ELECTRICAL CONDUCTION AND CRYSTALLIZATION PHENOMENA IN THIN LEAD FILMS AT TEMPERATURES BETWEEN 14°K AND 500°K

Thesis by

Edgar L. Armi

In Partial Fulfillment of the Requirements for the
Degree of Doctor of Philosophy

California Institute of Technology
Pasadena, California
1941

Abstract

This thesis presents a description of the design of and the results obtained with an apparatus constructed for producing thin metal films, by the method of evaporation in high vacuum, and to study the electrical behavior of such films at various temperatures.

Experimental investigations were carried out in a temperature range from 14°K to 500°K. Electric resistances were measured with adequate accuracy between 10^2 and 10^{15} ohms. Evaporation rates against furnace temperatures were determined by weighing of deposits and were found to be in good agreement with specific predictions of Kinetic Theory.

Formation and destruction of electric conductivity were analyzed in their dependence upon temperature, time and vacuum conditions. Part of the experiments were carried out at temperatures low enough to prevent crystallization, thus permitting to study the undisturbed process of the building up of metallic conduction. Formulas are suggested to describe the behavior of the films investigated.

TABLE OF CONTENTS.

I. Introduction.

The literature on the subject of thin metal films numbers a few hundred and among these several excellent surveys of the field containing quite complete bibliographies; attention in this regard may be drawn to the papers of Reinders and Hamburger,(20,11) Richter,(21) Lange,(17) Anderson,(1) and Foster(8). The author of this thesis does not intend to present a discussion of similar scope; only a few essential facts will be sketched briefly before he enters upon the description of his experimental work.

The measurement of electric resistance offers a singularly sensitive tool for the registration of structural alterations in a film; indeed, changes of resistivity by a factor 10^{12} within a few minutes are observed - a "magnification" of an order rarely found in any field. On the other hand, the interpretation of the experimental results is rather involved, due to the indirect approach of the method, the extreme difficulty of standardizing experimental conditions of the occurring high complexity and therefore, unfortunately, the contradictory character of experimental data found in the literature.

Thin films can be produced easily by electrolysis or chemical processes, however more direct methods of depositing are preferred. Cathode sputtering has played a very important role in this field, most earlier workers having used this method. But with the progress of high vacuum technique, evaporation has become almost standard, the reason being that thin films are quite sensitive to even traces of gases, (see the systematic investigation by Johnson and Starkey,(12) also Kirchner,(13) Lovell(18)), so that evaporation in extreme vacuum seems to be the only method furnishing reasonably uncontaminated films.

Thickness determinations of deposited films are not very satisfactory; since optical etc. methods fail at the small dimensions involved (down to 1 Å and less), it is usual to weigh the films or to determine their mass by semi-microchemical methods. The thickness is then calculated from mass and area of the deposit, assuming the density of the metal in a film to be the same as in bulk. That this assumption however is hardly justified, since films display a porous structure, is shown for thin films by Reinders and Hamburger(20) and for thicker films by Beeck, Smith and Wheeler(5).

Numerous are the investigations on the structure of films by X-rays and electron diffraction. While these methods give very accurate results, the application of such high-energy beams affects and alters the object investigated, in particular causing crystallization and favoring growth of already existing crystallites in the film exposed - see Trillat and Oketani,(28) Was and Tol,(29,30) Kramer(5).

While there is agreement about the general character of the resistance-thickness curve, controversies are still raging on all further details. It seems that, with the development of the technique of extremely high vacua and the use of low temperatures (see Lovell,(18) Appleyard,(34) Bristow(6)), the "critical thickness," at which conductivity sets in, is being pushed back to values of less than monomolecular dimensions. However, substrata and specific properties of the metals chosen for depositing play roles yet to be clarified.

The subject of temperature effects is specially controversial. While it would be tempting to embrace the ideas of Zahn and Kramer,(31,14,15,16) who postulate the existance of "amorphous" metal modifications with well determined transformation temperatures ("Umwandlungstemperaturen"), their experimental evidence, up to now, does not seem to be quite conclusive enough to prompt acceptance of these ideas. (See also Suhrmann and Barth,(23,24) Berndt,(25) Tammann(26).

It is the endeavor of the author of this thesis to contribute towards a clearer understanding of the mechanism of formation and destruction of conductivity in thin metal films. The investigation was carried out over a range of temperatures from 500°K down to 14°K (solid hydrogen). Lead was chosen as deposit metal for its relatively large vapor pressure at not-too-high temperatures and because, owing to its great specific mass and large atomic dimensions, its mobility and hence its rate of crystallization could be expected to be slowed down to negligibility at temperatures well within reach of this investigation, thus allowing to study the formation of metallic conduction without the masking effects of crystallization. It is intended, later on, to extend this research to other metals.

II. Description of Apparatus.

1. General.

In order to avoid, as much as possible, effects of gases present during deposition of the film, the method of evaporating in high vacuum was chosen. The lead, held in a crucible, was heated by an electric furnace to the desired temperature of evaporation. The metal atoms evaporated were collected on a glass plate at controlled temperatures. A shielding system cut out stray evaporation. The thickness of films deposited was determined by weighing. The method of measuring the electrical resistance was essentially the one described by Townsend,(27) compensating leakage across the film by an opposite potential and using a sensitive electrometer as null instrument.

Since liquid hydrogen had to be used extensively in some of the experiments, certain special precautions were necessary to eliminate the danger of hazards from handling that substance and influenced in a large degree the design of the whole apparatus.

Part of the equipment and apparatus is that used previously by Anderson(12) and Foster(8) for their work on the process of electric conduction and the author wishes to express his indebtedness to them.

2. Vacuum Apparatus and Manometers.

Pumps and Traps: A rotating oil pump (Hyvac, BL 80361C) was used as roughing pump, being capable by itself to reach a vacuum of 10^{-2} mm Hg or better. As high vacuum outfit, two mercury pumps were used in series. On the forevacuum side connections were made of glass and rubber hose, shellac coated; on the highvacuum side only glass and copper tubing was used, connections here were sealed with Picein wax. Wide bore cocks were used on the highvacuum side. A large glass balloon was included in the forevacuum side to increase the capacity of the system. Several stop cocks were inserted to separate the different parts of the system and to admit gases when needed. A vessel containing P_2O_5 was installed in the forevacuum to protect the rotating pump against contamination with water.

Two traps were provided, cooled with liquid air, one (for quart flask) immediately after the mercury pumps and a second one (for pint flask) directly below the main vacuum chamber. The liquid air for these traps had to be refilled about every 12 to 14 hours; continuous runs of a week and longer could therefore easily be carried out.

Vacuum Chamber: The main vacuum chamber had cylindrical shape, was 7 cm wide and 47 cm long, with a widening in the furnace region to about 9 cm. It possessed a large ground joint at each end and in its upper half was equipped with four small ground joints for copper plugs, to which were attached the wires for electrical and temperature readings. Of the two large ground joints of the main vacuum chamber, the lower (glass-glass, 6 cm diameter) was sealed with Picein wax, whereas for the upper (glass-metal, 7 cm diameter), after much experimenting and some damage due to sticking, a mixture of Airco Hyvac Stopcock Lubricant with graphite flakes was adopted and proved to be very satisfactory. The lower ground joint was cooled by a continuous stream of compressed air while the furnace was in use, thus preventing the Picein wax from warming up. Airco Hyvac Stopcock Lubricant was used on stopcocks in the forevacuum part, Apiezon Grease L in the highvacuum section (only here, because of its high price).

Manometers, General: Four types of manometers were used, for overlapping ranges: A simple U tube filled with mercury (400 to 1 mm Hg) was located in the forevacuum system, a McLeod manometer (10^{-1} to 10^{-6} mm Hg), was installed in the highvacuum system between the mercury pumps and the stopcock of the main vacuum chamber, while the vacuum chamber proper was equipped with an electrical discharge gauge (5 to 10^{-2} mm Hg), operated by a 6 volt battery and an ordinary Ford coil, and an ionization gauge (10^{-2} to 10^{-7} mm Hg). This multiplicity of vacuum measuring devices, located at different spots in the vacuum system, was not only very useful for precisely determining vapor pressures over a wide range, but was also extremely handy for occasional leak hunts, since it permitted to test separately the different parts of the system. While the U tube and the electrical discharge gauge need no detailed description, some additional information will be given on the two other gauges.

McLeod Manometer: The McLeod manometer, with ordinary quadratic scale from 10^{-1} to 10^{-6} mm Hg pressure, was connected to the vacuum system by wide copper tubing and could be separated from it by a wide bore cock. The glass ball had a volume of 215 cc, the capillaries a diameter of 1 mm. The mercury was pushed up by compressed air (available at a pressure of 50 lbs.); to regulate air pressure, a quarter inch needle valve was installed; only a small part of the air stream was used to lift the mercury column, most of it was let out by a bypass hole after traversing the valve. Though this arrangement was satisfactory by itself, a considerably finer adjustment was possible after installing a worm gear (ratio 1:20) on the needle valve.

Ionization Gauge: The set-up of the ionization gauge was essentially the one described by Simon(22) as method "B", with a Western Electric 101 J tube (experiments with other types of radio tubes were less successful). The emission current was easily controlled by adjusting the heating current, kept usually around 0.4 A (D.C. ammeter BL 8731). The heating current was furnished by a 6 volt battery, grid and plate current by a set of 5 Burgess radio "B" batteries. The emission current was measured by a Rawson double pivot "Multimeter" (BL 8245) with adjustable range. To read the ionization current, a Leeds & Northrup galvanometer (BL 80198) was installed

(16 ohms resistance, sensitivity 10.8 mm/μV, 50 ohms damping resistance used). The distance of the scale was so adjusted that, with an emission current of 0.50 mA, the reading in mm gave directly the pressure in 10^{-6} mm Hg (see graph). For higher sensitivity, a Leeds & Northrup Ayrton shunt (BL 8675) was provided, cutting down the sensitivity by powers of 10, thus permitting direct readings in 10^{-5}, 10^{-4}, etc., mm Hg. Calibration of the ionization gauge was carried out against a McLeod manometer in the region of 10^{-2} to 10^{-4} mm Hg (using a liquid air trap to condense mercury vapors) and extrapolated to lower pressures, since, as Simon(22) and others have shown, pressure and ionization current are perfectly proportional at these pressures.

3. Furnace, Shield and Shutter

Furnace: The furnace was constructed along the lines of the one described by Goetz,(9) however, since it was not intended to go up to very high temperatures, soapstone was used instead of magnesium oxide. The soapstone block was turned in a lathe and then baked for 40 hours in an electric oven at 1100°C. The inside of the inner piece was bored conically so as to receive the conically shaped crucible and had a small circular hole through the bottom for passage of the thermocouple wires; the outside of it was grooved to receive 35 turns of #20 Nicrome wire. The outer piece had cylindrical shape and fitted tightly over the inner part after the wire had been applied. Shrinkage during the outbaking process amounted to approximately 1%. Two nickel bands around top and bottom of the furnace insured both mechanical stability and electrical contact with two heavy copper wire electrodes. The crucible itself was turned from cast iron, with slightly conical walls and a few threads at the top; a rod provided with matching threads was used to insert the crucible into or take it out of the furnace.

Thermocouple: Through the hole in the bottom of the furnace, a copper-constantan thermocouple was inserted into the lower part of the crucible, protected by a small iron tube. In spite of this seemingly good location, almost in the center of the furnace, the indications of the thermocouple were several percent low (in the working range of around 400 to 600°C) and had to be corrected for that amount. The thermocouple had been calibrated beforehand, at the boiling point of water and the melting points of tin, lead and aluminum. The millivoltmeter connected for the temperature readings was a Siemens & Halske precision instrument (courtesy Dr. A. Goetz).

Shield and Furnace Shutter: In order to limit the spreading of the molecular beam and thus avoid stray deposits of metal, a shielding tube (made of a 35 mm glass tube, 10 cm long), was fastened to the top of the furnace; it was so designed in its dimensions as to permit the molecular beam to cover amply all the area desired to be exposed to it, without using the penumbra region. Cutting out of the penumbra by inserting a stop with a small opening at the "focus" was not considered desirable, because this would have caused "imaging" of the emitting surface onto the film with all possible inhomogeneities of the former. The shielding tube had a shutter at its top, consisting of a circular nickel lid turning on hinges at one side, with a small counterweight of soft iron. By the aid of an electromagnet, this shutter was very easily opened and closed from the outside.

Temperature Control: A 15 ohm slide wire rheostat (BL 8748), together with a set of Polarcub heater resistors and a Weston A.C. ammeter (BL 80156) permitted a precise adjustment of the furnace current over a wide range. However, lack of constancy in the voltage of the current supply was quite disturbing; despite constant watch of ammeter and thermocouple millivoltmeter and readjustment of the furnace current, the accuracy of deposit rates reported is likely to be affected by this source of errors.

4. Film Support and its Temperature Control.

Film Support: All films were deposited on circular micro cover glasses (Braun Corp. "Diamond Brand", 22 mm diam., 0.2 mm thick), which had been subjected to a thorough cleaning in acid, distilled water and solvents before being inserted in the apparatus. In order to insure low-resistance contact with the electrodes, platinized areas were prepared between and over which the film was deposited; strips of thin tin foil, folded several times, were interposed between platinum layer and electrodes and the latter then screwed on, under gentle pressure, "Liquid Lustre for China" (Chapman-Bailey, Los Angeles) was found very satisfactory to obtain well platinized surfaces and was applied in several coats. Outbaking was done for several hours in a small electric oven at a temperature of about 400°C.

Shutter: In order to keep any particles from reaching the film support (a precaution important especially during the outgassing process), a shutter mechanism was placed immediately in front of the cover glass. It consisted mainly of a sort of small sled hanging on copper bars and carrying pieces of soft iron at both ends; upon application of an electromagnet from outside in one direction it would cover up entirely the glass plate, in the other direction it would give free a rectangular area, about 1.3 x 1.4 cm^2 between the electrodes.

Thermal Contact: While for room and higher temperature investigations mechanical contact of the glass plate with the well leveled backing was considered sufficient, special precautions were taken for low-temperature runs to insure good thermal contact with the cooling reservoir. A 1 mm thick plate of cast iron, of approximately the same thermal expansion coefficient as the glass used, was soldered to the bottom of the copper reservoir and covered with a fine solder film. The cover glass was platinized on its entire back (in the same way as the conducting strips on the front were prepared) and then electrolytically copper-plated. Between the so treated cover glass and the iron plate, a thin sheet of soldering metal was laid (it had been prepared by dropping liquid solder on a glass plate). After completing assemblage of the whole apparatus and having attained good vacuum, a high-frequency induction furnace was employed to raise the temperature up to around 250 to 300°C, thus soldering the cover glass to the backing.

High Frequency Induction Furnace: A coil of copper tubing wound around the outside of the vacuum chamber constituted the high-frequency induction furnace just mentioned, which was operated by a water-cooled double mercury spark gap. Since the latter had to work under streaming hydrogen, a simple mechanism was devised, the "bubble-indicator," which showed whether hydrogen was flowing and blocked admittance to atmospheric air in case of breakdown in the hydrogen supply. Before each run, the lines were flushed with hydrogen until a whistle at the exhaust gave the "hydrogen sound." The spark gap, together with some coils and condensers, was wired to the secondary of a G.E. 230/16500 volt 10 KVA transformer (EE 7). Intensity control was effectuated by a large variable water-resistance in the primary, in connection with ammeter (BL 8145) and voltmeter (BL 8052).

Electrodes and Thermocouple: The first set of electrodes employed consisted of two similarly shaped elastic copper pieces holding the glass plate from both sides. One of the electrodes rested on a little copper block making direct contact with the cooling reservoir, the other was fastened to a glass bridge and thus well insulated. This glass piece was shaped to the desired dimensions by hand grinding, and received several holes with the aid of a high speed drill. In order to create more symmetrical conditions for heat equilibrium, it was however found advisable to replace the uninsulated copper electrode by a less heat conductive material and therefore German silver was used instead, leaving out the copper block support entirely. From the insulated electrode, a copper wire led to one of the four copper plugs in the wall of the vacuum chamber. A copper-constantan thermocouple was located in the bottom of the cooling reservoir, its copper wire hard soldered to the inside of the copper tank and passing through the German silver filling tubes, its constantan wire also connected to one of the copper plugs; two of these were therefore in constant use leaving the other two available for additional thermocouples, etc.

Temperature Control Outfit: Temperature control was effectuated by keeping a reservoir at constant temperature and having heat or cold transmitted to the film in the way described further below. The reservoir was built of 2" copper tubing with copper bottom and top plates; all seams were hard soldered. German silver tubing, because of its small thermal conduction, was used for carrying the cooling or heating substance to the tank. A 2-tube system was used; a 1/8" diameter inner tube for the cooling liquids (liquid air, liquid hydrogen) and a 1/2" outer tube for the return of the cold gas; for heating, steam was admitted through the outer tube and the inner tube was used as water return. Copper gauze was placed inside the tank to avoid splashing of the cooling liquids during the filling. When heating to higher temperatures was desired, the high frequency furnace described above was applied; about 15 minutes' heating was required to raise the temperature of the copper tank from room temperature to 250°C.

To reduce the amount of heat radiation received by the film from the furnace, the distance furnace-film support was chosen rather large (16 cm); to avoid heat influx by conduction,the length of poorly conducting German silver tubing "insulating" the copper tank was also made large (13 cm). This entailed a quite elongated shape of the vacuum chamber, but the adiabasy thus attained was remarkably good; with a filling of liquid air, the reservoir remained at constant temperature for several hours.

Flow-Meter: As it was found desirable to determine quantitatively evaporation rates of liquid air and liquid hydrogen in the cooling tank, a "flow-meter" with three ranges was constructed, similar to the one described by Goetz,(10) but of slightly different dimensions. Two capillaries were of equal length (90 cm), but of different diameters (1 and 2 mm); the third range, for high evaporation speeds, had a 2 mm capillary, 12 cm long. As a rough calculation had revealed that turbulence phenomena were to be expected at least in the fastest range, an exact calibration was undertaken with both air and hydrogen. The hydrogen data were obtained by having the gas stream from a gasometer through the flow-meter, at different speeds, and reading volume lost against time elapsed. To calibrate for air, liquid air was placed in containers of various heat insulation qualities (thermos flask, thermos flask without silvering, metal can completely covered by wool, metal can partly embedded in wool, etc.), and the gas evaporated directed through the flow meter; the amount evaporated was determined directly by the loss of weight of the container, kept on a balance during the measurements.

As may be anticipated from the formula for Reynolds' number $R = usd/\eta$ (u velocity, s specific mass, d diameter of tube, η viscosity), turbulence effects are much more pronounced in the air curves than in the hydrogen curves; the specific mass of air being 14.5 times larger than that of hydrogen, the viscosity however larger only by a factor 2, the critical Reynolds number will be reached by an air stream at speeds about 1/7 that of hydrogen under otherwise equal conditions. Indeed, while the hydrogen curve III is just slightly bent upwards, the corresponding air curve shows, for higher speeds, an increase of pressure by almost a factor 2 over that to be expected under laminar flow conditions.

Vacuum Chamber and Temperature Control: As mentioned before, the vacuum chamber was closed at its upper end by a large metal ground joint (brass, 7 cm diameter, slope of walls 6°), provided with water circulation to keep the sealing stopcock grease near room temperature. It had been planned originally to use a 3-tube assembly to carry the cooling liquid across this large metal plug, thus assuring highest efficiency, since the two inner tubes would have carried liquid and gas in the two directions while the outer tube would have served to insulate by a vacuum space, thus eliminating all contact of the "cold" with the metal plug. In order however to simplify the construction and judging that strictest economy in the use of liquid hydrogen was not essential, since its supply was assured at this Institute, a 2-tube assembly finally was executed. Thus, the two German silver tubes coming from the copper tank passed through the plug, the inner tube German silver all the way up, the outer brazed to the wall of the metal plug. A short distance above the metal plug, an outlet was soldered to the outer tube; finally, at the top of the apparatus and insulated by a length of 12 cm German silver tubing, came the opening of the inner tubing, so constructed that it fitted the evacuated siphons used at this Institute for transvasating cold liquids. The connection to the siphon could be made vacuum-tight, thus permitting to lower the vapor pressure over the cooling liquid by the use of a high speed rotating pump; with this method, temperatures down to 14°K (solid hydrogen) were reached.

As the metal plug with its attachments had a considerable weight which it was considered dangerous to let act continually on the glass apparatus, a counter-weight was installed, with a steel wire running over pulleys, to hold the plug weightless in its place.

Using liquid hydrogen entailed the adoption of special precautions to eliminate danger of explosion. The major part of the apparatus was built into one of the "stations" described by Goetz,(10) with sloping roof and powerful ventilation. Switches, heaters, all sources of sparks, flames, etc., were relegated to the outside of this "station"; in fact, no unpleasant experience whatsoever, up to now, has sprung from the use of liquid hydrogen.

5. Electrical Measuring Apparatus.

The apparatus employed to measure the electric resistance of the metal films was the same as that described by Foster,(8) with only minor alterations. A potential V' charged a condenser (capacitance C) by leakage across the film; by applying an opposite potential V (moving slide wire resistances by hand as the leakage went on), this charge was compensated and a sensitive string electrometer (BL 9345) kept at zero. By Foster's derivation, the resistance of the film is $R = tV'(1 - t/2T) / CV$, which in most cases simplifies to $R = tV'/CV$, as $t/2T \ll 1$.

t	time read on a stop watch (BL 2316)
V	compensating potential read on a Weston D.C. voltmeter (BL 8128), adjusted by slide wire resistances (BL 8531, 8279)
V'	potential across film, read on a Weston A.C. voltmeter (BL 8953) adjusted by a slide wire resistance (BL 8363)
C	capacitance of condenser (see below)
T	time constant of condenser (see below).

Replacement of one of the condensers used by Foster and recalibration of the whole set of six condensers by the cascade method was found advisable.

Number of condenser	Capacitance to electrometer, farads	Time constant, seconds
C_0	2.3×10^{-11}	260
C_1	1.95×10^{-10}	570
C_2	1.65×10^{-9}	2300
C_3	2.0×10^{-8}	1400
C_4	1.9×10^{-7}	3100
C_5	2.1×10^{-6}	12000

For the measurement of lower resistances, not feasible with this leakage method, a simple circuit was added, consisting of a 1.6 volt dry-cell and a sensitive milliammeter (Rawson Multimeter BL 8245, the same as that used for measurement of the emission current of the ionization gauge) in series with the film.

III. Experimental Procedures.

1. Manipulation of Apparatus.

To obtain good vacuum conditions, the apparatus was assembled and pumping started usually the day before depositing was to take place. All lead deposits from the preceding run were removed with dilute nitric acid; traces of grease, Picein, etc., dissolved in carbon tetrachloride and alcohol before assemblage was started; after soldering of the wire connections was done, all traces of soldering paste were carefully cleaned off. Outgassing of metal parts and soldering of the glass plate (see under "Thermal Contact") with the high frequency induction furnace was begun only after a reasonably good vacuum had been established. At the same time, the furnace was raised to a temperature somewhat higher than to be attained during the depositing process.

Depositing was started, i.e. the furnace shutter was opened, after the furnace had been allowed sufficient time to reach the desired equilibrium temperature. Potential at the electrometer and across the glass plates was switched on at least one hour before the deposit was to begin, to be sure that electrical equilibrium was reached when depositing was actually started.

During the run, temperatures of furnace and copper tank were closely watched and kept at the values wanted. Vacuum was checked periodically on ionization gauge and McLeod manometer. Water circulation in the metal plug at the upper end of the vacuum chamber and air stream around the Picein seal at the lower end were kept going continually. Liquid air around the traps in the pumping line was maintained at a high level. Electric resistance was measured and recorded at short intervals during the entire length of the run and continually during periods of rapid change.

2. Rate of Deposit.

Deposit rates for various furnace temperatures were determined experimentally, using the same set-up as for resistance measurement runs except that the cover glass had not received any platinizing treatment. The weight of the film was determined as the difference between the weights of the cover glass before and after depositing had taken place. For a check, the cover glass was weighed again after the deposit had been removed by dilute nitric acid. All the weighings were done on a Sartorius precision microbalance (courtesy Dr. A. Goetz), adjusted to a sensitivity of 1×10^{-5} g/div. Dividing the mass of material deposited by its area and the exposure time gave directly the deposit rate (on the graph in $g^{1} cm^{-2} min^{-1}$).

Kinetic theory derives the following formula for the vapor pressure, valid if $dS \ll$ mean free path of the effusing molecules:

$$p = (dN/dt)(2\pi MRT)^{\frac{1}{2}} (760) \,/\, dS\, d\omega \cos\theta \,(1.0132 \times 10^{6})$$

p vapor pressure(in mm Hg) M molecular weight

dN/dt number of moles per second, effusing from an opening of area dS cm^2 into a solid angle $d\omega$, at an angle θ with the normal to dS

R gas constant per mole T absolute temperature

Substituting values from the geometry of the apparatus

$dS = 0.70^2, \qquad d\omega = (\text{area of film})/16.0^2, \qquad \cos\theta \approx 1,$

also $M = 207$ and p from the formula for the vapor pressure of Pb given in the International Critical Tables (Vol. III, p. 207), $\log_{10} p = -52.23\, A/T + B$, where $A = 188.5$ and $B = 7.82$, we are able to draw the curve of deposit rates against furnace temperatures as given in graph IX. However, plotting the actually measured deposit rates in this graph will not furnish points on the theoretical curve, as we may expect some reevaporation to take place from the glass shield, when the latter assumes in its lower part temperatures near to that of the furnace. It was, therefore, necessary to determine this increase in the deposit rate by making deposits also without the shielding. After this correction factor is applied (1.32 in the average), the experimental points fit the theoretical curve very well indeed.

Whenever in the following, thicknesses are given in Ångstroms, they have been obtained from the deposit rates of graph IX, multiplied by the time of exposure and divided simply by the density of lead in bulk (11.3). Though as mentioned before, this cannot by any means be called a quantitative determination of thickness, it will give a fair indication of its order of magnitude.

IV. Electrical Measurements and their Interpretation.

1. Uninterrupted Deposits, "Critical Thickness."

a. High temperature deposits.

Curve I on graph X may be regarded as typical for room temperature deposits. At the start of the deposit, the resistance measured (of the order of 10^{14} ohms) is that of the glass plate; then, after the heat influx by radiation from the furnace has acted for several minutes, we observe a small drop in the background resistance, due to higher conductivity of the glass plate at a slightly raised temperature. No effect of the lead deposited on the resistance is measured until the film reaches a considerable (average) thickness; in our case, after about 80 minutes (corresponding to a thickness of 160 Å), the first signs of film conductivity are observed, then however, the resistance falls very rapidly with each new layer of lead atoms added; after 120 minutes total deposit time (240 Å), the resistance measured is only $1 \times 10^{+5}$ ohms and is still falling.

This pattern of behavior of film resistance versus deposit time is quite general and perfectly reproducible; in all cases a "critical thickness" is observed and then a rapid drop of resistance. It should however be noticed that the value of this "critical thickness" is highly dependent upon vacuum conditions prevalent during the depositing process. Film I on graph X was deposited under a gas pressure of the order of 10^{-5} mm Hg;

higher vacua tend to lower the "critical thickness", whereas poorer vacuum conditions make much heavier deposits necessary to obtain conductivity. On a film deposited under about 5 x 10^{-5} mm Hg, conductivity was observed only after a thickness of 1000 Å was reached; a film produced under still poorer vacuum displayed no conductivity at all up to a thickness of 6500 Å (where the depositing was stopped). It seems that this dependence upon the quality of the vacuum has not always received quite the attention it deserves; "critical thicknesses" reported in the literature might, in some instances, represent not so much a property of the films investigated but an indication of the vacuum conditions in the apparatus.

Curve II on graph X represents a deposit made under similar conditions as I, here however the copper tank was cooled by liquid air. Nevertheless only a temperature of about -50°C can safely be claimed to have been maintained during the deposit, since the method of insuring good thermal contact with the cooling reservoir (discussed in II, 4) had not yet been developed when this film was produced. Considering that some wandering in the film towards the cold electrode has taken place, we see that this film has an effective average thickness of about the same magnitude as film I and is displaying a much similar behavior.

b. Low temperature deposits.

An entirely different behavior is shown by the group of curves III. These deposits were made at low temperatures, with very good thermal contact of cooling reservoir to film. We see here that conductivity sets in after as small a thickness is reached as 8Å. Raising the temperature annihilates the conductivity of these films (as shown in detail in IV, 3b), which effect permitted to deposit all five films of this group on top of each other; before each exposure all traces of conductivity were destroyed by warming up to room temperature.

We see that the presence of non-conductive remnants of previous deposits does not essentially affect the establishment of new conductive layers, except that with increasing thickness more atoms are needed to obtain the same conductivity. Thus the deposit times, until conductivity sets in, for consecutive runs are 4, 5, 8, 10 and 12 minutes. Only the first three of these were made at the temperature of liquid hydrogen (20°K), the fourth at solid air (65°K), the fifth at liquid air (90°K). It is not astonishing that this variety in the background temperatures during deposition should be of little effect; we must remember indeed that during the exposure the film is subjected to the heat radiation of the furnace as well as to the direct energy transfer of the impinging lead atoms, which leave the furnace with a temperature of more than 500°C. Thus we should expect, in spite of good heat transfer conditions in the backing, that the actual film temperature during depositing may be around -150°C for these films, with little difference whether liquid air or liquid hydrogen is in the cooling tank. After closing the shutter, however, the film rapidly assumes the temperature of its backing and then, as shown further below, its behavior is not the same at liquid hydrogen and liquid air temperatures.

2. Interrupted Deposits and Air Admission.

Graph XI exhibits the resistance curves of two films produced under similar conditions as those in graph X, here however the exposure was interrupted during the process of conductivity formation. Film I, deposited at room temperature, clearly demonstrates that, after the beam is cut off, the resistance of the film climbs up (dotted curves) and tends to join the value of the background resistance if left to itself for a sufficiently long time; we also notice that the loss of conductivity will be the more rapid the lower a level of conductivity had been reached when the deposit was interrupted. Film II, deposited with liquid air cooling (and mediocre thermal contact), displays a different pattern of behavior: When thermal equilibrium is reached (some minutes after closing the shutter), the resistance first decreases, then reaches a minimum, and finally goes up in a way similar to I, though somewhat slower.

Graph XII illustrates the effects of air admitted to the film under various pressures. In the first part of curve I, the film is left to itself in high vacuum (1×10^{-5} mm Hg); only a slight increase in resistivity is noted. At A, some dry air is let into the vacuum chamber, to a pressure of 0.5 mm Hg; immediately the resistance of the film shoots up (by a factor 10^4 in 5 minutes) and reaches the level of the background, i.e. all conductivity of the film is entirely destroyed. Film II, starting from a lower resistance level, is practically stationary in high vacuum, shows a slow increase of resistance under 0.1 mm Hg air pressure and a jump upwards by a factor 10^2 in a few minutes, when air under atmospheric pressure is admitted, without however losing its conductivity as completely as film I.

Attention may be drawn to the branch AS of curve II in graph XI , where at A a small amount of air is admitted (to a pressure of 1×10^{-3} mm Hg), while the depositing process is still going: For a short time the resistance falls back until the pumps have reestablished normal vacuum conditions, then the resistance curve resumes its downward move, though first at a slower pace than before the disturbance had taken place.

It is interesting to compare the foregoing behavior to that of a "non-conductive" lead film of 6500 Å thickness. Heating this film up from 20°C to 220°C results in a perfectly reversible decrease of resistance by a factor 10^5, due entirely to the increase of conductivity of the glass substratum and following the law $R = R_o \exp(\gamma/KT)$ or $\log R = a + b/T$, i.e. a straight line, when log R is plotted against 1/T. Admission of air into the vacuum chamber, while this film is kept at 100°C by a flow of steam through the copper tank, also shows an entirely reversible effect, namely a decrease of resistance by a factor ca 5 (from 2.1×10^{12} in vacuo to 4.5×10^{11} at 1 mm Hg and 3.7×10^{11} at 25 mm Hg).

3. Temperature Effects.

a. Formation of conductivity.

Graph XIII should be considered as a continuation of graph X; it shows in detail the behavior of group III of that graph after the beam is shut off. We see that when thermal equilibrium is reached after a few minutes, a decrease in resistivity can be observed in all cases, following the pattern of an asymptotic decrease towards final values. Apparently it does not make much difference whether cooling is done by liquid or solid hydrogen, however, change-over to solid or liquid air results in a definite increase in the "rate of reaction" and in establishment of a lower final resistivity. This final value of resistivity is reached the more rapidly the higher the temperature applied to these films - up to a specific temperature, in our case about 100°K, above which destruction of conductivity sets in as described further below. It might be possible to explain this process of continued formation of conductivity after the supply of new metal atoms has been cut off, by assuming a transformation of "amorphous" metal atoms into the "metallic" state (possibly in line with Kramer's ideas) or by some other mechanism capable to account for the increase of the number of current carriers. It is likely that any such process is activated by higher temperature and it stops when the supply of transformable units is exhausted. Surmising that the process follows the pattern of a monomolecular reaction, we may venture the following derivation:

Calling R the resistance of the film at the time considered and R_T the final resistance when all atoms capable to do so under the circumstances (temperature, history and present conditions of film, etc.) have changed over to the "conductive modification," it seems reasonable to assume that the rate of decrease of resistance $(-dR/dt)$ is proportional to $(R - R_T)$, i.e. $-dR = K_T(R - R_T)\,dt$, where K_T is the "reaction constant." Integrating and setting $R = R_o$ at $t = 0$, $(R - R_T)=(R_o - R_T)\exp(-K_T t)$ or $\log (R - R_T) = \log (R_o - R_T) - K_T t$ which, when plotted in a semi-logarithmic representation, should be a straight line, K_T determining its slope and $\log (R_o - R_T)$ its starting point at $t = 0$.

On graph XIV the two curves I and II of graph XIII are plotted with t as abscissa and $\log (R - R_T)$ as ordinate (R_T being chosen 5×10^9 for I and 1.3×10^{10} for II). We notice that while for the first 15 to 20 minutes the curves follow the law derived, later on the resistance values measured are higher than calculated from our simple formula, meaning that the transformation actually progresses at a somewhat slower pace. To correct for this defect, we can write t^s instead of t, where $s \geqq 1$, thus $\log (R - R_\tau) =$ $\log (R - R_\tau) = \log (R_o - R_\tau) - K_\tau t^s$.

Plotting our two curves with a value $s = 3/2$ (i.e. reducing in our diagram the time scale by an exponent 2/3), furnishes indeed well behaved straight lines; it needs further investigation however, to decide whether this value of the exponent has any deeper significance. It also is yet to be determined which law governs the establishment of the values K_τ and R_τ. Qualitatively it may be said (see graph XIII) that K_τ increases rapidly with the temperature, meaning that for higher temperature the process will be very fast and R_τ be reached almost instantaneously. Furthermore, both K_τ and R_τ are linked in an, up to now, only vaguely explained way to initial resistance, thickness and previous treatment of the film.

b. Destruction of conductivity.

Curves I to III on graph XV show the effect of raised temperature on a group of films deposited at low temperature. They all exhibit the same, very definite pattern of behavior: Rapid, irreversible increase of resistance towards a final value which is the higher, the higher the temperature applied; at about -100°C the last traces of conductivity are quickly destroyed. Looking for a mechanism that might adequately explain this highly temperature dependent decay of conductivity, we should consider that while at the temperatures discussed in the preceding chapter (solid hydrogen to liquid air), mobility of the lead atoms on the glass plate is greatly reduced, this is not true here any more. Thus we might now expect the lead atoms to use their higher mobility to leave the random positions in which they were "frozen" during the low temperature deposit and tend to form thermodynamically more stable clusters or crystallites. As Estermann(7) has shown, atoms are indeed capable to move over quite considerable distances; we should therefore expect that already at relatively low temperatures their mobility would be large enough to break up a conductive layer into small agglomerations.

We may derive a mathematical formulation for the decay of conductivity in analogy to the one for the decrease of resistivity in the last chapter. Calling $G = 1/R$ the conductance at the time considered and G_τ the "final" conductance at that temperature, we may assume that the rate of decrease ($-dG/dt$) is proportional to $(G - G_\tau)$, hence $-dG = K'_\tau(G - G_\tau)dt$, with K'_τ as "reaction constant." Setting $G = G_o = 1/R_o$ at $t = 0$, $(G - G_\tau) = (G_o - G_\tau) \times \exp(-K'_\tau t)$ or $\log (G - G_\tau) = \log (G_o - G_\tau) - K'_\tau t$, giving a straight line, with $\log (G_o - G_\tau)$ at $t = 0$ and the slope K'_τ. As seen on graphs XVI and XVII this law indeed is closely followed in the curves investigated. (For curve I on both graphs see further below.) We may finally render the formula more flexible by attaching an $s \geqq 1$ as exponent to t, in the same way as in the last chapter, so that $\log (G - G_\tau) = \log (G_o - G_\tau) - K'_\tau t^s$.

While the formula derived, with an exponent $s = 1$ or possibly $s = 3/2$, fits well the experimental data as shown by the almost straight lines in graphs XVI and XVII, both curves I take exception to this rule. Now, these curves I represent the destruction of conductivity by admission of air to films deposited at room temperature - an entirely different phenomenon, though externally similar in its final effects upon the resistance of a film. We may safely assume that adsorption and even chemical action take place in these films upon raising of the gas pressure and we cannot expect our formula to hold in the same way as for the crystallization process for which it was devised; indeed, values of s of the order of 10 are required to transform these curves into approximately straight lines.

Returning to graph XV, curve III exhibits the life-story of a film from the time the shutter was closed through various warming and cooling experiences to the final annihilation of the conductivity by heat. It also gives by comparison with IV and V, a good illustration of the connection of R_τ with the "equilibrium temperature", the temperature at which the process of formation of conductivity has already stopped and the destruction has not yet set in (i.e. $K'_\tau = 0$), the observed rule being that the "equilibrium temperature" is the higher the lower the value of R_τ.

It may be mentioned in this connection that film II in graph X, which is stationary as long as kept at liquid air temperature, suddenly drops in its resistance by a factor 10^5 when warmed up to 225°K; this is another illustration, in this case for a "heavy" film, of the temperature dependence of both the "equilibrium temperature" and R_r. As shown below, the value of R_r however is not only affected by the initial conditions of conductivity formation of the film, gases present in the vacuum chamber, temperature of background, etc., but also by the electric potential applied to measure the film's resistance.

4. Effect of Electric Currents.

As mentioned in III. 1., the electric potential across the glass plate (usually of the order of 40 volts) was switched on at least an hour before the deposit was started and maintained for the entire length of the measurements. This implies that all films actually were grown under the permanent influence of an electric potential, and when conductivity had set in were traversed by electric currents which locally might have reached quite considerable densities. It has not been possible, up to now, to isolate the action of these currents; we should not anticipate however that their effects are entirely negligible. Curve V on graph XV shows that for an extreme case, by passing a current of 5 mA, the resistance of a film has been made to drop by a factor 10^4 and the "equilibrium temperature" to rise from 180°K to 220°K; we may expect that some action will be exerted also by the minute currents traversing films of very high resistivity - it might very well be possible that these currents even play an essential role in the process of conductivity formation.

V. Conclusions from Experimental Work.

While part of the phenomena reported need more extended investigation before definite new quantitative conclusions can be drawn, a few facts stand out clearly enough to be enumerated here, partly confirming and extending results of others workers in this field and partly opening up new aspects.

Results of studies on Pb films, deposited at low temperatures, led to the assumption that two entirely different processes are acting in such films, one causing formation, the other destruction of conductivity.

A group of investigations dealt with films deposited at temperatures sufficiently low to inhibit crystallization. At average thicknesses of ca 8 Å, detectable conductivity was observed to set in for these films. After the molecular beam had been shut off, the conductivity continued to increase by factors 10^2 to 10^3 towards specific final values and at rates increasing with temperature. An irreversible transformation of deposited "amorphous" molecules into the "metallic modification" may explain this phenomenon. The formula $\log (R - R_\tau) = \log (R_o - R_\tau) - K_\tau t^s$ (R_τ "final" value of resistance, K_τ "reaction constant," $s \approx 3/2$), tentatively derived, is found to fit well the experimental data.

Above a specific temperature (ca 100°K for this last group of films), a *decrease* of conductivity was observed, at rates rapidly rising with higher temperatures. It may be assumed that with increasing temperatures the mobility of Pb atoms becomes sufficient to account for agglomeration into crystallites ("recrystallization") and thus destruction of possibly existing conductive formations (chains, networks, layers). A formula is suggested, fitting the measured values.

Films of higher initial conductivity were found to change at higher temperatures from the process of formation of conductivity to that of its destruction; a quantitative connection however between the values of R_r, K_r and the initial conductivity could not yet be established.

The behavior of films under air at different pressures was studied and the decrease of conductivity occurring was found to be of a different type than that observed under the influence of temperature (crystallization). Absorption and/or chemical action (oxidation) are assumed to be responsible for this type of phenomena.

Decrease of resistivity was observed when an electric current was passed through a film in analogy to the effect of raising the temperature within the region below the "critical" temperature.

Finally, "critical thicknesses" were found to be highly sensitive to vacuum conditions and criticism is expressed with regard to the significance of some of the "critical thicknesses" reported in the literature.

Acknowledgements.

The author wishes to express his appreciation to Prof. A. Goetz for suggesting and directing this research and for many valuable ideas; to Dr. A. Dember thanks for his untiring and ever helpful advice and assistance.

Bibliography

(1). A. B. C. Anderson, Thesis C.I.T. (1933).

(2). A. B. C. Anderson and A. Goetz, Phys. Rev. 45, 293 (1934).

(3). E. T. S. Appleyard, Proc. Phys. Soc. 49, E118 (1937).

(4). E. T. S. Appleyard and A. C. B. Lovell, Proc. Roy. Soc. A158, 718 (1937).

(5). O. Beeck, A. E. Smith and A. Wheeler, Proc. Roy. Soc. A177, 62 (1940).

(6). J. R. Bristow, Phys. Soc. Proc. 51, 349 (1939).

(7). J. Estermann, Zeits. f. physik. Chemie 106, 403 (1923).

(8). M. G. Foster, Thesis C.I.T. (1939) and Phys. Rev. 57, 42 (1940).

(9). A. Goetz, Zeits. f. Physik 42, 329 (1927).

(10). A. Goetz, Rev. Sci. Inst. 6, 217 (1935) and 7, 307 (1936).

(11). L. Hamburger, Ann. d. Physik 10, 789 and 905 (1931).

(12). M. C. Johnson and T. V. Starkey, Proc. Roy. Soc. A140, 126 (1933).

(13). F. Kirchner, Zeits. f. Physik 76, 576 (1932).

(14). J. Kramer, Ann. d. Physik 19, 37 (1934).

(15). J. Kramer, Zeits. f. Physik 106, 675 and 692 (1937).

(16). J. Kramer, Zeits. f. Physik 111, 409 and 423 (1938).

(17). H. Lange, Kolloid-Zeits. 78, 109 and 231 (1937).

(18). A. C. B. Lovell, Proc. Roy. Soc. A157, 311 (1936).

(19). A. C. B. Lovell, Proc. Roy. Soc. A166, 270 (1938).

(20). W. Reinders and L. Hamburger, Ann. d. Physik 10, 649 (1941).

Bibliography (continued).

(21). K. Richter, Kolloid-Zeits. 61, 208 (1932).

(22). H. Simon, Zeits. f. techn. Physik 5, 221 (1924).

(23). R. Suhrmann and G. Barth, Phys. Zeits. 35, 971 (1934).

(24). R. Suhrmann and G. Barth, Zeits. f. Physik 103,133 (1936).

(25). R. Suhrmann and W. Berndt, Phys. Zeits. 37, 146 (1936).

(26). G. Tammann, Ann. d. Physik 22,73 (1935).

(27). J. S. Townsend, Phil. Mag. 6, 598 (1903).

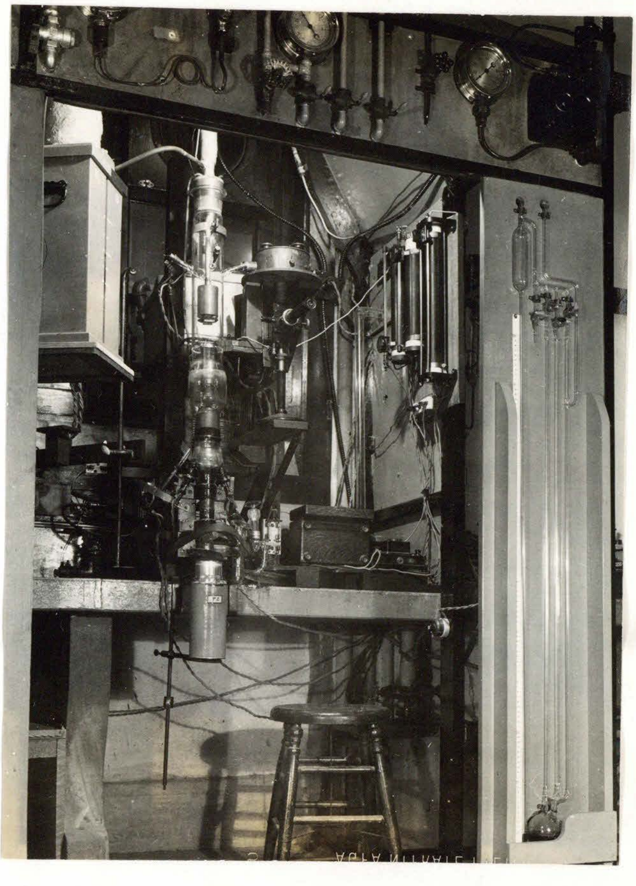
(28). J. J. Trillat and S. Oketani, J. de Phys. et Radium 8, 59 and 93 (1937).

(29). D. A. Was, Physica 6, 382 and 390 (1939).

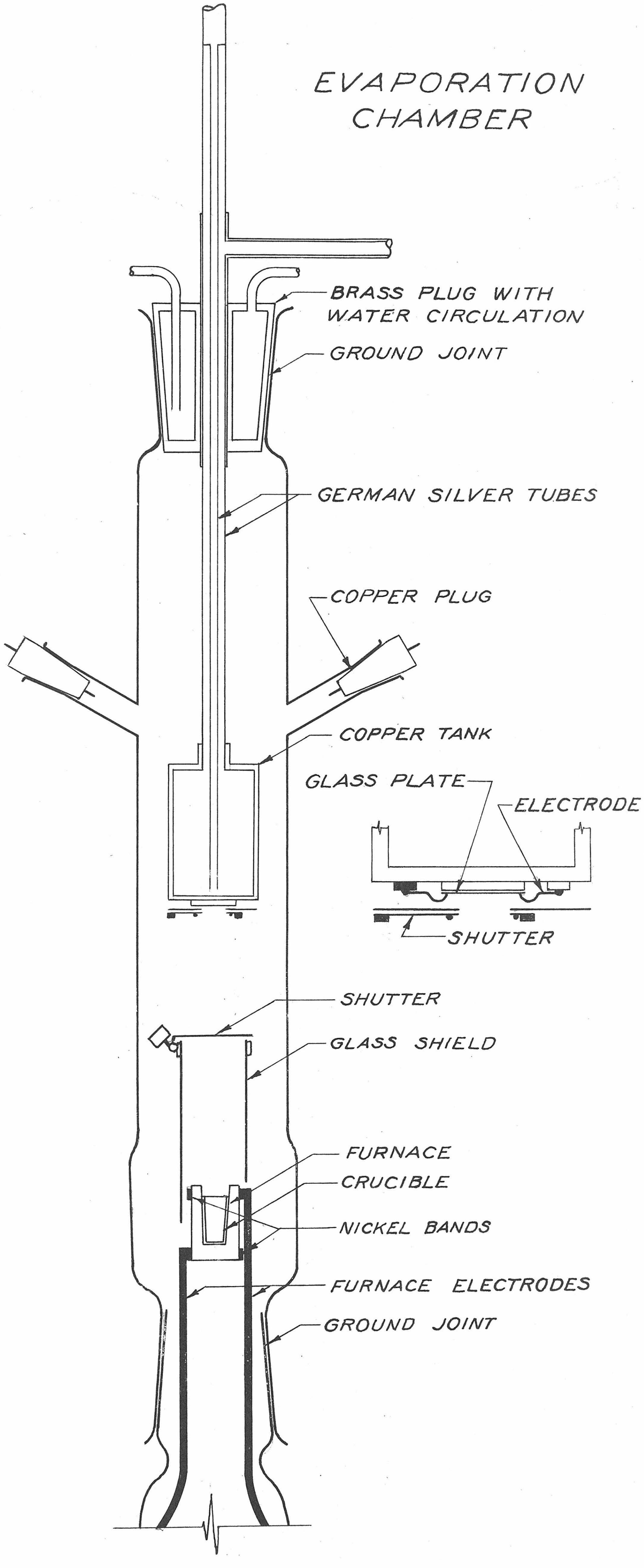
(30). D. A. Was and T. Tol, Physica 7, 253 (1940).

(31). H. Zahn and J. Kramer, Zeits. f. Physik 86, 413 (1933).

I.



EVAPORATION CHAMBER



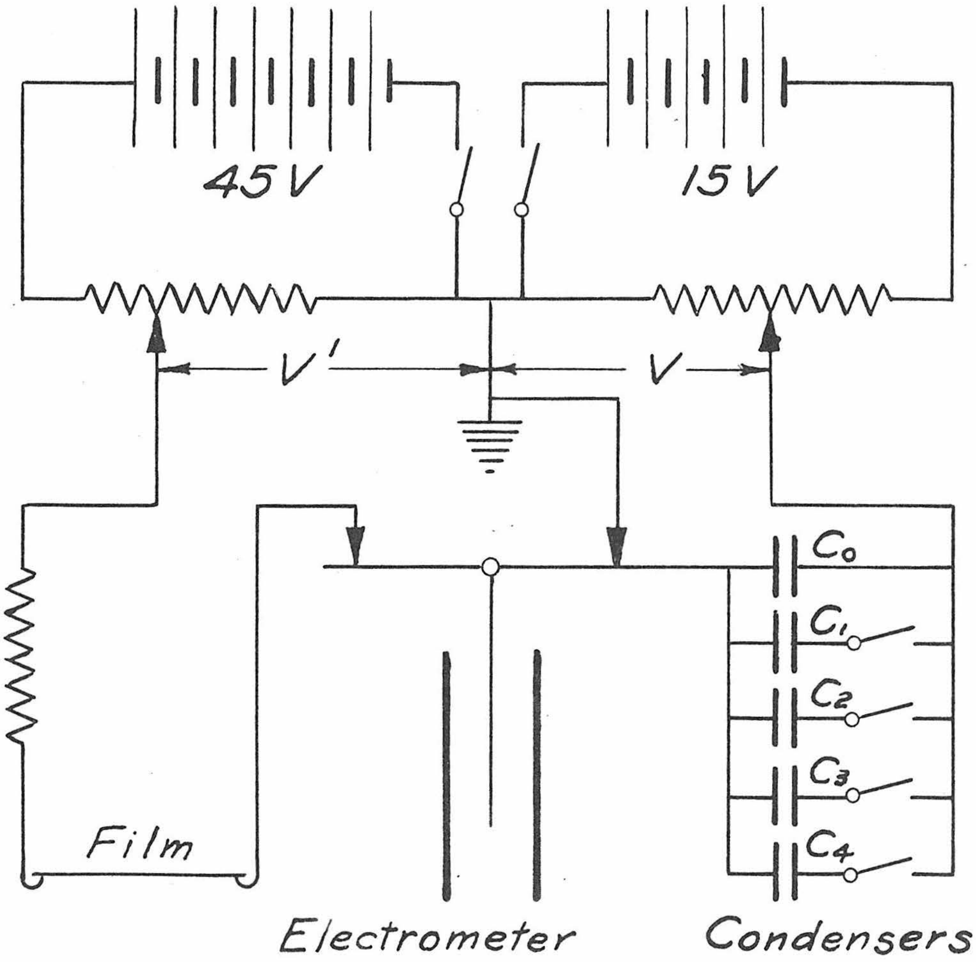
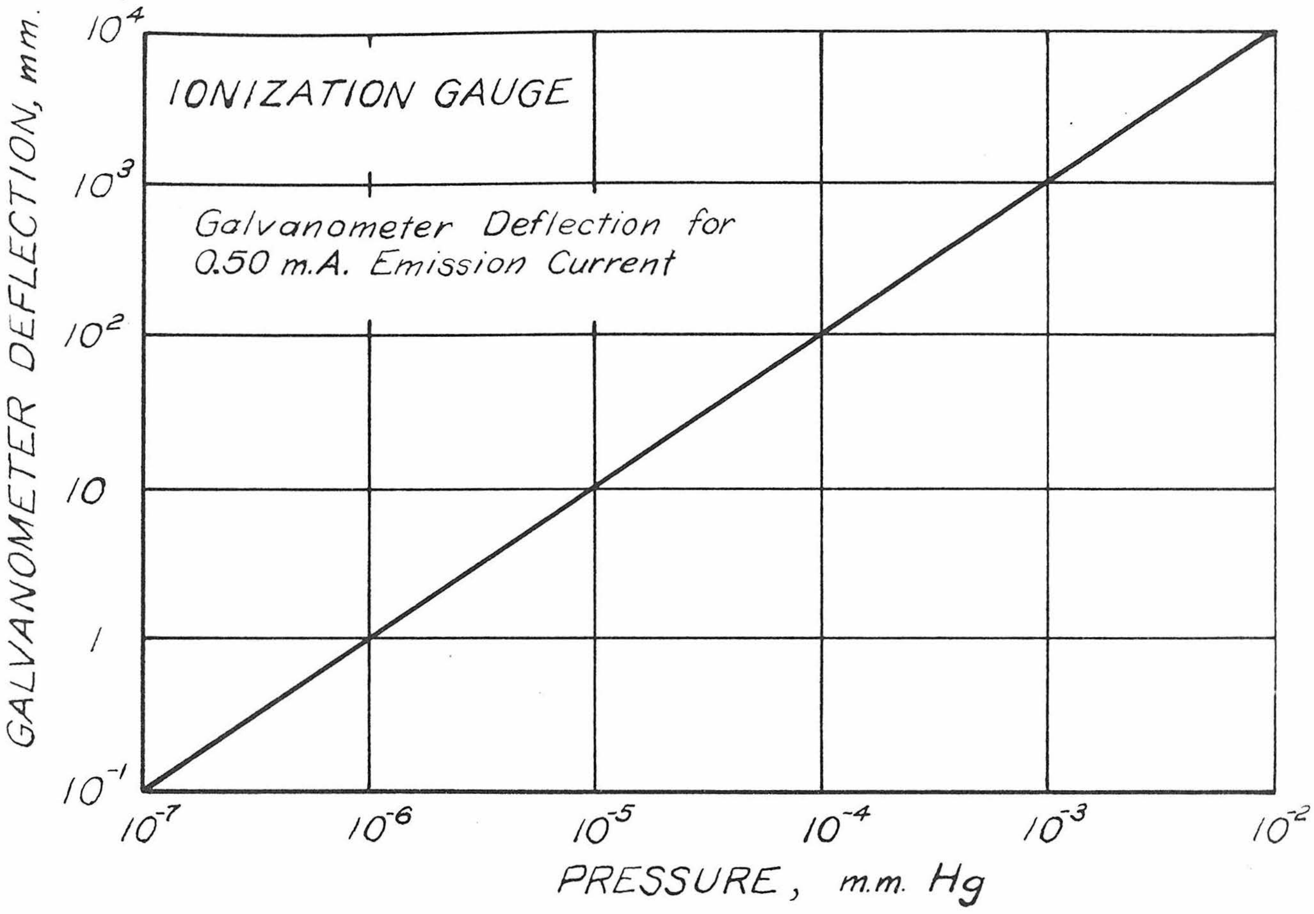
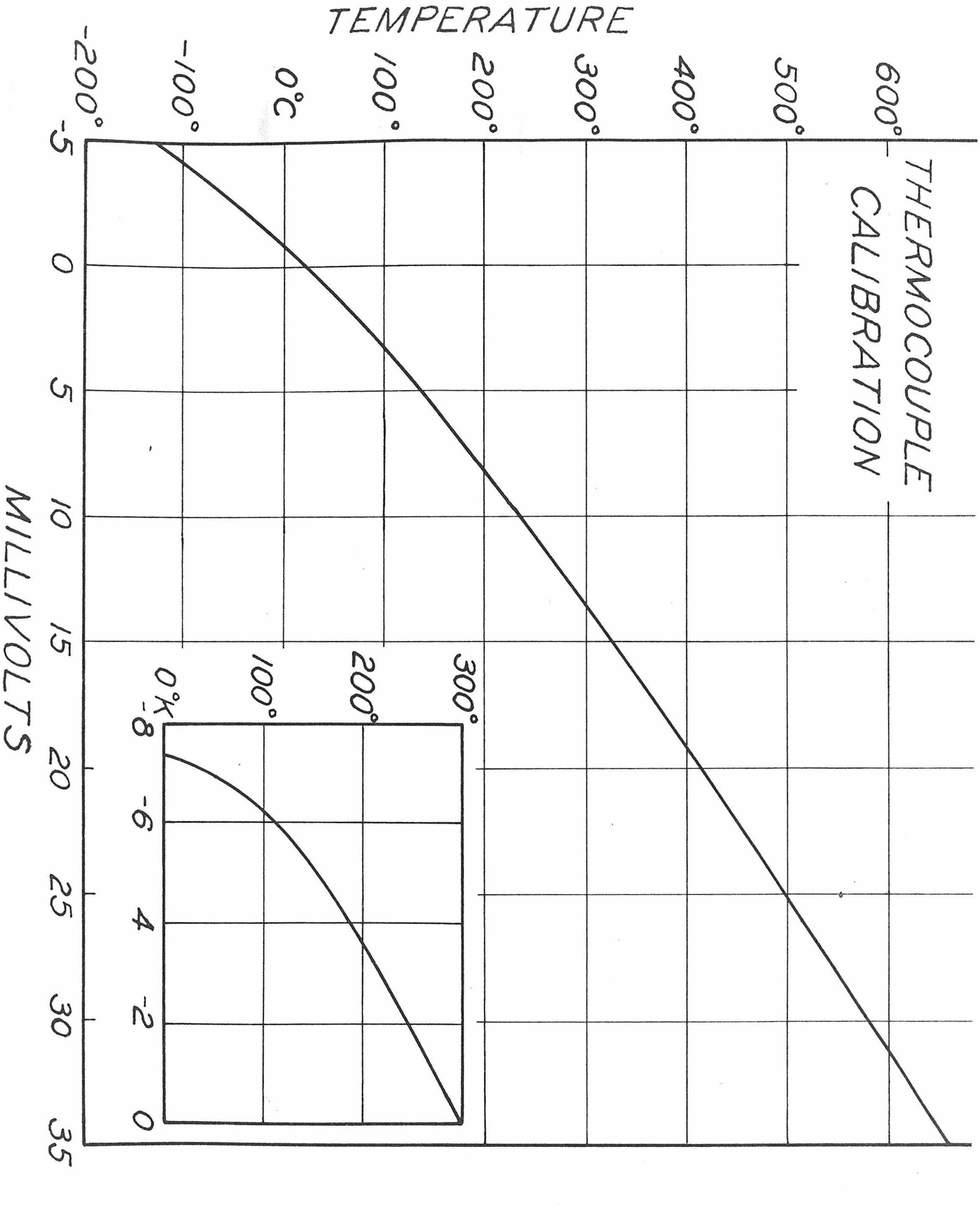
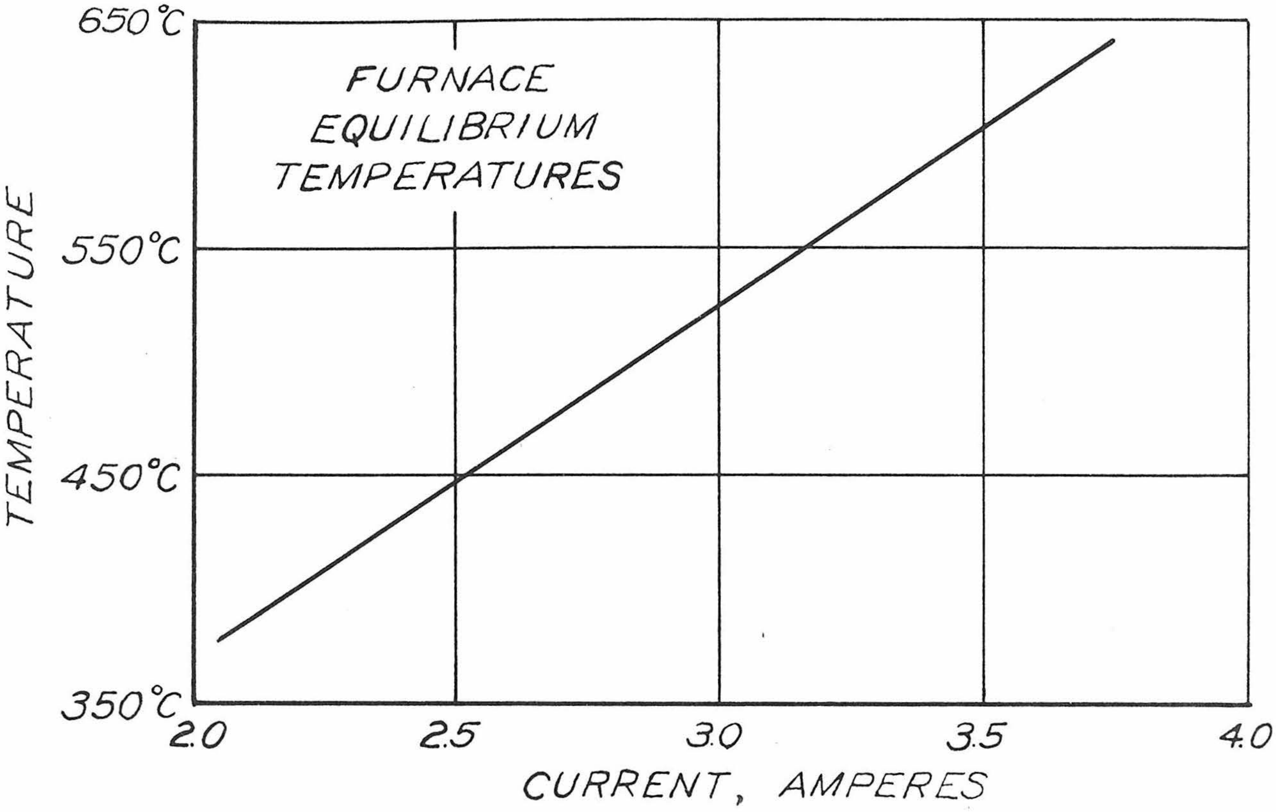


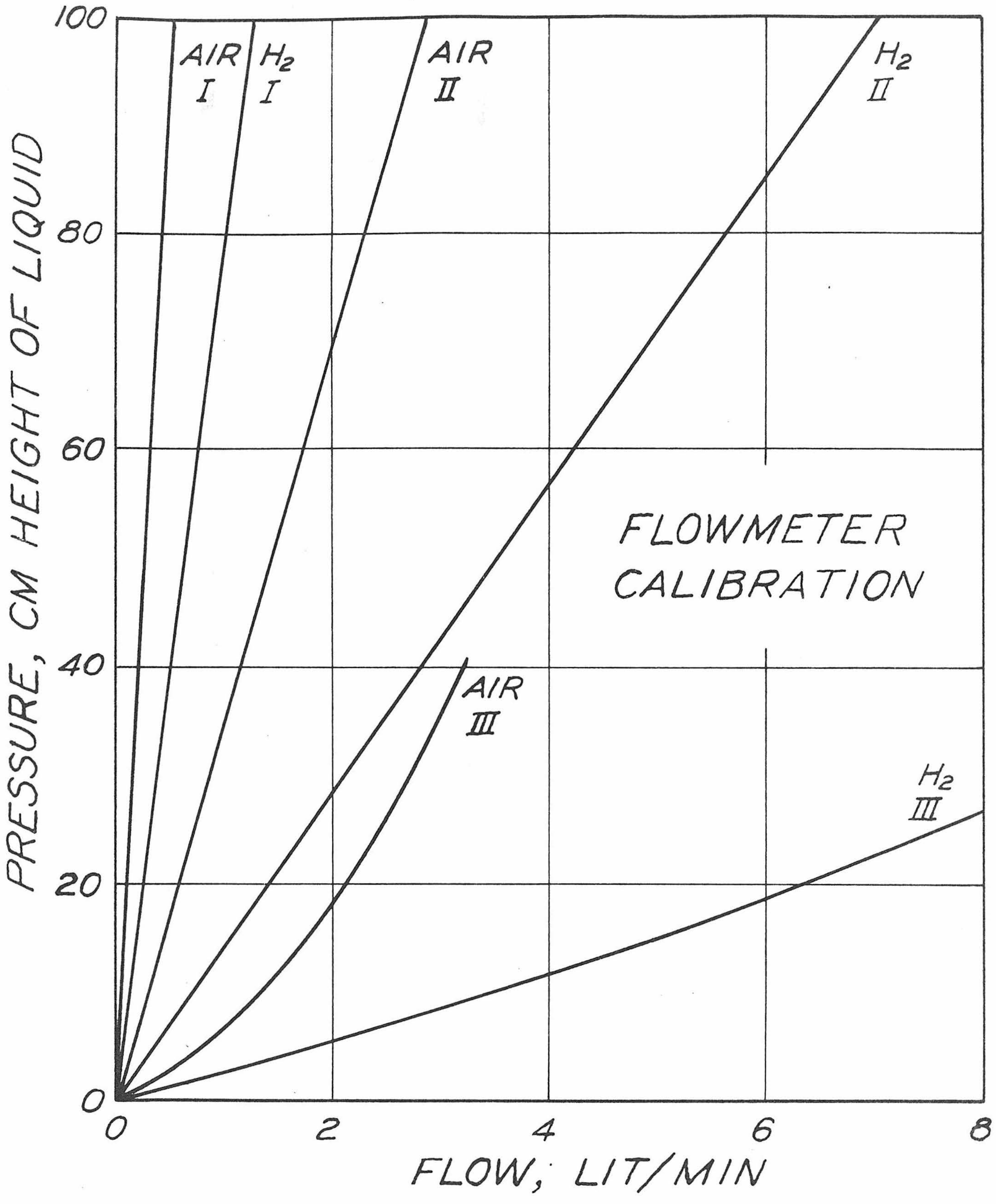
DIAGRAM OF MEASURING CIRCUIT

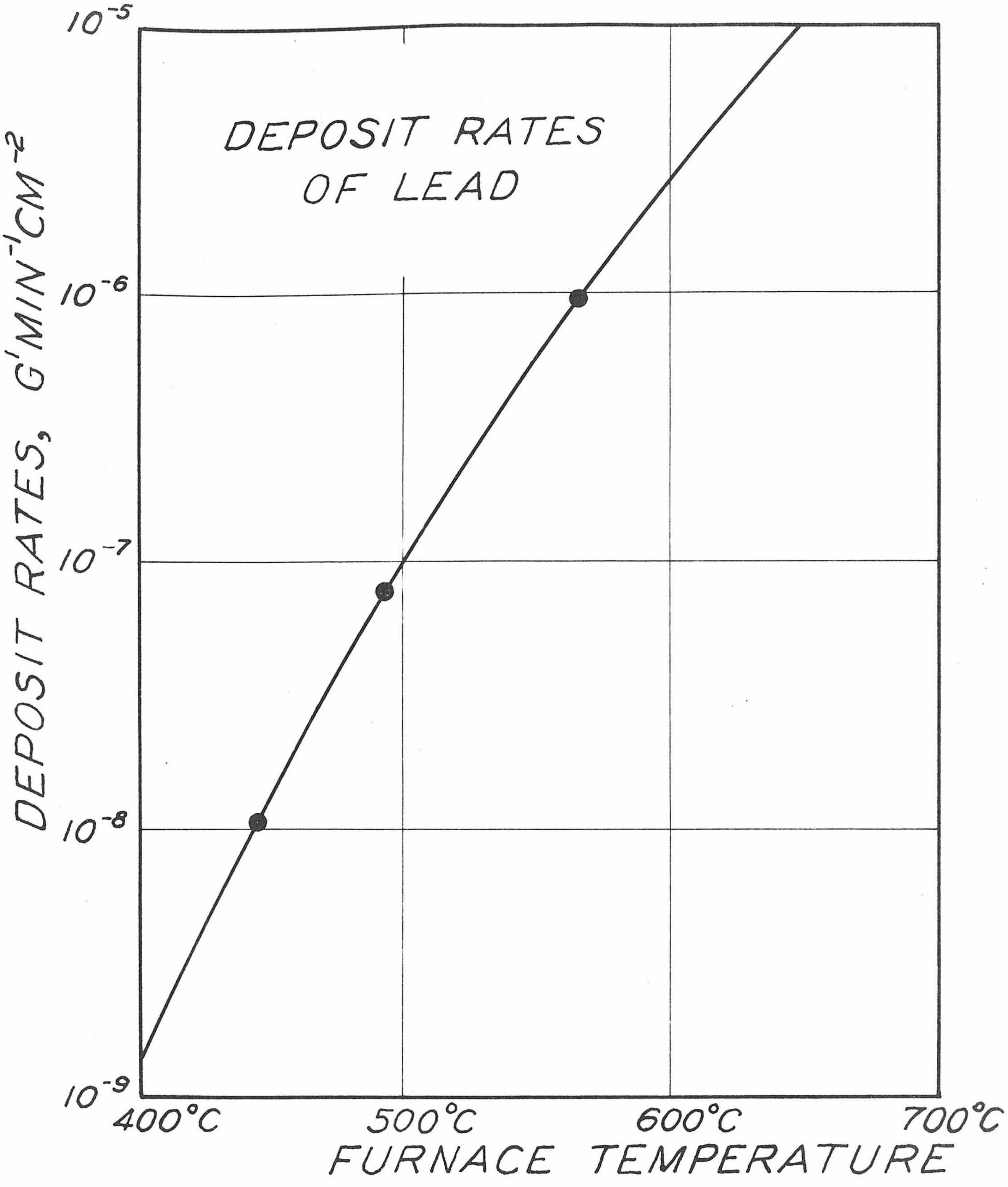

IONIZATION GAUGE
Galvanometer Deflection for 0.50 m.A. Emission Current
GALVANOMETER DEFLECTION, mm.
10^4
10^3
10^2
10
1
10^{-1}
10^{-7}
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
PRESSURE, m.m. Hg

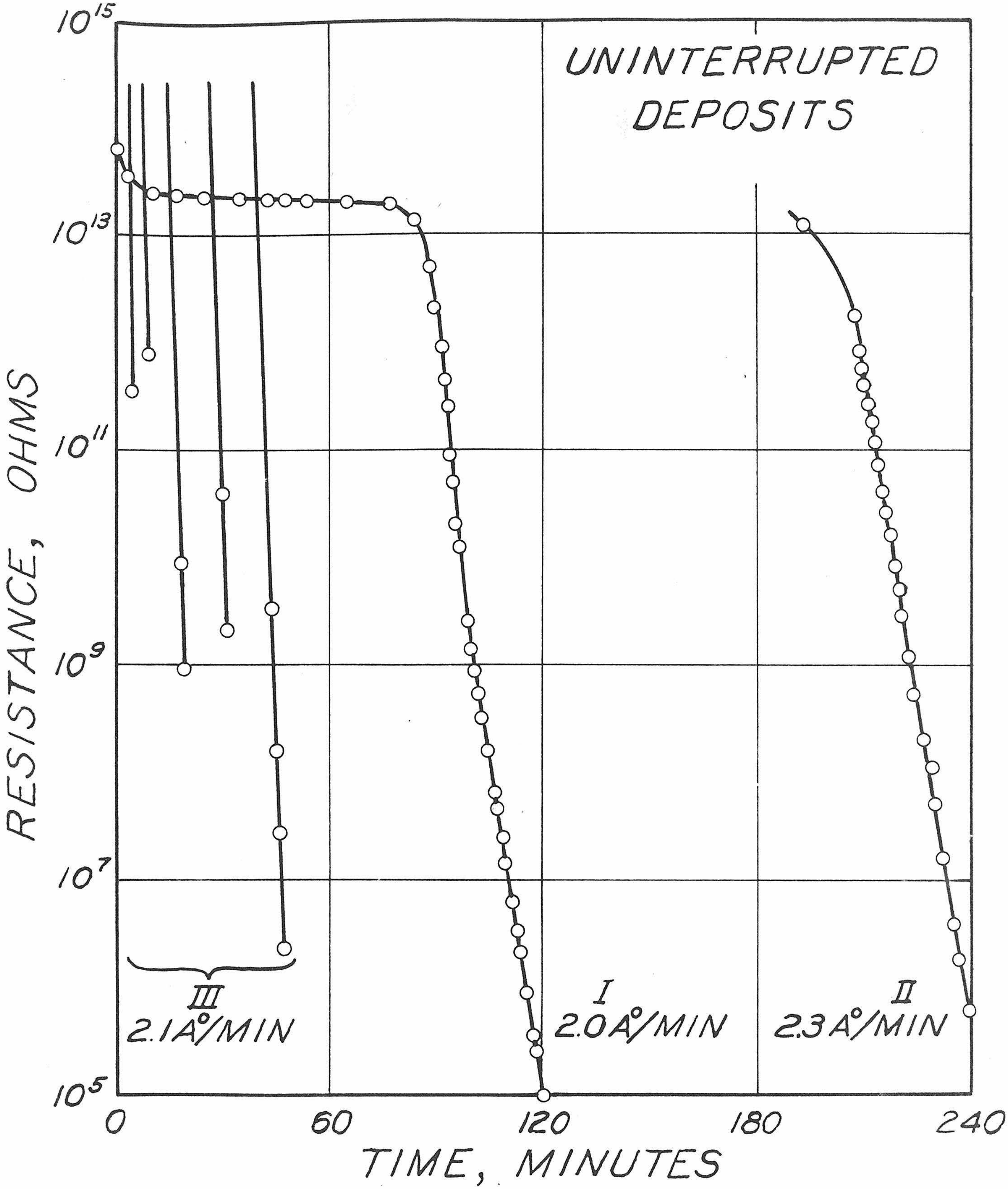


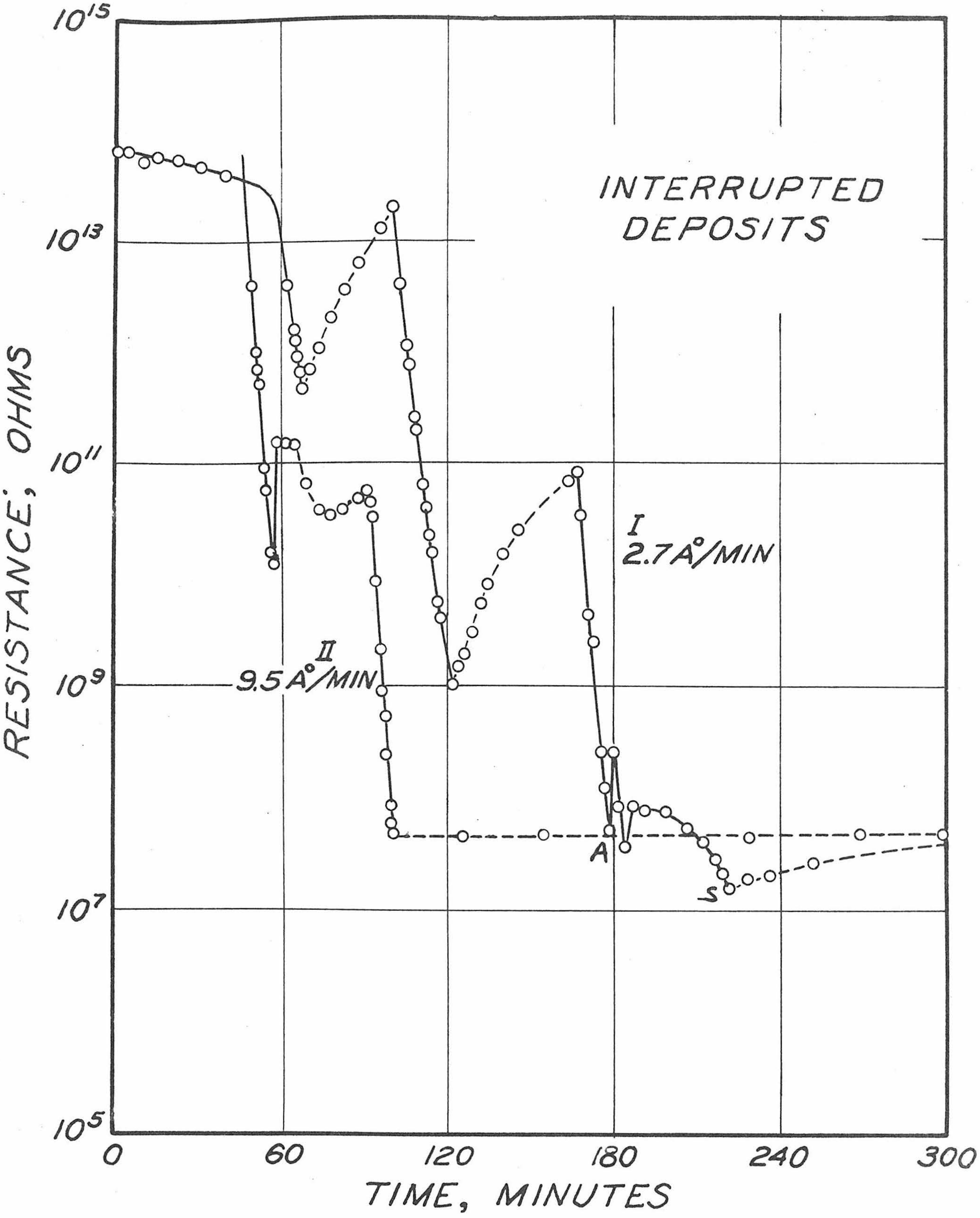
THERMOCOUPLE CALIBRATION


FURNACE
EQUILIBRIUM
TEMPERATURES
TEMPERATURE
650°C
550°C
450°C
350°C
2.0
2.5
3.0
3.5
4.0
CURRENT, AMPERES

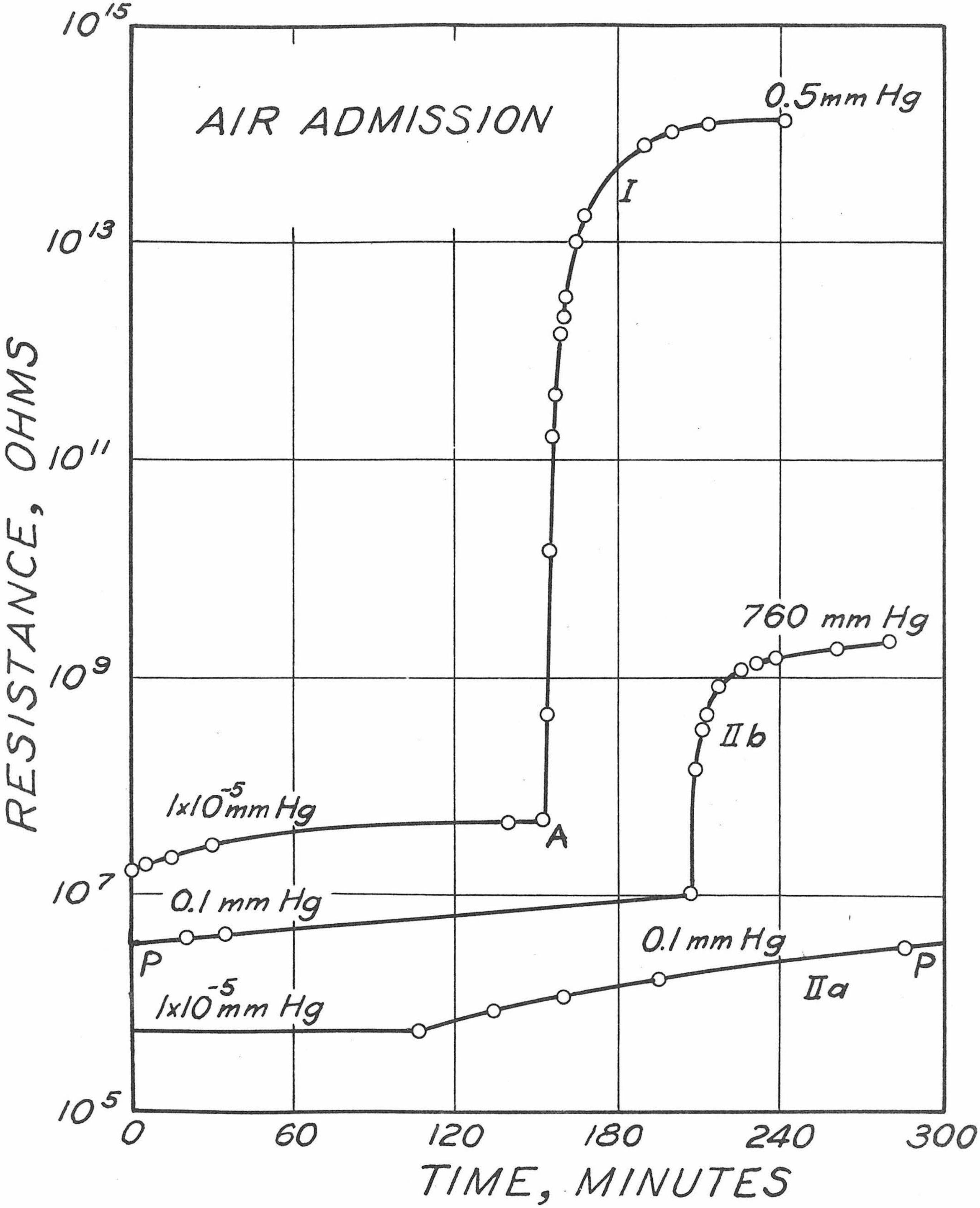

100
80
60
40
20
0
PRESSURE, CM HEIGHT OF LIQUID
0
2
4
6
8
FLOW, LIT/MIN
AIR I
H$_2$ I
AIR II
H$_2$ II
AIR III
H$_2$ III
FLOWMETER CALIBRATION

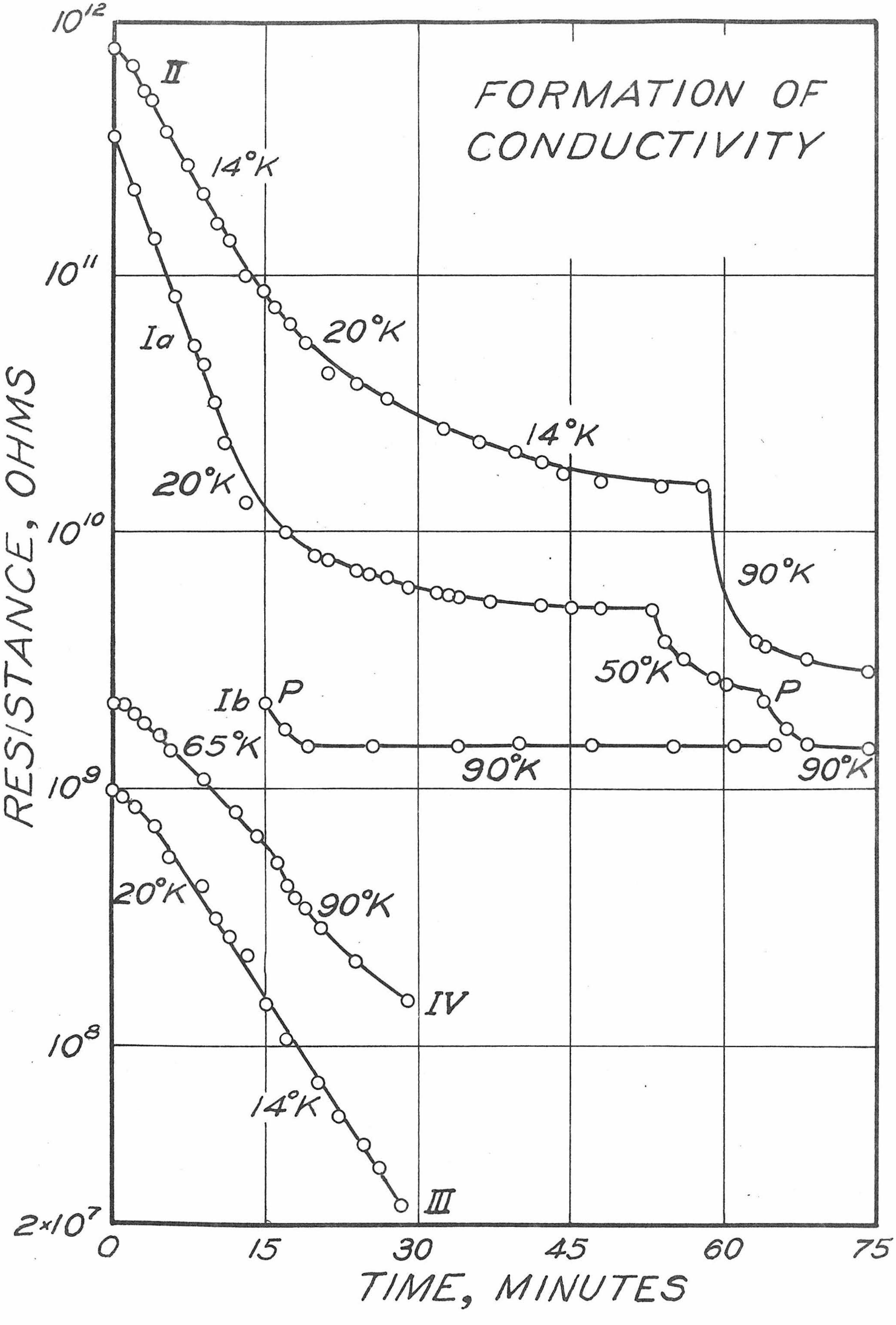

DEPOSIT RATES
OF LEAD
DEPOSIT RATES, G'MIN⁻¹CM⁻²
10⁻⁵
10⁻⁶
10⁻⁷
10⁻⁸
10⁻⁹
400°C
500°C
600°C
700°C
FURNACE TEMPERATURE

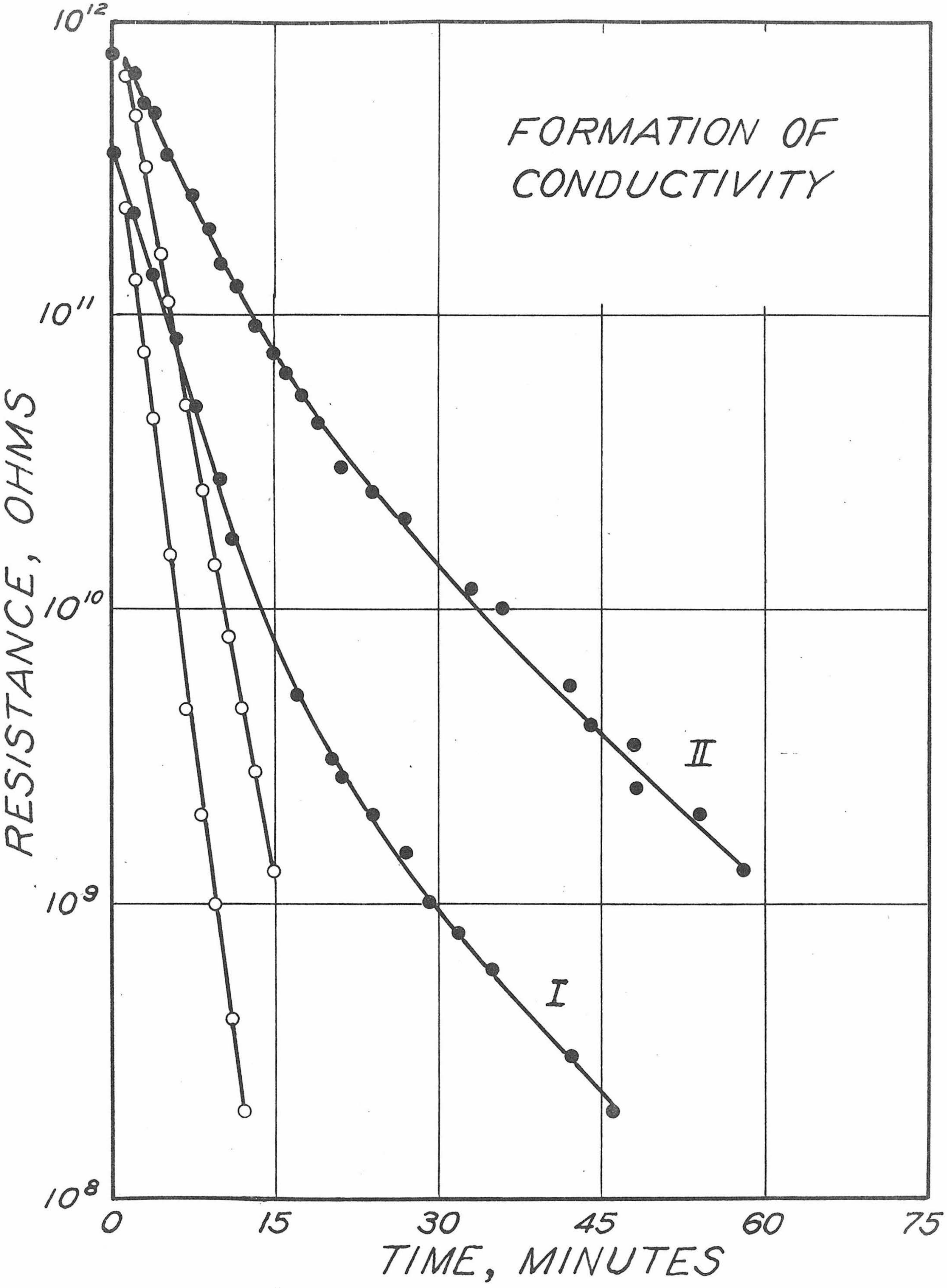

UNINTERRUPTED
DEPOSITS
10^{15}
10^{13}
10^{11}
10^{9}
10^{7}
10^{5}
RESISTANCE, OHMS
0
60
120
180
240
TIME, MINUTES
III
2.1A°/MIN
I
2.0A°/MIN
II
2.3A°/MIN

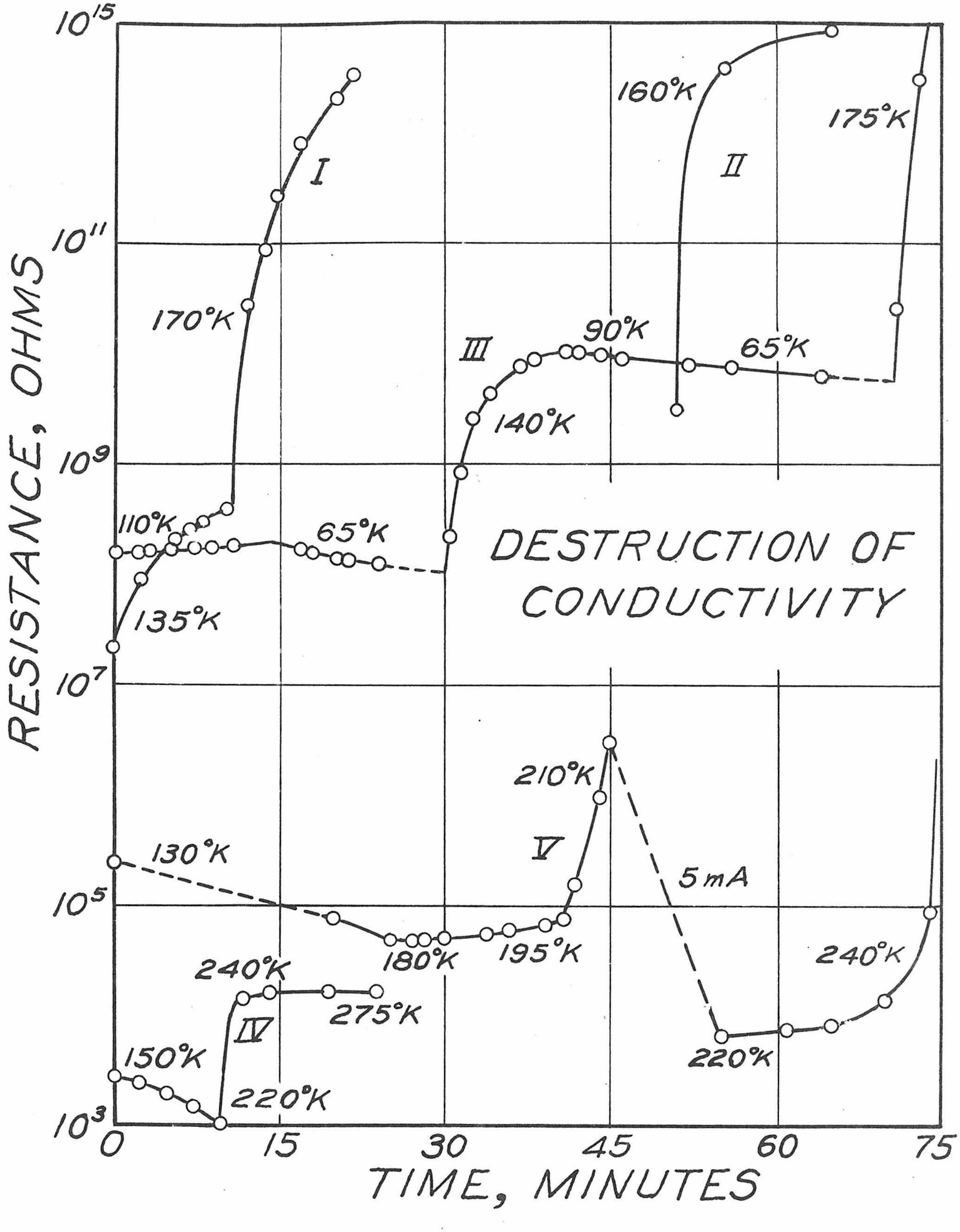


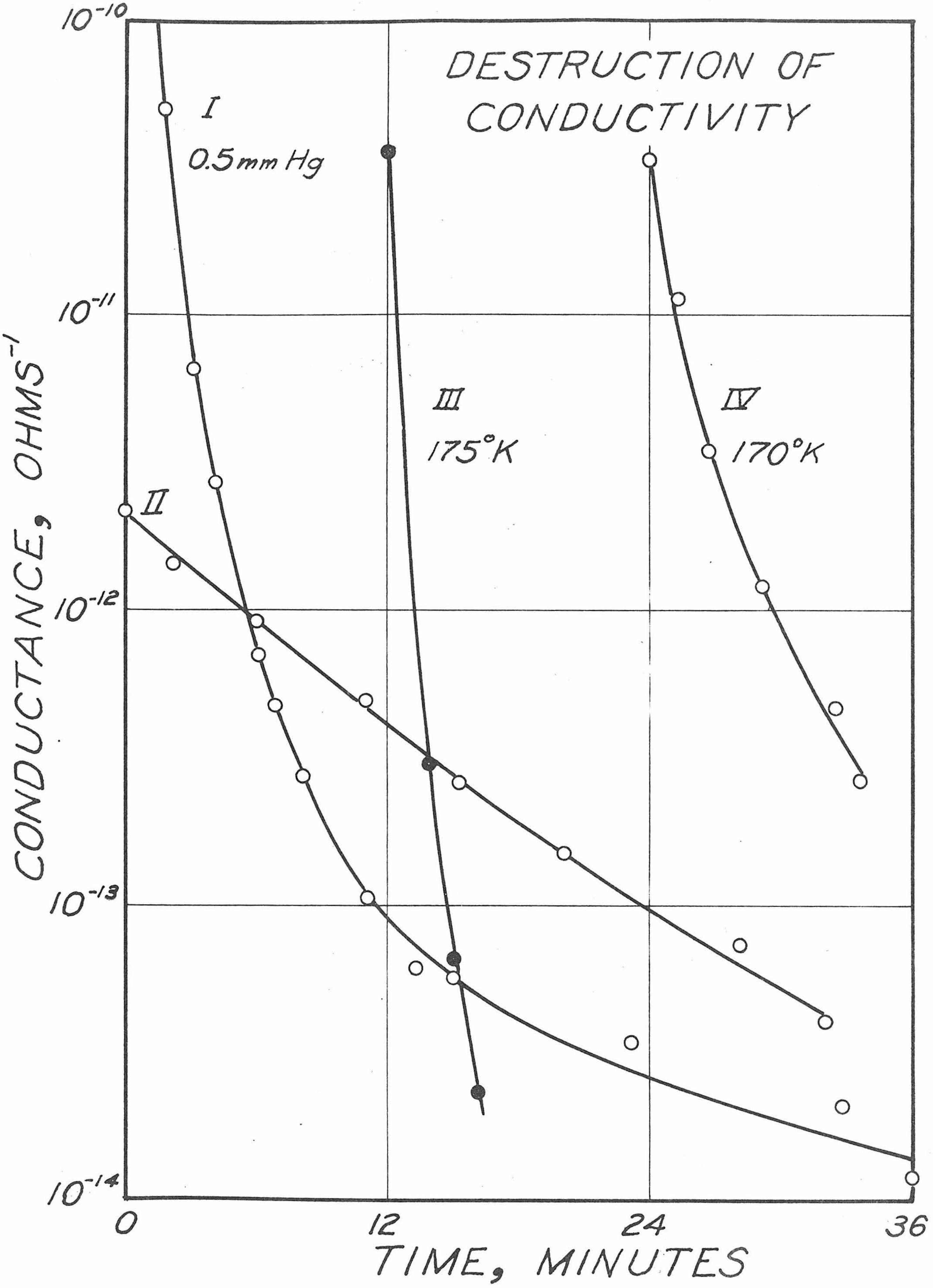
INTERRUPTED DEPOSITS
RESISTANCE, OHMS
TIME, MINUTES
10^{15}
10^{13}
10^{11}
10^{9}
10^{7}
10^{5}
0
60
120
180
240
300
I
2.7 A°/MIN
II
9.5 A°/MIN
A
S

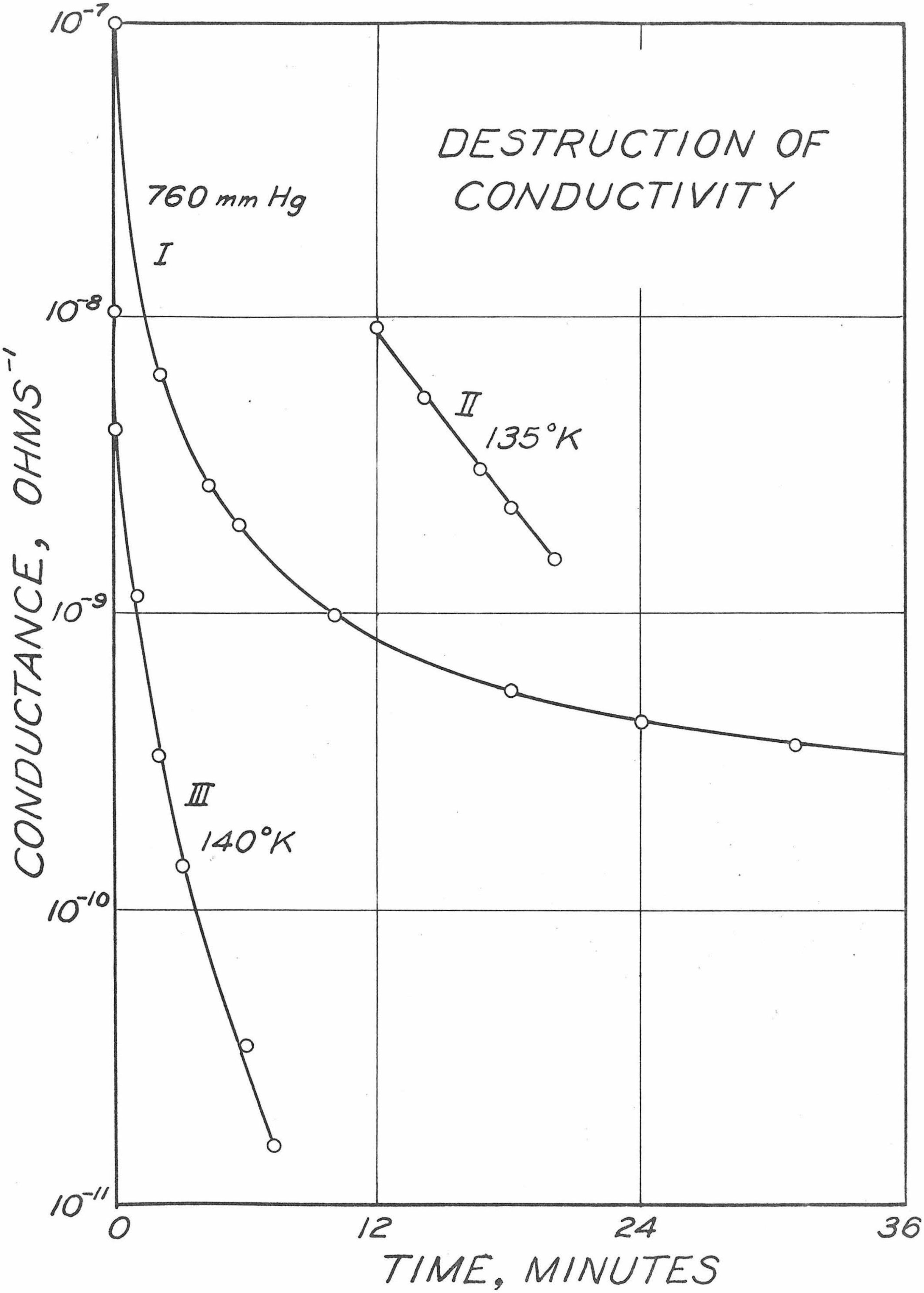

AIR ADMISSION
RESISTANCE, OHMS
TIME, MINUTES
10^{15}
10^{13}
10^{11}
10^{9}
10^{7}
10^{5}
0
60
120
180
240
300
0.5 mm Hg
I
760 mm Hg
IIb
1×10^{-5} mm Hg
A
0.1 mm Hg
P
0.1 mm Hg
P
IIa
1×10^{-5} mm Hg


FORMATION OF CONDUCTIVITY
RESISTANCE, OHMS
TIME, MINUTES
10^12
10^11
10^10
10^9
10^8
2×10^7
0
15
30
45
60
75
II
14°K
20°K
14°K
90°K
Ia
20°K
50°K
P
90°K
Ib
P
90°K
65°K
90°K
IV
20°K
14°K
III


FORMATION OF CONDUCTIVITY
RESISTANCE, OHMS
TIME, MINUTES
10¹²
10¹¹
10¹⁰
10⁹
10⁸
0
15
30
45
60
75
I
II


DESTRUCTION OF CONDUCTIVITY
RESISTANCE, OHMS
TIME, MINUTES
10^{15}
10^{11}
10^{9}
10^{7}
10^{5}
10^{3}
0
15
30
45
60
75
I
II
III
IV
V
170°K
160°K
175°K
90°K
65°K
140°K
110°K
65°K
135°K
210°K
130°K
5 mA
180°K
195°K
240°K
240°K
275°K
150°K
220°K
220°K


DESTRUCTION OF CONDUCTIVITY
I
0.5 mm Hg
II
III
175°K
IV
170°K
CONDUCTANCE, OHMS⁻¹
10⁻¹⁰
10⁻¹¹
10⁻¹²
10⁻¹³
10⁻¹⁴
0
12
24
36
TIME, MINUTES


DESTRUCTION OF CONDUCTIVITY
760 mm Hg
I
II
135°K
III
140°K
CONDUCTANCE, OHMS⁻¹
10⁻⁷
10⁻⁸
10⁻⁹
10⁻¹⁰
10⁻¹¹
0
12
24
36
TIME, MINUTES