THE PROCESS OF ELECTRIC CONDUCTION IN THIN LEAD FILMS

Thesis by

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A. Introduction. The work of other investigators:

I. Thin films in general:

Experiments have been made for many years* on the properties of thin metallic layers. Hamburger 4) (1931), Schultze 3) (1933), Anderson 1) (1933) and Andrade 2) (1936) give extensive summaries of results up to the times indicated. These results, and those of subsequent workers, have been characterized by pronounced lack of quantitative agreement, although certain phenomena are found qualitatively by most observers.

It is nearly always found, disregarding minor details, that the conductivity phenomena of metals are volume phenomena, since when in a thin layer they are quite different from those of the same metal when in massive pieces. The Hall effect (Mackeown 5) does not find the deviations obtained by Riede 6) and others), and the thermoelectric coefficients (Holmes 10)) have been observed to show unexpected variations for thin layers of metal. Extensive work has been done on the optical anomalies exhibited by thin films (Bauer 11), Fukuroi 12, 13), Hass 14), Kirchner 68), Ornstein 15), Rouard 16), and Schultze 3) give copious references), and of late the question of crystal structure under thin layer conditions has received direct treatment at the hands of many investigators using optical and electron-optical methods. (References 2, 4, 14, 49, 17--30.) Caution is required in the interpretation, however; Was 40), for example, shows that the disturbance to the film caused by exposing it to electron rays cannot be neglected, since changes in configuration are sometimes started prematurely by supplying this much energy. The most-measured property

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*See for example Kundt (Ann. d. Phys. 27, 59, 1886).

of thin films, however, has been the electrical conductivity. Since this thesis deals with investigation of electrical conductivity, the literature on this detail will be treated more specifically:

II. Detailed consideration of electrical conductivity:

There are several qualitative features common to the results of most workers:

(1) The (specific) conductivity observed for the metal in thin films depends strongly on the thickness, the value for the thinnest films being much less than that for the massive metal.

Anderson[1] finds that the measured resistivity of his evaporated silver layers increases by a factor of about 100 in the range from zero to 300 atomic layers, then falls rapidly toward the bulk value, some 10^{12} below, as the thickness is increased.

Braunbek[31], and Vollmer and Estermann[32], using evaporated mercury films; Fukuroi[12, 13], using cadmium and zinc as well; Hamburger[4, 23, 24], using silver, antimony nickel, platinum, and tungsten; Krautkraemer[38], using silver and gold; Lovell[33, 34, 35, 36], using rubidium, potassium, and caesium; Mitchell[37], using silver; Riedmiller[26], using nickel; and Was[39], using gold, all find that thin evaporated metal films have specific resistance much higher than the bulk metal. The various investigators differ as to the size of this effect, Lovell observing (under very clean conditions) only a factor of 10 between a 40 Angstrom film and the bulk metal, and the others larger factors, although the preliminary increase noted by Anderson does not seem to be recorded anywhere else.

Many investigators used films obtained by cathode sputtering

(Notably Andrade [2], Dembinska [19], Braunsfurth [41], Féry [42], King [46], Joliot [43], Kramer [44,45], and Perucca [47,48]) and obtain similar results, complicated by the effect of foreign atoms necessarily present due to the poor vacuum required for the sputtering process.

The chemical method of depositing metal films from a solution containing its ions (see, for example, Wait [67], Stone [50]) is now no longer used for conductivity experiments, due to the contaminations which this method provides in abundance.

(2) There exists a critical thickness, in the neighborhood of which the change in conductivity with thickness is very rapid.

Experiment (See Anderson [1] for summary to 1933) shows that as a film is first being deposited the observed conductivity is low, sometimes completely undetectable. (Although Lovell [34] observes some conductivity even with fewer atoms present than would be required to form a complete monolayer.) Then, as the thickness increases, conduction appears quite suddenly. The critical thickness for this to occur is always small, different observers finding values ranging from about 50 Angstroms (Krautkraemer [38]) to several thousand (Braunbek [31]), although most workers agree with Lovell [34] that films 10^4 or more Angstroms thick approach the normal metal very closely in specific properties.

(3) A thin film when first laid down is usually unstable, and irreversible changes occur with changing temperature, with time, with passage of heavy current, and with the addition and removal of foreign atoms.

The sharpest temperature changes are reported by Kramer [44], who finds that films sputtered at low temperatures exhibit a sudden irreversible decrease in resistance as they pass through a certain characteristic temperature as they are warmed up. Other workers (Fukuroi 13), Mitchell 37), and Suhrmann and Barth 52)) find similar changes which appear somewhat more gradually, allowing numerous measurements to be made as the resistance falls. Hamburger 23), Suhrmann and Barth 52) and others find that the resistance of a given film behaves in a reversible fashion below a maximum temperature to which the film has previously been raised, but if the temperature is increased beyond this maximum, irreversibility occurs once more, with changes now reversible under the new maximum. Lovell 35) reports, on the other hand, that his rubidium films condensed at 70° Absolute are stable and exhibit no hysteresis all the way up to 90° Absolute, providing sufficient care is taken with the cleaning and outgassing of the film backing.

Most workers who have examined the point agree that the resistance of a film changes with time, but the sign of the change is not the same for some authors as for others. Anderson 1) gives extensive data showing that the resistivity of a film increases with time, approaching stable values greater by factors as large as 10^2 about 40 minutes after deposit, although he obtained a decrease by relaxing his precautions to exclude foreign atoms. That experimenters using good vacua (Wright 53), and Lovell 35) for example) obtain an increase, and workers, e.g. Bartlett 54), using the sputter process, with its comparatively low vacuum, obtain the decrease lends the weight of more evidence to Anderson's explanation. Lovell and Wright both find, however, that careful outgassing of the backing reduces this aging effect, in some cases eliminating it entirely. Braunsfurth 41), and

and Perucca 48) have found complex anomalies due to admitting various gases to their sputtered films. Vand 58), however, finds a decrease with time for his evaporated films of silver and gold, together with fluctuations in resistance on admitting air to the apparatus. Mitchell 37) also finds a decrease with time.

(4) The observed properties depend strongly on the condition of the supporting surface on which the film is laid.

Here may be recorded the additional results of Ditchburn 55) and of Was 39). Ditchburn finds that a background of copper can be made uniform only by heating strongly in vacuo immediately before use. Was shows that the critical thickness of his gold films is increased from about 50 Angstroms to about 100 Angstroms on heating the background to drive off gases adsorbed. Anderson and Was have compared films condensed on various substances as backing, and find measurable differences between the properties of otherwise identical films.

III. Theories proposed in the past to account for these observations:

(1) Non-conducting layer theory:

Perucca 48) advances the idea that a metal surface is naturally of zero conductivity due to interaction of conduction electrons with the potential barrier at the surface. This explanation does not seem to be accepted by other workers, and against it must be set the experimental results of Lovell 35) and of Hamburger 23) which show directly that a film one atomic layer thick, or even less, does conduct electricity.

(2) Altered free electron-path theory:

On the assumption of a continuous film of uniform thickness,

J. J. Thomson and, more recently, Fuchs [57] have calculated the effect on observed conductivity of the shortening of the mean free path for conduction electrons due to collisions with the bounding surface of a thin film. Fuchs has extended the simple treatment of Thomson to include the statistical distribution of mean free paths, the Fermi-Dirac statistics, and the proportion between electrons reflected in specular and diffuse fashion from the surface. By proper thickness dependence of this last proportion, he is able to secure agreement with experimental data. Physically, this process means taking proper account of the degree of roughness of the surface, that is, departing slightly from the primary assumption of a plane parallel film. (It may be remarked here that Foersterling [58] decides, from results of optical experiments, that the assumption of a homogeneous isotropic geometrically ideal film is contrary to the facts.) The reflection correction must be made empirically in Fuchs' theory, and this limits its significance, but it appears that there is value in the fundamental idea that conduction is low because the conduction electrons have a thickness-limited opportunity to move freely. This theory provides no simple mechanism for the change of resistance with time.

(3) Granular structure theory:

A slightly different approach to the thickness-dependent interference with conduction electrons has been proposed by Swann [59] and adopted by many other investigators since. This theory starts with the fact that atoms when first deposited on a solid surface from a finely divided state are distributed in completely random fashion. As soon as an atom is deposited on the surface, however, its thermal motion (see Frenkel 69)) becomes one of sliding over the surface. (Andrade 2), Essig 21), Finch 22), and Was 40) give fairly direct experimental evidence that such an effect actually occurs.) Since the temperature is below the melting point of the bulk metal, the attractive forces between the atoms are important, and atoms which come close to each other tend to cling together. This process results in the formation of many nuclei, or centers of coagulation, so that the entire film becomes changed from the random distribution to the more stable configuration of many small patches (the decrease in potential energy furnishing the entropy required by thermodynamics). This result gives a film which is anything but uniform in thickness, and allows the observed time variations to be described in terms of surface mobility of the condensed atoms. Anderson 1) has carried out this extension along the following lines: Since these patches are distinct from each other unless there be more than a certain critical amount of metal present, electrons will have a difficult time crossing the spaces between, and high observed resistance will occur. As time passes, and more and more atoms are removed from circulation by striking a patch and staying there, the resistance of the film will increase still further, and for the thinnest films will soon become comparable with the resistance of the background, and therefore undetectable. On the other hand, once the patches become big enough so that many of them touch, conduction should become much easier, and resistance as observed exhibit a rapid drop. Thermal effects can be obtained by a little more extension of these ideas: Temperature increases, by increasing the agitation of the molecules might, under certain circumstances, establish contact between patches that could not reach each other when cold, and molecular cohesion will tend to conserve such contacts once made.

Of the three theories here presented, this granular structure theory seems the most promising, and has received the most support from experiments.

IV. Experimental methods of previous and contemporary investigators:

The problem that must be solved in making conductivity experiments with thin metallic films is a threefold one. A film must be produced under conditions as simple as possible and so that the average thickness is known, good electrical and thermal contact must be established between the film and the measuring instruments, and the resistance must be measured rapidly by methods which are adaptable to a wide range of values. The methods which have been employed in the past to do these things are discussed:

(1) Of the three methods of producing thin films outlined under A, II,(1) that of condensation from metal vapor in high vacuum seems to give least chance for contamination, although it possesses the disadvantage that the metal atoms are moving rapidly when they strike the backing, where best conditions would be expected if they had the smallest excess energy possible. Andrade seems to be the latest worker to use sputtered films for extensive investigations, and claims his films when first laid down exhibit no inhomogenieties visible under ultramicroscope examination, though a patch structure appeared later on heating.
It seems best, however, to have the fewest foreign atoms possible, i.e. to use high vacua, and evaporate the films. With present-day technique,

even the less volatile metals may be evaporated from tungsten filaments (Hass 25), Was 39,40)), platinum (Dembinska 19), Anderson 1)), tantalum (Bauer 11)), or directly from wires of the metal concerned (Riedmiller 26)) and in the case of more easily vaporized metals it is possible to use a more easily controlled resistance furnace (Pringsheim and Pohl 61), Goetz 60), Lovell 35)). Careful cleaning of the backing and surrounding apparatus is necessary if foreign atoms are to be effectively eliminated. Bauer 11), Riede 64), Beeching 17), and Anderson 1) employed various versions of the scrub-off in nitric acid method recommended by the Bureau of Standards 62) and others. Lovell 34) and Was 39) outgassed their backings for many hours at high temperature in vacuo. No one seems yet to have used the electronic clean-up method of Strong 63) in conductivity investigations. Anderson 1) deposited some of his films on a freshly cleaved calcite surface.

(2) Various methods have been proposed for measuring the thickness of deposited layers. Actually, all that can be measured is the average thickness over a considerable area. Optical methods of measuring thickness (Brueck 18), Rouard 16)) are doubtful since thin films exhibit, as has been noted above, imperfectly understood optical anomalies. Mayer 65) and Lovell 34) measure the density of atoms in the beam to the backing plate, using the ionization from a hot tungsten wire placed in the beam as an indicator. Anderson 1), Féry 42), Was 39), and Riedmiller 26) measured the deposit rate by weighing a thick film deposited at known setting of the apparatus, then assuming the rate was the same throughout. Methods which give

the number of atoms per unit area can be used to obtain the thickness only if it be assumed that the density of thin layers is related in a known fashion to that of the normal metal. Nearly all workers point out in assuming normal density for thin films that it is really an assumption, which future experiments may or may not disprove.

<u>(3)</u> Care is required to insure that the film makes good electrical and thermal contact with the surroundings where desired. Early methods of clamping electrodes on the film (Stone 50)) are not satisfactory, and it has become almost universal practice to lay down conducting areas on the background to which contact can be made, and deposit the thin film on top so that it bridges an otherwise bare gap. Thus, intimate molecular contact occurs over a considerable area. The materials used to obtain these predeposited contacts have been either a previous deposit of the same metal as investigated (Anderson 1), Riedmiller 26), King 46)), or of platinum (Fukuroi 12), Houllevigue 66), Suhrman and Barth 52)) or of graphite (Lovell 36)), gold (Féry 42)), or silver (Mitchell 37)). The question of proper thermal contact between the film and the material used to cool it and measure its temperature has not received much attention in the literature. Lovell, for example, measures the vapor pressure of the liquid oxygen poured behind the film backing, but does not differentiate clearly between this temperature and that of his film. Fukuroi finds, however, by comparing readings of several thermocouples, that his temperature gradients are all small between film and cooling fluid.

<u>(4)</u> Several methods of measuring the resistance of films have been

used. Some workers (e.g. Bartlett 55), Mitchell 37), Fukuroi 12)) have used the Wheatstone bridge, though Mitchell uses a galvanometer directly for the higher resistances, Anderson 1) used an electrometer circuit of variable capacity and measured the charging rate. Deubner 67) measured his resistances with alternating current, using an amplifier and a vibration galvanometer. The more recent electron tube D.C. amplifier circuits do not seem to have been much employed in this field.

V. Conclusions from previous work:

The time dependence of resistance of a thin metal film, together with the small-particle structure observed with the microscope (Andrade 2), Kramer 44)) under certain conditions, and the microcrystal structure given (Finch 22), Kirchner 68), Was 40)) by electron diffraction experiments on such films, makes it very probable that the patch-structure picture of the conduction process in thin layers outlined in A, III, (3) contains much truth. Disagreement in results between experiments of apparently comparable validity, particularly as to the sign of the time variation of resistance, makes it imperative that more light be shed on this phenomenon and on the other special features of thin-film conductivity before detailed theories can be constructed which take quantitative account of the differences between different metals.

B. The experiments reported in this thesis:

I. Purpose of the investigation:

The results described here were obtained, using apparatus adapted from that of Anderson, in an attempt to make somewhat clearer the picture of the conduction mechanism in thin metallic films, with particular emphasis on the aging process and its temperature-dependent aspects.

II. Experimental methods employed:

To obtain trustworthy results, the apparatus was arranged to fulfill the following conditions: (Details will be given below, but in this paragraph is included under each requirement a brief statement of the means employed to meet it.)

(1) The film must be produced with the smallest possible contamination, and small excess energy.

> The thin layers of lead were deposited from vapor in high vacuum on carefully cleaned glass surfaces held at various temperatures. Lead was chosen because of its appreciable vapor pressure at not-too-high temperatures, and deposit rates were kept slow so as to avoid extra kinetic motion in the film as far as possible. Careful cleaning of the entire apparatus preceded each run, and all metal parts were thoroughly outgassed with an induction furnace.

(2) The thickness of the film must be known as accurately as possible.

> Care was taken that the lead evaporate at uniform rate throughout each experiment, and the rate was measured

as a function of the temperature of the evaporating furnace by weighing several extra-heavy films with a microbalance. A magnetically operated shutter gave precise control over evaporation time.

(3) The best thermal contact must be obtained with the cooling fluid.

It will be seen from Plates 3 and 4 that the cooling fluid is contained in a quartz-bottomed chamber, and the film backing (a microscope slide cover glass) is platinized and carefully soldered into place.

(4) Reliable electrical contact must be maintained with the film to be measured.

Platinized contact areas were provided (Plate 4) so that the film bridged the gap between them, and the electric leads were soldered to these platinized places. Platinizing was done by painting platinum china paint where desired (See Plate 5A) and baking for some hours.

(5) The resistance of the film must be measured rapidly even as it varies over large ranges.

The resistance of the films was measured in the vacuum by applying a potential, and observing the rate at which the resulting current across a film charged condensers of various sizes. Part of the measurements were done using Anderson's 1) method (Plate 6), and part were done using an adaption of Townsend's 70) method (Plate 7). The advantages of the latter are that it maintains constant potential across the film, and it localizes leaks and capacitances so that more complete corrections for stray effects can be made. As in Anderson's work, condensers were calibrated against a standard cylindrical condenser of known dimensions.

It was found advisable to attach a thermocouple at the point indicated in Plate 3 to obtain a rough idea of the temperature of the film backing at various times.

III. Detailed description of the apparatus and its use:

(1) The vacuum chamber:

The assembled apparatus is shown in Plate 1, and is adapted from that of Anderson [1] using some of his glass parts. The vacuum system has been somewhat improved, however, by using two mercury diffusion pumps instead of one, and two liquid air traps in series (only one shown here). An ionization gauge (an ordinary 201-A electron tube, grid potential + 157 1/2 volts, plate potential - 22 1/2 volts) was installed as shown, connected by a long tube to the spot where the pressure of the system seemed likely to be highest, i.e. directly under the evaporation furnace. This gauge was not very precisely calibrated, but a claim of at worst 10^{-6} millimeters of mercury is believed conservative for the pressures obtaining during all the experiments. Further confirmation of the high vacua maintained is given by Plate 8A, which is a photomicrograph (dark field illumination) of the edge of a typical film deposited under normal conditions. The width of the penumbra observed is that calculated from the geometry of the apparatus, assuming straight-line paths of lead atoms from furnace to deposit plate. Scattering is seen to be negligible, hence collisions between lead atoms and remaining air molecules must be unimportant.

All glass and metal parts were thoroughly cleaned before each run, using the following procedure:

The glass parts were scrubbed with dilute nitric acid, rinsed thoroughly in distilled water and dried in air. This removed residual lead. Any stray bits of vacuum wax were removed by a thorough scrubbing with carbon tetrachloride. Metal parts received the same treatment, and in addition were systematically outgassed at red heat with an induction furnace.

The cover glass that was to receive the deposited lead was subjected to a particularly thorough cleaning. It had previously been platinized as required for contacts, and was scrubbed briskly with a cotton swab in concentrated nitric acid (as recommended by the Bureau of Standards 62)) until the distilled rinse water did not run off into drops, but clung evenly as a thin film all over the surface. Then the glass was rinsed several more times in distilled water, dried in air, and promptly inserted in the apparatus. As added protection to the film backing, an auxiliary shutter (Plate 3) was placed over the aperture to the final stop, and removed only after outgassing the rest of the apparatus, the iron portion responding to a magnet outside.

No part of the glass or metal that would ultimately be inside the high vacuum was touched directly with the hands in reassembling. Contamination from sealing compound (Picein or Apiezon W) was avoided by keeping the wax only on the outer portion of otherwise clean ground joints, and isolated from the main vacuum chamber by long capillary tubes at the wire seal-ins (Plate 5B).

Metal parts were made of molybdenum as far as possible, since this metal has a low vapor pressure at high temperatures, and does not lose its elasticity on heating below 1200°C. Outgassing was conducted in spurts of about one minute heating followed by several minutes pause for the pumps to clean out the dislodged atoms, until the ionization gauge showed practically no increase in pressure due to heating metal parts bright red for a minute.

(2) Evaporation:

The furnace used is the one described by Goetz 60), the chief addition being the wrought-iron lining to hold the lead. This was necessary, since melted lead in the bare MgO crucible gripped the sides so firmly that the crucible was nearly destroyed when the metal shrank on cooling. It will be observed from Plate 2 that the thermocouple junction used to measure the temperature of the lead is very close to the center of the furnace, with hot metal in nearly all directions from it. Hence the temperature as read must be typical of the furnace. The shields surrounding the crucible prevent the lead from condensing on the outer walls of the vacuum chamber, to be later re-evaporated onto the film backing. For the few hours exposures employed, lead re-evaporating from these shields and condensing on the thermocouple wires did not cause serious short circuit, but it was necessary to clean off the stray lead before each run to avoid trouble of this sort.

Above the furnace (Plate 2) are placed stops so as to collimate the beam of lead atoms (that is, to trap any which are not going in the right direction). The shutter shown is turned on its pivot by a magnet from outside the vacuum, opening and closing the route to the deposit area as desired. The entire stop and shield system is earthed, and so is one terminal for the heater current to the furnace. This reduces electric field changes inside the vacuum chamber to the point where conductivity measurements can be made while the film is being deposited, without the 60 cycle alternating current used to heat the furnace disturbing the sensitive electrometer of the measuring circuit.

Various evaporation rates for the furnace were determined by direct experiment, weighing the total amount of lead deposited on an unplatinized cover glass in a known length of time (about ten hours), the furnace temperature being kept constant throughout that time. The resulting curve of mass deposited per unit area per unit time against reading of the millivoltmeter attached to the copper-constantan thermocouple attached to the furnace is shown in Graph 1. As will be seen from the sample data of Table 1, the accuracy obtained in weighing the actual film is not high, since etching off the lead and weighing the backing plate alone gives another weight almost as big as that of plate and film together, hence the accuracy of the difference suffers. Also, it appeared from comparing thermocouple readings with values of heating current that the thermocouple might not be absolutely reliable in its response, though neither error is so large as to invalidate the curve. The chief source of thermocouple error is probably slight shifts in its position from run to run, although the furnace is constructed to make small changes in this position unimportant.

(3) The film:

Plate 3 shows the support for the film backing, with the two supporting hooks insulated from each other so they act as current leads to determine the conductivity as well as supporting the cover glass while it is being soldered. Cooling fluid can be poured in at the top, and circulates in close juxtaposition to the deposited film itself. To control the melting of solder used to fasten the backing down, a thermocouple was attached at the point indicated.

Proper electrical and thermal contact between the deposited film and its surroundings was obtained by using solder. Before inserting the film support into the vacuum chamber, carefully cleaned strips of solder were placed under the contact hooks, and under the cover glass itself. A previously tinned brass plate inserted as shown helped the solder to spread evenly over the platinized back of the cover glass when heated (Plate 4). Then, while outgassing the apparatus, the induction furnace was moved so that the temperature of the cover glass and brass backing plate remained a few degrees above the melting point of solder for several minutes. In this way, all crevices were filled, and dependable contact established both with the cooled quartz chamber and with the current leads. Sometimes there were a few small bubbles under the cover glass, but these seldom covered more than a small fraction of the total area cooled. The film backing was not heated except as noted here.

In using the apparatus, after the cleaning, loading, and outgassing procedure described above, the furnace would be brought to the desired temperature, (using two rheostats in parallel to control the current precisely) and held there for at least an hour with the shutter closed. After that, the shutter would be opened for a known length of time, thus depositing a known amount of lead on the backing. Conductivity measurements were made from time to time while the film was growing, and afterwards as well if growth was interrupted to study aging effects.

(4) Electrical measurements:

The electrometer was calibrated by connecting in parallel with a voltmeter and applying various potentials. Electrometer-indicated potentials required in the calibration of the auxiliary condensers (see below) were obtained by direct measurement for the point desired, instead of taking the result from the calibration chart.

Some of the earlier measurements were made using circuit No. 1 (Plate 6). This is essentially the circuit used by Anderson, and the experimental arrangement represents for the most part minor rearrangement of apparatus designed by him. The potential across the film sends a current onto the electrometer, and by measuring the time between indicated potentials the resistance of the film can be calculated using the ordinary exponential law of charging a condenser through a resistance. Serious charge leakage was avoided by insulating the electrometer system with amber, hard rubber, or lucite at points of support. Calibration of the various auxiliary condensers will be taken up with circuit No. 2, but for this case we need the capacitance of the electroscope system to ground. This quantity was found by comparing the charging rate when the electrometer alone was in the circuit with that when C_1 was also in, using a typical film when at the right thickness for the purpose. The accuracy of this calibration is not high, but the results obtained from this basis are consistent, and attempts to improve the accuracy by other means brought doubts concerning stray capacitances to ground or the electrostatic shielding (e.g. that of the contact hooks). Only the first readings were taken with circuit No 1, however. This circuit assumes that Ohm's law holds for the film, since the potential across the film varies several volts as the condenser charges up, and the exponential variation in voltage with time (assumed in reducing the data) is a result of the strict proportionality between current and potential difference. Since some of Anderson's work cast doubt on the validity of Ohm's law for thin films, a circuit was sought which would allow current to be measured at constant potential drop. Thus, if measurements be conducted rapidly enough so that the current would not have time to change appreciably due to other causes (time, or increasing thickness of the film), each measurement will be valid, even if current is not strictly proportional to potential drop. If the change from one potential drop to another be made convenient, the experimental check of this proportion becomes simple and precise.

Many of the room temperature data and all the liquid air temperature data were taken using circuit No. 2, due fundamentally to Townsend 70). It will be seen from Plate 7 that, as the potential of the film is raised by allowing charge to leak on through the film, it can be lowered by reducing the potential of the other side of the condenser bank, using contact L in the potentiometer shown. Thus, as more and more charge leaks on, the potential of the electrometer can be maintained at zero by manual adjustment of the 15-volt potentiometer. Hence, leakage of charge from the electrometer system becomes negligible except as it may occur across the condenser bank. Furthermore, the capacitance of the electrometer system disappears from the equations used to measure film resistance, affecting only the sensitivity of the circuit. Thus there is no longer need to worry about stray capacitances.

The theory of this circuit is simple, but will be given here to illustrate the correction for leakage across the auxiliary condenser. (It has been noted above that this is the only place where the electrometer system is influenced by a conductor of different potential, except across the film, and the leakage across the film is being measured.)

Let the capacitance of the entire electrometer system be C_e to ground.

Let the capacitance of the electrometer system to conductor (1), (Plate 7) be C_{1b}. (This can be varied by connecting in more auxiliary condensers.)

Let the auxiliary condenser have leakage resistance R, and let this resistance obey Ohm's law.

Let the time of measurement be short enough so that current to be measured will depend only on the potential drop across the film.

Then: Q = charge on electrometer system = $C_e V_e + C_{1b} V_1$

and if C_e be maintained at zero potential, $Q = C_{1b} V_1$

The rate of increase of this charge is the film current I_F, less the current leaking away across the auxiliary condenser. That is:

$\frac{1}{C_{1b}}\frac{dQ}{dt} = \frac{dV_1}{dt} = \frac{I_F}{C_{1b}} + \frac{V_1}{RC_{1b}}$ hence $V_1 = I_F R\left(e^{\frac{t}{RC_{1b}}} - 1\right)$ since I_F will be practically constant. (This is the only approximation so far.) If now we call $-RC_{1b} = \tau =$ the time constant of the auxiliary condenser, then if τ is large enough in comparison with our short time of observation, we may write:

$$I_F = \frac{V_1}{R(e^{-\frac{t}{\tau}} - 1)} \approx \frac{C_{1b} V_1}{t(1 - \frac{t}{2\tau})}$$

In all but a few cases, $\frac{t}{\tau}$ will be so small that even the correction term can be neglected.

The only changes necessary to adapt the Anderson apparatus to this circuit were to insulate the condenser bank from ground on both sides, set up the potentiometer rheostats (which need not be calibrated), and construct another auxiliary condenser having very large resistance and capacitance of the order of magnitude of the electrometer system (Plate 5C). The electrometer is now used only as a null indicator.

In using this circuit, one connects the film to the electrometer, releases the grounding key, allows the film to leak charges onto the insulated electrometer system for a known length of time, moving the potentiometer contact away from zero just fast enough to keep the electrometer reading zero, cuts off the film at a measured instant, adjusts the electrometer accurately to zero, and reads the resulting V_1. The manipulation is but slightly more complicated than that of circuit No. 1, and the error much less. Leakage corrections can be applied more easily, stray capacitances do not matter, and a constant potential drop is maintained across the film. By the use of the 45-volt potentiometer (Plate 7) this potential can be varied, and resistance measured for various potential drops, thus checking Ohm's law.

(5) Calibration of condensers:

The electrometer system is so shielded (Plate 7) that its two parts act like separate condensers connected. That is, the capacitance of (a) to (1) in the diagram can be neglected, due to the grounded shield between. Thus, if we keep the total charge on the electrometer system zero, we will always have Q_b = charge on (b) part of electrometer system $= -Q_a = -C_a V_a$ where V_a is the potential indicated by the electrometer, and C_a is the capacitance to ground (i.e. to the shielding) of the (a) part of the system.

But $Q_b = C_b V_a + C_{1b} V_1$ as before, hence $C_{1b} V_1 = -(C_a + C_b) V_a$

Let us connect C_s = capacitance of the standard condenser in parallel with C_a and adjust the potentiometer to V_1' so that the same potential V_a on the electrometer obtains. Hence we have:

$$C_{1b} V_1' = -(C_a + C_b + C_s) V_a \quad \text{or} \quad C_{1b} = \frac{-C_s V_a}{V_1' - V_1}$$

This method calibrates one auxiliary condenser against the standard, but is not convenient if $|C_{1b}| >> |C_s|$, since then V_1' differs so little from V_1 that measurement is difficult and inaccurate. The other condensers were calibrated against the known auxiliary in cascade fashion as follows:

Let the total charge on the electrometer system be Q, as obtained by putting a potential V_1 on the conductor (1) and grounding the electrometer, with only the known C_{1b} across the gap between (b) and (1). Now, with the electrometer insulated, we connect the originally uncharged C_{2b} in parallel with the C_{1b} , and adjust the applied potential to V_1' to bring the electrometer back to zero. In doing these things, we have

$$Q = C_{1b} V_1 = (C_{1b} + C_{2b}) V_1' \quad \text{hence} \quad C_{2b} = C_{1b}\left(\frac{V_1 - V_1'}{V_1'}\right)$$

Thus we calibrate the condensers in order, each against the last. The results are shown in Table 2, each value given being the result of at least ten capacitance readings. The calibration of C_0 against C_s is the result of 60 trials, but the spread is such as to make the probable error 2%. A further check is available near the other end of the cascade: The best auxiliary condenser (No. 4) is marked 0.2 μfd. by its maker (Carpentier, Paris), while the value obtained by the indirect method described here is 0.201 μfd. if carried out to three decimal places. The agreement with the experimental value is encouraging, but some of the apparent accuracy must be called good fortune.

Leakage rates and time constants were determined by keeping the electrometer system, charged, at zero potential, measuring at various times the value of V_1 required to do this. The results are included in Table 2. Since observation times were kept under 20 seconds for the most part, only the readings taken with C_3 have appreciable leakage corrections.

C. Results and their significance:

I. General:

The films used for the data recorded here were selected from those actually made by the method described as the films which exhibited uniform mirror-like appearance under careful visual inspection. It was found that, among other things, the slightest trace of grease vapor, even of slightly warm Apiezon W, inside the vacuum chamber itself gave rise to films of uneven thickness and non-metallic appearance. All such films were discarded for use in calculating results. On the other hand, essentially all the readings taken with films it was decided to use are found on the graphs; in order to include the dozen that do not appear, it would have been necessary to draw some of the curves on a smaller scale.

Thickness of the films was obtained by dividing the mass of lead per square centimeter (known from the evaporation rate of the furnace, Graph 1) by the density of bulk lead (11.3 gms. per cc.). A brief discussion of this assumption will be found above, on page 10.

The structure assumed by these lead films when allowed time to come to equilibrium was photographed with the ultramicroscope. Plate 8A has already been referred to as a photograph of the edge of a film taken by this method. Plate 8B is such a photograph, taken from the central region of a typical lead film deposited by this apparatus at somewhat higher magnification than 8A. The grainy structure is very obvious, and is typical of the appearance of these films under ultramicroscopic examination.

The conductivity plotted is the quantity $\sigma = \frac{L}{Rwd}$

where R is the measured resistance of the film (ratio of potential drop to current),

L is the length of the film between electrodes,

W is the width of the film,

and d is the thickness determined as above.

This quantity will certainly give the conductivity in mhos per centimeter cube of a thick piece of metal, but it is by no means obvious that the expression means much more than it actually says for a thin layer. The values of L and W were measured for each film, but were maintained very nearly 1.0 centimeters each by the construction of the apparatus. Also, care was taken that the sides of the film be as nearly as possible perpendicular to the electrode edges, but no correction was applied if the resulting film was out by a few degrees, since it is easily shown that the correction factor to be applied for a parallelogram film whose corner angle is α is somewhere between $\sin\alpha$ and $\csc\alpha$. For angles near 90°, both these functions have values very nearly unity.

Cutting off the potential from the film for a time was observed to have negligible effect on subsequent observations; passing current through the film seemed to increase its resistance slightly for a time, but if the film was allowed to rest a few minutes without current (with or without being electrically charged), it seemed to recover.

II. Preliminary observations:

The results given by eight preliminary runs of the apparatus are shown in Graph 2. The films were obtained by exposing the water-cooled backing continuously to the beam of lead atoms, measuring the conductivity from time to time. The speed of deposit was kept as nearly constant as possible during each run, but different speeds were used for different runs; the rate of deposit in Angstroms increase of thickness per minute is attached to each curve on the graphs.

It will be observed that the conductivity of the thinner films decreases slightly with thickness, a result that is in harmony with the preliminary increase in resistivity noted by Anderson (page 2), although it must be emphasized that this change with thickness really means that the measured resistance of the film is not decreasing as fast as the thickness is growing. In most cases, the film exhibits detectable conduction after a short time of deposit, and then the resistance remains almost constant for a considerable number of Angstroms increase in thickness.

Soon, however, there comes a point (depending more, apparently, on the conditions obtaining for the individual film than on the controlled variables, e.g. speed of deposit; as will be seen here and later, correlation between deposit speed and film properties is very slight) where the conductivity begins to rise rapidly toward the bulk value about 10^{12} higher. It will further be observed that these points are in the neighborhood of 150 Angstroms for most of the films, there being three at about 100 Angstroms, and two at about 200 Angstroms.

It will also be seen that for several of the films the curve begins to have an inflection point, as though conductivity began to come with a rush. then slowed down a bit later. This effect is not very prominent on these curves, but will be more so on those to come later.

III. Films condensed at room temperature:

After these first few films described above were deposited and measured, a more rigorous outgassing technique was adopted, with corresponding improvement in the vacuum obtained in the apparatus, hence it was felt that the films obtained under these new conditions gave sufficiently more reliable results to justify their being discussed separately. The results on five more runs of the apparatus are plotted on Graph 3.

It will be observed here that the thickness where a film begins the swift rise toward the bulk value of conductivity is more nearly the same for the different specimens measured than was the case for the films described under II, being about 60 Angstroms for four of the films, and only a little over 100 for the other one. Furthermore, the inflection point is more prominent in these data, showing definitely that the conductivity of the films deposited under these conditions starts its rapid rise, then slows down a little, but is still increasing very rapidly when its value becomes too large to be measured on the apparatus in its present form.

It is particularly interesting to notice how far the conductivity of a film decreases with time when the beam is cut off, and the film left to itself. Two of these curves show how the conductivity decreases by more than an order of magnitude under these circumstances. (Stable lower values were approached after about half an hour). When the lead is turned on again, it is seen that the rise toward bulk value is particularly rapid, until the curve becomes practically a continuation of the former portion.

These effects were tested more thoroughly by the subsequent experiments depicted in Graphs 4 and 5. Graphs 4a and 5a are the results obtained from two runs of the apparatus under the same high vacuum conditions as the other films discussed in this section, the difference being that deposit was interrupted at regular intervals, and the film allowed to come to equilibrium after each partial deposit. The curves of conductivity against time while this approach to equilibrium process was occurring are given in Graphs 4b and 5b. The symbol B is attached to the curves at the points where the conductivity becomes so low that the conduction of the film was lost in that of the background. It will be seen that the conductivity of the thinner films rises rapidly to a value in the neighborhood of 10^{-5} mho $cm.^{-1}$, then decreases slightly as the thickness increases until the film is cut off from the lead beam, then swiftly falls back to become indistinguishable from the background. On the next exposure, the same process is repeated almost as on a fresh background, and so on until the total average thickness is several hundred Angstroms. Then the rises become higher and the falls not quite so low.

Graph 5b exhibits a very interesting feature that will be seen again in the data to be discussed below. The curves obtained using 20 volts across the film to measure its conductivity lie always below or coincident with the curves obtained by using 40 volts across the same film. The thick film does not show this separation within the error of the experiment, but the thinner ones quite definitely disobey Ohm's law, in that as the applied potential is halved the current is reduced by a factor slightly larger than 2. This result is in qualitative agreement with a result given by Anderson[1)], although the effect observed here is not as large as the one he records, and seems to depend less on the previous voltage history of the film. An attempt will be made in paragraph VII of this section to assign reasons for these modes of behavior in terms of accepted ideas as to the physical state of metals in thin films.

IV. Films condensed on liquid-air-cooled background:

A significant number of experiments were made while cooling the background with liquid air. A thermocouple was attached at various places on the film backing itself and on the brass underplate (See Plates 3 and 4) in an attempt to decide what relation existed between the temperature of the liquid air and the temperature of the film itself. No more definite conclusion was reached than that temperature differences as high as 50°C. could exist between the film and the fluid, and this difference increased when the film was exposed to thermal radiation from the evaporating furnace. Therefore, the evaporation was conducted in spurts of a few minutes each, with the shutter closed in between intervals of deposit, long enough so that the film approached equilibrium, both thermally as indicated by the thermocouple and in configuration as indicated when the conductivity settled down toward a constant value. Thermal contact between the thermocouple and the glass surface holding the film was rather uncertain, but it is believed from the readings obtained that the methods described above maintained the film temperature below -100°C. throughout each liquid-air-cooled run.

The results obtained in five runs with the apparatus with liquid air cooling are plotted on Graphs 6,7,8, and 9. These plots have been made as nearly self-explanatory as possible: With each curve is included the rate of deposit, with the aging curves the average thickness of each film measured, and the curves taken with 20 volts potential drop across the film are clearly distinguished from those taken with 40 volts wherever such distinction exists.

The most striking difference between these curves and the similar ones (Graphs 4 and 5) obtained for the higher temperatures is that in the present case the phenomena of rapid increase of conductivity with thickness toward the bulk value, and of rapid decay with time into the background conduction, seem to occur much sooner, and in more intense fashion. The points where conductivity begins to increase rapidly are in every case in the neighborhood of 30 Angstroms average thickness. However, when the beam is cut off, the conductivity falls again to low values, Graph 9a being a particularly good example of the high peaks and low valleys obtained. For some of these films, however, it will be noted that, while the first increase of conductivity still begins very early, later the film seems nearly stable as it is laid down (e.g. Graph 6a or 8a). Departures from Ohm's law are seen to be less striking for the most part. The slope of the aging curve of film conductivity (a quantity proportional to the fractional rate of change of conductivity with time, since these curves are plotted on semilog coordinates) will be observed to become less steep with increasing thickness. This point will be brought out more plainly in Graph 10 (same page as Graph 1), which is a direct plot of the initial rate of decrease in log σ with time against the thickness for the various films for which a significant number of such data exist.

V. Rates of time-decrease in conductivity:

Graph 10 is, as noted above, a plot of the negative numerical slope of the initial part of the aging curve against the thickness of the film being aged. It will be seen that this initial slope (proportional to $-\frac{1}{\sigma}\frac{d\sigma}{dt}$) becomes smaller for the cold backing with increasing thickness of film, and reference to any b-graph will show that this rate of decrease of log σ decreases with the time. The maxima observed in the curves for room-temperature backing on Graph 10 are quite amazing, though caution whispers that two data are hardly enough to use as a basis for a new theory. These maxima might, of course, be due to insufficient aging of previous layers, that is, the lead be applied to an undercoating not yet fully in equilibrium. However that this "underaging" phenomenon should happen preferentially at high temperatures would be amazing also, since presumably the equilibrium state should be approached more rapidly at higher temperatures. The total time of aging was about 30 minutes for all these films. For the liquid air temperature data, it is seen that, for 100 Angstroms, say, the films deposited more rapidly tend to have a higher rate of initial decay in conductivity. This tendency is so slight, however, that it could not be regarded if it were not the result to be expected on the basis of the picture to be presented in paragraph VII.

VI: Conclusions from the above observations:

Apparently, with these experiments as with many others in the field, the quantitative results depend in such measure on seemingly minor details of experimental technique that, until more standardized methods are worked out, it is of doubtful validity to look much deeper into the actual numerical results than their orders of magnitude. It seems, however, that the trends exhibited in these data are qualitatively true, and the results therefore not without application to the problem at hand.

In addition to the general statements about electrical conductivity under which the results of other experimenters were classified in A, II, (i.e. thickness dependence of conductivity, critical thickness for rapid changes, instability leading to irreversible changes with time and temperature, and the importance of deposit conditions) the results described here allow the following more specific statements to be made, true under the conditions obtaining for the experiments:

(1) Deposited metal films ultimately exhibit a non-uniform, or grainy structure under ultramicroscopic examination.

(2) The critical thickness for rapid change of conductivity of a continuously deposited lead film is smaller for lower temperature of deposit. After this thickness is reached, the increase is at first very rapid, then less rapid.

(3) Films deposited at room temperature show a slight decrease in conductivity with thickness when this is less than the critical thickness of (2).

(4) The conductivity of these films decreases with time after the film is deposited, the fractional rate of decrease being more rapid for the thinner films, though there is indication of a maximum in this rate for intermediate thickness at higher temperatures.

(5) The total change of conductivity with time is larger in some cases for smaller applied potential used to measure the conductivity, and is larger in most cases for lower temperatures.

The bearing of these ideas on the process of electrical conduction in thin metallic films will now be examined.

VII. Qualitative mechanism of thin-film conductivity:

On the basis of the experimental facts quoted and obtained in the above sections of this thesis, the following picture of atomic behavior giving rise to the observed conductivity phenomena can be drawn:

The freshly deposited film will consist of atoms condensed from the vapor, dispersed at random on a cooled solid backing surface. In view of the large energy changes available if the atoms become adsorbed on the backing plate or move close to each other and form groups, the random configuration cannot be expected to be an equilibrium one. It is known, however, that only a very few atoms of the metal (compared to the number available in a few minutes deposit with the lead beams used) are sufficient to neutralize the Van der Waals adsorptive forces, particularly if other atoms (e.g. material not removed by the outgassing process) have been adsorbed first. Hence the next possibility for a more stable configuration is that of forming groups of atoms, the added stability being due to reduction of free surface and to lattice formation. The equilibrium state actually observed in these experiments is thus the one to be expected on this picture, since the presumably fixed first few layers are inaccessible to accurate observation with this apparatus, and therefore the atoms which can be observed are those coming a little later. These will appear mobile, and draw apart into many small groups. This process results in the formation of areas unoccupied by observable atoms, unless the total number of atoms available is sufficient to fill these areas with more groups. The rate at which this aggregation will take place will depend on the mobility of the atoms on the surface; the equilibrium configuration will be approached more rapidly if the atoms are more mobile.

Since this approach to equilibrium has been going on all the time deposit was taking place, the degree of instability existing at the instant of stopping the deposit will depend on the relative rates° of deposit and aggregation, being presumably greater for faster deposit.

Two mechanisms of conduction may be considered as possible for the thin layers under these conditions: either electronic or ionic conduction. On this picture of group formation, either mechanism will give a

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°The rate of deposit can be controlled with satisfying accuracy by the methods described above, but adequate standardization of the deposit surface to give really reproducible values of the rate of aggregation was apparently not assured by the methods used here. It may be that success in this direction lies along the line of rigorously outgassing the deposit surface as done by Lovell, although it is uncertain how much such heroic heat treatment will injure the structure of the surface itself while driving off adsorbed atoms.

conductivity decrease with time: A conduction electron is able to leap small gaps, but when the film draws up into closely packed groups the path of a conduction electron becomes interrupted by a smaller number of larger gaps, and these inhibit conductivity. On the other hand, any electrolytic conduction which occurs will doubtless be motion of ionized "free" atoms, since the temperature is far enough below the melting point so that any atom which joins one of the groups is unlikely to escape from the strong forces binding it there. That is, only uncombined atoms will have appreciable mobility, and as the number of such atoms decreases the conductivity decreases.

The ionic mechanism gives, on this picture, complete absence of conduction when the atoms are all combined. Many of the thicker films included in these experiments have shown conduction when the resistance became practically constant, and therefore equilibrium conditions had supposedly been reached, and all the "free" atoms had given up their freedom in exchange for stability. This residual conduction indicates that a substantial part, at least, of the conduction is electronic. On the electron picture, when no more current is carried by the film itself (i.e. resistance is that of the backing plate), it means that aggregation has pulled the film into separated pieces so thoroughly that the different pieces have lost all connection with each other.

That room-temperature films (See Graphs 4 and 5) do not become as conducting at the start as do those deposited at lower temperature (Graphs 6,7,8, and 9), although both kinds fall rapidly back to the conduction of the background, may mean that the extent of instability in the high-temperature film is less than that in the low-temperature film, due to the presumably more complete aggregation that occurred while the high-temperature film was being deposited.

The results of Anderson1) support his assertion that the rate at which atoms disappear into the centers of aggregation is roughly proportional to the number of atoms as yet uncombined. It is reasonable to suppose, then, that when deposit is first started on a plate containing no uncombined atoms (i.e. all previous layers have been allowed to come to equilibrium), the average space between atoms will decrease very rapidly at first, until enough uncombined atoms are present so that the rate of aggregation becomes comparable with the rate of deposit. This viewpoint is consistent with the rapid initial rise in conductivity noted on Graphs 4,5,8, and 9 particularly. When the state is reached where new atoms are being supplied as fast as they disappear into the growing isolated patches, conductivity should become sensibly constant and the degree of dispersion existing when the supply is cut off will be measured by the total decrease in conductivity occurring after this as the film approaches equilibrium. Measurements of this sort on a properly standardized background should give much information about the rate of aggregation of the atoms in a newly deposited thin film, although the changing size of the patches of metal complicates the picture. Consideration, however, of Graphs 4, 5, and 9, shows that under proper conditions, even for many layers of fully aged lead, new deposits behave almost exactly as on a fresh background. From this it follows that the patches cover only a very small portion of the backing at such times.

The more sudden appearance of conduction (i.e. smaller critical thickness) for cold films than for room-temperature films (C, IV) would be attributed on this picture to the smaller degree of rearrangement occurring while the cold film is being deposited. The smaller conductivity plotted for increasing thickness of the thinnest films has been discussed above as being due mainly to the increase of the thickness (d in the formula for σ in paragraph C,I.), the resistance remaining essentially at the same high value while the thickness increases.

When the patches of metal on the backing become large enough so that appreciable forces are exerted by the edges of one group on those of other groups in the neighborhood, these surface forces will tend to close the gaps between the patches. Thus we should have a sudden increase in the equilibrium conductivity. It seems reasonable to suppose that the first few occurrences of this sort will create a very few paths of easy conduction ("through highways" , so to speak) across the film, and that subsequent increases in conductivity come from forming a more and more dense network of such paths. When this process begins, the higher conductivity obtained,after all the free atoms have completed aggregation, would be taken on the basis of the mechanism considered here as an indication of the degree to which the patches are connected.

Whether such a path as is considered above is a conducting path or not would be expected to depend somewhat on the energy available to push the electrons across the gaps. Hence, when the film is aging, some paths may very well become, due to slowly widening gaps, non-conducting for 20 volts applied potential before this happens for 40 volts applied. This is the sign of the deviation found from Ohm's law. A conduction mechanism of this kind requires the existence of a voltage threshold. The apparatus described does not, however, permit the accurate determination of conductivity in the region of contact potentials that would be necessary to investigate this expected threshold.

D. Summary

The apparatus of Anderson has been improved and altered so as to allow experiments with lead films. Thin layers of lead were deposited under clean conditions very carefully achieved; the rate of condensation on glass surfaces was varied, and the surfaces were held at room temperature with circulating water, or below -100°C. with liquid air. The electric conductivity of these films was measured, and the following correlations between results and experimental conditions obtained:

The critical thickness at which the low-conductivity film begins to increase its conduction rapidly, approaching the conductivity of the bulk metal a factor of 10^{12} away, is found to be about 60 Angstroms for room temperature, and about 30 Angstroms for liquid-air-cooled films, if obtained by continuous evaporation.

If the deposit is interrupted (i.e. the film isolated from external influences), the conductivity of the metal layer falls rapidly toward zero, for the thinner films becoming undetectable very soon due to its being masked by the conduction of the backing plate of glass.

The rate at which this decrease starts was found to be greater for thinner films as a rule, and the total range covered by the decrease was almost always greater for low temperature films.

These conductivity-time curves gave lower conductivity for 20 volts measuring potential than for 40 volts used to measure the conductivity for all cases where the two could be distinguished.

The observed effects were fitted into the following picture of the conduction process in thin metal films: The time changes observed in resistance are due to structure changes in the film, such that its tendency to draw into small patches removes the mobile atoms from circulation, and opens gaps which obstruct the conduction electrons. The effects of temperature and time on this aggregation process have been discussed, with regard to the stability of the groups, and the possibilities of ionic and electronic conduction. The smaller atomic mobility expected at low temperatures has been shown to give the type of results actually found.

The deficiency in quantitative reproducibility is ascribed to lack of sufficiently good control of the physical surface conditions on the plate where the film is condensed.

E. Acknowledgments:

The writer has drawn extensively on the ideas and experience of others in carrying out these experiments. He has tried to note in detail his dependence on the results of Dr. A.B.C.Anderson, but there has been other valuable help which cannot be so definitely specified. To Dr. Goetz, who proposed the problem, utmost thanks are due for his many fruitful suggestions during the work and in supervising the preparation of this record; the help of Mr. E.L.Armi was most welcome in several vital places; the glass parts were skilfully made and kept in repair by Mr. W.Clancy; Mrs. W.J.Rodekohr has given much help in typing this report.

Table 1. Sample weighing of calibration film

Date of observation	Feb. 4, 1939
Time of deposit	480 minutes
Thermocouple reading	11.70 divisions
Area of film	1.53 sq. cms.
Sensitivity of microbalance	7.7×10^{-6} gms/div.
Weight of film and cover glass	0.217798 gms.
	0.217804
	0.217805
	0.217804
	0.217813
	0.217809
Average	0.217806gms.
Weight of cover glass (lead etched off)	0.217759 gms.
	0.217756
	0.217758
	0.217771
	0.217755
	0.217755
Average	0.217759 grams
Weight of film	4.7×10^{-5} grams.
Grams per square centimeter per minute	6.4×10^{-8}

Table 2. Condenser capacitances and time constants

Condenser number	Capacitance to electrometer, µfd	Time constant, seconds
C_0	— 2.3×10^{-5}	2040
C_1	— 2.16×10^{-4}	3300
C_2	— 1.81×10^{-3}	8600
C_3	— 1.55×10^{-2}	220
C_4	— 2.01×10^{-1}	4300
C_5	— 2.16	9540

Table 3. Apparatus numbers

Rheostats	BL8710 BL8712 BL8531 BL8363 BL 8379
A.C.Ammeters	BL8301 BL8145
A.C.Voltmeter	BL8052
D.C.Voltmeters	BL8953 BL8114
D.C.Millivoltmeter	BL80433
D.C.Milliammeter	BL8018
Hyvac pump	BL80361C
Electrometer	BL9345

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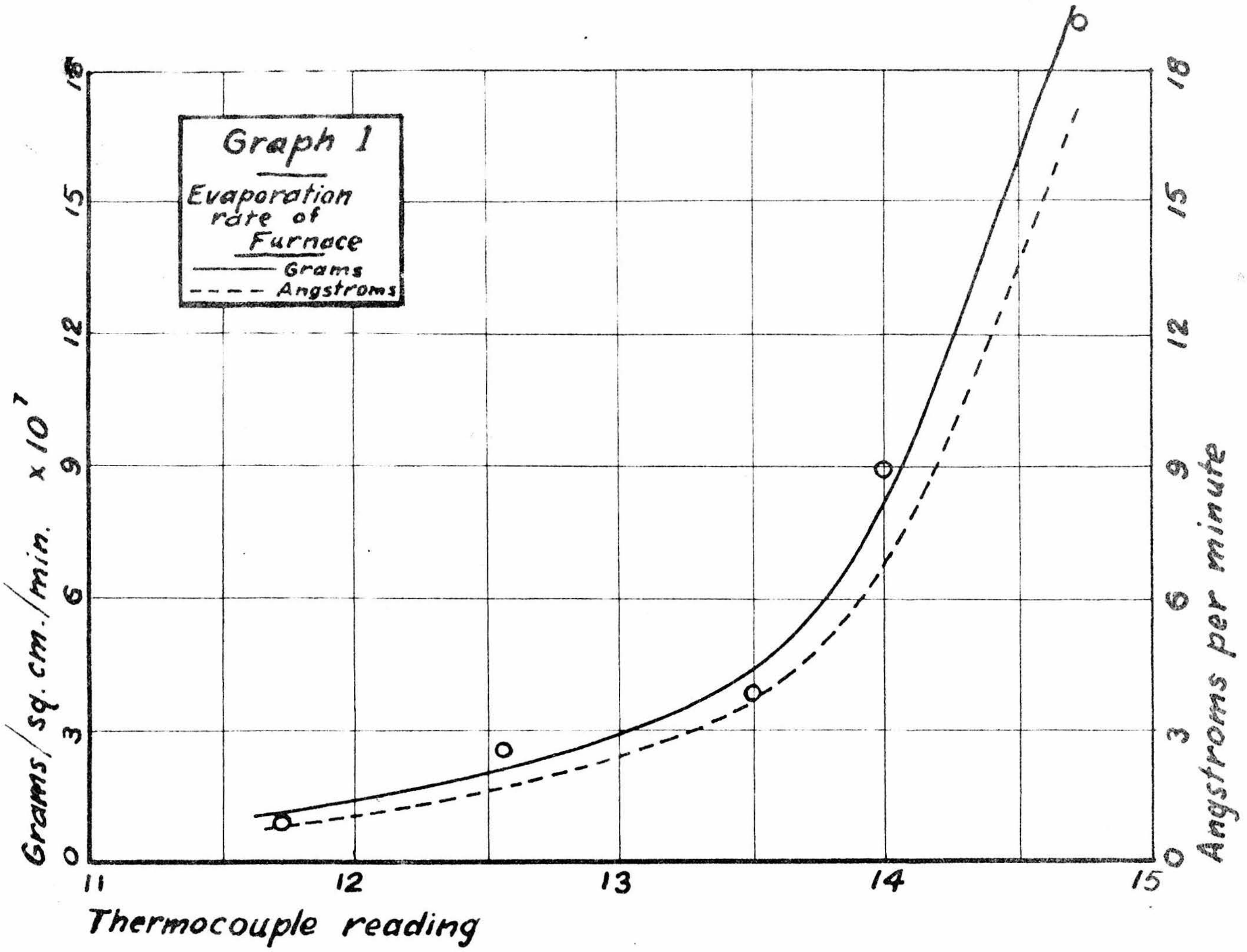
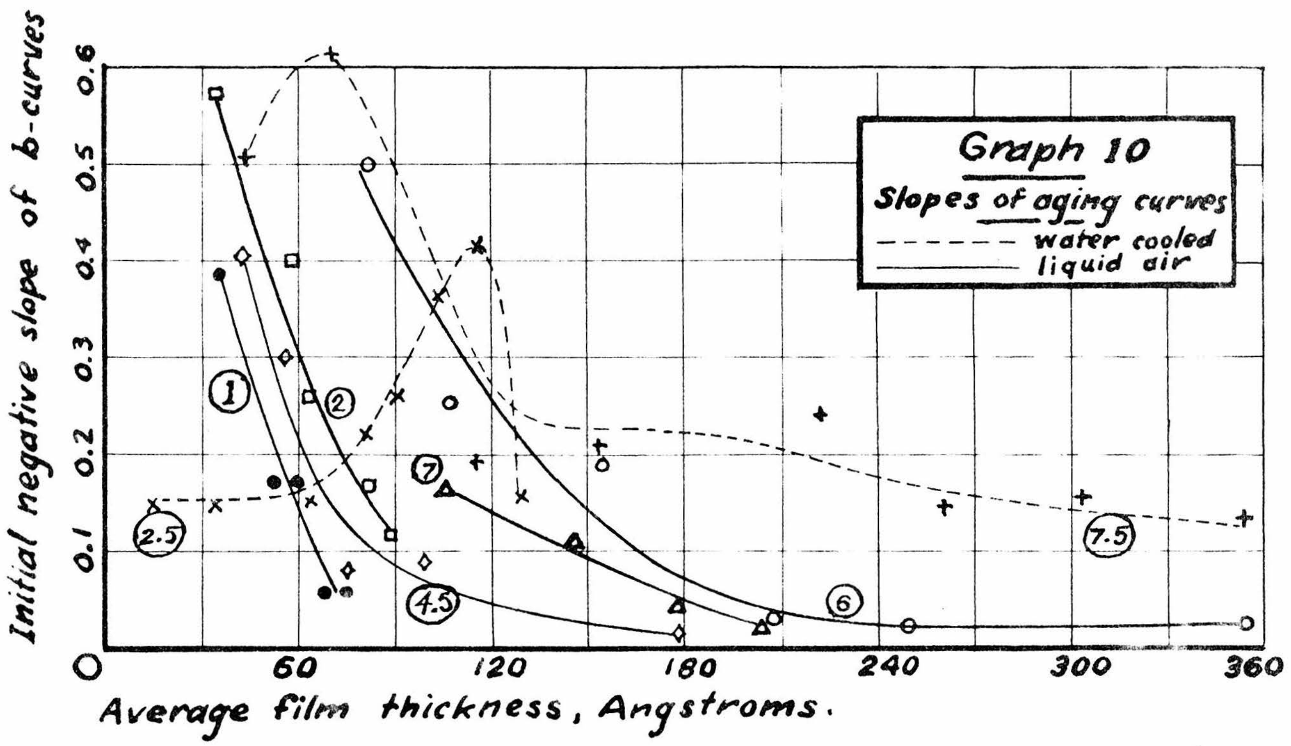
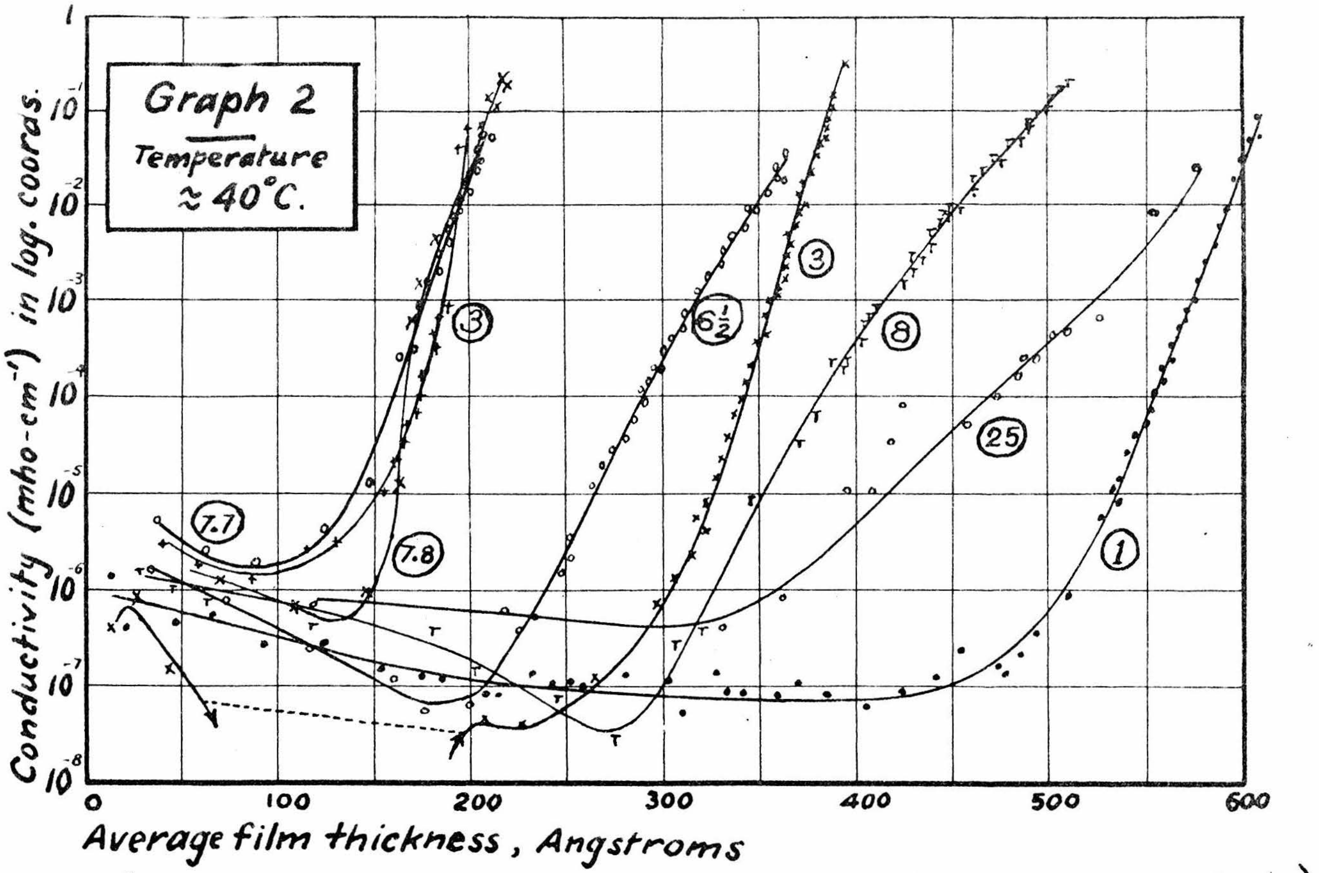
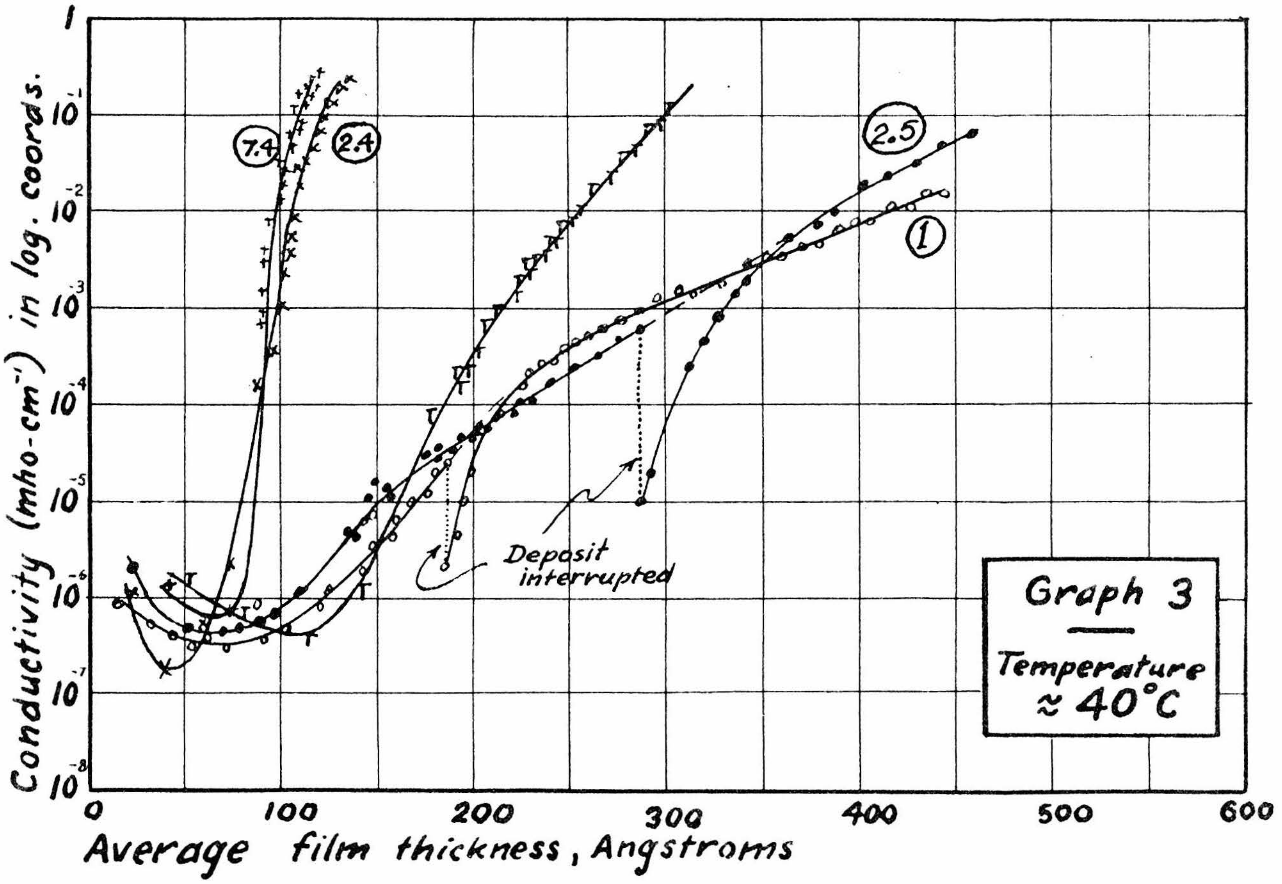


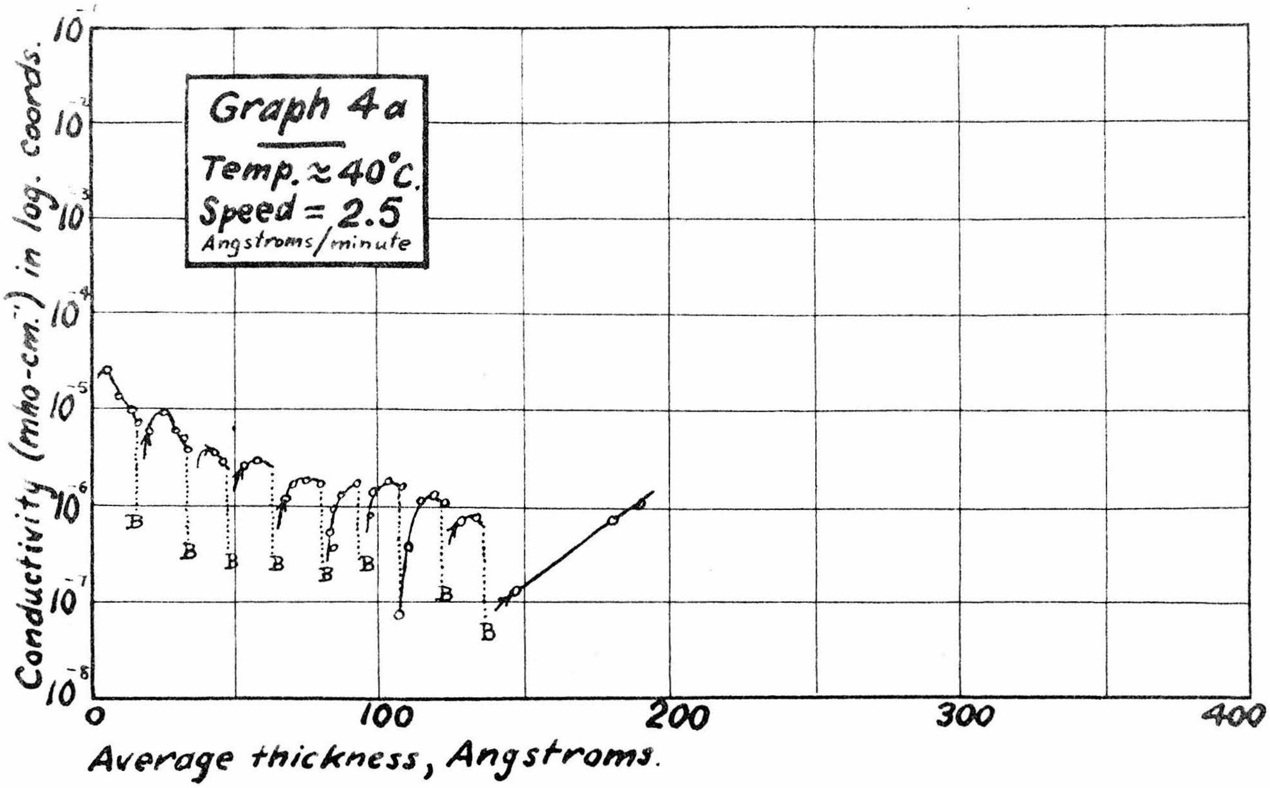


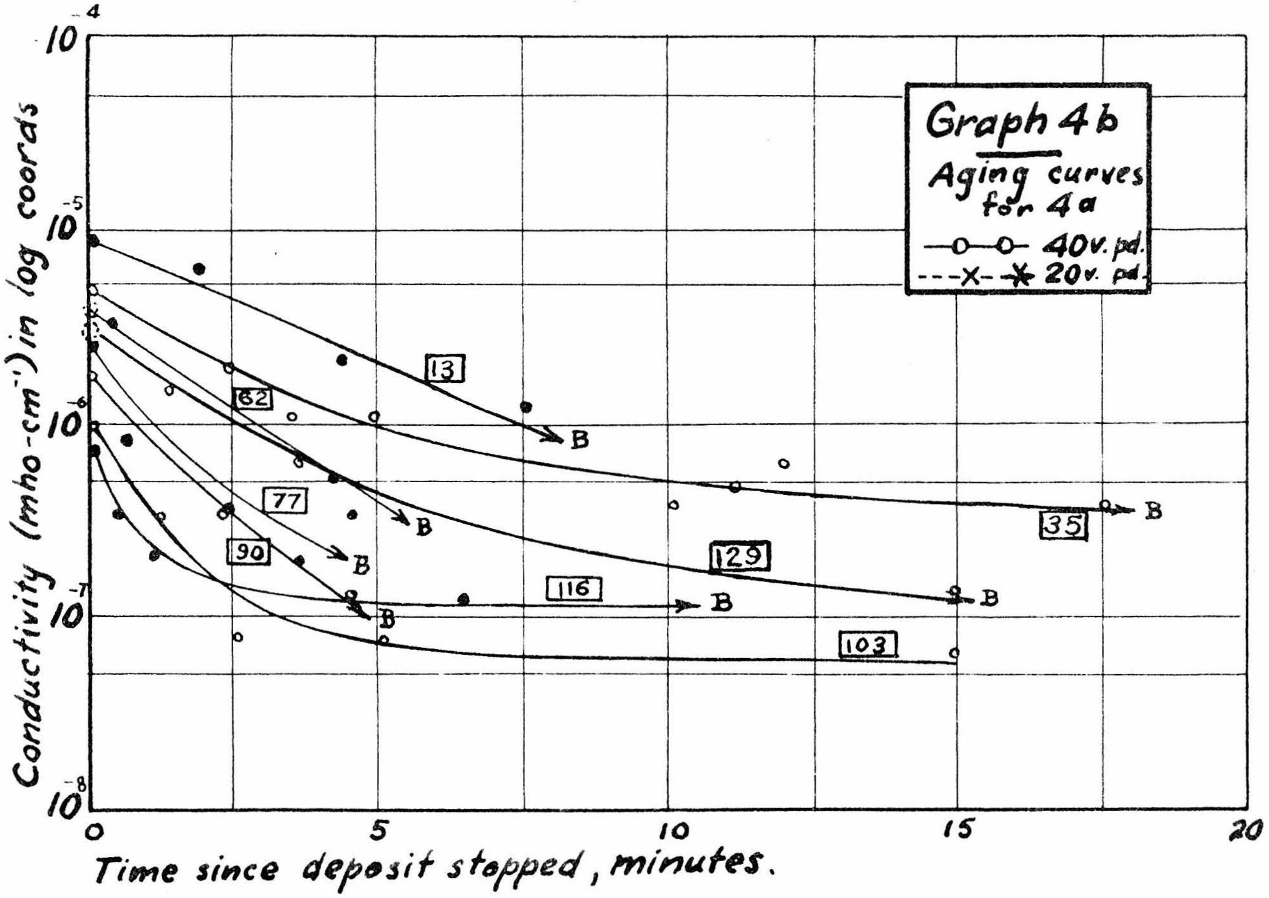
(Note: circled numbers indicate speed of deposit, Angstroms/minute)



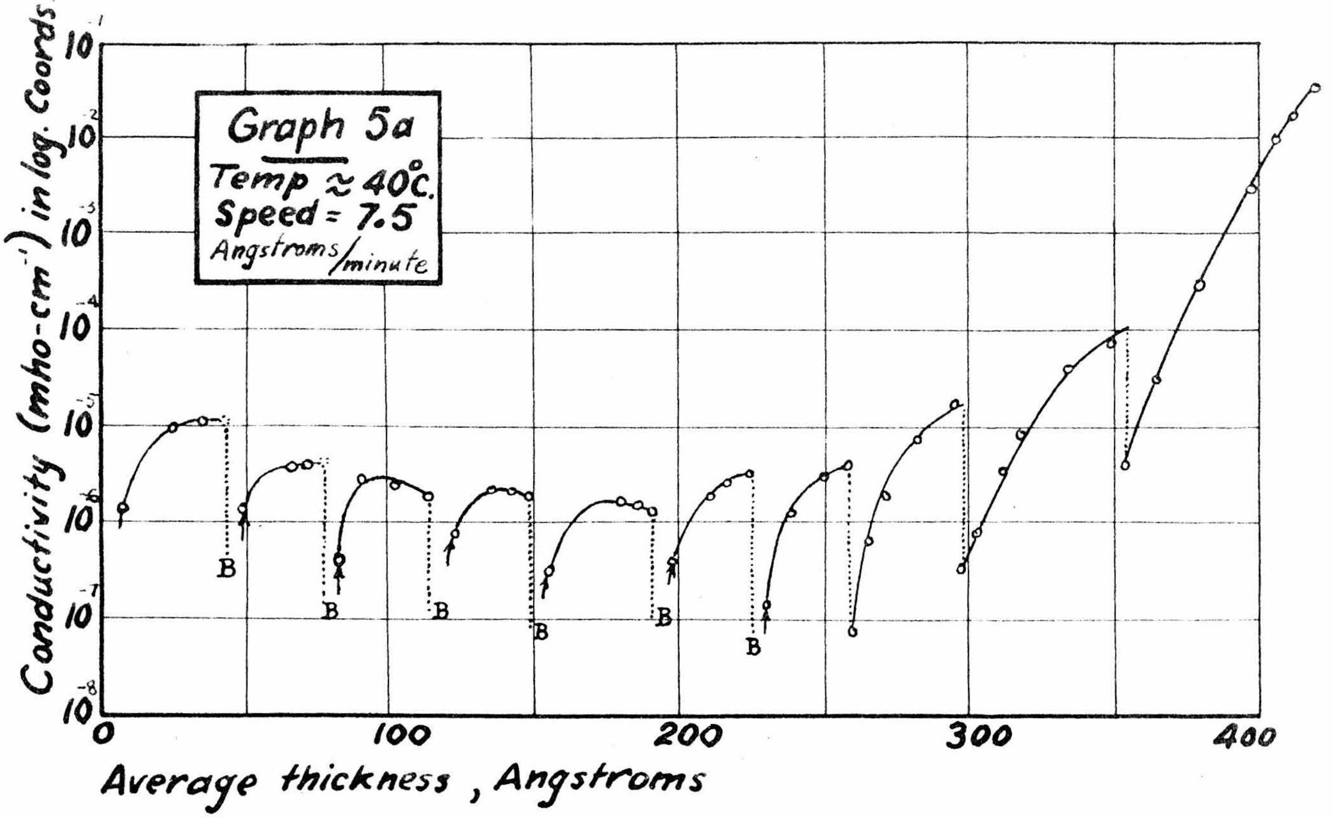
(Note: circled numbers indicate speed of deposit, Angstroms per minute.)

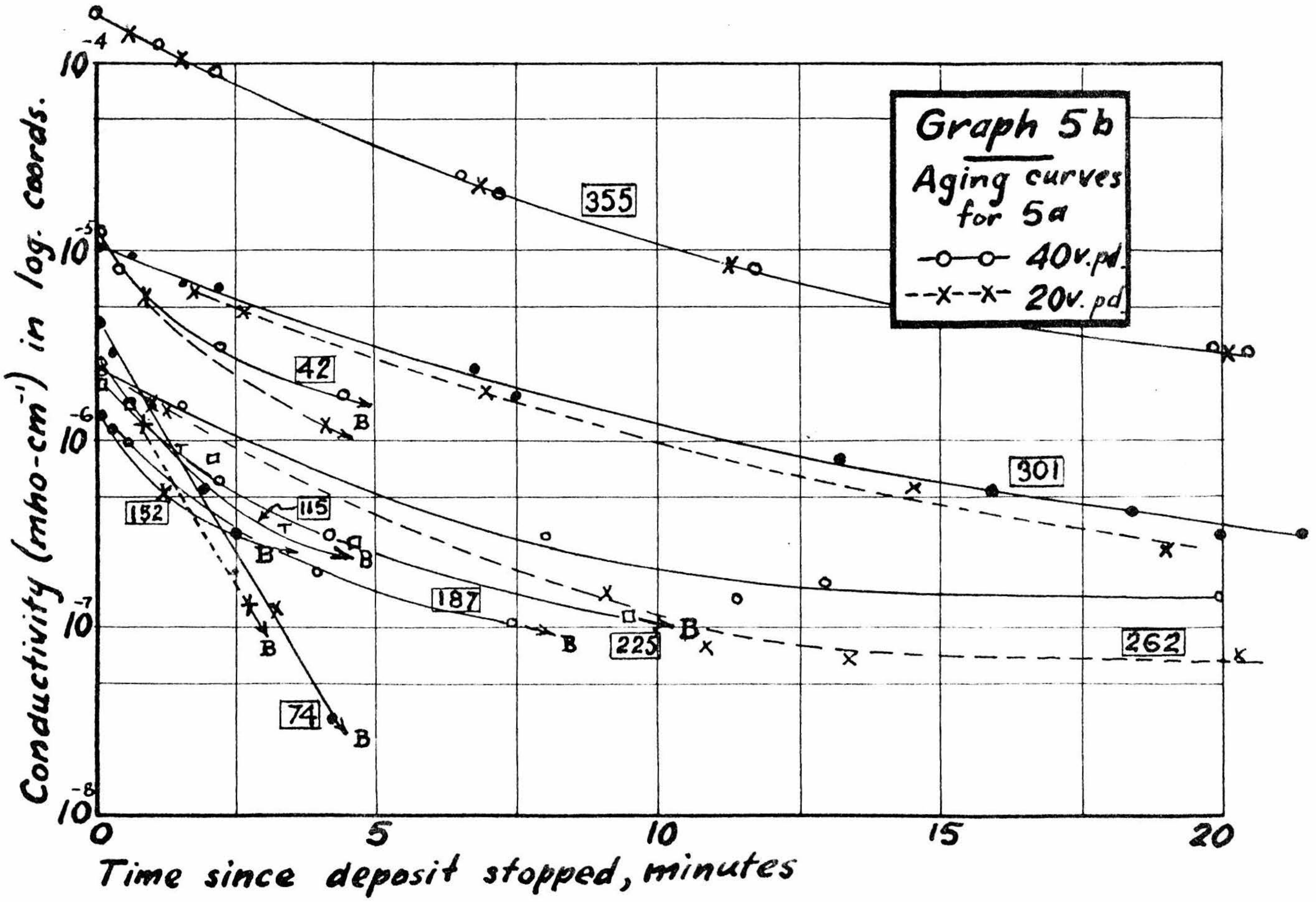




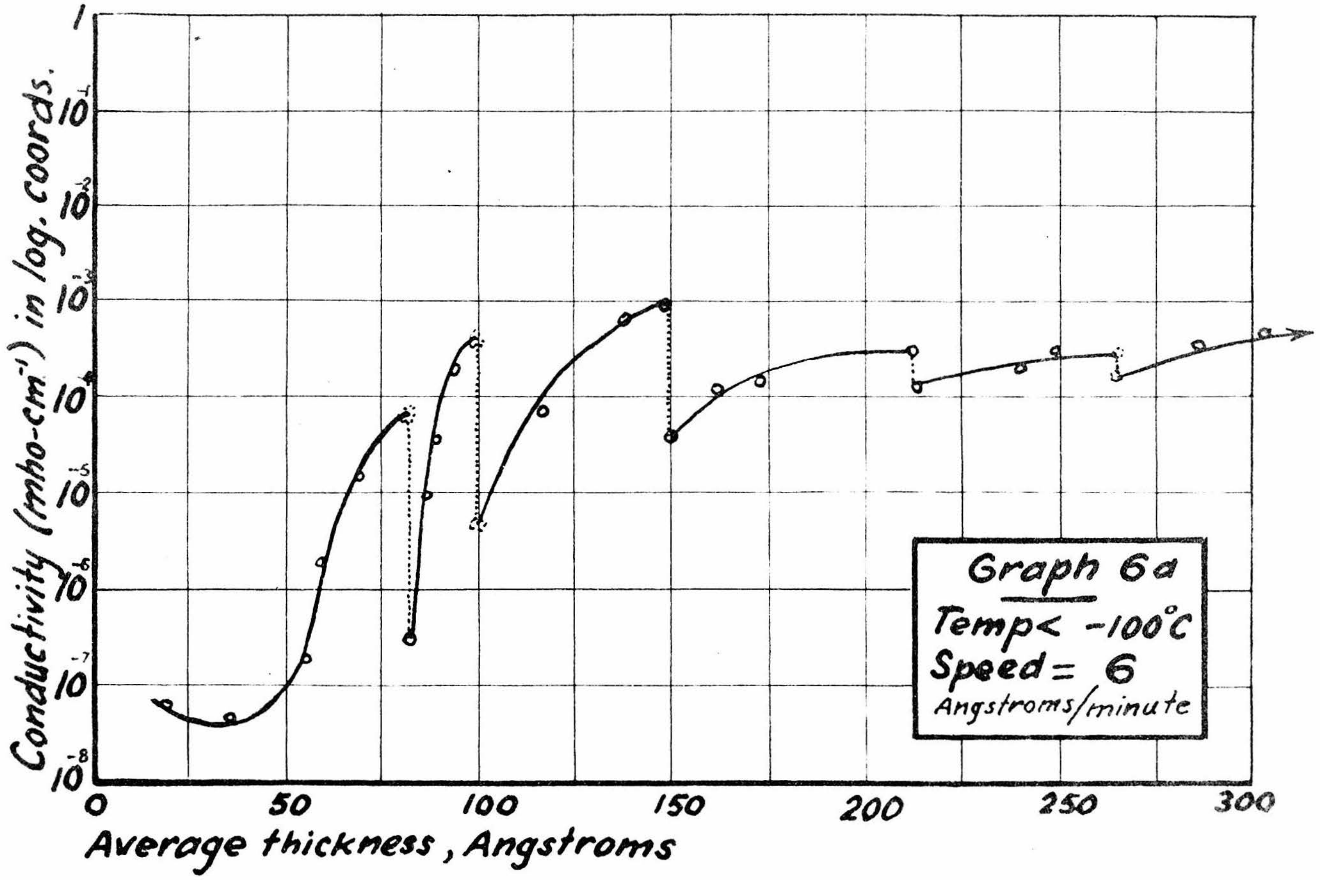


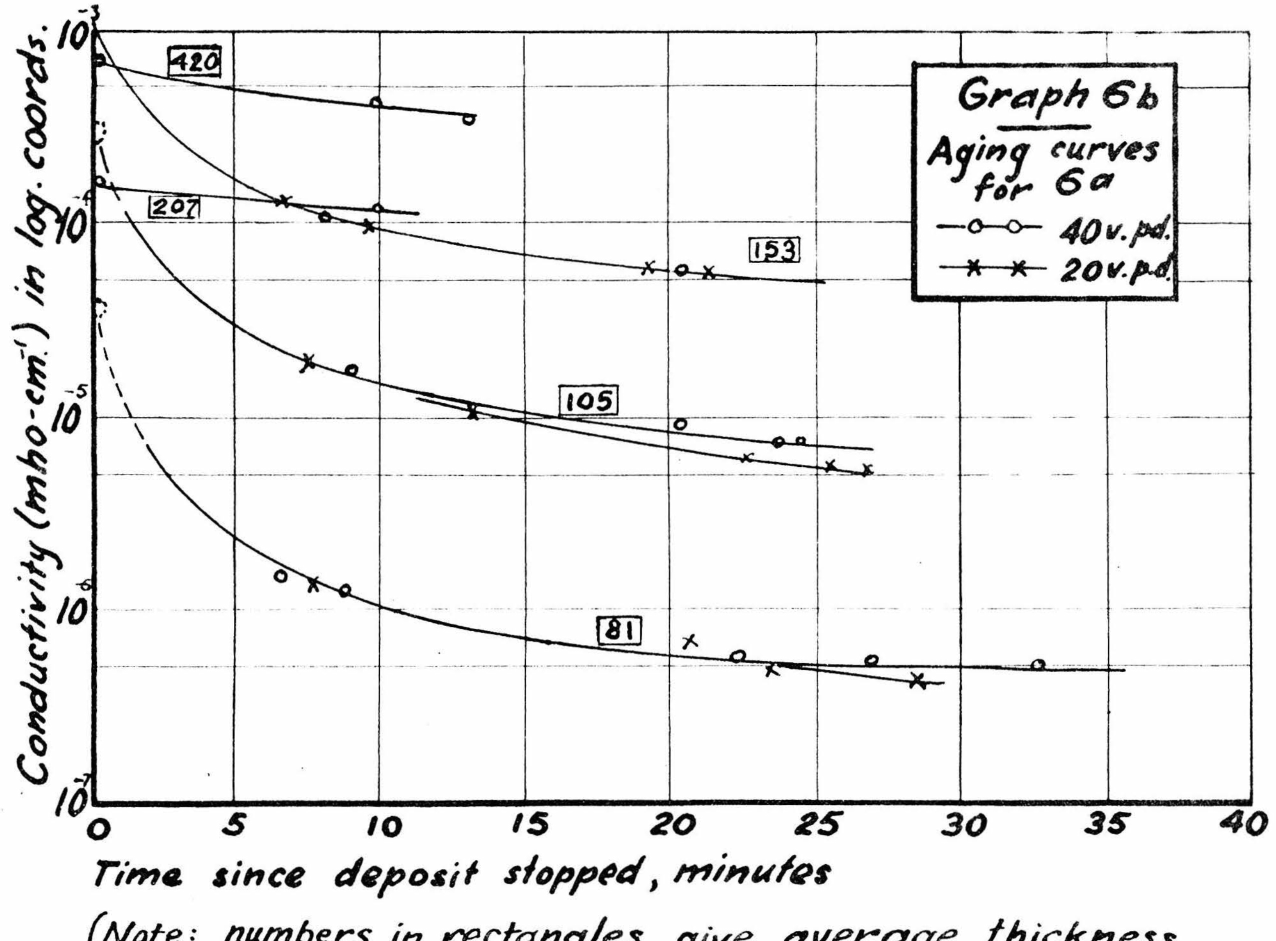
(Note: numbers in rectangles give average thickness of film for the curve concerned)



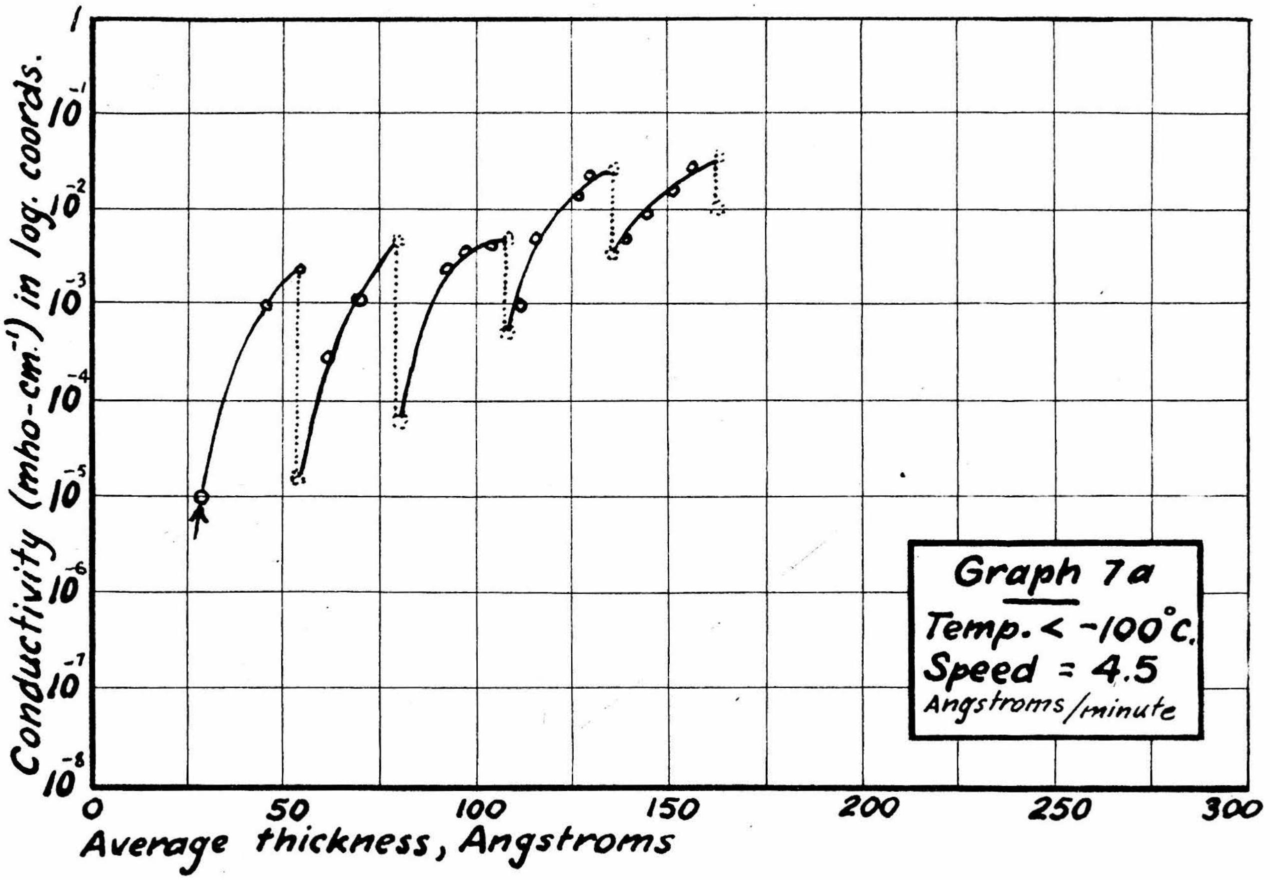


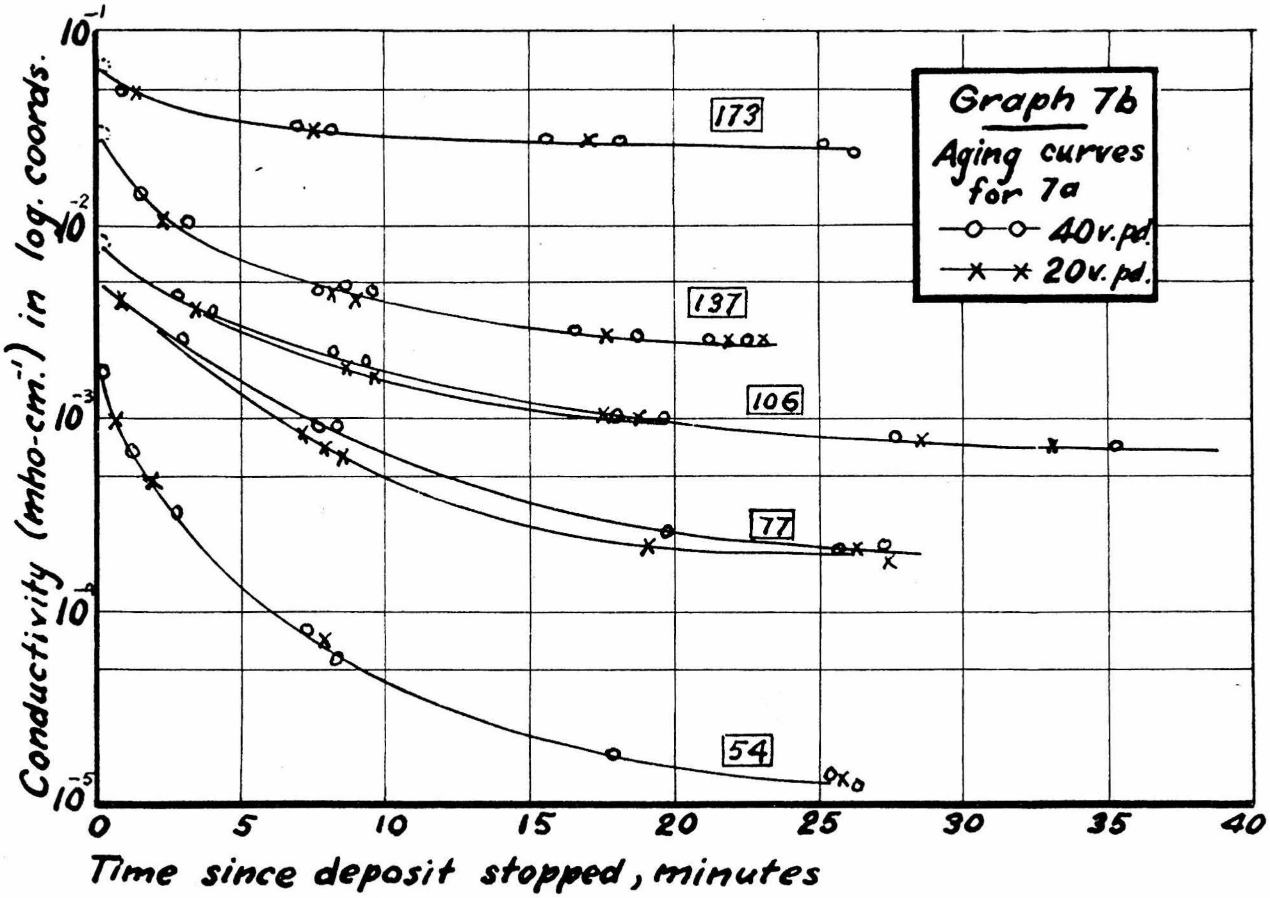
(Note: numbers in rectangles give average thickness of film for the curve concerned)



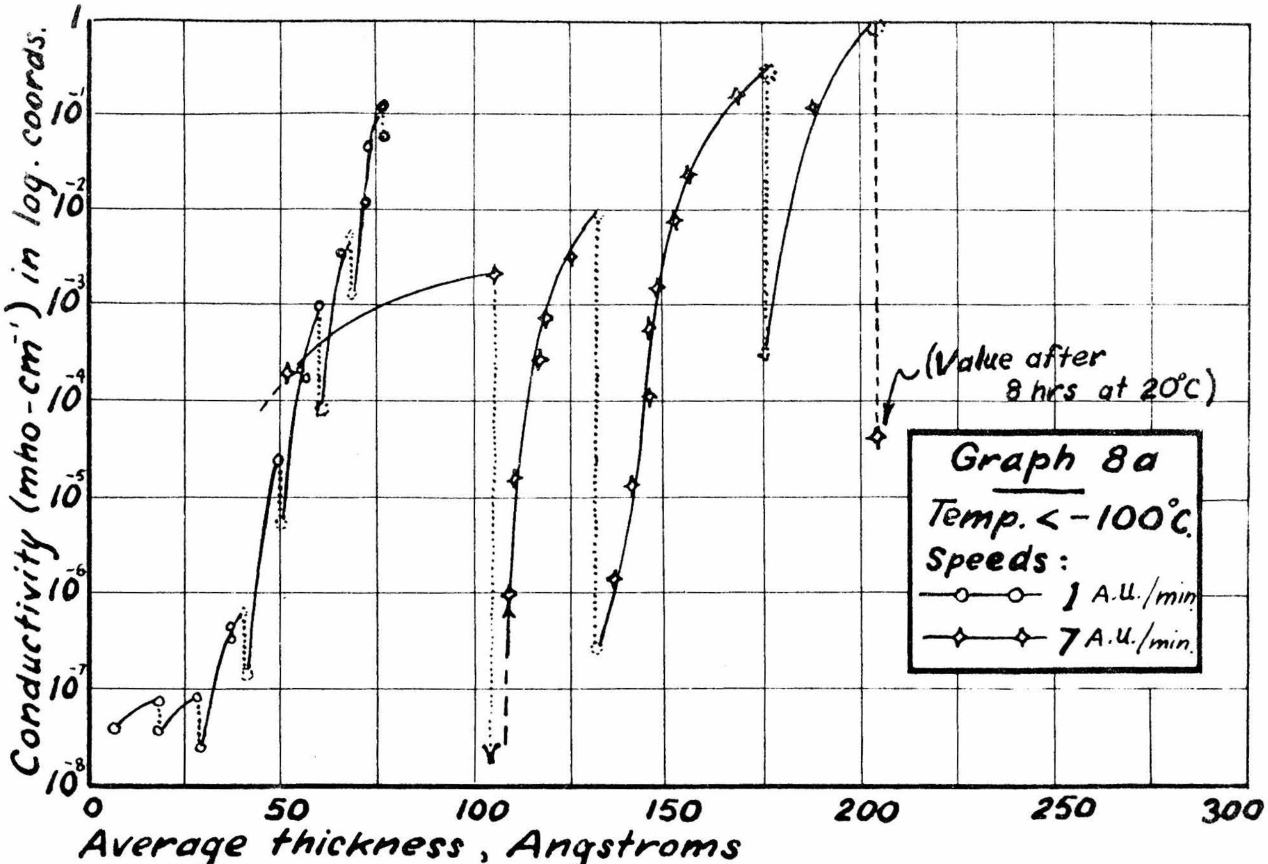


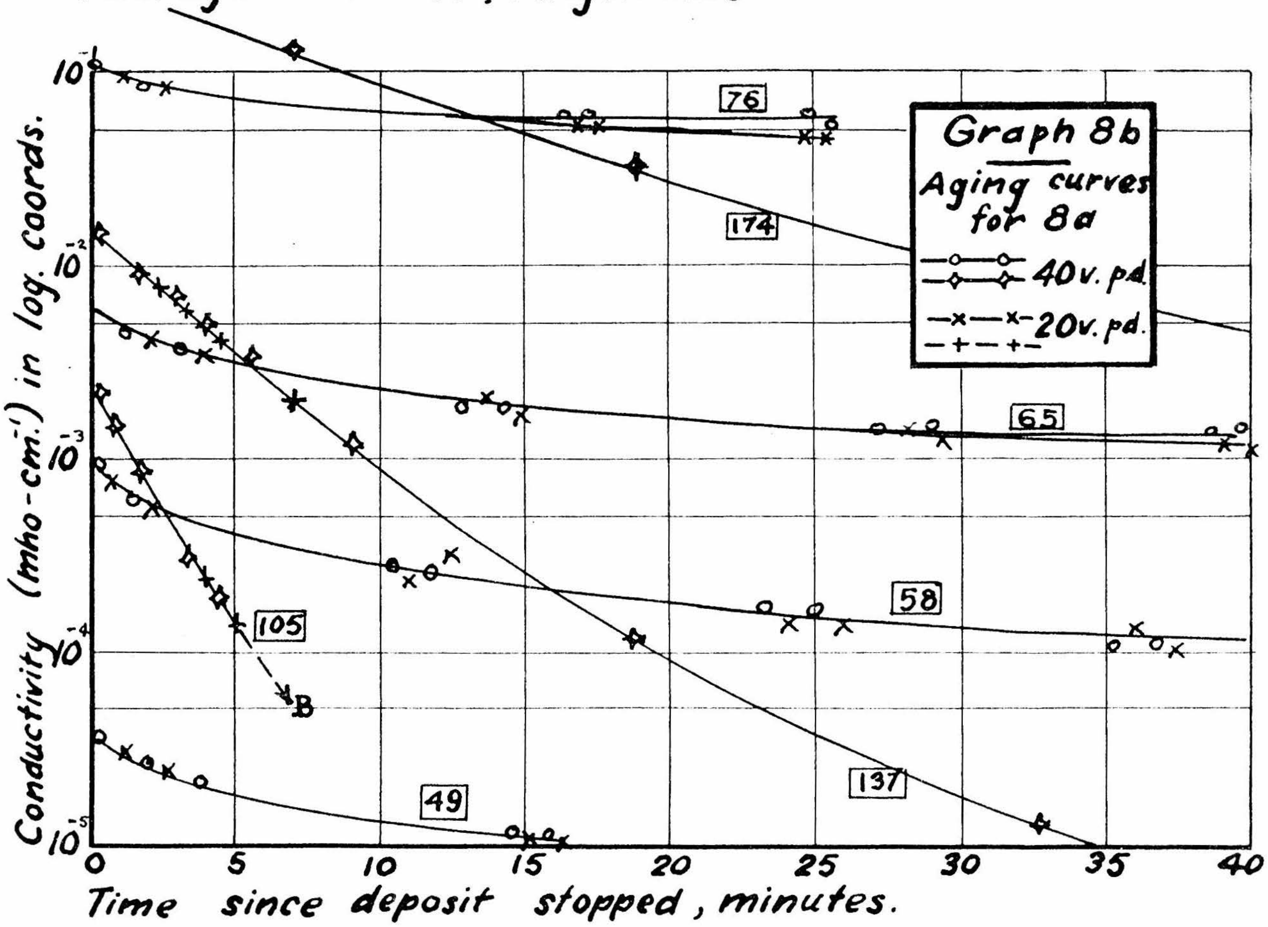
(Note: numbers in rectangles give average thickness of film for the curve considered.)



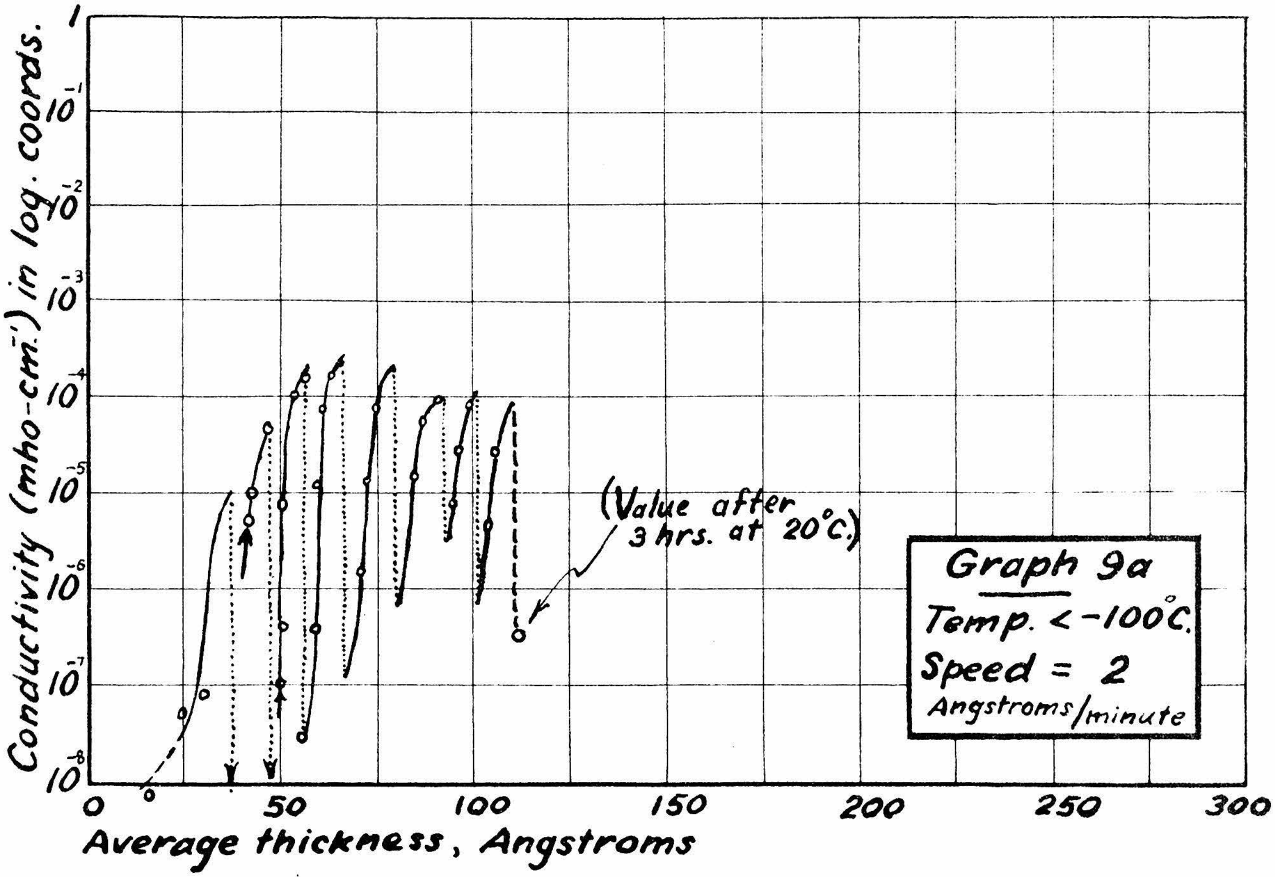


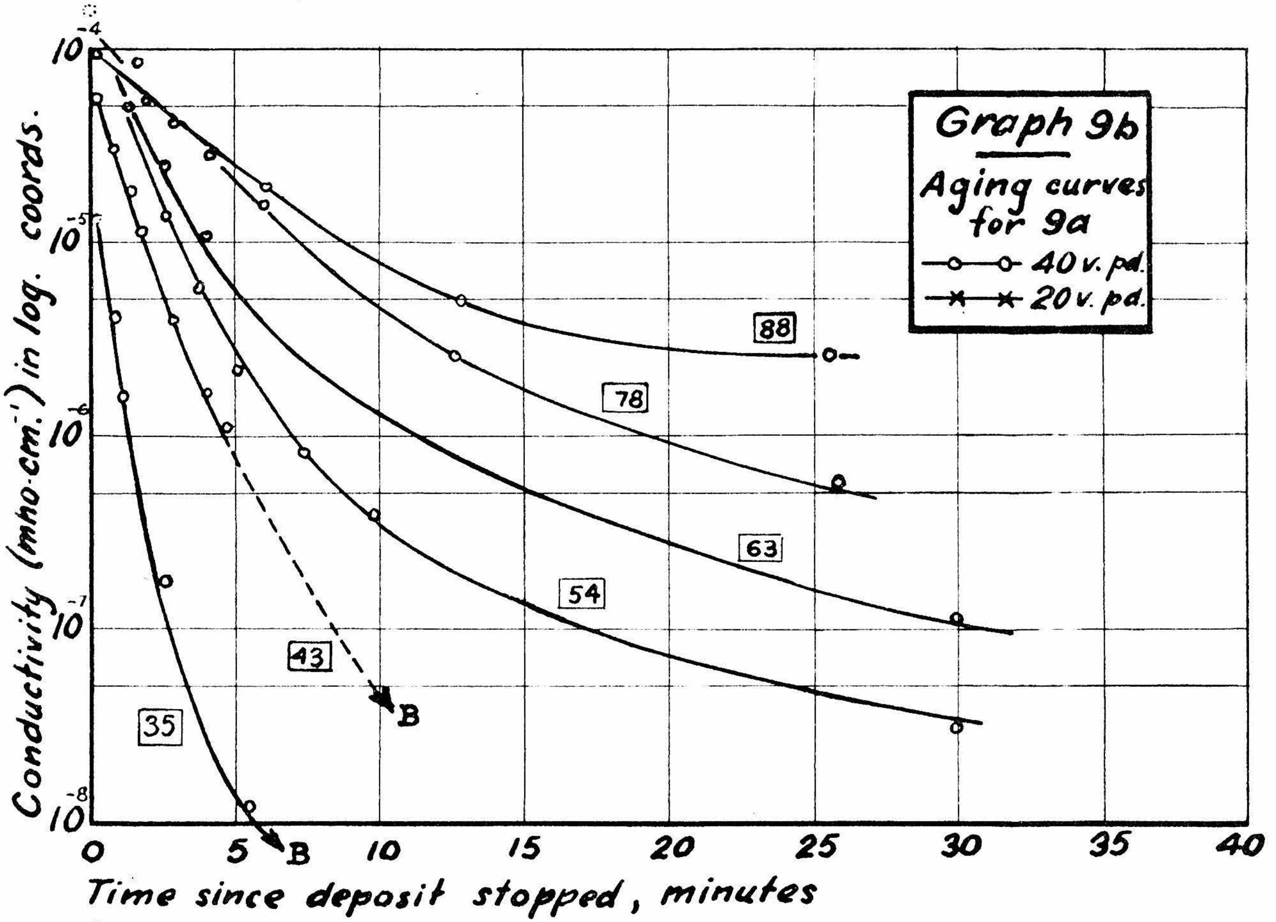
(Note: numbers in rectangles give average thickness of film for the curve considered.)





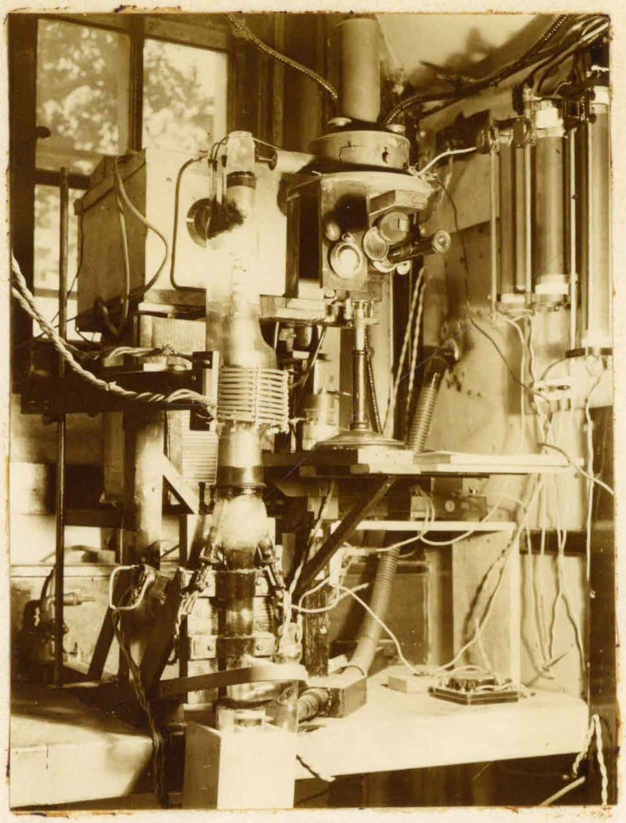
(Note: numbers in rectangles give average thickness of film for the curve considered.)



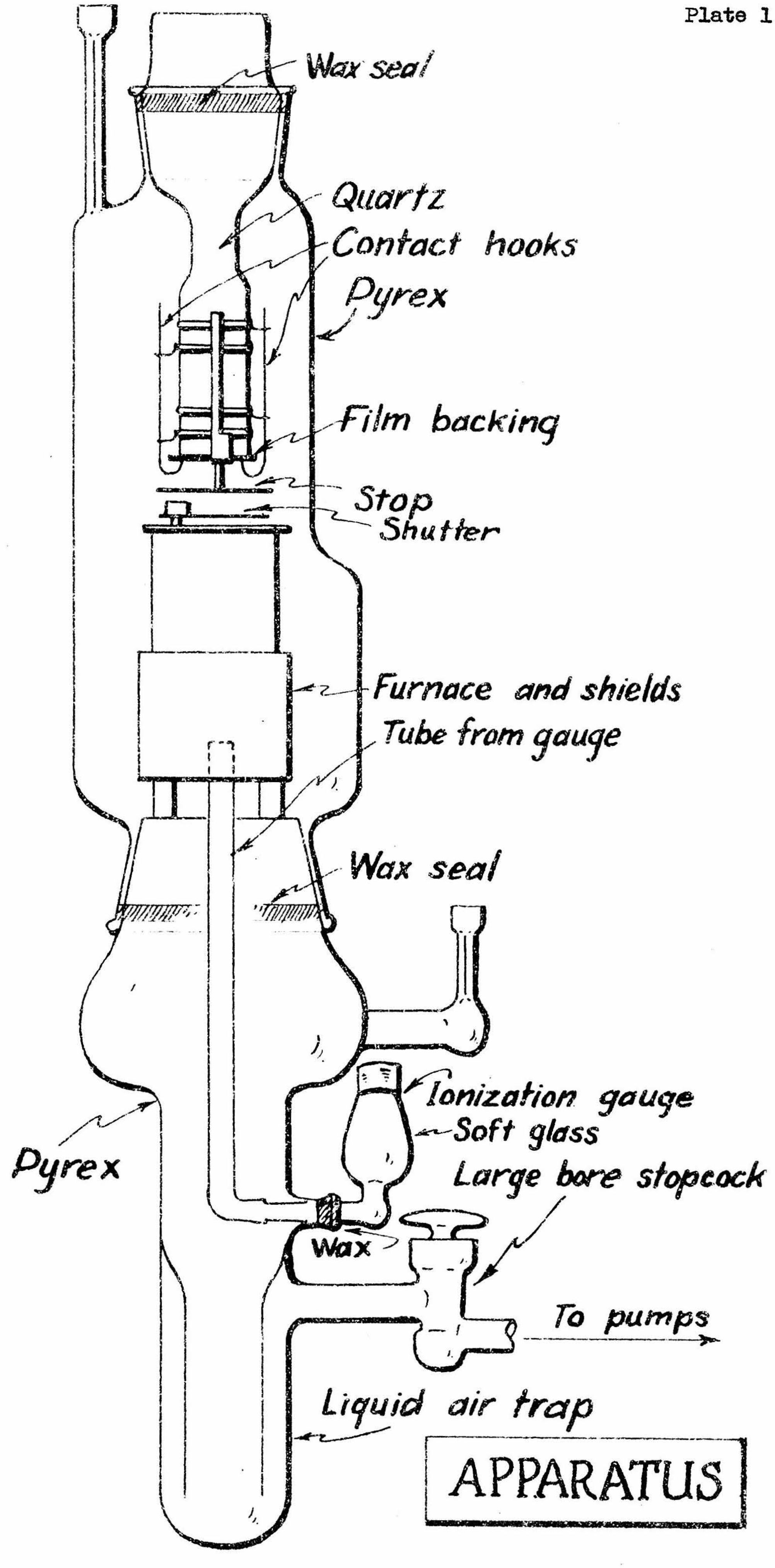


(Note: numbers in rectangles give average thickness of film for the curve considered.)

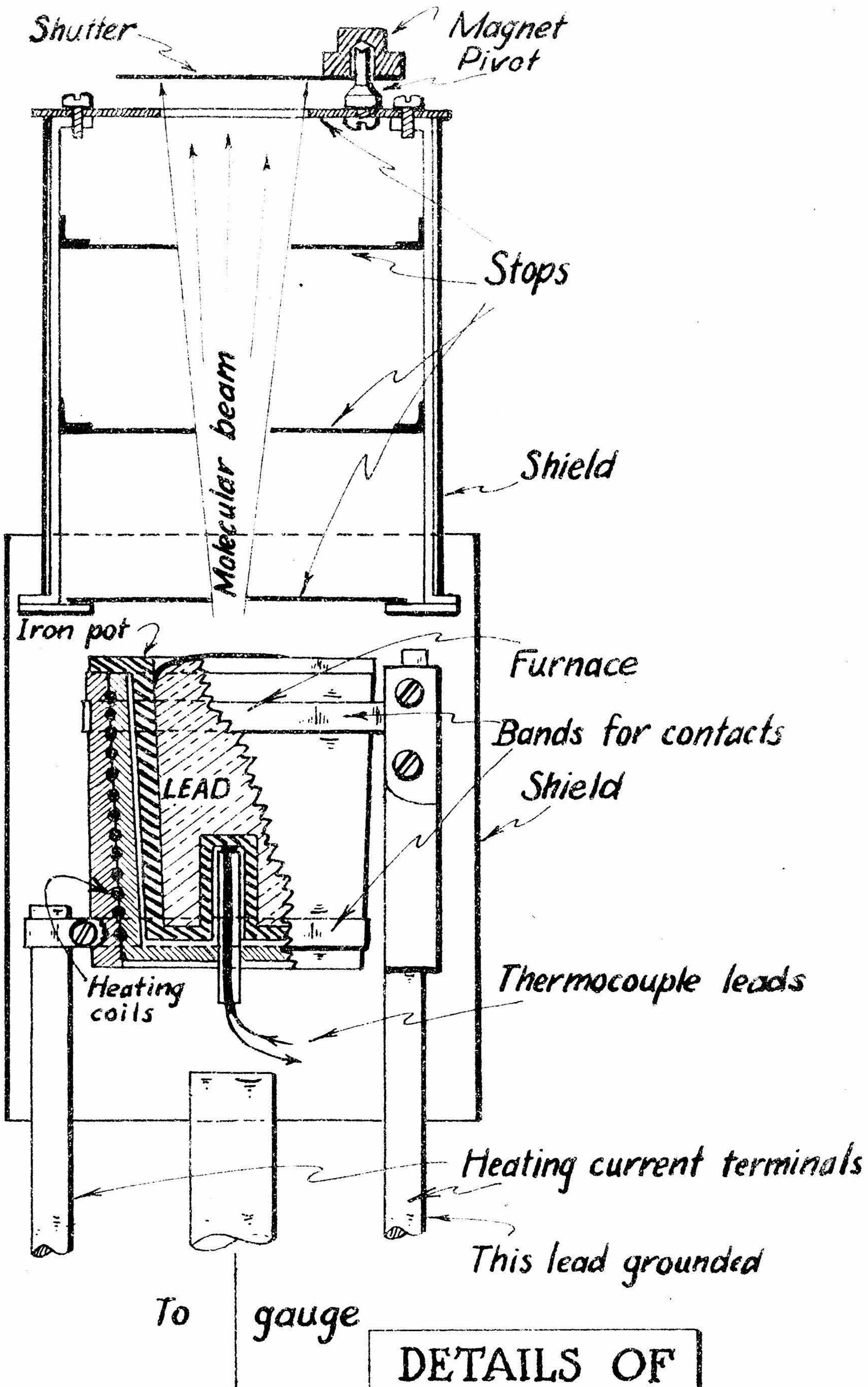
Plate 1 A.



Photograph of apparatus

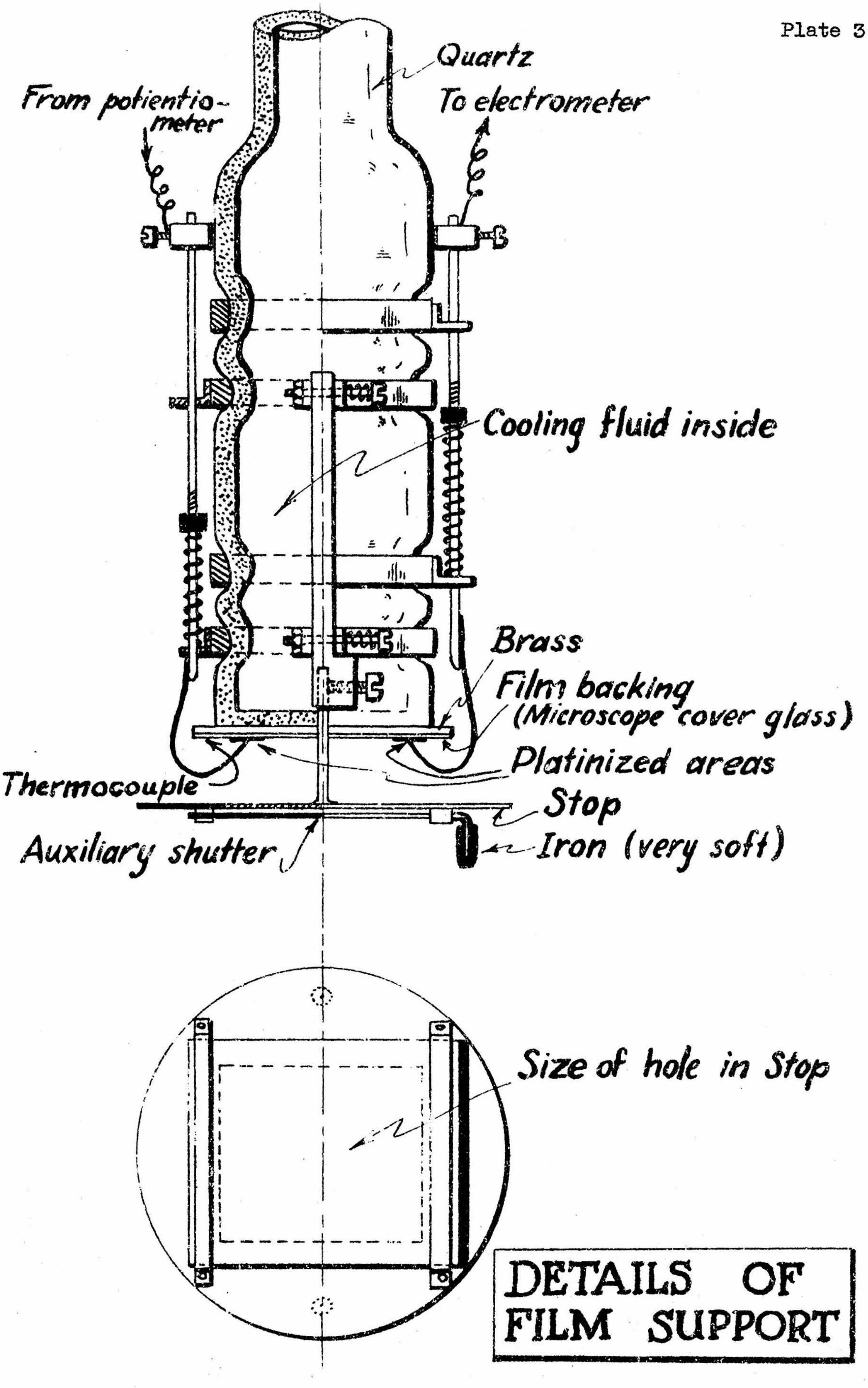

Wax seal
Quartz
Contact hooks
Pyrex
Film backing
Stop
Shutter
Furnace and shields
Tube from gauge
Wax seal
Ionization gauge
Soft glass
Pyrex
Large bore stopcock
Wax
To pumps
Liquid air trap

APPARATUS



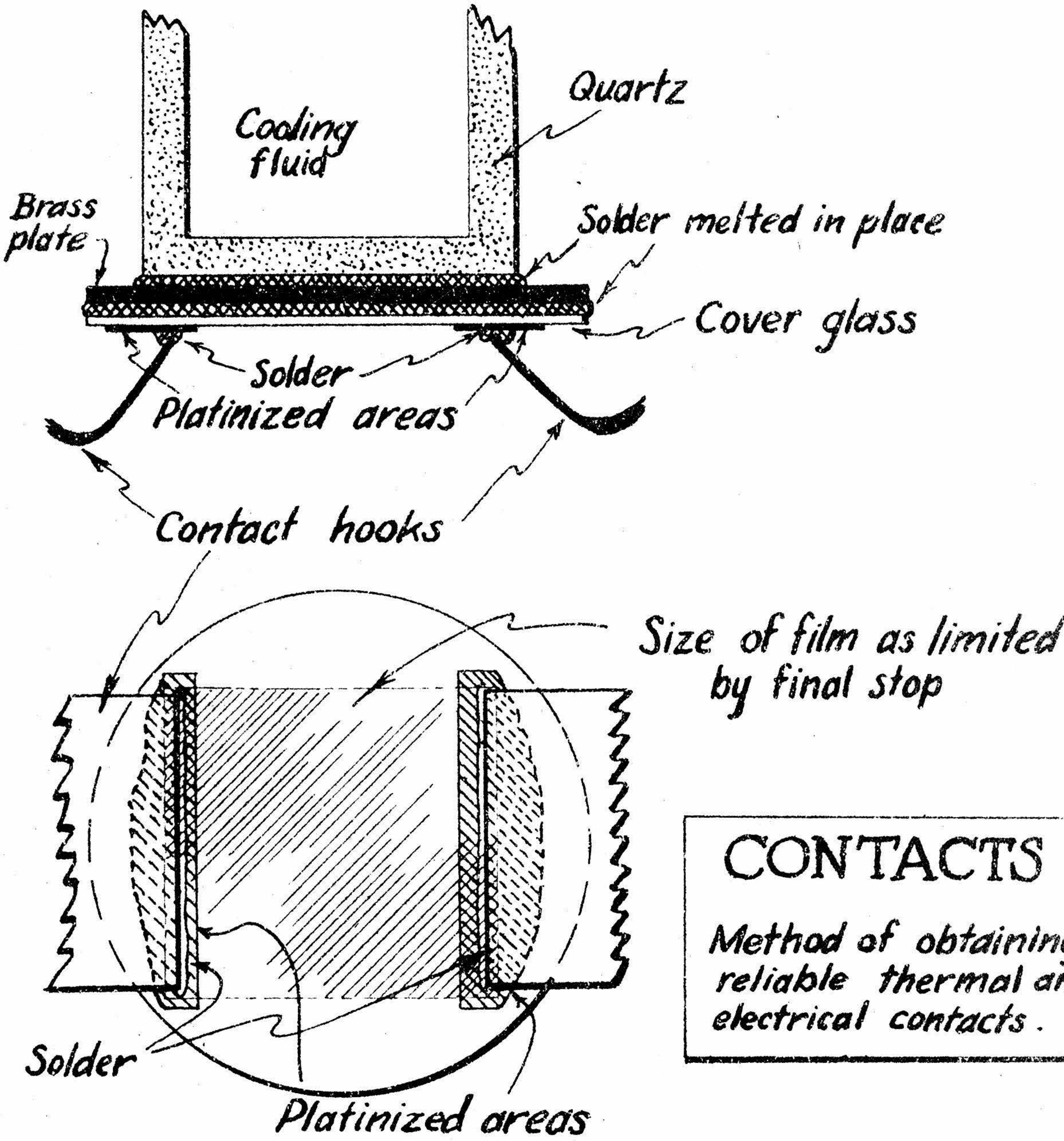
DETAILS OF FURNACE

Plate 3.



DETAILS OF FILM SUPPORT

Plate 4.

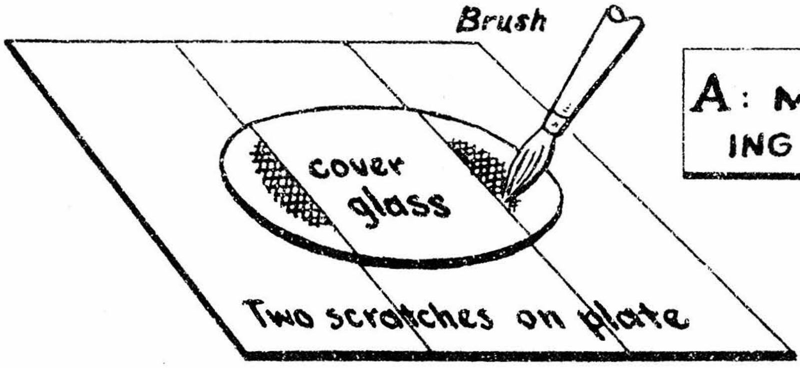


CONTACTS

Method of obtaining reliable thermal and electrical contacts.

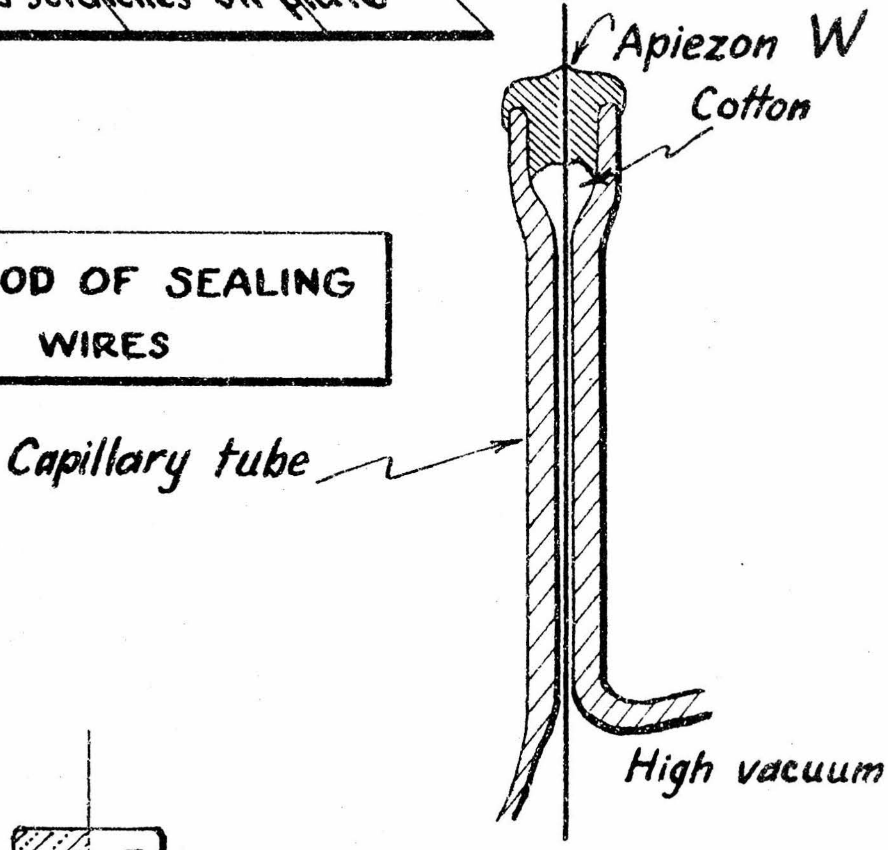
Note: solder is melted in the vacuum by careful application of the induction furnace.

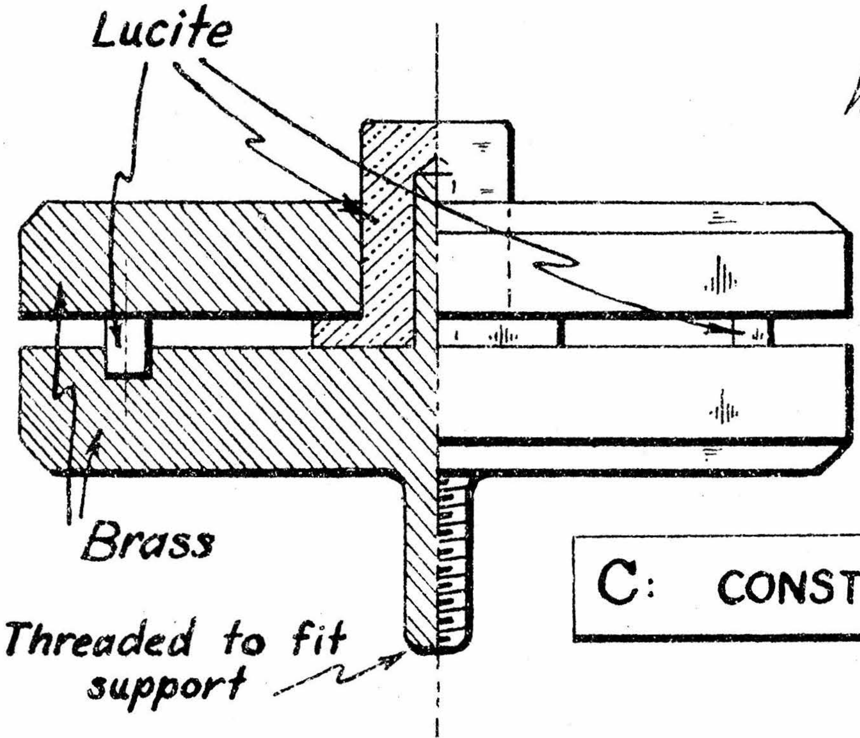
Plate 5.



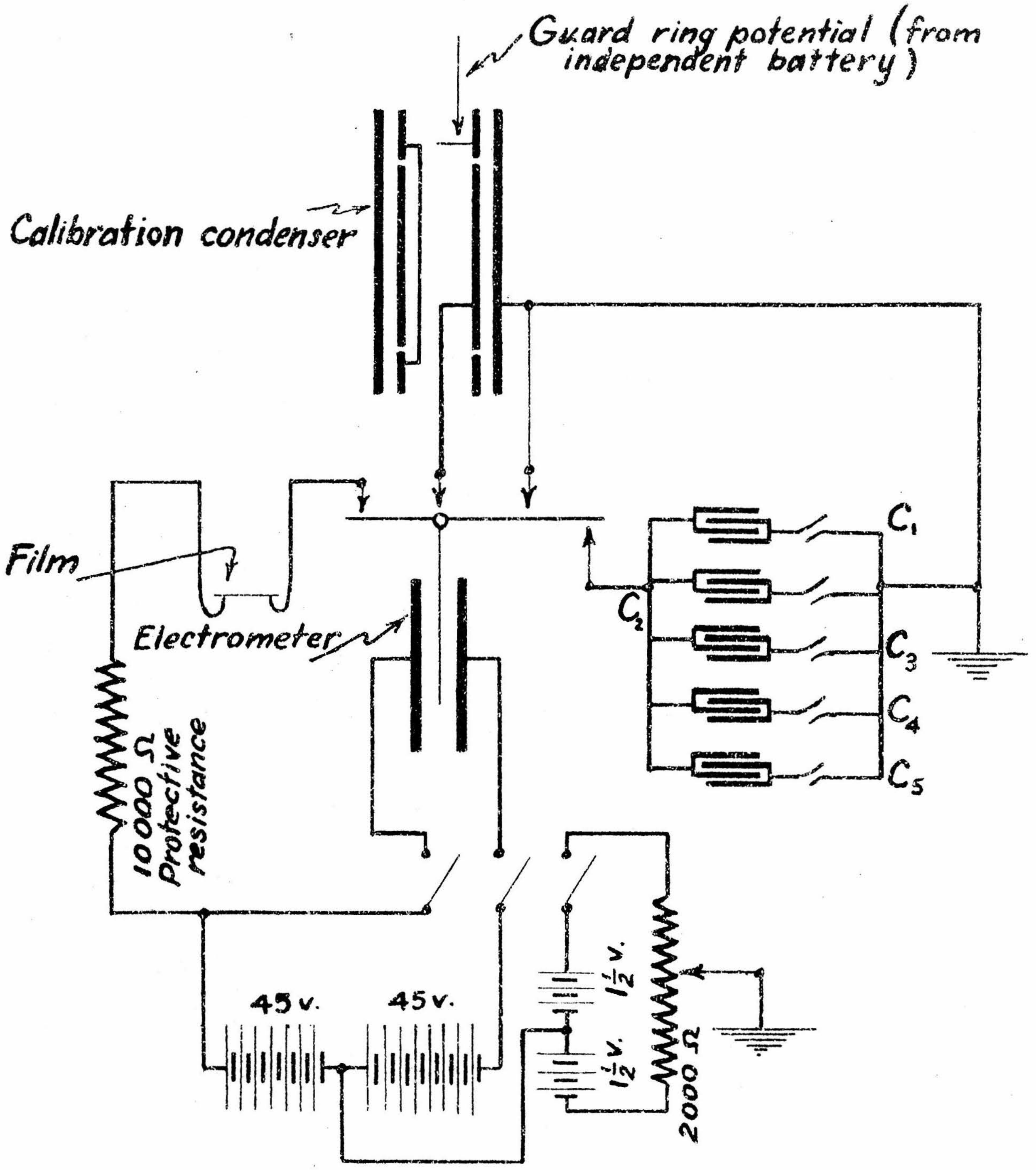
A: METHOD OF APPLYING PLATINUM CONTACTS

B: METHOD OF SEALING IN WIRES



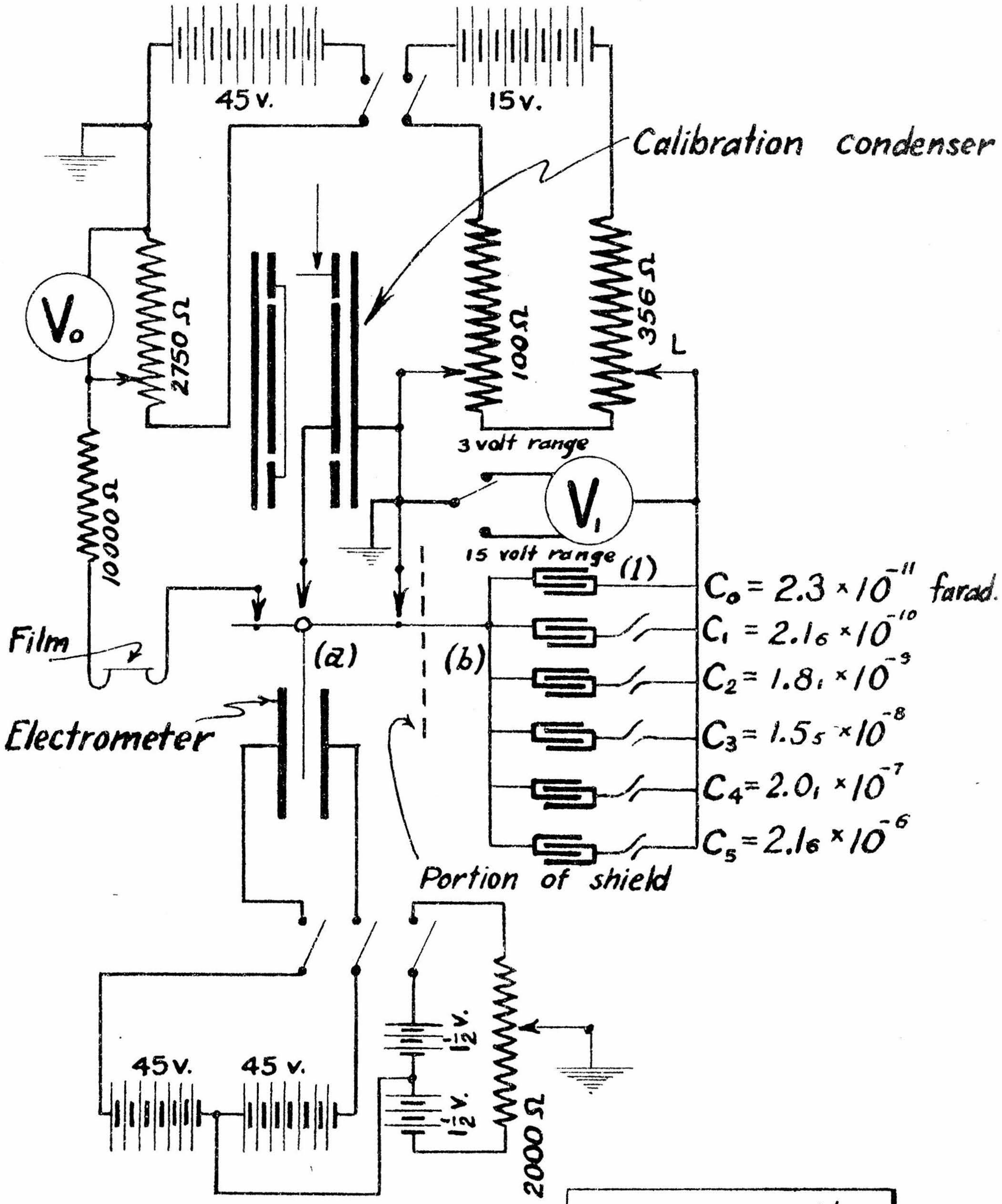


C: CONSTRUCTION OF C_0



(Entire apparatus shielded)

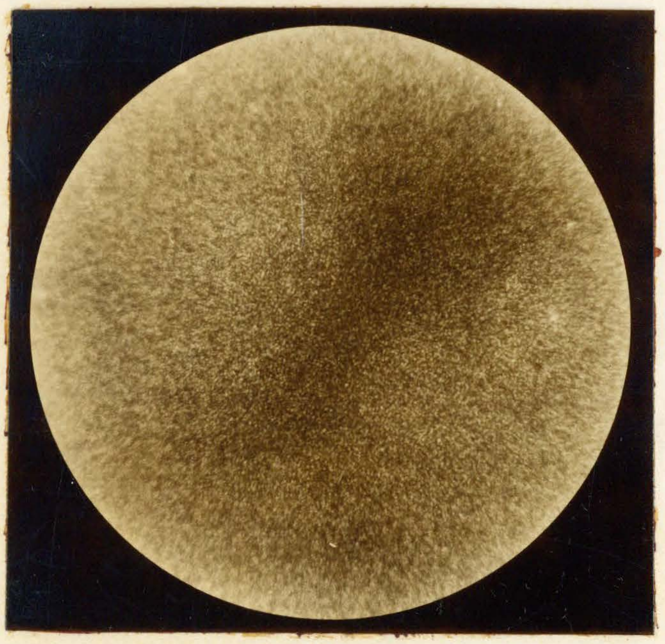
CIRCUIT #1


45 v.
15 v.
Calibration condenser
V_o
2750 Ω
100 Ω
356 Ω
L
3 volt range
V_1
15 volt range
10000 Ω
Film
(a)
(b)
(1)
Electrometer
$C_0 = 2.3 \times 10^{-11}$ farad.
$C_1 = 2.1_6 \times 10^{-10}$
$C_2 = 1.8_1 \times 10^{-9}$
$C_3 = 1.5_5 \times 10^{-8}$
$C_4 = 2.0_1 \times 10^{-7}$
$C_5 = 2.1_6 \times 10^{-6}$
Portion of shield
45 v.
45 v.
$1\frac{1}{2}$ v.
$1\frac{1}{2}$ v.
2000 Ω

CIRCUIT #2

A. Edge of film

130 diameters
Ultramicroscope illumination
Cardioid condenser
Achromatic objective (Zeiss)
Photo eyepiece



B. Center of film

850 diameters
Ultramicroscope illumination
Cardioid condenser
Glycerin immersion objective (Zeiss)
Photo eyepiece