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The Complete Photo-electric Emission from Potassium.

THE COMPLETE PHOTO-ELECTRIC EMISSION FROM POTASSIUM

ABSTRACT

This thesis is in two parts, the first portion of which describes experiments which were carried out to detect a positive photo-electric emission from potassium. The result of these was that if such an emission occurs it is of the order of 10^{-7} times the negative emission at most, i.e. a thousand times as small as the value found by Dember, who claimed to have definite evidence of a photo-electric effect.

The major portion concerns the two or more threshold frequencies of potassium. A brief historical account is given ending with the work of Richardson and Young in which they predict for the sensitised potassium surface a threshold at 10,000 AU and another at 30,000 AU. Precautions were taken to obtain a clean surface in a high vacuum, the apparatus being of a form which made the saturation of the photo-electric currents easy and the potassium was subjected to approximately black body radiation. Using Richardson's formula for the saturated currents $C = AT^{\lambda} e^{-\frac{b\nu}{T}}$, the work functions, b, and the corresponding threshold frequencies were determined. The values of the frequencies found were 7,100 A.U., 10,000 A.U. 21,000 A.U. A tentative explanation is given of certain Hysteresis phenomena which were observed.

The COMPLETE PHOTO-ELECTRIC EMISSION FROM POTASSIUM

The earlier part of the experimental work described in this thesis was undertaken with the purpose of detecting a positive photo-electric emission from potassium, if any such emission actually occurs. The experiments indicate that any positive emission from the metal under the influence of light is so small that it is doubtful whether it occurs at all.

The later and major portion of the thesis is devoted to an investigation of the photo-electric (negative) emission from the metal under the influence of black body radiation. The experiments indicate the existence of at least two work functions whose values and the associated threshold frequencies have been determined.

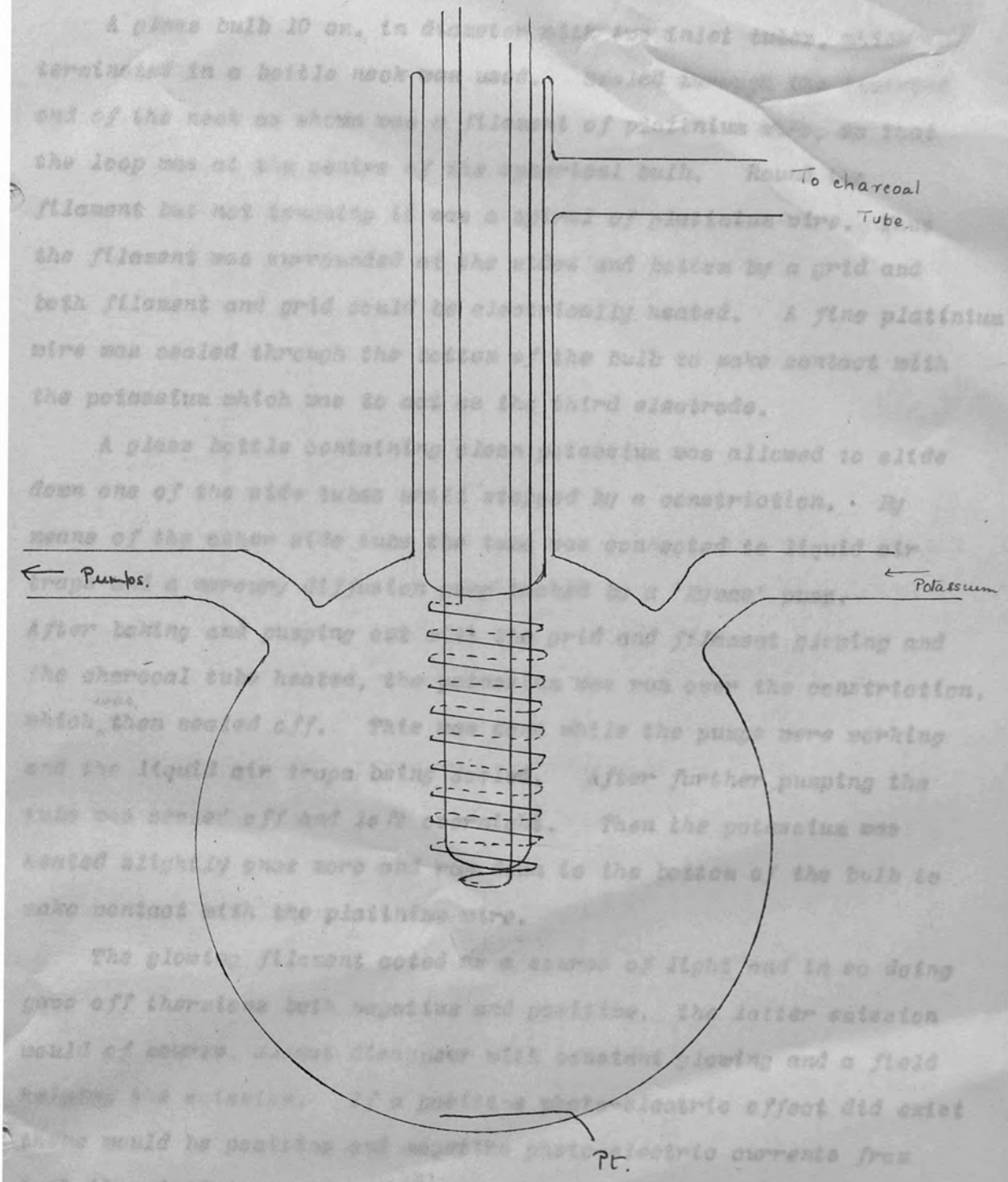
POSITIVE PHOTO-ELECTRIC EFFECT

Dember (Ann.d.Phys. 30) states that a cylinder surrounding a metal plate aquired a positive charge when the plate was illuminated with ultra violet light, a suitable field being applied, and attributed this charging up to the emission of positive ions by the plate. Bär and Lucksinger (Phys. Zeitschr. 1921) working with small particles of paraffin and selenium in a Millikan electron apparatus found some particles become negatively charged when illuminated with ultra violet light. This so-called 'inverse' effect seems to point to photo-electric emission of positive particles, but it can also be accounted for, if some stray light is allowed to fall on metal parts in the apparatus, which give off photo-electrons to be picked up by the particles under examination. In neither of the above experiments were precautions taken to shield the metal parts from the stray short wave light. S. Taubes (Ann.D.Phys. V1 1925) found that when the condenser plates in the electron apparatus were coated with wax the 'inverse' effect did not appear, but with bare metal plates it did.

Du Bridge (Phys. Rev. Feb.1925) also found that he could account for Dember's results by the effect of the ultra violet light on the cylinder itself. M. Hake (Zeitschr.für Phys. Band XV Heft 23 1923) worked with nineteen materials in an Ehrenhaft's form of Millikan's electron apparatus and found that metals show both effects, depending on the gas surrounding them and that insulators -glycerine- always show the inverse effect in gases. Wasser (Zeitschr. für Phys. Band 27 Heft 4 1924) finds that mercury drops in nitrogen and carbon-dioxide give the inverse effect when of certain sizes only (small). E.J.Lorentz (Phil. Mag. Vol. 1 1926) covers the same range of radii as the previous experimenter but cannot obtain the effect. He worked with fifty drops of oil of varying diameters in air, nitrogen, hydrogen, carbon-dioxide, oxygen and helium, fifty drops of glycerine in air, nitrogen, and hydrogen, and with fifty drops of mercury in air and nitrogen. In no one case did he notice the inverse effect, until the screens keeping the light off the plates were removed.

None of the above observers, however, have worked with the alkali metals, though if the positive photo-electric emission exists it seems a priori probable that these metals would exhibit the effect to a greater degree than other metals, ~~known to be much less active as regards the normal effect.~~ Also the recent observers, with the exception of Du Bridge, observed the behaviour of a certain number (say fifty) of drops of the substance. Dember, however, found that the positive current was of the order of 10^{-13} amps. as compared with a ~~negative emission of~~ 10^{-9}, so that the probability of a drop being charged negatively is 10^{4} times as great as the probability of it picking up a positive charge. With only fifty drops being considered it would be possible to overlook the effect even if it did exist.

Diagram I



EXPERIMENTS ON THE POSITIVE PHOTO-ELECTRIC EFFECT

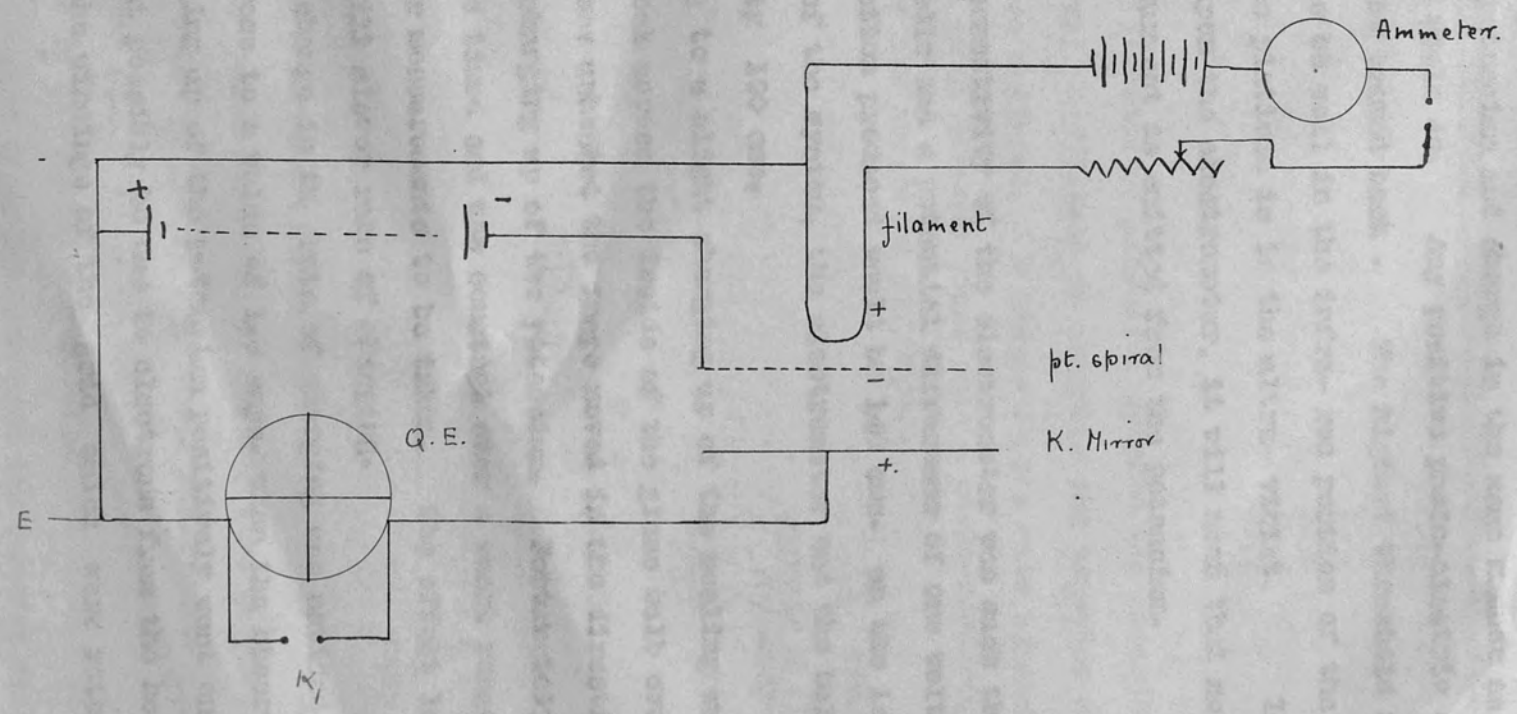
Apparatus used.

A glass bulb 10 cm. in diameter with two inlet tubes, which terminated in a bottle neck was used. Sealed through the inverted end of the neck as shown was a filament of platinium wire, so that the loop was at the centre of the spherical bulb. Round the filament but not touching it was a spiral of platinium wire. Thus the filament was surrounded at the sides and bottom by a grid and both filament and grid could be electrically heated. A fine platinium wire was sealed through the bottom of the bulb to make contact with the potassium which was to act as the third electrode.

A glass bottle containing clean potassium was allowed to slide down one of the side tubes until stopped by a constriction. By means of the other side tube the tube was connected to liquid air traps and a mercury diffusion pump backed by a 'Hyvac' pump. After baking and pumping out with the grid and filament glowing and the charcoal tube heated, the potassium was run over the constriction, which was then sealed off. This was done while the pumps were working and the liquid air traps being cooled. After further pumping the tube was sealed off and left overnight. Then the potassium was heated slightly once more and run down to the bottom of the bulb to make contact with the platinium wire.

The glowing filament acted as a source of light and in so doing gave off thermions both negative and positive, the latter emission would of course, almost disappear with constant glowing and a field helping the emission. If a positive photo-electric effect did exist there would be positive and negative photo-electric currents from both the platinium grid and the potassium. When the connections are arranged as shown in diagram 2, the negative current from the grid and the positive from the ~~alloy~~ potassium alone affect the quadrant electrometer. The grid is negative with respect to the potassium so that any electrons from the metal are turned back, while any positive particles from the potassium are attracted across to the grid leaving a negative charge

Diagram II



on the potassium, which when the key K, is open, causes a deflection of the needle of the electrometer. The field between the filament and grid will turn back any electrons emitted from the filament. There may be a negative photo-electric current from the grid, which could reach the potassium and charge in the same manner as the positive current leaving it would do. Any positive photo-electric current from the grid will be turned back. The highest threshold frequency of potassium is known to be well in the infra- red portion of the spectrum, while that of the platinum is in the ultra- violet. If no effect is produced upon the electrometer, it will mean that no positive photo-electric current is emitted from the potassium.

Results.

The sensitivity of the electrometer was such that with 120 volts on the needle and a potential difference of one volt between the quadrant the deflection produced would be 140 cms. on the lamp scale. The capacity of the system, the electrometer and the bulb in series, was very nearly 100 cms.

Owing to a slight charging up of the sealing wax key and also to a small leak across the inside of the glass bulb even when the filament was unheated the image moved in the direction indicating a positive charging up of the potassium. Fortunately it was not too fast to be timed and was constant over a short range of time, long enough for measurements to be taken. The effect looked for would mean a still slower rate of charging.

No change in the rate of charging was noticed until the filament current rose to a value of 1.8 amps. when the observations showed that the charging up of the potassium positively went on at a slower rate This might possibly be due to electrons from the hot filament escaping between the windings of the grid which were rather wide. However at this

particular temperature the negative current was quite large (greater than 10^{-6} amps).

A stop clock reading to .2 seconds was used and it would have been easy to detect a change of rate of 1 cm. in ten seconds.

Filament current	Time for image to traverse 22cm.
0	10.2 seconds
1.5 amps.	10.2 "
0	10.4 "
1.6 "	10.2 "
0	10.2 "
1.7 "	10.4 "
0	10.2 "
1.8 "	11.2 "

The difference of potential between the potassium and the grid was 96 volts; sufficient to saturate the negative currents at the temperatures employed. A change in the rate of charging up of one centimetre in 10 seconds would mean a photo-electric current of 10^{-13} amps. For the potential difference

$$= \frac{1}{140 \times 300} \text{ electro static units.}$$

$$= \frac{\text{current} \times \text{time}}{\text{capacity}}$$

$$= \frac{C \times 10}{100} \text{ E.S.U.}$$

$$C = \frac{10}{140 \times 300}$$

$$= \frac{10^{-3}}{4.2} \text{ E.S.U.}$$

$$= \frac{1}{4.2} \times \frac{1}{3} \times 10^{-12} \text{ amps,}$$

$$< 10^{-13} \text{ amps.}$$

Hence a current of this order could easily have been detected.

Dember found the ratio of his negative to positive photo-electric currents to be $\frac{10^{-9}}{10^{-13}} = 10^{4}$, whereas these experiments give the ratio as more than $\frac{10^{-6}}{10^{-13}} = 10^{7}$.

Hence if the positive photo-electric effect does occur it is at least a thousand times smaller than the current which Dember attributed to the emission of positive ions.

THRESHOLD FREQUENCIES OF POTASSIUM

Hertz was the first to observe photo-electric phenomena and one of the first facts which appeared was that only certain kinds of light were instrumental in liberating electrons. In experiments in connection with electric oscillations he noticed, while using two spark gaps, that the maximum length of the spark was smaller if one was enclosed in a dark box. By inserting plates of glass so as to screen one spark gap from the other the change did not occur, while rock salt did not hinder the action. Thus Hertz showed that ultra violet light was the cause of the lengthening of the maximum spark. Hallswach investigated the effect of ultra violet light on electro statically charged bodies and found that negatively charged bodies became discharged, no effect being produced on positively charged bodies. Again the effective portion of the light used, that from an arc lamp, was found to be in the ultra violet portion of the spectrum. Hallswach also found that metal discs exposed to ultra violet light aquired a positive charge and as a result of his investigations concluded that the light caused the plate to lose electrons which travelled away from it along the direction of the lines of force.

Elster and Geitel (Ann. d. Physik 52 1894) found that ordinary daylight was effective in the case of the more electro-positive metals. They experimented on rubidium, potassium and sodium, using a series of filters and found that only with rubidium was there any appreciable effect with red light while maxima occured with yellow. The more electro positive the metal the longer the wave length with which it becomes active. J.J.Thomson found that a positively charged metal plate placed opposite a surface of sodium-potassium (NaK) alloy or rubidium lost its charge even in the dark, presumably due to the influence of long waves. Experiments carried out with other metals showed that the photo-electric activity increased with decreasing wave length, and Hallswach found the same occured with the alkali metals. The apparent disagreement between the results of Elster and Geitel and Hallswach for the alkali metals was explained by Pohl and Pringsheim

who showed that the activity depended on the angle of incidence of the light. With normal incidence, when the electric vector is parallel to the surface the activity increases with the frequency of the light but in other cases the electric vector, which is parallel to the plane of incidence, produces a maximum for some particular wave length. In the case of sodium potassium alloy it is at about 4000 au. These are the "normal" and "selective" effects. Compton and Richardson found two maxima for the photo-electric activity in the case of sodium and concluded that the normal effect also exhibits a maximum, but that it is further in the ultra violet part of the spectrum than that produced by the selective effect.

The relation between the wave length of the incident light and the velocity of the emitted photo-electrons engaged the attention of investigators for some time. Ladenburg and Markau obtained velocity distribution curves, by measuring the photo-electric current with different values of retarding and accelerating potentials. Ladenburg found that his results could be represented by the relation $\sqrt{V}\lambda$ = constant, (where V is the stopping potential) or that the initial velocity was proportional to the frequency $v \propto \nu$. Joffé, however, pointed out that they also could be fitted to the relation, that positive accelerating potential i,e, the square of the initial velocity was proportional to the frequency. With the short range of ~~the experiments, light of~~ wave lengths 2000 au to 2700au, it was impossible to say whether points of the graph lay on a straight line or the practically straight portion of a parabola. J.Kunz, working with Nak alloy was in favour of the second conclusion but the difficulty of obtaining a perfectly clean surface and so of preparing the metal in the same condition on two successive occasions again introduced some doubt. The work of Hughes gave evidence in favour of $v^2 \propto \lambda^{\nu}$. He also produced much cleaner surfaces by distilling the metals on to a strip in vacuo and used an improved type of monochromator. Results obtained with various metals showed the second relation to be the one which best explained the facts.

Thus

Hughes found $V = h\nu - V_0$, where V is the stopping potential, V_0 is constant. The emission will cease altogether below a certain definite frequency determined by the relation $V_0 = h\nu_0$

As early as 1903 Richardson had measured the thermionic work function, ~~the result being given in equivalent volts and obtained from readings on the thermionic currents~~. The thermionic emission from a heated metal is governed by the relation $C = AT^n e^{-\frac{b}{T}}$, where n may be 2 or $\frac{1}{2}$ T being the temperature to which the metal is raised, A a constant, b is $\frac{\varphi}{k}$, where φ & k are respectively the work function and ~~k is~~ the gas constant for one molecule or the entropy constant. By plotting the $\log_{10} \frac{C}{T^{\frac{1}{2}}}$ against $\frac{1}{T}$ the results gave a curve convex to the origin, of which the left hand portion approximated to a straight line. ~~This straight line being considered,~~ a value for the constant b can be obtained by measuring the slope of the line with respect to the $\frac{1}{T}$ axis. For sodium the value of b obtained was 3.16×10^{4}, which corresponded to a value 2.63 in equivalent volts. The measurements were obtained using a steel tube which could be placed in a small furnace. Inside was a hollow semi circular cylinder of brass, while a platinium wire was stretched along the axis of the cylinder. Small cubes of sodium were placed on the brass cylinder and after heating in the evacuated tube formed a fairly evenly distributed film over the inside of the steel tube. The tube was evacuated by means of a Gaede pump and liquid air on a charcoal tube and the leak from the tube to the wire gave the thermionic currents. The method of introducing the metal would necessitate the presence of some oxide and gases which the Gaede pump could not remove. These would doubtless give rise to a thin film on the metal surface, thus giving a high value for the threshold frequency. It was suggested that the platinium wire might gradually give off its absorbed hydrogen and this also would lead to a high result. Also difficulty was experienced in saturating the thermionic currents.

In 1910 Pohl and Pringshein's work on measurements of the position of the maximum for the selective photo-electric effect gave approximate values for the threshold frequency Vo. ~~If~~

If ν_{max} represents the frequency at which the maximum occurs then $\nu_{max} = \frac{3}{2}\nu_0$. Pohl and Pringshein found λ_{max} for potassium to be about 4400 AU and for sodium 3350 AU. These results would indicate that Vo for potassium is somewhere near 4.5×10^{14} and for sodium 6.0×10^{14}

When Richardson and Compton were investigating the relation between exciting frequency and the velocity of the ejected electron they also found a maximum photo-electric activity occuring in the case of sodium. They were using a new type of monochromatic illuminator, which gave a strong and accurately monochromatic beam of light, and exhausting the bulb by means of a Gaede pump and using liquid air on a charcoal tube. The sodium was placed in position, the bulb exhausted and then the sodium cut by a razor blade drawn downwards by the attraction of an external magnet on a piece of soft iron attached to the blade. Difficulty was experienced in making observations because the surface fatigued very rapidly owing to the freshly cut surface being immediately attacked and contaminated. However, the curves showed that a maximum occured in the currents and its position showed that a Vo was in the neighbourhood of 5.15×10^{14}.

The next year1913, Richardson and Compton repeated their observations with sodium, using the same procedure to exhaust the bulb as before, but instead of cutting the sodium in vacuo the clean surface was distilled on to a metal strip. This time, although the currents showed fatigue the maximum did not shift with the lapse of time. The range of wave lengths used was greater than before and two maxima occured, the first with a wave length of 3600AU and the second further in the ultra violet at 2270 au, It was noticed that the work function depends very largely on the state of oxidation of the surface and that the first maximum decreases more rapidly with fatigue than the second. There was considerable overlapping in the visible spectrum so that the critical wave length could not be definitely determined but was somewhere about 5500 AU. The maximum at 3600 AU would give a value 5.5×10^{14} for ν_0 while the 5500 AU value for ν_0 gives 5.4×10^{14} for ν_0. The second frequency as indicated by the second

maximum at 2270 AU would have a value 8.8 X 10^{14}.

Millikan published in the Physical Review of 1916 an account of a long and careful piece of work, the aim of which was to verify Einstein's law and in particular to obtain a photo-electric measurement of Planck's constant h. He worked with the metals sodium and lithium and took great precautions to obtain film free surfaces. The metals were mounted, so that a knife operated by electro magnets could shave films from the surface at any desired time in a vacuum which corresponded to about a ten millionth of a millimeter of mercury pressure. The apparatus was exhausted by means of a Gaede molecular pump and the shavings of metal helped to raise the vacuum by chemical action. A wide range of incident wave lengths 6800 AU to 2400 AU, were used and the photo-electric currents excited by the different wave lengths measured by means of an ionisation chamber. It was found that in high vacuum the contact electro motive force did not alter greatly just after the surface had been shaved, but that the photo-electric currents would drop to a third or fourth of t their initial value in half an hour. This was the case with sodium, but lithium remained strongly photo-electric for an indefinite period, no decay being shown over a period of six months. Plotting volts (P. D) against frequency gave a straight line, and when the contact potential difference between the sodium and the copper of the ionisation chamber i.e. 2.51 volts had been allowed for, the line intercepted the axis at ν_0 = 4.39 X 10^{14}. This threshold frequency corresponds to a limiting wave length of λ_0 = 6800 AU. In spite of the great precautions taken Millikan still thought that λ_0 might be in error by about 100 AU.

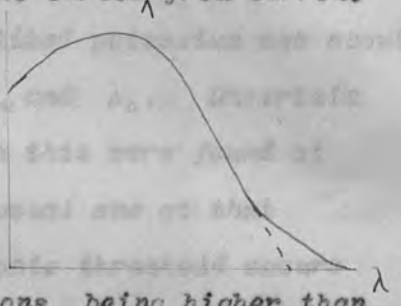
In 1917 W.Wilson measuring the complete photo-electric effect from sodium potassium alloy obtained a value for Vo of 6.2 X 10^{14} The relation between the saturated photo-electric current i and temperature T is the same as that governing the thermionic emission namely $i = C T^{k} e^{-\frac{b}{T}}$ k being either 2 or $\frac{1}{2}$. b again is $\frac{\varphi}{R}$ where φ is work function. The alloy was capable of being tapped about in the exhausted vessel so as to produce a fresh surface at will, but

in spite of that, fatigue was noticed and as might be expected a high value for Vo obtained. The graph of log $\frac{i}{T^2}$ and $\frac{1}{T}$ gave a straight line in the final experiments though earlier results had indicated two straight lines inclined to each other.

Later, in 1922, Richardson obtained values for Vo which agreed with those of W.Wilson. He was working with alloy (K.Na) in an atmosphere of $COCl_2$, and obtained very small currents with incident light of wavelength λ5460, indicating that the threshold is just on the low frequency side of it. Repeating using Hilger colour filters he found a very small current with λ 4916 which gives Vo = 6.02 X 10^{14}. The clean alloy was kept in a funnel and allowed to drop through a nozzle at such a rate that the drops of alloy remained clean. If the rate was too slow films appeared on the drops. Richardson found that different gases affected the photo-electric threshold frequency and Vo apparently varies with trifling changes in conditions. In one experiment with the alloy in $COCl_2$ it was not possible to obtain a current with the full illumination of a mercury lamp through the λ 4355 filter, while in other cases, apparently no different, large currents were obtained. The threshold wave length is higher than λ 5460 when the alloy is in $COCl_2$, but when in chlorine it is less than λ 4355. In some cases with water vapour present currents were obtained with wave lengths λ 4355, λ 5460, λ 5790, so that when water vapour is present the value of Vo can lie in the infra red. The method of exhaustion in this case was with a Gaede pump backed by a Geryk.

In the following year Young carried out some experiments on the thermionic and photo-electric properties of potassium. The metal was put in a side tube, freed from naptha by exhausting with a rough pump, warmed so as to run through into the main tube. At first a film formed over the surface but after continued heating the surface remained bright indefinitely. On plotting log $\frac{i}{T^2}$ against $\frac{1}{T}$ the graph obtained was not in general rectilinear, although in some cases, on first heating the metal after a day or two's rest a straight line was obtained. The curves were continuous from the solid to the liquid state, no break occuring at the change of state. The current

potential difference curves however were of peculiar shape in some cases, especially near the bend, corresponding to currents just less than the saturated current. For temperatures near 200°C values of b from 1.39 to 1.58 X 10^{4}, corresponding to equivalent volts .99 to 1.32 were obtained. b for temperatures about 30°C varied from ,502 to .576 X 10^{4} corresponding to .463 to .694 equivalent volts. All these are less than Richardson's value obtained in 1903. Young's photo-electric measurements gave higher values. The curves obtained by plotting current against wavelength being as shown gave 1.86 to 2.02 in equivalent volts or if the tail of the curve is attributed to scattered light 1.72 to 1.77 volts.



The threshold wave length was between λ 6640 and λ 6120. Richardson has given an explanation of the photo-electric work functions being higher than the thermionic ones. This is the theory of 'patches'. With a metal surface having areas each with its characteristic work function, two or more, local electrostatic fields will be set up under the influence of heat or incident light of the correct wave length. It was suggested that the thermionic current comes from the parts of the surface having low work functions while the photo-electric currents are more evenly distributed over the whole surface. The local fields at the boundaries of the patches could also explain the greater difficulty in saturating the thermionic currents from a surface. The peculiar shape of the current potential curves plotted by Young might also be accounted for by the local fields.

In 1925 Richardson and Young published another paper on the same subject. First Richardson's results of 1903 are recalculated from the aspect of the curve being two straight lines instead of one and neglecting some of the points. This gives the two work functions in equivalent volts as 3.96 and 1.37. The first agrees fairly well with Richardson and Compton's photo-electric value for the second threshold i.e. 3.63, but 1.37 is very low when compared with the photo-electric values 1.82 to 3.56 volts. These experimenters worked with potassium in a vacuum obtained with mercury diffusion pumps and the metal surface obtained by melting the metal away from

from the oxide skin and continuing heating until the surface remained clean. The potassium surface was sensitised by passing a luminous discharge between the the metal surface and the electrode when in an atmosphere of about ,1mm. of hydrogen, introduced by heating palladium tubes. The hydrogen was then pumped out. The photo-electric current was plotted against the wave length and one maximum was found before sensitising while two were present after. This sensitised surface gave an emission corresponding to a threshold of about λ_0 = 10,000AU. The threshold of the unsensitised potassium was about 7000 AU which agrees with other values of λ_{max} and λ_0. Uncertain traces of a thermionic threshold agreeing with this were found at 200°C, but the usual ones are much lower; a usual one at that temperature being 10,000 AU. Another thermionic threshold occurs at about 30,000 AU, but even the sensitised potassium showed no trace of this. The glow discharge being passed in the presence of hydrogen or water vapour, besides bringing out undeveloped thresholds increases the normal emission.

Richardson and Brotherton have shown that the presence of various gases ~~decreases~~ reduces the value of the threshold frequency. Dealing with sodium potassium alloys of different compositions the threshold frequendy in vacuo varied between 5.2 and 5.4 X 10^{14} while in an atmosphere of $COCl_2$ the values of Vo were from 5.0 to 5.4 X 10^{14} Water vapour also makes the threshold frequency a little lower than in vacuo. In this paper the disagreement between chemical and photo-electric determinations of the contact potential differences is also explained by Richardson's theory of patches. The stopping potentials for the various alloys were measured and graphs plotted between σV and V. The values in $COCl_2$ were higher than in vacuo. If i is the current against an opposing potential V then $i = i_0(1 + \sigma V)e^{-\sigma V}$ i_0 is the saturation current and $\sigma = e/kT$. In one case the zero on the V scale given by the chemical emission was 1.82 volts. If V_s is the stopping potential and K the contact potential between the two surfaces then

$$e(V_s + K) = \tfrac{1}{2} m v^2 = h(\nu - \nu_0)$$

ν_0 = threshold frequency and ν = frequency of incident light.
In one case of photoelectric determination 14 $\nu_0 = 5.0 \times 10^{14}$ when using a group of wave lengths 4347 - 58 AU making $\frac{h}{e}(\nu - \nu_0) = 0.77$ volts which gives a zero as determined photo-electrically = 2.46 volts. With a different ~~band~~ range of wave lengths incident the zero = 2.49 volts. Thus the photo-electric determinations agree among themselves, but are larger than that given by the chemical emission. The difference can be accounted for if it is assumed that the chemical action does not take place over the whole surface. Then the value for Vo is higher in the absence of $COCl_2$, and the surface acted on by the gas is electro positive to the clean alloy. This agrees with the low thresholds which have been found when water vapour is present. Let ν_p be the photo-electric threshold frequency for contaminated areas and ν_c for the clean alloy. Photo-electric measurements determine the smaller of these two, so far ν_p in all cases. Contact potential differences determined from the chemical or photo-electrons which come from different areas with different intrinsic potential differences. The theory of patches also accounts for the difficulty of obtaining saturation and the breaking down of Maxwell's plateau in the neighbourhood of zero emission. If electrons are ejected at the periphery of a positive patch the slow ones will be pulled into the positive area.

Date	Observer	Substance	Photoelectric Threshold	Equivalent Volts	Thermionic Threshold	Equivalent Volts
1903	Richardson	Na				2.63
1910	Pohl and Pringsheim	K Na	4.5×10^{14} 6.0×10^{14}			
1912	Richardson and Compton	Na	5.15×10^{14}			
1913	Richardson and Compton	Na	5.2×10^{14} 5.56×10^{14} 8.81×10^{14}	2.14 2.29 3.63		
1916	Millikan	Na	4.4×10^{14}	1.82		
1917	W. Wilson	K Na	6.2×10^{14}	2.56		
1922	Richardson	K Na	$6.02 \rightarrow 6.25 \times 10^{14}$			
1923	Young	K		1.86 - 2.02		1.32 - .99 .694 - .463
1925	Richardson's results of 1903 recalulated					3.96 1.37
1925	Richardson and Young	K	4.3×10^{14} 3.0×10^{14} (about)		3.0×10^{14} 1×10^{14}	
1927	Richardson and Brotherton	Alloys of K and Na	$5.0 \rightarrow 5.4 \times 10^{14}$			

EXPERIMENTS ON THE THRESHOLD FREQUENCIES OF POTASSIUM

The apparatus used to investigate the existence of the positive photo-electric effect was also used to measure the threshold frequency of potassium, by measuring the complete photo-electric effect when in equilibrium with black body radiation of known temperature. By heating the potassium at the bottom of the bulb with a small electric heater, it was vapourised and then deposited in a thin film over the cool part of the spherical surface. To prevent the vapour settling on or near the filament and grid both were heated throughout the operation and another electric heater was wound round the outside of the bottle neck. By repeated heating and cooling of the potassium it was possible to obtain a comparatively thick mirror over the whole spherical surface, the gap on the glass in contact with the heater being covered by tipping the tube while the metal was still in the liquid state. In the earliest experiments the mirror of potassium was apparently not of sufficient thickness to make good electrical contact over the whole of the surface, for inconsistent readings of the photo-electric currents were obtained: doubtless due to certain portions of the surface becoming charged up after subjection to radiation for a few minutes. When the film of potassium was made thicker this difficulty disappeared. Owing to repeated reflections of the radiation emitted by the filament at the bright potassium surface the interior space is filled with approximately black body radiation and at the same time a fresh metal surface could easily be obtained by heating and vapourising the potassium. Furthermore each heating would improve the conditions until all the substances which had been left in the bulb capable of reacting with potassium had been used up.

The law governing the relation between current and temperature in the case of the complete photo-electric effect is expressed by

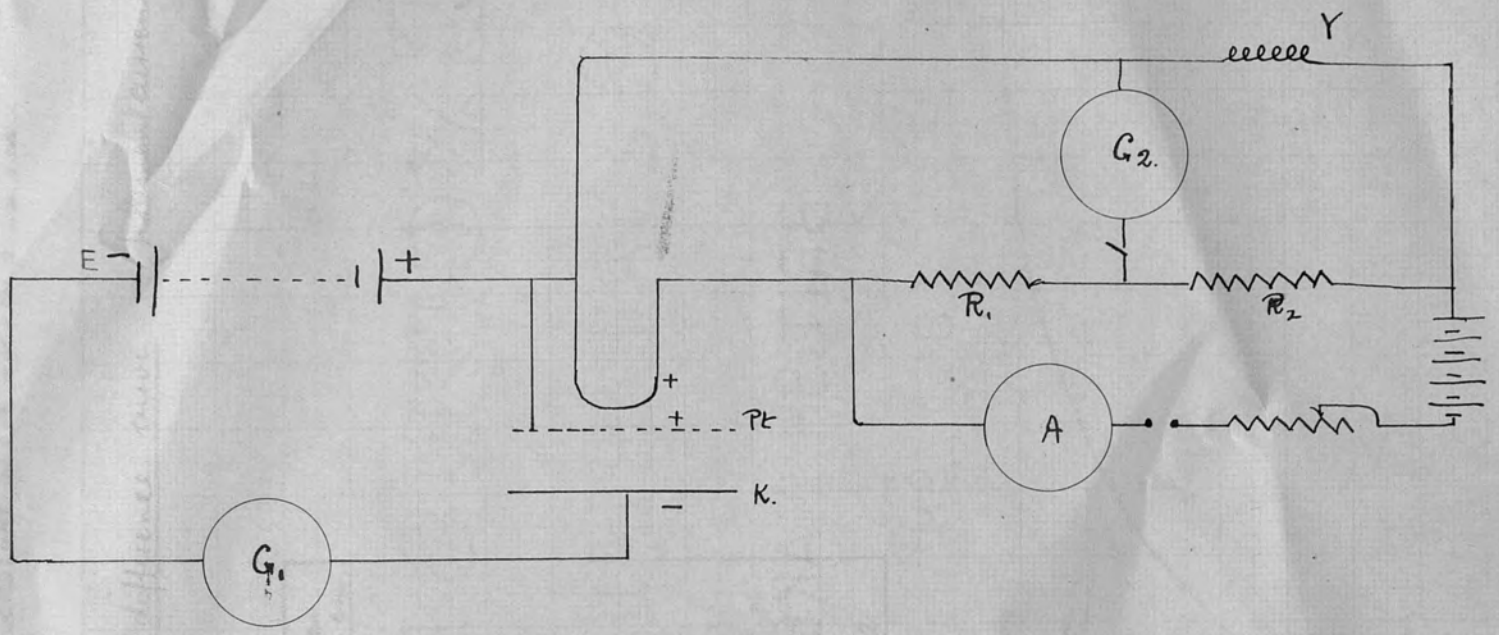
$$C = A T^{n} e^{-\frac{b}{T}}$$ (see Richardson Phil. Mag. Vol.1. 1912)

where C is the saturated current

A is a constant

T is the temperature of the radiator

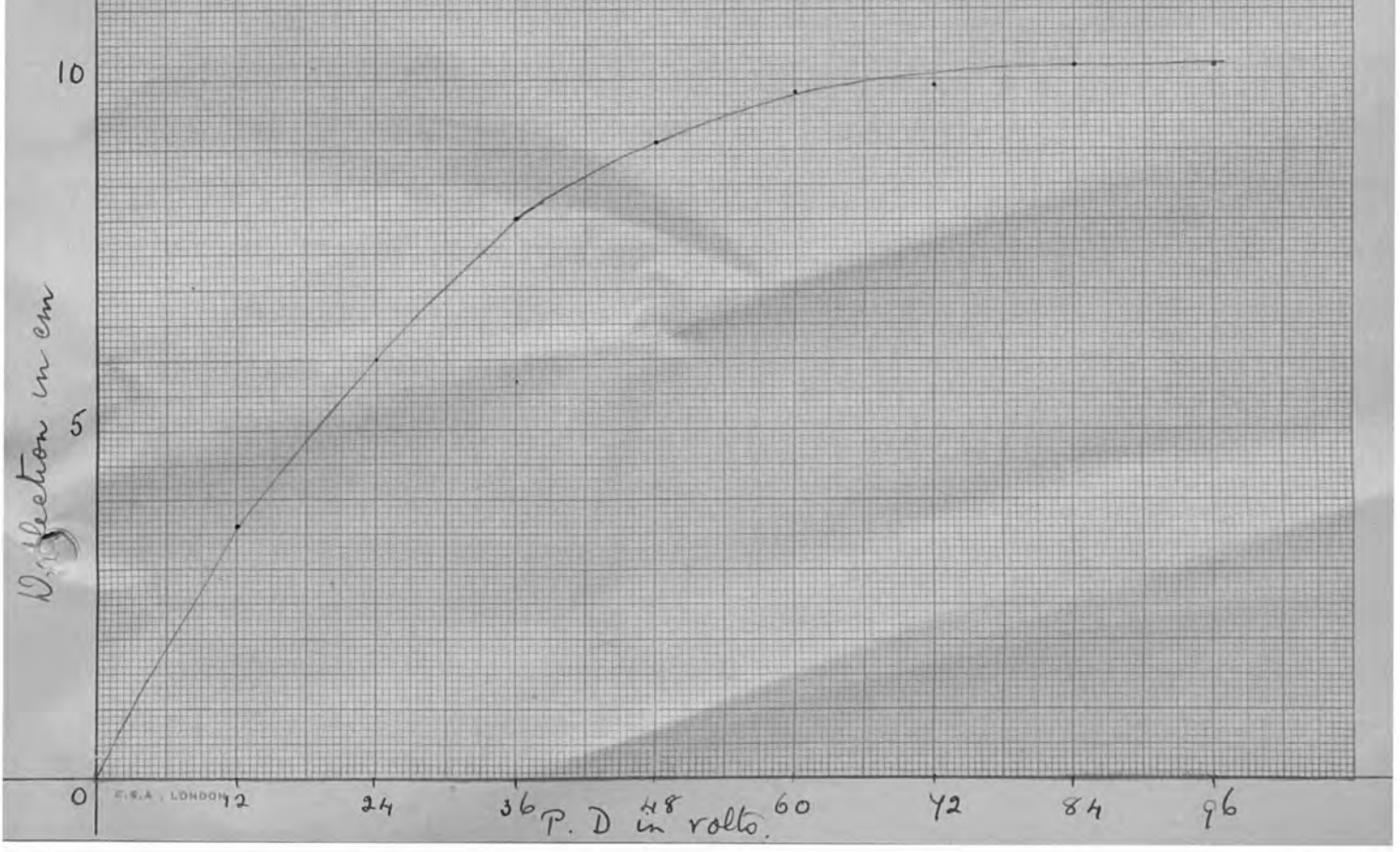
Diagram III



Current potential difference curve filament current is 2·5 amps.

P.D on filament volts	Deflection cm.
12	3·6
24	6·0
36	8·0
48	9·1
60	9·8
72	9·9
84	10·2
96	10·2

Fig 1



n is a constant which equals 2 or 1/2
b is $\frac{\varphi}{R}$ i.e. $\frac{\text{work function}}{\text{gas constant for one molecule}}$

therefore plotting log $\frac{C}{T^n}$ against $\frac{1}{T}$ should give a straight line - the slope giving the value of b.

The saturated currents C were comparatively large and a sensitive galvanometer was used to measure them ~~the photo-electric currents~~. The connections were as shown in III. The two grid connections and one side of the filament were connected to the positive side of a lamp board in which the 10 lamps were arranged in series and connected to the 240 volt mains. One terminal of the galvanometer G1 was connected between two of the lamps, the other ~~galvanometer terminal~~ being connected straight to the potassium mirror. The resistance of the filament was measured at the various temperatures by means of a Wheatstone's bridge arrangement, R1 and R2 were two arms of a Post Office box, and X was a coil of eureka wire 2 metres long immersed in a flask filled with paraffin oil, which in turn was surrounded by a water bath. The resistance of the coil was 2.056 ohms. Its resistance was previously measured at 20° C and at 100° C, no difference being detectable, and when surrounded by a water bath the temperature varied over a range of less than 10° C, when the largest currents were used. Consequently under the conditions of the experiment it was an invariable resistance. The filament was heated by a battery of accumulators and the steady balance in the bridge found, using a dead beat Onwood galvanometer, which gave a deflection of about 10 cm. on the scale for a change of resistance of one ohm in the variable arm of the box. The photo-electric currents were well saturated as is shown by Figure I, the current potential difference curve corresponding to a filament current of 2.6 amps. With the largest filament currents used (3.5), saturation was secured by having 108 volts potential difference between the potassium and the filament, so this value was used throughout.

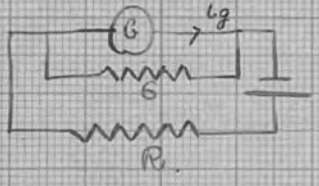
The graph plotted between galvanometer (G_1) deflection and resistance in the variable arm of the box i.e. between current and filament temperature in arbitrary units, was of the form shown in

Calibration curve for galvanometer G_1.

Fig II

R. ohms.	S ohms.	Current i_g $\times 10^{-7}$ amps	Deflection cms.
10^6	10	·29	1·3.
10^6	20	·54	2·4
5×10^5	20	1·14	5·6
10^6	60	1·39	6·9
4×10^5	20	1·45	7·3
9×10^5	50	1·54	7·9
3×10^5	20	1·93	10·6
7×10^5	50	1·98	10·9
10^6	100	2·59	16·5.
6×10^6	50	2·48	19·0
5×10^5	50	2·48	19·4
10^5	10	2·93	20·0

$G = 682$ ohms.
$E = 2·03$ volts



$$i_g = \frac{E}{R} \cdot \frac{S}{S+G}$$

Fig III

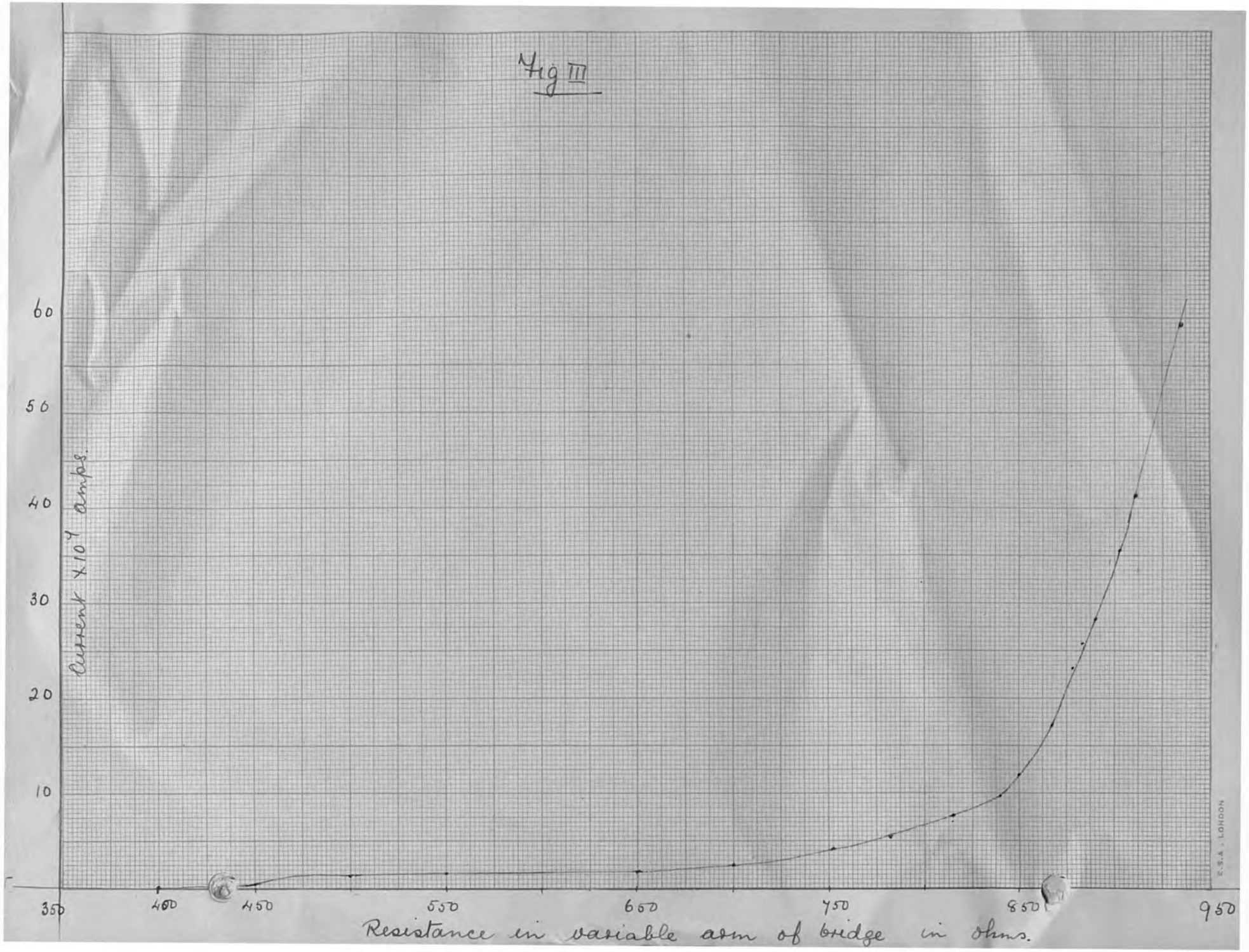

60
50
40
30
20
10
Current x10⁻⁴ amps.
350
400
450
550
650
750
850
950
Resistance in variable arm of bridge in ohms.
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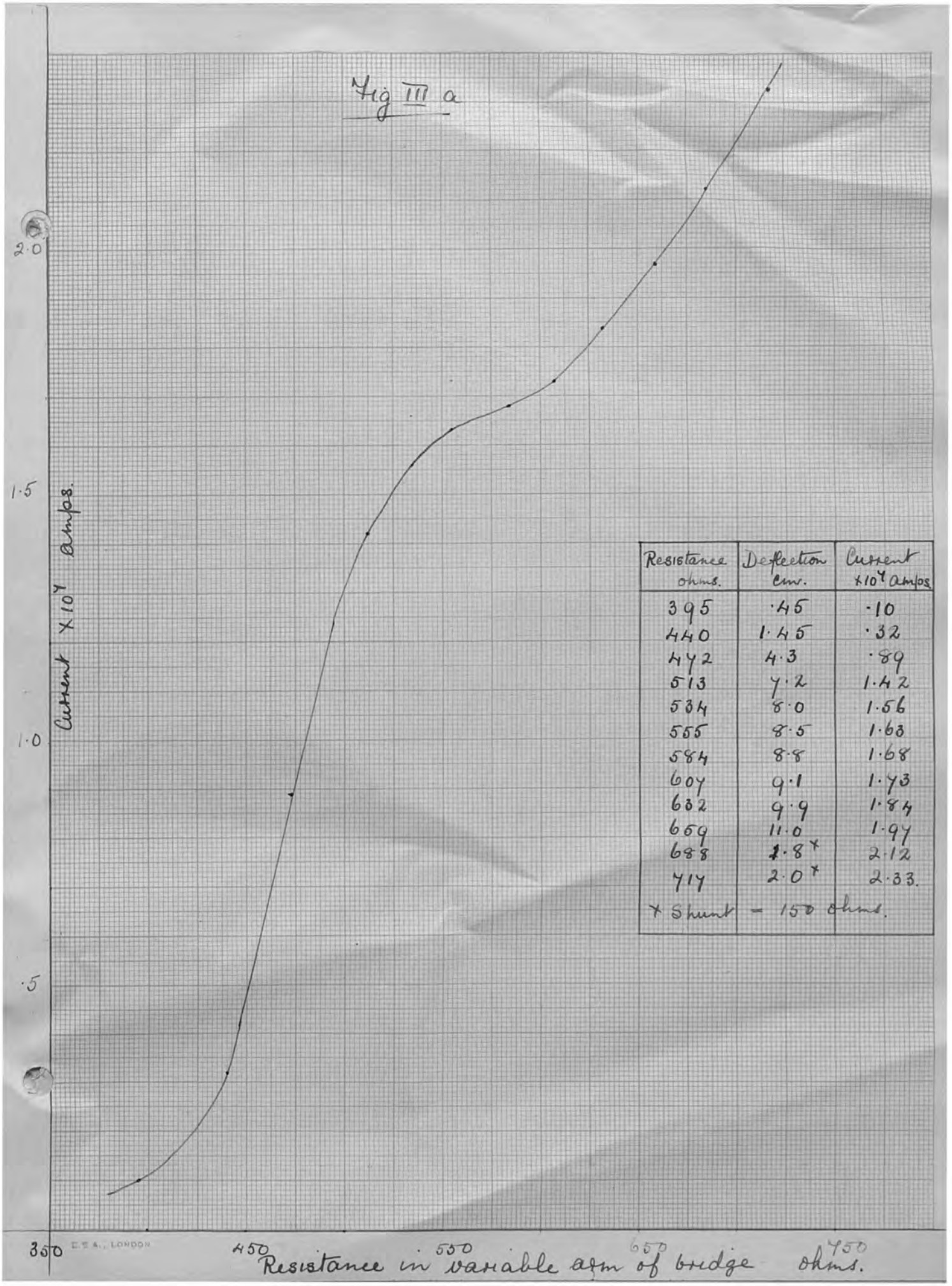
Fig III a

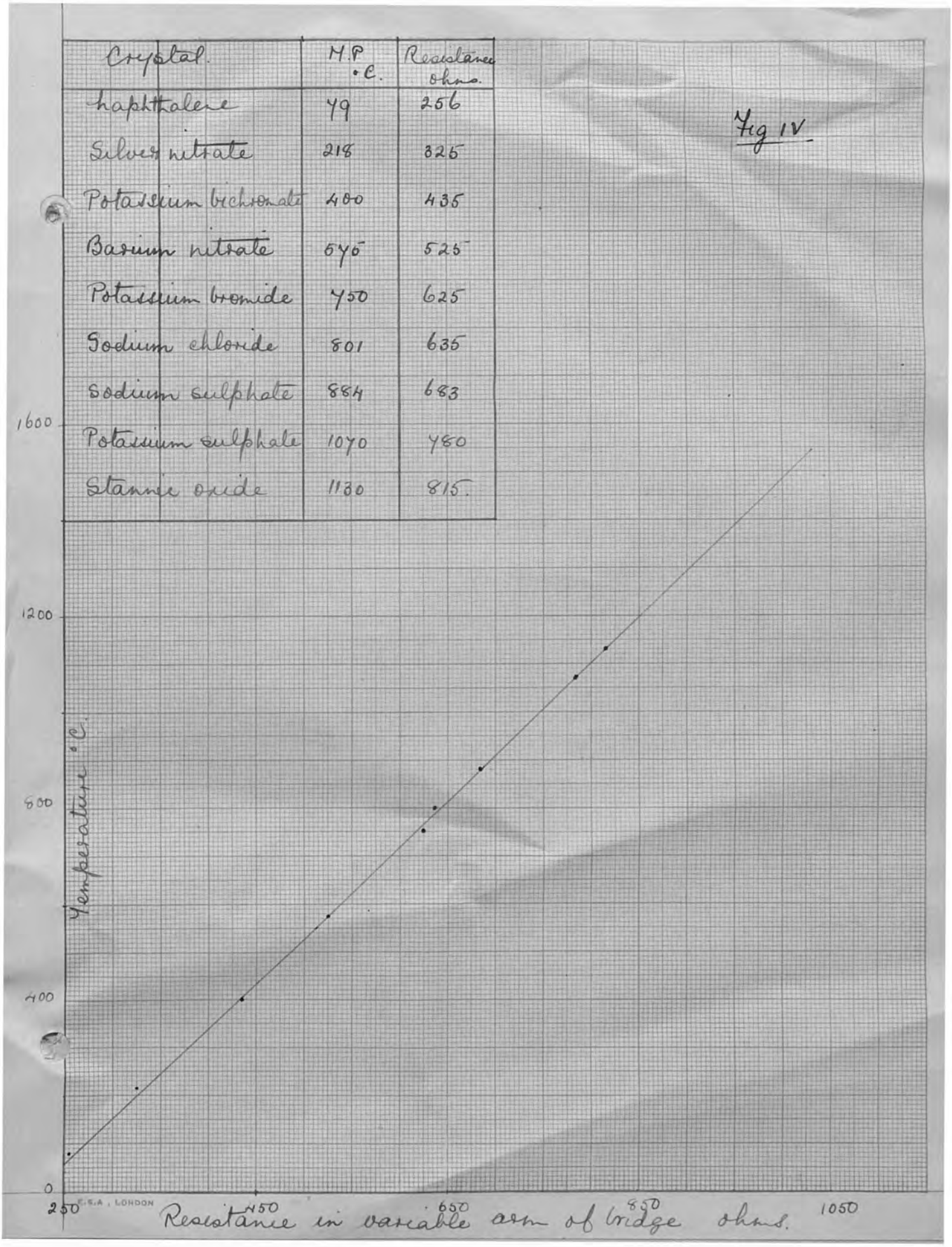


Resistance ohms.	Deflection cm.	Current $\times 10^4$ amps
395	·45	·10
440	1·45	·32
442	4·3	·89
513	7·2	1·42
534	8·0	1·56
555	8·5	1·63
584	8·8	1·68
604	9·1	1·73
632	9·9	1·84
659	11·0	1·94
688	1·8 *	2·12
714	2·0 *	2·33.

* Shunt = 150 ohms.

Crystal.	M.P. °C.	Resistance ohms.
Naphthalene	79	256
Silver nitrate	218	325
Potassium bichromate	400	435
Barium nitrate	570	525
Potassium bromide	750	625
Sodium chloride	801	635
Sodium sulphate	884	683
Potassium sulphate	1070	780
Stannic oxide	1130	815.

Fig IV



figures 3 and 3a.

In order to ensure the best possible conditions the potassium was then melted off the walls of the bulb, and a completely fresh film deposited. As soon as this film was sufficiently thick the charcoal tube was immersed in liquid air. A set of deflection — resistance readings was taken about half an hour after the mirror had been deposited and another set taken after the lapse of two and a half hours. Neither at this time nor next morning was any fatigue noticed, in fact as will be mentioned later, the current over a certain range increased with time. The curves obtained with this fresh film agreed with those previously obtained.

Hysterisis effects were considerable. Readings were taken when the filament current was gradually increased, but if taken in the reverse order the difference between corresponding current readings was so great, that for the lowest temperatures used, the descending reading would be as much as twice the ascending reading. The effect disappeared quite rapidly with time, in the case of the high temperatures, so rapidly as to be imperceptible. Though the decay at lower temperatures was slower, the original ascending reading would be reached by leaving the apparatus for ten minutes. The descending readings are inconsistent depending as they do on the time that elapses between altering the filament current and taking the readings of the current and filament resistance. The effect did not appear to be dependant on the degree of evacuation of the bulb.

The relation between filament resistance and temperature was found by opening the bulb and withdrawing the filament and grid and then finding the resistances of the filament at the melting points of certain crystals. The bridge arrangement was exactly the same as when taking readings of the photo-electric current, and minute crystals of substances having well defined melting points were placed on the filament at its hottest part. The current passing through the

Resistance ohms	Deflection ohms	Shunt ohms	Temperature °C	$\frac{1}{T} \times 10^4$	Current $\times 10^3$ amps	$\log \frac{C}{T^2} + 13$	$\log \frac{C}{T^2} + 10$
400	.50		340	16.3	.12	.504	.685
425	1.05		380	15.3	.23	.732	.954
437	1.60		405	14.8	.35	.882	1.129
450	2.35		425	14.3	.49	1.002	1.268
462	3.35		445	13.9	.70	1.133	1.417
475	4.40		470	13.5	.90	1.202	1.519
487	5.30		485	13.2	1.08	1.274	1.594
500	6.75		505	12.9	1.35	1.348	1.685
525	7.60		553	12.1	1.50	1.340	1.717
550	8.25		605	11.4	1.60	1.317	1.732
575	8.60		657	10.8	1.65	1.281	1.733
600	9.25		712	10.2	1.75	1.256	1.756
625	9.65		777	9.25	1.80	1.213	1.745
650	10.40		830	9.09	1.90	1.194	1.738
675	1.75	150	890	8.62	2.05	1.181	1.779
700	1.95		920	8.40	2.25	1.199	1.814
717	2.00		945	8.19	2 33	1.196	1.825
755	3.60		1005	7.80	4.16	1.406	2.066
782	4.60		1070	7.46	5.21	1.461	2.133
815	6.60		1135	7.09	7.32	1.568	2.290
839	9.40		1180	6.89	9.82	1.674	2.413
850	5.20	50	1200	6.80	12.00	1.743	2.495
867	5.80		1230	6.66	17.13	1.880	2.645
876	8.20		1248	6.58	23.28	2.003	2.776
883	10.4		1260	6.55	25.72	2.019	2.817
890	10.8		1275	6.53	28.65	2.078	2.862
903	16.6		1302	6.39	35.33	2.154	2.950
911	5.80	20	1308	6.33	41.10	2.216	3.014
935	8.85	20	1360	6.15	59.30	2.347	3.167
After lapse of three days							
542	9.3		600	11.5	1.75	1.361	1.773
579	1.9	150	675	10.6	2.22	1.393	1.858
607	2.1		725	I0.0	2.44	1.389	1.888

649	2.3	150	810	9.25	2.79	1.376	1.920
654	2.5		820	9.17	2.88	1.382	1.900
706	2.8		915	8.41	3.33	1.393	1.885
715	3.1		935	8.27	3.60	1.392	2.015
751	3.9		1000	7.87	4.44	1.438	2.095

RESULTS

$$C = A_1 T^{\frac{1}{2}} e^{-\frac{b_1}{T}}$$

$$\log_e C = \log_e A - \tfrac{1}{2}\log_e T - \frac{b_1}{T}$$

$$\text{or} \quad \log_e \frac{C}{T^{\frac{1}{2}}} = \log_e A_1 - \frac{\varphi}{kT}$$

$$\text{Hence } \varphi = \frac{\text{slope} \times 10^{4}}{\log_{10} e} \times 1.37 \times 10^{-16} \text{ ergs}$$

Since $k = 1.37 \times 10^{-16}$ ergs/°C

$$\text{Then } \lambda_c = \frac{3 \times 10^{10}}{\nu_c} = \frac{3 \times 10^{10} \times h}{\varphi}$$

where h = Planck's constant = 6.547×10^{-27} ergs sec.

$$\text{Also } \log_{10} A = \log_{10} \frac{C}{T^{\frac{1}{2}}} + \frac{b_1}{T} \log_{10} e$$

Hence having determined the values of b_1 and b_2 the constants A_1 and A_2 may be calculated, taking points on the graph within the ranges, where first one and then another work function predominates.

To determine A_1

T = 1308°C
C = 41.10×10^{-7} amps.

To determine A_2

T = 1135°C
C = 7.32×10^{-7} amps.

To determine A_3

T = 405°C
C = $.35 \times 10^{-7}$ amps

PORTION OF CURVE	AA_1	A_1B	CD
SLOPE	.875	.62	.30
$b \times 10^{-4}$ °C	2.01	1.43	6.91×10^{-1}
$\varphi \times 10^{12}$ ergs	2.76	1.96	9.46×10^{-1}
λ_c A.U.	7,120	10,000	20,800
Multiplying constant	.038	4.59×10^{-4}	3.58×10^{-5}

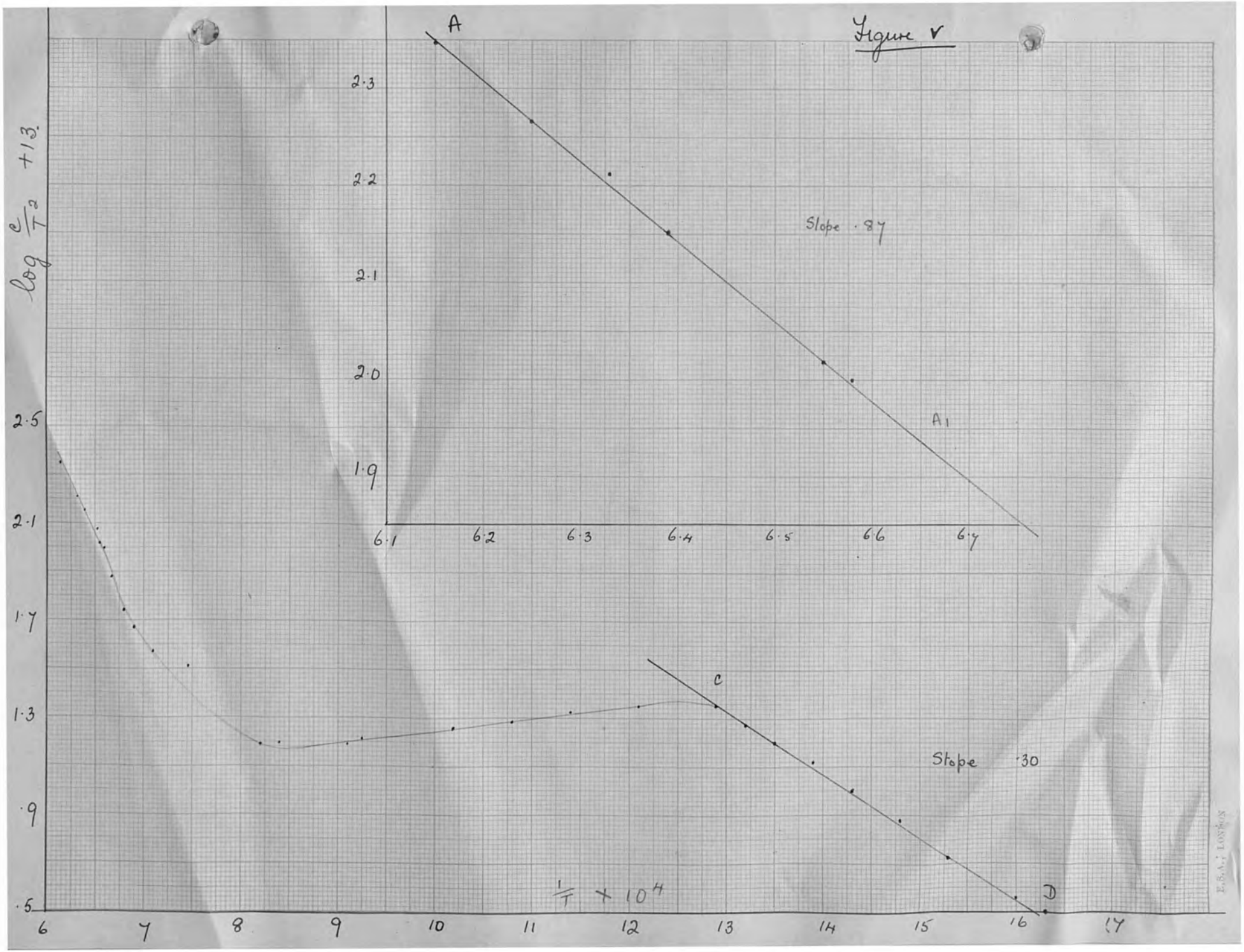


Figure V
A
A1
C
D
Slope .84
Slope .30
log e/T² + 13.
1/T × 10⁴
2·3
2·2
2·1
2·0
1·9
2·5
2·1
1·7
1·3
·9
·5
6·1
6·2
6·3
6·4
6·5
6·6
6·7
6
7
8
9
10
11
12
13
14
15
16
17

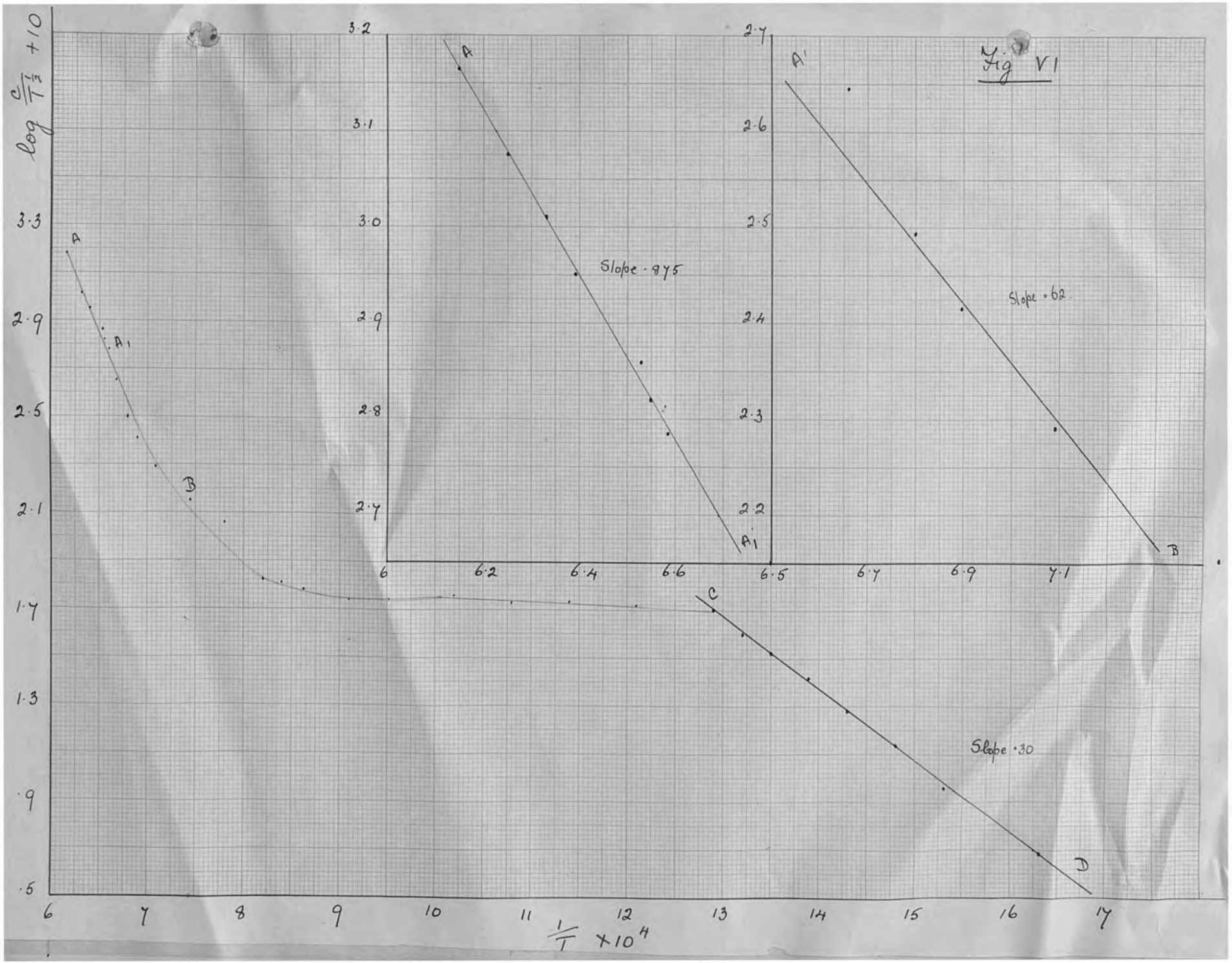


Fig VI
log C/T^3/2 + 10
1/T ×10^4
A
A1
B
C
D
A'
B'
Slope · 875
Slope · 62
Slope · 30

filament was gradually increased, the Wheatstone balance being readjusted continually until the crystal, which was viewed through a microscope melted. The graph obtained by plotting the melting point against the resistance in the variable arm of the box was a straight line (Figure 4)

Having determined the temperatures and corresponding currents graphs were plotted between $\log C/T^2$ and $1/T$ and also between $\log C/T^{\frac{1}{2}}$ and $1/T$ (Figures 5 and 6). In both cases nearly all the points lie on three straight lines, and the slopes of the portions AA_1, , A_1B and CD are the same in both graphs. The intermediate portion BC, however, is rather different. When taking $\log C/T^2$ we have a line BC sloping downwards from fortunes right to left, while in the other case the central line is very nearly horizontal, but has a slight downward slope from left to right. This central portion corresponds to the almost horizontal part of the current - temperature curve in Figure 3 and this does not appear to be very stable. The currents in this region gradually increased with time , not becoming absolutely constant until about three days after the potassium mirror had been deposited. Using readings obtained after this lapse of time the general characteristics of this central part of the logarithmic curves are unaltered but the slopes are slightly different. The slope of the part BC of both $\log C/T^2$ against $1/T$ and $\log C/T^{\frac{1}{2}}$ against $1/T$ is very small compared with the slopes of the lines AA_1 and CD i.e. .013 as compared with .675 and .30 .

The results obtained show that potassium has at least two, possibly three work functions, corresponding to critical wave lengths at 7,100 A.U. , a more doubtful one at 10.000 A.U. and one at 21,000 A.U. and so the relation governing the photo-electric current can be approximately represented by

$$C = A_1 T^n e^{-\frac{b_1}{T}} + A_2 T^n e^{-\frac{b_2}{T}} + A_3 T^n e^{-\frac{b_3}{T}}$$

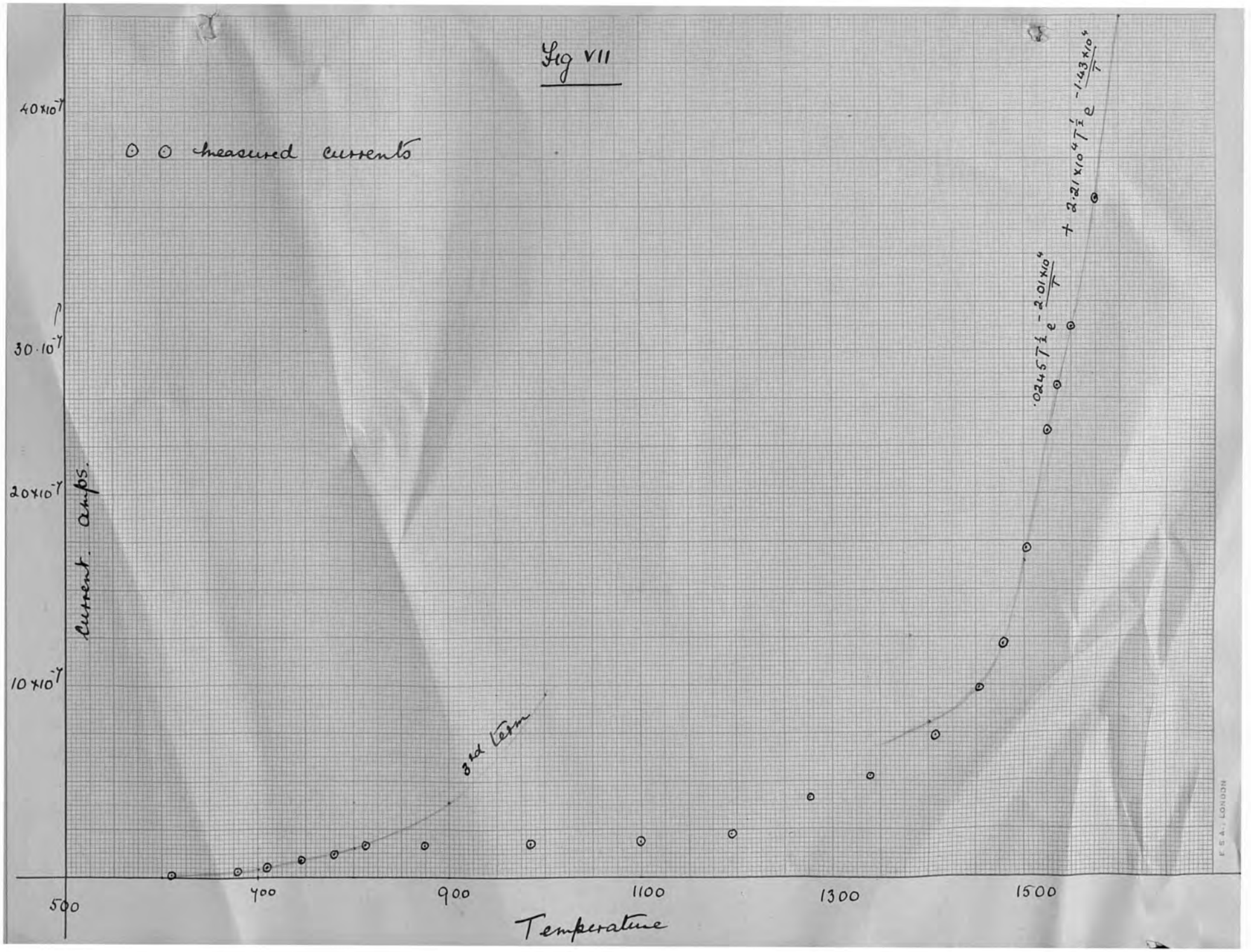


Fig VII
⊙ ⊙ measured currents
40×10⁻⁷
30·10⁻⁷
20×10⁻⁷
10×10⁻⁷
Current. amps.
3rd term
·0245 T^½ e^(-2·01×10⁴/T)
+ 2·21×10⁴ T^½ e^(-1·43×10⁴/T)
500
900
1100
1300
1500
Temperature
F.S.A. LONDON

or putting inthe numerical values

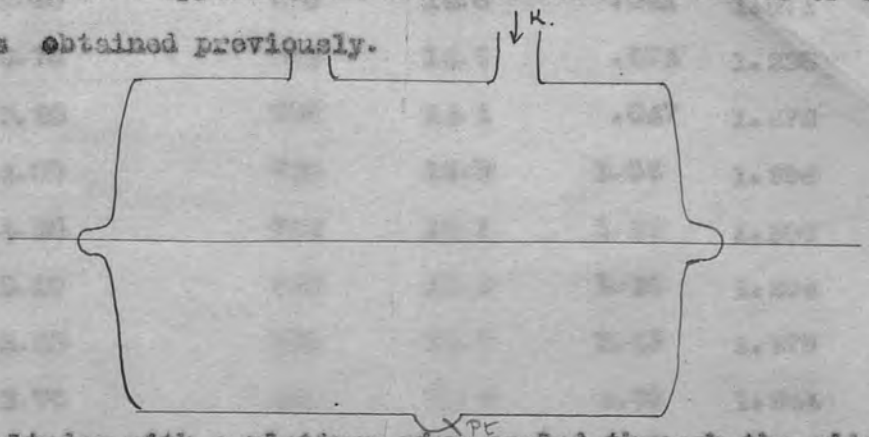
$$C = \cdot 038\, T^{\frac{1}{2}} e^{\frac{-2.01\times10^{4}}{T}} + 4.59\times10^{-4}\, T^{\frac{1}{2}} e^{\frac{-1.43\times10^{4}}{T}} + 3.58\times10^{-5}\, T^{\frac{1}{2}} e^{\frac{-6.91\times10^{3}}{T}}$$

at low temperatures, where the first terms are negligible compared with the third. At higher temperatures the first term alone is necessary and indeed the third term gives currents of a greater order of magnitude than those measured. Consequently it seems as though the low work function must cease to exist, in the neighbourhood of the flat part of the logarithmic curves. The presence of the work function at 10.000A.U. and thus of the second term seems rather doubtful, but it may exist since the part BAA of the logarithmic curves can also be represented by the sum of the first two terms , if the multiplying constants A and A are altered in a suitable manner. In Figure VII are plotted the curves obtained by calculating values of the third term and then of the sumof the first two terms with the new constants for a few temperatures, showing also the measured current values. These curves show that the third term cannot be included when calculating the currents at higher temperatures and that the flat part of the current – temperature curves lies between the two calculated curves .

The constant A_3, multiplying the term with the largest work function is 1.1 x 10 times as great as A_8, The above results support the theory of multiple work functions put forward by Richardson and Young (Pro.Roy.Soc. A 1925) . Evidently the area associated with the greatest work function is very many times the area associated with the smaller work functions. The hysteresis effects noted in these experiments and in those of Richardson and Young may be due either to small variations of one or more work functions or to the variation of the areas associated with the work functions, especially while the lowest value of ϕ is disappearing.

Further Experiments on the Threshold Frequencies of Potassium

It was felt to be a little doubtful if the radiation from the filament at the low temperatures ~~was~~ approximated to really black body radiation. Consequently the experiments described above, were repeated with slightly different apparatus in order to test the values of the work functionss obtained previously.



A glass cylinder with a platinum wire sealed through the side and two side tubes was covered on the inside with a thick film of silver, formed by reducing a solution of silver nitrate. The inner surface of the silver was found to be bright after being rinsed out with water several times. The ends of the cylinder had been drawn down to narrow tubes and through these the axial platinum filament was sealed after the silvering of the cylinder, so that the filament and the silver film were not in contact. As before the potassium was run into a side tube so as not to touch the silver film and the tube sealed off from the pumps.

The film was connected to one terminal of the galvanometer G_1 as in diagram 3. No deflection of the galvanometer occurred with the maximum filament current, when the silver film was negative with respect to the filament, so no emission of positive ions from the filament could be detected with the apparatus used. The potassium was then run down into the tube and heated to deposit it in a thin layer over the silver. Nor was any thermionic emission from the potassium detectable, since even with the largest filament currents, the galvanometer image returned immediately to zero on suddenly switching off the filament current.

As before the photo-electric current – filament resistance curve showed an initial rise, and the logarithmic curve (Figure 8) showed

Readings

Resistance ohms	Deflection cms.	Shunt ohms	Temperature abs.	$\frac{1}{T} \times 10^4$	Current $\times 10^4$ amps	$\log \frac{C}{T^2} + 13$	$\log \frac{C}{T^{\frac{1}{2}}} + 10$
2855	.55		603	16.5	.141	.589	.759
2969	.70		613	16.3	.168	.650	.831
3052	1.00		628	15.9	.243	.790	.987
3120	1.30		645	15.5	.321	.887	1.102
3243	2.20		676	14.8	.541	1.071	1.318
3270	2.70		683	14.6	.673	1.238	1.411
3387	3.35		708	14.1	.847	1.272	1.503
3505	4.00		738	13.5	1.02	1.296	1.575
3600	4.55		763	13.1	1.15	1.300	1.619
3800	5.20		823	12.2	1.35	1.294	1.673
4000	5.55		858	11.7	1.45	1.279	1.695
4115	5.70		888	11.3	1.50	1.244	1.702
4340	5.95		943	10.6	1.56	1.220	1.706
4585	6.30		1003	10.0	1.66	1.209	1.720
4920	7.20		1083	9.26	1.90	1.234	1.762
5080	8.15		1123	8.93	2.16	1.269	1.810
5255	9.52		1168	8.55	2.54	1.284	1.871
5415	2.55	200	1203	8.33	2.78	1.298	1.904
5680	2.95		1273	7.87	3.22	1.369	1.956
5820	3.55		1303	7.69	3.97	1.411	2.041
5914	4.05		1328	7.53	4.54	1.410	2.095
5978	4.60		1348	7.46	4.63	1.410	2.102
6015	5.50		1353	7.40	6.21	1.529	2.169
6090	5.65		1373	7.30	6.37	1.529	2.235
6125	6.00		1378	7.25	6.86	1.558	2.267
6220	7.80		1408	7.09	9.08	1.661	2.374
6290	8.10		1423	7.04	9.37	1.665	2.395
6340	11.25		1433	6.98	13.23	1.809	2.543

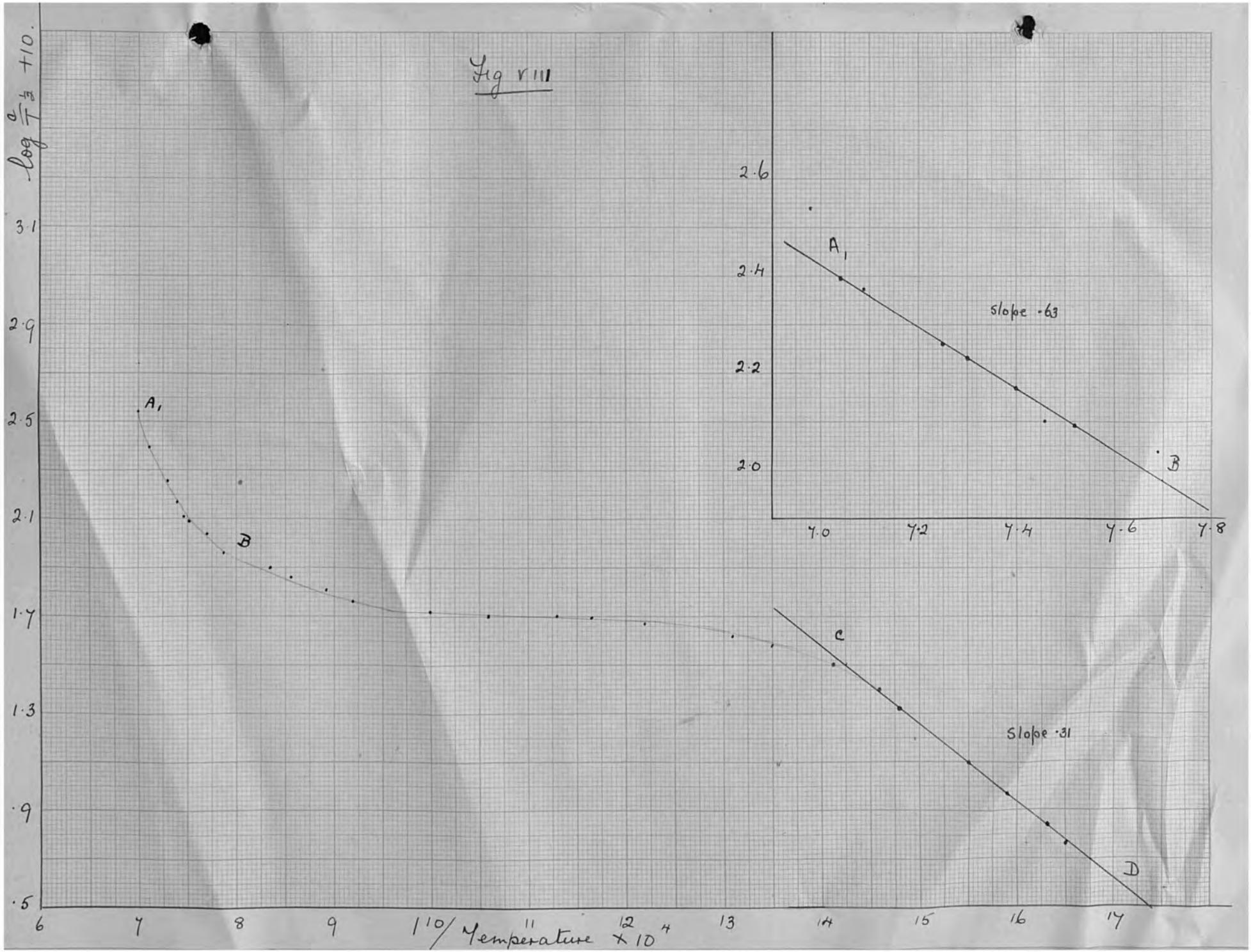


Fig VIII
log a/T^½ +10.
3·1
2·9
2·5
2·1
1·7
1·3
·9
·5
A,
B
C
D
6
7
8
9
11
12
13
14
15
16
17
1/0 Temperature X 10^4
2·6
2·4
2·2
2·0
A,
Slope ·63
B
7·0
7·2
7·4
7·6
7·8
Slope ·31

precisely the same features as those of Figures 5 and 6. The highest temperature used was 1200 C as compared with 1400 C in the earlier experiments and on referring to the earlier curves it is seen that between these temperatures only does the greatest value of φ predominate. so the line of slope .87 is absent. The slopes of the lines AB and CD were found to be .63 and .31 which agree with the values found before. Also the flatter central part sets in and finishes at the same readings on the axes as it did in the previous curves. Again the central part BC is a little different when $\log C/T^2$ and when $\log C/T^{\frac{1}{2}}$ are used, although the slopes of the lines AB and CD are the same.

RESULTS

Portion of curve	AB	CD
Slope	.63	.31
$b \times 10^{-4}$ °C	1.44	.71
$\varphi \times 10^{12}$ ergs	1.99	.98
λ_c A.U.	9,890	20,100
Multiplying constant	5.9×10^{-4}	8.1×10^{-5}

As before the measured currents can be represented by the sum of the terms at low temperatures, while the lowest work function must vanish at higher temperatures.

Summary

No evidence has been found for the existence of a positive photo-electric emission and it has been shown that if such an effect does exist it is less than 10^{-7} times the negative emission, from the same surface measured in these experiments. It is shown that potassium has at least three work functions corresponding to the wave lengths 7,100 A.U. 10,000 A.U. and 21,000 A.U. The results indicate that the 'patches' of lower work function form a very small part of the whole surface.