The Photoelectric Method for the Determination of h/e

Thesis by

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Contents

Abstract

The experimental foundations of the photoelectric method for the determination of h/e have been re-examined. The theory of the normal energy distribution of photoelectrons has been modified by including the effect of contact potentials; it is shown that the stopping potential at 0° K. should be independent of variations of the cathode work function.

Apparatus has been constructed for the precise determination of the normal energy distribution of photoelectrons from sodium. Photoelectric currents emitted by monochromatic light were accurately measured after passage through a retarding field. The results of such measurements are found to vary with changes of the anode potential barrier.

Energy distribution curves taken at different frequencies exhibit very satisfactory mutual consistency; when plotted logarithmically they are of identical shape. This shape does not agree with the theoretically predicted normal energy distribution. The reasons for this discrepancy are discussed, and an explanation is given in terms of the structure of the anode potential barrier.

A method for the determination of h/e based on the consistency in shape of the empirically determined curves has been developed, and preliminary results have been obtained. The errors of the method are discussed, and modifications for its further improvement are suggested.

The Quantum Constant and its Determination

On December 14, 1900, Max Planck[1)] read to the Deutsche Physikalische Gesellschaft a paper on "the Theory of the Energy Distribution Law in the Normal Spectrum", in which he introduced the concept of light quanta with the prophetic words, "Moreover, further relations have resulted in this connection, which appear to me to be of considerable significance in extensive regions of physics and also of chemistry". In the same address, which, more than any other single contribution, marks the transition from classical to modern physics, Planck gave a numerical value to the constant h which connects the energy of an elementary oscillator with its frequency. From measurements by Kurlbaum[2)] of the Stefan-Boltzmann constant, and by Lummer and Pringsheim[3)] of the constant of Wien's Law, Planck obtained $h = 6.55 \cdot 10^{-27}$ erg cm. The striking agreement of this figure with many of the more recent determinations is rather fortuitous; nevertheless, more than fifteen years elapsed before inherently more precise methods of measurement were developed.

These newer methods were gradually suggested by the development of the quantum theory and by the growing realization of the importance of the quantum concept in many of the most fundamental physical processes. Omitting from the present consideration the attempts by Lewis and Adams[4)] and Eddington[5)] to obtain the values of natural constants purely by speculation, there remain essentially nine methods for the experimental determination of the quantum constant h. For the numerical values given below in connection with these different methods, the author is indebted to Professor R. T. Birge, who kindly communicated to him the results of a number of unpublished calculations. A summary of all quoted results will be found on page 12.

I. Wien's Displacement Law.

The equation which Planck derived for the energy distribution of heat radiation from a black body may be stated in the form,

$$E_\lambda = 2\pi c^2 h \lambda^{-5} \frac{1}{e^{\frac{ch}{\lambda kT}} - 1} , \tag{1}$$

where $E_\lambda d\lambda$ denotes the emission per unit surface of unpolarized radiation of wave length λ in the range $d\lambda$, and k the Boltzmann constant. By equating the derivative of this expression to zero, Wien's Displacement Law is obtained:

$$\lambda_{max} T = \frac{c_2}{\beta} = \frac{ch}{k\beta} , \tag{2}$$

where $\beta = 4.9651$ is a purely numerical constant. In Planck's original calculation k is indirectly furnished by the Stefan-Boltzmann constant. At the present time it appears preferable to use the relation

$$k = \frac{R}{N_0} = \frac{Re}{Fc} , \tag{3}$$

where R is the gas constant per mol, N_0 Avogadro's number, and F the value of the Faraday, and to consider e as unknown:

$$\frac{h}{e} = \frac{R c_2}{F c^2} . \qquad (4)$$

In his comprehensive 1929 report on the physical constants Birge6) adopts the value $c_2 = (1.432 \pm 0.003)$ cm deg, in close agreement with the results of Coblentz7). Using the best values available at this time for the auxiliary constants R, F, and c, Birge8) obtains from this,

$$h/e = (1.37\,296 \pm 0.00288)\,10^{-17} \text{ erg sec e.s.u.}^{-1}$$

II. The Stefan-Boltzmann Law.

Integration of Planck's equation (1) yields the Stefan-Boltzmann Law for the total radiation from a black body,

$$E = \sigma T^4 , \qquad (4)$$

where σ , in terms of previously discussed constants, may be written as

$$\sigma = \frac{2\pi^5}{15} \frac{R^4}{F^4 c^6} \frac{e^4}{h^3} . \qquad (5)$$

Thus,

$$\frac{h}{e^{4/3}} = \left(\frac{2\pi^5}{15} \frac{R^4}{F^4 c^6} \frac{1}{\sigma} \right)^{\frac{1}{3}} . \qquad (6)$$

A critical review of all experimental work on the Stefan-Boltzmann constant has been given by Birge6) in 1929. He has more recently come to the conclusion, however, that the accuracy at present obtainable in this type of determination is too poor to warrant comparison with other methods of determining h/e.

III. Photoelectric Effect.

In 1905, Einstein$^{9)}$ advanced the hypothesis that the subdivision of energy into discrete quanta of magnitude $h\nu$ should apply to the radiation itself as well as to Planck's elementary oscillators. This view, according to which radiation may be thought of as consisting of "photons" of energy $h\nu$, led Einstein immediately to a simple interpretation of photoelectric phenomena, and to the establishment of the equation

$$h\nu - P = eV_{max} , \qquad (7)$$

where P is the work rendered by the electron in leaving the metal, and eV_{max} the maximum energy which a photoelectron emitted by light of frequency ν may have. This equation was experimentally confirmed by Millikan$^{10)}$ in a series of experiments which, in 1916, yielded the first direct precision determination of the quantum constant. Subsequent determinations by this method were made by Lukirsky and Prilezaev$^{11)}$ in 1928, and by Olpin$^{12)}$ in 1930. Using a weighted mean of these three determinations, Birge$^{8)}$ obtains as the most probable value of h/e from photoelectric determinations

$$h/e = (1.37\,348 \pm 0.00\,295)\cdot 10^{-17} \text{ erg sec e.s.u.}^{-1}$$

The further development of this method, and the modifications of Millikan's procedure, which recent theoretical and experimental advances have necessitated, form the subject matter of this thesis. A detailed discussion of these photoelectric results will therefore be given later.

IV. Continuous X-Ray Spectrum.

The applicability of the photoelectric equation (7) to x-ray processes was first demonstrated experimentally by Duane and Hunt13) in 1915, although Wien14) and Stark15) suggested as early as 1907 that the equation might be valid in the x-ray region. For the purpose of determining the value of the quantum constant, one generally uses the inverse photoelectric effect, to which equation (7) applies. The quantity P appears in this case as a small correction to the applied voltage V. The equation predicts that, for a given frequency of emitted x-radiation, there is a sharply defined minimum voltage through which the primary electrons must have fallen to produce x-rays of this frequency. This cut-off can be experimentally determined with high precision. Birge8) has computed a weighted mean of

$$h/e = (1.37\,587 \pm 0.00\,029)\,10^{-17} \text{ erg cm e.s.u.}^{-1}$$

from the results of four different investigations, of which the most accurate one is that of Kirkpatrick and Ross16). Very recently, DuMond and Bollman17) have made another very precise determination at this laboratory; their result,

$$h/e = (1.37\,62 \pm 0.00\,03)\ 10^{-17} \text{ erg cm e.s.u.}^{-1},$$

is in close agreement with the previously mentioned mean.

V. Ionization Potentials.

The suggestion that the quantum constant h enters into the treatment of the emission of radiation by atomic collision processes was made by Stark[18)] in 1907, but the first adequate interpretation of resonance and ionization potentials was given in 1913 by Bohr[19,20)] in his fundamental papers on atomic theory. In terms of Bohr's atomic model, the energy which must be supplied by collision to the electron in an atom, in order to move it from the ground state to an excited state, is related to the frequency which the electron emits upon its return to the ground state by the simple relation

$$eV = h\nu \quad . \tag{8}$$

For ionization potentials, the left side becomes the energy necessary to remove the electron from the ground state to infinity; the right side is replaced by $hc\nu_0'$, where ν_0' is the "term value", expressed in cm^{-1}, of the ground state, which can be accurately determined from the spectral series relations. From the results of E. O. Lawrence[21)] on the ionization potential of mercury, and from the work of Van Atta[22)] on helium, Birge[8)] has calculated the value

$$h/e = (1.37\,500 \pm 0.00\,121)\ 10^{-17} \text{ erg cm e.s.u.}^{-1}$$

VI. Rydberg Constant and Specific Electronic Charge.

Another major success of Bohr's atomic theory consisted in the simple and direct interpretation of the Rydberg constant, for which Bohr obtained the expression

$$R_\infty = \frac{2\pi^2 e^5}{h^3 c^2 \left(\frac{e}{m}\right)} , \qquad (9)$$

where e/m is expressed in electromagnetic units. Hence,

$$\frac{h}{e^{5/3}} = \left[\frac{2\pi^2}{c^2 R_\infty \left(\frac{e}{m}\right)}\right]^{\frac{1}{3}}$$

and

$$\frac{h}{e} = \left[\frac{2\pi^2 e^2}{c^2 R_\infty \left(\frac{e}{m}\right)}\right]^{\frac{1}{3}} \qquad (10)$$

Since the adopted value of the Rydberg constant R_∞ is generally held to be more reliable than the values of almost all other physical constants, equation (10) provides an excellent test of the mutual consistency of determinations of h/e, e/m, and e. At the present time, the best values for the latter two constants appear to be Bearden's[23)] weighted mean of x-ray diffraction determinations of e, and Birge's[24)] weighted mean of five e/m determinations. These values are,

$$e = (4.8029 \pm 0.0005)\ 10^{-10} \text{e.s.u.}$$

and $$e/m = (1.75\,762 \pm 0.00\,016)\ 10^{7} \text{ e.m.u. g}^{-1}.$$

On the basis of these figures, and of Houston's25) determination of the Rydberg constant, Birge24) obtains

$$h/e = (1.37985 + 0.00\,012)\ 10^{-17} \text{ erg cm e.s.u.}^{-1}$$

The discrepancy between this value and the results of direct h/e determinations will be further discussed at the end of this section.

VII. X-ray Photoelectrons.

The investigation of the velocities of photoelectrons ejected from atoms by incident x-rays was started, in 1914, by Robinson and Rawlinson26) who applied the methods of magnetic β-ray spectroscopy to this problem. The simple and direct interpretation of the velocities in terms of the photoelectric equation (7) and Bohr's atomic theory was discovered seven years later by M. de Broglie27,28) who showed the existence of photoelectrons satisfying the equation

$$E_{kin} = h\nu_0 - h\nu_q \qquad (11)$$

These electrons are ejected from the q shell by incident photons of energy $h\nu_0$; $h\nu_q$ represents their original energy in the q shell. The term P of the equation (7) reduces to a negligible correction. If the kinetic energy E_{kin} of the emitted electron is measured by the radius of curvature r of its path in a magnetic field H, one obtains the expression

$$\left(\frac{e}{h}\right)\left(\frac{e}{m}\right) = \frac{2c^2\,(\nu_0 - \nu_q)}{(Hr)^2 - \left(\frac{h}{e}\right)^2 (\nu_0 - \nu_q)^2} \quad , \qquad (12)$$

which gives a very useful relation between e/h and e/m; it should be noticed that the second term in the denominator is a small relativistic correction term. Precise measurements on this basis have been recently performed by Robinson29) and Kretschmar30); assuming e/m to be 1.7575 10^7 e.m.u. g^{-1} Birge8) has obtained from this work the value

$$h/e = (1.37\,801 \pm 0.00\,138)\ 10^{-17}\ \text{erg cm e.s.u.}^{-1}$$

VIII. Compton Effect.

One of the most convincing arguments in favor of the quantum concept was advanced in 1923 by A. H. Compton31). The process involved in the Compton effect differs from the photoelectric process in that the energy $h\nu$ of the incident photon is only partly communicated to the electron; the remainder appears as photon of the modified frequency $h\nu'$. According to Compton, this modified frequency is related to the incident frequency and the scattering angle by the simple relation

$$\lambda' - \lambda = \frac{h}{mc}(1 - \cos\varphi) = \left(\frac{h}{e}\right)\left(\frac{e}{m}\right)\frac{(1 - \cos\varphi)}{c} \quad . \qquad (13)$$

Later investigations have shown that corrections must be applied to the trigonometric term, and the theoretical situation is not entirely cleared up at this time. The best experimental work on the absolute amount of the shift appears to be that of Ross and Kirkpatrick32), who used different incident wave lengths, and allowed for the correction terms by extrapolating their results to zero incident wave length. With the value of e/m used in the preceding section, their determination, according to Birge8), leads to the value

$$h/e = (1.37\,787 \pm 0.00\,325)\,10^{-17}\ \text{erg cm e.s.u.}^{-1}$$

IX. Electron Diffraction.

The major difficulty which confronted the early quantum theory was the impossibility of accounting for diffraction and interference phenomena with the corpuscular model of radiation which the photon concept seemed to imply. In 1924, L. de Broglie33) suggested that motion of a body and propagation of a wave were associated by the relation

$$\lambda = \frac{h}{m v} \quad , \qquad (14)$$

an hypothesis which has since been amply verified by experiments on the diffraction of beams of moving particles. Such experiments can now be carried out with a precision comparable to that attained by most of the methods previously mentioned. If the velocity of a beam of electrons is measured by means of the applied voltage V, and if the wave length λ of such electrons is obtained from the crystal diffraction pattern, one obtains the expression

$$\lambda = \left(\frac{h}{e}\right) \frac{1}{\sqrt{2\left(\frac{m_0}{e}\right) V \left(1 + \frac{e}{m_0}\,\frac{V}{2c^2}\right)}} \quad , \qquad (15)$$

which represents an experimentally available relation between the constants e, h, and e/m. If e/m is assumed to be known, a value of h/e may be calculated. The best determination of this type appears to be that of v. Friesen34); a similar experiment by Gnan35) depends on a different and less accurate method of measuring the velocities of the electrons. The calculation of a final corrected value of h/e from v. Friesen's work has not yet been carried out; it appears, however, from a preliminary calculation by Birge8) that this result agrees, within the limits of probable error, with the determinations previously discussed.

Summary

Table I

(A) Direct Determination of h/e

Method	Section	h/e (erg sec e.s.u.$^{-1}$)
Radiation constant c_2	I	$(1.37\ 296 \pm 0.00\ 288)\ 10^{-17}$
Photoelectric effect	III	$(1.37\ 348 \pm 0.00\ 295)\ 10^{-17}$
Cont. x-ray spectrum	IV	$(1.37\ 587 \pm 0.00\ 029\ \ 10^{-17}$
Ionization potentials	V	$(1.37\ 500 \pm 0.00\ 121)\ 10^{-17}$

(B) Determinations involving e/m

Method	Section	h/e (erg sec e.s.u.$^{-1}$)
X-ray photoelectrons	VII	$(1.37\ 801 \pm 0.00\ 138)\ 10^{-17}$
Compton effect	VIII	$(1.37\ 787 + 0.00\ 325)\ 10^{-17}$

(Calculated with $e/m = 1.7575 \cdot 10^7$ e.m.u. g^{-1})

(C) Weighted Mean of all Results in (A) and (B)

Methods I, III, IV, V, VII, VIII (1.37 588 ± 0.00 027) 10^{-17}

(D) Interrelation with Determinations of e

Method	Section	h/e (erg sec e.s.u.$^{-1}$)
Rydberg Constant	VI	(1.37 985 ± 0.00 012) 10^{-17}

(Calculated with R = (109 737.42 ± 0.006) cm^{-1}

e = (4.8029 ± 0.0005) 10^{-10} e.s.u.

e/m = (1.75 762 ± 0.00 026) 10^{7} e.m.u. g^{-1})

A graphical representation of the results quoted in this summary is given in Fig. 1, p. 14.

The methods which have been reviewed are, of course, not the only relations between h and other constants, which are available for experimental investigation. The degree of precision which has been achieved by other methods is, however, not sufficiently high at this time to permit a comparison of their results with those indicated above. On the other hand, there is every reason to believe that, within the next few years, our knowledge of these constants will be supplemented by the results of new and different determinations, particularly in connection with spectroscopic fine structure measurements36).

It will be clear from this outline that the numerous interrelations between the three fundamental constants e, e/m, and h make

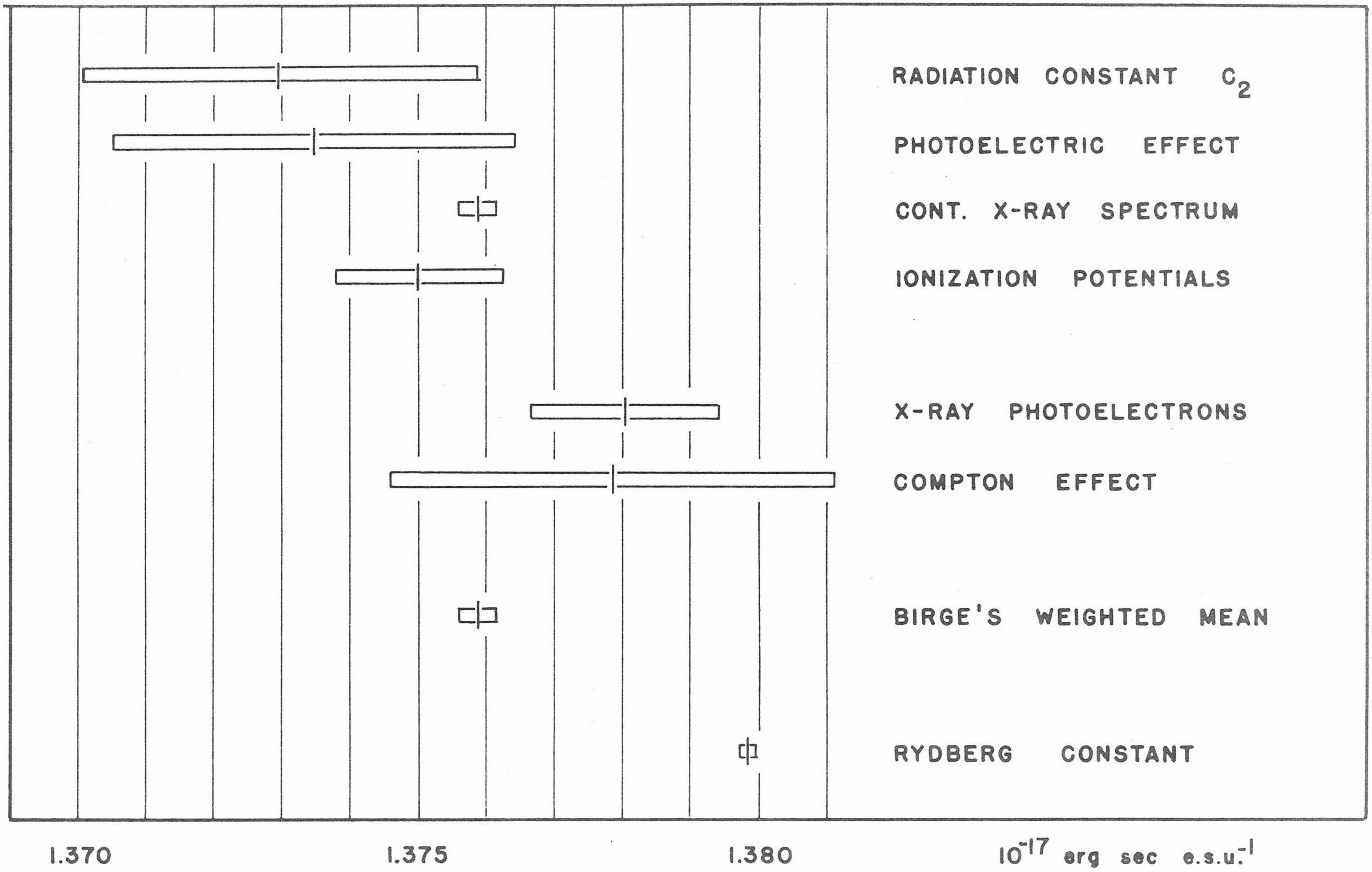
RADIATION CONSTANT C_2
PHOTOELECTRIC EFFECT
CONT. X-RAY SPECTRUM
IONIZATION POTENTIALS
X-RAY PHOTOELECTRONS
COMPTON EFFECT
BIRGE'S WEIGHTED MEAN
RYDBERG CONSTANT
1.370
1.375
1.380
10^{-17} erg sec e.s.u.$^{-1}$

FIG. I

it a difficult task to establish accurate comparisons between the results of all such determinations. The correlation of such results, and, more particularly, the examination of their mutual consistency has been extensively discussed in a series of papers by Bond[37-39], Ladenburg[40-43] and especially by Birge[6,8,24,44-49].

Recent investigations have resolved many of the difficulties which existed at the time when the present program of research on fundamental constants was started at this laboratory. The discrepancy between the results of spectroscopic e/m determinations and deflection measurements no longer exists, and, in his last report, Birge[24] gives $e/m = 1.75762 \cdot 10^7$ e.m.u. g^{-1} as the weighted mean of the five latest results (by four different methods), with a probable error smaller than 0.02%. Recent redeterminations of the viscosity of air indicate that the results of the direct determination of e by the oil-drop method are not inconsistent with the values determined from x-ray diffraction. Since the latter method is more precise, Birge[47] has now adopted Bearden's[23] weighted mean of all precise determinations of this type, $e = 4.8029 \cdot 10^{-10}$ e.s.u., with a probable error of 0.01%.

The outstanding discrepancy at this time seems to exist between the values of h/e determined from measurements of the continuous x-ray spectrum (method IV), and the value obtained from the Rydberg constant and the above values for e and e/m (method VI). The results are, respectively, $1.37\,587 \cdot 10^{-17}$ and $1.37\,985 \cdot 10^{-17}$ erg cm e.s.u.$^{-1}$. Moreover, the x-ray method, which far exceeds in accuracy all the other experimental methods, gives results in excellent agreement with the weighted mean of all other determinations (cf. Table I, p. 12). Thus Birge[24)] excludes the possibility of systematic and possibly theoretical errors in the h/e determinations, and suggests that the difficulty lies either with the method of calculating e from x-ray diffraction results, or with Bohr's formula for the Rydberg constant. It is not generally agreed, however, that the present state of the experimental evidence necessitates such drastic conclusions. In the past history of such measurements, the concept of probable error has not always given a reliable indication of experimental consistency, and the calculated errors mentioned above may be similarly misleading. This view gains further support from hitherto unpublished results on e/m by Dunnington. The ultimate decision of the problem will depend on further experimental material.

The present investigation was undertaken in order to re-examine the experimental foundations of the photoelectric method, to improve its technique, and to study its inherent limits of precision.

The Stopping Potential Method

The basis of all early photoelectric determinations of h/e was Einstein's equation (7), which may once more be stated in a variety of customary forms:

$$\frac{1}{2} m v^2_{max} = eV_{max} = e\left(V'_{max} + K\right) = h\nu - \varphi e = h\nu - h\nu_0 \cdot \quad (7)$$

$\frac{1}{2}mv^2_{max}$	is the maximum kinetic energy which a photoelectron ejected by a quantum of frequency ν can have.
eV_{max}	is similarly its maximum gain in potential energy under the action of an opposing electric field.
V'_{max}	is the largest externally applied opposing field which it can traverse.
K	is the contact potential difference between anode and cathode, considered positive when the cathode is positive with respect to the anode.
φ	is the classical work function of the cathode.
ν_0	is the lowest ("threshold") frequency at which a quantum will be able to release electrons.

This equation evidently implies that the initial kinetic energies of the electrons within the metal are zero or negligible. In view of the experimental inaccuracies of the early photoelectric investigations, it appeared reasonable, at that time, to neglect the small initial energies predicted by the Maxwell-Drude-Lorentz theory of metals.

Equation (7) immediately leads to the so-called "stopping potential method" of measuring h/e. We consider a photoelectric cell of any design, whose cathode is illuminated by a monochromatic beam of light, and determine experimentally the relation between current and applied voltage. The result will be a curve of the type shown in Fig. 2, p. 19. The principal features of this curve are the horizontal section for $V > 0$, and the sharp intercept with the axis. If the effective retarding field is zero or negative, all electrons ejected from the cathode will reach the anode, and the current will be saturated. On the other hand, if

$$V'_{max} = \frac{h}{e}(\nu - \nu_0) - K, \qquad (16)$$

even the fastest ejected electrons will no longer be able to reach the anode; accordingly the curve will intersect the axis at this point at a finite angle. The shape of the intermediate section of the curve is much more difficult to predict. It will primarily depend on the frequency, on the geometry of the cell, and on the energy and momentum distributions of the emitted electrons. The development of a theory predicting this shape could naturally not be attempted at a time when neither the photoelectric mechanism nor the metallic state were sufficiently understood.

For the purpose on hand, however, it is sufficient to find V'_{max} for a number of different frequencies. In accordance with the equation above, the different values of V'_{max}, when plotted against frequency, will fall upon a straight line, whose slope is h/e. This is shown in Fig. 3, p. 19, which is taken from Millikan's[10)] paper.

The accuracy with which the slope of this line can be determined will clearly depend on the range of frequencies used in the investigation. For this reason the alkali metals, which are sensitive to a large portion of the visible region as well as to ultraviolet light, were used by Millikan, in spite of the complications in experimental technique.

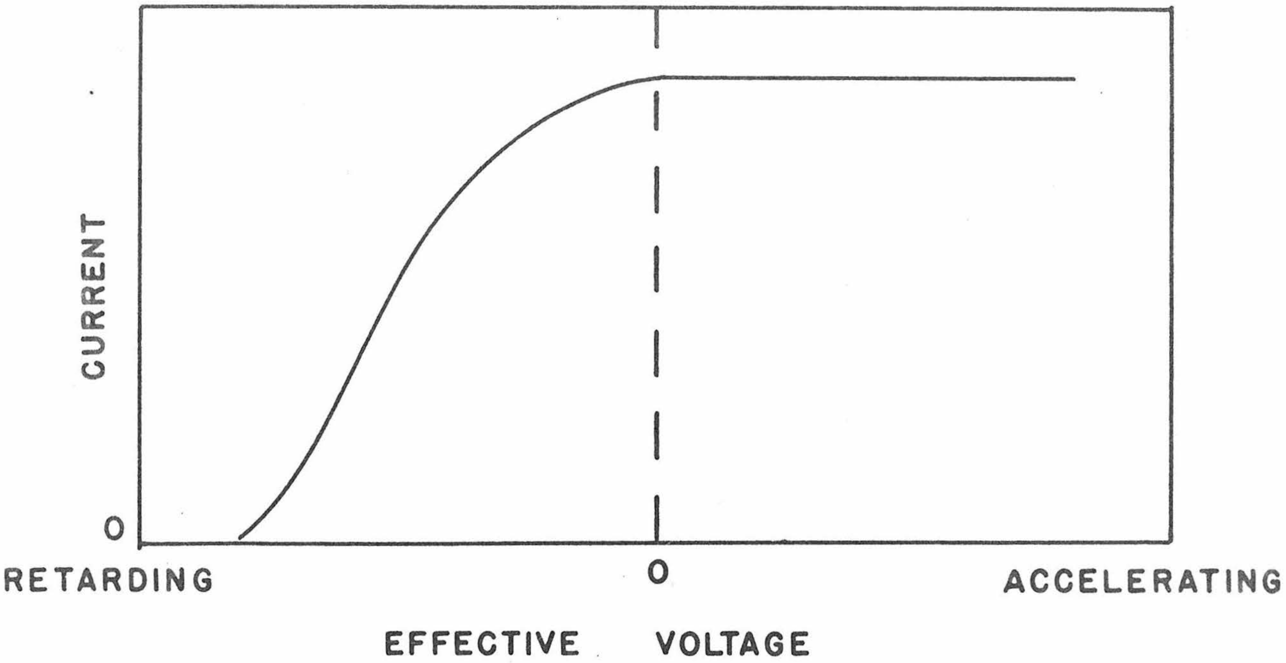
CURRENT
0
RETARDING
0
ACCELERATING
EFFECTIVE VOLTAGE

FIG. 2

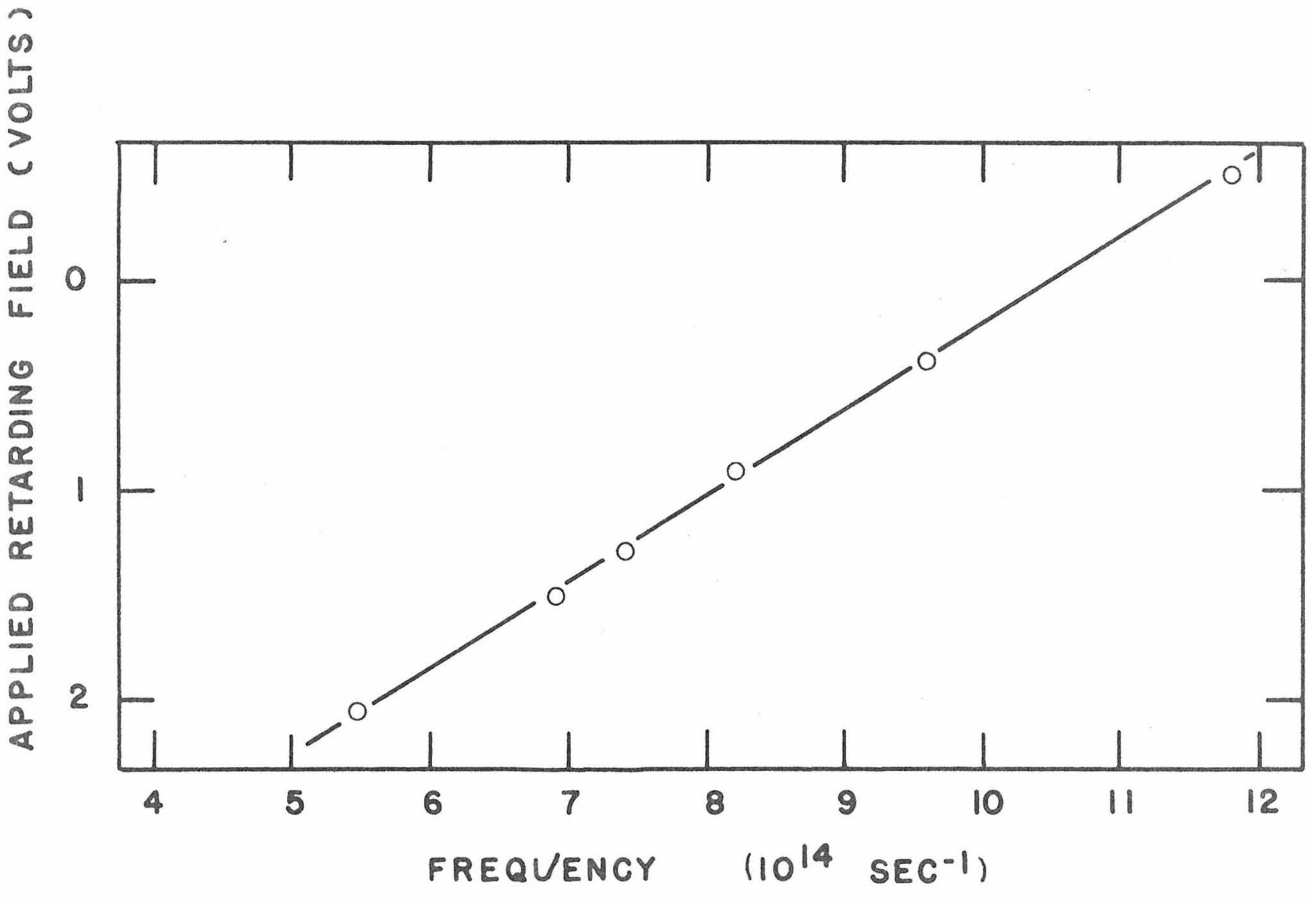
APPLIED RETARDING FIELD (VOLTS)
0
1
2
4
5
6
7
8
9
10
11
12
FREQUENCY (10^14 SEC^-1)

FIG. 3

The principal difficulty of this type of experiment consists, of course, in the precise determination of the intercept. Evidently the limitations of current measuring devices prevent the measurement of a curve of the type of Fig. 2, p. 19, as far down as the actual intersection with the axis. From the lowest measured point down to the axis, it becomes necessary to invoke some process of extrapolation. If one assumes the existence of a well-defined maximum energy, there is no reason to doubt the validity, within suitable limits of error, of the results so obtained.

In the course of the actual measurements, however, it was occasionally found that the curves, for a given frequency, had long asymptotic feet. This was first pointed out by Ramsauer50), and subsequently carefully studied by Millikan51). By excluding all stray light of frequency higher than ν , Millikan succeeded in proving conclusively that the "feet" which were observed in these early experiments were caused by stray light. Nevertheless, the complete elimination of stray light by means of filters involved so considerable a reduction of the intensity that the corresponding photocurrents were too small to be measured with precision. Hence, in the actual measurements10) no filters were used; the spurious effects of the asymptotic feet were partially circumvented by not determining the lowest points of the curve at all. This method of extrapolation seemed, to a certain extent, justified by the fact that, in the h/e diagram, (Fig. 3, p. 19), no point was separated from the straight line by more than 0.01 volt.

A similar method of extrapolation was subsequently used by Lukirsky and Prilezaev[11)], who found that the shape of the current-voltage curve near the axis could be expressed by a simple quadratic form. While the process of extrapolation was thus made less subjective, their experimental procedure, compared with that of Millikan, suffered from two other causes of inaccuracy. The use of a silver anode entailed the presence of fairly large reverse currents (up to several per cent of the current to be measured) at the highest frequencies, for which special corrections had to be introduced. The very disturbing influence of these reverse currents, which will be more fully discussed below, was altogether avoided in Millikan's experiment by the use of a copper oxide anode. Again, Lukirsky and Prilezaev worked with ordinary metals, and were thus restricted to relatively narrow frequency ranges.

Olpin[12)], in the course of a long investigation of the sensitization of photoelectric surfaces, made a number of stopping potential measurements on a sodium surface sensitized with sulphur vapor. With such cathodes, he was able to extend the frequency range through the entire visible region into the near infrared. Reverse currents were completely avoided by the use of an anode made of soot-coated nickel. There is no indication in his paper as to how the extrapolation to zero current was performed. The slope of the straight line in the h/e plot was determined graphically; Birge[45)] has since recalculated it by least squares methods, and arrives at a result which is higher by 0.3%.

On the basis of the three determinations mentioned in this section, Birge[8)] has further calculated a weighted mean (cf. p. 5):

$h/e = (1.37\ 348 \pm 0.00\ 295)\ 10^{-17}$ erg cm e.s.u.$^{-1}$.

The magnitude of the probable error indicates a satisfactory degree of mutual consistency between these experiments. That the possibility of systematic error as a result of the extrapolation process must nevertheless be recognized, will be clear from an inspection of the current voltage curves of Fig. 10, p. 69. The lower ends of these curves, whose accurate determination has been made possible by recent improvements in photoelectric technique and electrical measuring devices, show a very slow asymptotic approach to the axis, and emphasize the difficulty of extrapolating to a particular stopping potential. Moreover, serious misgivings against any attempts to assign definite values to such limiting potentials have arisen from our present theoretical interpretation of the photoelectric effect.

New Theories of the Photoelectric Effect

One of the basic requirements for any theory of photoelectric phenomena consists evidently in establishing a satisfactory model of the metal. Millikan[51)] had determined, as early as 1916, that the photoelectric process affects the electrons which are responsible for metallic conduction. The classical concept of conduction was based upon the electron gas of Drude and Lorentz; it suffered from the notorious difficulty that it predicted specific heats for this electron gas which were independent of temperature, and altogether too large.

This difficulty was completely removed in 1928 by Sommerfeld's theory of metallic conduction. In the preceding year, Pauli53) had succeeded in explaining the paramagnetism of the alkalis by applying the statistics of Fermi54) and Dirac55) to the electron gas. Sommerfeld56) extended the application of this principle to conduction phenomena, and to the closely related thermionic and thermoelectric effects.

The Sommerfeld theory agrees with the classical theory in assuming a constant potential inside the metal. The electron gas is thus composed of entirely free electrons; the potential variations in the neighborhood of the individual atoms of the crystal lattice are entirely neglected. A more refined theory which takes into account the periodic character of the potential in the metal has since been developed by Bloch57). For the treatment of the photoelectric effect, however, the free electron model of Sommerfeld has so far been found adequate. The reason for this lies primarily in the circumstance that for the valence electrons of the alkalis the effective potential in the metal is shown by the new theory to be very nearly constant. Moreover, it has been shown (cf. p. 29) that the electrons which are responsible for the photoelectric effect near the threshold absorb the energy of the photons in force field at the surface of the metal. The potential variations in the interior of the crystal can therefore probably be neglected. The following theoretical discussion will thus be based on the concept of free electrons.

According to Sommerfeld56), the distribution in energy of these free electrons inside the metal is given by the formula,

$$N(\epsilon)\,d\epsilon = \frac{8\pi\sqrt{2}\,m^{3/2}}{h^3}\,\frac{1}{e^{\frac{\epsilon-\mu}{kT}}+1}\,\epsilon^{\frac{1}{2}}\,d\epsilon\,, \qquad (17)$$

which gives the number, per unit volume, of electrons in the energy range from ϵ to $\epsilon + d\epsilon$. This equation is supplemented by the expressions for μ,

$$\mu = \mu_0\left[1 - \frac{\pi^2}{12}\left(\frac{kT}{\mu_0}\right)^2\right]\,; \qquad \mu_0 = \left(\frac{h^2}{2m}\right)\left(\frac{3n}{8\pi}\right)^{\frac{2}{3}}\,, \qquad ((18)$$

where n is the number of electrons per unit volume. The term involving T^2 can, in general, be neglected; in the subsequent work it is always assumed that $\mu = \mu_0$. The function N(ϵ) is shown for T = 0° and T = 1500° K. in Fig. 4, p. 25, which is taken from Richtmyer58).

It is evident from equation (17) that, at 0° K., a sharply defined maximum energy exists, for which $\epsilon = \mu_0$. As the temperature rises, the sharp angles in this distribution curve are gradually rounded off, and the high energy end of the curve descends asymptotically to the axis of abscissae.

The difference between this and the classical energy distribution becomes still more striking if one considers the actual values of μ_0. According to equation (18), these represent energies of the order of five to six volts, corresponding to mean energies of nearly four volts, whereas, in classical theory, the energies at ordinary

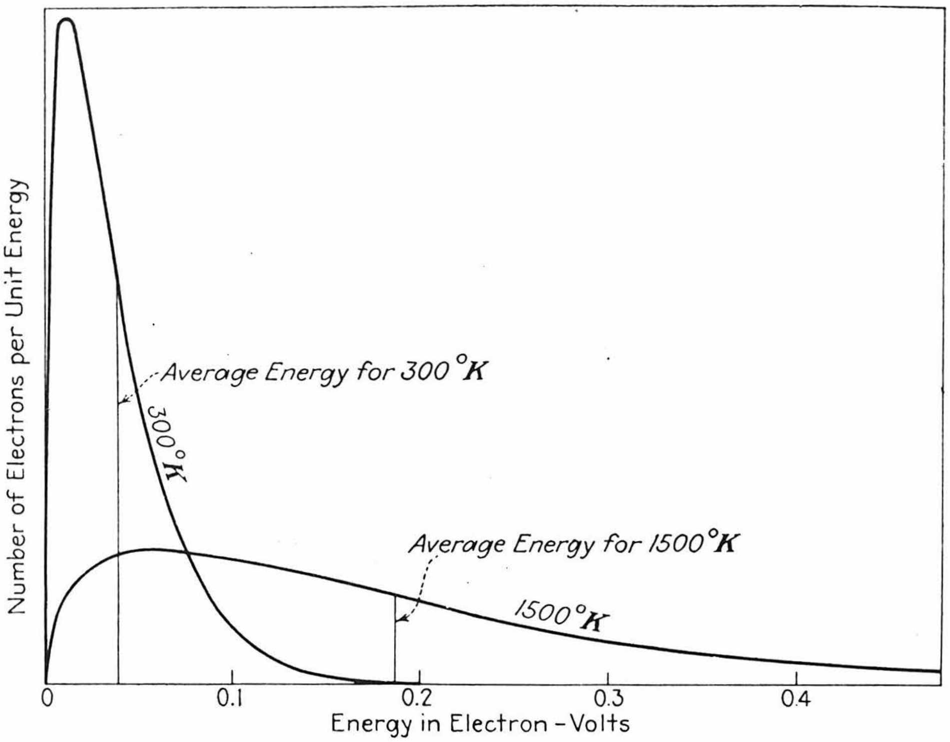

FIG. 42.—Distribution of energy among (conduction) electrons at temperatures of 300°K. and 1500°K., according to the Maxwell (*i.e.*, classical) distribution law.

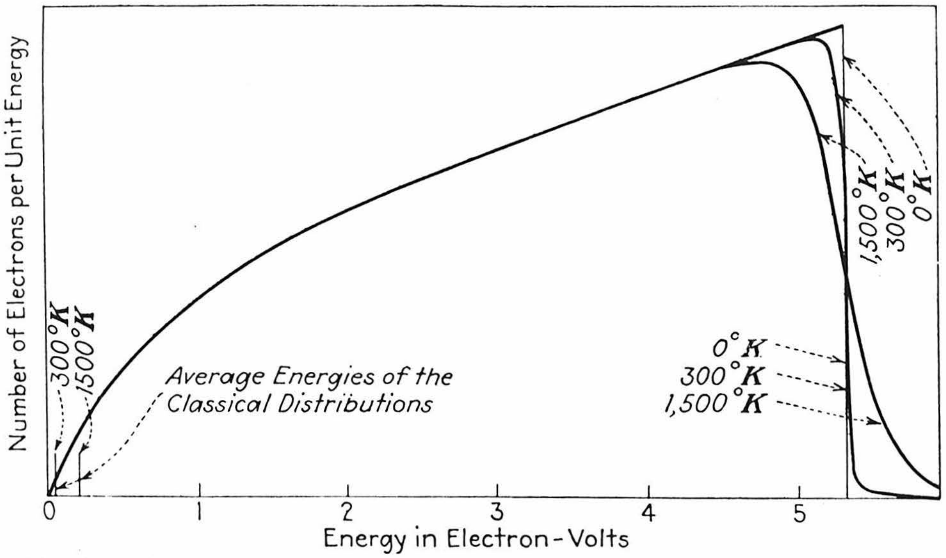

FIG. 43.—Distribution of energy among the (conduction) electrons of platinum at temperatures of absolute zero, 300°K., and 1500°K., according to the Fermi-Dirac statistics.

Fig. 4

temperatures were distributed around mean values of a few hundredths of a volt.

By a reconsideration of the thermionic effect, Sommerfeld was similarly forced to conclude that the surface potential barrier, W_a, of the metal was much larger than previously assumed. Richardson's work function φ appears in the new theory as the difference $\frac{1}{e}(W_a - \mu_0)$; thermionic data thus fail to provide a test of these new values. Experiments on electron diffraction by crystals, however, have yielded values of μ_0 in agreement with those calculated from (18) on the assumption that the number n of free electrons in the metal is equal to the number of atoms.

This new state of affairs necessitates a careful revision of the earlier statements concerning the photoelectric effect. Since the initial energies of the electrons are no longer negligible, the energy balance for an individual electron is now

$$\frac{1}{2} m v_n^2 = eV = \epsilon_n + h\nu - W_a \quad . \tag{19}$$

ϵ_n is used to designate the energy which is associated with the component of the momentum normal to the surface; for the sake of brevity, this quantity will be called the "normal energy". v_n is similarly the velocity normal to the surface. The assumption, that the entire energy $h\nu$ of the photon should be added to the normal energy of the electron, is discussed on page 31.

The distribution function of the normal energies ϵ_n, according to Sommerfeld's theory, is given by the expression,

$$n(\epsilon_n)\,d\epsilon_n = \frac{(2m)^{3/2}\,\pi kT}{h^3}\,\log\left(1+e^{-\frac{\epsilon_n-\mu}{kT}}\right)\epsilon_n^{-\frac{1}{2}}\,d\epsilon_n, \quad (20)$$

where n is referred to unit volume.

A definite maximum value of ϵ_n exists only at 0° K., where the Einstein equation may now be written

$$\frac{1}{2}\,m\,v_{n_{max}}^2 = e\,V_{max} = h\nu - \left[W_a - \mu_0\right] = h\nu - \varphi e. \quad (21)$$

At all higher temperatures, the Einstein relation fails. With sensitive current measuring devices, it is possible, moreover, to demonstrate the absence of definite maximum energies of emission. The current voltage curves of Fig. 10, p. 69, which were taken at room temperature, exhibit a slow asymptotic approach to the axis, rather than the sharp intercept demanded by classical theory. The fact that the earlier experimenters did not detect these "feet" must apparently be attributed to the lower sensitivity of their current measuring devices.

The implications of these new developments with respect to the determinations of h/e will be considered in the following section. In connection with the present theoretical survey, the question presents itself whether it is possible, on the basis of this new model, to predict the dependence of the photoelectric emission on various factors which can be experimentally controlled.

Of the large number of such experiments, which can be and have been performed, the only type which is of interest in h/e determinations consists in investigations of the energy distribution of emitted photoelectrons. Once this energy distribution is known, the current voltage relation can be derived from a knowledge of the field between the emitting electrode and the collector. Such a calculation is feasible only in the case of relatively simple fields, particularly those existing between parallel plates and concentric spheres. The former case, which is the one chosen for the present investigation, will involve the normal energies of the emitted electrons, while the latter is concerned with their total energies. A third, and more difficult type of experiment is the magnetic analysis of the photoelectrons ejected in some particular direction.

With the present quantum mechanical understanding of the interaction between the electrons in metals and incident quanta, the results of such experiments can be predicted in many cases. It must be emphasized, however, that such calculations are possible only under certain simplifying assumptions. In each case, of course, the validity of such assumptions can only be upheld as long as experimental results are not consistently at variance with the predictions made by the theory.

In the treatment of the interaction of the incident photon with the free electrons of the metal, a major obstacle is introduced by the well-known fact that energy and momentum cannot be simultaneously conserved in such an encounter. This difficulty was circumvented in the theory of Wentzel[59] by treating the incident radiation as a damped wave. Since the damping of the light wave can only be caused by bound electrons, this theory appears to lack internal consistency.

Tamm and Schubin[60] suggested the existence of two different types of photoelectric effect. The electrons forming the first of these are supposed to receive the energy of the photons in the force fields of the atoms in the crystal lattice; this phenomenon is designated as "volume effect". In the second type, called "surface effect", the encounter between photon and electron takes place in the force field of the surface. Tamm and Schubin have further attempted to show that the volume effect will be of negligible importance in the range of frequencies, near the threshold, which are usually involved in photoelectric experiments. While the general validity of this conclusion is perhaps not too well established[61,62], no adequate theoretical treatment of the volume effect is available at this time. The further discussion will therefore be restricted to the surface effect.

An earlier calculation of this surface effect is included in a paper by Fröhlich[63], which contains, however, no clear statement of the distinction made above. His results, as well as those of more refined calculations by Penny[64], apply to photoelectric currents from very thin films, in which emission takes place at two surfaces; they are therefore of no further interest here.

The results of Tamm and Schubin on the surface effect have been criticized for mathematical defects by Mitchell[62,65]), who has given a new and complete treatment of the surface effect, for a discontinuous potential barrier, and a temperature of 0° K. While this procedure is satisfactory, in general, the results cannot be applied in the immediate neighborhood of the threshold. In the first place, the temperature dependence becomes of major significance in just this region; secondly, the form of the surface potential barrier becomes essential because of the small velocities of escape which the electrons have near the threshold. Inasmuch as any modification of the stopping potential method will involve the region near the foot of the current voltage curve, these two factors will be of particular importance.

The first successful attempt to develop a theory taking these factors into account was made by Fowler[66]). Starting with a number of definite assumptions, Fowler was able to derive a rather simple and extremely useful expression for the dependence of the photoelectric emission upon frequency in the neighborhood of the threshold. Subsequently, DuBridge[67]) published a slightly modified form of this theory, and applied it to the problem of normal and total energy distributions. A brief outline of the procedure will serve to clarify much of the subsequent discussion.

The first assumption made in Fowler's derivation is that 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. Thus the normal energy of a photoelectrically emitted electron of initial energy

ϵ_n will be $\epsilon_n + h\nu - W_a$. In the idealized case of metals with plane surfaces, it is possible to support this assumption with a quantum mechanical derivation$^{68,69)}$.

Similar quantum mechanical considerations indicate that the transition probability, i.e, the probability that an electron will be put into a state of higher energy by a quantum, is dependent, in general, upon ν and ϵ_n. In the present application, the energy distribution is to be determined for constant ν ; the important factor, in this case, is the dependence on ϵ_n. The explicit assumption will now be made that the transition probability is proportional to the velocity normal to the surface, or,

$$P(\epsilon_n) = C\sqrt{\frac{2\epsilon_n}{m}} \tag{22}$$

This assumption has been shown to be valid in terms of a more exact quantum mechanical procedure by Mitchell$^{68)}$.

Concerning the transmission coefficient at the boundary, the assumption will be made that

$$\begin{aligned} D(\epsilon_n) &= 0, \quad \text{when } (\epsilon_n + h\nu) < W_a \\ D(\epsilon_n) &= 1, \quad \text{when } (\epsilon_n + h\nu) \geq W_a . \end{aligned} \tag{23}$$

The principal support for this statement must consist in the consideration that, after passage through the boundary, the electron emerges into a retarding field; under such conditions selective transmission and reflection should not take place.

With these assumptions, a more specific choice of the shape of the surface potential barrier is not necessary on the elementary theory. Mitchell established the result just mentioned for an image field; while this may not be an exact representation of the actual surface, it appears to be the best approximation which can be suggested at this time.

The total number of electrons, per incident quantum, which are able to cross a retarding field V, and reach the anode, can then be obtained by multiplying equation (20) by $P(\epsilon_n)$, and integrating from $(Ve - h\nu + W_a)$ to infinity:

$$N_1 = C\,\frac{4\pi m kT}{h^3}\int_{Ve-h\nu+W_a}^{\infty}\log\left(1+e^{-\frac{\epsilon_n-\mu}{kT}}\right)d\epsilon_n \tag{24}$$

Upon introducing the variable,

$$y = \frac{h\nu-(W_a-\mu)-Ve}{kT}, \tag{25}$$

the result of the integration may be stated in the form

$$N_1 = C\,\frac{4\pi m kT}{h^3}\,\varphi(y),$$

$$\varphi(y) = \begin{cases}\left(e^{y}-\dfrac{e^{2y}}{2^2}+\dfrac{e^{3y}}{3^2}-\dfrac{e^{4y}}{4^2}\pm\cdots\right), & Ve \geqslant h\nu-(W_a-\mu)\\[2ex] \left(\dfrac{y^2}{2}+\dfrac{\pi^2}{6}-\left[e^{-y}-\dfrac{e^{-2y}}{2^2}+\dfrac{e^{-3y}}{3^2}\mp\cdots\right]\right), & Ve \leqslant h\nu-(W_a-\mu).\end{cases} \tag{26}$$

The current per unit surface and unit intensity can then be obtained by simple substitutions:

$$\frac{I}{JA} = \alpha T^2 \varphi(y) , \tag{27}$$

where the constant α will, in general, depend on ν .

In an experiment of the type here considered, the dependence of current upon voltage will be determined for a number of frequencies. For each frequency, it is possible to ensure constant values of the intensity, of the illuminated area, and of the temperature of the cathode. Under those conditions the expression for the current may simply be written,

$$I = C_\nu \varphi(y) . \tag{28}$$

The particular advantage of this form consists in the fact that $\varphi(y)$ is a universal function of the argument y. If, therefore, the logarithms of the photoelectric currents are plotted, identical curves for all frequencies should result except for horizontal and vertical displacements. This circumstance suggests a simple procedure by which the results of energy distribution experiments can be applied to the determination of h/e. The details of this method will be presented in the next section.

It has already been indicated that the derivation above has since been supplemented by a more rigorous quantum mechanical treatment, which furnishes a theoretical basis for some of the assumptions introduced ad hoc in the elementary derivation. Assuming a free electron model with image field boundaries, Mitchell68) has been able to derive the expression,

$$J_x \propto \left(\frac{kT}{h}\right)^2 \int_0^\infty dy \log\left[1 + \exp\left\{-y + \frac{h(\nu-\nu_g)}{kT}\right\}\right], \qquad (29)$$

which, by simple transformations, can be shown to be identical with equation (24).

A cursory inspection of the expressions (27) and (25) seems to suggest that the voltage dependence of the photoelectric currents will be functionally related to the work function ($W_a - \mu$) of the cathode. While this is undoubtedly the case in experiments in which the total emission is measured as a function of frequency, it does not seem to be generally realized that there is no theoretical basis for such a conclusion in connection with retarding field experiments. In fact, a closer investigation of the argument (25) shows that y is not a function of ($W_a - \mu$). A retarding field V, existing between two electrodes, arises, in general, from two contributions. In addition to an externally applied potential difference V_p, it is necessary to consider the contact potential difference V_c between the metals of anode and cathode. All potentials will, as before, be considered positive when retarding. With this convention, the contact potential difference can be re-expressed as:

$$V_c = \frac{1}{e}\left[\left(W_a^{(2)} - \mu^{(2)}\right) - \left(W_a^{(1)} - \mu^{(1)}\right)\right] \qquad (30)$$

where the superscripts (1) and (2) refer to the cathode and anode, respectively (cf. Fig. 13A, p. 81). The quantities W_a and μ used heretofore refer to the emitting metal; they are therefore identical with $W_a^{(1)}$ and $\mu^{(1)}$. Since $V = V_p + V_c$, the argument y now may be rewritten in the form

$$y = \frac{h\nu - (W_a^{(2)} - \mu^{(2)}) - V_p e}{kT} . \qquad (31)$$

This substitution, which was first pointed out to the author by Professor Houston, is of considerable importance in the analysis of some of the results of this investigation. It has frequently been observed that current voltage curves, taken at different times with the same frequency, are displaced with respect to each other along the voltage axis. At 0° K., such displacements could be more concisely described as changes in stopping potential. According to the previous development, such shifts can be attributed to changes in the work function of the anode. The underlying physical principle, as will be clear from the schematic representation in Fig. 13A, p. 81, consists in the fact that the effect of any change in the work function of the cathode is nullified by a corresponding change in the contact potential difference.

Because of the numerous difficulties involved in the technique of determining photoelectron energy distributions, there exists only a very limited amount of experimental material which is sufficiently precise for comparison with the theory which has been presented. The only available work on normal energy distributions is that of DuBridge and Hergenrother70) on molybdenum, in which good general agreement with the theory is obtained for a range of temperature from 300° to 965° K., and for frequencies between 2400 and 2700 A.

If the retarding field between the emitting electrode and the collecting electrode is a radial field, instead of a homogeneous one, total energy distribution curves can be obtained in a manner quite analogous to the previously discussed normal energy distributions. The theoretical analysis for this case has first been given by DuBridge67); the method, however, is not as direct as in the case of normal energies, and involves additional approximations and assumptions. Roehr71) has confirmed this theory by experiments with molybdenum at temperatures between 300° and 1000° K. and for three frequencies between 2400 and 2700 A. Brady72,73) has investigated the total energy distribution of photoelectrons from potassium films of varying thickness; in all cases, the curves showed good agreement with the theory. A similar investigation on sodium by Brady and Jacobsmeyer74) yielded results exhibiting definite differences from the theoretical predictions. Broadwell75) likewise investigated the total energy distribution of photoelectrons from sodium; again the agreement with the theory was very poor. The same observation was reported, on the basis of preliminary experiments, by DuBridge and Hill76,77), who have been able, however, to improve the agreement with the theory by the use of extremely pure surfaces.

An investigation, by the method of magnetic analysis, of the energy distribution of photoelectrons from calcium has been reported very recently by Liben78). The results for pure surfaces agree with the theoretically predicted distribution, while pronounced differences are exhibited by oxydized surfaces.

The experiments which have just been mentioned should be clearly distinguished from measurements of the "spectral distribution curve", in which the total photoelectric emission is measured as a function of frequency, usually with the object of securing values of the work function of a particular material. In connection with the large amount of published material in this field, the frequent use of the terms "distribution function", "Fowler curve", etc., has led to some confusion. Fowler's theory[66)] was originally developed for such spectral distribution measurements, and the mathematical treatment in the two cases is very similar. Nevertheless, there is an essential difference in physical content between spectral distributions and energy distributions. At any given frequency, the former simply gives the total number of photoelectrons emitted per incident quantum, whereas the latter establishes the energy distribution of these electrons. Corresponding to the greater amount of information furnished by the energy distribution curve, the experimental requirements for its determination are more exacting.

The Modification of the Photoelectric Method

The theoretical development which has been outlined in the preceding section has involved a complete change in the foundations of the photoelectric method for the determination of h/e. The realization that, at ordinary temperatures, sharply defined maximum velocities of emission do not exist has emphasized the uncertainty of the extrapolation process in the stopping potential method, and eliminated its theoretical justification. At the same time, however, it has provided the basis for a different, and inherently more precise method of establishing the value of h/e from photoelectric measurements.

This method requires the measurement, at a number of different frequencies, of the normal or total energy distribution of the photoelectrons. For reasons indicated on p. 36, the normal energy distribution was chosen for this investigation. The construction of the photocell used in these measurements had to provide, therefore, for the application of a homogeneous retarding field between anode and cathode. For each frequency, the actual measurements then consisted in determining the photoelectric currents for various retarding potentials in the region near the foot of the current voltage curve. The result was a series of curves of I vs. V_p, for a number of different frequencies. If now the illumination was constant during the time required to measure each one of these curves, and if, moreover, the anode work function, the temperature, and the metallic constitution of the cathode were constant during the time required to measure the entire set, then all conditions had been fulfilled for the comparison of such results with the theoretical predictions of equations (28) and (31).

Following in principle a method first indicated by Fowler$^{66)}$, such comparisons can be conveniently effected by graphical analysis.

Taking logarithms on both sides of equation (28), one obtains,

$$\log I = K_\nu + \log \varphi(y) , \tag{32}$$

or

$$\log I = K_\nu + \Phi(y) , \tag{33}$$

with

$$y = \frac{h\nu - (W_a^{(2)} - \mu^{(2)}) - V_p e}{kT} \tag{31}$$

In accordance with this equation, a "theoretical" or "Fowler" curve may be constructed, in which Φ (y) is shown as a function of y. Tables79) have been published which give the values of Φ (y) over a large range of y.

From the experimentally established values, it is possible, on the other hand, to plot a curve of log I against $-\frac{V_p e}{kT}$. An arbitrary value of e/k will be assumed temporarily.

Now, if the experimental data are in agreement with the theoretical predictions, it is evident that these curves will be identical, except for horizontal and vertical displacements; from the schematic drawing (Fig. 5, p. 40), it will further be clear that the horizontal displacement is

$$\Delta = -\frac{V_p e}{kT} - y = \frac{(W_a^{(2)} - \mu^{(2)}) - h\nu}{kT} . \tag{34}$$

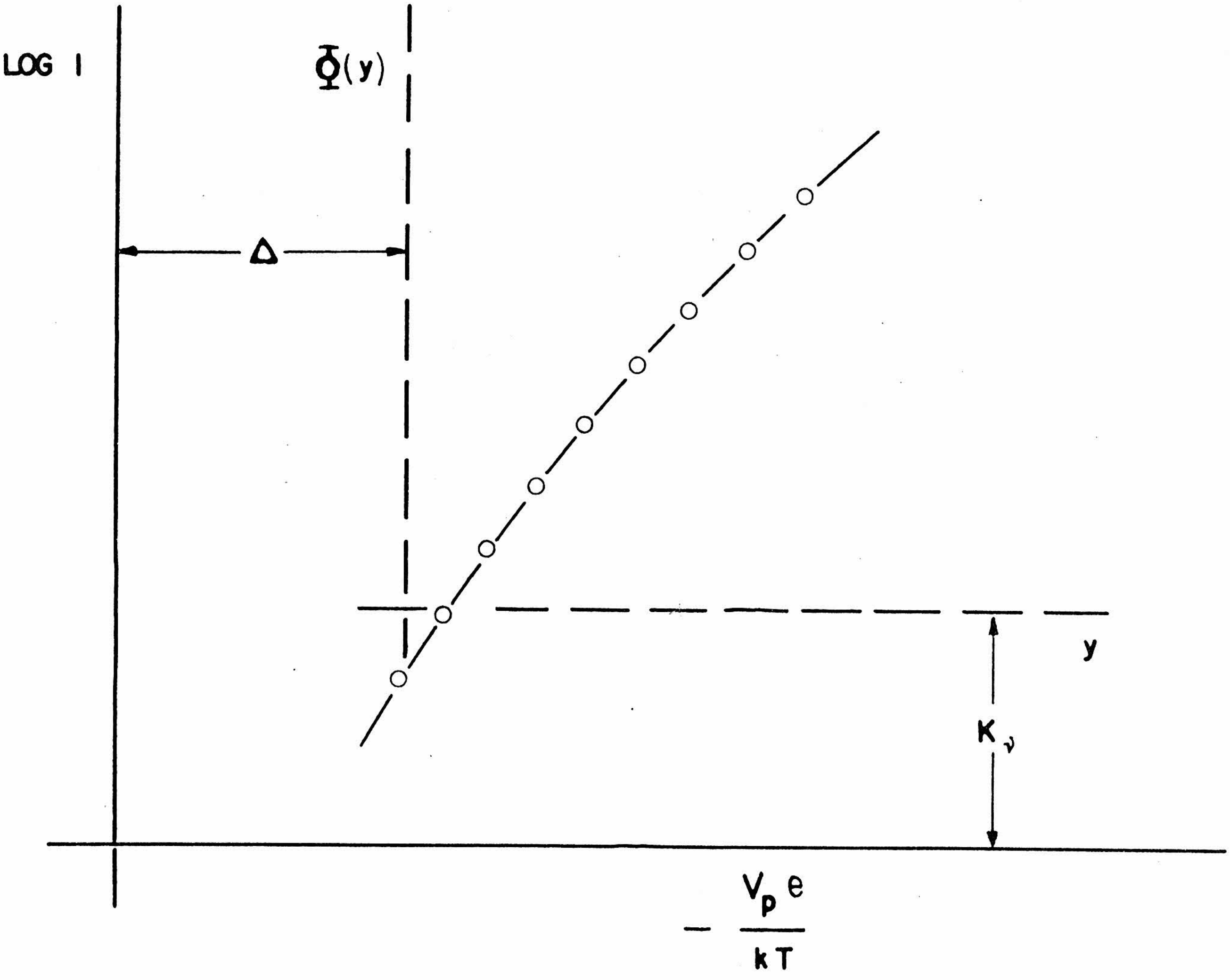

FIG. 5

By superimposing the experimentally obtained points upon the theoretical curve, it is thus possible to determine a horizontal displacement for each of the n frequencies at which the current voltage curve has been measured. For convenience in plotting, it is customary to use the logarithm of the relative current, log I/I_0 in the experimental curves. I_0 is usually chosen to be the largest current measured at each frequency, so that the logarithms will all be zero or negative. It is evident that this introduces no change, since the term log I_0 may be absorbed in the constant factor K .

In general, then, n values of Δ can be determined:

$$\Delta_i \equiv -\frac{V_i^* e}{kT} = \frac{\left(W_a^{(2)} - \mu^{(2)}\right) - h\nu_i}{kT} \quad . \tag{35}$$

Division by the previously assumed value of $\frac{e}{kT}$ yields n equations of the type,

$$V_i^* = \frac{h}{e}\nu_i - \frac{W_a^{(2)} - \mu^{(2)}}{e} \quad . \tag{36}$$

The values V_i^* thus appear in a role analogous to that of the stopping potentials in the older method. If they are plotted against the corresponding frequencies, they should similarly lie on a straight line. The solution for its slope h/e can then be performed graphically, or preferably by least squares procedure.

From the point of view of the theory which has been outlined, the present investigation was to have a two-fold object. Accurate measurements of the current voltage curves of photoelectrons ejected from a sodium surface into a homogeneous retarding field by monochromatic light were to be taken, and compared with the theoretically predicted normal energy distribution law. If the results were found to be in agreement with the theory, the same measurements were to be used for a new photoelectric determination of h/e.

The Experimental Arrangement

The principal features of the experimental equipment required for the present investigation were implicitly determined by the theoretical aspects of the problem. The photoelectric cell had to be so constructed that its two electrodes formed a parallel plate condenser. The cathode had to be illuminated by monochromatic light of constant intensity. A number of known frequencies of such light had to be available. For each frequency, different retarding electric fields had to be applied between anode and cathode. These potentials had to be accurately measured. Finally, a sensitive and accurate current measuring device had to be provided for the determination of the resulting photoelectric currents.

The photoelectric tube.

The choice of the photoelectric substance was governed by two essential requirements. A high yield, in terms of electrons per quantum, was necessary in order to obtain, in the temperature-dependent high energy range, a quantity of electrons sufficient for the precise determination of the energy distribution. In the second place, a high limiting threshold, well up in the visible range, was desirable because it would permit the use of a large range of incident frequencies. Both properties are found in the alkali metals, which have the additional advantage of representing a close approximation to the free electron metal of Sommerfeld. Sodium was selected from this group because it is least difficult to handle, and because its relatively low vapor pressure retards the gradual diffusion throughout the photoelectric cell.

On the other hand, the major difficulties of the experiment were directly connected with the use of sodium. Very high vacua are necessary to ensure stable photoelectric surfaces with this material. Its vapor pressure, even at room temperature, is still high enough to cause the gradual formation of a thin film on all parts of the tube. When such films attain a thickness of a few molecules72), they not only become conductive, but they also lower the photoelectric work function of any material on which they are deposited73,74,80-82). Two important difficulties are consequently encountered in the construction of a satisfactory experimental tube. In the first place, the formation of a molecular film of sodium on the glass wall between anode and cathode must be circumvented, because the resulting leakage currents would vitiate the determination of the true photoelectric currents. Secondly, a high anode work function must be maintained, in spite of the gradual accretion of sodium on the surface. This work function must be large enough to prevent, for all frequencies used in the experiment, the emission of photoelectrons by diffusely reflected light; for, any electrons thus liberated from the anode would be accelerated toward the cathode in the existing electric field. In spite of the much weaker illumination producing them, these "reverse currents" would thus be of the order of magnitude of the currents to be measured. Finally, the preparation of a supply of pure sodium, and the application of this material to the cathode, gave rise to a number of difficulties in technique, which had to be overcome in connection with the design of the experimental tube.

In the course of the investigation, several tubes were constructed, each representing a different effort to avoid the difficulties which have been outlined. In the first of these, an attempt was made to reduce the vapor pressure of the sodium by maintaining the cathode at liquid air temperature. The tube had a long indentation with a flat surface on one side. Silver was evaporated onto this surface to form a conducting support for the sodium, which was subsequently applied by evaporation from a side tube. The entire cavity was filled with liquid air. A movable anode was placed opposite the cathode whenever measurements were to be taken. The essential reason for the failure of this scheme appears to have been the accumulation of residual gases on this cooled surface. It was found impossible to obtain stable photoelectric surfaces. Reverse currents were often encountered in spite of the liquid air cooling; this may, however, have been connected with the then rather imperfect method of applying the sodium.

In the two following tubes, a solution was attempted by making the anode of a material which would retain a high work function in the presence of sodium vapor. In view of Millikan's10) success with copper oxide, an anode was made of this material. The cathode, which originally consisted of molybdenum, could be moved to a different section of the tube for application of the sodium. This tube was later modified by using tungsten as the cathode material, and by providing more elaborate precautions for the satisfactory insulation of the anode. While it was possible, in these tubes, to avoid reverse currents by using very thin sodium films of the cathode, these films were found to be photoelectrically very unstable. The inherent difficulty lay in the impossibility of ensuring adequate vacua in these copper oxide anode cells. Whenever the tube was baked at a sufficiently high temperature to dislodge the residual gas from the glass walls, the anode was simultaneously reduced to pure copper. After a number of unsuccessful attempts to find a compromise solution between two apparently contradictory requirements, this design was rejected.

At this stage, Professor Houston suggested to the author the possibility of effecting the differentiation between electrons of different energies by the simultaneous application of longitudinal magnetic and radial accelerating electric fields between two concentric cylindrical electrodes. In such a device, which is somewhat analogous to a magnetron oscillator, both electrodes may consist of sodium, since the fields may always be adjusted so as to make it impossible for electrons to pass from anode to cathode, even if only the fastest electrons from the cathode are permitted to reach the anode. The theory which has been given for the case of the homogeneous electric field must naturally be modified for this more complicated case. The same assumptions which Fowler made were therefore used to derive the photoelectric current as a function of the electric and magnetic fields. It developed, however, that, even at 0° K., the resulting expressions were not integrable, and the approximate expansions much too complicated to be of experimental utility.

It was therefore decided to return to the simple electric field, and to attempt to inhibit the evaporation of sodium by carefully controlled deposition of a moderately thin film on the cathode. At the same time, provisions were to be made, by which the anode could be heated, and accumulated sodium atoms removed, without opening the apparatus, or interrupting any of its normal functions. The choice of anode materials was to be made from the Ni-Pd-Pt group of elements, which exhibit the highest work functions found among the metals[83-86]. According to Glasoe86), the work function of pure nickel is 5.01 volts, corresponding to a threshold of 2463 A. Since the pure metal would accordingly permit the use of the Hg line at 2536 A, it was considered satisfactory for this purpose. In the design of the anode support, particular attention was given to the problem of ensuring adequate insulation in spite of the presence of small amounts of sodium vapor.

The construction of the entire tube was compatible with the requirements of high vacuum technique.

The general features of the tube will be clear from Fig. 6, p. 48; its individual parts are represented in detail in Fig. 7, p. 49. The central chamber contained the electrodes in their normal position. A quartz window, attached by means of a graded seal, provided for the illumination of the cathode at a large angle of incidence. The specularly reflected portion of the light was absorbed in a light trap. The pump connection was attached to the bottom of the central chamber.

Two $2\frac{1}{2}$ inch lateral tubes, whose axes enclosed an angle of 135°, were attached to the sides of this chamber. The electrodes were supported by glass tubes sliding in somewhat larger tubes, which, in turn, were rigidly attached to the outer walls. At their opposite ends, these movable supporting tubes carried magnetic armatures; these consisted of iron wires fused in glass to prevent gas contamination. By means of these armatures, the electrodes could be withdrawn from the central chamber into the side tubes, and rotated around the axes of the latter. Each electrode had a total excursion of $4\frac{1}{2}$ inches.

In the retracted position, the anode, which was mounted normal to the axis of its side tube, was located in the field of a high frequency furnace, by which the electrode could be brought to incandescence, and thus deprived completely of adsorbed sodium. Particular attention is called to the very careful insulation of the anode, Fig. 7 A, p. 49. The anode was not supported on the main stem, which slid

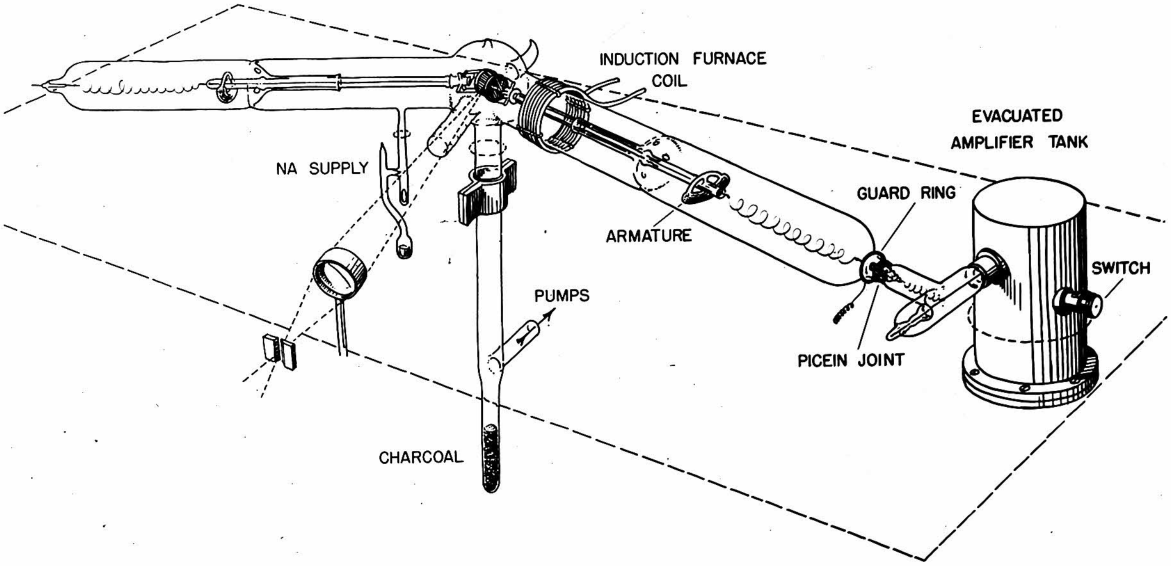
INDUCTION FURNACE
COIL
EVACUATED
AMPLIFIER TANK
NA SUPPLY
GUARD RING
ARMATURE
SWITCH
PUMPS
PICEIN JOINT
CHARCOAL

Fig. 6

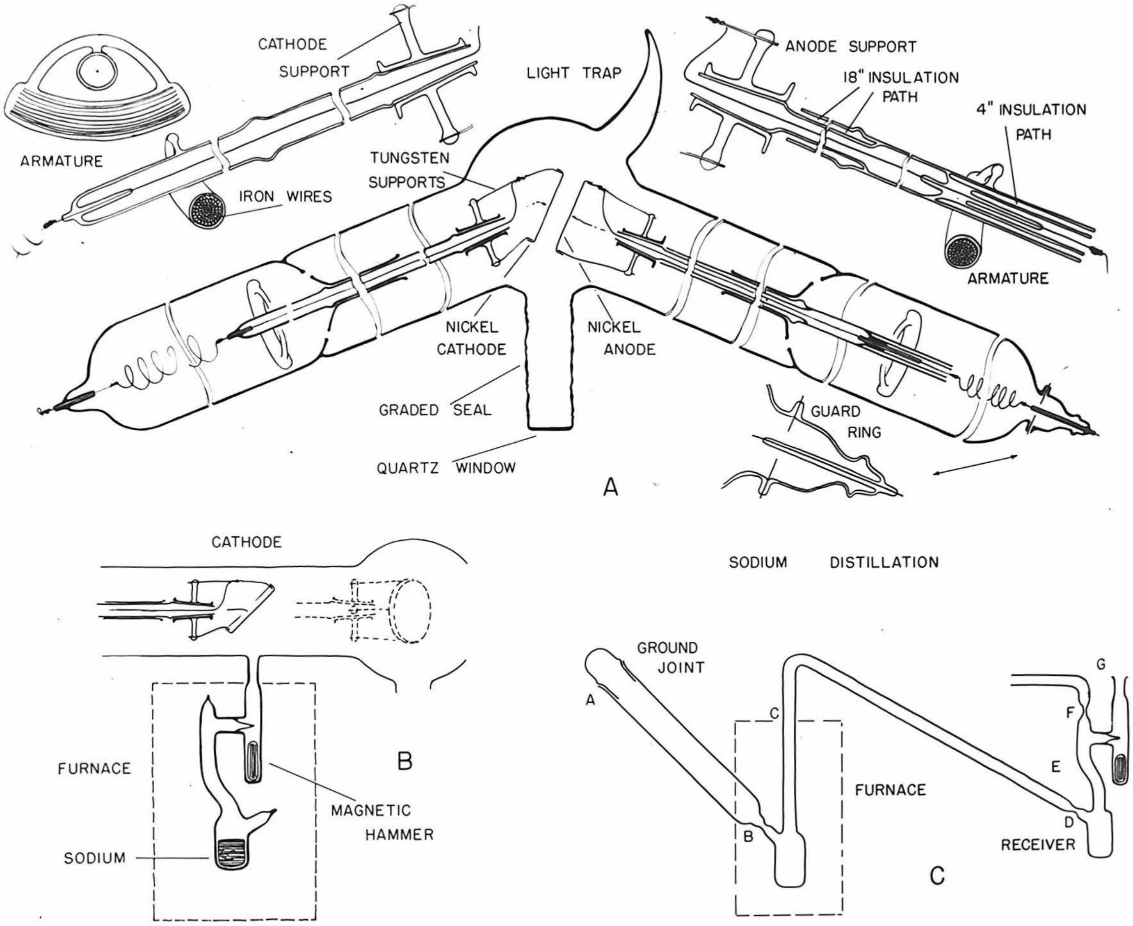
CATHODE
SUPPORT
ARMATURE
IRON WIRES
TUNGSTEN
SUPPORTS
LIGHT TRAP
ANODE SUPPORT
18" INSULATION
PATH
4" INSULATION
PATH
ARMATURE
NICKEL
CATHODE
NICKEL
ANODE
GRADED SEAL
QUARTZ WINDOW
GUARD
RING
A
CATHODE
FURNACE
B
MAGNETIC
HAMMER
SODIUM
SODIUM DISTILLATION
GROUND
JOINT
A
C
B
FURNACE
G
F
E
D
RECEIVER
C

Fig. 7

in the fixed bearing, but on an inner tube, which was sealed to the main stem nine inches back from the open end. In this fashion, a carefully baffled pyrex insulation path, over 18 inches long, was provided. A similar shorter apron was constructed over the far end of the stem, where the danger of sodium contamination was not so great. The arrangement has been found entirely adequate to suppress internal leakage currents; with four volts between the electrodes, such "dark currents" were less than the limit of sensitivity ($< 10^{-15}$ amps.) of the current measuring equipment.

The cathode was mounted in such a way that its normal made an angle of 45° with the axis of its side tube. In the retracted position, it could thus be rotated 90° around the latter axis, so that its surface was exposed to the opening of the sodium vapor inlet, as shown in Fig. 7 B, p. 49. The angular disposition of the side tube served the additional purpose of preventing the heated anode from "looking" directly at the retracted cathode, thus avoiding the further evaporating of sodium by radiated heat.

The electrodes themselves were circular nickel discs, 1.75 inches in diameter, each with a cylindrical crimped edge 1/8 inch wide. They were made from 0.008 inch nickel sheet by means of a special steel die. Four tungsten wires were spotwelded to the inside of the crimped edge of these electrodes; the far ends of these wires were fused to a pyrex supporting body, which was fitted to the end of the sliding rod by means of a ground joint. This arrangement facilitated the assembly and dissection of the tube.

The design of the electrodes has, after protracted use, exhibited a defect in connection with the heating of the anode. In the course of many hours' heating to a temperature sufficient to evaporate the nickel from the hottest parts of the anode, the flat surface has gradually bulged outward so as to show, in the end, a pronounced convexity toward the cathode. A centrally supported disc electrode has since been tried, but, after thorough heat treatment, the warping was even more pronounced in this case. Further work on this problem is in progress.

Electrical connections to the electrodes were made through helical tungsten springs of sufficient tension to prevent contact with the outer walls of the side tubes. All connections inside the tube were welded. On the anode side, to which the current measuring equipment was connected, the final seal was protected from external leakage currents by a fused-in Housekeeper disc seal.

The separation of the electrodes, in the working position, was between 3/8 and 1/2 inch. The adjustment of the two electrodes to a parallel position was facilitated by the angle between the cathode and its axis of rotation. The development of frictional electric charges by the sliding glass parts made it impossible to use the current amplifier immediately after moving the electrodes; if necessary, this could be circumvented by using grounded metal wire runners87).

The apparatus was evacuated by a double mercury diffusion pump, backed by a Cenco Hyvac oil pump. Two liquid air traps in series were inserted between pumps and tube, and a charcoal side tube was arranged directly below the central chamber of the tube.

During evacuation, the entire tube was surrounded by an electric furnace, and kept at a temperature of about 450° C. for one week. The furnace was then temporarily removed, and each electrode heated for thirty minutes to at least 900° C. by induced high-frequency currents. The tube furnace was then re-installed, and the tube baked for another week. After this second heating, the charcoal tube was kept immersed in liquid air. While this outgassing treatment would not be adequate for determinations of the characteristic photoelectric properties of pure metals, it has proven sufficient to ensure stable sodium surfaces, which could be used for periods of over fifty days. It should be recalled, in this connection, that the location of the current voltage curves with respect to the voltage axis has been shown to be independent of the work function of the cathode. (cf. p. 35 .) If, therefore, the work function of the cathode was not that of absolutely pure sodium, the results should not have been affected, provided only that the work function was constant during the measurements. The possible effect of complicated compound thresholds will be discussed later.

The Preparation of the Sodium.

The sodium used as the photoelectrically active material in this investigation was prepared from the commercial product in a separate pyrex distillation apparatus (Fig. 7 C, p. 49). After removal of the oxide crust, cleaning in benzene, and drying with filter paper, small lumps of sodium were introduced into the apparatus through the ground joint A. Evacuation with a double mercury diffusion pump was immediately started, and the joint at A was sealed with picein wax. After about two hours' pumping, the entire apparatus was flamed off; next, the sodium was melted and driven through the narrow constriction B. In this process, most of the coarser impurities were removed. The inlet tube was then removed at B. An electric furnace was placed around the sodium bulb, and the metal heated at 400° C, for about six hours. The vapor condensed in the section between the top of the furnace (C) and the bend of the tube. The location of the point C could be adjusted in such a way that no vapor travelled beyond the bend. At the end of six hours, most of the gas contained in the metal appeared to be removed, and, after repeated flaming of the receiver, the transfer into the latter was slowly effected during the next four hours. This was accomplished by electrical heating of the section CD, which had previously been covered with asbestos, and wound with chromel wire. The rate of transfer of the vapor could be regulated by a resistance in series with the chromel windings; it was usually kept at about 1 cc per hour. When a sufficient supply had accumulated, the still was sealed off at D, and removed from the pumps at F. The sodium supply was then in an evacuated container, ready for attachment to the photoelectric tube.

The method devised by Burt[88)] of cleaning sodium by electrolysis through soda glass was also attempted. Although it was found possible to speed up the rate of deposition of the sodium to over 0.5 grams per hour, the method was abandoned because of the difficulties connected with the transfer of the sodium from the lamp bulbs into the pyrex apparatus.

A number of preliminary experiments were then performed with a dummy tube, in order to determine a properly controlled precedure for evaporating the sodium onto the cathode. Upon surrounding the supply bulb with an electric furnace, it was found that a fairly well-defined conical beam could be obtained, without the use of a liquid air cooled "atomic gun", by simply exposing the top section of the inlet tube to air at room temperature. Thus, after attachment of the supply bulb to the main tube, the destruction of the breakable tip with a glass-covered magnetic hammer, the spread of the beam could be adjusted by shifting the furnace up and down, while the rate of deposition was controlled by the furnace temperature. A visible deposit of matte white appearance was formed upon the cathode. During the evaporation, the cathode was moved back and forth to enable the beam to cover all parts of its surface.

The Source of Illumination.

The primary sources of illumination, used throughout this investigation, were quartz mercury arcs. The first of these was a 220 volt d.c. horizontal Uviarc, operated at about 80 volts by a special voltage-regulated 230 volt generator through suitable series resistance and inductance. The other was a Schott 110 volt d.c. capillary arc of the type described by Johnsrud[89]. While the latter seemed to be more stable, the available intensity was so much greater with the former arc that it was used for all the more important measurements.

Radiation from the mercury arc was passed, in succession, through two Hilger quartz monochromators of 30 mm aperture. A single slit was used between the instruments. Two sets of values were adopted for the openings of the different slits:

	A	B
Source slit	0.019 in.	0.025 in.
Intermediate slit	0.004 "	0.014 "
Exit slit	0.010 "	0.020 "

By means of a two inch quartz lens, an image of the exit slit was formed on the cathode. An electrically operated shutter intercepted the beam between monochromator and focussing lens.

The effective absence of stray light, for both sets of openings, is indicated principally by the results of the energy distribution determinations, which will be discussed later on. In addition, several individual tests were made to establish the absence of scattered light of higher frequencies. After the system had been adjusted for transmission of a single spectral line, the wave-length drum of the second monochromator was rotated toward shorter wave-lengths, until the original beam was just cut off by one of the slit edges. The retarding field was then adjusted to values corresponding to those used near the lower end of the current voltage curve in the actual measurements taken at that particular frequency. With the current amplifier at maximum sensitivity, it was in no case possible to detect any photoelectric current.

The other important requirement placed upon the source of illumination consisted in the necessity for a constant value of the illumination of the cathode. It will be clear from the theoretical development that this constancy was only required over the length of time necessary for the determinations at one particular frequency. This time varied from one to two hours. The one conclusive test for constant conditions, which was consistently applied in all measurements, consisted in the use of the resulting curve itself: The individual points on the curve were not taken in simple succession from one end of the measured range of currents to the other, but, beginning at the low current end, alternate points were determined, until the high current end was reached, whereupon the intermediate points were determined in the reverse order. If the points thus obtained were found to lie consistently on smooth curves, it could safely be assumed that the required constancy of illumination prevailed throughout the run. If, on the other hand, there was evidence of a "staggering" of the points toward the low current end of the curve, it had to be concluded that one or several conditions did not remain constant during the measurement. It was not possible, in such cases, to ascribe the difficulty unambiguously to the arc, since a changing anode work function, for example, might have produced the same result.

For this reason alone, a direct and independent check on the illumination would be valuable. Moreover, the proportionality between photoelectric current and illumination would permit corrections to the observed currents to be applied, if the changes of illumination could be followed quantitatively. Several attempts were made to achieve such illumination measurements by relatively simple means, but it became evident that the only adequate method consisted in intercepting the beam by a quartz plate immediately in front of the apparatus, and measuring the reflected portion with a linear photocell. Preliminary tests with a commercial caesium cell of the vacuum type (RCA-919) have been made, but the resulting currents were too small to be used quantitatively without amplification. A simplified linear amplifier, of the type described by Huntoon90), has recently been constructed for this purpose by Mr. A. Hemmendinger of this laboratory, but it has not been used in any of the work to be reported here. Inspection of the set of current voltage curves reproduced in Fig. 9, p. 68, and Fig. 10, p. 69 will show, however, that it has been possible to obtain curves in which the "staggering" of alternate points is either negligible, or altogether absent. Only such curves, which clearly indicated that no spurious variations had occurred, were used for quantitative analysis.

The Electrical Equipment.

The essential features of the electrical apparatus for the production and measurement of the retarding field, as well as that for the measurement of the photoelectric currents, are shown in Fig. 8, p. 61. The potential for the retarding field was obtained from a six volt storage battery by means of a potential divider consisting of two decade boxes, whose total resistance was maintained at 10,000 ohms. This potential was applied to the cathode, while the anode was connected to ground through the grid resistance of the amplifier tube. The potential of the anode with respect to ground was thus not the actual potential across the electrodes, but the correction for the drop between anode and ground could be easily and accurately determined, as will be shown later.

For the measurement of the potential of the cathode, a Leeds & Northrup Type K potentiometer was used in connection with a heat insulated Weston standard cell. The latter was calibrated by Dr. F. G. Dunnington against an Eppley standard cell with a recent Bureau of Standards certificate. In order to extend the range of the potentiometer, a special volt box for ratios of 4:1 and 2:1 was constructed with Shallcross precision wire-wound resistors. The rated values of the two smaller resistances were 2500 ohms, of the larger one, 5000 ohms. The exact values were established both with a precise Leeds & Northrup Wheatstone Bridge, and with the main potentiometer.

In order to expediate the collecting of data, the different settings of the decade boxes, which supplied the retarding potentials, were carefully calibrated, in steps of 100 ohms, against a standard setting (5000 ohms on each box). During the actual measurements, it was thus only necessary to check this standard setting from time to time, as the supply voltage decreased.

All the voltage determinations made with this equipment were consistent and repeatable to within 0.01%. Comparison of some of the calibrated decade box settings with an older, and less reliable potentiometer of the same type indicated discrepancies as large as 0.03%. Although these differences were almost certainly reducible to the poor condition of this second instrument, an upper limit of 0.05% was assigned to the voltage determinations.

The photoelectric currents were measured by means of a direct current amplifier using a General Electric FP-54 pliotron. With a grid resistance of $2.6 \cdot 10^{10}$ ohms, made by the S. S. White Dental Company, this tube was employed as a steady deflection instrument. While the maximum sensitivity, which can be obtained in this manner, is less than in the rate-of-discharge method, the much greater rapidity of the former method suggested its use in the present investigation. The amplifying circuit itself was of the type designed by DuBridge and Brown91). The The construction of this circuit underwent a number of successive modifications, until a final maximum voltage sensitivity of 200 000 mm per volt was attained. With the grid resistance mentioned above, this is equivalent to nominal current sensitivity of $2 \cdot 10^{-16}$ amps. per mm.

Because of unavoidable small fluctuations at this sensitivity, and the presence, in this tube, of grid currents of this magnitude, the smallest currents measured in the actual determinations were of the order of 10^{-15} amps.

In the course of the gradual development of the final circuit, it was also tried to use the circuits suggested by Barth92) and Pennick93), but their performance was not found as satisfactory as that of the older DuBridge and Brown circuit. Macdonald94), in a comprehensive analysis of d.c. amplifying circuits, has recently come to the same conclusion on a theoretical basis.

Once the maximum voltage sensitivity of an amplifier of this type has been attained by proper adjustment of the constants of the circuit, the major problem consists in the elimination of fluctuations and drifts. By gradual improvements in the details of construction, it has been found possible to reduce these to a satisfactory minimum level.

The amplifying tube itself, the grid resistance, and a calibration switch were contained in an evacuated brass chamber (Fig. 6, p. 48, Fig. 8, p. 61). An evacuated glass connecting piece surrounded the lead from the end of the photoelectric tube to the grid of the amplifier tube. The only place at which this lead touched the glass wall was protected against leakage by a special apron.

The entire photoelectric tube as well as the glass connecting piece were carefully shielded by copper sheet and copper wire cloth,

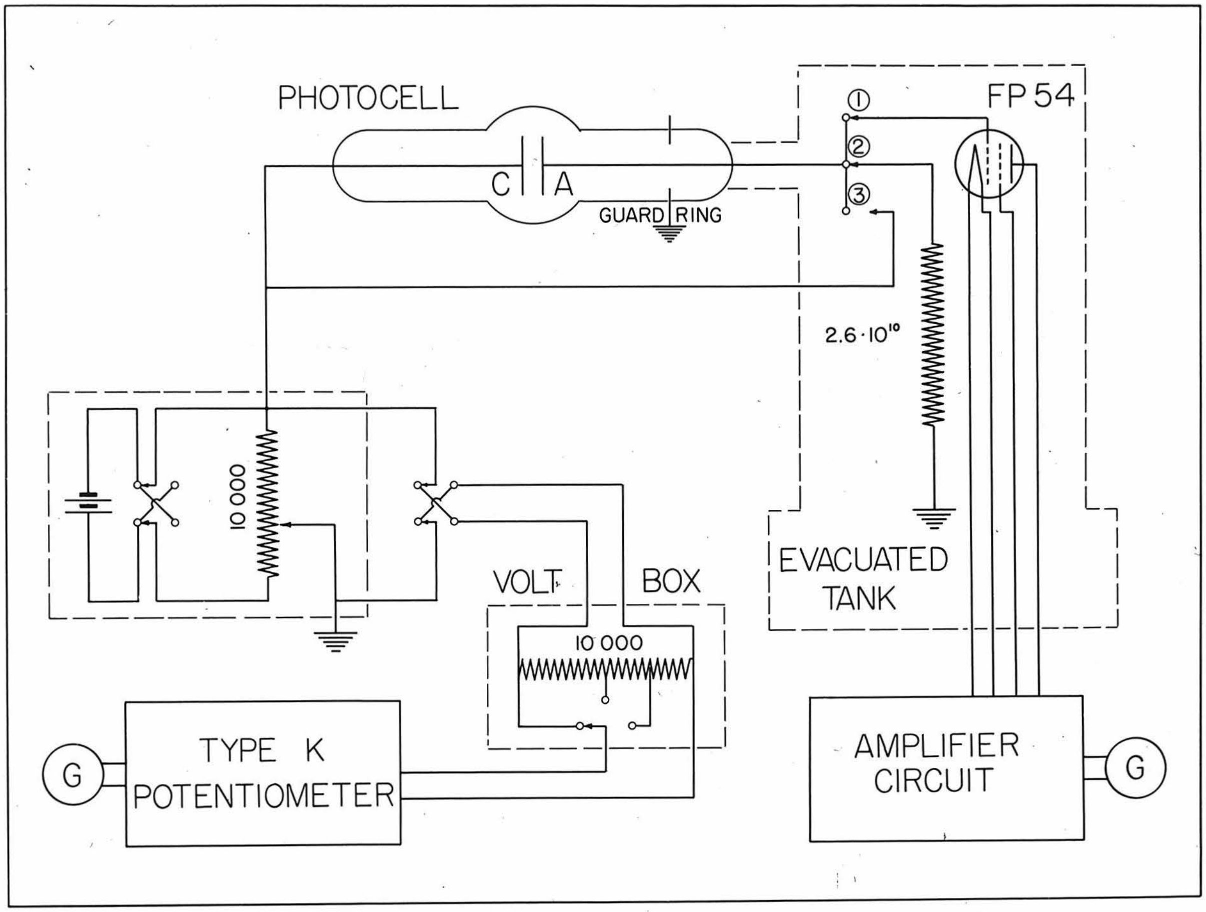
PHOTOCELL
C
A
GUARD RING
①
②
③
FP 54
2.6·10¹⁰
10 000
VOLT BOX
10 000
EVACUATED TANK
G
TYPE K POTENTIOMETER
AMPLIFIER CIRCUIT
G

Fig. 8

which were installed as close to the leads as possible, in general directly over the glass wall of the tube. All electrical connections to the photoelectric tube and the amplifier case consisted of high-insulation shielded cable. The remainder of the amplifying circuit, including the Ayrton galvanometer shunt, was included in an aluminum box. The batteries for the operation of the tube were similarly in a shielded container, as were also the battery and potential dividers for the production of the retarding field. Because of the contact difficulties experienced with variable resistors, they were gradually replaced by fixed wire-wound resistors, with the exception of a filament rheostat, and two rheostats for the adjustment of the galvanometer zero point.

With these precautions, the random fluctuations, at maximum sensitivity, did not, under ordinary conditions, exceed a magnitude of a few millimeters. The occurrence of more violent extraneous disturbances during the daytime made it necessary, however, to make all the more important measurements during the night.

Steady drifts of the zero point could not be completely eliminated with the present equipment. The principal source of such drifts consists in slow temperature changes of the various resistances, with fluctuating room temperature. To a large extent, this difficulty might be removed by immersing the entire network in an oil-filled reservoir. During the night, however, these drifts did not exceed a few millimeters per minute at maximum sensitivity. By applying a linear correction for such drifts, as explained in the next section, the remaining error was certainly much smaller than that introduced by random fluctuations.

The circuit for the supply and measurement of the retarding potentials was also used for the calibration of the amplifier. Any arbitrary potential with respect to ground could be applied to the control grid of the pliotron by means of the cam-operated switch in the amplifier case. In Fig. 8, p. 61, this switch is shown in the usual measuring position, in which the grid resistance shunts the amplifying tube. By opening contact (2) and closing (3), potentials from the voltage divider could be directly impressed on the grid of the tube. The switch itself consisted of platinum points, which were insulated by 1/2 inch amber plugs; the contacts were closed by means of strong phosphor bronze springs.

For each position of the galvanometer shunt, varying nominally from full sensitivity to 0.001 sensitivity, the deflections were determined for a series of suitable voltages. For the higher sensitivity ranges, the resulting calibration curves (deflections vs. grid potentials) were very nearly straight lines. Inasmuch as the theory of the experiment requires merely a knowledge of relative currents, which are strictly proportional to the voltage drops along the grid resistance, the desired ratios could be directly determined from the voltage ratios. The determination of the accurate value of the grid resistance was therefore not necessary; the required voltage ratios could be immediately determined from the calibration curves which showed the control-grid voltage for any deflection of the galvanometer.

The control grid voltage, which is accurately obtained in this manner, is further applied to the calculation of the exact retarding potential between the electrodes, as indicated on p. 67.

The amplifier was completely calibrated whenever measurements were made; in determinations of complete sets of data, calibrations were performed both before and after the actual measurements. In all cases, the variations of the amplifier sensitivity over short periods were found to be negligible.

The magnitude of the random fluctuations under the most unfavorable conditions would suggest that a value of 10^{-15} amps. should be assigned to the uncertainty of the current determinations. This is also the rated order of magnitude of the residual grid currents of the FP-54 pliotron. It has not always been possible, however, to repeat measurements of photoelectric currents with this accuracy. Such discrepancies did not necessarily originate in defects of the current measuring equipment, but may have resulted from changes in the illumination. Since the requirements to be imposed on the accuracy of the relative current determinations arise ultimately from the method of superimposing logarithmic current voltage curves, a satisfactory estimate of all random errors in the determination of such curves may be derived from their mutual consistency. The quality of this agreement is graphically represented in Fig. 11, p. 75; the best quantitative 75 index of the total uncertainty consists in the deviations between determinations, by different observers, of the horizontal shifts necessary to bring these curves to coincidence (cf. Table II, p. 84).

Measurements and Results

With the apparatus described in the preceding pages, altogether 42 energy distribution curves have been measured, on two different sodium surfaces. It became apparent, almost immediately after deposition of the first coat of sodium, that very considerable changes of the electrode work functions took place, so that the majority of the measurements were determinations of individual curves made with the object of studying these changes. When conditions became sufficiently stable to permit measurements of complete sets of data, two such sets were taken. A new surface was then applied, and additional measurements were made shortly afterwards. The results from these last sets indicate considerable instability, and necessitate the conclusion that, with the present tube, adequate stability is not reached until at least four weeks after deposition of a new surface. For this reason, the quantitative analysis of the normal energy distribution has been limited to the two complete sets of curves which were obtained under conditions of maximum stability. Nevertheless, the study, on the basis of the remaining data, of the nature of the gradual changes in the behavior of the tube has led to valuable conclusions, without which the proper interpretation of the principal results would not have been possible.

The discussion of these results will be preceded by an outline of the process by which the data were obtained and calculated.

The mercury arc was ignited several hours before the beginning of a run. While it was attaining temperature equilibrium, the amplifier was calibrated, and a number of simple tests were made to establish the absence of leakage currents and reverse currents. Next, the potential ranges to be used for each incident frequency were determined by some rough preliminary measurements. The exact potential supplied by the potential divider at the standard setting (cf. p. 59) was then measured with the potentiometer.

Next, the monochromators were adjusted to the desired frequency, and the retarding potential set to the lowest value to be used. Simultaneously with the opening of the shutter, a stopwatch was started, and the zero point of the galvanometer was recorded. After twenty seconds, the galvanometer deflection was recorded, and the shutter closed. Again twenty seconds were allowed for the galvanometer to return to its zero position, which was then recorded. The whole process was then twice repeated. After this, a new setting of the retarding field was established, and a second point determined in the same manner. The same procedure was followed for all successive points, which were taken in the particular order explained on p. 56. When currents became too large to be measured at the maximum sensitivity of the amplifier, the procedure was slightly modified to allow for the underdamped condition of the galvanometer at the lower sensitivities. In such cases, thirty seconds were allowed for each excursion, but only two readings at each point were taken, instead of three. After all points at one frequency were measured, the standard setting of the voltage divider was again determined with the potentiometer. At the end of an entire run, the amplifier calibration was repeated.

As already indicated, a linear drift of the galvanometer zero point was then assumed; the interpolated values of the deflection were simply determined by subtracting the mean of two successive zero readings from the intermediate reading. For the mean of the three values thus obtained, the grid voltage was determined from the amplifier calibration curves.

Next, the potential of the cathode was determined from the known ratio of the particular potential divider setting to the standard setting, from the known volt box factor, and from the potentiometer reading corresponding to the standard setting. By adding the grid potential, the applied retarding potential V_p was then determined.

Current voltage curves of the type shown in Fig. 9, p. 68, and Fig. 10, p. 69, could then be plotted. In order to effect the comparison with the theoretical curves, the logarithms of the currents were next determined, and these logarithms were plotted against the product of V_p and an arbitrarily adopted value of $e/kT = 38.705$ int. volts^{-1} (cf. p. 39), corresponding to a temperature of 300° K. For convenience in drawing, a constant term was generally added to the logarithms of the currents; the theoretical development shows that this is always

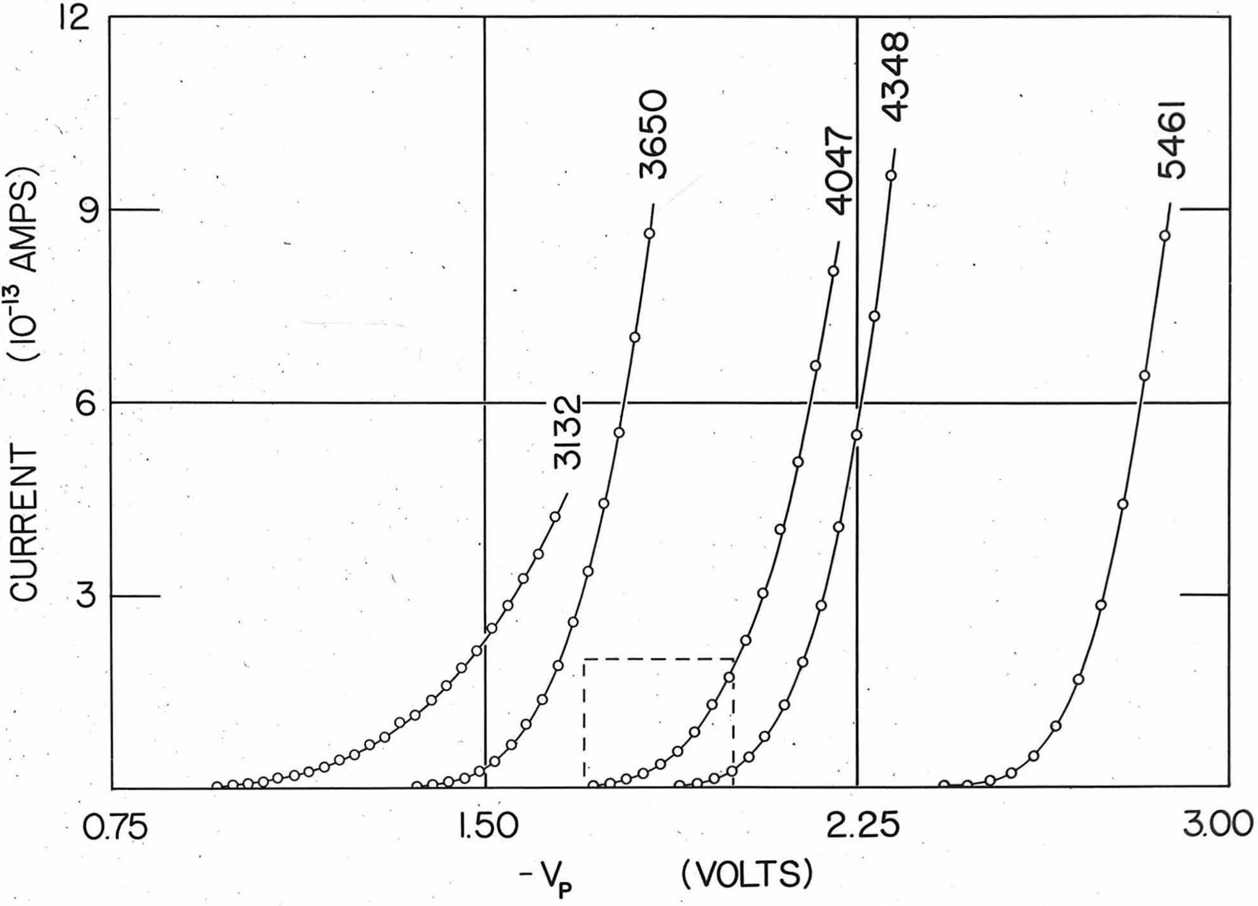
12
9
6
3
CURRENT (10^{-13} AMPS)
0.75
1.50
2.25
3.00
- V$_P$ (VOLTS)
3132
3650
4047
4348
5461

Fig. 9

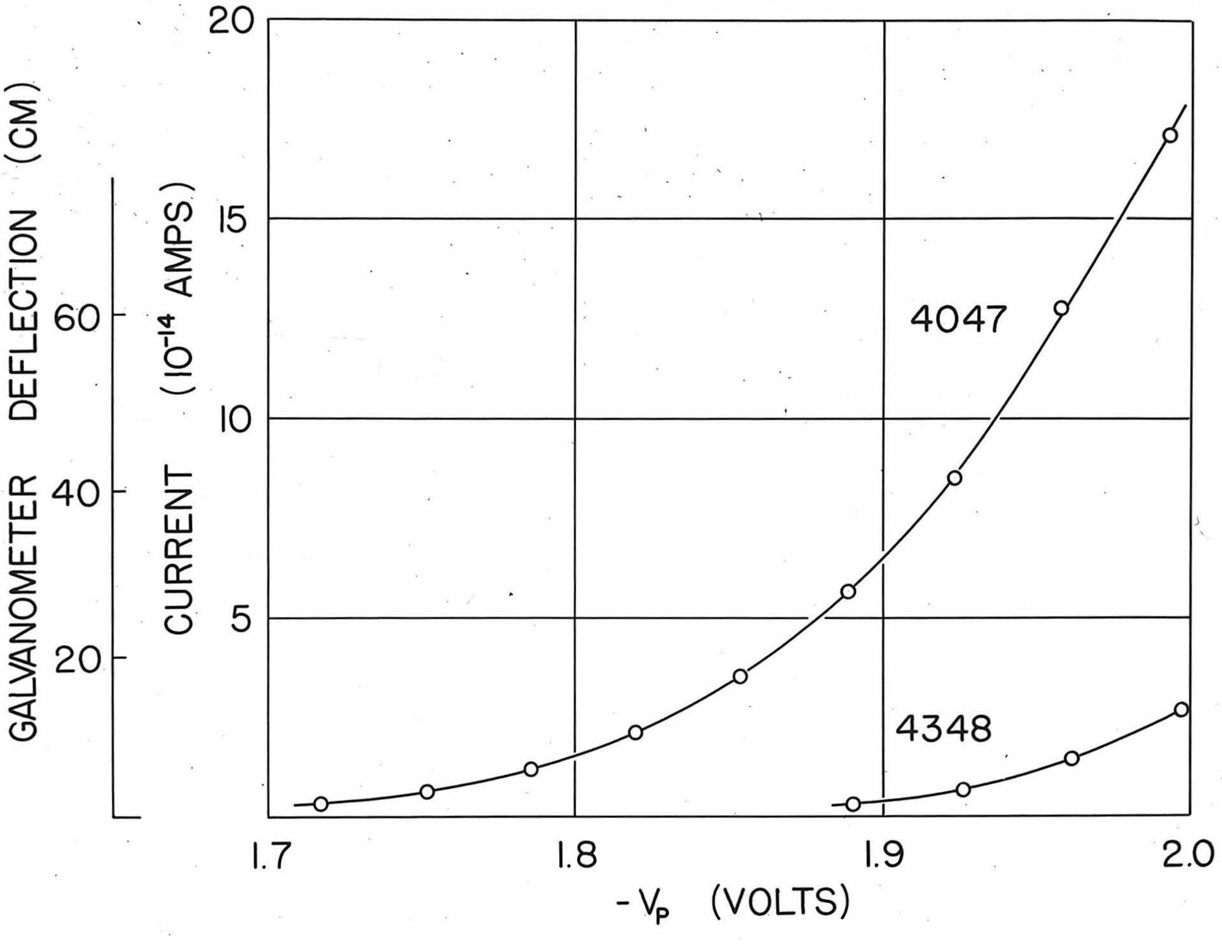
GALVANOMETER DEFLECTION (CM)
20
40
60
CURRENT (10^{-14} AMPS)
5
10
15
20
4047
4348
1.7
1.8
1.9
2.0
$-V_P$ (VOLTS)

Fig. 10

permissible. The data were then in a form suitable for superposition on the theoretical curve log (x) vs. x, drawn to the same scale (cf. 41 p. 41). The results of such comparisons will be discussed in the following section. 41

The previously mentioned systematic changes in the behavior of the tube manifested themselves primarily in shifts, along the voltage axis, of the entire set of current-voltage curves. It has been shown, in the theoretical section, that such shifts are not functionally related to the cathode potential barrier, but rather to that of the anode. The variations in question will therefore be discussed in terms of changes of the anode work function. The observed phenomena can be summarized as follows:

(1) Immediately after deposition of the first layer of sodium, the curves shifted rapidly in the direction corresponding to decreasing anode work function, i.e. toward the left in Fig. 9, p. 68. A total displacement of about 0.8 volts was observed during the first twelve hours after deposition.

(2) During the next seven days, a more gradual shift of altogether about 0.5 volts took place in the opposite direction.

(3) The anode was then heated to incandescence for a total period of 45 minutes. Measurements taken immediately afterwards indicated that a large shift had occurred in the direction of increasing anode work function. The curves were displaced about 0.8 volts toward the right.

(4) A steady and rather slow displacement of the curves in the direction of decreasing work function was noticed during the following five weeks. Initially, the rate of displacement was about 0.05 volts per week, but the process appeared to slow down later. The two most reliable complete sets of data, which form the basis of the discussion in the following two sections, were taken during the last week of this period.

(5) A new and somewhat heavier coat of sodium was then deposited on top of the old one, and, immediately afterwards, the anode was heated for 25 minutes. Readings taken a day later showed that the curves had shifted about 0.6 volts in the direction of decreasing anode work function; this shift continued during the seven hours in which measurements were made.

(6) The anode was again heated to incandescence for about 45 minutes. This resulted in a shift of about 0.7 volts in the direction of increasing anode work function.

(7) Further determinations were made two days later. While the rate of displacement of the curves was much less than during the measurements mentioned in (5), the results contained definite evidence of a shift in the direction of decreasing anode work function.

(8) Frequent tests on the existence of reverse currents showed that, during the use of the first sodium surface, the long-wave limit of the anode never went higher than 3100 A; after application of

the second surface, very small reverse currents could be detected at 3132 A and 3650 A, although these did not interfere with the measurements. In all cases, the work function of the anode was lower than that of pure nickel, so that no measurements could be made at 2536 A.

With the exception of the observations (2), all of the described variations can be plausibly interpreted as the result of the gradual accretion of sodium on the anode. In every case, heat treatment of the anode was followed by a pronounced effect in the direction of increasing work function. All other variations, except (2), are consistent with an assumed decrease of the work function. It is well established[73,74,80-82)] that the presence of alkalis, even in layers of atomic dimensions, on ordinary metals involves a considerable decrease of the work functions of such metals. The increased rate of the process in observations (5) to (7) can easily be accounted for by the known fact that much more fresh sodium was introduced into the tube on that occasion than in the application of the first deposit.

No satisfactory explanation has been found for the anomalous behavior represented in the observations (2). Several authors[75,78)] have noticed changes in intrinsic sensitivity of evaporated alkali surfaces shortly after deposition. The suggestion that such changes might have simulated a displacement of the curves along the voltage axis is open to the objection that a displacement of 0.5 volts would not have been possible, under such conditions, without considerable alteration in the shape of the curves. On the basis of the data now available, it has not been possible to observe a definite change of that type.

Further investigations of these time-dependent changes of the anode work function are planned, particularly in connection with simultaneous observations of the photoelectric long wave limit of the anode.

Comparisons with Theoretical Predictions

Since the principal result obtained from the logarithmically plotted current voltage curves consists in their definite disagreement with the theoretically predicted curve, it is essential to establish first the absence of systematic errors in the determinations of the experimental curves. One of the sets of actual current voltage curves from which these were derived is shown in Fig. 9, p. 68. An enlarged view of the dotted area is shown in Fig. 10, p. 69. In view of the particular alternating order, in which the points of these curves were measured, the appearance of the curves may be taken to indicate conclusively that variations of the illumination or of the anode threshold were not present to the extent of causing any alteration in the shapes of these curves. The experimental points follow smooth curves even in the region of the lowest measured currents, where the errors introduced by such changes would be considerable (cf. p. 56).

The logarithmic curves themselves exhibit very satisfactory agreement among each other. This is shown in a composite diagram, Fig. 11, p. 75, which was obtained by selecting one curve, in this case λ 4047, as a standard, and displacing the other curves along the horizontal and vertical axes, until their points fell along the standard curve. The amounts of the horizontal displacements are listed on the diagram. With the exception of two high points originating from λ 5461, the mutual consistency of the different curves appears to be well-established. Regarding those two points, it should be realized that λ 5461 is very close to the low frequency limit of the cathode; the photon energy is therefore only slightly larger than the work function of the cathode. As soon as the rather small range of potential has been covered, which corresponds to the difference $(h\nu - (W_a - \mu))$, all electrons emitted from the cathode will reach the anode, i.e. the current is saturated. The situation in this case is schematically represented in Fig. 13 B, p. 81. The two points in question represent the approach of this saturation.

The validity of the energy-distribution represented by this composite curve is especially demonstrated by the fact that the points derived from different frequencies represent electrons which have left the sodium with vastly different energies. While each curve represents a region of about 0.6 volts near the high energy end of the distribution, the total range of the energies, with which these electrons were emitted from the cathode material, is over two volts. The identical shapes of the corresponding curves not only show that the distributions are

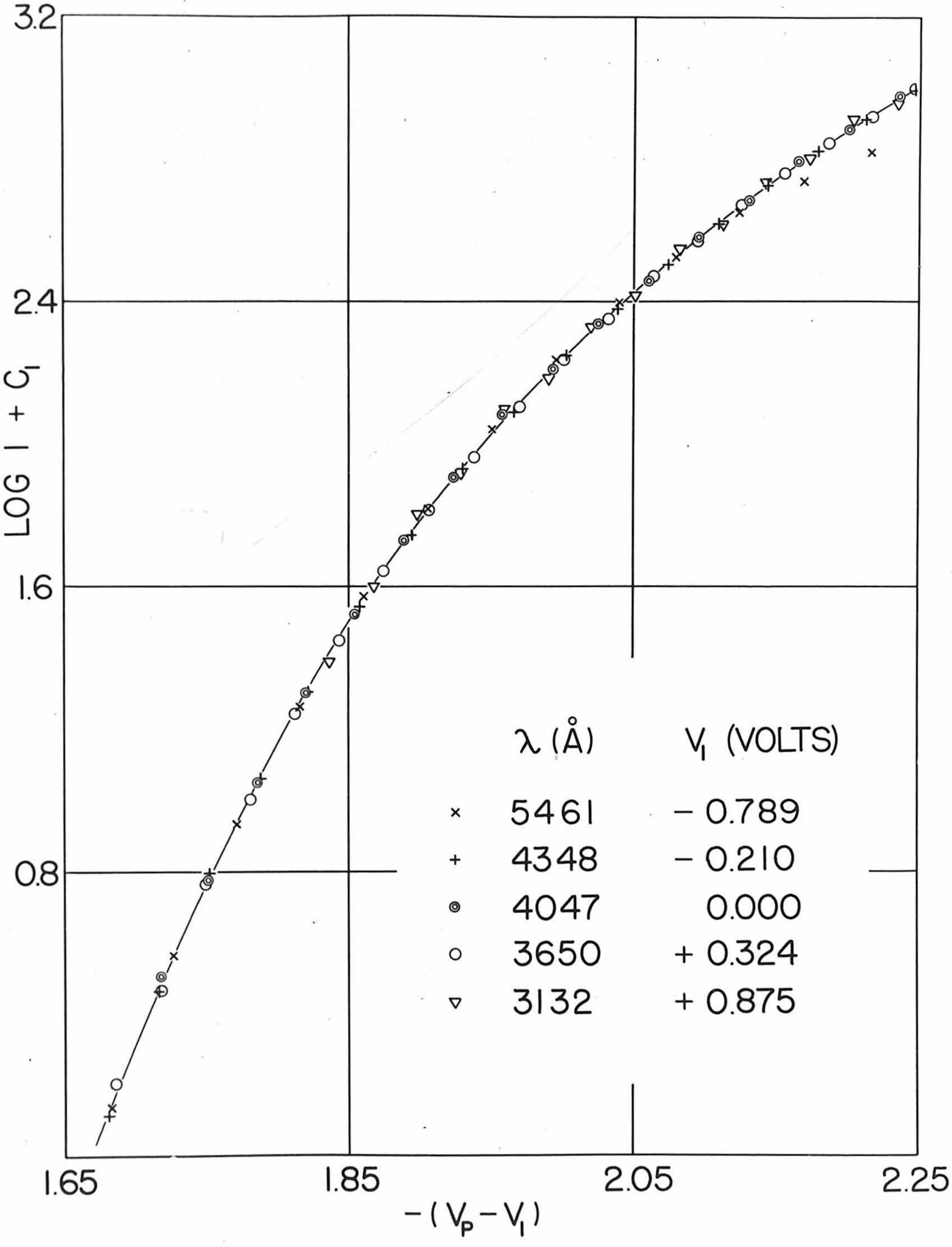
3.2
2.4
1.6
0.8
LOG I + C$_1$
1.65
1.85
2.05
2.25
$-(V_P - V_1)$
λ (Å)
V$_1$ (VOLTS)
× 5461 − 0.789
+ 4348 − 0.210
◎ 4047 0.000
○ 3650 + 0.324
▽ 3132 + 0.875

Fig. 11

independent of the absolute energy of emission, but they also suggest the probable absence of disturbing effects dependent on emission energies, such as might be introduced, for example, by the earth's magnetic field, or the distortion of the electric field produced by the slight warping of the electrodes.

Moreover, each curve represents ratios up to nearly one thousand in the number of electrons in different energy ranges. Again, the agreement obtained in the lower parts of these curves constitutes definite evidence for the absence of stray light of higher frequencies; for any distortions of the energy distribution curve as a consequence of scattered light from adjacent spectral lines would certainly not be identical for all five lines. Finally, it will be evident from the curves of Fig. 9, p. 68, that the different curves also represent different ranges of total photoelectric current. Thus two points with the same ordinate in Fig. 11, p. 75, do not at all represent the same magnitudes of photoelectric current, a fact which finds further expression in the differences between the vertical shifts necessary to bring the different curves to coincidence. The mutual agreement of the curves thus argues against the possibility of a systematic distortion introduced in the current measuring device, e.g. by failure of Ohm's Law in the grid resistance, or by grid currents in the amplifying tube.

It thus appears unavoidable to accept the conclusion that the curve represented in Fig. 11, p..75, represents the normal energy distributions of the photoelectrons for the particular barriers which existed in the tube at that time. Curves obtained with the same sodium surface a week later show the same degree of mutual consistency; moreover, the distribution curves agree with the ones previously taken, in spite of an intervening small change in the anode work function.

The disagreement of the observed distribution with the one theoretically predicted for a temperature of 300° K. is shown in Fig. 12, p. 78. It is of interest to mention here that, in 1936, DuBridge and Hill[77)] reported, in a preliminary note, a similar discrepancy in the total energy distribution, and indicated that it was not observed in very pure sodium. No further information has been published on this point, but, very recently, another investigation by Mann and DuBridge[95)] on absolute photoelectric yields revealed that also in this type of experiment the behavior of sodium did **not** agree with theoretical predictions. The very careful work by Brady and Jacobsmeyer[74)] on total energy distributions of photoelectrons from sodium also shows that definite agreement with the theoretical curve cannot be obtained (cf. especially Fig. 6 in their paper). In all these cases, the shapes of the observed curves were roughly similar to the theoretically predicted distribution at much higher temperatures. In order to subject this point to a closer examination, a series of theoretical curves was drawn for different temperatures 50° apart. The curve which most nearly fits the observed data is that at 600° K.; inspection of the two curves in Fig. p. 78, clearly shows, however, that systematic differences exist between these two curves. This is not surprising in view of the

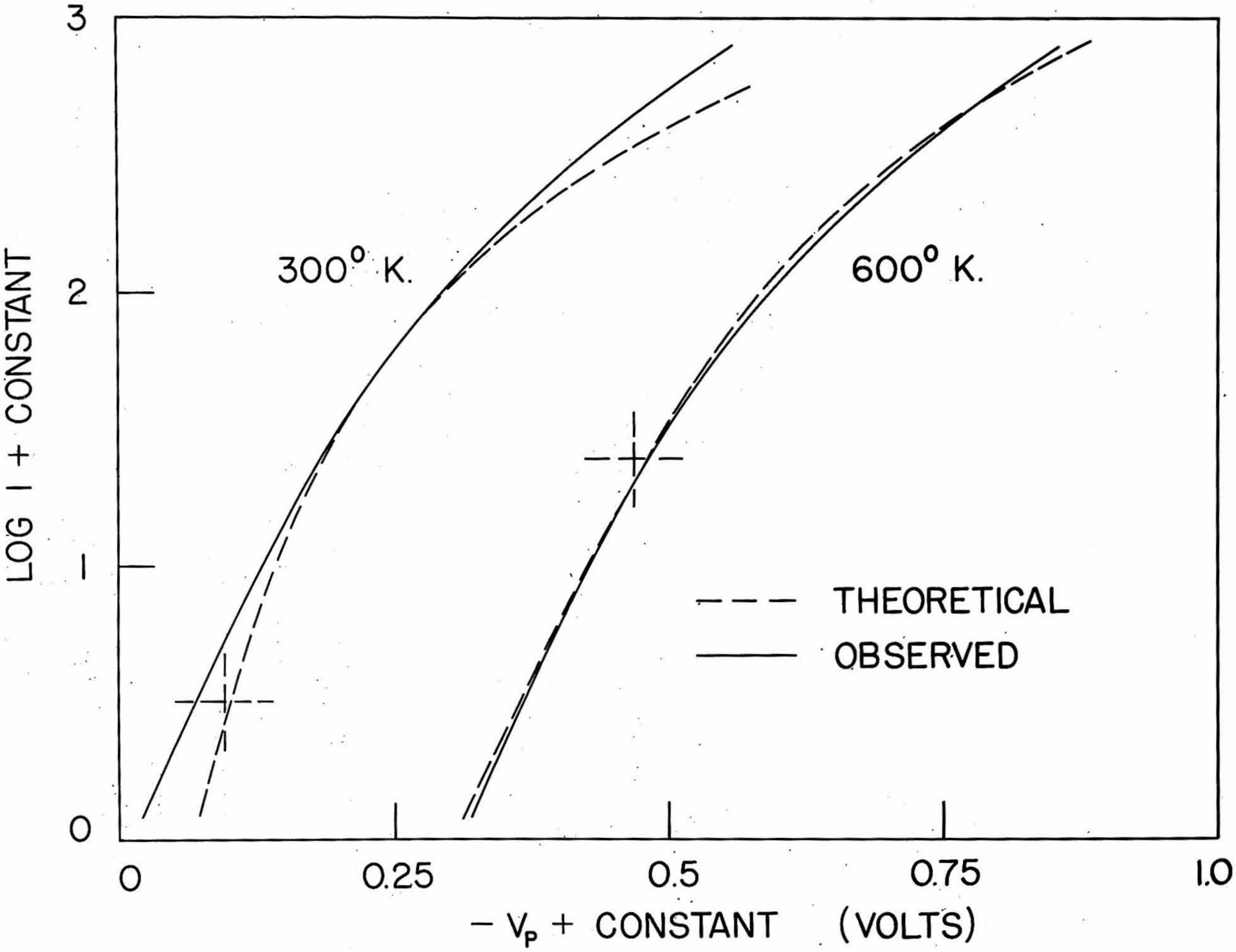
3
2
1
0
LOG I + CONSTANT
0
0.25
0.5
0.75
1.0
− V_P + CONSTANT (VOLTS)
300° K.
600° K.
THEORETICAL
OBSERVED

Fig. 12

absence of cogent theoretical reasons demanding a satisfactory agreement at these fictitiously high temperatures.

In order to explain the difference between observed and theoretical energy distributions, it has most frequently been suggested[73,77,96)] that slight gas contaminations are responsible for the altered shapes of the curves. In spectral distribution experiments, in which the total emission of the cathode is measured in accelerating fields as a function of frequency, such effects have often been observed[97,98)]. It must be emphasized, however, that in such experiments the work functions of cathode and anode appear in entirely different roles. The conditions in such experiments are schematically represented in Fig. 13 C, p. 81. In such a situation, it is plausible enough, on a theoretical basis, that a cathode potential barrier of complicated shape, such as would be produced by gas contamination, would have a decided effect on the transmission of the electrons. On the other hand, DeVoe[99)] has found, in an investigation of the effects of gases on the spectral distribution of photoelectrons from evaporated zinc surfaces, that agreement with the theoretical curve could be obtained in all stages of gas contamination.

In the present type of experiment, which deals with energy distributions at individual frequencies, the situation is, however, quite different. Here a retarding field is joined directly to the cathode potential barrier (cf. Fig. 13 A, p. 81), and it is difficult to see why a change in the shape of the cathode barrier should have any effect on the transmission of the electrons. Furthermore, Professor Houston has succeeded in showing that the transmission probabilities, which govern the interaction between photons and electrons are approximately independent of the shape of the cathode potential barrier, provided that the highest point of that barrier is lower than the top of the anode barrier. From the mutual consistency of the curves, and from the fact that the position of the top of the anode barrier was changed by more than 1.5 volts in the process of obtaining data at different frequencies, it seems safe to assume that this restriction was not violated. Thus, while it is not contended that the sodium surfaces used in the present experiment were absolutely pure, the explanation of the shapes of the observed curves on the basis of gas contamination is considered inadequate.

On the other hand, under the conditions prevailing in this type of experiment, the nature of the anode potential barrier becomes an important factor. If this barrier should be of a more complex type than the plain discontinuous threshold, and, more particularly, if it should be of the type shown in Fig. 13 D, p. 81, then theoretical considerations would certainly suggest an alteration in the shape of the current voltage curve. Moreover, this type of surface potential barrier is just the one which should be expected to result from the deposition of small quantities of sodium on the anode surface. In view of the experimental evidence for the existence of such adsorbed layers of sodium on the anode, this appears to be altogether the most plausible explanation of the shape of the observed distribution curves. In fact,

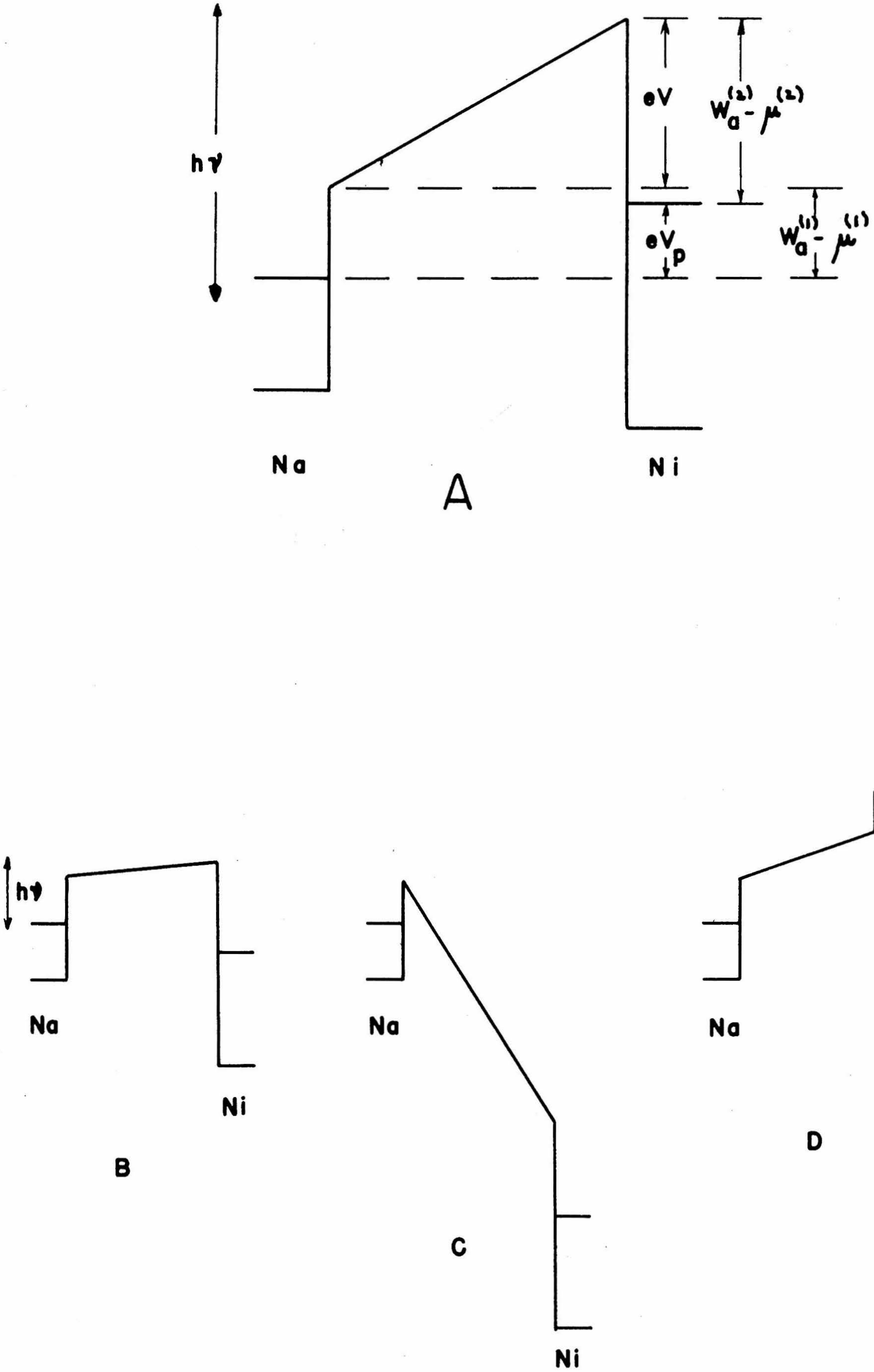

FIG. 13

some preliminary results which Professor Houston has obtained from calculations on this basis agree remarkably well with the observed results; by more careful adjustment of certain parameters, it is hoped that complete agreement will be achieved.

Another possible cause for the disagreement of the observed curves with the predicted ones of the ordinary theory may consist in the release of electrons by volume photoelectric processes (cf. p. 29). Although some rough calculations by Tamm and Schubin[60)] indicate that the limiting frequency for this phenomenon should lie above the range used in the present investigation, their conclusions have not generally been accepted. The theoretical treatment, which has so far been considered, concerns only the surface effect, i.e. the interaction of photons and electrons in the force field at the surface of the metal. On the other hand, it does not seem very likely that photoelectrons released in the force fields surrounding the atoms of the lattice should contribute to the total distribution in exactly the same proportion at λ 5461 as at λ3132; in the absence of more complete information on this point, it may perhaps suffice to invoke once more the observed mutual consistency between the curves at different frequencies as evidence against the existence of volume photoelectric processes.

Finally, it should be recalled that all the theoretical treatments, which have been presented, are based on an ideally plane metal surface. It is very doubtful whether an evaporated film of sodium satisfies this condition to a sufficient degree. Although Mitchell[65)] has called attention to this problem, the calculation of the effects of surface roughness caused by microcrystalline aggregates presents such difficulties that no adequate theoretical treatment is available.

The Determination of h/e.

From the point of view of the photoelectric determination of h/e, the most important aspect of the mutual agreement of the logarithmic current voltage curves consists in the assumption that the horizontal displacements necessary to bring the curves to coincidence are identical with the differences $\frac{h}{e}\Delta\nu$. This assumption would, of course, be considerably strengthened by an adequate theoretical explanation of the shape of those curves. In the meantime, it was thought to be of interest to evaluate the two most reliable sets of data on this assumption.

The displacements listed in Fig. 11, p. 75, represent the mean values of six determinations by three different observers. The subjoined table shows the individual determinations; the wave-length given beside their initials indicate the reference curve, to which the other curves were fitted. Graphs approximately 30 x 30 cm in size were used for this purpose.

Table II

Wave-lengths	5461	4348	4047	3650	3132
WVH(4047)	-0.789	-0.209	0.000	0.326	0.875
WVH(4348)	-0.788	-0.211	0.000	0.323	0.875
AHH(4047)	-0.793	-0.211	0.000	0.323	0.882
AHH(4348)	-0.787	-0.209	0.000	0.323	0.873
CFJO(4047)	-0.791	-0.211	0.000	0.318	0.873
CFJO(4348)	-0.788	-0.209	0.000	0.323	0.871
Mean	-0.789	-0.210	0.000	0.323	0.875

(All displacements are referred to λ4047, and listed in volts)

The resulting mean values were then plotted against the corresponding frequencies, as shown in Fig. 14, p. 85. The exact wave-lengths for the several lines were taken from Kayser's Tables$^{100)}$; in the case of groups, the line of lowest wave-length was chosen. The adopted values were the following:

Nominal Designation	I.A.
5461	5460.724
4348	4339.21
4047	4046.56
3650	3650.15
3132	3125.62

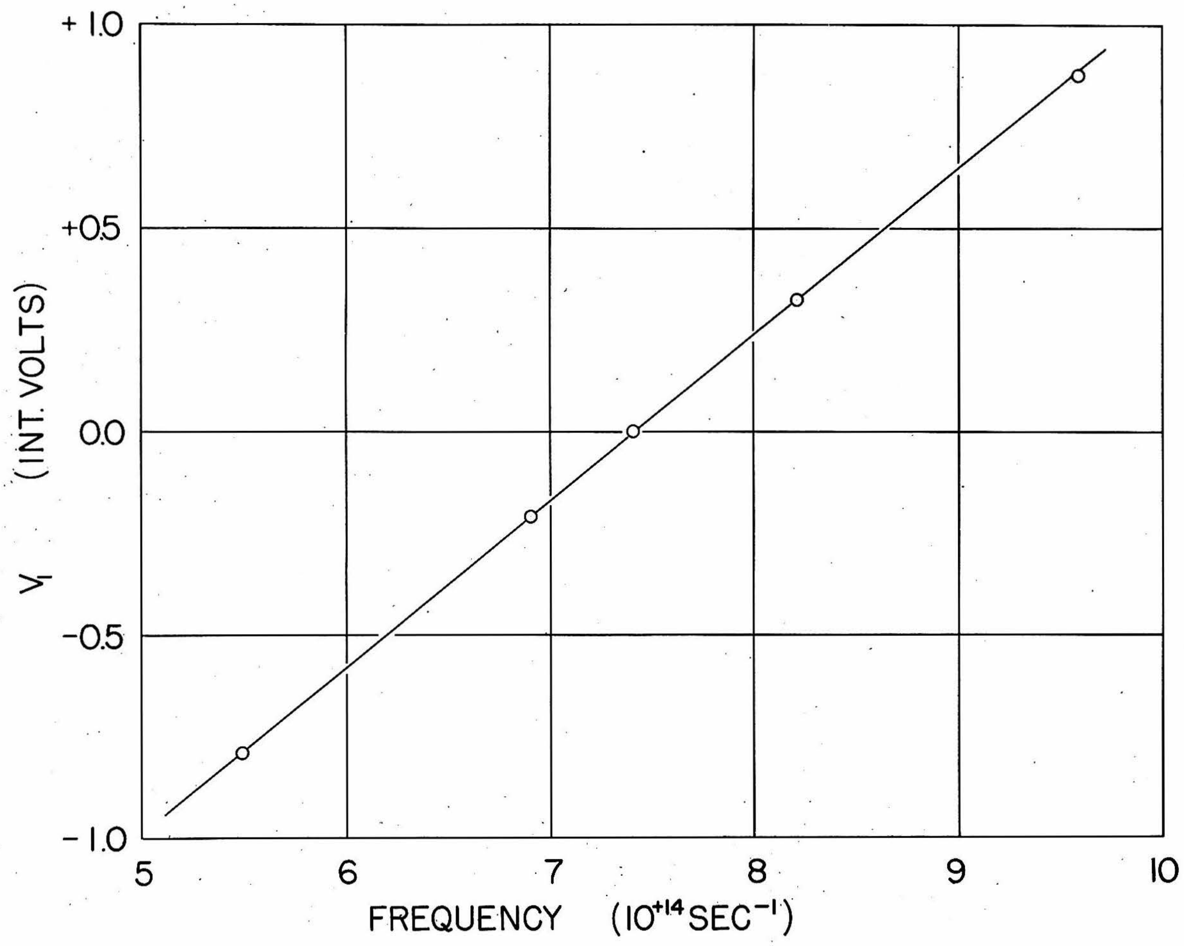

Fig. 14

Fig. 14, p. 85, shows that the five points cannot be joined by a straight line. In fact, a larger diagram would exhibit a very slight upward convexity of the curve joining the points. The same defect is shown by the results of the second set of data. In order to gain some information on this matter, a set taken under much less stable conditions with the second sodium surface was analyzed; the resulting points showed the same defect in a more pronounced manner. When this latter fact is considered in connection with the circumstance that the data for the different wave-lengths were taken in the order λ5461, λ3122, λ4348, λ3650, λ4047, and in similarly alternating sequence in the other runs, the conclusion suggests itself that small changes in the anode work function must have taken place, while the entire set of data was taken. The fact that evidence of such shifts was not noticed in the current voltage curves, Fig. 9 and Fig. 10, pp. 68 and 69, may be taken to indicate either that possible traces of systematic "staggering" were misinterpreted as random variations, or else that the amounts of the shifts were below the level of the fluctuations of the amplifier.

The straight line shown in Fig. 14, p. 85, was determined from the five points by the usual least squares procedure; the individual points were weighted in accordance with the deviations of the six shift determinations (cf. Table II, p. 84) from the mean. Equal weights were applied to λ4348 and λ4047, since both curves were used as reference curves. The slope of the least squares line was found to be

$0.4094 \cdot 10^{-14}$ int. volt-seconds, corresponding to a value of $h/e = 1.366 \cdot 10^{-17}$ erg sec e.s.u.$^{-1}$. The second set of curves yielded $h/e = 1.390 \cdot 10^{-17}$ erg sec e.s.u.$^{-1}$. It may be of interest to note that the mean of these two values, $h/e = 1.378$, lies fairly close to Birge's[24)] weighted mean value, $h/e = 1.376$. DuBridge and Hill[76)], on the basis of preliminary experiments on total energy distribution of sodium photoelectrons, have reported results 2% above the accepted mean value. In accordance with Birge's[101)] recommendation, the ratio r_e/r_i was calculated for the two results which have been quoted; from the values obtained, it was evident that the usual least squares error by internal consistency was not applicable here.

The question of the inherent limits of precision of the method which has been investigated cannot be definitely answered on the basis of the available material. The outstanding defect at present consists in the slight curvature of the points in the final h/e diagram. From observations of the first sodium surface over a period of five weeks, it seems reasonable to assume that, after a longer interval, the anode threshold would come sufficiently close to absolute equilibrium to reduce variations during the measurements to a negligible level. The development of more rapid methods of securing a complete set of data would further decrease errors from this source; it would also permit the reduction of the probable error by the use of a larger number of incident frequencies. The deviations between the results of different determinations of the voltage displacements, shown in Table II, p. 84, are more difficult to interpret quantitatively. Closer agreement could certainly be effected if it were possible to measure the photoelectric currents with greater precision. It seems doubtful, however, whether the amplifying equipment can be improved much beyond its present performance. The most promising line of attack seems to consist in a search for more powerful sources of monochromatic radiation.

On the other hand, the process of the graphical superposition of curves of the type here involved will introduce personal errors even with perfect data. In fact, DuBridge[96)] has suggested that a photoelectric determination of h/e would not be possible without a more precise method of analyzing the experimental data. It is certain that a great advance in precision could be achieved by the development of a least squares method of determining these voltage displacements. Such a method, of course, would have to be based on an adequate theoretical expression for the observed distribution curve. Further work in these different directions is in progress; meanwhile no definite limits of uncertainty have been assigned to the values of h/e obtained in the present survey of the method.

While it does not appear probable that this method can be developed to a precision comparable to that attained by the x-ray method, the present investigation indicates definitely that determinations of h/e by the photoelectric method are possible on the basis of empirically established curves of normal energy distribution. Even in the absence of an adequate theoretical interpretation of such curves, the removal, by this method, of the uncertainties of extrapolation constitutes an essential advantage over the previous stopping potential method.

Conclusion

The author takes pleasure in acknowledging his indebtedness to Professor W. V. Houston, who suggested this investigation, and has taken an active interest in its progress, and to all staff members of the Norman Bridge Laboratory who have generously contributed their advice on many technical problems. Special acknowledgment is due to the Institute's glass blower, Mr. W. Clancy, whose unusual skill and patience in the construction of the experimental tubes contributed materially to the progress of the investigation.

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