Publications, 1931 - 1940

PHOTOELECTRIC AND THERMIONIC EMISSION FROM COMPOSITE SURFACES

BY

WAYNE B. NOTTINGHAM

Photoelectric and Thermionic Emission from Composite Surfaces

By Wayne B. Nottingham*

Massachusetts Institute of Technology

(Received August 6, 1932)

Classical methods when applied to photoelectric and thermionic emission from composite surfaces often lead to inconsistent results. A study of the thermionic emission, with a new thyratron circuit for heating tungsten and thoriated tungsten filaments, reveals that many points can be explained if we take into consideration the complex form of the potential barrier produced by an atom layer of electropositive metal when deposited on an "electronegative" base. From an experimental knowledge of the transmission coefficient of the barrier as a function of electron energy and the use of the Wentzel approximation for the transmission coefficient $D(v) = \exp - (4\pi/h)\int_{x_1}^{x_2} (2mH)^{1/2}dx)$, it is possible to calculate the shape of the barrier which turns out to be practically parabolic and about 4.3×10^{-8} cm in width one electron-volt below the top of the hill. Since the width and perhaps the height of the barrier seem to depend upon the temperature, it becomes clear that the Richardson-Dushman equation $I = AT^2 \exp(-b_0/T)$ is applicable only as an empirical representation of the data obtained with composite surfaces as emitters. This surface model explains very naturally the fact that the electrons emitted from a composite have an apparently Maxwellian distribution of velocities corresponding to a temperature fifty percent higher than that of the filament as reported by Koller and Rothe. It also gives a qualitative explanation of the observed dependence of the photoelectric long wavelength limit on the applied potential for thin films of sodium on nickel using very low fields.

Introduction

A COMPOSITE surface may be formed by depositing a thin layer of "electropositive" metal on a more "electronegative" one. Many investigators have found such surfaces to be more active thermionic and photoelectric emitters of electrons than either of the metallic constituents when taken in bulk. The thermionic current from a composite surface has been observed to depend on the temperature according to the Richardson equation $I = AT^2 \exp(-e\phi_0/kT)$ but differences between values of the work function ϕ_0 for different surfaces are not in satisfactory agreement with measurements of the contact difference in potential.[1]

The thermionic current varies with the accelerating field according to the Schottky mirror image theory[2] only for high fields.[3] At low fields the current falls much more rapidly than might be expected. Electrons emitted from a

---

* Fellow at the Bartol Research Foundation, Swarthmore, Pennsylvania, while carrying on the experimental work reported in this paper.

[1] I. Langmuir and K. H. Kingdon, Phys. Rev. **34**, 129 (1929).

[2] K. T. Compton and I. Langmuir, Rev. Mod. Phys. **2**, 123 (1930). See part B (5) for complete discussion.

[3] J. Becker and D. Mueller, Phys. Rev. **31**, 431 (1928); N. B. Reynolds, Phys. Rev. **35**, 158 (1930).

clean tungsten surface have been found to have a Maxwellian distribution of velocities[4] with a temperature equal to that of the filament but according to the results of Koller[5] and Rothe,[6] the apparent temperature of the electrons emitted from a composite surface is at least fifty percent higher than that of the emitting surface.

The above difficulties serve to illustrate the nature of some of the broader aspects of the problem at hand. We see that the observed results follow more or less according to the theories which have been well able to describe the thermionic emission from clean surfaces, but in almost every case there is a definite difference between observation and theory which is much larger than the experimental error. It is the object of the first part of this paper to describe as concisely as possible a series of experiments on the thermionic emission from thoriated filaments and the photoelectric emission from films of sodium deposited on nickel. In the latter part of this paper an attempt will be made to coordinate these new, and many of the old, results into a theory.

The experimental work upon which this paper depends was carried on at the Bartol Research Foundation with the liberal support of the Franklin Institute of Philadelphia between January, 1929, and August, 1931.

THE EXPERIMENTAL PROBLEM

From his studies of *photoelectric emission*, Dr. Ives[7] reported that as a thin film of sodium is deposited on a platinum surface, "the long wave limit of the emission first moves toward the red as the film increases in thickness and then, after the maximum of the photoelectric sensitiveness is passed, moves back toward the violet." Later, Ives and Olpin[8] reported that in the cases of lithium, sodium, potassium, rubidium and caesium this maximum "excursion" of the long wave limit was "found to coincide with the first line of the principal series, i.e., the resonance potential." Stimulated by these researches an attempt was made to investigate the energy distribution of the emitted electrons and test the linearity of photoelectric response of these surfaces to light of a wave-length very near that of the threshold. What was thought to be a nonlinearity in the response[9] and reported as such was later found[10] to be due to a nonlinearity in the amplifier system used to measure the extremely small currents. These studies also yielded results which were interpreted as a departure from Einstein's photoelectric equation.[11] The experimental data, which are now being published in detail for the first time, can apparently be explained on the wave-mechanical theory of electron transmission through a potential barrier.

[4] L. H. Germer, Phys. Rev. **25**, 795 (1925).
[5] L. R. Koller, Phys. Rev. **25**, 671 (1925).
[6] H. Rothe, Zeits. f. Physik **37**, 414 (1926).
[7] H. E. Ives, Astrophys. J. **60**, 209 (1924).
[8] Ives and Olpin, Phys. Rev. **33**, 281 (1929); **34**, 117 (1929).
[9] W. B. Nottingham, Phys. Rev. **33**, 633 (1929).
[10] W. B. Nottingham, Phys. Rev. **35**, 669 (1930).
[11] W. B. Nottingham, Phys. Rev. **33**, 1081 (1929).

In the field of *thermionic emission*, Reynolds[12] reported work which might be considered as an extension of that of Becker and Mueller[13] on the variation of the thermionic emission from a thoriated tungsten filament as a function of the electric field. The fact that the results reported by Reynolds could be interpreted qualitatively with the same "surface models" as those used in the interpretation of the photoelectric[14] emission data made it clear that a thorough investigation of the problem of the thermionic emission from a thoriated tungsten wire using small retarding and accelerating potentials on the collector, might greatly extend our understanding of the general problem of composite surface emitters. Two important difficulties of the experiment not satisfactorily disposed of by Reynolds were (1) the lack of uniformity of potential difference between the filament and the collector due to the filament heating current and (2) the adequate insulation of the collector. Preliminary work done by the author before these difficulties were overcome verified the general experimental results of Reynolds, but suggested new explanations.

With the help of wave mechanics, it is now possible to explain many of the observed facts of electron emission from composite surfaces by considering the transmission *through* the potential barrier produced by an atom layer of an electropositive element when deposited on a more electronegative base. These points will be discussed in detail later in this paper. Since practically all of the experimental work being reported in this paper was done before an application of the present theory[15] was made, it will not be difficult to discover points in the argument which can be disposed of by additional experiments. Although there are a number of such investigations under way already, it has been thought worth while to report in detail on the results obtained to date, partly to help other workers in the field and partly to invite criticism of the experiments and theories presented here.

Electric Circuits

a. Filament heating circuit

In order to heat the filament and yet have no drop in potential over it during measurement an intermittent heating system like that used so successfully by Germer[16] was employed. Instead of using a 500 cycle generator and tungar rectifiers as done by Germer, a thyratron "inverter" circuit was developed at the suggestion of Dr. A. W. Hull and patterned essentially after his circuit.[17] This is shown in Fig. 1.

With thyratron T_1 conducting 0.25 ampere the plate P_1 is only about 12 volts positive with respect to the filament and there is a difference in potential of 250 volts across the condenser C. When the oscillator voltage carries

[12] N. B. Reynolds, Phys. Rev. **35**, 158 (1930).
[13] J. Becker and D. Mueller, Phys. Rev. **31**, 431 (1928).
[14] W. B. Nottingham, Phys. Rev. **35**, 669 (1930).
[15] W. B. Nottingham, Phys. Rev. **38**, 1918 (1931).
[16] L. H. Germer, Phys. Rev. **25**, 795 (1925).
[17] A. W. Hull, Gen. Elec. Rev. **32**, 390 (1929).

the grid G_2 of thyratron T_2 *positive*, this tube suddenly becomes conducting and the quick drop of potential at P_2 causes that of P_1 to become very negative with respect to F_1. If the de-ionization time is shorter than the time required for the condenser C to charge up through the 1000 ohm resistance, then thyratron T_1 will remain nonconducting until the next half cycle of the oscillator at which time G_1 is made positive and the cycle of operation as described above is repeated. It is easy to see that the wave form of the current through T_1 will be qualitatively that of Fig. 2.

The part of the cycle during which the filament is heated is shown crosshatched. The sharp peaks showing reverse current for an extremely short
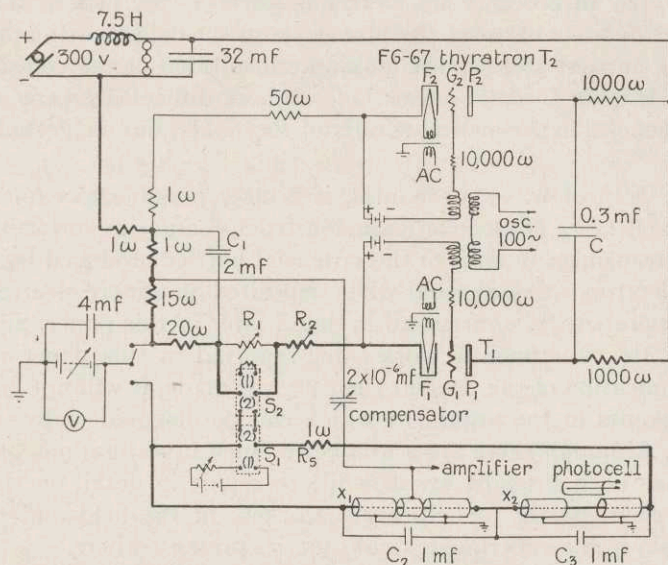

Fig. 1. Thyratron[18] inverter circuit for heating filament with pulsating current.

time were assumed to be there on indirect evidence only. The condensers C_1, C_2 and C_3 were introduced to eliminate the effect due to this reverse current. Now that a cathode-ray oscillograph which can follow such rapid

[18] Since the thyratron has not yet come into common use in physical research, it will perhaps be desirable to describe very briefly its operating characteristics.

The thyratron is a gas filled (mercury vapor) three-electrode tube containing a cathode, anode and grid. With positive potentials of a few hundred volts on the plate, a few volts negative grid potential prevents the electron current flow from cathode to anode. At a certain critical value of grid bias enough current flows, however, to start ionization in the gas. Within a few microseconds an arc is fully developed with the current limited only by the external circuit under normal conditions. After the formation of the arc the grid has no control over the flow of current. Thus in a circuit with a d.c. plate supply, provision must be made for stopping the flow of current through the thyratron after it has once been started by effectively cutting off the plate supply. It is for this reason that we have the plates of the two thyratrons of Fig. 1 connected together by the 0.3 mf condenser.

For detailed discussion see: A. W. Hull, reference 17; W. B. Nottingham, J. Frank. Inst. **211**, 271 (1931); W. B. Nottingham, J. Frank. Inst. **211**, 751 (1931).

changes in potential is available, the exact nature of this objectionable reverse peak is to be investigated.

The power was supplied by a 300 volt d. c. generator driven by a three-quarter hp, three phase synchronous motor. With the generator brushes in good condition the output voltage was steady to within about 0.1 percent for a considerable period of time.

An inductance and condenser were used as shown to eliminate the commutator ripple.

b. Adjustment of filament temperature

The Langmuir and Jones[19] temperature scale for pure tungsten was used. Approximate values of the temperature were calculated from measurements of the current flowing and the diameter of the filament. With this approximate temperature, the end loss correction was calculated[20] and the final temperature was determined from the Langmuir-Jones table for $V'(A')^{1/3}$ which involves measurement of the filament length, voltage drop, and current.
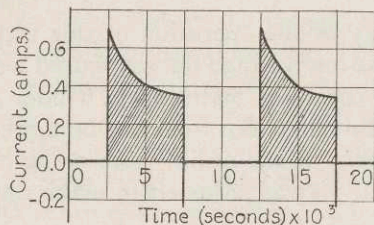

Fig. 2. Wave form of current through thyratron T_1.

The current was determined by measuring the drop in potential over a standardized one ohm resistance R_s using a Leeds and Northrup type K potentiometer. The voltage drop over the filament was accurately measured using a type K potentiometer with ten times the usual current flowing through the coils and slide wire. With this method, it was possible to measure accurately d.c. voltages as high as 16.1 volts. By throwing the switch S_1 to position (1) the filament under test X_1 and the auxiliary filament X_2 were heated by d.c. These two filaments were of approximately equal length and from the same stock. Under this condition the temperature of the test filament could be determined and the light emitted from the auxiliary filament accurately measured by a null method. With switches S_1 and S_2 both in position (2) filaments X_1 and X_2 could be heated with pulsating current. By adjusting R_1 and R_2 the temperature of X_2 was brought very accurately to that previously determined by observing the photoelectric current produced by the light emitted from X_2. It was then assumed that the temperature of the test filament was the same as that determined from the d.c. measurements. The frequency of the pulsating current was varied from 100 to 500 cycles per second with no change in the thermionic current observed. Prac-

[19] I. Langmuir and H. A. Jones, Gen. Elec. Rev. **30**, 310, 354, 408 (1927).
[20] Langmuir, McLane and Blodgett, Phys. Rev. **35**, 478 (1930).

tically all measurements were therefore carried out with the oscillator set to deliver 100 cycles.

c. Amplifier circuit for photoelectric current

The photoelectric current produced by the light from the auxiliary filament X_2 was measured with the circuit shown in Fig. 3.
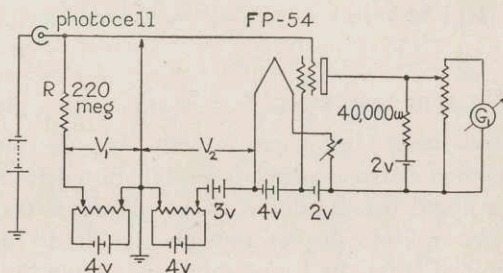

Fig. 3. Amplifier circuit for photoelectric current.

The underlying theory of the operation of this type of circuit has been discussed elsewhere.[21] The low voltage batteries used were 150 amp.-hr. storage batteries and were carefully maintained. Under these conditions the single tube amplifier circuit has been found to be more steady than the two tube circuit and much easier to maintain. With no light on the photoelectric cell and V_1 zero, potential V_2 was adjusted to make the current through the galvanometer G_1 zero.
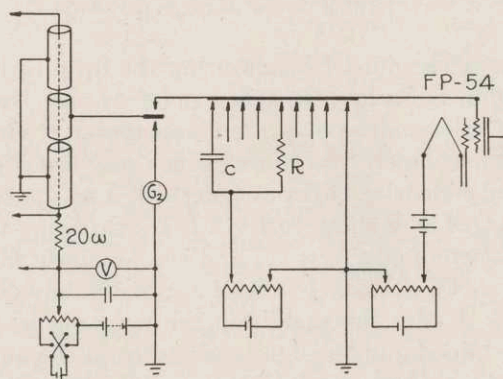

Fig. 4. Grid circuit of vacuum tube amplifier used to measure thermionic current.

When the filaments X_1 and X_2 were heated by direct current, the light from the auxiliary filament X_2 falling on the cell caused a current to flow through R. The potential V_1 was then adjusted to bring the galvanometer to zero. The pulsating current was adjusted to maintain the light emitted from X_2 constant as indicated by the galvanometer.

[21] W. B. Nottingham, J. Frank. Inst. 209, 287 (1930); L. A. DuBridge, Phys. Rev. 37, 392 (1931).

d. Amplifier circuit for thermionic current

The circuit for measuring the thermionic current was very similar to that of Fig. 3, except that a 25,00-b type *R* galvanometer was used in place of a 2500-e instrument. Instead of a standard FP-54 vacuum tube, an early model of the same general design having a higher mutual conductance was used with a resulting maximum sensitivity of about 10.5 cm per millivolt applied to the grid. Certain special features incorporated in the grid circuit are shown in Fig. 4.

Condensers or resistances were used in the grid circuit to give a means of varying the sensitivity. The capacities of a specially selected set of fixed condensers ranged from 0.002 mf to 8.0 mf and the values of resistance ranged from 5000 megohms to zero. With the capacities it was possible to use the rate of deflection method of measurement for the current range of 10^{-13} to 5×10^{-8} amp after which the galvanometer G_2 could be used directly.

EXPERIMENTAL TUBES

a. Construction and preparation

The filaments, kindly furnished by the Research Laboratory of the General Electric Company, were of types known as "*T*," "*E*," and "*C*" wire. "*T*" and "*E*" were thoriated tungsten, the latter being free from carbon and the "*C*" wire was pure tungsten. The wire diameter was approximately 1.6 mils and the length of the filaments were about 10.8 cm. The collector was 1 cm in diameter and about 2.5 cm long. Cylinders of the same diameter and about 4 cm long were used to make the field uniform near the ends of the collector and also receive the emission from the cool ends of the filament.

The collector was supported on long "beads" held by "sealed-in" tungsten connections maintained at the collector potential. A special lead was brought out for the collector to give high insulation from the other leads coming through the press. All the metal parts were made of "baked out" nickel or tungsten. A rather elaborate outgassing schedule was carried out with oven baking at temperatures up to 400°C and heating of the collectors with the induction furnace as well as extensive heating of the filament.

b. Activation of the filament

Langmuir and Rogers[22] found that tungsten wire containing about one percent of thorium oxide could be made, by a proper heat treatment, a much more efficient emitter of electrons than pure tungsten at filament temperatures of less than 2000°K. The details of this process are given in full by Langmuir[23] and also by Dushman[24]. At a filament temperature of 2700°K to 2900°K some of the thorium oxide decomposes leaving a small amount of thorium between the tungsten crystals and near enough to the surface so that the thorium can diffuse, at the activation temperature, to the surface and form a layer of thorium atoms. The filament temperature must be 1800°K

[22] I. Langmuir and W. Rogers, Phys. Rev. **4,** 544 (1914).
[23] I. Langmuir, Phys. Rev. **22,** 357 (1923).
[24] S. Dushman, Rev. Mod. Phys. **2,** 381 (1930).

or greater for this "activation" to take place at a reasonably rapid rate. After a long time of activation the equilibrium surface condition is governed by the rate of diffusion and the rate of evaporation.

Fig. 5 shows a typical set of curves[25] representing the first activation carried out in steps at $T_a = 1920°$K.

The accumulated time is plotted along the abscissa while the thermionic current observed at a test temperature of $T_t = 1230°$K and a collector potential of $+20.0$ volts is plotted as the ordinate. The maximum found after 90 minutes' acitvation is undoubtedly related to the maxima found by Becker[26] in his studies of the thermionic emission from a caesium covered tungsten filament. In Becker's work the surface coverage corresponding to the maximum emission was thought to correspond to a monatomic layer of caesium
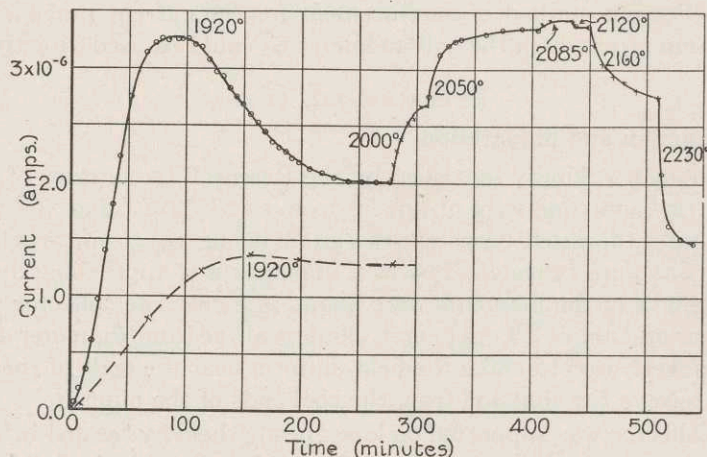

Fig. 5. Activation of a thoriated filament with test temperature 1230°K (T wire). Solid curves applied accelerating potential 20 volts; dashed curve potential 2.0 volts.

atoms on the tungsten and by analogy it is thought that the maximum in Fig. 5 corresponds to a monatomic layer of thorium atoms on tungsten. With $T_a = 1920°$K the equilibrium condition was practically reached after 280 minutes of activation. By raising the activation temperature to 2000°K this equilibrium was disturbed immediately and a sharp *rise* in the curve was observed. At about 2100°K the *equilibrium* condition corresponds very closely to that of the maximum observed at 90 minutes. Activation at still higher temperatures, leaves the surface only partly covered. At low fields the maximum practically disappears. The significance of this observation will be discussed later.

The main features of the activation curve shown in Fig. 5 are thus easily understood. There are, however, many details concerning the activation process which may be of importance in the explanation of results obtained with more complicated composite surfaces. For example, after a filament has been

[25] W. B. Nottingham, Phys. Rev. **35**, 1128 (1930).
[26] J. A. Becker, Phys. Rev. **28**, 341 (1926).

fully activated, the emission has been observed to *increase* two to six fold in the cource of time even though the filament is maintained at liquid air temperature between observations. This effect is undoubtedly brought about by the adsorption of some gas. A detailed examination of this effect is being undertaken.

MEASUREMENT OF THERMIONIC CURRENT

a. Velocity distributions

The experimental difficulties associated with the measurement of the thermionic emission from composite surfaces have long been recognized. For example, work function measurements involving a change in temperature of
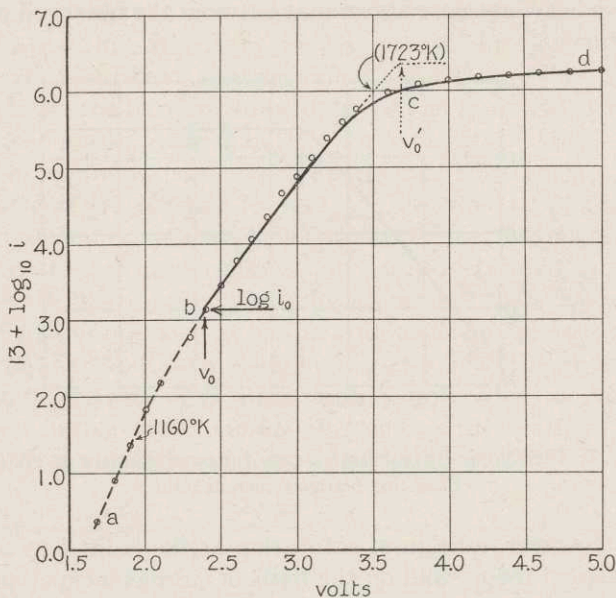

Fig. 6. Thermionic current from a fully activated filament at 1160°K (pulsating filament current used). Range *ab* calculated by Schottky equation. Range *bcd* identical to that observed with tungsten filament at 1723°K.

the emitter are often invalidated because the surface conditions may change with the temperature. Some of these changes are slow enough to be observed; others may be rapid and escape observation. Surface conditions also change with an alteration in the current drawn from the filament and may thus be subject to variation with applied field and temperature. Changes at the surface of the collector as indicated by a shift in contact potential have also been observed.[27] In order to minimize these difficulties a definite procedure of measurement was adopted. Before beginning a set of measurements, maxima of accelerating potential (usually less than 10 volts) and temperature (about 1200°K) were decided upon. During the run these standard conditions were maintained except during the time required for each reading, i.e., after

[27] W. B. Nottingham, Phys. Rev. **39**, 183 (1932).

making a reading standard conditions were reproduced before taking the next. In Fig. 6 a typical curve is given showing the thermionic current received by the collector as a function of the applied potential difference between the collector and the filament.

The points enclosed in circles are the observed points. The curves drawn through the points are of theoretical significance. The dashed curve from *a* to *b* is the theoretical curve, computed from the classical equation developed by Schottky,[28] for the current received against a retarding potential by a cylindrical collector from a filament of small diameter supported along the axis of the cylinder, with the distribution of velocities assumed to be Maxwellian and the temperature that of the filament. Over the part of the range covered, there is a very close agreement between the observed points and the theoretical curve.
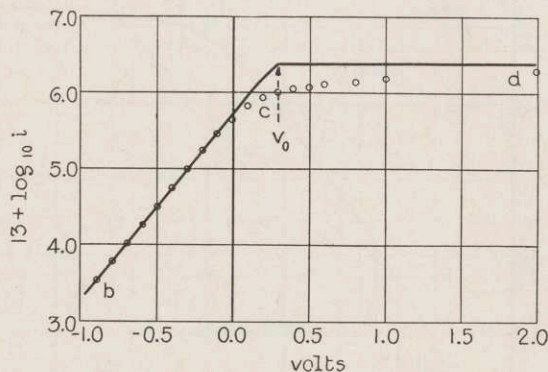

Fig. 7. Thermionic current from a pure tungsten filament at 1723°K.
(Pulsating filament current used.)

There is, however, no sign of saturation at the point *b* as one would expect from classical theory and on the basis of Germer's experience with pure tungsten filaments. It is only natural to suggest that the observed results are distorted by space charge effects which would invalidate a calculation using the Schottky theory. In order to test this point measurements were made on a filament of "*E*" wire in the *completely deactivated* state and also on a pure tungsten "*C*" wire. These filaments were heated to such a temperature that the saturation current was exactly equal to that observed on the activated filament with about 6 volts applied potential. The results of one of these tests are shown in Fig. 7.

In the case of the clean tungsten filament, the Schottky curve and the observed points agree almost perfectly up to within about 0.2 volt of the theoretical saturation point. At lower temperatures the agreement is even closer. These results are in very close agreement with those of Germer which showed that space charge effects could be neglected in the case of pure tungsten filaments up to about 1830°K. Since space charge phenomena are controlled

[28] Walter Schottky, Ann. d. Physik **44**, 1011 (1914). Germer's table in Phys. Rev. **25**, 795 (1925) was used for all of these computations.

primarily by the current density and the electric field near the surface of the filament, the fact that the space charge can be neglected in the case of the pure tungsten indicates that it can also be neglected in the case of an activated thoriated filament for temperatures less than 1200°K.

A comparison was made between the observed curves for clean tungsten at 1723°K and thoriated tungsten at 1160°K and it was found that the curves were almost identical over the range *b c d* of Figs 6 and 7. The range *bc* in the case of pure tungsten indicates that the velocity distribution of the electrons is Maxwellian with a temperature of 1723°K. *But the similar range bc for the thoriated filament is also characteristic of* 1723°K, *although the temperature of the filament was only* 1160°K. This is a fundamentally important result, and it will be shown that the new theories of transmission through potential barriers can give just this result, i.e., given a potential barrier of the required dimensions, the distribution of electron velocities of those electrons which are transmitted through the barrier can be described as Maxwellian with a temperature 45 to 50 percent *higher* than that of the filament.

Measurements of the velocity distribution of the electrons from thoriated filaments operated at 987°K, 1045°K and 1103°K showed the same agreement between observed points and the Schottky curve for the range of applied potential negative to that designated as "v_0," while over the range of potential positive to "v_0" the distribution was quite accurately the same as that of a pure tungsten filament operated at temperature high enough to give the same saturation current at about 6 volts applied potential. With the filament in a particular state of activation all of the values of "v_0" for the various temperatures were the same within about ±0.1 volt and the ratio of these temperatures was extraordinarily constant, as indicated by Table I.

TABLE I.

Thoriated fil. temp.	Case 1		Case 2	
	Tungsten	Ratio	Tungsten	Ratio
987	1458	1.48	1490	1.51
1045	1540	1.47	1570	1.50
1103	1620	1.47	1650	1.50
1160	1685	1.45	1723	1.48

It will be noticed that these results check well with the estimations made by Koller[5] and Rothe[6] that the electron temperature as indicated by the apparent velocity distribution is 50 percent higher than that of the filament, although their work applied to the oxide-coated filament. The theory to be proposed here would presumably be approximately applicable also to this more complicated type of surface.

These experiments have therefore suggested the existence of two groups of emitted electrons, the one with higher speeds classically characteristic of the filament temperature and the other (comprising nearly 99.9 percent of the saturation emission) being apparently characteristic of a 50 percent higher temperature. The discovery of the former group is due to the experimental extension of the velocity distribution curve through a larger range of

values than is usually done. The latter group, which has heretofore been treated classically is, on the present theory, a group which could not escape classically but is allowed to escape by wave mechanics according to a probability factor which depends jointly on the "potential barrier" created by the adsorbed electropositive layer and on the applied potential.

b. Work-function measurements

Really accurate determinations of the thermionic constants ϕ_0 and A of the Richardson equation $I = A\ T^2 \exp\ -e\phi_0/kT$, are exceptionally difficult when the range of permissible temperature variation is small. Data which were obtained show definitely that both of the constants depend very decidedly on the exact state of the surface. No two activation and filament aging curves have been observed which are exactly alike and therefore no two values of ϕ_0 and A are the same although attempts have been made to control activation conditions accurately. Studies now under way will no doubt throw new light on this question.

With an applied accelerating potential of 6.0 volts, the observed values of ϕ_0 ranged from 2.38 to 2.83 electron-volts while the value of A ranged from 0.56 to 10.2 amp. per cm² per deg.².

One of the best determinations gave $\phi_0 = 2.64$ and $A = 3.2$ which compare very satisfactorily with those of Dushman and Ewald[29] of $\phi_0 = 2.63$ and $A = 3.0$. Measurements with applied potentials of 2.0 and 2.4 volts, corresponding to values of v_0 as defined above for various conditions of activation, gave ϕ_0 between 3.1 and 3.5 electron-volts and A between 10 and 60 amp. per cm² per deg.².

The results reported[30] for solid thorium are $\phi_0 = 3.35$ v with $A = 60$. This suggests that the effective work function of a composite surface measured at a very low potential such as v_0 changes from that of the base metal to that of the surface metal as the film thickness increases to that of a single layer or greater. Thus we have a qualitative explanation of the fact that the activation curve of Fig. 5 taken at a very low field shows no maximum. The analogous result has been found photoelectrically.

PHOTOELECTRIC EXPERIMENTS

Although considerable work was done on the problem, photoelectric emission from composite surfaces, very little of it is of permanent value since the problem must be reinvestigated in the light of the recent theories of photoelectric effect such as that of Fowler.[31] The results reported here are therefore preliminary and show simply some of the more easily observed facts.

A sketch of one of the experimental tubes is shown in Fig. 8.

[29] S. Dushman and J. W. Ewald, Phys. Rev. **29**, 857 (1927).

[30] Dushman, Rev. Mod. Phys. **3**, 394 (1931). (Calculation based on data of C. Zwikker, Proc. Amst. Acad. Sci. **29**, 792 (1926). W. Espe gives $\phi_0 = 3.39$ v and $A = 70$ in Zeits. f. tech. Physik **10**, 489 (1929).

[31] R. H. Fowler, Phys. Rev. **38**, 45 (1931).

The collector c_1, c_2, c_3 was made in three parts and the circuit arranged so that only the current collected on c_2 was measured. The emitter was a nickel cylinder 8 mm in diameter and about 6 cm long mounted on a movable support. By means of the iron weight sealed into a glass envelope, this electrode could be moved to positions I, II or III. During the baking and exhaust it
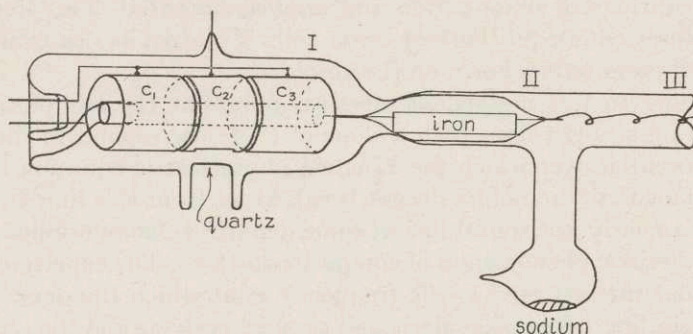

Fig. 8. Tube for study of photoelectric emission from a thin film of sodium on nickel.

was in position III. In position II sodium could be deposited on the surface by evaporation from the side tube. While in position I, the electrode was supported concentric with the collecting cylinders by a glass tube sealed in the end as shown. A slit in collector c_2 permitted the light to fall on the emitter after having entered the tube through the quartz window.
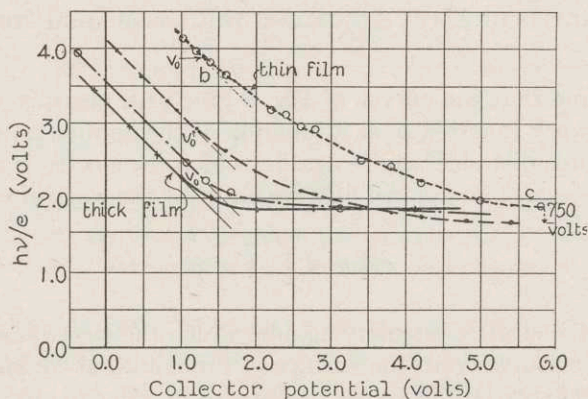

Fig. 9. Minimum-frequency limit as a function of applied potential.

The primary object of the study was to observe the dependence of the effective photoelectric long wave limit on film thickness and applied potential. The range of applied potential varied from a few volts retarding to about 700 volts accelerating. The most interesting results were obtained at low potentials and are shown in Fig. 9.

Over the range of applied potentials greater than 3 volts, the current was measured as a function of the wave-length holding the potential constant. The curve covering a range of current from 10^{-13} to 10^{-14} amp. was then extra-

polated into the axis to give the long wave limit. Over the range of small positive and negative potentials, the current was measured as a function of applied potential while the light frequency was constant. The extrapolation of these curves thus gave additional points for the limiting frequency at which an emission of the order of 10^{-14} amp. would take place under the particular conditions of illumination and applied potential. This limiting frequency expressed in equivalent electron volts is plotted as the ordinate while the applied potential is shown on the abscissa.

According to this method of plotting, points at the left of each curve which fall on straight lines with a slope of (-1) correspond to the range of applied potential over which the Einstein photoelectric equation is applicable. The fact that the points do not break away from this line and quickly approach a nearly horizontal line at some definite value of applied potential is a characteristic phenomenon of composite surfaces. The experimental facts of particular interest are (1) the frequency ν_0 at which the departure from the Einstein line takes place decreases progressively as the thickness of the film increases, presumably starting at that for nickel and finally reaching that for solid sodium; (2) with an accelerating potential of five volts or more the minimum-frequency "limit" undoubtedly decreases as the film thickness increases going through a "maximum excursion" and then returning to that of sodium in bulk. This fact was demonstrated by Ives[8] some years ago but it is interesting to note that the extent of this "excursion" is considerably greater than that of the resonance lines of sodium.

Analysis of Data According to Classical Methods

a. Theory*

If we assume that the curves of Fig. 9 give us a measure of the *effective* photoelectric work function ϕ_e as a function of the applied potential, we can deduce the "force-distance" curve against which the electrons must be working. In the absence of an applied field we have for the work of escape:

$$e\phi_0 = e \int_0^\infty F(s)ds \tag{1}$$

where $F(s)$ is the electric intensity against which the electron is working and s is distance measured from the surface of the metal. If we have an applied field the force against which an electron works in order to escape is increased or decreased. The decrease in work which the electron must do in order to escape with the help of an accelerating field is

$$\Delta\phi_e = \int_0^{s_c} V\phi(s)ds + \int_{s_c}^\infty F(s)ds. \tag{2}$$

Here s_c is the critical distance which the electron must go in order to escape V is the difference in potential between the electrodes and $\phi(s)$ depends on

---

* The theory presented here has undoubtedly been worked out by others. A less general discussion is given by Hughes and DuBridge, *Photoelectric Phenomena* p. 210.

the geometry of the electrodes. The critical distance is of course given by the condition

$$V\phi(s_c) = F(s_c). \tag{3}$$

If we make a small variation in V we obtain

$$\Delta\phi_e + (d(\Delta\phi_e)/dV)\delta V = \int_0^{s_c+(ds_c/dV)\delta V} (V + \delta V)\phi(s)ds + \int_{s_c+(ds_c/dV)\delta V}^{\infty} F(s)ds. \tag{4}$$

After subtracting Eq. (2) from Eq. (4) it follows that

$$d(\phi_e)/dV = \int_0^{s_c} \phi(s)ds \tag{5}$$

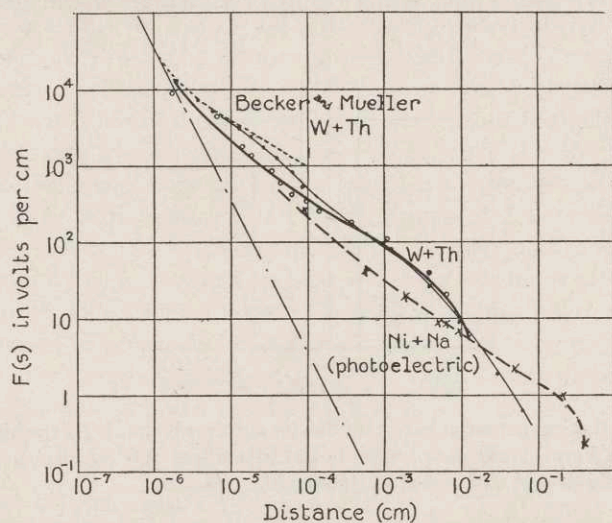since $d(\Delta\phi_e)/dV = d(\phi_e)/dV$.

Fig. 10. Computed force functions for various composite surfaces. Solid lines thoriated tungsten; dotted line Becker-Mueller data thoriated tungsten; dashed line sodium on nickel observed photoelectrically. Dot-dash line given by mirror image theory.

The left-hand side of Eq. (5) comes from the slope of such curves as those of Fig. 9. If $\phi(s)$ can be integrated s_1 can be determined as a function of V and using Eq. (3), $F(s)$ can be deduced. For infinite cylinders we obtain

$$s_c = r\big[(R/r)^{d\phi_e/dV} - 1\big] \tag{6}$$

where R = radius of outer and r = radius of inner cylinder.

Thermionic data can also be analyzed in this way if we assume that all current changes with applied potential are due to an alteration in the work function. Differentiating the Richardson equation we obtain

$$d(\log i)/dV = -(e/kt)(d\phi_e/dV). \tag{7}$$

In this way $d\phi_e/dV$ as a function of V can be obtained from observed data and Eqs. (6) and (3) can be used to determine the "force function" $F(s)$.

b. Experimental test of classical method

The results of the experimental test of this method of analysis are best illustrated by the curves of Fig. 10.

It is interesting to note that the general trend of the curves is remarkably uniform. It is not difficult to show that data taken at different temperatures, such as that summarized in Table I above, will give the same force function if the temperature ratios of columns three and five are constant.

There are at least two serious objections to this method of analysis which are (1) forces as great as 5.0 to 10.0 volts per cm at distances as great as 10^{-2} cm from the surface are certainly impossible, and (2) determinations of the thermionic constant A made with applied potentials between 2.6 and 6.0 volts have not been found to be constant as is required if the entire change in thermionic current with field is the result of a change in the effective work function.
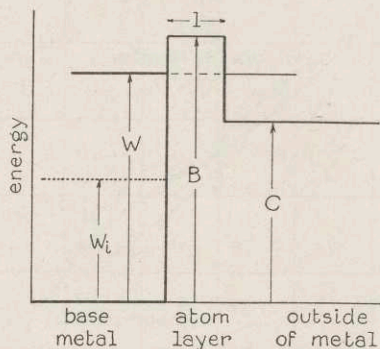

Fig. 11. Hypothetical potential barrier of Fowler and Nordheim. W_i is the highest electron energy assuming a Fermi-Dirac distribution in the base metal at $0°$K. Electrons with energy $B > W > C$ must pass *through* a barrier of width l in order to escape.

TRANSMISSION THROUGH POTENTIAL BARRIER EXPLAINS RESULTS AT LOW FIELDS

a. Theory and application to thermionic data

Although the theories of Fowler[32] and Nordheim[33] and the approximate solution to the wave equation used by Wentzel[34] and others have been known for some years, no applications of these results to the voltage-current thermionic curves were made until last year.[15] It is clear that a hypothetical potential barrier of the Fowler-Nordheim type, shown in Fig. 11, will give results qualitatively like those shown in Fig. 6.

Upon heating, the electrons in a metal acquire energies greater than W_i. Those with energy greater than B can escape and the probability of escape upon approach to the boundary should be independent of the energy. The distribution of velocities of these electrons will of course follow the classical

[32] R. H. Fowler, Proc. Roy. Soc. **A122**, 36 (1929).
[33] L. Nordheim, Phys. Zeits. **30**, 177 (1929). Further bibliography here.
[34] Wentzel, Zeits. f. Physik **38**, 518 (1926).

laws and therefore be practically Maxwellian as is indicated by the observed curve ab of Fig. 6. For electrons of energy $W < B$ the probability transmission is distinctly less than that for $W > B$ and is furthermore a function of the energy W. Since the transmission coefficient decreases as W decreases the group of electrons with energy $B > W > C$ received by a collector will certainly not have a Maxwellian distribution at the temperature of the filament and if they have anything like a Maxwellian distribution at all it will certainly correspond to a temperature considerably higher than that of the filament since the transmission coefficient decreases with decreasing W thus favoring the high velocity electrons.

With a barrier of this type in mind, we see that the electron emission received with the collector at the potential v_0 (Fig. 6) corresponds to all of the electrons with energies greater than B.

From the fact that the velocity distribution of these electrons is Maxwellian at the temperature of the filament, we can calculate the number of electrons with energy greater than W which approach the barrier from within the metal and can therefore calculate the transmission coefficient as a function of W which must be obtained in order to produce the observed current-voltage curve. This was done using the Nordheim equation. For this B and C of Fig. 11 were held constant and three values of l were determined for three arbitrary values of W. The smooth curve drawn through the points looked very much like a parabola and the width at 1.0 electron-volt below the top of the "hill" was 4.5×10^{-8} cm. This result suggested that the barrier might be assumed to be parabolic and the Wentzel equation used.

The current-voltage characteristic of Fig. 6 can be idealized as shown in Fig. 12. The line abb' is given by the equation

$$\log_\epsilon i = \log_\epsilon i_0 + (e/kT_1)(v - v_0)/300 \tag{8}$$

while the line $c'c$ is given by

$$\log_\epsilon i = \log_\epsilon i_2 + (e/kT_2)(v - v_0)/300. \tag{9}$$

We know that the complete curve must be given by

$$i = i_0 \frac{e}{300 kT_1} \int_{-\infty}^{v} \epsilon^{e(v-v_0)/300 kT_1} D(v) dv \tag{10}$$

where $D(v)$ is the transmission coefficient. Our experiments show that we may take

$$D(v) = 1 \text{ for } (v - v_0) < 0 \tag{11}$$

and

$$D(v) = \epsilon^{e(v-v_0)(1/T_2 - 1/T_1)/300 k} \text{ for } v - v_0 > 0, \tag{12}$$

for then Eq. (10) reduces to

$$i = i_0 \epsilon^{e(v-v_0)/300 kT_1} \text{ for } (v - v_0) < 0 \tag{13}$$

and

$$i = i_0 \left[1 + T_2/T_1(\epsilon^{e(v-v_0)/300 kT_2} - 1)\right] \text{ for } v - v_0 > 0. \tag{14}$$

For values of $(v-v_0) > 0.3$ volt, this equation reduces to Eq. (9) with $i_2 = i_0 T_2/T_1$. The complete curve given by Eqs. (13) and (14) is shown by the solid line of Fig. 12.
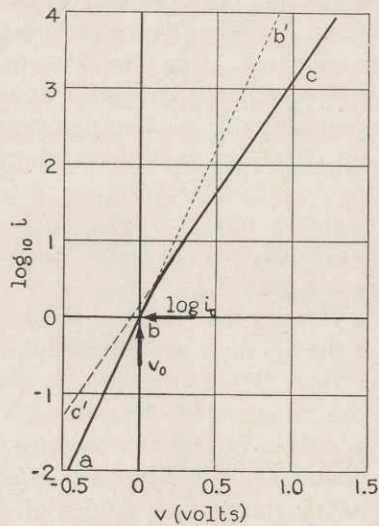

Fig. 12. Idealized current-voltage characteristic; equivalent to observed curve Fig. 6.

The Wentzel approximation gives the transmission coefficient for a barrier like that of Fig. 13 as

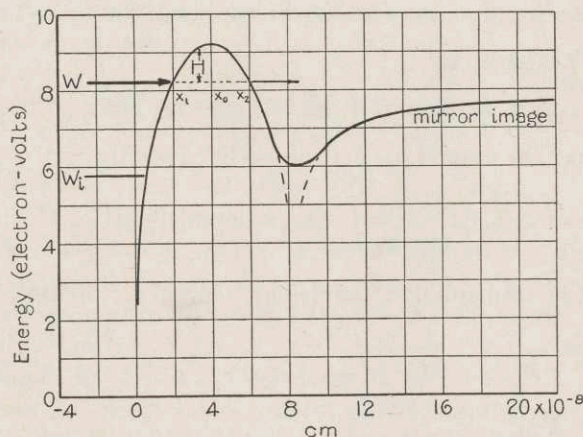$$D(v) = \epsilon^{-(4\pi/h)\int_{x_1}^{x_2}(2mH)^{1/2}dx}. \tag{15}$$

Fig. 13. Potential barrier calculated from observed data on thoriated filament $T = 1160°K$.

Let us assume that the potential curve is a parabola above the line at W and is given by

$$H = [e(v - v_0)/300] - C^2(x - x_0)^2 \tag{16}$$

where C is a constant and x_0 is the value of x at the maximum. Remembering that $H=0$ at x_1 and x_2 Eq. (15) reduces for this case to

$$D(v) = \epsilon^{[-2\pi^2(v-v_0)\epsilon(2m)^{1/2}/300\,hC]}. \tag{17}$$

Equating the empirical Eq. (12) and the theoretical Eq. (17) we can solve for C to get

$$C = [2\pi^2k(2m)^{1/2}/h]T_1T_2/(T_2 - T_1) \tag{18}$$

$$= 17.54 \times 10^{-3}T_1T_2/(T_2 - T_1). \tag{19}$$

The width of the barrier at any point is thus given as a function of v by

$$(x_2 - x_1) = 1.438 \times 10^{-4}[(T_2 - T_1)/T_1T_2](v - v_0)^{1/2}. \tag{20}$$

Putting in $T_1=1160$ and $T_2=1723$ we obtain $(x_2-x_1)=4.05\times10^{-8}$ cm with $(v-v_0)=1.0$ volt which is a reasonably good check on the result obtained using the Nordheim formula which gave 4.5×10^{-8} for the same data.

Using Eq. (20) we can calculate the appropriate barrier widths at one volt under the hill to fit the data summarized by Table I. The results are given in Table II.

TABLE II.

T_1	Barrier width $(v-v_0)=1$ volt Case I.	Case II.
987	4.77×10^{-8} cm	4.92×10^{-8} cm
1045	4.39	4.6
1103	4.15	4.33
1160	3.87	4.05

According to these data the effective width of the barrier seems to be *decreasing* with *increasing* temperature. This may be due to the inaccuracy of determining the appropriate value of T_2 although it is possibly a real effect since the transmission coefficient is probably determined more by the minimum distance of approach of the thorium atom to the tungsten surface rather than by its average position. If this result is true, it is evident that the use of the equation $I=AT^2\exp(-b_0/T)$ to determine the thermionic work function for composite surfaces cannot be of much theoretical significance since the observed current must depend on some "effective" work function which must be a complicated time average and also a function of the temperature. The area over which the emission actually takes place would also be decreased with the result that the surface area of the filament could not be used as is usually done to calculate a value of A.

This method of analysis thus provides a possible explanation for that part of the current-voltage characteristic which has been most troublesome for the classical theory, namely, that of the low voltage range. It also shows how the apparent velocity distribution of the electrons can very well be described as Maxwellian with a temperature 50 percent higher than that of the emitting surface as first pointed out by Koller.[5]

b. Application to photoelectric data

It is evident that a surface model similar to that of Fig. 13 is in qualitative agreement with the results shown by Fig. 9 in which we have the observed minimum-frequency limit shown as a function of the applied field. We see that if the collector potential is adjusted to turn back all electrons transmitted through the barrier, as the potential is varied, then the measured results can be expected to follow the Einstein equation and we will obtain a linear relation between potential and the minimum-frequency limit. Since the minimum-frequency limit as measured depends on the reception of a current of about 10^{-14} amp. at the collector over the range of small positive potentials, the apparent minimum-frequency limit will decrease less rapidly than before, thus accounting for the range bc of the curve shown in Fig. 9. With moderate accelerating fields the minimum-frequency limit is set primarily by the height of the plateau (Fig. 13) above the highest occupied energy level in the metal W_i. It is at once clear that photoelectric and thermionic studies should be carried out on the same filament under well controlled conditions for results so obtained are complimentary in many respects and would almost certainly give us the necessary information out of which a detailed picture of composite surface phenomena could be constructed.