

a small third harmonic is present and has been studied by H. P. Hastings.

At the suggestion of one of us, Leeds and Northrup arranged with Vreeland to develop a smaller and less expensive instrument giving 500 and 1000 cycles, which they are now selling. After we had tested the first of these and the development of our work had shown the desirability of certain modifications, especially a wider range of frequency, Vreeland consented to the sale of an instrument giving 500, 750, 1000 and 1500 cycles, which are ample for most work on the simple measurement of the conductivities of solutions. Fig. XIV gives the oscillogram of the wave form of the small Vreeland oscillator at 130 cycles. It should be emphasized that this Vreeland was built by Leeds and Northrup to give frequencies of 500 and 1000 and that we had to add extra capacity in order to get the lower frequency. Even under these extreme conditions the wave form for this lower frequency is still very good. The wave form for 500 cycles in Fig. XV is practically a pure sine wave and gives excellent results in conductivity work.

After making the above study on the best source of alternating current for this conductivity work practically all of our measurements have been made with the Type B Vreeland oscillator. The development of the best types of bridges, telephones, inductances, capacities, cells, baths, etc., and the applicability of various types of bridge set-ups in this work will be described in the succeeding articles. Especially will it be shown that the apparent resistance changes with frequency when bright electrodes are used but that by the proper methods and calculations the true electrical conductivity can be obtained.

MADISON, Wis.

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## STUDIES IN THE MEASUREMENT OF THE ELECTRICAL CONDUCTIVITY OF SOLUTIONS AT DIFFERENT FREQUENCIES.

### VI. INVESTIGATIONS ON BRIDGE METHODS, RESISTANCES, CELLS, CAPACITIES, INDUCTANCES, PHASE RELATIONS, PRECISION OF MEASUREMENTS, AND A COMPARISON OF THE RESISTANCES OBTAINED BY THE USE OF INDUCTANCE AND CAPACITY BRIDGES.<sup>1</sup>

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During the last few years, chemists have made decided improvements in the Kohlrausch method of measuring the electrical conductivities of solutions.

<sup>1</sup> We are indebted to the Carnegie Institution of Washington for aid in this work.

A. A. Noyes<sup>1</sup> and his co-workers made great strides by using weighed solutions and fine bomb-cells, and their work probably has an accuracy of 0.10%.

Washburn<sup>2</sup> published the first fine article on a general improvement of the Kohlrausch method in which he described notable advances by the use of tuned telephones, pure resistances, better cells, a 1000 cycle current of sine wave form, better capacities for securing a minimum, and methods of grounding.

Chapman and Hibbard<sup>3</sup> have recently published an excellent bulletin in which they describe similar apparatus and especially the use of an alternating current galvanometer as a detector for the 60-cycle current obtained from a Holtzer-Cabot generator.

Hartley and Barrett<sup>4</sup> showed an apparent change of resistance with change in frequency, and Schlesinger<sup>5</sup> has described some noteworthy improvements.

The general methods here described had their origin in 1908-9 in the repeated observations that the resistance of solutions apparently changed with a change in the frequency of the current from the induction coil. As this source of error was seen to be a possible explanation of the discrepancies in the results obtained by different investigators using different frequencies and different cells it was decided to investigate as deeply as possible the frequency, resistance and capacity relations. Washburn and Chapman and Hibbard used 1000 and 60 cycles, respectively, and considered that the resistances observed are the true electrical resistances, but our work shows the necessity for measurements at different frequencies, if we are to understand clearly all the phenomena involved in the solution and at the electrodes, and to measure the true electrical conductivities. By deliberately magnifying the different sources of error we have been able to understand them and develop methods for their elimination.

In this study we have been greatly aided by Dr. H. L. Curtis of the National Bureau of Standards, and especially by Prof. Edward Bennett, of the University of Wisconsin, and by other colleagues who have made many important suggestions on the interpretation of our results and on the methods, which are well known to electrical engineers and physicists, but not to chemists in general. Most of the data here reported were worked out by Taylor in Washington with the excellent equipment kindly placed at our disposal by the Bureau of Standards.

In this research the writers have tried (1) to solve the ordinary mechan-

<sup>1</sup> Noyes, Carnegie Inst. Monograph.

<sup>2</sup> Washburn and Bell, *THIS JOURNAL*, 35, 177 (1913).

<sup>3</sup> Hibbard and Chapman, Mich. Agr. Coll., Expt. Sta., *Tech. Bull.* 23.

<sup>4</sup> Hartley and Barrett, *THIS JOURNAL*, 103, 786 (1913).

<sup>5</sup> Schlesinger, *Ibid.*, 36, 1589 (1914).

ical and electrical difficulties connected with the measurement of the conductivity of electrolytes, (2) to make a fundamental study of the *electrode phenomena* and their bearing on the resistance and capacity of a solution in a conductivity cell at different frequencies and voltages, and (3) to eliminate the importance of these electrode phenomena as far as possible so as to make the *apparent* resistance of a solution in a cell as nearly as possible only the *true electrical resistance* of the solution.

**Source of Current.**—The first requisite for securing a bridge balance when resistances, inductances, and capacities are measured, is a source of alternating current which has a pure sine wave form of any desired voltage, and of constant frequency, which frequency may be varied at will through a wide range. This is necessary to prevent unsymmetrical polarization at the electrodes and to annul the influence of harmonics on the telephone, and to enable us to study the effects of changes in voltage and frequency on the resistances of solutions in the cells. After testing the ordinary "buzzer," the Holtzer-Cabot and General Electric generators and the 60-cycle current of Madison, we have found that the Type A or B Vreeland oscillator sold by the Western Electric Company best suited our requirements for many reasons previously published. We are making measurements at 250 to 3000 cycles per second. Arrangements have now been made with Dr. Vreeland, however, for Leeds and Northrup to sell a small instrument for use at 500, 750, 1000 and 1500 cycles, which are sufficient for most work. We use calibrated tuning forks and the beat method to secure the correct frequency.

**Resistances.**—In order to make measurements with a precision or accuracy of 0.001% with alternating currents, the resistances must be so made as to be free from errors from inductance and capacity at all frequencies used. Curtis<sup>1</sup> has shown that average American and German resistances of 1000 ohms and over, including our own Chapeyron coils, may have errors greater than 0.05% arising from inductance and capacity effects, and has devised coils which are practically free from these defects. These coils have been used in our work. These have been used recently by Washburn and by Chapman and Hibbard. Washburn formerly used platinum strips on glass rods devised by physicists and we are indebted to Professor H. Pfundt for the use of one of his type of platinum film on glass plates. It seems to the writers that the great objection to platinum films on glass or quartz is the high temperature coefficient, the fragility, and the inconvenience in mounting or inclosing them.

**Telephones.**—We have used telephones made by the Western Electric Company which are very sensitive and which can be tuned to the particular frequency of the alternating current employed, in order to get the

<sup>1</sup> Curtis and Grover, *Bull. Bur. Standards*, Vol. 8, No. 3 (1911).

greatest accuracy in bridge settings. The attachment of a stethoscope to the telephone, suggested by Curtis, has been a very great aid. We have also used an alternating current galvanometer at low frequencies.

**Bridge.**—Two well-known types of the Wheatstone bridge were recommended to us by Leeds and Northrup, Curtis, and Bennett, and Mr. H. P. Hastings has begun the use of several others. We have employed throughout the work the substitution method used regularly in the Bureau of Standards and suggested to us by Dr. Curtis, and have compared it with others. The arrangement of the bridges is shown in Figs. I and II, and

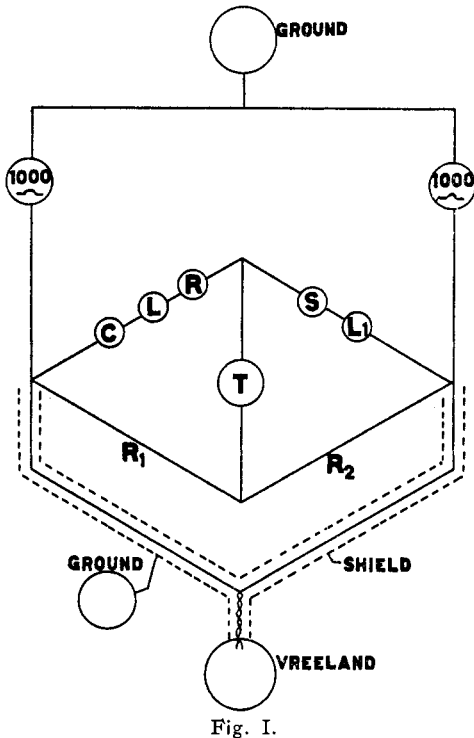


Fig. I.

the substitution method used is explained below.  $R_1$  and  $R_2$  are Curtis ratio coils of 100, 500, or 1000 ohms each,  $C$  the cell,  $T$  the telephone,  $S$  the variable resistance in the bridge,  $L$  a variable standard inductance,  $L_1$  a fixed inductance greater than the smallest value of  $L$ ,  $K$  a standard variable condenser,  $K_1$  a variable or fixed condenser with a capacity larger than the lowest value of  $K$  if the bridge cannot be balanced by  $K$ , and  $R$  a set of fine variable Curtis resistances with a range from 10,000 to 0.001 ohm. In making a reading with the bridge shown in Fig. I,  $R$  is set on zero, and, with the cell in circuit,  $S$  and  $L$  are varied until there is no sound in the telephone. The cell is then removed and the bridge again balanced by vary-

ing  $L$  and  $R$ . The reading of  $R$  is then the sum of the "apparent" resistances of the cell and of the cell leads and electrodes, whose resistances are known, and the difference between the two inductance readings gives the inductance corresponding to the cell "capacity." It is then necessary simply to regulate the temperature of  $R$  and by this method we eliminate any error due to changes in the other resistances, or in the inductances, arising from changes in room temperature. With good temperature regulation measurements on a cell can be duplicated to one part in 100,000. In making a reading with the bridge shown in Fig. II a similar procedure should be employed, *i. e.*, the bridge is first balanced with the cell and the

condensers  $K$  and  $K_1$  in circuit. Then the cell is removed and the bridge again balanced by changing  $R$  and  $K$ . The resistance and capacity of the cell are then obtained as above.

The method of grounding the bridge was developed by Curtis and Taylor and other methods and improvements will be described later by Mr. H. P. Hastings.

This bridge set-up in Fig. II, with the exception of the substitution method and the grounding, is the one devised by Kohlrausch and improved with great success first by Washburn and Bell<sup>1</sup> and later by Hibbard and Chapman. These workers, however, did not use Curtis ratio coils but employed the circular Kohlrausch slide wire bridge. It will be shown in a subsequent article that even a mechanically perfect circular Kohlrausch slide wire bridge must be used with very great caution as errors as large as 1% can arise in some bridge set-ups because of the self-induction in the circular slide wire and the capacity between the metal cover and the slide wire.

We have now devised and used extensively a special bridge containing Curtis ratio and dial coils and inclosed Curtis alternating current standards similar to the National Bureau of Standards' fixed resistances for direct currents. These are all immersed in oil at constant temperature and the resistances can be relied upon very accurately. They are furthermore calibrated by direct current against a set of four National Bureau of Standards resistances of the inclosed type. This apparatus was built for us by Leeds and Northrup and it will be described and the measurements reported in the near future in other articles.

**Capacities.**—Our condensers consist of (1) a Western Electric Company box of standard mica units from 0.001 to 1.1 microfarads and paper units up to 41.1 microfarads and (2) a Leeds and Northrup variable air condenser, giving from  $25 \times 10^{-6}$  to  $1500 \times 10^{-6}$  microfarads. We have

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<sup>1</sup> THIS JOURNAL, 35, 197 (1913) and Catalog No. 48 of Leeds and Northrup (1915).

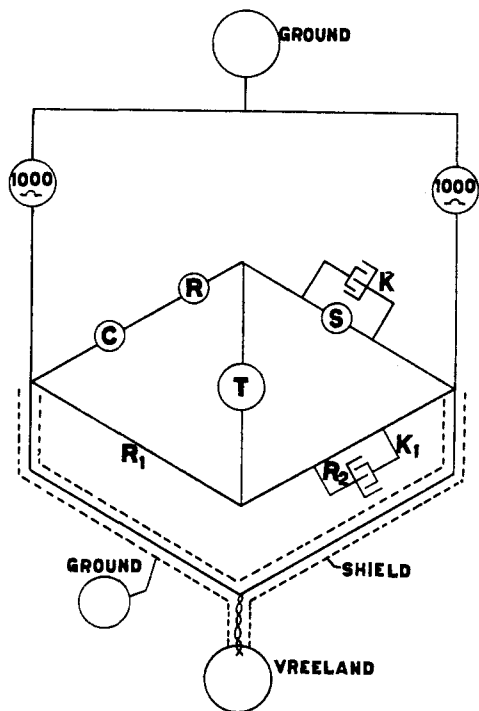


Fig. II.

also three other variable air condensers of low range. These standards have either been calibrated by the Bureau of Standards or checked by us against our standards. These measurements were, of course, made at the different frequencies used by us.

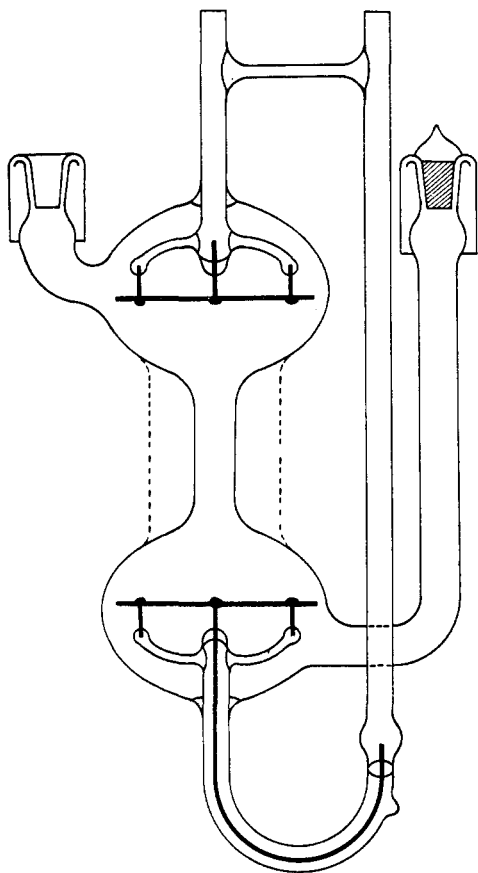


Fig. III.

**Inductances.**—Our fixed inductances are wound in a single layer on mahogany spools, as we have found that multiple layers produce changes in resistance and inductance when the frequency is changed. Stranded and braided enameled silk covered wire should be used at high frequencies to prevent errors from "skin effects." Our variable inductances are improved forms of the Ayrton and Perry types on mahogany frames worked out in coöperation with Professor Edward Bennett and are so devised as to be practically free from changes in resistance and inductance arising from changes in frequency. They are arranged with verniers and mechanical devices which allow us to obtain quickly and accurately values from  $10^{-3}$  millihenries upward. They will be

described in detail in separate articles.

**Phase Relations.**—The resistance of a solution in a conductivity cell is made up of the *true resistance* of the solution and certain phenomena which we shall call *electrode effects*. A cell behaves toward an alternating current as if it were made up of a resistance in series with a condenser with a small leak, and it offers an impedance to the harmonically varying current, changes the phase in that bridge arm, and gives an unbalance in the telephone. It is, therefore, impossible to obtain a perfectly sharp minimum in the telephone unless the capacity is accurately balanced by one of the several well-known methods, such as (1) a capacity in parallel with the resistance arm of the bridge, as recommended by Kohlrausch, (2) a capacity in series with the resistance arm of the bridge, (3) an in-

ductance in series with the cell (in R, Fig. I), or (4) an inductance in the opposite side of the bridge (in R<sub>2</sub>, Fig. I). We have used all of these methods and have compared them with others and our results will be given in a later report.

Mr. H. P. Hastings has observed the very interesting and fundamentally important phenomenon that in cells with small bright electrodes a disturbing third harmonic accompanies the low fundamental note from the Vreeland oscillator at low frequencies, and this has also been observed in oscillograph measurements by Dr. G. H. Gray. This harmonic can, of course, be balanced out by an inductance or capacity, and its frequency can be thus calculated. We have devised methods for balancing out the fundamental notes, and the harmonics simultaneously, in order to study the electrode phenomena more carefully. A Vreeland oscillator giving simultaneously two or more frequencies of any desired values is greatly to be desired,

**Cells.**—Our cells are dumb-bell types which we have developed since 1908 and are shown in Figs. III and IV. They are made by Otto Haak, 545 N. 5th Street, Philadelphia. The advantages of these cells are the following: (1) The ground glass joints are not exposed but are under the

liquid of the bath and hence prevent evaporation of the solvent and consequent changes of concentration. (2) The electrodes are supported in four places so that they cannot change position and thus change the cell constant. They can be made of Jena 16<sup>III</sup> or 297<sup>III</sup> glass or of quartz. Our criterion of excellent cells is that *whatever the solutions used the ratios of the resistances of any solution in two such cells, or of two solutions in any*

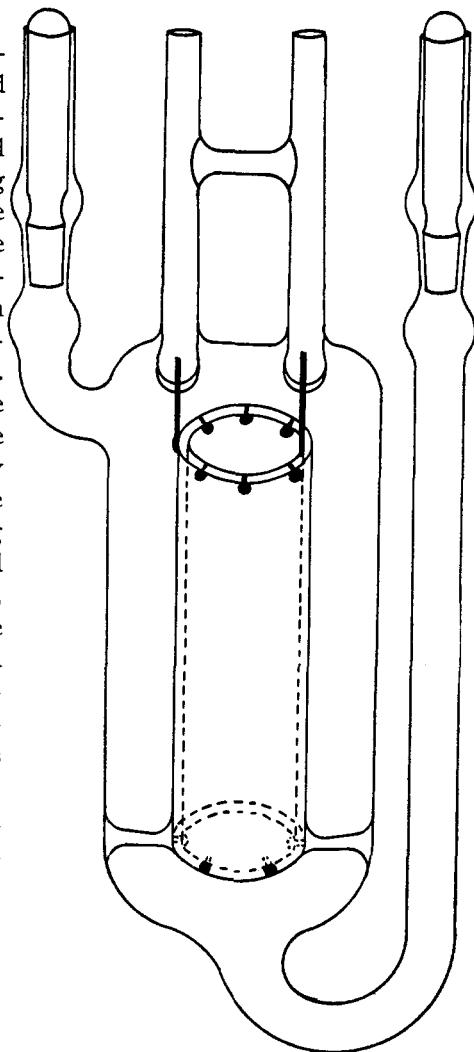


Fig. IV.

cell, must be constant to within 0.01% at infinite frequency. Only in this way can we be certain that the electrode effects have been practically eliminated and that we are measuring the *true electrical resistance* of the solution with great accuracy. This we have now succeeded in attaining.

**Solutions.**—The solutions should be made up and analyzed by weight methods in resistance glass or quartz containers and transferred by means of apparatus which will be described in a later report, *under the water* of the constant temperature bath into *clean cells* containing air in which the vapor pressure is that of the solution to be measured. In the present work the solutions were not made up with any great degree of accuracy as we were concerned first with developing accurate *methods* for making conductivity measurements and this problem could be solved as well by relative as by absolute measurements of conductivity.

**Precision of Resistance Measurements on Solutions.**—Using the apparatus described and the method outlined above it will be seen from the TABLE I.—DATA SHOWING PRECISION OF RESISTANCE READINGS ON A GIVEN SOLUTION IN A GIVEN CELL.

Cell V— $\frac{1}{2}$ -inch platinized electrodes.

0.2 N NaCl.	
Time.	Res. at 1000.
3.25.....	...
3.38.....	89.142
3.41.....	89.143
3.43.....	89.143
3.45.....	89.143
3.48.....	89.143
3.51.....	89.142
4.12.....	89.143
Next day	
9.31.....	89.143
9.35.....	89.144
Maximum difference, 0.0022%.	

Cell II—1-inch silver plated electrodes.

0.1 N NaCl.	
Time.	Res. at 1000.
3.25.....	...
3.46.....	163.573
3.49.....	163.574
3.51.....	163.573
4.05.....	163.573
4.09.....	163.573
Maximum difference, 0.0006%.	

Cell II—1-inch bright electrodes.

0.05 N NaCl.	
Time.	Res. at 1000
1.45.....	...
2.14.....	313.474
2.17.....	313.474
2.19.....	313.472
2.22.....	313.471
2.24.....	313.470
2.27.....	313.470
2.45.....	313.472
2.57.....	313.471

Maximum difference, 0.0013%.

Cell IX—2-inch sand-blasted electrodes.

0.2 N NaCl.	
Time.	Res. at 1000.
9.35.....	...
10.12.....	282.090
10.14.....	282.092
10.15.....	282.091
10.48.....	282.092
10.51.....	282.094
10.53.....	282.095
10.55.....	282.095
11.04.....	282.092
11.07.....	282.093
11.33.....	282.091
11.35.....	282.091
11.40.....	282.090
Maximum difference, 0.0018%.	



data given in Table I that readings on a given cell with a given solution can be repeated easily with an average deviation within  $\pm 0.001\%$ .

**Checks on the Resistance of Different Parts of the Same Solution in the Same Cell.**—Resistance measurements were then made on different parts of the same solution in the same cell to see how closely these measurements would check. The following table shows that the maximum variation is about  $0.01\%$ . Each measurement given is the average of a large number of readings for the same portion of the solution. Considering the fact that the electrodes in most of the older cells made in 1908 were not absolutely rigid, that the solutions were poured into the cells, etc., these values check remarkably well.

TABLE II.—CHECKS ON DIFFERENT PARTS OF THE SAME SOLUTION IN THE SAME CELL.

	Res. at 1000.	Max. dif. in per cent.
Cell I—1-inch bright electrodes, 0.05 <i>N</i> NaCl.....	197.714	0.000
	197.714	
Cell II—1-inch bright electrodes, 0.2 <i>N</i> NaCl.....	84.260	
	84.254	
	84.259	
	84.256	0.007
Cell III—1-inch platinized electrodes, 0.2 <i>N</i> NaCl.....	78.481	
	78.482	
	78.479	
	78.487	0.010

**Constancy of Resistances of Solutions in Cells Over Short and Long Time Periods.**—Dr. G. H. Gray's oscillograph measurements at 60 and 240 cycles and our conductivity data show that after two cycles the current does not cause an appreciable change in the resistance and capacity of the cell during short time periods such as ten minutes. It seemed desirable in the practical use of the conductivity method to see whether measurable changes occur in longer time intervals. Table III illustrates

TABLE III.—DATA SHOWING CONSTANCY OF RESISTANCES OF SOLUTIONS IN CELLS OVER LONG TIME PERIODS.

	Time.	Res. at 1000.	% change in R.	Time.	Res. at 600.	% change in R.
Cell I						
1" bright electrodes, 0.2 NaCl.....	4.18	53.099	0.043	4.11	53.327	0.081
Next day.....	9.36	53.122		9.45	53.370	
Cell II						
1" bright electrodes, 0.2 <i>N</i> NaCl... ..	11.46	84.187		12.19	84.444	
	4.08	84.200	0.044	4.04	84.460	0.055
Next day.....	10.00	84.224		9.53	84.490	
Cell III						
1" platinized electrodes, 0.2 <i>N</i> NaCl	10.25	78.486		11.05	78.486	
	4.15	78.486	0.001	4.22	78.486	0.003
Next day.....	10.12	78.487		10.22	78.488	
Cell V						
$\frac{1}{2}$ " platinized electrodes, 0.2 <i>N</i> NaCl	3.38	89.143		3.59	89.156	
	9.35	89.144	0.001	9.40	89.156	0.000

some of our characteristic data, each measurement given being the average of a number of readings. These data show that in cells with platinized electrodes the resistances of the solutions do not change appreciably on standing in the cells for 24 hours. On the other hand in cells with bright platinum electrodes there is an increase in the resistance and the change seems to be larger when the resistance is measured at 600 cycles than when measured at 1000 cycles.

**A Comparison of the Resistances Obtained at 600 and 1000 Cycles by the Use of Inductance and Capacity to Balance the Capacity of the Cell.**—As was mentioned above, in order to obtain a perfectly sharp minimum in the telephone, the capacity in the cell must be accurately balanced by some method such as by another capacity in parallel with the resistance arm of the bridge, or by an inductance in series with the cell. Some measurements were made on resistances of solutions in different cells at 600 and 1000 cycles by using both methods of balance to see how closely the two would check. The data are shown in Table IV.

In order to use the substitution method with a condenser in parallel with the resistance arm,  $R_4$ , as in Fig. II, a balance was first made with the cell inserted, the cell was then removed and the substitution resistance,  $R_3$ , balanced against the resistances of the bridge. When this method is used a correction must be made on the substitution resistance according to the following equation worked out for us by Professor Edward Bennett:  $R_3/R_4 = R_1/R_2 - K/C$ , in which  $R_1$  and  $R_2$  are the values of the ratio coils,  $R_3$  the value of the substitution resistance,  $K$  the capacity in parallel with the resistance  $R_4$  which is necessary to balance the capacity of the cell, and  $C$  is the capacity of the cell calculated from the inductance, or by other methods which will be described later. When this correction is made for the three cases given in Table IV the values for the apparent resistances obtained by the use of an inductance and those obtained by the use of a condenser check extremely well. The largest variation is 0.004%, and in this case the data are not very satisfactory, but all of the remaining values check to within about 0.001%, which is not more than the experimental error.

The first part of the table gives the data for 0.2 *N* NaCl in Cell IX with roughened electrodes 2 inches in diameter. The readings were taken in the following order: First, Group 1, then Groups 2, 3, 4, etc. At both 600 and 1000 cycles the uncorrected resistance measured with the condenser is only about 0.002% higher than the one measured with the inductance, and the corrected resistances do not vary more than 0.001%. The second part of the table gives duplicate measurements, (a) and (b), of the data for 0.05 *N* NaCl in Cell I with 1-inch bright electrodes. Measurements were made in this case only at 1000 cycles. Here the uncorrected resistance measured with the condenser is about 0.013% higher than that measured

with the inductance, but the corrected resistances differ only 0.001%. The third part of the table gives the data on 0.025 *N* NaCl in Cell I at 600 and 1000 cycles. In this case there is practically no difference in the uncorrected readings with the condenser and inductance at 1000 but at 600 cycles the uncorrected resistance measured with the condenser is about 0.01% higher than that measured with the inductance. The corrected resistances, however, differ only 0.002% at 600 and 0.004% at 1000 cycles.

It will be seen from the data with both the condenser and the inductance that the apparent resistance decreases when the frequency is raised from 600 to 1000 cycles, which is in conformity with all of our other results. The changes in resistance obtained by using the 2-inch roughened electrodes with inductances or condensers were practically only 0.025%, whether corrected or not, because of the large capacity of these large electrodes. The 1-inch bright electrodes, with much smaller surfaces and capacities, however, showed a change of resistance of 0.0925% when the inductance method was used and 0.095% when we employed the corrected data from the condenser method. If the data are not corrected, however, this difference of 0.0025% experimental error becomes four times that large, namely, 0.010%. All of the above facts, then, show that both the inductance and the condenser methods give practically the same results when the proper corrections are made.

TABLE IV.—A COMPARISON OF THE RESISTANCES OBTAINED BY THE USE OF INDUCTANCE AND OF CAPACITY TO BALANCE THE CAPACITY OF THE CELL.  
Cell IX—0.2 *N* NaCl.

	Inductance res. in ohms.		Condenser res. in ohms.	
	600.	1000.	600.	1000.
	282.159	282.088	282.166	282.098
(1)	282.161	282.090	(2) 282.169	282.097
	282.163	282.092	282.168	
	282.160	282.091		
	282.162	282.092	282.166	282.096
	282.163	282.094	282.167	282.095
(3)		282.095	(4)	282.096
		282.095		
		282.092		
		282.093		
	282.162	282.091		282.096
(5)	282.163	282.091	(6)	282.097
Aver. before correction.....	282.162	282.092	282.167	282.096
Aver. after correction.....	282.162	282.092	282.162	282.094

Dif. in uncor. res by the two methods at both 600 and 1000, 0.002%.

Dif. in cor. res. by the two methods at 600, 0.000%.

Dif. in cor. by the two methods at 1000, 0.0007%.

Cell I.—0.05 N NaCl.

Inductance res. in ohms 1000.		Condenser res. in ohms 1000		
(a).	(b).	(a).	(b).	
197.715				
197.715				
197.717		197.740		
197.712		197.740		
197.713	197.711	197.740		
197.713	197.714	197.740	197.740	
197.713	197.714	197.740	197.740	
197.713	197.714	197.740	197.740	
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Aver. before correction.....	197.714	197.713	197.740	197.740
Aver. after correction.....	197.714	197.713	197.711	197.711

Dif. in uncor. res. by the two methods, 0.013%.

Dif. in cor. res. by the two methods, 0.001%.

Cell I.—0.025 N NaCl.

Inductance res. in ohms.		Condenser res. in ohms.		
600.	1000.	600.	1000.	
	381.009			
	381.010			
	381.012		381.000	
381.361	381.007	381.391	381.009	
381.361	381.000	381.395	381.007	
381.361	381.000	381.398	381.007	
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Aver. before correction.....	381.361	381.006	381.397	381.006
Aver. after correction.....	381.361	381.006	381.352	380.989

Dif. in uncor. res. by the two methods at 600, 0.010%.

Dif. in cor. res. by the two methods at 600, 0.002%.

Dif. in uncor. res. by the two methods at 1000, 0.000%.

Dif. in cor. res. by the two methods at 1000, 0.004%.

### Conclusions.

(1) We have found that the Vreeland oscillator is the best and most convenient source of alternating current tried for conductivity work because (1) it is practically noiseless and can be started and stopped conveniently; (2) it gives practically a pure sine wave form; (3) it gives a constant frequency independent of the variation in the actuating direct current; and (4) this frequency can be changed easily to anything desired in our work.

(2) Curtis coils on porcelain spools should be used for all resistances above 10 ohms to prevent errors due to inductance and capacity effects.

(3) For greatest accuracy in balancing the bridge one should use a telephone which can be tuned to any desired frequency, and can be attached to a stethoscope, as suggested by Curtis.

(4) A substitution method suggested by Curtis for measuring resistances is advantageous as, by simply regulating the temperature of R in Fig. I, it prevents errors due to any changes in the resistances of the bridge

coils, or in the inductance, caused by variations in temperature, and allows the experimenter to read the resistances directly instead of having to make involved calculations.

(5) The bath, if made of metal, and also the bridge, should be grounded to prevent errors from capacity effects.

(6) In order to prevent changes in the resistance of the solutions during measurements the cells should be made (1) with the ground glass joints below the surface of the liquid of the bath to prevent evaporation of the solvent in the cell, (2) with the electrodes well supported by several glass arms and platinum posts to prevent changes in position of the electrodes, and (3) with the leads to the electrodes sealed off at the end in the glass tubes to allow the experimenter to keep these ends clean and to prevent changes in the resistance of the leads.

(7) Solutions should be made up and analyzed by weight methods in clean, resistance glass or quartz containers and transferred *under* the water of the bath into clean cells.

(8) Resistance measurements on a given solution in a given cell can be duplicated to within 0.001%.

(9) Resistance measurements on different parts of the same solution in the same cell, even when no special precautions were taken in filling the cell, checked to within 0.01%.

(10) The resistances of aqueous solutions in cells with platinized electrodes did not change appreciably on standing in the cells 24 hours. Cells with bright electrodes showed changes in resistance from 0.05 to 0.14% in 24 hours.

(11) A comparison of the resistances obtained by the use of (1) an inductance and (2) a condenser to balance the capacity of a cell shows that the values of the resistances obtained by the two methods are practically the same, the variation being only  $\approx 0.001\%$ .

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## STUDIES IN THE MEASUREMENT OF THE ELECTRICAL CONDUCTIVITY OF SOLUTIONS AT DIFFERENT FREQUENCIES.

### VII. INVESTIGATIONS ON THE TRUE AND APPARENT RESISTANCES, VOLTAGE, APPARENT CAPACITY, SIZE AND CHARACTER OF ELECTRODES, RATIO OF INDUCTANCE CHANGES TO RESISTANCE CHANGES, AND THE RELATION OF INDUCTION AND CAPACITY TO FREQUENCY.<sup>1</sup>

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In the preceding papers we have shown that the resistances of solutions of electrolytes can be measured with a precision of 0.001% and an

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