratories, and of deriving a basis for the voltameter measurements made in Washington. The results obtained also served the further purpose of establishing the magnitude of one of the corrections to be applied to the voltameter measurements previously made by the delegates, to reduce them to a strictly comparative basis. The unit of resistance which it was agreed to adopt will also be employed in the voltameter work to be undertaken in the immediate future. The opinion is further expressed that as soon as primary mercurial standards, in strict conformity with the specifications adopted by the London Conference, have been realized in the four institutions, a common unit of resistance, based upon all such mercurial standards, will be adopted for international use.

# Description of the Standards

(a) The Standards of the National Physical Laboratory.—Two coils, L 17 and L 87, were submitted for comparison. L 17 is a sealed standard, otherwise embodying the main features of the Reichsanstalt type. The coil is wound with manganin wire, but is not provided with potential terminals. It bears the date 1902, the case having been reconstructed in 1909.

The temperature formula, as calculated from the chart submitted, was found to be

 $R_t = R_{20} \{1 + 0.000 \text{ o20 o } (t - 20) - 0.000 \text{ o00 } 4_t (t - 20)^2\}$  in the range 10° to 22°

As this range did not include 25°, the temperature at which practically all the measurements were made, the 20°-25° difference in value was directly determined in Washington, and was used in reducing the results, as was also the case with all the other coils except the Carpentier box of the Laboratoire Central, described below.

L 87 is an open coil, provided with potential terminals and constructed for high-current carrying capacity, being wound with manganin strip about 8 mm wide on a frame composed of six insulating posts, 12 cm long, equally spaced in a circle 8 cm in diameter. It was brought to Washington for inclusion in the voltameter circuit, and was not submitted as a resistance standard.

The temperature formula, calculated from the chart submitted and covering the range  $10^{\circ} - 22^{\circ}$ , is as follows:

$$R_t = R_{20} \{ 1 + 0.0000140 (t - 20) - 0.00000048 (t - 20)^2 \}$$

The differences in millionths between the values at 20° and 25° by the above formulæ, and by direct observation, are given below. The agreement may be regarded as entirely satisfactory, particularly as the original observations did not extend to 25°.

Coil	Differences by formula 25°-20°	Observed difference 25°-20°
<b>L</b> 17	89	89
L 87	58	57

(b) The Standards of the Physikalisch-Technische Reichsanstalt.—Two open 1-ohm standards of the Reichsanstalt type, with potential terminals, and one sealed small type 1000-ohm coil, all constructed by Otto Wolff, were submitted.

The 1-ohm coils are provided with an extra pair of binding posts so that they may be connected in a circuit without the aid of mercury cups.

Wolff No. 2836 bears the mark K 108, and Wolff 2838 bears the mark K 109. The following values were certified by the Reichsanstalt:

Coil	R <sub>18</sub> °	a <sub>l8</sub> °	β <sub>18</sub> °
2836	1.000 0705	+.000 013 5	000 000 42
2838	1.000 0695	+.000 013 4	000 000 3 <sub>3</sub>

the temperature formula being of the form

$$R_t = R_{18^{\circ}} \{ \mathbf{1} + \alpha(\mathbf{t} - \mathbf{18}) + \beta(\mathbf{t} - \mathbf{18})^2 \}$$

The 1000-ohm coil, No. 4089, contains paraffin oil which had stood for a long time exposed to air of 55 per cent humidity. The value certified from measurements made in the laboratory of Prof. Lindeck, over the period December 30, 1909, to March 9, 1910, is 1000.055 ohms, at 18° C. The values given for  $\alpha$  and  $\beta$  of the above formula are  $\alpha = +.000$  014 0,  $\beta = -.000$  000  $4_3$  corresponding to an increase in resistance of 77 parts per million between 18° and 25° C.

(c) The Standards of the Laboratoire Central d'Électricité.—These consisted of an open 1-ohm Wolff standard, No. 3961, of the Reichsanstalt type, marked PTR 97 1908, and a Carpentier box of five 1-ohm sections. The values found for No. 3961 and given by M. Jouaust 5 are as follows:

TABLE I

Date	Resistance at 18°	Measurements at
Sept., 1908	0. 999 981	
July, 1909	0. 999 994	PTR
Apr., 1909	0. 999 977	NPL
Oct., 1908	1.000 10	1
Jan., 1909	1.000 13	1
May, 1909	1.000 115	LCE
Aug., 1909	1. 000 116	

<sup>5</sup> Bull. Soc. Int. Elect., 10, p. 187; 1910.

The Carpentier box is marked "1417 K." The coils are wound on threaded porcelain tubes, three coils in parallel forming each 1-ohm section. The terminals of the sections are permanently connected, each by an independent rod, to six rectangular brass blocks, situated between two parallel brass bars to which the coils may be connected by the aid of plugs connecting the blocks

to the bars. The plugs are of special construction, the milled head being hollow and threaded to receive the stem, which carries near its lower end a rectangular projection of such size as to pass through the rectangular spaces between the bars and blocks. On turning the head, the rectangular contact piece is rotated against stops, and further rotation of the head clamps it against the under side of the block and bar. The bars terminate in heavy copper rods (bent downward at 8 cm from the bars) which serve to make external electrical connections. As used at the Laboratoire Central, the box is placed in series with a standard, with which it is to be compared, the standard or box being alternately short circuited, which is accomplished in the case of the box by inserting the two plugs in the holes at the ends of the same block. The measurements are thus made by the substitution method, the connecting resistance remaining practically the same. The variable length of the bar included is eliminated by making measurements with the plugs in the two possible positions, measurements of the comparison coil being made with the plugs at the opposite ends of both contact blocks in turn. For purposes of the very highest precision, all forms of plug contacts are to be considered objectionable, as the plug contact resistance is subject to some variation which may amount to several hundred-thousandths of an ohm. The measurements given below were made at 20°, and for the above reason the values of the coils were determined between potential terminals.

These may be chosen in two ways, as each section can be connected through the contact blocks to the bars by inserting the plugs at the two pairs of diagonally opposite ends of the terminal blocks, thus including slightly different connecting resistances, the coils being connected to the blocks by independent rods to either side of the center. For this reason the connections were always made in the following way: With the box turned so that its terminals are to the left of the observer, the plug making connections to the upper bar was to the right of the corresponding plug making connections to the lower bar. The small binding posts on the blocks were used as current terminals, and the large binding posts on the bars were used as potential terminals.

The values certified by the LCE from measurements by the method of substitution were:

Coil	Value at 20°
1	. 1.000572
2	1. 000544
3	1. 000104
4	1. 000405
5	1. 000180

(d) The Standards of the Bureau of Standards.—The coils of the Bureau of Standards here employed were 5 in number, all of the sealed type.6 Three of them, numbered 3, 7, and 8, were constructed and sealed at the Bureau in 1907. Nos. 3939 and 3940 are coils especially constructed in 1909 by Otto Wolff, and sealed at the Bureau in June 1909. In Nos. 3, 3939, and 3940, manganin wire, and in Nos. 7 and 8, manganin strip, is used. The values assumed for them were derived from comparisons made at the Physikalisch-Technische Reichsanstalt in 1907 of two 1-ohm and 2 tenth-ohm well-seasoned Wolff standards of the PTR type. On their return to the Bureau in September, 1907, they were compared with 8 other 1-ohm and 5 other tenth-ohm standards of the same type, and the 2 sets were interconnected by directly determining their ratio, thus giving the relative values of all the coils on the same basis. The values assigned to them were obtained by giving equal weight to the comparisons made at the Reichsanstalt for each of the 4 coils. The ten units and seven tenths were used as a reference set until May, 1909, when they were replaced by 10 sealed units, equal weight being given to the values obtained through the 10 units and through the seven tenths previously used as the basis of reference. The values assigned in this report to the 5 sealed units above described were expressed on this basis by measurements on March 8 and 9, 1910. A recomparison made May 23 showed that none had changed relatively to reference set by more than I part in I ooo ooo.

<sup>6</sup> Bulletin, Bureau of Standards, 5, p. 413; 1908.



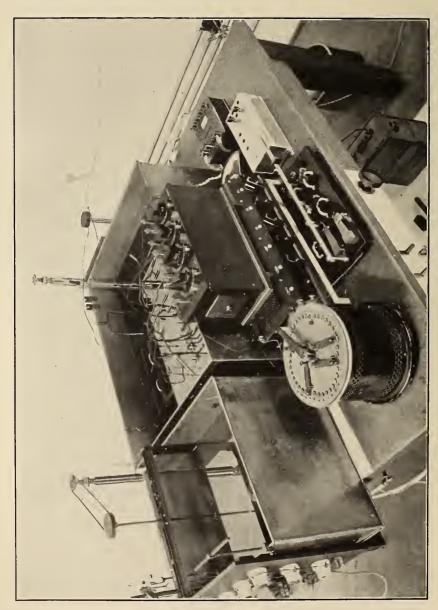


Fig. 1.—Bridge used in Resistance Comparisons

# The Resistance Comparisons

The necessary comparisons were all made in a thermostatically controlled and well stirred oil bath, by Dr. F. Wenner, the standards being substituted in turn in the same arm of a Kelvin double bridge. The connecting resistance, between the standard and an auxiliary 1-ohm coil, was eliminated without further adjustment of the 10-ohm ratio coil employed on account of the relatively small magnitude of the resistance in question, the coils under comparison all having approximately the same values, and the resistance of the connections to the auxiliary ratio coils being also very low.

The main ratio arms consisted of a 10-ohm coil on the same side of the bridge as the auxiliary 1-ohm standard, the other arm being in a number of sections, four of which were provided with shunt dials producing changes in resistance of respectively, 0.00001, 0.00001, 0.00001 and 0.001 ohms per step, the minimum resistance of the shunts corresponding to the zero setting of the shunt dials. The bridge was quickly balanced by finding the setting of the shunt dials corresponding to zero deflection of the galvanometers. Neglecting, for the moment, the connecting resistance to the main ratio arm, the differences in the dial readings represent directly differences, in parts of the whole, between the coils under comparison, the next lowest dial giving parts per million.

The small correction above referred to was determined by transferring the battery connection from the current terminal of the standard to a terminal cup on the ratio arm, and rebalancing. One-eleventh of the difference found corresponds to the correction, to be added to the dial reading for the corrected balance, since the adjacent arms had resistances in the ratio of 1:10, and the resistance in question was included in the ratio arm in finding the principal balance.

Since with a test current of o.1 ampere, a change in balance of one-millionth corresponded to a deflection of 1 mm on current reversal, the settings could be readily made to an accuracy of con siderably better than one part per million. In the tabulated results below, these are rounded off to the nearest o.5 millionth.

Since the galvanometer was permanently connected to the bridge and the resistance under oil, the only source of error from thermoelectromotive forces was in the galvanometer circuit external to the bridge. These were small and sufficiently constant between reversals of the battery current to be entirely negligible.

# The Results

The measurements are expressed in terms of the mean value of five sealed 1-ohm coils as derived through comparisons of a number of 1-ohm coils at the Reichsanstalt. In each case the difference in parts per million between the given coil and the unit thus defined has been given.

The resistances were all measured between the potential terminals except in the case of L 17, which has current terminals only. According to M. Laporte, the LCE coil, Wolff No. 3961, is generally measured between the current terminals at the Laboratoire Central d'Électricité. The resistance in this case has been tabulated, using the observed difference of 18 millionths between the potential terminals and the current terminals.

TABLE II

Physikalisch-Technische Reichsanstalt Coils

Date (1910)	Temp.	Measured value	PTR value	PTR value— NBS value in millionths	Mean
		No. 2836			
Apr. 6	25°	+156.5	+144. 5	12.0	
7	20	+107.0	+ 96.0	-11.0	
11	25	+150.5	+144.5	- 6.0	
19–20	25	+143.0	+144.5	+ 1.5	-2
30	25	+139.0	+144.5	+ 5.5	
May 7	25	+140.0	+144.5	+ 4.5	
14	25	+139.5	+144.5	+ 5.0	
		No. 2838			
Apr. 6	25°	+146.0	+147	+ 1.0	
7	20	+101.5	+ 95	- 6.5	
11	25	+144.0	+147	+ 3.0	
19-20	25	+137.5	+147	+ 9.5	+6
30	25	+134.5	+147	+12.5	
May 7	25	+135.5	+147	+11.5	
14	25	+133.5	+147	+13.5	
		Relative values 28	336-2838		
Apr. 6	25°	+10.5	-2.5		
7	20	+ 5.5	+1.0		
11	25	+ 6.5	-2.5	1	
19–20	25	+ 5.5	-2.5	1	
30	25	+ 4.5	-2.5		
VIay 7	25	+ 4.5	-2.5		
14	25	+ 6.0	-2.5		

The values in the fourth column are taken from the Physikalisch-Technische Reichsanstalt data, using the Reichsanstalt formula. In the last part of the table is given the difference between the two coils as measured on the different days together with relative values as given by the Reichsanstalt.

The two coils showed a decrease with respect to those of the Bureau of Standards for the first four comparisons, and, further, the difference between the two coils is about eight millionths greater than that given by the Reichsanstalt. The fifth column contains the difference between the values of each coil as measured at the Physikalisch-Technische Reichsanstalt and as measured at the Bureau.

Sealed 1000-ohm No. 4089 of the Reichsanstalt at 25°

Date	Diff. in millionths	Reference coils
Apr. 22		Referred to 2 NBS coils Referred to same 2 coils Referred to 6 NBS coils Referred to 5 NBS 1-ohm coils

In the first comparison two 1000-ohm coils of the Bureau of Standards were used; in the measurement of May 17 six 1000-ohm coils, including the first two, were employed. The values of the Bureau of Standards coils were assumed to have remained constant since the step-up made from the five sealed units in February, 1910. The value for May 23 was obtained by stepping up from two units to two thousands. The units were two of the five referred to below, and were compared with the other three on this date. The standard 4089 was compared directly with the 1000-ohm standards used in the step-up. All measurements are expressed in millionths of the nominal value.

The Physikalisch-Technische Reichsanstalt value given by measurements from December 30, 1909, to March 9, 1910, is 1000.055 ohms at 18°.

$$\alpha = +14.0 \times 10^{-6}$$
  $\beta = -0.4_3 \times 10^{-6}$ 

The value at 25° calculated from these temperature coefficients is +132<sup>m</sup> in terms of the Physikalisch-Technische Reichsanstalt standard of reference. Hence, values given by Physikalisch-Technische Reichsanstalt minus values given by Bureau of Standards equals +8 millionths.

The value found in the intercomparisons of November, 1908, to January, 1909, for this same quantity was Physikalisch-Technische Reichsanstalt minus Bureau of Standards equals +8 millionths.

The Physikalisch-Technische Reichsanstalt standard is periodically checked against the primary mercurial standards, but the unit as represented by four 1-ohm manganin standards has not been altered recently.

TABLE III

National Physical Laboratory Coils

Date (1910)	Temp.	Measured values	NPL values	NPL value— NBS value in millionths	Mean
		L 17			
Apr. 6	25°	+113.0	(+123)	(+10.0)	
7	20	+ 22.5	+ 34	+11.5	
11	25	+111.0	(+123)	(+12.0)	
19–20	25	+111.0	(+123)	(+12.0)	+12
30	25	+110.5	(+123)	(+12.5)	
May 7	25	+112.0	(+123)	(+11.0)	
14	25	+110.5	(+123)	(+12.5)	
		L 87			
Apr. 6	25°	+327.5	+325	- 2.5	
7	20	+278.0	+263	-10.0	
11	25	+342.0	+325	-17.0	
19–20	25	+334.5	+325	- 9.5	-12
30	25	+334.0	+325	- 9.0	
May 7	25	+341.0	+325	-16.0	
14	25	+347.0	+325	-22.0	
	I	Relative values L	87—L 17	'	
Apr. 6	25°	+214.5	(+202)		
7	20	+255.5	(+234)		
1	25	+231.0	(+202)		
19–20	25	+223.5	(+202)		
30	25	+223.5	(+202)		
May 7	25	+229.0	(+202)		
14	25	+237.5	(+202)		

The values in the parentheses are calculated using the mean difference between 20° and 25° measured at the Bureau of Standards, since the National Physical Laboratory observations did not extend beyond 21°5.

The open coil L 87 has been unsteady since its arrival, and has a relative value, with respect to L 17, larger by more than 20 millionths than before leaving Teddington. L 87 is a strip coil of manganin capable of carrying a current of 10 amperes, and was brought to the Bureau of Standards for inclusion in voltameter circuits, and not primarily as a resistance standard.

The sealed coil L 17 is steady and indicates a difference in the values of resistance at the two laboratories of

$$NPL - NBS = + 12$$
 millionths.

The value found in the intercomparisons of November 1908, to May, 1909, was about

$$NPL - NBS = +25$$
 millionths.

The National Physical Laboratory standard is that obtained from the NPL mercury standards of resistance. No resistance coils are assumed constant except over a short period of time.

TABLE IV

Laboratoire Central d'Électricité Coil

		Measure	ed values	/			
Date	Temp.	Potential terminals	Current terminals	LCE value	LCE value— NBS value	Mean	
			No. 3961				
1910							
pr. 6	25°	+104.0	+122.0	+234	+112.0		
7	20	+ 27.5	+ 45.5	+151	+105.5		
11	25	+101.0	+119.0	+234	+115.0		
19-20	25	+ 96.0	+114.0	+234	+120.0	+117	
30	25	+ 94.0	+112.0	+234	+122.0	*	
[ay 7	25	+ 95.0	+113.0	+234	+121.0		
14	25	+ 93.5	+111.5	+234	+122.5		

This coil has also been measured at the Reichsanstalt and at the National Physical Laboratory, and these determinations are given in the following table for comparison with those just made:

Date	Place	Temperature	Value
Apr., 1909 July, 1909 Apr., 1910	NPL PTR NBS	20° 20° 20°	Millionths +15. 5 +32. 4 +27. 5

Assuming that the coil has remained constant over this period, this would indicate a value NPL-PTR = -17 millionths, whereas the value derived from the comparisons on the Bureau coils November, 1908, to May, 1909, was NPL-PTR = about + 20, that is a value of about the same magnitude but with the opposite sign. The values in each case are for the resistance between the potential terminals.

This coil showed relative changes, as did the other open coils with respect to the Bureau of Standards basis of reference.

The measurements on 1417-K are:

Coil	Apr. 11	Apr. 20	Apr. 21	
1	+438.0	+433	+436.5	
2	+443.0	+448	+450.5	
3	+ 13.0	÷ 10	+ 13.0	
4	+312.0	+309	+310.5	
5	+ 83.5	+ 82	+ 84.5	

These measurements were made at 20° between potential terminals. For the most part these coils, which are of bare wire on porcelain, have remained very steady during the intercomparisons.

# Bureau of Standards Coils

In the above comparisons the standard of reference was the mean of five of the sealed standard unit coils of the Bureau. There has been no change in their relative values greater than one-millionth during these intercomparisons, and no relative change greater than three millionths during the last year, except in the case of No. 3. The following table gives an idea of their relative constancy during this period:

# TABLE V

# The Bureau of Standards Coils

# 1909

Coil	January	February	March	April	May	July	October
3	+45	44	46	46	47	48	49
7	+53	54	54	54	54	55	55
8	+61	62	62	61	61	62	62
3939 3940	Sealed June, 1909						

#### 1910

Coil	February	March	Apr. 6	Apr. 7	Apr. 11	Apr. 20	Apr. 30	May 7	May 14	May 23
3	50	52	52	52	52	52	52. 0	52. 5	52. 5	53
7	54	56	56	56	56	56	55. 5	55. 5	55. 5	55
8	60	62	62	62	62	62	61.0	62. 0	61. 5	61
3939	89	91	90	91	91	91	91.0	91. 0	91. 0	91
3940	88	89	.89	89	89	89	89. 5	89. 0	89.0	89

If we assume that the Physikalisch-Technische Reichsanstalt corrections to coils No. 2836 and No. 2838 correspond to the mean values obtained in the seven comparisons, we have the difference between the values of these coils, as measured at the Physikalisch-Technische Reichsanstalt and at the Bureau of Standards, equal in the case of one coil to -2, and for the other +6 millionths. Taking the mean of these and the results on the sealed National Physical Laboratory standard L 17, we have

The state of the s	Millionths.
PTR-NBS	+ 2
NPL-NBS	+12
Mean	+ 7

This is the correction recommended by the subcommittee to be applied to the values given in the above tables and expressed in terms of the Bureau of Standards basis of reference. The new unit thus defined is intended to represent the mean values of the Physikalisch-Technische Reichsanstalt and the National Physikalische Reichsanstalt and the Reichsanstalt a

sical Laboratory mercury units as represented by the coils submitted.

The following table gives the values of the coils referred to the new unit:

TABLE VI

Coil	Туре	Apr. 6, 25°	Apr. 7,	20°	Apr. 11, 25°	Apr. 19-20, 25°	
2836		+163.5	+114	4. 0	+157.5	+150.0	
2838	Open	+153.0	+108		+151.0	+144.5	
L 17	Sealed	+120.0	+ 29		+118.0	+118.0	
L 87	)	+334.5	+285		+349.0	+341.5	
3961	Open	+129.0	+ 5		+126.0	+121.0	
				1		1	
Coil	Туре	Apr.	30, 25°	May	7, 25°	May 14, 25°	
2836	)	( +1	46. 0	4.	147. 0	+146.5	
2838	Open	12	41. 5		142. 5	+140.5	
L 17	Sealed		17. 5		119. 0	+117. 5	
L 87	Dealed		41.0		348. 0	+354.0	
3961	Open		19. 0		120. 0	+118.5	
3901	,	( +1	.19. 0	Т.	120.0	Ţ116. J	
Coil of 1417-K	Туре	Apr.	11, 20°	Apr. 19	9–20, 20°	Apr. 21, 20°	
Number 1	1	[	45. 0	-1	-440	+443.5	
Number 2			50. 0		-455	+457.5	
Number 3	Open		20. 0		- 17	+ 20.0	
Number 4	1		319. 0		-316	+317.5	
Number 5			90.5		- 89	+ 91.5	
Coil	Туре	Apr. 6, 25°	Apr. 7	, 25°	Apr. 11, 25°	Apr. 19-20, 25°	
3	1	+59	+5	9	+59	+59	
7		+63	+6	3	+63	+63	
8	Sealed	+69	+69 +6		+69	+69	
3939		+97	+97 +98		+ <sub>0</sub> 8	+98	
3940		+96	+9	6	+96	+96	
Coil	Coil Type		Apr. 30, 25°		7, 25°	May 14, 25°	
3	1	( +:	59. 0	+	59. 5	+59.5	
7		+1	52. 5	+	62. 5	+62.5	
8	Sealed		68. 0	+	69. 0	+68.5	
3939		+9	98. 0		98. 0	+98.0	
3940		+9	96. 5		96. 0	+96.0	
	ľ	,					

No. 3961 measurements include resistance between current terminals.

22451°—12——7

#### 2. STANDARD CELL COMPARISONS

Each of the delegates brought with him a considerable number of cells, which have been repeatedly compared, under the most favorable conditions, with those of the Bureau of Standards, thus furnishing a basis for expressing the results of the voltameter work undertaken at Washington, as well as for further work in the home laboratories. In addition, this made possible the direct comparison of the standards of electromotive force employed in the four institutions, and furnished data of value on the accuracy attainable in the reproduction of the Weston Normal Cell. Further data on the last question were obtained from 48 cells 7 set up in Washington, with four samples of mercurous sulphate representing the methods of preparation adopted in the four institutions. Portions of each sample were washed according to the procedure followed in the four laboratories, and three cells were set up with each washed sample as stated below. In addition, two cells were set up with each of four samples of cadmium sulphate submitted; comparative tests were also made of four samples of mercury and of cadmium or cadmium amalgam.

The comparisons were made in a basement room especially fitted up for such work. Fig. 2 shows the general arrangement of the apparatus. No important modifications of the installation have been made since 1907, when a full description was published.<sup>8</sup>

All cell comparisons are made in automatically controlled petroleum baths, each of which is provided with coils for electric heating, a cooling coil for water circulation when operating at temperatures below that of the room, an efficient stirrer and means for directing the circulation in the bath, and a sensitive thermoregulator, in addition to a rack for mounting the cells.

The cells are mounted on wooden strips and held in place by sheet metal clips. The strips were supported by a metal frame work so that the cells were 3 or 4 cm above the level of the thermo regulator grid and several cm below the surface of the oil. Between the cells were mounted hard rubber blocks, carrying, near the ends, copper blocks provided with a pair of holes for

<sup>&</sup>lt;sup>7</sup>Four additional cells were also set up by Mr. Smith. These are not included in the report, since it was previously agreed that each delegate should set up only 12 cells.

<sup>8</sup> Wolff and Waters, Bulletin, Bureau of Standards, 4, p. 1; 1907. (Reprint No. 70.)

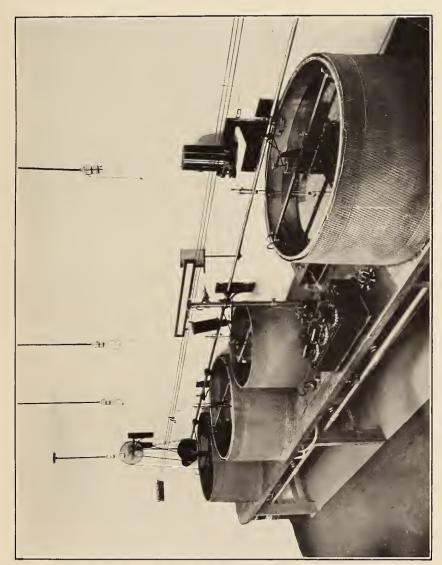


Fig. 2.—View of Standard Cell Room, Showing Four of the Five Baths



mercury cups, one pair serving for the cell terminals and the other pair for external connections. The holes for the latter purpose were spaced at equal distances so that the cells could be put in circuit by inserting a pair of stiff contact wires mounted in a hard rubber block.

Connections to the potentiometer were made by the aid of three insulated line wires extending over the baths, and to which the leads from the contact wires and the potentiometer terminals could be connected in any desired manner by the aid of copper clips.

The Electrical Measurements

The measurements given below were all made by means of a 5-dial Wolff potentiometer of the usual construction having a resistance of 10 000 ohms per volt, the units of the tenth ohm dial corresponding therefore to 10 microvolts. The potentiometer current was furnished by a storage cell of ample capacity, which was continuously left in circuit and covered with sheet asbestos to reduce temperature variations. Under these conditions the current, regulated by a manganin rheostat, was sufficiently constant for all purposes.

A high sensibility D'Arsonval galvanometer, made by the Cambridge Scientific Instrument Co., was employed throughout. A difference of 10 microvolts produced a deflection of several millimeters, so that the values could be readily measured to microvolts, even with the high resistance potentiometer employed.

The comparisons of the cells were made by the differential method, each cell being measured in opposition to one of the lot taken as a standard of reference. As the differences measured were small, no errors are introduced by possible variations of the potentiometer current likely to occur during a complete set of measurements. From the differences thus measured, the results could be expressed in terms of any particular cell or the mean value of certain selected cells, by applying a suitable correction.

### Sources of Error

Errors due to temperature measurement may be considered as practically eliminated on account of the very small temperature coefficient of the Weston Normal Cell, about 50 microvolts per degree at 25°. The error made in the employment of a carefully calibrated mercurial thermometer graduated to tenth degrees can hardly exceed 0.01° under the very favorable conditions here met. The perfect regulation of temperature also reduced the effect of hysteresis to negligible proportions, except in the case of a very few of the cells which seemed to show an abnormal hysteresis.

On account of the differential method employed in the standard cell comparisons and the small differences in electromotive force found, errors due to variation in the potentiometer current, and errors in the calibration of the potentiometer, are also practically eliminated. Care must, however, be taken to keep the switch contacts of the potentiometer in good working order, as some trouble has been occasionally found owing to a gradual yielding of the hard rubber blocks carrying the contact brushes. Thermoelectromotive forces were practically absent, as shown by occasional tests, made in the customary way by reversals of both the potentiometer battery and the connections to the cells compared. Measurements had previously been made of all insulation resistances, including the resistance between cell terminals in the bath on a blank cell with the cross arm sealed off, but in every case the resistances were found so high that this error could not exceed one microvolt.

In view of the constancy of the results given below, as shown by this agreement of measurements on successive days, the errors in the relative values of the cells can hardly exceed one or two microvolts.

### The Cells and their Relative Values

The standard cells submitted by the four laboratories (types of which are shown in Fig. 3), and others included for various reasons in the comparisons, are listed in the following tables which give details concerning the source and the methods of preparation or purification of the various materials employed, the washing of the mercurous sulphate, the date of setting up, and other information which may be of interest.

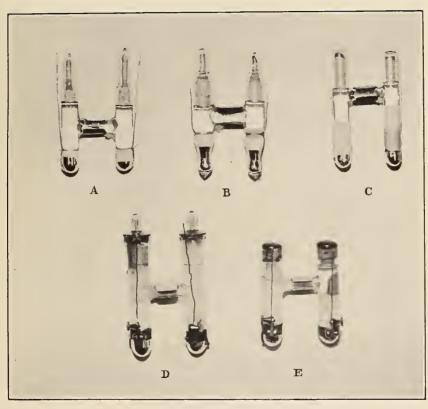


Fig. 3.—Types of Standard Cells

A, National Physical Laboratory; B, Physikalisch-Technische Reichsanstalt; C, Bureau of Standards; D and E, Laboratoire Central d'Électricité



The tables also give the results of the comparisons made at the Bureau of Standards, for the most part by Mr. M. P. Shoemaker. For the older cells these include, for completeness, data obtained before the comparisons made under the auspices of the International Committee. In all cases the values are expressed in terms of the basis of reference adopted by the Bureau of Standards, and originally defined as the mean value of twelve cells set up with mercurous sulphate prepared by various methods. Unfortunately, seven of these cells were accidentally short-circuited in 1908 during the determination of the temperature coefficient of the Weston Normal Cell, and subsequently showed considerable relative changes. They were, therefore, replaced by seven other cells, set up by Wolff and Waters, which had previously shown exceptionally uniform differences with respect to the first reference set though differing from them in the mean by approximately 14 parts 9 in 1 000 000. To preserve the continuity of values, this difference has since been applied as a correction to the measurements.

TABLE VII
Bureau of Standards Reference Cells

#### Data

Cell	Date	Hg <sub>2</sub> SO <sub>4</sub>	Method of washing	Remarks
20 21	June, 1906	b <sub>15</sub>	Acid, alcohol, CdSO4	Untreated sol CdSO4 used.
7 10	do	b <sub>15</sub> b <sub>15</sub>	do	CdSO <sub>4</sub> shaken with Cd amalgam, cloudy solution. Basic CdSO <sub>4</sub> or Cd(OH) <sub>2</sub> formed; filtered solution used.
23	do	<b>b</b> <sub>15</sub>	do	CdSO <sub>4</sub> sol. unsaturated, shaken in atmosphere of C. P. nitrogen 48 hours.
25	do	<b>b</b> <sub>15</sub>	do	CdSO <sub>4</sub> sol. unsaturated, shaken in atmosphere of C. P. hydrogen 48 hours.
13	do	<b>b</b> <sub>15</sub>	do	CdSO <sub>4</sub> sol. saturated, shaken with Cd amalgam in vacuo 48 hours.

<sup>&</sup>lt;sup>9</sup> In most of these cells, the CdSO<sub>4</sub> solution had been shaken under various conditions, for <sub>24</sub> hours or more, with Cd amalgam before it was used, to determine whether any change ensued which might affect the electromotive force.

### TABLE VII---Continued

### Bureau of Standards Reference Cells-Continued

Differences, at 25° C, in Microvolts, from Bureau of Standards Basis of Reference

Cell	Feb. 7	Mar. 1	Mar. 18	Apr. 6	Apr. 7	Apr. 8	Apr. 11	Apr. 15	Apr. 22	Apr. 29	May 10	<b>M</b> ay 16
20	-27	-25	-26	-25	-25	-24	-24	-26	-25	<b>—25</b>	-25	-24
21	-16	-15	-14	-13	-14	-13	-13	-12	-14	-15	-13	-13
7	- 1	- 1	- 0	- 1	<b>—</b> 2	- 1	- 1	- 1	- 1	<b>—</b> 2	<b>—</b> 2	- 1
10	- 4	<b>–</b> 3	- 3	- 4	- 5	- 4	- 4	- 4	<b>-</b> 4	<b>–</b> 5	<b>–</b> 5	- 4
23	-20	-21	-22	-22	-22	-22	-22	-22	-23	-23	-24	-24
25	-14	-14	-13	-12	-13	-12	-12	-12	-11	-11	-11	-10
13	-21	-21	-21	-21	-22	-21	-21	-22	-21	-22	-22	-23

Untreated  $CdSO_4$  solutions were used in making up all pastes; 12.5 per cent cadmium amalgam was employed.

### TABLE VIII

Differences, in Microvolts, between Cells Employed in Voltameter Work and the Bureau of Standards Basis of Reference. Temperature, Approximately 25° C.

Date	No. 37	No. 180	No. 109	No. 56
Арг. 9	-15	<b>—5</b>	+3	+7
13	-14	-2	+4	+8
14	-14	-4	+4	+8
15	-14	-4	+4	+8
20	-14	<b></b> 5	+2	+6
26	-15	-4	+3	+7
28	-16	<b>-4</b>	+4	+6
29	· —15	-4	+3	+6
30	-15	<b>—</b> 7	+2	+5
May 2	15 -	5	+3	+7
3	-14	-4	+4	+7
5	-15	-4	+3	+7
7	15	-4	+3	+7
9	15	-4	+4	+7
12	-15	-5	+2	+5
17	-18	-7	0	+4
19	-20	8	0	+3
	15. 2	-4.7	+2.8	+6.4

TABLE IX

## Cells Submitted by the Physikalisch-Technische Reichsanstalt

Differences, at 25° C, in Microvolts, from Bureau of Standards Basis of Reference

Cell	Date	Hg <sub>2</sub> SO <sub>4</sub>	Apr. 610	Apr. 6 11	Apr.	Apr.	Apr. 11	Apr. 15	Apr.	Apr. 29	May 10	May 16
D <sub>1</sub> D <sub>2</sub> D <sub>3</sub> D <sub>4</sub> E <sub>10</sub> E <sub>11</sub> E <sub>12</sub> E <sub>13</sub> F <sub>7</sub> F <sub>8</sub> F <sub>9</sub> F <sub>10</sub> H <sub>1</sub> H <sub>2</sub> H <sub>3</sub>	Oct. 29, 1909	ym zm	\begin{array}{cccccccccccccccccccccccccccccccccccc	+21 16 12 26 +17 8 17 18 +43 43 41 59 +34 37 31	+17 15 15 28 +17 7 14 15 +44 41 43 +33 35 29	+22 18 16 29 +18 8 15 15 +44 42 42 +32 36 29	+21 19 15 28 +18 8 16 16 +44 42 42 42 436 29	+21 17 15 28 +18 8 15 15 +42 41 41 +31 35 28	+21 17 15 28 +18 8 15 15 +43 43 41 42 +31 35 28	+21 16 15 28 +17 8 15 15 +43 43 41 41 +29 33 27	+19 14 12 28 +15 7 13 14 +42 41 40 +28 31 25	+19 15 13 29 +16 7 13 14 +41 42 40 40 +27 31 25
Mean				+26	+26	+27	+27	+26	+27	+26	+25	+25
Avera	Average deviation from mean			±12	±11	±11	±10	±10	±10	±10	±10	±10

<sup>10</sup> Cells measured five to twelve minutes after putting in bath.

### FURTHER DATA SUPPLIED BY THE REICHSANSTALT.

The mercury was taken from a specially purified supply prepared for ohm work. The remaining materials ( $CdSO_4 + 8/3 H_2O$ , Cd,  $H_2SO_4$ ,  $H_2O$  and  $HNO_3$ ) were obtained from Kahlbaum, and are to be considered, according to tests made in the chemical division, as the purest. The Cd was nevertheless examined by the Mylius test for zinc, and found to be free from zinc; the mercurous nitrate was recrystallized once; the cadmium sulphate employed was also recrystallized, that for the preparation of the saturated cadmium sulphate solution once and that for the crystals twice.

<sup>11</sup> Cells measured one hour after putting in bath.

The four samples of mercurous sulphate employed were prepared by slowly adding a solution of mercurous nitrate and nitric acid to a warmed solution of sulphuric acid (1:6 by volume). After settling, the precipitate was washed, by decantation, about three times with 1:6 sulphuric acid, and then washed in portions with about 150 cc  $\rm H_2O$  on a large Gooch filter. Finally it was washed several times with small quantities of saturated cadmium sulphate solution and preserved under saturated cadmium sulphate.

The cadmium amalgam was prepared by melting together the calculated quantities of Cd and Hg, and contained 12.5 per cent Cd.

The paste for the cells, set up the same day, was prepared in sufficient quantity for all of them by lightly mixing the ingredients to form an easily flowing paste. Both electrodes were finally covered with a layer of  $CdSO_4 + 8/3 H_2O$  crystals.

The following table gives further data for the four samples of Hg<sub>2</sub>SO<sub>4</sub>:

Designa- nation	Date of preparation	HgNO <sub>3</sub>	HNO <sub>3</sub>	H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub>	H <sub>2</sub> O	Time of precipitation
		o	g	g	o	g	Minutes
xm	Oct. 26, 1909	150	15	150	77	100	5
ym	Oct. 28, 1909	150	15	150	77	150	5±
zm	Nov. 12, 1909	150	15	300	75	300	3.5
βm	Nov. 27, 1909	150	24	276	75	150±	1. 3

The cells had not shown any appreciable relative changes before they were taken to Washington.

TABLE X

### Cells Submitted by the National Physical Laboratory

Differences, at 25° C, in Microvolts, from Bureau of Standards Basis of Reference

Cell	Date	Hg <sub>2</sub> SO <sub>4</sub> (by chemical precipitation)	Apr. 612	Apr. 6 13	Apr.	Apr.	Apr. 11	Apr. 15	Apr. 22	Apr. 29	<b>M</b> ay 10	<b>M</b> ay 16
A <sub>1</sub> A <sub>2</sub>			(+ 9 + 9	+ 9 + 7	+11 + 9	+15 +13	+15 +12	+14 +13	+15 +15	+15 +15	+14 +14	+13 +12
$A_3$		Sample 1	+ 7	+ 7	+10	+13	+13	+12	+14	+13	+12	+12
A4			+ 4	+ 3	+ 2	+ 6	+ 7	+ 6	+ 7	+ 6	+ 6	+ 6
$\mathbf{A}_5$	Oct., 1909		+ 4	+ 1	0	+ 5	+ 4	+ 4	+ 4	+ 4	+ 4	+ 3
$\mathbf{B}_1$	0 0, 2505		(+ 7	+ 5	+ 5	+ 9	+10	+ 9	+ 9	+ 9	+ 8	+ 8
$\mathbf{B}_2$		Sample 2	+ 9	+ 8	+ 8	+10	+10	+ 9	+ 9	+ 9	+ 7	+ 6
$\mathbf{B}_3$			+ 4	+ 4	+ 1	+ 5	+ 6	+ 3	+ 3	+ 3	+ 1	- 1
Cı		Sample 3	{+17	+12	+13	+19	+20	+20	+20	+20	+20 +17	+19 +15
C <sub>2</sub>	,		(+ 9	+11	+ 9	+14 +32	+16	+17	+16 +31	+16 +31	+31	+29
$\mathbf{D}_1$ $\mathbf{D}_2$		Sample 4	$\begin{cases} +29 \\ +31 \end{cases}$	+31	+28	+31	+32	+31	+31	+32	+32	+30
D <sub>2</sub>		Sample 4	+34	+29	+25	+27	+28	+28	+27	+28	+27	+25
E <sub>1</sub>			(+29	+31	+25	+29	+30	+29	+29	+30	+29	+27
$\mathbf{E}_{2}$			+31	+29	+27	+30	+32	+31	+31	+32	+31	+29
E <sub>3</sub>	Nov., 1909	Sample 5	+31	+29	+28	+31	+32	+31	+30	+31	+30	+28
E4			+29	+36	+32	+35	+37	+35	+33	+34	+33	+30
F <sub>1</sub>			(+27	+29	+26	+29	+32	+30	+29	+29	+30	+29
F <sub>2</sub>			+33	+25	+22	+25	+27	+26	+26	+25	+25	+25
F <sub>3</sub>		Sample 6	+29	+27	+20	+27	+29	+28	+26	+25	+25	+25
F4	J		+41	+31	+28	+31	+35	+33	+33	+34	+35	+34
G <sub>1</sub>	}	ſ	(+37	+36	+33	+37	+39	+38	+36	+35	+35	+33
G <sub>2</sub>			+35	+39	+35	+40	+41	+40	+37	+38	+36	+35
G <sub>3</sub>		Sample 7	+33	+36	+32	+36	+38	+36	+35	+35	+34	+32
G <sub>4</sub>			+29	+30	+28	+31	+33	+32	+30	+31	+30	+29
G <sub>5</sub>	Jan., 1910	·	+29	+35	+31	+35	+36	+34	+32	+32	+31	+30
$\mathbf{H}_1$	,		+34	+36	+33	+37	+38	+37	+35	+35	+34	+34
$\mathbf{H}_2$			+36	+37	+32	+36	+37	+36	+35	+35	+35	+33
H <sub>3</sub>		Sample 8	+37	+37	+34	+38	+39	+38	+36	+35	+34	+33
H4			+31	+32	+30	+34	+35	+35	+34	+35	+33	+32
H <sub>5</sub>	)		+37	+31	+27	+29 +21	+31 +22	+31 +20	+31	+31 +18	+30	+29 +16
K <sub>1</sub> K <sub>2</sub>	Feb 1010	Sample 0	+22 +25	+22	+18 +23	+21	+22	+20	+26	+18	+17	+10
K <sub>2</sub> K <sub>3</sub>			+23	+27	+23	+19	+21	+19	+18	+18	+17	+16
173	,					T19	7-21	719	710	710	-1/	710
	Mean			+24	+22	+25	+26	+25	+25	+25	+24	+23
Averag	ge deviation		±10	± 9	± 9	±10	± 9	± 9	± 9	± 9	± 9	

<sup>12</sup> Cells measured five to twelve minutes after putting in bath.

The following additional data were supplied by the National Physical Laboratory:

The mercury for all cells was distilled twice, and electrolytically purified before distilling for some of the cells.

<sup>13</sup> Cells measured one hour after putting in bath.

The cadmium sulphate was recrystallized from slightly acid, pure commercial salt. Most of the cadmium amalgam was prepared by depositing cadmium into mercury by electrolysis. All the cells contained 10 per cent amalgam.

The methods of washing the mercurous sulphate, preparing the paste, etc., were in the main identical with those described in the appendix to the report of the London Conference.

The same paste mixture was used in setting up cells designated by the same letter.

TABLE XI

Cells Submitted by the Laboratoire Central d'Électricité

Differences, at 25° C, in Microvolts, from the Bureau of Standards Basis of Reference

Cell	Apr. 6 14	Apr. 6 15	Apr.	Apr. 8	Apr.	Apr. 15	Apr. 22	Apr. 29	<b>M</b> ay 10	May 16
$\mathbf{E}_{9}$	-74	-41	-17	-12	-19	-18	-21	-23	-29	<b>–</b> 3
$\mathbf{E}_{12}$	<b>—</b> 46	-31	- 2	- 1	- 2	-11	-14	-12	<b>—19</b>	-21
$\mathbf{E}_{13}$	-16	+ 2	+ 6	+ 4	<b>—</b> 9	-15	-19	-22	-31	-33
E14	<b>–</b> 3	+15	+27	+29	+20	+19	+15	+14	+ 8	.+8
$\mathbf{D}_2$	+73	+79	+45	+49	+49	+49	+49	+49	+52	+55
$\mathbf{D}_3$	+68	+78	+46	+49	+50	+48	+48	+47	+45	+45
$\mathbf{P}_{\mathbf{I}}$	+72	+61	+65	+67	+67	+64	+64	+63	+61	+62
$\mathbf{P}_2$	+62	+63	+68	+69	+69	+68	+68	+67	+67	+67
$P_3$	+79	+67	+68	+69	+69	+68	+68	+68	+67	+65
$S_2$	- 1	+16	+27	+31	+34	+35	+43	+53	+80	+98
S <sub>4</sub>	+ 9	+17	+27	+31	+34	+34	+33	+31	+28	+26
S <sub>5</sub>	+37	+35	+26	+27	+26	+24	+23	+18	+14	+11
S <sub>7</sub>	+39	+47	+55	+57	+55	+53	+53	+52	+48	+46
S <sub>8</sub>	+11	+17	+30	+35	+38	+38	+37	+37	+31	+29
$\mathbf{Z}_2$	+56	+61	+66	+69	+68	+67	+66	+65	+64	+64
Mean			+35	+38	+37	+35	+34	+34	+32	+35
Average deviation from mean			± 22	± 22	±23	± 21	± 25	±26	±30	±30

<sup>14</sup> Cells measured five to twelve minutes after putting in bath.

The following additional data concerning the above cells were submitted by M. Laporte:

Cells designated by the same letter were made of the same materials and at about the same time.

The methods of preparation and purification of the materials were the same as those described in the paper by Janet and Jouaust. (Bull. Soc. Int. des Élect., 8, 409; 1908.)

The washing of the  $Hg_2SO_4$  was always done at the time of making up the cells. Concentrated  $CdSO_4$  was used for this purpose and continued until congo paper showed no blue color after 10 minutes contact with the filtrate.

The  $Hg_2SO_4$  sample in the D and S cells was prepared by D. C. electrolysis. The sample for the P and Z cells, as also a second sample for the E cells, was made by A. C. electrolysis.

<sup>15</sup> Cells measured one hour after putting in bath.

TABLE XII

New Cells Submitted by the Bureau of Standards

Data

A	
Description   Description   Description   Description	
Description   Page 201	
Description of the control of the	te.
A. E. V.   Feb., 1910   A. E. V.   A. E. V	
232	
Description of the content of the	
240 241 242 242 243 244 Feb., 1910  h 61 h 44 A. E. V. h 61 h A. E. V. h 61 A. E. V. Solution admitted. Washed 1908; materials mixed dry; cell exhausted a solution admitted. Washed 1908; materials introduced dry; cell exhausted a solution admitted. Washed 1908; materials introduced as in cell Same paste; Hg <sub>2</sub> SO <sub>4</sub> washed and digested	
241 242 243 244 Feb., 1910  1	
CdSO <sub>4</sub> solution admitted.  Duplicates of cell 222.  Materials introduced dry; cell exhausted a solution admitted.  Peb., 1910  h 61  A. E. V.  Materials introduced dry; cell exhausted a solution admitted.  Washed 1908; materials introduced as in cell Same paste; Hg <sub>2</sub> SO <sub>4</sub> washed and digested.	haustod c-d
243 244 Feb., 1910  b 61 A. E. V. h 61 A. E. V. Materials introduced dry; cell exhausted a solution admitted. Washed 1908; materials introduced as in cell Same paste; Hg <sub>2</sub> SO <sub>4</sub> washed and digested of the solution admitted.	лацыец анц
243 244 Feb., 1910 Feb., 1910 A.E. V. Materials introduced dry; cell exhausted a solution admitted. Washed 1908; materials introduced as in cell Same paste; Hg <sub>2</sub> SO <sub>4</sub> washed and digested of the solution admitted.	
Feb., 1910   Solution admitted. Washed 1908; materials introduced as in cell   Same paste; Hg <sub>2</sub> SO <sub>4</sub> washed and digested	,
245 h 44 A. E. V. Washed 1908; materials introduced as in cell Same paste; Hg <sub>3</sub> SO <sub>4</sub> washed and digested to the same paste; Hg <sub>2</sub> SO <sub>4</sub> washed and digested to the same paste; Hg <sub>2</sub> SO <sub>4</sub> washed and digested to the same paste; Hg <sub>2</sub> SO <sub>4</sub> washed and digested to the same paste; Hg <sub>2</sub> SO <sub>4</sub> washed and digested to the same paste; Hg <sub>2</sub> SO <sub>4</sub> washed and digested to the same paste; Hg <sub>2</sub> SO <sub>4</sub> washed and digested to the same paste; Hg <sub>2</sub> SO <sub>4</sub> washed and digested to the same paste; Hg <sub>2</sub> SO <sub>4</sub> washed and digested to the same paste; Hg <sub>2</sub> SO <sub>4</sub> washed and digested to the same paste; Hg <sub>2</sub> SO <sub>4</sub> washed and digested to the same paste; Hg <sub>2</sub> SO <sub>4</sub> washed and digested to the same paste; Hg <sub>2</sub> SO <sub>4</sub> washed and digested to the same paste; Hg <sub>2</sub> SO <sub>4</sub> washed and digested to the same paste; Hg <sub>2</sub> SO <sub>4</sub> washed and digested to the same paste; Hg <sub>2</sub> SO <sub>4</sub> washed and digested to the same paste; Hg <sub>2</sub> SO <sub>4</sub> washed and digested to the same paste; Hg <sub>2</sub> SO <sub>4</sub> washed and digested to the same paste; Hg <sub>2</sub> SO <sub>4</sub> washed and digested to the same paste to the same pa	and CdSO4
h 61 A. E. V. F. Same paste; Hg <sub>2</sub> SO <sub>4</sub> washed and digested	
	with alcohol
h 61 A. E. V. F. and ether.	
248 h 61 A. E. V. F. Same paste; same materials as in cells 246 at	nd 247.
249   n 61   A. E. V. F.	
250 h 61 A. E. V. F. Two pastes for cells 246-249 mixed and let sta	
251 h 44 A.E.V. Washed 1908; rewashed 1909; ingredients of mixed dry.	of paste not
252 h 44 A. E. V. Washed 1903; rewashed 1909; ingredients of dry.	paste mixed
257 h 44 A.E.V. Same material as in cells 251 and 252; H	g <sub>2</sub> SO <sub>4</sub> sifted
through Pt. gauze.	
259 ) ( b 67 A. E. V. Exposed to air 5 hours altogether; sealed in v	acuo.
275 h 67 A. E. V. Hg <sub>2</sub> SO <sub>4</sub> sealed in vacuo; sifted through Pt. g	
Mar., 1910 using.	
b 67 A. E. V. Duplicate of cell 275.	
277 h 67 A. E. V. Exposed to air 1 month; sifted through Pt. ga	uze.
B22 ) ( h 62   A. E. V. F. )	
B24 h 63 A. E. V. F. Hg <sub>2</sub> SO <sub>4</sub> also digested with alcohol 1 hour, an	d rewashed
B25 b 64 A. E. V. F. and dried.	
B26 h 67 A. E. V. F.	
B27 h 61 A. E. V. Hg <sub>2</sub> SO <sub>4</sub> let stand in air and redigested in cold	10% H.SO.
Feh., 1910 washed as in B22.	
B29 h 43 A. E. V. After washing, Hg <sub>2</sub> SO <sub>4</sub> kept in sealed hottle washed as B22.	e 1 year; re-
B32 Chem. F. A. E. V. Hg2SO4 made according to NPL specification	S.
B38 b 67 A. E. V. Washed as in B22.	
B39 Chem. F. A. E. V. Same as in B32.	
B40 A. E. V. Under house vacuum 4 hours after washing.	
B41 b 67 A. E. V. Hg <sub>2</sub> SO <sub>4</sub> exposed to air several days, and then vacuum.	kept under
B43 Mar., 1910 h 61 A. E. V. Hg <sub>2</sub> SO <sub>4</sub> let stand in air for several weeks.	
B45 b 67 A. E. V. Same as cell 259.	
B49 h 61 A. E. V. Hg <sub>2</sub> SO <sub>4</sub> exposed to air of hasement 1 month,	
B50 h 67 A. E. V. Same as B45.	

# TABLE XII—Continued

New Cells Submitted by the Bureau of Standards—Continued Differences, at 25° C, in Microvolts, from Bureau of Standards Basis of Reference

Cell	1-4 days	9-20 days	Apr. 7	Apr. 8	Apr. 11	Apr. 15	Apr. 22	Apr. 29	May 10	<b>M</b> ay 16
222	+28	+12	+ 1	+ 5	+ 7	+ 7	+ 6	+ 7	+ 6	+ 5
226	+72	+44	+36	+37	+37	+38	+36	+34	+33	+31
228	+71	+46	+38	+39	+38	+38	+36	+34	+33	+33
230	+27	+20	+15	+17	+17	+17	+17	+16	+16	+18
231	+20	+19	+19	+21	+21	+20	+21	+20	+19	+20
232	+16	+18	+24	+27	+26	+25	+26	+25	+25	+26
233	+18	+17	+21	+23	+22	+22	+22	+22	+22	+24
240	+47	+19	+12	+15	+18	+16	+18	+18	+17	+17
241	+14	+ 6	+ 8	+ 9	+12	+ 9	+10	+10	+ 9	+ 9
242	+29	+17	+16	+16	+17	+15	+16	+16	+15	+15
243	+26	+12	+11	+12	+13	+11	+12	+11	+10	+10
244	+14	+ 8	+10	+ 9	+12	+10	+11	+10	+10	+10
245	+53	+29	+24	+25	+28	+25	+24	+22	+22	+21
246	+30	+18	+15	+15	+17	+15	+14	+13	+13	+11
247	+42	+28	+21	+22	+22	+19	+18	+17	+16	+15
248	+32	+22	+14	+14	+16	+15	+15	+14	+14	+13
249	+30	+19	+15	+15	+16	+15	+14	+14	+13	+12
250	+53	+39	+30	+31	+32	+29	+27	+26	+25	+24
251	+41	+22	+17	+19	+19	+17	+16	+16	+16	+15
252	+28	+17	+14	+16	+17	+15	+15	+15	+13	+13
257	+37	+27	+24	+25	+27	+24	+24	+23	+20	+21
259	+17	+15	+11	+12	+12	+12	+12	+10	+ 7	+ 7
275	+13	+ 4	+ 4	+ 5	+ 7	+ 6	+ 6	+ 6	+ 3	+ 4
276	+12	+ 2	+ 2	+ 4	+ 5	+ 5	+ 5	+ 5	0	0
277	+35	+24	+24	+26	+27	+25	+26	+26	+19	+18
B22	+21	+22	+20	+21	+22	+22	+22	+21	+19	+20
B24	+22	+20	+19	+19	+20	+20	+20	+19	+18	+19
B25	+25	+18	+11	+12	+13	+14	+13	+13	+12	+13
B26	+14	+14	+11	+11	+12	+13	+13	+13	+12	+13
B27	+29	+24	+20	+19	+20	+20	+19	+18	+17	+17
B29	+12	+10	+10	+10	+10	+11	+11	+11	+10	+10
B32	+37	+27	+22	+20	+21	+20	+20	+19	+18	+19
B38	+14	+12	+14	+13	+15	+15	+16	+17	+17	+18
B39	+39	+36	+28	+28	+29	+28	+28	+27	+25	+26
B40	+32	+25	+23	+22	+23	+22	+23	+22	+20	+21
B41	+38	+32	+30	+29	+29	+29	+29	+28	+27	+27
B43	+20	+17	+20	+18	+20	+19	+20	+20	+18	+19
B45	+13	+ 9	+ 8	+ 7	+ 8	+ 7	+ 7	+ 7	+ 6	+ 7
B49	+20	+19	+18	+18	+18	+18	+19	+18	+18	+19
B50	+10	+10	+ 9	+11	+ 9	+10	+10	+10	+ 9	+ 9
Mean	+29	+20	+17	+18	+19	+18	+18	+17	+16	+16
Average deviation from mean	±11	± 7	± 7	± 6	± 6	± 6	± 6	± 6	± 6	± 6

#### METHOD OF WASHING AND DRYING THE MERCUROUS SULPHATE

A indicates washing with absolute alcohol.

E indicates washing with anhydrous ether.

V indicates drying in vacuo.

F indicates that material was flooded with the wash liquid and allowed to stand one hour or more.

The general procedure was the same in other respects as described elsewhere except that 10 per cent cadmium amalgam was employed throughout. The cells were set up by F. A. Wolff and E. C. McKelvy.

### Discussion of the Results

It will be seen from the foregoing tables that the relative values of the same cell, as obtained in the various comparisons, show, with few exceptions, a most excellent agreement which must be attributed in great part to the very perfect temperature regulation maintained throughout the whole period of the measurements.

Bureau of Standards Reference Cells.—The constancy of the relative values of the reference cells used by the Bureau of Standards, as shown by Table VII and by measurements extending over a long period, led to the provisional adoption of the Bureau basis of reference for expressing the results of all the measurements, particularly as no decision could be reached in advance as to any other basis for expressing the results.

Bureau of Standards Cells employed in Voltameter Work.—Table VIII shows the relative constancy of W 109, the cell employed throughout in the voltameter work, and that of three others maintained in the same bath. These cells were selected from a large number employed in the determination of the temperature coefficient of the Weston cell in 1908, 16 on account of the small hysteresis shown. Slight differences are in part due to the temperature not having been exactly 25° throughout. No correction is, however, required for this, as the cells were compared with the reference cells at 25° and were used at the temperature of the bath.

The measurements made by the aid of a special line, highly insulated, are in almost exact agreement with check comparisons made on transferring one of the cells to the bath containing the reference cells.

The Cells Submitted by the Four Laboratories.—The relative values of the separate cells constituting four groups (Tables IX–XII) show changes from their means which do not exceed  $\pm 3$  microvolts except in a few instances, excluding the first two sets of comparisons made ten minutes and one hour after they were placed in the comparing baths.

From the tables it appears that the mean values of the normal cells submitted by the four laboratories are in most excellent agreement, and, also, that the average deviations of individual cells from their respective group means are quite small.

The values of the French mean and the average deviation of the individual cells from the group mean may, as suggested by M. Laporte, be affected in part by the cells of high value, set up with mercurous sulphate prepared by alternating current electrolysis, since similar high values have been found at the National Physical Laboratory and at the Bureau of Standards with a sample of mercurous sulphate prepared by this method at the Laboratoire Central, and also with the French sample employed in Washington. Moreover, the values of some of these cells show relative changes from the comparisons previously made in the home laboratory, thus increasing the average deviation from the group mean. As indicated by M. Laporte, most of the French cells are several years old, as it was impossible to set up new cells before the Washington meeting, since arrangements for the participation of the Laboratoire Central d'Électricité were not completed until shortly before the meeting.

## Summary

From Table XIII, which shows the values of the separate group means for eight series of comparisons (the first two series being excluded for reasons stated above), it is seen that the average variation of any of the group means hardly exceeds  $\pm 1$  microvolt, and that the average deviation of all of the groups from the mean of the group means is approximately  $\pm 5$  microvolts, which may, indeed, be considered as a most excellent agreement.

For this reason, it was decided by the committee that the voltameter results should be expressed in terms of the mean of the group means of the four sets of cells, thus necessitating a correction of +26 microvolts to the results expressed in terms of the basis of reference of the Bureau of Standards. Assuming, further, that the cells now set up have the same value as the cells which formed the original basis of reference of the Bureau, it would appear from Table VII that these reference cells have decreased by approximately 2 parts in 100 000 since 1907.

The mean value of W 109 employed in the voltameter work, after applying the above correction of 26 microvolts, is equal to the mean value of the group means less 23 microvolts. This correction has been applied in the tables below giving the results of the voltameter experiments.

### TABLE XIII

Differences, in Microvolts, between Separate Group Means and the Bureau of Standards Basis of Reference

Group	Mean-NBS	Basis of	Reference
-------	----------	----------	-----------

Number of cells	Apr.	Apr.	Apr. 11	Apr. 15	Apr. 22	Apr. 29	May 10	May 16	Means	Means minus group mean	Average deviation of individ- ual cells from sepa- rate group means
PTR 15	+26	+27	+27	+26	+27	+26	+25	+25	+26	0	±10
NPL 34	+22	+25	+26	+25	+25	+25	+24	+23	+24	-2	± 9
LCE 15	+35	+38	+37	+35	+34	+34	+32	+35	+35	+9	±25
NBS 40	+17	+18	+19	+18	+18	+17	+16	+16	+17	9	± 6
Mean of group	+25	+27	+27	+26	+26	+26	+24	+25	+26		

### New Cells set up at Washington by the International Committee

In order to determine the effect of different methods of preparation and of washing the mercurous sulphate, it was agreed by the committee (see minutes of the seventh meeting) "that representatives from each of the four laboratories receive samples from representatives of each of the other laboratories, and that with this material and his own he make up 12 cells—three from each of the samples, using the method of preparation which he chooses." It was further agreed that the mercury, cadmium amalgam, cadmium sulphate crystals, and solution, should be

taken from a common supply furnished by the Bureau of Standards.

In addition it was agreed to permit the representatives of the Bureau of Standards to set up eight cells—two each with the samples of cadmium sulphate from the four institutions, the other materials being the same, and to compare the mercury and cadmium amalgams brought to the Bureau with those used in setting up the 48 cells.

This program was carried out in so far as time permitted. Owing to the numerous voltameter experiments made, and the sessions of the committee, and the impracticability of more than one person setting up cells at the same time, the operation of washing the mercurous sulphate by M. Laporte, was done under most unfavorable conditions, and extended over a number of days. Prof. Jaeger washed only his own sample of mercurous sulphate, Mr. McKelvy washing the remaining samples in accordance with the instructions furnished, preparing the pastes, and setting up the 12 cells representing the Physikalisch-Technische Reichsanstalt procedure.

### The Mercurous Sulphate

Three samples of mercurous sulphate were prepared in Washington by the following methods:

- 1. By the precipitation method, by Prof. Jaeger.
- 2. By the precipitation method, by Mr. Smith.
- 3. By direct current electrolysis, by Mr. McKelvy.

Three samples of mercurous sulphate were made, using a current density of 4.7 amperes per dm² for 5.5 hours. The sulphuric acid used was J. T. Baker's best, diluted to 1:6 by volume (23.5 per cent H<sub>2</sub>SO<sub>4</sub> or 2.8 N). The mercury used was the same as that used in constructing the cells. The three samples were mixed thoroughly and kept under 1:6 acid. The sample was separated from the excess metallic mercury by decantation.

An apparatus was also constructed for preparing mercurous sulphate by alternating current electrolysis, as prepared by the Laboratoire Central d'Électricité. With the particular apparatus, the yield was so small, using a 60-cycle current, that no solid mercurous sulphate had been precipitated at the end of two hours.

With a frequency of 42 cycles per second, the yield with a current of 5 amperes was insufficient after 24 hours' continuous operation to set up the 12 cells agreed upon. A sample prepared by the same method at the Laboratoire Central d'Électricité, by M. R. Jouaust, was therefore used instead. This sample had been prepared in 24 hours. The more rapid production of mercurous sulphate is attributed to a stronger agitation of the surface of the mercury.

# The Washing of the Mercurous Sulphate

Physikalisch-Technische Reichsanstalt.—The white sample precipitated chemically by Dr. Jaeger was washed with water three times by decantation, then five times with small portions of a saturated CdSO<sub>4</sub> solution in a Gooch crucible provided with a filter paper disk as filtering septum. The PTR sample was kept under saturated CdSO<sub>4</sub> solution until used. The three other samples were used immediately after washing.

Bureau of Standards.—The four samples used in making up the 12 cells representing the Bureau of Standards procedure were washed twice with pure absolute alcohol in a Gooch crucible, then let stand under alcohol in a beaker for an hour. On again transferring to the crucible, they were washed twice with alcohol and then twice with anhydrous ether. These samples were then placed in a high vacuum and so kept until used.

Laboratoire Central d'Électricité.—The washing of the four samples was made in a Gooch crucible using a disk of filter paper. It was washed twice with H<sub>2</sub>SO<sub>4</sub> of spec. grav. 1.15, then several times with a concentrated solution of CdSO<sub>4</sub>, until a piece of congo paper placed in contact with the last wash water showed only a slight tendency to become blue. As a result of the meetings and other circumstances, the washing was interrupted several times, and lasted several days. The cells were then set up under very unfavorable conditions.

National Physical Laboratory.—The sample precipitated chemically by Mr. Smith was washed with dilute H<sub>2</sub>SO<sub>4</sub> (1 to 6) twice by decantation. The precipitate was then filtered, washed three times with dilute H<sub>2</sub>SO<sub>4</sub> and afterwards 6 times with a neutral saturated solution of cadmium sulphate to remove the acid. The

mercurous sulphate was then flooded with cadmium sulphate solution and left for one hour. It was then washed twice more with cadmium sulphate solution.

### The Remaining Materials

The Mercury.—All the Hg used in this investigation was first subjected to a preliminary purification by electrolysis. It was then further purified by distilling it at least twice in a current of air under greatly reduced pressure, according to Hulett and Minchin.<sup>17</sup>

The essential feature of this method is the oxidation of any metals, that may distill with the mercury, by means of a slow current of air, admitted through a tube drawn out at one end to a very fine capillary extending almost to the bottom of the distilling bulb.

The Cadmium Amalgam.—The 10 per cent amalgam was made up by direct weighing from Kahlbaum's electrolytic cadmium and the purest mercury. The thin film of oxide on the surface of the cadmium was removed by means of dilute sulphuric acid. This was removed by thorough washing with pure water, the amalgam then being dried before weighing.

The Cadmium Sulphate.—Kahlbaum's cadmium sulphate, prepared especially for standard cells, was treated in the manner prescribed by Wolff and Waters. The final product was crushed and thoroughly mixed to give a uniform sample. This cadmium sulphate was used for this entire series of cells.

The Cadmium Sulphate Solution.—The cadmium sulphate described above was added in excess to the purest water, and the whole rotated at 25° in liter bottles for at least a day. The solution was then filtered. This solution was used in washing the mercurous sulphate, and in constructing the cells by all the representatives, and was made in such quantity as to cover these operations for all the cells set up, where it was desired to keep the cadmium sulphate constant.

# Setting up the Cells

All the cells were set up in the manner described in the appendix to the report of the London Conference.

<sup>17</sup> Physical Review, 21, p. 388; 1905.

# Sealing

All the cells were hermetically sealed in glass without overheating the cell contents in any case.

### The Results

The differences, at 25° C, found between these 48 cells and the mean of the group means, used as the basis of the voltameter experiments, are given in the following Table XIV:

TABLE XIV

Cells set up by the International Committee

Set up by Dr. Wolff and Mr. McKelvy, May 9, 1910

Cell

Hg<sub>2</sub>SO<sub>4</sub> May 12 May 14 May 16 May 24 May 27 May 31 June 6 June 14 June 20

Cen	1162001	IVIAY IL	IVIUJ IT	iviay 10	Iviay Dr	IVI dy 27	iviay 51	June 0	June 14	June 20
301	)	( - 5	- 8	-10	-13	-15	-16	-16	-17	-18
302	NBS	- 5	- 8	-10	-14	-17	-17	-17	-18	-18
303		+ 1	- 3	<b>-</b> 5	-10	-13	-14	-13	-14	-15
304	h	( +15	+14	+15	+16	+15	+15	+18	+19	+19
305	LCE	+13	+13	+14	+16	+16	+16	+18	+18	+18
306	1)	+17	+17	+18	+18	+17	+17	+19	+19	+20
307	h	ſ <b>−</b> 26	-30	-30	-34	-35	-36	-35	-35	-34
308	NPL	-39	-41	-42	-40	-41	-41	-39	-39	-38
309	)	-25	-29	-31	-33	-35	-36	-34	-35	-34
310	1	( +12	+ 9	+10	+11	+ 9	+ 9	+12	+12	+12
311	PTR	+12	+ 9	+11	+10	+ 9	+ 9	+11	+11	+11
312	J)	+11	+10	+10	+10	+ 8	+ 8	+10	+10	+10
Mean		-1.6	-3. 9	-4. 2	-5.2	-6.8	-7. 2	-5.5	-5. 8	-5.6
Average deviation f	rom mean.	±15.4	±16.1	±17.2	±18.8	±19.2	±19.5	±20.2	±20.6	±20.6
	Set up by Mr. Smith, May 13, 1910									
313	1	ſ	-15	-27	-29	-31	-32	-31	-31	-31
314	NBS	{	- 5	-23	-31	34	-35	-35	-35	-36
315	)	l	<b>–</b> 4	-10	-14	-18	-18	20	-21	-21
316	1	ſ	+34	+29	+22	+18	+17	+18	+16	+16
317	} LCE	<b>{</b>	+27	+22	+19	+16	+15	+17	+16	+16
318	)	l	+50	+42	+31	+29	+26	+26	+23	+23
319	1	·	+44	+22	+ 8	+ 2	+ 1	- 1	<b>-</b> 5	<b>—</b> 6
320	NPL	<b>{</b>	+34	+17	<b>—</b> 2	<b>–</b> 9	-10	-13	-18	-18
321	)	l	+33	+13	+ 3	- 3	<b>—</b> 4	- 7	-11	-12
322		[	+ 8	+ 6	+ 5	+ 2	+ 3	+ 3	+ 3	+ 2
323	PTR	{	+ 2	+ 3	+ 3	0	0	+ 2	+ 2	+ 2
324	324		+18	+13	+10	+ 8	+ 8	+ 9	+ 7	+ 6
Mean	Mean			+8.9	+2.1	-1.7	-2.4	-2.7	-4.5	-4.9
			+18.8							

### TABLE XIV—Continued

# Cells set up by the International Committee—Continued

# Set up by M. Laporte, May 24, 1910

Cell	Hg <sub>2</sub> SO <sub>4</sub>	May 12	May 14	<b>M</b> ay 16	May 24	May 27	May 31	June 6	June 14	June 20
325	)	(				+163	+157	+154	+144	+132
326	NBS	{				+199	+182	+172	+158	+143
327	)	l				+236	+214	+199	+183	+166
328	)	ſ				26	+ 22	+ 48	+ 49	+ 46
329	LCE	<b>{</b>				+ 91	+ 84	+ 80	+ 75	+ 69
330		L				+ 92	+ 85	+ 81	+ 76	+ 71
331	1	ſ				+171	+163	+157	+143	+134
332	NPL	<b>{</b>				+200	+179	+166	+150	+139
333		L				+208	+193	+179	+164	+153
334	í	1				+165	+162	+150	+138	+127
335	PTR	<b>{</b>				+105	+130	+131	+124	+114
336	J	l				+171	+154	+143	+133	+123
Mean						+147. 9	+143.8	+138.3	+128. 1	+118.1
Average deviation fr	om mean.					± 54. 9	±42.2	±35.7	±31.4	±28.8

### Set up by Mr. McKelvy for Dr. Jaeger, May 26, 1910

337	1		 1	 -32	-38	-37	-36	-35
~ 338	NBS	\	 	 15	-29	-32	-33	-32
339		l	 	 -41	48	-41	-38	36
340	1	[	 	 +16	+11	+13	+13	+15
341	LCE	<b>{</b>	 	 +29	+17	+17	+16	+18
342	J	l	 	 +14	+ 7	+10	+10	+12
343	)	{	 	 + 4	-12	-15	-18	-18
344	NPL	<b>{</b>	 	 + 3	12	-14	-17	-17
345	J	l	 	 + 8	- 9	-13	-15	-15
346	)	ſ	 	 +39	+25	+25	+24	+23
347	PTR	<b></b>	 	 +65	+40	+34	+30	+27
348	J	l	 	 +35	+15	+12	+11	+ 8
Mean			 	 +10.4	-2.8	-3.4	-4.4	-6.7
Average deviation fr	om mean.		 ļ	 ±22.6	±21.9	±21.9	±21.8	±21.3
-		·	 	 				

The agreement of the separate cells of each group of three is quite close, as might have been expected, since the same paste mixture was employed.

The average deviations from the respective group means of the separate cells in each group of 12, representing the four samples of mercurous sulphate washed by the same method, are, however, considerably larger than were found in the case of the cells submitted by the four laboratories, where each group was set up according to the same specifications. The means for the groups, with the exception of the cells set up by M. Laporte, which, as already explained on p. 111, were constructed under abnormal conditions, are, however, practically identical with the mean of the group means given in the main body of the report, thus indicating apparently that no differences are introduced by the differences in procedure followed.

TABLE XV

Group Means for New Cells set up in Washington by International Committee

TI- 00		Set up by—								
Hg <sub>2</sub> SO <sub>4</sub>	NBS	LCE	NPL	PTR	omitting LCE					
NBS	-17	+147	-29	-34	-27					
LCE	+19	+ 62	+18	+15	+17					
NPL	-35	+142	-12	-17	-21					
PTR	+11	+121	+ 3	+19	+11					
Means	- 6	+118	5	<b>- 4</b>	<b>–</b> 5					

The comparison of the separate means for the four samples of mercurous sulphate, as shown by the values given on the same horizontal line, Table XV, is also fairly satisfactory, omitting the cells set up by M. Laporte for the reasons stated above. Differences are, however, indicated, by the means given in the last column, between the four samples of mercurous sulphate, the NBS and NPL samples both giving, respectively, values 27 to 21

parts in 1 000 000 lower than the mean of the group means adopted by the committee, and the LCE and PTR samples higher values by 17 and 11 parts in 1 000 000. To establish these as real differences considerable more investigation would be required.

In particular, the fact that the mercurous sulphate prepared by alternating current electrolysis gives cells whose emf is a little higher than usual, has been observed by several experimenters. This is not to be explained by the dimensions of the crystals of the  $\mathrm{Hg_2SO_4}$ . Measurements made at the LCE have shown that the crystals have a magnitude of from 3 to 6 thousandths of a mm to more than .02 mm. This corresponds closely with the dimensions given by Mr. Smith for crystals prepared by other methods.

### Other Cells set up

It was agreed by the committee to permit representatives of the Bureau of Standards to set up two cells with the four samples of cadmium sulphate submitted by the four laboratories, using the same sample of mercury and cadmium amalgam as used in the 48 cells, and a common sample of mercurous sulphate. The latter was prepared by the electrolytic method, and washed with alcohol and ether, and since preserved in a highly evacuated glass tube, thus eliminating sources of error due to washing. The dry sample was freed from lumps by sifting through platinum gauze, and was then thoroughly mixed.

The cadmium sulphate samples, except in the case of the Bureau of Standards, do not represent the stock employed in setting up the main group of cells. Samples of crystals and saturated solutions were submitted by three of the laboratories, but only crystals were submitted by the Laboratoire Central d'Électricité. From the latter a saturated solution was made.

The results on the cells set up in this manner are given in Table XVI.

TABLE XVI

Cells set up with Different Samples of CdSO<sub>4</sub>
Differences, in Microvolts, from Mean of the Group Mean

Cell	CdSO <sub>4</sub>	May 10	May 12	May 14	May 16	May 24	May 27	May 31	June 6	June 14	June 20
349	NBS	{ - 3	-14	-16	-19	-21	-23	-25	-25	-22	-25
350		- 2	-11	-12	-15	-19	-20	-22	-22	-21	-23
351	LCE	{ −27	-29	-28	-29	-29	-30	-30	-28	-27	-28
352		−27	-29	-29	-30	-30	-31	-30	-29	-28	-29
353	NPL	{ -19	-21	-22	-23	-24	-25	-25	-25	-23	-24
354		-14	-20	-21	-22	-23	-24	-24	-23	-21	-23
355	PTR	{ +11	- 1	- 3	- 4	-12	-14	-19	-20	-22	-25
356		+10	- 2	- 4	5	-12	-15	-19	-20	-23	-28
1	Mean	<b>–</b> 9	. —16	-17	-18	-21	-23	-24	-24	-23	-26
Averag from	ge deviation mean	±13	± 9	± 8	± 8	± 5	± 5	± 3	± 3	± 2	± 2 1

From Table XVI it will be seen that at the last measurement the cells are in practical agreement; the initial difference between them has been steadily decreasing. Their mean value is now less than the mean of the group means adopted as a basis of reference. It is particularly noteworthy that the two cells set up with the Laboratoire Central d'Électricité sample attained their normal value immediately after they were set up. As this is one of the principal objects sought, it is felt that further investigation of the CdSO<sub>4</sub> solutions is highly desirable. Three other cells, since set up with the same sample of CdSO<sub>4</sub>, also showed an exceptionally small hysteresis.

Two four-limb cells were set up to compare the samples of mercury and cadmium or cadmium amalgam with those employed in setting up the Bureau of Standards cells and the cells set up by the committee in Washington. Here, again, the samples submitted, except in the case of the Bureau cells, did not represent the materials employed for the particular cells submitted by the respective laboratories. It was, however, thought that a comparison might be interesting.

The samples of mercury compared were the following:

- (a) Purified at Bureau of Standards by Hulett's method.
- (b) Purified at Bureau of Standards by making the mercury the anode in electrolysis.

- (c) Purified at Physikalisch-Technische Reichsanstalt.
- (d) Purified at National Physical Laboratory.

The samples were covered with the same paste mixture. The differences in electromotive force, in microvolts, are given in the following table, from which it appears that, although one of the samples differed by 17 microvolts initially, all the samples were in practical agreement after six weeks.

TABLE XVII

Comparison of four samples of Mercury

			1		
Sample	May 10	May 11	<b>M</b> ay 12	May 14	June 20
(b)—(a)	- 1	0	- 1	0	0
(c)-(a)	+17	+16	+13	+12	+4
(d)—(a)	+ 3	+ 3	+ 3	+ 4	+2

Differences, in Microvolts

The cadmium amalgam samples, all containing 10 per cent cadmium, were the following:

- (a) Prepared at Bureau of Standards from Kahlbaum's best electrolytic cadmium.
- (b) Prepared at Laboratoire Central d'Électricité by electrolysis (originally 12.5 per cent).
  - (c) Prepared at Physikalisch-Technische Reichsanstalt.
- (d) Prepared from sample of 15 per cent amalgam submitted by the National Physical Laboratory.

The amalgams were introduced into the cell, covered with CdSO<sub>4</sub> crystals and saturated CdSO<sub>4</sub> solution, and the cell sealed. The differences, in microvolts, are given in the following table:

# TABLE XVIII Comparison of four samples of Cadmium Amalgam

Differences, in Microvolts

Sample	<b>May</b> 10	May 11	<b>M</b> ay 12	May 14	June 6
(b)—(a)	<b>–</b> 3	<b>–</b> 3	<b>–</b> 3	<b>–</b> 3	<b>–</b> 3
(c)—(a)	0	0	0	0	<b>–</b> 3
(d)—(a)	-36	<b>—</b> 36	-37	-37	<b>—37</b>

The National Physical Laboratory amalgam is one of a series investigated by Mr. Smith in 1908,<sup>18</sup> and showed surface change which reminded one of tin "plague." It was taken to Washington to point out this appearance to the committee. It was made from electrolytic cadmium and originally the amalgam had been completely melted and chilled by sudden cooling to – 30°. In making up the 10 per cent amalgam, it was heated with the required amount of mercury until the whole was melted and then filtered through a capillary to remove the surface contamination, and introduced into the cell on remelting. This should, however, have given normal values, since any effect of chilling the original amalgam should have been eliminated by diluting and remelting.

It is suggested that in the future international coöperative work the cells submitted by each laboratory be set up from the same supply of mercury, amalgam, and cadmium sulphate, and that samples be preserved for subsequent comparison.

# Report on Measurements made on the Cells submitted for Comparison to determine the Magnitude of the Hysteresis following Temperature Changes

After the 10 measurements above discussed, supplementary observations were made at 30°, 20°, and 25°, to determine whether there were any marked differences between the cells with respect to the rapidity with which they adjusted themselves to temperature changes.

The baths were first regulated at 30° by increasing the electrical heating, and this temperature was maintained within 0.02° for 48 hours. The temperature was then reduced to 20° by ice water circulation, the regulation being effected by the method which had been found most satisfactory in the determination at the Bureau of the temperature coefficient of the Weston Normal Cell.<sup>19</sup>

As was there pointed out, the difficulty of regulating and maintaining a small steady flow of ice water through the coils of two or

<sup>18</sup> Phil. Mag., 19, p. 250; 1910.

<sup>19</sup> Bulletin, Bureau of Standards, 5, 316; 1908. (Reprint No. 104.)

more tanks in parallel, due to the separation of air bubbles in the pipes, was overcome by the use of an auxiliary water tank provided with an overflow and maintained at a temperature of 17–18° C by regulating the flow of ice water admitted to it. The water from this tank was circulated through the cooling coils of the two tanks containing the cells by the aid of a rotary pump, the water being returned to the auxiliary tank, thus forming a closed system. No difficulty was found except from an inadequate supply of ice.

In the following tables are given the differences between the observed values of the separate cells and the values found in the last series of observations at 25°. For comparison, it will be noted that the 25°-30° difference, according to the formula of Wolff adopted by the London Conference, is 266 microvolts, and the corresponding 20°-25° difference is 226 microvolts.

TABLE XIX

Cells submitted by the Physikalisch-Technische Reichsanstalt

Differences, in Microvolts, from 25°

Cell	24 hours 30°	48 hours 30°	24 hours 20°	48 hours 20°	24 hours 25°	4 days 25°	10 days 25°	18 days 25°	35 days 25°	36 days 25°
$\mathbf{D}_1$	-255	-260	+254	+253	+5					
$\mathbf{D}_2$	-261	-264	+218	+221	-3					
$\mathbf{D}_3$	-260	-262	+233	+229	-2	-3	-2	-4	-5	<b>—</b> 5
$\mathbf{D}_4$	-265	-269	+220	+230	-1					
E10	-263	-263	+221	+221	-2					
E11	-264	-263	+221	+222	-1	-1	-1	-2	-2	-1
$\mathbf{E}_{12}$	-265	-263	+220	+220	-2					
$\mathbf{E}_{13}$	-266	-264	+220	+221	-2					
$\mathbf{F}_{7}$	-261	-263	+223	+226	-2					
$\mathbf{F}_8$	-261	-263	+225	+228	-1					
$\mathbf{F}_{9}$	-263	-263	+224	+225	-2	-2	-3	<b>—</b> 5	-4	<b>-</b> 5
$\mathbf{F}_{10}$	-261	-262	+216	+220	-3					
$\mathbf{H}_{1}$	-264	-263	+216	+216	-4					
$\mathbf{H}_2$	-264	-263	+220	+219	-4					
$\mathbf{H}_3$	-262	-262	+221	+221	-4	-4	<b>—</b> 5	-6	-2	6
Mean	-262.3	<b>—263.</b> 1	+223.5	+224.8	-2					

TABLE XX

# Cells submitted by the National Physical Laboratory

Differences, in Microvolts, from 25°

Cell	24 hours 30°	48 hours 30°	24 hours 20°	48 hours 20°	24 hours 25°	4 days 25°	10 days 25°	18 days 25°	35 days 25°	36 days 25°
$A_1$	-262	-261	+225	+225	-2					
$\mathbf{A}_2$	-260	-260	+229	+228	-3					
$A_3$	-262	262	+226	+225	-4					
$\mathbf{A}_4$	-262	-262	+224	+223	-5	-2	+2	-3	-1	-1
A5	-262	-263	+224	+223	<b>-</b> 5					
$\mathbf{B}_1$	-262	-262	+229	+229	-2					
$\mathbf{B}_2$	-262	-263	+245	+243	+6					
$\mathbf{B}_3$	-262	-263	+223	+224	-4					
$C_1$	-262	-262	+229	+228	-2					
$C_2$	-261	-262	+234	+233	0					
$\mathbf{D}_1$	-261	-262	+225	+225	-2			1		
$\mathbf{D}_2$	-261	-263	+225	+226	-4					
$\mathbf{D}_3$	-261	-263	+224	+225	-2					
$\mathbf{E}_1$	-262	-263	+228	+228	-1					·
$\mathbf{E}_2$	-262	-262	+226	+226	-2	-1	-1	-4	0	-2
$\mathbf{E}_3$	-26i	-261	+226	+226	0					
$\mathbf{E}_4$	-262	-262	+221	+222	-1			1		
$\mathbf{F}_1$	-262	-260	+222	+222	-3					
$\mathbf{F}_2$	-261	-261	+222	+222	0					:
$\mathbf{F}_3$	-259	-260	+222	+222	+1					
$\mathbf{F}_{4}$	-262	-262	+222	+222	0					
Gı	-263	-263	+219	+223	-4					
$G_2$	-261	-262	+221	+223	-3					}
G <sub>3</sub>	-265	-262	+224	+225	-3	-2	-2	-4	-1	-3
G <sub>4</sub>	-259	-262	+222	+224	-1					
$G_5$	-263	-263	+220	+225	-2					
$\mathbf{H}_1$	-265	264	+220	+222	-3					
$\mathbf{H}_2$	-262	-263	+221	+223	-2					
$H_3$	-263	-264	+223	+224	-3	-3	-3	-6	-2	-4
H <sub>4</sub>	-263	-264	+218	+222	-3					
$\mathbf{H}_{5}$	-262	-262	+219	+222	-2					
K <sub>1</sub>	-262	-262	+223	+222	-1					
$\mathbf{K}_2$	-262	-262	+223	+223	-1					
$\mathbb{K}_3$	-262	-261	+210	+211	-2					
Mean	-261.8	-262.1	+223.9	+224.6	-2					

### TABLE XXI

# Cells submitted by the Laboratoire Central d'Électricité

Differences, in Microvolts, from 25°

Cell	24 hours 30°	48 hours 30°	24 hours 20°	48 hours 20°	24 hours 25°	4 days 25°	10 days 25°	18 days 25°	35 days 25°	36 days 25°
E <sub>9</sub>	-183	-228	+644	+587	+ 59					
$\mathbf{E}_{12}$	-203	-222	+460	+445	+ 33					
$\mathbf{E}_{13}$	-162	-194	+676	+630	+ 62					
E14	-197	-218	+514	+495	+ 75					
$\mathbf{D}_2$	-261	-261	+209	+218	+ 18	+28	+32	+41	+68	+69
$\mathbf{D}_3$	-251	-254	+235	+241	+ 12					
$P_1$	-261	-261	+214	+214	<b>–</b> 5					
$\mathbf{P}_2$	260	-260	+227	+222	- 2	- 1	- 1	<b>–</b> 2	- 1	- 3
$P_3$	-263	-264	+229	+224	<b>→</b> 3					
$S_2$	-261	-261	+410	+417	+129					
S <sub>4</sub>	-246	250	+274	+275	+ 20					
$S_5$	-241	-247	+235	+249	+ 11	+10	+ 9	0	- 9	<b>—</b> 7
S <sub>7</sub>	-235	-239	+273	+284	+ 51					
S <sub>8</sub>	-240	-245	+199	+228	+ 12					
$\mathbf{Z}_2$	-253	-258	+290	+284	+ 11	+ 9	+ 4	- 1	- 1	- 3
Mean	-234	-244	+339	+334	+ 32					

TABLE XXII

# Cells submitted by the Bureau of Standards

Differences, in Microvolts, from 25°

Cell	24 hours 30°	48 hours 30°	24 hours 20°	48 hours 20°	24 hours 25°	4 days 25°	10 days 25°	18 days 25°	35 days 25°	36 days 25°
222	<b>—</b> 264	-265	+247	+247	+ 6	+ 5	+4	+3	÷2	+2
226	267	-268	+268	+268	+ 6	+ 4	÷2	0	-3	-3
228	-269	-270	+266	+266	+ 3	+ 2	0	-2	-6	-6
230	- 269	<b>—</b> 269	+243	+246	- 1	- 1	-1	-1	0	-1
231	-265	-265	+232	÷236	- 1	- 1	0	0	-1	-1
232	-268	-268	+230	+234	— 5	- 3	-2	-2	-2	-3
233	-268	-268	+229	+233	- 3					
240	-270	-270	+224	+233	<b>-</b> 9			1		
241	-262	-263	+221	+226	— 5					
242	-262	-264	+227	+228	- 3					
243	- 263	-263	+227	+227	— 2					
244	-263	-263	+222	+225	— 5					
245	-264	-265	+234	+239	+ 1	+ 4	+3	+2	+1	+1
246	-261	-263	+220	+223	- 4					
247	-262	-264	+220	+223	— 5					
248	-263	-265	+218	+223	<b>-</b> 7					
249	-263	-265	+221	+225	— 5			0	1	
250	-263	-263	+229	+232	<b>— 3</b>	<b>—</b> 3	-3	-4	-4	-4
251	-262	-263	+233	+236	- 1	- 1	-1	-1	-1	-1
252	-262	264	+230	+233	— 2	<b>—</b> 2	-1	-2	-1	-1
257	-264	-264	+234	+235	<b>–</b> 2	<b>–</b> 2	-1	-2	-2	-1
259	-267	-267	+227	+231	<b>—</b> 6					
275	-263	-264	+209	+216	-10	<b>—</b> 6	-5	5	-5	-8
276	-263	-265	+217	+221	+ 2					
277	268	-269	+203	+218	-18	-12	<b>-</b> 9	-9	-7	<b>-</b> 9
B22	-262	262	→+ 230	+230	0	0	-2	-4	-4	-4
24	260	-261	+235	+233	+ 2	+ 1	-1	-3	-3	-3
25	-260	-262	+240	+239	+ 2	+ 2	-2	-4	-5	-5
26	-262	-262	+231	+231	0	0	-1	-3	-3	-3
27	-262	-263	+255	+253	+ 6	+ 5	+1	-2	-1	-2
29	-261	-261	+239	+236	+ 3	+ 2	+2	-1	-1	-2
32	-250	-255	+255	+252	+ 3	+ 1	-3	-4	-3	-4
38	-264	-265	+237	+237	+ 2	+ 2	+2	-1	0	0
39	-259	-261	+226	+224	0	<b>←</b> 1	0	-3	-3	-2
40	- 263	-264	+227	+228	<b>—</b> 3	- 3	<u>-5</u>	-6	-7	-6
41	-262	-263	+237	+236	+ 1	+ 1	-1	-3	-5	-4
43	- 262	- 263	+226	+226	- 1	- 1	-1	-3	-3	-3
45	-262	262	+239	+238	+ 3	+ 1	+1	-3	-3	-4
49	-262	-263	+242	+243	+ 4	+ 4	+3	0	-1	-1
50	264	- 264	+243	+241	+ 5	+ 1	0	-1	-2	-3
Mean	<b>—263.</b> 2	-264. 2	+232.3	+234.3	- 2					

### TABLE XXIII

## Cells Set up by the International Committee

Differences, in Microvolts, from 25°

### Set up by Dr. Wolff and Mr. McKelvy, May 9, 1910

Cell	Hg <sub>2</sub> SO <sub>4</sub>	24 hours 30°	48 hours 30°	24 hours 20°	24 hours 20°	48 hours 25°	5 days 25°	6 days 25°
301	)	( -269	-269	+266	+255	+ 5	+ ·1	+ 1
302	NBS	-270	-271	+266	+256	+ 4	0	0
303	J	-269	-270	+266	+255	+ 4	- 1	- 1
304	)	(-266)	-266	+231	+224	- 4	- 3	_ 2
305	LCE	-265	-266	+231	+225	_ 4	- 3	_ 2
306	J	-266	-266	+230	+224	4	<b>–</b> 4	_ 2
307	)	-267	-268	+231	+232	- 3	<b>–</b> 5	_ 2
308	NPL	<b>−267</b>	-268	+240	+231	- 3	4	<b>–</b> 2
309	}	-267	-268	+244	+234	<b>–</b> 3	<b>–</b> 5	<b>–</b> 3
310	1	( -265	-267	+235	+228	- 3	_ 2	- 1
311	PTR	-265	267	+235	+228	<b>–</b> 2	- 1	- 1
312	)	-265	-266	+234	+230	- 1	- 1	0
Mean		-267	-268	+242	+235	- 1	- 2	- 1

### Set up by Mr. Smith, May 13, 1910

313		( -271	-271	+303	+288	+20	+12	+12
314	NBS	-271	-271	+310	+290	+20	+11	+11
315	}	-276	-276	+291	+274	+13	+ 7	+ 6
316	1	-268	269	+245	+233	— 3	<b>–</b> 3	— 3
317	LCE	<b>−268</b>	-269	+245	+232	<b>–</b> 3	<b>—</b> 3	_ 2
318	lj l	<b>—267</b>	-268	+247	+229	- 3	- 3	<b>– 2</b>
319		( -272	-273	+291	+267	+16	- 1	0
320	NPL	-274	-275	+298	+274	+ 7	<b>— 3</b>	<b>– 2</b>
321	}	_274	-276	+293	+268	+ 5	- 4	- 3
322	)	-276	-277	+242	+234	- 1	- 2	0
323	PTR	277	-277	+237	+230	<b>– 2</b>	- 2	0
324	J	-266	-267	+244	+236	- 1	0	0
Mean		-272	-272	+270	+255	+ 8	+ 1	+ 1

TABLE XXIII—Continued

# Cells Set up by the International Committee—Continued Set up by M. Laporte, May 24, 1910

Cell	Hg <sub>2</sub> SO <sub>4</sub>	24 hours 30°	48 hours 30°	24 hours 20°	24 hours 20°	48 hours 25°	5 days 25°	6 days 25°
325	1	_296	-294	+452	+368	+14	-13	-16
326	NBS	280	-281	+435	+353	+10	-10	-10
327		-280	-281	+462	+374	+13	- 9	-12
328	h	( -249	-248	+216	+204	- 1	<b>—</b> 2	- 1
329	LCE	-265	-267	+269	+249	<b>—</b> 2	<b>–</b> 5	- 4
330	J	266	-266	+264	+247	<b>—</b> 2	- 5	- 4
331	1	∫ <b>—280</b>	-283	+368	+315	+12	-13	-13
332	NPL	-283	-285	+423	+350	+16	-11	-11
333	J	<b>—286</b>	-287	+438	+362	+17	- 8	<b>-</b> 9
334	1	√ −276	-279	+387	+314	+ 4	-13	-13
335	PTR	-269	-271	+353	+290	+ 9	5	6
336	J	-283	-282	+389	+317	+ 1	- 8	<b>–</b> 9
Mean		-276	-277	+372	+312	+ 8	- 8	<b>–</b> 9

### Set up by Mr. McKelvy for Dr. Jaeger, May 26, 1910

337		(-270)	-270	+254	+245	+ 1	+ 2	+ 3
338	NBS	-269	-269	+262	+251	+ 3	+ 4	+ 6
339	J	-269	-269	+256	+254	+ 6	+ 6	+ 7
340	h	ſ <b>−</b> 270	-270	+246	+236	- 7	- 7	<b>–</b> 5
341	LCE	270	-270	+245	+235	- 6	<b>–</b> 5	- 4
342	J	-269	-268	+247	+241	- 3	- 3	- 1
343	1	-268	-270	+254	+243	0	- 1	+ 1
344	NPL	-269	- 269	+254	+240	- 2	- 3	<b>- 2</b>
345	J	-269	-270	+254	+241	- 2	- 3	- 3
346	1	∫ <b>-279</b>	-277	+282	+259	- 1	- 3	<b>–</b> 2
347	PTR	-272	-273	+279	+258	- 1	- 4	- 2
348	J	-272	-271	+293	+268	+ 3	0	+ 2
Mean		-270	-270	+260	+248	- 1	- 2	0
						1		1.

### TABLE XXIV

# Cells Set up to Test Different Samples of Cadmium Sulphate Differences, in Microvolts, from 25°

Cell	CdSO <sub>4</sub>	24 hours 30°	48 hours 30°	24 hours 20°	24 hours 20°	48 hours 25°	5 days 25°	6 days 25°
349	NBS	∫ <b>—263</b>	-263	+243	+237	+2	+2	+2
350		-264	-264	+241	+235	0	0	+1
351	LCE	∫ <b>—264</b>	-264	+125	+217	-5	-2	-1
352	LCE	€ <b>—263</b>	-264	+227	+227	0	0	+1
353	NPL	∫ <b>—264</b>	-265	+241	+235	+2	+1	+2
354	}NPL	-265	-265	+241	+237	+2	+2	+3
355	PTR.	-272	-273	+285	+266	+5	-4	-1
356	JPIR	270	-270	+288	+268	+9	-2	+1
Mean.		-266	-266	+236	+240	+2	0	+2

### 3. DESCRIPTION OF THE EXPERIMENTS ON THE VOLTAMETER

The persons who took part in the voltameter experiments were: Mr. Smith of the National Physical Laboratory, Dr. Jaeger of the Physikalisch-Technische Reichsanstalt, M. Laporte of the Laboratoire Central d'Électricité, and working under the direction of Dr. Rosa, Messrs. Vinal, McDaniel, Post, Grover, Dellinger, and McBride, of the Bureau of Standards.

General Arrangement of the Apparatus.—The general arrangement of the circuits and the apparatus used is shown in Fig. 4 and the photograph (Fig. 5). The current was taken from a 120-volt storage battery, no one else using the battery at the same time. After the first experiment of this series, a special line was

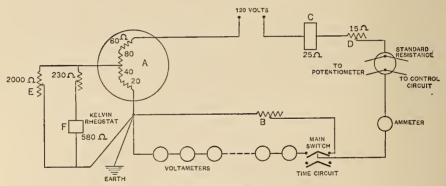


Fig. 4 .- The Voltameter Circuit

Before beginning the experiment, the current flows through a resistance B approximately equal to the resistance of the voltameters

run from the battery to the voltameters to guard against troubles due to uncertain contacts and plug resistances, such as might arise at the switchboard, and the connections between the separate cells of the battery were investigated and found satisfactory. The voltameter circuit included five manganin coils of 40 ohms, and one of 20 ohms in an oil bath A (Fig. 4), which coils constituted the main portion of the resistance in the voltameter circuit. In series with these was a variable rheostat B of 30 ohms range, which could be substituted in the circuit in place of the voltameters before the beginning of the experiment by means of the main switch. From the latter the current passed through a Weston



Fig. 5.—Arrangement of the Voltameters



ammeter of 1.5 amperes range, a resistance standard of 2 ohms, a rheostat D of 15 ohms, variable in steps of less than one-tenth ohm, to a rheostat C of 25 ohms, variable in steps of one-half ohm.

Arrangement for Holding the Current Constant.—Before the beginning of the experiment, the resistance of the rheostat B was set to a value which past experience would indicate as the probable resistance of the voltameters. With this resistance in the circuit, the current was adjusted to approximately the desired value, by means of the rheostats C and D. For the fine regulation of the current, two circuits were arranged in parallel with a portion of the manganin resistance A of 60 ohms resistance. One of these circuits consisted of a variable rheostat E of about 2000 ohms, while the other contained a Kelvin rheostat F having a total resistance of 580 ohms, in series with a variable rheostat G of about 230 ohms. Before an experiment, the current was allowed to flow for some time with the rheostat B in place of the voltameters. The current having been found to be satisfactorily steady, and having been adjusted to the proper value, the main switch was thrown to its other contacts, thus introducing the voltameters into the circuit in place of the rheostat B. The change in the current (usually small) due to the difference between the actual and the predicted resistance of the voltameters, was in a very few seconds corrected by rapidly sliding the contact of the rheostat D in the direction indicated by the deflection of the galvanometer, the correct current being quickly attained by oscillations of rapidly decreasing amplitude about the correct value. The current was then maintained constant by means of the Kelvin rheostat.

The Adjustment of the Value of the Current.—The current was adjusted to the desired value by means of a Wolff potentiometer and standard cell. The connections are shown in Fig. 6. The potentiometer was of the Wolff form as modified for the Bureau of Standards, according to suggestions of Mr. H. B. Brooks. The main circuit of the potentiometer includes eighteen 1000-0hm coils, nine 100-0hm coils, nine tens, nine units and ten tenths, and, in addition, fixed coils of 800 ohms and 190 ohms, together with an extra dial A of ten 1-0hm coils. The total resistance in the

main circuit is therefore 20 000 ohms plus a variable external resistance depending on the voltage of the storage cell, and the usual Wolff arrangement of double dials, as shown in the figure, provides that the total resistance shall be independent of the setting of the dials. Permanent connections are made to the end of the eighth 1000-ohm coil, and to the sliding contact of the extra dial of units, so that by placing the switch on the points N, the standard cell may be placed across a resistance of 10 190 ohms plus the resistance up to the contact on the extra unit dial A. For example, a cell having a value of 1.0195 volts can thus be instantly placed across 10 195 ohms, and the main current adjusted by means of the external resistance, without disturbing the setting of the dials.

The current was held at such a value that the drop of potential over the 2-ohm resistance standard, Fig. 4, was equal to the electromotive force of the standard cell used. To correct, however, for errors in the potentiometer, such as errors in the adjustment of the relative values of the coils, thermoelectromotive forces; changes in the potentiometer current and the like, a control circuit was arranged as shown in Fig. 6. The cell No. 100, whose value was to be determined by means of the voltameters, was joined in series with a sensitive galvanometer, so that by depressing a key the drop of potential over the standard resistance could be opposed directly to that of the standard cell. This circuit served as the ultimate control for the current. The procedure adopted was as follows: While one observer adjusted the current until the electromotive forces in the circuit just described were balanced, a second observer at the potentiometer took note of the resting place of the potentiometer galvanometer which corresponded to this balance. The reading of the potentiometer galvanometer was then held at this point, by means of the Kelvin rheostat, with an occasional check on the correct resting point by the method just described. This procedure not only allows the errors of the potentiometer to be eliminated, but permits a second observer to judge of the steadiness of the current at the same time.

The sensibility of the arrangement adopted was such that a change of current of one part in a hundred thousand produced a deflection of 6 mm in the potentiometer galvanometer, while the

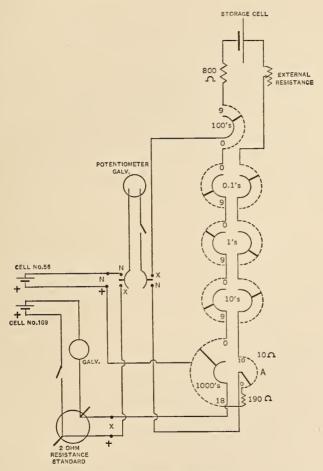


Fig. 6.—Diagram of Potentiometer

The small dial marked A enables the observer to place the standard cell across the proper resistance so that the battery current may be checked without changing the setting of the dials.

deflection corresponding to the same lack of balance in the control circuit galvanometer was 2 cm. Under normal conditions the current could be held so close that the potentiometer galvanometer

uffered no deflection, positive or negative, as great as half a centimeter. As a rule, no correction is applied for these small fluctuations of the current since special experiments, in which a record has been taken of the deflections of the galvanometer during the entire experiment, have shown that the integrals of the positive and negative deflections over the duration of the experiment balance one another very completely.

The Standard Resistance was an open 2-ohm manganin coil by Otto Wolff, No. 2342, kept in an oil bath which was stirred by a motor, the temperature of the bath being taken both at the beginning and end of an experiment. No attempt was made to control the temperature of the bath. The following determinations of the resistance of this coil will give an idea of its constancy. The values observed are here corrected by 7 millionths to conform to the basis of reference adopted by the committee.

Date	Resistance at 25°
	Ohms
1909: Feb. 8	2. 000124
Mar.12	134
Apr. 5	136
July 21	132
Aug.30	150
Oct. 2	150
1910: Mar. 2	150
Apr. 8	134
May 2	136

The resistance at any other temperature is given by the formula

$$R_t = R_{25} \left[ 1 + 7.4^{\text{m}} \left( t - 25 \right) - 0.4^{\text{m}} \left( t - 25 \right)^2 \right]$$

The Standard Cell used was a Weston cell, No. 109. This, with three others, was kept in an oil bath whose temperature was automatically maintained at 25° by a thermostat regulating to 0°01. Previous to this series of experiments, this cell had, with others, been carried downstairs for occasional comparisons with the reference cells of the Bureau of Standards. At the beginning of this series of experiments a specially insulated line was run from the

laboratory on the second floor through a shaft to the standard cell room. The insulation resistance was found to be greater than 1000 megohms, so that no error as great as one microvolt could have been introduced. As a further check, one of the cells was transferred to the reference bath, and the measurements repeated. The difference, after reduction to exactly the same temperature, was found to agree with that found with the special line to within 2 microvolts. This arrangement was found very convenient, allowing as it did measurements of the cells to be made in place. Accordingly, frequent comparisons of these four cells with the reference cells of the Bureau of Standards were made during the course of the series of voltameter experiments. The results of these comparisons have already been given in Table VIII, p. 100. It was there shown that the variations of cell No. 100 with respect to the standard of reference were less than 2 microvolts, the mean value being equal, on the scale adopted by the committee, to -23 microvolts.

Measurement of the Time.—The connections used are shown in Fig. 7. A chronograph, with two pens, was used. One of the pen magnets was placed in series with the secondary of a relay, which received a signal once a second from the standard Riefler clock. The other pen magnet was joined to one set of blades of the main switch.

This was a double-pole, double-throw switch, whose blades were so shaped that when thrown in either direction contact was made on one side just as it was being broken on the other. One side of this switch was used to throw either the voltameter or an equivalent resistance into the circuit as already described; the other side was connected to the time circuit. When this switch was to be thrown up, to insert the voltameters in the circuit, the single pole double-throw switch B was previously thrown up, so that at the instant the current was made through the voltameters the pen magnet was energized. At the end of the experiment, the switch B was thrown down, so that at the instant when the main switch was thrown in the same direction to break the current through the voltameters, the pen magnet was energized exactly as before. Thus, any possible inequality in the working of the magnet on

make and break circuit was avoided by recording both the beginning and the end of the experiment by means of closing the circuit of the pen magnet.

The chronograph used was made by the Société Génèvoise. The speed of the electrical driving motor is controlled by a centrifugal governor which acts on the field circuit of the motor. Three speeds of the drum may be obtained. That used in these

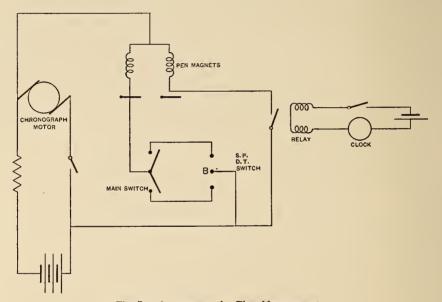


Fig. 7.—Arrangement for Time Measurement

The main switch of the voltameter circuit, Fig. 4, is mechanically joined to the main switch of the time circuit so that they act simultaneously, the latter operating one pen of the chronograph, the other being operated by a standard clock.

experiments was one revolution in 10 seconds, a distance of 5 cm on the record corresponding to one second, thus allowing one hundredth of a second to be easily read with certainty. As the duration of an experiment was about two hours, the determination of the time correctly to one part in a million should not be a difficult matter. Evidence on this point was obtained in an experiment, previous to those of this series, in which the current was started and stopped nine times, so that any systematic error in

the measurement of the time should be magnified and detected in the weight of the deposit, as compared with that obtained under otherwise the same conditions but with no interruption during the experiment. From this experiment it seemed probable that no systematic error in the determination of the time greater than a few parts in a million is to be expected.

Dimensions of the Cathodes and Anodes Used.—These are given, roughly, in the tables below, together with the approximate capacity of the cathodes in cc. Photographs of these have also been made.

TABLE XXV
Dimensions of the Cathodes

Laboratory	Designation of cup	Material	Shape	Diam. at top	Depth	Capacity
				cm	cm	сс
LCE	LC <sup>A</sup>	Platinum	Hemisphere	10.0	4.5	250
LCE	SC <sup>R</sup>	do	do	9.0	4.0	200
PTR	I	do	Cylinder	5.0	6.0	120
PTR	ш	do	do	5.0	6.0	120
NPL	A	do	Nearly cylinder	10.0	9.0	400
NPL	В	do	do	10.0	9.0	400
NBS	92, 93, 95	do	do	10.0	7.5	350
NBS	127, 128	do	Hemisphere	7.5	5. 0	165
NBS	27, 28	do	Crucible	6.0	8.0	125
NBS	125, 126	Gold	do	6.0	8. 0	125

TABLE XXVI
Dimensions of the Anodes

Laboratory	Form	Diameter or transverse dimension	Axial dimension
		cm	cm
LCE			
LCE	Disk	5.0	0.3
PTR	Rod	1.0	3.0
NPL	Disk	5.0	1.0
NBS	Rod	1.5	3. 0
NBS	Disk	3.0	0.3

### Description of the Voltameters

Form used at the Laboratoire Central d'Électricité.—The platinum cup rests on a ring of sheet copper, a projecting lug and binding post serving to lead in the current. The ring and cup are contained in a cylindrical glass vessel, and to insure good contact between the ring and cup the latter rests on sheets of tin foil wrapped on the ring. A vulcanite cross arm, sliding on an upright, carries the anode. Connection is made to the latter by a screw connector soldered to a flexible cord, which terminates in a second binding post on the vulcanite base. The filter paper, used as septum, is formed by the aid of sealing wax, into a cylinder closed at the bottom, and is suspended by silk threads from the cross arms. The general arrangement is shown in the photograph (Fig. 8).

Form used at the Physikalisch-Technische Reichsanstalt.—The top edge of the cylindrical platinum cup is turned over to form a flat rim, which is made fast by winged nuts to a metal holder partly embracing the cup. The cylindrical anode is held by a metal cross arm provided with adjustments for centering the anode, and for holding it at the height desired. When silk is employed as a septum, two layers are generally used, the silk being wrapped completely about the anode and tied around the supporting rod with a silk thread from the same sample of silk. Whether used with silk or without a septum, a little hemispherical glass dish is supported below the anode by three glass rods, bent to hang from the top edge of the cup. The assembled voltameter is shown in the subjoined photograph (Fig. 9).

Form used at the National Physical Laboratory.—This is referred to in presenting the results of the experiments as the "new form." In this the platinum cup rests on a ring of brass, attached to the vulcanite base, and joined to a binding post. The large disc anode is supported by an eccentrically placed rod, protected from the action of the current by a glass tube. The anode rests in a shallow glass cup provided with a ground edge. This glass cup is supported by a glass rod, fused to its center and passing through a hole in the center of the anode. The supporting rods of both anode and cup are held by a metal cross arm, adjustable on a metal upright. A cylinder of glass, about 7 cm in diameter and

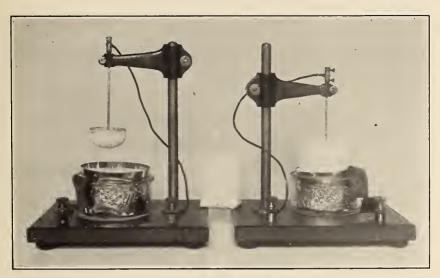


Fig. 8.—The French Voltameters

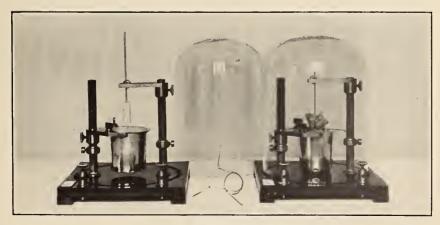


Fig. 9.—The German Voltameters





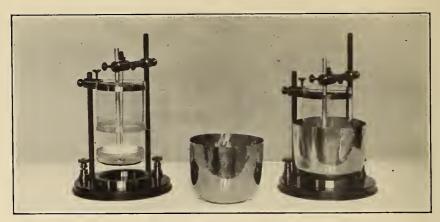


Fig. 10.—The English Voltameters

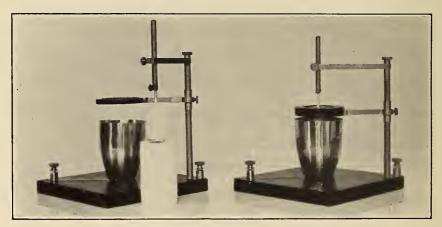


Fig. 11.—The American Voltameters. Porous Pot Form

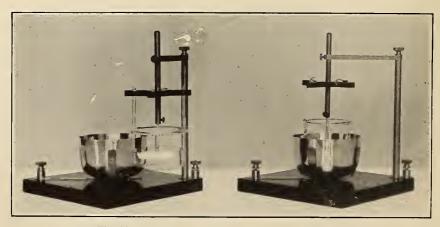


Fig. 12.—The American Voltameters. No septum form

7 cm axial length, is ground to fit over the edge of the glass cup. This cylinder is embraced by a metal collar carried by a piece of brass, which is in turn borne on an adjustable clamp on a second metallic upright. The cylindrical piece is first adjusted to rest on the edge of the glass cup, the whole being centered in the platinum cup. The inner and outer chambers thus formed are next filled with electrolyte to the same level in both, and the glass shield raised until its lower edge is just below the surface of the electrolyte. After the deposit has been made, the cylindrical shield is again lowered to close the anode chamber, and the whole system, filled with electrolyte, is removed from the platinum cup. An assembled view is given in the subjoined photograph (Fig. 10).

The Porous Pot Voltameter as used at the Bureau of Standards.— The platinum cup is held by gold-plated spring clips, mounted on a vulcanite base and screwed to a gold-plated strip bearing a binding post. The porous pot is held in a friction ring of vulcanite, which sets on a second vulcanite ring of somewhat larger aperture, carried by a metal arm terminating in a sleeve which is adjustable on a metal upright. The anode is carried by another metal arm, with adjustments both in a vertical and in a horizontal plane. The porous pots are cylindrical, those used in the smaller platinum cups being 3.5 cm in diameter and 5 cm deep, and those used in the largest cups 4.2 cm in diameter. (See photograph Fig. 11.)

The no-septum form as used at the Bureau of Standards.—When no septum is used, the disk anode rests in a glass cup 5 cm in diameter and 2.5 cm deep, which is suspended from two glass rods bent to hook over a strip of vulcanite carried on the supporting arm. A glass ring is fused to the supporting rods about 2.5 cm above the cup, and the position of the latter is so adjusted that the ring lies in the surface of the electrolyte. This prevents any anode slime, which may rise to the top of the solution, from reaching the cathode. (See Fig. 12.)

If silk is to be used as a septum, the supporting rod of the anode is slipped through a small hole in the silk, and the latter is tucked between the anode and the cup. The anode then holds the silk in place by its weight.

# Methods of Washing and Drying the Cathodes and of Preparing Them for the Next Experiment

Procedure at the Laboratoire Central d'Électricité.—At the end of the experiment the electrolyte is removed from the cathode by means of a pipette, taking care not to remove any loose particles of silver. Any particles which may be drawn into the pipette are carefully replaced. The wash water is renewed eight times, the deposit ordinarily being left several hours, or over night, in the fifth wash water. The electrolyte and all the wash waters are carefully examined for particles of silver, and any which may be found are replaced in the cathode. The latter is then dried at about 140° before weighing.

After weighing, the voltameter is assembled and a small current is sent through in the opposite direction so that at the same time in which the deposit is removed from the cup, an adherent deposit is laid down on the anode. When the deposit has been entirely removed, the cup is washed out, first with nitric acid, and then with a concentrated solution of caustic soda and with distilled water, and dried at 140°.

Procedure at the Physikalisch-Technische Reichsanstalt.—At the end of the experiment, the electrolyte is first poured out, the deposit is rinsed several times with distilled water, after which the cathode is submerged in a beaker of distilled water for an hour or more. The cathode is then rinsed off, both inside and out, into the beaker, to collect any loose silver, and the cup is dried in an oven at a temperature of from 120° to 140°. The electrolyte, as well as all the wash water, is then filtered in a Gooch crucible (covered with a hard filter) in order to collect all the silver particles. This crucible is then set in a porcelain crucible without holes, and dried in the manner described above. The silver particles are added to the deposit before weighing. After weighing, the deposit is removed by electrolysis as already described, or simply dissolved by nitric acid, and the cup washed and dried.

Procedure at the National Physical Laboratory.—For the usual procedure, see page 18 of the appendix of the report of the London Conference. The procedure adopted in this series of experiments was somewhat modified. The solution was first removed

from the bowl, which was then nearly filled with distilled water and allowed to stand for at least an hour. This wash water was then removed and the deposits washed eight times with small quantities (about 50 cc) of distilled water. The bowl was dried in an electric oven at about 160°. If any loose silver was observed in the solution or in the wash waters, these liquids were filtered, the filter paper dried, and the loose silver added to the bowl after drying the deposit. The bowl was cooled in a dessicator and weighed.

After weighing, the deposit is removed by passing a current through the voltameter in the opposite direction (a small current density being used in order to obtain an adherent coating of silver on the anode), and the cup was washed with strong nitric acid and distilled water and dried in an electric oven.

Procedure at the Bureau of Standards.—The electrolyte is drawn off by means of a small siphon or pipette, care being taken not to remove all on account of the danger of losing particles of loose silver. The amount of electrolyte left in the bowl will depend on the quantity of loose silver present, which is usually very small. Four wash waters are successively poured into the cup from an Erlenmeyer flask, which eliminates the danger of splashing. wash waters are each drawn off by means of the siphon into large beakers, and these wash waters are examined for loose silver by placing the beakers on black paper in a strong light, the inspection being aided by stirring the liquid in order that any particles present may collect in the center of the beaker. In case any particles are found, they are entrapped in a pipette and replaced in the cathode. Four more wash waters are then added, if necessary, the number depending on the amount of electrolyte left orignally in the cup. The final wash water is not entirely removed from the cathode, but a few cc are left, the quantity depending on the amount of loose silver. The cup is then dried in an oven for an hour at about 150°, then cooled and weighed. After weighing, the deposit is removed by electrolysis, the cup soaked in strong nitric acid, washed with caustic soda, dil. HNO3, and distilled water, and then dried in the oven.

Treatment of the Porous Pots.—These are removed from the electrolyte after an experiment, and kept in silver nitrate until the

next experiment. If they are not to be used again for a long time, they may be kept in distilled water or may be washed and dried.

Description of the Balances Used.—The balances used were four in number. The larger cups, 92, 93, 95, A and B, were weighed on an Oertling balance, those of medium size, 127, 128, LCA and SCB, on one by Rueprecht, and the smaller cups, I, III, 27, 28, 125, and 126, on a balance by Stückrath. The latter was arranged so that the cups could be transposed and the sensibility could be determined without opening the balance case. These three balances are set up on piers in a vault 3 m by 3.5 m, provided with a double wall, access being possible through a double door in the two walls. The deflections of the balances are observed from outside by telescope and scale. The temperature and humidity conditions in this room, with a single observer present, have been very satisfactory. If care be taken to keep the doors closed, and to remain in the room no longer than is necessary,20 the temperature rise during a day's weighing is rarely more than a tenth of a degree, and the change in humidity not more than I per cent.

In practice it was found necessary to wait at least 15 minutes after the balance case had been closed before a reading of the balance could be made. With the Stückrath balance, where it was not necessary to open the case so often, and where the vibration of the small pans is not important, weighings could be made more rapidly.

After the first experiment the Physikalisch-Technische Reichsanstalt cups were weighed on a second Rueprecht balance, similar to that already mentioned, but situated in the room where the regular precision measurement and adjustment of weights by the Bureau of Standards is carried on. The constancy of temperature and humidity in this room (which has several windows and walls of a single thickness only), while good, is naturally not as good as is attainable in the vault when only one observer is present.

Description of the Methods of Weighing.—Since the methods used by the delegates had to be, in some cases, somewhat modified from those previously used to conform with the conditions existing at the Bureau of Standards, and the nature of the balances, the

<sup>&</sup>lt;sup>20</sup> This room was intended for use by only one observer at a time. When several observers were present the conditions were naturally not so favorable as just described.

method used in weighing the Bureau of Standards cups will first be indicated, and the deviations in the practice of the other delegates noted.

The cups are weighed in pairs against a counterpoise, the weights of the two cups and the counterpoise being adjusted very closely to the same value, the differences being in every case less than a milligram and for the most part less than 0.5 mg, except in the case of Nos. 127 and 128, which are, respectively, 2 mg and 3 mg lighter than the cup No. 25, used as counterpoise. The cups 92, 93 and 95 were weighed against a platinum cup, No. 94, while for the small cups, 27, 28, 125, and 126, a square of sheet platinum had been adjusted to serve as counterpoise.

For weighing the cups after an experiment, an additional weight, closely equal to the weight of the silver, was added to the counterpoise. The weights used for this purpose on the Oertling and Stückrath balances, which weights will be referred to as S and S, are of silver, gold-plated. Their values, 4098.26 and 4098.36 milligrams, respectively, were originally adjusted to be as closely equal as possible to the normal deposit in one hour, with a current of I ampere. With the voltameters as now used, it is found necessary with a current of half an ampere (potential drop on the 2-ohm standard equal to the emf of the Weston cell) to let the current flow for about 2 seconds more than two hours, in order that the deposit may be sensibly equal to these weights. Since they are of silver, no buoyancy correction has to be applied. For weighing the deposit in the cups 127 and 128, a weight of platinum, designated as  $\Sigma$ , and having a weight of 4095.23 milligrams, was used. This was purposely made lighter than S and S on account of the fact, already mentioned, that these cups 127 and 128 are 2 to 3 milligrams lighter than their counterpoise. A buoyancy correction of 0.24 mg had to be applied to the weight of the deposit in this case because  $\Sigma$  is of platinum instead of silver.

With the counterpoises and cups adjusted as described, the process of weighing is very much simplified, and the necessity for introducing the hand into the balance case is very much decreased, with an increase in accuracy and saving of time, which amply justify the labor of the adjustment.

The following examples will illustrate the method of making the weighings and recording the results:

[Test, Large Cups, Empty; Date, April 13, 1910; Temperature, 2291; Balance, Oertling; Humidity, 51%; Observer, F. W. G.]

Pans		Rea	dings	Equilib-	Dif-		Observed
Left	Right	Left	Right	rium reading	fer- ence	Computation	differ- ence
93+△ (△=0.4 mg)	94	22. 93 22. 98	25. 70 25. 62 25. 53	22. 96 25. 62 48. 58		(1) $95-94 = \frac{4.52}{5.59} \times 0.399 =$ (2) $93-95 = \frac{6.27}{5.59} \times \frac{0.399}{2} =$	mg -0.322 +0.224
∆removed	94	25. 17 25. 28	29. 06 28. 94 28. 84	25. 22 28. 95		(3) $93-94 = \frac{0.88}{5.59} \times 0.399 =$	-0.063
93	95	23. 13 23. 22	(26. 56) 26. 47	54. 17 26. 47 23. 18	5. 59 4. 52	= sensibility for 0.4 mg  From (1) and (3) 93-95=0.259 mg (calculated)	
95	93	26.99 27.05	(28.97) 28.90	49. 65 27. 02 28. 90 55. 92	6. 27	93-95= 0.224 (observed) Discrepancy= 0.035 mg	
95	94	27. 39 27. 43	29. 44 29. 38 29. 32	27. 42 29. 38 56. 80	0.88		

Here the weight  $\triangle$ , used in determining the sensibility, was a rider whose effect, when applied to the fourth division of the beam, was the same as 0.399 mg on the pan.

It will be seen that the differences of the individual cups and the counterpoise are determined by substitution. The difference between the weights of the two cups is determined by transposition. No discrepancy greater than 0.04 mg between the value thus measured and the value calculated from the two measurements by substitution was tolerated. The average value of this discrepancy, with this balance, was about 0.02 mg or five parts in a million of the weight of the deposit.

From the above measurements we find by least squares adjust-

$$93-94 = -0.075 \text{ mg}$$
  
 $95-94 = -0.310 \text{ mg}$ 

The cups were then used in the third international experiment and, on weighing, the adjusted values were

$$(93 + Deposit) - (94 + \dot{S}) = +0.333 \text{ mg}$$
  
 $(95 + Deposit) - (94 + \dot{S}) = +0.091 \text{ mg}$ 

from which we find

Deposit on 
$$93 = \dot{S} + 0.408 \text{ mg} = 4098.67 \text{ mg}$$
  
Deposit on  $95 = \dot{S} + 0.401 \text{ mg} = 4098.66 \text{ mg}$ 

With the Stückrath balance the procedure was a little different, as is shown in the following example. The discrepancy here in the observed and calculated values of 28–27 is only 0.01 mg.

[Test, Small Platinum Cups, Empty; Date, April 22, 1910; Temperature, 2391; Balance, Stückrath; Humidity, 60%; Observer, G. W. V.]

	Pans	Read	lings	Equilib-			
Left	Right	Left	Right	rium reading	Differ- ence	Computation	Observed Difference
27	С	(124. 6) 124. 3	104.7 105.0	124.3 104.9		$ 27-C = = 28-C = \frac{47.8}{38.6} \times \frac{1}{2} \text{ mg} =  $	mg 0.000 0.619
С	27	(130.7) 130.2	98.7 99.2	229. 2 130. 2 99. 0 229. 2	0.0	$28-27 = \frac{47.0}{38.6} \times \frac{1}{2} \text{ mg} =$ $28-27 \text{ calculated} =$ $\text{Discrepancy} =$	0. 609 0. 619 0. 010
С	added △=1 mg	(116.8) 116.2	74.0 74.6	116. 2 74. 3	38.7	=sensibility for 1 mg	
С	28	( 97.9) 98.1	108.0 107.8	107. 9 98. 1	30.7	- Schstomy to 1 mg	
28	С	(102.8) 103.4	150. 8 150. 0	206. 0 103. 4 150. 4			
28	added △=1 mg	(100.3) 100.5	114.8 114.6	253.8 100.5 114.7	47.8		
28	27	(110. 2) 110. 7	141.9 141.4	215. 2 110. 7 141. 6	38.6	=sensibility	
27	28	(108.3) 108.2	97.0 97.1	252.3 108.2 97.1			
				205. 3	47.0		

The adjusted values were

$$27 - C = +0.003 \text{ mg}$$
  
 $28 - C = +0.616 \text{ mg}$ 

These cups were then used in the sixth experiment, and reweighed on April 25th, the values found being

$$(27 + \text{Deposit}) - (C + \ddot{S}) = +0.458 \text{ mg}$$
  
 $(28 + \text{Deposit}) - (C + \ddot{S}) = +1.151 \text{ mg}$ 

which give

Deposit on 
$$27 = S + 0.455$$
 mg =  $4098.82$  mg  
Deposit on  $28 = \ddot{S} + 0.535$  mg =  $4098.90$  mg

The National Physical Laboratory cups were weighed on the Oertling balance against 94. To do this, a small platinum weight of about 0.114 gram was added to 94, whenever these cups were to be weighed, and the difference between A and B (about 0.496 gram) necessitated the preparation of a second weight equal to this difference, to be added to B. Otherwise, the weighings of these cups were made exactly as in the example already given. At the suggestion of Mr. Smith the weighings were made by Dr. Grover or Mr. Vinal and occasionally checked by himself.

The Laboratoire Central d'Électricité cups were weighed against a set of brass weights, NBS 6550, which were calibrated at the beginning of the experiments. The following example will make clear the method of procedure:

[I, Weight of Cathode A, Empty; Date, April 19, 1910; Balance, Rueprecht; Observer, Laporte]

	Pans		dings		
Left	Right			Means	Computation
Tare	A+10.+1+0.5		22.75		
(100 g)	+0.1.+0.005	22. 51	22.73	22.51	This gives
	+0.002.+0.002	22. 52	22.71	22.73	Tare=A+11.619 $-\frac{10.69}{12.73}$ mg
				45.24	=A+11.61815 g
Tare	50+20+10.+10			26.34	
(100 g)	+5+2.+2+1	1		29.59	
				55.93	1 mg on right gives-12.73 divi-
Tare	Added 1 mg			19.87	sions.
(100 g)				23.33	
				43.20	

[II, Weight of the Cathode A with the Deposit]

	Pans	Read	lings		0
Left	Right	Left	Right	Means	Computation
Tare	A+Deposit +5+2.+0.5+0.02			19. 20 19. 40 38. 60	Tare= A+Deposit+7.520 $-\frac{18.04}{24.51}$ × 2 mg= A+Deposit+7.51853 g
Tare	50+20+10.+10 +5+2.+2+1		,	24.97 31.67	
Tare	Added 2 mg			56.64 13.75 18.38	2 mg on right gives -24.51 divi- sions.
				32.13	

### [III, Weight of Deposit]

For weighing the PTR cups, a platinum counterpoise of about 60 g was used, various small weights of a fraction of a mg being used to bring the equilibrium nearer the center of the scale. For weighing the silver, the Bureau of Standards gold-plated silver weight S was used.

The following example will serve to show the method of weighing and the form of record:

[Weighing No. 9; Date, April 14, 1910; Cup I, Empty; P=Cup I; G=B<sub>1</sub>+0.5 mg; Balance, Stückrath B<sub>1</sub>=Counterpoise; Observer, Jaeger]

Pans		Readin	an and	Position	Mean	
Left	Right	Readill	ıgs	Position	iviean	
G	P	106. 2	106.4	120.15	GP=119.5 Zero position=121.1 PG=122.7	
P	G	104.3 140.8	105.0	122.72	P-G=+3.2 Correction to 0.5 mg=+0.009 mg	
G	P	104.6	105.0	118.9	) <sub>18.4</sub>	
G	P+1	122.8	121.8	100.5	J .	
	mg	78.2		1	Sensibility= $\frac{1}{18.4}$ = 0.0543 mg	

$$P = G + 3.2 \times \frac{0.0543}{2} = G + 0.087 \text{ mg}$$
  
 $P = B_1 + 0.509 + 0.087 = B_1 + 0.596 \text{ mg}$ 

[Weighing No. 11; Date, April 16, 1910; Cup I, with Silver of Experiment No. 3; P=Cup I+Deposit; Baiance, Rueprecht; G=B<sub>1</sub>+S+(0.5+0.3) mg correction of 0.5+0.3 mg=+0.015 mg]

Pa	ans	Readings		Position	Mean
Left	Right		Readings	Fosition	Mean
G	P	87.3	87. 7 114. 0	100.75	GP=101.0 PG=101.75 Zero=101.4
P	G	107. 2	107.0	101.75	P-G=+0.75
G	P	91. 2	91.6	101.25	8.25=0.420 mg
G	P+0.4	116.4	116.9	109.5	
	mg		102.3		Sensibility= $\frac{0.420}{8.25}$ = 0.051 mg

$$P = G + 0.75 \times \frac{0.051}{2} = G + 0.019 \text{ mg}$$

$$= B_1 + \ddot{S} + 0.815 + 0.019 \text{ mg} = B_1 + \ddot{S} + 0.834 \text{ mg}$$
Therefore,

Cup I + Deposit = 
$$B_1$$
 +  $\ddot{S}$  + 0.834 mg  
Cup I =  $B_1$  + 0.596  
Deposit =  $\ddot{S}$  + 0.238 mg  
= 4098.602 mg

## APPENDIX D. TABLES OF RESULTS OF THE EXPERIMENTS WITH THE SILVER VOLTAMETER

## INDEX OF EXPERIMENTS TABLE XXVII

April 9, 1910 (Experiment No. 1<sup>21</sup>)

			April 9,	1910 (	Experiment N	0. 1 21)	
No. of deposit	Labora- tory	Cup	Weight	Weston cell at 20°	Type of voltameter	Electro- lyte	Remarks
						Per cent	
1	LCE	LC <sup>A</sup>	mg		Filter paper	15 B	Filter paper touched
2	LCE	SC <sup>B</sup>	4021.3		do	15 B	
3	PTR	1	4017.04		No septum	20 C	Good deal of anode
	1						slime
4	PTR	III	4011.36		Silk	20 C	Lost some silver
5	NPL	A	4017. 2		New form	11 A	
6	NPL	D	4017. 4		do	11 A	D1 - 1- 1 - 1 1 1 1 1
7	NBS	93	4016. 95		Porous pot	10 D	Black band around top
8 9	NBS	95 27	4019.91		do	10 D	of deposit
10	NBS NBS	28	4017. 16 4016. 61		do	10 D 10 D	
10	NES	40	4010.01		do	10 D	J
		1	April 15,	1910	(Experiment I	No. 3)	
15	LCE	$LC^{A}$	4098. 8	1.01842 <sub>8</sub>	Filter paper	15 B	
16	LCE	SC <sup>B</sup>	4098.8	8428	do	15 B	
17	PTR	I	4098.58	8373	No septum	20 C	Anode slime in cup
18	PTR	III	4098.30	8304	Silk	20 C	
19	NPL	A	4098. 27	8310	New form	10 A	
20	NPL	В	4098. 20	828 <sub>e</sub>	do	10 A	
21	NBS	93	4098. 67	8397	Porous pot	10 D	
22	NBS	95	4098. 66	8394	do	10 D	
23	NBS	127	4098.40	8328	Glass and silk	10 D	
24	NBS	128	4098. 18	8274	do	10 D	
		1	April 20	), 1910	(Experiment I	No. 5)	
29	LCE	LCA	4099. 6	1.018538	Filter paper	15 B	
30	LCE	scB	4099.1	8414	đo	15 B	
31	PTR	I	4098. 54	8275	Double silk	20 C	
32	PTR	III	4098.95	8378	do	20 C	Good deal of loose sil- ver
33	NPL	A	4098.68	8310	New form	10 A	
34	NPL	В	4098. 57	8283	do	10 A	
35	NBS	93	4098. 94	8375	Porous pot	10 D	
36	NBS	95	4099. 01	8392	do	10 D	
37	NBS	127	4098. 23	8201	Glass and silk	10 D	Silk became detached
38	NBS	128	4098. 59	8288	do	10 D	
		1-	I.				

<sup>21</sup> The current was interrupted for 15 seconds or more. Values are comparative only.

# TABLE XXVII—Continued April 26, 1910 (Experiment No. 7 22)

			71pm 20	, 1710	(Experiment 1	(O. 1 )	
No. of deposit	Labora- tory	Cup	Weight	Weston cell at 20°	Type of voltameter	Electro- lyte	Remarks
			mo			Per cent	
43	LCE	LCA	4099. 3	1. 018469	Filter paper	15 B	
44	LCE	SCB		·	do	15 B	Contaminated
45	PTR	1	4098. 36	8236	Double silk	20 C	
46	PTR	III	4098. 25	8209	do	20 C	
47	NPL	A	4099.06	8415	New form	10 A	
48	NPL	В	4099.10	8420	do	10 A	
49	NBS	93	4099.29	8468	Porous pot	10 D	
50	NBS	95	4099. 29	8468	do	10 D	
51	NBS	27	4098. 82	8352	do	10 D	
52	NBS	28	4098. 87	8363	do	10 D	
			May 2,	1910 (	Experiment N	o. 10)	
62	LCE	$\mathbf{LC}^{\mathbf{A}}$	4098. 25	1.018246	New form	15 B	
63	LCE	$SC^{B}$	4099.1	8457	Filter paper	15 B	
64	PTR	1	1 4000 ==	0.05	(Filter paper	20 C	Mean of the two de-
65	PTR	III	4098.77	8376	Double silk	20 C	posits
66	NPL	A	4098.34	8270	New form	10 A	
67	NPL	В	4099. 17	8475	Filter paper	10 A	
68	NBS	127	4098.41	8288	Porous pot	10 A	
69	NBS	128	4099. 48	8552	Glass and silk	10 A	More silk than usual
70	NBS	125	4098. 40	8284	Porous pot	10 A	
71	NBS	126	4099.71	8608	Silk on porous pot	10 A	100 sq. cm of silk on pot
	1.50	150			1		200 847 622 61 812 62 941
			May 7,	1910 (	Experiment No	o. 13)	
86	LCE	LCA	4098. 28	1. 018196	New form	15 B	Electrolyte A was 2 in 106 alkaline
87	LCE	scB	4098. 95	8362	Filter paper	15 B	
88	PTR	I	4099. 44	8482	do	20 C	
89	PTR	III	4098. 48	8246	Double silk	20 C	
90	NPL	A	4098. 66	8290	Silk	10 A	One layer of silk (Jaeger)
91	NPL	В	4098. 96	8363	New form	10 A	
92	NBS	92	4098. 72	8304	Glass and silk	10 A	Two layers of silk
93	NBS	93	4098.96	8363	Porous pot	10 A	
94	NBS	27	4098. 78	8319	Silk	10 A	100 sq. cm of silk on pot
95	NBS	28	4098.30	8200	Porous pot	10 A	Very small porous pot
			May 14,	1910 (	Experiment N	o. 16)	
116	LCE	LCA	4202. 59		Porous pot	15 B	
117	LCE	SCB			Silk	15 B	Very small anode
118	PTR	I	4201.58		Double silk	10 C	
119	PTR	III	4200.19		do	10 C	
120	NPL	95	4202. 99		New form	10 A	Neutralized
121	NPL	A	4202.77		do	10 A	1
122	NPL	В	4201. 29		do	10 C	
123	NBS	92	4202.70		Porous pot	10 A	
124	NBS	93	4203.19		do	10 A	Made 2 in 106 alkaline
125	NBS	128	4202. 77		Glass	10 A	No septum
126	NBS	127	4202. 90		do	10 A	Do.
127	NBS	27	4202. 50		Porous pot	10 A	Made 10 in 106 acld
128	NBS	28	4202.60		do	10 A	Made 5 in 108 acld
		1			1.4		_

 $<sup>^{22}</sup>$  The current in this experiment was unusually unsteady. Error perhaps  $\pm_{10000}$ .

### INDEX OF EXPERIMENTS OF THE SUBCOMMITTEE

### TABLE XXVIII

### April 14, 1910 (Experiment No. 2)

No. of deposit	Cup	Weight	Weston cell at 20°	Type of voltameter	Electrolyte	Remarks
		mg			Per cent	
11	125	4098, 36	1. 018256	Porous pot	10 A	
12	•126	4098. 16	8206	do	10 B	
13	27	4098, 40	8265	do	10 D	
14	28	4098. 50	8288	do	10 C	
		A	pril 18, 19	010 (Experim	ent No. 4.)	
25	125	4098. 84	1. 018292	Porous pot	10 D	
26	126	4098. 61	8234	do	10 C	
27	27	4098. 86	8295	do	10 B	
28	28	4098. 80	8281	do	10 A	
			1	910 (Experin		1
39	125	4098. 72	1. 018276	Porous pot	10 C	
40	126	4098. 73	8278	do	10 D	*
41 42	27 28	4098. 82 4098. 90	830 <sub>0</sub> 832 <sub>0</sub>	dodo	10 A 10 B	
42	20	4096, 90	0320	do	10 15	
		A	pril 28, 19	910. (Experir	ment No. 8)	
53	125	4098. 58	1. 018277	Porous pot	10 B	
54	126	4098. 61	8284	do	10 A	
55	27	4098. 79	8328	do	10 C	
56	28	4098. 97	8374	do	10 D	•
		A	pril 30, 1	910. (Experi	ment No. 9)	
57	92	4098. 19	1. 018287	Porous pot	10 A	
58	93	4098. 73	8420	do	10 D	Glass shield under por-
				TT .		
59	95	4098. 29	8311	New form	10 A	
59 60	95 27	4098. 29 4098. 15	831 <sub>1</sub> 827 <sub>5</sub>	Porous pot	10 A 10 A	

### TABLE XXVIII—Continued

### May 3, 1910. (Experiment No. 11)

		M	ay 3, 191	0. (Experime	ent No. 11)	
No. of deposit	Cup	Weight	Weston cell at 20°	Type of voltameter	Electrolyte	Remarks
		mg			Per cent	
72	92	4099.60	1.018543	Porous pot	10 B	
73	93	4099.33	8476	do	10 C	
74	95	4098.59	829 <sub>2</sub>	do	10 A	
75	27	4098.57	8287	do	10 C	
76	28	4098. 26	8209	do	10 A	
		M	ay 5, 191	.0. (Experime	ent No. 12)	
77	92	4099. 22	1. 018457	Porous pot	10 B	
78	93	4098.99	840a	do	10 C	
79	95	4099. 16	8441	New form	10 C	
80	27	4098.33	8233	Porous pot	10 C	
81	28	4098.54	8286	do	10 A	
82	A	4099, 30	8476	New form	10 B	
83	В	4098.50	8279	do	10 A	
84	I	4099. 19	8448	Filter paper	20 C	
85	ш	4098, 25	8216	Double silk	20 C	
		10707-0	5-20			
		Ma	y 10, 19	10. (Experim	ent No. 14)	
96	,92	4096. 32		Siphon	10 B	1
97	*93	4096. 10		do	10 old Baker	
98	125	4095. 84		do	10 B	
99	126	4096.70		do	10 old Baker	Current not held ex-
100	28	4095. 16		do	10 A	cept approximately
101	27	4094.78		Porous pot	10 A	and time not meas-
102	A	4095. 16		Siphon	10 A	ured.
103	В	4094.66		New form	10 A	
104	I	4093.41		Double silk	10 C	li .
105	ш	4093.62		do	10 C	
		1/Γ-	10 10:	10 (E	NI- 15)	K.
		IVIA	y 12, 19	io. (Experim	ent No. 15)	
106	LC'A	4098. 35	1. 018215	Porous pot	15 B	Very small anode
107	95	4098. 51	8254	New form	10 A	
108	A	4098. 26	8193	do	10 A	Made 1 in 104 acid
109	В	4100.50	8753	do	10 A	Made 10 in 106 alkaline
110	93	4099.34	8462	Porous pot	10 Recovered	
111	92	4099.17	8420	do	10 Recovered	
112	127	4099. 82	8581	do	10 Recovered	Made 5 in 106 alkaline
113	128	4098.00	8129	do	10 Recovered	Made 1 in 104 acid
114	27	4098.18	8174	do	10 Recovered	
115	28	4098.72	8307	do	10 Recovered	
		Ma	y 19, 19	10. (Experim	ent No. 17)	
129	92	4098, 39	1. 018269	Porous pot	10 E (new)	
130	95	4098.30	8249	do	10 E	
131	27	4098.40	8272	do	10 E	
132	28	4098. 37	8265	do	10 E	
		1030.07	0203			

#### COMPLETE TABLES OF EXPERIMENTS

### TABLE XXIX

### First Experiment, April 9, 1910

No.	Labora- tory	Cup	Туре	Anode	Electro- lyte	Vol- ume	Weight of silver	Remarks
1	LCE	LC <sup>A</sup>	Filter paper	Hemi- sphere	Per cent Twice re- crystal- lized	cc 250	mg	Filter paper touched bowl
2	LCE	SC <sup>B</sup>	do	Disk		200	4021. 3	
3	PTR	I	No septum	Cylinder	C 20	110	4017.04	Anode slime
4	PTR	ш	Silk	do	C 20	110	4011.36	Lost some silver
5	NPL	A	New form	Disk	A 11	350	4017. 2	Black substance near
6	NPL	D	do	do	A 11	350	4017. 4	upper boundary
7	NBS	93	Porous pot	Rod	<b>D</b> 10	300	4016. 95	Disels substance see
8	NBS	95	do	Disk	<b>D</b> 10	300	4019.91	Black substance near
9	NBS	27	do	Rod	<b>D</b> 10	90	4017.16	upper boundary of
10	NBS	28	do	do	<b>D</b> 10	90	4016. 61	deposit

The current was interrupted during this experiment so that no calculation of the value of the Weston cell could be made.

The filter paper in cup LCA touched the cathode, causing discoloration of the deposit. The twice recrystallized electrolyte used in the LCE cups was believed to be contaminated on the journey from Europe, and was not used in the other experiments.

The PTR Cup III met with an accident, and silver was lost, and there was a good deal of anode slime in Cup I.

The deposits in the NPL and NBS cups were abnormal, in the opinion of Messrs. Smith and Rosa, a black substance being deposited with the silver near the upper boundary of the deposit. It was observed that on heating this black deposit became white, and Dr. Rosa suggested the possibility that it was colloidal silver.

### TABLE XXX

### Second Experiment, April 14, 1910

#### Experiment of Subcommittee

[Room temperature, 2195; time, 7202.24 seconds; standard resistance No. 2342, at 2290,=2.000090 ohms; standard cell No. 109 was 23 microvolts lower than the group mean of the cells of the four laboratories; the current was estimated as correct within  $\pm \frac{1}{100\,000}$  except during the first 20 minutes, giving an average deviation of not more than  $\pm \frac{3}{100\,000}$ 

No.	Cup	Туре	Anode	Electrolyte	Vol- ume	Weight of silver	Weston cell at 20°
11 12 13 14	125 126 27 28	Porous pot	Roddododo	Per cent A 10 B 10 D 10 C 10	95 95 95 95	mg 4098. 36 4098. 17 4098. 40 4098. 50	1.018256 8206 8265 8288

This experiment had for its object the comparison of the deposits obtained with the electrolyte of the various laboratories. The solutions were electrolyzed in cups of the same size and shape, and with porous cups of the same size, treated in the same manner. The anodes were all of the same shape and practically identical in size. Cups 27 and 28 are of platinum, cups 125 and 126 of gold.

### TABLE XXXI

### Third Experiment, April 15, 1910

[Room temperature, 2299; time, 7201.86 seconds; standard resistance No. 2342, at 2396,=2.000112 ohms; standard cell No. 109 was 23 microvolts lower than the group mean; the current was estimated as correct to within  $\pm \frac{1}{1000000}$ ]

No.	Labora- tory	Cup	Туре	Anode	Electro- lyte	Vol- ume	Weight of silver	Weston cell at 20°	Remarks
					Per cent	сс	mg		
15	LCE	$LC^A$	Filter paper	Hemisphere	B 15	250	4098.8	1.018428	
16	LCE	SC <sup>B</sup>	do	Disk	B 15	200	4098.8	8429	
17	PTR	I	No septum	Cylinder	C 20	110	4098.58	8373	Anode
	1								slime in
									cup.
18	PTR	III	Silk	do	C 20	110	4098.30	8304	
19	NPL	A	New form	Disk	A 10	370	4098. 27	8310	
20	NPL	В	do	do	A 10	370	4098. 20	8280	
21	NBS	93	Porous pot	do	D 10	300	4098.67	8397	
22	NBS	95	do	Rod	D 10	300	4098.66	8394	
23	NBS	127	Glass and silk.	Disk	<b>D</b> 10	175	4098.40	8328	
24	NBS	128	đo	do	<b>D</b> 10	175	4098. 18	8274	

There was a good deal of anode slime in Cup I, some of which reached the bottom of the cup. All the wash waters and filtrates were free from dissolved silver.

The deposits in Cups A and B were free from striae, and were very fine and adherent. There was no loose silver at all in Cup A, and only a few crystals in B.

#### TABLE XXXII

### Fourth Experiment, April 18, 1910

#### Experiment of Subcommittee

[Room temperature, 23°; time, 7202.89 seconds; standard resistance No. 2342, at 23°3, =2.000108 ohms; standard cell No. 109 was 23 microvolts lower than the group mean; the current was estimated as correct to within  $\pm \frac{1}{100.000}$ 

No.	Cup	Type Anode		Electrolyte	Volume	Weight of silver	Weston cell at 20°
25 26 27 28	125 126 27 28	Porous potdododododododododo	Roddodododo	Per cent D 10 C 10 B 10 A 10	95 95 95 95	mg 4098. 84 4098. 61 4098. 86 4098. 80	1. 01829 <sub>2</sub> 823 <sub>4</sub> 829 <sub>5</sub> 828 <sub>1</sub>

This experiment was for the purpose of comparing the four different electrolytes, and differed from Experiment 2 only in that the porous pots and the cups were interchanged among the electrolytes.

### TABLE XXXIII

### Fifth Experiment, April 20, 1910

[Room temperature, 2275; time, 7202.47 seconds; standard resistance No. 2342, at 2392, =2.000105 ohms; standard cell No. 109 was 24 microvolts lower than the group mean; the current was estimated as correct to within  $\pm \frac{2}{100.0000}$ 

No.	Labora- tory	Cup	Туре	Anode	Electro- lyte	Vol- ume	Weight of silver	Weston cell at 20°	Remarks
					Per cent	СС	mg		
29	LCE	LCA	Filter paper	Hemisphere	B 15	250	4099. 6	1. 01853 <sub>8</sub>	
30	LCE	SCB	do	Disk	B 15	200	4099.1	8414	
31	PTR	I	Double silk	Cylinder	C 20	110	4098. 54	8275	
32	PTR	ш	do	do	C 20	110	4098.95	8378	Loose sil-
									ver
33	NPL	A	New form	Disk	A 10	370	4098.68	8310	
34	NPL	В	do	do	A 10	370	4098. 57	8283	
35	NBS	93	Porous pot	đo	D 10	300	4098.94	8375	
36	NBS	95	do	do	D 10	300	4099. 01	8392	
37	NBS	127	Glass and silk.	do	<b>D</b> 10	175	4098. 23	8201	Silk de-
									tached
38	NBS	128	do	do	<b>D</b> 10	175	4098, 59	828 <sub>8</sub>	

The deposit in Cup I was much more adherent than that in III, where there was a good deal of loose silver. The same silk was used in I and III as in the third experiment.

The same silk was used in the cups 127 and 128 as in the third experiment. Since that time the silk had been kept in weak AgNO<sub>3</sub> solution, being washed just before the experiment. The silk in 127 became detached during the experiment, and considerable anode slime escaped.

### TABLE XXXIV

### Sixth Experiment, April 22, 1910

#### Experiment of the Subcommittee

[Room temperature, 22°; time, 7202.72 seconds; standard resistance No. 2342, at 22°4, =2.000090 ohms; cell No. 109 was 23 microvolts lower than the group mean; the current was estimated as correct to within  $\pm \frac{1}{10000}$ 

No.	Cup	Туре	Anode	Electrolyte	Volume	Weight of silver	Weston cell at 20°
39 40 41 42	125 126 27 28	do	Roddodododo	Per cent C 10 D 10 A 10 B 10	95 95 95 95	mg 4098. 72 4098. 73 4098. 82 4098. 90	1. 01827 <b>s</b> 827 <sub>8</sub> 830 <sub>0</sub> 832 <sub>0</sub>

This experiment was similar to Experiments 2 and 4, the only difference being that the cups and porous pots were still further interchanged.

### TABLE XXXV

### Seventh Experiment, April 26, 1910

[Room temperature, 22%; time, 7202.41 seconds; standard resistance No. 2342, at 22%9=2.000100 ohms; cell No. 109 was 23 microvolts lower than the group mean; the current was unusually unsteady, the possible error being estimated at  $\pm \frac{1}{10000}$ 

No.	Labora- tory	Cup	Туре	Anode	Electro- lyte	Vol- ume	Weight of silver	Weston cell at 20°	Remarks
					Per cent	сс	mg		
43	LCE	LCA	Filter paper	Hemisphere	B 15	250	4099.3	1.018469	
44	LCE	SCB	do	Disk	B 15	200			Contami-
			l l						nated.
45	PTR	I	Double silk	Cylinder	C 20	110	4098.36	8236	
46	PTR	III	do	do	C 20	110	4098. 25	8209	
47	NPL	A	New form	Disk	A 10	370	4099.06	8415	
48	NPL	В	do	do	A 10	370	4099. 10	8420	
49	NBS .	93	Porous pot	Rod	<b>D</b> 10	150	4099. 29	8468	
50	NBS	95	do	do	D 10	330	4099. 29	8468	
51	NBS	27	do	do	<b>D</b> 10	90	4098. 82	8352	
52	NBS	28	do	do	D 10	90	4098. 87	8363	

The Cup SCB was soiled externally by a drop of AgNO3 on the tin foil.

The deposits in the NPL bowls were absolutely free from striæ, and were very firm, there being no loose silver.

Cup 93 was used with only half the usual quantity of electrolyte.

### TABLE XXXVI

### Eighth Experiment, April 28, 1910

#### Experiment of Subcommittee

[Room temperature, 22°; time, 7202.47 seconds; standard resistance No. 2342, at 2294=2.00090 ohms; standard cell No. 109 was  $22\frac{1}{2}$  microvolts lower than the group mean; the current was estimated to be correct to within  $\pm \frac{1}{100000}$ 

No.	Cup	Type	Anode	Electro- lyte	Vol- ume	Weight of silver	Weston cell at 20°
				Per cent	сс	mg	
53	125	Porous pot	Rod	B 10	95	4098. 58	1. 018277
54	126	.:do	do	A 10	95	4098. 61	8284
55	27	do	do	C 10	95	4098. 79	832 <sub>8</sub>
56	28	do	do	D 10	95	4098. 97	8374

This was the fourth experiment where the four electrolytes were compared in the small porous pot voltameter. Each electrolyte has now been measured in each of the platinum cups and the porous pots.

### TABLE XXXVII

### Ninth Experiment, April 30, 1910

#### Experiment of the Subcommittee

[Room temperature, 23%; time, 7201.90 seconds; standard resistance No. 2342, at 25%5=2.000138 ohms; standard cell No. 109 was 24 microvolts lower than the group mean; the current was estimated as correct to within  $\pm \frac{1}{100\ 000}$ 

No.	Cup	Туре Ало	ede Electro- lyte	Vol- ume	Weight of silver	Weston cell at 20°	Remarks
57	92	Porous pot	Per cent A 10	cc 300	mg 4098. 19	1. 018287	
58	93	do	D 10	300	4098. 73	8420	Glass shield under po- rous pot
59	95	New form	A 10	320	4098. 29	8311	
60	27	Porous pot	A 10	95	4098. 15	8275	
61	28	do	<b>D</b> 10	95	4098.62	8392	

### TABLE XXXVIII

### Tenth Experiment, May 2, 1910

[Room temperature, 24°; time, 7202.26 seconds; standard resistance No. 2342, at 2496,=2.000133 ohms; standard cell No. 109 was 23 microvolts lower than the group mean]

No.	Labora- tory	Cup	Туре	Anode	Electro- lyte	Vol- ume	Weight of silver	Weston cell at 20°	Remarks
62	LCE LCE	LC <sup>A</sup> SC <sup>B</sup>	New form	Disk	Per cent B 15 B 15	cc 250 200	mg 4098. 25 4099. 1	1.01824 <sub>6</sub> 845 <sub>7</sub>	
64 65	PTR PTR	III	Double silk		C 20 C 20	110 110	4098.77	8376	Mean of silk and filter pa- per
66	NPL .	A	New form	Disk	A 10	350	4098.34	8270	
67	NPL	В	Filter paper	do	A 10	400	4099. 17	8475	
68	NBS	127	Porous pot	Rod	A 10	150	4098. 41	8288	
69	NBS	128	Glass and silk.	Disk	A 10	175	4099. 48	8552	More silk than usual
70	NBS	125	Porous pot	Rod	A 10	90	4098.40	8284	
71	NBS	126	Silk on pot	do	A 10	90	4099.71	8608	100 sq cm silk on pot

The silver particles from Cup III were added to those from Cup I by mistake. The combined particles were weighed by themselves. The weight found was 1.585 mg, but "after scraping out some of the finer particles 1.858 mg." This last weight was used and the mean of the two cups found.

On first weighing cups 125 and 127, the weights 4098.68 and 4098.74, respectively, were found. It was then noticed that there was on the outside of each a white spot which, on being removed and tested, was found to be crystallized AgNO<sub>3</sub>, probably spattered from a pipette. On rebaking the cups and reweighing, the weights given in the table were found.

The silk in Cup 128 and Cup 126 was pure raw silk which had been thoroughly washed, but had been kept dry for about two months, and was washed just before the experiment.

#### TABLE XXXIX

### Eleventh Experiment, May 3, 1910

#### Experiment made by the Subcommittee

[Room temperature, 24°; time, 7202.56 seconds; standard resistance No. 2342, at 25?4,=2.000142 ohms; standard cell No. 109 was 22 microvolts lower than the group mean; the current was estimated as correct to within  $\pm \frac{2}{100\ 000}$ 

No.	Спр	Туре	Anode	Electro- lyte	Vol- ume	Weight of silver	Weston cell at 20°	Remarks
				Per cent	cc	mg		
72	92	Porous pot	Rod	B 10	300	4099.60	1.018543	
73	93	do	do	C 10	300	4099. 33	8476	
74	95	do	do	A 10	300	4098.59	8292	
75	27	do	do	C 10	95	4098. 57	8287	
76	28	do	Disk	A 10	95	4098. 26	8209	Porous pot 4.3 cm diam. 5.5
								cm deep
70	20		2.54	11 10	33	1090.20	0209	-

The porous cup in Cup 28 in experiment 76 was prepared by Mr. Smith who first boiled it in strong HNO<sub>3</sub> and then in several lots of distilled water. The pot was afterwards baked in an electric oven to drive off any remaining acid and was then soaked in several lots of distilled water.

### TABLE XL

### Twelfth Experiment, May 5, 1910

#### Experiment made by the Subcommittee

[Room temperature, 21°; time, 7202.26 seconds; standard resistance No. 2342, at 21°5,=2.000074 ohms; standard cell No. 109 was 23 millionths lower than the group mean; the current was estimated as correct to within  $\pm \frac{2}{100-000}$ 

No.	Cup	Туре	Anode	Electro- lyte	Vol- ume	Weight of silver	Weston cell at 20°	Remarks
				Per cent	сс	mg		
77	92	Porous pot	Rod	B 10	325	4099. 22	1.018457	
78	93	do	do	C 10	315	4098.99	8400	
79	95	New form	Disk	C 10	315	4099.16	8441	
80	27	Porous pot	Rod	C 10	90	4098.33	8233	
81	28	do	do	A 10	90	4098. 54	8286	
82	Α	New form	Disk	B 10	350	4099. 30	8476	
83	В	do	do	A 10	350	4098.50	8279	After removal of
								spot of AgNO3 on outside of cup
84	I	Filter paper	Cylinder	C 20	110	4099. 19	8448	
85	III	Double silk	do	C 20	110	4098. 25	8216	

The same silk was used in Cup III which has been used in the PTR cups in the previous experiments. A washed filter paper tube was used in Cup I.

### TABLE XLI

### Thirteenth Experiment, May 7, 1910

[Room temperature, 23°; time, 7202.58 seconds; standard resistance No. 2342, at 2393, =2.000109 ohms; standard cell No. 109 was 23 microvolts lower than the group mean; the current was estimated as correct to within  $\pm \frac{2}{100.000}$ . It was unusually unsteady during the last 10 minutes]

No.	Labora- tory	Cup	Туре	Anode	Electro- lyte	Vol- ume	Weight of silver	Weston cell at 20°	Remarks
					Per cent	сс	mg		
86	LCE	LCA	New form	Disk	B 15	230	4098. 28	1. 018196	
87	LCE	$SC^B$	Filter paper	đo	B 15	160	4098.95	8362	
88	PTR	I	do	Cylinder	C 20	110	4099. 44	8482	
89	PTR	III	Double silk.	do	C 20	110	4098. 48	8246	
90	NPL	A	Silk	Disk	<b>A</b> 10	370	4098.66	829 <sub>0</sub>	One layer of silk
91	NPL	В	New form	do	<b>A</b> 10	370	4098.96	8363	
92	BS	92	Glass and	do	A 10	315	4098. 72	8304	Two layers silk
93	BS	93	Porous pot	Rod	A 10	315	4098.96	8363	
94	BS	27	Silk and po- rous pot	do	A 10	95	4098. 78	8319	Silk on porous
95	BS	28	Porous pot	Small rod.	A 10	95	4098. 30	8200	Porous pot 1½ cm diam, 4 cm deep

The same filter paper tube was used in Cup I as in the experiment of May 5.

The silk in Cup A was some of that used by Dr. Jaeger which had been soaked during the preceding experiments. The silk in cups 92 and 27 was the same as that used on May 2, and had been kept in weak AgNO<sub>3</sub> solution since that time.

### TABLE XLII

### Fourteenth Experiment, May 10, 1910

#### Experiment of the Subcommittee

In this experiment with the siphon form of voltameter, the current was held only approximately constant and no accurate measurement of the time was made. The results are therefore only relative.

No.	Cup	Туре	Anode	Electrolyte		Weight of silver	Relative weights
				Per cent	cc	mg	
96	92	Siphon	Hemisphere	B 10	435	4096. 32	1. 00028
98	125	do	Ring	B 10	195	4095. 84	1.00014
97	93	do	do	Old Baker 10	400	4096.10	1.00023
99	126	do	do	Old Baker 10	195	4096.70	1.00037
102	A	do	đo	A 10	480	4095. 16	1.00000
100	28	do	do	A 10	195	4095. 16	1.00000
101	27	Porous pot	Rod	<b>A</b> 10	95	4094. 78	0. 99990
103	В	New form	Disk	A 10	400	4094.66	0. 99988
104	1	Double silk	Cylinder	C 10	110	4093. 41	0. 99957
105	ш	do	đo	C 10	110	4093. 62	0. 99962

The volumes of the electrolyte were taken as the sum of the volume of the cathode liquid+one-half the volume of the siphon.

The relative values are referred to the mean of all as unity. The following table gives the difference obtained with each electrolyte:

Туре	Differences, parts in 100 000
New form.	0
Porous pot	+ 2
Siphon, small	+12
Siphon, large	+12
Siphon, small	+26
Siphon, large	+40
Siphon, small	+49
Siphon, large	+35
Silk	-31
do	-26
	New form. Porous pot. Siphon, small. Siphon, large Siphon, small. Siphon, large. Siphon, small. Siphon, large. Siphon, small. Siphon, small. Siphon, small. Siphon, large.

### TABLE XLIII

### Fifteenth Experiment, May 12, 1910

#### Experiment of the Subcommittee

[Room temperature, 2295; time, 7202.54 seconds; standard resistance No. 2342, at 2298, -2.000100 ohms; standard cell No. 109 was 24 microvolts lower than the group mean]

No.	Cup	Туре	Anode	Electrolyte	Vol- ume	Weight of silver	Weston cell at 20°	Remarks		
				Per cent	cc	mg				
106	LCA	Porous pot	Small rod	B 15	230	4098.35	1.018215			
107	95	New form	Disk	A 10	300	4098.51	8254			
108	A	do	do	A 10	350	4098. 26	8193	Made 1 in 1	104	
								acid		
109	В	do	do	A 10	350	4100. 50	8753	Made 10 in 1	106	
							1	alkaline		
110	93	Porous pot	Rod	Recovered	300	4099. 34	8462			
111	92	do	do	Recovered	300	4099. 17	8420			
112	127	do	Disk	Recovered	150	4099. 82	8581	Made 5 in 1	106	
								alkaline		
113	128	do	do	Recovered	150	4098.00	8129	Made 1 in 1	104	
,								acid		
114	27	do	Rod	Recovered	95	4098. 18	8174			
115	28	do	do	Recovered	95	4098. 72	8307			

The electrolyte designated as "recovered" was obtained from impure Baker AgNO<sub>3</sub> by repeated fusion and recrystallizations. The salt was tested after this experiment and found to contain a very appreciable amount of reducing agents.

The alkaline solutions were made so by the addition of NaOH in the quantities recorded in the table. The solutions were opalescent. The acid solutions were obtained by adding r part in 10 000 of HNO<sub>3</sub>.

#### TABLE XLIV

### Sixteenth Experiment, May 14, 1910

The current was interrupted during the experiment by the failure of the supporting rod of the anode in Cup SC<sup>B</sup>. The values are therefore relative only.

No.	Labora- tory	Cup	Туре	Anode	Electro- lyte	Vol- ume	Weight of silver	Relative weights	Remarks
					Per cent	cc	mg		
116	LCE	LCA	Porous pot	Rod		230	4202.59	0.99995	
117	LCE	SCB	Silk	do	B 15	200			Anode 2 cm
									long 0.5 cm
									diam
118	PTR	1	Double silk	Cylinder	C 10	110	4201.58	0.99971	
119	PTR	Ш	do	eb	C 10	110	4200.19	0. 99938	
120	NPL	95	New form	Disk	A 10	270	4202.99	1.00004	Neutralized
121	NPL	A	do	do	A 10	350	4202. 77	0.99999	
122	NPL	В	do	do	C 10	350	4201. 29	0.99964	
123	BS	92	Porous pot	Rod	A 10	300	4202.70	0.99997	
124	BS	93	do	do	A 10	300	4203.19	1.00009	Made 2 in 10 <sup>6</sup>
									alkaline
125	BS	128	Glass	Disk	A 10	175	4202.77	0. 99999	No septum
126	BS	127	do	do	A 10	175	4202.90	1.00002	Do.
127	BS	27	Porous pot	Rod	A 10	95	4202.50	0.99993	Made 10 in 105
									acid
128	BS	28	do	do	A 10	90	4202.60	0. 99995	Made 5 in 10 <sup>5</sup>
									acid
120	20	20			12 10	,0	1202.00	0. 79993	

The relative weights are referred to the mean of the deposits with electrolyte A as unity.

The "neutralized" electrolytes were first made 2 in 10 $^6$  alkaline with NaOH, which was then neutralized by the addition of  $\mathrm{HNO}_3$ .

The anodes used in Cups 127 and 128 were prepared by the deposition of a coating of electrolytic silver, using a small current, as is always done with the anode in the "new form."

#### TABLE XLV

### Seventeenth Experiment, May 19, 1910

#### Experiment of Subcommittee

[Room temperature, 2295; time, 7202.21 seconds; standard resistance No. 2342, at 2299=2.000101 ohms; standard cell No. 109 was 23 microvolts lower than the group mean; the current was estimated as correct to within less than  $\pm \frac{1}{100.000}$ 

No.	Спр	Туре	Anode	Electro- lyte	Vol- ume	Weight of silver	Weston cell at 20°
129 130 131 132	92 95 27 28	Porous potdododo	Roddodododo	Per cent E 10 E 10 E 10 E 10	cc 315 315 95	mg 4098. 39 4098. 30 4098. 40 4098. 37	1. 01826 <sub>9</sub> 824 <sub>9</sub> 827 <sub>3</sub> 826 <sub>3</sub>

The electrolyte E used in this experiment was made from  ${\rm AgNO_3}$  recently purified by Dr. McDaniel from Merck's salt.

### APPENDIX E. REPORTS OF SUBCOMMITTEES

(The reports of the subcommittees on resistances and standard cells have been incorporated in the Appendixes C,  $\tau$  and C,  $\iota$ .)

### 1. SUBCOMMITTEE ON WEIGHTS

By E. B. Rosa and F. Laporte

The following weights were brought by the different members of the committee:

One gold-plated brass weight of 10 g from the Laboratoire Central d'Électricité.

Four brass weights of 1, 1, 2, and 3 g, together with 12 platinum and aluminum weights of values ranging from 1 mg to 400 mg from the Physikalisch-Technische Reichsanstalt.

Two gold-plated brass weights of 2 g and 5 g from the National Physical Laboratory.

The results of the comparisons of the above weights with the standards of the Bureau of Standards are given below, together with the values to the same standard of reference of the principal Bureau of Standards' weights used in the voltameter experiments.

# Laboratoire Central d'Électricité

Correction found = -0.19 mg.

The following is taken from the certificate of the Bureau International des Poids et Mesures.

Mass of the weight=9999.863 mg+1.2094 $\triangle$ where  $\triangle$  is the difference between the real and the assumed volume.

Volume assumed (density taken as 8.5)=1.1764 ml at o°.

# Physikalisch-Technische Reichsanstalt

#### Corrections Found

Nominal value	PTR, July-Aug., 1909	NBS, Apr., 1910	
g	mg	mg	
3	+0.117	+0.116	
2	+0.046	+0.049	
1	+0.020	+0.020	
1	+0.027	+0.024	
0.4	0.009	0. 004	
0.3	+0.064	+0.061	
0. 2	-0.005	-0.009	
0. 1	+0.041	+0.040	
0.04	-0.004	-0.005	
0. 03	+0.001	+0.001	
0.02	+0.005	+0.002	
0. 01	+0.028	+0.030	
0.004	+0.020	+0.020	
0.003	+0.025	+0.023	
0. 002	-0.001	0.004	
0.001	-0.006	-0.009	

# National Physical Laboratory

NBS values 5 g + 0.055 mg  

$$\frac{5 \text{ g} + 0.003}{2 + 0.003}$$
  
Sum 7 g + 0.058 mg

The value certified by the National Physical Laboratory was 7.00000 g in vacuo. The difference may be, perhaps, explained by the fact that one of the weights had in some way become contaminated by a minute spot of mercury.

# Bureau of Standards Weights Employed in the Voltameter Experiments

The following weights, which had been adjusted to be closely equal to the mass of silver deposited by a current of one-half ampere in two hours, had in terms of the NBS standards the values below:

Designation	Material	Mass	
Ś	Gold-plated silver.	mg 4098. 262	
ä	dodo	28 4098. 364	
Σ	Platinum	4095. 232	

 $<sup>^{23}</sup>$  On Apr. 21, 1910, this weight was checked against the PTR weight by Dr. Jaeger using the Rueprecht balance and the value 4098.388 mg. was found.

Besides these, determinations of the corrections of a box of weights, NBS 6550, used by M. Laporte in the voltameter experiments, were made with the appended results taken from the certificate.

Nominal value	Correction	Distinguishing mark
g	mg	
100	+0.02	
50	+0.12	
20	-0.02	1
10	-0.04	One dot
10	-0.04	Two dots
5	-0.006	
2	-0.124	One dot
2	-0.005	Two dots
1	-0.003	
mg		
500	+0.018	
200	+ 0. 005	
100	+0.012	One dot
100	0	Two dots
50	-0.011	
20	+0.011	
10	-0.004	One dot
10	+0.005	Two dots
5	+0.006	
2	+0.001	One dot
2	-0.012	Two dots
1	+0.008	One dot
1	+0.007	Two dots
6 (rider)	+0.011	Shape
6 (rider)	+0.017	Shape
6 (rider)	+0.006	Shape

The last figure in a number of the corrections is only approximate, but is given for the sake of greater accuracy in using the corrections.

# 2. REPORT OF COMPARISONS OF FOUR DIFFERENT ELECTROLYTES IN SMALL POROUS CUP VOLTAMETERS

By E. B. Rosa

On April 12 the committee authorized some special experiments to be made by the Bureau of Standards under Dr. Rosa's direction, to compare four different electrolytes submitted to the committee by the four delegates, using the smallest sized porous cup voltameters. Four such experiments were made, using four voltameters each time (two platinum and two gold crucibles), and it was so arranged that each electrolyte was used in each of the four crucibles, and with each of the four porous cups. The

results are exhibited in the accompanying table. The electrolytes were as follows:

- A. Three times recrystallized silver nitrate, prepared at the National Physical Laboratory.
  - B. As purchased from Poulenc Frères.
- C. As purchased from the Gold-und Silber-Scheide-Anstalt, Frankfurt, being fused by the manufacturer.
  - D. As purchased from same firm, not fused.

The three samples of silver nitrate, B, C, and D, were used as supplied by the manufacturer, without further purification.

In the column headed "Means" are given the mean values obtained in four experiments with each salt. These agree remarkably well, so well that one might infer either that all samples of silver nitrate are pure, or that the impurities present are negligible. Other experiments with larger volumes of these electrolytes show very considerable differences in the weights of deposits with these same electrolytes. One may conclude from these and other experiments that when the electrolytes are not quite free from organic impurity, the excess above the normal deposit is very slight in so small a voltameter (100 cc of electrolyte), the excess being not greater (and possibly less) than one-third as much as in a voltameter of 300 cc capacity.

TABLE XLVI

Electro- lyte	Gold Platinum				Porous cups				
	125	126	27	28	Means	2	3	5	6
A	8256	8284	830e	8281	8280	830e	8284	8281	8256
В	8277	8206	8295	832e	8274	8277	8206	832e	8295
С	8276	8234	8328	8288	8282	8234	8276	8288	8328
D	8292	8278	8265	8374	8302	8265	8292	8374	8278
Mean	8275	825 <sub>0</sub>	8297	8316		8269	8264	8316	8289
		1.01	8284				1.01	8284	

Mean=1.018285 for Weston Normal Cell:

First experiment, mean equals	1. 018254
Second experiment, mean equals	8277
Third experiment, mean equals	
Fourth experiment, mean equals	8316

The mean of the deposits in the gold crucibles is equal to that in the platinum (within experimental error) and the average deposit, using each of the four porous cups, is also sensibly the same.

The mean of all values obtained in these experiments is 1.01828<sub>5</sub>, in close agreement with the values obtained using other electrolytes believed to be pure. (See Table XLVII in the report of the subcommittee on the investigation of special questions, etc.)

# 3. REPORT OF SUBCOMMITTEE ON THE INVESTIGATION OF SPECIAL QUESTIONS REGARDING THE SILVER VOLTAMETER

### By F. E. Smith and E. B. Rosa

The subcommittee of two, appointed April 29 to investigate certain special questions concerning the silver voltameter, have conducted six sets of experiments, and have made chemical tests to study the following questions:

- 1. The volume effect, or the difference in deposit in large and small voltameters with different electrolytes.
- 2. The comparison of the siphon form of voltameter with others, with three different electrolytes.
- 3. The effect of silk as used in the voltameter, on the weight of deposit.
  - 4. The effect of acid and alkali in the electrolyte on the deposit.
- 5. The relation between chemical tests for impurity and the evidence of the deposits concerning impurity of electrolyte. The deposits are in runs No. 9, 11, 12, 14, 15, and 16. Runs 10 and 13, made according to the decision of the committee April 29, to compare the various forms of voltameter, have afforded some additional information. Most of the information we have obtained is presented in a series of tables.

Our object in compiling these tables is to present the results in a form convenient for discussion. We suggest that other tables be added, and the present ones modified if such a procedure renders the results more intelligible.

1. The Volume Effect.—Table XLVII gives a summary of 24 deposits made between April 15 and May 12 in the new form, and in the porous cup form of voltameter, using three sizes of the latter, using the same AgNO<sub>3</sub> in all, namely, that prepared by Smith at

the National Physical Laboratory by recrystallizing three times and fusing. It is now neutral when tested by iodeosine, and shows no reaction when tested by potassium permanganate, after fusing, for the presence of organic matter or other reducing substances. It was the purest AgNO<sub>3</sub>, judged by this chemical test, that was available.

The conclusion seems justified, that at least for the porous cup voltameter, the volume effect, which is pronounced in the case of impure electrolytes, is entirely absent in this electrolyte, which is neither acid nor alkaline, and seems very pure.

Table XLVIII gives the differences obtained with three electrolytes which are not pure according to the test described above. These three electrolytes have all been employed in the international experiments. It was shown by experiments Nos. 2, 4, 6, and 8, that these electrolytes agree very closely when used in the small porous cup voltameters, but previous work had shown that the differences in deposits of different electrolytes due to varying impurity is exaggerated in larger voltameters, so it was deemed necessary to try all the various electrolytes that showed reduction of potassium permanganate in large voltameters. The unrecrystallized AgNO<sub>3</sub> from Frankfurt, that had been used by the Bureau of Standards, requires 2 cc of permanganate solution; the fused AgNO<sub>2</sub> from same manufacturer (used by Physikalisch-Technische Reichsanstalt) and the crystallized salt from Poulenc (used by Laboratoire Central) before fusion required 0.5 cc and after fusion required 5 or 6 cc of permanganate solution, showing in the latter case a higher percentage of reducing agents present.

Table XLVIII shows that the first named electrolyte gives 8.5 in 100 000 heavier deposit in the large porous cup voltameter than in the small one, the second 16.4 in 100 000, and the third 21.7 in 100 000 greater, according to the deposits 72, 77, and 82. But, according to the deposits 62, 86, and 106, the volume effect is negative, that is, minus 5.6 in 100 000. The last experiments are made with different sized cups of intermediate values. These 1esults would seem to show the advantage of purifying by successive recrystallizations the AgNO<sub>3</sub> until the products are pure as

tested by permanganate of potash, and as further tested by giving identical deposits in large and small voltameters. More evidence on this subject is furnished by the experiments with the siphon voltameter.

2. The Siphon Voltameter.—On May 14 we used six siphon voltameters in series with four others, there being three large and three small voltameters, and three different electrolytes. The latter included the NPL pure electrolyte, the LCE slightly impure, being the third in Table XLVIII, and an electrolyte made from Baker AgNO<sub>3</sub>, supposed to be more impure than the others, as judged by chemical tests. The results obtained are as follows:

Taking the mean of all the deposits as 1.00000, in the small porous cup voltameter the deposit is 1.00001, and the new form is 0.99988, the English electrolyte in two siphons averaged 1.00000, the French electrolyte in two siphons averaged 1.00021, and the Baker electrolyte in two siphons averaged 1.00030. In the voltameters using silk the mean was 0.99960.

It is evident from the table that the deposits with the siphon voltameter are in every case the heavier, the excess being greater, the more impure the electrolyte, but from these experiments no precise relation can be drawn as to the relation between the excess and the volume of the electrolyte. Whether the excess of II in 100 000 with the NPL is due to very slight impurities, or due to the mere fact that a siphon was used, or is purely accidental, cannot be decided without further experiment.

3. The Effect of Silk.—The experiments of May 2 (deposits 69 and 71) appear to show that silk can greatly increase the deposit. If it is washed and soaked long enough to avoid giving an excess of silver it may cause too small a deposit, perhaps because of the acidity which develops in the electrolyte. Pure washed silk appears to produce two effects of quite different character. According as one or the other predominates, the deposit may be too heavy or too light. Every test of electrolyte that has been made when silk is used, shows a pronounced acidity at least five or ten times as great as should, in our opinion, be permitted in a normal voltameter.

In Table L a comparison is made between the deposits in the five different experiments with and without silk. In two experiments, the value of the standard cell is not determined, and the results are relative. The differences, however, are expressed in parts in 100 000 in all cases.

4. The Effect of Acid and Alkali.—This was tested in the deposits made May 12, the results of which are shown in Table LI.

Five or ten parts in a million of alkali produces a large excess, and two parts in a million an appreciable excess, in the weight of the deposit. The effect of acid appears not to be proportional to the quantity of acid, one part in 10 000 not reducing the deposit much more than one part in 100 000 of acid. More information on this subject seems to be needed.

5. We present in a separate paper a report prepared by Dr. McDaniel on the chemical testing of silver nitrate. We have discussed above the effect of acid and alkali, and the volume effect which we have attributed to impurity other than acid. Tests by permanganate seem to show that the impurity which produces the volume effect may be detected by the permanganate reaction. The evidence is that the electrolyte which seems to be fully free from volume effect shows no permanganate reaction, and the three or four different samples of silver nitrate which show the permanganate reaction to a greater or less degree also show a slight volume effect.

## TABLE XLVII

# Experiments Using National Physical Laboratory Electrolyte

No. of deposit 24	New form voltameter	Small porous cup voltameter	Large porous cup voltameter	Medium-size porous cup voltameter
<b>[19</b>	1. 018310			
[20	280			
[33	310			
(34	283			
11		1.018256		
28		281		
41		300		
54		284		
[47	25 415			
(48	25 420			
(57			1. 018287	
<b>5</b> 9	311			
(60		275		
(66	270			
68				1.018288
(70		284		
<b>§74</b>			292	
76		26 209		
<b>[81</b>		286		
[83	279			
(91	27 363			
93			27 363	
95		. 28 200		
107	254			
Mean	. 1. 018287	1. 018281	1. 018290	1. 01828 <sub>8</sub>

<sup>24</sup> Deposits included in braces are deposits in the same experiment.

<sup>25</sup> Current unusually unsteady.

<sup>&</sup>lt;sup>26</sup> The porous cup was a larger one than usual, 4.3 cm. diameter, and the deposit had the appearance of one from an impoverished electrolyte.

<sup>27</sup> Different solution from the others, 2 in 10 6 alkaline.

<sup>&</sup>lt;sup>28</sup> A porous pot only 1½ cm. in diameter was used in this experiment. The electrolyte became 10 in a million acid during the experiment.

Omitting 47, 48, and 91, new form gives 1.018287.

Omitting 76, 93, and 95, porous cup gives 1.018284.

The NBS value with small cups, and using German salt not recrystallized, was 1.018 27.

# Report on Concrete Standards

# TABLE XLVIII

# Tests of Volume Effect on Three Electrolytes

Size	tals of the Gol	From crys- AgNO <sub>3</sub> from d-und Silber- e-Anstalt	AgNO	From fused from Gold-und Scheide-Anstalt	(3) LCE—From crystals of AgNO <sub>3</sub> from Poulenc		
	No. of deposit	Value for cell	No. of deposit	Value for cell	No. of deposit	Value for cell	
Small voltameter	13	1. 018265	14	1. 018289	12	1. 018206	
	25	292	26	23,	27	295	
	40	278	39	27 <sub>ô</sub>	42	320	
(Volume approxi-							
mately 100 cc)	51	352	55	328	53	27,	
	52	363	75	288			
	56	374	80	233			
	61	392					
Mean		1. 018331		1. 018275		1. 018275	
Large voltameter	21	1. 018397	73	1.01847 <sub>7</sub> (p. c.)	72	1.01854 <sub>3</sub> (p.c.)	
	22	394	78	40 <sub>0</sub> (p. c.)	77	45 <sub>7</sub> (p. c.)	
	35	374	79	44 <sub>1</sub> (Sm.)	82(370 cc)	47 <sub>6</sub> (Sm.)	
(Volume 300 cc except							
where noted)	36	392			62(250 cc)	246	
	49	468			86(230 cc)	196	
	50	468			106(250 cc)	215	
	58	420					
Mean		1.018416		1. 018439		1. 018492 219	
		331		275		275 275	
Differences		. 000085		. 000164		. 00021 <sub>7</sub> —. 00005 <sub>6</sub>	

### TABLE XLIX

# Comparative Results, with and without Silk

The two deposits of each pair below were with substantially the same volumes, except where noted as large and medium:

No. of deposit	Type of voltameter	Electrolyte	With silk	With- out	Differ- ence, parts in 100 000
90	With new form	NPL electrolyte	290		
91	do	do		363	<b>—</b> 7 <sub>3</sub>
18	With Jaeger form	Frankfurt, fused (PTR)	304		
17	do	do		373	— 6 <sub>9</sub>
23	With NBS glass cup and silk (medium)	Frankfurt, not fused (NBS)	328		
21	With NBS porous cup (large)	do		397	— 6 <sub>9</sub>
24	With NBS glass cup and silk (medium)	do	274		
22	With NBS porous cup (large)	do		394	-12 <sub>0</sub>
37	With NBS glass cup and silk (medium)	do	201		
35	With NBS porous cup (large)	do		375	-174
38	With NBS glass cup and silk (medium)	do	288		
36	With porous cup (large)	do		392	-104
69	With NBS glass and silk (double). (medium)	do	552		
68	With NBS porous cup (medium)	do		288	29+264
71	With NBS porous cup and silk (double)	do	608		
70	With NBS porous cup	do		284	29+324
92	fore) (large)	NPL electrolyte	304		
93	With porous cup (large)	do		363	— 6 <sub>9</sub>
94	With porous cup and silk (small)	do	319		
95	With porous cup-acid electrolyte	do		<sup>30</sup> 20 <sub>0</sub>	80+119
Mean	·				97

<sup>&</sup>lt;sup>29</sup>Striated deposits. The silk was thoroughly washed, but had not been soaked in water a long time. The same silk gave a negative difference the next time, after having been soaked for several days,

<sup>&</sup>lt;sup>30</sup> The electrolyte in the porous cup voltameter was acid by ro in ro<sup>6</sup> at the end of the run, and we suppose this accounts for the light deposit, which makes the difference *positive* instead of negative as in the other pair of deposits. In four pairs the voltameters were larger with the porous cup than with the silk, so that the difference is larger than otherwise, due to whatever "volume effect" (if any) there may be.

## TABLE L

# Comparisons of Deposits with and without Silk

# Different Electrolytes

Ex- peri-	No. of Small porous		No. of	Nove form	No. of	PTR voltame-		es, parts fn 0000
ment 31	deposits	cups	deposits			deposits ters (with silk)		From por- ous cup
3			2	1. 018295	1	1.018304	+ 0-9	
5			2	297	2	327	+ 3.0	
7	2	1. 018357	2	418	2	222	-19.5	13. 5
12	2	26 <sub>e</sub>	1	279	1	216	- 6.3	- 4.4
14	1	0. 99990	1	0. 99988	2	0.999595	-28.5	-30.5
16	2	32 1. 00000 <sub>5</sub>	1	0. 99999	2	0. 999545	-44.5	46, 0

 $<sup>^{31}</sup>$  The experiments 14 and 16 did not allow of calculating the value of the cell. The relative values of the weights of the deposits are given for these experiments.

TABLE LI Effect of Acid and Alkali

No. of		Alkaline	Neutral	Acid	Differ- ence in
deposit	Notes		weight, parts in 100 000		
108	NPL electrolyte $\frac{1}{10\ 000}$ acid			1.018193	- 6 <sub>1</sub>
107	NPL electrolyte neutral		1.018254		<b></b>
109	NPL electrolyte alkaline $\frac{1}{100\ 000}$	1.018753			+49 <sub>9</sub>
113	New NBS electrolyte acid $\frac{1}{10\ 000}$	, 		1.018129	+452
112	New NBS electrolyte alkali $\frac{5}{10^6}$	1.018581			•••••
		We	ight of dep	osit	
121	)				
125	NPL electrolyte neutral, mean of 3		4202.82		
126 127	J NPL electrolyte acid $\frac{10}{106}$			4202-50	- 8
124	NPL alkaline $\frac{2}{10^6}$				+ 9
128	NPL electrolyte acid $\frac{5}{10^6}$				- 5
123 120	NPL alkali and acid to neutralize (mean)		4202.85		+ 1

<sup>32</sup> In experiment 16 the value 1.000005 was obtained when no septum was used.

TABLE LII

Value of Deposits with Filter Paper

Number of deposit	Value for cell	Laboratory	
15	1. 018428	LCE	
16	428	LCE	
29	<b>53</b> <sub>8</sub>	LCE	
30	41₄	LCE	
43	469	LCE	
63	457	LCE	
88 64	376	PTR	
67	475	NPL	
84	448	PTR	
87	362	LCE	
88	482	PTR	
Меап	1. 018450		

<sup>33</sup> The value with this deposit is the mean of the two deposits in the German cups with filter paper and gilk. It has been excluded in taking the mean.

# 4. METHODS OF TESTING FOR VARIOUS IMPURITIES IN SILVER NITRATE By A. S. McDaniel

Free Acid or Alkali.—The usual methods of testing the neutrality of salts do not apply to silver nitrate solutions. Thus, toward litmus, silver nitrate solutions react alkaline even after the addition of 1 part in 100 000 of nitric acid, while the same sample will show an acid reaction toward methyl-orange even after the addition of an unlimited amount of alkali, so long as any undecomposed silver nitrate remains (i. e. so long as the Ag is not completely precipitated as AgOH).

If, however, the Ag be precipitated as AgCl by means of neutral KCl or NaCl solution, and the AgCl filtered off through asbestos, the filtrate shows a neutral reaction toward all indicators if the original AgNO<sub>3</sub> contained no acid or alkali. Samples of silver nitrate purified by repeated recrystallization have been obtained which show a neutral reaction toward iod-eosine when tested in this manner, whereas if so little as I part in I 000 000 of nitric acid (or alkali) be added to the original solution it can be detected in the filtrate from the precipitated AgCl. In testing for amounts of acid less than several parts in 100 000, the AgCl must be filtered off by means of asbestos instead of filter paper, for the reason that pure distilled water extracts a small amount of cellulose

hydrates from filter paper which show an alkaline reaction toward both iod-eosine and methyl-orange.

By the use of standard  $\frac{N}{1000}$  HNO<sub>3</sub> and  $\frac{N}{1000}$  NaOH with iodeosine indicator the amount of free acid or alkali in a solution of silver nitrate may be determined to within one part in one million. The procedure is as follows:

10 cc of a 10 per cent solution of AgNO, in a beaker are treated with just sufficient of 20 per cent solution of carefully purified and neutral KCl to completely precipitate the whole of the silver as AgCl. The precipitated AgCl is filtered off through asbestos, and the whole of the filtrate titrated with standard  $\frac{N}{1000}$  NaOH (or HNO<sub>3</sub>) using iod-eosine as indicator. The titration is carried out in a 25 cc glass-stoppered cylinder. The indicator must be used in an aqueous-ether solution. An aqueous layer and an ethereal layer must always be present. The iod-eosine is soluble in the ether without coloration, whereas the alkaline compound of iod-eosine is soluble in water with a pink color. Two cubic centimeters of the ethereal solution of iod-eosine (5 to 10 mg per liter) are used for each titration. Before adding the solution to be titrated, the iod-eosine, in presence of ½ cc of water, is first neutralized with  $\frac{N}{1000}$  acid or alkali. The solution to be tested is then added and the whole brought back to the neutral point. A blank determination is carried out in the same way, except that no silver nitrate solution is used; and the solution is not filtered. The reading obtained for the blank is subtracted from that obtained in the titration. Each cc of  $\frac{N}{1000}$  NaOH for a 10 cc sample of silver nitrate solution represents approximately 4 parts in 1 000 000 of free HNO3 in the original solution; and each cc of  $\frac{N}{1000}$  HNO<sub>3</sub> represents 6 parts of NaOH in 1 000 000 in the original solution. The results are expressed in terms of HNO<sub>3</sub>.

Reducing Agents.—These are tested for by means of  $\frac{N}{1000}$  KMnO<sub>4</sub> solution in the following manner:

10 cc of a 66.6 per cent solution of AgNO<sub>3</sub> to be tested are placed in a 25-cc glass-stoppered cylinder and made acid by the addition of 1 cc of concentrated nitric acid free from reducing substances. This mixture is then titrated with the standard permanganate solution. The permanganate is added in ½ cc portions until the pink color persists for one minute. Each cubic centimeter of permanganate solution is equivalent to approximately 2 parts of metallic silver, 4 parts of AgNO<sub>2</sub>, or 0.4 parts of furfural in 1 000 000 parts of dry AgNO<sub>3</sub>. One-half cc of the permanganate solution is required to give a permanent color to 10 cc of distilled water, hence this amount is subtracted from the value obtained in any titration. H<sub>2</sub>SO<sub>4</sub> may be used in place of HNO<sub>3</sub>.

Carefully recrystallized samples of AgNO<sub>3</sub> have been prepared which show no permanganate reduction, whereas samples which during their preparation have come in contact with filter paper or unwashed silk reduce from 2 to 70 cc of the permanganate solution. Also, concentrated solutions of pure recrystallized AgNO<sub>3</sub> to which colloidal metallic silver has been added reduce appreciable amounts of permanganate. Likewise, silver nitrite or hyponitrite dissolved in concentrated silver nitrate solutions also reduce permanganate. In fact, any strong reducing agent capable of reducing a neutral solution of AgNO<sub>3</sub> to metallic silver, when added to concentrated silver nitrate solutions causes the latter to reduce permanganate, whereas the addition of certain other organic substances of a mild reducing character such as cane sugar, do not appreciably modify the amount of permanganate reduced by the solution (except after fusion of the solid AgNO<sub>3</sub>).

We have previously stated in detail our explanation of the action of strong reducing agents (derived from filter paper, silk or other source) in producing abnormally heavy deposits in the silver voltameter on account of their precipitation of colloidal silver. The test with permanganate is a sure method for detecting the presence of such strong reducing agents, and hence a sample of silver nitrate which is intended for use in the voltameter should fulfill this test. It is true that other milder reducing agents may reduce permanganate and their presence may not appreciably affect the electrochemical equivalent of silver, but the only safe course is to prove

the entire absence of any substances capable of reducing permanganate. In other words, no *safe* method for differentiating the strong and harmful from the weak and harmless reducing agents is known to us. Besides, the AgNO<sub>3</sub> used should approach the state of absolute purity as nearly as possible.

Some samples of carefully recrystallized AgNO<sub>3</sub> upon fusion, at a temperature as little above the melting point as possible, showed no permanganate reduction after such treatment whereas other samples, in the preparation of which organic material had not been carefully excluded, showed considerable permanganate reduction after fusion. We, therefore, conclude that this method of testing AgNO<sub>3</sub> for reducing substances (i. e. fusion and subsequent titration with permanganate) is the most efficient. If the fusion be carried out at a temperature of about 50°, or more, above the melting point, for a half-hour or longer, a pure sample of AgNO. will afterwards show permanganate reduction. Prolonged fusion at very high temperatures results in the complete reduction of AgNO<sub>3</sub> to metallic Ag, hence in applying the above test care must be exercised not to raise the temperature above 250° C (the melting point is about 208° C) and not to heat the salt longer than necessary for its complete fusion. The crystals of silver nitrate to be tested must show an acid reaction toward iod-eosine in 10 per cent solution.

Summary of the Action of the Various Septa used in Voltameter Work upon Silver Nitrate Solutions as Shown by the Tests just Described

Filter Paper.—Filter paper (or aqueous extract of filter paper) precipitates colloidal metallic silver of varying color. This colloidal silver can be coagulated and collected, and is easily converted into ordinary metallic silver by heating to 150° C or by long contact with very dilute HNO<sub>3</sub>. This reduction of AgNO<sub>3</sub> to metallic silver by filter paper is due to the decomposition of the cellulose of which the filter paper is composed into strongly reducing aldehydes, consisting chiefly, if not entirely, of furfuraldehyde (see previous reports).

This precipitation of metallic silver is accompanied by the liberation of free nitric acid, which can be detected after the solution has stood for a considerable time, varying from a few hours to several days, depending upon the amount of cellulose used. The reason that this HNO<sub>3</sub> can not be detected immediately is because it is neutralized by the *excess* of basic cellulose hydrates present; until these cellulose hydrates are completely neutralized or decomposed the solution reacts alkaline. As already stated, aqueous extracts of filter paper show a basic reaction toward iodeosine and methyl-orange. The rate of formation of HNO<sub>3</sub>, due to the reduction of AgNO<sub>3</sub> by filter paper, may be determined by determining from time to time the decrease in the basicity due to the cellulose hydrates.

Silk.—Unwashed raw silk (or aqueous extract of silk) precipitates colloidal metallic silver from silver nitrate solutions. This colloidal silver may be collected and converted into ordinary metallic silver, as already described, under "filter paper" or its presence in *concentrated solutions* may be shown by its reduction of permanganate solution.

This reduction of AgNO<sub>3</sub> to metallic silver by unwashed silk we believe to be due to the partial decomposition of the latter into strongly reducing aldehydes. Very strong evidence for this explanation is found in the fact that such unwashed silk is actually decomposed into aldehydes by a solution of nitric acid containing only a few parts of acid in 100 000. Now, 10 per cent of silver nitrate solution contains about this amount of nitric acid, due to the hydrolysis of AgNO<sub>3</sub> into AgOH and HNO<sub>3</sub> as determined colorimetrically by means of methyl-orange.

Thoroughly washed raw silk does not reduce AgNO<sub>3</sub> solution to metallic Ag, at least to any considerable extent, as shown by the absence of any color which might be due to colloidal silver. Also, further evidence on this point is furnished by the fact that such washed silk does not yield aldehydes upon treatment with very dilute nitric acid, as is the case with unwashed silk.

However, thoroughly washed silk and silver nitrate solutions do act upon each other chemically in some way. This is con-

<sup>22451°—12——12</sup> 

clusively proven by the fact that neutral silver nitrate solutions become distinctly acid after contact with thoroughly washed silk. We believe that this acid results from the hydrolysis of the protein material of the silk into amino-acids. The evidence so far accumulated, which favors this explanation of observed fact, is that the AgNO<sub>3</sub> solution is slightly acid (due to hydrolysis) and it is well known that protein materials, in general, are hydrolyzed by dilute acids into a class of substances known as amino-acids. But further evidence must be accumulated on this point before such an explanation can be established. However, there is ample experimental proof that there is some kind of a chemical reaction between thoroughly washed silk and silver nitrate which results in this solution becoming acid, and, so far as our present knowledge goes, no treatment of the silk renders it inactive.

Unglazed Porcelain Pots.—These can be cleaned and treated in such a manner that they are without action upon silver nitrate solutions so far as the chemical tests already described are capable of showing. This method of treatment consists in first filling the pot with about 10 per cent HNO<sub>3</sub> and allowing it to filter through the pores. The strength of acid required, and the number of filtrations necessary, depend upon the previous treatment of the pot. This treatment is continued until the pot is free from stains. If necessary the pot is first heated to 600° or 1000° C before treatment with acid. This effectually removes all stains. Successive portions of distilled water are now allowed to filter through until the filtrate is neutral toward iod-eosine.

Pots have been prepared in this manner which were so insoluble that the conductivity of water having a specific conductivity of  $1.2 \times 10^{-6}$  reciprocal ohms was not appreciably altered by filtration through them. Successive portions of silver nitrate solution are now filtered through the pot until the filtrate is again neutral toward iod-eosine; about three filtrations are usually necessary. The pot is then ready for use in the voltameter.

# 5. NEUTRALITY TESTS OF ELECTROLYTES (USED IN EXPERIMENTS) TABLE LIII

	_	. NPL electrolyt	е	NBS electrolyte		
Date	Ex- peri- ment	Notes	Acid (parts in 106)	Alka- line	Notes	Acid (parts in 106)
Apr. 14	2	Before experiment	0		Before experiment	0.6
14	2	Porous pot	3. 5		Porous pot	3. 4
15	3				do	1.3
15	3				Glass and silk	14. 4
15	3				do	12.0
18	4	Porous pot	1.4		Porous pot	1.3
20	5	Before experiment	0		Before experiment	0.6
20	5	New form	0	0	Porous pot	0.6
20	5				do	1.0
20	5				Silk (Kohlrausch)	
20	5				do	
30	9	New form	0.9		Porous pot	0.9
May 3	11	Porous pot	0.9	0.3	r orous pol	0.9
<b>May</b> 5	12	do	0.9			
. 5	12	New form	0.9	0	••••••••••	
, 3	13	Before experiment		-		
7		_		1.2		
	13	New form.			• • • • • • • • • • • • • • • • • • • •	
7	13	Silk (large cup)	5. 0			
7	13	Very small porous pot	10.0			
7	13	Double silk (Kohlrausch,	8. 4		•••••	
		large cup)				
7	13	Silk on porous pot (small cup).	19. 2			
10	14	Siphon		0.6	Old Baker (siphon)	1. 2
10	14	Porous pot		0.3	do	1. 2
10	14	Siphon		0.6		
10	14	New form		0.6		
12	15	do	1. 2		New electrolyte (before)	0
12	15	Solution made 10 in 106 alka- line		1. 5	Porous pot	0. 5
12	15	Made acid 1	109. 2		do	
		10 000			do	1.6
12	15	Made 10 in 106 alkaline		1.5	do	1.1
				110	do	0.4
12	15				Made acid 1	64. 8
12	13				10 000	
12	15				Made 5 in 106 alkaline	2. 1
14	16	Neutralized	0.3		Wade 5 in 10- aikaime	
14	16	do	0.3			
	_	Made 10 in 10° acid			Now Morely (before)	
14	16		6.6	· · • · · · · ·	New Merck (before)	0
14	16	Made 2 in 106 alkaline	0.6		Porous pot, large	0.6
14	16	New form	0. 6		do	0.9
14	16		• • • • • • • • • • • • • • • • • • • •	•••••	Porous pot, small	2.4
14	16				do	2. 7

<sup>&</sup>lt;sup>24</sup> The silk itself gave wash waters which were alkaline. There is probably hydrolysis of the silk to form amino acids. The values in the table all refer to the end of the experiment unless expressly stated otherwise.

## TABLE LIII—Continued

		_	LCE electrolyte		PTR electrolyte		
Date		Ex- peri- ment	Notes	Acid (parts in 10°)	Notes	Acid (parts in 10 <sup>6</sup> )	
Apr.	14	2	Before experiment	3	Before experiment	0	
	14	2	Porous pot	41/4	Porous pot	5	
	15	3					
	18	4	Porous pot	3. 6	Porous pot	1.2	
	20	5	Before experiment	3	Before experiment	0	
	20	5	Filter paper	0.6	Silk I	42	
	20	5	do	(Alk.0.3)	Silk III	27	
May	7	13	New form	0.6	Filter paper	30	
	7	13	Filter paper	1.8	Silk (small cup)	42	
	12	15	Before experiment	3. 5			
	12	15	Porous pot (anode)	0.9			
	12	15	Porous pot (cathode)	3. 3			
	3	11			Porous pot	2.1	
	5	12	Porous pot	3. 6	do	1.5	
	5	12	New form	3.0	New form	0.9	
	5	12			Porous pot	0.6	
	5	12			Washed filter tube	174	
	5	12			Double silk	25	
	10	14	Siphon	1.2	do	33	
	10	14	do	3. 0			
	14	16	Anode	0	Double silk	16. 2	
	14	16	Cathode	2. 4	New form	0.3	

#### 6. PERMANGANATE TESTS

Ten cubic centimeters of a 66.6 per cent solution of the salt is made acid with 0.3 cc of 30 per cent  $H_2SO_4$  and titrated with  $\frac{N}{1000}$  KMnO<sub>4</sub> solution until the color remains permanent for one minute. The precipitated  $Ag_2SO_4$  does not interfere with the titration.

Nitric acid may also be used (see p. 173).

Twenty-five cubic centimeters of  $\frac{N}{1000}$  KMnO<sub>4</sub> is equivalent to 0.006 per cent of Ag or 0.010 per cent of AgNO<sub>2</sub>, or 0.001 per cent furfural in the dry salt.

TABLE LIV

Tests of the Permanganate Reduction of Different Samples of Silver Nitrate

Sample tested				
,	сс			
Old Baker, not recrystallized	25. 0			
New Baker (received Jan. 15, 1910) not recrystallized	67. 0			
New Baker, after fusion and filtering	14.0			
New Baker, repeatedly recrystallized (after fusion)	0.5			
New German, not recrystallized	0.5			
New German, twice recrystallized	0. 5			
New German (after fusion)	2. 0			
New German, twice recrystallized (after fusion).	0.5			
French (crystallized)	0.5			
French (after fusion)	5. 0			
German (Dr. Jaeger) fused	6.0			
English (fused)	0. 5			
"New" NBS electrolyte (more than)	6.0			

#### 7. SPECIAL TESTS ON THREE SAMPLES OF SILK

## By A. S. McDaniel

Three samples of raw silk, one furnished by the Bureau of Standards and two furnished by Prof. Jaeger were each treated with portions of the same solution of silver nitrate in glass-stoppered flasks in a thermostat kept at a temperature of 25° C. The silver nitrate solution used was a 10 per cent solution of "New German" silver nitrate which was tested for acid before the experiment and found to contain approximately 1.8 parts of acid in one million parts of solution. The silk furnished by Prof. Jaeger was rinsed once with distilled water before using. It was divided into two approximately equal portions (200 cm²) and each portion treated separately with the silver nitrate solution. The silk furnished by the Bureau of Standards had been thoroughly washed with hot HNO3 solution and rinsed until the water showed no acidity toward iod-eosine indicator.

The amount of silk used in each test was approximately 200 square centimeters, and the volume of solution 160 cc. The flasks were fastened in a rotating device immersed in the water of the thermostat, and were sealed by a thin coating of paraffin over the stopper, which was further protected by a rubber cap. After 24 hours, the flasks were removed and the solutions tested for acid after filtering off the suspended particles of silk by means of an asbestos filter. The results are tabulated in the accompanying table:

### TABLE LV

Sample of silk	Treatment <sup>35</sup>	Volume solution	Acidity, parts 10 <sup>6</sup> (at end)
I. NBS, 200 cm <sup>2</sup> (new)	Acid washed and rinsed free from acid	160 cc 10% AgNO <sub>3</sub> (1.8 parts	22
II. Jaeger, 200 cm <sup>2</sup> (old)	As furnished, rinsed with dis-		37
	do		23
IV. No silk		do	(Alk)-0.3

35 All shaken for 24 hours at 25°.

# APPENDIX F. VARIOUS REPORTS GIVEN TO THE COMMITTEE 1. CONNECTION WITH PREVIOUS WORK

Mr. Smith thought it advisable to connect the results obtained by this committee with the results obtained by the various delegates before meeting in Washington. Such links would be valuable, as they would serve to indicate the reproducibility of the various forms of the silver voltameter. In connection with this matter, he had perused the reports presented by the delegates and believed that good agreement had been obtained. In the report he had presented from the National Physical Laboratory, the probable value of the Weston cells was given as 1.01827 ±0.00002 international volts at 20° C or 1.0183 international volts, if the value be given within 1 part in 10 000.

This value is founded on the latest experiments at the National Physical Laboratory, details of which are given in the National Physical Laboratory report.

The mean value obtained from all the results given in Table XLVII of the report of the subcommittee on the voltameter, is 1.01829 international volts, in very good agreement with the previous one.

In his work of 1906, when filter paper was used, the value of the cell at 20° C was given as 1.01843 volts. M. Laporte's value is 1.01844 and the value now obtained at Washington is 1.01845.

Following are similar statements from Dr. Rosa, M. Laporte and Dr. Jaeger.

PTR.—Dr. Jaeger communicated the results of earlier measurements at the Reichsanstalt on the electromotive force of the Weston cell and on the silver voltameter.

According to these measurements (see Jaeger and von Steinwehr, Investigations on the Silver Voltameter, Zeitsch. f. Instrk., 1908, p. 327) the mean value 1.01834 international volts was obtained for these standard cells, which were in good agreement with those of America and England. The values obtained with the porous pot were on the average about 5 in 100 000 lower. Those without the porous pot, for the most part with silk, about 5 in 100 000 higher than this mean value. Further relative measurements have, however, given the result that there is no difference between voltameters with and without porous pot. (Compare loc. cit., p. 366.) Likewise, later measurements, whose results have been communicated to the committee, have shown that no appreciable difference appears to exist between voltameters of the Kohlrausch form with and without silk.

The mean values obtained with the Reichsanstalt's voltameter in the joint work at Washington, 1.01829 and 1.01833, as also the mean of all the experiments—1.01833, and, finally, the value 1.0183 recommended by the committee for the Weston Normal Cell, all are in good agreement with the earlier values found at the Reichsanstalt.

At the present time, measurements of the same kind are in progress at the Reichsanstalt, but the results are not yet at hand.

LCE.—By using at Paris the English unit of resistance and assigning to the Weston Normal Cell the value 1.01818, adopted in England, the result of the experiments on the silver voltameter was

By calculating, however, the value of the Weston Normal Cell, by taking 1.11800 for the electrochemical equivalent of silver, we have

$$1.01818 \times \frac{1.11829}{1.11800} = 1.01845$$

The mean of the result obtained in the cooperative experiments at Washington, with the voltameters set up with filter paper, with four different electrolytes and four different observers, is

and the mean of the results obtained in the seven experiments made with the electrolyte and the cathodes used at the Laboratoire Central d'Électricité is

# 1.018438

NBS.—As shown in the report of the subcommittee on the silver voltameter, and the third report of the Bureau of Standards on work done on the silver voltameter, the value found for the emf of the Weston Normal Cell by the Bureau of Standards before April 1, 1910, using the small porous cup voltameters, was 1.01824+0.00003=1.01827 volts. This is in very close agreement with the mean value found in the experiments made with two pure electrolytes, using two different types of voltameters (and both large and small sizes) as shown in Table I of the report of the subcommittee, the latter mean being 1.01828 volts. As the electrolyte was not quite pure, we know the value found with large voltameters was a little too large (see Table XLVIII), but we have shown that the different electrolytes agree very closely when using the smallest size of voltameter, and hence the results obtained in this form are considered most reliable.

#### 2. INTERPRETATION OF RESULTS

By W. Jaeger [Translation.]

Dr. Jaeger submitted three tables showing the results obtained with the silver voltameter:

Table LVI contains the means of all the separate experiments; those only to be excluded in which impurities were purposely added.

Table LVII contains the means of the experiments which were carried out with the voltameters of the Reichsanstalt.

Table LVIII contains a summary of the three principal experiments in which the voltameters of the different countries were used in the same way as usual.

The grand mean of Table LVI is 1.01832, and if the experiments on filter paper are excluded, 1.01831. These numbers are in good agreement with the value 1.0183, recommended to the committee.

The mean of Table LVII, using all the observations (not excepting those with filter paper) is 1.01833. Excluding the experi-

ments with filter paper, the value 1.01827 (or 1.01829) is obtained. These numbers are also in good agreement with the value adopted by the committee. From this I conclude that the use of silk is practically without influence, which is also in agreement with the measurements at the Reichsanstalt (submitted to the committee) in voltameters with and without silk.

The summary LVIII gives also, for the three measurements (Nos. 3, 5 and 7) with the cups of the Reichsanstalt, very nearly the same mean value, 1.01829, as with all the measurements (Table LVII). The measurements with the cups of the National Physical Laboratory give the mean value 1.01833, which is also in good agreement with the adopted value, and also agrees well with the experiments of the Reichsanstalt. Since, according to the opinions of some of the members of the committee, that the English salt is the purest and that the method used by Mr. Smith avoids all organic septa, this agreement is, in my opinion, a further proof that the use of silk as septum had no appreciable influence on the silver deposit. The numbers obtained with filter paper (France) seem to indicate that filter paper, in agreement with the opinions derived from observations of the Bureau of Standards increases the deposit. The differences between the large and the small cups of the Bureau of Standards appear, likewise, to indicate that under certain circumstances a difference between the deposits of silver in large and small cups can occur. I incline, however, to the opinion that this phenomenon, which has been designated as the "volume effect" could be ascribed to the influence of the porous pot.

In the 15th experiment, May 12, those electrolytes, which were made alkaline by the addition of NaOH became "opalescent," which appears to indicate that precipitation of silver hydroxide took place. In such a case the weight of silver must naturally be found too large. This measurement appears, therefore, to me to be inconclusive with regard to the influence of alkali.

The relative experiments, Nos. 14 and 16 of the 10th and 14th of May, show such abnormal differences that one must be very careful in drawing conclusions from these experiments. It is, indeed, not impossible that faults in the insulation were present,

which influenced the distribution of current among the different voltameters. The values found for the PTR voltameters appear to me very improbable. Also it is not easy to see why the siphon voltameters gave strongly varying values in experiment 14, while, according to Mr. Smith, they gave values at Teddington, which agreed well with those of the "new form." All these circumstances make the experiments concerned appear rather questionable, and I prefer, therefore, not to subscribe to the conclusions drawn from them.

On the other hand, the experiments with cups of the same kind and different electrolytes (see special table) indicate that the different salts give the same deposit. This would have to be interpreted that all the electrolytes used are sufficiently pure.

TABLE LVI

Mean of all the Experiments in which the Mean for each Experiment is Obtained, excluding those Deposits [Experiment 15] in which Acid was Purposely Added to the Electrolyte

Number of experiment	Date (1910)	Weston cell at 20° (corrected to the mean of resistances and standard cells)	Differences, parts in 100 000	
2	Apr. 14	1. 01825	<b>—</b> 7	
3	15	35	+3	
4	18	275	<b>-4.</b> 5	
5	20	34	+2	
6	22	295	-2.5	
7	26	38	+6	
8	28	32	0	
9	30	34	+2	
10	May 2	39	+7	
11	3	36	+4	
12	5	36	+4	
13	7	31	-1	
15	12	30s	-1.5	
17	19	26	-6	
		Mean, 1. 01832	±3.5	

These figures include 93 deposits, of which 10 or 11 were made using filter paper. If the latter are excluded, the mean 1.01831 is obtained.

Probable error of a series  $=\pm 2.8 \times 10^{-5}$ Probable error of the result= $\pm 0.8 \times 10^{-5}$ 

TABLE LVII Mean of the Experiments with the Cups I and III of the Reichsanstalt

Number of experiment	Cup	EMF cell at 20°	△37
3	I	38 1. 01837	+ 8
3	III	30	+ 1
		Mean, 1.01834	+ 5
5	I	1. 01827	<b>–</b> 2
5	III	38	+ 9
		Mean, 1.01832	+ 3
7	I	1. 01824	- 5
7	III	21	<b>–</b> 8
		Mean, 1.01822	- 7
10	I	<sup>39</sup> 1. 01838	+ 9
10	Ш		
12	I	39 1. 01845	+16
12	ш	22	- 7
		Mean, 1.01836	+ 7
13	I	<sup>39</sup> 1. 01848	+19
13	III	25	<b>- 4</b>
		Mean, 1.01836	+ 7
		Mean of all, 86 1. 01833	

 $<sup>^{36}</sup>$  If the experiments with filter paper are excluded, the mean 1.01829 is obtained,  $^{37}$   $\bigtriangleup$  is the difference of the individual values and the value 1.01829.  $^{38}$  Without septum.  $^{39}$  With filter paper.

#### TABLE LVIII

Summary of the Results of the Three Experiments, Each with 10 Cups, in the Forms Used in the Different Countries

## Experiment No. 3, April 15, 1910

Cup	Germany	Cup	England	Cup	France	Cup	U. S. A.	Cup	U. S. A.
III	1. 01837 +3 30 -4 1. 01834	A B	1.01831 +1 28 -2 1.01830		1. 01843 0 43 0 1. 01843	93	1. 01840 +1 39 0	127	1. 01833 +3 27 -3 1. 01830

### Experiment No. 5, April 20, 1910

I	1.01827 -5 38 +6	1.01831 +1 28 -2	1. 01854 +7 416	1		1.01820 -4 29 +5
	1. 01832	 1. 01829	 1. 01847		1. 01838	 1. 01824

# Experiment No. 7, April 26, 1910

III	1.01824 +2 21 -1		1.01841 0 42 +1	1.01847	93 95	1.01847 0 47 0	127 128	1.01835 0 36 +1
	1. 01822		1. 01841	 1.01847		1. 01847		1. 01835
Mean.	1. 01829		1. 01834	 1. 01846		1-01841		1. 01830

### 3. INTERPRETATION OF RESULTS

### By E. B. Rosa

Table LIX gives a summary of the results obtained in 14 international experiments, containing 98 deposits. Three experiments are not included in this table, two (1 and 16) because of accidents whereby the current became interrupted, one (14) because of the inclusion of six siphon voltameters having a total resistance of about 200 ohms, and the current could not therefore be maintained constant enough to permit an accurate determination of its average value. All other experiments were made with very steady current, the average uncertainty in its mean value in each of the 13 experiments being probably not greater than 1 part in 100 000.

Twenty-four deposits were made with electrolytes which do not reduce potassium permanganate. At the Bureau of Standards we have found that the reaction with potassium permanganate is large with very impure electrolytes, which give striated deposits and a large volume effect; that it is less with less impure electrolytes which give a smaller volume effect, and that there is no reaction with those samples of silver nitrate which give no volume effect. We should, therefore, conclude that a small reaction with potassium permanganate is not only an evidence of a small quantity of impurity in the silver nitrate, but that this small impurity will increase the deposit appreciably in a large size voltameter (300 to 400 cc), and we think this conclusion is justified by our work. In other words, the permanganate test seems to be a searching test for reducing agents which tend to make the deposit too heavy. Most of these 24 deposits were from silver nitrate purified by Smith at the National Physical Laboratory, but four were from silver nitrate purified by McDaniel at the Bureau of Standards. The deposits agree very accurately in the two types of voltameters, and in the several sizes of the porous cup voltameters, and the average deviation of the 24 deposits from the mean of all is a little over I part in 100 000. This surprising agreement with so many deposits under so many conditions can not be altogether accidental, but indicates the possibility of very high reproducibility when the electrolyte is pure and all the conditions suitable, even though the size and type of voltameter be varied, with different treatment in detail of the deposits. regret that only two samples of silver nitrate were available, which were entirely pure as tested by potassium permanganate. but we have prepared some others since the international experiments were finished, and shall be prepared to report on these later. We may add that the purification of silver nitrate so that it will stand this very severe test is not difficult when one knows exactly how to proceed, and we mean to communicate the process to some of the chemical manufacturers, so that they may supply nitrate that will be strictly pure as tested in this way.

Ten deposits were made, using filter paper, by three experimenters, using different voltameters and different electrolytes. The mean value is 15.1 in 100 000 higher than the value with

pure electrolyte, using porous cups or no septum (as in Smith's new form). There is a very good agreement among these values, although the mean deviation from the mean of all is about three times as great as in the first set. It may be remarked that a single sheet of filter paper was used in each case. If heavier paper, or two sheets of the same, had been employed, the excess in weight would have been greater. (See third report of the Bureau of Standards on this subject.) As no member of the committee favors the use of filter paper in the normal voltameter, it is not necessary to discuss these results further.

Fifteen deposits were made with silk, by three experimenters, in several different types of voltameters. Two deposits were made with new raw silk that had been washed thoroughly but not soaked in water a long time before using. These two deposits average 29.4 in 100 000 higher than the mean of the others. other 13 deposits were with washed silk that had been kept in water a long time before using and then used repeatedly. average is closely in accord with the results of group 1. This, however, would seem to be largely accidental, inasmuch as silk seems to produce two disturbing effects which are in opposite directions, as pointed out in the report of the subcommittee. first is to increase the deposit by producing reducing agents, which effect is large at the start but decreases rapidly with continued washing. The second is to produce acid, which decreases the deposit. The special tests on three samples of silk (see report by Dr. McDaniel) in which silk was placed in neutral AgNO3 in a bottle for 24 hours, which was rotated to keep the liquid stirred, show that acid is produced by silk, even outside of the voltameter, when current is not flowing. Two of these samples were Dr. Jaeger's silk, and one was supplied by the Bureau of Standards. All tests of the electrolyte that have been made at the end of experiments in which silk has been used, show acid in relatively large quantities, about 20 to 40 parts in a million; enough to reduce the deposit appreciably, according to the special tests on the effect of acid. That, on the average, the deposits in the above table are as high as with the pure electrolytes, in spite of the presence of acid, shows to my mind that the silk probably is also producing simultaneously the first effect mentioned above.

Reference may be made also to the deposits with silk in the Physikalisch-Technische Reichsanstalt voltameters in the relative experiments 14 and 16. As compared with the voltameters 27 and B, of experiment 14 (in which pure electrolyte was used, and in which a normal value of the deposit may fairly be assumed to have occurred) the silk voltameters gave deposits 3 in 10 000 too small; whereas the mean of the siphon voltameters was 3 in 10 000 greater than the two taken as normal. In experiment 16, the mean of the deposits 121, 125, and 126, was taken as normal, these three having pure, neutral silver nitrate and no septum to contaminate the electrolyte. Here the silk voltameters are 3 and 6 parts, respectively, in 10 000 too low, a departure from the normal value greater than produced by filter paper in any of these experi-Possibly these four deposits are only accidentally low; if so, no suggestion was made as to the nature of the accidents. The presence, however, of silk (producing 10 times as much acid in the electrolyte as, I believe, is permissible) gives some ground at least for suspicion, even though something else may have operated to produce so considerable deviations from the mean value.

In the fourth group of results there are 35 separate deposits in which various electrolytes have been employed, all of which, judged by the chemical tests applied, were slightly impure. By this is meant that they were, judged by ordinary standards, pure. But, judged by the permanganate test, they carried an appreciable quantity of organic impurities or reducing substances that result from organic impurities. Many of these deposits are the same as those given in Table XLVIII of the subcommittee, showing the volume effect. That is, the deposit is larger from large volumes of electrolyte than from small when the electrolyte is impure. In 13 deposits in large voltameters (2 National Physical Laboratory and 11 National Bureau of Standards), the mean is 15 parts in 100 000 greater than for the 18 deposits in the small National Bureau of Standards voltameters. To our view this is unmistakable evidence of impure electrolytes. If our view is correct, all purchased samples of AgNO<sub>3</sub> which have been at the disposal of the committee, from German, French, and American makers, have been slightly impure, and only the two samples referred to above, purified by Smith and McDaniel, are strictly pure. I regard

it as a fortunate discovery by Dr. McDaniel that a comparatively simple chemical test should show (as the potassium permanganate test seems to do) the presence of small quantities of impurities so difficult to detect by other means.

Faraday's law is the underlying principle of the silver voltameter. When the latter is employed as a standard for current measurements, the quantity of the deposit should be proportional to the quantity of electricity. If large and small voltameters do not agree, there is something wrong with the voltameter or with the manipulation, or with the electrolyte. We think that there is no doubt whatever in this case as to where the trouble lies. The voltameters and the manipulation are the same (for the most part) as in the first group of results. The electrolytes differ. We do not need to trust the chemical test alone to prove the electrolytes are impure; the voltameter experiments show it also. Hence we clearly should not give the same weight to the results of the experiments in group 4 in determining the true value of the emf of the Weston cell in international volts, as to the results of experiments not open to these objections.

In groups 5 and 6 the results of adding small quantities of alkali and acid are given. Very small quantities of either affect the weight of the deposit, alkali increasing and acid reducing the deposit. We have made other experiments on this subject at the Bureau of Standards, and shall make still others. We can not say precisely how much of either is safe, but a slight decrease in weight is caused by a few parts of acid in a million, and probably one in a million of alkali, if always present, would be noticeable in the mean of several experiments.

Finally, we call attention to the fact that many of the deposits made by the Bureau of Standards in these investigations with impure electrolytes were made for the purpose of demonstrating the "volume effect" (as we have called it) as a test for impurity.

Four cups were used by the Bureau of Standards, instead of two as the others did, in order to have two different volumes of electrolyte (one 100 cc and the other 300 cc) to show how important it was to have silver nitrate of the highest purity, and it was stated at the time that the salt was purchased and was not quite pure, and would give a higher value in the large cups. All the AgNO<sub>3</sub> used in these experiments was tested by the permanganate test, and although it was considered very pure, the permanganate reaction if trustworthy showed slight impurity in all except the English. The representatives of the Bureau of Standards have great confidence in this test, but as it is a new test and has not been used before by others, its trustworthiness was not accepted by all the delegates.

At the end of Table LIX is given a summary of the results obtained in the 70 deposits of groups 1, 3, and 4, omitting those made with filter paper and those in which acid or alkali was added. There is a difference of opinion among the delegates as to how these results should be weighted in taking the mean, but for the purpose of fixing the value of the Weston Normal Cell to five figures it fortunately makes little difference how the results are combined. If equal weight is given to all, the result is nearly the same as though the weights were unequal.

# TABLE LIX

Summary of Results of 89 Deposits, excluding relative values of Experiments 1, 14, and 16

1 With Voltameters Using Porous Cups or without any Septum (with Electrolyte neutral by the iod-eosine test and free from reducing substances by the permanganate test)

(1) Mean of 10 40 deposits, NPL, new form voltameter	28 <sub>9</sub> 28 <sub>5</sub>	±4.3 ±0.7 ±1.0 -0.2
Mean 24 deposits, two types, several sizes of voltameters  Mean excluding two determinations with unsteady current  2. Using Filter Paper	71	
(6) Mean of 3 deposits, PTR, with filter paper	1. 01846 <sub>9</sub>	1. 7
	437	4. 4
(15) Mean of 1 deposit, NPL, with filter paper	475	2. 5
Mean of 10 deposits	1. 018450	±3.4

 $<sup>^{40}</sup>$  Two deposits in NPL, new form in seventh experiment, gave 1.018418. The current in this experiment was unusually unsteady. If these two determinations be excluded, the mean of 8 deposits is 1.018287 and the mean of 22 is 1.018286.

<sup>22451°-12-13</sup> 

### 3. Using Silk

2

4

3

(5) Mean of 6 deposits, PTR, with silk	1. 01828 <sub>2</sub> 58 <sub>0</sub>	±4.
(13) Mean of 6 deposits, NBS, with used silk	28 <sub>5</sub>	±3.
alkaline)	290	0.
Mean of 15 deposits	1. 01832 <sub>3</sub> 1. 01828 <sub>6</sub>	3•
4. Electrolyte indicated by the chemical tests to be Slightly In	npure	
<ul> <li>(7) Mean of 1 deposit, PTR, with no septum.</li> <li>(9) Mean of 2 deposits, LCE, with no septum.</li> <li>(16) Mean of 2 deposits, NPL electrolyte, with no septum, large</li> </ul>	1. 01837 <sub>3</sub>	
voltameter	458	
voltameter	430	
voltameter	280	
voltameter	214	
Mean of 35 deposits	1. 018335	
5 Electrolyte Slightly Alkaline, NaOH added		
(18) Mean of 2 deposits, electrolyte, alkaline, added 2.1/106 NaOH.  Mean of 1 deposit, electrolyte, alkaline, added 5/106 NaOH  Mean of 1 deposit, electrolyte, alkaline, added 10/106 NaOH	1. 01836 <sub>3</sub> 58 75	
Mean of 4 deposits.	1. 018515	
6. Electrolyte Slightly Acid, HNO <sub>3</sub> added		
Mean of 1 deposit, electrolyte acid, added 10/10 <sup>6</sup> HNO <sub>3</sub>	1. 01820 <sub>0</sub> 16 <sub>0</sub>	
Mean of 3 deposits	1. 018173	
Summary		
Mean of 22 experiments, group 1 equals	1. 018286	
Mean of 13 experiments, group 3 equals	1.018286	
Mean of 35 experiments, group 4 equals.	1. 018335	
Mean of 70, giving each equal weight, equals	1. 01831 <sub>0</sub> 1. 01830 <sub>2</sub>	
Mean of 70, giving group 4 han weight, equals	•	4

Mr. Smith makes the following comments on Dr. Rosa's interpretation of the results:

Dr. Rosa's conclusions are naturally on very similar lines to those of the subcommittee on the silver voltameter, of which I was a member, and in consequence I am in almost complete agreement with his conclusions.

The possible action of silk has been discussed by the full committee and I think it well that further experiments should be made with it and with porous pots or any other medium which may contaminate the electrolyte. These experiments must of course be supplemented by others on the effects of small quantities of acid and alkali.

The question of the purity of the electrolyte is most interesting. To obtain pure silver nitrate very considerable care was taken in the early and recent experiments at the National Physical Laboratory and, I believe, even greater care in the recent experiments by M. Laporte at the Laboratoire Central. In these cases I think that there is no doubt but that very pure salt was obtained, although in the early National Physical Laboratory experiments, and in some of the experiments at the Laboratoire Central, the solutions were afterwards contaminated by filter paper.

It will be observed that the tests made by Dr. McDaniel on silver nitrate from the National Physical Laboratory showed the fresh electrolyte to be free from organic matter and to be never acid. On one occasion a sample of fused salt was given to Dr. McDaniel and this he found to be free from acid and alkali. I was surprised. therefore, to find on May 7 that a solution was alkaline to the extent of 2 parts in I 000 000 and at that time I was at a loss to explain the alkalinity. However, a report submitted by Dr. McDaniel shows that in 24 hours a 10 per cent solution which was originally acid by 1.8 parts in 1 000 000 became slightly alkaline (0.3 in 1 000 000) after agitation in a flask. As some of the bottles in which the electrolytes were stored. were fresh from the stores of the Bureau and in many cases the electrolyte remained in the bottles for 14 days—perhaps more—the slight alkalinity observed on May 7 was probably produced by interaction with the glass. It is of interest to note that on May 7 the results obtained with the NPL electrolyte were higher than usual by about 8 parts in 100 000, and that this was the only occasion when such an abnormal value was obtained. It is true that there was one other occasion when high values resulted. but the current was unusually unsteady and the results are not therefore of much weight. I conclude that solutions should be freshly prepared or stored in special glass bottles.

With regard to Dr. Rosa's statement to the effect that "if we were to restrict the volume of electrolyte to 100 cc, something might be said for permitting the use of electrolyte which is not quite pure," I think that the statement should refer to the degree of electrolysis and not to the volume. According to my own experiments, the reason why, from a small volume of impure electrolyte, a lighter deposit is obtained than from a larger volume of the same electrolyte, when the two are placed in series, is because the degree of electrolysis is greater in the first case than in the second. For equal concentrations the degree of electrolysis is inversely as the volumes. If alkali or other impurity tending to increase the deposit, is present in an electrolyte at the commencement of an experiment there is less present at the end of the experiment; the average quantity of impurity present during the experiment varies, therefore, with the degree of electrolysis and hence the deposit varies with the latter. It also follows that the deposit from an impure electrolyte depends on the concentration of the solution. 100 cc of a 20 per cent solution (impure) will give a heavier deposit than 100 cc of a 10 per cent solution of the same salt, if the two are placed in series.

Hence, while I entirely indorse Dr. Rosa's remarks on the desirability of having a pure electrolyte, I suggest that the uniform results obtained with the four small voltameters were due to the high degree of electrolysis.

# 4. INTERPRETATION OF RESULTS By F. E. Smith

Mr. Smith submitted the following table, which gives the weighted means of all experiments with the forms of voltameters stated at the heads of the columns. To obtain these weighted means, values were assigned to the results in proportion to the degree of accuracy with which the current was estimated to be known. Each mean is accompanied by a number, in parentheses, denoting the number of values from which the mean was obtained; the mean deviation from the mean is also given, but in calculating this one deviation (associated with the experiment in which the value of the current was estimated to be known with an accuracy not greater than I in 10 000) has been omitted.

TABLE LX

Electrolyte	New form, 370 cc	Porous pot, small bowl, 100 cc	Porous pot, large bowl, 300 cc	
NPL Poulenc Frankfurt (fused) Frankfurt recovered	(1) 441		$(4) \ 30_4 \pm 2_6$ $(3) \ 35_7 \pm 14_3$ $(2) \ 43 \pm 3_9$ $(9) \ 41_5 \pm 2_3$	
NBS, purified		$\begin{array}{c} (2) \ 26_9 \ \pm 0_4 \\ (30) \ 28_5 \end{array}$	$\begin{array}{c} (2) \ 25_9 \ \pm \ 1_0 \\ (20) \ 38_0 \end{array}$	

Electrolyte	Filter paper, 100 to 350 cc	Silk, 70 cc to 350 cc	No septum (Jaeger), 70 cc	Weighted mean
NPL	(1) 47 <sub>5</sub> (7) 43 <sub>8</sub> ±3 <sub>9</sub>			(28) 30 <sub>8</sub> (17) 36 <sub>2</sub>
Frankfurt (fused)	(2) $46_5 \pm 1_7$	(7) 28 <sub>3</sub> ±4 <sub>6</sub> (4) 28 <sub>2</sub> ±3 <sub>5</sub>	(1) 343	(19) 32 <sub>8</sub> (22) 34 <sub>6</sub>
NBS, purified		(14) 31 <sub>3</sub>	(1) 34 <sub>3</sub>	(4) 26

Weighted mean of all (89)=1.01833e

Mr. Smith stated that he would interpret the results in the table submitted by him as showing that with some of the electrolytes a larger mass of silver was deposited from a larger volume than from a small volume, and his deduction from this was that some of the electrolytes were impure. This was admitted in the case of the two first electrolytes (Frankfurt crystallized; also recovered silver nitrate) from the Bureau of Standards, both in the Bureau of Standards' reports and during the experiments.

A further deduction from the table is that, with filter paper, a contamination of the electrolyte results which increases the mass of the deposit.

It was worthy of notice that the results obtained (mean = 1.018264) with the purified salt of the Bureau of Standards agreed substantially with those obtained (excluding filter paper and silk, mean = 1.018286) with the purified salt from the National Physical Laboratory and these two electrolytes showed very little or no volume effect. It was also well to point out that the values obtained with the four electrolytes in small voltameters of the porous pot type agreed remarkably well, both among themselves (mean = 1.018285) and with the two values stated above.

M. Laporte and Dr. Rosa expressed themselves as being in agreement with these remarks.

#### 5. INTERPRETATION OF RESULTS

By F. Laporte [Translation.]

Before the experiments in Washington, the results obtained in the different laboratories for the electromotive force of the Weston Normal Cell, as deduced from the value of the ohm and the deposit of silver, may be considered to be as follows:

	41 1908	<sup>42</sup> 1910
PTR	1. 01834	
NPL	1. 01843	1. 01827
NBS	[1.01837 [1.01863	<sup>4</sup> 31. 01827
LCE	1. 01879	1. 01845

<sup>41</sup> Introduction, p. 6.

The results obtained at Washington, as is shown by Appendix F, page 180, prove that the experimental conditions employed by the different laboratories in 1910 are reproducible with precision. This is a first important point gained. The measurements made by the four laboratories are now comparable.

The use of filter paper as a septum has the effect of increasing the weight of the deposit in the voltameter in question. This fact is very strikingly established by the experiments; however, under

<sup>42</sup> Appendix F, pp. 180 et seq.

<sup>&</sup>lt;sup>43</sup> The results given by the NBS relate only to deposits obtained in voltameters of small size and with the porous pot.

given experimental conditions, its action always appears to be the same. That is, the "Rayleigh" form is also as reproducible as the others.

One sees also that traces of alkali increase the weight of the deposit, and that free acid added to the electrolyte decreases it. The action of alkali is more distinct and more important than that of acid. The experiments are entirely insufficient to evaluate numerically the importance of this action or to fix upon allowable limits in the specifications.

The use of silk as septum would appear to necessitate fulfilling certain experimental conditions (nature of silk, preliminary washing). The same is probably true of the porous pot, which gave in one or two experiments results which were too low, which results were regarded as abnormal. But it would not appear to me that any conclusion can be drawn.

Excepting the points just indicated, no other fact appears to have been indubitably proved. The measurements of the acidity or alkalinity of the electrolyte, before and after the experiments, no acid or alkali having been purposely introduced, gave results which were not markedly systematic. Even with filter paper, the results of the tests have indicated alkalinity as often as acidity, and it is necessary to enter into complicated chemical considerations to explain the results.

As regards the volume effect and the test with permanganate of potash, the results are not entirely conclusive.

The experiments which may be regarded as establishing it were all made with the porous pot, the four electrolytes evidently gave the same results in the small voltameters, the test with the larger voltameters was not made in such a systematic manner. It can also be seen from the table on page 168 that very noticeable differences were obtained with voltameters of the same volume. Further, the question was not settled as to whether or not the fusion of the silver nitrate, necessary for the test with permanganate, has an effect on the weight of the silver deposit.

The volume effect, then, although very probable, does not seem to me to have been indisputably established by the experiments.

I wish, however, to make clear that I consider the electrolyte of the National Physical Laboratory as the purest of the solutions employed. The voltameter without septum seems to me to offer the greatest amount of security and to be above suspicion. Accordingly, in discussing the experiments, all should be rejected with the exception of those made with the new form, using the National Physical Laboratory electrolyte, and in which the acidity of the electrolyte was controlled.

These experiments are as follows:

Experiment	Deposit	Acidity 10 <sup>-6</sup>	Value of Weston cell
5	33	0 .	1. 018310
5	34	0	283
9	59	0.9	311
12	83	0	279
15	95	1. 2	254
Mean			1. 018287

But these experiments are truly too few to allow of taking their mean as representing the value of the electromotive force of the Weston cell; I think, therefore, that it will be better to take as the provisional value of the Weston cell the mean which results from including all the deposits obtained in the experiments of the International Committee (excepting those in which filter paper was used and those carried out under abnormal conditions). In fact, we have just seen that if an attempt is made to discuss and analyze all the results, point by point, difficulties or impossibilities are met with. Why, for example, should certain results a little different from the mean (Experiments 7 and 13) be eliminated, or their importance be diminished, because the current was noted to be unsteady or because the electrolyte was found acid or alkaline, while other deposits of the same experiment are too light or normal, the test of acidity not having been made systematically for all the electrolytes in all the experiments?

Taking the mean, then, of the 40 values contained in the following table, the value

1.0183,

is obtained.

I think, then, that the value to be adopted should be

1.0183

# Report on Concrete Standards

# TABLE LXI

Experi- ment	Deposit	Electro- lyte	Туре	Value of Weston cel
	( 17	С	No septum	1.018373
3	18	С	Silk	304
	19	A	New form.	310
	20	A	do	280
	21	D	Porous pot	397
	22	D	do	394
	23	D	Glass and silk	328
	24	D	do	274
	{ 31	С	Double silk	1.018275
	32	С	do	378
	33	A	New form	310
	34	A	do	283
5	35	D	Porous pot	375
	36	D	do	392
	37	D	Glass and silk	201
	38	D	do	288
7 45 46 47 48 49	{ 45	С	Double silk	1.018236
	46	С	do	209
	47	A	New form	415
	48	A	do	420
	49	D	Porous pot	468
	50	D	do	468
	51	D	do	352
	52	D	do	363
	f 62	В	New form.	1.018246
10	66	A	do	270
10	68	A	Porous pot.	288
	70	A	do	284
1	{ 86	В	New form.	1.018196
89	89	С	Double silk	246
	90	A	Silk	290
13	91	A	New form	363
13	92	A	Glass and silk	304
	93	A	Porous pot.	363
	94	A	Silk	313
17	95	A	Porous pot.	200
	129	E	do	1.018269
	130	E	do	249
	131	E	do	272
	132	E	do	265
Mean				1.01831

#### 6. PROVISIONAL SPECIFICATIONS FOR THE SILVER VOLTAMETER

For work of highest precision. Prepared by E. B. Rosa at the request of the committee and submitted for consideration, but not acted upon

- 1. The electrolyte shall consist of a solution of silver nitrate in distilled water, having from 10 to 20 g of silver nitrate in 100 cc of the solution.
- 2. The electrolyte must be free from organic or other reducing substances, as shown (a) by a suitable chemical test, (b) by giving a crystalline deposit free from striations, and (c) by giving the same weight of deposit in a large and in a small voltameter.
- 3. The silver nitrate is purified by crystallization and fusion, and if the chemical test for purity is omitted it should be purified until further crystallization does not change the weight of the deposit.
- 4. The voltameter should contain not less than 75 cc in the cathode chamber, and the deposit should not continue long enough to reduce the mean concentration of the electrolyte in the cathode chamber below 5 per cent. If no septum is used, no greater weight of silver should be deposited in a single experiment than is contained in the electrolyte at the start.
- 5. The electrolyte when ready for use must be neutral or very slightly acid, as tested by iod-eosine. As one part in a million of alkali may increase the deposit appreciably, it may be better to have a slight acidity (say one part in a million) than to take the risk of slight alkalinity in attempting to make it strictly neutral. The electrolyte must be neutral or slightly acid at the end of the experiment, no alkalinity, and only a trace of acid, if any, being present. In any case there must not be enough acid present to affect the weight of the deposit. Any septum or other substance which contaminates the electrolyte or produces appreciable alkalinity or more than a trace of acid must be avoided.
- 6. The cathode should be a crucible or bowl, preferably of platinum (although gold may be used) of from 125 cc to 400 cc capacity. The surface should preferably be smooth and bright and the deposited silver should be removed by electrolysis or by acid, without scratching or marring the surface of the platinum by any instrument.
- 7. The anode should be of pure silver and is preferably coated with electrolytic silver. This is conveniently done when a previous deposit is being removed from the cathode bowl, using a relatively small current. The anode should have as large an active area as the size and type of voltameter permit.
- 8. The current during a deposit should be maintained constant, and is preferably not more than one ampere, and the time not less than one hour.
- 9. If the surface of the platinum is perfectly clean and the electrolyte pure the silver will be adherent and there will be little if any loose silver. After thorough washing, the cathode bowls are dried at about 150° C, preferably in an electric oven and after cooling are weighed. In the weighing a similar platinum dish adjusted to the same weight is advantageously used as a tare.
- 10. The electromotive force of the standard cell employed is calculated from the weight of silver deposited, the resistance, and the time, using 1.11800 mg per second as the electrochemical equivalent of silver.

## 7. REPORT OF SUBCOMMITTEE ON THE MAINTENANCE OF THE UNITS

By F. A. Wolff and F. Laporte

In the opinion of the subcommittee, it is considered of the highest importance for the additional work outlined on the silver voltameter and for similar international cooperative work in the future to adopt measures which would enable such results to be expressed in terms of the same resistance standards and standard cells here employed.

The following are therefore recommended with regard to the unit of resistance:

- 1. An intercomparison of the coils of the PTR, the NPL, and the LCE in the home laboratories with other reference standards immediately upon the return of the delegates to their laboratories.
- 2. The periodic recomparison of the coils employed at the NBS by the aid of at least two coils selected on account of their relative constancy and sent to each laboratory in turn at least once a year.
- 3. The general adoption of sealed coils as reference coils to eliminate at least one source of variation.
- 4. The early completion of primary mercurial standards in precise realization of the London specifications and the determination of their relation to the unit here employed.

Our recommendations in reference to standard cells are as follows:

- 1. An intercomparison of the cells taken back to the home laboratories with the cells serving as the previous basis of reference.
- 2. The periodic recomparison of the cells here employed by the aid of a number of cells sent to each laboratory in turn.
- 3. The construction of new cells from time to time as a further check on the constancy of the reference cells. These should include cells set up with materials derived by exchange between the various laboratories.
- 4. Cooperative work along lines to be agreed upon to be made the basis of suitable specifications to insure the highest possible accuracy of reproduction as well as uniformity of procedure.
- 5. The completion of arrangements for the preparation of standard cell materials made according to the specifications agreed upon, and their distribution under the auspices of the International Scientific Committee.

With regard to the silver voltameter the following recommendations are made:

- 1. The adoption of general specifications in so far as they may be agreed upon.
- 2. Further experiments on matters not considered as settled at this conference and as indicated in the minutes of the sixteenth meeting of May 23 to serve as a basis for final specifications.

In addition the following general recommendations are made:

- 1. That the results obtained in any of the above work by any member of this committee be promptly communicated to the other members.
- 2. That every effort be made to complete the results of the silver voltameter experiment and the construction of mercury ohms by the spring of 1911.
- 3. That every assistance be given to members of the International Scientific Committee not represented in Washington who may be working or who desire to work on the questions here taken up.
- 4. That researches bearing on these questions be published as soon as possible after their completion.

# V. RÉSUMÉ

By F. Laporte

[Translation]

The state of the question of the electrical units and standards at the time of the opening of the Conference of London, in 1908, and in the following year (1909) was as follows:

## THE INTERNATIONAL OHM

The National Physical Laboratory and the Physikalisch-Technische Reichsanstalt only had realized mercurial standards representing the international ohm. These standards, dating as they do, from before 1908, do not fulfill all the conditions laid down at London in the specifications for ohm standards to be constructed later. The Laboratoire Central d'Électricité referred its measurements to legal ohms, constructed in 1884, and preserved at the Post and Telegraph office at Paris. The Bureau of Standards had, as base of reference, wire coils compared with the German and English ohms.

#### STANDARD CELLS

The standard cells constructed in the different laboratories, according to slightly differing procedures, principally as regards the preparation of the mercurous sulphate, agreed in value, in so far as it had been possible to detect by exchanging cells and samples. However, the cells prepared from mercurous sulphate, obtained at the LCE by alternating current electrolysis, and constructed in this and the other laboratories, had shown a slightly higher electromotive force than the others.

#### SILVER VOLTAMETER

Adopting 1.11800 as the electrochemical equivalent of silver, the values found for the electromotive force of the Weston Normal Cell are as follows, each laboratory having employed different electrolytes, voltameters, and experimental conditions:

At the NPL with filter paper	1.01843
At the PTR with silk and porous pot	
At the NBS with the porous pot	37
At the NBS with filter paper	
At the LCE with filter paper	79

This statement shows that differences of several ten-thousandths existed between the results.

The London Conference recommended, subject to later experiments, as provisional value of the emf of the Weston cell, 1.0184 at 20° C.

Following a vote of the International Committee on the proposition of Mr. Stratton, a technical committee was formed and met at Washington to make joint experiments. The aim of this work was to determine what value should be recommended for the emf of the Weston Normal Cell at 20° C as determined from measurements made by means of the silver voltameter.

This committee was composed of Messrs. Rosa, of the Bureau of Standards, chairman; Jaeger, of the Physikalisch-Technische Reichsanstalt; Laporte, Laboratoire Central d'Électricité; Smith, National Physical Laboratory; and Wolff, Bureau of Standards.

The work continued from April 4 to May 25, 1910. The delegates made and had made, during this time, numerous experiments and comparisons of the silver voltameter, resistance coils, and standard cells.

The results of the experiments were presented in the reports of the subcommittees and discussed in the meetings of the technical committee.

The work of the committee may be summarized as follows:

### RESISTANCES

The resistance coils, which were brought by the delegates, were intercompared. The experiments were made at two temperatures, 20° and 25° C. The numerous comparisons made have led to the following conclusions:

The Technical Committee decides to choose, actually and until new mercury ohms shall have been constructed, as the value of the international ohm, to be recommended to all countries, the mean of the values of the units realized at the Physikalisch-Technische Reichsanstalt and National Physical Laboratory. Although the international ohm, as defined by the London Conference, has not been strictly realized, the committee believes that its value has been obtained in two independent laboratories, with a good degree of precision, and that future work will not change its value by more than 2 or 3 in 100 000.

The committee expresses the hope that new international ohms, fulfilling all the specifications of the London Conference, may be realized as soon as possible in different laboratories.

The results of the comparisons of the different metallic resistances have been as follows (see p. 94):

Ohm PTR – Ohm NBS = 
$$+2 \times 10^{-6}$$
  
Ohm NPL – Ohm NBS =  $+12 \times 10^{-6}$ 

From these can be deduced that the differences between the values of the ohms in use in the different laboratories and the value adopted by the Technical Committee, are as follows:

```
For the PTR ohm - 5 \times 10^{-6}
For the NPL ohm + 5
For the NBS ohm - 7
For the LCE ohm + 110
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The relative measurements of the metallic resistances seem to show that the resistances inclosed in sealed boxes gave, during the experiments in Washington, results more regular than have the metallic resistances for which this precaution had not been taken.

#### WESTON STANDARD CELL

Standard cells constructed in each laboratory were brought by the delegates. From the point of view of the methods of preparation of the mercurous sulphate, the following differences exist among the cells.

At the PTR, by precipitation by adding hot sulphuric acid to acid mercurous nitrate, or the reverse.

At the NPL, by precipitation by adding mercurous nitrate to sulphuric acid.

At the NBS, by electrolysis with direct current.

At the LCE, part by electrolysis with direct current, the rest by alternating current electrolysis.

All these cells were compared at different times during the work of the delegates (for the results, see p. 96 et seq.). As a result of these comparisons, the Technical Committee has decided to choose as "value of the Weston Normal Cell, the mean value of the cells submitted by the delegates of the four laboratories. This mean has been calculated in the following manner: The mean of the values of the standard cells, presented by each delegate, has first been taken, and then the mean of the four numbers thus found."

The results are summarized in Table XIII, page 109.

Ceils		Mean of group minus general	Average deviation of single	
No.	Laboratory	mean; difference in 10-6	cells from mean of group	
15	PTR	0	±10	
34	NPL	-2	± 9	
15	LCE	+9	±25	
40	NBS	<b>-</b> 9	± 6	

TABLE LXII

The committee expressed the opinion that new experiments were necessary for the completion or modification of the specifications of the London Conference on the subject of the standard cell, and that the time was not sufficient to enable them to carry these out during their stay in Washington.

The delegates had, however, carried out at the Bureau of Standards the following work:

Each delegate prepared mercurous sulphate according to the method of preparation used in his own laboratory. And then each delegate constructed three standard cells with each of the four samples of mercurous sulphate thus obtained; that is, 12 cells in all.

The results given by these 48 cells are given in Table XV, page 115. They show that excepting several abnormal cells, the cells are in very good agreement.

During the work of the committee at Washington, members of the Bureau, under the direction of Dr. Wolff, carried out a systematic series of researches, having for their aim the comparing of the materials brought by the different delegates. The results given in the report (pp. 116 to 119) show that the different materials are equivalent in their effects on the emf of the cell, but the Technical Committee has been able to discuss neither the results of this research nor that following.

An important investigation was made on a large number of cells to throw light on the anomalies, which certain of them present, when their temperature is changed, and to study the lag exhibited by the cell in taking up the value given by the formula connecting the variation of the emf with the temperature.

### THE SILVER VOLTAMETER

The delegates have sought to determine the value of the emf of the Weston Normal Cell in international volts by joint experiments on silver voltameters connected in series, the standard cell and the international ohm being defined as has been done above.

In all the experiments with the silver voltameter, the strength of the current was maintained constant at the value of approximately 0.5 ampere, the length of time of its passage being two hours, and the weight of silver deposit being slightly greater than 4 grams.

The delegates have employed the silver nitrate and the voltameters which they brought with them. They carried out the work under experimental conditions similar to those used by them ordinarily in their respective laboratories.

In the greater part of the experiments Dr. Jaeger used a form of voltameter, employing silk and a glass cup to separate the anode from the cathode.

Mr. Smith employed the arrangement designated by him by the name of "the new form."

Prof. Rosa made use ordinarily of the porous pot of porcelain.

M. Laporte employed filter paper and the so-called Rayleigh form.

In certain experiments, certain of the delegates have exchanged materials and have used the apparatus of one another.

While the delegates carried out their experiments, members of the Bureau of Standards, under the direction of a subcommittee, made other experiments on the silver voltameter, with the end in view of studying the different electrolytes and forms of voltameter used. The results have shown that voltameters in which filter paper is used as septum lead to results which are too high. The delegates were unanimously of the opinion that the results of experiments made under these conditions should not be used for the determination of the value of the emf of the Weston Normal Cell.

The committee is of the unanimous opinion that "the mean of the results which they have obtained will not be modified by more than several parts in one hundred thousand when the specifications shall have been completed.

"The committee decides to recommend to the International Committee for Electrical Units and Standards the following value for the emf of the Weston Normal Cell:

# E = 1.0183 international volts at 20° C"

The results of all the experiments are given in the tables of Appendix D (p. 145), and in Appendix F will be found the remarks of each of the delegates.

Although the experiments on the silver voltameter have been numerous, the committee (owing to the opposition of Dr. Jaeger and of M. Laporte) "thought best not to complete the specification of the silver voltameter until new experiments have been made by the members of the committee in their respective laboratories on those points which are not considered as actually settled, and that the committee shall complete the general specifications after these experiments."

These electrolytes rendered acid or alkaline by the addition of a certain quantity of free acid or alkali have given rise to deposits different from that corresponding to a neutral electrolyte. Acidity brings about a diminution of the deposit, and alkali an augmentation; the effect of alkali is more important than that of acid.

Messrs. Jaeger and Laporte have called attention to the fact that the precision of the methods for testing the acidity or alkalinity had not been sufficiently investigated to allow of fixing the limits permissible in the electrolyte.

The electrolytes used by the four delegates were tested comparatively in voltameters of small dimensions (volume about 100 cc and the porous pot form), and in voltameters of more than

double the volume of the first (porous pot and new form). The four electrolytes give the same weight of deposit in the small voltameters; they give different results in the larger voltameters. One only of the electrolytes, that of the National Physical Laboratory, and, later, an electrolyte obtained from a nitrate purified by the labors of members of the Bureau of Standards, have given with certainty the same results in both small and large voltameters. The volume effect obtained in these experiments has not been admitted as certain by Mr. Jaeger, and the correspondence of these results with those obtained by the permanganate test for organic material has not been considered as definitely established by both Messrs. Jaeger and Laporte.

Although in a large part of the experiments the silk used as septum gave normal values for the silver deposit, there is a possibility, as some of the experiments show, that under certain conditions the weight of the silver deposit can be changed. Dr. Jaeger is of the opinion that pure silk, if sufficiently washed, can be used as septum without error.

Experiments with siphon voltameters were also carried out. They were only comparative owing to the variations of resistance which this form of voltameter introduces into the circuit. They gave deposits heavier than those of the other forms. Mr. Smith calls attention to the fact that at the National Physical Laboratory the siphon and the new form have given identical results.

