THE WORK FUNCTION IN THERMIONIC AND PHOTOELECTRIC EMISSION

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A Dissertation for the M.Sc. Degree.

ProQuest Number: 10097179

ProQuest 10097179

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I. INTRODUCTION

The fact that air in contact with the surface of a
metal lost its insulating properties was known about two hun-
dred years ago, and during the nineteenth century much work
was done in investigating the phenomenon.   As a result of
this work it was found that at comparatively low temperatures
and high pressures a solid readily lost a positive charge,
but at high temperatures and low pressures both negative and
positive charges were lost.

In 1883 Edison found that there was a flow of elec-
tricity across a relatively good vacuum in a bulb containing
a glowing carbon filament. When he mounted an independent
electrode in the tube and connected this to a galvanometer,
he found that the galvanometer indicated a current when the
electrode was made positive with respect to the heated fila-
ment, but that there was no effect when it was made negative.
Preece and later Fleming showed that this effect was due to
the fact that negative electricity was lost by the heated
filament and collected by the positive electrode.

The precise nature of the carriers of the charge was
determined by J.J. Thomson, who found, by the cycloid method,

that the ratio of their charge to their mass was the same as for the negative charges of the Geissler tube, i.e., electrons.

At the same time as the experimental investigations on the loss of an electric charge from a hot metal were being carried out the phenomenon of the loss of an electric charge from an illuminated body was also being investigated. In 1887 Hertz found that a spark would pass across the spark gap in a secondary circuit when the gap was illuminated by the spark of the primary circuit, whereas no spark passed in the secondary circuit when the spark gap was shielded from the light of the primary circuit spark; in the next year Hallwachs found that a negative charge was lost from a plate illuminated by ultra-violet light, Elster and Geitel also found that some metals were sensitive to visible light, a plate acquiring a positive potential when illuminated.

The actual nature of the charge was established by J. J. Thomson, who showed that it is the negative electron as in the case of loss of charge from a hot metal. Lenard found that the energy of the emitted electron is independent of the intensity of the incident light, while the total number of emitted electrons is directly proportional to the intensity of the light. It was assumed, therefore, that the source of emitted electrons must be in the body of the metal, in all

probability being the free conduction ones which are held within the metal by the forces at the surface.

Lenard's discovery that the energy of an emitted electron is independent of the intensity of the light is inexplicable by the wave theory of light, this led Einstein to take the step of considering light as being corpuscular, each corpuscle or quantum having energy $h\nu$ where ν is the frequency of the light and h is Planck's radiation constant. If therefore the whole energy of the quantum is absorbed by the emitted electron the energy of the emitted electron is given by

$$E = \tfrac{1}{2}mv^2 = h\nu - w$$

where w is the work done in dragging the electron through the surface.

An electron emitted from a hot solid must also receive enough energy in order to pass through the surface. O.W. Richardson in 1901 developed a formula using the same assumptions as those of the classical theory of conduction in metals; he found the number of electrons whose energy at a temperature T is great enough for them to pass through the potential barrier at the surface of the metal. By this method he established the formula

$$i = AT^{\tfrac{1}{2}}e^{-w/kT}$$

where i = current per sq. cm. of the metal

T = absolute temperature

A, w and k are constants.

Soon after Richardson's derivation of this formula H.A. Wilson considered the emission of electrons from a hot metal as a reversible thermodynamical process and applied Clapeyron's latent heat equation to the evaporation of electrons from the metal obtaining the equation

$$i = A'T^{\frac{1}{2}}e^{-l_0/kT}$$

where A' and l_0 are constants.

In both phenomena, therefore, the electron must draw energy from some source in order that it may pass through the potential barrier at the surface of the metal. It would seem that, for any given metal, external conditions being the same, this amount of energy or the "work function", should be the same for both phenomena.

The development of the Sommerfeld electron theory has introduced new conceptions of the work function, and this, together with the improvement of vacuum technique, give sound evidence of the equality of the work functions in these two phenomena.

## II. EXPERIMENTAL DETERMINATION OF THE WORK FUNCTION

Considering Einstein's[1] photoelectric equation

$$\tfrac{1}{2} mv^2 = h\nu - w$$

where $\tfrac{1}{2} mv^2$ is the kinetic energy of the emitted electron, $h\nu$ is the energy given to the electron by a light quantum of frequency ν and w is the work done by the electron in escaping from the metal, if the frequency of the light is decreased the velocity of the emitted electrons will be decreased until they are finally stopped; if ν_0 is the frequency corresponding to zero velocity of the emitted electrons, then $w = h\nu_0$ and ν_0 is known as the threshold frequency for the given metal. In order to determine this threshold frequency experimentally the metal must be illuminated by monochromatic light of known frequency, and the emitted electrons collected at an electrode after being accelerated by an electrostatic field. The apparatus must be at the lowest possible pressure in order to avoid secondary ionisation effects and contamination of the surface of the metal. Also the shape of the collecting electrode must be such that all the electrons emitted from the metal reach the electrode and not exposed glass surfaces of the apparatus. The metal itself must be extremely carefully prepared so that its surface is uncontaminated and gas free.

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1. Einstein, Ann. d. Phys. 17, p. 132 (1905).

The two most usual designs of tube are a) spherical, b) cylindrical. The spherical type consists of a glass bulb with the metal M under experiment at its centre. The collecting electrode E is a metal
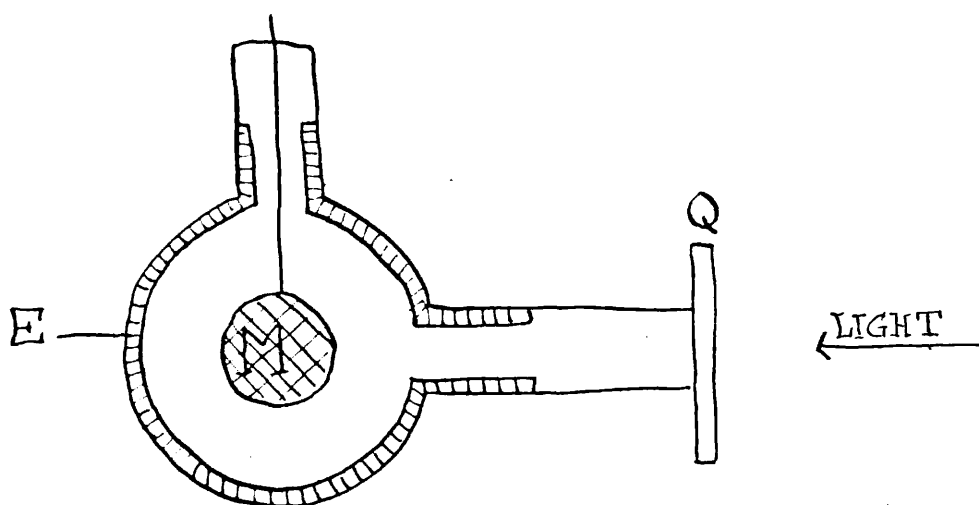
deposited on the glass walls of the bulb; light enters through the quartz window Q. In this type of tube all the light that passes through the window will fall either directly or by reflection on the metal M, and hence the maximum photoelectric current is obtained for a given intensity of the incident light. The collecting electrode E is made positive with respect to the metal M and therefore photoelectric emission from it is not possible and thus ensures that any emission currents measured arise from the metal at M alone.
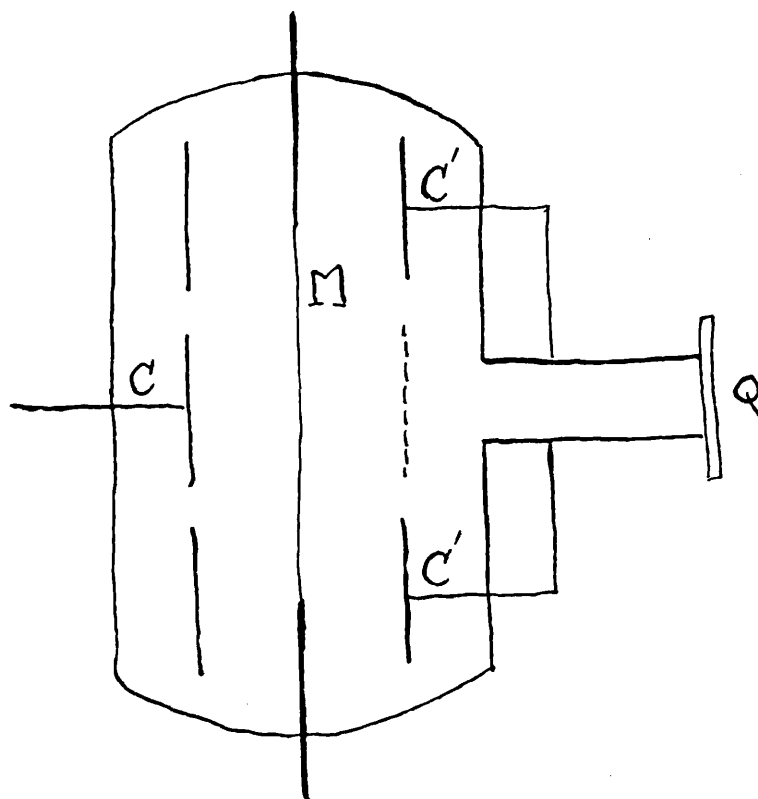
The cylindrical tube is also designed to give the maximum possible photoelectric current for a given intensity of incident light. In this tube the metal M under experiment is in the form of a wire and the collecting electrode C is cylindrical. A small patch of this electrode is perforated to admit the light that passes through the quartz window Q. The two cylinders C' act as guard rings. This has the advantage that it may also be used for thermionic measurements.

Since the value of the work function is dependent on the forces at the surface of the metal, it is essential that the metal shall be uncontaminated and free from all adsorbed

gases. The specimen of the metal is heated to a high temperature for many hours in a very high vacuum. The importance of this cleaning is shown by the fact that Du Bridge found that the photoelectric work function of platinum increased from 5 electron volts to 6·3 electron volts during the cleaning process. Allowance must also be made for the Schottky[1] effect, since the electron is emitted in an accelerating field.

It was found in determining the threshold frequency that its value was not definite but depended on the sensitivity of the measuring instruments; that is, if a graph is plotted of photoelectric current against frequency of the incident light, the curve approaches the frequency axis asymptotically. It will be seen in section III that the maximum kinetic energy of the electron within the metal before emission must be taken into account when considering the work function of a surface; on the basis of the Fermi statistics there is only a sharply defined maximum value of this kinetic energy at $0^\circ K$, it is seen therefore, that in determining the photoelectric threshold allowance should be made for this temperature effect, and the threshold corresponding to $0^\circ K$ determined.

The method of calculating the threshold at $0^\circ K$ from measurements made at other temperatures is due to Fowler[2], whose method was later modified by Du Bridge.[3]

1. Schottky, Zeits. f. Phys. 14, p. 63 (1923).
2. Fowler, Phys. Rev. 38, p. 45 (1931).
3. Du Bridge, Phys. Rev. 39.

Fowler deduced from theoretical considerations the following relationship:

$$I = AT^2 (W_a - h\nu)^{-\frac{1}{2}} f(x)$$

where I = photoelectric current per unit intensity of incident light.

W_a = potential drop at the surface of the metal.

$$x = (\frac{h\nu - \phi}{kT}) \quad \text{where} \quad \phi = h\nu_0$$

Vo being the threshold frequency corresponding to $0^{\circ}K$.
Fowler also found the following values for $f(x)$:

$$f(x) = e^x - \frac{e^{2x}}{2^2} + \frac{e^{3x}}{3^2} - - - - - - - x \lessgtr 0$$

or,

$$f(x) = \frac{\Pi^2}{6} + \frac{x}{2} - (e^{-x} - \frac{e^{-2x}}{2^2} + \frac{e^{-3x}}{3^2} - - -) \text{ for } x \geq 0$$

For frequencies near the threshold $(W_a - h\nu)^{\frac{1}{2}}$ is practically constant, so that

$$\log \left[\frac{I}{T^2}\right] = B + F(x)$$

B being constant and independent of ν and T, and $F(x) = \log f(x)$.
The theoretical curve of $F(x)$ and x may be constructed and from experimental observations $\log (\frac{I}{T^2})$ may be plotted as a function of $\frac{h\nu}{kT}$; the difference between the theoretical curve

and the experimental curve on the $\frac{h\nu}{kT}$ axis is then $\frac{\phi}{kT}$, so that ϕ, the photoelectric work function may be determined.

Du Bridge modified this method by plotting $F(x)$ as a function of $\log x$ instead of x. Observations are made of the photoelectric yield for a given frequency at a series of temperatures and an observational graph is plotted of $\frac{I}{T^2}$ against $\log (\frac{1}{T})$, the shift of the observational curve in order to give coincidence with the theoretical curve gives $h.(\frac{\nu - \nu_0}{kT})$ and hence knowing ν, ν_0 may be calculated. This method eliminates the necessity of reducing I to the photoelectric current per unit intensity of absorbed light and hence avoids the troublesome measurement of the intensity of the light.

Another method of determining the photoelectric work function is to determine the maximum energy of the electrons emitted by light of known frequency, and then the work function may be calculated by Einstein's equation. The energy of the emitted electrons may either be determined by a stopping potential method or by determining their deflection in a magnetic field. In the stopping potential method allowance must be made for contact difference in potential if the collecting electrode is not composed of the same material as the emitting metal.

In order to determine the thermionic work function of a metal measurements must be made of the current emitted from

a metal at a known temperature. For a metal which is easily obtainable in the form of a wire the design of the tube is similar to that used for determining the photoelectric work function. The metal under consideration is heated by means of an electric current and the current emitted from the metal, if saturation current cannot be reached by the application of a suitable electric field, is determined when there is a known accelerating field between the metal and the collecting electrode. If the current is determined for a series of accelerating fields it is possible to determine the current for no accelerating field, as is shown in section IV.

$$I = I_0 \, e^{-\sqrt{F}a/kT}$$

where I is the current when the field is F_a

and I_0 is the current when there is no accelerating field. Also it will be shown in section III that

$$I_0 = AT^\lambda e^{-\phi/kT}$$

where A = a constant

T = Temperature of the metal

ϕ = the work function of the surface

If, therefore, a graph is plotted of log I - 2 log T and $\frac{1}{T}$ it should result in a straight line the slope of which is $\frac{\phi}{k}$

and hence ϕ may be found. [For actual method of the determination of the work function see section III.]

The temperature of the metal may be found from the determination of its resistance at the lower temperatures of the experiment, or at higher temperatures the emissivity of the metal may be used in order to calculate the temperature. As in the case of photoelectric emission the metal must be "clean". All cleaning processes should be performed at a temperature considerably higher than the maximum temperature of the experiment.

Yet another method of determining the work function of a surface is by measuring the current emitted from a metal when illuminated by black body radiation. It will be shown in section III that the current emitted from the metal varies with the temperature of the source of radiation in the same way as the thermionic current from a metal varies with the temperature of the metal. The apparatus used by Roy[1] to determine the work function by this method is indicated in the following diagram.

1. Roy, Proc. Roy. Soc. 112, p. 599 (1926).
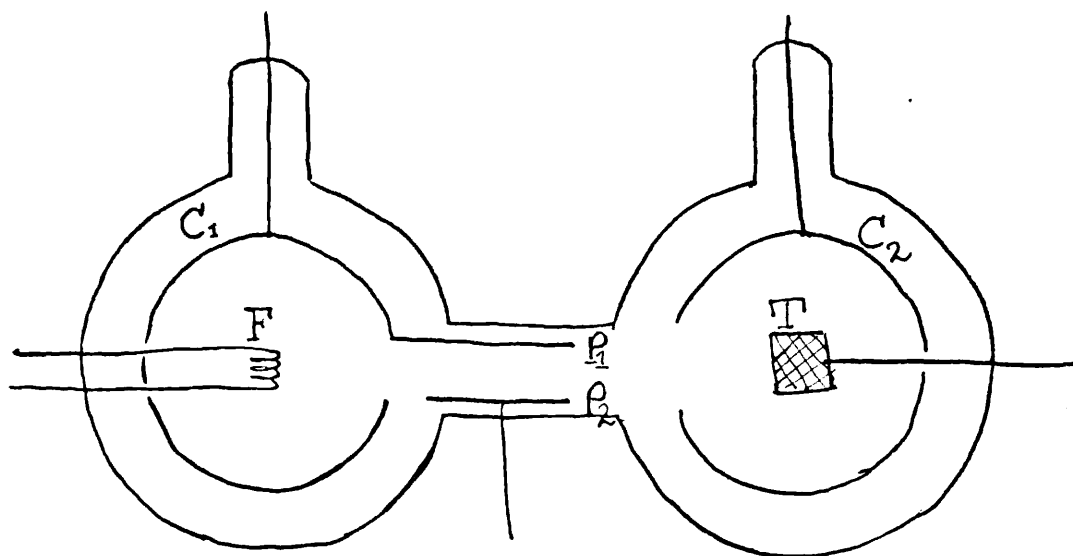
The source of radiation is a tungsten filament F which may be heated by means of an electric current, and F is kept positive with respect to the cylinder C_1, so that thermionic emission from F is not possible. The radiation leaving F passes between the plates P_1 and P_2 across which a difference in potential is applied so as to remove any stray charges. T is the metal under experiment which is made negative with respect to the cylinder C_2 so that the electrons emitted from T by the radiation are collected by the cylinder C_2. W. Wilson,[1] when using a similar method to determine the emission from sodium-potassium alloy, illuminated by black body radiation from a platinum filament, showed that, since the emission ceased directly the radiation was shut off, the emission is due to the radiation and not to thermionic emission.

1. W. Wilson, Proc. Roy. Soc. 93A. (1916).

Unfortunately the values of the work function found by this method do not show agreement with other methods as the experiments have not been carried out with the modern method of preparation of the surface of the metals, and hence the values cannot be considered as characteristic of the pure metal.

Experimental determination of the work function of the alkali metals has shown some interesting phenomena. Two values of the work function were found for a given specimen of the metal when the emission was due to thermionic, photoelectric, and "complete" photoelectric emission; further, Ives and Olpin[1] have found complete agreement between the work function of the alkali metals and their resonance potential. It will be seen from the accompanying graph that the work functions of the alkali metals are considerably less than that for any other metal.

Recent values of the photoelectric work function calculated by Fowler's method show very good agreement with the thermionic work function for the same specimen of the metal and where values for the two work functions have been measured at several temperatures the agreement is within the limit of experimental error. The variation of the work function with temperature is so small, however, that there

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1. Ives and Olpin, Phys. Rev. 34, p. 117.

does not seem to be convincing experimental evidence of the equality of the temperature coefficients of the two work functions.

Metal	Thermionic work function	Photoelectric work function. Fowler's method.
Iron	4.77 equi.volts	4.77 equi. volts
Nickel	5.03 ±.05　"	5.01　"
Molybdenum	(303°K 4.14　"	4.14　"
	(940°K 4.18　"	4.16　"
Palladium	4.99 ±.04　"	4.97 ±.02　"
Tantalum	(293°K 4.09　"	4.10　"
	(973°K 4.14　"	4.14　"
Tungsten	4.54　　"	4.54　"

Variation of Work Function with Atomic Number.

Work Function in equivalent volts.

Atomic Number.
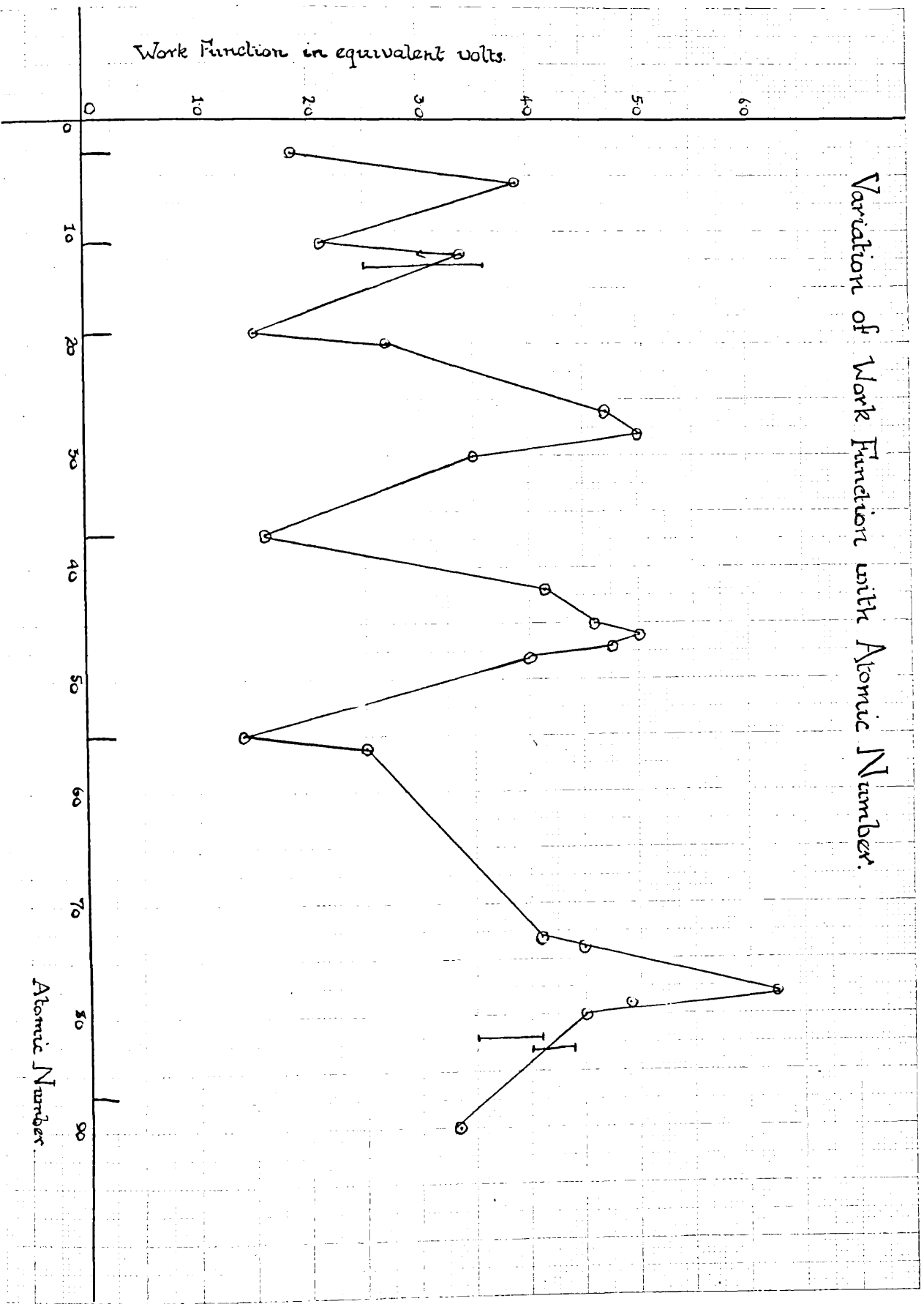
III.   THEORIES   OF   EMISSION

Using the classical electron theory of conduction in metals, a theoretical formula for the emission of electrons from a hot metal was first derived by O.W. Richardson in 1901.[1] He calculated the emission on the assumption that all those electrons whose velocity normal to the surface gives them sufficient energy to pass through the potential barrier at the surface of the metal,will escape from the metal.

Let ϕ = the potential step at the surface of the metal

   e = charge on an electron

   m = mass of an electron

   u_0 = minimum velocity normal to the surface for an electron to escape

then $\phi e = \frac{1}{2} mu_0^2$

According to the Maxwellian velocity distribution, the number dN of electrons per unit volume having normal velocity components between u and u + du is given by

$$dN = N \sqrt{\frac{m}{2 \pi kT}} \; e^{-\frac{mu^2}{2kT}} \; du$$

where N = total number of free electrons per unit volume of the metal.

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1. O.W. Richardson, Proc. Roy. Soc. (1903).

The number n of electrons that escape from unit area of the
surface per second is then

$$n = \int_{u = u_0}^{u = \infty} u\,dN = N\sqrt{\frac{m}{2\pi kT}} \int_{u_0}^{\infty} e^{\frac{-mu^2}{2kT}}\, u\,du$$

$$= N\sqrt{\frac{kT}{2\pi m}}\; e^{\frac{-mu_0^2}{2kT}}$$

If i = current emitted per unit area

i = ne

$$i = Ne\sqrt{\frac{kT}{2\pi m}}\; e^{\frac{-mu_0^2}{2kT}}$$

It will be seen from this that at $0^\circ K$ the energy of the electron
is considered as zero.

Shortly after Richardson's derivation of the above
equation H.A. Wilson[1] showed that thermionic emission is analo-
gous to the evaporation of a liquid.

If p = vapour pressure of a liquid at absolute temperature T

L = latent heat of the liquid per gm. molecule,

then $L = (v_2 - v_1)\; T\frac{dp}{dT}$

where v_1 = volume of the liquid

v_2 = volume of the resulting vapour.

1. H.A. Wilson, Proc. Roy. Soc. (1904).

neglecting v_1 and putting $v_2 = \dfrac{RT}{p}$

$$L = \frac{RT^2}{p} \frac{dp}{dT}$$

Let Q = the internal work done in evaporating the liquid

let $Q = Q_0 + aT$ where a is some constant

then $L = Q + pv_2$

so that $Q_0 + aT + RT = \dfrac{RT^2}{p} \dfrac{dp}{dT}$

Hence if p_1 is the vapour pressure at temperature T_1 and p_2 that at T_2

$$\log \left(\frac{T_1^{R+a} + p_1^{R}}{T_2^{R+a} + p_1^{R}} \right) = Q_0 \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

But $p = bmVN$

where m = mass of a molecule

V = root mean square value of the velocities of the molecules

N = number of molecules leaving square cm. of the liquid per second

b = a constant

but $V^2 \propto T$, hence let $p = b'\sqrt{T}$ where b' is a constant,

then

$$\log \left(\frac{T_1^{\frac{1}{2} + a/R} \, N_2}{T_2^{\frac{1}{2} + a/R} \, N_1} \right) = \frac{Q_0}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

If the electrons emitted from a hot metal are considered as behaving in the same way as evaporated molecules, the current i

emitted must be Ne where N is given by the above equation and

e is the electronic charge,

$$\therefore \quad \log\left(\frac{T_1^{\frac{1}{2}+a/R}\, l_2}{T_2^{\frac{1}{2}+a/R}\, l_1}\right) = \frac{Q_0}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\text{or} \quad l = AT^{\frac{1}{2}+a/R}\, e^{-\frac{Q_0}{RT}} \quad \text{where A is a constant.}$$

If Q is independent of temperature, $a = 0$ and this formula

has the same form as that deduced by Richardson.

A further development of this method is to express the

latent heat of evaporation in terms of the specific heat of

the two phases, i.e.,

$$L = L_0 + \int_0^T C_p\, dT - \int_0^T c_p\, dT$$

where L_0 = latent heat of evaporation at $0^\circ K$

$\quad\quad C_p$ = specific heat of the electrons at constant pressure
in the vapour state

$\quad\quad c_p$ = specific heat of the electrons at constant pressure
in the solid state.

But $C_p = 5/2\, k$ for one molecule of a monatomic vapour

and $c_p = 0$

$$L = L_0 + \frac{5}{2}\, kT$$

But also $\dfrac{L}{kT^{2}} = \dfrac{d(\log p)}{dT}$

$$Lo + \frac{5}{2}kT = \dfrac{d(\log p)}{dT} kT^{2}$$

or $\quad p = AT^{5/2} e^{-Lo/kT}$

Frpm the kinetic theory of gases the number of electrons striking unit area of the metal surface per second is given by

$$n = \dfrac{p}{(2\pi m kT)^{\frac{1}{2}}}$$

hence the current emitted from unit area of the surface is

$$i = ne = AT^{2} e^{\frac{-Lo}{kT}}$$

If the value of c_p as given by the classical electron theory has been used, this equation would correspond to that derived by Wilson; it is not possible to determine from experimental results which is the more accurate.

In the derivation of this formula the actual mechanism of emission has not been taken into account nor has the state of the electron before and after the evaporation process been considered, so that L_0(orQ_0) measures the excess amount of work that has to be done in order to remove an electron from the metal. The fact that the electron may have an appreciable

amount of energy at $^\circ$K has not been considered, whilst Richardson's derivation on the basis of the classical electron theory of metals assumed that the electron has zero energy at 0°K.

Although in certain cases the treatment of the free electrons in metals as a perfect gas has met with success, in others the results from theory show no agreement with experimental observations. In 1927 Pauli[1] introduced an entirely new conception of the electrons in a metal. He assumed that the free electrons should be considered as belonging to a degenerate gas, that is one obeying the statistical laws of Fermi and Dirac. On the basis of these laws an electron of a degenerate gas at 0°K has an appreciably large kinetic energy of the order 6 to 12 equivalent volts, but the measured value of the work function gives the extra energy that must be supplied to the electron in order that it may pass through the potential step at the surface of the metal. If then the initial energy of the electron is of the order 6 to 12 volts, and the excess energy that must be given to the electron before it is emitted is from 2 to 6 volts, the actual potential step at the boundary of the metal must be of the order 8 to 18 volts.

The velocity distribution function in the Fermi-Dirac statistics is given by

$$dn_{u\,v\,w} = \frac{2m^3}{h^3} \frac{du\ dv\ dw}{e^{\alpha+E/kT}+1}$$

1. Pauli, Zeits. f. Phys. 41, p. 81 (1927).

where $dn_{u\,v\,w}$ = the number of electrons whose velocity components u,v,w lie in the range du, dv, dw.

α = a parameter dependent on T and the number of electrons per unit volume.

and $E = \frac{m}{2} (u^2 + v^2 + w^2)$

The thermionic current is calculated by determining the number of electrons whose velocity components normal to the surface have a minimum value given by $\frac{1}{2}mu_0 = W_a$, where W_a is the potential step at the surface of the metal.

$$i = \frac{2m^3 e}{h^3} \int_{u_0}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{u}{e^{\alpha + E/kT} + 1} \, du \, dv \, dw$$

Let $\mu = -\alpha kT$, then μ is the maximum kinetic energy of an electron at $0^C K$

$$i = 2 \, AT^2 e^{-(W_a - \mu)/kT}$$

Comparison of this equation with that deduced from thermodynamical considerations shows that

$$W_a - \mu = L_0$$

It is seen from the derivation of the expression for the thermionic emission of electrons by statistical methods that if all the electrons which have sufficient energy to pass

through the surface do so, A should be a universal constant.
For electrons moving in the metal before being emitted the
reflection is small, so that on this account the deviation
of the observational value of A from the theoretical value
should also be small. The value of A as given by plotting
$\log i - 2 \log T$ against $\frac{1}{T}$ is not constant. Becker and
Brattain have shown that this inconstancy of A is allied to
the dependence of the thermionic work function on the tem-
perature of the emitting surface.

The equation for emission from a surface may be written

$$i = AT^{\gamma} e^{\frac{-b}{T}}$$

where A and b are constants. Becker and Brattain distinguish
between three quantities, viz., b, h and w. The quantity b
is obtainable from the slope of the line $\log i - 2 \log T$
against $\frac{1}{T}$ since $-\frac{b}{2.3}$ is the slope of this line; h is defined
as the "heat function" and is equal to $(\frac{L_p}{R} - \frac{5T}{2})$, where L_p
is the latent heat at   constant pressure of evaporation of
the electrons from the metal, and w is the work function.
Using the method of Becker and Brattain, first consider the
derivation of the thermionic equation by thermodynamical
methods. It can be shown, by using Clapeyron's latent heat
equation that

1. Becker and Brattain, Phys. Rev. 45 (1934).

$$\log i - 2 \log T = \log H + \log(1-r) - [\frac{h}{2.3}]_{T'} + \frac{1}{2.3} \int_{T'}^{T} \frac{h}{T^2} \, dT$$

where H is a constant independent of T but dependent on T',
which is a fixed temperature in an experimental range, and
r is the "reflection coefficient", that is, the ratio of the
number of electrons that pass through the surface to the num-
ber coming up to the surface and having sufficient energy to
pass through it. If this is differentiated with respect to
$\frac{1}{T}$

$$\frac{dy}{d(\frac{1}{T})} = \frac{-1}{T^2} \frac{dy}{dT} \qquad\qquad y = \log i - 2 \log T$$

$$\therefore \quad \frac{-1}{T^2} \frac{dy}{dT} = \frac{-1}{T^2} \left(\frac{d \log(1-r)}{dT} + \frac{h}{2.3 T^2} \right)$$

$$= \frac{-h}{2.3} \quad \text{If} \quad \frac{dr}{dT} = 0 \text{ or } \frac{1}{T^2} \cdot \frac{d \log (1-r)}{dT}$$

is small in comparison with $\frac{h}{2.3}$. If h is dependent on T,
$\log i - 2 \log T$ and $\frac{1}{T}$ will be a curve, the slope at any point
T' being given by $\frac{h}{2.3}$ and the tangent to the curve at any
point is given by

$$\log i - 2 \log T = \frac{b}{2.3T} + \log A.$$

Up to the present for pure metals the graph has been shown
to be a straight line, so that b = h and log A = log H(1 - r).

The value of the current emitted from a surface when calculated by statistical methods is given by

$$1 = U(1 - r) T^2 e^{\frac{-w}{T}}$$

or log 1 - 2 log T $=$ log $U(1 - r)$ $-\frac{w}{T\,2.3}$

where U is a universal constant the value of which is

120 amps/cms $/^{\circ}K$ and wk $= W_a - W_1$

where W_a is the difference in potential energy between an electron inside and outside the metal and W1 is an integration constant which is dependent on temperature as it involves the number of atoms in unit volume of the metal. w in general will depend on the metal, its surface and on the temperature. If $\frac{dw}{dT} = \alpha$ where α is a constant

$w = w_0 + \alpha T$ w_0 is an integration constant.

The curve given by plotting log 1 - 2 log T and $\frac{1}{T}$ is a straight line whose slope is $\frac{-w_0}{2.3}$ and whose intercept is log $U(1-r) - \frac{\alpha}{2.3}$

so that log A $=$ log $U(1 - r) - \frac{\alpha}{2.3}$ or $\alpha = 2.3(\log U(1 - r) - \log A)$

In order to calculate the value of α it is necessary to know something of the value of the reflection coefficient r. It seems that the value of r is so small that it may be neglected since in the most accurate experiments comparatively large

errors are introduced in the determination of **A**. The method
of finding the work function at any temperature T' is as
follows, the line log i - 2 log T and $\frac{1}{T}$ is plotted from ex-
perimental observations.
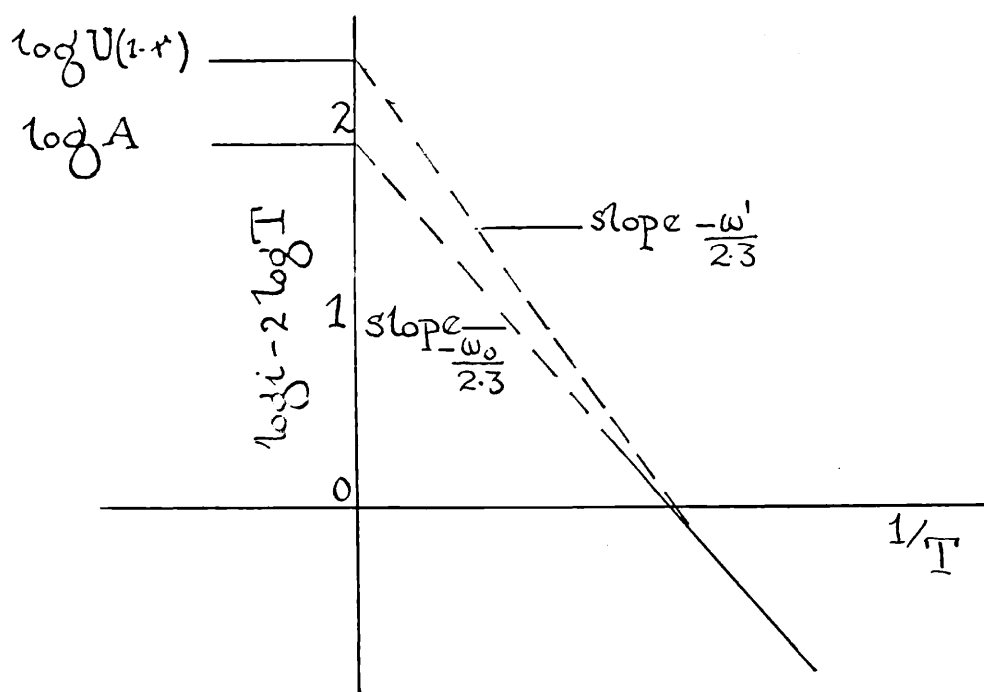
The point on the line corresponding to $\frac{1}{T}$ is then joined to
log U and the slope of this line is $\frac{-w'}{2.3}$ where w' is the work
function at the temperature T'. The value of   can also be
determined; it has been found to yield a variation of the work

function of the order 10^{-4} equivalent volts per $^{\circ}K$.

Reimann[1] has also pointed out the dependence of the thermionic work function on temperature because of the expansion of the metal.

The most fundamental of photoelectric relationships is that due to Einstein[2], i.e., $E = \frac{1}{2}mv^2 = h\nu - w$

where $E = \frac{1}{2}mv^2$ is the kinetic energy of the emitted electron

   w = work done in dragging the electron through the surface

   h = energy of the light quantum,

the electron being able to absorb the whole energy since it is in a field of force. Then if νo is the minimum value of ν in order that an electron shall be emitted $w = h\nu o$. This is assuming that the kinetic energy of the electron within the metal is negligible. If, however, the electron gas is considered as a degenerate one this is not so, but at $0^{\circ}K$ the maximum kinetic energy is μ so that a nearer approximation is

$$\frac{1}{2}mv^2 = h\nu + \mu - W_a$$

If the maximum velocity distribution function from the Fermi-Dirac statistics is plotted as a function of the energy E of the electrons, it is found that at $0^{\circ}K$ there is a

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1. Reimann, Nature, 133.

2. Einstein, Ann. d. Phys. 41 (1905).

discontinuous drop to zero in the function at a point where

$E = \mu$. At higher temperatures, however, this drop is not dis-

continuous, the maximum energy of an electron being slightly

greater than μ, hence $h\nu_0$ when measured experimentally will be

slightly less than $W_a - \mu$.

This dependence of the photoelectric threshold on tem-

perature has been calculated by Fowler.[1] Considering only the

case when the metal is illuminated by light of frequency

which is near the threshold, he determined the number of elec-

trons N within the metal whose velocity components u normal

to the surface, are greater than some critical value u_0 given

by

$$\tfrac{1}{2}mu_0^2 + h\nu = W_a$$

If $n(u)du$ is the number of electrons per unit volume whose

normal velocity components lie in the range du, then

$$N = \int_{u_0}^{\infty} n(u)\,du$$

But from the Fermi-Dirac statistical laws

$$n(u)\,du = \frac{4\pi kTm^2}{h^3} \log\left(1 + e^{\frac{\mu - \tfrac{1}{2}mu^2}{kT}}\right)du$$

When ν is not very different from ν_0, the case that Fowler con-

sidered, the logarithm can be expanded and integrated term by term.

Putting $\phi = W_a - \mu = h\nu_0$

and $x = \dfrac{h\nu - \phi}{kT} = \dfrac{h}{kT}(\nu - \nu_0)$

1. Fowler, Phys. Rev. 38 (1931).

$$N = \frac{2\sqrt{2\pi} \; m^{3/2} k^2 T^2}{h^3 (W_a - h\nu)^{\frac{1}{2}}} \left(e^X - \frac{e^{2X}}{2^2} + \frac{e^{3X}}{3^2} \; \text{------} \right)$$

for $x \lesssim 0$

or $\qquad N = \frac{2\sqrt{2\pi} \; m^{3/2} k^2 T^2}{h^3 (W_a - h\nu)^{\frac{1}{2}}} \left[\frac{\pi^2}{6} + \frac{x^2}{2} - \left(e^X - \frac{e^{-2X}}{2^2} + \frac{e^{-3X}}{3^2} \; \text{---} \right) \right]$

for $x \gtrsim 0$

At the threshold when $\nu = \nu o$ $\;\; N \propto T^2$, also it can be assumed that the photoelectric emission $I \propto N$.
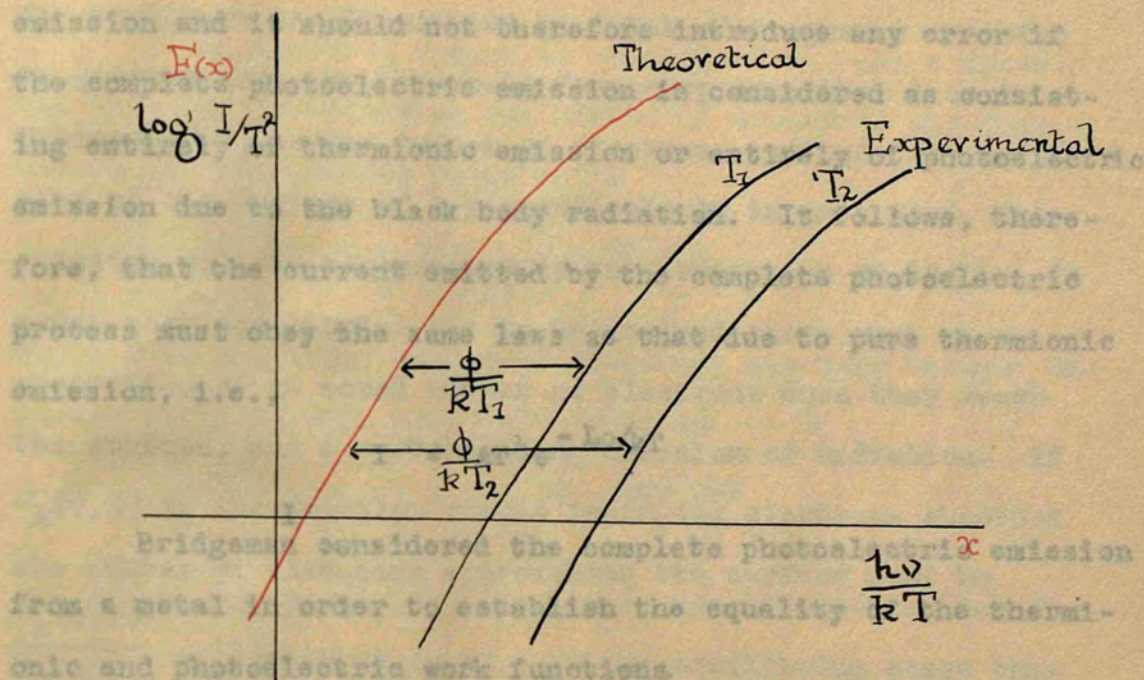
$$I = AT^2 (W_a - h\nu)^{-\frac{1}{2}} f(x)$$

or $\qquad \dfrac{I}{T^2} = A(W_a - h\nu)^{-\frac{1}{2}} f(\dfrac{h\nu - \phi}{kT})$

But for frequencies near the threshold $(W_a - h\nu)^{\frac{1}{2}}$ is practically constant and so may be included with the constant A

$$\log I/_{T^2} = B + F(x) \qquad F(x) = \log f(x)$$

If the theoretical curve $F(x)$ against x and the experimental curve $\log I/_T$ and $\dfrac{h\nu}{kT}$ are plotted on the same graph as below the horizontal shift of the experimental curve in order that it may coincide with the theoretical curve gives $\phi/_{kT}$ and hence the true threshold at 0^oK may be calculated

$F_{(x)}$

$\log I/T^2$

Theoretical

Experimental

T_1 T_2

$\dfrac{\phi}{kT_1}$

$\dfrac{\phi}{kT_2}$

x

$\dfrac{h\nu}{kT}$

Another interesting case of the emission of electrons from a metal is that due to black body radiation — the complete photoelectric effect.   This was first considered theoretically by O.W. Richardson in 1912, who treated it as a reversible thermodynamic process, as later did W. Wilson, Roy and Bridgeman.

Since the metal must be considered as being in temperature equilibrium with an infinite enclosure, it is not possible to distinguish between thermionic and "pure" photoelectric emission in the process of complete photoelectric

1. O.W. Richardson, Phil. Mag. 24 (1912).

emission and it should not therefore introduce any error if
the complete photoelectric emission is considered as consist-
ing entirely of thermionic emission or entirely of photoelectric
emission due to the black body radiation. It follows, there-
fore, that the current emitted by the complete photoelectric
process must obey the same laws as that due to pure thermionic
emission, i.e.,

$$I = AT^2 e^{-Lo/kT}$$

Bridgeman[1] considered the complete photoelectric emission
from a metal in order to establish the equality of the thermi-
onic and photoelectric work functions.

Consider two metals A and B metallically in contact in
an evacuated enclosure at temperature T; the whole enclosure
is in thermal equilibrium.

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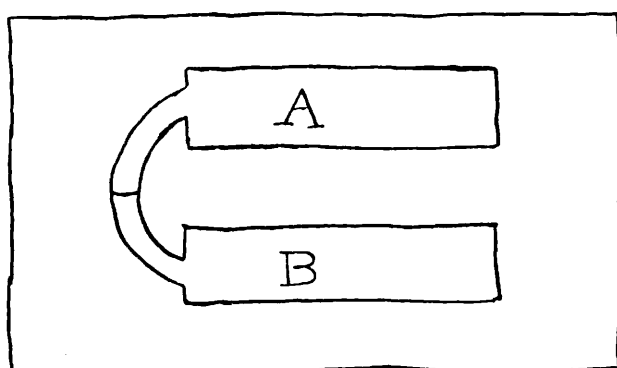
1. Bridgeman, Phys. Rev. 31 (1928).

The enclosure is illuminated by light of frequency ν which is greater than the threshold frequency of either A or B. Taking $f_A(\nu,T)$ as the number of electrons emitted from unit area of the surface of A perpendicularly in unit time, this emission will be accompanied by the absorption of light. In order that equilibrium may be maintained there must be an absorption of an equal number of electrons when they reach the surface, and a corresponding emission of radiation. If $\alpha_A(\nu,T)$ is the fraction of the impinging electrons absorbed the number of electrons approaching the surface must be

$$\frac{f_A(\nu,T)}{\alpha_A(\nu,T)}$$ call this $F_A(\nu,T)$. In the equilibrium state this must also be equal to the number of electrons that leave the surface. Also all the electrons that leave A must reach B and be absorbed there or

$$F_A(\nu,T) = F_B(\nu,T)$$

or $F_A(\nu,T)$ must be independent of A. Using the threshold frequency ν_0 as a characteristic parameter of the substance $F(\nu,\nu_0,T)$ must be independent of ν_0 when $\nu > \nu_0$. In the case of complete emission the photoelectric mechanism cannot be separated from the thermionic and so the condition limiting F can be obtained from thermionic considerations.

If an electron vapour is considered to have a Maxwellian velocity distribution the number of electrons per unit volume in the velocity range dv is

$$dn_v = \frac{n}{3} \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} e^{-mv^2/kT} dv$$

where n is the total number of electrons per unit volume; the number striking unit area per second is

$$dN_v = \tfrac{1}{4}vdn_v = \frac{n}{6} \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} e^{-mv^2/kT} v \, dv$$

But Bridgeman showed from thermionic considerations that the number n is given by

$$n = \frac{(2\pi mkT)^{3/2}}{h^3} \exp \frac{(S_\rho - S_m)_0}{k} - \frac{L_0}{kT} - \frac{1}{kT} \int_0^T (C_{p\rho} - C_{pm}) \, dT$$

$$+ \frac{1}{k} \int_0^T \frac{C_{p\rho} - C_{pm}}{T} \, dT$$

where $C_{p\rho} - C_{pm}$ is the difference in the specific heats at constant pressure of the charged and the uncharged metal and $(S_\rho - S_m)_0$ is the difference in entropy at $0^\circ K$ of the charged and the uncharged metal. Also from Einstein's photoelectric equations $\tfrac{1}{2}mv^2 = h(\nu - \nu_0)$ and $vdv = \frac{h}{m} d\nu$. The number dN_v is the number of electrons in photoelectric equilibrium under the stimulation of light of frequency ν and intensity $I(\nu)d\nu$ where

$I(\nu)$ is the distribution function for black body radiation at temperature T

$$dN_v = F(\nu, \nu_0, T) \; I(\nu) \; d\nu$$

But $I(\nu) = \dfrac{8\pi}{c^3} \dfrac{h\nu^3}{e^{h\nu/kT} - 1}$

$$\therefore \quad F(\nu, \nu_0, T) = -\frac{\dfrac{n}{6}\left(\dfrac{m}{2\pi kT}\right)^{\frac{1}{2}}\dfrac{h}{m}\; e^{-\dfrac{h(\nu - \nu_0)}{kT}}}{\dfrac{8\pi}{c^3}\dfrac{h\nu^3}{e^{h\nu/kT} - 1}}$$

Substituting for n, it is found that

$$\frac{S_\rho - S_m}{k} + \frac{h\nu_\rho - L_o}{kT} - \frac{1}{kT}\int_0^T (C_{p\rho} - C_{pm})\, dT + \frac{1}{k}\int_0^T \frac{C_{p\rho} - C_{pm}\, dT}{T}$$

must be independent of the metal — that is, a universal temperature function. If the above equation is differentiated with respect to T and multiplied by kT^2: $\left[- h\nu_0 + L_o + kT \dfrac{d\nu}{dT} +\right.$ $\left.\int_0^T (C_{p\rho} - C_{pm})\, dT\right]$ = a universal temperature function. If T approaches $0^\circ K$ as the limit, the right-hand side approaches a universal constant. The integral and $T\dfrac{d\nu}{dT}$ will become zero so that $L_o - h\nu_0'$ = a universal constant where ν_0' is the threshold frequency measured at $0^\circ K$.

Lo of the above expression is proportional to the "heat function" which has been shown by Becker and Brattain to be

equal to w_0 where $w = w_0 + \frac{dw}{dT}$, w being the thermionic work function at any given temperature. But it has been shown by experiment (see Section II) that $w = h\nu_0$ where ν_0 is the threshold at the same temperature, so that if $\frac{d\ h\nu_0}{dT} = \frac{dw}{dT}$ the universal constant of Bridgeman's calculation will be zero. Although in all probability this is so, the variation of the work functions with temperature is so small that experimental verification seems outside the range of present experimental measurements.

IV. THE NATURE OF THE WORK FUNCTION

It being an established fact that there is a drop of potential across the surface of a metal, an explanation of its existence is necessary. This drop of potential would exist if there were a double electric layer on the surface of the metal with the negative charges on the outside; this conception is useful for explaining work function phenomena and was used by Richardson and H.A. Wilson,[1] but there is no evidence of the existence of such a layer.

Another possible explanation suggested by Debye[2] and Schottky,[3] is that as the electron comes up to the surface the image force comes into play. For an electron distance x from the surface the image force — in ordinary E.S.U. — is $\frac{e^2}{4x^2}$, and the potential at this point is $- \frac{e^2}{4x}$ — the potential at infinity being zero. This in the case of a continuous surface makes the potential of the metal and hence the work function infinite. Debye and Schottky therefore assumed that the image law breaks down near the surface, and

1. H.A. Wilson, Phil. Trans. Roy. Soc. A. (1908).

2. P. Debye, Ann. d. Phys. 33 (1911).

.3. W. Schottky, Zeits. f. Phys. 14 (1923).

that the force is constant within a distance x_0 from the surface. This assumption then gives the work function a finite value.

Another consideration that must be taken into account is that in experimental investigations of thermionic and photoelectric emission, the electron is always emitted in an electric field, hence if $F(x)$ is the force on an electron distance x from the surface due to the surface forces, and F_a is the applied electric field, the resulting field distance x from the surface is $(F(x) - F_a)$, and the potential at that point is given by

$$V = \int_0^\infty [F(x) - F_a]\ dx$$

An electron will leave the metal entirely if it can be removed to a point x' where the external applied field just neutralizes the field towards the metal.

Let w = work function for zero applied field
and w' = work function for applied field F_a,
then

$$ew' = \int_0^{x'} [F(x) - F_a]\ dx$$

$$= \int_0^\infty F(x)\ dx - \int_{x'}^\infty F(x)\ dx - \int_0^{x'} F_a\ dx$$

$$= ew - \int_{x'}^\infty F(x)\ dx - F_a x'$$

If F(x) is the image field $F(x) = \dfrac{e^{\lambda}}{4x^{\lambda}}$ and at x'

$$F_a = F(x) = \frac{e^{\lambda}}{4x'^{\lambda}}$$

$$\therefore \quad w' = w - \sqrt{F_a}$$

If the Sommerfeld electron theory is used instead of the classical one as above, F(x) must be associated with the drop of potential W_a across the surface of the metal and the measured value of the work function is then $w' = W_a' - \mu$ and $w = W_a - \mu$, $W_a' = W_a - \sqrt{F_a}$. Thus the relationship between work function and applied field holds for both classical and Sommerfeld conceptions of the electron gas.

The above relationship has been tested experimentally for both thermionic and photoelectric emission. Substituting $w' = w - \sqrt{F_a}$ in the Richardson thermionic equation

$$I = AT^{\lambda} e^{-w'e/kT}$$

the expression

$$I = I_0 e^{-\sqrt{F_a}/kT}$$ is obtained, where

I_0 is the current for zero applied field. It was found that using the results of experimental investigations on pure metals $\log_e I$ plotted against F_a yielded a straight line, hence verifying the relationship. When the relationship was tested for composite surfaces, however, large deviations

from the law were found. Becker and Müller working on
thoriated tungsten found that for large applied fields the
law is very nearly obeyed, but for small applied fields the
deviation is great. Lawrence and Linford found agreement
with the Schottky law for the photoelectric emission from a
thick layer of potassium on tungsten.

Bartlett[1] and Waterman have questioned the soundness,
when calculating the work function, of neglecting the space
charge in the near neighbourhood of the metal, particularly
if the electron gas is a degenerate one. They have developed
an expression for the emission of electrons from a metal into
an accelerating field on the assumption that the whole of the
potential step at the surface of the metal is due to space
charge. Their expression gives the value of the difference
of potential of the order 15 to 20 volts, which is in agree-
ment with the value given by calculations based on the assump-
tion of the Sommerfeld theory. In their calculations, how-
ever, they have used Poisson's equation which is applied to an
infinite plane. The validity of its application to the
emission of electrons from a metal surface is questionable.

Zwikker[2] has found an expression for the potential step
at the surface of a metal using the assumption that both space

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1. Bartlett and Waterman, Phys. Rev. 37 and 38 (1931).

2. Zwikker, Physica, XI.

charge and image force are contributing to the work function.
He has also estimated the relative values of the potential
difference due to the image force and due to the space charge:
he found that the image force contributes 97% of the work
function and the space charge 3%. He acknowledges that pro-
bably the image laws cannot be applied to such small distances
as used in his calculations, and that some allowance (perhaps
1%) must be made for structural forces at the surface of the
metal. Unfortunately Zwikker has also used Poisson's equa-
tion when considering the contribution due to space charge.

It is seen therefore that there is considerable dis-
agreement over the actual origin of the potential drop at the
surface of the metal. Although the Schottky law gives the
correct variation of work function with applied field and it
has been shown by Zwikker to contribute a very large percent-
age to the work function, Bartlett and Waterman have in their
calculations obtained a correct value of the work function by
completely neglecting the image force. It would seem possible
that this variance lies in the conception of the actual posi-
tion of the surface of the metal.

V. CONCLUSION

It is seen that the development of both theoretical and experimental investigations of thermionic and photo-electric emission leads to the conclusion of the numerical equality of the work functions of two phenomena at any given temperature. This is to be expected as the electron in both these cases of emission must have the same energy in order that it may be removed from the metal. The existence of the complete photoelectric effect suggests the possibility that thermionic emission is an autophotoelectric effect. The difficulty which arises in the comparison of the two effects is that in the case of pure photoelectric emission produced by some external source of illumination the light will be absorbed by a thin layer of the metal, whereas in the complete photoelectric effect which can also be treated as a thermionic process, the temperature radiation is present all through the body of the metal. Experiments show that the intensity of black body radiation is too small to account for the emission, if it is only to be considered as a surface effect, so that if thermionic emission is to be considered as

an autophotoelectric effect it must be treated as a volume effect.

The unsatisfactory disagreement as to the actual mechanism of the work function may arise from different interpretations of the surface of the metal, as when distances comparable with atomic dimensions are considered it seems possible that surface roughness may play some part.