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VIII. *On the Origin of the Electron Emission from Glowing Solids.*

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Recent researches on the negative ionisation from glowing solids have thrown doubt upon the accuracy of the view of the origin of this ionisation which has been developed by O. W. Richardson.* This view is based upon the electron theory of metallic conduction, and supposes that an electron entering the surface layer with a normal velocity component greater than a certain amount is able to escape into the surrounding space and to take part in carrying the thermionic current. On this view, as Richardson has shown, the electron emission increases rapidly with the temperature, the connection between these quantities being given by an exponential formula, $i = A\theta^{\frac{1}{2}}\epsilon^{-\frac{Q}{2\theta}}$, where i is the thermionic current, θ the absolute temperature, and A and Q are constants. That this formula represents, with fair accuracy, the observed results in the case of platinum and of certain other substances for temperatures up to about 1500° C. has been shown by the experiments of Richardson,* by H. A. Wilson,† by the author,‡ and by other experimenters. Experiments made at higher temperatures, however, have generally shown that the current increases less rapidly with the temperature than is required by this formula. Even if in all cases the temperature variation of the thermionic current were in agreement with the above formula, this could not be taken as a proof of the theory of the origin of the effect, for it has been shown by H. A. Wilson that the current measured at any temperature depends very largely upon the nature of the residual gas present in the apparatus.§ This has led to the view that the ionisation is entirely due to chemical action between these gases and the heated solid—a view which is also in agreement with the exponential relation between the current and the temperature, for such chemical changes as might occur would probably increase with the temperature in this manner.

* O. W. Richardson, 'Phil. Trans.,' A, vol. 201, p. 297, 1903.
† H. A. Wilson, 'Phil. Trans.,' A, vol. 202, p. 243, 1903.
‡ F. Horton, 'Phil. Trans.,' A, vol. 207, p. 149, 1907.
§ *Loc. cit.*

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This chemical action theory has received considerable support from the experiments of HABER and JUST,* and of FREDENHAGEN† on the alkali metals, and of PRING and PARKER‡ on carbon. The experiments with the alkali metals have shown that by repeated purification (re-distillation) and continued improvement of the vacuum the electron emission from these substances can be continually reduced. If, however, a small amount of air or of any gas having chemical action upon the metal under test is allowed to enter the apparatus a large increase in the thermionic current at once occurs.

Similarly with carbon, the negative thermionic current decreases continuously as the gas pressure is reduced and with progressive purification of the carbon, and, moreover, by admitting small amounts of different gases to the carbon an increased current is obtained, the increase being proportional to the known chemical activity of these gases.

RICHARDSON§ has recently described some experiments with a tungsten filament heated to a high temperature in a good vacuum, and has considered the following different hypotheses as to the possible mode of origin of the electronic emission :—

(1) The emission is due to the evolution of gas by the filament;

(2) The emission is caused by chemical action or by some other cause depending on impacts between gas molecules and the filament;

(3) The emission is the result of some process involving consumption of tungsten.

Experiments were devised for the purpose of testing each of these theories, and in each case it was found that the observed emission was very much greater than could be accounted for by the hypothesis. It was, therefore, concluded "that the emission of electrons does not arise from any interaction between the filament and the surrounding gases or vapours, nor from any process involving consumption of the material of the filament. It thus follows that the emission of electrons from hot tungsten, which there is no reason for not regarding as exhibiting this phenomenon in a typical form, is not a chemical but a physical process." These experiments cannot be regarded as conclusive, for there is a possible cause of the electron emission which has not been considered, namely, that it arises from an action between the metal filament and gases contained in it. In testing the second hypothesis mentioned above, RICHARDSON considers only the possibility of chemical action between the metal filament and the gas surrounding it. The fact that the thermionic emission from a hot wire in a good vacuum decreases on driving out the gas by long continued

* HABER and JUST, 'Ann. der Phys.,' vol. XXX., p. 411, 1909, and vol. XXXVI., p. 308. 1911.

† FREDENHAGEN, 'Verh. d. Deutsch. Phys. Ges.,' vol. 14, p. 384, 1912.

‡ PRING and PARKER, 'Phil. Mag.,' vol. 23, p. 192, 1912, and PRING, 'Roy. Soc. Proc.,' **A**, vol. 89, p. 344, 1913.

§ RICHARDSON, 'Phil. Mag.,' vol. 26, p. 345, 1913.

heating is evidence that the emission depends either upon the evolution of gas, or upon the gas remaining in the hot wire. RICHARDSON'S experiments to test the former hypothesis may be taken as showing that the emission does not depend upon the evolution of gas, but there remains the possibility that it depends upon the gas which is still in the wire. This latter view was put forward by H. A. WILSON* to explain the results of some experiments with a platinum wire heated in hydrogen gas. A series of observations were made at different pressures and it was found that on changing the gas pressure the resulting change in the thermionic current took some time to become established. A similar effect was obtained when the temperature of the wire was altered, keeping the gas pressure constant, in which case the current variation lagged behind the alteration of temperature. These experiments indicate that the increase in the thermionic emission produced by hydrogen is due to the gas inside the platinum, and that it takes time for equilibrium between the gas in the wire and that surrounding it to become established after any change in the conditions has been made.

It appeared probable that information as to the origin of the electron emission from glowing solids could be obtained by experimenting with those substances which give rise to exceptionally large emissions, namely, the oxides of the alkaline earth metals. These oxides are all stable substances and ones which would not be expected readily to enter into reaction with the residual gases left in the apparatus. The possibility of chemical action in these cases would appear to depend on the oxide being electrolysed by the passage of the discharge, in which case there might be some re-combination of the constituents. The view that the electron emission from glowing lime occurs as a result of the re-combination of calcium and oxygen which have been liberated electrolytically has been put forward by FREDENHAGEN.† The author does not think that there is very strong experimental evidence that such chemical changes do give rise to the emission of electrons, but this point will be referred to later. If, for the present, we admit the possibility of the chemical union of calcium and oxygen giving rise to an emission such as is observed in the case of the Wehnelt cathode, the plausibility of FREDENHAGEN'S theory depends upon whether the conductivity of these oxides can be shown to be accompanied by electrolysis.

In 1905 the writer investigated the electric conductivity of lime at high temperatures and came to the conclusion that the conductivity is mainly carried on by electrons set free in the interior of the oxide, but that some electrolysis also occurs. Thus there is the necessary condition for the hypothesis as to the origin of the activity of a lime cathode put forward by FREDENHAGEN. The following experimental results are given by FREDENHAGEN as supporting this hypothesis:—

* H. A. WILSON, 'Phil. Trans.,' A, vol. 202, p. 243, 1903.

† K. FREDENHAGEN, 'Ber. K. Sächs. Ges. Wiss.,' Leipzig, vol. 65, p. 42, 1913.

(1) The emission from calcium is increased when traces of oxygen are present;

(2) After much use a Wehnelt cathode becomes "exhausted." The oxide gradually disappears and the metallic surface of the supporting strip is perceptibly altered, probably owing to the action of the liberated calcium or oxygen;

(3) When lime is heated so that no current goes through it there is no large emission of electrons.

The only one of these which appears to the writer to be conclusive is the last. The first result follows from the fact that the emission from lime is much greater than that from calcium,* and it is not necessary to attribute the emission to the process of oxidation. The second result supports the view that electrolysis takes place, but does not support the theory further than that; but from the third result it appears that electrolysis is essential in order to obtain a large electronic emission from lime.

The experiments described in the present paper were performed to test the "chemical action" theory of the working of an oxide cathode. FREDENHAGEN experimented with a mixture of lime and magnesia which is a better conductor than lime alone. The experiments about to be described were made with Nernst filaments which consist of a mixture of oxides having a much larger conductivity than the mixture used by FREDENHAGEN. It has been found by OWEN† that these filaments give a large electron emission at high temperatures. The following points have been investigated:—

(1) Does the electron emission from a Nernst filament depend upon whether the heating current is alternating or continuous? One would expect that, if the conduction through these filaments is electrolytic, the re-combination of the constituents would be more complete with an alternating current than when a continuous current is employed; so that, if the electron emission depends upon this re-combination, the thermionic current at a given temperature should be greater in the former case.

(2) Is the emission from a Nernst filament the same when it is heated by conducting an electric current and when it is heated by a metal wire passing through it, the wire being raised to incandescence by an electric current? In the latter case practically the whole of the heating current is carried by the metal wire, and any electrolysis which occurs is due to the thermionic current; so that re-combination must be very much less under these circumstances than when the filament itself conducts the heating current.

* F. HORTON, 'Phil. Trans.,' A, vol. 207, p. 149, 1907.

† G. OWEN, 'Phil. Mag.,' vol. 8, p. 230, 1904.

(3) The emission from a Nernst filament heated in the ordinary manner has been compared with that given by the same material when powdered and heated upon platinum. This experiment is similar to that just mentioned.

The discharge tube used in these experiments is similar to that described in a former paper,* the only difference being that in the present apparatus the two parallel platinum plates which form the anode are 1·5 cm. apart. The cathode, when in position, is parallel to these plates and mid-way between them. It can easily be removed from, or replaced in, the discharge tube. Experiments were made with twenty different Nernst filaments of the B type and meant for use on a 100-volt alternating supply. They were all of about the same dimensions, the length of the glowing portion being about 9·5 mm. and the diameter about 0·78 mm. When a filament was to be heated by passing an electric current through it, the platinum wires attached to it were welded on to the platinum leads of the discharge tube. When an alternating current was used, this was obtained from the secondary of a transformer, the primary coil of which was connected to the alternating town supply, and the current through the filament could be varied by changing the resistance in both the primary and the secondary circuits. One of the fine iron wire resistances supplied with Nernst lamps was always kept in series with the filament. As this resistance has a large positive temperature coefficient, it tends to steady the current through the circuit. In order to start the filament glowing it had to be taken from the discharge tube and heated by holding it above, and near to, a glowing "heater" of the kind supplied with an ordinary Nernst lamp. It was then replaced in the apparatus which could be rapidly exhausted, when required, by means of a water-pump, a mercury pump, and a charcoal tube cooled in liquid air. In this way the gas pressure in the apparatus could be reduced to ·0001 mm. within twenty minutes from the time that the filament was started glowing.

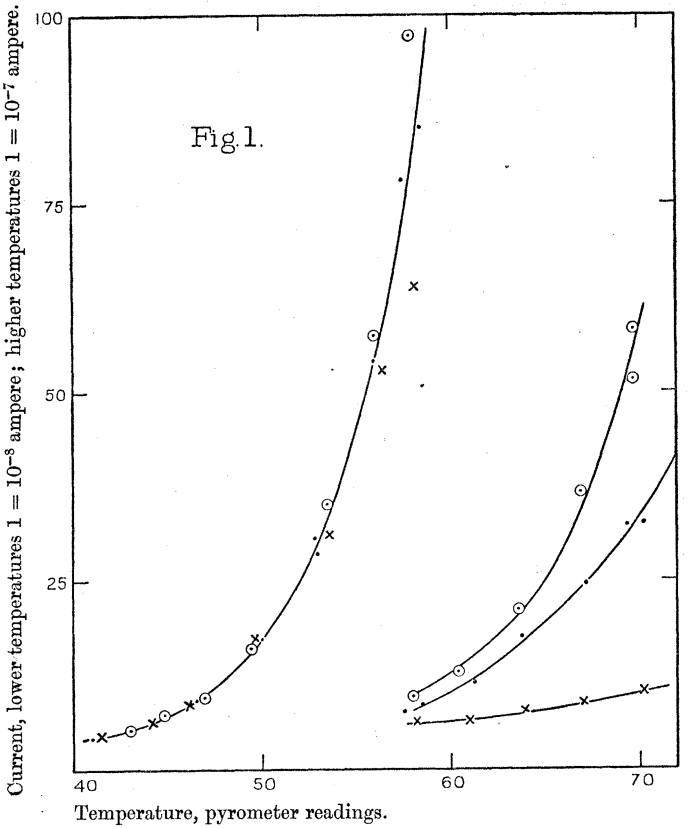
The temperature of the glowing filament was determined by means of a Féry optical pyrometer for the use of which I am indebted to Prof. T. Mather, of the City and Guilds College, London. This instrument was standardised by observations of the readings corresponding to different temperatures of a platinum tube of about the same diameter as a Nernst filament and having a standardised thermocouple of fine wires of platinum and platinum-rhodium welded to it. In order that the surface of the platinum tube should be exactly similar to that of the filament, a filament was finely powdered and mixed with water, and the platinum tube was then covered with a thin layer of Nernst filament material by evaporating this mixture upon it. This platinum tube was fitted up in the place of the filament in the discharge tube, and observations of the thermo-electromotive force and readings of the optical pyrometer were taken at several temperatures between 900° C. and 1600° C. From these observations, the temperature of a Nernst filament corresponding to any reading of the pyrometer between these limits can be ascertained with fair accuracy.

* 'Roy. Soc. Proc.,' A, vol. 88, p. 117, 1913.

I. *A Comparison of the Electronic Emissions from a Nernst Filament when Heated by Continuous and by Alternating Currents.*

It was originally intended to perform this experiment with the filament in a vacuum, but it was soon found that, although with an alternating current the filament continued to glow steadily in a vacuum, when a continuous current was used one end of the filament became much hotter than the other end. At the same time the gas pressure in the apparatus increased, so that evidently some electrolysis of the material of the filament was proceeding. It was always the positive end of the filament which became the hotter, probably because some metallic constituent of the filament is set free by electrolysis at the negative end and lessens the resistance in that part of the circuit. In order to maintain the whole of the glowing portion of the filament at a uniform temperature when a continuous heating current was used, it was found to be necessary to have oxygen present in the discharge tube. This no doubt oxidises the metal liberated by electrolysis and so maintains the uniformity of the filament. The comparison was therefore performed with air in the apparatus at atmospheric pressure, and the observations were taken in the following manner:— The leads to the filament were connected to a switch so that either an alternating current from the transformer or a continuous current from a battery of storage cells could be used. In addition to the adjustable resistances in the transformer circuit there was another set of adjustable resistances in the battery circuit, so that the E.M.F. applied from the storage cells could be made equal to that being supplied at any instant by the transformer before switching the filament on to the continuous current circuit. In this way observations at about the same temperature could be made alternately, with the filament connected to the transformer or to the storage cells. A filament was first of all heated on the alternating circuit and a series of observations of the negative thermionic current at different temperatures was taken, the potential difference applied across the discharge tube, in addition to that due to the heating circuit, being 210 volts. The negative emission at atmospheric pressure from a new Nernst filament generally increased during the first day's heating, after which it remained fairly constant. When the steady state had been reached a comparison of the emissions from the filament heated on the "alternating" circuit and on the "continuous" circuit was made. The temperature of the filament was adjusted to be as low as practicable, and readings of the thermionic current and of the pyrometer were made; the filament leads were then switched on to the continuous current circuit, and the pyrometer and galvanometer readings were again taken. The filament was immediately switched back on to the alternating circuit, so that it never remained for more than a minute or two with a continuous current flowing through it. The direction in which the continuous current was to flow through the filament was then reversed by means of a reversing key connected with the storage cells, and the observations of the emission and temperature, with alterna-

ting and with continuous current heating, were repeated. The temperature of the filament was then raised by lessening the resistance in the transformer circuit. A corresponding alteration was made in the battery circuit, and measurements of the thermionic emission and the temperature of the filament were made on both circuits. The observations were repeated at gradually increasing temperatures up to about 2050° C., after which the temperature was gradually lowered again, the measurements being repeated at frequent intervals. In this way three series of measurements of the thermionic current at different temperatures were obtained, with the filament heated (1) by an alternating current; (2) by a continuous current in one direction;



Points marked ● are for heating by alternating current.
Points marked ⊙ are for one direction of continuous current.
Points marked × are for reverse direction of continuous current.

(3) by a continuous current flowing in the opposite direction through the filament. The values of these thermionic currents were plotted against the corresponding temperatures, and it was found that for temperatures up to about 1750° C. the points all fell fairly well upon one curve, but that at temperatures much higher than this they separated out into three curves; the curve corresponding to the alternating heating current falling between the two curves corresponding to the different directions of the continuous current. A set of curves obtained with one of the filaments experimented on is given in fig. 1. In this the thermionic currents for the

higher temperatures are plotted to one-tenth the scale used for the lower temperatures. The temperatures are represented by the pyrometer readings, to which they are roughly proportional. I was unable to calibrate the pyrometer accurately in degrees centigrade up to the highest temperatures used in these experiments. The lowest temperature represented in the figure (pyrometer reading = 40) corresponds to 1637° C.; the highest temperature represented (pyrometer reading = 72) corresponds to about 2050° C.

The curious difference between the values of the thermionic current at a high temperature for the two directions of the continuous heating current arises from the potential difference of the heating circuit. There was a fall of potential of some 80 volts along the glowing portion of the filament, and a steady potential difference of 210 volts was maintained between one end of the filament and the anodes. The potential difference between the anodes and a point near the other end of the filament therefore changes considerably when the direction of the heating current is reversed. At the lower temperatures the current does not vary very rapidly with the potential difference when this is in the neighbourhood of 200 volts, but at the higher temperatures used in these experiments the current is far from being saturated with 200 volts, so that the total thermionic current will change considerably when the direction of the current in the heating circuit is reversed. If this explanation is correct we should expect that the difference between the emissions in the two cases would be much less if a considerably larger potential difference were maintained between the electrodes of the discharge tube. To test this, the potential difference was increased to 600 volts and the experiment was repeated. It was then found that even up to 2000° C. there was no marked difference in the value of the thermionic current when the direction of the continuous heating current was reversed. The experimental points for both alternating and direct current heating fell equally nearly to a single curve, showing that the electron emission from the filament under these conditions is the same whether an alternating or a direct heating current be used.

On the theory that the electron emission depends upon the re-combination of the electrolytically separated constituents of the oxides of which a Nernst filament is made, it would be expected that a larger emission would be obtained when an alternating heating current is employed, for then the re-combination is complete. The experiment just described would be more conclusive in disproving this theory if it could have been performed in the absence of oxygen, but, as already stated, the filament could not be made to continue uniformly hot with a direct heating current for long enough to enable accurate observations to be made. When the experiment was tried in a vacuum there was the further difficulty that the liberation of oxygen by the continuous current altered the gas pressure in the apparatus, and ionisation by collisions greatly increased the measured thermionic current. Experiments were also made at as low temperatures as possible in pure nitrogen gas at atmospheric

pressure so that this increase in pressure should be negligible, but the results only justify the statement that there was no great difference between the emissions when the filament was switched momentarily from the alternating circuit on to the continuous current circuit, the resistances in the two circuits having been adjusted so as to maintain the temperature of the filament as nearly constant as possible. Since the filament could not be left on the direct current circuit for more than a second or two at a time, the comparison was very difficult to make. For this reason the following experiments were devised.

II. *A Comparison of the Electronic Emissions from a Nernst Filament when heated by conducting an Electric Current and when heated without conducting the Heating Current.*

The ideal method of making this comparison would, at first sight, appear to be to heat the filament in a vacuum, firstly in the usual manner by means of an alternating current, and secondly by placing the discharge apparatus in some form of furnace. Such an experiment is, however, not practically possible, for a good vacuum cannot be maintained in a vessel at a high temperature; not only do the walls of the vessel evolve gases, but the material which would otherwise be most suitable for the experiment—quartz—becomes permeable to gases at about 1000° C.

A Nernst filament is in the form of a fine tube and the method of thermal heating adopted was by placing the filament upon a tantalum wire which just fitted it, and heating the wire by an alternating current from the transformer. Tantalum wires of the required diameter were prepared for me by Messrs. Siemens, and supplied in straight pieces about 5 cm. long. In performing the experiment the negative emission from a filament was investigated when the filament was heated by an alternating current in a vacuum obtained by the use of charcoal cooled in liquid air. The thermionic current as a rule decreased slightly during the first few hours heating of a new filament; after this it was fairly steady even when tested on different days. The filament was then disconnected from the platinum leads and its two ends were cut off, leaving the middle glowing portion only. This was mounted on a tantalum wire cut to such a length that about 3 mm. of wire protruded from each end of the filament. The ends of the tantalum wire were fitted inside two short pieces of platinum tube which had already been welded on to the platinum leads of the discharge tube. The platinum tubes were of about the same dimensions as the filament, and were pinched up tightly on to the tantalum, thus making good electrical contact. In this way none of the tantalum wire was exposed; the central part was covered by the filament and the ends were encased in the platinum tubes through which the heating current was conducted. These leads never became sufficiently hot to give a thermionic emission comparable with that given by the filament. After exhausting the apparatus, the tantalum wire was heated by an

alternating current and in this way the temperature of the filament was raised, and its electron emission was investigated at different temperatures. The thermionic currents were plotted against the corresponding temperatures and a curve was drawn through the points so obtained. Some readings from this curve are given in the following table which also contains, for comparison, the values of the thermionic current from the filament at the same temperatures when heated by an alternating current passing through it. In both cases the potential difference applied between the terminals of the discharge tube was 208 volts, and the pressure of the residual gas in the apparatus was 0·0002 mm.

Temperature, degrees Centigrade.	Thermionic currents : 1 = 10^{-7} ampere.	
	Filament heated by alternating current.	Filament heated on tantalum wire.
1754	585	480
1690	319	256
1637	163	146
1590	78	78·5
1546	35·2	42·8
1503	22·6	23·4
1466	8·6	9·7

An inspection of the above table shows that the electron emission is about the same whichever method of heating the filament be employed. The greatest difference is about 20 per cent., which is not large considering the experimental difficulties. From the table it appears that the emission from the filament when heated by conducting a current increases more rapidly with the temperature than it does when heated upon a tantalum wire. This was not always the case. Several filaments were tested and it was found that the emission was sometimes greater with one method of heating and sometimes with the other. The rate of increase with temperature of the thermionic emission from a Nernst filament heated by an alternating current in a vacuum depends very largely upon the previous heating of the filament. With filaments which had been heated for many hours at a high temperature it was generally found that the thermionic current above about 1500° C. increased with the temperature much less rapidly than with a new filament.

It is clear that in these experiments there must be very much more electrolytic decomposition of the Nernst filament, followed by re-combination of the constituents, when the filament is itself conducting the heating current, than when it is heated on the tantalum wire. In the latter case only a very small portion of the heating current flows through the filament, for the resistance of this, even at the highest temperature, is very large compared with that of the tantalum wire.

In comparing the electron emission in the two cases it is necessary to consider the

possible effect of the electron emission from the tantalum wire itself. If the electrons emitted by the wire escape through the Nernst filament they would take part in carrying the measured thermionic current. In order to see whether the current so carried is likely to be a considerable fraction of the whole, a piece of tantalum wire of the same dimensions as that used inside the filament was fitted in the apparatus, and the emission from this was measured at different temperatures. At the highest temperature recorded in the table the emission was only $9{\cdot}7 \times 10^{-7}$ amperes. It is, however, probable that in the experiment proper the wire was considerably hotter than the filament surrounding it, and there is therefore some doubt as to what part of the measured current may be due to the tantalum; but I think it can safely be stated that the emissions from the filament alone with the two methods of heating are of the same order of magnitude, and there is certainly no such difference as would be expected if the emission were caused by the re-combination of the electrolytically separated elements of which the filament is composed. In order to eliminate the uncertainty as to the effect of the heating wire the following experiment was made.

III. *A Comparison of the Electronic Emission from a Nernst Filament Heated in the Ordinary Manner with that given by the same Material when Heated upon Platinum.*

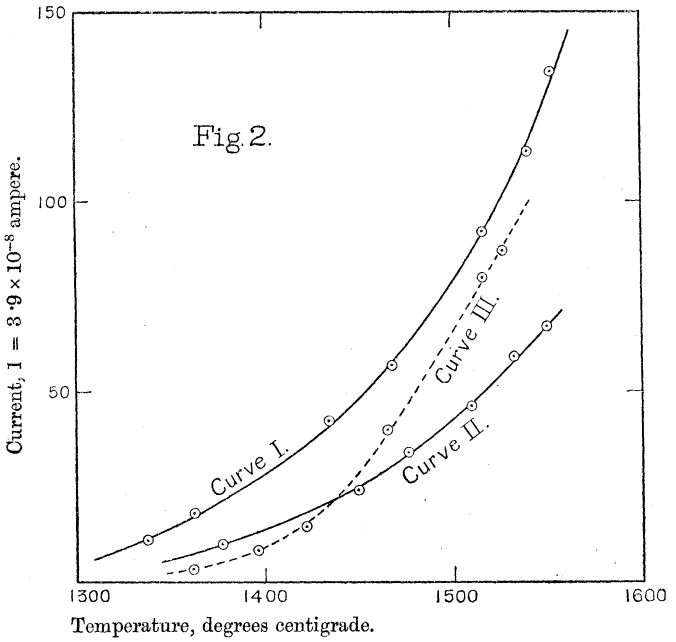
In making this comparison the emission from a filament at different temperatures when heated by an alternating current in a good vacuum was investigated as before. When the thermionic current tested under similar conditions on different days had become fairly constant, the filament was detached from the apparatus and a piece of fine platinum tube was substituted for it. The external diameter of the platinum tube was a little less than that of the filament, and the internal diameters of the two were the same. The length of the tube used was rather greater than that of the glowing part of the Nernst filament so as to make the surface areas about the same in the two cases. A thermocouple of fine wires of platinum and platinum-rhodium was carefully welded on to middle of the platinum tube. This junction was standardised in the usual manner and served to determine the temperature of the tube during the experiments. Observations of the negative emission from this platinum tube were then made under similar conditions to those employed with the Nernst filament, except that the temperature was determined by the thermocouple and not with the pyrometer. The emission from this platinum tube was rather larger than I had expected it would be, and much larger than that measured from the tantalum wire. It was therefore taken down and boiled in strong nitric acid and afterwards heated for some time in air at atmospheric pressure. This treatment reduced the emission considerably, but the thermionic current at 1516° C. was found to be 9×10^{-6} amperes per sq. cm. of heated surface, which is about 20 times the value to which the emission from a platinum wire can be reduced. However, this value of the current was fairly constant, and the values now obtained at different

temperatures were therefore taken as measuring the steady emission from the platinum.

The glowing portion of the filament, the emission from which had already been tested, was finely powdered in an agate mortar; a little water was added, and the particles in suspension were transferred to the platinum tube by evaporating this mixture upon it, a drop at a time. In this way a thin uniform coating of Nernst filament material was obtained upon the platinum tube, which was heated to a bright red heat in the air for a few minutes before being fitted into the apparatus. After reducing the gas pressure to 0·0001 mm. the thermionic emission from the heated tube was again investigated, with, as usual, a potential difference of about 210 volts between the terminals of the discharge tube. A series of observations at gradually increasing temperatures was made, and it was found that the negative emission was now very much smaller than the emission from the uncoated platinum tube had been. The observations showed, however, that the emission was tending to increase, and the tube was therefore left heating for some three or four hours, after which another series of measurements at different temperatures was made. The emission was found to have increased to about 30 times the original values and was now remarkably constant. It was thought desirable to treat the tube exactly as the Nernst filament had been treated when its emission was measured, so before testing on the following day, air was let into the apparatus to atmospheric pressure, and the tube was raised to incandescence for a few minutes, after which the apparatus was evacuated with the platinum tube still glowing. The emissions at various temperatures were at once measured and were found to be about 30 per cent. smaller than those finally obtained on the previous day. On continuing the heating, however, the emission soon rose to about the same value as before. These operations were repeated on four days, and in every case the final steady values of the thermionic current were within 5 per cent. of the steady values first obtained after the initial increase had taken place. It was assumed that these currents represented the sum of the emission due to the platinum tube and that due to the material upon it, and to obtain the effect of the material alone the previously determined values of the emission from the clean platinum tube at corresponding temperatures were subtracted. In making this correction the current from the thermocouple welded on to the platinum tube was used as an indicator of its temperature, and the part of the thermionic current taken as being due to the platinum at each temperature was the value which had been obtained from the tube alone at a temperature giving the same deflection of the galvanometer attached to the thermocouple.

In comparing the corrected value of the emission from the filament material heated on the platinum tube with the emission from the whole filament at the commencement of this series of experiments, the optical pyrometer readings were used for temperature measurements in both cases. The comparison is best made by means of emission-temperature curves, and in fig. 2 three such curves are given. Of these, Curves I.

and II. are for the Nernst filament when heated in the usual manner by conducting an alternating current. Two curves are given so as to show the magnitude of the variation of the negative emission with this method of heating. The curves represent the last two series of observations made before the filament was broken up. Curve II. was obtained immediately after heating at a high temperature in air at atmospheric pressure, and Curve I. shows the values to which the emission had risen after heating for some hours in a vacuum. The increase is rather greater than that obtained when the material on the platinum tube was similarly treated. The corrected "steady values" of the emission from the material of this filament when heated on the platinum tube are shown in Curve III. The differences between these values and those given by the filament itself are not greater than the differences often obtained in observations



Curves I. and II. are for a Nernst filament heated by an alternating current.
Curve III. is for the material of a Nernst filament heated upon platinum.

of the thermionic current from a glowing cathode under apparently identical conditions at different times, and we may safely conclude that there is no marked difference between the emission from the material heated upon platinum—when practically none of the heating current flows through it—and that obtained when the material is heated by conducting an electric current. Such a result could not be obtained if the electrons are liberated only as a result of the chemical action between the products of electrolysis of the material of the filament.

It has been mentioned that the emission from the material heated upon platinum was, at first, considerably less than that from the platinum alone, and that this emission gradually increased up to a steady value in the course of three or four hours' heating.

The fact that the negative emission from a Wehnelt cathode often takes some time before it reaches its full strength is considered by FREDENHAGEN to support his view of the action of these cathodes. An investigation of this effect was therefore made in the case of the Nernst filament material heated upon platinum. For this purpose a strip of platinum foil was welded on to the platinum leads of the discharge tube and was covered with the material of a Nernst filament in the manner which has already been described. The temperature of this strip was determined by means of a thermo-junction welded on to it, and the thermionic emission was tested under different potential differences and with different gas pressures in the apparatus. At a low pressure and with 40 volts applied potential difference the negative emission was, at first, very much smaller than that from platinum alone; the measured current at 1440° C. being 10^{-8} amperes cm.^{2}, and at 1500° C. $3{\cdot}2 \times 10^{-8}$ amperes cm.^{2}—values which remained fairly constant during two hours' heating.

The positive emission was also tested, and this was very much larger. At 1260° C. it began by being $2{\cdot}3 \times 10^{-5}$ amperes cm.^{2} and decreased to $1{\cdot}7 \times 10^{-6}$ amperes cm.^{2} after heating for 40 minutes, the platinum strip being charged to +40 volts throughout this period. It was found that leaving the strip charged positively for some time did not cause any increase in the negative emission when tested immediately afterwards, but that after the strip had been charged negatively for a few minutes, the positive emission was abnormally large. On FREDENHAGEN'S view of the activity of the oxide cathode, the passage of the feeble negative thermionic current from the platinum strip is supposed to start the electrolytic decomposition of the oxide, and the re-combination of the elements separated by electrolysis is supposed to give rise to a further electron emission, thus increasing the current through the oxide layer and causing the gradually increasing effect sometimes observed with these cathodes. The material of a Nernst filament certainly appears to suffer electrolysis when a current flows through it, so that electrolytic decomposition may be produced by a thermionic current flowing through the material on the platinum strip; but although a strong positive thermionic current was measured at 1265° C., no negative emission could be detected at this temperature on reversing the direction of the electric field. This experiment shows that the activity of the oxide cathode does not arise in the manner suggested by FREDENHAGEN.

On the day following that upon which the observations just recorded were made, the effect of a stronger electric field was investigated. A potential difference of 209 volts was used between the electrodes and the temperature of the platinum strip was gradually raised to 1500° C. The negative thermionic current at this temperature was $1{\cdot}9 \times 10^{-7}$ amperes cm.^{2}. It began to increase, very slowly at first, but after about 10 minutes a sudden rapid increase to $1{\cdot}3 \times 10^{-6}$ amperes cm.^{2} took place, after which the slow increase again continued during a further 10 minutes' heating which was given. The apparatus was then left until the following day when the temperature was at once raised to 1500° C. The negative emission was $2{\cdot}0 \times 10^{-6}$ amperes

cm.^{2} and gradually increased to $7{\cdot}7 \times 10^{-6}$ amperes cm.^{2} during two hours' heating; but the increase did not stop here, and further heating on the two following days increased the emission to $1{\cdot}1 \times 10^{-5}$ amperes cm.^{2} at 1500° C., at which value it remained constant for some time. This gradual increase in the thermionic current was not due to an increasing gas pressure, for this was kept constant by continual pumping; nor did it depend upon the passage of the thermionic current, for it took place when the potential difference was removed from the electrodes during part of the heating, and, as will be seen from the figures already given, the increase continued on one occasion when the cathode was left cold over night with no electric field on. Experiments showed that the current at 1500° C. and 0·005 mm. pressure was approximately saturated with 20 volts, but that complete saturation was never obtained, the current increasing very slightly with each increase of the applied E.M.F. up to 400 volts.

It seems possible that the smallness of the negative emission from the freshly coated platinum may be due to an electrical double layer at its surface which tends to prevent the escape of electrons, so that a large electric field has to be applied to counterbalance this action. Continued heating may have the effect of removing this double layer and hence causing the gradual increase of the thermionic current to a steady maximum value. The existence of such double layers is not easily proved, and further experiments in this direction are necessary.

The Chemical Action Theory of the Electron Emission.

The connection between ionisation and chemical action has been investigated by many observers and very inconsistent results have been obtained. The inconsistency is perhaps most marked in the case of the alkali metals. By recent experiments Haber and Just* and Fredenhagen† claim to have shown that when the alkali metals enter into chemical action there is a liberation of electrons. On the other hand Broglie and Brizard‡ have concluded that the ionisation which occurs when sodium oxidises is due to the formation on the surface of a host of microscopic bubbles, and that the effect is merely an example of "ionisation by bubbling." A similar result has been announced by Reboul,§ who also states that the presence of water vapour is essential. A large number of chemical reactions which are not accompanied by ionisation have been investigated by L. Bloch‖; these even include certain cases where the action is accompanied by flame as in the combustion of sulphur or arsenic. But the literature of this subject is so extensive that it is impossible to give an adequate summary of it in the present paper.

* Haber and Just, 'Ann. der Phys.,' vol. xxx., p. 411, 1909, and vol. xxxvi., p. 308, 1911.
† Fredenhagen, 'Verh. d. Deut. Phys. Ges.,' 14, p. 384, 1912.
‡ Broglie and Brizard, 'Comptes Rendus,' vol. 149, p. 923, 1909.
§ Reboul, 'Comptes Rendus,' vol. 151, p. 311, 1910.
‖ Bloch, 'Ann. de Chim. et de Phys.,' vols. 22 and 23, 1911.

The arguments in support of the chemical action theory of the origin of the electron emission from glowing solids are based upon two experimental results :—

(1) The reduction which takes place in the electron emission on purifying the element under test and on improving the vacuum in which the test is conducted.

(2) The increased activity which is produced when substances known to have chemical action upon the cathode are introduced into the discharge chamber.

These results point to a connection between electron emission and the possibility of chemical action, and it is claimed that the small value of the emission which is still obtained after continued purification must not be regarded as a true thermal effect, for it can be accounted for as being due to remaining traces of gaseous or other impurities. On the other hand, it can be urged with equal force that this remaining effect should not be regarded as due to chemical action until it has been shown to occur under conditions which preclude the possibility of an emission of electrons as a result of an increase in their thermal energy by rise of temperature. Experiments which have been made with these precautions have almost invariably indicated that chemical action is not by itself the cause of ionisation. Evidence to this effect was obtained by the author some time ago when comparing the electron emission from calcium with that from lime. In these experiments a platinum strip was covered with calcium by sublimation in a vacuum ; an excess of oxygen was let into the discharge tube and the calcium was oxidised to lime. No detectable ionisation occurred during this process of oxidation in the cold, nor even at a temperature of 500° C. or 600° C., under which conditions the oxidation must have been very rapid. It was only when the lime formed had been raised to 700° C. or 800° C. that a measurable electron emission was obtained. In the case of the strongly electro-positive alkali metals it is not impossible that an electron emission (as a result of thermal energy) occurs at the ordinary temperature of the laboratory, and if an increased emission does occur in the presence of a reacting gas, this may be due, not directly to the chemical action, but to the rise of temperature which accompanies it. This momentary increase of temperature may be very considerable in the case of the surface layer, although the rise in temperature of the bulk of the metal may be quite inappreciable. The fact that chemical action and rise of temperature are usually closely associated in the type of reaction with which we are concerned makes it very difficult to prove that an observed thermionic emission is a result of either chemical action or temperature alone.

A process which causes the liberation of electrons from matter must act either by increasing the kinetic energy of the electrons or by diminishing the work which an electron must do in order to escape. An increase of temperature acts in the former manner, but a disturbance of the motions of some of the electrons would also

appear to be an inevitable result of an atom taking part in a chemical reaction, and if this does occur, it would be not improbable that such disturbance should lead, in some cases, to an electron emission. Experimental evidence shows that when atoms enter into chemical reactions at ordinary temperatures, it is rarely (if ever) that the accompanying disturbance increases the kinetic energy of any of the electrons sufficiently to enable them to escape; but if the conditions are arranged so that the electrons already possess considerable kinetic energy in virtue of their thermal agitation, it would seem possible that the stimulus of chemical action should have the effect of increasing this energy sufficiently to cause some of the electrons to overcome the forces tending to retain them in the substance. It seems, therefore, that chemical action at a high temperature might be expected to result in an electron emission in cases where the temperature itself is not sufficient to produce this effect, or where it produces it only to a much smaller extent. This conclusion is supported by the fact that an increased emission occurs when certain chemically active gases are allowed to enter the discharge tube, but it must be remembered that there is another manner in which these gases may act in aiding the escape of electrons from the glowing cathode, namely, by causing an alteration in the surface conditions whereby the minimum amount of energy an electron must possess in order to escape from the cathode is reduced. Such a reduction might be caused by the formation of an electric double layer at the surface of the cathode which would create a force tending to drag out the electrons. There is already a considerable amount of evidence of the existence of these double layers in certain cases, and this view has been put forward to explain the action of hydrogen in increasing the electron emission from platinum.*

The author is of opinion that at present there is not sufficient experimental evidence to enable us to explain the manner in which the presence of a gas in the discharge tube acts in increasing the negative thermionic emission, but it is not improbable that the method by which this increase is brought about is different in different cases; for instance, when oxygen comes in contact with a calcium cathode at a high temperature, the increased emission is doubtless due to the fact that the emission from the product of the chemical action—lime—is greater than the emission from calcium at the same temperature. The possibilities of ionisation by collisions need also to be carefully investigated. Recent experiments have shown that the electric intensity required to produce this effect is very much smaller than has been supposed, and the process is probably always going on near a glowing cathode at low pressures. It must be remembered also that the gas pressure in the neighbourhood of a cathode which is continually evolving gas may be considerably greater than that measured in more remote parts of the apparatus, so that it is difficult to estimate the magnitude of the effect of ionisation by collisions.

* 'Conduction of Electricity through Gases,' Camb. Univ. Press, 1906, p. 203.

Summary and Conclusion.

The experiments with Nernst filaments have shown that the oxides of which these are made suffer electrolysis when conducting an electric current, but that the electron emission which occurs at high temperatures is not due either directly or indirectly to this electrolysis, for the magnitude of the emission at a given temperature is the same whether the current through the material is great or small. It is therefore concluded that the emission from lime in a Wehnelt cathode is not due to the re-combination of electrolytically separated calcium and oxygen, as has been suggested.

Owing to the increasing chemical activity of substances at high temperatures, and to the impossibility of removing all traces of impurities from the discharge tube, it is very difficult to prove conclusively that any known case of electron emissions is purely a thermal effect; but, on the other hand, there is no satisfactory evidence that ionisation is ever produced by chemical action alone. It would seem, therefore, that the theory that thermal agitation is by itself sufficient to cause the emission of electrons from matter could only be disproved by reducing the thermionic current from a metal at the highest attainable temperature to zero.

The increased ionisation from a glowing cathode which occurs when a chemically active gas is allowed to enter the discharge tube may arise in several ways :—

(1) It may be directly due to chemical action ;
(2) It may be indirectly due to chemical action, arising as a consequence of an increase of temperature resulting therefrom, or from the product of the action having a greater activity than the original substance of the cathode ;
(3) It may be due to an alteration of the surface conditions at the cathode in such manner as to make it easier for the electrons to escape, for instance, by the formation of an electric double layer ;
(4) It may be due to ionisation by collisions.

It seems probable that the cause of the increased activity is different in different cases.

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