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 ±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.[1]

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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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[1] We are indebted to the Carnegie Institution of Washington for aid in this work.

accuracy of 0.01% by the use of (1) Curtis resistances free from capacity and inductance; (2) a Vreeland oscillator giving a pure sine wave of uniform frequency which can be varied widely; (3) proper grounding and shielding of the electrical apparatus and the bath; (4) a telephone which can be tuned to any desired frequency; (5) cells whose electrodes are fixed and whose ground joints are immersed to prevent evaporation; and (6) the use of different bridge methods which give the same true electrical conductivities of the solutions.

In the present article[1] we will discuss chiefly (1) the relation of the resistances of solutions of electrolytes to the voltage, the frequency of the alternating current, and the area of the electrode surface; (2) the relation between the area of the electrode surface and the magnitude of the apparent "capacity" of the cell; (3) the relation between the electrolytes, electrode material, size and character of electrode surface, and change of inductance and resistance with change in frequency; (4) the measurement of the true electrical conductivity of solutions; (5) the explanation of the apparent "capacity" of the cell; (6) the relation between the inductances necessary to valence the capacity of the cell at different frequencies; and (7) the ratio of the change in resistance to the change in inductance produced by a change in frequency.

Effect of Change of Voltage on the Apparent Resistance of Solutions of Electrolytes.

The first point to be investigated was the influence of change in voltage on the resistances of solutions in different cells. The bridge was first tested to see whether the resistances changed with change in voltage. It was found that a given resistance in the bridge did not vary as much as 0.001%, with change in voltage from one-eighth to 10 volts. Experiments along this line were carried out with the bridge coils alone, and also with inductances in two adjacent arms of the bridge.

We then took up the study of various solutions and in Table I are given the resistances of different solutions in several cells at a number of voltages. Each measurement given is the average of a number of readings. The range of voltage was from $^1/_4$ to 2 v., at which the polarization voltage 1.23 is not reached at the electrodes. Above 4 volts there was in most cases such an appreciable heating effect that it was difficult to make accurate measurements. From an inspection of the data in Table I it is seen that the variation in the resistance is not more than ±0.001%. This is true only when the cells, solutions and containers are kept scrupulously clean, as the slightest trace of grease or dirt causes a measurable

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[1] Part of this work was done by Dr. Taylor at the Bureau of Standards, and we are indebted to Dr. H. L. Curtis for many valuable suggestions. We desire to express our thanks especially to Professor Edward Bennett of the the University of Wisconsin for the coöperation which will appear in joint articles later.

variation in the resistance with change in voltage. Since with unclean cells we have found variations in resistance as large as 0.08% when the voltage is changed from $^1/_4$ to 2 v. constancy of resistance and inductance with change in voltage can be used as a very reliable test for cleanliness of cells and containers for the solutions.

TABLE I.—VALUES FOR THE RESISTANCES AND INDUCTANCES OF DIFFERENT SOLUTIONS IN VARIOUS CELLS, MEASURED AT DIFFERENT VOLTAGES.

		Res. $^1/_4$ v.	Ind. in μ h.	Res. $^1/_2$ v.	Ind. in μ h.	Res. 1 v.	Ind. in μ h.	Res. 2 v.	Ind. in μ h.
Cell I,	0.2 *N* NaCl..	53.099	280	53.099	280	53.098	280	53.099	280
	0.1 *N* NaCl..			101.108	315	101.109	315		
	0.05 *N* NaCl..			195.303	350	195.302	350		
	0.1 *N* KCl...	85.870	435	85.869	435	85.871	435		
Cell III,	0.2 *N* NaCl..	78.482	15	78.483	15	78.482	15	78.481	15
	0.2 *N* NaCl..	78.491	16	78.492	16	78.491	16		
	0.2 *N* NaCl..	78.481	13	78.480	13	78.479	13		
	0.1 *N* NaCl..			149.923	7	149.921	7		
Cell II,	0.2 *N* NaCl..	84.187	310	84.187	310	84.187	310		
	0.2 *N* NaCl..			84.260	380	84.259	380		
Cell V,	0.2 *N* NaCl..	89.143	40	89.143	40	89.143	40	89.143	40

These data also show that there is no change in the inductance necessary to balance the cell capacity and, therefore, no change in the capacity of the cell with this change in voltage. This would most probably not be true if we did not have a perfectly reversible system, for otherwise more ions would be discharged at one electrode than at the other during a given complete oscillation, and we would, therefore, expect the inductance to change. But even in perfectly reversible systems the constancy of resistance and of capacity, or inductance, with change in voltage below the polarization voltage 1.23 is one of the most important factors which must be considered in interpreting the "electrode phenomena." With a higher voltage at each pulse there is a greater number of electrons discharged, a greater change of concentration at the electrodes, the deposition of more gas ions on the electrodes, and a greater reverse contact potential, and Dr. G. H. Gray has now been able to show by oscillograph measurements that the resistance and capacity do not change with varying electrode potentials below the polarization voltage 1.23, but do change continuously above this point. Experiments to cover all phases of this problem are in progress.

Effect of Change of Frequency on the Apparent Resistance of Solutions of Electrolytes.

A study of the effect of change of frequency on the apparent resistance of electrolytes was next taken up. Acree and Robertson had noticed in their work that a change in the buzzer note caused a change in the apparent resistances of solutions in cells with bright electrodes. This point has doubtless been observed by many others and has recently been confirmed in conversations with Professor Mathews of the Department of Physical Chemistry in the University of Wisconsin, Dr. E. P. Wightman, and others. This naturally suggested the study of this phase of the problem, which, as far as we know, had never been investigated before 1909. and which is the most important phase of conductivity work.

We have studied solutions of different kinds and concentrations of electrolytes in cells differing in construction, size, and character of electrodes, etc. The frequencies used have been chiefly 600 cycles and 1000 cycles, although 60, 500, 2000 and 3000 were used in a few cases, and Mr. H. P. Hastings has now employed 60, 250, 500, 750, 1000, 1500, 2000 and 3000. In Table

TABLE II.

	Res. 1000 cycles.	Res. 600 cycles.	Dif. in res. at 1000 cycles and 600 cycles in Per cent.
Cell II, 1″ bright electrodes.			
0.2 *N* NaCl	84.256	84.541	0.337
0.1 *N* NaCl	160.424	160.729	0.190
0.03 *N* HCl	149.036	149.378	0.229
0.1 *N* KCl	146.003	146.360	0.244
0.05 *N* NaCl	310.202	310.544	0.110
Cell II, 1″ bright electrodes, silver plated.			
0.1 *N* NaCl	163.573	163.658	0.052
0.1 *N* $AgNO_3$	162.723	162.757	0.021
Cell VI, 1″ bright electrodes.			
0.2 *N* NaCl	11.492	11.803	2.635
0.1 *N* NaCl	21.540	21.939	1.819
0.05 *N* NaCl	41.052	41.476	1.022
0.025 *N* NaCl	79.391	79.962	0.714
Cell IV, 1/2″ bright electrodes.			
0.2 *N* NaCl	146.930	148.720	1.203
0.1 *N* NaCl	277.703	279.785	0.744
0.05 *N* NaCl	534.40	536.30	0.355
0.1 *N* KCl	241.24	244.17	1.200
Cell XII, 2″ cylindrical electrodes.			
0.005 NaCl	170.160	170.265	0.062
0.001 *N* KI	81.623	81.685	0.076
Cell III, 1″ platinized electrodes.			
0.2 *N* NaCl	78.490	78.490	0.000
0.1 *N* NaCl	149.922	149.922	0.000
0.05 *N* NaCl	290.269	290.269	0.000
0.2 *N* $CuSO_4$	155.884	155.882	0.001
0.1 *N* KCl	131.093	131.094	0.001
Cell V, 1/2″ platinized electrodes.			
0.2 *N* NaCl	89.143	89.156	0.015
0.1 *N* NaCl	170.273	170.285	0.007
0.05 *N* NaCl	329.769	329.770	0.000

Cell IV, 1/2″ bright electrodes.

Frequency	250	500	750	1000	1500	2000	3000
Res.	292.32	287.13	285.24	284.30	283.28	282.74	282.16
Ind. in Mili. hen.	21.79	6.19	2.95	1.90	0.98	0.64	0.21

II is given a summary of the values for the resistances of many different solutions in the same cells at 600 and 1000 cycles, and the difference between these two values in per cent. Each resistance given is the average of a number of readings. At the end of the table we have given the resistance and inductance measurements on 0.1 *N* NaCl in Cell IV at frequencies varying from 250 to 3000 cycles. These last measurements were made by Mr. H. P. Hastings.

From an inspection of these data it is seen that there is only a very small change in resistance with change in frequency from 600 cycles to 1000 cycles in the cells with *platinized* electrodes. With these cells it is also possible to get a balance with an accuracy of ±0.01% without the use of either an inductance or condenser.

In the case of the cells with bright platinum electrodes, which must be used in some cases to prevent the decompositions caused by spongy platinum, there is a decrease in resistance with increase in frequency. This fact is shown particularly well by Mr. Hasting's data at the end of Table II. In this case the change in resistance with change in frequency from 250 to 3000 cycles is about 3.2%.

It is evident from the data that as the concentration of any given solution is decreased, and consequently the resistance is increased, in a given cell with bright electrodes, the change in resistance with change in frequency decreases. It, therefore, follows that the resistance should be made as high as possible and the voltage raised to get a good minimum, since the change in voltage used causes no change in the inductance or resistance. To accomplish this end, the solutions used in a given cell should be as dilute as possible and the electrodes should be at least 1 inch in diameter and 2 inches is preferable. If the resistance is above 10,000 ohms the errors will generally be less than 0.01% when the resistance at 1000 cycles is assumed to be the true resistance. In order to measure concentrated solutions, cells with constructions between the electrodes[1] should be used in order to make the resistance high.

It was also found that as the size of the electrode surface is increased the change in resistance with change in frequency decreases. This is best seen from Table III below, in which each measurement given is the average of a number of readings. We have selected cells and solutions giving as nearly as possible the same resistance so that the values may be comparable.

Table III also shows that as the surface of the electrodes is increased, the inductance necessary to obtain a balance decreases and hence the apparent "capacity" of the cell, acting as a condenser, increases. It is also seen that the higher the apparent capacity the lower the inductance

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[1] Ref. to preceding article.

TABLE III.—MEASUREMENTS OF RESISTANCES AND INDUCTANCES ON SOLUTIONS HAVING ABOUT THE SAME RESISTANCES IN CELLS VARYING IN AREA OF ELECTRODE SURFACE.

	Res. at 1000 cycles.	Ind. in μh at 1000 cycles.	Res. at 600 cycles.	Ind. in μh at 600 cycles.	Diff. in res. at 600 cycles and 1000 cycles in per cent.
Cell IV, $^1/_2$″ bright electrodes, 0.1 N NaCl...	277.703	2229	279.785	5849	0.744
Cell II, 1″ bright electrodes, 0.05 N NaCl....	310.202	425	310.544	1295	0.110
Cell X, 2″ bright electrodes, 2 N NaCl.......	421.200	134	421.489	326	0.068
Cell IX, 2″ roughened electrodes, 0.2 N NaCl	282.092	115	282.162	310	0.025
Cell V, $^1/_2$″ platinized electrodes, 0.05 N NaCl	329.769	25	329.770	85	0.000
Cell III, 1″ platinized electrodes, 0.05 N NaCl	290.269	0	290.2697	0	0.000

and hence the smaller the change in resistance with change in frequency. It is, therefore, evident that the electrical "capacity" of the cell should be made as large as possible. This may be done by increasing the surface area of the electrodes. It follows naturally that platinizing the electrodes best accomplishes this end. Spongy platinum may also increase the rapidity of the reversible ionization of molecular gas. We have found that solutions of different salts having about the same resistance in the same cell with platinum electrodes give approximately the same change in resistance with change in frequency from 600 cycles to 1000 cycles. This is shown in Table IV, in which each measurement given is the average of a number of readings.

TABLE IV.—RESISTANCE MEASUREMENTS ON SOLUTIONS OF DIFFERENT ELECTROLYTES HAVING APPROXIMATELY THE SAME RESISTANCES IN THE SAME CELLS.

	Res. at 1000 cycles.	Res. at 600 cycles.	Dif. in res. in per cent.
Cell II, 0.1 N NaCl....	164.024	164.404	0.23
0.03 N HCl....	149.036	149.378	0.23
0.1 N KCl.....	146.003	146.360	0.24
Cell I, 0.2 N NaCl....	53.103	53.329	0.42
0.1 N HCl.....	58.270	58.531	0.45

While this is true for platinum electrodes it is also apparent that there is a specific relation between the electrolytes, the electrode material, the character of the electrode surface, and the change of capacity and resistance with change in frequency. The above fact is shown in such data as the following in Table V. For this work the electrodes of one cell were plated electrolytically with silver. The oscillograph will also be used in these cases in the study of valve action and passivity.

TABLE V.—DATA SHOWING RELATION BETWEEN ELECTROLYTES, ELECTRODE MATERIAL, CHARACTER OF ELECTRODE SURFACE, AND CHANGE OF CAPACITY AND RESISTANCE WITH CHANGE IN FREQUENCY.

Character of electrode.	Solution.	Ind. in μh.	Change in res. with change in frequency from 600 cycles to 1000 cycles.
1″ bright platinum.......	0.1 N $AgNO_3$	155	0.12%
1″ rough, silver plated...	0.1 N $AgNO_3$	25	0.012%
1″ rough, silver plated...	0.1 N NaCl	95	0.052%

It is seen also that we have here the same relation between the inductance and the change in resistance with change in frequency as was noted above; that is, the lower the inductance and, therefore, the higher the capacity of the cell, the smaller the change in resistance with change in frequency.

The Measurement of the True Electrical Conductivity of Solutions.—In order to make accurate conductivity measurements, the cells and methods must be so perfected that the ratio of the resistances for any given solution in two cells, or of two solutions in any cell, must be constant to within 0.01%. This will not be the case unless we can eliminate electrode effects. We, therefore, compared two cells with platinized electrodes, in both of which the electrode effects have been shown to be zero or very small. Cell III has electrodes 1 inch in diameter and Cell V electrodes one-half inch in diameter. 0.2 N, 0.1 N and 0.05 N solutions of NaCl were measured in both cells and the ratios of the resistances calculated. The ratios are given in Table VI below, in which each measurement given is the average of a number of readings.

TABLE VI.—RATIOS OF THE RESISTANCES OF 0.2N, 0.1N AND 0.5N NaCl MEASURED AT 1000 FREQUENCY IN TWO CELLS WITH PLATINIZED ELECTRODES.

	Res. of 0.2 N NaCl.	Ratio of res.	Res. of 0.1 N NaCl.	Ratio of res.	Res. of 0.05 N NaCl.	Ratio of res.
Cell III.......	78.482		149.922		290.269	
Cell V........	89.156	1.1360	170.285	1.1358	329.770	1.1361

The deviation in the ratio of resistances is only ±0.013%, which is not much more than the experimental errors. We can, therefore, conclude that one inch *platinized* electrodes give nearly the true electrical resistance of these solutions when the resistance is above 100 ohms.

As it was found that the change in resistance with change in frequency of any solution in a cell with *bright* platinum electrodes becomes smaller and smaller as the frequency increases, we attempted to eliminate the "electrode effects," or polarization, and thus obtain the *true electrical resistance* of the solution, by extrapolating the resistances to infinite frequency. In order to do this measurements were made at three different frequencies, 600, 1000 and 2000 cycles, with two cells, both of which had electrodes 1 inch in diameter. The electrodes in Cell II were bright and in Cell III were platinized. 0.1 N and 0.05 N solutions of NaCl were used in each cell. We then plotted the results as curves[1] by using the resistances at different frequencies as ordinates and the reciprocal of the frequencies as abscissas. The points where these curves cut the X axis give approximately the values for the resistances at infinite frequency. The data used in plotting the curves are given in Table VII.

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[1] The first calculations were made by Taylor and Curtis in *Physical Review*, **6**, 61, following the suggestion by one of us.

TABLE VII.—RATIOS OF THE RESISTANCES OF 0.1 *N* AND 0.05 *N* NaCl MEASURED AT 60 CYCLES, 600 CYCLES, 1000 CYCLES, AND 2000 CYCLES IN TWO CELLS, ONE OF WHICH HAS BRIGHT AND THE OTHER PLATINIZED ELECTRODES 1 INCH IN DIAMETER, AND THE EXTRAPOLATION OF THESE RESISTANCES TO INFINITE FREQUENCY.

	Res. at 60 cycles.	Ratio of res. at 60 cycles.	Res. at 600 cycles.	Ratio of res. at 600 cycles.	Res. at 1000 cycles.	Ratio of res. at 1000 cycles.	Res. at 2000 cycles.	Ratio of res. at 2000 cycles.	Res. at ∞ cycle.	Ratio of res. at ∞ cycle.
Cell III, 0.1 *N* NaCl.....	166.3[1]		153.145		153.145		153.145		153.145	
0.05*N* NaCl.....	294.0[1]	1.7679	293.092	1.91382	293.092	1.91382	293.092	1.91382	293.092	1.91382
Cell II, 0.1 *N* NaCl.....	183.6[1]		164.149		163.844		163.580		163.365	
0.05*N* NaCl.....	319.3[1]	1.7396	313.491	1.90979	313.158	1.91132	312.895	1.91279	312.665	1.91390
Difference in ratios in %..		1.60		0.21		0.13		0.05		0.004

[1] These solutions are different from those used in the remaining measurements and as neither set of solutions was made up at all accurately the resistance measurements for the two sets do not check; nevertheless, these solutions serve well for purposes of comparison of the difference between the ratios for bright and platinized electrodes.

TABLE VIII.—DATA SHOWING R_{∞} CALCULATED BY MEANS OF THE EQUATION $R_{\infty} = R_f - KL_f f$ AND THE DIFFERENCE BETWEEN THIS VALUE AND THAT OF R_{∞} OBTAINED BY EXTRAPOLATING THE RESISTANCE TO INFINITE FREQUENCY.

	R_{∞} found by extrapolation.	Res. at 500.	Ind. at 500 in mh.	R'_{∞} calc.	% dif. in R_{∞} and R'_{∞}.	Res. at 1000.	Ind. at 1000 in mh.	R'_{∞} calc.	% dif. in R_{∞} and R'_{∞}.
Cell 1/2″ bright Pt elec., 0.2*N* NaCl	147.45	150.98	3.76	147.56	+0.07	149.20	0.99	147.30	−0.10
Cell 1″ bright Pt elec., 0.1*N* NaCl	164.30	165.42	1.09	164.42	+0.07	164.90	0.28	164.39	+0.05
Cell 2″ etched Pt elec., 0.1*N* NaCl	455.42	455.74	0.38	455.40	−0.004	455.61	0.13	455.37	−0.01
Cell 1″ etched gold elec., 0.2*N* NaCl	101.58	102.39	0.84	101.62	+0.04	102.02	0.22	101.62	+0.04

It is seen that the ratios of the resistances of these solutions in the two cells varied 1.62% at 60 cycles, 0.21% at 600, 0.13% at 1000 and 0.05% at 2000. As the resistances in cells with platinized electrodes do not change with change in frequency from 600 to 2000 cycles the resistance at infinite frequency would in all probability be the same as at the lower frequencies. By comparing the ratios for the two cells at infinite frequency the difference is only 0.004%, which is not more than the errors involved in the experiments and the extrapolation. We must, therefore, conclude that cells with bright platinum electrodes give approximately the true electrical conductivity of solutions only at high frequencies approaching infinity.

In order to eliminate the necessity of making resistance measurements at several different frequencies and extrapolating the resistance to infinite frequency to obtain the true electrical resistance of solutions of electrolytes, we have been able to derive an equation by which the resistance at infinite frequency can be calculated approximately from the resistance and inductance measurements at any given frequency. Professor Bennett has developed the full equations for expressing the changes in the apparent resistance and capacity of a system behaving like a cell, namely, a resistance in series with a "leaky" condenser. In his equations the value of n in the function (f^n) varies with frequency and our value (f^1) seems to hold approximately for our frequencies from 250 to 3000. By using the equation $(R_f - R_\infty)/L_f f = K$, when R_f and L_f are the resistance and inductance (millihenries) measurements, respectively, at any given frequency, f, R_∞ the resistance at infinite frequency, and K a constant, we have calculated the value of K and found it to be about 0.00182. In order to obtain this constant we have used several different solutions in various cells. Cells with bright and etched platinum, and etched gold and silver electrodes were used, as with these we obtain the largest values for L_f and $R_f - R_\infty$ and thus minimize the errors.

By using this value for K and substituting the values for R_f, L_f, and f at 250, 500, 750, 1000, 1500 and 2000 cycles, in the equation $R_\infty = R_f - KL_f f$ we then calculated the resistance at infinite frequency, R_∞, for several different solutions in different cells, many of which were not used in obtaining the constant K. A few of the data for frequencies of 500 and 1000 are given in Table VIII in this article. The values for R'_∞ calculated by using the equation differ by only 0.01 to 0.10%, from those for R_∞ obtained by extrapolation even though R_f differs from R_∞ as much as 2.4% in some cases. The average of the values for R'_∞ by using ALL of the above frequencies for any given cell and solution varied only from ± 0.01 to ± 0.025% from those obtained for R_∞ by extrapolating the resistance to infinite frequency and will be reported in detail in another article on the development of these equations. This gives us a method for determining approximately the true electrical resistance of the solution by measuring the "apparent" resistance and the inductance (or capacity) at any one frequency. The apparent resistance at 1000 cycles will be within 0.01% of the true resistance if the solution used in the given cell is so dilute that the inductance in henries is less than 0.5×10^{-4} times the resistance. It is thus a simple matter to tell approximately how dilute the solution must be in a given cell to give the true resistance within 0.01% at 1000 cycles.

Another way to get the true resistance within 0.01% at 1000 (1500) cycles is to make use of the fact discussed above that the difference between the apparent resistances at 500 and 1000 cycles, or at 750 and 1500 cycles, is exactly the difference between the true resistance and the apparent resistance at 1000 (1500) cycles. For a given cell, therefore, we measure once for all what resistance is needed to make $R_{500} - R_{1000}$ or $R_{750} - R_{1500}$ less than 0.01% of R_{1000} or R_{1500} and always employ solutions giving about that resistance or more. This procedure avoids the use of standard inductances or capacities.

The change in resistance with change in frequency shown above will make it clear why different careful workers have found different values for the molecular conductivity and ionization of the same carefully prepared solution of the same salt, as some measurements were made at 60 cycles, others at 1000 cycles, etc. In calculating the ionization the equation $\alpha = \mu_v/\mu_\infty$ is used. In obtaining μ_v, cells with small electrodes are ordinarily used and often the resistances are comparatively small. It has been shown above that the error in such cases may be from 3 to 4%. On the other hand, in obtaining μ_∞ cells with large electrodes placed close together are ordinarily used and the resistances are usually large. In such cases the error will be small, such as from 0.05 to 0.1%. It is thus seen that large errors may occur in μ_v and hence in α, and that the extent of this error will depend on the resistance and on the frequency used in making the measurement. In all cases α, μ_v and μ_∞ should be extrapolated to infinite frequency to obtain correct values.

The Effect on the Capacity of Deposition of Gas on the Electrodes.—When a current passes in one direction in an aqueous solution of a salt, for instance, a metal or hydrogen is deposited at one electrode and an anion or oxygen at the other. These gases can either remain on the plates, thus decreasing their surface and increasing the resistance and inductance, or dissolve in the water, or become ions on the reverse pulse of the current. A study of these points is being made by Mr. H. P. Hastings by saturating the electrodes and the liquid around the electrodes with H_2, O_2, etc., by pumping out the solution before and during electrolysis and by adding nonelectrolytes (and electrolytes) to combine with the gases. Experiments which have been carried out up to this time apparently show that the changes in resistance and inductance with change in frequency cannot be accounted for by the deposition of neutral gases on the electrodes, but are probably due to a concentration of the ions of the electrolyte and solvent at and on the electrode and hence to an attendant contact potential.

That the changes are not due to gas deposited on the electrodes is shown by the data in Table IX. These measurements were made at 60 cycles because we would expect the greatest changes in capacity to occur at low frequencies. We shall, however, investigate this subject at higher frequencies of 1000, 1500, etc., where settings can be made with much higher accuracy.

TABLE IX.—DATA SHOWING EFFECT ON THE CAPACITY OF DEPOSITION OF GAS ON THE ELECTRODES.

Cell V, $^1/_2''$ platinized electrodes.

Solution.	Res. in ohms.	Ind. in μ *h*.
0.1 *N* NaCl, before passing H through cell	147.98	5.9
H passed through cell 2 min.	147.98	5.9
H passed through cell 2 min.	147.93	5.5
0.05*N* NaCl	306.4	6.2
H passed through cell 2 min.	306.5	6.2
H passed through cell 10 min.	306.5	5.9
H passed through cell 20 min.	306.5	6.2
H passed through cell and solution 30 min.	306.0	5.9

If the electrode phenomena are not due to deposited neutral gas it seems likely that they arise from a double layer formed by the deposition of the ions of the solvent and solute on the electrode and by the change in concentration of the electrolyte at the electrode. If this is the case we should expect these changes to be so closely connected with the electrical factors that very definite relations should be found (1) between the inductances and the frequencies, and (2) between the change in resistance and the corresponding change in inductance produced by changes in frequency. That these relationships are very definite is shown in the next two sections.

Relation between the Inductances Necessary to Balance the Capacity of the Cell at 600 and 1000.—By a study of both water and alcoholic solutions in nine different cells it was found that the inductance necessary to balance the capacity of the cell is much larger at 600 than at 1000 cycles and that the inductance is nearly inversely proportional to the square of the frequency. This is shown by the data given in Table X. The average of fifty values for the calculated ratio is 2.66 while the value for the ratio of the square of the frequencies is 2.77. As this relation holds true for a "leaky" condenser the cell seems to act as a simple condenser with a leak.

Ratio of Change in Resistance to Change in Inductance Produced by a Change in Frequency.—All of the data given above show that as

TABLE X.—DATA GIVING THE RATIO OF INDUCTANCES NECESSARY TO BALANCE THE CAPACITY OF THE CELL.

		Ind. in μ h.		
		600.	1000.	Ratio.
Cell I, 1" bright electrodes,	0.2 N NaCl	715	280	2.55
	0.1 N NaCl	835	315	2.65
	0.05 N NaCl	915	350	2.61
	0.025 N NaCl	1045	395	2.65
	0.2 N $AgNO_3$	560	210	2.67
	0.1 N KI (alc.)	1500	580	2.58
Cell IV, 1" bright electrodes,	0.2 N NaCl	6138	2272	2.70
	0.1 N NaCl	5849	2229	2.62
	0.1 N KI (alc.)	6700	2500	2.68
Cell IX, 2" sand blasted electrodes,	0.2 N NaCl	310	115	2.70
Cell XI, cylindrical electrodes, 1/2" long,	0.001 N KI	2450	910	2.69
Cell XII, cylindrical electrodes, 2" long,	0.0005 N NaCl	475	175	2.71
	0.001 N KI	365	145	2.52

the frequency of the alternating current approaches infinity, the change of resistance of a given solution in a given cell, and also the inductance necessary to balance the capacity of the cell, approach zero. In Table XI are given the resistances at 1000 cycles, the differences between the inductances in millihenries and the differences between the resistances in ohms at 600 and 1000 cycles, and the ratios of the differences in inductance to the difference in resistance. It will be seen that the ratios are very close to a constant 2.0. A few of the values calculated for different solutions in different cells are given in Table XI below. Many other cells of different types give this same constant, as they should theoretically.

TABLE XI.—DATA SHOWING RATIO BETWEEN THE DIFFERENCE IN RESISTANCE AND THE DIFFERENCE IN INDUCTANCE WITH CHANGE IN FREQUENCY FROM 600 TO 1000 CYCLES ON A GIVEN SOLUTION IN A GIVEN CELL.

Cell I, 1" bright electrodes.

		Res. at 1000.	Dif. in Ind. in μ h.	Dif. in R in ohms.	μ h/ohms.
	0.2 N NaCl	53.103	0.435	0.226	1.925
	0.1 N NaCl	101.108	0.520	0.250	2.080
	0.05 N NaCl	195.302	0.565	0.276	2.050
	0.025 N NaCl	381.005	0.650	0.356	1.826
	0.2 N $AgNO_3$	54.521	0.350	0.176	1.990
	0.03 N HCl	149.251	0.630	0.340	1.853
	0.1 N KI	130.134	0.790	0.350	2.260
	0.1 N KI (alc.)	609.263	0.920	0.520	1.770
Cell II,	0.2 N NaCl	84.259	0.605	0.289	2.093
	0.1 N NaCl	160.424	0.600	0.305	1.970
Cell IV,	0.05 N NaCl	534.400	3.866	1.900	2.030
Cell VI,	0.2 N NaCl	11.492	0.635	0.311	2.040
	0.1 N KI (in alc.)	90.000	0.930	0.468	1.990

Considering the fact that most of this work was done before the method was finally perfected, the values are remarkably constant. Mr. H. P.

Hastings has now secured much more elaborate data confirming these results at widely different frequencies, resistances, capacities, and inductances, and we have devised some simple equations for developing the theoretical aspects and for correlating these phenomena approximately, especially with the equation $R_\infty = R_f - KL_f f^n$ discussed above.

Apparent Capacities of Various Solutions in Different Cells.—In Table XII we have given the values in microfarads for the capacities of several different solutions in different cells at both 600 and 1000 cycles, calculated from the inductance measurements by means of the equation $C = 1/L\omega^2$. These data show that the values for the cells with platinized electrodes are very high, and also that the values for the capacities at the two frequencies are nearly the same. It is also seen that the values for the cells with platinized electrodes do not check very satisfactorily and this is due to the fact that L is very small and thus a small error in L causes a very large change in C.

TABLE XII.—CAPACITIES OF DIFFERENT SOLUTIONS IN VARIOUS CELLS AT 600 AND 1000 CYCLES, CALCULATED FROM THE EQUATION $C = 1/L\omega^2$.

	Solution.	C in $\mu f.$ at 600 cycles.	C in $\mu f.$ at 1000 cycles.
Cell V, $^1/_2''$ platinized electrodes,	0.2 *N* NaCl.........	787	633
Cell II, 1″ bright Pt electrodes,	0.2 *N* NaCl.........	88	82
Cell VI, 1″ bright Pt electrodes,	0.2 *N* NaCl.........	68	63
Cell III, 1″ platinized electrodes,	0.1 *N* NaCl.........	5405	3623
Cell V, $^1/_2''$ platinized electrodes,	0.1 *N* NaCl.........	781	725
Cell II, 1″ bright Pt electrodes,	0.1 *N* NaCl.........	70	72
Cell VI, 1″ bright Pt electrodes,	0.1 *N* NaCl.........	53	50
Cell III, 1″ platinized electrodes,	0.05 *N* NaCl........	..	..
Cell IV, $^1/_2''$ bright Pt electrodes,	0.05 *N* NaCl........	12	11.5
Cell II, 1″ bright Pt electrodes,	0.05 *N* NaCl........	55	59
Cell X, 2″ bright Pt electrodes,	0.05 *N* NaCl........	213	190
Cell IX, 2″ etched Pt electrodes,	0.05 *N* NaCl........	227	222
Cell V, 1″ platinized electrodes,	0.05 *N* NaCl........	826	1010

In Table XIII are given the values for the capacities of several different solutions in various cells calculated from the equation (1) $C = 1/L\omega^2$, and (2) $C^2 - C/L\omega^2 = -1/R_3{}^2\omega^2$, which latter equation will be discussed more fully in a later paper. The values calculated for the capacity by the two methods check very well.

The changes of concentration of the electrolyte at the electrode and the deposition of ions on the electrodes both doubtless give rise to the reverse electromotive force which makes the cell act like a condenser and diffusion and neutralization phenomena make the condenser "leak." Professor Bennett has devised equations for treating such phenomena mathematically and a full report on this subject will be given later.

The most important part of our work planned is to study the electrode phenomena and the phase relations. In order to do this we are devising

TABLE XIII.—CAPACITIES OF DIFFERENT SOLUTIONS IN VARIOUS CELLS CALCULATED FROM THE EQUATIONS (1) $C = \frac{1}{L\omega^2}$, (2) $C^2 - \frac{C}{L\omega^2} = -\frac{1}{R_3^2\omega^2}$.

Cell.	Solution.	Res. at 600 cycles.	Ind. at 600 cycles. in μ h.	Res. at 1000 cycles.	Ind. at 1000 cycles in μ h.	Cap. in μ f. $C = \frac{1}{L\omega^2}$.	Cap. in μ f. $C^2 - \frac{C}{L\omega^2} = -\frac{1}{R_3^2\omega^2}$.
IV	0.2 *N* NaCl	148.7	6138	.....	....	11.5	11.3
IV	0.1 *N* NaCl	280.0	5849	.....	....	12.0	12.2
IV	0.1 *N* NaCl	.....	....	277.7	2230	11.4	11.3
IV	0.05 *N* NaCl	536.3	4752	.....	....	15.0	15.0
II	0.2 *N* NaCl	84.4	800	.....	....	88.0	88.0
II	0.05 *N* NaCl	310.5	1295	.....	....	55.0	55.5
VII	0.1 *N* NaCl	29.0	990	.....	....	72.0	70.5
VIII	0.1 *N* NaCl	43.5	1210	.....	....	58.0	58.8
IX	0.2 *N* NaCl	282.0	310	.....	....	227.0	229.0

alternating current potentiometer methods to study the electromotive force and phase changes near the electrodes. We are using some cells with very small movable plate and point electrodes which are brought close together to magnify the electrode effects and are devising other cells with plane parallel electrodes which can be adjusted as close together as desired by interferometer methods, and we can thus make the known distance between the electrodes so small that the ions move from one plate to the other and back at each cycle and make the electrode phenomena play the chief role. Professor Bennett has available a very fine triple oscillograph with a period of 0.0003 second, with which it is possible to detect and measure changes in phase, voltage, current, capacity, and other phenomena in very short-time periods and at different frequencies, and Dr. G. H. Gray has already made important studies which will be reported later in detail.

Conclusions.

(1) There is no measurable change in the resistance of a solution, or the inductance, with the change in voltage needed, provided the cells, solutions, and containers are kept scrupulously clean. If the cells are not clean, however, there is a change in resistance with change in voltage, and this fact can be used as a very reliable test for cleanliness of cells.

(2) In order to make accurate conductivity measurements the cells and methods must be so perfected that the ratios of the resistances for any given solution in two cells or of two solutions in any cell, must be constant to within 0.01%. This will not be the case unless we can eliminate electrode effects. The ratios of the resistances of 0.2 *N*, 0.1 *N* and 0.05 *N* NaCl in two cells, one with 0.5 and the other with 1 inch *platinized electrodes* did not vary more than 0.01% which is about the experimental error shown to be due to the 0.5 inch electrodes and other causes. Since there is no measurable change in the resistance of a solution with change in frequency around 500 to 2000 cycles in our cells *with platinized*

electrodes 1 inch or more in diameter, we can, therefore, conclude that one-inch platinized electrodes give approximately the true electrical resistance of these solutions at such frequencies, and certainly do so at infinite frequencies, if the resistance is above 100 ohms.

(3) In cells with *bright platinum electrodes* there is a change in resistance with change in frequency from 600 to 1000 cycles and higher, and this change depends upon several factors: (1) as the concentration of any given solution is decreased, and, therefore, the resistance increased, the change in resistance with change in frequency is decreased; (2) as the area of the electrode surface is increased the change in resistance with change in frequency is decreased; (3) as the area of the electrode surface is increased the inductance necessary to obtain a balance is decreased, and, hence the apparent "capacity" of the cell is increased. (4) The higher the apparent "capacity" of the cell, and, therefore, the smaller the inductance necessary to balance this capacity, the smaller the change of resistance with change in frequency becomes. As the apparent "capacity" of a cell is increased by increasing the surface, platinized electrodes should give the smallest change in resistance with change in frequency and this is borne out by all our data. (5) Solutions of different salts having about the same resistance in the same cell with bright platinum electrodes give approximately the same change in resistance with change in frequency from 600 cycles to 1000 cycles. (6) There is a specific relation between the electrolyte, the electrode material, the character of the electrode surface and the change of capacity and resistance with change in frequency. This is shown by the fact that for a change in frequency from 600 cycles to 1000 cycles. 0.1 N $AgNO_3$ in a cell with 1 inch bright platinum electrodes gives a change of 0.12%; 0.1 N $AgNO_3$ in this cell with the 1-inch electrodes, rough, silver plated, gives a change of 0.012%, and 0.1 N NaCl in the same cell a change of 0.052%.

By comparing the resistances of 0.1 N and 0.05 N NaCl in two cells, one of which had bright and the other platinized electrodes one inch in diameter, it was seen that the ratio for the cell with bright electrodes was much lower at the lower frequencies than that for the cell with platinized electrodes, but as the frequency was increased the ratio for the cell with bright electrodes approached that for the cell with platinized electrode. Extrapolating the resistance for the cell with bright electrodes to infinite frequency the ratio was found to differ by only 0.004% from that given by the cell with platinized electrodes. It is thus shown that the true electrical resistance of solutions can be measured in cells with bright platinum electrodes only at infinite frequency. We, therefore, recommend for all conductivity work involving an accuracy of 0.01% the use of a Vreeland oscillator, giving three or more frequencies, for example, 500, 750, 1000 and 1500, or 2000 cycles, and the extrapolation of the corresponding resistances to that at infinite frequency.

(4) By substitution in the equation $(R_f - R_\infty)/L_f f = K$, where R_f and L_f are the resistance and inductance measurements, respectively, at any given frequency f, R_∞ the resistance at infinite frequency, and K a constant, we can calculate R_∞ for any given cell and solution. The values found for R_∞ by this equation differ from those found by extrapolation by only ±0.01 to ±0.025%.

(5) The fact that there is a change in the resistance of electrolytes with change in frequency makes it clear why different workers have found different values for the molecular conductivity and ionization of the same solution, as some measurements were made at 60 cycles, others at 1000 cycles, etc. The resistances or conductivities at *infinite frequency* should be used in all cases.

(6) Saturation of bright and platinized electrodes with hydrogen produces no appreciable change in the "capacity" of the cell at 60 cycles. This and a great deal of other evidence seems to show that the "capacity" does not arise simply from a neutral gas layer deposited on the electrodes and acting as an air condenser. It is probably due to a "double layer" of ions of the electrolyte and of the solvent at and on the electrodes and hence to "contact potential" by these changes of concentration arising from electrolysis.

(7) The ratio between the inductance measurements at 600 and 1000 cycles with various solutions in many different cells is a constant, the value being about 2.66. This shows that the inductance is nearly inversely proportional to the square of the frequency, the ratio for the square of the frequency used being 2.77. As this relation holds true for a leaky condenser the cell seems to act as a resistance in series with a simple condenser with a leak.

(8) As the frequency of the alternating current is increased the change in apparent resistance of a given solution in a given cell, and also the inductance necessary to balance the capacity of the cell, are decreased and both approach zero at infinite frequency. It was found that the ratio of the difference in the inductance in millihenries to the difference in the resistance in ohms between 600 and 1000 is a constant, being about 2.00.

(9) The electrical capacities of the cells acting as leaky condensers have been measured by different consistent bridge methods. The capacities vary with the solution, size of electrode, character of surface, resistance, and other factors, and range from 10 to 1000 microfarads for bright electrodes and from about 500 to 5000 microfarads for platinized electrodes.

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