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2. "On the fine structure of the spectrum lines of Thallium in the ultraviolet", by W.Mohammad & S.B.L.Mathur, (Phil.Mag., 5, 1111-1114, 1928).
3. "On the fine structure of the arc lines of Lead and Tin", by S.B.L.Mathur (Phil. Mag., Ser.7, Vol. 14, 270-275, 1932.
4. "An arrangement of atomic nuclei and the prediction of isotopes", by S.B.L.Mathur, (J.Am.Chem.Soc., 55, 3053-3056, 1933).
5. " Circumzenithal arc tangential to a corona of 46 degrees", by S.B.L.Mathur (Ind. J. of Phys., 15, pt.ii, 123-129,1941).
6. "The Laws of electrodynamics and Newton's third law of motion" by S.B.L.Mathur (Science & Culture, 5, no. 2, 1939)
7. "Biot-Savart Law and Newton's Third Law of Motion", by S.B.L. Mathur (Phil. Mag., Ser.7, Vol.,22, 171-176, 1941).
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A NEW METHOD OF DETERMINING THERMIONIC CONSTANTS.

Introduction.

The theory of metals is of increasing importance these days and any contribution related to that subject will be of interest. This dissertation deals mainly with a new thermionic method of determining the constants A_o and ϕ in the well-known Richardson equation

$$i = A_o T^2 e^{-\frac{\phi}{KT}}$$

developed under the guidance of Prof. Dr. Sir K.S. Krishnan, Kt., F.R.S at the University of Allahabad. Before, however, the new method is discussed it will, perhaps, not be out of place to review briefly the salient features of the concept of the Work Function and of the existing methods of determining it.

Potential barrier at the surface of a metal.

There have been several views of the concept of the Work Function. According to the electrical image theory of Scottky[1] the potential barrier at the surface of a metal may be roughly given by the image force. Another view, which attained its final expression in the treatment of Dushman[2], considered the thermal emission of electrons from a metal as thermodynamically equivalent to the evaporation of a monatomic gas of molecular weight $N_a m$, where N_a is Avogadro number and m, the electronic mass. Using the Clausius-Clapeyron equation an emission equation was derived which was the same established already by the pioneer work of O.W. Richardson. The work function thus was taken to be the latent heat of evaporation of an electron at 0° K. These views are rather mechanistic and crude and do not give so detailed a picture as that furnished in the treatment of Sommerfeld[3] based on Fermi-Dirac Statistics. The Richardson equation, however, still stands as the practical embodiment of thermionic theory.

It is well-known that most metals are crystalline in structure and consist of an array of ions built by a regular repitition in three dimensions of some structural unit. Fig.1 illustrates the variation of potential energy, U, due to the nuclei $\alpha, \beta, \gamma \ldots$ and the regions of intense local potential variations near the latter. Since the greate

portion of the metal is the volume between the nuclei, the potential between the nuclei may be taken as nearly constant as shown by the arched portions. It will be noted that since there are no nuclei to one side of the surface of the metal there will be no lowering of the potential energy curve such as prevails in the region between the nuclei within the metal. This is the origin of the potential barrier at the surface of the metal.

An electron in the metal that possesses energy corresponding to the point A in Fig.1 collides with and rebounds from the potential walls a and b and remains confined within them. It, therefore, is strongly bound to the nucleus, N, and cannot drift away. But an electron with energy corresponding to the point B will, at no point within the metal, have its total energy entirely converted into potential energy and hence it will travel, more or less, freely within the metal. But when it reaches the surface of the metal, it collides with the potential barrier at C there. Its kinetic energy is reduced to zero and the electron is turned back into the body of the metal. It is such electrons which have energies in the region of the potential plateau and are subject to no forces, whatever, that form the "free electron gas" within the metal. Since they are atleast as many as the number of atoms they are of the order of 10^{23} /gm. molecule and form a degenerate Fermi gas.

In order to show more details Fig.1 has been redrawn as Fig.2 with all potential variations within the metal being omitted with the exception of the barrier at the surface. The zero of energy has been chosen at the level of the plateau in Fig.1. The electrons, even at 0° K of temperature, possess varying amounts of kinetic energy ranging from zero to a definite maximum, μ, called the Fermi energy, as shown by the horizontal line. According to Sommerfeld, who applied the Fermi-Dirac statistics to the electron gas in metals, the number N_E of electrons per unit volume with energies between E and (E+ dE) is given by

$$N_E\,dE = \frac{8\pi}{h^3}\,\frac{\sqrt{2m^3E}}{e^{\frac{(\mu-E)}{kT}}+1}$$

where $E = \frac{1}{2}m(u^2+v^2+w^2)$,

μ, already indicated in Fig. 2, $= \frac{h^2}{8m}\left(\frac{3\gamma N_0}{\pi}\right)^{\frac{2}{3}}$ approximately,

N = the number of atoms in unit volume of the metal,

γ = the number of free electrons per atom (usually assumed to

be equal to the number of electrons in the outermost shell of the atom),

and T, h, and K have their usual significance.

Fig. 3 illustrates the energy distribution of the electrons in metals. It will be seen that at 0° K, N_E varies as $\sqrt{E}$ upto $E=\mu$, after which it drops to zero. Hence μ represents the maximum kinetic energy of the electrons at 0° K. The distribution is represented by the full line curve. At temperatures above 0° K, the distributions are approximately such that for $E<\mu$, N_E still varies as $\sqrt{E}$; but for $E>\mu$, it falls to zero exponentially according to the Maxwell Law as indicated by the dotted line curve. If these higher energy electrons are imparted a sufficient energy , given by the following relation and shown in Fig. 2:

$$\phi = V_a - \mu$$

they can surmount the potential barrier V_a and escape from the metal. This ϕ is defined as the electron Work Function of the metal. It is different for different metals.

Methods of measuring Work Functions.

The Work Function, ϕ, has been measured by the following methods:

1. Thermionic Emission.
2. Cooling effect when electrons are emitted, or heating effect when electrons are collected.
3. Electron reflection from the surface of metals.
4. Contact potentials.

and 5. Photoelectric Threshold values.

Since the nature and the arrangement of the surface atoms determine the nature of the surface forces, and, hence, the magnitude of the Work Function, it is essential for the obtaining of significant data to experiment on metals of which the surface, at least the immediately underlying regions are free from impurities. Hence the utmost care has to be taken to take not only metals of the highest chemical purity but also to further purify the surface of all occluded and adsorbed gases by a course of prolonged heat treatment in the highest vacuum available and to maintain this vacuum throughout the measurements.

(1) The Thermionic Emission method.

This method consists in imparting, by heating, to the relatively few electrons of energies greater than the "zero point energy", μ, enough kinetic energy to enable them to cross the potential barrier (Fig. 2) at the surface of the metal.

The experimental arrangement consists of a thin cylindrical wire, or a strip of uniform cross-section, of the metal under investigation disposed along the axis of a cylinder of some refractory metal, both being enclosed in a bulb which can be kept highly evacuated. The walls of the bulb, as well as the metallic parts within, are thoroughly degassed by a prolonged course of heat treatment. The filament is heated to various high temperatures by a current from a low tension battery and the electrons emitted form a space charge which has to be neutralised by applying increasingly positive voltages on the cylinder before the latter can collect the saturation current. Since the cylinder, or anode, consists of 3 sections, the end ones acting as guard rings while the middle one acting as the collector, hence by attracting all the emitted electrons from the middle of the filament, the end effects due to the filament leads, the effects due to the cooling of the ends of the filament, and any distortion of the electric field at the ends of the anode are all eliminated. From the specifications of the filament the area of the central segment enclosed by the middle cylinder is calculated. The temperature of the emitter is measured by an optical pyrometer, or by a thermocouple welded to the segment, or from observations on the resistance of the wire, or from the watts radiated from the surface.

An early form of an emission equation was suggested on the basis of the classical kinetic theory of gases by Richardson as follows:

$$i = A T^{\frac{1}{2}} e^{-\frac{b}{T}}$$

but later developments, both from the thermodynamical point of view and from the Fermi Statistics point of view gave the equation already described as:

$$i = A T^2 e^{-\frac{\phi}{kT}} \qquad \text{——— (1)}$$

where i is the electronic emission from a unit area and A is a universal constant given by $(1-r)\frac{4\pi m e k^2}{h^3}$ which, on substitution of the various constants, comes out to be 120 amperes/cm^2 deg^2. Here r is the average relection coefficient. Since both the equations predict the same exponential dependence upon the temperature and since the

the exponential factor overshadows the effect of the $T^{\frac{1}{2}}$ or the T^2 factor it is not possible to decide experimentally whether the one or the other is the proper one. However, owing to its theoretical significance, the T^2 equation is used to express the emission relation Taking the logarithms of both the sides we get

$$\log \frac{i}{T^2} = -\frac{\phi}{KT} + \log A$$

so that if the values of $\log \frac{i}{T^2}$ are plotted against the values of $\frac{1}{T}$, the slope of the straight line, called the Richardson line, gives the value of the Thermionic Work Function, ϕ, while the intercept gives the constant A. It will thus be seen that in order to determine the thermionic constants A and ϕ, the quantities to be determined are:

(a) the area of the emitting surface,

(b) the electronic emission from that surface, and

(c) the temperature of the emitter.

The following corrections have to be applied to mimimise the errors:

(i) Area of the emitter

Although the area can be easily determined before the filament is put in position, the measurement becomes inaccurate after the degassing treatment. Owing to the heat, the metal gets evaporated unevenly along the filament and gets pitted. Crystallisation also may occur thus changing the very nature of the surface. The area of the filament, with its hills and dales on the surface, cannot, therefore, be found with accuracy for the emission measurements.

(ii) Temperature.

Optical pyrometer measurements consist in a photometric measurement for $\lambda = 0.665\,\mu$ of the radiation emitted by the filament. The temperature scale is based upon Wien's Law, which is sufficiently accurate for the purpose of that wave length. But since the material of the filament is not a black body the intensity of radiation will be a fraction, E_λ, of the above so that for knowing the true temperature the emissivity E_λ has to be found. Actually the emissivity varies with temperature and so must be determined for different temperature for each metal to be investigated. Such data are now generally available for metals.

(iii) Lead Losses.

These are altogether avoided by using either the guard ring principle or by using different lengths of the same filament over the same range of temperature values. Otherwise, corrections have to be applied. I.Langmuir, S.MacLane, Blodgett[4] have given a comprehensive discussion of the effect of the End Losses on the characteristics of filaments of Tungsten and other metals. The accurate determination of the corrections is a very tedious matter.

(iv) Corrections for the Anode Voltage.

Equation (1) applies to emissions which have not been affected by any external fields. But, except when the temperatures are small and hence the emissions are little the mutual repulsions of the electrons set up a space charge around the emitter which prevents the electrons from reaching the anode. Hence an increasingly positive potential has to be applied to the anode to enable it to neutralise the space charge and attract to itself all the electrons emitted. It is found that the electron current to the anode increases slightly even when the saturation value is reached so that strictly speaking saturation is never quite realised. Schottky[5] has shown that if F_c, the accelerating field due to the collector potential is not disturbed by the space charge and F_c is proportional to V_c, the collector potential, the observed emission i_1 is related to i_o, the emission for zero field at the emitter by the relation:

$$i_1 = i_o e^{4.39 (F_c)^{\frac{1}{2}} / T}$$, whence, by taking logarithm we get

$$\log_{10} i_1 = \log_{10} i_o \frac{1.905 (SV_c)^{\frac{1}{2}}}{T},$$

where S is the constant of proportionality and is calculable from the electrode geometry by means of electrostatic laws. Hence, if a graph of $\log_{10} i_1$ is plotted as a function of $V_c^{\frac{1}{2}}$ it should be a straight line whose slope is $\frac{1.905 (S)^{\frac{1}{2}}}{T}$ and whose intercept at $V_c = 0$ gives $\log_{10} i_o$.

(v) and (vi) Corrections due to the rise of the temperature of the filament on account of the radiation received from the heated anode and due to the variation in the heating current of the filament due to the return of the space charge from the anode are given later under Davisson & Germer's work relating to the determination of W

mination of Work Function by the cooling of the filament on the emission of electrons from it.

It will be seen that the thermionic method is very suitable for the measurement of thermionic constants of refractory metals whose surface can be rid of adsorbed or occlided foreign matter by a course of rigorous heat treatment. It is direct and straightforward as it seeks to measure the entire emission from the metallic filament. But it suffers from certain defects . Firstly, in the theoretically derived emission equation, whether derived from thermodynamical grounds as by Dushman or from Fermi Statistics by Sommerfeld, the right hand side of equation (1) has to be multiplied by a transmission factor (1-r), where r is the reflection coefficient for electrons incident perpendicularly on the surface of the metal. This r has different significance in the two theories; but it does occur. Nordheim[6] has shown that the two reflection coefficients are numerically equal and Becker and Brittain[7] have shown that since all available evidence seems to show that the reflection coefficient is less than 0.1 so that since the values of A are usually not accurate to within 10%, the reflection coefficient is neglected in the emission equation. Hence, for all practical purposes the Dushman-Richardson equation of emission is written as (1). But, whatever be the importance of the coefficient theoretically, in the practical measurements of the thermionic constants A and ϕ, an element of uncertainty, however small, is introduced.

Next, the determination of i, the thermionic emission from a unit area of the filament, is not free from difficulties. most of which arise from the fact that prior to the emission measurements the filament has to be given a rigorous degassing heat treatment in the course of which the surface of the emitter gets pitted and even crystallisation may occur thereby changing the very nature of the emitter. The area of the emitter surface, with its hills and dales, is not easy of an accurate determination. On account of uneven cross section the emission varies from point to point. There is no single potential difference between the

anode

anode and even the central segment of the filament as the potential gradient along the latter due to the heating current from the low tension battery will vary on account of the varying cross-section. This results not only in an uneven emission but also in collection by the anode. It also makes the Lead loss and Schottky corrections inaccurate. The last named correction needs a further discussion as its measurement requires something more than a mere knowledge of the potential difference between the filament and the anode.

In the correction for the Schottky effect S, the constant of proportionality, has to be calculated from the electrode geometry by electrostatic laws. But, although some special cases, e.g., a heated straight filament surrounded by a coaxial cylindrical anode, have been studied theoretically the general investigation of the space charge effect for any given disposition of the electrodes, such as might occur in any actual experiment, is very difficult. Even in the simple case, mentioned above, the theoretical investigation, as pursued by Langmuir [8], Langmuir and Blodgett [9] and others, could give a solution only for the particular case of the velocity of electron emission being zero- an assumption unrelated to facts since the electrons are emitted with a Maxwellian velocity distribution. Hence, the value of i, the saturation electronic current for a zero field at the emitter, cannot be determined with any certainty.

The measurement of the true temperature presents similar diffuculties. Due to the unevenness of the filament the temperature varies from point to point and there is no single temperature. Further, a temperature scale has to be set up for each metal to be investigated. It has been pointed out that now data for the emissivity of most metals for different temperatures are available. But the emissivity for different temperatures has to be known for the metal under conditions of heat treatment as nearly identical in condition as possible with those used in the measurement of electron emission. Since conditions of heat treatment vary from sample to sample and, in the event of change of nature of the surface occuring due to crystallisation, the condi-

tions may vary from point to point even in the same sample. Hence an element of uncertainty creeps into the measurement of temperatures. Wahlin and his coworkers[10] now have adopted the practice of setting up a temperature scale for each sample of the metal under investigation.

It will be shown later that the thermionic method developed under the guidance of Sir K.S. Krishnan, F.R.S., at the University of Allahabad eliminates the various defects mentioned above.

(2) The Calorimetric method.

Richardson[11] was the first to suggest that since the work function is the net work done at the expense of the thermal energy in taking an electron out of the metal and putting it at rest outside the surface and since the emitted electrons have a Maxwellian velocity distribution corresponding to the temperature T of the emitter, and, therefore, have an average kinetic energy 2 KT, the emitter will lose an average energy $\left(\frac{\phi_e \epsilon}{300} + 2KT\right)$ ergs per emitted electron, where ϕ_e denotes the work function of the emitter in electron volts. If the emission is i amperes, the energy lost is

$$E_e = i\left(\phi_e + \frac{2T}{11600}\right) \text{ watts} \quad \ldots\ldots\ldots\ldots (2)$$

On the other hand, if electrons are recived by an anode at potential V volts positive with respect to the emitter, the average energy received per electron by the collector is

$$\left(\frac{\phi_c \epsilon}{300} + 2KT + \frac{V\epsilon}{300}\right) \text{ ergs.}$$

Hence for i amperes thermionic electron current received, the collector will receive

$$E_c = i\left(\phi_c + \frac{2T}{11600} + V\right) \text{watts} \ldots\ldots\ldots\ldots (3),$$

where ϕ_c is the work function of the collector.

Hence, there are two types of experiments. In the first, the cooling produced as a result of the emission of electrons is measured; while in the second, the heating of the anode is measured.

There has been a variation in the second type of experiment due to Holst and Oisterhuis[12], Penning[13], Schttky[14] etc., the last worker being Van Voorhis and Compton[15]. The idea is that if a Langmuir collector is placed near the anode in a

gaseous discharge it will be surrounded by both positive ions and electrons. Now if the potential of the collector is kept at a constant, slightly negative value V_o with respect to the space potential, positive ions will reach it at a constant rate due to their velocity of agitation in the gas and the small attracting potential V_o. Electrons also will reach it at a constant rate as, owing to the Maxwellian distribution of their velocities, there will always be some electrons which will have large enough energies to overcome the retardation V_o. Hence, in unit time the collector will receive an amount of heat H_o made up of H_r the heat transfer by radiation; H_c the heat transfer by conduction; the heat contribution of the positive ions due to their average energy of agitation, E_+, in the gas, their acceleration by the voltage V_o, and their heat of neutralisation ϕ_+ at the metal surface; and lastly, the heat contribution of the electrons due to their energy of agitation, E_-, and also due to their heat of condensation ϕ_- into the metal. Hence, we get

$$H_o = H_r + H_c + i^+(E_+ + V_o + \phi_+) + i^-(E_- + \phi_-) \quad \ldots\ldots\ldots(4),$$

where the i's denote the corresponding type of current received by the collector.

Now, if the potential of the collector is then suddenly altered to a less negative value, V_f, there will be, immediately after this change, no appreciable variation in H_r and H_c. The change in i^+ also will be negligibly small. But i^- will change i_f, say. Hence

$$H_f = H_r + H_c + i^+(E_+ + V_f + \phi_+) + i_f^-(E_- + \phi_-) \quad \ldots\ldots\ldots(5)$$

Subtracting (4) from (5), we get

$$H_f - H_o = i^+(V_f - V_o) + (i_f^- - i^-)(E_- + \phi_-) \ldots\ldots\ldots(6)$$

The difference between H_f and H_o may be deduced from the heat capacity of the collector and its rate of temperature rise from the thermocouple embedded in the collector when the potential is changed from V_o to V_f. Hence ϕ_- may be calculated since all the remaining quantities in the above equation are measurable directly or by the Langmuir collector methods. However, in view of the complexity of the phenomena and of the many corrections that have to be applied it appears that this method, as at present pursued, may not prove of much value.

Hence, the experiments on the determination of ϕ by the cooling and by the heating effects will be discussed.

(i) Determination of ϕ by the Cooling Effect.

Although Wehnelt and Jentzsch[16] were the first to utilise the cooling effect for the determination of ϕ and, subsequently, Cook and Richardson[17] established that work functions could be accurately measured by this method, it is Davisson and Germer[18] whose work approaches perfection in technique. It will, therefore, be discussed briefly though later work by Krüger and Stabenow[19] and also by Fleming and Henderson[20] cannot be ignored.

In Davisson and Germer's work the filament to be tested is provided with potential leads far enough removed from the ends of the filament to avoid effects arising from the end cooling and by means of guard rings the emission of electrons from the filament is limited to the region between these points.

Suppose that with the plate at a negative potential and a heating current of I amperes through the filament the difference in potential between the leads is E volts. If now the plate is made positive an electron current of i amperes flows from the filament and, simultaneously, a cooling of the filament occurs. Hence, the resistance of the filament is reduced and the heating current as well as the potential drop across the leads will also be affected.

Now so long as the plate is negative and there is no electronic emission reaching the anode from the filament the power $\overline{W}$ supplied to the filament is equal to the power W radiated from it. But when the emission occurs from the filament these are no longer the same and the difference between $\overline{W}$ and W is the power absorbed by the thermionic emission. Expressing this as a voltage, times the emission i, it can be shown that

$$\phi i = \Delta\overline{W} - \Delta W = \left[\frac{2EI}{E - I\frac{dE}{dI}}\right]\left(\Delta E - \frac{dE}{dI}\Delta I\right) \qquad \ldots\ldots(7)$$

Davisson and Germer kept ΔI zero by compensating the change in filament resistance by an appropriate alteration in the resistance r_o in the heating circuit. Hence

$$\phi = \frac{2EI}{E - I\frac{dE}{dI}} \cdot \frac{\Delta E}{i} = Q \cdot \frac{\Delta E}{i} \qquad \ldots\ldots(8)$$

In order that this relation shall yield the true value

of ϕ, the value of ΔE employed must be the voltage change actually due to the cooling effect of the emission. Hence, the following corrections have to be applied:

(i) There are a number of changes in E which reverse sign relative to the true effect if the direction of the heating current is reversed. These are eliminated from the results by averaging observations made with the two directions of I.

(ii) There are other changes which do not reverse their sign, e.g., effects resulting from geometrical dissymmetry and from variations in thermionic properties from point to point along the filament. All first order errors arising from these causes are eliminated from the results by averaging observations for the two directions of I.

(iii) Under the bombardment of the electrons the plate gets heated and a part of the radiation from the plate is absorbed by the filament which, therefore, rises in temperature thereby increasing the resistance and, hence, the voltage across the filament. The most satisfactory method of correcting for this error is to observe the value of $\frac{\Delta E}{i}$ at constant filament current for a series of plate voltages, and then to extrapolate to the value of $\frac{\Delta E}{i}$ corresponding to plate voltage zero. This follows from the consideration that $\Delta\phi$, the change in the work function due to this cause, can be shown to be equal to $-fV$, where f is the fraction of the radiation from the plate absorbed by the filament and V is the potential difference between the plate and the filament so that at $V = 0$ the change $\Delta\phi$ also will be zero and at that voltage $Q\frac{\Delta E}{i}$ will be the value of ϕ in accordance with equation (8).

(iv) Yet another spurious effect is due to the space current returned to the filament. If the electronic current, i, reaching the anode is not small compared with I, the heating current, there is an addition of the returned space current to the normal heating current with the result that there is a variation of the total effective heating current from point to point along the filament. This defect can be removed by so arranging the return of the space current to the filament that the voltage change due to the redistribution of the heating current is eliminated. It can be shown that if the current returned to the middle point of the filament

of the filament is four times as great as the current returned to ~~the~~ each end by suitable resistances being put as in figure 4, ΔE is zero.

Determinationsof by this method have been very accurate and are as reliable as by the thermionic emission method.

(ii) Work Function from the Heating Effect.

This type of experiment based on ~~the~~ equation (3) has been performed by Richardson and Cook[21]. Two short Osmium filaments heated to a high temperature were used to supply the copius stream of electrons needed. The metal to be investigated, in the form of very thin strips, was wound on a very light glass frame so as to lie in one plane and to expose as much surface as possible. The frame was insulated from the Osmium filaments and suitably mounted between them. By applying various small potential differences the electrons emitted by the Osmium strips were made to impinge on the metal strips, which formed one arm of a very sensitive Wheatstone bridge. The effect was tested by the change of resistance and temperature experienced by the strip. The strip thus acted as a bolometer. These experiments gave the value of ϕ of the proper order of magnitude. In fact, Richardson[22] was inclined to the view that, owing to the way in which the contact potential entered, the effect found rather measured the cooling effect at the surface of the hot electrode than the heating effect at the surface of the cold one. Since the precautions of high vacuum and degassing were not taken the results obtained in the experiment were not satisfactory.

3. Electron reflection from the surface of metals.

This method consists in measuring the potential barrier, V_α, at the surface of the metal by using electrons as probes which are diffracted by the crystal lattices . Knowing from the X-ray data the crystal structure of the metal, V_α can be calculated. The value of μ, the zero point energy, is known so that an estimate of ϕ could be made from the relation:

$$\phi = V_\alpha - \mu$$

It will be remembered that Davisson and Germer[23] found that

the directions of the electron beams diffracted by the space lattice could not be predicted by assigning to the electrons the wave length given by the de Broglie relation:

$$\lambda = \frac{h}{mv} .$$

Instead, it was necessary to assume a contraction of the crystal lattice, or else, to assign to the electrons a smaller wave length, λ'. The interpretation of this apparant discrepancy was given by Rosenfeld and Witmer[24] and Bethe[25], who pointed out that, on entering the crystal, the electron would be refracted and, hence would suffer a change in wave length such that $\lambda' = \frac{\lambda}{\beta}$, where β is an index of refraction. β was found to be > 1, implying that the electrons get speeded up on entering the crystal on account of their falling through the surface potential barrier, V_α, after having been accelerated through the applied potential V between the electron gun and the (111) face of the nickel crystal used by Davisson and Germer. The de Broglie wave length on account of the applied potential, V, is given by

$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2m\varepsilon V}}$$

On passing through the surface potential, V_α, the electron is accelerated so that the changed wavelength λ' is given by

$$\lambda' = \frac{h}{\sqrt{2m\varepsilon (V + V_\alpha)}}, \text{ so that}$$

$$\beta = \frac{\lambda}{\lambda'} = \sqrt{1 + \frac{V_\alpha}{V}} .$$

Since β and V are determined experimentally, one can find V_α.

Since the errors of the electron diffraction experiments give V_α to an uncertainty of ± 5 volts, and, there is an uncertainty in the value of χ, the number of free electrons per atom in the expression of μ, the zero point energy, this method of determining ϕ has its limitations and can be considered only of qualitative significance. The values of ϕ found out by this method are of the right order of magnitude. Of the five methods of determining work functions, listed before, this one is the least developed as is the case with the method depending on the heating effect.

4. Work Function from Contact Potentials.

It is well-known that the Contact Potential, V_{cp}, between two metals A and B of work functions ϕ_A and ϕ_B, respectively, is related by the equation:

$$V_{cp} = \phi_B - \phi_A .$$

Contact potential measurements are usually made by methods based on Kelvin's, since that affords practically instantaneous determinations of Contact Potentials allowing distinction between rapid and slow changes of work function. In Kelvin's method the two metals, A and B, form a condenser, which tends to become charged to their contact difference of potential, equal in magnitude to the difference in the work functions of the two metals. When the Contact Potential is compensated by an applied potential, a change in the capacity of the condenser is unaccompanied by an electrical discharge.

Using this idea Zisman[26] has devised a method of measuring the contact potential between two parallel plates, whereby he varied their capacity at an audio frequency by making one plate vibrate at the end of a flexible reed. The other plate was coupled to an audiofrequency vacuum tube amplifier. An applied potential in series with a high resistance between the plates was adjusted until no signal appeared in the amplifier. At this point the applied potential had the value of V_{cp} between the plates.

But the best determinations[27] are those of P.A. Anderson. A beam of 4 to 8 volt electrons is directed by an electron gun against a small area near the centre of the strip of Tungsten foil and the current to the foil plotted as a function of the retarding potential applied to the strip. A similar characteristic is taken of the electron flow to the second metal. The voltage displacements of these two characteristics from one another then measures the contact potential between the two metals- tungsten being taken as a standard because being one of the most refractory metals it can be thoroughly purified of all adsorbed and occluded foreign matter by a rigorous course of heat treatment. The Work Function of tungsten being known, that of the other metal is established. Care is taken that after a thorough outgassing the tube is sealed from the pumping system, gettered by the vapourisation of Barium, and

immersed in liquid air during measurement. Clean Tungsten is chosen as a reference surface to which the difference of the pair of metals is referred. Then the metal surface to be measured against tungsten is formed by thermally vapourising the metal and the purity of the metal finally checked by measuring the contact potential of each of a succession of films formed in a fractional distillation of the metal. The attainment of a constant potential unaltered by further distillation, is taken as a criterion of a clean film. Thus, a method of measurement has been used which makes it possible to follow closely any changes in work function which may be experienced by the tungsten immediately after it is flashed, or by the freshly distilled metal immediately after it is formed. Further, this method, unlike the thermionic one, is applicable to all metals, not necessarily refractory. Unlike the photoelectric method, to be discussed shortly, it yields measurements of uniformly high sensitivity and, taken altogether, seems to offer a promising road to a systematic knowledge of the work function charateristics of non-composite, viz., pure, metal surfaces.

5. Work Function from Photoelectric Effect.

This method is based on the imparting of energy, ϕ, viz., $V_a - \mu$, to the Fermi electrons within a metal having energy μ by means of photons of just enough frequency ν_0 to enable the electrons to come out of the metal. Thus

$$h\nu_0 = V_a - \mu = \phi$$

Naturally, precautions have to be taken about the purity of the surface of the metal and that no scattered light of shorter wave length than that to which the monochromatic illuminator is set should be allowed to enter the cell containing the metal under investigation. The contact potential between the metal and the collector has also to be determined. High vacuum has to be maintained.

The photoelectric threhold, ν_0, is determined by any of the follwing methods:

(a) The stopping potential method.

If the photoelectric surface is mounted in an evacuated enclosure, with a second electrode near it so as to collect all the photoelectrons reaching it and if this second electrode is made increasingly negative with respect to the photo surface, a retarding potential V is reached at which the photo current is zero. The experiment is repeated for various values of ν, and ν plotted against V. Where the curve cuts the frequency axis, $\nu = \nu_0$. A correction must be made for contant potential when estimating V. In the work of Millikan[28] an arrangement was made to cut a fresh surface of the metal within the evacuuated bulb itself so that a new surface free from adsorbed or occluded gases was exposed to the photons. In general, such experiments suffer from the difficulty that measurements of stopping potentials are difficult to make.

(b) The spectral distribution curves method.

In this method the rate at which electrons are ejected from a given surface by a unit intensity of absorbed light of given frequencies, viz., the spectral sensitivity or the photoelectric yield, is plotted against the frequencies. The point at which the extrapolated curve plunges into the frequency axis gives the desired threshold ν_0. The collecting electrode is here charged positively so as to collect all the electrons ejected. The relative intensities of the various spectral lines furnished by the monochromator supplemented by filters opaque to short wavelengths are found with the help of a sensitive thermocouple. In order to reduce the measurements to unit intensity of absorbed light, it is necessary to know the reflectivity of the surface for various wavelengths. This is the method most commonly used.

(c) The "Complete" Photoelectric emission method.

Richardson[29] from thermodynamical reasoning concluded that if a metal surface be exposed to the total thermal radiation from a black body at a temperature T, the total photoelectric current from the surface should vary with T according to the equation:

$I = A_1 T^2 e^{-\frac{h\nu_0}{KT}}$ where A_1 is a Constant and the other terms have their usual significance. This equation is thus identical with Richardson's thermionic emission equation for the temperature T for a surface whose work function

is $h\nu_o$. The photoelectric current under these conditions has been called the"complete" photoelectron emission.

Temperature correction.

Having determined the photoelectric threshold at any temperature, T, one has to remember that for all temperatures above 0 K the spectral distribution curves show an asymptotic approach to the frequency axis so that the "threshold" loses quantitative significance. At 0 K the experimentally determined threshold would be the same as the true threshold defined by

$$h\nu_o = W_a - \mu.$$, where W_a is the height of the potential barrier in exp.

But at higher temperatures this is not so because when electrons are ejected by light of frequency near the threshold it is only the electrons of maximum energy which are available for ejection, and the effect of temperature on these is of considerable importance. Fowler[30] has shown that if

$$\phi = W_a - \mu \text{ and}$$

$$x = (h\nu - \phi)/ KT = h(\nu - \nu_o)/ KT,$$

the photoelectric emission, I, is given by

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

where A is a constant and $f(x) = e^x - \frac{e^{2x}}{2^2} + \frac{e^{3x}}{3^2} - \ldots\ldots$, for $x \leqslant 0$

and $= \frac{\pi^2}{6} + \frac{x^2}{2} - \left(e^{-x} - \frac{e^{-2x}}{2^2} + \frac{e^{-3x}}{3^2} \ldots\right)$ for $x \geqslant 0$.

f(x) is thus a universal function of (x), whose form is the same for all metals and all temperatures.

Now, since for frequencies near ν_o the quantity $(W_a - h\nu)^{\frac{1}{2}}$ is practically a constant and may be included with the factor A, therefore, taking logarithms, we get

$$\log(I/T^2) = B + F(x),$$

where B is a new constant independent of ν and T, and $F(x) = \log f(x)$.

The theoretical curve F(x) may be plotted as a function of x and if the observed values of the photoelectric yield I are plotted in the form $\log (1/T^2)$ versus $\frac{h\nu}{KT}$, it is apparant that if the experimental curve is shifted horizontally and then vertically to coincide with the theoretical curve, the amount through which the horizontal shift will have to take place will be $\frac{\phi}{KT}$ and that through which the vertical shift will occur will be B. The horizontal shift, therefore, determines ϕ and hence ν_o, the true threshold.

~~The form of the theoretical curve and the method~~

The form of the theoretical curve and the method of shifting the observed curves are indicated in Fig.5.

It will be seen that the photoelectric method of determining the electron work function of metals is as satisfactory as the thermionic emission or the contact potential measurement methods. For less refractory metals it shares suitability with the latter method.

A new Thermionic method.

An altogether new method of measuring the thermionic constants, A and ϕ, which, besides being direct and straightforward minimises or eliminates the various defects pointed out in the Richardson type of thermionic emission measurements, has been developed under the guidance of Sir K.S. Krishnan, F.R.S. at the University of Allahabad.

A small hollow cylinder of the metal under investigation is closed from all sides except for a small hole of about 1 mm. diameter at one end. This cylinder is heated to various high temperatures by being kept within, but insulated from, a graphite furnace tube through which a heavy current is passed from a transformer. The electrons emitted by the inner surface of the metal cylinder at any temperature soon acquire equillibrium with the emitting metal surface and ~~form~~ an electronic gas pressure within the cavity of the cylinder. On account of this pressure the electrons effuse out through the hole and are caught by a Faraday Cylinder a cm. or so away from the hole. The electron effusion current is, naturally, proportional to the gas pressure within the cavity and this gas pressure will depend both on the temperature of the emitter as well as on the work function of the metal. The whole arrangement is enclosed within a water cooled vacuum chamber and measurements of the effusion current are recorded after ~~both~~ the metal cylinder, the graphite furnace tube and the entire contents are thoroughly degassed in vacuum, and the value of the work function acquires a steady value. Full details are given in the report on the investigations on the thermionic constants of Molybdenum.

If the radius of the diaphragm of the Faraday Cylinder, kept d distance away from the effusion hole of ~~area~~ area, S, is r, the saturation current, i_o, collected by the Faraday Cylinder has been shown by B.N. Srivastava[31] to be given by:

$$p = \frac{\sqrt{2\pi m K}}{\varepsilon S} \cdot \frac{r^2+d^2}{r^2} \cdot i_o \cdot T^{\frac{1}{2}},$$

where p is the equillibrium pressure of the electron gas within the metallic cavity, ε is the electronic charge and K and T are respectively the Boltzmann constant and the absolute temperature of the metal.

The effect of the space charge on the electronic current under such an arrangement of measurement has been worked out theoretically [32] and also verified experimentally [33] by B.N. Srivastava and A.S. Bhatnagar.

Applying the Clausius- Clapeyron equation to the equillibrium vapour pressure of a monatomic gas, the electronic gas pressure within the metal cavity is also given by

$$\log_{10} \frac{p}{T^{\frac{5}{2}}} = -\frac{\phi}{KT} \log_{10} e + C \log_{10} e \qquad \ldots\ldots(10)$$

ϕ being the work function of the metal.

Substituting the value of p given in (9), above, we get

$$\log_{10} \frac{i_0}{T^2} = -\frac{\phi}{KT} \log_{10} e + C \log_{10} e - \log_{10} \frac{(2\pi mK)^{\frac{1}{2}}}{\varepsilon S} \cdot \frac{r^2+d^2}{r^2} \qquad \ldots\ldots(11)$$

so that if, as usual, the experimental values of $\log_{10} \frac{i_0}{T^2}$ are plotted against those of $\frac{1}{T}$, the value of the work function, ϕ, can be determined from the slope of the curve.

Taking into account the spin of the electrons, since according to Sackur and Tetrode

$$C = \frac{2(2\pi)^{3/2} K^{5/2} m^{3/2}}{h^3},$$

$$C \log_{10} e - \log_{10} \frac{(2\pi mK)^{\frac{1}{2}}}{\varepsilon S} \cdot \frac{r^2+d^2}{r^2} = \log_{10} \frac{2(2\pi)^{\frac{3}{2}} K^{\frac{5}{2}} m^{\frac{3}{2}}}{h^3 \cdot (2\pi mK)^{\frac{1}{2}}} \cdot \frac{\varepsilon S r^2}{r^2+d^2}$$

$$= \log_{10} \frac{4\pi mK^2}{h^3} \cdot \frac{\varepsilon S r^2}{r^2+d^2}$$

But $\frac{4\pi \varepsilon m K^2}{h^3} = A_0$, the thermionic constant in Richardson's well known thermionic emission equation as derived from Thermodynamical considerations by Dushman. Hence, the above is equal to $\log_{10} A_0 \frac{S r^2}{r^2+d^2}$.

Hence, (11) becomes

$$\log_{10} \frac{i_0}{T^2} = -\frac{\phi}{KT} \log_{10} e - \log_{10} A_0 \frac{S r^2}{r^2+d^2} \qquad \ldots(12)$$

from which, knowing ϕ, A_0 can be calculated.

It will be seen that this method has the following advantages:

(1) It is direct and straightforward as it seeks to measure the electronic gas pressure within the cavity of the metallic cylinder.

(2) There is no complication about reflection coefficients.

(3) Since the metal under investigation is enclosed within the graphite furnace tube, it is heated by the radiation within the graphite enclosure which acts as a black body. Hence, the temperature of the furnace tube, as measured by an Optical Pyrometer sighted through a window in the vacuum chamber, gives the temperature of the metal under investigation without any recourse to a temperature scale for the metal.

for the metal under conditions identical with those of emission measurements.

(4) Any variations in the area of the emitting surface due to evaporation of the metal at places does not affect the temperature or emission of the metal under investigation. The area of the emitter does not enter into calculation.

(5) Corrections due to Lead losses and to Schottky effect are not needed. Instead of any high potential on the anode as required in the Richardson type of emission measurements, the potential difference between the effusion hole and the diaphragm of the Faraday Cylinder is of the order of 1 volt to bring about saturation in the measurement of the effusion currents.

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ON A NEW METHOD OF DETERMINING THE THERMIONIC CONSTANTS OF MOLYBDENUM.

Introduction.

Most of the investigations on the Thermionic Work Function of metals are based on the pioneer work of O.W. Richardson. In such methods the relation used has been

$$i_o = A_o T^2 e^{-\phi/KT},$$

in which i_o is the saturation electronic current collected by the anode from a unit area of the filament heated to the absolute temperature, T; A_o is a constant, found by Dushman to be theoretically the same for all metals; K is Boltzmann's constant and ϕ is the work function for the metal under investigation. Such thermionic determinations suffer from certain defects.

In the theoretically derived equation of thermionic emission, whether obtained on thermodynamical grounds by Dushman, or by the use of Fermi-Dirac statistics by Sommerfeld, the right hand side of the above equation has to be multiplied by a transmission factor, (1-r), where r is the reflection coefficient for electrons incident perpendicularly on the surface of the metal. This r is the external coefficient in the case of Dushman's theory and the internal one in that of Sommerfeld. However, it does occur. But, as has been shown by Becker and Brittain[1], since all available evidence seems to show that the reflection coefficient is less than 0.1 and since the values of A_o are usually not accurate to within 10%, the reflection coefficient is neglected and the emission equation is, for all practical purposes, taken as above thereby introducing a certain amount of uncertainty in the value of the work function obtained.

Next, the determination of i_o involves some difficulties. When the filament is subjected to the intensive heat treatment for degassing purposes, it gets unevenly evaporated and its surface gets pitted. The area of the emitting surface, with its hills and dales, is not easy of an accurate determination. Then, on account of the uneven cross-section of the filament, whose nature of surface, even, may get changed on account of crystallisation occuring during ~~the hat~~

the heating, the emission may vary from point to point. From the point of view of collection by the anode also uncertainties occur. Although the guard rings minimise the effect of the potential gradient along the filament due to the heating current during emission measurements, there is no single potential difference between the anode and even the central portion of the filament and large variations, due to the unevenness of the filament, may arise in the potential difference between the collector and the emitter. This results in an uneven thermionic collection by the anode. The unevenness of the filament produces difficulties in the correction for Lead losses and for Schottky effects also. The last-named effect needs further discussion as its measurement does not require merely a knowledge of the potential difference between the anode and the filament.

In the correction for Shottky[2] effect, S, the constant of proportionality in the equation

$$\log_{10} i_1 = \log_{10} i_o + \frac{1.905(SV)^{\frac{1}{2}}}{T}$$

has to be calculated from the electrode geometry by electrostatic laws. But, although some special cases, e.g., a heated straight filament surrounded by a coaxial cylindrical anode, have been studied theoretically, the general investigation of the space-charge effect for any given disposition of the electrodes, such as might occur in any actual experiment, is extremely difficult. Even in the simple case, mentioned above, the theoretical investigations, as pursued by Langmuir[3], Langmuir and Blodgett[4] and others, could give a solution only for the particular case of the velocity of electron emission being zero- an assumption quite unrelated to facts since the electrons are emitted with a Maxwellian velocity distribution. Hence, the value of the saturation current for a zero field at the emitter, i_o, cannot be determined with any certainty.

The measurement of T is equally uncertain. Due to the uneven cross-section of the filament, the heating current varies from point to point and there is no single temperature of the filament. Further, since the radiation emitted by the metal has to be chosen for the measurement of temperatures by the Optical Pyrometer,

a temperature scale for each metal to be investigated has to be set up under conditions of heat treatment as nearly identical as possible with those used in the measurement of electronic emission. Since conditions of heat treatment vary from sample to sample and, in the event of crystallisation occuring, from point to point even in the same sample, an element of uncertainty in the value of the temperature of the emitter creeps in.

The present report deals with a new method of determining Thermionic Constants developed in the Physics Laboratory of the University of Allahabad. It will be seen that it eliminates the various defects, enumerated above, in the usual Richardson type of experiments.

A.S. Bhatnagar[5] has determined the Thermionic Work Function of Graphite from the rate of effusion of electrons through a tiny hole in an otherwise closed cylindrical cavity made in a rod of graphite which could be heated electrically in vacuum to various high temperatures.

It is obvious that, for any given temperature, the electron gas produced in the graphite cavity will attain a saturation pressure in equilibrium with the surface of the cavity and that the rate of effusion of the gas through the hole will be proportional to this pressure. If the effused electrons are collected by a Faraday Cylinder with a limiting diaphragm of radius, r, placed, d, distance away from the effusion hole of area, S, the saturation current, i_o, has been shown by B.N. Srivastava[6] to be given by

$$p = \frac{\sqrt{(2\pi mk)}}{\varepsilon S} \cdot \frac{r^2 + d^2}{r^2} \cdot i_o \cdot T^{\frac{1}{2}},$$

where, p, is the equilibrium pressure of the electrons within the cavity, ε, is the electronic charge, and k and T have the usual significance.

The effect of the space charge on the electronic current under such an arrangement of measurement has been worked out theoretically by B.N. Srivastava and A.S. Bhatnagar[7] and the conclusions also experimentally verified by them.[8]

Applying the Clausius-Clapeyron equation to the equilibrium vapour pressure of a monatomic gas, the electronic gas pressure within the cavity is given by

$$p = e^{c} T^{5/2} e^{-\phi/kT},$$ ϕ, being the Work function.

Whence,

$$\log \frac{p}{T^{5/2}} = -\frac{\phi}{KT} \log e + c \log e$$

Substituting the value of p, given before, we get

$$\log_{10}\frac{i_o}{T^2} = -\frac{\phi}{kT}\log_{10}e + c\log_{10}e - \log_{10}\frac{(2\pi mk)^{\frac{1}{2}}}{\varepsilon S}\cdot\frac{r^2+d^2}{r^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

so that, as usual, if the experimental values of $\log_{10}\frac{i_o}{T^2}$ are plotted against those of $\frac{1.}{T}$, the value of the work function, ϕ, can be determined from the slope of the curve.

Considering the spin of the electrons, since according to Sackur and Tetrode,

$$e^c = \frac{2(2\pi)^{3/2}k^{5/2}m^{3/2}}{h^3},$$

$$c\log_{10}e - \log_{10}\frac{(2\pi mk)^{\frac{1}{2}}}{\varepsilon S}\cdot\frac{r^2+d^2}{r^2} = \log_{10}\frac{2(2\pi)^{3/2}k^{5/2}m^{3/2}}{h^3(2\pi mk)^{\frac{1}{2}}} \times \frac{\varepsilon Sr^2}{r^2+d^2}$$

$$= \log_{10}\frac{4\pi mk^2}{h^3}\cdot\frac{\varepsilon Sr^2}{r^2+d^2}$$

But $\frac{4\pi\varepsilon mk^2}{h^3} = A_o$, the Thermionic constant in Richardson's well-known equation $i_o = A_o T^2 e^{-\frac{\phi}{kT}}$, as derived from Thermodynamical considerations by Dushman.

Hence, the above is equal to $\log_{10} A_o\frac{Sr^2}{r^2+d^2}$.

$\therefore$ (1) becomes

$$\log_{10}\frac{i_o}{T^2} = -\frac{\phi}{kT}\log_{10}e - \log_{10}A_o\frac{Sr^2}{r^2+d^2} \qquad \ldots(2)$$

from which, knowing ϕ, A_o can be calculated.

particularly of those with values of work function lower than that of graphite,

It was thought that the work function of metals could be determined by noting the increase in the saturation pressure if the metal were introduced in the graphite cavity. ~~provided the work function of the metal was less than that of graphite~~. Since the pressure of the electron gas due to the metal in that case would be higher than due to graphite alone, there should be an excess of the effusion current, which should enable the work function of the metal to be calculated.

With this end in view, the following metals were tried. The temperatures at which an appreciable electronic effusion current from the metal could be expected to begin were calculated from the value of the work function of the metal and the sensitivity of the galvanometer connected to the Faraday cylinder ~~xxxgixxx~~ and are given below:

Metal	Melting point.	Work Function in electron volts.	Temperature in °C at which a measurable extra effusion current was due.
1.Barium	850° C	2.2	520° C
2.Strontium	800° C	2.2	520° C
3.Magnesium	651° C	2.4	600° C
4.Titanium	1715° C	3.9	1090° C
5.Zirconium	1930° C	4.1	1150° C
6.Silver	961° C	4.7	1300° C

Along with the above, MgO also was tried.

With graphite alone (work function: 4.8 e.v.), an appreciable effusion current began occuring at about 1450°C. It was found, though after each experiment some of the metal introduced was found present in the cavity since very little could get out of the tiny effusion hole, when heated, the effusion current began at about the same temperature of 1450° C. This showed that there was no evidence, whatsoever, of any extra electronic pressure being developed within the graphite cavity due to the metal of lower work function introduced within it. ~~the cavity~~. The graphite surface of the cavity would not allow any increase in the equilibrium pressure appropriate to it at that temperature. ~~This phenomenon needs~~

~~further investigation.~~

In the light of the above results it was decided to make a closed chamber with a small effusion hole of the metal itself so that the electrons emitted by the metal may acquire equilibrium with the surface of that metal and may not be affected by the presence of any foreign surface like that of Graphite. The experimental details are described below.

Experimental Arrangement.

(a) The Molybdenum Tube.

A spectroscopically pure cylindrical rod of Molybdenum, about 8 cms. in length, was bored throughout its length so as to form a tube. This tube was provided at each end with a tightly fitting plug of the same metal. One of the plugs was solid, while the other, facing the Faraday cylinder, was hollow and had a central hole of diameter 0.724 mms. It was through this hole that the electrons, produced within the cavity of the Molybdenum tube, when heated, effused out to the Faraday cylinder. The overall length of the Molybdenum tube, thus prepared, was 8.5 cms. and the outer diameter 8.5 mms. ~~(Figure 1)~~ Fig. 1.

The inner surface of the Molybdenum tube was cleaned of all greasy matter with carbon tetrachloride after which a new emitting surface was produced by etching the metal with dilute HCl.

This Molybdenum tube was heated in vacuum by being enclosed within, but insulated by from quartz rings from, a graphite furnace tube through which a heavy electrical current could be sent from a transformer (Fig.). Lest the molybdenum tube should acquire a positive potential due the emission of electrons from its surface, the end having the effusion hole and facing the Faraday cylinder was earthed by means of a molybdenum wire which could not only stand any high temperatures, in the presence but could also avoid the production of any Contact Potentials between the Molybdenum tube and the earthing wire itself. The flow of effused electrons was thus made regular between the hole and the Faraday cylinder without the occurence of any extraneous electric fields.

(b) The Graphite Furnace Tube.

The furnace tube of Acheson graphite was altogether 14.7 cms. long and was made by boring a hole, ~~1.3 cms. in diameter,~~ in a cylindrical rod of graphite 1" in diameter. Leaving a length of 6 cms. at one end and of 1.7 cms. at the other to act as collars, the middle portion of about 7 cms. was thinned so that its wall had a thickness of only 2 mm. and acted as the furnace proper with an outer diameter of 1.4 cms. and an inner diameter of 1.2 cms. The inner diameter of the collars was 1.3 cms. (Fig 1). ~~The whole furnace tube was turned out on a lathe out of one piece of graphite rod. The shape and specifications of the furnace tube together with the Molybdenum tube in position are illustrated in Figure 2.~~

The collars at the ends were held tight between holes of corresponding size in graphite blocks, which themselves were tightly clamped to water cooled plates p_1 and p_2 of copper which acted as electrodes for the heavy heating current (Figs 2 & 3) ~~Fig. 2~~ from the transformer. Since a heating current of the order of 500 to 1,000 amperes had to be passed through the furnace tube, the electrical contacts between the copper electrodes and the graphite blocks as well as between the blocks and the collars had to be very good, indeed, if arcing and the consequent fluctuations in the galvanometer deflections and the far more serious consequences of the pitting of the surface of the copper plates by arcing were to be avoided. Hence, in order to improve the contacts, copper foils were introduced between the various contacting surfaces. Care was also taken that when tightly clamped between the graphite blocks on the copper ~~electrodes~~ plates, the furnace tube rested in a horizontal position so that there was no uneven strain anywhere on the ~~furnace~~ tube resulting in its fracture.

Figure 1 shows the disposition of the Molybdenum tube resting on fused quartz rings within the graphite furnace tube. These rings were 5 mms. wide and had an inner diameter of about 1 cm. so as to allow for the expansion of the Molybdenum cylinder, which had an external diameter of 8.5 mms. only. They were kept in the collars near the ends of the furnace portion of th

graphite tube and since they had an external diameter between 1.2 and 1.3 cms. there was no risk of their accidentally entering the furnace part of the tube. Since the thick copper plates on which the graphite blocks carrying the thick graphite collars were clamped were water cooled, there was no ~~risk~~ chance of the temperature of the quartz rings rising much and causing them to emit any electricity or acquiring any electric potential. As will be shown later, this was also verified experimentally. In this way, the Molybdenum tube was heated by the radiations of the graphite furnace tube without being in contact with it.

Care was taken that the plugs of the Molybdenum tube projected a little beyond the fused quartz rings so that no complications from the production of any electrostatic charges may arise.

(c) <u>The Furnace and Vacuum Chamber</u>.

The furnace worked in vacuum and was originally set up by Saha and Tandon[9] for their studies on Thermal Ionisation. Subsequently some minor changes were effected to suit the present investigations.

Briefly, the chamber consists of a water-cooled cylindrical drum, A, of cast iron and two hollow cast iron plates, B, and, C, which close the open ends of the drum (Figures 2 and 3) when the furnace is working. The drum and the plates are all vertically mounted on a horizontal lathe bed. The axis of the drum also is horizontal. ~~so that when the latter is moved on its four small wheels on the lathe bed it makes a vacuum tight contact against. The plate, B, fixed at one end of the lathe bed in~~ The plate B is fixed at one end of the lathe bed in a framework of cast iron tightened to the bed by the supports SS. The vertical plate, C, was permanently joined to the drum so that when all the processes of assembling the graphite furnace tube with its contents of the Molybdenum cylinder and its accessories were complete, all that was necessary to seal the furnace effectively against the atmosphere was to slide the drum on its wheels and put it in contact with the water cooled plate B. Although the contact faces between A and B had been accurately ground, a gasket of para rubber was put between the

areas of contact, care being taken that no portion of the rubber projected into the chamber to give off any vapours ~~although,~~ Since the plates B and C and the drum A were water-cooled, there was no chance of the gasket ever getting hot enough to give off any gases.

Figure 3 gives a vertical section of the vacuum chamber. The fixed plate, B, has 4 holes a, b, c, and d, as shown in Figs. 2 and 3. Through the holes a and b are inserted two water cooled annular tubes, t, which are insulated from B by mica sheets rolled on the tubes. The tubes, t, were made by scooping out from solid brass rods. On the water cooled ends they carry exactly fitting heavy copper collars ending in horizontal thick copper plates p_1 and p_2 provided with slots as shown in Fig. 3. The electrode carrying the copper plate p_2 was earthed. It is on these plates p_1 and p_2 that the graphite blocks, which in their central cylindrical holes tightly carry the furnace tube, are clamped by means of nuts and bolts passing through the slots. The surfaces of the plates p_1 and p_2 were machined and made accurately smooth so that the graphite blocks could make as intimate an electrical contact with them as possible and there may be no arcing between them.

The holes c and d, each 1" in diameter, in the plate B were for the insertion of two brass tubes, each soldered to a length of tombac tubing, each of which, in turn, was connected t a carefully ground conical mouthpiece to a four stage mercury diffusion pump manufactured by Messrs. E. Leybold Nachfolger A. The coupling between the tombac tubings and B were, as in the c of that between the tubes t and B, ~~were~~ vacuum tight. (Fig. 3). The brass piece of one of the two Tombac tubings had also a hole closed vacuum tight with an ebonite plug which carried through i the well insulated wires of ~~the~~ a Pt-Pt 10 % Rhodium Thermocouple as well as a copper lead to the ~~anode~~ Central electrode of the Faraday cylinder. (Fig. 3). On one of the heating current electrodes, t, viz., the one earthed, was fixed a clamp which bore the fused quartz sheath of the thermojunction of the thermocouple. The ends of the wires of the couple which emerged out of the ebonite plug were connected to a millivoltmeter.

The water cooled drum A was furnished with a side tube on which a glass window was sealed. An Optical Pyrometer sighted through the window enabled the temperature of the furnace to be measured (Fig.2)

The plate C, which also was water cooled, had a hole which served as a means of communication between the Vacuum chamber and a Vacuum gauge.

(d) The Heating Arrangement.

The water cooled electrodes, t, carrying the copper plates p_1 and p_2 on which the graphite furnace was clamped, were connected by thick stranded copper leads to a low tension transformer of capacity 12 KW. and fed by a current from an A.C. generator worked off 250 volts D.C. mains. This transformer had five ranges so that the temperature of the furnace could be regulated both by adjusting the generator as well as by varying the range of the transformer. The voltage across the electrodes could be thus varied between 1 and 7 volts so that a heating current of several hundreds of amperes could be sent through the furnace producing temperatures above 1850° C. But these temperatures were not exactly reproducible as neither the settings of the generator nor of the transformer were capable of fine adjustments.

As has been shown in Fig. 2, the electrode, t, carrying the copper plate p_2, on which the end of the Molybdenum cylinder having the effusion hole lay in its surroundings of graphite tube and block, was earthed by means of a copper wire soldered to the electrode outside the vacuum chamber. The molybdenum wire wound on the groove between the Molybdenum cylinder and the end plug having the effusion hole was earthed simply by being clamped to p_2 which also carried the base plate and the outer cover with the diaphragm of the Faraday cylinder so that they also were automatically earthed (by)

(e) The Electrical Circuit for measuring the Thermionic Current.

The electrical circuit for the measurement of the thermionic current is given in Fig.4.

The galvanometer was a Leeds & Northrup instrument and a universal shunt was used to vary the sensitiveness, which, for different ratios of the shunt is given below:

Shunt ratio	1	1/3	1/10	1/30	1/100	1/300
Galvanometer sensitivity in 10^{-9} amps/mm of deflection.	1.7	5.8	17.4	52.4	196	755

(f) Degassing and Vacuum.

As the various components of the furnace or vacuum chamber were water cooled they needed no degassing of the rigorous type required for the Molybdenum and the graphite furnace tubes. After the Cenco Hyvac pump and then the two Mercury Diffusion pumps had produced the vacuum of the order of 10^{-4} mms., a heavy heating current used to be passed for hours during the day to degass the chamber and, more particularly, the graphite and the Molybdenum tubes. At the end of the day the chamber was sealed for the night so that it retained the vacuum and the furnace could be restarted the next day. This daily routine was pursued till the value of the work function of Molybdenum, which fluctuated from day to day, acquired a steady value.

(g) Measurement of the Temperature.

Temperatures were measured with a Leeds & Northrup Optical Pyrometer of the disappearing filament type. Since the Molybdenum emitter was enclosed within the graphite furnace tube, the Optical Pyrometer read the temperature of the outer surface of the graphite tube. But since the cavity of the furnace had its ends closed by the ends of the Molybdenum Tube and the fused quartz rings, the radiations within the cavity were practically those of a Black Body and it was not unreasonable to suppose that the temperature of the Molybdenum tube was, after some time, the same as that of the cavity and, consequently, that of the outer surface of the graphite furnace tube. To verify this, the solid plug of the Molybdenum tube was removed and the thermojunction of the Pt-Pt 10% Rh Thermocouple was inserted so that the junction was held at the centre of the Molybdenum tube. The thermocouple thus gave directly the temperature of the inner, viz., the emitting

surface of the Molybdenum Cylinder while the Optical Pyrometer measured that of the outer surface of the graphite furnace tube. The following gives the two temperatures:

Temperature of the inner surface of the Molybdenum tube as given by the Pt-Pt-10% Rh Thermocouple.	Temperature of the outer surface of the graphite furnace tube as read by the Optical Pyrometer.
975° C	980° C
1260° C	1260° C
1440° C	1435° C
1500° C	1500° C

Considering that the least change in temperature that could be read by the Optical Pyrometer was 5° C., the agreement between the readings of the two instrument may be taken to be very satisfactory and Hence the Optical Pyrometer alone was used in the investigations to measure the temperature of the furnace and, therefore, of the emitting surface of the Molybdenum tube.

The cailbration chart of the Pt-Pt 10% Rh thermocouple had been tested previously by determinations of the melting points of Zinc and of NaCl and was found to be accurate.

(h) Effect of fused Quartz rings.

Before any measurements on Molybdenum could be taken it was necessary to determine whether the two rings of fused quartz, on which the Molybdenum tube rested within the graphite furnace, themselves emitted any thermionic current. Hence, the Molybdenum Cylinder was removed and the two rings of fused quartz were kept in position in the collars of the furnace tube and the Pt.-Pt 10% Rh Thermojunction was put in contact with the ring away from the Faraday Cylinder. It was found that even when the furnace was kept at a temperature of 1640° C for about an hour there was no appreciable thermionic current received by the Faraday Cylinder. The temperature of the ring was only 260° C which must have been due to the fact that the temperature of the collars even near the furnace was not allowed to rise by the thick graphite blocks which were in intimate contact with the water cooled thick copper plates p_1 and p_2. This comparatively low temperature of the rings also explains the absence of any emission from them.

Incidentally, the above blank experiment established the absence of any appreciable amount of spurious thermionic currents reaching the Faraday Cylinder, whose diaphragm was too small to admit any ions other than those from the effusion hole in the Molybdenum tube a few mms. distance in front of it.

Experimental Procedure.

Before putting the Molybdenum tube in position, the following measurements were made:

1. The radius, r, of the diaphragm of the Faraday Cylinder was 0.426 cms.
2. The ~~distance~~ radius, r_e, of the effusion hole of the Molybdenum tube was 0.0362 cms.
3. The distance between the effusion hole and the edge of the graphite collar after the Molybdenum tube had been put on fused quartz rings within the furnace, as described before, was measured. It was 1.3 cms.

The Molybdenum tube, thus enclosed within the graphite tube, was carefully placed in the hole in the graphite blocks and the whole kept on copper foils on the plates p_1 and p_2. The bed plate of the Faraday Cylinder was placed below p_2 and iron bolts passing vertically through appropriate holes in the graphite blocks and ~~held tight by means of~~ the slots in p_2, when tightened by nuts below p_2, held not only the graphite furnace but also the Faraday cylinder in position. One end of the molybdenum wire having been previously tightly wound ~~between~~ round the depression between the Molybdenum tube and the Molybdenum plug with the effusion hole, the other end was clamped to p_2 by inserting it between p_2 and a nut, tightening the graphite block of the bed plate of Faraday Cyl. Thus the collar, the molybdenum plug with the effusion hole, the bed plate and the outer cover with the diaphragm of the Faraday cylinder were all automatically earthed since the electrode, t, carrying the plate p_2 ~~was~~ had already been earthed by a copper wire ~~soldered~~ from outside the vacuum chamber. Care was taken that the wire did not anywhere come in the path of the effused electrons between the effusion hole and the diaphragm of the Faraday cylinder. The effusion hole and ~~the centre of~~ the diaphragm were ~~at the same height~~ coaxial. All these operations were

very delicate lest the effusion hole should change its position with respect to the edge of the Graphite furnace tube.

The distance between the edge of the collar and the diaphragm of the Faraday cylinder was measured. The total distance between the effusion hole and the centre of the diaphragm was thus found to be 1.5 cms.

The other collar of the furnace tube was similarly clamped on p_1. The drum A was then moved to contact B and thus seal the vacuum chamber against the atmosphere.

Water having been started to flow through A, B, C, and t, and the backing pump and then the two Mercury Diffusion Pumps having produced the necessary vacuum, a heating current was sent through the furnace. The temperature of the graphite was gradually raised to over 1850 C at which it was kept for about an hour. Then the temperature was reduced to about 1650 C when measurements on the thermionic currents were begun. An interval of about 15 minutes sufficed for the temperature of the furnace to become steady after every reduction in the heating current.

Positive as well as negative voltages upto about 4 volts in steps of 0.2 volts were applied on the central electrode of the Faraday cylinder. Usually saturation currents were found to occur at about 1 volts on the central electrode. Readings of the galvanometer were thus obtained to determine the saturation values of the emission currents for various temperatures from about 1650 C to the lowest at which any appreciable thermionic current was found. Usually the thermionic positive currents were negligible in comparison with the electronic currents.

After the readings for the emission currents for various temperatures had been taken, the furnace was allowed to cool and the stop cock connecting the vacuum chamber with the backing pump was closed so as to preserve the vacuum in the furnace chamber till the furnace was reworked the same or the next day. The vacuum pumps were then stopped till the furnace was worked again. In this way, both the graphite furnace and the Molybdenum cylinder were degassed for several weeks during which the value of the work function of Molybdenum varied from day to day. It was only

when the values of the work function had become steady that it was concluded that the process of degassing was completed.

That the ~~process~~ thermionic emission for a given temperature was reproducible is shown by the fact when the degassing was complete and the value of the work function had attained a steady value, the values of $\log i_o / T^2$ plotted against $1/T$ for various working days all fell on the same straight line. The slope of the line gave the value of the Work Function and the intercept enabled the constant A to be calculated.

Observations.

The observations, taken on different days, of the galvanometer deflections for various temperatures and for different voltages applied on the Faraday Cylinder are given below: A graph of $\log i_o / T^2$ against $1/T$ for all the days during which the above observations were taken is also given. The numbers 1, 2, 3, 4 and 5 written against the various points on the graph denote the number of the day on which the data were obtained.

I- Thermionic Emission from Molybdenum.

	Optical Pyrometer reading in C.	Galv. Shunt ratio.	Sign of the voltage on the Faraday Cylinder.	Galvanometer deflections in mms. when the voltage applied on the central electrode of the the Faraday Cylinder was 0.0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.5	3.0	3.5	4.0
1.	1610	1/ 10	plus	20.0	34.0	49.0	62.0	68.0	72.0	72.0	72.0	72.5	72.5	72.5	73.0	73.5	73.5	74.0
			minus															- 5.0
2.	1575	,,	plus	7.0	12.0	23.0	32.0	39.0	43.0	43.5	44.0	44.0	44.0	44.5	45.0	46.0	46.5	47.0
			minus															- 3.0
3.		1/ 3	plus	20.0	47.0	82.0	110.0	120.0	127.5	127.5	128.0	128.0	128.5	128.5	129.0	130.0	130.5	131.0
			minus															- 8.0
3.	1540	,,	plus	10.0	24.0	42.0	56.0	67.0	73.5	74.0	74.0	74.5	74.5	74.5	75.0	76.0	76.5	77.0
			minus															- 5.0
4.	1530	,,	plus	8.0	18.0	30.0	42.0	54.0	63.0	63.5	63.5	64.0	64.0	64.5	65.0	65.5	66.5	67.0
			minus															- 4.0
5.	1515	,,	plus	2.0	12.0	25.0	37.0	49.5	49.5	49.5	50.0	50.0	50.0	50.5	51.0	51.0	51.5	52.0
			minus															- 3.0
		1/ 1	plus	35.0	87.0	139.0	155.0	167.0	167.5	167.5	168.0	168.0	168.5	168.5	169.0	169.5	170.5	171.0
			minus															-12.0
6.	1495	,,	plus	20.0	58.0	95.0	108.0	119.0	119.0	119.0	119.0	119.5	119.5	119.5	120.0	120.5	120.5	121.0
			minus															- 8.0
7.	1460	,,	plus	10.0	32.0	50.0	65.5	66.0	66.0	66.5	67.0	67.0	67.5	68.0	68.5	69.5	70.0	71.0
			minus															- 5.0
8.	1450	,,	plus	7.0	22.0	37.0	55.5	55.5	56.0	56.0	56.5	56.5	57.0	57.0	58.0	58.5	59.5	60.0
			minus															- 4.0
9.	1425	,,	plus	5.0	15.0	25.0	36.0	36.0	36.0	36.5	36.5	37.0	37.0	37.5	38.0	38.5	39.5	40.0
			minus															- 2.0
10.	1395	,,	plus	3.0	10.0	20.5	21.0	21.0	21.0	21.5	22.0	22.0	22.0	22.5	23.0	24.0	24.5	25.0
			minus															- 2.0
11.	1350	,,	plus	2.0	6.0	8.5	9.0	9.0	9.0	9.5	9.5	10.0	10.0	10.0	10.5	11.0	11.5	12.0
			minus															- 1.0
12.	1325	,,	plus	1.0	4.0	5.0	5.5	5.5	5.5	5.5	5.5	6.0	6.0	6.0	6.0	6.5	6.5	7.0
			minus															- 0.0

II- Thermionic Emission from Molybdenum.

	Optical Pyrometer reading in C.	Galv. Shunt ratio.	Sign of the voltage on the Faraday Cylinder	Galvanometer deflections in mms. when the voltage applied on the central electrode of the Faraday Cylinder was														
				0.0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.5	3.0	3.5	4.0
1.	1600	1/30	plus	7.5	12.5	17.5	20.0	21.0	21.5	21.5	22.0	22.0	22.5	22.5	23.0	24.0	24.5	25.0
			minus															- 2.0
2.	1570	,,	plus	4.5	7.0	9.5	12.0	13.0	13.5	14.0	14.0	14.0	14.5	14.5	15.0	15.0	15.5	16.0
			minus															- 1.0
3.	1550	,,	plus	4.0	5.5	7.0	8.5	9.5	10.0	10.0	10.0	10.5	10.5	10.5	11.0	11.5	11.5	12.0
			minus															- 1.0
4.	1535	,,	plus	3.0	4.0	5.0	6.0	7.0	8.0	8.0	8.0	8.0	8.0	8.0	8.5	8.5	9.0	9.0
			minus															- 0.0
5.	1520	,,	plus	1.5	2.5	3.5	4.5	5.5	6.0	6.0	6.0	6.5	6.5	6.5	6.5	6.5	7.0	7.0
			minus															- 0.0
6.	1510	1/10	plus	3.0	6.0	10.0	14.0	16.5	16.5	17.0	17.0	17.5	18.0	18.0	19.0	19.5	20.0	21.0
			minus															- 2.0
7.	1500	,,	plus	1.0	4.0	7.0	11.0	13.0	13.5	13.5	14.0	14.0	14.0	14.0	14.5	15.0	15.5	16.0
			minus															- 1.0
8.	1475	1/3	plus	9.0	18.0	22.0	25.0	25.0	25.5	25.5	25.5	26.0	26.0	26.0	27.0	27.0	27.5	28.0
			minus															- 2.0
9.	1435	,,	plus	4.0	8.0	11.0	12.5	12.5	13.0	13.0	13.0	13.0	13.5	13.5	14.0	14.0	14.5	15.0
			minus															- 1.0
10	1415	1/1	plus	8.0	18.0	29.5	29.5	30.0	30.0	30.5	30.5	31.0	31.0	31.5	32.0	32.5	33.5	34.0
			minus															- 4.0
11.	1400	,,	plus	6.0	14.0	22.5	22.5	23.0	23.0	23.5	23.5	24.0	24.0	24.5	25.0	25.5	26.5	27.0
			minus															- 2.0

III- Thermionic Emission from Molybdenum.

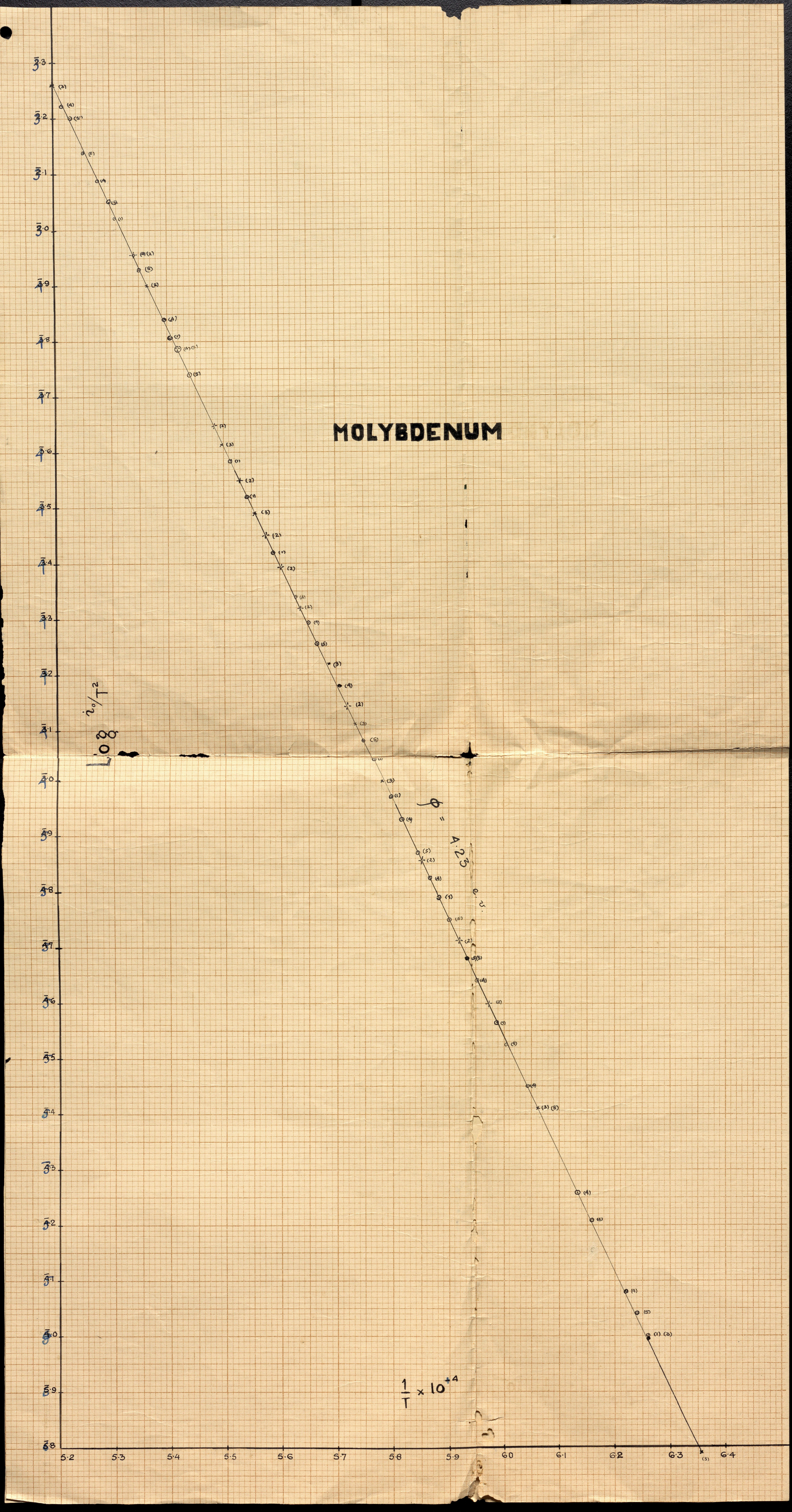
Optical Pyrometer reading in C.	Galv. Shunt ratio.	Sign of the voltage on Faraday Cylinder	Galvanometer deflections in mms. when the voltage applied on the central electrode of the Faraday Cylinder was														
			0.0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.5	3.0	3.5	4.0
1. 1630	1/30	plus	12	22	32	37	41	45	44	44	44.5	44.5	45	45.5	46	46.5	47
		minus														-	3
2. 1590	,,	plus	2	5	10	14	17	18.0	19	19	19	19.5	19.5	20.5	21	21.5	22
		minus														-	2
3. 1545	,,	plus	0	2	4	5	7	9.5	9.5	10	10	10	10.5	10.5	11	11.5	12
		minus														-	1
4. 1525	1/10	plus	1	5	11	16	19	20.5	21	21	21.5	22	22	23	23.5	24.5	25
		minus														-	2
5. 1485	,,	plus	0.5	3	6	8	10.5	10.5	11	11	11.5	11.5	12	12.5	13	13.5	14
		minus														-	1
6. 1470	1/ 3	plus	8	16	21	23.5	23.5	24	24	24	24.5	24.5	25	25.5	26	26.5	27
		minus														-	2
7. 1435	,,	plus	3	9	15	18	18	18	18.5	18.5	19	19	19	19.5	20	20.5	21
		minus														-	2
8. 1410	1/1	plus	10	22	27	27	27.5	28	28	28	28.5	29	29	30	30.5	31	32
		minus														-	2
9. 1375	,,	plus	4	10	14	14	14.5	14.5	15	15	15.5	15.5	16	16.5	17	17.5	18
		minus														-	1
10. 1325	,,	plus	1	4	5	5.5	5.5	5.5	6	6	6	6	6.5	7	7	7.5	8
		minus														-	0
11. 1300	,,	plus	0	2	3	3.5	3.5	3.5	4	4	4	4	4.5	5	5	5.5	6
		minus														-	0

IV- Thermionic Emission from Molybdenum.

	Optical Pyrometer reading in C.	Galv. Shunt ratio.	Sign of the voltage on the Faraday Cylinder	Galvanometer deflections in mms. when the voltage applied on the central electrode of the Faraday Cylinder was														
				0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.5	3.0	3.5	4.
1	1645	1/ 10	plus	30	48	68	88	108	116	120	120	120.5	120.5	121	122	122.5	123	124
			minus															- 4
2	1620	,,	plus	25	35	46	58	68	81	86.5	87	87	87.5	88	89.5	90.5	91.5	92.5
			minus															- 3
3.	1600	,,	plus	21	29	38	48	58	63.5	64	64.5	64.5	65	65.5	67	68	69	70
			minus															- 2
4.	1580	1/3	plus	25	52	88	124	134	138	139	139	139.5	139.5	140	140.5	141	142	142.
			minus															- 2
5.	1570	,,	plus	22	44	70	102	114	118.5	118.5	119	119	119.5	120.0	120.5	121	122	122
			minus															- 2
6.	1505	,,	plus	15	21	28	36	41	41	41.5	41.5	42	42.5	42.5	43.5	44.5	45	46
			minus															- 1
7.	1480	1/ 1	plus	30	58	86	91.5	92	92	92.5	93	93	93.5	94	95	96	97	98
			minus															- 4
8.	1445	,,	plus	14	30	46	51	51	51.5	52	52.5	53	53	54	55	56	57	58
			minus															- 2
9.	1430	,,	plus	10	22	34	39.5	40	40	40.5	41	41	41.5	42	43	44	45	46
			minus															- 2
10.	1405	,,	plus	7	17	25	26	26.5	26	26	26.5	27	27.5	28	29	30	31	32
			minus															- 1
11.	1380	,,	plus	2.5	10	15.5	16	16.5	16.5	17	17.5	18	18	18.5	19.5	20	21	22
			minus															- 1
12	1355	,,	plus	2	6	10	10	10.5	11	11.5	11.5	12	12.5	12.5	13.5	14.5	15	16
			minus															- 0
13.	1335	,,	plus	1.5	4	6.5	7	7.5	7.5	8	8.5	9	9	9.5	10.5	11	12	13
			minus															- 0

V- Thermionic Emission from Molybdenum.

	Optical Pyrometer reading in C.	Galv. Shunt ratio.	Sign of the voltage on the Faraday Cylinder	Galvanometer deflections in mms. when the voltage applied on the central electrode of the Faraday Cylinder was														
				0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.5	3.0	3.5	4.0
1	1640	1/ 10	plus	28	45	62	81	100	110	114	114	114.5	115	115.5	117	117.5	119	120
			minus															- 4
2	1630	,,	plus	27	38	50	61	76	92	98	98.0	98.5	98.5	99.0	99.5	100.5	101	102
			minus															- 3
3	1615	,,	plus	23	30	40	50	60	72	79	79.5	80	80	80.5	81.5	82.5	83	84
			minus															- 2
4	1595	,,	plus	20	27	36	44	52	59	59	59.5	60	60.5	61	62	63	64	65
			minus															- 1
5	1565	1/3	plus	20	35	66	80	96	108.5	109	109	109.5	110	110.5	111.5	112	113	114
			minus															- 4
6	1490	1/1	plus	30	52	78	104	110.5	111	111	111.5	112	112	112.5	113.5	114.5	115	116
			minus															- 4
7	1465	,,	plus	20	34	48	64	72	72	72.5	72.5	73.0	73	73.5	74.0	74.5	75.5	76
			minus															- 3
8	1440	,,	plus	10	18	26	36	43.5	43.5	43.5	44	44	44	44.5	45	45	45.5	46
9	1420	,,	plus	8	12	20	28	32	32	32	32.5	32.5	32.5	32.5	33	33.5	33.5	34
			minus															- 1
10	1410	,,	plus	5	10	16	22	27	27.5	27.5	27.5	28	28	28	28.5	29	29.5	30
			minus															- 0
11	1390	,,	plus	4	9	14	19	19	19	19.5	19.5	19.5	20	20	20.5	21	21.5	22
12	1375	,,	plus	2	7	14	14.5	14.5	14.5	15	15	15.5	15.5	16	16.5	17	17.5	18
13	1330	,,	plus	0	3	6	6	6	6.5	6.5	7	7	7	7.5	8	8.5	9	9.5


MOLYBDENUM
log i_d/T^2
1/T × 10^+4
φ = 4.23 e.v.
3.3
3.2
3.1
3.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
5.9
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.2
5.3
5.4
5.5
5.6
5.7
5.8
5.9
6.0
6.1
6.2
6.3
6.4

Results.

The following values of ϕ were thus obtained:

1	2	3	4	5	Mean
4.231	4.226	4.229	4.232	4.234	4.23 e.v.

The values of A for ϕ = 4.23 e.v. for various temperatures are given below:

Temp. in °C	1	2	3	4	5	6	7	
	1650	1600	1550	1500	1450	1400	1350	
A	243	244	237	239	240	244	241	
								Mean 241 amp./ cm^2 /deg^2

In this connection it must be stated that whereas the values of the Thermionic Work Function obtained on different occasions are reliable, those of the constant A are not so. This is because the distance between the effusion hole of the Molybdenum cylinder and the edge of the graphite furnace tube, which had been measured prior to the fixing of the furnace on the copper plated p_1 and p_2 was found changed when the furnace was being unclamped from the plates and could not, therefore, be verified. It will be recalled that in order to allow for the expansion of the Molybdenum cylinder during heating the cylinder had to be supported in fused quartz rings of a size larger than that of the diameter of the cylinder which was, therefore, liable to be displaced during the process of not only fixing the or removing the furnace but also of clamping or unclamping the earthing wire.

Discussion.

The Thermionic work function of Molybdenum was first determined by I. Langmuir[10], who found the value of b in Richardsons' $T^{\frac{1}{2}}$ equation to be 50,000, corresponding to ϕ equal to 4.08 e.v. Later on he[11] found the value of the function to be 4.05 e.v. Probably the difference in the temperature scales used and in the surfaces account for this divergence. Stoekle[12] obtained a value corresponding to 4.39 e.v., but as he could not degass the metal properly, the values obtained were irregular and varied from condition to condition and were not very reliable. Amongst the

early workers must be mentioned also Lester,[13] who by comparing the loss of heat due to the emission of the electrons with the gain in heat when a known increment of current was supplied to the filament and assuming that the change in heat supplied was proportional to the change in the resistance of the filament, determined the work function. The value he found was 4.59 e.v.

These early workers' technique was not very highly developed. A definite advance was made by Dushman, Rowe, Ewald and Kidner[14] and by Zwikker,[15] who worked under good vacuum conditions. The values obtained by these workers- 4.44 and 4.38 e.v. respectively- are in good agreement with eachother and undoubtedly represent the best values heretofore obtained for outgassed metal. However, Dushman reported that great difficulty was encountered in eliminating the last traces of oxide from the Molybdenum specimens so that completely consistent values of the thermionic emission were never obtained.

Martin[16] studied the photoelectric properties of Molybdenum during outgassing and found that after 150 hours of heating at temperatures upto 1700° K the work function reached an apparantly stable value of 3.2 e.v., while the value of the thermionic work function for the same specimen was 3.48 e.v. While these two values are in fair agreement with eachother, the large discrepancy between these values and those obtained by Dushman and Zwikker led Dushman[17] to suggest that the heat treatment had not been carried out in this case at high enough temperatures to eliminate all impurities.

Decidedly the best determinations on Molybdenum were made by DuBridge and Roehr,[18] who studied the photoelectric and thermionic emission ~~for~~ from pure Molybdenum during a prolonged process of outgassing by heat treatment at temperatures upto 2100° K. In a sealed off tube with a vacuum well below 10^{-7} mms. an equilibrium condition was reached which was not changed by further treatment upto 1600 hours. Photoelectric curves taken at room temperatures and at 940° K and analysed by Fowler's method yielded a true work function for the outgassed Molybdenum of 4.15 ± 0.02 volts. Thermionic data for the same specimen also yielded a work function of

4.15 volts and a value of the constant A close to the theoretical value of 60 amp./ cm^2 $deg.^2$ That the cause of the low value of the work function obtained by Martin was the degassing of the specimen for an insufficient time and at an insufficiently high temperature was proved by DuBridge and Roehr as they also got values of the same order as those reported by Martin during their early stages of heating. Similarly, they found that many of their specimens did show a work function of the order of 4.4 volts obtained by Dushman and his coworkers and also by Zwikker, but those of the samples which stood a more prolonged heat treatment gave the lower value of 4.15 so that the latter value may be taken to be characteristic of a very gas free state of Molybdenum. It is possible that the prolonged heating causes a microscopic recrystallisation of the surface which results in a slight reduction of the work function.

Some equally reliable work seems to be that of A.J. Ahearn[19] who in the course of his investigations on the effect of temperature on the emission of electron field currents from Molybdenum using high vacuum technique as well as a rigorous conditioning of the filament found the work function to be 4.32 e.v. The value of 4.33 e.v. was obtained by H. Freitag and F. Kruger[20] at a vacuum of 10^{-7} mms. F.Kruger and G. Stabenow[21], however, measured the work function of electrons by compensating the cooling due to the emission by raising the heating current and measuring this compensating current by a resistance in an a.c. Wheatstone bridge circuit. The work function could be obtained to a fraction of 1 % and was found to be 4.40 e.v. Rentschler and Henry[22] by sputtering on glass surfaces determined the photoelectric threshold corresponding to ϕ equal to 4.35 e.v. But the surfaces were highly contaminated. Some of the most recent determinations with the most advanced vacuum technique and degassing have yielded values near to those of DuBridge and Roehr. Wahlin and Reynolds[23], Grover[24], and Wright[25] have found the value of the electron work function to be 4.17, 4.2, and 4.2 e.v., respectively.

The following table summarises the most reliable values of the electron work function and gives also the value found in the present investigations by an altogether different method from those pursued by any of the previous workers on the metal.

Electron Work Function of Molybdenum.

Investigator	Year	Work function in e.v.	A in amps/cm^2/deg^2
1. DuBridge & Roehr	1932	4.15	-
2. Ahearn	1933	4.32	-
3. Freitag & Kruger	1935	4.33	-
4. Kruger & Stabenow	1935	4.40	-
5. Wahlin & Reynolds	1935	4.17	51
6 Rentschler + Henry	1936	4.17	51
7. Groover	1937	4.2	-
8. Wright	1941	4.2	55 for strip and 115 for round filament.
9 Present work	1949	4.23	241* ~~(not reliable)~~

* This value of A will be confirmed.

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24. Wright — Phys. Rev., 60, 465, 1941.

23 Wahlin & Reynolds — Phys. Rev. 48, 751, 1935

24 Grover — Phys. Rev. 52, 982, 1937.

25 Wright — Phys. Rev. 60, 465, 1941

Summary.

By measuring the electronic current effusing out through a small hole in an otherwise closed chamber of Molybdenum, heated in vacuum to various high temperatures in a graphite furnace, the electronic work function of the metal was found to be 4.23 e.v. The constant A, which could not be determined to an equal certainty, was found to be 241 amp./cm.^{2} deg.^{2}. This method has several advantages over the usual thermionic ones based on that of Richardson. It avoids the uncertainties in the value of the reflection coefficient occuring in the theoretically derived thermionic emission equation. Being dependent on the effusion current, which depends on the saturation electronic vapour pressure within the metallic chamber, the method is a very direct one. Since the emitting surface of the metallic chamber is completely enclosed within the graphite furnace tube, the temperature of the emitter, after some time, becomes the same as that of the graphite tube. Hence the whole of the metal under investigation is at one uniform temperature and no temperature gradients requiring complex corrections are needed. Further the temperature of the emitter could be determined by means of an Optical Pyrometer without the help of any temperature scale of the metal under investigation. Evaporation of the metal or any changes in the surface did not affect the temperature. As all the fittings in the vacuum chamber were water cooled the troublesome task of degassing was confined to that of the graphite furnace tube and its contents. Since high anode voltages were not needed, the unceratinties of determining saturation currents on account of Scottky effect did not occur. The lead loss corrections also were avoided. The value of the thermionic constants ~~A was~~ were capable of being determined without any measurement of the area of the emitting surface. Thus the method avoids the major defects of the usual Richardson type of experiments and is suitable for the determination of the thermionic constants of refractory metals.

THE THERMIONIC WORK FUNCTION OF IRON.

Introduction.

In an earlier paper[1] details have been given as to how from the effusion electron current from a hole in an otherwise closed chamber of Molybdenum heated in vacuum to different temperatures the thermionic constants of the metal could be determined. The present report gives the results obtained with Iron investigated in the same way. Iron is of interest from the point of view of the transitions that occur at various temperatures from one form to another. The measurements under report were confined to the δ and the γ forms- mostly the former.

Preparation of the Emitting Surface.

A cylindrical tube with a tightly fitting plug at each end was made of an ordinary piece of iron. As in the case of Molybdenum, one of the plugs was solid, while the other was hollow excepting for a thin wall at the end which had a central circular hole of radius 0.751 mms. The overall length of the cylindrical tube with the plugs fitted was 8.5 cms. and the diameter was 0.8 cms.

On the inner walls of the cylindrical tube and the plugs a coating of iron was deposited by electrolysis from a ferrous chloride solution. The prepared surface was cleaned of all grease and other organic impurities by dipping in chromic acid and washing. This was followed by a slight etching with dil. HCl which was finally washed away with hot distilled water. This tube was then dried and carefully put in the previously degassed graphite furnace tube on fused quartz rings and the vacuum chamber assembled as already described in the earlier paper.

The degassing of the iron cylinder was a problem. Although iron melts at 1530° C, it softens at a much lower temperature. Hence the cylinder sagged and short circuited the furnace tube. A heavy electric current from the furnace would then flow through the iron which would get melted and ruin not only the graphite furnace

but also the surface of the copper plate electrodes and make them unfit for further use. This behaviour of iron may be connected with the equilibrium distribution of crystal planes on its surface on passing from the γ to the β form. H.B. Wahlin[2] also remarks that "each time the filament passed through the A[3] point, it warped and with repeated transitions twisted sufficiently to short circuit portions of the specimen." In the light of the above experience it was decided to do the major part of degassing the iron cylinder at temperatures less than 850° C and to degass at higher temperatures only for very short durations until the value of the thermionic work function of the iron attained a steady value. It thus took several weeks to prepare the specimen for observations.

When the sample had been degassed, the usual practice was to raise the temperature to about 750° C in about an hour. The temperature was then sent up to about 1500° C and the readings of the thermionic emission were quickly taken with decreasing temperatures till about 1350° C was reached when no appreciable currents could be found with the galvanometer. The heating current was then lowered slowly and then switched off to be made on the next day.

The observations taken when the degassing was complete are given below: The values of $\log \frac{i_0}{T^2}$ and $\frac{1}{T}$ as plotted on the graph were obtained from these observations. The numbers 1, 2 and 3 written against the points on the graph denote the day on which the data were collected.

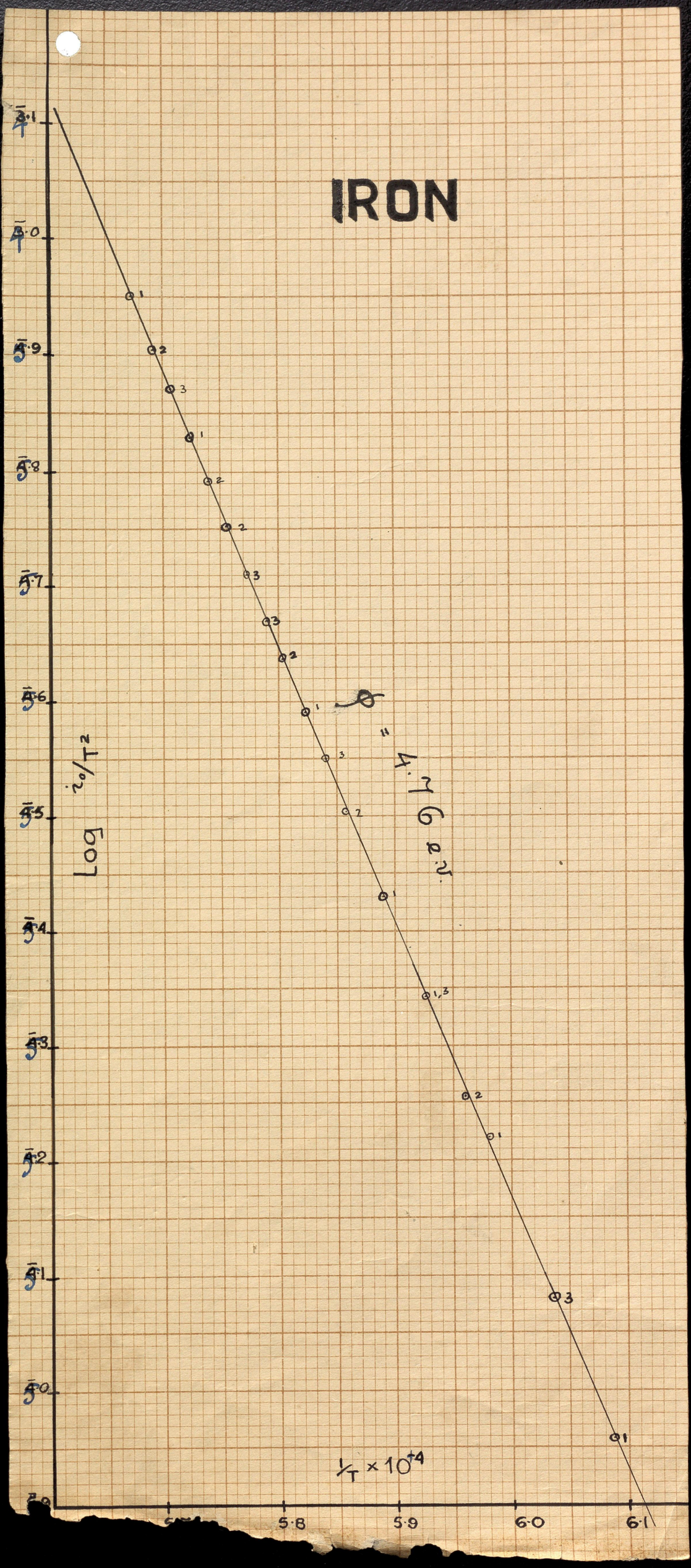
1- Thermionic Emission from Iron.

	Optical Pyrometer readings in C.	Galv. Shunt ratio	Sign of voltage on the anode of the Faraday Cylinder.	Galvanometer deflections in mms. when the voltage on the central electrode of the Faraday Cylinder was														
				0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.5	3.0	3.5	4.0
1	1490	1/1	plus	18	26	36	46	52	56	56.5	57	57	57.5	57.5	58.5	59.5	60	61
			minus															- 5
2	1475	,,	plus	14	22	34	40	41.5	42	42	42.5	42.5	43	43	44	44.5	45	46
			minus															- 4
3	1445	,,	plus	6	14	20	23	23	23.5	23.5	24	24	24	24.5	25	25.5	26	26.5
			minus															- 2
4	1425	,,	plus	4	8	12	16	16	16	16.5	16.5	16.5	17	17	17.5	18	18.5	19
			minus															- 1
5	1415	,,	plus	2	4	10	13	13	13	13.5	13.5	13.5	14	14	14.5	15	15.5	16
			minus															- 1
5	1400	,,	plus	1	7	9.5	9.5	9.5	10	10	10	10	10	10.5	11	11	11.5	12
			minus															- 0
7	1370	,,	plus	0.5	5	5	5	5.5	5.5	5.5	6	6	6	6.5	7	7	7.5	8
			minus															0

	Optical Pyrometer reading in C.	Galv. Shunt rea-ratio	Sign of voltage on the anode of the Faraday Cylinder.	Galvanometer deflections in mms. when the voltage on the central electrode of the Faraday Cylinder was														
				0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.5	3.0	3.5	4.0
1	1485	1/1	plus	17	25	32	39	45	49.5	49.5	50	50	50	50.5	50.5	51	51.5	52
			minus															- 4
2	1470	,,	plus	13.5	21	28	35	37.5	37.5	38	38	38	38	38.5	39	39	39.5	40
			minus															- 3
3	1465	,,	plus	12	17	24	32	34	34	34.5	34.5	34.5	35	35	35.5	36	36	36.5
			minus															- 3
4.	1450	,,	plus	9	14	18.5	24	26	26	26	26	26	26.5	26.5	27	27.5	27.5	28
			minus															- 2
5	1435	,,	plus	5	10	16	18.5	19	19	19	19	19	19.5	19.5	20	20	20.5	21
			minus															- 1
6.	1405	,,	plus	1.5	7	10	10	10.5	10.5	10.5	10.5	11	11	11	11.5	12	12	12.5
			minus															- 1

III- Thermionic Emission from Iron.

	Optical Pyrometer reading in C.	Galv. Shunt ratio.	Sign of voltage on the anode of the Faraday Cylinder.	Galvanometer deflections in mms. when the voltage applied on the central electrode of the Faraday Cylinder was														
				0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.5	3.0	3.5	4.0
1	1480	1/ 1	plus	15	21	29	36	42	45	45.5	45.5	46	46	46	46.5	47	47.5	48
			minus															- 2
2	1460	,,	plus	13	18	24	29	30.5	31	31	31	31.5	31.5	31.5	32	32	32.5	33
			minus															- 1
3	1455	,,	plus	11	15	20	26	28	28	28	28	28.5	28.5	28.5	29	29.5	29.5	30
			minus															- 1
4	1440	,,	plus	8	11	15	18	20.5	21	21	21.5	21.5	21.5	22	22.5	23	23.5	24
			minus															- 1
5	1415	,,	plus	2	5.5	10	13	13	13	13.5	13.5	14	14	14	14.5	15	15.5	16
			minus															-0.5
6	1385	,,	plus	0	3	7	7	7	7.5	7.5	8	8	8	8.5	8.5	9	9.5	10
			minus															- 0


IRON
$\bar{4}$·1
$\bar{4}$·0
$\bar{5}$·9
$\bar{5}$·8
$\bar{5}$·7
$\bar{5}$·6
$\bar{5}$·5
$\bar{5}$·4
$\bar{5}$·3
$\bar{5}$·2
$\bar{5}$·1
$\bar{5}$·0
$\bar{5}$·9
5·8
5·9
6·0
6·1
Log i_0/T^2
$\frac{1}{T} \times 10^{+4}$
θ = 4.76 eV

Calculations.

In the paper on the determination of the thermionic work function of Molybdenum[1] the following equation has been developed:

$$\log_{10} i_o / T^2 = -\frac{\phi}{KT} \log_{10} e + \log_{10} A_o \frac{Sr^2}{rd},$$

where i_o is the saturation electronic current collected by the Faraday cylinder having a diaphragm of radius r; T is the absolute temperature of the Iron cylinder under investigation; ~~is the electronic charge;~~ ϕ is the work function; A_o is the constant in Richardson's T^2 emission equation; S is the area of the effusion hole; K is Boltzmann's Constant; and d is the distance between the effusion hole and the diaphragm of the Faraday Cylinder.

Hence, if a graph of $\log_{10} i_o / T^2$ is plotted against the values of 1/T, the work function, ϕ, will be given by

$$\frac{\text{The intercept on the } \log \frac{i_o}{T^2} \text{ axis}}{\text{The intercept on the } 1/T \text{ axis}} \times \frac{1.371 \times 10^{-16} \times 300}{10^{-4} \times 4.77 \times 10^{-16} \times 0.4343} \text{ e.v.}$$

In the following, data for $\log_{10} i_o / T^2$ and 1/T have been taken from observations taken on different days which have all been plotted on one graph:

	Intercept on the $\log_{10}$ axis	$\log_{10} i$	Intercept on 1/T axis in units of 10^{-4}	1/T	ϕ in e.v.
1	$\bar{5}.8686 - \bar{5}.0879$	0.7807	6.032 - 5.706	0.326	4.75
2	$\bar{5}.7100 - \bar{5}.3427$	0.3673	5.924 - 5.771	0.153	4.76
3	$\bar{5}.6688 - \bar{5}.5510$	0.1178	5.837 - 5.788	0.049	4.77

Mean value of ϕ = 4.76 e.v.

Taking the above value of ϕ, r = 0.426 cms., d = 1.3 cms., and the radius of the effusion hole = 0.0751 cms., the following values were found for A_o at different temperatures:

	Temperature of Iron in C	A in amp/ cm / deg
1	1490	706.9
2	1465	697.1
3	1440	708.6
4	1415	695.2
5	1370	719.4

No particular effect of transition from the γ to the δ form could be discernible in the present investigations.

Discussion.

The earliest attempt to measure the thermionic work function of iron was made by Jentzch[3], who found it to be 4.04 e.v. R. Hamer[4] found the limiting wave length for the photoelectric effect from a sand papered commercial sample of iron under ordinary conditions to be λ=3050 $\pm$ 50 Å. In the next paper[5] he published he finds this limit to be at λ=2870 $\pm$ 40 Å, which would correspond to a work function of 4.3 e.v. In this work he took more care and exhausted his cell of air by means of a Gaede Mercury pump. S.C. Roy[6] determined the value from photoelectric emission to be 4.2 e.v Similarly, G.B. Welch[7] using a pure sample of iron found the photoelectric threshold at λ=3150. But in a more careful work using clean surfaces of iron of the highest purity and in vacuum of the order of 10^{-6} mms. he finds the limit to be at λ 3155 corresponding to a work function of 3.91 volts.

Although the work of Roy and Welch are distinct advances in technique there is no doubt that the values of 4.2 volts and 3.91 volts respectively, obtained by them are those that, according to Cardwell[8], would correspond to the early stages of a long outgassing process and cannot be said to be characteristic of the well outgassed material.

The first really reliable determination seems to be that of Cardwell who found the threshold of iron, after extended outgassing in a high vacuum, to be between λ2580 and 2652 A, corresponding to a work function of 4.72 $\pm$ 0.07 e.v. He found the photoelectric sensitivity of his specimen to be considerably less after cooling suddenly than after cooling slowly from above 1180° K (β - γ transition point). He attributed this to a retention in the former case of part of the γ form (face-centred cubic), this being the photoelectrically less sensitive. The β and α forms, which are stable below 1180° K are body-centred cubic crystals.

The corresponding thermionic properties of iron above and below the β - γ transition point have been studied by Siljeholm[9]. He found the Richardson line to consist of two parallel parts with a discontinuity at the transition point. From the slope of this line for the specimens which had been most thoroughly outgassed the value 4.77 e.v. was obtained for the work function. This is in perfect agreement with the value obtained photoelectrically by G.N. Glasoe[10]

who has used Fowler's method to determine the photoelectric work function of electrolytic iron outgassed for several hundreds of hours at temperatures upto 1220 K in a vacuum of the order of 10^{-8} mms. Glasoe also determined the contact potential difference between specimens of electrolytic iron and nickel and found it to be 0.21 ± 0.01 volts. The photoelectric long wave length limit of the same specimens and under identical conditions used for the contact potential measurements gave a work function of 5.01 for Nickel and 4.77 for iron so that the difference of these functions is equal to the measured contact potential difference between the two metals within the limits of error of the photoelectric measurements.

W. Distler and G. Monch[11] found 4.04 volts for the value of the thermionic work function of iron. But the main interest of these workers seems to have been the verification of the relation between the work function and the distance between the atoms.

However, to the careful work of Cardwell and Glasoe must be added that of H.B. Wahlin[12], who determined the thermionic properties of the Iron group. In order to obtain reliable results Wahlin determined the temperature scale of the metals under conditions of heat treatment as nearly identical as possible with those used in the thermionic studies. A prolonged heat treatment was carried out and a vacuum of the order of 3.10^{-8} mms was kept. The temperature of the filament was raised slowly to a final degassing value of 1250 A during several days. Care was taken that the temperature did not at any time fall below the A_3 point (β - γ transition). After a stable condition had been reached, and the thermionic data taken, the temperature was lowered into the β region and the heating continued. When a steady state had again been reached and the data were obtained, the temperature was again raised with two of the specimens into the γ region and further thermionic results recorded. These were found to be in agreement with the first ones. The average of the results for 4 filaments which showed no appreciable temperature gradients is

below β-γ transition: $\varphi = 4.48 \pm 0.06$ e.v.
$A = 26$ amp./ cm^2 deg^2.

above ,, ,, : $\varphi = 4.21 \pm 0.06$ e.v.
$A = 1.5$ amp/ cm^2 deg.^{2}

The values of the Work Function of Iron obtained by different workers have been listed below. Those which appear to be particularly reliable have been marked with an asterisk.

	Invstigators	Method	Year	Work Function in e.v.	A in amp/Cm^2 Deg^2
1.	Jentsch	Thermionic	1908	4.04	-
2.	Hammer	Photoelectric.	1924	4.72	-
3.	Roy	,,	1926	4.2	-
4.	Welch	,,	1928	3.91	-
5.	Cardwell	,,	1928	4.72*(γ-iron)	-
6.	Siljeholm	Thermionic	1931	4.77*(,, ,,)	-
7.	Galsoe	Photoelectric & Contact Potential	1931	4.77*	
8.	Distler & Monch	Thermionic	1933	4.04	
9.	Wahlin	,,	1942	4.48*(below β-γ transition.)	26
				4.21*(above β-γ transition)	1.5
10.	Present work	,,	1949	4.76 (δ_{Fe} and γ_{Fe})	705 = (120)

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THE THERMIONIC WORK FUNCTION OF GRAPHITE.

Although it was from an incandescent fliament of carbon that in 1883 Edison[1] first observed the effect known after him, the data about the thermionic constants of Carbon are neither consistent nor satisfactory. This may be as much due to the lack of the use ~~of~~ by the earlier workers of the modern technique of degassing under high vacuum as to the fact that carbon readily disintegrates and makes the surface of the emitter pitted under an intensive heat treatment. Hence a roughness factor comes in and introduces a certain amount of unceratinty not only in the area of the emitter but also upon the nature of the surface as the compactness of the mass of the sample may change. Thus for the constants A and in Richardson's equation, Langmuir[2] obtained the value $pA = 5.10^{-4}$ amp/ cm^2/deg^2 and $\phi = 2.54$ e.v., where p represents the roughness factor. Such values are altogether too small and it is likely that the surface used was not quite clean. Earlier, Richardson[3] had obtained 6.48 e.v. for the value of ϕ, whereas F. Deininger[4] had obtained 4.48 e.v. for it. But these two workers had not degassed the emitter nor used any high vacuum. In 1916 Langmuir[5] obtained 3.88 and then 3.94 e.v. for ϕ. No value for A was given in the first work, but in the latter[6] one, Langmuir's value for pA was 5.93 amp/cm^2/deg^2 which is much nearer the expected order of magnitude. At about the same time, Lester[7] from the latent heat of evaporation of electrons from the graphite surface calculated the work function to be 4.5 e.v.—a value greater than the latest value of Langmuir. There is no doubt that the low values of Langmuir were due to an insufficient pre-heating.

Realising the value of a rigorous heat treatment in high vacuum Reiman[8] subjected his graphite filament to a prolonged pre-heating and obtained 4.34 e.v. for the work function and 30 amp/ cm^2/deg^2 for A. Earlier, S.C. Roy[9] had found 4.82 e.v. for ϕ of diamond and graphite from the total photo electric effects, while R. Hamer[10] from the same method found ϕ to be 4.72 e.v. In 1947 Braun and Busch[11] by heating the Specimen in oven the walls of which served as anode have found ϕ equal 4.39 & A = 15. A little earlier, ~~More recently~~, A.S. Bhatnagar[12] has determined the work function of graphite by determining the pressures of the electron gas in equi-

librium with the emitting graphite surface at different temperatures. He made a closed graphite chamber with an effusion hole at one end and by measuring the electron effusion current found the work function to be 4.84 e.v.

The work under report is a continuation of the investigations on work function by the method adopted in the papers on Molybdenum[13] and Iron.[14] In essence the method is that of Bhatnagar.

A hollow cylinder of ~~the metal~~ Acheson graphite under investigation was provided with a solid plug of the same material at one end and a similar hollow plug with a thin wall having a central effusion hole of radius 0.0502 cms. at the other. This cylinder was, ~~as before,~~ put inside a graphite furnace tube. The end with the solid plug was insulated from the furnace tube by means of a fused quartz ring, while the other end was slightly raised by keeping a piece of graphite between the cylinder end and the furnace tube. The cylinder was thus made horizontal and the end with the effusion hole also automatically earthed. The effusion hole and the diaphragm of the Faraday Cylinder were thus coaxial. The distance between the effusion hole and the diaphragm of the Faraday Cylinder was 1.3 cms. The rest of the details were the same as in the previous papers.

This investigation was undertaken to act as a check on the method adopted in the previous work.

The observations taken on 5 different occasions, after the degassing was complete, are reproduced below. From these observations the values of $\log \frac{i_0}{T^2}$ and $\frac{1}{T}$ were calculated and plotted on a graph paper. The numbers 1, 2, 3, 4 and 5 written against the points on the graph denote the days on which the data were collected.

I- Thermionic Emission from Graphite.

	Optical Pyrometer reading in C.	Galv. rea-ratio.	Sign of Shunt voltage on the anode of the Faraday Cylinder.	Galvanometer deflections in mms. when the voltage applied on the central electrode of the Faraday Cylinder was														
				0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.5	3.0	3.5	4.0
1	1710	1/1	plus	36	58	82	104	121	140	154	158.5	158.5	159.5	159	160	160.5	161.5	162
			minus															- 4
2	1680	,,	plus	22	42	58	74	86	95	99.5	100	100.5	100.5	101	101.5	102.5	103	104
			minus															-2.5
3	1655	,,	plus	18	36	50	58	66	68.5	69	69	69.5	70	70	71	71.5	72	73
			minus															- 2
4	1630	,,	plus	13	24	35	44	45.5	46	46	46.5	46.5	47	47	48	48.5	49	50
			minus															- 1
5	1615	,,	plus	10	20	28	35.5	36	36.5	36.5	37	37	37.5	38	38.5	39.5	40	41
			minus															- 1
6	1585	,,	plus	9	17	21.5	21.5	22	22.5	22.5	23	23	23.5	24	24.5	25.5	26	27
			minus															- 0
7	1580	,,	plus	5	15	20	20	20.5	20.5	21	21	21.5	21.5	22	23	23.5	24	25
			minus															- 0
8	1565	,,	plus	2	12	15	15.5	15.5	16	16	16.5	16.5	17	17	18	18.5	19	20
			minus															- 0
9	1530	,,	plus	0	8	8.5	8.5	9	9.5	9.5	10	10	10.5	11	11.5	12.5	13	14
			minus															- 0

II- Thermionic Emission from Graphite

	Optical Pyrometer reading in C.	Galv. shunt ratio.	Sign of voltage on the anode of the Faraday Cylinder.	Galvanometer deflections in mms. when the voltage on the central electrode of the Faraday Cylinder was 0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.5	3.0	3.5	4.0
1	1720	1/1	plus	40	67	93	110	142	167	179	185	187.5	188	188	189	189.5	190	191
			minus															- 5
2	1685	,,	plus	23	42	59	76	92	105	107	107	107	107.5	108	108.5	109	109.5	110
			minus															- 3
3	1655	,,	plus	18	35.5	47	60	64.5	68.5	69	69	69.5	70	70	71	71.5	72	73
			minus															- 2
4	1620	,,	plus	12	22	33	39	39.5	39.5	40	40	40.5	41	41	42	42.5	43	44
			minus															- 1
5	1595	,,	plus	7	17	24	25.5	26	26	26.5	27	27.5	27.5	28	29	30	31	32
			minus															- 1
6	1570	,,	plus	3	13	16.5	17	17.5	17.5	18	18	18.5	19	19	20	20.5	21	22
			minus															- 0
7	1545	,,	plus	1	9	11	11	11.5	12	12	12.5	12.5	13	13	14	14.5	15.5	16
			minus															- 0

III- Thermionic Emission from Graphite.

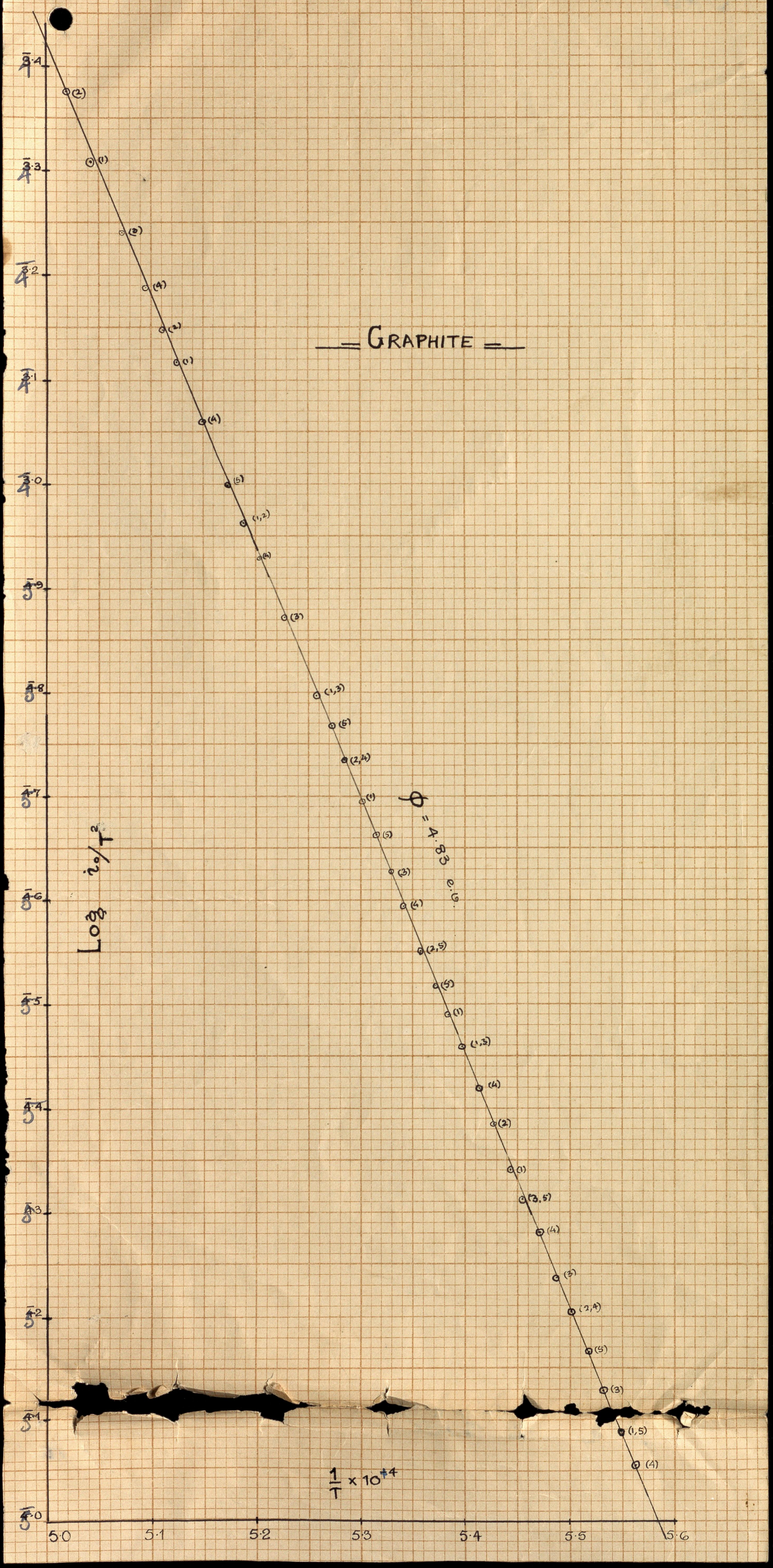
	Optical Pyrometer reading in C.	Galv. Shunt ratio.	Sign of the voltage on the anode the faraday cylinder.	Galvanometer deflections in mms. when the voltage applied on the central electrode of the Faraday Cylinder was														
				0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.5	3.0	3.5	4.0
1	1700	1/1	plus	35	66	94	122	128	132	134.5	135.5	136	136	136.5	137.5	138.5	139	140
			minus															- 4
2	1640	,,	plus	16	32	46	52	53.5	53.5	54	54.5	54.5	55	55	56	56.5	57.5	58
			minus															- 1
3	1630	,,	plus	13	24	35	44	45.5	46	46	46.5	46.5	47	47	48	48.5	49.5	50
			minus															- 1
4	1605	,,	plus	7	20	28	30.5	30.5	31	31.5	31.5	32	32.5	32.5	33.5	34.5	35	36
			minus															- 1
5	1580	,,	plus	5	15	20	20	20.5	21	21	21.5	21.5	22	22	23	23.5	24.5	25
			minus															- 0
6	1560	,,	plus	2	11.5	14	14.5	14.5	15	15	15.5	15.5	16	16	17	17.5	18.5	19
			minus															- 0
7	1550	,,	plus	1	10	11.5	12	12	12.5	12.5	13	13	13.5	13.5	14	15	15.5	16
			minus															- 0
8	1535	,,	plus	0	9	9	9.5	10	10	10	10.5	11	11	11.5	12	12.5	13.5	14
			minus															- 0

IV- Thermionic Emission from Graphite.

	Optical Pyrometer reading in C.	Galv. Shunt ratio.	Sign of voltage on the Faraday Cylinder.	Galvanometer deflections in mms. when the voltage applied on the central electrode of the Faraday Cylinder was														
				0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.5	3.0	3.5	4.0
1	1690	1/1	plus	28	45	63	82	100	110	117	118.5	119	119.5	119.5	120.5	121.5	122	123
			minus															- 5
2	1670	,,	plus	23	39	54	72	83	86.5	87	87	87.5	88	88	89	89.5	90	91
			minus															- 2
3	1650	,,	plus	18	28	40	52	62	64	64	64.5	65	65	65.5	66.5	67.5	68	69
			minus															- 1
4	1620	,,	plus	12	23	34	39	39	39.5	40	40	40.5	40.5	41	41.5	42.5	43	44
			minus															- 1
5	1600	,,	plus	7	17	25	28	28	28.5	29	29	29.5	29.5	30	31	31.5	32	33
			minus															- 0
6	1575	,,	plus	4	12	18	18.5	18.5	19	19	19.5	20	20	20.5	21	21.5	22.5	23
			minus															- 0
7	1555	,,	plus	1.5	9	13	13.5	13.5	14	14.5	14.5	15	15.5	15.5	16.5	17.5	18	19
			minus															- 0
8	1545	,,	plus	1	8	11	11	11.5	12	12	12.5	12.5	13	13	14	14.5	15.5	16
			minus															- 0
9	1525	,,	plus	0	7.5	7.5	8	8	8.5	8.5	9	9	9	9.5	10	11	11.5	12
			minus															- 0

V- Thermionic Emission from Graphite.

	Optical Pyrometer reading in C	Galv. Shunt ratio.	Sign of voltage on the Faraday Cylinder	Galvanometer deflections in mms. when the voltage applied on the central electrode of the Faraday Cylinder was														
				0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.5	3.0	3.5	4.0
1	1660	1/1	plus	26	38	50	62	70	74.5	74.5	75	75	75.5	76	76.5	77.5	78	79
			minus															- 2
2	1625	,,	plus	14	32	39	42.5	43	43	43.5	44	44	44.5	45	45.5	46.5	47	48
			minus															- 1
3	1610	,,	plus	12	26	32	33	33.5	33.5	34	34	34.5	35	35	36	36.5	37.5	38
			minus															- 1
4	1595	,,	plus	9	20	25	25.5	25.5	26	26	26.5	27	27	27.5	28	29.5	30	31
			minus															- 0
5	1590	,,	plus	6	18	23	23.5	24	24	24.5	25	25	25.5	26	26.5	27.5	28.5	29
			minus															- 0
6	1560	,,	plus	2	12	14	14.5	14.5	15	15	15.5	16	16	16.5	17	17.5	18.5	19
			minus															- 0
7	1540	,,	plus	1	9	10	10	10.5	10.5	11	11	11.5	12	12	12	13.0	14.5	15
			minus															- 0
8	1530	,,	plus	0	8	8.5	8.5	9	9	9.5	10	10	10.5	10.5	11.5	12	13	13.5
			minus															-0



GRAPHITE
Log i_0/T^2
$\frac{1}{T} \times 10^{+4}$
$\phi = 4.83$ e.v.
5·0
5·1
5·2
5·3
5·4
5·5
5·6

Calculations.

In the paper on Molybdenum the following equation has been developed:

$$\log i_o / T^2 = - \frac{\phi}{KT} \log \varepsilon + \log A_o \frac{Sr^2}{r^2 + d^2},$$

where i_o is the saturation electronic current collected by the Faraday Cylinder having a diaphragm of radius r; T is the absolute temperature of the Graphite cylinder under investigation; ϕ the work function; A_o is the constant in Richardson's emission equation; S is the area of the effusion hole; d is the distance between the effusion hole and the diaphragm, and K is Boltzmann's Constant, ε being the electronic charge.

Hence, if a graph of $\log i_o / T^2$ is plotted against the values of 1/T, the work function, ϕ, will be given by

$$\phi = \frac{\text{The intercept on the } \log \frac{i_o}{T^2} \text{ axis}}{\text{The intercept on the } 1/T \text{ axis}} \times \frac{1.371 \times 10^{16} \times 300}{10^{-4} \times 4.77 \times 10^{-10} \times 0.4343} \text{ e.v.}$$

In the following, data for $\log \frac{i_o}{T^2}$ and $\frac{1}{T}$ have been taken from observations taken on different days which have all been plotted on one graph.

	Intercept on the $\log \frac{i_o}{T^2}$ axis	$\log \frac{i_o}{T^2}$	Intercept on $\frac{1}{T}$ axis in units of 10^{-4}	1/T	ϕ in e.v.
1	$\bar{4}.3799 - \bar{5}.0551$	1.3218	5.561 - 5.018	0.543	4.831
2	$\bar{5}.9648 - \bar{5}.0877$	0.8771	5.546 - 5.187	0.359	4.848
3	$\bar{5}.9320 - \bar{5}.1277$	0.8043	5.531 - 5.200	0.331	4.822
4	$\bar{5}.8627 - \bar{5}.2054$	0.6573	5.500 - 5.228	0.272	4.795
5.	~~$\bar{4}.7669 - \bar{5}.2769$~~	0.4900	5.470 - 5.269	0.201	4.838
6	$\bar{5}.7330 - \bar{5}.3115$	0.4215	5.455 - 5.282	0.173	4.835
7	$\bar{5}.6273 - \bar{5}.7834$	0.2439	5.426 - 5.326	0.100	4.840
8*	$\bar{5}.420 - \bar{5}.000$	0.420	5.584 - 5.000	0.584	4.825

Mean value of ϕ in e.v. = 4.83

The data marked with an * were obtained directly from the graph.

Taking the above value of ϕ, r = 0.426 cms., d = 1.3 cms, and the radius of the effusion hole = 0.0502 cms., the following values of A_o were obtained for different temperatures of the emitter:

	1	2	3	4	5	Mean
Temp. in °C	1720	1680	1625	1580	1525	
A_o in amp/ cm^2/ deg^2	172.2	168.2	168.3	172.4	171.5	170

(170)

The following table summarises the values of the thermionic constants as found by different workers. The values that seem to be reliable are marked with an asterisk.

	Investigators	Year	Method	A in amp. cm^{-2} deg^{-2}	Work function in e.v.
~~xxxx~~	~~Langmuir xxxxxxxxxx~~	~~1913~~	~~Thermionic~~	~~A 5 x 10 xx~~	~~xxxxxxxxx 2.5 xxxx~~
1.	Richardson	1903	Thermionic	-	6.48
2.	Deininger	1908	Thermionic	-	4.48
3.	Langmuir	1913	Thermionic	A 5. 10^{-4}	2.5
4.		1916	Thermionic	A 5.93. ~~10~~ 10^{-}	3.88 3.94
4.	Lester	1916	Latent heat of evaporation.	-	4.5
5.	~~Reiman~~ x Hamer	1924	Photoelectric		4.72
6.	S.C. Roy	1926	Photoelectric	-	4.82*
7.	Reiman	1938	Thermionic	30	4.34*
8.	Bhatnagar	1944	Thermionic	-	4.84*
9.	Braun and Busch	1947	Thermionic	15	4.39
10.	Present worker ~~s~~	1949	Thermionic	170	4.83

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