A STUDY OF THE EFFECT OF ADSORBED GAS ON THE HIGH-FREQUENCY RESISTANCE OF COPPER WIRE.

BY AUSTIN BAILEY.

SYNOPSIS.

Effect of Adsorbed Gas on the High-frequency Resistance of a Loop of Copper Wire.—This resistance is known to be greater than would theoretically be expected if the surface layers have the same resistivity as the core. The experiments described were undertaken to determine whether this increased resistance is due to gas adsorbed by the surface layer of oxide. A square loop, 60 cm. on a side, was formed by enclosing copper wires inside of glass tubes connected to a vacuum pump, and after several hours' preliminary heating and pumping, the wire was glowed, and then its resistance for radio-waves of 20 meters length was found to increase in 20 minutes by several per cent., though the residual pressure was only 10^{-5} atm. After successive glowings the effect became progressively less as the oxide layer disappeared. With higher pressures the increase to an equilibrium value came more rapidly. These results indicate that the gas adsorbed by the copper-oxide layer does increase the resistance, and suggest that possibly copper wire whose surface is covered with a thin layer of metal such as tin, might have a lower high-frequency resistance than oxidized copper wire of the same size.

Short radio-waves, of less than 20 meters were produced by using only the capacity of the oscillating triode tube in the high-frequency circuit. The wave-length was measured to within $\frac{1}{2}$ per cent. by use of a modified Lecher System, with a hot-wire galvanometer at a current loop. Currents in the square loop were measured by means of a loosely coupled circuit containing a special vacuum thermo-element with minimum coupling in the galvanometer circuit.

Adsorption of Gases by Copper Oxide and Copper.—The observations indicate that copper oxide readily absorbs gases at room temperature and liberates them when glowed, while copper does not.

An arc-type diffusion pump is described, which has an iron wire ballast resistance wound around the tube which conducts the vapor to the condensation chamber. This enables the pump to get into operation quickly.

INTRODUCTION.

AT very short wave-lengths, measurements made of the high frequency resistance of a one meter square loop of wire show a much larger value than that calculated from the formula for the resistance of a straight wire of the same length. The comparison between the observed and calculated values of the resistance of a one meter square loop of No. 18 B. & S. gauge copper wire are shown in Fig. 1.

This discrepancy may be due to a number of causes, one of which may be gas adsorbed on the surface of the wire. Langmuir[1] has pointed out that there is probably a very close packing of the gas molecules adsorbed

[1] I. Langmuir, PHYS. REV., *8*, 149 (1916).

on the surface of a metal. Such a condensation would doubtless alter materially the physical properties of the surface. Since at high frequency, a large part of the current will flow in a thin skin near the surface, a change in the high-frequency resistance would be expected if we changed the properties of that surface.

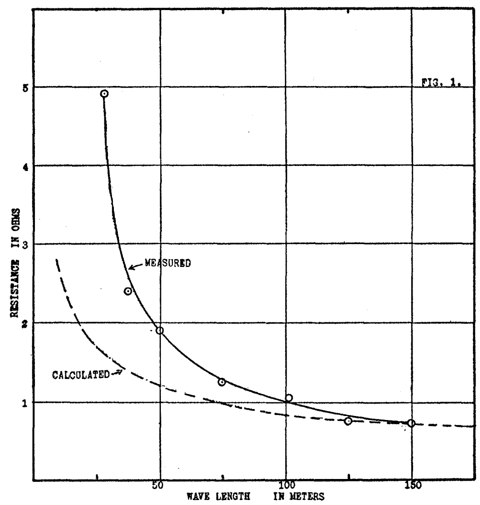

Fig. 1.

The experiments described below were undertaken in order to determine whether such a change of resistance due to a gas skin could be detected. The effect, if it exists, would be especially marked in some material which is known to adsorb gases strongly. Now Merton[1] has found that "copper strongly absorbs most gases." I, therefore, formed a square loop of copper wire, enclosing it in a glass tube so that the condition of the wire surface could be altered at will and measured the current flowing in the wire. A change in the resistance in the circuit, if capable of detection under the limitations of these experiments would then be indicated by a change in the reading of the galvanometer, since the electromotive force induced in the circuit was maintained constant.

Test Circuit.

The copper wire 0.045 cm. in diameter and about 240 cm. long was mounted at the center of a glass tube. The tube was made in two L sections which were so placed together as to form a square 64 cm. on each side, and were interconnected to the vacuum system as shown in Fig. 2. At the corner of each L tube the wire was supported by a Pyrex

[1] T. R. Merton, Chem. Soc. Jour., *105*, 645 (1914).

glass insulator I, connected at its far end to a spring S, which extended out into a small side arm which made equal angles with the sides of the L. By this means the wire was kept taut.

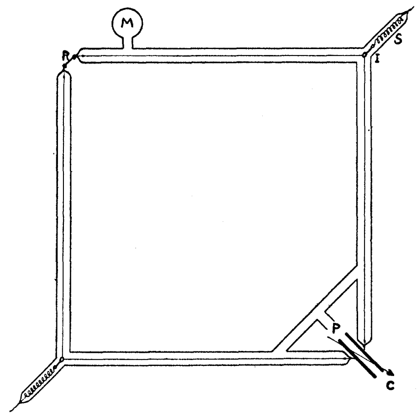

Fig. 2.

At the ends of each L the wire was attached to a piece of 1.05 mm. platinum wire and sealed out through the end, so that two of the corners of this square could be used for connecting additional apparatus. At one of these corners a single plate variable air condenser C was connected, and at the other corner an arrangement was made for connecting in various standard high frequency resistances, R, by means of mercury cups. Thus the resistance of the circuit could be measured by adding into the circuit known resistances.

Measuring Circuit.

To determine the change in current in the test circuit produced by different conditions of the wire, a circuit containing a 20 cm. loop of

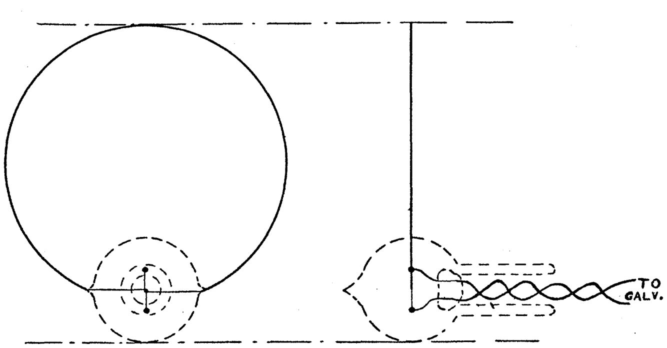

Fig. 3.

wire closed at its end by a thermo-element was inductively coupled to this circuit. The thermo-couple was especially designed and constructed so as to have as small currents as possible induced in the galvanometer circuit. This was done by making the plane of the loop at right angles to the galvanometer connections and by twisting together the insulated leads to the galvanometer as shown in Fig. 3. The copper-constantan element itself was mounted in a bulb which was evacuated to reduce thermal losses.[1] This increases the sensitiveness of the couple.[2] The measuring circuit being very sensitive could be loosely coupled to the test circuit and thus introduce only a very small resistance into the latter. At the same time it could be so placed that its loop plane was perpendicular to that of the oscillator circuit and thus reduce to a minimum direct action from the source of the power.

Oscillator.

A three-electrode vacuum tube connected as shown in the diagram (Fig. 4) was used as a high-frequency generator.

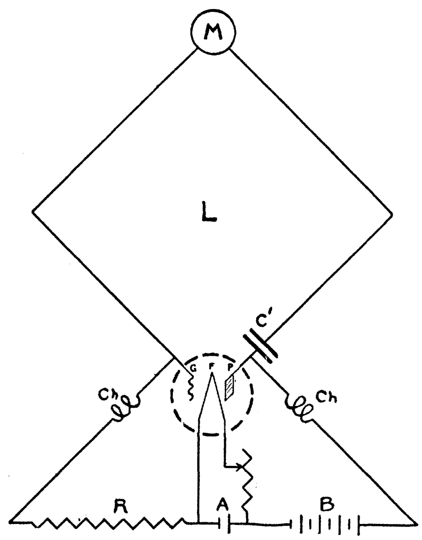

Fig. 4.

From the diagram it can be seen that the oscillating circuit contains only the capacity of the tube, in series with a blocking condenser C', of $\frac{1}{2}$ μf. and the inductance of a loop of wire 100 cm. square, L. The hot-wire ammeter M is placed at a current loop so that it will indicate that the circuit is oscillating. The chokes Ch were so adjusted that they

[1] I. Klemencic, Wied. Ann., 42, 416 (1891).

[2] P. Lebedew, Ann. d. Phys., 4 s., 9, 209 (1902).

were resonant at a frequency slightly greater than the frequency generated by the oscillating circuit. Such an adjustment makes the chokes have a high inductive reactance at the frequency used, and prevents the high-frequency current from going back into the direct-current circuits. A negative potential of about 100 volts is maintained on the grid by means of the grid-leak resistance *R*. Any desired potential on the plate could be obtained by means of a potentiometer contact on a resistance, through which the current from a 300-volt generator was maintained constant by means of a ballast lamp. This circuit, with the exception of the power supply, was mounted on a movable base, so that the angle of the loop with reference to the test circuit could be altered by rotation about two axes. The coupling could also be changed by altering the position of the oscillator with reference to the test circuit.

Measurement of Frequency.

A wave-meter was made of a variable air condenser with a maximum capacity of 670 $\mu\mu$f. and a single loop of No. 10 B. & S. gauge copper wire 20 cm. in diameter. The resonance point was indicated by a hot-wire galvanometer inductively coupled to this. By courtesy of the Commanding Officer, Radio Laboratories, Camp Alfred Vail, New Jersey, use was made of the Lecher system of parallel wires, constructed there by the author during the war, for the purpose of calibrating the wave meter. In Fig. 5 is shown the arrangement of the circuit. The single-

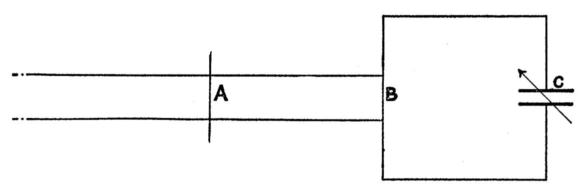

Fig. 5.

plate variable air condenser *C* was adjusted so that resonance with an outside source was obtained in the loop circuit. The resonance point was very sharp, due to the low resistance of the circuit, and was indicated by placing the hot-wire galvanometer at the point *B*. By this method the parallel wires were directly coupled to a circuit of fixed frequency and standing waves were produced on them. The wires were very long in comparison with the wave-lengths to be measured.

To measure the wave-length, a wire-bridge mounted on a long insulating handle was slid along the parallel wires until the hot-wire galvanometer at *B* showed a sudden decrease in reading to about half of its former value. Suppose this position was A, then the distance AB is some number of half wave-lengths. If the position A is the first such position found after leaving B, then AB is one half wave-length. A large number of current loops could be located in this manner, but since each position was more accurate than required, only two such determinations were made. While the method employed to determine the wave-length is similar to that described by Rubens,[1] the use of a small hot-wire galvanometer immediately at a current loop to indicate the positions of other current loops is believed to be of considerable advantage.

With an oscillating vacuum tube used to excite the system, the positions of A could easily be located so that the value of the wave-length thus determined was accurate within 0.5 per cent. The accuracy of this method for giving the correct indication of wave-length was checked down to 38 meters wave-length by a wave-meter composed of a standard inductance,[2] and a variable air condenser, both calibrated by the Bureau of Standards.

Vacuum System.

An oil pump which was capable of reducing the pressure to about 1 mm. of Hg was connected through a three-way stopcock to a drying tube containing P_2O_5. To the other end of the drying tube there was connected a system of two mercury condensation pumps in series. These pumps were made of Pyrex glass and connected by means of graded glass seal[3] to the McLeod gauge[4] and mercury trap. The design of the pumps is shown in Fig. 6. An arc[5] was used as the source of the vapor which was then conducted to the condensation chamber through a half-inch tube wound its entire length with No. 18 B. & S. gauge soft iron wire, with a cord, soaked in water-glass, wound between turns for insulation. To reduce the heat loss a covering of woven asbestos tape was wound on outside of the wire layer. The iron wire keeps the tube conducting the vapor warm[6] and at the same time acts as a ballast resistance for the arc. Tests made with this pump showed that its maximum rate of pumping was obtained when it consumed 300 watts and that the way in which this power was applied made no difference, *i.e.*, it could all be put into the arc, using external resistance, or it could be put into the arc and the resistance wound around the tube conducting

[1] H. Rubens, Wied. Ann., *42*, 154 (1891).
[2] Circular 74 of the Bureau of Standards, page 320.
[3] W. C. Taylor and Austin Bailey, Jour. Ind. Eng. Chem., *13*, 1158 (1921).
[4] Austin Bailey, Phys. Rev., *15*, 319 (1920).
[5] L. T. Jones and H. O. Russell, Phys. Rev., *10*, 301 (1917).
[6] Gaede, Ann. Phys., *4*, 46, 357 (1915).

the mercury vapor to the condensation chamber. The latter method of applying the power was, however, found to have the distinct advantage of making the pump effective sooner after closing the switch and at the same time of requiring a smaller current for operation.

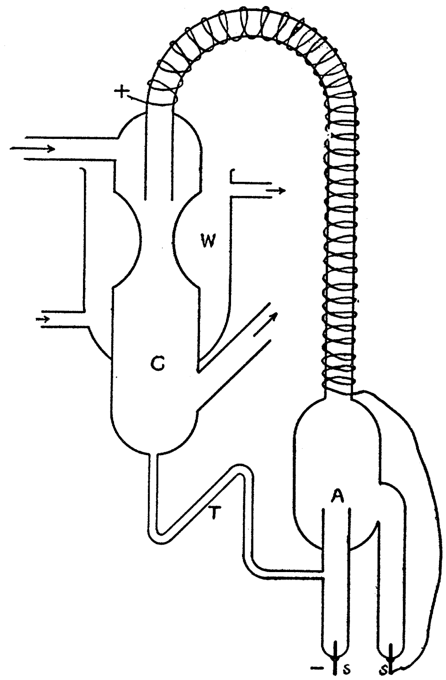

Fig. 6.

Observations and Conclusions.

With the apparatus arranged as described above, I first removed from the surface of the wire and the walls of the containing glass tube much of the adsorbed gas. This was accomplished by placing around the tube containing the wire an electrical resistance furnace and heating the glass to about 250° C., while at the same time the wire was raised to a much higher temperature by passing a current of about 2 amperes through it. This boiling-out process was continued for from three to four hours and then the tube containing the wire was sealed off from the pumping system. I then removed the furnace from the wire and allowed the apparatus to cool to the temperature of the room.

At the end of this process the surface of the wire was apparently covered with a layer of oxide. To remove any adsorbed gas from this surface layer, the wire was heated as hot as possible without burning out, and the observations begun immediately afterwards. The observations were continued until there appeared to be no further change in the resistance of the wire. Expansion of the wire caused by the increase in temperature, temporarily changed the inductance of the circuit. To compensate for this change, the circuit was constantly retuned during the cooling of the wire by adjusting the variable condenser C shown in Fig. 2. This adjustment was made at a distance from the circuit by means of a cord wound around the condenser handle, which enabled the observer to tune accurately without influencing the circuit by the close proximity of his body. The position of the observers remained fixed during each set of observations.

The attached curves show the results of several such runs. Fig. 7 shows successive runs on a wire which had previously been boiled out as described above. Two heatings of the wire to red heat were made to drive off adsorbed gas. This raised the pressure in the tube to about 4×10^{-3} mm. of Hg as indicated by the appearance of the discharge through the tube from a spark coil. One day later the wire was again heated red hot and beginning twenty minutes later the series of observations shown in Fig. 7 were made. The initial decrease in the resistance

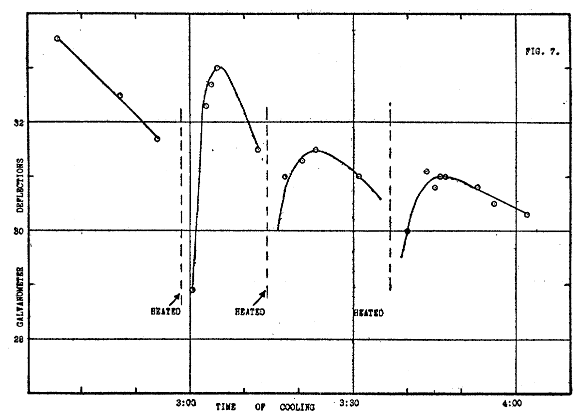

Fig. 7.

of the wire, shown by the rising portion of the curves, is obviously due to the cooling of the wire, for the tests made of the time required to obtain a maximum reading with the temperature of the test circuit constant proved that this gradual increase could not be due to the sluggishness of the measuring circuit. The subsequent decrease of reading is attributed to the readsorption of a film of gas by the oxide surface. As this takes place slowly at low pressures the galvanometer deflections go through a maximum, showing that the wire has a decreased resistance for a few minutes after the wire has cooled and before the gas has had time to be completely readsorbed. The progressive decrease in the ordinates of successive curves in the series shown in Fig. 7 is probably due to the discharge of the storage battery of 40 amp.-hours' capacity which was running the motor-generator and discharging at an 8 amp. rate. The increase in the brightness of the appearance of the wire after successive heatings indicated that the flattening out of the maximum was probably due to the removal of the oxide covering, thus decreasing the asdorbing surface.

The same wire used in Fig. 7 was heated in the resistance furnace again for four hours at about 250° C. and the appearance of the wire surface changed from a bright copper color to a reddish brown, showing that the oxide layer which had been decomposed by the heatings previously given to it had been partially reformed. The behavior of this wire, plotted in Fig. 8, was similar to that shown in Fig. 7. No quantita-

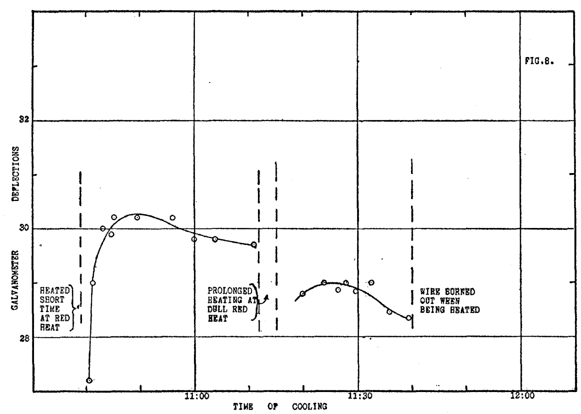

Fig. 8.

tive comparison can be made between these two figures or those following because of changes made in the position of the measuring circuit. Unfortunately the wire burned out during the third heating and a complete series could not be obtained.

The curves plotted in Figs. 9 and 10 are made with a different wire. Previous to the first curve plotted in Fig. 9 the wire had been boiled out and sealed off in a tube, and had been allowed to stand several days. The pressure in this tube was not as low as in the tube previously used. An interval of $7\frac{1}{2}$ hours elapsed before the first curve in Fig 9, during which time the storage battery was recharged. The curve following this charge of the storage battery is very erratic and full of accidental variations but it shows strong indication of a maximum. The next curve is more consistent in its points and fewer abrupt changes in galvanometer deflections were observed.

On allowing the air to again fill the tube at atmospheric pressure no marked change occurred. (See Fig. 9.) After heating the wire in air

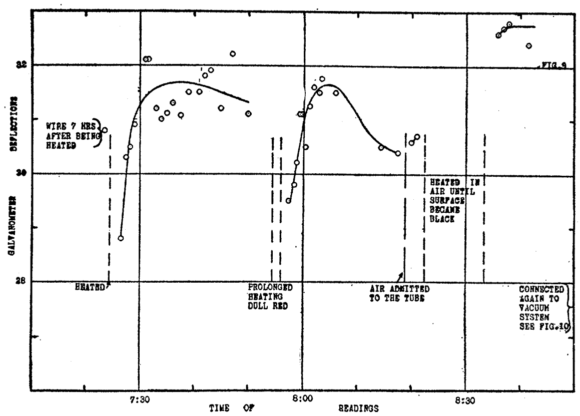

Fig. 9.

for ten minutes its surface appeared almost black, due undoubtedly to the formation of cupric oxide, CuO. Immediately after the heating current was turned off the oscillator was started again and observations made of the galvanometer deflections. These show a slight indication of a maximum. If this is a true maximum it is probably due to the same cause as before but is much sharper because the wire was initially at a lower temperature, could cool more quickly, and would probably readsorb gas more rapidly at atmospheric pressure.

The oscillator was again stopped, the tube connected to the vacuum

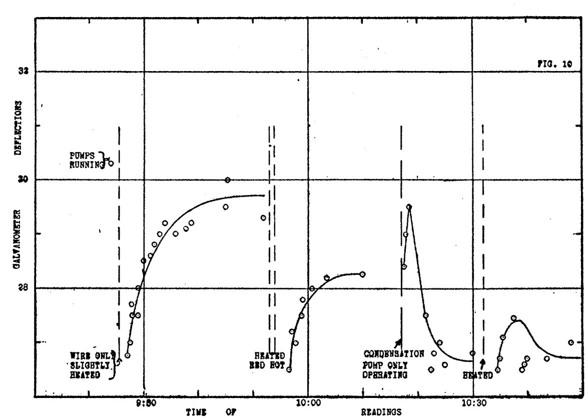

Fig. 10.

system and the pressure reduced to 3×10^{-4} mm. of Hg. The next two curves (Fig. 10) taken while the pumps were running, shows no maximum, probably because at this low pressure the gas was readsorbed more slowly by the oxide layer after heating. After the second heating at this low pressure the wire was apparently covered with the red oxide, Cu_2O. When the mercury condensation pumps were turned off and the backing pump still kept operating, the pressure gradually increased. The mercury in the pumps was so hot that it continued to go over and condense for some time after the current was turned off. This continued operation of the mercury pumps thus allowed the pressure to increase gradually. The first abrupt rise of the third curve shown in Fig. 10 may be due to some cause connected with stopping the operation of the mercury pumps, since the circuit at this frequency is very subject to variations from slight changes in nearby circuits. The final decrease of the galvanometer deflection however is probably due to the readsorption of the gas as the pressure increased.

Any single curve taken by itself would probably have little or no significance owing to the large fluctuations in the readings, due to accidental influences, but all the curves taken together strongly indicate: (1) that gas is readily adsorbed by copper oxide, and is easily liberated by heating, (2) that copper either does not adsorb gases as readily or that the adsorbed layer is not as easily liberated from the copper by heating, (3) that the resistance of the wire to high frequency currents is increased by the presence of the gas skin.

The "precipitated copper" as used by Merton was doubtless largely cuprous oxide as he describes it as "very dark brown in color," and as "prepared by reducing a solution of the copper salt." As is well known Cu_2O is prepared in this way. Finely divided copper can also be prepared in this way by the addition of suitable reducing agents such as $N_2H_4H_2O$. His statement that "if the copper is too strongly heated, it undergoes a change in color and loses its absorbing power," would also tend to show that the "precipitated copper" was largely Cu_2O and that on heating too strongly it underwent a chemical change, probably becoming metallic copper. Thus interpreted, his results are in entire agreement with the conclusions given above.

Copper wire when used commercially is doubtless covered with a thin layer of oxide, which strongly adsorbs gases, and which therefore according to the above results increases the resistance of the wire. Covering the surface of the wire with some metal which does not easily oxidize and at the same time does not appreciably adsorb gases would probably decrease the resistance of the wire. Possibly tin-covered copper wire would prove to have a lower high-frequency resistance than copper wire of the same size.

In closing, I wish to express my keen appreciation of the interest shown and encouragement given in this work by Professor Ernest Merritt and of the coöperation of Professor R. C. Gibbs in obtaining the material necessary to work out this problem. The advice and suggestions given by other members of the Department of Physics throughout the progress of this research is also greatly appreciated. Likewise, I wish to acknowledge the generous assistance which I have received from Professor Ernest Merritt and Doctor Gordon S. Fulcher in preparing this material for publication.

Cornell University,
June, 1920.