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A STUDY OF THE ELECTRICAL CONDUCTIVITY OF GLASS

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June 7, 1926

*W. Worden Day*  
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A thesis, presented to the Department of  
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in Chemistry by

W. Worden Day

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June 7, 1926.



# A STUDY OF THE ELECTRICAL CONDUCTIVITY OF GLASS

## INTRODUCTION

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This work was undertaken with the view of finding the alternating-current resistance of a specimen of soda-lime glass, and of determining how it changes with time, temperature, and amount of current passed. In all runs, we have restricted our work to the case of a one to one replacement of sodium ions for sodium ions by using a fused mixture of sodium-nitrate and sodium-nitrite as the electrolyte which makes contact to each side of the glass. Electrodes of both platinum and nickel were used to make contact with the fused salts.

## HISTORY

It has been known for a long time that glass at high temperatures will conduct electricity, but definite knowledge as to the process of this conduction was not obtained until 1884 when Warburg<sup>1</sup> definitely established the fact that it is electrolytic in nature. He showed that the current is carried by ions which



move through the glass. Warburg used mercury electrodes in his experiment and found, upon passing a direct current through the glass, that a layer of very high resistance was formed at the anode surface.

This theory was confirmed by Le Blanc and Kirschbaum<sup>2</sup> who, repeating Warburg's experiments, came to the conclusion that glass is ionized to about 80% at a temperature of 250 degrees centigrade. They also concluded, since the conduction is accompanied by a transfer of matter, that the process is electrolytic and due entirely to the movement of the sodium ions. The speed of this motion in soda-lime glass was found to be  $1 \times 10^{-8}$  centimeters per second at a temperature of 250 degrees centigrade. They found, also, that when the current is reversed, the original glass can be regenerated.

Other investigators have since conclusively proved, in case of soda-lime glass, that conduction is effected by the mobile sodium ions and that the cumbersome silicate ions are nearly immobile and therefore do not enter into the process.<sup>3</sup>

Much work has since been done in an attempt to accomplish conduction through soda-lime glass by



replacing the sodium ions with ions of other metals. Tegetmeir<sup>4</sup> worked with amalgams, whereas Heydweiller and Kopfermann<sup>5</sup> used fused salts as electrolytes. After replacement, they observed color effects which they attributed to the presence of the metal in a colloidal state. They also noticed that the resistance increases as the electrolysis continues, and they explained this fact with a theory that the resistance of the glass changes with the solubility of the replacing ion.

Working with the replacement of sodium in soda-lime glass with other metal ions, Kraus and Darby<sup>6</sup> found that the resistance increases rapidly as the electrolysis continues, and that the glass becomes completely permeated with fine cracks. These men also found that sodium enters the glass very readily, and that no change in weight occurs as the process continues----- indicating that it is a case of a one to one replacement of sodium ion for sodium ion.

The effect of temperature upon the conductance of soda-lime glass was studied by Rowe<sup>7</sup>, who found that the conductance increases exponentially with the temperature, but that the continual maintenance of the glass at a high temperature causes a decided increase in

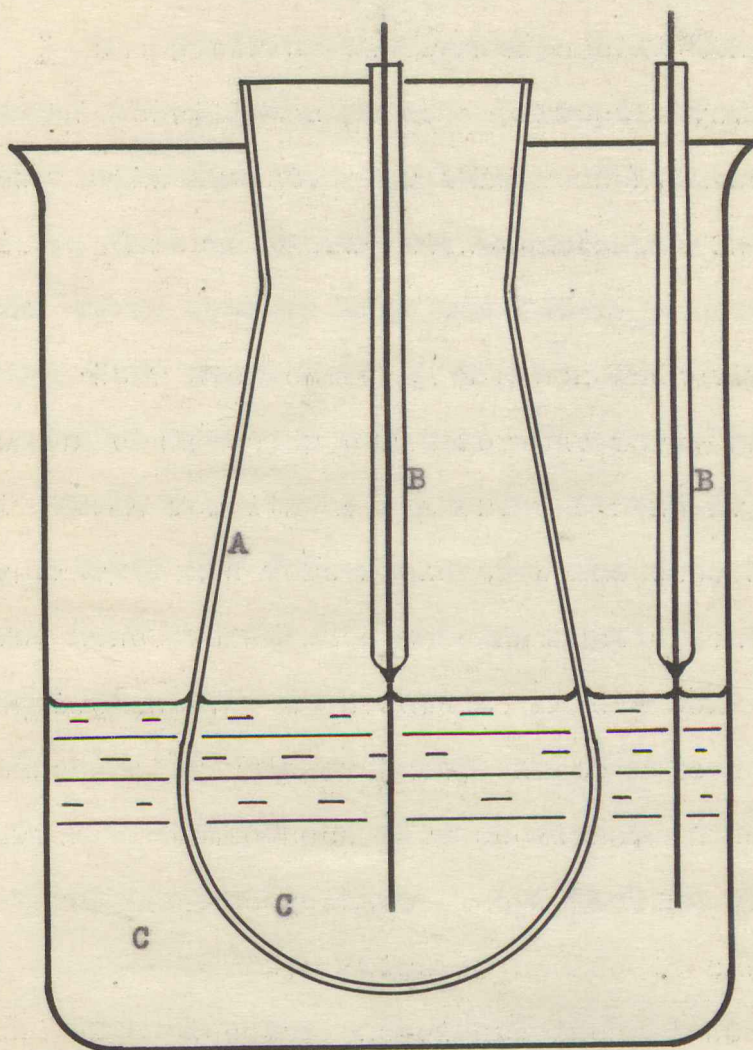


the resistance. For example: a sample of glass 1.17 centimeters thick, maintained at a temperature of 257 degrees centigrade for a period of twenty-four hours, increased its resistance by 1800 ohms.

In 1925, Engel<sup>8</sup> carried out a series of experiments on this subject and showed that the replacement is total in the case where sodium is substituted for sodium. The amount of replacement and its resultant effect upon the conductance of the glass is dependent upon the nature and solubility of the replacing ion. In every case the resistance of the glass increases.

The present work was undertaken with the hope that some accurate data could be obtained as to the absolute resistance of soda-lime glass and as to the way in which this resistance changes with respect to time, temperature and amount of current passed. We believe that we can thus clear up numerous questionable features of the work that has already been done.

CONDUCTIVITY UNIT



A--Conductivity glass.

B--Electrodes.

C--Electrolyte (sodium nitrate and  
sodium nitrite).



### APPARATUS

In attacking this problem from the experimental standpoint, certain features of previously described apparatus were employed. The glass used was in the form of unfinished incandescent lamp bulbs. We chose these because they would have properties identical with those used by Engel<sup>8</sup>, and also because they would be more uniform than any other form of glass. These bulbs were suspended in a bath of fused sodium nitrate and sodium nitrite; the eutectic mixture was used because its melting point is much lower than that of either salt alone. Some of the same fused mixture was placed inside the bulb and contact was made with the liquid on each side of the glass by means of platinum electrodes. For part of the work, nickel electrodes were used.

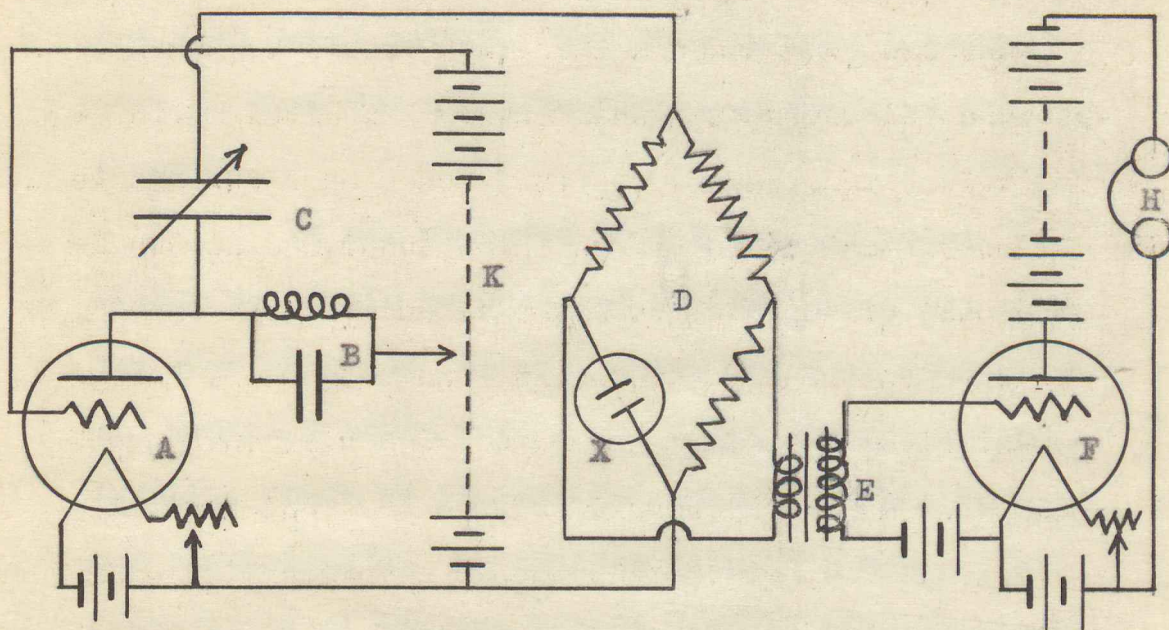
The unit just described was placed in an air thermostat which is electrically heated. A motor-driven fan continually agitates the air within the thermostat and the temperature is maintained constant within one degree by means of a mercury control. A complete description of the furnace will not be given here.

A high frequency sine wave oscillator was constructed, making use of a Dynatron vacuum tube.



PLATE I.

CIRCUIT DESIGNED FOR HIGH FREQUENCY RESISTANCE MEASUREMENTS



A--Dynotron (oscillator).

B--Tuned circuit to regulate frequency.

C--Variable condenser to regulate output.

D--Non-inductive Wheatstone's Bridge.

E--Permalloy transformer (audio frequency).

F--Pliotron (amplifier).

H--Phones.

K--150 volt "B" Battery.

X--Conductivity Unit.



PLATE I shows wiring diagram of oscillating circuit. This oscillator gives a perfect wave, but has very small output. For this reason, a second tube is used for amplification---as shown in same diagram.

It was expected that a non-inductive bridge box could be procured for our work, but when the time came for its use, there was none available. All ordinary boxes were found to be hopelessly inductive, hence we started to construct a box to suit our requirements. We decided to make a box using resistances of varying values, and to make settings by shorting out the necessary sections. A number of units were made according to the following method:

First, a wire is sealed to each end of a piece of one-eighth inch glass rod which is about one inch in length. The surface of the glass is etched or ground so that a smooth, fine line can be drawn on it with a lead pencil or piece of hard carbon rod. Connection is made between the wire and graphite mark by means of a cap of aqua dag which is painted over the ends of the glass.



These resistances are non-inductive and can be made with any desired resistance between one hundred ohms and fifty million ohms (.0001 to 50 megohms). After they have been completed thus far, they are baked until thoroughly dry and sealed into a glass tube. This keeps the moisture away and, therefore, makes the unit very constant and dependable. It was found that the construction of such a box would require a length of time greater than that at our disposal, so the work was turned into other channels. Volt-ampere readings were taken on both alternating and direct current and much interesting data was obtained in this manner.

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### RESULTS

Rowe<sup>7</sup> pointed out that the resistance of a piece of glass changes if the glass is maintained at a high temperature for a long period of time. We made careful resistance calculations from data obtained. over a period of ninety-nine hours, on a certain



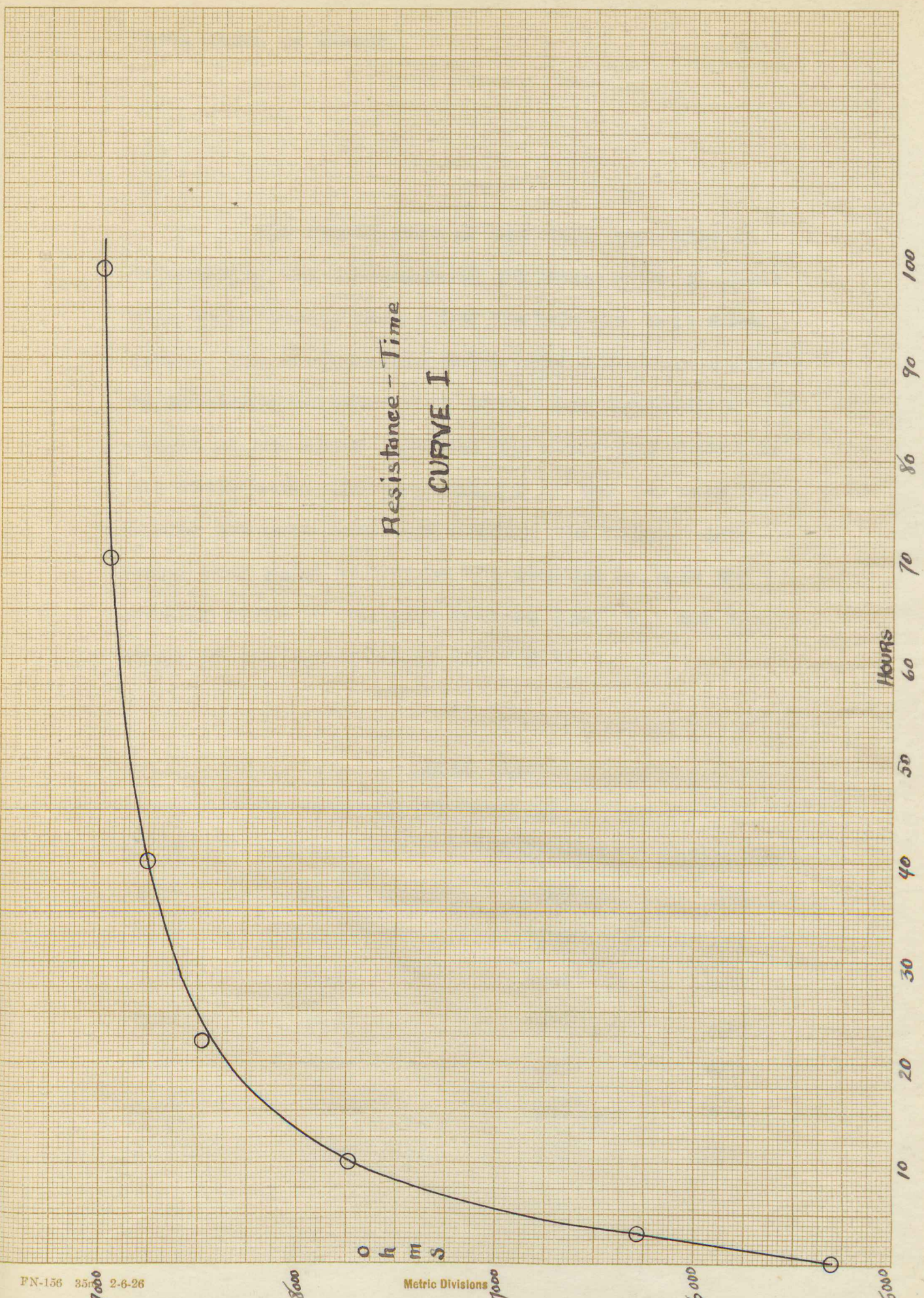
specimen of glass. Voltages were applied only long enough to take readings and then the circuit was shorted until the time came to take the next reading. We used the same potential in every case and kept the temperature constant throughout the experiment.

TABLE I.

<u>Temperature</u>	<u>Time</u>	<u>E.M.F.</u>	<u>Current</u>	<u>Resistance</u>
(Degrees Centigrade)	Hrs.	Volts	(Micro- amps.)	Ohms
276	0	.735	137	5360
276	3	.735	111	6350
276	10	.735	94.7	7750
276	22	.735	86.6	8470
276	40	.735	83.7	8780
276	70	.735	82.2	8930
276	99	.735	80.6	8990

(Nickel  
electrodes)







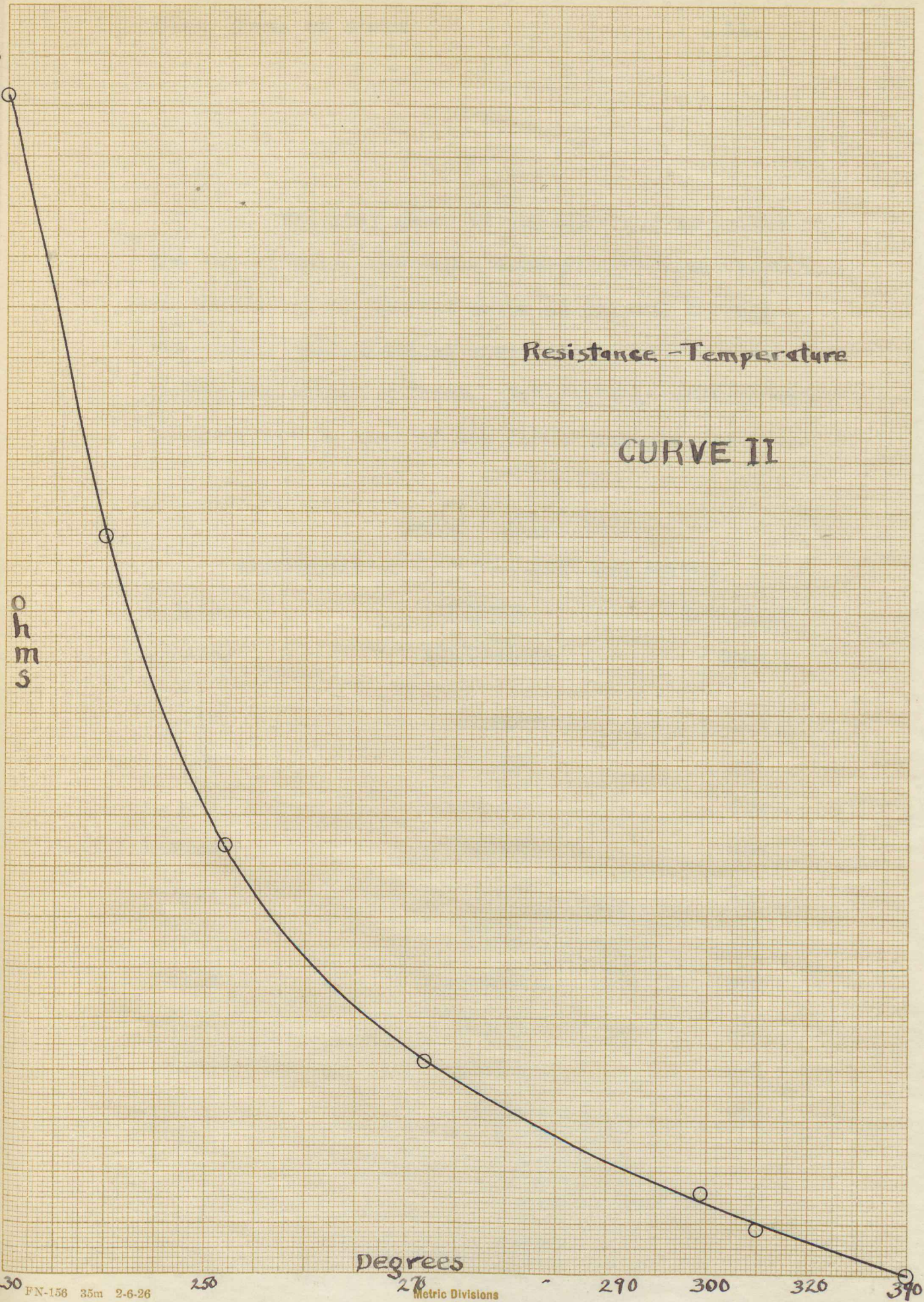
The second part of our work consisted in determining the variation of the resistance of glass with temperature, when other factors are kept constant. Two thermometers which were carefully corrected against each other were used. One thermometer was placed in the inner bath and the other was placed in the outer bath; the temperatures of the two were absolutely the same when each reading was taken. The range over which we worked was limited by both the melting point of the salt mixture ( $230^{\circ}$  C.) and the range of the thermometers ( $360^{\circ}$  C.).

TABLE II.

A. C. Readings

<u>Volts</u>	<u>Milli-amps.</u>	<u>Temperature</u>	<u>Resistance</u>
3.47	17.3	$340^{\circ}$	200
3.47	14.0	$310^{\circ}$	247
3.47	12.2	$299^{\circ}$	284
3.47	8.47	$272^{\circ}$	409
3.47	5.56	$252^{\circ}$	623
3.47	3.74	$240^{\circ}$	925
3.47	2.5	$230^{\circ}$	1387





Resistance - Temperature

CURVE II

ohms

Degrees



The last phase of our work was to follow the way in which the resistance changes with respect to the amount of current which is passing through the glass. Calculations were made with both alternating and direct current. Polarization effects were balanced out in case of the direct current readings.

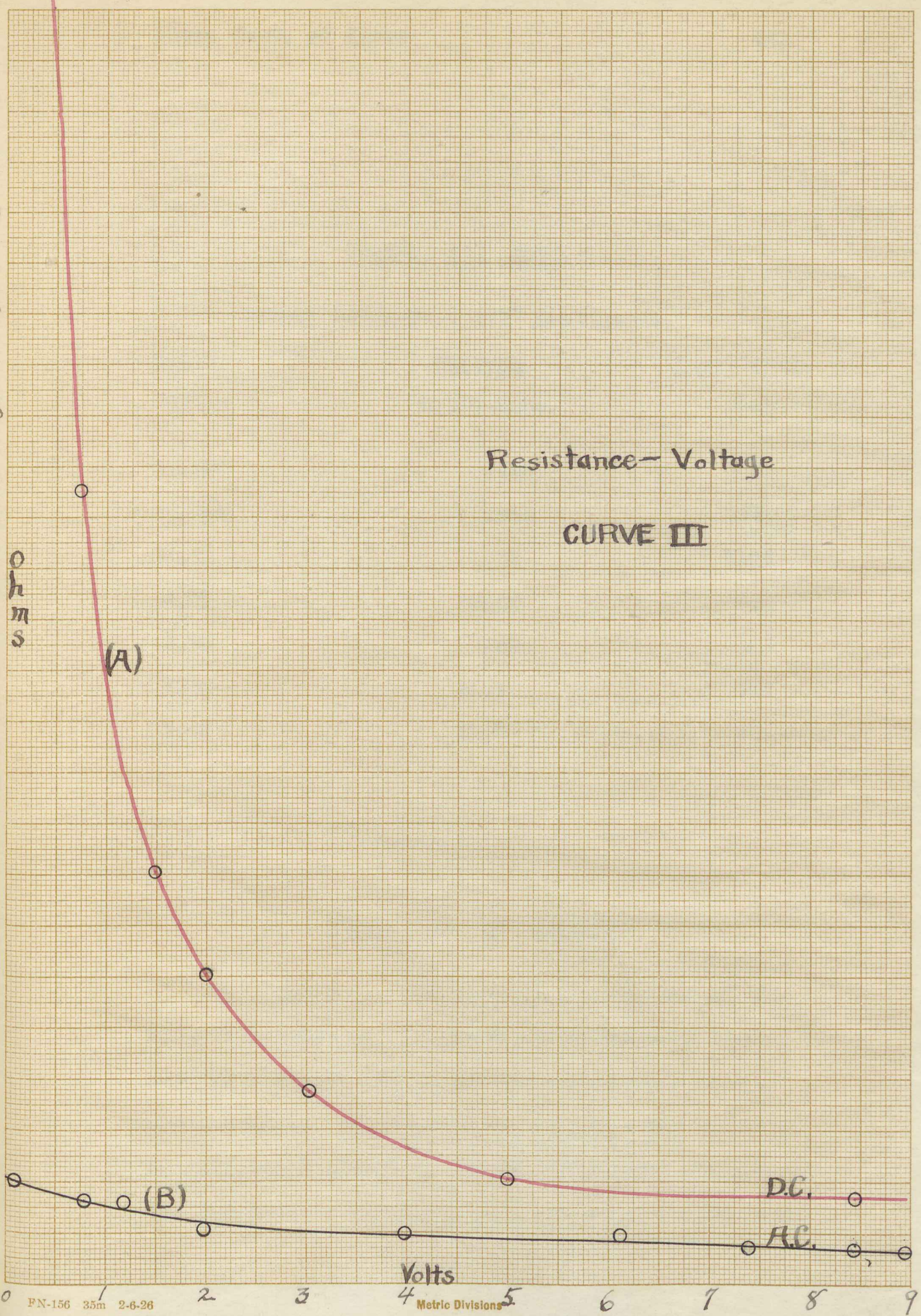
TABLE III.

ALTERNATING CURRENT----275<sup>0</sup> Centigrade

<u>E.M.F.</u>	<u>Current</u>	<u>Impedance</u>
(Volts)	Milli-amps	Ohms
.10	.194	515
.40	.85	471
.70	1.52	462
1.12	2.45	457
2.00	5.40	400
4.00	10.03	399
6.28	15.80	398
7.42	19.80	375
8.48	22.90	370
8.97	24.90	366



IF SHEET IS READ THE OTHER WAY (VERTICALLY), THIS MUST BE LEFT-HAND SIDE.  
THIS MARGIN RESERVED FOR BINDING



Resistance - Voltage

CURVE III

ohms

(A)

(B)

D.C.

A.C.

Volts

Metric Divisions

0 PN-156 35m 2-6-26 2 3 4 5 6 7 8 9



(TABLE III CONT.)

DIRECT CURRENT-----275° Centigrade.

<u>E.M.F.</u>	<u>Current</u>	<u>Resistance</u>
Volts	Milli-amps.	Ohms
.390	.125	3120
.750	.415	1850
1.50	1.36	1102
2.00	2.22	900
3.05	4.60	685
5.02	10.0	502
8.47	19.6	433

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### DISCUSSION OF RESULTS

CURVE I was plotted from values of the D.C. resistance of the glass and shows that there must be a change in the internal structure of the glass when its temperature is raised. The increase in resistance cannot be due to polarizing effects in the electrolyte or electrodes because, between read-



ings, the unit was short-circuited and, while readings were being taken, the electrodes were kept in motion. This motion agitated the electrolyte and thus overcame any localized concentration differences which might develop from the electrolysis.

CURVE II was made from data on the alternating current impedance of a specimen of soda-lime glass. Since the potential difference was constant throughout, the capacity effect is the same for each reading and, therefore, does not affect the shape of the curve. It shows that the resistance drops rapidly to a low value as the temperature is raised. The resistance of a piece of glass of an area of (approximately) 30 square centimeters and of a thickness of .1 cm. is only 200 ohms at 340° Centigrade.

CURVE III-A shows how the resistance, determined by D.C. measurements, varies as the potential difference increases. Polarization effects are cancelled out by stirring and taking readings in both the direct and reversed directions, and then taking the mean value of these readings. We believe that the decrease in resistance is caused by heating in the glass. The reason why CURVE III-B does not show so great a change is that there is an appreciable



capacity factor to be considered. This capacitative current varies directly as the applied voltage and tends to counteract the internal heating effect. If this capacity could be eliminated, CURVES III-B and III-A would be very nearly parallel.

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#### SUMMARY

We have made a large number of resistance measurements using soda-lime glass and have shown that the resistance varies exponentially with respect to the time during which the glass is maintained at a high temperature. The resistance reaches a saturation value after about seventy hours.

We have shown, also, that the resistance decreases exponentially: first, as the temperature increases; second, as the applied voltage increases; third, as the amount of current carried by the glass increases.

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