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A STUDY OF POLARIZATION CAPACITY OVER A WIDE FREQUENCY BAND

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Abstract

The polarization capacity of platinum electrodes in sulphuric acid and also of gold electrodes in sulphuric acid has been studied from 200 to 200,000 cycles per second. An alternating current bridge was used to make the measurements in the audible range and a bridge with heterodyne detector for the higher frequencies. If the *relation connecting capacity and frequency* is put in the form $C=C_0/f^P$ where C_0 and P are constants then at the lower frequencies P is nearly equal to .3 while at the higher frequencies it approaches .5. At the same time, the phase angle of the capacity shifts from about 20 to about 40 degrees. Voltage measurements made to determine the *limiting value of the initial capacity* show that it is of the same order of magnitude for alternating current as for direct charge. When *two harmonic alternating currents of differing frequencies are simultaneously impressed on a cell*, the polarization capacity measured by means of either one is independent of the presence of the other.

THE study of polarization capacity phenomena by alternating current methods has taken on a new interest in recent years. The development of alternating current measuring methods during the past decade, particularly the adoption of the vacuum tube for these purposes, has made possible accurate measurements of capacity over a wide range of frequency formerly inaccessible. Predictions which had been made for the action of cells at high frequencies can now be verified or shown in need of modification. On the theoretical side, the views of electrode phenomena which connect polarization with surface reactions afford some very interesting subjects for theoretical investigation.

The first attempt to use frequencies above a few thousand per second for polarization measurements was made by Kruger[1] in 1906. He used a very ingenious method with a damped oscillatory discharge, but not enough points were taken and the frequency range was not sufficiently extended so that very definite conclusions could be drawn. The first serious attempts to get polarization capacity measurements above audible frequencies were made by Merritt[2] and Jolliffe.[3] It is to follow up their work that the present investigation was undertaken.

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[1] Kruger, Ann. d. Physik **21,** 301 (1906).

[2] Merritt, Phys. Rev. **17,** 524 (1921).

[3] Joliffe, Phys. Rev. **22,** 293 (1923).

M. Wien[4] had studied the change of capacity with frequency for platinum electrodes in solutions of sulphuric acid at various audible frequencies, and his results, as well as the theorectical explanations given of them by Warburg[5] and Kruger,[6] had led to the expectation that at the higher frequencies the rate of change of capacity with frequency should be lessened, and in fact it was predicted that the capacity would become constant as the frequency was raised. Symbolically, if the relation between P, the back e.f.m. of polarization, and I, the alternating current through the cell is put in the following form (first suggested by Wien[4]) $P=I/C\omega\sin(\omega t-\pi/2+\psi)$, C should tend to become constant and ψ should approach zero as ω becomes greater. Jolliffe has found however that at frequencies from 100,000 to 2,000,000 per second C becomes proportional to $1/\omega^{\frac{1}{2}}$ and ψ is near 45° in the case of gold and for platinum C has been found proportional to $(1/\omega^{\frac{1}{2}}+\text{small const.})$. It is well known that the value of the polarization capacity depends very much on the particular piece of metal used in the cell and even for the same piece varies very much under different conditions. It seemed entirely possible therefore that these discordant results might have been due to the fact that the cells used were different. In order to test the hypothesis a single cell should be carried through both frequency ranges.

APPARATUS

A bridge shown in Figs. 1 and 2 was used to make these measurements, a vacuum tube oscillator supplying the alternating current. The arms R_1 R_2 R_3 are non-inductive resistances while a variable inductance is used to balance the capacity in arm 4. Since, as will be shown below, it is necessary to use small potentials across the cell to get the most information from polarization capacity measurements, a three stage amplifier was used in the detector arm of the bridge. In order to get most satisfactory operation of a bridge with an amplifier the Wagner[7] earth connection should be used as shown in diagram. In making measurements, arms 1 and 3 were kept equal. The cell was placed in arm 4 and the variable inductance in this arm and the resistance in arm 2 were adjusted so that the bridge was balanced. A switch was arranged so that a variable capacity box in series with a resistance, wound by the Ayrton method, could be substituted for

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[4] Wien, Ann. d. Physik **294,** 37 (1896).

[5] Warburg, Ann. d. Physik **303,** 492 (1899); **311,** 125 (1901).

[6] Kruger, Phys. Zeits. **45,** 1 (1904).

[7] Wagner, Elect. Tech. Zeits. **32,** 1001 (1911).

the cell. It was thus possible to read off directly from this capacity and resistance the capacity and resistance of the cell. The frequency was at the same time easily calculated by noting the value of the variable inductance required to balance this capacity; f then being equal to $1/2\pi\sqrt{LC}$. These calculated values were checked at several points by means of tuning forks. At frequencies above the audible range a heterodyne beat method of detection was used, the beating current being supplied by a vacuum tube oscillator. This circuit and the de-

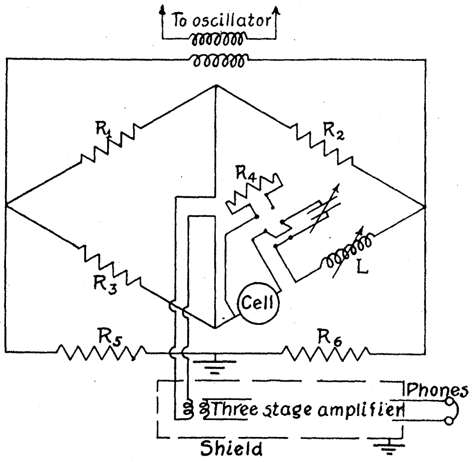

Fig. 1. Audio frequency bridge.

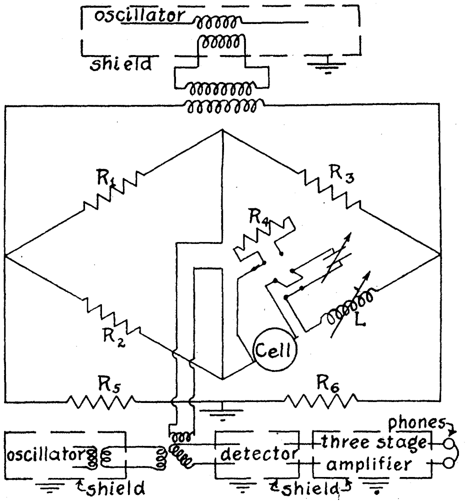

Fig. 2. High frequency bridge.

tector circuit from the bridge were loosely coupled to a third coil which led to a detector and amplifier. The frequency was measured by means of a S. C. R. Signal Corps wavemeter.

In order to make these measurements strictly comparable with Jolliffe's results the cells he had used (shown in Figs. 3 a "Cell A") were again employed in the first part of this work. The electrodes consisted of either gold or platinum rods of 1 mm radius sealed into glass tubes with DeKotinsky cement and then ground down so that only the cross section was exposed. They were usually placed so as to be between .5 and 1 mm apart.

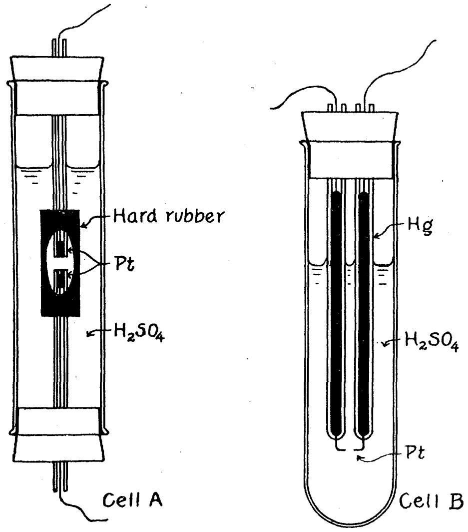

Fig. 3. Diagrams of electrolytic cells.

RESULTS

Before giving the results of the capacity-frequency runs several of the precautions which were needed to secure consistent results will be described. The earliest experimenters found that the polarization capacity was a function of the applied voltage but that a constant value was approached as the polarization potential was reduced. This so-called initial capacity has the most significant theoretical explanation and is therefore of the most interest. Since this change of capacity with potential had only been determined for direct charge, however, it was thought worth while to make a few rough determinations of this relation at several frequencies. To measure the potential drop across the cell a transformer with an input impedance of about 15,000 ohms was shunted across; and a vacuum tube was attached to the output as a detector. The change in plate current was read by means of a d.c. galvanometer. The whole transformer, vacuum tube, galvanometer system was calibrated throughout the frequency range and gave very satisfactory service, showing a change after a year's use which was less than the calibration errors. As all the curves giving the relation between capacity and potential were similar only one is shown in Fig. 4. The capacity C and phase angle ψ as defined above are both plotted against the potential drop at the electrodes, i.e., the total drop over the cell minus the drop due to the resistance of the electrolyte. The resistance of the cell was calculated from known conductivity data and from the dimensions of the cell. The most important points to be noted in these curves are the asymptotic values approached by the capacity and phase angle below .1 volt and their more rapid increase above this value. This limit for the initial capacity corresponds well with that found by direct charge methods.

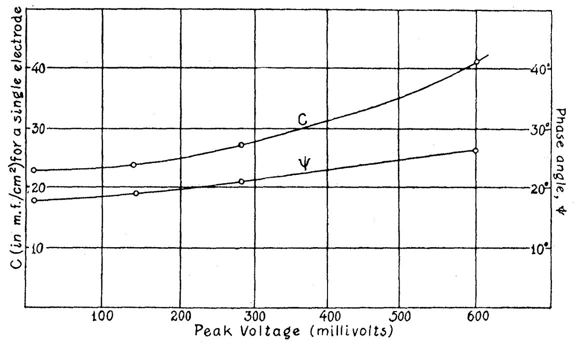

Fig. 4. Curve 1. Polarization capacity as a function of peak voltage at 1340 cycles per sec. Cell *A*, Pt−10% H_2SO_4.

In making the capacity-frequency measurements the potential applied to the cell was always kept below this critical value by determining the potential applied by means of the volt-meter, or, when this instrument could not be used, by reducing the current through the cell until further reduction caused no change in the bridge setting.

When the first measurements were made it was found that if it had taken some little time to make the reading with the comparison capacity, the cell did not immediately return to the same condition that it had previously shown. This was traced to a slight polarization which was set up in the cell when it was in the bridge circuit. Apparently even after the cell had been in the solution for a number of days some dissimilarities still existed in the electrodes which caused a small current to flow and polarize the cell. When the comparison capacity was substituted for the cell the circuit was open and under the influence of diffusion and other causes this polarization gradually disappeared, to build up again when the cell was placed in the bridge circuit. It was thought best to eliminate this small variation by always measuring the capacity when the cell was self polarized. To do this connections were arranged always to keep the cell on short circuit while the comparison capacity was being used.

In making capacity tests it was at first thought that a very pure sine wave should be used in order to get reliable results because of the change of capacity with frequency. Now, although the vacuum tube oscillator gives a wave which is quite satisfactory for most alternating current bridge purposes it cannot be said to be entirely free from overtones. As no data were available on the effects of these overtones on the capacity measurements an investigation of their possible effect was made with some very interesting results. The method of procedure was as follows: Two oscillating circuits of different frequencies were simultaneously loosely coupled to the bridge input. The pitches were kept sufficiently different so that they could readily be distinguished and the bridge could be balanced with respect to either of them while the other was sounding. In this way capacity and resistance measurements were made with an alternating current of a certain frequency while one of any other desired frequency and intensity was at the same time present.

The results of this test showed conclusively that overtones were not affecting the measurements. The balance point determined by means of either pitch was absolutely independent of the presence or absence of the other. This was even true when the supposed disturbing pitch had an intensity greater than that of the pitch being used for measurement.

These facts have further application of interest. It has been suggested by various experimenters, laterly by Haworth[8] and Gunther-Schultze,[9] that the capacity in certain cells might be due to the formation of a thin gas film, or sometimes a poorly conducting layer varying from one to a few molecules in thickness, this film acting as the leaky dielectric of a thin parallel plate condenser. In order to explain on the basis of this theory the change of capacity with frequency, it is necessary to assume that the thickness of this film changes. Since it is the thickness of this film that determines the capacity and only one thickness is possible at any particular time, we must draw the conclusion

[8] Haworth, Far. Soc. Trans. **16,** 365 (1920).

[9] Gunther-Schultze, Zeits. f. Physik **2,** 36 (1920).

that when two frequencies are simultaneously impressed on the cell the capacity shall be the same for each. This is in contradiction with the observed facts. The theories of Warburg[5] and Kruger,[6] however, predict just the results that have been found true. The back electromotive force of polarization in their theories is determined by the solution of a partial linear differential equation of the second order in two variables, time and distance from the electrode, with one boundary condition determined by the form of the impressed current and the other by the fact that the function must vanish at ∞. Now it is known that if the function defining the first boundary condition be expressed as a sum of simple harmonic terms, the solution of such an equation will be of the same form, the coefficient of each term being independent of the other. Applying this to the experiment given above, the back electromotive force corresponding to each applied sine current will be independent of the presence of the other and therefore each pitch will keep its own capacity in agreement with the results of these experiments.

It is well known that the resistance of an electrolyte and also its polarization capacity have considerable temperature coefficients. To guard against the errors due to possible temperature changes while the measurements were in progress, the cells were in the later experiments constantly kept in ice filled Dewar flasks.

Another possible source of error enters when it is desired to make the measurements of capacity shortly after the electrodes have been immersed in the electrolyte. After a cell has been set up, its capacity changes quite rapidly for some time, so that it is necessary to make a correction for this effect. It was found that the rate of change of capacity was almost constant over a short time interval and that the proportionate change was nearly the same for the different frequencies. A true temperature coefficient of capacity could therefore be determined for some mean frequency, and the correction computed for each measurement when necessary.

With these precautions and corrections, very consistent results could be secured as will be shown by the succeeding curves. Curves 2, 3, and 4 (Fig. 5) show the results of some tests taken with Jolliffe's cell using sulphuric acid. A diagram of the electrodes of this cell is shown in Fig. 3 under the heading "Cell A." In these curves, there are plotted against frequency the polarization capacity C in Wien's formula and the phase angle ψ.

In order to make the interpretation of the results easier, logarithmic paper has been used. The slope at any point thus shows the power relation that holds at that point between the capacity and frequency.

The data plotted in curve 2 were taken before the radio frequency bridge had been set up, and while Jolliffe was still taking data. There is a gap, therefore, between 6000 and 120,000 cycles per second, but the change in the slopes of the capacity-frequency curves between these points is very apparent. The slope of the capacity curves plotted on logarithmic paper, although changing at the low frequencies, is very nearly .3; at high frequencies it is close to .5, as also determined by Jolliffe in other cases, who found at these frequencies that the capacity was almost inversely porportional to the square root of the frequency. This curve also shows the increase in the phase angle which might have been expected from a comparison of the previous work in the low and high frequency ranges.

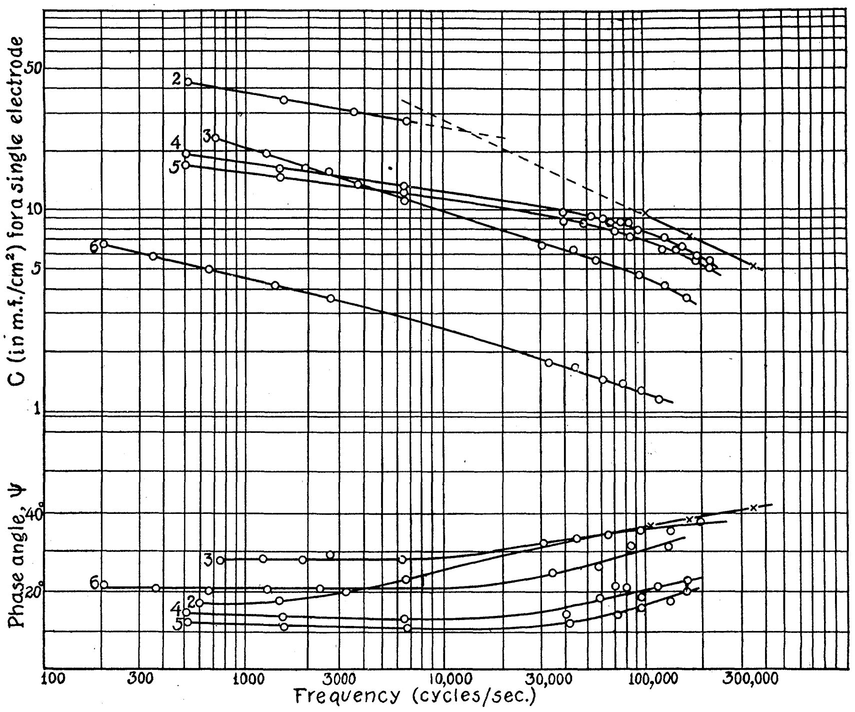

Fig. 5. Curves showing change in capacity with frequency. Curve 2, cell *A*, Pt -10% H_2SO_4; curve 3, cell *A*, Pt -1% H_2SO_4; curve 4, cell *A*, Pt -6% H_2SO_4; curve 5, cell *B*, Pt -6% H_2SO_4; curve 6, cell *A*, Au -1% H_2SO_4.

Curves 3 and 4 were taken with the same electrodes. The data for curve 3 were taken after the electrodes had been standing in the air for almost a year since last used. Before taking the data shown in curve 4 the electrodes were remounted and polished and then left standing in distilled water until used. Both curves 3 and 4 are very similar to 2.

There was some doubt as to whether the change in the stream lines as the frequency became higher might not have been the cause of the change in the law at the higher frequencies. A cell with an entirely different arrangement of electrodes was therefore built to test this supposition. It is shown in Fig. 3 as "Cell B." The capacity-frequency relation for this cell is shown by curve 5. It will be noticed that it is very nearly of the same form as the others.

Curve 6 shows the same relations for a cell of the Jolliffe type using gold electrodes in sulphuric acid. It will be noted that although the capacity in this case happens to be approximately one quarter as great as in the case of platinum the curve form both for capacity and phase angle is substantially the same.

CONCLUSIONS

1. When two harmonic alternating currents of differing frequencies are simultaneously impressed on a cell, the polarization capacity measured by means of either one is independent of the presence of the other.

2. The previous discordant observations giving change of capacity with frequency in a platinum sulphuric cell and gold sulphuric acid cell at low and high frequencies have been coordinated by showing that the law connecting capacity with frequency changes between 3000 and 100,000 cycles per second.

3. This change is due to a true polarization capacity effect and is not caused by change in stream lines in cell at high frequencies.

4. The initial capacity begins to change at the same potential for alternating current as it does for direct charge.

5. Confirming Jolliffe's[3] observations the Warburg and Kruger theories require modification in order to explain the change of phase angle and the increasing rate of change of capacity with frequency as the frequency is raised. These modifications in the theory will be discussed in an article to appear shortly.

In concluding the author wishes to express his appreciation to Professors C. C. Murdock and Ernest Merritt for their kindly help and genuine interest in the above work.

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