The Effect of Hydrogen on the Discharge of Negative Electricity from Hot Platinum

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VI. *The Effect of Hydrogen on the Discharge of Negative Electricity from Hot Platinum.*

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THE effect of hydrogen on the discharge of negative electricity from hot platinum was examined by the writer in 1903 ('Phil. Trans.,' A, 352, vol. 202, 1903); it was found to produce a very large increase in the current carried by the discharge. At pressures below 0·1 millim. of mercury the leak was found to increase with the pressure and to fall when the pressure was reduced. The experiments in the paper just referred to were all done with nearly new platinum wires which had not been heated in the gas for any great length of time, because it was known that long continued heating caused the wire to disintegrate, its surface becoming covered with a network of cracks. The present paper contains an account of a series of experiments in which wires were heated for long periods in hydrogen, so that any gradual changes in the effect of the hydrogen could be observed. It appears that continued heating in hydrogen alters the character of the effects observed, so that the behaviour of an old wire may be very different from that of a new one.

In the previous paper I suggested that the effect of hydrogen was due to the presence of hydrogen in the surface layer of the platinum, and this view appeared to be supported by the facts. Professor O. W. RICHARDSON ('Phil. Trans.,' A, 413, vol. 207, 1906) puts forward a different theory, viz., that the hydrogen alters the state of the platinum, so that the effect may remain even after the removal of all the hydrogen.

If the wire is heated in oxygen the large leak always immediately disappears, so Professor RICHARDSON supposes that the oxygen destroys the change in the state of the platinum produced by the hydrogen. According to the other view the oxygen burns up the hydrogen present at the surface of the platinum.

The very large increase in the negative leak produced by hydrogen has been recently confirmed by several observers, including O. W. RICHARDSON (*loc. cit.*), F. HORTON* and G. H. MARTYN.†

Measurements of the current at different temperatures enable the energy required

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* 'Phil. Trans.,' A, 416, 1907.

† 'Phil. Mag.,' August, 1907.

for the liberation of an ion to be calculated. This method of estimating this quantity was first used ('Phil. Trans.,' A, 296, 1901) by the writer to find the energy required to liberate one gram-molecule of ions formed at the surface of hot platinum in air at atmospheric pressure. The mean result then obtained was 60000 calories. RICHARDSON (*loc. cit.*) finds 49200 calories for the same quantity.

It has been suggested that in my experiments the current was very small compared with the saturation current, and that the variation of the current with the temperature was determined by the variation of the velocity of the ions with the temperature and not by the variation of the ionisation. But curves are given in my paper, showing the variation of the current with the E.M.F., which show that 220 volts produced very approximate saturation, and that with 40 volts the current was about one quarter of the saturation current and was then very nearly proportional to the E.M.F. The value 60000 calories was obtained from measurements of the currents due to 40 volts. If the saturation currents, which are also given in my paper, are used instead, the mean result is 50000.

The apparatus used in the present experiments was essentially similar to that employed in the previous investigation. The wire was heated by passing a current through it, and its temperature was estimated by measuring its resistance with a Wheatstone bridge. The wire consisted of a loop of about 11 centims. of wire 0·1 or 0·2 millim. in diameter. The loop was surrounded by an aluminium cylinder contained in a glass tube which could be exhausted. The current from the cylinder to the wire was measured with a galvanometer provided with suitable shunts.

The first part of this paper contains a discussion of the former results with new wires. The paper is divided into the following sections:—

(1) The effect of hydrogen on the leak from new wires.
(2) Variation of the current with the pressure at constant temperature.
(3) Variation of the current with the temperature.
(4) Variation of the current with the time.
(5) The effect of hydrogen on the resistance of the platinum.
(6) Effects due to passing a self-luminous discharge.
(7) A comparison of the negative leak in hydrogen with the positive leak in oxygen.
(8) The theory of the negative leak.
(9) A theory of the variation of the energy necessary for the liberation of an ion with the temperature.
(10) Conclusion.

1. *The Effect of Hydrogen on the Leak from New Wires.*

The variation of the negative leak with the temperature can be represented by the formula $x = \mathrm{A}\theta^{\frac{1}{2}}e^{-\mathrm{Q}/2\theta}$, where x denotes the current per square centimetre, θ the absolute temperature, and A and Q are constants.

It was shown in the previous paper that Q and A depend on the pressure of the hydrogen. I propose now to consider this variation of A and Q, and it will be shown that it can be deduced from the assumption that $x = \mathrm{B}p^n$, where p denotes the pressure of the hydrogen, and B and n depend only on the temperature.

The values of A and Q given in the previous paper were calculated from some of the observed currents, and when put in the formula $x = \mathrm{A}\theta^{\frac{1}{2}}e^{-\mathrm{Q}/2\theta}$ give nearly the observed values of x. I have recalculated them, using all the observations in turn, and taking the mean of the results. The new values of Q so obtained from the currents and temperatures given in the previous paper differ to some extent from the old values, and since a small error in Q produces a large error in A, the new values of A are considerably different. The following table contains the new values:—

Gas.	Pressure.	Q.	A.
	For a Wire Treated with HNO_3 for 24 Hours.		
Air	Small	145000	$1 \cdot 14 \times 10^8$
	Wire Boiled in HNO_3 for 1 Hour.		
Air	Small	131000	$6 \cdot 9 \times 10^7$
H_2	0·0013 mm.	110000	10^6
H_2	0·112 ,,	90000	5×10^4
H_2	133 ,,	56000	2×10^2

The new values, of course, represent the results a little better than the old ones.

Any one measurement of the negative leak is subject to a large possible error, but since the values of Q are obtained from a considerable number of observations, it is probable that the effects of errors are to some extent eliminated in the values of Q. For this reason I have attempted to establish the relation between the leak and the pressure by means of the values found for Q and A.

The results given in the previous paper (*loc. cit.*) on the variation of the leak with the pressure of the hydrogen show that the leak is proportional to a power of the pressure less than unity.

In fig. 1 the logs of the pressures and currents given on p. 265 are plotted, and the points fall nearly on a straight line, the slope of which shows that the current varies as $p^{0 \cdot 75}$ nearly.

Let x denote the current per square centimetre of platinum, then at each constant temperature assume $x = \mathrm{B}p^n$, where p denotes the pressure of the hydrogen and B and n depend only on the temperature. This is to be consistent with $x = \mathrm{A}\theta^{\frac{1}{2}}e^{-\mathrm{Q}/2\theta}$, where θ denotes the absolute temperature and A and Q depend only on the pressure.

Hence A must be equal to Kp^{-c}, and Q must be equal to $P-2\alpha \log p$, where K and P are constants. Also $n = \alpha\theta^{-1}-c$.

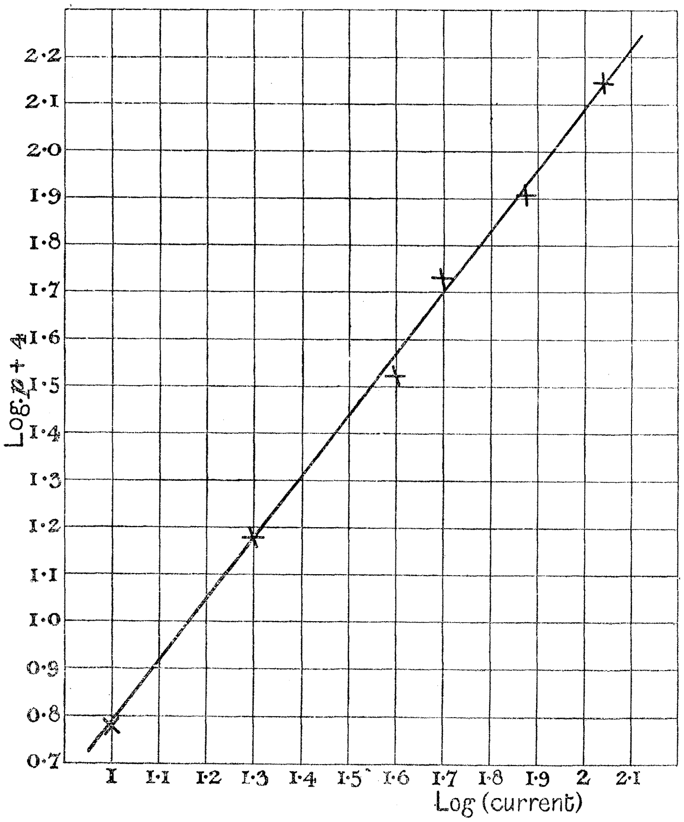

Fig. 1.

The following table contains values of Q calculated from the results given in the previous paper, together with $Q+2\alpha \log p$, taking $\alpha = 2400$.

p.	Q.	$Q+2\alpha \log p$.
millims.		
0·0013	110000	78000
0·112	90000	79500
133	56000	79500

It will be seen that $Q+2\alpha \log p$ is nearly constant, so that we have

$$Q = 79000-2\alpha \log p.$$

It appears therefore that the observed variation of Q with p agrees very well with that calculated on the assumption that $x = Bp^n$ at constant temperature.

Since $n = 0·75$ at 1350° C., and $\alpha = 2400$, we have $c = \alpha\theta^{-1}-n = 0·73$, so that A varies inversely as $p^{0·73}$.

The following table is calculated from the results given in the previous paper :—

p.	A.	$Ap^{0·73}$.
millims.		
0·0013	10^6	7800
0·112	5×10^4	10100
133	2×10^2	3600

Thus, while p is increased 10^5 times, $Ap^{0·73}$ only varies by a factor of 3. Only the order of magnitude of A can be obtained from the experimental results, so that it appears that the observed variation of A with p is consistent with the equation $Ap^{0·73}$ = constant.

The equations $A = Kp^{-c}$ and $Q = P - 2\alpha \log p$ give $A = Ke^{\frac{c}{2\alpha}(Q-P)}$.

Putting $P = 79000$, $\alpha = 2400$, $K = 9000$, and $c = +0·73$, and calculating Q from the values found for A, the following results are obtained :—

$$Q = 6580 \log A + 19100.$$

Gas.	Pressure.	A.	Q (calculated).	Q (found).
	millims.			
Air	—	$1·14 \times 10^8$	142000	145000
Air	—	7×10^7	138000	131000
H_2	0·0013	10^6	110000	110000
H_2	0·112	5×10^4	90300	90000
H_2	133	2×10^2	54000	56000

It appears, therefore, that this relation is satisfied by the values of A and Q for a wire in air as well as by those for a new wire in hydrogen.

If we put $p = 0$ in the equations $Q = P - 2\alpha \log p$ and $A = Kp^{-c}$, we get $Q = \infty$ and $A = \infty$. These equations therefore require modifying to enable them to represent all the values of A and Q. If we suppose $A = A_0/(1+ap^c)$, where a is a constant, then, when ap^c is large compared with unity, this formula will agree with $A = Kp^{-c}$, and when $p = 0$, it gives $A = A_0$.

We have $K = A_0/(1+a)$, which gives $a = 1·27 \times 10^4$. When $p = 0·001$, $ap^c = 100$, so that even at this pressure the present formula differs from $A = Kp^{-c}$ only by one per cent.

Since $A = A_0 e^{\frac{c}{2\alpha}(Q-Q_0)}$, we get $Q = Q_0 - 2\alpha c^{-1} \log(1+ap^c)$. This formula gives $Q = Q_0$ when $p = 0$, and for all measurable values of p does not differ appreciably from $Q = Q_0 - 2\alpha \log p - 2\alpha c^{-1} \log a$. When $p = 1$, $Q = P$, so that this is the same as

$Q = P - 2\alpha \log p$, which has been shown to agree with the observed values of Q at different pressures.

Since $n = \alpha\theta^{-1} - c$ at the temperature $\theta = \alpha/c$, the leak should be independent of the pressure.

If we substitute the expressions found for A and Q in the equation $x = A\theta^{\frac{1}{2}}e^{-Q/2\theta}$, we get

$$x = A_0(1+ap^c)^{(\alpha/\theta c - 1)}\theta^{\frac{1}{2}}e^{-Q_0/2\theta}.$$

If

$$R' = Q_0 + 2(\theta - \alpha c^{-1}) \log (1+ap^c)$$

and

$$D' = A_0(1+ap^c)^{(\alpha/\theta c - 1)},$$

this takes the forms

$$x = A_0\theta^{\frac{1}{2}}e^{-R'/2\theta} \quad \text{and} \quad x = D'\theta^{\frac{1}{2}}e^{-Q_0/2\theta}.$$

In the equation $x = A\theta^{\frac{1}{2}}e^{-Q/2\theta}$, which represents the variation of the leak with the temperature, Q is usually taken to be the energy required for the liberation of one gram-molecule of electrons, while A is proportional to the total number of free electrons present per cubic centimetre in the surface layer of the platinum. The experiments show that Q and A are both diminished by hydrogen. If we suppose that R denotes the true value of the energy required for the liberation of one gram-molecule of electrons, and that this quantity is a function of both θ and p, then, for example, if $R = R'$, we have $x = A_0\theta^{\frac{1}{2}}e^{-R'/2\theta}$, and this equation shows that all the results with new wires can be represented by supposing that the true value of A is A_0, whatever the temperature and pressure. On the other hand, if we denote the true value of A by D, then, for example, if $D = D'$, we have $x = D'\theta^{\frac{1}{2}}e^{-Q_0/2\theta}$, which shows that all the results can be represented by supposing that D is a function of θ and p, while R is always equal to Q_0.

In general, if $R = f(\theta, p)$, where $f(\theta, p)$ denotes a function of θ and p, then D will be given by the equation

$$\log \frac{D}{A_0} = \frac{1}{2\theta}(R - Q) + \left(\frac{\alpha}{\theta c} - 1\right) \log (1+ap^c),$$

so that, in general, both D and R may be any functions of θ and p which satisfy this equation, and the observed results will still be represented equally well by the equation $x = D\theta^{\frac{1}{2}}e^{-R/2\theta}$ at any pressure and temperature.

It appears, therefore, that on the view that R and D may be functions of θ as well as of p the results considered so far are not sufficient to determine the values of either of these quantities.

Let x denote the leak in air and x' that in hydrogen at the same temperature; then we have

$$x'/x = (1+ap^c)^{(\alpha/\theta c - 1)}.$$

At 900° C. in hydrogen at 26 millims. pressure RICHARDSON (*loc. cit.*, p. 45) found x'/x to be 4×10^8. The above equation gives $x'/x = 2 \times 10^9$. Since a small error in c produces a large error in x'/x, the agreement in this case is as good as could be expected. Thus, if we take $c = 0{\cdot}78$ instead of $0{\cdot}73$, we get $x'/x = 3 \times 10^8$. At 1570° C. in hydrogen at 760 millims. pressure, G. H. MARTYN (*loc. cit.*, p. 309) found $x'/x = 4{\cdot}4 \times 10^4$. The above formula gives $x'/x = 6{\cdot}5 \times 10^4$. At 1343° C. in hydrogen at 0·0013 millim. I found $x' = 5 \times 10^{-8}$. Taking $A_0 = 1{\cdot}14 \times 10^8$ and $Q_0 = 143000$, we get $x = 3 \times 10^{-10}$ at this temperature. Hence $x'/x = 170$. The formula gives $x'/x = 122$.

It appears, therefore, that the formula represents the observed values of x'/x as well as could be expected at pressures from zero to 760 millims., and at temperatures from 900° C. to 1600° C. Within these limits x'/x varies by a factor of more than 10^8.

It should be observed that the results so far considered are those obtained with new wires, and in each case, before measuring the current, some time was allowed to elapse to enable the wire to get into equilibrium with the hydrogen.

The agreement of the formulæ obtained with the observations shows that the equation $x = Bp^n$, which was assumed at the start, is approximately true.

If p is not less than 0·001 millim., the formula for x'/x is approximately $x'/x = a^{(\alpha/\theta c - 1)} p^{(\alpha/\theta - c)}$, so that x' varies as a power of the pressure. The following table gives the values of $\alpha\theta^{-1} - c$ at several temperatures, and some values of the power of the pressure calculated directly from recorded observations.

Temperature.	$\alpha\theta^{-1} - c$.	Observed.	Observer.
° C.			
800	1·50	1·12* at 860°	O. W. R.
1000	1·15	—	—
1200	0·90	0·22* at 1181°	O. W. R.
1400	0·70	0·75 at 1350°	H. A. W.
1600	0·55	0·57 at 1490°	H. A. W.
1800	0·43	0·6 at 1550°	H. A. W.

The number 0·22 calculated from RICHARDSON'S results at 1181° C. does not agree with $\alpha\theta^{-1} - c$. This is probably due to the wire not being new. After a wire has been heated a long time in hydrogen at high pressures it may take a very long time for the current to rise after the pressure has been increased. This is probably the explanation of the small value 0·22.

It should be said that since the formulæ from which the formula for x'/x is derived were shown to agree with the values found for A and Q, it was, of course, certain that the calculated values of x'/x would agree with the observed values if these were taken

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* These numbers are calculated from results given by RICHARDSON (*loc. cit.*).

from the same sets of observations as were used in getting the values of A and Q. It is interesting to find that observations by other observers over a very wide range also agree with the calculated values of x'/x.

The following table gives some values of x'/x calculated from the formula when $p = 1$ millim.

Temperature.	x'/x.	x'.
°C.		amperes per sq. centim.
800	$3 \cdot 4 \times 10^{8}$	$1 \cdot 8 \times 10^{-11}$
1000	$3 \cdot 4 \times 10^{6}$	$6 \cdot 8 \times 10^{-9}$
1200	$1 \cdot 1 \times 10^{5}$	$5 \cdot 1 \times 10^{-7}$
1400	$0 \cdot 9 \times 10^{4}$	$1 \cdot 4 \times 10^{-5}$
1600	$1 \cdot 2 \times 10^{3}$	$2 \cdot 0 \times 10^{-4}$
1800	$2 \cdot 4 \times 10^{2}$	$1 \cdot 6 \times 10^{-3}$

It will be seen that x'/x diminishes rapidly as the temperature rises.

Without making any assumption as to whether the hydrogen changes R or D, or both, we may draw an important inference from the results so far considered if we assume that the effect of the hydrogen is due to its presence in the platinum. Since the effect varies continuously with the pressure at constant temperature, we may conclude that the amount of hydrogen in the surface layer of the platinum varies continuously with the pressure. It follows from this that the hydrogen is in the platinum in a state of solution and not in a state of definite chemical combination. If a definite compound were formed, then the amount of combined hydrogen would be zero when the pressure was below its dissociation pressure, and constant when the pressure was above this. The results obtained with new wires indicate therefore that the hydrogen is in solution in the platinum.

2. *Variation of the Current with the Pressure at Constant Temperature.*

A wire, which had been heated for several hours in hydrogen at pressures up to one atmosphere, was kept at a constant temperature, and the leak observed at a series of pressures from one atmosphere downwards. At each pressure the leak was observed until it became nearly constant. The resistance of the wire at 0° C. was determined from time to time, and its resistance when hot was kept proportional to its resistance at 0° C., so that its temperature was kept nearly constant. The difference of potential used was proportional to the pressure, except at low pressures. The following table contains the results obtained in this way:—

Temperature 1310° C.

Pressure.	Potential difference.	Current.
millims.	volts	amperes
784	784	168×10^{-8}
385	385	83×10^{-8}
183	184	35×10^{-8}
71	72	26×10^{-8}
46	46	26×10^{-8}
23	30	16×10^{-8}
10	20	36×10^{-8}
0·85	20	78×10^{-8}
0·45	20	60×10^{-8}
0·24	20	46×10^{-8}
0·13	20	38×10^{-8}
0·068	20	40×10^{-8}
0·006	20	40×10^{-8}
0·000	20	40×10^{-8}

It will be seen that below 200 millims. the current does not vary much with the pressure. The rise at 0·8 millim. is probably due to ionisation by collisions. In the previous paper the following results were obtained with new wires :—

Temperature 1340° C.

Pressure.	Potential difference.	Current.	$\frac{\text{Current}}{\text{Pressure}}$.
millims.	volts	amperes	
766	40	3×10^{-3}	$3·9 \times 10^{-6}$
450	40	$1·5 \times 10^{-3}$	$3·3 \times 10^{-6}$
156	40	$2·2 \times 10^{-4}$	$1·41 \times 10^{-6}$
14	40	6×10^{-5}	$4·3 \times 10^{-6}$
0·11	40	4×10^{-6}	36×10^{-6}
0·0013	40	5×10^{-8}	39×10^{-6}

It ought also to be said that the last two results in this table were obtained with a wire which had never been in hydrogen at more than a small fraction of a millimetre pressure. The first four results were obtained by letting hydrogen in, keeping the temperature constant. Comparing the two tables, we see that there is a surprising difference between them. The first table shows very little variation with the pressure, while the second shows that the leak increased 10^5 times when the pressure was increased 10^6 times.

The difference between the old results and the new ones is so large that it was considered worth while to repeat the old experiments. A new wire was put up and heated in air, and was found to give a small current. The air was then pumped out and small quantities of pure hydrogen were successively admitted. The current was measured at each pressure, keeping the temperature constant. The following table contains the results obtained.

TEMPERATURE 1564° C.

Pressure.	Current.
millim.	amperes
0·006	$2·5 \times 10^{-7}$
0·028	$4·5 \times 10^{-7}$
0·056	$1·8 \times 10^{-5}$
0·337	$5·2 \times 10^{-5}$
0·169	$1·2 \times 10^{-5}$
0·090	$2·4 \times 10^{-6}$
0·003	$5·0 \times 10^{-8}$

The last three pressures were obtained by pumping out the hydrogen.

These results show that with a new wire the leak rises with the pressure and falls when it is reduced. The experiment was repeated immediately, and similar results were obtained. Next day, after the wire had been all night in hydrogen at a low pressure, the following results were obtained :—

Pressure.	Current.
millim.	amperes
0·001	5×10^{-8}
0·017	5×10^{-8}
0·146	2×10^{-7}
0·297	9×10^{-7}
0·618	11×10^{-7}
0·281	11×10^{-8}
0·146	6×10^{-8}
0·073	5×10^{-8}

It appears, therefore, that with a new wire the results are very different from those obtained with an old wire.

If a wire which has been heated in hydrogen at high pressures and is giving a large leak nearly independent of the pressure is heated in air, the leak falls at once to a small value. If the air is pumped out and a little hydrogen admitted, the leak at high temperatures is not affected at first, but after heating in the hydrogen for some time it usually develops rather quickly. The leak then rises when the pressure is increased, and has about the same value as with a new wire. On pumping out the hydrogen the leak only falls very slowly with the time.

The following table gives the currents at several pressures with a wire treated in the way just described. This wire, after heating in air, was heated to 1490° C. in hydrogen at 0·005 millim. pressure. The leak remained unchanged for two hours and then rose to about 4×10^{-6} ampere per square centimetre. After this, on increasing the pressure, the leak rose at once and remained steady.

Temperature 1490° C.

Pressure.	Current.
millim.	amperes
0·0135	$6 \cdot 56 \times 10^{-6}$
0·0168	$7 \cdot 80 \times 10^{-6}$
0·0281	$10 \cdot 50 \times 10^{-6}$
0·0399	$12 \cdot 70 \times 10^{-6}$
0·0579	$17 \cdot 20 \times 10^{-6}$
0·0776	$20 \cdot 50 \times 10^{-6}$
0·1151	$24 \cdot 60 \times 10^{-6}$

This experiment was repeated several times with similar results. On diminishing the pressure the leak fell off very slowly with the time, so that the pressure could be reduced to nothing without much diminishing the leak. This shows that the increase in the leak is not due to ionisation by collisions.

If the logs of the numbers just given are plotted, the points fall nearly on a straight line, the slope of which shows that the current is proportional to $p^{0 \cdot 57}$. At 1490° C. $\alpha\theta^{-1} - c$ is equal to 0·63. Thus the variation of the leak with the pressure is nearly that calculated from the old results with new wires. The value of the leak at 1490° C., with $p = 0 \cdot 1151$, given by the formula obtained in Section 1, is $1 \cdot 3 \times 10^5$, which does not differ much from the leak found. This wire, therefore, which had been heated in hydrogen at high pressures for a long time and then in air, gave the same leak in hydrogen as a new wire. It differed from a new wire only in that the leak fell very slowly with the time when the pressure was diminished, and that on first admitting the hydrogen the leak did not rise for a considerable time.

If we regard the leak from a wire which has not been heated in hydrogen at a high pressure as due to dissolved hydrogen, then, since in the case just described the leak was the same as that given by a new wire, we must regard the leak in this case also as due to dissolved hydrogen. Thus the difference between an old wire and a new one appears to be that the old wire absorbs and evolves hydrogen much more slowly than the new wire.

A wire which has been heated in hydrogen at high pressures differs from a new wire and from an old wire that has been heated in air. It always gives a very large leak which is nearly independent of the pressure. Even when it is heated in a good vacuum for many hours the leak does not fall.

Professor O. W. Richardson (*loc. cit.*) found that the leak in hydrogen was independent of the pressure when this was reduced from a few millimetres to nearly zero.

His wires, therefore, appear to have had the properties of old wires. He has described some experiments in which a wire giving a leak independent of the pressure was heated for many hours in a good vacuum and a slow evolution of gas was observed. The total volume of gas evolved, measured at 760 millims. pressure, was about 30 times that of the wire. I have repeated this experiment of RICHARDSON'S and have confirmed his result that the leak does not fall even after heating the wire for many hours in hydrogen at a low pressure. In my experiments the wire appeared to cease evolving an appreciable amount of gas after heating for about one hour.

The following table contains some numbers obtained in one series of observations with a wire kept between 1500° C. and 1600° C. The leak at 1600° C. was about 10^{-3} ampere. The wire had previously been heated in hydrogen and was giving a leak very large compared with the air leak. The volume of the apparatus was approximately 1000 cub. centims.

Time.		Pressure.
h.	m.	millim.
10	55	0·0017
12	7	0·0028
16	48	0·0028

In this experiment the pressure did not rise 0·0002 millim. in the last five hours. It seems certain, therefore, that a wire giving a large leak due to its having been heated in hydrogen can be heated to a very high temperature in hydrogen at a very small pressure for several hours without evolving an appreciable amount of gas.

On another occasion a wire was kept at about 1400° C. from 5 P.M. to 10 A.M., and the pressure did not rise more than 0·005 millim., although the wire was giving a large leak, due to its having been heated in hydrogen. If we admit that a wire giving a large leak does not necessarily evolve gas, we may explain this in two ways. Either the wire contains no hydrogen, or it contains hydrogen in a state of very stable combination. In the section of this paper on the effect of hydrogen on the resistance of the wire it is shown that heating in air diminishes the resistance at the same time that it destroys the leak. This seems to show that the surface layers of the wire contain hydrogen which is burnt up by the air. The fact that platinum black absorbs very much more hydrogen than solid platinum also points to the conclusion that the absorption is mainly a surface effect. The presence of hydrogen in a wire can be tested by heating it in oxygen and observing the pressure before and after heating. If hydrogen is present it will form water which will be absorbed by the P_2O_5, and so the pressure will be diminished. RICHARDSON (*loc. cit.*, p. 45) describes an experiment of this kind and observed a diminution in the pressure. In this experiment of RICHARDSON'S a wire at 900° C. in hydrogen at 26 millims. pressure gave a negative leak 4×10^8 times greater than the leak at the same temperature in oxygen. On heating in oxygen the pressure fell from 1·067 millims. to 1·026 millims. I have tried a similar experiment with a wire giving a large leak independent of the pressure which was heated in hydrogen at a small pressure until it ceased to evolve gas. A new wire was put up and heated for a few hours in hydrogen at atmospheric pressure. It was then left cold in hydrogen all night, and in the morning gave a large leak nearly independent of the pressure. The gas was then pumped out till the pressure was 0·0011 millim. The wire was then heated to a temperature of about 1200° C. for four hours, during which time the leak was about 3×10^{-5} ampere, but rose slightly towards the end of the experiment. After one and a-half hours the pressure had risen to 0·01 millim., but it remained constant during the next two and a-half hours. The wire was then allowed to cool, and oxygen was let in to a high pressure and pumped out several times. The oxygen was then pumped out to 0·0015 millim. The wire was then heated for a few seconds to about 1100° C., and after ten minutes the pressure was 0·0012 millim. The wire was then heated for two minutes and after a time the pressure fell to 0·0009 millim. The wire was now heated for two minutes to about 1500° C., and after a time the pressure was again 0·0009 millim.

On first heating the wire in the oxygen a large leak was observed which very quickly fell to a very small value. The capacity of the apparatus in the above experiment was 500 cub. centims., so that the volume of hydrogen (measured at 760 millims.) contained in the wire was 8×10^{-3} cub. centim. The volume of the wire was $10 \times \frac{22}{7} \times \frac{1}{(100)^2} = 3 \times 10^{-3}$ cub. centim., so that the wire contained about three times its volume of hydrogen, although it had been heated for two and a-half hours without evolving any gas. The gas evolved during the first one and a-half hours may have come from the wire, but some of it probably came from the surrounding electrode, which, of course, got warm during the long continued heating. When the wire was heated in oxygen, the electrode was not heated appreciably, because the current was only kept on a short time. I think this experiment shows that a wire which has ceased to evolve hydrogen when heated in hydrogen at a small pressure may still contain several times its volume of hydrogen.

If the wire absorbed oxygen when heated in it this would account for the fall in the pressure. The oxide of platinum, PtO, which is formed at 510° C., decomposes completely at 560° C. The temperature in the above experiment was much higher than 560° C., so that it is not likely that any oxide was formed. According to Bodländer, platinum absorbs oxygen energetically at from 700° C. to 900° C., but these temperatures are also lower than the temperature used.

If we admit that a wire giving a large leak independent of the pressure contains hydrogen, to which the leak is due, then it is necessary to suppose that the hydrogen is not all merely dissolved in the platinum. Since the leak is independent of the pressure, the amount of hydrogen in the wire must be independent of the pressure. If the temperature of the wire is raised while it is in a good vacuum, the leak on cooling to the original temperature is often a little lower than before. After standing cold the leak is usually higher on first heating the wire, and then falls off quickly at first and then more slowly. I think these variations may be ascribed to hydrogen dissolved in the wire like that in a new wire. The leak does not fall below a certain value at a given temperature, however long the wire is heated in a vacuum, even if the temperature is raised and lowered. RICHARDSON'S experiments show this very clearly, and I have confirmed this result. Very often the leak rises slightly while the wire is being heated in hydrogen at a very low pressure. To explain these results on the theory that the large leak is due to hydrogen contained in the surface layer of the platinum, it is necessary to suppose that a very stable compound of hydrogen and platinum is formed in the surface layer which has a dissociation pressure less than about 0·002 millim. even at high temperatures. In addition to the combined hydrogen the wire may contain dissolved hydrogen, but this will be got rid of by heating in a vacuum. The absorption of hydrogen by platinum at high temperatures has been investigated by several people, and they have all found that part of the gas can be driven off by heating in a vacuum, while part cannot be driven off in this way. It should be observed that the pressure of the hydrogen is never really reduced to zero by pumping out. It is possible that by reducing the pressure sufficiently the combined hydrogen could be removed, but if it has a finite dissociation pressure this must be very small.*

I think, therefore, that the difference between a new wire and a wire which has been heated in hydrogen at a high pressure is mainly due to the presence of combined hydrogen in the latter.

When the combined hydrogen has been burnt out of an old wire by oxygen the wire gives the same leak in hydrogen at a low pressure as a new one, but the leak takes a long time to appear and does not fall much when the pressure is reduced. This seems to show that the old wire only dissolves the hydrogen very slowly. Continued heating in hydrogen and air appear, therefore, to produce a change in the state of the platinum. This change of state does not appear to affect the final value of the leak, and is not destroyed by heating in oxygen, which at once destroys the leak.

This change of state may very likely be due merely to long continued heating; it probably consists of an alteration of the crystalline structure of the platinum. The formation of a compound of platinum and hydrogen in the surface layer, and its subsequent destruction by oxygen, might be expected to produce a change in the state of molecular aggregation of the platinum. Another thing which may have something to do with this change of state is the slow evaporation of the wire at high temperatures.

In my paper on the electrical conductivity of air and salt vapours ('Phil. Trans., A, 1901) I observed that the leak from hot platinum in air falls off during long continued

[**Added March* 20, 1908.—Since writing the above I have found that on heating to above 1600° C. at a very low pressure the large leak rapidly disappears.]

heating, at first rapidly and then much more slowly, and I suggested that this was due to a change in the state of molecular aggregation of the platinum. The platinum in these experiments was heated by a coal-gas flame and so no doubt contained hydrogen, so that this effect was probably due to the same cause as that just described.

3. *Variation of the Current with the Temperature.*

The leak from wires which had been heated in hydrogen at high pressures and were giving a leak independent of the pressure was measured at a series of temperatures on several occasions. The following table contains a set of results obtained in this way at a pressure of 0·003 millim.

Temperature.	Current.
° C.	ampere per sq. centim.
1578	$9 \cdot 51 \times 10^{-5}$
1613	$19 \cdot 26 \times 10^{-5}$
1648	$38 \cdot 7 \times 10^{-5}$
1683	$72 \cdot 3 \times 10^{-5}$

The mean values of A and Q in the formula $x = \mathrm{A}\theta^{\frac{1}{2}}e^{-\mathrm{Q}/2\theta}$ calculated from the above results are $\mathrm{A} = 1 \cdot 67 \times 10^{10}$ and $\mathrm{Q} = 135300$, and with these values the formula represents the observations very well.

The value of Q for a new wire in air is probably about 135000, so that Q for an old wire in hydrogen is nearly the same as for a new wire in air.

With the same wire, about a month later, the following results were obtained. The wire was heated in air, which was then pumped out and hydrogen was let in to a small pressure. After a time a leak developed which increased with the pressure. After heating for several hours at low pressures, hydrogen was let in to 0·084 millim. pressure. The leak then rose, but became constant after one hour. At each temperature the leak was then steady.

Pressure 0·084 millim.

Temperature.	Current.
° C.	ampere per sq. centim.
1265	$6 \cdot 8 \times 10^{-7}$
1377	$51 \cdot 0 \times 10^{-7}$
1496	$317 \cdot 0 \times 10^{-7}$

These numbers give $\mathrm{Q} = 89000$ and $\mathrm{A} = 6 \times 10^{4}$. The formulæ $\mathrm{A} = \mathrm{K}p^{-c}$ and $\mathrm{Q} = \mathrm{P} - 2\alpha \log p$ obtained in Section 1 give $\mathrm{A} = 5 \cdot 5 \times 10^{4}$ and $\mathrm{Q} = 83000$ at this pressure. The leak obtained in this experiment was nearly the same as with a new wire at the same pressure. This confirms the conclusion that an old wire after heating in air gives the same leak in hydrogen as a new wire, although the current takes much longer to get to its final value at any pressure.

The results obtained with the wire after heating in hydrogen at a high pressure are quite different from those given by a new wire. The values of A and Q, $1 \cdot 67 \times 10^{10}$ and 135300, obtained do not satisfy the relation $A = A_0 e^{c(Q-Q_0)/2a}$, which has been shown to hold for all the other values of A and Q.

According to the view suggested in the last section, the wire after heating for some time in hydrogen at a high pressure contains a stable compound of platinum and hydrogen having a dissociation pressure less than 0·002 millim. The amount of combined hydrogen is consequently independent of the pressure.

The amount of combined hydrogen must be independent of the temperature as well as of the pressure. For if on raising the temperature some of it escaped, this would show that its dissociation pressure was greater than that of the hydrogen outside, and so the whole of the compound would decompose. But a wire giving a large leak independent of the pressure can be heated in a good vacuum to 1400° C. without the leak falling; hence, at any rate below this temperature, the amount of combined hydrogen must be independent of the temperature.

Since Q for a wire containing combined hydrogen is nearly the same as Q for a new wire in air, it follows that the ratio of the leaks should be independent of the temperature. The following table contains the values of the leak given above and those for a new wire in air taken from my previous paper.

New wire in air.		Old wire.		
Temperature.	Leak.	Temperature.	Leak.	Ratio.
° C.		° C.		
1686	4×10^{-8}	1683	$7 \cdot 23 \times 10^{-4}$	$1 \cdot 81 \times 10^{4}$
1651	2×10^{-8}	1648	$3 \cdot 87 \times 10^{-4}$	$1 \cdot 93 \times 10^{4}$
1616	1×10^{-8}	1613	$1 \cdot 93 \times 10^{-4}$	$1 \cdot 93 \times 10^{4}$

It will be seen that the ratio is nearly constant.

The leak from wires which had been heated in hydrogen was measured in air at various temperatures many times during the course of this investigation. The leaks obtained were of the same order of magnitude as those given in the previous paper for new wires in air. They were from 2 to 10 times greater than the leak given in the previous paper for a wire which had been treated with nitric acid for 24 hours. One wire, which had been used a long time in hydrogen, was made the positive electrode in HNO_3 for several hours, and was then heated in air at a small pressure. It was found to give nearly the same leak as that from the wire just mentioned.

4. *Variation of the Current with the Time.*

In the previous paper the variation of the current with the time was considered in detail, and it was shown that the results obtained could be explained by supposing that the leak depended on the amount of hydrogen in the wire, and that a considerable time was required for the hydrogen in the wire to get into equilibrium with that outside. For example, it was shown that on diminishing the pressure at constant temperature the leak fell slowly. The previous results were obtained with new wires. With wires which have been heated in hydrogen at high pressures the variation with the time is similar to that with new wires, but the leak does not fall below a certain value, however much the pressure is reduced. The following table contains a series of observations on a wire at 1310° C. in hydrogen. The wire was left cold during each night.

Time.		Current.	Potential difference.	Pressure.
Days.	Minutes.			
		ampere	volts	millims. of Hg.
0	0	$8{\cdot}6 \times 10^{-5}$	200	195
	10	$4{\cdot}4 \times 10^{-5}$	200	195
	35	$4{\cdot}5 \times 10^{-5}$	200	195
	100	$5{\cdot}2 \times 10^{-6}$	200	195
1	0	$8{\cdot}4 \times 10^{-5}$	784	784
	10	$2{\cdot}8 \times 10^{-5}$	784	784
	50	$9{\cdot}5 \times 10^{-6}$	784	784
	100	$2{\cdot}8 \times 10^{-6}$	784	784
2	0	$3{\cdot}5 \times 10^{-6}$	784	784
	100	$1{\cdot}5 \times 10^{-6}$	784	784
	120	$1{\cdot}5 \times 10^{-6}$	784	784
	130	$7{\cdot}0 \times 10^{-7}$	385	385
	180	$7{\cdot}4 \times 10^{-7}$	385	385
	220	$1{\cdot}3 \times 10^{-7}$	30	23
3	0	$7{\cdot}5 \times 10^{-7}$	30	23
	60	$1{\cdot}9 \times 10^{-7}$	30	23
	200	$3{\cdot}4 \times 10^{-7}$	30	0·84
4	0	$6{\cdot}2 \times 10^{-7}$	20	0·84
	60	$5{\cdot}4 \times 10^{-7}$	20	0·84
	120	$5{\cdot}6 \times 10^{-7}$	20	0·84
5	0	$4{\cdot}4 \times 10^{-7}$	20	0·24
	60	$3{\cdot}5 \times 10^{-7}$	20	0·24
	180	$3{\cdot}5 \times 10^{-7}$	20	0·24
	300	$3{\cdot}6 \times 10^{-7}$	20	0·000
6	0	$3{\cdot}2 \times 10^{-7}$	20	0·006
	60	$3{\cdot}6 \times 10^{-7}$	20	0·006
9	0	$3{\cdot}8 \times 10^{-6}$	20	1·64
	60	$3{\cdot}7 \times 10^{-7}$	20	1·64
	120	$5{\cdot}0 \times 10^{-7}$	40	1·64

The wire was left cold between the seventh and tenth days. After several weeks' further experimenting with this wire at various temperatures and pressures, the leak at the same temperature as that at which the above results were obtained was

2×10^{-7}, and almost independent of the pressure. It will be seen that the leak fell rapidly at first and was usually greater after leaving the wire cold all night. It was nearly independent of the pressure below 200 millims. The variation of the leak with the time can usually be represented roughly by a formula of the type $Ae^{-\alpha t} + Be^{-\beta t} + C$, in which α is much greater than β, and A greater than B or C. The term C represents the final value of the leak, which is nearly constant, but it also falls off very slowly. The term $Ae^{-\alpha t}$ represents the large leak at first, and falls to half value in from a few seconds to 20 minutes, according to the temperature and state of the wire. The second term falls to half value in several hours. Irregular variations in the leak sometimes take place which make it impossible to determine α and β exactly. Moreover, these quantities are not the same on different occasions, but depend greatly on the previous treatment of the wire.

I think these facts indicate that the wire absorbs hydrogen in the cold, and that part of this hydrogen is given off fairly rapidly on heating, part is given off very slowly, and part not given off at all, even in a vacuum

If an old wire which has been heated in hydrogen for a long time is heated in air, and then again to a very high temperature (above 1600° C.) in hydrogen, the leak is nearly the same in hydrogen as in air. On reducing the temperature the leak remains small for a time, but then begins to increase rapidly and after a time gets to about the usual value for a wire in hydrogen. At first, while the leak is increasing with the time, it falls when the temperature is raised. After further heating the leak becomes more steady, and then always rises with the temperature. These facts seem to show that an old wire does not absorb hydrogen above a certain temperature, or only does so very slowly.

The fact that while the leak is rising with time it falls on raising the temperature is difficult to explain. This effect was obtained on several separate occasions. The leak, then, has a definite maximum value at a certain temperature. The leak in these experiments was saturated, so that the decrease on raising the temperature was not due to a diminution in the velocity of the ions. The leak rose when the temperature was diminished. In one experiment the current was 10^{-7} ampere at 1300° C., 4×10^{-7} at 1400° C., and 4×10^{-8} at 1500° C.

An increase in the leak while heating in hydrogen at constant temperature is usually accompanied by a small fall in the pressure, showing that the wire has absorbed hydrogen. Much weight cannot be given to observations showing a small change in the pressure, because small quantities of gas may be evolved or absorbed by the glass or the electrodes, so that a small change in the pressure is not necessarily due to gas evolved or absorbed by the wire.

One wire which gave a large leak in hydrogen when it was new, after heating in hydrogen for several days was heated in air and then gave the usual small air leak. On again heating in hydrogen to above 1600° C. for ten hours the leak remained small and showed no signs of rising with time.

5. *The Effect of Hydrogen on the Resistance of the Platinum.*

It is well known that when platinum is saturated with hydrogen its resistance is increased by a small amount. It was thought that this effect might be employed as a test of the presence of hydrogen in the wire. A wire which had been heated for some time in hydrogen and which gave a large leak independent of the pressure was used. It was heated for some hours in a very good vacuum and still gave the same current as in hydrogen at several millimetres pressure. Its resistance at 0° C. was then carefully determined and it was then heated to 1400° C. for a few seconds in air. The leak immediately fell to the air value. The resistance at 0° C. was again determined and was about one part in a thousand less than before. On again heating in hydrogen the resistance rose again.

This experiment shows that the increase in the resistance due to hydrogen is probably a purely surface effect, for oxygen does not diffuse into platinum. If we regard the increase in the resistance as due to the formation of the compound discussed in Section 2, then it is necessary to suppose that this compound is only formed in the surface layer of the platinum. It is well known that finely divided platinum absorbs much more hydrogen than platinum in large pieces, which also suggests that the compound formed is confined to the surface. The effect of the hydrogen on the negative leak is, of course, a surface effect and so depends only on the state of the surface layer.

6. *Effects due to Passing a Self-Luminous Discharge between the Wire and surrounding Electrode.*

After heating an old wire in air it gives a very small leak in hydrogen, at any rate for a time. If, while it is giving a very small leak, a luminous discharge is passed between the wire and the surrounding electrode by means of a large battery of cells, the leak on stopping the discharge is enormously increased. If the discharge is only passed for a few seconds, a moderate increase can be obtained, and then the leak has a maximum value at a certain temperature. After passing the discharge for some minutes the leak obtained always rises with the temperature.

These effects, it will be seen, are very similar to the effects observed during the increase of the leak when an old wire which had been heated in air was heated to a moderate temperature in hydrogen. The discharge appears to accelerate the recovery of the leak. The maximum value of the leak was obtained both with rising and falling temperatures. The current was nearly independent of the potential difference in all these experiments. This was tested specially at every temperature by taking two measurements with different potentials. The maximum value is, therefore, not due to the currents at the higher temperatures not being saturated. I hope to make further experiments on these effects.

7. *A Comparison of the Negative Leak in Hydrogen with the Positive Leak in Oxygen.*

The positive leak in oxygen has been studied very fully by Professor O. W. RICHARDSON ('Phil. Trans.,' A, 413, 1906), who attributes it to the presence of oxygen in the surface layer of the wire, and this view is undoubtedly in accordance with the facts. I attribute the negative leak in hydrogen in the same way to the presence of hydrogen in the surface layer of the platinum. If this view is correct, the behaviour of the positive leak in oxygen might be expected to be closely analogous to the behaviour of the negative leak in hydrogen. As a matter of fact, there is an extremely close analogy between the two, as will be shown presently.

In my previous paper I showed that treating a wire with nitric acid and heating it in air diminished the negative leak to a value very small compared with that usually obtained on heating a wire in a vacuum. This diminution was explained as being due to the removal of traces of hydrogen or other substances from the wire, and I suggested that possibly a complete removal of such traces would entirely destroy the negative leak. Since then RICHARDSON (*loc. cit.*) has described an experiment in which the leak from a platinum tube in air at atmospheric pressure was measured while hydrogen was allowed to diffuse through the platinum from the inside of the tube out into the air. He found that the small negative leak was unchanged by the hydrogen. I have repeated this experiment and confirmed his result. As RICHARDSON points out, this experiment shows clearly that the very small negative leak given by platinum in air is not due to traces of hydrogen in the platinum. In addition, measurements of the negative leak from clean platinum wires in air and other gases, except hydrogen, give fairly concordant results, so that I think there is now no doubt that there is a small negative leak due to the platinum itself. In fact, since traces of hydrogen in the surface of the platinum must be burnt up at once when it is heated in air, it is almost impossible that such traces could be the cause of the small leak given in air. This conclusion, of course, does not apply to the much larger leaks which are obtained when an ordinary platinum wire is heated in a vacuum without any special precautions. I think there is no doubt that they are due, as I suggested, to traces of hydrogen. In the present paper, when the negative leak in hydrogen is referred to, it is not intended to imply that there is not a small negative leak due to the platinum itself.

To return to the comparison of the positive and negative leaks, the variation with the pressure at constant temperature will be taken first. RICHARDSON shows that the positive leak increases with the pressure of the oxygen at low pressures rapidly, but at high pressures more slowly. The relation between the leak and the pressure is $x = \alpha p^n/(\beta+p^n)$, where α, β, and n are constants. The constant n varies with the temperature, being $\frac{1}{2}$ at 820° C. and 1 at 1170° C. Assuming that the leak depends on the amount of oxygen in the surface layer of the platinum, this shows that the oxygen dissolves in the platinum at low pressures, while at high pressures—since the leak becomes nearly independent of the pressure—there is an indication of chemical combination.

It will be seen that these results are very analogous to the results obtained with the negative leak in hydrogen. This increases proportionally to a power of the pressure at first, but in the course of time a compound is formed, and the leak is then nearly independent of the pressure. The difference between the two cases is that the positive leak always gets to a definite value at any pressure if enough time is allowed. This means that the compound formed can easily dissociate. The negative leak at first, before the stable compound is formed, exhibits hysteresis effects, that is, it lags behind changes in the pressure. RICHARDSON finds precisely the same thing with the positive leak, and it is almost certainly due in each case to the gas in the wire taking time to get into equilibrium with that outside.

The negative leak is often large on first heating a wire, and falls off with the time. The same thing applies to the positive leak, and in each case it is almost certainly due to the escape of gas absorbed while the wire was cold. The variation of both leaks with the temperature is represented by the formula $x = A\theta^{\frac{1}{2}}e^{-Q/2\theta}$.

I think, therefore, that the negative leak in hydrogen bears the same relation to the hydrogen that the positive leak in oxygen does to the oxygen. If one of them is due to the presence of the gas in the surface layer of the wire, then the other is also. The precise manner in which the presence of hydrogen in the surface layer alters the negative leak will be considered in Section 9.

8. *The Theory of the Negative Leak.*

Professor O. W. RICHARDSON ('Phil. Trans.,' A, 343, 1903) has given a very simple and elegant theory of the negative leak from hot bodies. According to this theory the metal contains electrons which move about freely inside the metal and have a velocity distribution like the molecules of a gas. Those electrons which collide with the surface with a normal velocity greater than a certain value escape. This theory leads to the formula $x = A\theta^{\frac{1}{2}}e^{-Q/2\theta}$, and according to it A is proportional to the number of free electrons per cubic centimetre in the metal. According to this theory A ought to be nearly independent of the pressure and nature of the gas present, because the electrical conductivity of the metal is very little affected, even by hydrogen.

In my previous paper I showed that hydrogen changed the value of A by a very large factor, and therefore I suggested that RICHARDSON's theory required modification in order to enable it to account for the facts.

It is shown in Section 1 of the present paper that if the true values of Q and A are denoted by R and D, and if we suppose that R and D may be functions of the temperature θ as well as of the pressure, then the variations of Q and A can be explained either by supposing that D is constant and R a function of θ and p, or that

R is constant and D a function of θ and p. Let us suppose, then, that D is constant, which is in accordance with RICHARDSON'S theory. We have, then,

$$R = Q + 2\theta \log (D/A).$$

According to this equation R increases uniformly with the temperature, and R cannot be calculated unless D is known. To determine D it is necessary to make some hypothesis to explain the variation of R with the pressure and temperature. This is done in the next section.

The negative leak from lime can, like that from platinum, be represented by the formula $x = A\theta^{\frac{1}{2}}e^{-Q/2\theta}$; and Dr. HORTON ('Phil. Trans.,' A, 1907) has shown that the electrical conductivity of lime at high temperatures can also be represented by a formula of the same type. He concludes that the number of free electrons per cubic centimetre of lime must increase rapidly with the temperature, so that, if A in the formula giving the negative leak were proportional to the number of electrons, then A ought to increase rapidly with the temperature. Dr. HORTON found A to be nearly independent of the temperature, and hence concluded that A was not proportional to the number of free electrons per cubic centimetre. It is easy to show that this conclusion is not really required by the results, which can be reconciled as follows:—Let N denote the number of free electrons per cubic centimetre of lime, and suppose that the electrical conductivity is proportional to $N\theta^{\frac{1}{2}}$, so that N varies as $e^{-Q'/2\theta}$, where Q' is the value in the formula giving the conductivity.

Suppose the negative leak from lime is given by the formula $x = D\theta^{\frac{1}{2}}e^{-R/2\theta}$; then, according to RICHARDSON'S theory, D varies as N, which varies as $e^{-Q'/2\theta}$. Hence we get $D = Ae^{-Q'/2\theta}$, where A is a constant, which gives

$$x = Ae^{-Q'/2\theta}\theta^{\frac{1}{2}}e^{-R/2\theta}.$$

The quantities found by Dr. HORTON are, therefore, A and $Q'+R$, and the independence of A and the temperature agrees with RICHARDSON'S theory if the assumptions here made are allowed.

9. *A Theory of the Variation of* R *with the Temperature.*

To explain the energy necessary to enable an electron to escape from the platinum, we may suppose that an electrical double layer exists at the surface. Let this consist of an infinitely thin layer of electricity at a distance t from the platinum, having a charge σ per square centimetre. If no electrons were present, the difference of potential between the layer and the platinum would be $4\pi\sigma t$; but, actually, electrons will be present in between the layer and the platinum and will increase the electric force. This effect will increase as the temperature rises, so that if R is due to such a layer it will vary with the temperature.

Let n denote the number of electrons per cubic centimetre at a point at a distance x

from the platinum surface. Let p denote the gas pressure due to the electrons and let ρ denote the electric volume density, so that $\rho = ne$. Then, when there is equilibrium, we have $-dp/dx+\mathrm{F}\rho = 0$, where F denotes the electric force inside the layer. Outside the layer, in the same way, $-dp/dx+\mathrm{F}'\rho = 0$, where F′ denotes the force outside. Then at the layer $x = t$ and $\mathrm{F}_t+4\pi\sigma = \mathrm{F}'_t$; also, since ρ must be continuous and $d\mathrm{F}/dx = 4\pi\rho$, we have $d\mathrm{F}/dx_t = d\mathrm{F}'/dx_t$.

At a great distance from the platinum we have for equilibrium $\mathrm{F}' = 0$ and $d\mathrm{F}'/dx = 0$, and at $x = 0$, $d\mathrm{F}/dx = 4\pi\rho_0$, where $\rho_0 = n_0 e$ and n_0 denotes the number of electrons per cubic centimetre in the platinum. These relations enable V, the difference of potential between the layer and the platinum, to be calculated.

Let $p = -\beta\rho$, where β is a constant at constant temperature, so that

$$-\frac{dp}{dx} = \beta\frac{d\rho}{dx} = \frac{\beta}{4\pi}\frac{d^2\mathrm{F}}{dx^2}.$$

Hence

$$\beta\frac{d^2\mathrm{F}}{dx^2}+\mathrm{F}\frac{d\mathrm{F}}{dx} = 0,$$

which gives

$$\beta\frac{d\mathrm{F}}{dx}+\tfrac{1}{2}\mathrm{F}^2 = c.$$

In the same way

$$\beta\frac{d\mathrm{F}'}{dx}+\tfrac{1}{2}\mathrm{F}'^2 = c' = 0.$$

Hence

$$-\frac{\beta}{\mathrm{F}'} = -\frac{x}{2}+\text{constant},$$

which gives

$$\beta\left(\frac{1}{\mathrm{F}'}-\frac{1}{\mathrm{F}'_t}\right) = \tfrac{1}{2}(x-t).$$

When $x = 0$, we have $4\pi\rho_0\beta+\tfrac{1}{2}\mathrm{F}_0^2 = c$, and when $x = t$, since

$$\frac{d\mathrm{F}}{dx_t} = \frac{d\mathrm{F}'}{dx_t} = -\frac{\mathrm{F}'^2_t}{2\beta},$$

we get $\mathrm{F}_t^2-\mathrm{F}'^2_t = 2c$, or $\mathrm{F}_t^2-(\mathrm{F}_t+4\pi\sigma)^2 = 2c$, which gives $\mathrm{F}_t = -c/4\pi\sigma-2\pi\sigma$. Now in the case of hot platinum we know that only a very small fraction of the electrons which collide with the surface escape, so that ρ outside the layer is very small; hence, when t is small and σ large, it is clear that F'_t will be small compared with F_t. Consequently $\mathrm{F}_t^2 = 2c$ very nearly, so that $2c = (-c/4\pi\sigma-2\pi\sigma)^2$, which gives $c = 8\pi^2\sigma^2$, so that $\mathrm{F}_t = -4\pi\sigma$. Hence

$$\beta\frac{d\mathrm{F}}{dx}+\tfrac{1}{2}\mathrm{F}^2 = 8\pi^2\sigma^2.$$

Integrating this gives

$$\frac{F}{a} = \frac{F_0 - a + (F_0 + a)\,e^{ax/\beta}}{F_0 - a - (F_0 + a)\,e^{ax/\beta}}, \text{ where } a = -4\pi\sigma.$$

The equation $8\pi\rho_0\beta + F_0^2 = a^2$ gives $F_0 - a = -8\pi\rho_0\beta/(F_0 + a) = \rho_0\beta/\sigma$ very nearly, because F_0 and a must be nearly equal. Hence

$$-F/4\pi\sigma = \left(1 - \frac{\rho_0\beta}{8\pi\sigma^2}\,e^{4\pi\sigma x/\beta}\right)\Big/\left(1 + \frac{\rho_0\beta}{8\pi\sigma^2}\,e^{4\pi\sigma x/\beta}\right).$$

This gives

$$V = -\int_0^t F\,dx = -\beta \log\left(1 + \frac{4\pi\sigma^2}{\rho_0\beta}\,e^{-4\pi\sigma t/\beta} + \frac{\rho_0\beta}{16\pi\sigma^2}\,e^{+4\pi\sigma t/\beta}\right)$$

$$-\beta \log\left(1 + \frac{4\pi\sigma^2}{\rho_0\beta} + \frac{\rho_0\beta}{16\pi\sigma^2}\right).$$

In this expression

$$\frac{\rho_0\beta}{16\pi\sigma^2}\,e^{4\pi\sigma t/\beta}$$

is quite negligible for platinum, and $\rho_0\beta/16\pi\sigma^2$ is small compared with $4\pi\sigma^2/\rho_0\beta$, hence

$$V = -\beta \log\left(1 + \frac{4\pi\sigma^2}{\rho_0\beta}\,e^{-4\pi\sigma t/\beta}\right) - \beta \log\left(1 + \frac{4\pi\sigma^2}{\rho_0\beta}\right).$$

This is almost the same as

$$V = -\beta \log e^{-4\pi\sigma t/\beta}\left\{1 - \frac{\rho_0\beta}{4\pi\sigma^2}\right\}$$

or

$$V = 4\pi\sigma t + \rho_0\beta^2/4\pi\sigma^2.$$

Let $4\pi\sigma te = w$, and then

$$Ve = w + 4\pi\rho_0 e^3 t^2 \beta^2 w^{-2}.$$

Now Ve is the work which an electron must do before it can escape, so that if N denotes the number of electrons in one gram-molecule, $R = NVe/J$, where J is the mechanical equivalent of heat. Let $\beta = \beta_0\theta$, and we get

$$R = \frac{Nw}{J} + \frac{4\pi N\rho_0 e^3 t^2 \beta_0^2 \theta^2}{Jw^2}.$$

If θ increases one degree, R therefore increases by $8\pi N\rho_0 e^3 t^2 \beta_0^2 \theta/Jw^2$.

In the last section we got $R = Q + 2\theta \log(D/A)$, according to which R increases uniformly with θ. But the experiments only extend over a small range of temperature, so that they are not sufficient to distinguish between the equations $R = Q + k\theta$ and $R = Q + k'\theta^2$, where k and k' are constants. The equation $R = Q + 2\theta \log(D/A)$ depends on the assumption that Q, D, and A are all independent of the temperature.

The experiments show that Q and A do not vary much with the temperature, but it is quite possible that they really vary to some extent, for they cannot be found very exactly. Consequently I think it is justifiable to regard the two formulæ for R as equivalent over the range of temperature of the experiments, and so to put

$$2 \log (\mathrm{D}/\mathrm{A}) = 8\pi \mathrm{N} \rho_0 e^3 t^2 \beta_0{}^2 \theta / \mathrm{J} w^2.$$

Now $\mathrm{N}w/\mathrm{J} = 4\pi\sigma te\mathrm{N}/\mathrm{J}$ is the value of R when $\theta = 0$, so it will be approximately equal to Q.

Hence we get $w = \mathrm{QJ}/\mathrm{N}$ and $\mathrm{Q}^2 \log (\mathrm{D}/\mathrm{A}) = 4\pi \mathrm{N}^3 e^3 \rho_0 t^2 \beta_0{}^2 \theta / \mathrm{J}^3$.

If we suppose that the hydrogen in the layer consists of positively charged atoms, it will increase σ without altering t. If, then, a value of D can be found which will make $\mathrm{Q}^2 \log (\mathrm{D}/\mathrm{A})$ a constant, this may be taken to be the true value of D. Let $\mathrm{Q}^2 \log (\mathrm{D}/\mathrm{A}) = \mathrm{C}$, and then D and C can be found from two values of A and the corresponding values of Q. Taking the values

Q.	A.
145000	$1 \cdot 14 \times 10^8$
90000	5×10^4

gives $\mathrm{D} = 1 \cdot 44 \times 10^{10}$ and $\mathrm{C} = 10 \cdot 2 \times 10^{10}$. Using these values of C and D, we obtain the following values of $\mathrm{Q}^2 \log \mathrm{D}/\mathrm{A}$:—

Q.	A.	$\mathrm{Q}^2 \log \mathrm{D}/\mathrm{A}$.
145000	$1 \cdot 14 \times 10^8$	$10 \cdot 2 \times 10^{10}$
131000	$6 \cdot 9 \times 10^7$	$9 \cdot 0 \times 10^{10}$
110000	10^6	$11 \cdot 6 \times 10^{10}$
90000	5×10^4	$10 \cdot 2 \times 10^{10}$
56000	2×10^2	$5 \cdot 7 \times 10^{10}$

The five values of C agree as well as could be expected. We have, therefore,

$$10^{11} = 4\pi \mathrm{N}^3 e^3 \beta_0{}^2 t^2 \rho_0 \theta / \mathrm{J}^3.$$

According to RICHARDSON's theory we have

$$\rho_0 = n_0 e = \mathrm{D} \times 3 \times 10^9 (\pi \mathrm{N} m/\mathrm{J})^{\frac{1}{2}},$$

where m is the mass of one electron. This gives, taking $e/m = -1 \cdot 8 \times 10^7$ in E.M. units and $\mathrm{N}e = -2 \cdot 9 \times 10^{14}$ in E.S. units, $\rho_0 = -2 \cdot 73 \times 10^{14}$ electrostatic units per cubic centimetre.

We have also $\beta_0 = 2{\cdot}8 \times 10^{-7}$, so that at $\theta = 1600$ we get

$$(4{\cdot}2 \times 10^7)^3 \times 10^{11} = 4\pi t^2 (2{\cdot}9 \times 10^{14})^3 (2{\cdot}8 \times 10^{-7})^2 \, 1600 \times 2{\cdot}73 \times 10^{14},$$

which gives $t = 2{\cdot}6 \times 10^{-8}$ centim.

The thickness of the double layer on platinum polarised by depositing hydrogen on it from dilute sulphuric acid has been calculated from the polarisation capacity by several observers who have found t about 2×10^{-8} centim. We should, of course, expect the thickness to be about of the order of the diameter of a molecule, which is believed to be about 2×10^{-8} centim. I think the fact that the theory proposed here leads to a value of t in agreement with that which might have been expected on other grounds shows that the theory is substantially correct.

Since platinum is an octovalent element we may take the number of free electrons associated with each atom as 8. The charge ρ_0 carried by the free electrons in one cubic centimetre of platinum ought therefore to be $8s\mathrm{N}e/\mathrm{M}$, where s denotes the density and M the atomic weight of the platinum. This gives

$$\rho_0 = -8 \times 21{\cdot}5 \times 2{\cdot}9 \times 10^{14} \div 195 = -2{\cdot}6 \times 10^{14},$$

which agrees very well with the value $-2{\cdot}7 \times 10^{14}$ obtained from the negative leak. The agreement between these two values of ρ_0 shows that all the 8 electrons associated with each atom of platinum are included in n_0, the number per cubic centimetre on which the negative leak depends.

Substituting the values found for D, A and Q in the formula $\mathrm{R} = \mathrm{Q} + 2\theta \log(\mathrm{D}/\mathrm{A})$, we get the following values of R :—

Gas.	Pressure.	R.
	millims.	
Air	—	$145000 + 9{\cdot}68\theta$
H_2	0·0013	$110000 + 19{\cdot}15\theta$
H_2	0·112	$90000 + 25{\cdot}14\theta$
H_2	133·0	$56000 + 36{\cdot}18\theta$

At $\theta = 2000$ these values are 164000, 148300, 140280 and 128360. The values of R at other pressures can be calculated, if desired, by means of the formula given in the last section.

A difficulty in the electron theory of the conductivity of metals has been pointed out by J. J. THOMSON in his book 'The Corpuscular Theory of Matter.' If the energy required to raise the temperature of the electrons one degree is calculated, it comes out greater than the specific heat of the metal. We have

$$p = -\beta\rho_0 = -\beta_0\rho_0\theta = \tfrac{1}{3} m n_0 \mathrm{U}^2,$$

where U^2 is the mean value of the square of the velocity of agitation of the electrons.

Thus $-\beta_0\rho_0\theta = \frac{2}{3}E$, where E is the kinetic energy of the electrons. Hence the energy required to raise the temperature of the electrons in 1 cub. centim. of platinum one degree is $dE/d\theta = -\frac{3}{2}\rho_0\beta_0 = \frac{3}{2} \times 2{\cdot}73 \times 10^{14} \times 2{\cdot}8 \times 10^{7}$ ergs. This gives $dE/d\theta = 2{\cdot}7$ calories, which is about three times the heat required to raise the temperature of 1 cub. centim. of platinum one degree at high temperatures.

It is possible that the number of free electrons per cubic centimetre is greater close to the surface of the platinum than inside. The value of ρ_0 deduced from the negative leak is, of course, the value close to the surface. Another very possible explanation of the difficulty is that D and ρ_0 have been over-estimated. If D is taken ten times smaller, or $1{\cdot}44 \times 10^{9}$, the energy required per cubic centimetre is only 0·27 calories per cubic centimetre, which is about one-third of the heat capacity per cubic centimetre. This value of D makes the thickness of the double layer 2×10^{-8} centim. instead of $2{\cdot}6 \times 10^{-8}$, and with it $Q^2 \log (D/A)$ is nearly as constant as with the value used. In fact, the possible error in D is at least a factor of 10, so that the difficulty about the specific heat is not very serious in the case of platinum if the value of ρ_0, deduced from the negative leak, is taken.

10. *Conclusion.*

The view taken in the above paper is that the effect of the hydrogen on the negative leak is due to its presence in the surface layer of the platinum. To explain this it is supposed that the hydrogen atoms are positively charged, so that they diminish the charge per unit area in the electrical double layer covering the surface of the platinum. The hydrogen appears to dissolve in the platinum at first, but at high pressures in time forms a stable combination, having a very small dissociation pressure. With new wires, before the stable compound has been formed, the leak is proportional to a power of the pressure of the hydrogen.

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