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Harold A. Wilson

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VII. *On the Discharge of Electricity from Hot Platinum.*

By HAROLD A. WILSON, *D.Sc., B.A., Fellow of Trinity College, Cambridge.*

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THE following paper contains an account of the results obtained in a series of experiments on the loss of electricity from hot platinum in several gases at various pressures. I shall begin by giving a brief account of some of the results obtained by previous workers on this subject, confining myself to those results which appear to bear more or less directly on the present investigation. Further information on the results of the earlier investigations may be found in WIEDEMANN'S 'Elektrizität,' vol. 4, in J. J. THOMSON'S 'Recent Researches,' in STARK'S 'Die Elektrizität in Gasen,' and in the papers referred to.

ELSTER and GEITEL ('Wied. Ann.,' vol 37, p. 315, 1889) found that hot platinum, in air and oxygen, produces positive electrification of the surrounding gas and bodies immersed in it, except at low pressures, when negative electrification is obtained. In hydrogen they found the electrification is always negative.

J. J. THOMSON ('Phil. Mag.' [5], vol. 29, pp. 358–441, 1890) measured the current due to a constant P.D. between two parallel platinum plates immersed in various gases and vapours at a bright red heat. He found that the current depends very greatly on the nature of the gas. Gases which dissociate into atoms when heated, such as HCl and salt vapours, conduct very much better than gases such as air and ammonia, which do not dissociate into atoms. Unless both electrodes are hot enough to glow, very little current can be obtained.

ARRHENIUS ('Wied Ann.,' vol. 42, p. 18, 1891) measured the current between two parallel platinum plates immersed in a Bunsen flame, by which they were kept at a bright red heat. He found that the current with increasing P.D. increases at first proportionately to the P.D., but when the P.D. is more than one or two volts, the curve connecting the current and P.D. bends over, and then becomes nearly parallel to the axis of P.D. The current is greatly increased when an alkali salt vapour is introduced into the flame. He investigated the relative conductivities due to various salts, but it is not necessary to describe here the results he obtained, since they do not bear directly on the present investigation.

The results obtained by ARRHENIUS were confirmed and extended in a research by

Professor A. Smithells, Dr. H. M. Dawson, and the writer ('Phil. Trans.,' A, vol. 193, pp. 89–128). Using as electrodes two concentric cylinders of platinum, it was found that the current was much greater when the outer cylinder was made the kathode than when it was made the anode. Also when the electrodes were simply connected to the galvanometer a current was observed from the inner to the outer cylinder through the flame. Phenomena of this kind have been known for a long time to occur when metal electrodes are immersed in a flame. They are evidently closely analogous to the effects described by Elster and Geitel, referred to above.

The discharge of electricity from platinum immersed in a Bunsen flame was further investigated by the writer ('Phil. Trans.,' A, vol. 192, pp. 499–528). In this paper it is shown that the ions concerned in the discharge between hot platinum electrodes immersed in a flame are nearly all produced at the surface of the platinum, and that the negative ions have a much greater velocity, due to an electric field, than the positive ions. Consequently, nearly all the current is carried by negative ions which start at the negative electrode. These results enable the polar properties of the conductivity of flames to be very simply explained. Hot platinum in a flame consequently discharges negative electricity very much more readily than positive electricity.

In the 'Phil. Mag.' for December, 1899, J. J. Thomson gave an account of some experiments on the ratio of the charge (e) to the mass (m) of the negative ions emitted by a hot carbon filament in a vacuum. He found that it is impossible to obtain consistent results unless precautions are taken to ensure that the filament is in an atmosphere of pure hydrogen. The cause of this is the gas evolved by the filament when it is heated. He found that by heating the filament for a long time, and repeatedly pumping out the apparatus and letting in pure hydrogen, regular results could be obtained. When this had been done, the filament only lost negative electricity, whereas before it lost sometimes only positive and sometimes only negative, and sometimes both. He found that e/m was equal to about 10^7, which is nearly the same as e/m for kathode rays, so that it is clear that the filament emits negatively charged corpuscles or electrons. The importance of taking such precautions as those described by Professor Thomson, in experiments on the leak from hot wires at low pressures, is very great. Unless this is done, the gases evolved by the wire fill the apparatus, and the leak observed is very irregular in its behaviour. It is probable that the gas evolved by platinum wires is mainly composed of hydrogen, which, as will be shown below, has a very large effect on the leak, even when present in very small quantities.

A further investigation of the leak from hot platinum was published by the writer in 1901 ('Phil. Trans.,' A, vol. 197, pp. 415–441). In this paper it is shown that hot platinum in air at atmospheric pressure in general discharges positive more readily than negative electricity, and that the rate of discharge at constant temperature falls off gradually with the time and ultimately becomes very small compared with its original value. The current between platinum electrodes in air with a constant P.D. increases rapidly with rise of temperature. If x_1 is the current (due to a small P.D.) at the absolute temperature θ_1, and x_2 that at θ_2, and Q the energy required to produce a gramme molecular weight of positive and negative ions, then it is shown that

$$Q\left\{\frac{1}{\theta_1}-\frac{1}{\theta_2}\right\}=2\log\frac{x_2{}^2\theta_1}{x_1{}^2\theta_2};$$

and Q is found to be nearly independent of the temperature, so that we may put $x = A\theta^{\frac{1}{2}}\epsilon^{-Q/4\theta}$, where A is a constant quantity. This formula is deduced on the assumption that the air close to the surface of the platinum dissociates into ions.* The value found for Q is 60,000 small calories. This gives 2·6 volts for the P.D., through which the ionic charge must fall to obtain enough energy to ionize one molecule of air in contact with hot platinum. [When a large P.D. is used, so that the current is the maximum, the appropriate formula is $x = A\theta^{\frac{1}{2}}\epsilon^{-Q/2\theta}$, p. 259 *infra.*]

It is also shown in this paper that the maximum current between hot platinum electrodes immersed in a stream of an alkali salt vapour is equal to the current required to electrolyse in a solution the amount of salt passing between the electrodes.† It is therefore clear that the leak is due to the ionization of the salt in contact with the platinum.

Professor McClelland, in 1902, published the results of some experiments on the leak from hot platinum in air at comparatively low pressures ('Proc. Camb. Phil. Soc.,' vol. 11, Part IV., p. 296). A fine platinum wire surrounded by a cylindrical electrode could be heated by passing a current through it. The current from the wire to the electrode was measured with various differences of potential between them. It was found that, at pressures below 1 millim., the current is much greater when the wire is negatively charged than when it is positively charged. The current with the wire positively charged is nearly independent of the P.D. between the limits 40 and 200 volts, but above 200 volts it rises rapidly with the P.D. When the wire is negatively charged, the current at $\frac{2}{3}$ millim. always rises rapidly with the P.D., but at $\frac{1}{10}$ millim. the rate of rise diminishes as the P.D. increases. These results can be explained by supposing that the ions coming from the wire produce others by colliding with the gas molecules when the electric intensity is large enough. This effect was discovered by Professor Townsend‡ for the ions produced in air by Röntgen rays, and it was shown by him that the negative ions produce others by collisions when the electric intensity is comparatively small. The intensity required to make the positive ions produce others by collisions is probably nearly that required to start an ordinary discharge through the gas, but in McClelland's

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* No assumption need be made as to the nature of the ions; they may be molecules, atoms or corpuscles carrying the ionic charge $e = 3 \times 10^{-10}$ E.S. unit.

† See also "The Laws of Electrolysis of Alkali Salt Vapours," 'Phil. Mag.,' August, 1902.

‡ 'Phil. Mag.,' February, 1901.

experiments the electric intensity near the fine wire approaches this value even when the P.D. is only 100 volts or less.

McClelland states in this paper that the negative leak from the wire is nearly independent of the air pressure from $\frac{1}{25}$ millim. to $\frac{1}{240}$ millim., and he suggests that the negative leak at low pressures is caused by the escape of negative ions from the metal.

Mr. O. W. Richardson ('Proc. Camb. Phil. Soc.,' vol. 11, Part IV., 1902, p. 286) has published the results of a series of measurements of the negative leak from hot platinum in gas at low pressures. He finds that the variation of the leak with the temperature can be represented by a formula of the type $x = A\theta^{\frac{1}{2}}\epsilon^{-Q/2\theta}$. This formula Richardson deduces from the assumption that the platinum contains negative corpuscles which can only get through the surface layers when their velocity exceeds a definite value. The value he obtains for Q corresponds to a fall of the ionic charge through 4·1 volts, which does not differ much from the value 2·6 volts found by the writer in air at atmospheric pressure. According to Richardson's theory, Q is the energy required to drive a gramme molecular weight of the corpuscles out of the metal through the surface layers. It is shown below that the formula $x = A\theta^{\frac{1}{2}}\epsilon^{-Q/2\theta}$ can be deduced without making any further assumption than that ions are produced at the surface of the metal, so that the agreement of the experimental results obtained with this formula cannot be regarded as evidence in favour of any particular theory with regard to the way in which the ions are produced. Richardson also shows that on his theory it is possible to deduce from the constant A in the above equation the number (n) of corpuscles in a cubic centimetre of the platinum. He obtains $n = 1{\cdot}3 \times 10^{21}$, which is of nearly the same order of magnitude as the values of n deduced from experiments* on the variation of the electrical resistance of platinum in a magnetic field. Richardson has recently read a paper† before the Royal Society on this subject, in which he has examined the negative leak from some other metals besides platinum in gas at low pressures. The results with platinum described in that paper are the same as those just referred to. In all these experiments the positive leak was very small compared with the negative leak.

W. Wien ('Annalen der Physik,' vol. 8, 1902, p. 244) has described some experiments on the leak from hot platinum wires in high vacua. He finds that even in a very good vacuum a hot wire can still discharge electricity to a distant small electrode if it is charged to a rather high potential. In the best vacuum the P.D. necessary was 800 volts for negative electricity and 3000 volts for positive.

According to C. D. Child ('Phys. Review,' Nos. 4 and 5, 1902) the negative leak from a hot platinum wire, using a large P.D., increases very rapidly with diminishing pressure from one atmosphere down to a small fraction of a millimetre of mercury. It will be shown below that this large increase is due to ionization by collisions with

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* Patterson, 'Phil. Mag.,' June, 1902.

† See 'Phil. Trans.,' A, vol. 201, 1903.

the gas molecules, and that below a certain pressure the leak in air diminishes with the pressure unless the P.D. used is too small to produce ions by collisions.*

In the following paper the results are given of experiments on the variation of the leak from hot platinum wires with the temperature of the wire, the pressure of the gas, and the nature of the gas. Some results are also given on the leak from a hot palladium wire. The rest of the paper is divided into the following sections:—

(1.) Description of apparatus, &c.
(2.) The leak in air, nitrogen and water vapour.
(3.) The variation of the negative leak with the temperature.
(4.) The leak in hydrogen.
(5.) The leak from palladium in hydrogen.
(6.) Summary of principal results.
(7.) Conclusion.

(1.) *Description of Apparatus, &c.*

The apparatus used is shown in fig. 1. The leak was measured from a platinum wire PP to a thin cylinder of platinum AB surrounding it. The cylinder was 1·4 centim. in diameter and 5 centims. long. The wire PP was in the form of a loop hanging vertically downwards. The cylinder was contained in a glass tube which

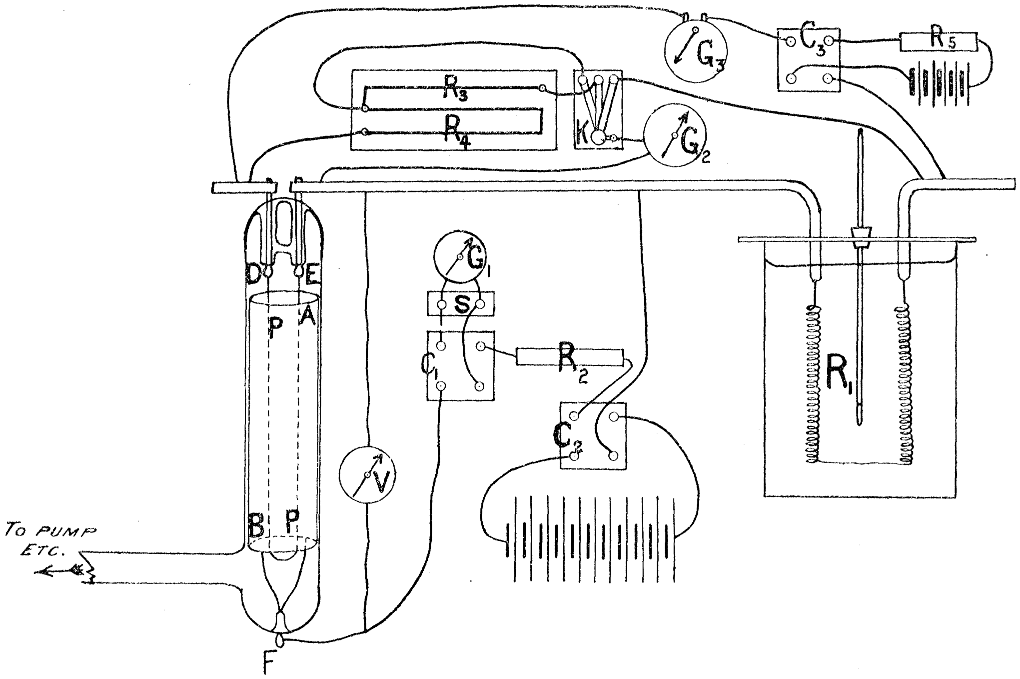

Fig. 1. PP, platinum wire; V, voltmeter; $C_1C_2C_3$, commutators; R_5, rheostat; G_3, ammeter; AB, cylinder; K, key; $R_1R_2R_3R_4$, resistances; G_1G_2, galvanometers; S, shunt.

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* Child also made measurements in hydrogen and found the leaks greater in hydrogen than in air. He did not measure the temperature of his wire, so that his results are purely qualitative.

fitted it loosely and was welded to two platinum wires sealed through the end of the tube at F. The loop was welded to two platinum wires D and E, which were sealed through the other end of the tube as shown. These wires were each 1 millim. thick and 2 centims. long, and the current used to heat the loop entered through them.

The cylinder was connected through a reversing commutator to an Ayrton-Mather galvanometer G_1, and then through a liquid resistance of about 10^5 ohms and another reversing commutator to one pole of a battery of small secondary cells, the other pole of which was connected to the loop. The P.D. between the loop and cylinder was measured by means of an electrostatic voltmeter V.

The resistance of the loop was measured by means of a Wheatstone's bridge arrangement. The loop was connected in series with a resistance coil R_1 of thick German silver wire spirals immersed in a jar of paraffin oil, the temperature of which was indicated by a normal thermometer.

The coil R_1 and the loop formed two arms of the bridge, and for the other two arms the coils of a P.O. box were used. The coil R_1 had a resistance of about 1·3 ohms, and 1000 or 200 ohms was usually used for the adjacent arm in the box. The fourth arm then had a value, usually several thousand ohms, depending on the resistance of the loop. The current through the loop, which nearly all passed through the coil R_1, was supplied by a battery of from 4 to 10 secondary cells, and was measured by means of a Weston ammeter. Another Ayrton-Mather galvanometer was used with the bridge arrangement, and was connected to the wire E and the opposite corner of the bridge. A key was used with this galvanometer, which closed first the two arms of the bridge in the P.O. box and then the galvanometer circuit. In this way the current only passed through the coils in the box when the key was pressed down. The resistance of these coils was so large compared with that of R_1 and the loop that no appreciable change in the current through the loop occurred when the key was pressed down. A rheostat in the battery circuit enabled the current through the loop to be varied, and the method used was to give the resistance of the variable arm of the bridge the desired value, and then by altering the current through the loop by means of the rheostat balance the bridge. At high temperatures the bridge was very sensitive and the resistance of the loop could easily be kept constant to one part in 5000 by adjusting the rheostat. When it was desired to measure the resistance of the loop cold, a single Leclanché cell in series with a resistance of 10 ohms was substituted for the secondary cells, and the variable arm of the bridge adjusted till a balance was obtained. This measurement could be made to one part in a thousand. The temperature of the loop was got in this case by a thermometer placed close to the tube, and whenever possible this measurement was made with the apparatus filled with gas at atmospheric pressure, because at low pressures a very small current is sufficient to heat the loop appreciably. The current through the loop in this case, therefore, was only kept on for a few seconds at a time, in order to prevent the loop from being heated above the surrounding temperature.

The resistance of 0° C. was calculated from the resistance at the temperature of the room, using the known value (0·0038) of the temperature coefficient at low temperatures of the wire used. The loop and wires D and E were made from pure platinum supplied by Messrs. JOHNSON, MATTHEY and Co.

The temperature of the loop was deduced from its resistance in the following manner. The temperature coefficient of the wire used was determined by measuring the resistance of a piece of the wire cold and at the melting-point of pure K_2SO_4, which, according to HEYCOCK and NEVILLE, is 1066° C. The wire was hung horizontally, and screened from air currents, and a minute particle of K_2SO_4 put on it and observed through a microscope. It was then heated by passing a current through it until the particle of K_2SO_4 just began to melt, and its resistance when this occurred was measured by the bridge arrangement just described. This was done with a particle at several points along the wire, and the mean of the resistances when the particles melted, which were all very nearly the same, was taken to be the resistance at 1066° C.

The following are the results of one experiment of this kind :—

Resistance in variable arm of bridge required to balance resistance of 18 centims. of wire, 0·2 millim. in diameter, at 19° C., 1014 ohms.

Resistances required at 1066° C. : (1) 4098, (2) 4100, (3) 4102 ; Mean 4100 ohms.

Resistance at 0° C. $= \frac{1014}{1 + 19 \times 0 \cdot 0038} = 945 \cdot 7$.

Hence mean temperature coefficient of the wire between 0° C. and 1066° C. is

$$\frac{3154 \cdot 3}{1066 \times 945 \cdot 7} = 0 \cdot 003129 \text{ ohm per ohm at } 0° \text{ C.}$$

The "platinum temperature" of the wire loop in any experiment was first calculated from its resistances at 0° C. and at the required temperature by means of the formula $R = R_0 (1 + \alpha pt)$, where R_0 is the resistance at 0° C., R that at the required temperature (pt), and α the coefficient 0·003129. The "platinum temperatures" so determined were corrected to the centigrade scale by means of a table of corrections. These corrections were obtained by determining the resistance of the wire at the melting-point of platinum, which was taken to be 1820° C. This was done by heating a wire loop in the apparatus described above until it just melted. The wire was heated in a vacuum and the current increased (very gradually when close to the melting-point), and the resistance measured until the wire just melted. This method gave sufficiently concordant results. The following are the numbers obtained in two experiments of this kind :—

(1) Balancing resistance at 15° C. for wire 0·1 millim. in diameter and about 13 centims. long, 1320 ohms.

Ditto when just on point of melting, 7615 ohms.

Hence $R_0 = \frac{1320}{1 + 15 \times 0\cdot0038} = 1248\cdot8$ ohms,

$$pt = \frac{R - R_0}{R_0\alpha} = \frac{6366}{1249 \times 0\cdot003129} = 1629^\circ \text{ on the platinum scale used.}$$

(2) Balancing resistance at 18° C. for wire 0·2 millim. in diameter and about 13 centims. long, 694 ohms.

Ditto when just melting, 4000 ohms.

Hence $R_0 = \frac{694}{1 + 18 \times 0\cdot0038} = 650\cdot4$ ohms,

$$pt = \frac{3349\cdot6}{650\cdot4 \times 0\cdot003129} = 1647^\circ \text{ on the platinum scale used.}$$

The mean of these two results, 1638°, was taken to be the melting-point of platinum on the platinum scale used. The correction to the centigrade scale at the melting-point of platinum is therefore $1820 - 1638 = +182°$.

The correction at other temperatures was calculated from this by means of a parabolic difference formula as used by CALLENDAR and GRIFFITHS,

$$t - pt = A\left(\frac{t}{1066} - 1\right)\frac{t}{1066},$$

where t = temperature centigrade, pt = temperature on platinum scale used, A = a constant.

The constant A is given by the equation $182 = A\left(\frac{1820}{1066} - 1\right)\frac{1820}{1066}$, which gives $A = 151$. The following table gives the values of the correction at several temperatures:—

Temperature.	Correction.	Temperature on platinum scale.
° C.	°	°
1066	0	1066
1100	5	1095
1200	22	1178
1300	40	1260
1400	62	1338
1500	87	1413
1600	114	1486
1700	143	1557
1800	176	1624
1820	182	1638

A curve was plotted from these numbers giving the correction in terms of the temperature on the platinum scale. The following table gives some values of the correction taken from this curve:—

Temperature on platinum scale.	Correction.	Temperature.
°	°	° C.
1066	0	1066
1100	6	1106
1200	26	1226
1300	50	1350
1400	83	1483
1500	120	1620
1600	164	1764
1638	182	1820

The temperatures so determined in this way are subject to an error due to the ends of the wire being cooled by the thicker electrodes to which they are welded. There is also an error due to the resistance of these electrodes being measured along with the wire and changing with the temperature. These errors are, however, almost entirely eliminated by the method of standardising the wire adopted, for the wire was standardised under nearly the same conditions as it was used under in the experiments, consequently these errors are reduced to almost zero at 1066° and at 1820°, and are therefore very small at the intermediate temperatures. The numbers obtained consequently represent very nearly the temperature of the wire at some distance from the electrodes. There was no appreciable error due to thermo-electric effects.

It was found that after a wire had been just fused, as described above, the whole length of the wire, except about 1 centim. at each end, showed signs of fusion, although as soon as any part of the wire fused completely it broke, and so stopped the current. The wires used were always about 13 centims. long, but in calculating the leak per sq. centim. of platinum surface, their length was taken as 1 centim. less than their actual length to allow for the cooling of the ends near the electrodes. This amounts to counting the 1 centim. of wire at each end as leaking half as much per unit area as the rest of the wire.

The tube containing the platinum wire was sealed on to a tube which communicated with a Töpler pump and McLeod gauge. The connecting tubes between the different parts of the apparatus were made short to enable the gas to get into equilibrium as quickly as possible.

The methods used for preparing and purifying the different gases used will be described in the following sections.

(2.) *The Leak from Hot Platinum in Air, Nitrogen, and Water Vapour.*

The results obtained with air will first be described. The air was passed slowly through tubes containing soda-lime and calcium chloride and then let into the apparatus through a good mercury-sealed tap. A bulb containing phosphorus pentoxide was sealed on to the apparatus near the tube containing the hot wire. The P_2O_5 used was a specially good sample, which was found to be quite free from lower oxides and contained no lumps of meta-phosphoric acid. In some of the earlier experiments a small tube packed tightly with gold leaf was put in between the hot wire tube and the rest of the apparatus to absorb mercury vapour. About 50 gold leaves were packed into a tube 1 centim. in diameter and 3 centims. long, and it was found that the gold near the end of the tube next the pump and gauge became amalgamated, whereas the rest of the gold remained for months perfectly bright. I believe that such a tube entirely prevents the diffusion through it of mercury vapour, and that previous failures in using this method of absorption are due to too few gold leaves having been used and not sufficiently tightly packed. Of course, such a tube does not allow very free communication between its ends, so that some little time has to be allowed to elapse after changing the pressure in the apparatus before making any measurements. It was found that the leak was very little affected by the absorption of the mercury vapour, so that in the later experiments this gold-leaf tube was abandoned. Some of the experiments in which the gold leaf was used will be described in the section on the leak in hydrogen.

In the earlier experiments very inconsistent results were often obtained. This was found to be due to gas, probably mostly hydrogen, given off by the wire when heated. A very small quantity of hydrogen has a very large effect on the leak, as will be shown in Section (4). When the platinum wire is welded to its electrodes it is heated in a blow-pipe flame, and probably absorbs some hydrogen, which is afterwards given out when the wire is heated in a vacuum. A new wire was generally found to give very large leaks, which varied in an irregular manner with the time. Long-continued heating in a good vacuum ultimately nearly gets rid of these irregularities, but long continued heating also causes the wire to disintegrate, and its surface becomes roughened and covered with a network of deep cracks. It was found that the irregular behaviour of the wire could be entirely got rid of without long continued heating by the simple process of boiling it in strong nitric acid, after welding it to its electrodes and sealing them into the tube. The tube was about half filled with pure nitric acid and boiled over a spirit lamp for a few minutes, the acid then poured out, and the process repeated two or three times. The tube was then washed out with distilled water. If the platinum loop had been bent by the boiling process, it was straightened by a clean platinum wire hook introduced through the side tube, and then the tube was sealed on to the pump and gauge, &c. The apparatus was then pumped out and filled up with air several times, and then on heating the wire the negative leak at once took up an almost steady value. The positive leak was very small, and did not fall off with the time after the first few seconds. The process of filling the apparatus with air and pumping out several times with the wire kept hot all the time was repeated at frequent intervals to ensure that the apparatus should only contain pure dry air.

Fig. 2 shows the way in which the leak from the hot wire varies with the P.D. at pressures of 766, 211, and 27 millims. of mercury, the wire being negatively charged. When the P.D. is small, the current is nearly independent of the P.D., but with larger P.D.'s the current rises rapidly with the P.D., the rate of rise being greater the lower the pressure. The temperature of the wire in this case was 1648° C., and the wire was 13 centims. long and 0·1 millim. in diameter.

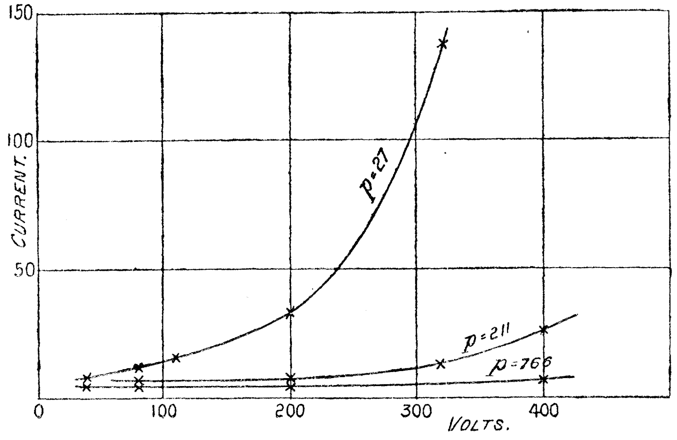

Fig. 2.

Fig. 3 shows the variation of the negative leak with the P.D. at pressures of 0·0036, 0·18, 0·29, 0·49, 0·81, and 12·1 millims. of mercury. At these pressures the rise of current with the P.D. is more rapid the higher the pressure. The temperature of the wire in this case was 1483° C.

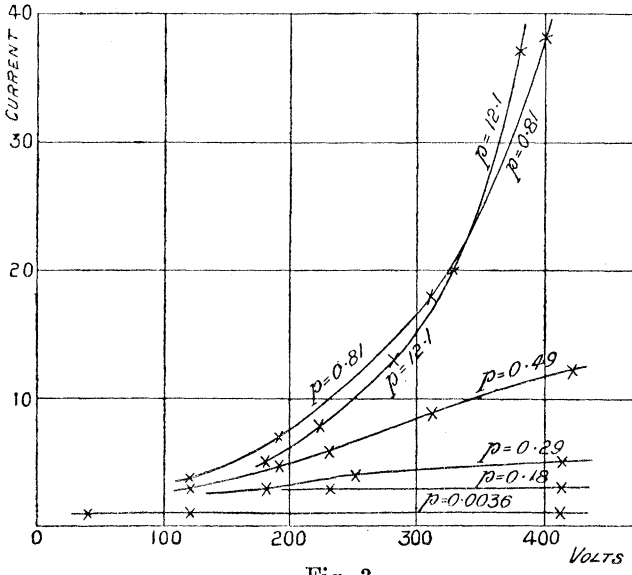

Fig. 3.

Fig. 4 shows the variation of the negative leak with the pressure, using constant P.D.'s of 250 and 40 volts. With 40 volts the current is quite independent of the pressure, but with 250 volts it rises rapidly to a maximum value at nearly 3 millims., and then falls with increasing pressure. The temperature in this case was 1483° C.

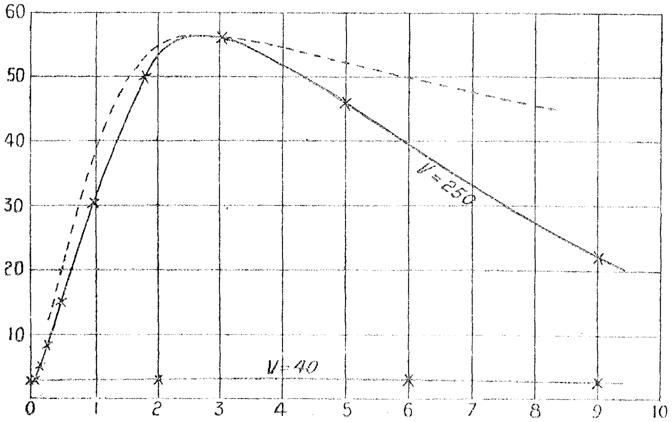

Fig. 4.

The above results on the variation of the current with the P.D. and pressure can be explained if it is assumed—

(1.) That the number of negative ions coming from the surface of the platinum per second is independent of the air pressure and so remains constant during each series of measurements, and

(2.) That the negative ions can produce ionization by collisions with the air molecules when moving with sufficiently great velocities.

It has been shown by Professor TOWNSEND* that negative ions produced in air and other gases at low pressures produce ionization by collisions with the molecules when moving under the influence of a sufficiently large electric intensity. He finds that if α is the number of negative ions produced by one negative ion in going 1 centim., then $\alpha = pf(X/p)$,† where p is the pressure, X is the electric intensity, and f denotes a function whose values he has determined.

The following table gives the values of $f(X/p)$ for air found experimentally by TOWNSEND (' Phil. Mag.,' vol. 5, 1903, p. 395) for several values of X/p :—

$\frac{X}{p}$.	$f\left(\frac{X}{p}\right) = \frac{\alpha}{p}$.	$N\epsilon^{-\frac{NEp}{X}}$.
70	0·25	0·07
100	0·73	0·33
200	2·5	2·2
400	5·8	5·8
600	7·9	8·0
800	9·4	9·4
1400	12	11·6

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* ' Phil. Mag.,' February, 1901, June, 1902, April, 1903, and ' Electrician,' April 3, 1903.

† TOWNSEND has determined a large number of values of α with various values of p and X, and he finds that they can be very accurately represented by an equation of this form.

When X/p is greater than about 200, α/p is given (as TOWNSEND shows) by the formula $\alpha/p = N\epsilon^{-NEp/X}$, where $N = 15{\cdot}2$ and $E = 25$ volts. The values of $N\epsilon^{-NEp/X}$ are given in the third column of the above table, and it can be seen that they agree with the experimentally determined values of α/p. X is measured in volts per centimetre and p in millimetres of mercury. Thus when X/p is large, α/p is nearly equal to 15·2.

If V is the P.D. between the wire loop and cylinder, and r the distance from the centre of the wire, then approximately near the wire $X = \dfrac{V}{r \log b/a}$, where b is the radius of the cylinder and a that of the wire. In the experiments just described $b = 0{\cdot}7$ centim. and $a = 0{\cdot}005$ centim., so that $\log b/a = 4{\cdot}94$ and $X = V/4{\cdot}94r$. Hence X at the surface of the wire is equal to 40 V.

Let n_r denote the number of negative ions, crossing a cylinder of radius r coaxial with the hot wire, per second. Then we have

$dn_r = n_r\alpha\, dr$; also $\alpha = Np\epsilon^{-NEp/X}$, and $X = \dfrac{V}{r \log b/a}$, so that $dn_r = n_r Np\epsilon^{-(NEpr/V)\log b/a}\, dr$.

Integrating, we get $\log n_b/n_a = \dfrac{V}{E \log b/a}\{\epsilon^{-(NEpa/V)\log b/a} - \epsilon^{-(NEpb/V)\log b/a}\}$. This equation should therefore be capable of approximately representing the variations of the current with the pressure and P.D. at constant temperature, when the P.D. is large enough to drag all the corpuscles which escape away from the wire. The value of N or the maximum number of negative ions produced by a corpuscle in going 1 centim. in air at 1 millim. pressure is equal, according to TOWNSEND's results (*loc. cit.*), to the number of collisions with air molecules made by the corpuscle. N should, therefore, be proportional to the number of molecules present at 1 millim. pressure, that is, it should be inversely proportional to the absolute temperature of the air.

The following table contains values of n_b/n_a taken from the curve in fig. 2 at 27 millims. pressure and those calculated by the formula taking $N = 3{\cdot}04$ and $E = 17{\cdot}7$, which values were obtained from the observed values of n_b/b_a at 150 and 300 volts.

V.	n_b/n_a found ($n_a = 5$).	n_b/n_a (calculated).
100	2·2	2·5
150	3·9	4·0
200	6·8	6·4
250	11·7	11·0
300	21·2	21·0
320	26·1	27·2

If N varies inversely as the absolute temperature, then, the value of N being 15 at 20° C., N at 1648° C. should be 2·3. The number 3 obtained is rather larger than this, as was to be expected, because the air near the wire must be cooler than the wire itself. It seems therefore that the results obtained are consistent with the view that N varies inversely as the absolute temperature.

The dotted curve in fig. 4 was calculated by means of the expression

$$\log n_b/n_a = \frac{\mathrm{V}}{\mathrm{E} \log b/a} \left\{ \epsilon^{-(\mathrm{NE}pa/\mathrm{V}) \log b/a} - \epsilon^{-(\mathrm{NE}pb/\mathrm{V}) \log b/a} \right\},$$

taking N = 8·04 and E = 16·55. These values were obtained by making the maximum on the calculated curve coincide with the observed maximum. Below 4 millims. pressure the observed and calculated curves agree fairly well, but at the higher pressures the calculated current is too large. At high pressures most of the ionization by collisions takes place near the wire where the gas is very hot, so that the value of N ought really to be taken smaller at the higher pressures, consequently the calculated currents are too large.

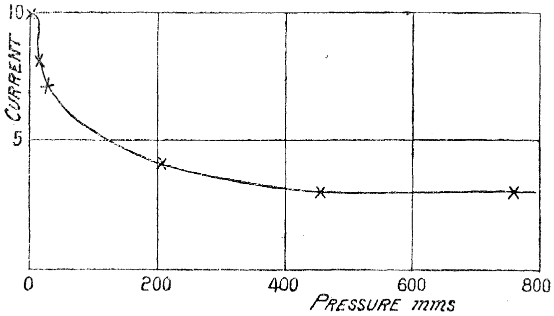

Fig. 5.

Fig. 5 shows the variation of the negative leak with the pressure using 40 volts only, so that practically no ions are produced by collisions. The current falls off as the pressure increases. This is probably due to the presence of the gas hindering the escape of the negative corpuscles from the surface of the wire.

Some measurements of the negative leak were also made in nitrogen and in water-vapour. The nitrogen was prepared from KNO_2 and NH_4Cl and passed over H_2SO_4 before admitting it into the apparatus. The last traces of oxygen were removed from it by sodium electrolysed into the apparatus through hot glass. The details of this process will be described in Section (4). The leak in nitrogen at pressures up to several millims. was nearly equal to that in a good vacuum from similarly treated wires, provided the P.D. used was not large enough to produce ionization by collisions. The effects with large P.D.'s were similar to those obtained in air.

The leak in water-vapour at temperatures below 1500° C. with a pressure of about 15 millims. was also very nearly equal to that in a good vacuum at the same temperature. The tube containing the wire was connected to a three-way tap, which was also connected to a tube leading to the pump and to a small bulb containing water. The tube and the bulb were exhausted separately and then connected together, several times, so that the tube containing the wire was filled with water-vapour. The current obtained was 25 divisions at 1446° C. The corresponding current in a vacuum was 27 divisions, using a wire which had been treated in a similar way.

The positive leak in air and other gases is very small at low pressures. When a platinum wire which has not been specially cleaned is first heated in a vacuum or in air at low pressures, it can discharge positive electricity to an extent appreciable on a galvanometer, but the current rapidly falls off and in a few seconds becomes inappreciable. A wire which has been cleaned by boiling HNO_3 usually only shows this effect to a very slight extent or not at all.

In air at high pressures the permanent positive leak is, of course, appreciable on a galvanometer. It increases with the pressure at constant temperature. In pure air at atmospheric pressure, using a wire cleaned with HNO_3 in the way described, the positive leak is about double the negative leak when the temperature is about 1550° C. The two leaks are nearly equal at a pressure of about 200 millims. at the same temperature.

(3.) *The Variation of the Negative Leak from Hot Platinum with the Temperature.*

The results in the preceding section show that the number of negative ions or corpuscles which start from the platinum is independent of the air pressure, provided that this is not more than a few millims., or that if the pressure is large the P.D. used is sufficient to drag away all the corpuscles which get out. In the present section the variation of the number of these corpuscles which escape from the platinum with the temperature will be considered.

The wire used was 13·0 centims. long and 0·1 millim. in diameter, and it was well cleaned with HNO_3 after it had been mounted as described above. The apparatus was filled with pure air and pumped down to a low pressure several times with the wire red hot. When it was thought that all gases evolved by the wire were got rid of, the apparatus was pumped down and the measurements made. If these precautions were not taken, the leaks were always much larger and very irregular.

The following table contains the results obtained with a particular wire treated in this way. Balancing resistances in P.O. box at 18·5° C. before experiments 1000 and 1669 ohms, and after the experiments 1000 and 1669 ohms.*

Balancing resistances 200 ohms and	Negative leak in galvanometer scale divisions. V = 40 volts.		
	$p = 0 \cdot 1$ millim.	$p = 0 \cdot 2$ millim.	Mean.
1600	(1) 5·0	(8) 5·0	5
1625	(2) 11·0	(9) 11·0	11
1650	(3) 25	(10) 23	24
1675	(4) 50	(11) 48	49
1700	(5) 108	(12) 100	104
1725	(6) 207	(13) 202	205
1750	(7) 412	(14) 410	411

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* In making a series of measurements, it is necessary to measure the resistance of the wire when cold from time to time, because at high temperatures the wire disintegrates and its resistance consequently rises with long continued heating.

The leak is the same at 0·2 millim. as at 0·1 millim., and it was verified carefully that no change occurred even on pumping down to 0·001 millim. The numbers in brackets refer to the order in which the measurements were made. The following table gives the values of the leaks in ampères and the temperatures deduced from the above numbers :—

	Temperature on platinum scale.	Temperature on Centigrade scale.	Leak in ampères.	Ampères per square centimetre of platinum.
	°	°		
(1)	1319	1375	$5 \cdot 8 \times 10^{-9}$	$1 \cdot 57 \times 10^{-8}$
(2)	1344·5	1408·5	$12 \cdot 7 \times 10^{-9}$	$3 \cdot 43 \times 10^{-8}$
(3)	1370	1442	$27 \cdot 6 \times 10^{-9}$	$7 \cdot 46 \times 10^{-8}$
(4)	1395·5	1476	$56 \cdot 4 \times 10^{-9}$	$15 \cdot 2 \times 10^{-8}$
(5)	1421	1510·5	$119 \cdot 6 \times 10^{-9}$	$32 \cdot 3 \times 10^{-8}$
(6)	1446·5	1545	236×10^{-9}	$63 \cdot 8 \times 10^{-8}$
(7)	1472	1580	473×10^{-9}	$128 \cdot 0 \times 10^{-8}$

It will be observed that as the temperature increases by nearly equal increments the current increases by nearly equal factors.

A theoretical proof of the formula $x = A\theta^{\frac{1}{2}}\epsilon^{-Q/2\theta}$ will now be given, and then it will be shown that the above results can be represented by this formula. The emission of negative corpuscles by hot platinum is analogous to the evaporation of a liquid, and whether the corpuscles come out of the metal or are produced at its surface, the number produced per second per unit area of platinum surface may be regarded as analogous to the number of molecules emitted per second by unit area of a liquid.

If p is the vapour pressure of a liquid at the absolute temperature θ, and L its latent heat of evaporation per gramme molecular weight, then $L = (v_2 - v_1)\theta\, dp/d\theta$, where v_2 = volume of vapour and v_1 = volume of liquid. Neglecting v_1 and putting $v_2 = R\theta/p$ we get $L = R\theta^2/p \,.\, dp/d\theta$. Let the internal work done in evaporating the liquid be Q and suppose $Q = Q_0 + a\theta$, where a is some constant, then $L = Q + pv$, so that we have

$$Q_0 + a\theta + R\theta = R\theta^2/p \,.\, dp/d\theta$$

or

$$\frac{Q_0 + (R + a)\theta}{\theta^2}\, d\theta = \frac{R\, dp}{p}.$$

Hence if p_1 is the vapour pressure at a temperature θ_1, and p_2 that at θ_2,

$$\log \frac{\theta_1{}^{R+a}\, p_2{}^{R}}{\theta_2{}^{R+a}\, p_1{}^{R}} = Q_0 \left(\frac{1}{\theta_1} - \frac{1}{\theta_2}\right).$$

Now $p = bmVN$, where m is the mass of a molecule, V the square root of the mean square of the velocities of all the molecules, and N the number leaving each square centimetre of the liquid surface per second and b a constant. But V^2 is proportional to θ, hence we may write $p = b'\text{N}\sqrt{\theta}$, where b' is a constant. Substituting this in the above equation we get

$$\log \frac{\theta_1^{\frac{1}{2}+\frac{\alpha}{\text{R}}}\text{N}_2}{\theta_2^{\frac{1}{2}+\frac{\alpha}{\text{R}}}\text{N}_1} = \frac{\text{Q}_0}{\text{R}}\left\{\frac{1}{\theta_1} - \frac{1}{\theta_2}\right\}.$$

In the case of hot platinum in an atmosphere of its own ions, if x is the current per unit area due to ions leaving the platinum surface, then $x = \text{N}e$, where e is the charge carried by one ion. Hence we get, putting R = 2, which is its value in small calories for one gramme molecular weight of any gas,

$$\log \frac{\theta_1^{\frac{1}{2}(1+\alpha)}x_2}{\theta_2^{\frac{1}{2}(1+\alpha)}x_1} = \frac{\text{Q}_0}{2}\left\{\frac{1}{\theta_1} - \frac{1}{\theta_2}\right\}.$$

The following table gives the values of Q calculated by means of this equation from the observed currents and taking $\alpha = 0$. The numbers in brackets indicate which pair of experimental numbers taken from the last table given above was used.

	Mean temperature.	Q.
	° C.	
(1, 2)	1392	138,500
(2, 3)	1425	132,000
(3, 4)	1459	124,400
(4, 5)	1493	133,500
(5, 6)	1528	126,300
(6, 7)	1563	132,000
	Mean . . .	131,100

The variations in Q are not greater than can be ascribed to experimental errors. The value of Q obtained corresponds to a fall of the ionic charge through 5·74 volts. RICHARDSON'S result for this quantity was 4·1 volts, but since the leaks which he obtained are about 1000 times greater than those given above, it was to be expected that his value of Q would be smaller than that which my experiments lead to.

The value of the constant A in the formula $x = \text{A}\theta^{\frac{1}{2}}\epsilon^{-\text{Q}/2\theta}$, calculated from the value of the current per square centimetre at 1580° C., is $6{\cdot}9 \times 10^7$, so that the equation becomes

$$x = 6{\cdot}9 \times 10^7\theta^{\frac{1}{2}}\epsilon^{-131{,}100/2\theta}.$$

The following table contains a comparison of the currents calculated by means of this formula and those found experimentally :—

Temperature.	Current per square centimetre found.	Current calculated.
°C.		
1375	1.57×10^{-8}	1.49×10^{-8}
1408·5	3.43×10^{-8}	3.33×10^{-8}
1442	7.46×10^{-8}	7.18×10^{-8}
1476	15.2×10^{-8}	15.3×10^{-8}
1510·5	32.3×10^{-8}	31.8×10^{-8}
1545	63.8×10^{-8}	64.5×10^{-8}
1580	128×10^{-8}	128.5×10^{-8}

The calculated and observed currents agree very well, so that we may conclude that a in the formula $x = A\theta^{\frac{1}{2}(1+a)}\epsilon^{-Q_0/2\theta}$ is really zero or nearly so. It is easy to show that the value of a cannot be greater than unity in order for the observed and calculated results to agree as well as they do. Consequently, since $Q_0 = 131{,}100$, Q does not vary as much as 1 part in 100,000 per degree centigrade.

The value found for Q is slightly more than double that found previously ('Phil. Trans.,' A, vol. 197, p. 430) for the work required to ionize a gramme molecular weight of air in contact with hot platinum.

All that it is necessary to assume to deduce the equation used to calculate Q either for the positive leak in air at atmospheric pressure, or for the negative leak in a vacuum, is that ions are produced in some way at the surface of the hot platinum. The results just described cannot, therefore, be regarded as any additional evidence in favour of the view that the negative leak from hot platinum is due to negative corpuscles coming out of the metal; they are, however, consistent with this view.

The positive leak in air at atmospheric pressure can be represented by the formula

$$x = A'\theta^{\frac{1}{2}}\epsilon^{-60{,}000/2\theta}.$$

The value of A′ may be obtained from the observation that the positive leak at 1550° C. is double the negative leak. This gives $A' = 0{\cdot}47$. The temperature at which the two leaks with the particular wire used were equal is, therefore, given by by the formula

$$6{\cdot}9 \times 10^{7}\theta^{\frac{1}{2}}\epsilon^{-131{,}100/2\theta} = 0{\cdot}47\,\theta^{\frac{1}{2}}\epsilon^{-60{,}000/2\theta},$$

which gives $\theta = 1895$ or 1622° C. Above 1622° C. the negative leak with this wire was greater than the positive leak, and below this temperature less.

At low pressures the positive leak is smaller. If we assume that it varies as the pressure, then it will be given at any pressure by the formula

$$x = \frac{0{\cdot}47p}{760}\,\theta^{\frac{1}{2}}\epsilon^{-60{,}000/2\theta}.$$

At 1 millim. pressure this gives $x = 6{\cdot}2 \times 10^{-4}\theta^{\frac{1}{2}}\epsilon^{-60{,}000/2\theta}$, and the temperature at which the positive and negative leaks are equal comes out 1127° C. These results afford an explanation of ELSTER and GEITEL'S observation that an insulated conductor near a hot wire becomes positively charged in air at atmospheric pressure, but negatively charged at low pressures.

The results described above show that the negative leak from a platinum wire is very little affected by the presence of air, nitrogen, or water vapour. It was found that putting some mercury into the tube containing the hot wire, so that it was filled with mercury vapour, increased the leak considerably at very high temperatures. The whole tube, of course, gets hot, so that the pressure of the mercury vapour must have been very considerable in this experiment. The following table gives the results obtained :—

Temperature.	Negative leak before introducing mercury.	Negative leak after introducing mercury.
° C.	divisions.	divisions.
1728	120	400
1645	37	78
1566	12	13

Thus above 1600° C. the presence of mercury in large quantities appears to increase the negative leak, but below this temperature it is without effect. The very small amount of mercury vapour ordinarily present can, therefore, safely be assumed to have no effect below 1600° C.

With different pieces of pure platinum wire cut from the same sample and treated in the same way with nitric acid fairly concordant results were obtained. Nevertheless, long continued heating of the wire diminishes the negative leak, provided the air is frequently changed. If the wire is simply left standing in air at a low pressure for a long time the leak is often greater than before on again heating the wire. The process of cleaning the wire with nitric acid and frequently changing the air in the apparatus diminishes the negative leak something like a thousand times usually. Thus the leaks given above are about one thousand times smaller than those given by RICHARDSON at the same temperatures.

These facts naturally suggest the question whether more thorough cleaning of the wire and purification of the air would not still further diminish the negative leak. To test this a wire was mounted as before and boiled in HNO_3 for about an hour. It was then left in the HNO_3 for 24 hours and a current passed from the wire to the cylinder through the HNO_3, so that the NO_3 ions were set free on the wire. The tube was then washed out and the leak measured in pure air at a low pressure, as before. The following table gives the results obtained :—

Temperature.	Negative leak per square centimetre of platinum.
° C.	ampères.
1686	4×10^{-8}
1651	2×10^{-8}
1616	1×10^{-8}

Thus the more thorough treatment of the wire with HNO_3 reduced the negative leak to about $\frac{1}{250}$th of that previously obtained, but the rate of variation of the leak with the temperature remained almost unchanged. These numbers give $Q = 155,000$ and $A = 6 \times 10^6$.

If $A = 6 \times 10^6$, then, on RICHARDSON'S theory, the number of corpuscles (n) in a cubic centimetre of the platinum would be 8×10^{19}. PATTERSON (*loc. cit.*) obtained $n = 10^{22}$ by experiments on the variation of the resistance of platinum in a magnetic field. It appears, therefore, that n cannot really be deduced from the constant A.

On one occasion some phosphorus pentoxide accidentally got into the tube containing the hot wire, and the negative leak was increased enormously by its presence. The current at 1490° C. was about 4×10^{-4} ampère, or 10^{-3} ampère per square centimetre. The negative leak was therefore increased about one million times by the presence of the phosphorus pentoxide. Now ordinary phosphorus pentoxide usually contains phosphorus acid and other impurities, and may give off some vapours when kept in a vacuum. If any such vapours were present in the tube containing the hot wire, this result shows that they would produce a leak of negative electricity from it.

It is clear, therefore, that minute traces of various substances such as hydrogen, phosphorus pentoxide, and alkali salts produce a large increase in the negative leak from hot platinum, and that the more thorough the precautions taken to remove traces of such substances the smaller the leak becomes. I have not succeeded in reducing the leak to less than 1 part in 250,000 of that observed by RICHARDSON, but I have little doubt that, if all traces of impurities could be got rid of, the negative leak in air would be reduced to a still smaller value.

There is considerable evidence in favour of the view that the negative leak in air is due to the presence of traces of hydrogen in the platinum.* It will be shown in the next section that the negative leak in hydrogen is enormous compared with that in air, and that at low pressures it is proportional to the pressure of the hydrogen. When the pressure of the hydrogen is very small, the value of Q in the formula $x = A\theta^{\frac{1}{2}}\epsilon^{-Q/2\theta}$ is nearly equal to its value in air, which makes it very probable that the small negative leak in air or a vacuum is due to the presence of traces of

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* This view was suggested long ago by BERLINER, 'Wied. Ann.,' vol. 33, p. 289 (1888).

hydrogen. It is well known that it is almost impossible to entirely get rid of the last traces of hydrogen from a vacuum tube.

This view is confirmed by the effect of nitric acid on the negative leak, for nitric acid oxidises hydrogen. It is also in agreement with the fact that the negative leak in air at low pressures falls off during long-continued heating of the wire. The rate at which the leak falls off diminishes as the leak gets smaller, so that with wires well cleaned with nitric acid the rate of fall is not very great.

Platinum wires not specially cleaned evolve gas when heated in a vacuum, and since hydrogen is the only gas which platinum is known to occlude in any quantity, this gas is no doubt hydrogen. It is practically impossible to get rid of this evolution of gas merely by long continued heating and pumping out. Thus WIEN (*loc. cit.*) states that his wires continued to evolve gas after weeks of heating in an extremely good vacuum. My wires, which had been treated with nitric acid and heated in air which was repeatedly changed, did not evolve anything like as much gas as those not so treated.

(4.) *The Leak in Hydrogen.*

In the experiments in hydrogen at low pressures the hydrogen was obtained sufficiently pure by allowing it to diffuse through platinum. A spiral of fine platinum tubing, 0·5 millim. external and 0·25 millim. internal diameter, was sealed on the apparatus at one end and the other end fused up. On heating this spiral in the flame of a spirit lamp, the hydrogen present in the flame diffused through into the apparatus. In this way the pressure could be increased several tenths of a millimetre in one minute when the total capacity of the apparatus was about 300 cub. centims.

The spectrum of a discharge in hydrogen let in in this way was examined, and appeared to consist almost entirely of the hydrogen lines. It was thought that faint traces of the CO spectrum could sometimes be seen, but it was not certain that any CO entered through the platinum spiral. For experiments at pressures above 10 millims. the hydrogen was obtained from pure zinc and hydrochloric acid, and passed into the apparatus through tubes containing soda-lime.

In some experiments the hydrogen was further purified by means of sodium let into the apparatus by electrolysis through hot glass, in the manner described by E. WARBURG.* This method was found to work very well, and a deposit of metallic sodium could easily be obtained. The sodium, of course, absorbed some hydrogen as well as the oxygen and other impurities possibly present.

The apparatus for this experiment is shown in fig. 6. A is the tube containing the hot wire, B a tube tightly packed with gold leaf, and C the sodium tube. This latter consisted of a thin glass tube about 15 centims. long and 1·5 centim. in diameter, with an aluminium wire electrode along its axis, as shown. It was immersed in

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[*] 'Wied. Ann.,' vol. 40, p. 1 (1890).

sodium amalgam contained in a test-tube. The test-tube was supported on asbestos wool in a thick brass tube DE, the lower end of which was closed by iron wire gauze. The gauze was heated by a small Bunsen flame and the temperature of the amalgam kept at about 280° C. At pressures above about 1 millim. a current from about 400 cells could then be passed from the amalgam to the aluminium electrode, and sodium deposited, forming a metallic mirror in the upper parts of the tube C. The discharge in C was a brilliant yellow colour, giving the D line. If oxygen was present, sodium oxide was formed, and the brilliant yellow light did not appear so strongly at first. This process did not appear to have any particular effect on the amount of leak obtained from the hot wire in hydrogen at any pressure, so that we may conclude that the increase of the leak due to letting in hydrogen is not due to the presence of impurities in the gas.

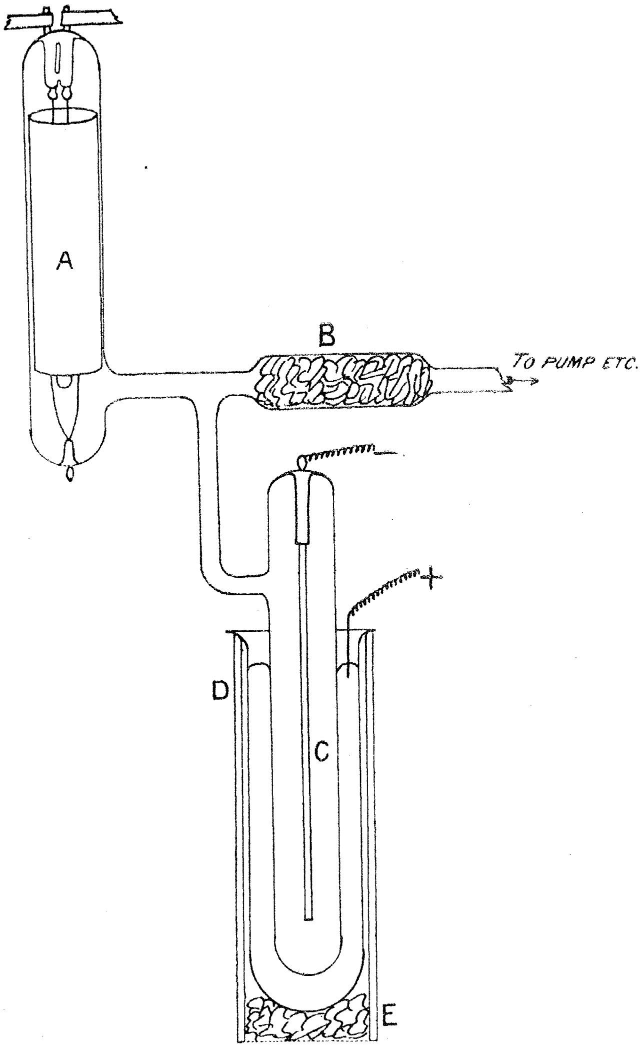

Fig. 6.

The following table gives some numbers showing the effect on the negative leak at a constant temperature of about 1350° C., due to letting in hydrogen :—

Pressure in millims. of mercury.	Current with 120 volts.
	divisions.
0·0006	10
0·0015	20
0·0033	40
0·0053	50
0·0080	75
0·014	110

This increase of the leak with the pressure cannot be ascribed to ionization by collisions, for at the highest pressure used, one negative ion can only produce 0·2 fresh negative ion in going 1 centim. The leak in air at 1350° C. from a clean wire would have given about $\frac{1}{250}$th division in the above experiment. Thus the leak in hydrogen at 0·014 millim. in this experiment was more than 25,000 times the leak from a very well cleaned wire at the same temperature in air.

In the experiment just described, the hydrogen was let in at intervals through the platinum spiral, so that the pressure increased during the experiment. Another way is to let in hydrogen to the highest pressure desired and then pump out during the experiment. It was found that the results were not the same in the two cases. On pumping down, the leak falls, but not so quickly as it rises on letting in the gas. It was soon discovered that the leak is not always a single-valued function of the pressure, but depends also on the previous treatment of the wire. The results can be explained on the hypotheses—

(1.) That the wire absorbs an amount of hydrogen depending on the pressure and temperature, and that when these are changed it takes a considerable time for equilibrium between the gas in the wire and that outside to be established; and

(2.) That the leak at any temperature depends on the amount of hydrogen in the wire, and not directly on the pressure outside.

Consequently, if the equilibrium is established at a particular temperature and pressure, then if the temperature is raised or the pressure lowered the leak should not be steady at first under the new conditions, but should gradually fall off, in consequence of gas leaving the wire, until equilibrium is again established. On the other hand, if the temperature is lowered or the pressure increased, the leak should gradually rise until equilibrium is again established. Experiments showed that these effects occurred exactly in the way expected.

The following tables give the results of some measurements of the negative leak in hydrogen, showing the effects of suddenly changing the temperature or pressure :—

Time.	Balancing resistance (p = 0·10 millim.).	Current.
minutes.		
12	3500	110
15	3500	100
16	3500	102
18	3500	102
19	3400	28
22	3400	30
23	3300	11
25	3300	15
28	3300	19
30	3300	22
33	3300	22

The above numbers show the effect of lowering the temperature at constant pressure. The current drops and then gradually rises, ultimately becoming steady when equilibrium has been established. Of course it is necessary to be sure that equilibrium has been reached at the higher temperature before changing to the lower temperature, in order to observe this effect, and to get equilibrium at the higher temperature may take a long time in some cases.

Time.	Balancing resistance (p = 0·34 millim.).	Current.
minutes.		
6	3200	16
8	3200	15
11	3600	1800
16	3600	1200
23	3600	900

These numbers show the effect of suddenly raising the temperature at constant pressure in hydrogen.

Time.	Pressure (Balancing resistance = 3700).	Current.
minutes.		
30	0·071	1100
60	0·071	1100
98	0·071	1200
114	0·012	1200
116	0·012	1000
118	0·012	720
157	0·012	280

The above numbers show the effect of lowering the pressure at constant temperature.

Time.	Pressure (Balancing resistance 3800).	Current.
minutes.		
47	0·0006	540
49	0·032	600
51	0·032	1740
59	0·032	1860
60	0·032	1980

The above numbers show the effect of raising the pressure at constant temperature. The effect of raising the temperature of the wire is most marked when a wire which has been standing at the ordinary temperature in hydrogen is suddenly heated to a high temperature. In this case an enormous current is obtained for a short time. Thus a wire at a certain temperature in hydrogen at 0·045 millim. pressure gave a current of $1·6 \times 10^{-6}$ ampère when equilibrium had been established. It was then allowed to stand cold for 20 hours when, on raising the temperature to the same value, the leak was at first more than 10^{-2} ampère, and only fell to its original value after long continued heating.

Some experiments were tried in which the temperature of the wire was raised by equal steps through a series of values and then lowered again through the same series of values, several times. The following are the results obtained in an experiment of this kind at a pressure of 0·112 millim. The numbers in brackets are the times in minutes at which the currents were measured.

Temperature.	Current.				
° C.					
1520	↓	550 (50) 770 (46)	↘	500 (90) 630 (87)	↘
1459	460 (12) 400 (15)	300 (45) 410 (40)	200 (51) 210 (55)	190 (85) 220 (81)	
1400	150 (20)	150 (40) 270 (35)	67 (57) 75 (60)	65 (80) 66 (76)	65 (95)
1341	42 (25)	42 (35)	24 (61) 25 (66)	24 (75) 25 (72)	
1284	12 (30)	↗	8 (67) 9 (70)	↗	

It will be noticed that when the temperature has just been raised the leak falls on waiting, whereas when it has just been lowered the leak rises on waiting. In spite of this, however, the numbers at each temperature keep fairly concordant towards the end of the experiment, which shows that they must approximately represent the variation of the leak with the temperature for a constant state of the wire with regard to the hydrogen. This means that the time between the observations was so short that very little change in the amount of hydrogen in the wire occurred during the latter measurements, in spite of the changes made in the temperature. This may be due to the amount of hydrogen absorbed by the wire varying very slowly with the temperature at the temperatures used in this experiment. It is stated in ROSCOE and SCHORLEMMER's 'Chemistry' (vol. 1, p. 139) that platinum at a red-heat absorbs 3·8 times its volume of hydrogen, and at 100° C. only 0·76 times its volume. If the volume absorbed were proportional to the absolute temperature, then platinum in equilibrium with hydrogen at any particular temperature would be in equilibrium at any other temperature. According to ROSCOE and SCHORLEMMER, the volume absorbed increases more rapidly than the absolute temperature up to a red heat, but on the other hand platinum certainly loses some of its hydrogen when heated to near its melting-point; consequently there must be a region of temperature between a red heat and the melting-point where the actual amount of hydrogen absorbed is nearly independent of the temperature at constant pressure. The very small variations with time in the latter of the above experiments seem to show that the range of temperature used in this experiment lies in this region. The latter numbers in the above experiment have been reduced to ampères per square centim. The results are given in the following table. The pressure in this experiment was 0·112 millim.

Temperature.	Current per square centimetre.
° C.	ampères.
1520	$7·55 \times 10^{-5}$
1459	$3·02 \times 10^{-5}$
1400	$1·15 \times 10^{-5}$
1341	$0·442 \times 10^{-5}$
1284	$0·145 \times 10^{-5}$

The formula $\frac{Q}{2}\left\{\frac{1}{\theta_1}-\frac{1}{\theta_2}\right\}=\log\frac{x_2\theta_1^{\frac{1}{2}}}{x_1\theta_2^{\frac{1}{2}}}$, when these numbers are substituted in it, gives Q = 85,900. A similar series of experiments done at a pressure of 0·0013 millim. of hydrogen gave the following results:—

Temperature.	Current per square centimetre.
° C.	ampères.
1516	127×10^{-8}
1457	70×10^{-8}
1400	$20 \cdot 4 \times 10^{-8}$
1343	$5 \cdot 0 \times 10^{-8}$
1287	$1 \cdot 6 \times 10^{-8}$

These numbers give Q = 120,000.

The variation of the negative leak with the temperature, using 40 volts, was also measured at a pressure of 133 millims. The following table gives the results :—

Temperature.	Current per square centimetre.
° C.	ampères.
1310	192×10^{-6}
1187	$33 \cdot 4 \times 10^{-6}$
1069	$5 \cdot 66 \times 10^{-6}$
961	$1 \cdot 04 \times 10^{-6}$

These numbers give Q = 36,000. The leak in air or in a vacuum, using a wire well cleaned with HNO_3, at 1310° C. is only about 2×10^{-11} ampère per square centimetre.

The following table gives the values of Q found at the different pressures, and also the approximate values of the constant A in the formula $x = A\theta^{\frac{1}{2}}\epsilon^{-Q/2\theta}$:—

Pressure of hydrogen.	Q.	A.
millims.		
0 (wire cleaned with HNO_3 for 24 hours)	155,000	6×10^{6}
0 (wire cleaned with HNO_3 for one hour)	131,100	$6 \cdot 9 \times 10^{7}$
0·0013	120,000	10^{7}
0·112	85,900	$5 \cdot 3 \times 10^{4}$
133·0	36,000	0·1

Thus the presence of hydrogen diminishes the amount of energy required in the production of the negative ions and consequently greatly increases the leak. It seems very probable from the above results that the action of the hydrogen depends on its absorption by the platinum, for the leak obtained depends apparently on the amount of gas absorbed by the wire and only indirectly on the gas pressure in the apparatus. The leak, when there is equilibrium between the wire and gas, is nearly proportional to the pressure at low pressures, but increases less quickly than the pressure at higher pressures up to a few millimetres. The leaks in the two sets of observations given above at 0·0013 millim., and at 0·112 millim., are nearly in the ratio of the pressures. If a large P.D. is used ionization by collisions comes in at higher pressures just as with air, and the current rises with the pressure, at pressures of a few millimetres, more quickly with large P.D.'s than with small. The following table shows the variation of the leak at a constant temperature of 1340° C. with the pressure up to 760 millims., using a P.D. of 40 volts, which is too small to produce ionization by collisions :—

Pressure.	Current.
millims.	ampères.
766	3000×10^{-6}
450	1500×10^{-6}
156	222×10^{-6}
14	60×10^{-6}

At high pressures the leak is again nearly proportional to the pressure.

Fig. 7 shows the variation of the negative leak in hydrogen with the P.D. at pressures of 133 and 766 millims. The current at 133 millims. is nearly saturated

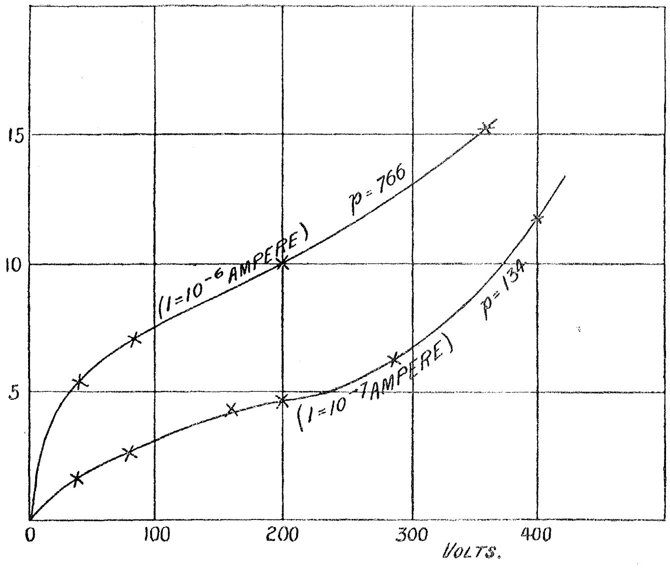

Fig. 7.

with about 200 volts, but then begins to rise rapidly owing to ionization by collisions coming in. The upper part of the curve can be represented approximately by the formula obtained in the section on the leak in air.

The positive leak, like the negative leak, is much increased by the presence of hydrogen. With clean wires it is, nevertheless, inappreciable on a galvanometer, except at pressures of several millimetres. The following values of the positive leak were obtained at 1300° C., using 160 volts :—

Pressure.	Positive leak.
millims.	ampères.
766	40×10^{-9}
156	24×10^{-9}
9	4×10^{-9}

The following table gives the values of the negative leak at a temperature of 1400° C. in hydrogen at several pressures :—

Pressure.	Current per square centimetre.
millims.	ampères.
133	1×10^{-3}
0·112	$1{\cdot}2 \times 10^{-5}$
0·0013	2×10^{-7}
0	$1{\cdot}2 \times 10^{-10}$

The last number is the leak from a very well cleaned wire in air at a low pressure. The leak obtained by Mr. RICHARDSON at 1400° C. was about 3×10^{-5} ampère per square centimetre, with a gas pressure of about 0·1 millim.

(5.) *The Leak from Palladium in Hydrogen.*

Some measurements were made of the leak from a palladium wire 0·2 millim. in diameter and 13 centims. long. The wire was left about 20 hours in hydrogen at a few millimetres pressure ; after mounting it and before it was heated the pressure was reduced to 0·0003 millim. The balancing resistance (R) of the wire was 320 ohms at 18° C. On heating to R = 1100, the negative leak with 200 volts was 3 scale divisions (1 division = 3×10^{-8} ampère) and the positive leak 750 divisions. After five minutes the leaks fell to 0·5 and 130 divisions respectively, while the pressure rose to 0·022 millim. The positive leak continued to fall with the time, and ultimately, after several hours' heating, became only 6 divisions with R = 1550 ohms. It was found that the positive leak was quite independent of the pressure of the hydrogen, while the negative leak increased nearly proportionally to the pressure at small pressures. Fig. 8 shows the variation of the leaks (P.D. = 200 volts) with the pressure, the resistance R being 1400 ohms.

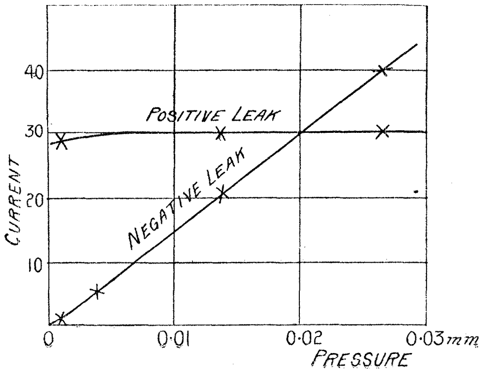

Fig. 8.

The palladium was found to "splutter" very much when hot, so that its resistance rose rapidly. The very large value of the positive leak from it when first heated is no doubt analogous to the positive leak from platinum not specially cleaned when it is first heated.

(6.) *Summary of Principal Results.*

(1.) The negative leak from a hot platinum wire in air, nitrogen, or water vapour is independent of the gas pressure, unless ionization by collisions occurs, and is the same as the negative leak from the same wire in a good vacuum.

(2.) The variation of the negative leak in air with the P.D. and pressure at constant temperature can be explained on the hypothesis that the negative ions produce ionization by collisions with the air molecules.

(3.) The number of collisions made by a negative ion probably varies inversely as the absolute temperature at constant pressure.

(4.) The variation of the negative leak per square centimetre with the temperature can be expressed by the equation $x = A\theta^{\frac{1}{2}}\epsilon^{-Q/2\theta}$, where x is the current in ampères, θ the absolute temperature, and Q and A are constants. For a wire very well cleaned with HNO_3, Q is 155,000 and A is about 6×10^6.

(5.) The negative leak in hydrogen is much larger than that in air or in a vacuum. At low pressures it is nearly proportional to the pressure of the hydrogen.

(6.) The presence of the hydrogen changes the value of the constants Q and A, the following being the values obtained at different pressures :—

Pressure.	Q.	A.
0	155,000*	6×10^6
0·0013	120,000	1×10^7
0·112	85,900	$5·3 \times 10^4$
133·0	36,000	0·1

(7.) It is extremely probable that the negative leak in air or in a vacuum is due to traces of hydrogen or other substances in the wire. The leak can be reduced to $\frac{1}{250,000}$th part of its ordinary value by taking precautions to remove such traces.

(8.) On first heating a positively charged palladium wire in a vacuum it can discharge positive electricity. The rate of discharge falls off rapidly with time and ultimately becomes inappreciable. A similar effect sometimes occurs with platinum, but the amount of the leak is very small and it disappears in a few seconds. The

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[* Of the three values of Q obtained at low pressures (viz. 155,000, 131,000 and 120,000) the value 131,100 is probably nearest the truth. The value 155,000 depends on measurements of very small currents and is probably too large. See Appendix.]

negative leak in hydrogen is proportional to the pressure at low pressures with palladium as with platinum.

(9.) In air and hydrogen, at pressures above several millimetres, there is a permanent positive leak from hot platinum which increases with the pressure. This leak is larger in hydrogen than in air at the same temperature.

(7.) *Conclusion.*

The question of most interest in connection with the leak of electricity from hot platinum is the method of production of the ions. RICHARDSON (*loc. cit.*) has proposed the theory that the negative leak is due to the escape of the corpuscles which, on the ionic theory of metallic conduction, metals contain. These corpuscles are supposed to move about freely inside the metal and to have a distribution of velocities the same as the molecules of an ordinary gas. All corpuscles entering the surface layers of the metal with a velocity component perpendicular to the surface greater than a definite value are supposed to escape; and from these assumptions a formula of the type $x = \mathrm{A}\theta^{\frac{1}{2}}\epsilon^{-\mathrm{Q}/2\theta}$ can be deduced, as RICHARDSON has shown. According to this theory the number of corpuscles in a cubic centimetre of the metal can be calculated from the value of the constant A, and according to this view the leak depends only on the state of the platinum and not on the surrounding gas.

The experiments described in this paper show that the phenomena cannot be explained completely by such a simple theory. There seems to be no doubt that the negative leak from hot platinum is due to the emission of negatively charged corpuscles or electrons, but the number of these emitted depends on the gases and other substances present at the surface of the platinum. With clean platinum in air at a low pressure there is, comparatively speaking, very little leak of electricity either positive or negative. In air at high pressures there is a small leak of positive electricity, while in hydrogen there is a comparatively enormous negative leak. In Mr. RICHARDSON'S experiments the gas present appears to have been that evolved by the hot metal, and so probably contained hydrogen.* This is, no doubt, the explanation of the comparatively very large currents which he obtained.

When occluded hydrogen molecules are present on the surface of the platinum, we may suppose that each molecule or atom of hydrogen has a corpuscle associated with it, and that these corpuscles have an energy distribution similar to the energy distribution of the molecules of a gas. If those corpuscles, having more than a certain amount of energy, are able to escape from the surface, these suppositions account for the existence of a negative leak in hydrogen.†

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* In RICHARDSON'S experiments the gas pressure rose considerably when the temperature of the wire was raised, showing that gases were being evolved by the wire.

† When a molecule of hydrogen has lost its corpuscle it may be supposed to combine with one of the corpuscles present in the platinum, so that on this view the hydrogen molecule serves as a sort of stepping stone to enable the corpuscles to escape from the platinum. [See Appendix.]

We may suppose also that the energy necessary to enable a corpuscle to escape from a hydrogen atom at the surface falls off as the concentration of the hydrogen atoms on the surface increases. In this way the diminution of Q by the presence of hydrogen can be explained. According to this view the number of corpuscles in a cubic centimetre of the metal cannot be deduced from the constant A.

It seems probable that the temporary positive leak from platinum and palladium, when they are first heated, is due to the presence ot a small amount of some decomposable compound or volatile impurity. This view is supported by the fact that platinum wires, well cleaned with nitric acid, do not give this effect to an extent appreciable on the galvanometer.

The positive leak in gases at high pressures is no doubt due to ionization of the gas molecules at the surface of the platinum.

In conclusion, I wish to say that my best thanks are due to Professor J. J. THOMSON for advice and kindly interest in these experiments while they were being carried out at the Cavendish Laboratory.

APPENDIX.

Added October 3, 1903.—Some interesting conclusions can be drawn from the way in which the negative leak from hot platinum or palladium in hydrogen varies with the pressure of the hydrogen. We have seen that when the pressure of the hydrogen is less than about 0·02 millim. the leak is nearly proportional to the pressure. Consider two temperatures θ_1 and θ_2. Let the leak at the temperature θ_1 be represented by the equation $x_1 = B_1 p$, where x_1 is the current per square centim., p the pressure, and B_1 a constant. Let the corresponding equation at θ_2 be $x_2 = B_2 p$. If these expressions for x_1 and x_2 are substituted in the equation

$$Q\left\{\frac{1}{\theta_1} - \frac{1}{\theta_2}\right\} = 2 \log \frac{\theta_1^{\frac{1}{2}} x_2}{\theta_2^{\frac{1}{2}} x_1},$$

we see that Q is independent of the pressure of the hydrogen. Consequently, when the pressure of the hydrogen is small, the energy required for the liberation of a corpuscle is independent of the pressure of the hydrogen.

Consider now the formula $x = A\theta^{\frac{1}{2}}\epsilon^{-Q/2\theta}$. Since Q is independent of p and $x = Bp$, it follows that A is proportional to p. It is clear, therefore, that A cannot be regarded as proportional to the number of corpuscles in a cubic centimetre of the platinum, because this latter number must be independent, or very nearly so, of p. A is evidently proportional to the number of corpuscles which are in a position to contribute towards the leak, so that we may conclude that this latter number is proportional to the amount of hydrogen present when this amount is small. Thus we are led to the conclusion that it is only those corpuscles which are in some way associated with hydrogen molecules or atoms which are able to escape from the platinum, at the temperatures at which it is possible to make observations.

In a note to his paper on "The Electrical Conductivity Imparted to a Vacuum by Hot Conductors" ('Phil. Trans.,' A, vol. 201, pp. 497–549) Mr. RICHARDSON suggests that the effect of hydrogen on the negative leak which I have observed can be explained on his theory by supposing that the hydrogen diminishes Q while A remains constant. But, as we have just seen, the fact that the leak is proportional to p shows that Q is constant and A proportional to p. When p is greater than about 0·02 millim. it is found that Q does diminish as p increases, but A does not remain constant.

Mr. RICHARDSON also suggests that my process of cleaning the platinum with nitric acid may deposit a layer of negatively charged oxygen on it which would increase Q and so diminish the leak. The leak can, however, be reduced without treating the wire with nitric acid. If the wire is simply heated in a good vacuum the leak falls off with time; and if the gases evolved by the wire are removed, the leak can be reduced in this way to as small a value as can be obtained by treating the wire with nitric acid. The nitric acid process was adopted because it enabled the hydrogen to be got rid of without long continued heating which causes the wire to disintegrate.

[Although it appears from the experiments that the negative leak obtained from hot platinum at low pressures is due to the presence of hydrogen or other substances, it is, of course, possible that with perfectly pure platinum at a sufficiently high temperature some negative leak would be obtained due to the emission of corpuscles by the platinum alone. Mr. RICHARDSON'S results for carbon, which show that there is a large emission of corpuscles from hot carbon even at very low pressures, make it probable that there would be a similar emission in the case of pure platinum at sufficiently high temperatures. The author has recently made some experiments with carbon which, as far as they have gone, confirm Mr. RICHARDSON'S results for that substance.]