

Normal Energy Distribution of Photoelectrons From Sodium and Gallium

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### Abstract

A new experimental method for the determination of the normal energy distribution of photoelectrons is outlined. The method involves separation of the electrodes by a large distance. The electrons are constrained to move along the axis of the phototube by applying a uniform axial magnetic field. The energy distribution is determined by measuring the photoelectric current as a function of retarding voltage between the emitter and the collector.

The theoretical justification for this method is worked out.

A phototube was made applying the above principles to measurements on liquid metal gallium. Another phototube was made for use with condensed surfaces of sodium. This tube was designed for extremely high vacuum use.

Improvements in the photocurrent measuring apparatus and in vacuum technique were made. The monochromators were used in a way similar to that described by Overhage. The sodium was also handled in the manner developed by him.

The uniformity of the magnetic field was checked and the currents in the coils adjusted to the most favorable value.

The results for gallium showed departures from theory but internal consistency similar to that observed by Overhage. The results for sodium show excellent agreement with the Fowler Theory, indicating a very simple form for the transmission coefficient of the surface potential barrier.

Measurements of  $h/e$  were possible from the data for sodium.

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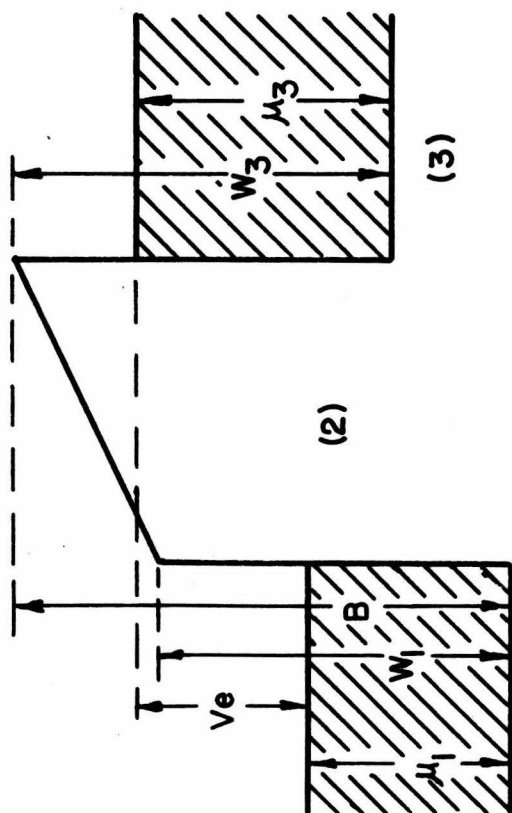
### Introduction

Previous measurements of the normal energy distribution of photoelectrons have yielded data at times approaching agreement with theoretical predictions and at other times disagreeing in various ways. The present work was undertaken in an attempt to check the existing theories. It was also hoped that information would be gained about the discrepancy existing between the values of  $h/e$  determined photoelectrically and those values obtained in other ways. The method here adopted is a modification of the usual one in which the photocurrent is measured as a function of retarding voltage.

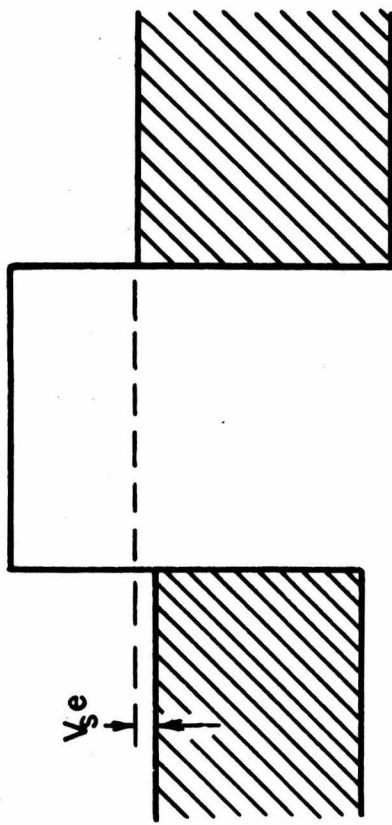
### Fowler Theory<sup>1)2)</sup>

Figure 1, page 2 is the energy diagram of the emitter (1), collector (3), and the intervening space (2), in a photoelectric tube. The electrodes are presumed to form a parallel plate condenser, with a uniform field between them. The kinetic energies of the electrons in the emitter lie between zero and , except for those few electrons having slightly greater energy than due to the effect of temperature: likewise, the kinetic energy of the electrons of the collector lie between zero and . The applied retarding potential is given by  $V$ . An electron must at least have a component of velocity normal to the surface of the emitter such that its "normal energy", is greater than or equal to  $W$  in order to overcome the surface potential barrier and escape from the emitter. Furthermore, it must at least have a





RETARDING FIELD PRESENT



NO RETARDING FIELD  
(SATURATION)

FIG. 1

normal energy equal to  $B$  ( $B = \mu_1 + V_e + W_3 \mu_3$ ) in order to reach the collector. It is clear that  $B$  is independent of  $W_1$  and thus, as pointed out long ago by Millikan, the current in a phototube where a retarding field is present is independent of the work function of the emitter, as long as this work function is low enough. (The classical work function is approximately  $\frac{W_1 - \mu_1}{e}$ ).

The theory we are about to develop is based on certain simplifying assumptions more or less justified. They are as follows:<sup>3)</sup>

1. The energy  $h\nu$  of the photon is communicated to the electron in such a way that only its momentum normal to the surface is changed. (This appears to be reasonable, since, in order to conserve both momentum and energy in the electron photon interaction, if the electron is to absorb the entire energy of the photon, the binding forces must absorb the excess momentum. The only binding of the "free" electrons is due to the surface potential barrier and hence is normal to the surface. Thus one would expect only the electron's velocity normal to the surface to be changed.)
2. The probability that an electron will be put into a state of higher energy by an incident quantum is proportional to the electron's initial velocity normal to the surface. (A quantum mechanical calculation of the excitation probabilities<sup>4)</sup> shows that this assumption is not far from the truth.)
3. The transmission coefficient at the boundary is one if the electron has a velocity normal to the surface greater than a certain value, and zero if it has less. (This assumption has been modified

by several authors. Professor Houston<sup>4)</sup> has calculated the energy distribution assuming an arbitrary function for the transmission probability. The form of this function has considerable effect on the predicted energy distribution, hence the results of the measurements can be used as a criterion of the validity of the simple assumption given above.)

Our calculations start from the Fermi-Dirac statistics. Taking velocity axes  $\xi$  normal to the surface of the metal and  $\eta$  and  $\zeta$  tangential to the surface we have

$$f(\xi, \eta, \zeta) d\xi d\eta d\zeta = \frac{2m^3/\hbar^3}{e^{(\epsilon - \mu)/kT} + 1}, \quad d\xi d\eta d\zeta$$

as the number of electrons per unit volume having velocities  $\xi, \eta$  and  $\zeta$  in the ranges  $d\xi, d\eta, d\zeta$ ,

$$\text{where } \mu = (\hbar^2/2m)(3n/8\pi)^{2/3} \quad \text{approximately}$$

$$\epsilon = \frac{1}{2}m(\xi^2 + \eta^2 + \zeta^2)$$

$n$  = total number of electrons per unit volume and the other symbols have their usual meaning.

Integrating over all  $\eta$  and  $\zeta$  we get

$$f(\xi) d\xi = (4\pi m^2 kT / \hbar^3) \int_0^\infty (1 + e^{(\mu - \frac{1}{2}m\xi^2)/kT})^{-1} d\xi$$

The next step is to multiply this by the probability of excitation (proportional to  $\xi$ ), by the number of photons per second, and by the transmission coefficient. Then integrating

over all  $\xi$  we get the number of electrons per second which pass over the barrier.

Multiplying in  $\xi$  and neglecting the proportionality factors in the excitation probability and in the number of photons we get

$$n(\xi) d\xi = (4 \pi m^2 kT / h^3) \log (1 + e^{(\mu - \frac{1}{2} m \xi^2) / kT}) \xi d\xi$$

$$\text{or } n(\epsilon_n) d\epsilon_n = (4 \pi m kT / h^3) \log (1 + e^{(\mu - \epsilon_n) / kT}) d\epsilon_n$$

where  $\epsilon_n = \frac{1}{2} m \xi^2$ , or the "normal" energy

$n(\epsilon_n)$  then gives us the number of electrons available for ejection.

Since the transmission coefficient is zero below a certain critical value of  $\epsilon_n$  and 1 above, we merely have to integrate  $n(\epsilon_n)$  from that critical value ( $B - h\nu$ ) to infinity.

Hence the number of electrons penetrating the barrier at the collector is

$$\begin{aligned} N &= \int_{B-h\nu}^{\infty} n(\epsilon_n) d\epsilon_n \\ &= (4 \pi m kT / h^3) \int_{B-h\nu}^{\infty} \log (1 + e^{(\mu - \epsilon_n) / kT}) d\epsilon_n \end{aligned}$$

$$\text{Let } (\mu - \epsilon_n) / kT = x'$$

$$[\mu - (B - h\nu)] / kT = x, \quad e^{x'} = u, \quad e^x = u_0$$

$$\text{Then } d\epsilon_n = -kT dx' = -kT du / u$$

and 
$$N = 4\pi m k^2 T^2 / h^3 \int_0^{u_0} \log(1+u) (du/u)$$

giving two values depending on the value of

For  $u_0 \leq 1$ , i.e.  $x \leq 0$  or  $h\nu \leq B - \mu$

$$N = (4\pi m k^2 T^2 / h^3) \left[ e^x - \frac{e^{2x}}{2^2} + \frac{e^{3x}}{3^2} - \dots \right]$$

For  $u_0 \geq 1$ ,  $x \geq 0$  or  $h\nu \geq (B - \mu)$

$$N = (4\pi m k^2 T^2 / h^3) \left[ \frac{x^2}{2} + \frac{\pi^2}{6} - (e^{-x} - \frac{e^{-2x}}{2^2} + \frac{e^{-3x}}{3^2} - \dots) \right]$$

In any case 
$$N = (4\pi m k^2 T^2 / h^3) \phi(x)$$

or 
$$N = AT^2 \phi(x), \text{ where } A = \frac{4\pi m k^2}{h^3}$$

$\phi(x)$  contains the variation in which we are interested since in our experiments  $T$  is constant.

$N$  should be proportional to the observed photoelectric current,  $J$ ; thus we have

$\log J = C + \Phi(x)$  when  $\Phi(x) = \log \phi(x)$ , and  $C = \text{constant}$

Since in our work the barrier,  $B = \mu_1 + V_e + W_3 - \mu_3$ ,

$$x = (h\nu - V_e - W_3 + \mu_3) / kT$$

If now we plot  $\log J$  against  $-V$ , the applied stopping potential, we should get a curve superposable on  $\Phi(x)$  plotted against  $\frac{kTx}{e}$ .

There will be a vertical shift equal to  $C$  and a horizontal shift equal to  $\frac{h\nu - W_3 + \mu_3}{e}$  necessary to accomplish the superposition.

Tables of  $\Phi(x)$  versus  $x$  are readily available<sup>2)</sup>.

The above is the test we apply to our data. Also, there should be a linear relation between the amount of the horizontal shift expressed in volts and the value of  $\nu$ . The slope of this line is  $h/e$ .

#### Previous Experimental Results.

The same method of analysis given above can be used to calculate the variation of photocurrent with temperature, light frequency, electrode work function and so on. One can also calculate the total energy distribution.

The experimental results on these points mostly agree well with theory, especially for the heavy metals. The heavy metals give good agreement in the case of the normal energy distribution, as measured by the parallel plate-retarding potential method, but Overhage using sodium as the emitter<sup>3)</sup> observed definite discrepancies, much larger than the experimental error. He found that his curves for

log J versus retarding voltage were superposable one on the other, but not on the theoretical curve; i.e. the theoretical curve had a greater curvature than the experimental. Henshaw<sup>5)</sup> on the other hand using thin films of potassium observed the opposite that the theoretical curve had less curvature than the experimental.

#### The New Experimental Arrangement

Much of the difficulty in previous work on the photoelectric properties of alkali metals has been held due to the evaporation of the metal from the emitter onto the collector. The work function of the collector is thus lowered and stray light will give rise to reverse currents in the tube. With this in mind and with the additional object of finding a more accurate method of determining the normal energy distribution, it was decided to separate the cathode and anode by a large distance, of the order of a foot, and constrain the electrons to move along the axis of the tube by applying an axial magnetic field. See figure 2, page 9 . As it turned out, there was no improvement in the reverse current situation and another method had to be used to correct for these stray currents; however, the improved internal consistency of the data seems to warrant the use of this new method of combined electric and magnetic fields.

The a-priori justification for the use of a magnetic field in this way is as follows:

The force F on an electron is given by

$$\vec{F} = e\vec{E} + \frac{e\vec{v}}{c} \times \vec{H}$$

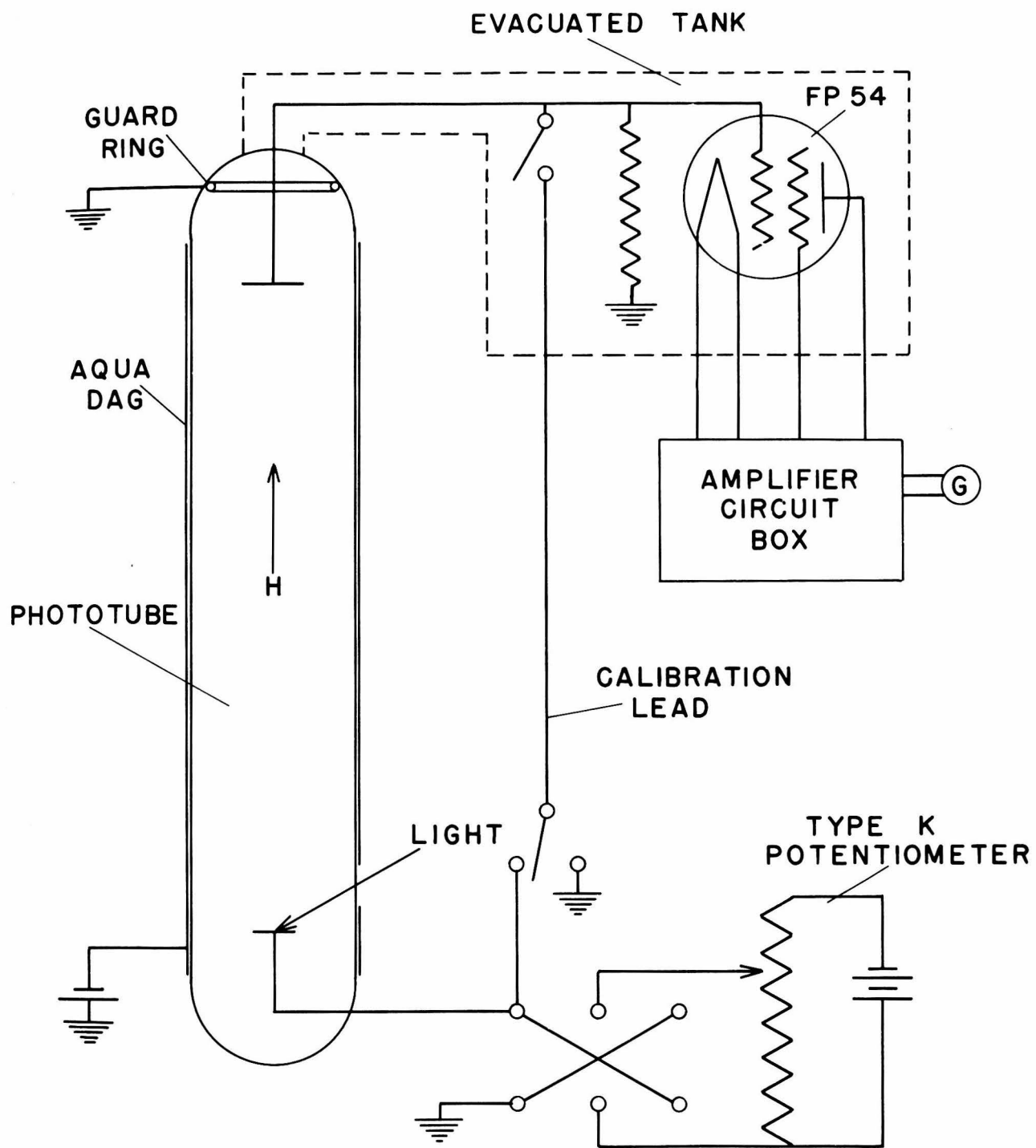


FIG. 2



$$\text{or } \frac{m}{e} \frac{d\bar{u}}{dt} = \bar{E} + \frac{\bar{v}}{c} \times \bar{H}$$

Take components and assume that H has only a z component,  
i.e. axial in the photo tube,

$$\frac{m}{e} \left( i \frac{dv_x}{dt} + j \frac{dv_y}{dt} + k \frac{dv_z}{dt} \right) =$$

$$i E_x + j E_y + k E_z + i \frac{v_y}{c} H_z - \frac{j v_x H_z}{c}$$

Take the z component

$$\frac{m}{e} \frac{dv_z}{dt} = E_z = - \frac{\partial \Phi}{\partial z}$$

Multiply both sides by  $v_z$  and integrate along the path taken by the particle

$$\frac{m}{e} \int_{z_0}^z \frac{dv_z}{dt} v_z dt = - \int_{z_0}^z \left( \frac{\partial \Phi}{\partial z} \right)_p dz$$

$$= - \int_{z_0}^z \left( \frac{\partial \Phi}{\partial z} \right)_p dz$$

$$= \frac{1}{2} \frac{m}{e} (v_z^2 - v_{z_0}^2)$$

$\left( \frac{\partial \Phi}{\partial z} \right)_p$  indicates the value at some point on the path.

One cannot off hand state the value of  $\int \left( \frac{\partial \Phi}{\partial z} \right)_p dz$ ; however,

if H is large enough, the path of the particle will be a spiral of some sort, and will stay as close as we wish to the same magnetic line of force. The electric field being continuous,

$\left( \frac{\partial \Phi}{\partial z} \right)_p$  can thus be made as close as we please to  $\left( \frac{\partial \Phi}{\partial z} \right)_H$

along the magnetic line of force.

$$\text{i.e.} \quad \left( \frac{\partial \Phi}{\partial z} \right)_P = \left( \frac{\partial \Phi}{\partial z} \right)_H + \mathcal{E}, \quad \begin{matrix} \mathcal{E} \rightarrow \bullet \\ H \rightarrow \leftarrow \end{matrix}$$

$$\begin{aligned} \text{and} \quad \int_{z_0}^z \left( \frac{\partial \Phi}{\partial z} \right)_P dz &= \int_{z_0}^z \left( \frac{\partial \Phi}{\partial z} \right)_H dz + \int_{z_0}^z \mathcal{E} dz \\ &= \int_{z_0}^z \vec{E} \cdot d\vec{s} + (z - z_0) \mathcal{E} \end{aligned}$$

$$\text{hence} \quad \frac{1}{2} m (v_z^2 - v_{z_0}^2) = e \Delta \Phi + e (z - z_0) \mathcal{E}$$

Thus, if the magnetic field is made large enough, whether or not an electron gets from the emitter to the collector depends on its initial  $v_z$  (i.e., on the normal energy) and on the potential difference between the electrodes. The magnitude of the error in the method could be calculated by assuming a value for  $\frac{\partial^2 \Phi}{\partial z \partial x}$ , multiplying it by the radius of curvature of the electron's path (proportional to  $\frac{1}{H}$ ) and by the electrode separation  $(z - z_0)$ . This would make  $\mathcal{E}$  of order  $\frac{1}{H}$ . However, this is undoubtedly too crude an approximation.  $\mathcal{E}$  is more than likely of order  $\frac{1}{H^n}$ ,  $n > 1$ , since the electron will spend part of its time on one side of the line of force and part of its time on the other, tending to cancel out the first order variation in  $\frac{\partial \Phi}{\partial z}$ .

### Apparatus and Method

In the course of the experiments, several different tubes and many electrode designs were tried, all of the general type shown in figure 2, page 9 . In an attempt to simplify the problem, it was decided to work first on the liquid metal gallium. It was felt that this metal would not give much of the trouble that the alkali metals do, since it has an extremely low vapor pressure ( $4 \times 10^{-4}$  mm Hg at  $1200^{\circ}\text{C}$ ) and hence would not so readily distill off and condense on the other surfaces in the tube. Also gallium has a low melting point ( $30^{\circ}\text{C}$ ) and can be easily super-cooled to room temperature. It was felt that the smooth liquid surface would offer advantages as an emitter.

At first, it was found difficult to hold the gallium in any sort of a cup, because it alloyed readily with the metals which were tried, especially at the elevated temperature necessary for outgassing.

A plain zinc electrode was then tried to test the principle of combined electric and magnetic fields. The apparatus functioned properly, but the measured photocurrent versus electrode voltage curves were far too extended and shallow; i.e. it was necessary to apply a large accelerating voltage to get any apprecable photocurrent, indicating that the glass walls of the tube were setting up a potential barrier between the electrodes. The solution to this difficulty was to apply a constant voltage to the glass walls of the tube by painting them with colloidal graphite solution

(Aqua-Dag) and connecting the resulting conducting layer to a battery. The justification for this will be discussed later.

After consulting the literature and finding that there are no known easily formed compounds of gallium and carbon, it was decided to try a graphite cup for holding the gallium. A tube was constructed essentially like figure 3, page 14 except that the emitter was a globule of gallium held in a graphite cup, 3 cm diameter, and the collector was a graphite disk, 3.5 cm diameter. These electrodes were held on tungsten wires tipped with platinum to avoid formation of brittle tungsten carbide during the frequent induction heating of the electrodes.

The gallium tube was not a sealed off system but was continuously evacuated by mercury diffusion pumps through two liquid air traps.

The chemical behavior of gallium is much like aluminum. At first several attempts were made to purify it and eliminate its persistent surface oxide film chiefly by heating in a current of hydrogen. It was possible to remove the oxide in this way, but upon exposing the gallium to air, the oxide returned. The most successful way to clean it was merely heating at  $450^{\circ}$  to  $500^{\circ}\text{C}$  for a day in its carbon cup, in a good vacuum. Considerable gallium distilled to cooler portions of the system, but that which was left behind was shiny (except for a few floating particles, probably carbon dust) and had a remarkably high surface tension. The shape of the globule was nearly spherical, whereas

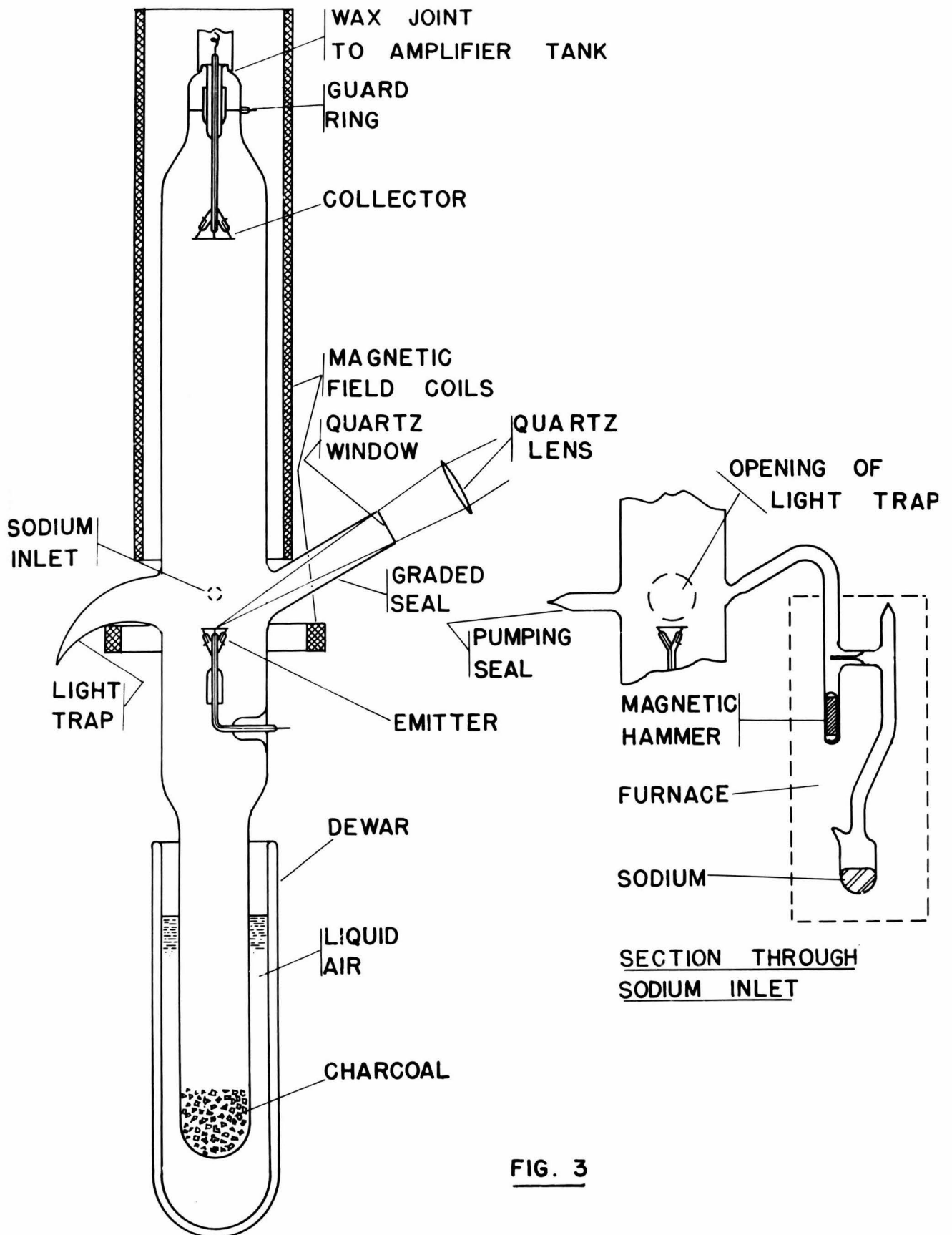


FIG. 3

before it had been quite flat. After the heating, a good vacuum was maintained until the photoelectric work was finished. At the end of the experiment, after exposure to air for a few hours, the globule again flattened out.

The tube used for sodium is shown in figure 3, page 14 . It was evacuated during outgassing and then sealed off permanently. The vacuum was maintained by a large charcoal trap immersed in liquid air. The electrodes were made of .001 inch tantalum sheet, spot welded to tungsten wires. The spot welding was greatly facilitated by the use of thin platinum sheet as a binder between the tungsten and the tantalum. The ends of the supporting wires were bent into a plane triangle and the electrode disk was welded to it, thus keeping the electrode approximately plane. The collector was made larger than the emitter so as to collect all of the electrons, even though they did not stay in a perfect beam. The glass mountings for the electrodes were made reentrant so as to provide a long insulation path on which sodium would not condense.

The magnetic field was created by two coils, shown in cross section in figure 3, page 14 . The upper coil was a long solenoid, consisting of five layers of number 18 enameled copper wire, 1850 turns in all or 46.50 turns per cm. The lower coil consisted of 190 turns of number 18 enameled copper wire in ten layers. A small blower was used to cool the coils. It was mounted so as not to transmit vibration to the rest of the apparatus.

For the work on gallium, the ratio of the currents in the coils was adjusted to a value which was found by an approximate calculation to give as uniform a field as possible. Before the work on sodium was undertaken, a small search coil, consisting of 8000 turns of number 44 copper wire was wound. Its dimensions were 1 cm long and 2 cm diameter. It was arranged to slide on a bakelite rod which was held axially to the coils. The field coils were put in their usual position and connected to their source of current. The search coil was connected to a sensitive galvanometer. With this arrangement, inhomogeneties of the magnetic field along the axis could be detected by sliding the search coil along its rod. The search coil was calibrated approximately by flipping it over in the Earth's field.

It was found that, using the best possible ratio of currents in the coils, (upper: lower 0.316), the emitter and collector were in regions of the same field strength ( $H$ ). The emitter was at a maximum of  $H$ , hence the lines of force were normal to its surface. 4 cm up from this electrode there was a minimum (3 percent below average) and 11 cm up a maximum (4 percent above average).  $H$  then returned gradually to its average value at the collector. There the rate of change of field strength was 0.5 percent per cm. This means that the line of force 1.5 cm (radius of collector) from the axis of the tube made an angle of 13 minutes with the axis. The work on sodium was done under these conditions.

The frame of the apparatus was largely of iron, except for those pieces of metal which were very near the tube. The latter were non magnetic. To check the effect of the iron frame on the magnetic field, pieces of iron were placed in orientations similar to those pieces already present. When they were quickly removed, there was no observable change in the axial magnetic field intensity, i.e. the change was less than 1 percent.

The total field strength was about 80 gauss. In such a field, the radius of curvature of a one volt electron moving at right angles to the lines of force is less than  $\frac{1}{2}$  mm.  $H$  was large enough so that the horizontal component of the Earth's field would cause a deflection of the field in the phototube amounting to less than 1 mm in the distance equal to the electrode separation.

With the coils in the orientation used for the work on gallium, the optimum current ratio was found to be 0.293. The actual work was carried out at a current ratio of 0.333 and repeated at 0.376. For the 0.333 ratio the maximum variations in field strength were probably 10 or 12 percent. For the 0.376 ratio, the variations were 15 or 20 percent. As will be discussed later, the ratio of these currents had no appreciable effect on the shape of the log  $J$  versus retarding voltage curve.

The effect of the total strength of the magnetic field on the photocurrent in the gallium tube was definite but small. Increasing the magnetic field strength 50 percent increased the photocurrent 0.4 percent at a point midway in the retarding potential curve.



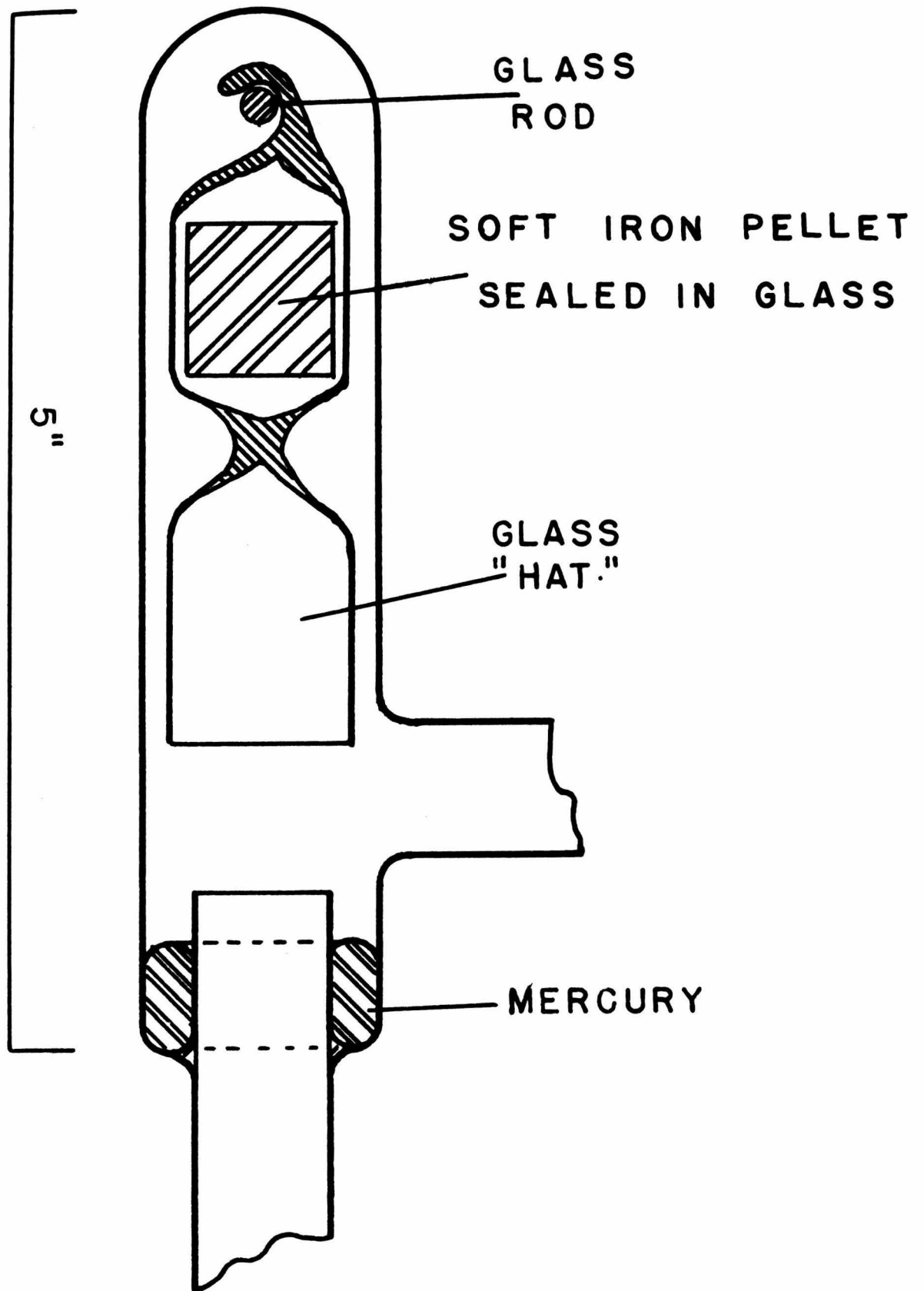
In the case of the sodium tube, decreasing the magnetic field strength by 13 percent decreased the saturation photocurrent 1 percent and had somewhat less effect on the current in the middle of the retarding potential curve.

To check the alignment of the magnetic field in the case of the sodium tube the upper coil was tilted at an angle to the vertical such that it moved 1.5 mm to one side at the level of the collector and the lower coil stayed where it was. There was no observable effect on the photocurrent. The indication is not only that the alignment of the magnetic field was correct, but that there were no troublesome inhomogenieties in the collector surface, since tilting the magnetic field coil should cause the electrons to hit in a different spot.

#### Vacuum System

At first, there was a great deal of trouble with leaks in the vacuum system. Various methods were tried in looking for the leaks, but the method which proved most successful was to seal off the high vacuum part of the system and watch the rate of change of the pressure while trying to stop the leak. The details of this method are discussed below.

A mercury seal valve, figure 4 on page 19, of the type first used to the author's knowledge by Dr. Townes in this laboratory was put into the vacuum system between the two stages of the mercury diffusion pump. By placing the poles of an electromagnet on opposite sides of the valve, it was possible to raise the glass hat up out of



VALVE

FIG. 4

the mercury. The hook could then be put on the glass rod and the valve would remain open. Since this valve was in a relatively high vacuum part of the system, it could be closed, the fore pump kept running, and the diffusion pumps turned off with no great change in the vacuum in the phototube proper.

To detect the leaks, a pirani gauge was used, figure 5 page 21 . It consisted of a 10 watt, 110 volt lamp bulb connected to the vacuum system by a pyrex-soft glass graded seal. This bulb formed one arm of a wheatstone bridge. The adjacent arm was a permanently evacuated bulb, as in the usual type of compensated pirani gauge. Both bulbs were kept in the same heavy, copper, water-cooled container, so as to minimize temperature differences between them. Of the other two arms of the bridge, one was a fixed resistor and the other a dial box, both presumably independent of temperature.

At first, it was found that the gauge was extremely sensitive to vibration, due to variable heat contact between the filament and its supports. This difficulty was obviated by removing these supports and letting the filament dangle between its lead in wires. It was found possible to remove the supports without destroying the bulb by putting a small pair of surgical scissors (or "cuticle" scissors) through the hole which had to be made in the bulb for evacuation. The support wires could be easily cut without damage to the filament. It was necessary to bend the lead in wires using a small pair of tweezers so that the filament would not hang against the glass.

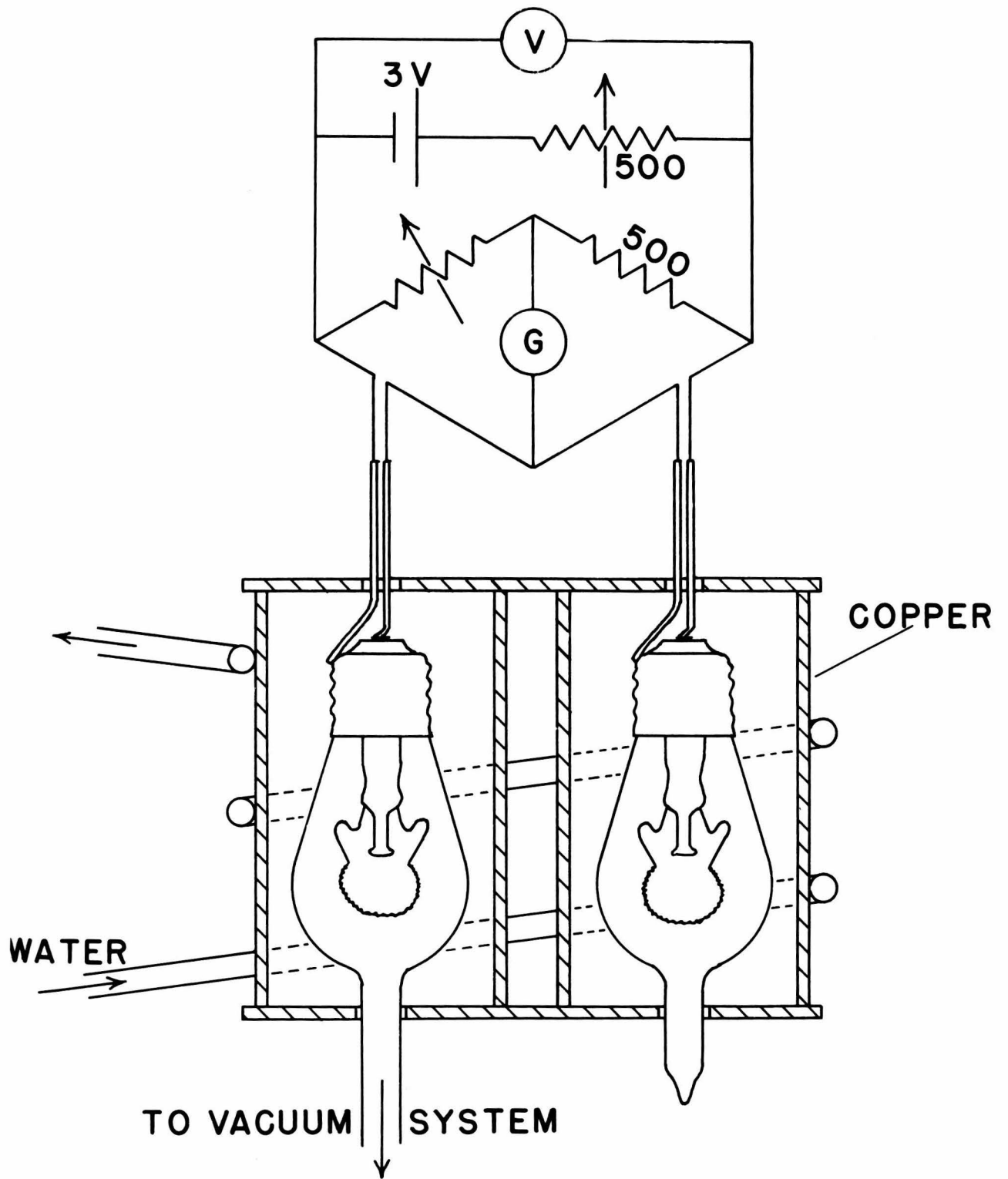


FIG. 5

When both the gauge bulb and the standard were modified in this way, the sensitivity to vibration was completely eliminated.

One other difficulty encountered was the sensitivity of the wheatstone bridge to the total voltage across it. The remedy was found to be a fixed resistor put in series with one of the pirani bulbs. The value of the resistor in this case was 16 ohms.

That it is possible thus to stabilize a pirani gauge may be seen as follows: Consider a wheatstone bridge with arms a,b,c,d. a and b are dependent on the current they carry and c and d are not. If the state of balance of the bridge is to be independent of the total current in the bridge,  $a/b$  must be constant, or, to a first approximation,  $d(a/b)/di$  must equal zero. This implies that  $a = \frac{b \, da/di}{db/di}$  which can be satisfied by adding a constant to a.

The gauge in its final form was found to be reliable over a period of days to a pressure of  $10^{-5}$  mm. Over short periods of time, however, pressure changes as small as  $10^{-7}$  mm could be detected, using a sensitive galvanometer in the wheatstone bridge circuit. The settings of the dial box and hence the readings of the galvanometer were approximately linear with pressure, 0.1 ohm corresponding roughly to  $10^{-5}$  mm Hg. Smaller pressure changes could be followed by watching the galvanometer. For small leaks, the rate of change of pressure in a sealed system is linear with time, so that the rate of drift of the galvanometer was constant. The procedure for finding leaks was to paint the suspected parts of the vacuum system in turn with Vultex (a water miscible latex

suspension which adheres readily to glass and dries into pure rubber in about 30 minutes) until the rate of drift of the galvanometer changed. If the leak was stopped in this way, as a check, it could be started again by stripping the rubber off the glass. Sometimes it was necessary to heat the glass with a gentle flame to start the leak again.

One of the most persistent causes of leaks was the longitudinal porosity of tungsten wire. As pointed out by other authors, this can be remedied by sealing a bead of nickel, copper or advance metal on the end of the tungsten wire.

For baking out the vacuum systems, a suggestion of Dr. R.M. Langer was put into practice, first by Dr. H. Bradner and then by the author. Furnaces were constructed from one layer of .001 inch aluminum foil, no other insulating material being used. The foil was somewhat crinkled up to give it rigidity. The pieces of foil were joined at the edges by folding twice. Large, entirely self supporting furnaces of odd shapes could be quickly constructed by this means. A carefully made furnace of this type, with as few holes in it as possible was as efficient as a furnace of the same size made by building up walls of fire-brick. For example, a space 26" x 20" x 10" was kept continuously at 450°C with a 1500 watt electric heater at the bottom.

The outgassing of the gallium tube was accomplished by heating the whole tube in an aluminum foil furnace at a temperature of 450°C for a day. The first set of data was run more than a month

after the outgassing, allowing ample time for conditions to stabilize.

After the first set of data, both carbon electrodes and the gallium were induction heated to a cherry red heat. Immediately after this, another set of data was run. The comparison between these two sets of data will be discussed later.

Since the sodium tube was to be a sealed off system, having the minimum amount of metal in it, it was felt that the technique of extremely high vacuum could be used.

First the tube proper, without the charcoal trap attached, was set up on the mercury pump and tested for leaks. The activated charcoal was given a preliminary outgassing by heating in vacuum at  $450^{\circ}\text{C}$  for several hours, cooling and exposing to air, then heating in vacuum at  $450^{\circ} - 500^{\circ}\text{C}$  for a day. After this, being careful to avoid contamination, the charcoal was put into the trap and the latter was sealed to the main tube. The sodium side arm (described in detail later) was attached to the tube and the whole thing connected to the vacuum system. A special aluminum foil furnace was built which allowed the sodium in its sealed off bulb to remain outside the furnace. This was necessary, since sodium attacks glass at high temperatures. Also the seal to the sodium reservoir had not as yet been broken, so that heating the reservoir would generate gas which could not be pumped away. The fact that the sodium reservoir was not heated along with the rest of the tube was not serious since it had been "flamed off" several times during the distillation of the sodium, and the reservoir would never be

connected to the main tube except through a hole about 1 mm in diameter.

The furnace was brought to 460°C for three days, then cooled down and dismantled. The coil of the induction furnace was next placed over one end of the tube and then the other, heating each electrode to incandescence for eight minutes. The aluminum foil furnace was again assembled and heated for another two days and cooled down. The electrodes were again induction heated, after which the furnace was brought to a temperature of 420°C and kept there for nine days. After this last heating the electrodes were induction heated and the tube left on the pumps at room temperature for a day. At the end of this time the tube was sealed off and the charcoal trap immersed in liquid air. The liquid air was kept in place till the end of the experiment. A final induction heating of the electrodes was carried out after allowing the charcoal time to clean up the residual gases.

It was found impossible to get the centers of electrodes as hot as the edges, with the result that the center of the collector remained visibly contaminated, even after the final induction heating. This contamination apparently had no effect on the results, however. The difficulty of not being able to heat the center of the electrode could be eliminated by making the center thicker, so that the eddy currents would be larger there, while the surface for heat dissipation would be approximately the same.



### Source of Monochromatic Light

The source of light used in these experiments was a vertical quartz arc (G.E. Uviac nominally 220 volt-1000 watt) operated from a special voltage regulated 220 volt D.C. generator. The manufacturer specifies 4.5 amperes and 160 volts drop in this lamp, but it was found that the light emission was too variable under those conditions even if a large inductance was put into the circuit. The values actually used were 3 amperes and 50 volts drop. Even so the arc was annoyingly unstable. For some of the measurements on the apparatus where accurate monochromatization was not required a tungsten filament bulb was used and found more constant. It would seem definitely possible to make a photoelectric - electronic stabilizer for the mercury arc. If such a device would permit use of the arc at its rated current, the photoelectric emission could be increased by a factor of 15.

The present measurements were conducted in such a way that any serious variation of intensity of the arc would manifest itself. Instead of taking all of the data for one curve in a sequence, the range of voltages was traversed in one direction, making readings at every other value of voltage. The rest of the readings were then taken going in the other direction. Any gradual change in intensity of the arc would then show up as staggering of the points of the curve. In no case was there any evidence of such changes.

The monochromatization was accomplished by means of one or two Hilger quartz monochromators, of 30 mm aperature. The light from

the last monochromator slit was focussed on the emitter by means of a 5 cm aperture quartz lens of 15 cm focal length. The axial position of the lens was adjustable so as to focus the various wavelengths used on the emitter. The lateral position of the lens was carefully adjusted so that the motion of focussing it would not displace the image from the center of the emitter. A wavelength scale was provided for setting the lens, the positions being calculated from the known indices of refraction of quartz at different wavelengths.

The photoelectric emission from gallium was so slight that reliable measurements could not be made using two monochromators in series, so that it was necessary to use only one, with rather wide slits. The only wavelengths which could be used were  $2483 \text{ \AA}$ ,  $2536 \text{ \AA}$ , and  $2653 \text{ \AA}$ . The second of these was so strong that part of the emission measured for the other two wavelengths was due to 2536. It was necessary to make a special correction for this.

A source (mercury discharge tube) was found which was rich in 2536, and gave very little of the other two wavelengths. The photoelectric current due to this light was measured as a function of monochromator setting, resulting in the curve shown in figure 6, page 28.

From the curve we can determine what part of the photocurrent is due to 2536 when the monochromator is set for the other wavelengths. The lines 2483 and 2653 are far enough from the points A,B,C and D so that they do not appreciably contribute to the

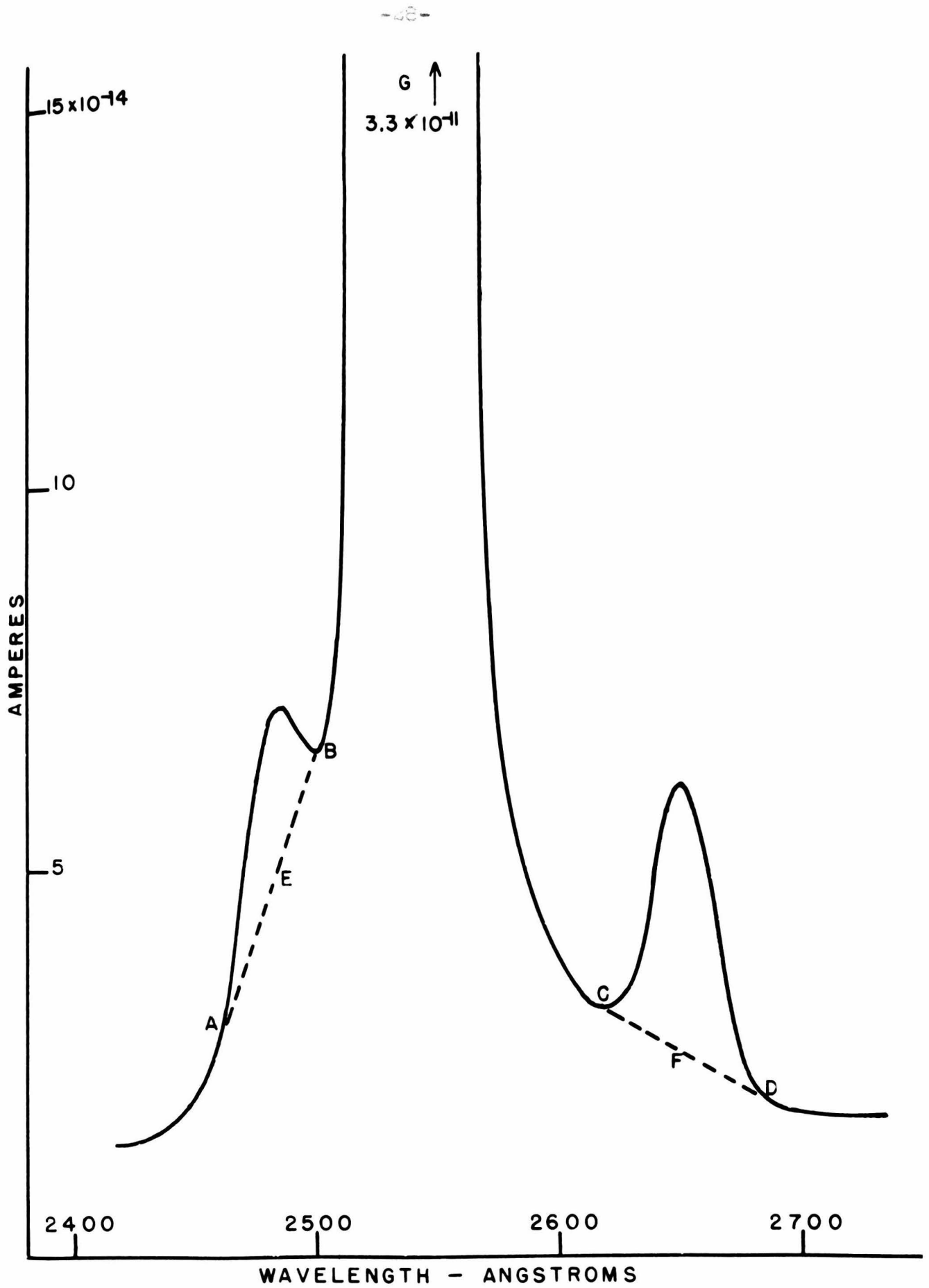


FIG. 6

photocurrent at these points. E is the average of the current values at A and B, F is the average of C and D.  $E/G$  is the ratio between the photocurrent due to 2536 when the monochromator is set at 2483 and that due to 2536 when set at 2536. The correction is applied by multiplying the ordinates of the current versus retarding voltage curve for 2536 by the ratio  $E/G$ . This gives the amount of current to be expected for the various retarding voltages when the monochromator is set at 2483. These current values can be subtracted from the observed currents for 2483 to get the true values. A correction is similarly applied for the wavelength 2653.

The work on sodium was done using two monochromators with a single slit between them. This slit was always set narrower than the first and last slits so that the monochromator wavelength settings would be less critical. A typical set of slit widths are as follows: .018, .014, .018 inches, although larger and smaller values were used.

The amount of light of unwanted wavelengths which gets through is negligible; for example, with one monochromator set at 2536 and the other 100 Å<sup>0</sup> off, the photocurrent is only .2 percent of the value obtained when both monochromators are set at 2536. Thus, if both monochromators were set 100 Å<sup>0</sup> off, only  $4 \times 10^{-6}$  of the 2536 intensity would get through.

In addition, a test (repeating Overhage's test (3)) was made to see whether there was any short wavelength contamination of the 4358 light. The first monochromator was set at 4358 and the second

at 4300 (so that the visible image due to 4358 had just disappeared). The retarding voltage was set so that only the most energetic electrons due to 4358 could have gotten through to the collector. There was no observed photocurrent, indicating no short wavelength contamination.

The lines of the mercury spectrum come in close groups with rather large separations between groups. The resolution of the monochromators, as indicated by the measurements described above, was such that all the lines of one group would come through the optical system, but none of any other. The following table gives the band widths for slit settings, .018, .014 and .018 inches.

<u>Wavelength - Å</u>	<u>Total Transmitted Band Width - Å</u>
4358	270
4047	210
3650	155
3125	85
2536	45

An electrically operated shutter intercepted the light beam from the last monochromator slit. The shutter could be operated from the observing station so that successive measurements could be made, with and without the light.

#### Amplifier

The photoelectric currents were amplified by an FP 54 phototube in the conventional DuBridge-Brown circuit<sup>6)</sup>.

The schematic hook up of the apparatus is shown in figure 2 on page 9 . The details of the amplifier circuit are shown in

figure 7 , page 32 .

The amplifier was used largely at a sensitivity of 60,000 divisions per volt, with a galvanometer of 7 seconds period and 2000 megohms sensitivity. The scale was 2 meters from the galvanometer. Part of the measurements were made at 400,000 divisions per volt, using a galvanometer of 13,000 megohms sensitivity and 15 seconds period. The grid resistors in the amplifier were S.S. White Dental resistors with a choice of  $1.24 \times 10^{11}$  ohms or  $2.6 \times 10^{10}$  ohms. The higher grid resistance and the more sensitive galvanometer used together gave a nominal current sensitivity of  $2 \times 10^{-17}$  amperes per scale division. Fluctuations were low enough that the current measurements were reliable to about  $10^{-16}$  ampere. Most of the measurements were made with the low sensitivity galvanometer and low grid resistance, since too great a time per reading was required with the others.

Various causes of fluctuating zero readings of the amplifier galvanometer were unearthed. Both magnetic and electrostatic shielding were found necessary before any work could be done. All parts of the amplifier were in grounded copper, brass, or aluminum containers, including the battery boxes and leads. The FP 54 tube itself was surrounded by a magnetic shield, made by rolling up a long piece of transformer lamination into a cylinder with ten layers wall thickness. The glass parts near the grid lead to the collector were painted with Aqua-Dag and connection made to ground. A second layer of shielding, made from copper sheet or screen, was used around



these parts and around the photo-tube itself. Even after this thorough shielding it was found that when a high frequency oscillator was used in the next room the galvanometer spot wandered around wildly.

Another source of trouble in the low resistance part of the amplifier circuit was contacts relying entirely on pressure, such as fuse clips, the tube base and slide wire rheostats. When possible, soldered connections were substituted. The ordinary radio type Clarostat was found satisfactory where the resistance was of the order of 1000 ohms. In that case, the variable contact resistance is a small fraction of the total. However, where a variable resistance of 10 or 20 ohms was needed, it was found necessary to use a fixed wire wound resistor of nearly the right value shunted with a large variable resistor. In that way, the effect of the variable contact resistance was minimized.

Even after the above precautions, there was some residual drift on the galvanometer zero, about 2 or 3 mm per minute. This drift was corrected for by taking zero readings before and after each photocurrent measurement. The true zero value was then taken as the average of the two zero readings. In all cases, either  $\frac{1}{2}$  minute or  $\frac{3}{4}$  minute, depending on the value of grid resistance used, was allowed for the galvanometer to come to rest before reading it; thus linear interpolation of the zero reading was justified.

The linearity of the amplifier grid resistance was checked by inserting rotating sectors in the light beam to the phototube, the



assumption being made that the average photoelectric current is proportional to the average light intensity. Sectors with 12.5 percent, 25 percent, 37.5 percent, 62.5 percent, 75 percent and 87.5 percent openings were used. Over the range of current values used in the experiments there was no observable departure from Ohm's Law in the grid resistor. i.e. the resistor was linear to within a few tenths of a percent. The test also proved that variations in grid current were negligible.

One defect of the S.S. White Dental resistors used in the grid circuit was that they tended to polarize. If a voltage was applied to the grid large enough to cause a full scale galvanometer deflection, and then the grid was grounded, the galvanometer spot would take much longer to return to its original position than one would expect from the time constant of the circuit.

The relation between grid voltage and galvanometer reading could be determined directly by applying a known voltage to the grid from the same potentiometer used for the retarding voltage, as shown in figure 2, page 9. The difference in potential between the collector and ground could always be determined from this calibration. The grounding switch shown in the calibration lead in figure 2 is merely to eliminate capacitative coupling between the type K potentiometer and the grid circuit while photoelectric measurements are being made. The applied retarding voltage  $V$ , in figure 1 on page 2, is equal to the positive voltage applied to the emitter from the potentiometer plus the voltage drop in the amplifier grid resistance, determined as above.

The type K potentiometer which supplied the retarding voltage

was used in the conventional way, except that its voltage range was doubled by passing twice the usual current through it. It was calibrated against two standard cells connected in series, the standard cell dial on the potentiometer being set to the average of the two values. The voltage delivered by the potentiometer was then twice the scale setting.

The standard cells used were frequently checked against those used in the recent work on  $h/e$  by Panofsky, Green and DuMond<sup>7)</sup>.

The latter cells were checked by the Bureau of Standards.

#### Necessity for Applying a Potential to the Glass

The Aqua-Dag coating on the outside surface of the glass tube, shown in figure 2, page 9, figure 3, page 14, proved to be necessary in the first experimental tube constructed, as previously mentioned.

If the apparatus were in a metal tube instead of a glass tube, whether or not an electron got from the emitter to the collector, with zero retarding field between these two electrodes, would clearly depend on the potential of the metal tube with respect to the two electrodes and on its work function. The glass tube behaves in the same way, that is, it appears to be a semi-conductor with an effective work function of about 5.4 volts.

The potential of the Aqua-Dag was maintained with respect to ground by using a varying number of dry cells. It was found in all cases that there was a rather sharp cut off value for this potential, below which no photocurrent would flow to the collector and above which the photocurrent was more or less constant. When the potential

on the glass gets too high, some electrons will migrate to the glass, causing a drop in the observed current.

With the gallium tube, the cut off value for the potential on the glass was about 1.0 volt. The current was constant from 1.5 volts to 6 volts and dropped 4 percent as the potential went to 40 volts.

With the sodium tube, the same definite cut off was observed, but there was some increase in the photocurrent as the potential on the glass was increased; e.g. as the potential was increased from 9 to 18 volts, the photoelectric current increased by 7 percent. This applies even if the emitter is made negative, so that all emitted electrons should get to the collector. The explanation for this fact is not evident. The tube was actually operated with 18 volts applied to the glass. The internal consistency of the data indicates that the presence of this potential did not alter the shape of the observed distribution curves, since the various curves were made in widely different energy ranges and one would not expect all energy ranges to be affected in the same way.

It was thought possible that the grounded guard ring at the collector end of the tube was neutralizing the effect of the potential applied on the outside of the glass. That possibility was eliminated by merely bringing the guard ring to the same voltage as the outside of the glass, with no effect. (The insulation of the collector inside the phototube was good enough so that it was unnecessary to keep the guard ring at ground potential).

### Sodium Distillation

The sodium used in this experiment was purified by double distillation in a pyrex still, (similar to the one used by Overhage) shown in figure 8 on page 38 . The still consisted of a set of receivers and connecting tubes as shown. The connecting tubes were covered with a layer of asbestos paper, applied wet to make it pliable. When the asbestos was dry, number 24 chromel wire was wound around the tube, 8 turns to the inch. Another layer of asbestos was applied on top of the windings.

The sodium was first cleaned of its oxide crust and cut into small pieces under dry benzene. The pieces were dried with filter paper and introduced into the system at A. The wax seal was made at A and the pumping started as quickly as possible. After an hour or so, the sodium was melted and allowed to run into the first receiver. When this had been accomplished, a seal was made at B.

The sodium was then slowly distilled into the second receiver, by heating the first in an electric furnace and passing current through the chromel windings on the connecting tube. A seal was then made at C. Throughout the process the whole apparatus was repeatedly torched off to outgas the glass walls.

The second distillation was preceded by six hours refluxing. The current in the windings was 1.2 amperes and the furnace temperature  $480^{\circ}\text{C}$ . The actual distillation took ten hours, with the furnace at  $490^{\circ}\text{C}$  and 2.9 amperes in the windings.

The final receiver was sealed off at D and E and was ready for

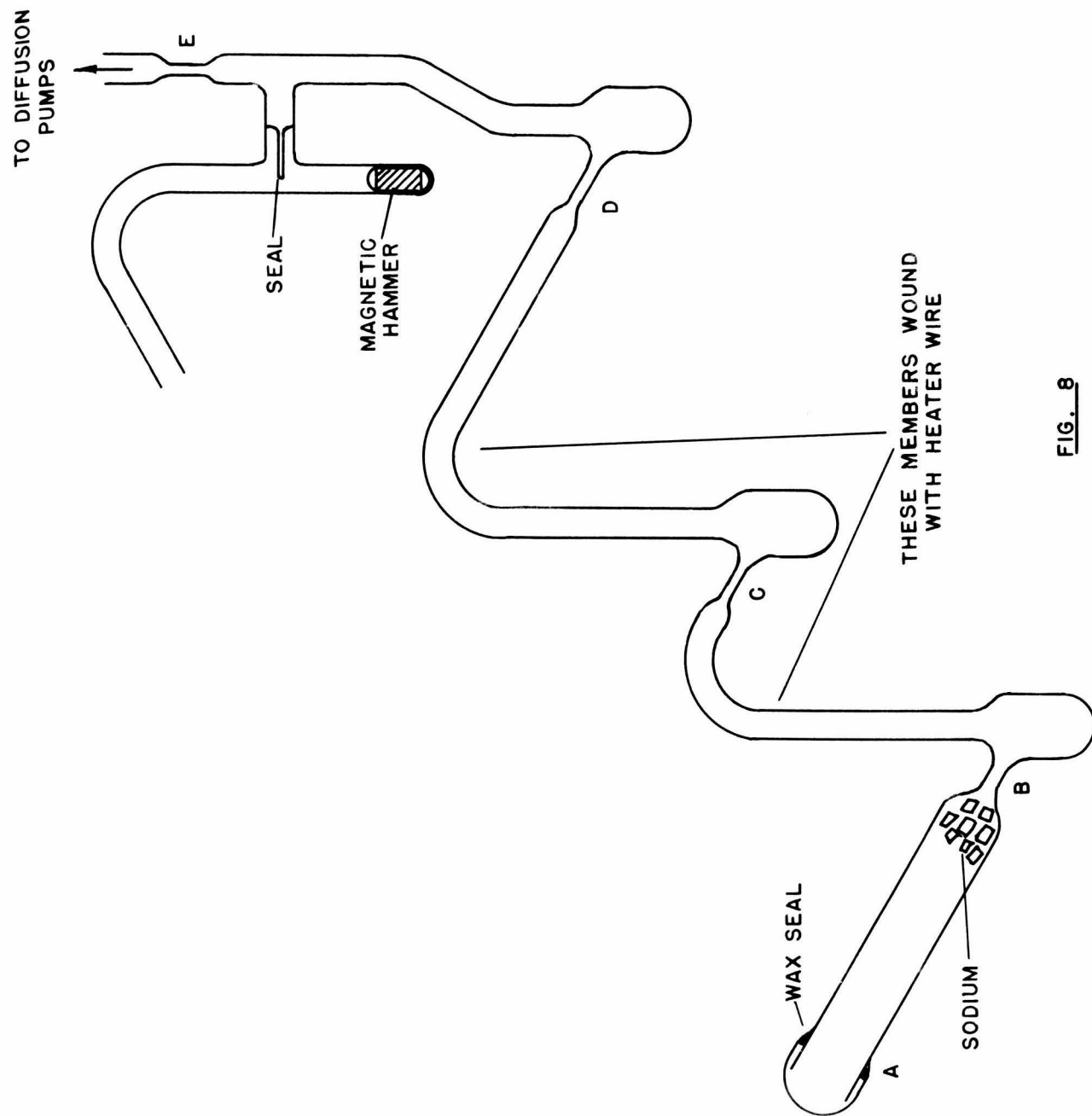


FIG. 8

attachment to the main phototube. The internal seal was not broken until all of the outgassing operations on the main tube were finished.

Before depositing the sodium on the emitter, the tube between the sodium reservoir and the phototube was wound with chromel wire as described above, all except the small constricted portion where the sodium tube joined the main tube. By keeping this portion cool enough to condense the sodium, a well defined conical beam could be formed. When everything was ready, the internal seal was broken with the magnetic hammer and the deposition carried out. Enough sodium was deposited on the emitter to form a heavy coating of matte white appearance.

### Results

By knowing the applied retarding potential for photocurrent saturation, ( $V$ ) the applied potential for photocurrent "cutoff" ( $V$ ) and the wavelength of the light, it is possible to make a rough estimate of the work function of both the emitter and collector.

Referring to figure 1 let

$$\begin{aligned}\phi_1 &= \text{work function of emitter (in volts)} = \frac{(W_1 - \mu_1)c}{e \cdot 10^9} \\ \phi_2 &= \text{work function of collector, } \frac{(W_2 - \mu_2)c}{e \cdot 10^9} \\ \frac{hc^2}{e \lambda \cdot 10^9} &= \text{energy of light used in electron volts.}\end{aligned}$$

$$\text{Then } \phi_2 = \frac{hc^2}{e \lambda \cdot 10^9} - V_c = \phi_1 - V_s$$

$$\text{Hence } \phi_1 = \frac{hc^2}{e \lambda \cdot 10^9} - V_c + V_s$$

Various work functions determined in the course of the research by this method are as follows:

Carbon	5.4 volts
Glass	5.4 volts
Gallium	3.8 volts
Sodium	2.3 volts

#### Gallium

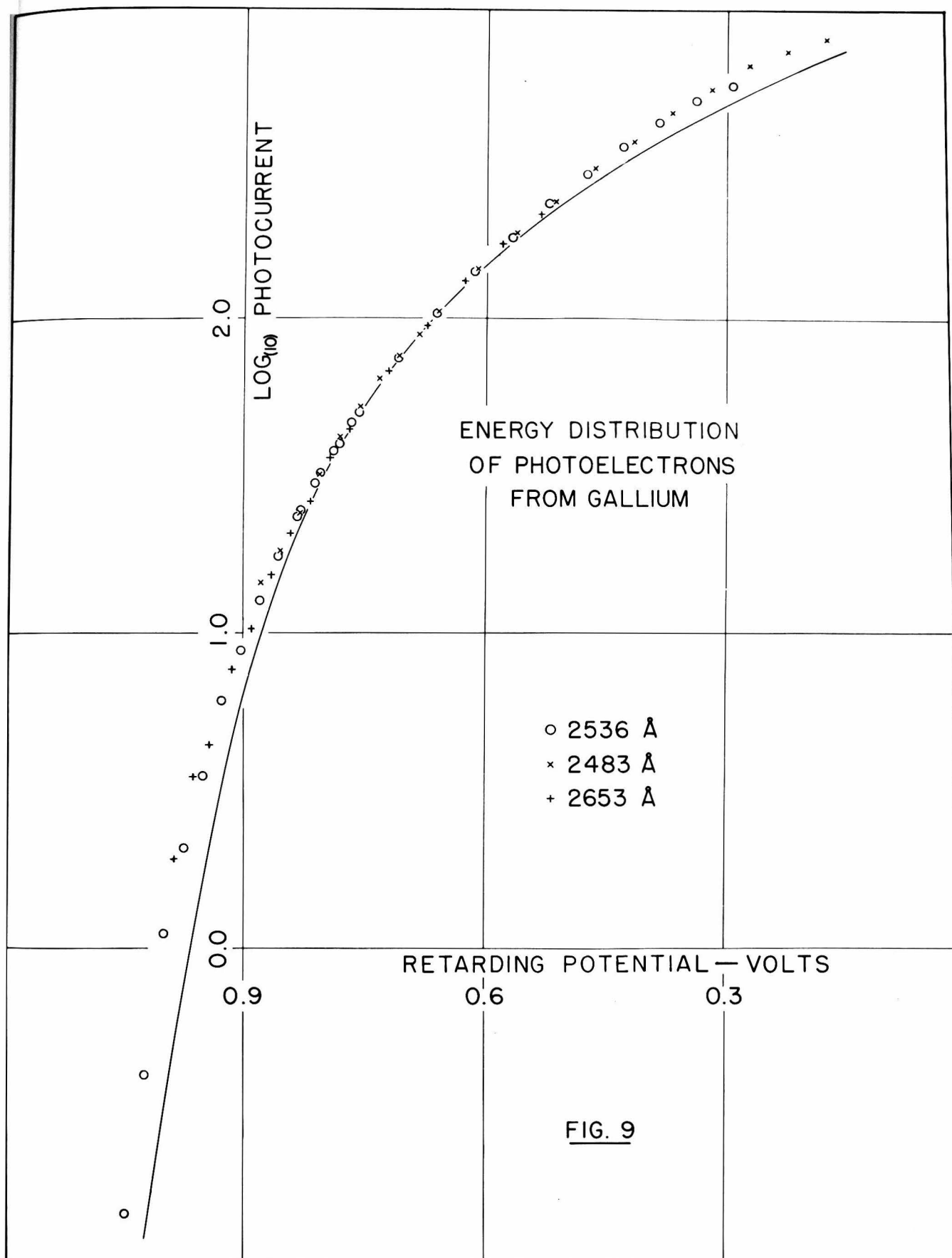
The data obtained with the gallium tube are plotted in figure 9 on page 41 . The abscissae are retarding voltages, i.e. the sum of the voltage applied to the emitter and the voltage drop in the amplifier grid resistor. The ordinates are logarithms of this same voltage drop in the grid resistor. The ordinate should differ only by a constant from the log of the true photocurrent.

The theoretical curve plotted on the same graph is  $\phi(x)$  plotted against  $\frac{ktx}{e}$  ( = .2556x for the temperature of 23.6°C at which the experiments were conducted.)

The curves for  $2483\text{\AA}^{\circ}$  and  $2653\text{\AA}^{\circ}$  have been corrected for stray light of  $2536\text{\AA}^{\circ}$ , as outlined in the section on light sources. These two curves have been drawn with arbitrary horizontal and vertical shifts to bring them into coincidence with the curve for  $2536\text{\AA}^{\circ}$ .

It can be seen that the mutual agreement of the data is good, but that there is a large discrepancy between the experimental and theoretical curves.

The experimental conditions for the data shown in figure 9 on page 41 were 3 volts applied to the glass walls and 1 and 3 amperes respectively in the upper and lower magnetic field coils.





To see what effect these factors had on the shape of the log J versus V curves, another set of data was taken a month later. The electrodes were induction heated to incandescence just before this last set of data was run. The conditions were 6 volts on the glass and 1.5 and 4.0 amperes in the coils. The agreement with the previous curve is good, discrepancies being within the experimental error, even though the work function of the collector had changed in the interim between the two runs and the experimental conditions were quite different.

In these experiments on gallium, there was no reverse photocurrent whatever.

#### Sodium

Immediately after depositing the sodium layer on the emitter, it was found that the work function of the collector was as low as that of the emitter.

A week after the deposition, the collector was induction heated to drive off condensed sodium. Immediately afterwards, the work function was nearly 4.5 volts but it began to decrease at once, going down to 2.5 volts in a day, indicating that it was impossible to prevent sodium from condensing on the collector. The work functions of both electrodes wandered around for some time, approaching constancy about two weeks after the last induction heating.

It was impossible to eliminate reverse currents, since the work function of the collector was so low. The reverse current

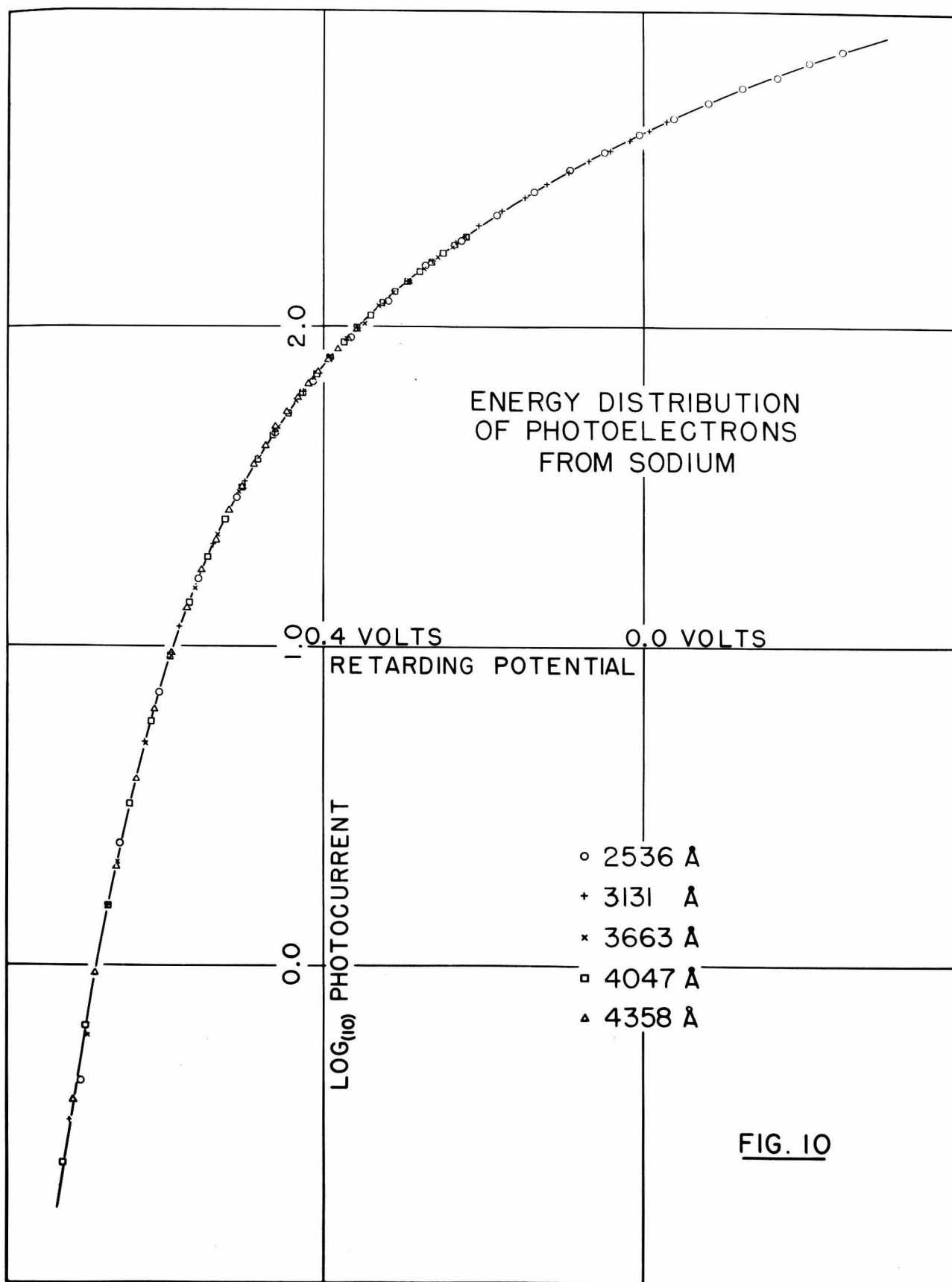
could be easily corrected for, however.

The fact that a retarding field (for electrons from the emitter) was present at all times during the measurements, meant that there was always an accelerating field for electrons from the collector. Thus any electron which left the collector would always be picked up by the emitter or by the walls of the tube, which were kept at 18 volts positive with respect to the collector. The reverse current then is merely a constant correction, to be determined by applying a large enough retarding voltage to cut off the direct photocurrent, and to be subtracted from all the values of photocurrent.

The data for sodium is plotted in figure 10, page 44. As before each curve has been given an arbitrary horizontal and vertical displacement to superpose it on the curve for  $4047\text{\AA}$ . Measurements were also made with  $4916\text{\AA}$ . This wavelength is so near the threshold that the retarding field must be very small. It is difficult to tell what portion of the curve represents current saturation and what portion is usable. For this reason, the data for  $4916\text{\AA}$  are not plotted.

The solid curve shown in figure 10 is the best curve which could be drawn to fit the results. The comparison between the theoretical and experimental curves is shown in figure 11, page 45. Here  $\frac{kt}{e} = .0259$  for the temperature  $27.5^{\circ}\text{C}$  at which the measurements were made.

A second set of data, taken under the same conditions, three days after that plotted in figure 10, agreed very well with the



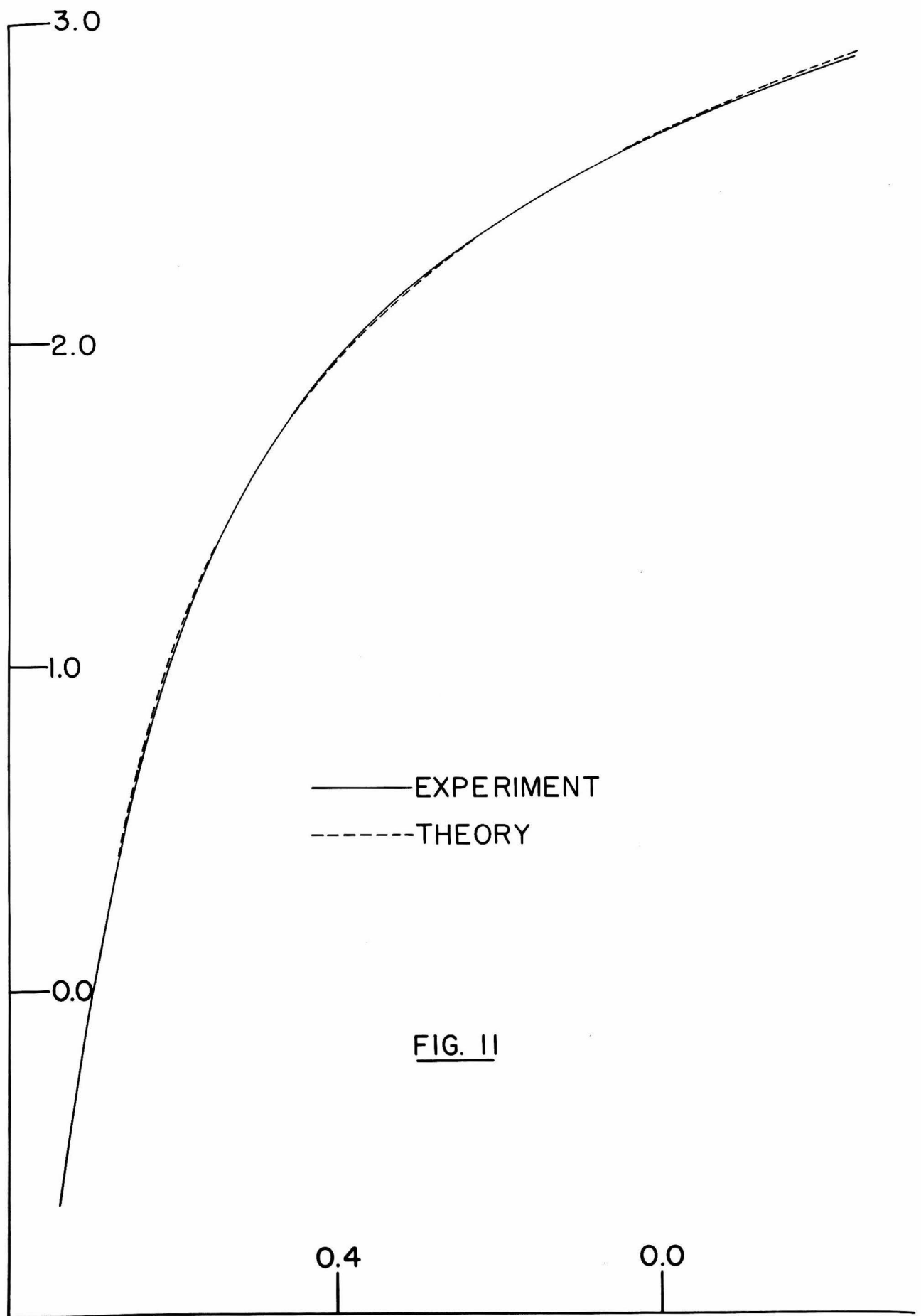
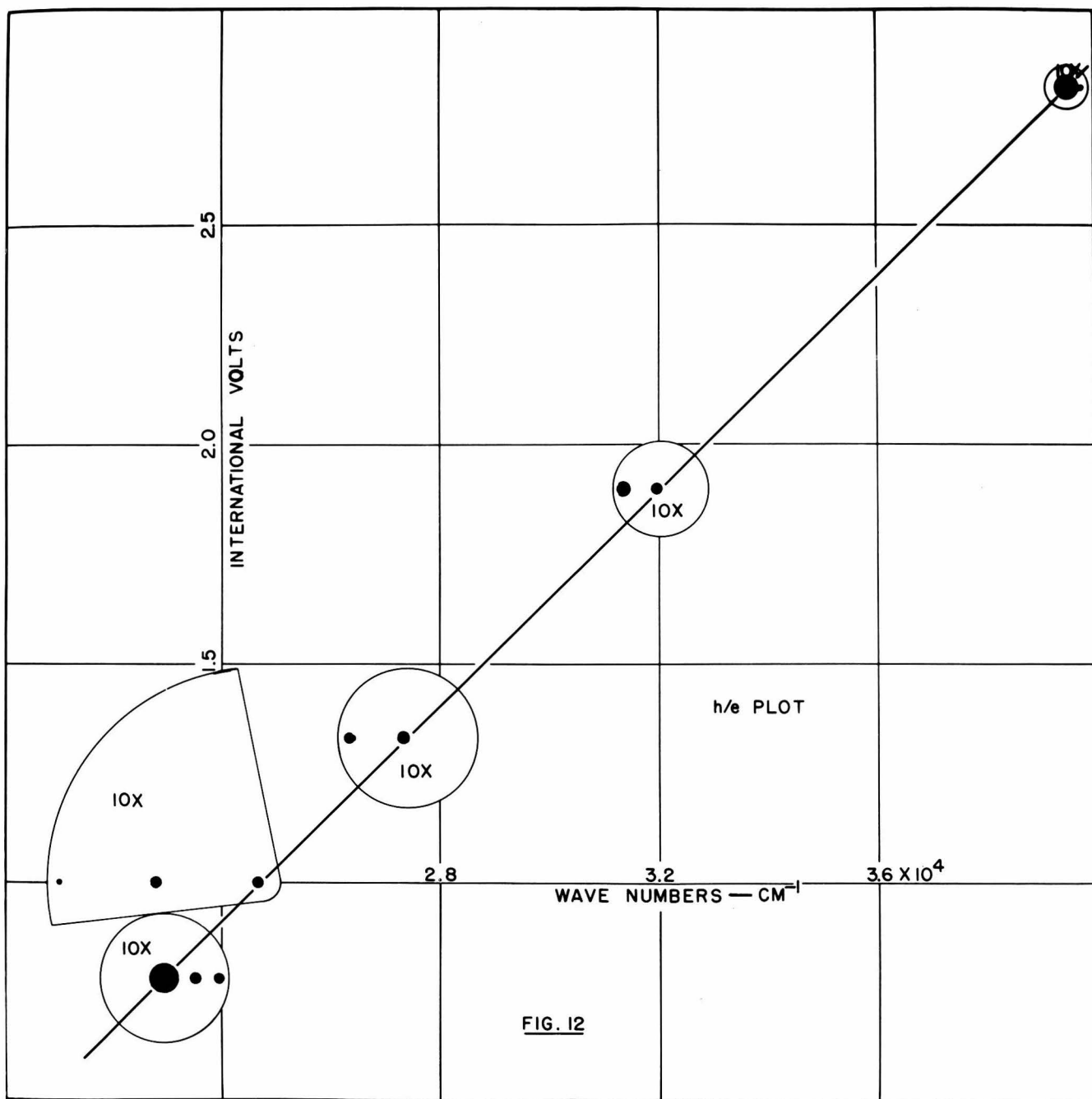


FIG. II



data shown. What deviations appeared were in the direction of better agreement with theory.

### The Determination of $h/e$ .

Figure 12, page 46 is a plot of the amount of horizontal shift in International Volts required to superpose each of the curves onto the reference curve (4047A), versus the wave numbers of the various spectral lines involved.

Each group of lines is shown plotted to a large scale, the areas of the circles showing the relative intensities. It may be seen that there is one straight line which will at least go through one point of each group, although this point does not necessarily correspond to the most intense spectral line. The lack of accurate intensity measurements (the best available are from the M.I.T. Wavelength Tables<sup>8)</sup>) makes it difficult to get a good mean for the effective wavelength of a group. It is not clear just what sort of a mean one would use if such measurements were available.

The slope of the straight line in figure 12, when multiplied by the proper constant should give  $h/e$ . The constant is  $x/c^2 \cdot 1.1132 \times 10^{-13} \text{ sec}^2 \text{ cm}^{-2}$  where  $x$  is the ratio of the international volt to the absolute volt, 1,00034, and  $c$  is the velocity of light,  $2.9978 \times 10^{10} \text{ cm/sec}$ . The values are taken from Birge<sup>9)</sup>.

The value of  $h/e$  so determined is  $1.375 \times 10^{-17} \text{ erg sec e.s.u.}^{-1}$

The  $h/e$  plot for the second set of data is not as good as the first, i.e. if a straight line is drawn through the points for 4358Å and for 2536Å, (bottom and top points, figure 12) it misses the other points by amounts varying from  $.004 \times 10^4$  to  $.009 \times 10^4$  wave numbers, all the deviations being in the same direction. From

the order in which the data was taken, this "curvature" could be attributed to a slow change in one of the constants of the phototube.

In any case, the value of  $h/e$  determined from the slope of the line through the points for  $4358\text{\AA}$  and  $2536\text{\AA}$  is  $1.383 \times 10^{-17}$  erg sec e.s.u.<sup>-1</sup>.

The average of the two  $h/e$  values is 1.379, lying between the x-ray value of Panofsky<sup>7)</sup>,  $1.3786 \pm 0.0002$ , and the most probable indirectly computed value of Birge<sup>9)</sup>,  $1.3793 \pm 0.0002$ . The author hesitates to assign limits of error to the value given here.

### Conclusion

The agreement between the data for  $2536\text{\AA}$  and the rest was not observed by Overhage<sup>3)</sup>, in his work on sodium. His difficulty may have been the fact that he did not refocus his condensing lens for each wavelength used. The change in the index of refraction of quartz between  $3131\text{\AA}$  and  $2536\text{\AA}$  is so large that his whole emitter would be illuminated instead of the center only. One would expect edge effects to be much worse under such conditions.

The unusually good agreement of the experimental results on sodium with theory would seem to indicate that the surface potential barrier is simpler than previously believed.

It can be seen from figure 1, that the factor which determines whether or not an electron is collected is the barrier at the collector. It is surprising that a collector whose surface is as definitely composite as this one should give such simple results.

Assumption 3. under Theory may thus be considered verified for

the surfaces involved in the sodium work.

The collector in the case of the gallium work was graphite, a semi-conductor for which deviations from the Sommerfeld free electron theory of metals may be expected.

There may also have been some trouble due to the fact that the emitter was a nearly spherical globule of gallium. The effect of electrode curvature could conceivably be similar to edge effect in the case of the parallel plate-retarding field method. In any case, the discrepancy between theory and experiment for gallium is quite like that observed by Overhage in his work on sodium.

The author is indebted to Professor W.V. Houston who suggested this problem and guided the course of the work.

The author also wishes to thank the many staff members of the California Institute of Technology without whose advice and encouragement the research could not have been a success. He especially wishes to thank Mr. W. Clancy, the institute glass blower who constructed the glass parts of the apparatus with great skill and patience.

The labor of the research was simplified by the fact that part of the apparatus had already been set up by Dr. Overhage and Mr. J.S. Wiggins before the author started to work. Mr. Wiggins also carried out the first part of the research on gallium.

Finally the author is grateful to his friends who helped in the preparation of this thesis.



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