voltage of five experiments with the above system at 25° with corrections for the potential of the calomel cell, for the barometric pressure, and for the vapor tension of the solution, and the final corrected voltage. The corrections for the potential of the calomel cell were determined as usual in our laboratory by comparing the working electrode with the mean of a large battery containing ten other electrodes. The couplets in the first column give the e. m. f. observed at first under atmospheric conditions and again at this pressure after having subjected the system to the increased pressure.

	Corrections.			
Meas. E. M. F.	Cal. cell.	Bar.	Vap. T.	Corrected. E. M. F.
0.42636	+0.00013	+0.00031	+0.00040	0.42720
0.42635	+0.00013	+0.00031	+0.00040	0.42719
0.42661	—0.00013	+0.00036	+0.00040	0.42724
0.42658	—0.00013	+0.00036	+0.00040	0.42722
0.42652	—0.00009	+0.00042	+0.00040	0.42725
0.42653	—0.00009	+0.00042	+0.00040	0.42726
0.42645	—0.00001	+0.00042	+0.00040	0.42726
0.42609	+0.00035	+0.00039	+0.00040	0.42723
				Average, 0.42723

Conclusions.

1. Experiments on the influence of the partial pressure of hydrogen on the potential of the hydrogen electrode show that near atmospheric pressure the changes can be expressed by the formula $E = RT/2F \log n\ H_2/H'_2$, in which H_2 and H'_2 are the partial pressures. The average change in potential found is 0.00001751 volt per millimeter which is only 0.3% larger than the value 0.00001746 volt calculated by the use of the above formula.

2. Five experiments on the system

$$H_2\text{–Pt–0.1 } N \text{ HCl–0.1 KCl–}Hg_2Cl_2\text{–Hg}$$

gave the potential 0.42723 ± 3, which is in very close agreement with the average of our earlier values and with those of Bjerrum, namely, 0.4272.

MADISON, WIS.

[CONTRIBUTION FROM THE CHEMISTRY OF FOREST PRODUCTS, UNIVERSITY OF WISCONSIN.]

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

V. INVESTIGATIONS ON THE USE OF THE VREELAND OSCILLATOR AND OTHER SOURCES OF CURRENT FOR CONDUCTIVITY MEASUREMENTS.[1]

BY W. A. TAYLOR AND S. F. ACREE.

Received August 26, 1916.

As the measurement of the true electrical conductivities of solutions

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[1] Robertson and Acree, *J. Phys. Chem.*, **19**, 381 (1915); Taylor and Curtis, *Phys. Rev.*, **6**, 61 (1915); Taylor, *Science*, **42**, 388 (1915). We are indebted to the Carnegie Institution of Washington for aid in this work.

of electrolytes and of heterogeneous systems, such as woods and other plant tissues and their liquid contents, skin and muscular tissues under different conditions, blood and many colloidal solutions and suspensions is of great importance to chemists, physicists, botanists, zoölogists, geologists, medical men, and others, we have been working during the past few years to develop methods for this purpose with an accuracy of 0.001%. The most important new aspects of the investigation were to determine the nature of the electrode processes, the polarization or capacity phenomena, and the phase relations, by the use of pure resistances, capacities, inductances, the oscillograph and an alternating current potentiometer. Since the ideal condition of being able to measure the true resistance at high frequencies approaching infinity cannot be realized today because of errors from skin effects and inductance and capacity in the resistance coils and leads, and because there are no current detectors giving the necessary precision at such high frequencies, we have tried to find methods for using lower frequencies. In this work it was first necessary to obtain 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. A pure sine wave is required in order to prevent unsymmetrical polarization at the electrodes and to annul the influence of harmonics on the telephone; that is, to obtain complete silence when the fundamental frequency is perfectly balanced by the use of the correct resistance and inductance or capacity in the bridge. Since we have found that the apparent resistance of a given solution in a cell with bright electrodes may vary as much as several per cent. with change in frequency, and that the true electrical resistance can be obtained only by making resistance measurements at several different frequencies and extrapolating the resistance to infinite frequency, or applying the formula $R_\infty = R_f - KL_f f$, it is obvious that we must be able to change the frequency at will, but that it must be constant at any given setting.

In our work we have tested the induction coil,[1] the 60-cycle city current of Madison, a Holzer-Cabot wireless alternating current generator, a General Electric type of large generator, a Siemen's-Halske alternating current generator, the small Vreeland oscillator sold by Leeds & Northrup for work at 500 and 1000 cycles, and the very fine type[2] B Vreeland oscillator which the Western Electric Company sells for work at frequencies varying from 160 to 4200 cycles. Oscillograms of the wave forms of the different machines are given in the figures below. These photographs show the wave form of the voltage, and also that of the current in some

[1] See Leeds and Northrup Catalogue 48, for oscillograms of their induction coils and of their small Vreeland oscillator, and for a description of this latter instrument.

[2] See "The Vreeland Oscillator" issued by the Western Electric Co., for a description of their Vreeland Oscillators, the oscillograms, and general applications of these instruments.

cases. In the case of the Madison city current the wave form of the charging current of a condenser supplied with this voltage is also shown to give an idea of the harmonics present. The writers are greatly indebted to Messrs. Curtis, Fitch and Fearing of the Bureau of Standards and to Professor Edward Bennett and Dr. G. H. Gray of the University of Wisconsin, for assistance in obtaining these oscillograms at various times since 1911.

The induction coil should be discarded when conductivity measurements of any great degree of accuracy are desired. It is especially unfitted for this work because (1) it does not give an alternating but a pulsating current having a large number of over-tones which prevent the operator from obtaining complete silence in the telephone, (2) the range of frequency is comparatively small, and (3) it is impossible to keep the frequency constant. Figs. I and II show the voltage wave form given by our induction coil, which is one of the best types made by Leeds and Northrup. This wave form is not only clearly far from sinusoidal, but is very unsymmetrical. The electromotive force below the axis is considerably larger than that above and the much slower rise to the maximum above is in decided contrast to the sharp break into the axis from below. The unreliability of an induction coil is clearly shown by the fact that although Figs. I and II were made without changing the setting of the induction coil, the difference between the amplitudes of the upper and lower peaks in Fig. I is much larger than in Fig. II. These facts show clearly not only that there is unsymmetrical polarization at the electrodes but that it varies so much from moment to moment when an induction coil is used that it is impossible to have the same current or voltage phases at the telephone terminals and secure silence.

Fig. III gives the oscillogram of the voltage wave of the 60-cycle city current of Madison. It is seen that the wave form is nearly sinusoidal, although the irregularities at the crest of the wave show that some harmonics are present. Fig. IV shows the oscillogram of the charging current of a condenser supplied by this voltage. In the charging current of a condenser the amplitude of any *n*th harmonic is *n* times as great as in the voltage wave form. Fig. V shows the pure sine charging current of the condenser after these harmonics have been tuned out by the use of the proper inductance and capacity. By tuning out the harmonics a very much better and more accurate minimum can be obtained. In Figs. IV and V, *e* denotes the voltage and *i* the current curves. Although the frequency is not quite steady a very good bridge balance can be obtained for such low frequencies and this purified source of current was useful in getting resistance, capacity and inductance measurements to compare with those at higher frequencies.

Figs. VI and VII give the oscillograms of a Holzer-Cabot wireless gen-

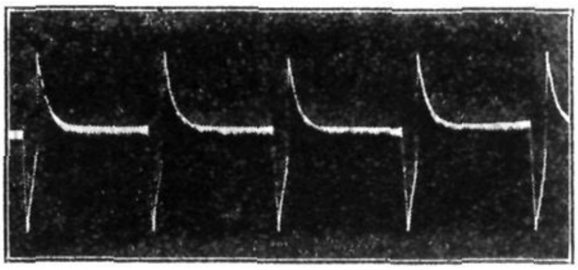

Fig. I.

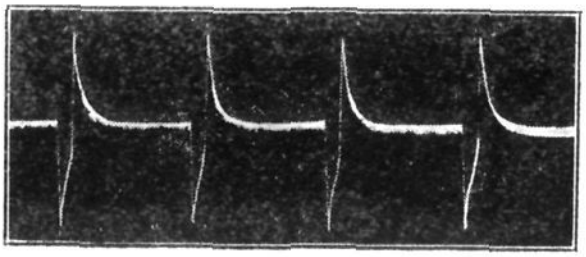

Fig. II.

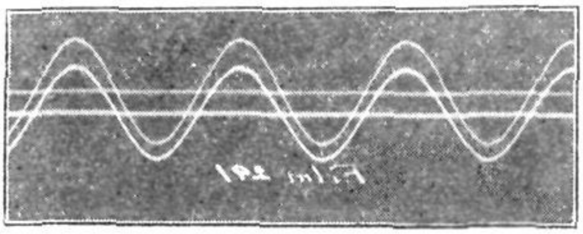

Fig. III.

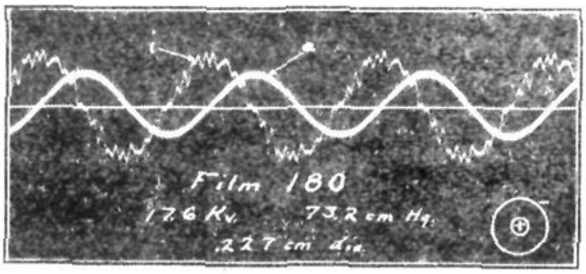

Fig. IV.

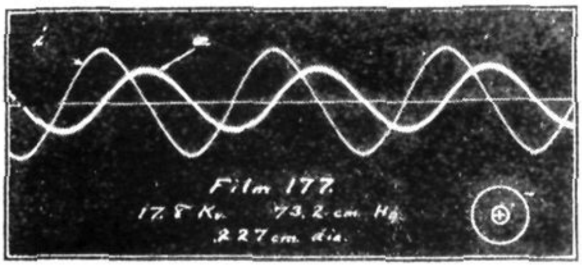

Fig. V.

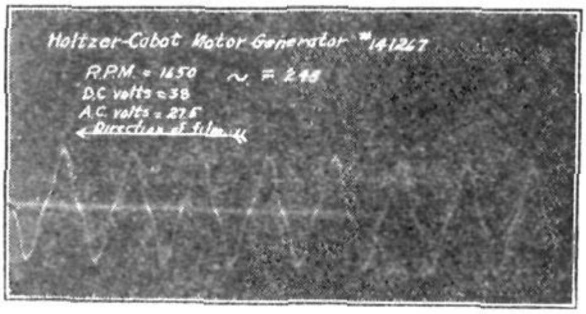

Fig. VI.

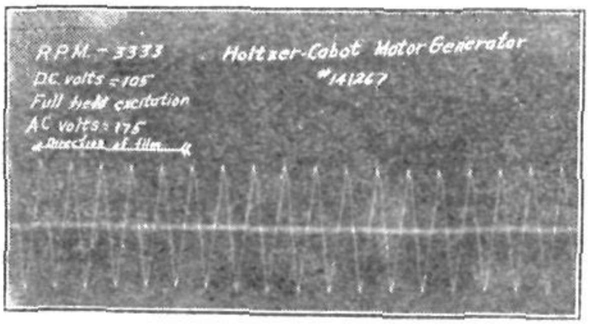

Fig. VII.

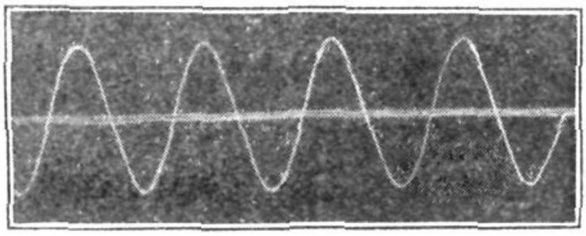

Fig. VIII.

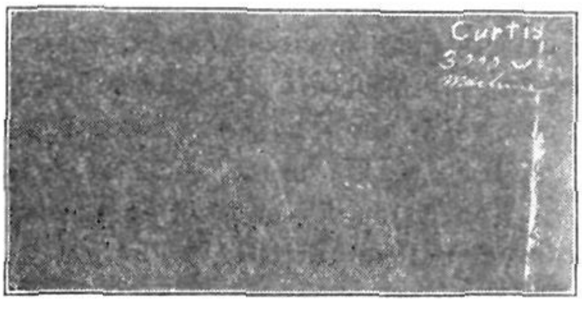

Fig. IX.

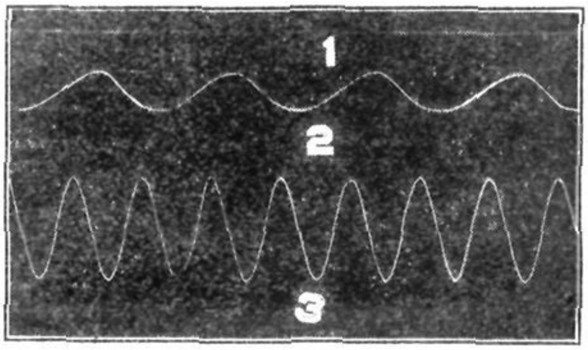

Fig. X.

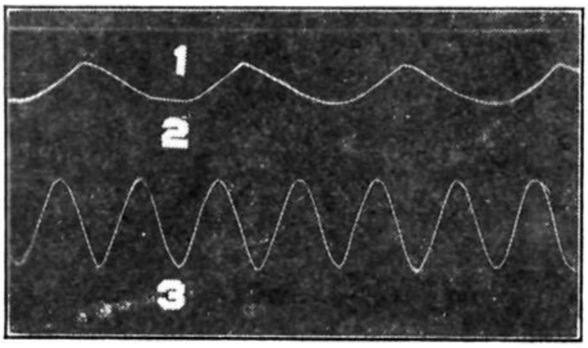

Fig. XI.

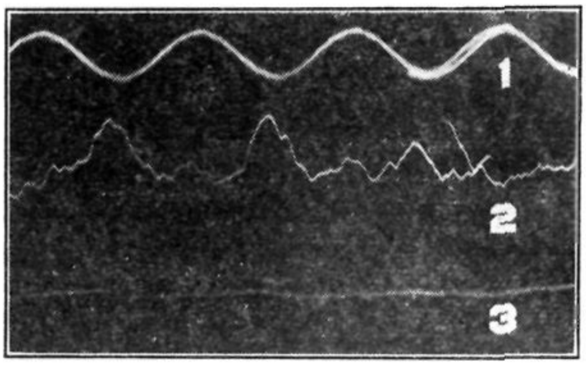

Fig. XII.

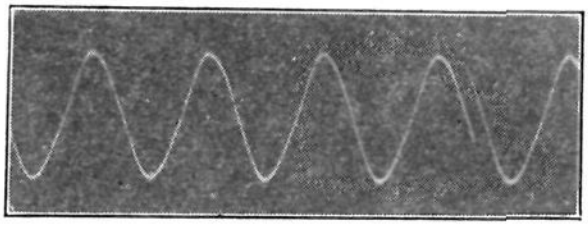

Fig. XIV.

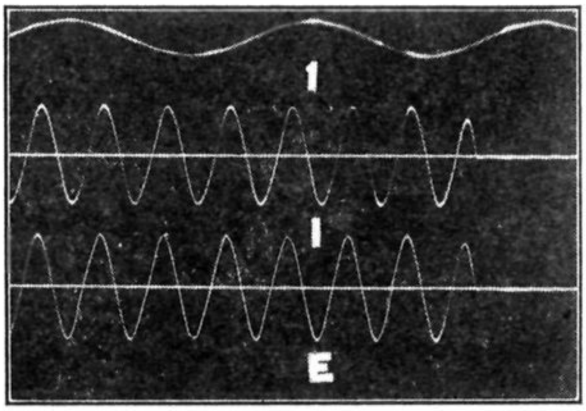

Fig. XIII.

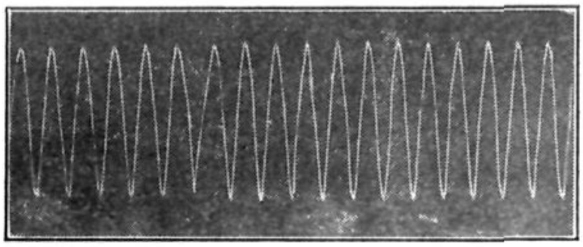

Fig. XV.

erator at 248 and 500 cycles, respectively. Although the wave form is very good for a machine of this kind, it is somewhat flat-topped because of the presence of a third harmonic. This prevents complete silence in the telephone when the fundamental is balanced. The greatest disadvantage is that the machine has no attachment for changing or regulating the frequency.

Figs. VIII and IX give the oscillograms of the wave forms obtained from the large General Electric Company generator made for frequencies from 160 to 3000. The first is for the 600-cycle side of the machine and the second for the 3000 side. These are practically sine waves and the freedom from harmonics allows us to obtain a much better minimum than that given by the Holzer-Cabot machine. But the frequency is not absolutely constant and the cost of the machine is very large. The energy output of the machine is so large that an alternating current galvanometer can be used as current detector at low frequencies with high precision.

Curtis in his work on resistances for alternating currents, and Washburn in his fine work on conductivities, and also Schlesinger have already tested the Siemens-Halske generator and found it excellent. The harmonics can be easily tuned out by the use of inductances and capacities. It can be made to give frequencies from 400 to 1800 but these are not constant unless a special regulating device is attached.

We have found the type B Vreeland oscillator sold by the Western Electric Company to be far the best source of current tried thus far, for the following reasons: (1) It is practically noiseless and can be started and stopped conveniently. (2) By the use of suitable secondary coils, which can be rotated easily, it can be made to give any voltage desired up to about 500; only a very small current can be obtained at this voltage but this is ample for measuring resistances up to 100,000 ohms or more. When a storage battery of constant voltage is used as a source of actuating current the alternating current obtained has a voltage steady enough for alternating current potentiometry. (3) It gives a constant frequency independent of variations in the actuating direct current or in the load and, hence, under even only fairly constant conditions, gives a note of constant pitch and loudness in the telephone, and, of especial importance, allows the cell capacity to be balanced out sharply so that an accurate bridge balance can be obtained. (4) The frequency is regulated by means of a set of mica and paper condensers with a range of 0.001 to 40 microfarads and in this way can be changed easily to any value between 160 and 4200 cycles and kept constant for weeks to within 0.10%. By changing the number of turns in the field coils of the Vreeland oscillator the frequency can be made as low as 30 to 40 without the use of additional condensers. By using extra condensers or inductances and these special field coils the frequency can be lowered to possibly 10; although Vreeland states that the wave form is not perfect at this frequency it is nevertheless good enough for all of our requirements. By the use of quartz bulbs frequencies up to 100,000 for wireless telegraphy can be obtained. An instrument for giving simultaneously any two frequencies within these ranges is much needed and may later be placed on the market. (5) It gives practically a pure sine wave free from harmonics which disturb the operator using the telephone and, hence, it is possible to obtain easily complete silence in the telephone. (6) It can be run by a mercury rectifier, but the wave form is then not so good, because the rectifier voltage is pulsating and not steady. Our unloaded rectifier gives the pulsating voltage wave form 2 in Fig. X, 1 being the zero of voltage in both Figs. X and XI. When loaded with the Vreeland the rectifier gives the voltage wave form 2 in Fig. XI, and the Vreeland gives the voltage wave form 3. This wave form 3 is seen to have a smaller amplitude every second cycle. The Vreeland gives a fine sine wave when run by the current from a good dynamo, especially if any small irregularity, such as that due to the dynamo brushes, is suppressed, and Fig. XII illustrates a study of their dynamo by Professor Bennett and Dr. Gray. Line 1 is the voltage oscillogram of the Madison 60-cycle city current and is used for reference. Line 2 shows the harmonics in the voltage wave form from the dynamo, and the entire film shows that the harmonics are repeated every six cycles. It was obtained by passing 3.5 amperes through the primary circuit of a 5 : 1 transformer and taking the voltage oscillogram of the secondary circuit. As the oscillograph was set so that the zero of voltage was 12 feet away and the transformer magnified the harmonics 5 times it is seen that the variation of about 1 inch in the oscillogram corresponds to a change of about 1/750 in the voltage from this cause. These harmonics can be suppressed by the use of a proper set-up of inductances and capacities. Line 3 illustrates the improvement secured by using an inductance of 1 henry in series with the primary of a second transformer set-up duplicating in every respect the one described above. As lines 1, 2 and 3 were taken simultaneously it is seen that this inductance chokes out the harmonics so nearly completely that there is no doubt that the current from any dynamo could be purified by using inductance and capacity, and hence the inductance and capacity in the Vreeland automatically tend to purify the dynamo current. When 3.5 amperes from a storage battery were passed through the transformer a perfectly straight voltage line, not illustrated, was obtained. The advantage of using such a purified current from a dynamo over that from a storage battery is simply one of less expense and avoidance of the labor of attending to storage batteries. The voltage, however, is not very constant in even the best dynamo. But a storage battery gives the steadiest current and hence the best wave form from the Vreeland, illustrated in 3, Fig. X, and should be used when convenient. Although the usual Type B instrument is made to operate on direct currents of 110 down to 75 volts, an instrument like ours can be ordered to operate from 120 down to 50 volts and thus effect distinct economy when storage cells are used. (7) In order to regulate the frequency we use calibrated tuning forks of 100, 250, 500, 750, 1000, 1500, 2000 and 3000 vibrations, and by changing the capacity the frequency can be fixed by the "beat" method with an accuracy of 0.10% for the lower frequencies and much better for the higher ones. Having calibrated the Vreeland at several frequencies, it is a simple matter to calculate the capacity necessary for any frequency. As such a set of tuning forks is expensive we shall be glad to lend them to anyone. (8) It is thus seen that no other available instrument so nearly meets ideal conditions for alternating current work in physics and chemistry and no investigator who has once used the Vreeland oscillator will be content with anything less satisfactory. Fig. XIII gives the practically pure sine voltage and current wave forms, *e* and *i*, for 240 cycles from the Type B Vreeland, when the current is passed through a conductivity cell;

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.

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.[1]

BY W. A. TAYLOR AND S. F. ACREE.

Received August 28, 1916.

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

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