The Ionisation Produced by Hot Platinum in Different Gases

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PHILOSOPHICAL TRANSACTIONS.

I. *The Ionisation Produced by Hot Platinum in Different Gases.*

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I.—§ 1. Introduction.

The principal objects of this investigation have been to examine the part played by the surrounding gas in the production of ions by hot metals and to discover, if possible, the mechanism by which the positive ions originate. In what follows, previous work on ionisation by hot metals will not be described, except in so far as it bears directly on the questions investigated, since the historical part of the subject has been fully treated in previous papers by the writer,[*] and others.

The present communication deals chiefly with the emission of positive ions from hot platinum, as earlier work has yielded much more information concerning the negative ionisation. In 1901 the writer[†] showed that a great number of facts in connection with the negative ionisation from hot metals could be explained by supposing that the electrons, of which the ions consist, were produced in the metal itself, from which they escaped by virtue of their kinetic energy. This theory makes the negative ionisation a function only of the metal surface and its temperature, and therefore independent of the nature and pressure of the surrounding gas, except in so far as this may have the effect of modifying the nature of the metallic surface. H. A. Wilson[‡] has confirmed this part of the theory by showing that the negative leak, except when ionisation by collision occurs, has the same value in air, nitrogen, and water vapour over a wide range of pressures. Wilson also showed, however, that hydrogen greatly modifies the negative leak. The experiments in the present paper seem to show that the effect of hydrogen is due to some change it produces in the platinum surface; its abnormal behaviour is probably bound up with its electro-positive character.

[*] 'Jahrbuch der Radioaktivität u. Elektronik.'

[†] 'Camb. Phil. Proc.,' vol. 11, p. 286.

[‡] 'Phil. Trans.,' A, vol. 202, p. 243.

All the known evidence relating to the ionisation from hot solids goes to prove that the positive and negative ionisations are, in the majority of cases, entirely separate effects. It is true that, generally speaking, a hot metal produces ions of both signs simultaneously, but by suitably altering the conditions the ratio of the two ionisations can be made to change to almost any required extent, even at constant temperature, and the one can be made to vary greatly whilst the other remains practically constant, so that it is evident that the two ionisations are produced by the operation of at least two independent causes. The leak from hot solids is, therefore, essentially unipolar.

In the 'Philosophical Magazine' (6), vol. VI., p. 80, the writer showed that the current from a fresh positively-charged hot platinum wire fell off asymptotically with the time the wire was heated at constant temperature. An effect of this kind was first recorded by ELSTER and GEITEL,* who noticed that an insulated plate near an incandescent platinum wire received a large positive charge when the wire was new, which gradually diminished, and ultimately changed sign with continued heating. This initial positive ionisation is presumably independent of the pressure, since it is very large in a good vacuum. Despite numerous experiments† its origin is still uncertain, but it is possibly due to some gas or volatile impurity present in the purest obtainable platinum.

By using a wire in which the initial positive leak had been reduced to a small value by heating in a good vacuum at a constant temperature at intervals extending over a long period of time, and subsequently letting in fresh air, the writer‡ succeeded in clearly showing that the leak, which was almost independent of the time, consisted of two parts, one proportional to, and the other independent of, the pressure of the air. So far as the writer is aware, this is the first experiment recorded which shows that any part of the positive leak from hot metals is a function of the pressure of the surrounding gas. The reasons which made such an effect difficult to detect are (1) the masking of the effect by the initial positive leak, if this has not been completely removed, and (2) irregularities and time effects in the part of the leak produced by the gas itself. These will be discussed at some length later in the paper.

In the present investigation a much more detailed study has been made of the ionisation in oxygen than in the other gases considered, for several reasons. In the first place, oxygen is a simple elementary gas which is easily prepared in a state of considerable purity. It has the additional advantage that small quantities of it produce a large increase in the positive ionisation which is readily measured. Finally, it acts as a self-purifying agent by oxidising, and so getting rid of, hydrogen—an impurity which it is of the utmost importance to avoid in experimenting on the ionisation produced by hot bodies.

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* 'Wied. Ann.,' vol. 37, p. 315 (1889).

† O. W. RICHARDSON, 'C.R. Congrès Liège,' 1905, p. 50.

‡ 'Camb. Phil. Proc.,' vol. 13, p. 58 (1905).

Besides oxygen, the present paper contains an account of measurements of the ionisation of both signs from hot platinum in air, nitrogen, helium, and hydrogen. There are also measurements of the ionisation from a platinum surface in air when a calculable quantity of hydrogen is diffusing out from the interior of the platinum. The last-named experiments shed a considerable amount of light on the mechanism of the processes by which the ions are produced.

It is necessary to say a word about the use of the term ionisation in this paper. By "the positive (or negative) ionisation" in a quantitative sense is meant the number of positive (or negative) ions liberated by 1 sq. centim. of the platinum surface per second under the conditions specified. The ionisations are, therefore, proportional to the respective saturation currents calculated per square centimetre of surface.

For convenience of reference the paper has been subdivided as follows:—

II.—§ 2. EXPERIMENTAL ARRANGEMENTS.

Except where the contrary is distinctly stated, the arrangement of apparatus used was similar to that in the author's previous papers.* The platinum wires were supplied by Messrs. JOHNSON MATTHEY AND Co., and were of the purest material obtainable. They were 0·01 centim. in diameter and were in the form of a loop, the wire being about 7 centims. long. The ends of the loop were welded on to stouter platinum leads (A, fig. 1) which were sealed into one end of a glass tube about

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* *Cf.* 'Phil. Trans.,' A, vol. 202, p. 243.

8 centims. in length. The wire was heated electrically as before, and in measuring its temperature the same Wheatstone's bridge method was made use of to determine its resistance. This method is an exceedingly sensitive one, and there is no difficulty in keeping the resistance constant to one or two degrees at the highest temperatures. This is a matter of considerable importance in working with hot wires when the leak is a rapidly variable function of the temperature.

The whole of the apparatus, which was in electrical connection with the leads A, was insulated on paraffin blocks and could be charged to any potential between 0 and ±800 volts. Owing to the heating current through the platinum filament there was a fall of potential along the wire amounting to from about 2 to 6 volts according to the temperature, which had to be taken into account at low voltages. The current from the wire was measured by means of a Dolezalek electrometer with a suitable capacity attached to the quadrants. For insulating the plate B the dry glass inside the tube was found to be good enough, but outside it was protected by sealing wax surrounded by a guard ring.

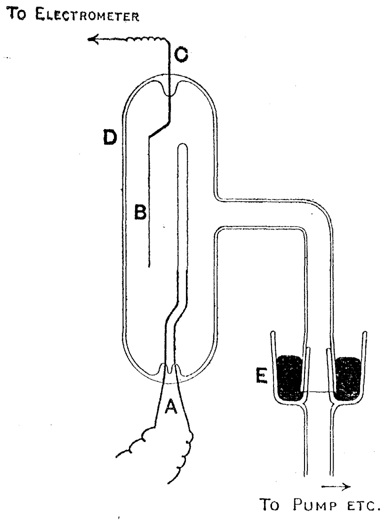

Fig. 1.

In work of this kind the cleanliness and purity of the materials employed are of the utmost importance. In the apparatus shown in fig. 1 it will be noticed that all the parts are of platinum and glass. This enabled the tube to be cleaned with boiling nitric acid and distilled water before the experiments commenced. The ground-glass joint E enabled a further refinement to be effected by obviating the necessity of finally fusing the side tube on to the pump connections and thereby bringing the cleaned wire into contact with the gases from the blowpipe flame. The ground joint was lubricated with carefully purified graphite and was sealed with mercury externally.

The oxygen used was prepared in two ways. When small quantities only were required it was obtained by heating potassium permanganate in a tube sealed on to the apparatus. It was found advisable to have the tube containing the permanganate shut off from the rest of the apparatus by a mercury trap as it gave off a small quantity of gas or vapour even when the salt had been dried by heating to 120° C. for two hours before it was sealed up. The oxygen produced in this way is freed from dust by plugging up the front end of the permanganate tube with glass wool. When larger amounts of oxygen were required the above method was found to be inconvenient, and the electrolysis of concentrated caustic potash was substituted for it. The oxygen evolved underwent a preliminary drying by passing through a tube packed with solid potassium hydrate before being admitted, through a glass tap, to the main apparatus, where it was subjected to the further action of phosphorus pentoxide. As thus prepared, the gas was liable to contain traces of hydrogen and hydrocarbons, but that these were not in sufficient amount to affect the results was proved by the fact that the oxygen prepared in this way gave the same results as that obtained from potassium permanganate, which must have been free from these impurities.

The resistance readings were reduced to platinum temperatures by the method described by CALLENDAR.* The wire was standardised by determining the melting point of potassium sulphate by the method previously described.† For the parabolic correction, which is small at all the temperatures considered, WILSON'S‡ value of the constant ($A = 151$) was assumed. This assumption seems justifiable as the value referred to the same kind of platinum wire.

It has been pointed out above that it is necessary to get rid of the initial positive leak from hot platinum before experiments can be made on the part of the leak which is due to oxygen. The following figures give the actual magnitude of the two leaks for the wire which was employed in this investigation. The wire was cleaned by boiling with nitric acid and distilled water before commencing and the apparatus was pumped out to a pressure of 0·00005 millim. The initial positive leak under these conditions at a temperature of 804° C. was found to be equal to $1{\cdot}62 \times 10^{-8}$ ampère. With the wire at a constant temperature this fell to half in about 10 minutes and, the rate of decay falling off with time, reached about one-tenth its original value after an hour's heating. Even after heating the wire for several hours a day for nearly a fortnight the part of the leak which was independent of the pressure could not be neglected in comparison with that which depended on the pressure, as the following numbers, which were obtained at a temperature of 721° C., testify :—

Pressure.	Current.
millim.	ampère
0·045	$1{\cdot}8 \times 10^{-12}$
0·03	$1{\cdot}52 \times 10^{-12}$
0·016	$1{\cdot}4 \times 10^{-12}$
0·004	$9{\cdot}6 \times 10^{-13}$
0·0003	$9{\cdot}6 \times 10^{-13}$

These numbers show that increasing the pressure from 0 to 0·045 millim. increases the leak from $9{\cdot}6 \times 10^{-13}$ to $1{\cdot}8 \times 10^{-12}$. The part of the leak due to the gas, for very small pressures like the above, is very nearly proportional to the gas pressure. The residual initial leak ($9{\cdot}6 \times 10^{-13}$ ampère) exhibited by these results was about equal to the leak produced in oxygen at a pressure of 0·05 millim. ; it was not permanent, however, but fell away till it could no longer be detected on the electrometer at this

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* 'Phil. Mag.' [5], vol. 48, p. 519.

† 'Phil. Trans.,' A, vol. 201, p. 497.

‡ 'Phil. Trans.,' A, vol. 202, p. 243.

temperature. In respect of falling away with time, the initial leak offers a very marked contrast to the part of the leak which depends on the surrounding oxygen. This was found to remain constant, except for a temporary variability, under the same conditions during the whole of the time the experiments were being carried out. The experiments on this particular wire lasted about three months and during that time it was heated at various high temperatures for about 150 hours.

In the sequel it will be shown that as the pressure of the oxygen is increased the current from the positively-charged wire asymptotically approaches a maximum value. It is interesting to compare this value, which is independent of the pressure, with the initial leak at the same temperature. The experiments show that at 804° C. the greatest positive leak from an old platinum wire of the above dimensions in oxygen $= 3{\cdot}6 \times 10^{-11}$ ampère, and is therefore about one five-hundredth part of the initial leak from a new wire.

Another source of trouble in these experiments arises from variations which take place in the leak when all the controllable conditions are kept constant. These variations, which will be considered more fully in the sequel, appear to fall into two classes. The first are of a hysteretic nature and depend on the previous treatment of the wire. For instance, if the gas pressure is suddenly lowered the leak does not decrease immediately, but only gradually settles down to its final steady value. Increasing the pressure gives rise to the converse effect. Sudden changes of temperature, and in some cases of potential, will be shown to give rise to similar hysteretic effects. These changes can be explained by supposing that the leak is due not to the external gas, but to oxygen, which is held chemically or otherwise in the superficial layers of the platinum, and that the amount necessary for equilibrium takes time to adjust itself.

The second kind of variation seemed to be of a purely irregular nature, and manifested itself by sudden jumps in the rate of movement of the electrometer spot across the scale. This effect was specially marked at high pressures, and at low pressures was not so noticeable. It may be due to the pressure of the contained oxygen becoming great enough to force a way through the overlying layer of platinum, and so giving rise to a sudden evolution of highly ionised gas.

To eliminate errors due to effects of the first kind, some time was always allowed to elapse after each change had been made, and readings taken from time to time until the leak became steady. At high pressures, where irregularities of the second kind occurred in addition, it was more difficult to obtain the equilibrium value of the leak; but by neglecting all readings where the movement of the spot was noticed to be jerky, by always taking the smallest values of the leak, and by waiting till two or more of these were identical, consistent results could always be obtained. This procedure was rather tedious in some cases, but it seemed to be the only method, as the irregularities concerned were not affected by any change in the controllable conditions (except by diminishing the pressure).

III.—The Ionisation in Oxygen.

§ 3. *Current and Electromotive Force.*

In considering the results of experiments under this head it is important to remember that owing to the thinness of the wires used most of the fall of potential occurred near the surface of the wire. For this reason there was always a considerable electric intensity near the hot wire even when the potential difference between the electrodes was quite small. As a sufficient approximation for the experiments described in the next three sections we may take the electric intensity at the surface of the wire to be 40 V for the wires 0·1 millim. in diameter, and 20 V for the wires 0·2 millim. in diameter, where V is the applied potential difference in volts.

Except within certain limited ranges of pressure and voltage the positive leak from a hot wire in oxygen was found to be independent of the applied electromotive force. A saturation current therefore always exists, and it follows that, except in certain special cases, the number of positive ions produced per second by a hot platinum surface does not depend on the external electric field. For instance, an experiment at 700 millims. pressure and a temperature of 793° C. gave the following values of the current with different E.M.F.'s, the experiments being made in the order indicated :—

Volts	80	40	200	400	80	200
Current . . . . (1 = $1 \cdot 19 \times 10^{-12}$ ampère)	23	23	23	24·5	23	20

The values of the current may be regarded as constant within the probable experimental error.

It is evident that at pressures near atmospheric, saturation is attained with a P.D. of less than 40 volts. As a matter of fact, in these cases, where all the ionisation is of one sign, there is, of course, no recombination and, provided the whole of the hot wire is at a positive potential great enough to overcome the tendency to diffuse back into the wire, all the ions produced reach the collecting electrode. A saturation current is thus obtained with a very small voltage. This is shown by some experiments made at a pressure of the same order of magnitude, 528 millims., as in the last experiment, and at a temperature of 706° C. The fall of potential along the filament, due to the heating current, was equal to 3·3 volts. The currents obtained with the various assigned *mean* voltages on the filament are as follows :—

Mean voltage	0	1·75	38	1·75	3·7	1·75	5·8	18	1·75	38	0
Current. . . . . . (1 = 6×10^{-13} ampère)	4	20	14·8	18·5	15·8	19·5	15·5	15	20	14·8	4·8

It will be seen that the maximum current is obtained with the potential at the middle point of the filament equal to +1·75 volts. Since there was a fall of potential of 3·3 volts along the filament due to the heating current, the more negative end would only be at a potential of +0·1 volt when saturation occurred; so that it is evident that the only competition the electrode experiences in collecting the ions is that due to the filament itself.

The mean potentials in cases where low voltages were used were determined by connecting a Weston voltmeter, one terminal of which was earthed, to each end of the filament in turn. The gradual decrease in the current as the potential rises from 1·75 to 38, which is very evident from the above numbers, will be dealt with later.

These current E.M.F. curves which show saturation at about 2 volts were only obtained at low temperatures. At higher temperatures the necessary voltage went up to about 40, as is shown by the following table:—

Mean voltage	+0	+4·1	+16	+42	+80	−40
Current . . . . (1 = $2 \cdot 4 \times 10^{-11}$ ampère)	5	36	57	63	68	0·04

Temperature = 1180° C. Pressure = 89 millims.

The greater difficulty experienced in reaching saturation at high temperatures may possibly be due to the relatively greater magnitude of the negative ionisation which would make recombination a factor to be reckoned with.

The experiments show that a potential of +80 volts is sufficient to saturate the current from a platinum wire at all the temperatures used. This is of great importance in the sequel, where the leak with 80 volts is used to measure the total number of ions produced by a platinum wire under various conditions.

When the pressure of oxygen in the apparatus was of the order of one millimeter, the current ceased to be independent of the voltage at high voltages. A careful series of measurements was therefore made of the way in which the current varied with the voltage at different pressures. The results are given in the next table and are also exhibited graphically in fig. 2. The measurements at the lowest pressure (0·06 millim.) were made at a temperature of 822° C.; for all the other pressures the temperature was 808° C. To eliminate time changes, the leak with +80 volts was taken as a standard and was measured both before and after each observation with another voltage. This precaution was not really necessary, as the steady state had been reached before the measurements commenced, but it served as a useful check. On account of the method of taking the observations, and also because they do not all refer to the same temperature, the absolute values of the leaks have not been given, but for each pressure they are referred to the current with +80 volts as a standard which is put equal to unity. The absolute values at different pressures can be obtained from the results for the pressure variation which will be given in a later section.

Pressure.	Current.								
	Voltage = +40.	Voltage = 80.	Voltage = 120.	Voltage = 200.	Voltage = 240.	Voltage = 280.	Voltage = 320.	Voltage = 360.	Voltage = 400.
millims.									
3·46	1·1	1	0·94	1·0	—	0·96	—	—	1·24
1·05	1·03	1	0·96	1·17	—	1·27	1·22	1·69	2·5
0·58	1·06	1	—	1·24	1·29	1·43	1·70	1·97	3·55
0·186	—	1	—	1·19	—	1·65	1·87	2·27	3·8
0·06	0·81	1	1·01	—	—	1·38	—	1·40	1·68

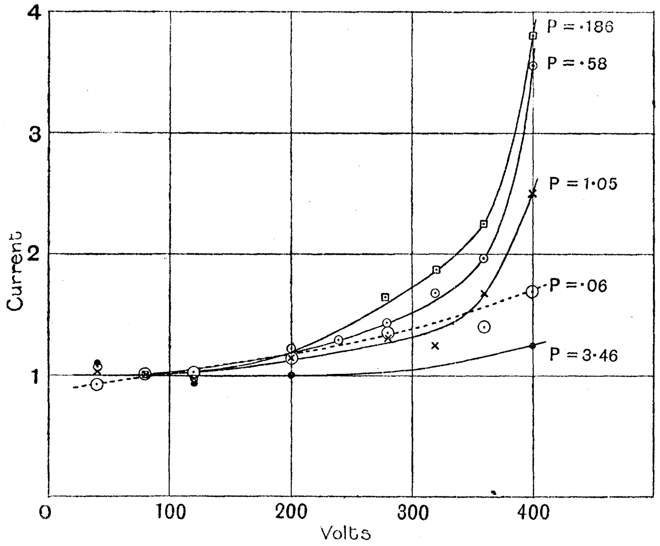

Fig. 2.

These results can readily be explained if we suppose that the wire produces at its surface a constant number of positive ions per second—which, however, depend, as will be seen later, on the pressure of the gas—and these ions are all collected unchanged by the electrode at low voltages. When the voltage increases to 200 or more, these positive ions produce others by collision and an increase in the current is obtained. The above increase in the current possesses all the features which are required by the view that it is due to ionisation by collision. The change produced by altering the P.D. from one to another assigned value increases as the pressure is diminished, reaches a maximum and ultimately disappears. Thus the ratio of the current under a given voltage to that under 80 volts reaches a maximum as the pressure is diminished.

The difference in the effect of the positive and negative ions from hot metals in producing other ions by collisions is readily seen when the above curves are compared with similar ones given by H. A. WILSON* for the negative leak from hot platinum in air at different pressures. WILSON used wires of the same thickness and an apparatus of about the same dimensions as the author, so that the two sets of observations are quite comparable. It will be noticed that with the negative leak a given P.D. changes the current in a given ratio at a much higher pressure than with the positive leak. In addition, the pressures for the maximum current with a given voltage are much lower for the positive than the negative leak. For instance, when $V = 340$, the maximum current for the negative leak is somewhere between 12·1 and 0·81 millim., whereas for the positive leak it is at a pressure somewhere near 0·2 millim. Thus for corresponding effects the value of X/p, where X is the electric intensity and p the pressure, has to be much greater when the positive ions are the active agents than when the negative ions are. The actual difference between the effects of the two kinds of ions is diminished owing to the fact that the negative ions which the original positive ions produce by collisions also act as ionising agents.

Curves resembling some of the above have been obtained previously by MCCLELLAND†, who also explained the increase in the current produced by the electromotive force as being due to the positive ions producing others by collisions.

The author has calculated the number of positive ions which reach a surrounding cylinder when a given number start from a wire of given radius at its centre and both the positive ions and the negative ions subsequently produced give rise to others by collision, in the hope that it might be applied to the further elucidation of the above experimental results. The expression obtained, however, is so complex that its manipulation, so as to fit the observations, did not seem likely to greatly advance our knowledge of the subject. There does not, however, so far as one can see, seem to be anything in these results contrary to the view that the positive ions from hot metals have about the same power as the positive ions produced by Röntgen rays in air of producing other ions by collisions, and that the other ions so produced consist, in any given case, of an ordinary positive ion together with a corpuscle.

§ 4. *Hysteretic Relations between Current and Electromotive Force.*

The numbers given in Table 4, § 3, exemplify the curious fact that in some cases the current increased with diminishing potential difference. The case cited was not found to be an isolated instance, as the following numbers, obtained at a temperature of 826° C. and a pressure of 0·4 millim., testify :—

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* 'Phil. Trans.,' A, vol. 202, p. 253 (1903).

† 'Camb. Phil. Proc.,' vol. 11, p. 300 (1902).

Mean volts	−0·9	0	+0·4	+0·6	+0·9	+3·2	+8·2	+8·5	+40
Steady current . . . (1 = 6 × 10^{-13} ampère)	0·9 — — —	1·5 — — —	2·8 — — —	12 — — —	13 13 — —	20·7 20 21·7 21	15·7 15·4 — —	14·8 — — —	13·4 — — —
Mean steady current . .	0·9	1·5	2·8	12	13	20·8	15·5	14·8	13·4

Similar results were obtained at a pressure of 0·0015 millim., so that this effect occurs at all pressures.

The numbers quoted do not give the value of the current immediately the potential was put on, but what it settled down to later. In all these cases it was found that on raising the potential the current was too big at first, and only settled down to its steady value after some minutes. Similarly, on changing to a low voltage the current was too small at first and subsequently increased somewhat. Effects of this kind were much more marked with wires which had not been heated very much, and will be considered more fully under § 13. They can obviously be explained if we assume that the electric field displaces the equilibrium condition in such a way as to reduce the number of ionising systems.

Effects of this kind could not be detected at higher temperatures, owing to the greater difficulty of attaining saturation already alluded to. In these cases it was found that, though no certain increase in the current could be detected on changing the potential from 40 to 80 volts, yet it increased by about 60 per cent. with a potential of 760 volts. This increase was approximately proportional to the voltage. When it occurred, 600 volts was used to measure the saturation current; it was not safe to go up to much higher voltages, owing to the possibility of ionisation by collisions occurring even at high pressures.

§ 5. *Current and Pressure.*

We come now to what has been regarded throughout as the main object of this investigation, namely, the relation between the ionisation produced by the wire and the pressure of the surrounding gas. In interpreting the results, it is important to remember (1) that the current was always saturated, and (2) that, at low temperatures at any rate, the negative leak in oxygen was always found to be small compared with the positive. These two results conjoined prove that volume ionisation of the gas round the wire is negligible, at any rate at low temperatures. Moreover, there is every reason to believe that the negative ionisation, which makes itself felt even in oxygen at higher temperatures, is the ordinary corpuscular emission from hot metals, so that everything points to the positive ionisation being due to an action which takes place at the surface of the metal.

In a previous paper, which has already been quoted,* it was shown that the leak from a hot platinum wire in air at low pressures fell off as the pressure was reduced from about 0·1 millim. to 0 in such a way as to indicate that the leak consisted of two parts, one proportional to the pressure, and one independent of it. A similar experiment was now made with pure oxygen, except that observations were started at a higher pressure. The results of this experiment are given in the next table. The temperature was 816° C., and the potential on the filament +80 volts.

Pressure in millims. . .	0·000008	0·00028	0·0183	0·116	0·207	0·374	0·675	1·26	2·18
Current . . . . . . (1 = 6 × 10^{-13} ampère)	2·15	2·15	5·2	9·5	13	15·5	17	20	24

The pressure was varied by making one stroke of the pump and then making an observation, after waiting for everything to become steady, at the reduced pressure thus obtained. The order in which the observations were taken was thus that of diminishing pressure, so that any secular change which might be going on would go entirely in the one direction and might vitiate the results. In order to test whether an effect of this sort was coming in, fresh air was let into the apparatus the next day and observations again taken over a similar range. The results are exhibited along with the previous ones in fig. 3. The points marked thus × refer to the observations in Table IX., whilst those marked thus ⊙ refer to those taken on the following day. The experimental conditions were the same in both cases.

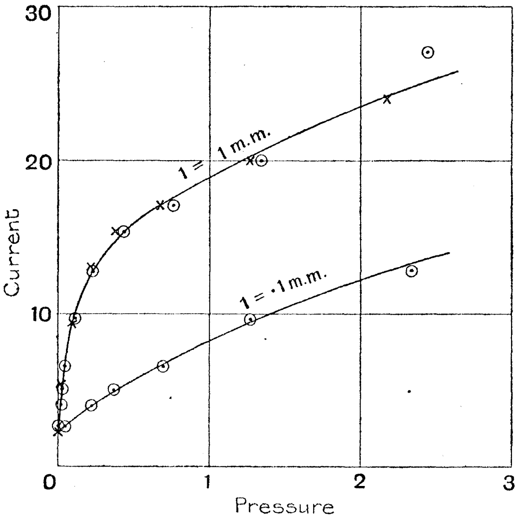

Fig. 3.

The lower curve may be compared with the numbers for air up to 0·11 millim. in the paper referred to above.* It will be seen that at these low pressures the part of the leak which depends on the gas is roughly proportional to the pressure, agreeing with what was previously found for air. The part of the leak which is independent of the pressure, which is clearly marked in fig. 3, is smaller relatively to the rest than in the previous experiments. It will not be noticed in the later curves, as it became too small to be noticeable after a few days' more heating.

Although the results given in fig. 3 show that hysteretic effects had been largely

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* 'Camb. Phil. Proc.,' vol. 13, p. 58, 1905.

eliminated from the experiments which they represent, still an inspection of the actual experimental numbers shows that such effects did occur. It was often observed, for instance, that if the wire had been heated for a time to a temperature higher than that at which observations were being taken, the value of the leak was too great for some time afterwards. For instance, in an experiment at 816° C., where the pressure was 1·4 millims. and the steady leak = 30, the unit being 6×10^{-13} ampère, after heating for a few minutes to about 1100° C. the wire was found to give the following values of the leak at the times in minutes stated.

Time	0	3	7	11	14	25	28	31
Current	90	70	56	44	40	30	31	30

It is evident from the above numbers that it took about 20 minutes for equilibrium to be established at this temperature, a fact which gives some indication of the prodigious labour required in taking the observations.

Another hysteretic effect, which is more likely to be a source of trouble in experiments on the effect of change of pressure, is a time lag of the change in the leak behind the change in the pressure. In testing for an effect of this kind it is evident, from the preceding paragraph, that it is necessary to keep the temperature constant while the pressure change is made. This is very difficult, since with a constant current through the wire its temperature is a function of the pressure of the surrounding gas, but by watching the galvanometer spot of the Wheatstone's bridge circuit, and manipulating the rheostats which control the heating current as quickly as possible, the temperature can be restrained from varying very much whilst the pressure change is being made. The following numbers represent the effect at 809° C. of suddenly reducing the pressure from 1·8 to 0·21 millim., the P.D. being +80 volts. The steady leak at 1·8 millims. had the value 18 ($1 = 1{\cdot}9 \times 10^{-12}$ ampère); the leak at 0·21 millim. had the values given at the times stated.

Time	hours . . .	12	12	12	12	12	12	1	1	2
	minutes . .	35	38	41	46	51	56	4	7	42
Current		14·8	13·7	13	10	9·5	8·1	9	7·8	7·3

In a similar way, on increasing the pressure, keeping the temperature constant, it was found that the leak at the higher pressure was too small at first and only gradually rose to its final steady value.

It is evident from what has been said that the lag in the leak behind pressure changes must have affected to some extent the results shown in fig. 3. The practically exact coincidence of the two curves might merely imply that the observations were taken at about the same rate in the two cases, so that the errors were about the same in each case. A check on this was, of course, afforded by the fact that values of the leak were only retained after they ceased to vary with the time; but partly owing to the great length of time required for equilibrium to be established, and partly owing to the invariable presence of irregularities of another kind, which will be considered later, it was very difficult to be sure that equilibrium had been attained in any specified case. For this reason it was thought desirable to have some further means of checking the extent to which these influences affected the measurements.

This was done by gradually increasing the oxygen pressure instead of diminishing it, as happened by taking readings after successive strokes of the pump. It is evident that under these conditions the pressure time lag will have the opposite effect to what it had when the pressure was being reduced, so that the lack of coincidence between the curves obtained with increasing and diminishing pressure will give a measure of the extent to which the lag effect has not been eliminated. What was required, then, was an arrangement which would deliver small adjustable quantities of oxygen into the main apparatus.

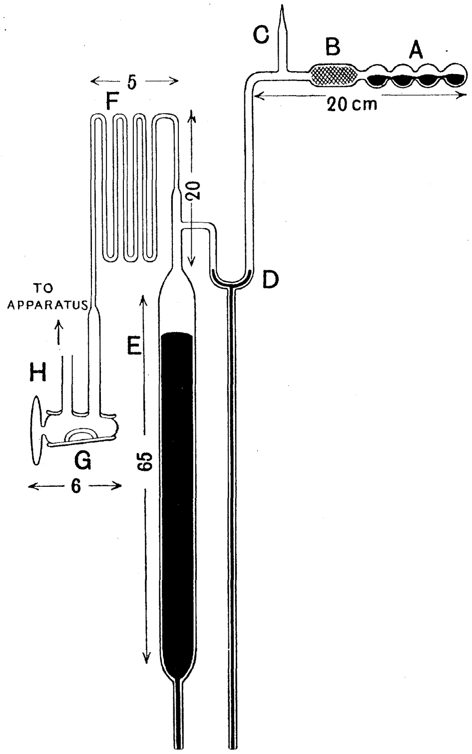

Fig. 4.

To do this, the apparatus shown in fig. 4 was devised. The principle of the method is to allow gas to flow into the apparatus through a very long narrow capillary tube under an adjustable difference of pressure for varying times. In the figure this part of the apparatus is shown together with the arrangement for furnishing the oxygen. The bulbous tube A contained pure dry potassium permanganate; by heating a small portion of it for variable lengths of time, any desired quantity of pure oxygen could be set free. Such a tube may be used time after time for long periods. B is a glass wool plug to stop the manganese dioxide dust which is produced when A is heated. C is a drawn-out glass tube which can be broken to let down the vacuum in this part of the apparatus if required. It is convenient to have the permanganate tube so that it can be shut off from the rest of the apparatus. This may be done by means of the mercury cut off D. At F is the fine capillary tube, bent as shown to economise space, through which the gas flowed into the main apparatus at H. This tube was about 140 centims. long, and was the narrowest available in the laboratory. By means of the tube E, which, like D, was filled with mercury, both being connected to separate reservoirs, the volume above the mercury at E could be regulated, and so any desired variation could be made in the pressure driving the gas through the tube F. Finally the glass tap E allowed the time during which the flow took place to be varied in any desired manner. By suitably varying the two controlling factors it was found that the pressure in the main apparatus could be increased by any amount from 0·001 millim. to several centimetres at will. This apparatus works very well and will probably be found to be very convenient for work of this kind. It permits of a much greater range of variation of pressure than a regulator which it has been found convenient to employ in previous experiments, which is practically a tube like E sealed directly on to the apparatus. With this the pressure is regulated by the change of volume produced when the height of the mercury column is altered.

Using the apparatus just described, a series of measurements of the leak was now made, with the pressure of the oxygen gradually increasing. The temperature was 826° C. and the potential on the filament = +40 volts. The numbers obtained were as follows:—

Pressure in millims.	0·0107	0·029	0·055	0·12	0·294	0·474	1·09
Current . . . . (1 = 6 × 10^{-13} ampère)	2·9	4·4	6·6	11·1	19·4	23	35

It will be observed that these numbers are very similar to those previously obtained with decreasing pressure, showing that the time effects do not play a very important part under the specified experimental conditions. In order to have a more exact test, two consecutive series of readings were taken, one with decreasing and the other with increasing pressure. The resulting observations are plotted in fig. 5. The temperature was 828° C. and the potential +38·2 volts. The points marked thus × were taken with the pressure decreasing, those marked thus ⊙ with the pressure increasing.

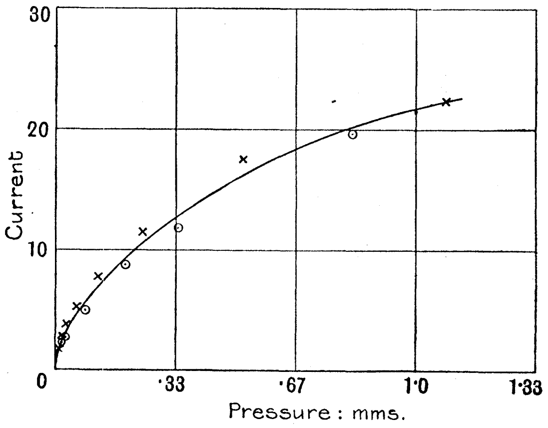

Fig. 5.

It will be seen that the two sets of points fall very nearly on the same curve, but that those with the pressure increasing tend to be lower than those with the pressure decreasing, in agreement with the time-lag effects previously described.

The experiments were now pushed to higher pressures, atmospheric pressure being the upper limit. In doing so, great difficulty was experienced owing to the purely irregular effects mentioned on p. 6. These effects were characterised by sudden changes in the rate of leak of a purely temporary kind, and were quite different from the hysteretic effects previously described. Very often in the midst of a reading, when the electrometer spot was moving quietly across the scale at the usual rate, it would suddenly give a kick and dart right off without any warning or apparent cause. These kicks were much more marked at high than at low pressures. At pressures of about 1 millim. it was rare for a kick to increase the leak in 15 seconds by 25 per cent., whereas values of the leak equal to six times the minimum have been recorded at atmospheric pressure. The following numbers, obtained at a pressure of 366 millims. and a temperature of 809° C., furnish an excellent example of this kind of thing.

Time.	Leak.	Spot movement.
h. m.		
10 31	31·7	steady
10 34	41	slight kick
10 37	33	steady
10 40	200	kick
10 43	31·5	steady
10 46	33	steady

The above represents the greatest value of the kick recorded. Generally speaking, the value of the leak only oscillated up to twice its minimum value. Further experiments on the source of these irregularities will be described later (§ 10). As no change in the arrangements has been found to eliminate them, they were avoided by always taking the minimum value of the leak, and readings were always taken until two consecutive minima agreed with one another. For instance, the true value of the current from the above observations was taken to be 32. This method was found to give consistent results.

The curves shown in fig. 6 represent the result of an experiment with the resistance of the wire maintained equal to that which it would have at a pressure of 1 millim. and a temperature of 816° C., the potential on the filament being +40 volts. The unit of current is 6×10^{-13} ampère. All the observations except two were taken with the pressure decreasing. The lower curve represents the same observations as the upper, but the pressure scale is magnified ten-fold. The two observations marked thus ⊗ are on the scale of the upper curve. They were made with the pressure increasing after the other series were finished, and were taken very rapidly, so that equilibrium was not fully established. They both fall well below the rest, owing to the time-lag effect described above. The other points fall very nearly on the curves drawn.

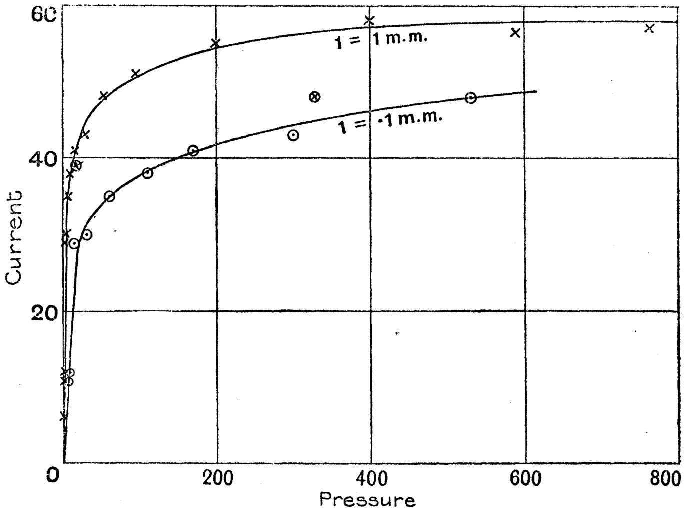

Fig. 6.

The independence of pressure exhibited by the leak at high pressures seemed at first sight a very surprising result and led the author to enquire whether there might not be something wrong with the temperature measurements at high pressures. As has been explained, the criterion employed to obtain a constant temperature so far has been a constant resistance of the wire. Now the resistance measures the average temperature of the wire across its section, whereas what is required in these measurements is a constant surface temperature, so that any change which alters the temperature gradient from the centre of the wire to the circumference will alter the surface temperature at constant resistance. Increasing the gas pressure facilitates the flow of heat from the surface of the wire and must therefore increase the internal radial temperature gradient. It is evident, then, that increasing the gas pressure lowers the surface temperature when the resistance is kept constant. It might be thought that this effect would be small in the thin wires used (0·01 centim. diameter), but the leak is a very rapidly varying function of the temperature, so a small temperature error produces a big change in the leak.

To eliminate this error, which only enters into the experiments on the pressure variation, and then is only important at somewhat high pressures, a method was devised by which the surface temperature was kept constant. A tube similar to that shown in fig. 1 was constructed, exhausted, and sealed up. The wire in it was then heated to a standard temperature by means of a constant current. A portion of this filament was then compared with a similarly situated portion of that from which the leak was being measured, and the heating current through the latter was adjusted until the two appeared to be of the same brightness. Both hot wire tubes were shut up in a black-lined box, and by looking into this through a tube furnished with paper slits the field of view could be limited to those portions of the filaments which it was desired to compare.

This method was rather rough and very tedious to use. Great care was necessary to get reliable results with it, and the strain this involved, added to the natural difficulties of the experiments, rendered the method almost impracticable. However, a number of series of observations were taken by this method of direct comparison. The results of one of them are given in the following table :—

Pressure in millims.	0·96	3·8	14	58	135	252	537	747
Current . . . . (1 = $1\cdot19 \times 10^{-12}$ ampère)	8·0	9·8	10·7	15	17	19·5	24	22

The temperature was about 800° C. and the voltage +200. Roughly speaking, these numbers serve to confirm those which were obtained by the resistance method; they show that the leak varies very little with the pressure at high pressures. On the other hand, there is a more rapid variation than that previously found, indicating that the resistance method did make the temperatures too low at the higher pressures.

It was found that a better way to make use of this optical method of obtaining a constant temperature was to determine the change of resistance required to keep the filaments equally bright when the pressure was varied, and to use the results thus got to correct the readings for the leak at constant resistance to what they would be at constant temperature according to the optical criterion. This procedure may appear pointless at first sight, but it is not. The advantage of it lies in the fact that it separates the difficulties of the optical regulation process from those which are due to the vagaries of the leak itself. The leak then was measured with the wire heated so that its resistance remained constant; this is done by the purely mechanical process of keeping a galvanometer spot at the middle of a scale, so that all the attention of the observer could be devoted to the actual measurement of the leak itself. Similarly, in finding the way the resistance changed for the same brightness, all the attention could be devoted to seeing when the two wires were equally bright. It was far easier to carry out both these operations separately and combine the results than to do both things at once, and the results obtained were far more consistent.

Working in this way a curve was obtained giving the resistance at various pressures corresponding to a constant temperature. A curve was also plotted, from experiments which will be described later, showing the relation between the leak at constant pressure and the resistance. On combining these two curves so as to eliminate the resistance, a third curve was obtained which gave the factor by which the leak at any pressure had to be multiplied to bring it to the value it would have at the temperature which the wire was at when the pressure was 1 millim.

Treated in this way the numbers plotted in fig. 6 yield those exhibited in fig. 7. As before, the temperature is 816° C., the voltage +40, and the unit of current 6×10^{-13} ampère, the pressure being expressed in millimetres.

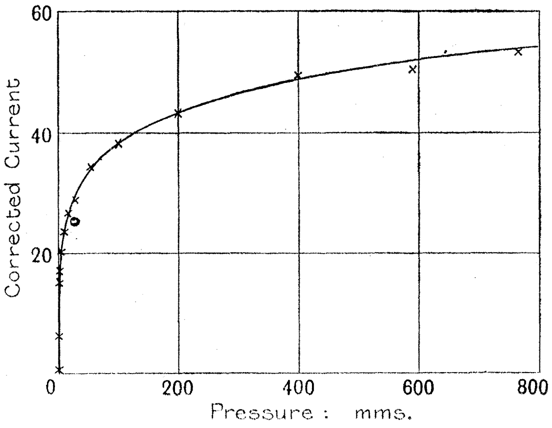

Fig. 7.

It will be seen that despite the temperature correction which has been made the leak varies very little with the pressure at high pressures and is probably asymptotic to a line somewhere about $y = 56$.

The preceding observations show that the positive ionisation produced by a hot platinum wire in oxygen at temperatures below 900° C. is approximately proportional to the square root of the pressure at low pressures. As the pressure is raised, the rate of increase of leak with pressure gradually diminishes so that the leak tends to approach a steady value asymptotically at high pressures. A similar result was found to hold at higher temperatures, with the difference that the rate of increase was greater at low pressures. At 1180° C. the leak was nearly proportional to the pressure below 2 millims., and the rate of increase at higher pressures fell off as before. The numbers supporting this conclusion will be found below in Part IV.

Before leaving this part of the subject it is necessary to consider another source of error to which the experiments were liable. This was due to the walls of the tube getting heated. During the course of the experiments the author tried the effect of heating the tube in which the measurements were being made by means of a Bunsen burner placed outside it. This was found to produce an enormous increase in the leak. In one instance, where the pressure before heating the tube was 0·0005 millim., heating for a few minutes with a Bunsen burner increased the leak from $2{\cdot}2 \times 10^{-13}$ ampère to 5×10^{-9} ampère, *i.e.*, in a ratio of 1 to 20,000. At the same time the gas evolved from the walls only sent up the pressure to 0·001 millim. This curious and interesting effect, which is being further investigated, does not appear to depend on the state of cleanliness of the tube, as it showed itself with apparently undiminished vigour after the tube had been taken down and boiled out three times with pure nitric acid and subsequently rinsed out seven times with boiling distilled water. The effect was also obtained in air at atmospheric pressure and in a vacuum produced by liquid air and charcoal, where it was impossible for the wire to come in contact with mercury vapour or vapours given out by phosphorus pentoxide.

Whatever the cause of this effect may turn out to be, it is clear that it might have completely vitiated the present measurements of the leak in oxygen and other gases. In fact, the following considerations will show that a small trace of the above effect might easily simulate the effects investigated. When the gas pressure is very low, very little heat is carried from the hot wire to the surrounding electrode and the walls of the tube, which consequently remain quite cold. As soon, however, as the pressure of the gas is increased the temperature of the walls increases too, and if the above effect were coming into play, the increase in the leak due to the heating of the walls might easily appear to be a steady function of the pressure of the gas in the tube.

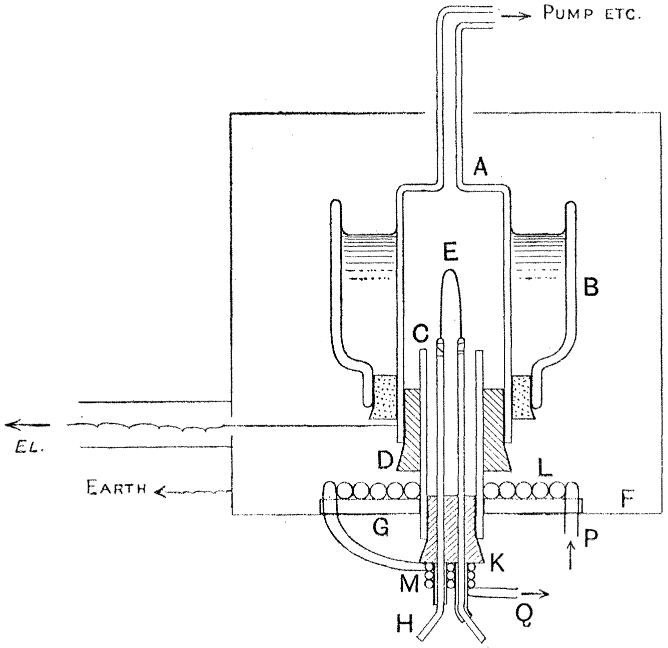

Fig. 8.

It was considered advisable to settle this question definitely by examining the leak in a vessel in which the only thing which could possibly get hot was the platinum wire itself. This was done by means of the apparatus shown in fig. 8. The metal tube A served as the electrode to which the leak was measured and thus replaced both the glass tube and the platinum electrode in the previous apparatus. This outer tube was kept cold by means of water placed in the inverted wide-mouthed bottle B. A heavy brass tube C, permanently connected to earth and insulated from A by a clean rubber stopper D, served as a guard ring to prevent leakage from the high potential wire E across the supports to the testing electrode system AB. The guard tube C had a heavy flange G soldered to it which formed a base for the apparatus and rested on the bottom of an earthed biscuit tin F. The lower end of the tube C projected through a hole in the tin. The hot platinum wire was bound to the thick copper leads H by means of fine copper wire, and the leads were supported and insulated from the guard tube C by means of the rubber stopper K. Both the hot wire leads and the guard tube were kept cold by a stream of water flowing through the composition spiral PLMQ. The part of this which was laced round the leads H was insulated from them by thin rubber tube. This was found to conduct heat well enough to keep the leads cold.

This apparatus, in which effects due to heating of the walls were prevented, was found to give exactly the same kind of results as the earlier experiments. For instance, the saturation current in oxygen at different pressures was found to have the following values:—

Pressure in millims. . .	2	0·43	0·07	0·014	124	56	12	2·6
Current	64	38	22	13	228	180	156	99

The temperature in this experiment was 976° C. and the unit of current 7×10^{-13} ampère. The observations were taken in the order of the numbers in the table.

Several other points were tested with this apparatus, one of which was to see whether the lag in the leak behind changes the pressure still held. The wire was giving a minimum leak of 36 divisions under a pressure of 0·64 millim. when the oxygen was pumped out as rapidly as possible to a pressure of 0·004 millim. The temperature was then adjusted to its former value, and the following minimum values of the leak were observed at the times stated, the time being reckoned from the point at which the temperature first became steady.

Time in minutes	5	10	14	20
Current.	24	20	15	15

Evidently the wire requires time to adjust itself to the changed conditions, so that this effect cannot be attributed to anything given off owing to the walls becoming heated.

The irregular changes in the leak previously noticed seemed to occur in this vessel to about the same extent as in the others, so they also cannot be ascribed to anything from the walls of the tube.

Some puzzling effects which have been observed may, however, probably be assigned to this cause, and it seems advisable to mention them for the benefit of other workers in this subject. The writer has several times obtained a large increase of the leak with the pressure at high pressures, especially with the wire at a high temperature. This effect has, however, only been found to occur when the whole tube became very hot and it could be reduced to a small value by simply blowing cold air on to the outside of the tube. Another effect which probably arises in the same way is an increase in the leak at a given temperature produced by heating the wire for a short time to a considerably higher temperature (see p. 13). Both these effects appear to be really due to the walls of the tube becoming heated.

Experiments were also made to see if the negative ionisation in oxygen varied with the pressure of the gas. The temperature was 1100° C. and the saturation currents with the wire charged positively and negatively respectively at the different pressures were those shown in the accompanying table.

Pressure in millims.	0·64	0·15	0·12	0·026
+ ve current	87	27	21	9
− ve current	19	22·5	21	21·5

The potentials used were +40 and −7·5 volts respectively. These were tested and found to produce saturation. With the potentials employed there was no possibility of the measurements being vitiated by ionisation by collisions. The results show that, whilst the oxygen increases the positive leak ten-fold, the negative remains unchanged within the limits of experimental error. The independence of negative ionisation and gas pressure, which had been previously observed by McClelland and H. A. Wilson, will be found to be of considerable importance later in interpreting the results on the positive ionisation.

§ 6. *Current and Temperature.*

The last section forms a fairly complete investigation of the way in which the positive ionisation from hot platinum in oxygen varies with the pressure, when the temperature is kept constant, for a considerable range of temperatures. The phenomenon was next investigated by measuring the ionisation at constant pressure when the temperature of the wire was varied.

The measurements were made with the glass tube apparatus previously described. Rough experiments were made at several pressures, but only those at pressures of 1 to 3 millims. have been retained. At very low pressures irregular results were got, doubtless owing to changes in the composition of the small quantity of gas present in the apparatus, whilst at pressures comparable with atmospheric it was feared that an error might creep in owing to the walls of the tube becoming heated. At pressures of about 2 millims., however, several wires were tried and found to give consistent results over a range from about 700° C. to 1250° C. It was found convenient to measure the negative current at each temperature along with the positive. The results therefore enable us to compare the positive and negative ionisations from wires under identical conditions. The ionisation would, no doubt, be proportional to the area of the hot metal surface if the surface were uniformly heated. As, however, the wires are colder at the ends owing to the heat being conducted away through the leads, the effects from wires of different lengths and thicknesses will not be strictly comparable with their superficial areas. To allow for this, 0·5 centim. was subtracted in every case from the length of the wire. The area thus reduced will be referred to as the effective area of the surface of the wire.

A wire 0·1 millim. in diameter, which had been heated in oxygen for a period of about three months (usually for several hours a day), was found to give the following values of the positive and negative saturation currents at the temperatures stated :—

Temperature.	+ Current.	− Current.
° C.	ampère	ampère
708	$1 \cdot 6 \times 10^{-12}$	—
770	$6 \cdot 7 \times 10^{-12}$	—
826	$1 \cdot 5 \times 10^{-11}$	—
883	$3 \cdot 2 \times 10^{-11}$	$1 \cdot 1 \times 10^{-14}$
940	$5 \cdot 8 \times 10^{-11}$	$6 \cdot 7 \times 10^{-14}$
999	$1 \cdot 1 \times 10^{-10}$	$8 \cdot 0 \times 10^{-13}$
1058	$3 \cdot 8 \times 10^{-10}$	$6 \cdot 2 \times 10^{-12}$
1119	$6 \cdot 4 \times 10^{-10}$	$3 \cdot 2 \times 10^{-11}$
1181	$1 \cdot 1 \times 10^{-9}$	$3 \cdot 3 \times 10^{-10}$
1227	$1 \cdot 7 \times 10^{-9}$	$1 \cdot 6 \times 10^{-9}$

The pressure of the oxygen in the above experiment was 1·47 millims., and the effective superficial area of the wire was 0·223 sq. centim. In this experiment the negative ionisation was measured with 40 volts P.D. This would probably give rise to ionisation by collisions at the pressure during the experiment, so that the values for the negative ionisation in the table are probably somewhat greater than the true saturation values.

In proceeding from a low to a high temperature it was usually found that the leak at the high temperature was too big at first and subsequently fell to a smaller value. This effect did not, however, occur in a wire which had been heated in oxygen for a very long time—for instance, it was not noticed in the above series of observations—and is probably due to the wire not really having reached a state of equilibrium.

It will be noticed that the value of the positive ionisation increases very rapidly with the temperature of the wire, though not so rapidly as the negative corpuscular radiation. The relationship between the two is brought out more clearly when the results are exhibited graphically as in fig. 9. The continuous curves with points thus × represent the positive, and the dotted curves with points thus ⊙ the negative, ionisation. The scale of current is different for the different curves. For curves (1) and (4) the unit is 10^{-12} ampère, for (2) and (5) $1 = 10^{-11}$ ampère, and for (3) and (6) $1 = 10^{-10}$ ampère. The two leaks become equal at about 1230° C., though the positive is far bigger than the negative at low temperatures.

Although the negative ionisation increases far more rapidly than the positive, both depend on the temperature in the same general kind of way; in fact, the positive ionisation, so far as its temperature relations are concerned, obeys the law originally

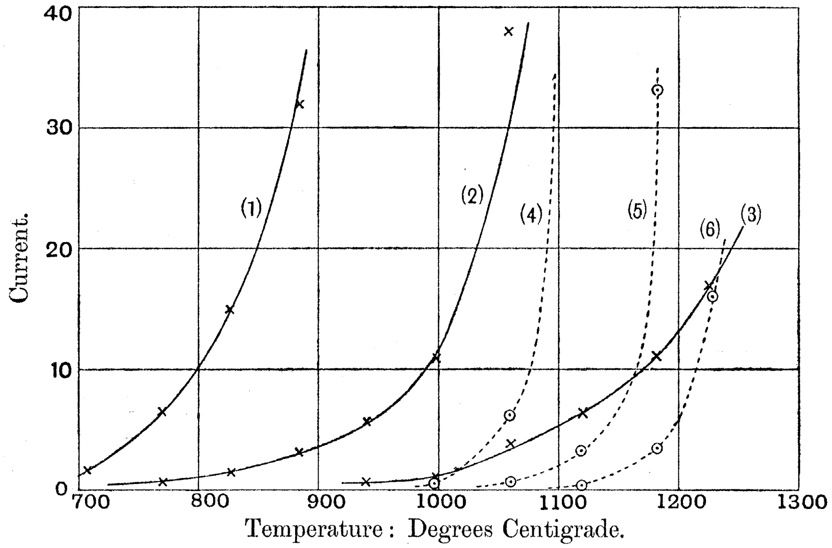

Fig. 9.

deduced by the author for the negative ionisation, and can be expressed by means of the formula $A\theta^{\frac{1}{2}}e^{-b/\theta}$, where A and b are constants and θ is the absolute temperature. The constant b which measures the work done in setting free an ion is, in general, much smaller in the case of the positive than the negative ionisation. This may be tested, as the writer has explained in previous papers, by taking logarithms, when, if L is the current and A′ a new constant,

$$\log_{10} L/\theta^{\frac{1}{2}} = A' - b/(2\cdot30\theta).$$

The value of the logarithm should therefore be a linear function of $1/\theta$. Values of $\log_{10} L/\theta^{\frac{1}{2}}$, where L is the current per unit area of surface for two wires of different lengths and diameters, have been plotted against $1/\theta$ in the accompanying diagram.

The extent to which the points fall on two straight lines furnishes a test both of the applicability of the above formula and also of the nature of the agreement between different wires. The data for the wires tested are (1) diameter = 0·01 centim., effective superficial area = 0·223 sq. centim., positive ionisation-points thus ×, negative ionisation-points thus ⊗; (2) diameter = 0·02 centim., effective area = 0·66 sq. centim., positive ionisation-points thus · , negative ionisation-points thus ⊙.

It will be observed that the points for the positive leak, and also for the negative leak, fall very nearly on the same straight line for the two wires. This shows not only that the leak may be expressed by a formula of the above type, but also that the constants A and b which enter into the formula are the same for both wires. The tangent of the angle the above lines make with the axis of $1/\theta$ is a measure of the work done in setting free an ion. This quantity is evidently much less for the positive than for the negative ions. The value of this work is conveniently expressed in calories per gramme molecule of ions, a gramme molecule of ions being the amount which would occupy 22·4 litres if in the state of gas at 0° C. and 760 millims.

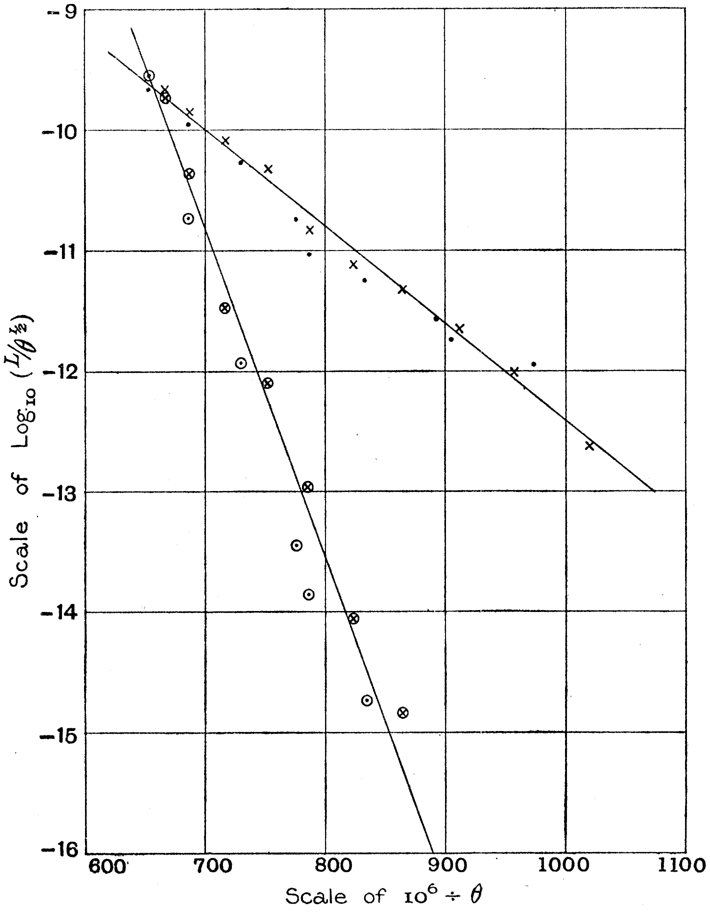

Fig. 10.

Expressed in this way, the numbers can at once be compared with the heats of various purely chemical reactions. The best series of experiments in oxygen (at 1·5 millims. pressure) gave for the work required to set free a corpuscle $\omega_- = 13{\cdot}55 \times 10^4$ calories. This is in good agreement with WILSON'S value $13{\cdot}11 \times 10^4$ for the negative leak from hot platinum in air at a low pressure.[*] The value of the work required to set free a positive ion was found to be $\omega_+ = 3{\cdot}04 \times 10^4$ calories. The heats of the most intense chemical actions involving only one valency range around 5×10^4 calories, so that the energy required to liberate a positive ion is somewhat smaller, and that required to set free a negative ion considerably bigger, than the greatest amount of energy set free in any known chemical reaction.

§ 7. *Uncontrollable Variations.*

We have seen (p. 16) that the positive leak in oxygen, particularly at high pressures, continually varies in an erratic manner, even when all the controllable

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[*] 'Phil. Trans.,' A, 352, vol. 202, p. 259.

conditions are apparently kept constant. The following numbers, which refer to a temperature of about 900° C., illustrate the kind of thing that occurs. The wire, which was 0·2 millim. in diameter, was maintained at a potential of +40 volts, the pressure of the oxygen being atmospheric. All the conditions were kept constant; the unavoidable variation in the temperature of the wire was continuously registered by the galvanometer spot, and was not sufficient to cause a variation of 5 per cent. in the value of the leak. Nevertheless, readings at 2-minute intervals gave the following values for the current:—146, 180, 178, 228, 158, 170, 150, 246, 166, 324, 198, 174, 198.

Naturally the existence of a variability of this kind makes it very difficult to find out what is the real effect of changing the controllable conditions, and the author has spent a great deal of time in trying to get rid of it. In this he has been unsuccessful. It looks, in fact, as though this variability is in some way or another an inherent part of the phenomena. In some respects it seems to follow definite laws. It is more marked at high than at low pressures, and at low than at high temperatures. The positive leak at temperatures above 1200° C. seemed to show very little variability. It is not due to trivial variations in the state of the gas in the tube, as the negative leak, measured under the same conditions as the positive, did not show it. For the same reason it cannot be due to discharges from points which might form on the surface of the platinum.

It was found to be present whatever the voltage on the filament. Boiling out the tube with nitric acid and distilled water left it unaffected. Slightly heating the walls of the tube with a Bunsen burner did not affect it, although heating the walls more strongly was found to give the big leak mentioned on p. 19. The big leak thus produced, on the contrary, was steady and did not vary capriciously with the time. The variability was not due to vapour given off intermittently from the heated walls of the tube, as it occurred in undiminished intensity in the tube whose walls, &c., were cooled with water. It might have been ascribed to the intermittent escape of occluded hydrogen, were it not that a wire which had recently been heated in hydrogen did not show the effect to a greater extent than a wire which had been heated in an atmosphere of oxygen over a period of about three months.

There seems to be no escape from the conclusion that this effect is caused by some periodic change in the state of the platinum surface. If the metal was continually undergoing recrystallisation accompanied by the emission of absorbed gas, equilibrium might possibly be incapable of ever being attained, and the results might simulate those which have been observed. It does not seem advisable to speculate further on this point. The real question from the point of view of this investigation is whether the selection of the minimum values in the case of the measurements at high pressures is legitimate or not. They certainly seemed far more definite than the maximum or the average values, but apart from this and the apparently remote possibility that the "jumps" are really due to the escape of some substance foreign to the platinum there is no reason for taking one set of values rather than the other. On these grounds the results at low pressures may be considered more reliable than those at high ones.

§ 8. *Comparison of Different Wires.*

After the last section it is refreshing to find that the ionisation from hot wires is capable in some ways of exhibiting a certain amount of constancy. The results given on pp. 24 and 25 show that two wires at any rate gave approximately the same amount of ionisation, both positive and negative, per unit area with the same pressure of oxygen at all temperatures from 700° C. to 1250° C. In the course of the investigation the positive ionisation in oxygen, under similar conditions of pressure and temperature, was measured for four different wires having different linear dimensions. It is interesting to compare the leaks from these per unit area of surface when reduced, by means of the results which have been obtained, to some standard pressure and temperature. The pressure selected is 1·5 millims., and the leaks at this pressure are given for two temperatures, viz., 770° C. and 880° C. The data will be found in the following table (see next page).

The wires numbered (1), (2), and (4) were each 0·1 millim. in diameter, while No. (3) was 0·2 millim. in diameter. It will be noticed that, although the area of the wires varied in the ratio of nearly one to four, and the different wires had been very differently treated, yet the values of the leak per unit area, as shown by the last two columns, are very nearly the same in every case. The values furnished by the first wire on May 5 and July 14 are especially interesting, since they show that, once the steady condition is attained, there is no further falling off due to continued heating in oxygen at a red heat. This wire was heated for several hours on most days between the two dates to a temperature varying between 750° C. and 1100° C. As the observations recorded with wire No. 3 near the temperatures of 770° C. and 880° C. were a little irregular, the values were selected by drawing a curve like fig. 9 and finding the values of the leak at these temperatures from the curve. In regard to this wire it is only fair to say that it was subsequently heated strongly in hydrogen, and after that treatment was found to give a much smaller leak (about one-third to one-fourth) than before. It seems probable, however, that this is due to a permanent change produced by the hydrogen in the texture of the metal surface. It has often been observed that the surface of platinum which has been heated in hydrogen develops a roughened crystalline appearance. This change does not appear to be produced by heating in oxygen, at any rate at temperatures below 1100° C. The alteration could not be due to an error in the temperature brought about by a change in the temperature coefficient of the resistance, as the negative leak was not reduced in as great a ratio as the positive. The figures for the last wire are of interest, as they were obtained in the tube with water-cooled walls and were therefore free from any effect from the walls.

No. of wire.	Effective area.	Date.	Pressure.	Temperature.	Observed current.	Total leak at P = 1·5 millims. and		Leak per unit area at 1·5 millims. and	
						θ = 770° C.	θ = 880° C.	770° C.	880° C.
	sq. centim.		millims.	° C.	ampère				
(1)	0·223	May 5, 1905	1·15	771	$7 \cdot 1 \times 10^{-12}$	$7 \cdot 5 \times 10^{-12}$	—	$33 \cdot 7 \times 10^{-12}$	—
(1)	0·223	,,	1·15	885	$28 \cdot 1 \times 10^{-12}$	—	$28 \cdot 5 \times 10^{-12}$	—	128×10^{-12}
(1)	0·223	July 14, 1905	1·47	769	$6 \cdot 6 \times 10^{-12}$	$6 \cdot 8 \times 10^{-12}$	—	$30 \cdot 5 \times 10^{-12}$	—
(1)	0·223	,,	1·47	882	$31 \cdot 2 \times 10^{-12}$	—	$30 \cdot 5 \times 10^{-12}$	—	137×10^{-12}
(2)	0·214	July 20, 1905	2·08	799	$7 \cdot 8 \times 10^{-12}$	$4 \cdot 93 \times 10^{-12}$	—	$23 \cdot 0 \times 10^{-12}$	—
(2)	0·214	,,	2·08	878	$25 \cdot 6 \times 10^{-12}$	—	$23 \cdot 0 \times 10^{-12}$	—	108×10^{-12}
(3)	0·66	February 26, 1906	2·00	—	—	$21 \cdot 0 \times 10^{-12}$	—	$31 \cdot 8 \times 10^{-12}$	—
(3)	0·66	,,	2·00	—	—	—	$85 \cdot 0 \times 10^{-12}$	—	129×10^{-12}
(4)	0·170	March 16, 1906	2·45	973	$69 \cdot 0 \times 10^{-12}$	$4 \cdot 7 \times 10^{-12}$	$23 \cdot 0 \times 10^{-12}$	$27 \cdot 6 \times 10^{-12}$	135×10^{-12}

§ 9. *Special Properties of New Wires.*

The writer* has shown that a new platinum wire, even when well cleaned with boiling nitric acid and distilled water, gives rise to an abnormally high positive ionisation when heated in a vacuum. This initial ionisation gradually falls off to a small value, but it is found that a wire which has lost most of this initial effect still exhibits peculiar properties when the leak from it in an atmosphere of oxygen or air is examined. These effects, which only seem to disappear after continued heating at a low pressure, are characterised by great variation of current with electromotive force together with time changes in the current under constant voltage.

It has been shown that an old wire exhibits little variation of the current with electromotive force with voltages above 40. Changing the voltage from +40 to +760 never more than doubled the current in the case of an old wire at atmospheric pressure. In the case of a new wire, however, a change in the voltage generally altered the current in the ratio of the applied voltage. The current did not, however, remain steady at the new value. If the voltage had been increased it gradually fell to a value much nearer that which it had at the lower voltage. The steady value which the current seemed to be approaching was greater the higher the voltage, and what may be called the steady increase with voltage was generally greater the newer the wire. The converse increase in the current subsequent to lowering the voltage was also sometimes observed, but was much smaller.

The following numbers, which were obtained in air at atmospheric pressure at a temperature of about 900° C., with a wire which was not very new and therefore did not show the effect in its most exaggerated form, will illustrate the kind of thing that occurred. The wire under +40 volts was giving a leak which oscillated from 33 to 44 divisions, the minimum value of 33 divisions being, however, fairly constant. The voltage was changed to +360, when readings every successive 3 minutes gave for the values of the leak 117, 97, 79, 68, 70, 73. On changing the voltage back to +40, the leaks at 3-minute intervals were 21, 25, 22, 23.

The above experiments were carried out in the glass tube apparatus first described. This apparatus relies for its insulation inside the tube solely on the surface of the glass. It seemed possible that queer effects like the above might be obtained on changing the voltage if the surface of the glass were getting charged up. This might be especially likely to happen after a new wire had been sealed into the tube, owing to the surface retaining a film of moisture, since it was necessary to introduce moisture to clean out the tube.

For these reasons it seemed advisable to test the question with a form of apparatus which was not liable to these objections. The apparatus used was really designed for some experiments on the leak from a platinum tube which will be described later (see fig. 16, p. 54). The hot wire was insulated along the axis of three equal cylindrical

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* ‘Phil. Mag.’ [6], vol. 6, p. 80.

tubes of aluminium. The two outside tubes acted as a guard ring, so that the leak was only measured from the uniformly heated central part of the wire to the surrounding middle cylinder. In addition to this, all the insulation was surrounded by earthed tubes, so that there was no possibility of it becoming charged up by strong ionisation. The effects previously observed were fully confirmed with this apparatus.

A new wire, not specially cleaned, placed in this apparatus gave with +40 volts a leak of 100 divisions which remained constant for 1 hour 40 minutes. On raising the potential to +760 volts the following values of the current were obtained at the times stated :—

Time	hours	2	2	2	2	2	3	3	3	3	3	3	4
	minutes . . .	44	47	50	53	58	4	9	20	31	38	44	0
Current		3570	1930	950	760	570	485	475	190	115	112	103	103

On returning to +40 volts, the leaks at successive six-minute intervals were 80, 84, 90, 94. The temperature in this experiment was 925° C. A similar experiment with a hot platinum tube 2 millims. in external diameter showed the same kind of effect, and also an increase in the positive leak, when the tube had been left negatively charged.

The obvious conclusion from these experiments is that part of the leak from a new wire is emitted by something which is itself positively charged, and is therefore removed when the wire is positive, but not when it is negative. Dust given off by the platinum might be expected to become positively electrified by virtue of point discharge action in the strong field in the neighbourhood of the hot wire whatever the sign of its electrification when it left the wire. It would thus be retained by a negatively, but not by a positively-charged wire. On the other hand, there appears to be no obvious reason either why dust should produce the observed effects or why a new wire should give off more dust than an old one. Blowing a current of air past the wire had no marked effect on the positive leak under a high voltage. The general complexity of these initial phenomena would seem, however, to indicate that there is more in them than the above simple explanation demands.

What the process of ageing a wire for the purpose of this investigation consists in is not quite clear. Mere heating alone will not do it. A new wire, which was heated for about a week in the air of the laboratory before being tested, was found to behave like a new wire when the leak was tested. The above experiments would seem to indicate that the presence of a big positive charge on the wire is instrumental in facilitating the decay of the initial leak, whilst, other things being equal, the rate of decay is greater at low than at high pressures. It looks as though the initial leak from a new wire was due to the presence of some gas which was positively charged when emitted by the wire.* Such a gas might be expected to diffuse away from the wire more readily at a low than a high pressure and under a high than a low field.

§ 10. *Theory of the Steady Positive Leak in Oxygen.*

The view which the author has been led to as the result of the foregoing experiments is that the positive, as well as the negative, ions are produced in the first instance inside the metal, or, at any rate, so far within the surface that their rate of production is in general uninfluenced by the external field. The experiments, in addition, afford strong support to the view that the positive ions are furnished not by the platinum itself, but by the oxygen absorbed or dissolved in the transition layer between the metal and the surrounding gas. That the positive ions do not arise in the space outside the free metal surface appears to be distinctly indicated by the following considerations.

We have seen that the positive and negative ionisations from hot platinum vary with the temperature according to the same kind of law, but quite independently of one another. This is exemplified by the fact that at a pressure of 1·5 millims. of oxygen the two leaks are equal to one another at about 1230° C., whereas at 700° C. the saturation current with the wire negative is about 10^{-7} of its value with the wire positive. The disparity between the two leaks points strongly to the view that they are the result of separate actions; it proves, in addition, that there is no considerable amount of volume ionisation, but it does not prove that the ions are not formed outside the wire. For instance, an oxygen molecule might attack a positively-charged platinum atom, with the result that of the two oxygen atoms present in the molecule the one carrying the negative charge combined with the platinum, whilst the other one was set free, forming a positive ion. Of course, the negative ion would in a sense be free while the interaction was taking place, but it would always be within a distance from the attracting positive ion comparable with the radius of the sphere of molecular action, and the interionic attraction would probably be enormous compared with the greatest external field of force (about 10^5 volts per centimetre) which could be applied.

There are two main objections to the foregoing view, which otherwise has the advantage of simplicity to recommend it. One of these is the way in which the leak lags behind change of pressure. It will be noticed that the above theory would make the leak proportional to the rate of reaction between the O_2 and the free platinum. In order to explain the variation of the leak with pressure under steady pressures, it is necessary to assume, what is otherwise probable, that the proportion of uncombined

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* This conclusion receives strong support from previous experiments by the writer, in which he showed that the ionising power of a new wire could be transferred to a second wire, previously rendered inactive by heating, if this were negatively charged. 'Phil. Mag.,' [6], vol. 6, p. 86.

platinum is smaller at high than at low pressures. Hence, if the pressure were suddenly changed from a high to a low value, the leak at constant temperature should be small at first and then gradually rise to a steady value, while suddenly increasing the pressure should give rise to the converse effect. As a matter of fact, the opposite of this is what has been observed in both cases, indicating that the ionisation is proportional to the "combined" rather than to the "free" platinum, if it is permissible to use these words in a rather wider sense than that usually understood by the term chemical combination.

The other objection depends on the way in which the steady leak varies with the pressure at low pressures. The preceding view would make the leak directly proportional to the pressure at low pressures at all temperatures, whereas the experiments show that at low temperatures and pressures the leak varies as the square root of the pressure. This result is also readily explained if we suppose the ionisation to be proportional to the amount of combined or absorbed oxygen rather than to the rate of chemical action between the oxygen and the platinum.

For the reasons stated, it seems necessary to seek the cause of the ionisation within the surface layer of the metal. On the molecular theory a metal, and in fact any solid, will possess a surface layer in which the molecules are more loosely held together than in the interior. On account of the well-known tenacity with which films of gas adhere to solid bodies, it seems reasonable to suppose that this layer will be capable of being penetrated by the surrounding gas, and that when equilibrium is established the absorbed gas will have a density which is very great compared with that of the free gas outside. This comes to assuming that a gas molecule loses potential energy when it enters the surface layer. To explain the results it is necessary to assume, in addition, that, for reasons connected with the structure of the metal, only dissociated oxygen atoms and not the ordinary molecules are capable of entering the surface layer. This assumption receives some support from the fact that the hydrogen which diffuses through hot platinum has been shown to be in the atomic form.* In order to make the problem definite we shall suppose the surface layer to be only a few atoms thick, and that each platinum atom is capable of retaining one oxygen atom in its immediate neighbourhood. The problem, then, reduces to what is virtually the determination of the condition of chemical equilibrium. Let the maximum concentration of the free platinum, *i.e.*, the concentration when no gas is present, reckoned as so much per unit area, be $= a$, and let the concentration of the platinum which is used up by retaining its sufficient quotum of gas at time $t = x$. Then the concentration of the free platinum at time $t = a-x$. Let the external gas pressure $=$ P, then the pressure of the dissociated oxygen $= p$, where p is given by the quadratic

$$p^2 = k(\mathrm{P}-p) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1),$$

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* *Cf.* WINKELMANN, 'DRUDE'S Ann.,' vol. 8, p. 388; and RICHARDSON, NICOL and PARNELL, 'Phil. Mag.' [6], vol. 8, p. 1.

k being the dissociation constant of free oxygen. The rate of formation of the Pt, O systems is evidently proportional to $p\,(a-x)$, whilst their rate of decomposition is proportional to x. The total rate of increase is therefore

$$\frac{dx}{dt} = \mathrm{A}p\,(a-x)-\mathrm{B}x,$$

A and B being constants. In the steady state $dx/dt = 0$, and

$$x = \frac{\mathrm{A}pa}{\mathrm{B}+\mathrm{A}p} = \frac{af(\mathrm{P})}{b+f(\mathrm{P})} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2),$$

if we write $b = \mathrm{B}/\mathrm{A}$ and $p = f(\mathrm{P})$. Assuming that the positive ionisation is proportional to the amount of adsorbed oxygen, its variation with the pressure will be given by the above expression.

The assumption that the ionisation is proportional to the amount of adsorbed oxygen does not commit us to the view that the ions are liberated by the decomposition of an oxide of platinum, though it is not inconsistent with that view. The phenomena of electrolysis show that, when molecular disruption is accompanied by electrical separation, the metal tends to receive a positive, and the non-metallic element a negative, charge. We might therefore expect the oxygen to be liberated from hot metals in the form of negative ions, whereas it is found that the oxygen receives a positive charge. This seems to indicate that the positive ions are not charged oxygen atoms when they are expelled from the system platinum-oxygen, which possibly becomes unstable owing to continued corpuscular bombardment. However, since we know so little of the material constitution of the positive ions, it seems unprofitable to dwell any longer on the question of their precise origin.

Returning to the consideration of the formula that has been obtained for the leak in equation (2), we see that when the amount of dissociation is small $p = k^{\frac{1}{2}}\mathrm{P}^{\frac{1}{2}}$. This will be the case at low temperatures if the pressure is not too small, so that under these circumstances the ionisation will vary with the pressure as $\alpha\mathrm{P}^{\frac{1}{2}}/(\beta+\mathrm{P}^{\frac{1}{2}})$, α and β being constants. This expression is evidently of the right form, for when P is small it varies as $\mathrm{P}^{\frac{1}{2}}$, whilst when P is great it becomes independent of P, and this is the kind of variation with pressure that was found experimentally. The numbers in the following table, which refer to an experiment at 730° C., furnish a means of examining the agreement with the formula in more detail. The unit of current is 10^{-12} ampère. The constants in the formula are $\alpha = 12$, $\beta = 3{\cdot}9$, the pressures being reckoned in millimetres of mercury.

The agreement between the observed and calculated values of the ionisation is as close as the experimental results warrant. In general, the observed leak tends to be smaller than the calculated at the very lowest pressures, owing to the concentration of the dissociated oxygen beginning to vary with the pressure more rapidly than as

Pressure in millims. of Hg.	$P^{\frac{1}{2}}$.	Calculated leak, $x = \alpha P^{\frac{1}{2}}/(\beta + P^{\frac{1}{2}})$.	Observed leak.
0·006	0·078	0·23	0·17
0·025	0·158	0·465	0·46
0·045	0·212	0·62	0·62
0·077	0·278	0·80	0·795
0·085	0·292	0·84	0·84
0·102	0·32	0·91	0·94
0·143	0·378	1·06	1·23
0·26	0·51	1·39	1·58
0·454	0·674	1·77	1·84
0·95	0·97	2·48	2·5
4·3	2·08	4·2	4·5
17·0	4·13	6·18	6·0
66·0	8·1	8·1	8·7

the square root. The above numbers yield, for the maximum current the above wire was capable of furnishing, at 730° C. the value 12×10^{-12} ampère, or, per square centimetre of surface, 54×10^{-12} ampère.

The following series refer to a somewhat higher temperature (820° C.) and furnish a more complete test of the way the formula works at higher pressures. In this case α was taken $= 56 \times 10^{-12}$ ampère and $\beta = 4{\cdot}0$ (millims. of mercury)$^{\frac{1}{2}}$.

Pressure in millims. of Hg.	$P^{\frac{1}{2}}$.	Calculated leak, $x = \alpha P^{\frac{1}{2}}/(\beta + P^{\frac{1}{2}})$.	Observed leak.
0·003	0·055	0·75	1·0
0·17	0·41	5·2	5·9
1·5	1·22	13·2	15
3·1	1·76	17·1	17
6·1	2·47	21·3	20·7
10·7	3·27	25	23·5
17	4·12	28·4	26·5
30	5·48	32·3	30
53	7·28	36·5	34
97	9·85	39·5	38
200	14·3	43·7	43
399	20	46·7	49·3
587	24·2	48·3	50·5
766	27·7	49	53·5

The maximum value of the positive ionisation in oxygen at 820° C. appears from these numbers to be $= 2{\cdot}5 \times 10^{-10}$ ampère per square centimetre. The values of the above leaks at the lowest pressures are probably somewhat high, as it was found to be impracticable to wait long enough to be certain that equilibrium had become fully established.

We have seen that the assumption that the denominator in the expression for the positive ionisation is of the form $\beta + P^{\frac{1}{2}}$ is an approximation which will only hold at low temperatures. The numbers given below show that at 1170° C. the leak is very closely represented by an expression of the form $\alpha P/(\beta+P)$, which would be the value given by the theory if most of the gas outside the wire were dissociated. This is likely enough to be the case at pressures of the order of 1 millim., and at higher pressures the exact form of $f(P)$ has very little influence on the result. No doubt a better agreement could have been obtained by putting in the theoretical value for p, viz., $\sqrt{kP+\frac{1}{4}k^2}-\frac{1}{2}k$, but this involves introducing a new constant k into the expression for the ionisation, a refinement which is not warranted by the exactitude of the experimental results. It appeared to be impossible to test the theory more fully by pushing the experiments to a higher order of accuracy, on account of the irregularities which have already been described.

The experimental values of the ionisation at 1170° C. and those calculated from the formula $\alpha P/(\beta+P)$ are given in the following table. α was taken $= 38 \times 10^{-10}$ ampère, and $\beta = 4{\cdot}8$ millims. of mercury :—

Pressure in millims. of Hg.	Calculated leak, $x = \alpha P/(\beta+P)$.	Observed leak.
0·14	0·96	1·08
0·30	2·0	2·24
0·39	2·56	2·85
0·62	3·9	4·35
1·27	7·2	7·9
2·06	10·4	11·3
5·3	18·8	19·9
23·5	30·8	31·5
89	36·0	35·9

The greatest value of the positive leak in oxygen at 1170° C. works out at $1{\cdot}7 \times 10^{-8}$ ampère per square centimetre of platinum surface. The smaller amount of variation with temperature exhibited by the constant β is a surprising result. At the two lower temperatures $\beta = Bk^{-\frac{1}{2}}A^{-1}$ in the notation previously employed, and its constancy with temperature implies that the heat of formation of the platinum-oxygen systems from *atomic* oxygen is nearly equal to the heat of formation of an oxygen molecule from two atoms. At the higher temperature β is equal to B/A, and its value in conjunction with the preceding result implies that B/A is small compared with 4·8 at the lower temperatures.

According to the present theory, the energy change associated with the action which gives rise to a positive ion is given exactly by the temperature variation of the maximum value of the leak and not by the temperature variation of the leak under a pressure of 1·47 millims. as was assumed on p. 25. The preceding results enable us to correct for this, but as the effect of the correction is smaller than the probable experimental error it has not been proceeded with.

IV.—§ 11. THE IONISATION IN NITROGEN.

The nitrogen used in the experiments was prepared from air and therefore contained the inert gases in the proportion in which they occur to nitrogen in the atmosphere. So far as was possible without using very elaborate refinements, care was taken to free it from oxygen, hydrogen, carbon dioxide, dust and organic impurities. The air of the laboratory was allowed to bubble very slowly through a wash bottle containing alkaline pyrogallate and then passed over (1) a red-hot tube about 60 centims. long containing copper and copper oxide, (2) a long tube packed with cotton wool, and (3) a tube 30 centims. long packed with fused potash and plugged with glass wool, before it was admitted into the apparatus. Inside the apparatus it was finally dried over P_2O_5 and further purified (1) at low pressures by exposure to sodium amalgam from a cathode of which a discharge could be passed from time to time, (2) at high pressures by heating a copper spiral red hot in it. The copper spiral had previously been heated in a vacuum to drive off occluded hydrogen. With regard to the discharge from the sodium amalgam cathode it was found advisable not to pass it too frequently, as it absorbs nitrogen rather quickly, but not so quickly as it absorbs oxygen. All the purifying arrangements were placed close to the testing bulb and between it and the rest of the apparatus so as to be as efficient as possible. After the nitrogen had been prepared, the copper in the hot tube was always found to be quite bright except at the front end.

The positive ionisation in nitrogen is small compared with that in oxygen, especially at low pressures. As we have seen, a small quantity of oxygen has a very big effect on the positive leak, and it might therefore be supposed that the leaks observed in nitrogen were due to traces of oxygen which had not been removed by the purifying processes. This, however, is rendered improbable by the fact that the ionisation in nitrogen differs in character in certain important respects from that in oxygen. The current requires a greater electromotive force to saturate it under similar conditions, and it also showed time changes, after altering the applied E.M.F., similar to those observed in a new wire. These changes were never observed in a wire which had been heated in oxygen for a long time.

On letting in fresh nitrogen the leak was always found to have a much bigger value than that at which it finally settled down. The rate of decay was very big at first, but after a time became extremely slow, so that there still seemed to be a slow decrease after several hours' heating at 900° C. This decrease may have been due to the gradual absorption of oxygen. No decrease in pressure could be observed, but this does not prove anything, as the decrease in the pressure required to account for the observed effects, supposing them due to oxygen, would fall within the probable experimental error. The measurements of the relation between the current and the applied E.M.F., &c., refer to the state in which the leak was varying very slowly, if at all, with the time.

The relation between current and E.M.F. at 2·8 millims. pressure and 905° C. is given by the following numbers :—

Volts	+0·3	+2·2	+7	+11	+40	+80	+160	+240	+360	−40
Current . . . . (1 = $3 \cdot 9 \times 10^{-12}$ ampère per sq. centim.)	0·19	0·52	0·66	0·77	1·0	1·1	1·3	1·33	1·58	0·53

At 760 millims. and 920° C. the values found were :—

Volts	+40	+120	+200	+360	+560	+760
Current . . . . (1 = $5 \cdot 3 \times 10^{-13}$ ampère per sq. centim.)	9	26	32	40	41	42

Compared with oxygen under similar conditions, these numbers, which are shown graphically in fig. 11, show that the ionisation in nitrogen requires a greater applied E.M.F. to produce saturation. With the above wire, which was 0·02 centim. in diameter, the current in oxygen showed very little increase with voltage after 40 volts. The increase with 360 volts at 2·8 millims. is due to the occurrence of ionisation by collisions.

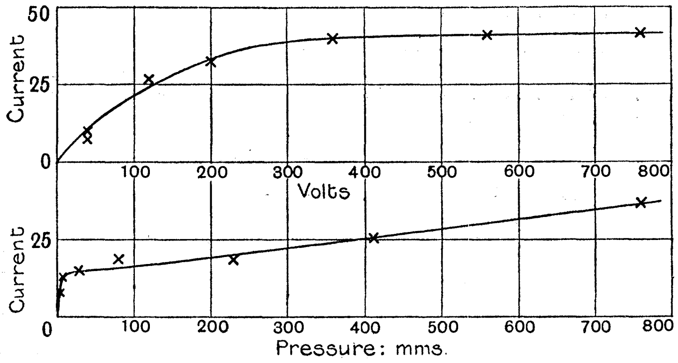

Fig. 11.

The variation with temperature of the leak in nitrogen at a pressure of 2·8 millims. was also examined. On raising the temperature the leak was too big at first and usually required about 20 minutes to fall to its minimum value. The numbers obtained for the positive and negative ionisation are given in the accompanying table :—

Temperature.	Saturation current.	
	+.	−.
° C.	ampère	ampère
827	$3 \cdot 0 \times 10^{-13}$	$4 \cdot 4 \times 10^{-14}$
900	$1 \cdot 7 \times 10^{-12}$	$5 \cdot 8 \times 10^{-13}$
907	$3 \cdot 8 \times 10^{-12}$	$1 \cdot 5 \times 10^{-12}$
984	$2 \cdot 76 \times 10^{-11}$	$3 \cdot 52 \times 10^{-11}$
1071	$9 \cdot 9 \times 10^{-11}$	$4 \cdot 71 \times 10^{-10}$

These numbers were found to obey the formula $A\theta^{\frac{1}{2}}e^{-\omega/2\theta}$.

The values of the energy changes associated with the liberation of a gram-molecule of positive and negative ions respectively are found to be $\omega_{+} = 7 \cdot 12 \times 10^4$ calories and $\omega_{-} = 11 \cdot 2 \times 10^4$ calories. Thus the work required to liberate a positive ion from platinum in an atmosphere of nitrogen is more than twice the value of the corresponding quantity in oxygen.

At low pressures the positive saturation current in nitrogen was found at 905° C. to consist of two parts, one independent of the pressure and the other nearly proportional to it. This is shown by the following numbers :—

Pressure in millims.	0·067	0·14	0·3	0·6	1·3	2·8
Current . . . . (1 = $3 \cdot 3 \times 10^{-13}$ ampère per sq. centim.)	2·6	2·6	2·2	3·0	4·3	6·6

The current did not continue increasing with the pressure at the above rate up to atmospheric pressure, but at slightly higher pressures than the above the current curve began to bend round towards the pressure axis. It did not, however, tend to become independent of the pressure as in the case of oxygen, but it increased at a rate proportional to the pressure at high pressures. The variation of saturation current with pressure up to atmospheric pressure is shown in the lower curve in fig. 11. The unit of current = $1 \cdot 05 \times 10^{-12}$ ampère per square centimetre. The temperature was 920° C.

The nitrogen used in the last experiment was allowed to remain all night in the apparatus, whilst both the platinum wire and the copper spiral were heated in it. During this time the leak with +40 volts decreased considerably, as is shown by the following numbers :—

Oxygen was certainly absorbed during the above heating by the copper spiral, for it was afterwards found to be blackened. It is therefore difficult to be certain that the final value of the ionisation was really due to nitrogen rather than to a small trace of oxygen which the copper spiral was incapable of removing. Assuming that

Time	P.M. 5.43	P.M. 6.01	P.M. 6.40	P.M. 7.11	P.M. 9.12	A.M. 10.06	A.M. 10.30	P.M. 3.00
Current (1 = 7×10^{-13} ampère per sq. centim.)	48	39	34	28	24	14·5	10·5	9

oxygen and nitrogen act quite independently of each other in producing the positive ionisation—reasons will be adduced later for showing that this is improbable—the proportion of oxygen to nitrogen required to account for the whole of the leak in nitrogen at atmospheric pressure would be about 1 to 10,000. Against this it is necessary to set the following facts:—

(1) The ions in nitrogen appear to be considerably bigger than those in oxygen, as shown by the current E.M.F. curves.

(2) The experiments on air indicate that nitrogen does not simply act as a diluent to oxygen, but exerts a marked retarding effect on its power of producing positive ionisation, so that a trace of oxygen present would exert a much smaller effect than that obtained on the basis of the above calculation.

(3) The positive ionisation in nitrogen varies more rapidly with temperature than that in oxygen. The numbers indicate that the energy necessary to liberate a positive ion from hot platinum in nitrogen is rather more than twice the value for oxygen.

On the whole, the balance of evidence seems to be in favour of the view that nitrogen produces a genuine positive ionisation which is considerably smaller than that in oxygen at about 900° C.

V.—§ 12. The Ionisation in Air.

The air used in these experiments was purified by passing slowly through two tubes, one packed with cotton wool and the other with fused caustic potash. It was subsequently dried over phosphorus pentoxide inside the apparatus. The general characters of the results in air are similar to those in oxygen, but the current was found to be more difficult to saturate under otherwise like conditions.

The relation between the current and the electromotive force at atmospheric pressure is given by the lower curve in fig. 12. The observations to which both the curves in fig. 12 refer were made with the water-cooled apparatus already described. The temperature was 976° C., the effective area of the wire 0·170 sq. centims., and the unit of current 7×10^{-13} ampère. The upper curve gives the value of the saturation current at different pressures. In this curve the leak at the four highest pressures was measured with +704 volts, the next with +512 volts, and the two lowest with +120 volts. This method of gradually decreasing the voltage as the pressure was lowered, so as to ensure approximate saturation and at the same time avoid the occurrence of ionisation by collision, was frequently adopted in this investigation.

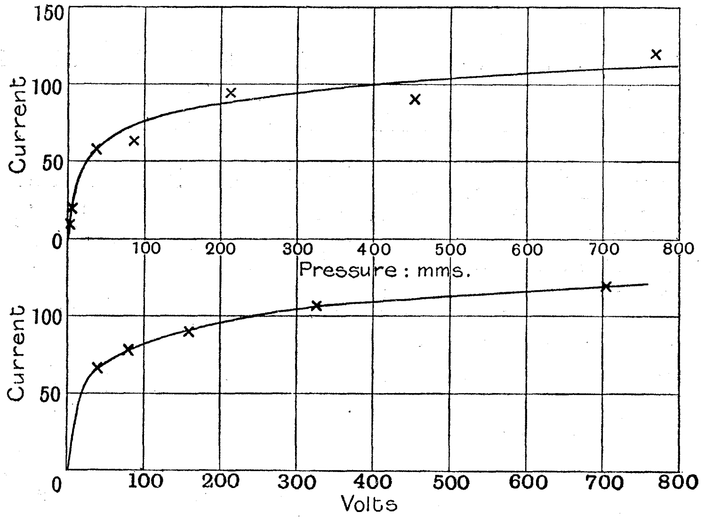

Fig. 12.

The temperature variation of the approximately saturated leak in air at atmospheric pressure was also examined with the wire 0·2 millim. diameter in the glass tube apparatus. The numbers obtained are given in the following table. The effective area of this wire was 0·66 sq. centim. :—

Temperature.	Current.	
	V = +560.	V = −40.
° C.	ampère	ampère
812	$9\cdot3\times10^{-12}$	—
893	$2\cdot2\times10^{-11}$	$3\cdot3\times10^{-14}$
900	$5\cdot2\times10^{-11}$	$5\cdot3\times10^{-14}$
978	$3\cdot3\times10^{-10}$	$3\cdot2\times10^{-13}$
1064	$8\cdot0\times10^{-10}$	$4\cdot2\times10^{-12}$
1150	$2\cdot0\times10^{-9}$	$3\cdot8\times10^{-11}$
1236	$6\cdot7\times10^{-9}$	$2\cdot6\times10^{-10}$

These numbers may be compared with the values for the leak in oxygen at different temperatures given on p. 23. In doing this it is necessary to multiply the latter by a factor of about 3·3, which varies slightly with the temperature, to bring the positive leak to its value at atmospheric pressure. Both sets of numbers have also to be divided by the effective areas of the respective wires. When this is done, it will be seen that the maximum leak in oxygen is greater than that in air at all temperatures, though the latter increases more rapidly with the temperature. Both the positive and negative leaks in air obey the formula $A\theta^{\frac{1}{2}}e^{-\omega/2\theta}$, the values of the constants which determine the energy change associated with the formation of one gram equivalent of each kind of ions being respectively $\omega_+ = 4{\cdot}92 \times 10^4$ and $\omega_- = 8{\cdot}97 \times 10^4$ calories. The value of ω_- for oxygen was $13{\cdot}5 \times 10^4$ calories; the lower value obtained in air is possibly due to -40 volts not being sufficient to produce saturation. Experiments were not made to test this at the time, but some results obtained by H. A. WILSON* indicate that this might have been the case. The value of $4{\cdot}92 \times 10^4$ for ω_+ is intermediate between the values $3{\cdot}04 \times 10^4$ and $7{\cdot}12 \times 10^4$ found for oxygen and nitrogen respectively.

Referring to the above table, we find for the maximum current in air the values $2{\cdot}2 \times 10^{-11}$ and $5{\cdot}2 \times 10^{-11}$ ampère at 893° C. and 900° C. respectively. Taking the mean of these, $3{\cdot}7 \times 10^{-11}$ ampère, to be the true value at 897° C., and dividing by 0·66 to reduce to unit area, we find for the maximum current at 897° C. the value $5{\cdot}5 \times 10^{-11}$ ampère per square centimetre. The corresponding quantity in oxygen deduced from fig. 9 (here we have to multiply by 3·3 on account of the low pressure) is $5{\cdot}8 \times 10^{-10}$ ampère per square centimetre, or ten times the corresponding quantity in air. Again, referring to fig. 12, we see that the maximum leak in air at 976° C. is $4{\cdot}5 \times 10^{-10}$ ampère per square centimetre, a number which agrees satisfactorily with the value $4{\cdot}95 \times 10^{-10}$ ampère per square centimetre given by the table on p. 40. The maximum leak in oxygen deduced from fig. 10 is $12{\cdot}2 \times 10^{-10}$ ampère per square centimetre, nearly three times the value for air. It is interesting to compare with these numbers what the values for air would be if the nitrogen had no effect. Since air contains 21 per cent. of oxygen by volume, on this basis the leak in air at 760 millims. would be the same as that in oxygen at 160 millims. Referring to fig. 7, we see that this should be equal to 0·775 of the value in oxygen at 760 millims. This would give 44×10^{-11} and $9{\cdot}5 \times 10^{-10}$ ampère per square centimetre at the two temperatures instead of the values $5{\cdot}5 \times 10^{-11}$ and $4{\cdot}5 \times 10^{-10}$ actually found.

This result, that the positive ionisation in air was smaller than if the nitrogen had been removed, seemed at first sight very surprising, and further experiments were made to test the question directly. This was done by letting air and oxygen into the apparatus immediately after each other and measuring the leak at atmospheric pressure. The experiments were carried out at 895° C. The values obtained are given in the subjoined table, that in nitrogen being added for comparison. The experiments were carried out in the order of the table, proceeding from above downwards. The unit of current is 7×10^{-13} ampère.

Gas.	Saturation current.
Nitrogen	29
Air	70
Oxygen	336
Air	70
Oxygen	244

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* 'Phil. Trans.,' A, vol. 202, p. 256, fig. 5.

The oxygen in the first experiment was prepared by electrolysing caustic potash, in the second by heating potassium permanganate. The difference in the values for oxygen is probably "accidental."

The disparity between the two leaks is considerably smaller than that calculated from the table, but it shows that nitrogen has a distinct inhibiting effect on the positive ionisation produced by oxygen. It may do this by combining with the free oxygen ions and so reducing their concentration, or by associating with the platinum and so reducing the amount available for combination with oxygen. The latter view would give a satisfactory quantitative explanation of the results.

VI.—§ 13. THE IONISATION IN HELIUM.

A few experiments were made in this gas chiefly with the object of finding out if hot platinum would liberate positive ions in an atmosphere in which the possibility of chemical action in the ordinary sense was excluded. The helium used was obtained from Messrs. TYRER AND Co., Sterling Chemical Works, Stratford, E. After admitting it into the apparatus it was dried over phosphorus pentoxide and purified by means of a discharge from a cathode of sodium potassium alloy. The tube used for this purpose is shown in fig. 13. After the apparatus had been completely exhausted, the liquid alloy was admitted through the stop-cock A. Care has to be exercised in doing this, as the alloy is liable to stick in the tube, and, when it begins to move again, to do so with such violence that it is projected into other parts of the apparatus. The electrical connection to the cathode was made by the platinum wire B sealed into the glass. The anode C was of aluminium. The side tubes D, E led to the pentoxide bulb and testing vessel and to the pump and McLeod gauge respectively.

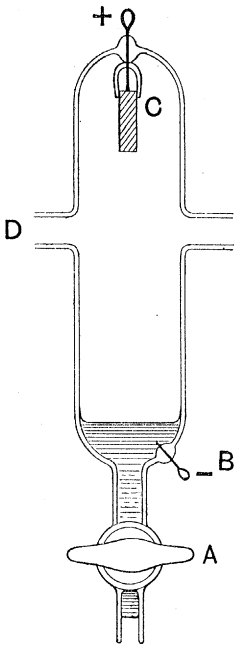

Fig. 13.

MEY* has shown that the discharge from a cathode of sodium potassium alloy given by an induction coil rapidly absorbs all gases except the inert ones. The discharge used was found to run down 3 millims. of air to a pressure comparable with that due to the residual argon in about 20 minutes. The discharge was allowed to pass for several hours before measurements of the leak were made. The helium must have been very pure to start with, as no decrease in pressure was observed with the McLeod gauge. The spectrum was also examined from time to time, and no lines belonging to any gas other than helium were noticed.

There is every reason to believe that the helium used in these experiments attained a very high degree of purity, and that the leak observed is really due to helium and not to traces of some other gas present. The leak resembled that

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* 'DRUDE'S Ann.,' vol. 11, p. 138.

in nitrogen in showing too big a value after the wire had been allowed to remain cold and only gradually settling down to a steady value. It is very difficult to explain this effect as being due to the absorption of impurities, as it appeared to be much the same whether the discharge had been run before the leak was tested or not. It seems far more likely to be due to a change taking place in the platinum. The following measurements at 907° C. of the leak at 2·4 millims. pressure with +11 volts on the filament show the way it varied with time:—

Time	A.M. 10.46	A.M. 10.48	A.M. 11.10	A.M. 11.25	A.M. 11.50	P.M. 12.09	P.M. 12.26	P.M. 2.21	P.M. 2.41
Current ($1 = 3 \cdot 3 \times 10^{-14}$ ampère per sq. centim.)	314	294	194	156	134	148	124	134	130

The values of the steady leak under +11 volts at the same temperature and different pressures are as follows:—

Pressure in millims. of Hg	0·07	0·32	2·4
Current ($1 = 3 \cdot 3 \times 10^{-14}$ ampère per sq. centim.)	18	54	130

The positive ionisation in helium at 2 millims. pressure and 907° C. appears to be, roughly speaking, about three times that in nitrogen and one-fortieth that in oxygen under like conditions.

The above experiments are not complete enough to enable us to deduce the law according to which the leak in helium varies with the pressure. The experiments were not pushed up to high pressures owing to the difficulty of ensuring the purity of the gas. They are chiefly of interest as showing that hot metals can produce ionisation in the inert gases when chemical action is out of the question.

VII.—§ 14. The Ionisation in Hydrogen.

A large number of experiments have been made with this gas, but the phenomena are very complicated, so that it is difficult to be quite certain of the interpretation of the results. This is largely owing to our ignorance of the absorption and diffusion of hydrogen in platinum at low pressures. Some of the effects observed seem to be of considerable interest and importance, and they will be described in order to give greater completeness to this account of the subject. Discussion of the theoretical bearing of the results will be avoided except in so far as it is necessary to render the purpose of the experiments intelligible, and generally speaking the writer is of opinion that this part of the work ought to be regarded as a preliminary exploration of a very complex question. So far as the negative leak is concerned, the ground has been previously examined, and valuable results obtained by H. A. WILSON.*

The hydrogen used in the experiments was prepared for the most part by the action of pure zinc on pure hydrochloric acid with a little ferric chloride added to make the action go. It was passed over solid potash and cotton wool before being admitted into the apparatus. In some cases, when only a little hydrogen was required, it was admitted into the apparatus by diffusion through the walls of a platinum tube heated in a spirit-lamp flame. This method is a very convenient one for obtaining a small quantity of hydrogen in a high degree of purity. As is well known, the negative ionisation produced by hot platinum in an atmosphere of hydrogen is very big, and it was found impossible to use the electrometer in the ordinary way, with a condenser attached to the quadrants, in order to measure the currents obtained. These currents, which amounted to as much as 10^{-4} ampère in some cases, were measured by taking the steady deflection when the electrometer quadrants were connected by a high resistance which could be varied from one to one million ohms. This was a very convenient arrangement, as it enabled the same instrument, by simply changing a few plugs, to be used for measuring any current from 10^{-1} to 10^{-14} ampère.

Interesting effects are observed when a wire, which has previously been heated in oxygen only is first heated in hydrogen. Such a wire gives rise to an abnormally high positive ionisation which gradually decays with time, whilst the negative ionisation increases simultaneously. The kind of thing that occurs is typified by the numbers in the subjoined table. The wire, which was 0·1 millim. in diameter and had an effective area of 0·214 sq. centim., had previously been heated in oxygen at 2 millims. pressure at a temperature of 800° C. Under these conditions it was giving about $8 \cdot 5 \times 10^{-12}$ ampère positive leak, the negative leak being small compared with this value. The wire was then allowed to cool, the oxygen pumped out, and hydrogen let in to a pressure of 27·5 millims. The currents, with potentials of -40 volts on the filament, were then measured at different times at a constant temperature of 800° C., with the result shown by the table.

Time hours . . .	3	3	3	3	3	3	3	3	4	4	4	4	4	4	4	4	5	5	5
Time minutes . .	32	36	42	44	47	52	56	58	2	6	10	15	18	21	24	27	15	20	28
Current, + ... ($1 = 10^{-12}$ ampère)	54	47·5	30·5	24	20	14	—	—	15·5	10	7·1	7·1	—	—	10	7·8	2·6	—	2·1
Current, − . . . . ($1 = 10^{-8}$ ampère)	—	—	—	—	—	—	3·06	3·4	—	—	—	—	8	8·4	—	—	—	75	—

It will be noticed that after the wire had been charged negatively, the positive leak was abnormally high. This may be a spurious effect due to the insulation

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* 'Phil. Trans.,' A, vol. 202, pp. 243 *et seq.*

becoming charged by the copious negative ionisation. It was impossible to test the question with the apparatus used.

A second wire, 0·2 millim. in diameter, was tested and found to give results almost identical with the above when it was heated in hydrogen for the first time at 860° C. This wire was afterwards heated in hydrogen and later in oxygen for several days, mostly at a temperature of about 1100° C. A long time after the wire had again got into a steady condition in regard to the ionisation in oxygen the oxygen was pumped out and hydrogen re-admitted. The wire was now heated in hydrogen at 26 millims. pressure at a temperature of 900° C., when it was found that the above slow time changes had almost disappeared. The negative leak when first measured about 10 minutes after first heating the wire was $6{\cdot}72 \times 10^{-5}$ ampère, whilst the positive was $4{\cdot}5 \times 10^{-12}$ ampère. They subsequently rose and fell to 8×10^{-5} ampère and $6{\cdot}7 \times 10^{-13}$ ampère respectively. The difference between the two cases seems to indicate that heating in hydrogen produces a permanent change in the constitution of the platinum. There are two other facts which support this contention. One is the permanent reduction of the value of the steady positive leak in oxygen produced by continued heating in hydrogen, which was mentioned on p. 27. The other is that the surface of a wire which has been heated for a long time in hydrogen becomes visibly pitted and cracked. This change does not appear to be produced by heating, to moderate temperatures at any rate, in oxygen.

Observations were also recorded of the variation in the ionisation when the gas in which the wire was heated was changed from hydrogen to oxygen. The change from one gas to the other was carried out in the same way as in the previous case. Oxygen was admitted to a pressure of 1·067 millims. and the wire maintained at 900° C. Under these circumstances the negative leak was found to fall at once to the small value previously obtained in oxygen. The negative leak when first measured registered 2×10^{-13} ampère per square centimetre, and it was found to possess the same value 20 minutes later. The positive leak, on the contrary, fell gradually during 3 hours from $4{\cdot}8 \times 10^{-11}$ to $8{\cdot}9 \times 10^{-12}$ ampère, more than half the fall occurring in the first half hour. This decrease in the ionisation was accompanied by a slight decrease in the pressure of the oxygen, which fell to 1·026 millims., indicating that hydrogen had been evolved by the wire, had combined with the oxygen, and that the water formed had been absorbed by the phosphorus pentoxide. This experiment indicates that hydrogen diffusing out of a hot platinum wire increases the positive leak in oxygen, but is without effect on the negative leak. This conclusion will be more fully established by experiments to be described later.

The last experiment shows that although a considerable amount of hydrogen may remain in the wire, the addition of a small quantity of oxygen at once reduces the negative ionisation to a small value. This indicates that the great negative ionisation produced by hydrogen in platinum is due to some change of a very superficial character. On the other hand, a wire which has previously only been heated in oxygen only appears to attain to the high value of the leak in hydrogen with extreme slowness when heated in that gas. It seems very difficult to reconcile these statements if the only time effect occurring is the diffusion of hydrogen into and out of the wire.

The relation between the negative leak in hydrogen and the applied electromotive force was next examined. It was found that the normal curve, exhibiting saturation and a definite relation between current and electromotive force, could only be obtained under very restricted conditions. The normal relation referred to is that exhibited by fig. 14. This experiment was made with the wire 0·2 millim. in diameter and 0·66 sq. centim. effective area; the pressure of hydrogen was 3·8 millims. and the temperature 900° C.

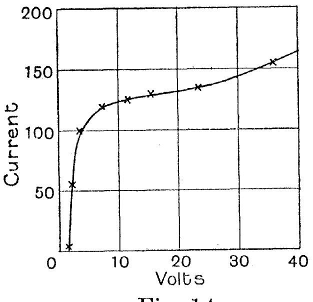

Fig. 14.

The heating current caused a fall of potential of about 5 volts along the filament; the potentials given are the potentials of the middle point of the filament. The unit of current is $1{\cdot}67 \times 10^{-10}$ ampère. The increase in the current with voltages greater than 20 indicates that ionisation by collisions was beginning to come in.

On pushing these experiments to higher potentials, it was found that the current ceased to be a definite function of the applied E.M.F. and varied in a curious way with the time. The mystery was cleared up when considerably higher potentials were applied. The experiments were carried out at 1084° C. with a wire 0·1 millim. in diameter and an effective area of 0·214 sq. centim. The pressure was 1·77 millims.; the unit of current to which the following numbers refer is 10^{-8} ampère. It was found that under a high voltage the steady current was *smaller* than under a low one. For instance, under 19 volts the wire had been giving a steady negative leak of about 147 divisions. At a certain instant the voltage was changed to 286, when the following values of the current were obtained after the intervals of time stated :—

Time (minutes)	2	3	5	7	10	13
Current . . . . (1 = 10^{-8} ampère) (V = -286)	62	44	37	33	28·5	26

The voltage was now reduced to 80, when the current was found to remain almost steady for some time at 7 divisions. It did not, however, stay at this value, but after a time began to increase, slowly at first, then more rapidly, then more slowly again, until it finally became steady at about 220 divisions. This great reduction of the leak by applying a big voltage and subsequent slow increase under a low voltage was observed time after time with two different wires under varied conditions of temperature and pressure. On the other hand, the absolute values of the leaks finally obtained seemed very capricious. The general character of these time changes is exhibited by fig. 15.

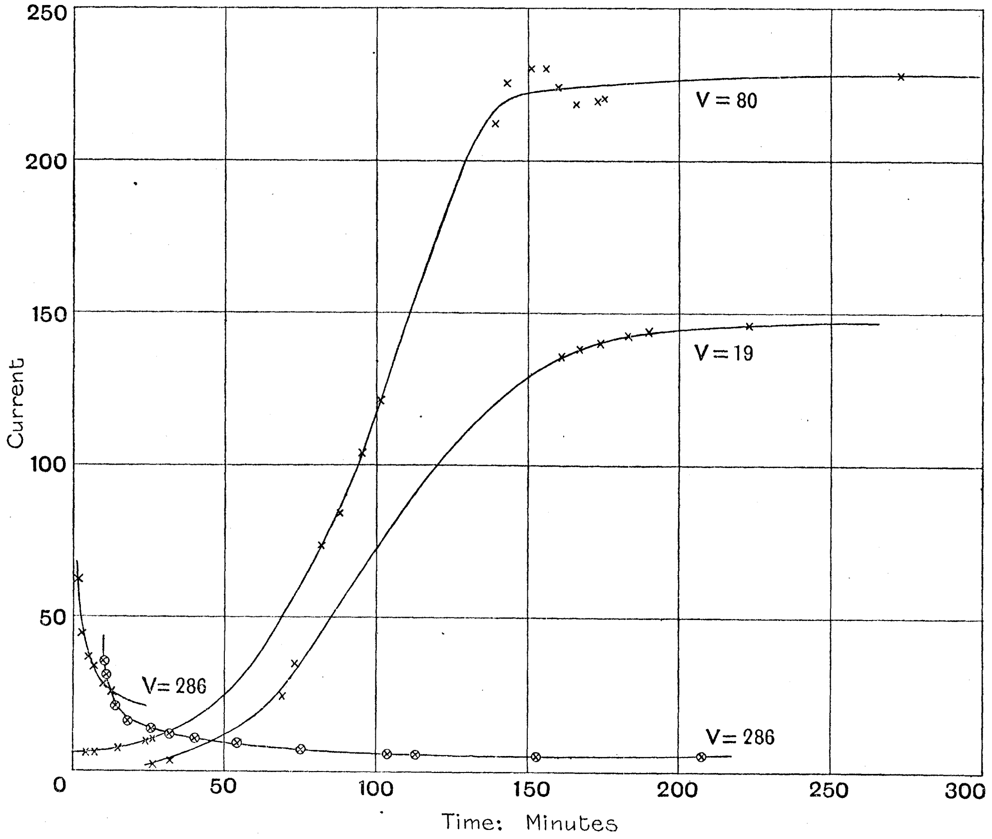

Fig. 15.

In order to make the experiments comparable, the wire was maintained at a potential of -286 volts for 120 seconds before the readings under any assigned voltage were commenced. For obvious reasons the voltage on the filament during any one set of readings was never changed.

The reduction in the negative leak by applying a big voltage does not occur under the following conditions:—(1) At very low pressures ($< 0\cdot1$ millim.), (2) at high pressures (200 millims.), (3) when the wire is positively charged. The subsequent increase in the ionisation occurs if the wire is either uncharged or charged positively as well as under a low negative potential. The time required for the establishment of the final equilibrium appears to decrease fairly rapidly as the temperature increases. The voltages employed in the previous experiments were never great enough to produce a luminous discharge, though the effect does occur if a luminous discharge passes. The reduction in the ionisation is greater if the wire is made the cathode than if it is made the anode.

All the above facts point to the view that the reduction of the negative leak in hydrogen produced by the application of a high potential is due to a change in the surface caused by the bombardment of the surface by the positive ions produced in the gas by ionising collisions. This view is supported by the fact that after the high potential had been applied a greater heating current was always required to maintain the wire at its original temperature. This shows that the amount of heat radiated from the surface at a given temperature was greater than before, so that the nature of the surface must have become changed in some way.

Two views which are not mutually exclusive may be taken as to the nature of the action by which the bombardment of the positive ions, which are really weak canal rays, reduces the negative leak. They may act either by destroying a layer of positively-charged hydrogen which helps the corpuscles out of the metal, or they may merely allow the absorbed hydrogen to escape from the wire. The last suggestion receives strong support from the recent experiments of SKINNER on the evolution of hydrogen from metallic cathodes under the influence of the luminous discharge.* On the other hand, it is difficult to conceive how bombardment by positive ions for two minutes can allow so much hydrogen to escape from a wire that it takes several hours for it to diffuse back again. On the whole, the evidence, though inconclusive, is in favour of the double layer theory.

The writer has examined the effect of changing the temperature on the value of the steady negative ionisation in hydrogen, and has confirmed WILSON'S† result that increasing the temperature gives a leak which is too big initially, whilst decreasing the temperature has the converse effect. The curve showing the recovery with time, after heating to a high temperature, is similar in form to that obtained after exposure to a high potential, although the ratio of final to initial value of the leak was smaller in the cases examined.

So far little has been said about the steady positive ionisation in hydrogen. We saw on p. 44 that a wire when first heated in hydrogen gives a considerable positive leak which gradually decays with time. It is an interesting question whether this decay would go on indefinitely, or if the positive leak has a minimum value depending in pressure, temperature, &c. The following experiments show that the steady positive leak due to hydrogen at 3·8 millims. pressure and a temperature of 900° C. is very small, even if it exists.

The wire (diameter = 0·2 millim. and effective area 0·67 sq. centim.) was maintained at a constant temperature of 900° C. in a hydrogen vacuum for about $3\frac{1}{2}$ hours. By pumping from time to time, the steady pressure was kept below 0·001 millim., though hydrogen was being given off by the wire. The values of the leak with +40 volts at various times were as follows:—

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* SKINNER, 'Phys. Rev.,' vol. 21, p. 1 (1905).

† H. A. WILSON, 'Phil. Trans.,' A, vol. 202, p. 265.

Time: hours	12	12	1	1	2	3
Time: minutes	2	55	12	26	44	31
Current (1 = $3 \cdot 5 \times 10^{-13}$ ampère)	13	12	10·5	9·5	6·7	6·0

The rate of evolution of hydrogen from the wire decreased considerably during the above experiment. During the first half hour the pressure in the apparatus rose by 0·0033 millim., and during the last half hour by 0·00016 millim. The volume of the apparatus was about 2000 cub. centims., that of the wire being 0·0033 cub. centim. The amount of hydrogen left in the wire would probably be comparable with that given out in the last half hour, so that the pressure of the hydrogen *inside* the wire would, according to the above numbers, still be considerable. The current 21×10^{-13} ampère at the end of the experiment might be due to the residual gas left in the wire, so that these experiments are not contrary to the view that the positive leak in hydrogen, such as it is, is due to absorbed gas.

The effect of letting in hydrogen to a pressure of 3·8 millims. was now tried, and the leak at 900° C. measured at various times, with the results shown.

Time: hours	3	3	3	3	3	4	4	5	5	6
Time: minutes	43	46	49	53	56	1	10	25	39	14
Current (1 = $3 \cdot 5 \times 10^{-13}$ ampère)	108	104	88	76	68	60	46	18	14	15

The big leak obtained on letting in the fresh gas is a somewhat surprising result, but might possibly be due to impurities which are gradually destroyed or removed. The point which seems most important is the small value, $5 \cdot 2 \times 10^{-12}$ ampère, of the steady leak at this pressure. This was only two and a-half times the value of the positive leak obtained after the wire had been heated for 3½ hours in a good vacuum. The value of the positive leak in oxygen at this pressure and temperature would have been about 10^{-10} ampère, or nearly twenty times the above number.

Owing to the smallness of the positive leak in hydrogen, together with other difficulties which arose, few other satisfactory measurements were made on it.

Measurements of the variation with pressure of the negative ionisation from hot platinum in hydrogen have been made by H. A. WILSON.[*] WILSON's method consisted in measuring the leak when hydrogen at successively increasing pressures

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[*] 'Phil. Trans.,' A, vol. 202, p. 243.

had been admitted to a wire previously oxidised in nitric acid. At a temperature of 1350° C. the ionisation increased rather less rapidly than if it were proportional to the pressure up to 0·014 millim. The writer* has made experiments to see if the same kind of results could be obtained by decreasing the pressure from a high initial value. The first experiments were made at 900° C., and indicated that the leak with −40 volts consisted of two parts, one proportional to, and the other independent of, the pressure. The part proportional to the pressure could be accounted for as being due to ionisation by collisions, so that the nett result was a leak independent of the pressure. This leak remained constant when the wire was left hot for 2¾ hours, although some gas was given off by the wire, the pressure rising from 0·00033 to 0·0017 millim. This result might be reconciled with WILSON's by supposing that the gas was retained by the platinum with extreme tenacity, and that the amount evolved during the 2¾ hours' heating was merely an insignificant fraction of what remained in the wire.

To test this supposition, an experiment was carried out at a much higher temperature (1390° C.), and an attempt was made to estimate the rate of evolution of hydrogen by the wire from time to time from the increase in the pressure of the McLeod gauge. Before commencing the experiment the wire had been heated for some time in hydrogen at a pressure of 1·35 millims., so presumably equilibrium at this pressure would have been approximately established. The amount of hydrogen still retained under these conditions appears to be very large. The rate of increase of pressure per hour after heatings for the time in hours stated is given by the following numbers :—

Increase of pressure (millims.) per hour.	0·0064	0·0055	0·0052	0·0050	0·0033	0·0014
Mean time (hours)	0	2	2·2	3	5·5	11

The numbers are only approximate, as the McLeod gauge was not well adapted for measuring small pressures accurately. The volume of the apparatus (pump, McLeod gauge, &c.) was of the order 2000 cub. centims., that of the wire being 0·0033 cub. centim. On the assumption that all the increase of pressure is due to hydrogen evolved by the wire, the concentration of hydrogen in a platinum wire at 1350° C. in equilibrium with hydrogen outside at a pressure not greater than 1 millim. (it may have been considerably less than this) must be of the order of that corresponding to a pressure of 2×10^4 millims. of mercury. It seems probable that most of the increase of pressure is really due to hydrogen evolved from the wire and not from the walls of

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* It is only fair to state that WILSON describes experiments on the effect of reducing the pressure of the hydrogen, which gave a much greater diminution in the leak than that observed by the writer (*vide* H. A. WILSON, *loc. cit.*, p. 266).

the vessel, since this protracted increasing of the pressure in a vacuum was not observed after a wire had been heated in other gases. Even if the above large amount of gas has to be got rid of the rate of escape seems very slow; in fact, the numbers show that the law for the rate of diffusion of hydrogen through hot platinum obtained by RICHARDSON, NICOL and PARNELL* at pressures greater than 1 millim. does not hold at low pressures. It is probable that at these pressures it is necessary to take external dissociation into account (*vide loc. cit.*).

Whilst the preceding measurements of the rate of evolution of hydrogen were being recorded, readings of the current with −13 volts on the filament were taken simultaneously. This value of the potential was used in order to ensure saturation (see fig. 15) and at the same time to avoid the occurrence of ionisation by collisions as far as possible. The readings were commenced at a pressure of 0·3 millim., and the current was found to decrease by about 40 per cent. of its value on reducing the pressure to 0·002 millim. This additional part of the current, which is nearly proportional to the pressure, may be accounted for by supposing it to be due to ionisation by collisions. The wire was then heated for $16\frac{1}{2}$ hours at a low pressure, during which time gas was given off at the rates indicated by the numbers in the last table. The values of the leak ($1 = 10^{-6}$ ampère) and the times, reckoned from the instant at which the apparatus was first pumped down to 0·002 millim. pressure, at which they were recorded are given in the next table:—

Time: hours	0	0	2	2	3	3	5	6	16	16
Time: minutes	0	15	16	44	6	17	45	0	10	37
Current	30	26	31	29	30	27	26	25	15	12

At a first glance these numbers indicate a continual falling off in the value of the leak at constant temperature as the gas escapes from the wire. The criterion for constant temperature was the resistance of the wire, and it was found that, owing to the spluttering of metal which takes place at high temperatures, the resistance of the wire at 0° C. had increased considerably during the course of the above experiment. When this was allowed for it was found that the average temperature of the wire at the close of the above experiment was 1280° C. instead of 1370° C., its value when the experiment started. The leak at 1280° C. should have been about three divisions instead of twelve, so that pumping out the gas had apparently increased the leak. This paradoxical result is probably caused by the fact that the above method of reckoning over-corrects for the effect of loss by spluttering. A calculation from the numbers in the last table but one shows that the wire had lost

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* 'Phil. Mag.,' vol. 8, p. 1.

about nine-tenths of the hydrogen originally present in it at the end of the experiment, so that the experiment appears to warrant the conclusion that the amount of the negative ionisation depends very little on the amount of hydrogen in the wire. In fact, the hydrogen appears to act by altering the condition of the surface of the wire, and once this change has taken place it is very little affected by changes in the amount of hydrogen either outside or inside. The most reasonable view appears to be to suppose that the positively charged hydrogen atoms form an electrical double layer, which helps the corpuscles out of the metal.

A few measurements of the variations of the ionisation, both positive and negative, with the temperature were made in hydrogen. Experiments at pressures of the order of 1 millim. were found to be particularly difficult to carry out on account of the length of time required for equilibrium to be established and the difficulty of being certain that it was established. The following values, with a pressure of 1·90 millims. represent the best series of measurements at this kind of pressure.

Temperature, ° C.	860	1017	1181
Current . . . . (ampères per sq. centim.) (V = +40)	$2\cdot5\times10^{-11}$	13×10^{-11}	112×10^{-11}
Current . . . . (ampères per sq. centim.) (V = −40)	$4\cdot7\times10^{-10}$	—	11×10^{-6}

These numbers for the positive ionisation will be seen to be considerably greater when the difference of temperature is allowed for than the minimum value given on p. 49. This indicates that the steady condition had not really been attained when the measurements were made, although the final reading was never recorded until the leak appeared to be varying very slowly, if at all, with the time. [Another possibility, which must be kept in view, is that these inconsistencies are due to some other undiscovered factor, which is not taken account of.] If we calculate from the above numbers the energy change associated with the liberation of a gramme molecule of ions of each sign we find $w_+ = 3\cdot58\times10^4$ calories and $w_- = 12\cdot0\times10^4$ calories.

A series of measurements was also made at a much higher pressure (226 millims.). The numbers obtained are given in the table following.

No regular change could be detected in the value of the positive ionisation at the lowest temperature over a space of half-an-hour. This tends to confirm the conclusion from the experiments on p. 49 that there is a positive leak in hydrogen which is a function of the pressure. At low pressures this is much smaller than the positive leak in oxygen, but it increases more rapidly with the pressure. It also

Temperature, ° C.	860	1017	1097	1181
Current (ampères per sq. centim.) (V = +560)	$4 \cdot 1 \times 10^{-11}$	$3 \cdot 8 \times 10^{-10}$	—	14×10^{-9}
Current (ampères per sq. centim.) (V = −40)	10×10^{-8}	—	$12 \cdot 5 \times 10^{-6}$	$2 \cdot 8 \times 10^{-5}$

appears to increase more rapidly with the temperature. The values of the negative leak are bigger than those obtained at the lower pressures for the same temperature, the difference being greatest at the lower temperatures. This would seem to indicate that the small increase in the negative leak with pressure obtained at the lowest pressure, and which it was suggested might be due to ionisation by collisions, is really a genuine direct effect of the gas and becomes greatly magnified at high pressures.

The values of the energy change associated with the liberation of one gramme molecule of each kind of ions at this pressure are $w_{+} = 5 \cdot 7 \times 10^{4}$ calories and $w_{-} = 5 \cdot 56 \times 10^{4}$ calories. Thus increasing the pressure of the hydrogen appears to increase the work required for a positive ion to escape from the metal, whereas it decreases it in the case of the negative ion. This result so far as it refers to the negative ionisation has previously been obtained by H. A. WILSON.*

VIII.—§ 15. EXPERIMENTS WITH A PLATINUM TUBE.

The writer has also made experiments on the change produced in the ionisation at the outside surface of a platinum tube in air when hydrogen was allowed to diffuse from the inside of the tube. A brief abstract of the results obtained has already been published†; the present section gives a more detailed account of the experiments. These platinum tube experiments, in the opinion of the writer, settle decisively a number of questions which have been, or might be, raised with regard to the origin of the ionisation produced by hot platinum. For instance, H. A. WILSON‡ has suggested that the negative ionisation produced by hot platinum in air is due to traces of occluded hydrogen which are retained by the wire in a very persistent manner. If this were the case, the small negative leak in air would be enormously increased by allowing any considerable quantity of hydrogen to diffuse out of the wire from inside. As a matter of fact, when hydrogen was allowed to diffuse out of the walls of the tube at a rate corresponding to 2 cub. centims. at

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* 'Phil. Trans.,' A, vol. 202, p. 269.

† 'Camb. Phil. Proc.,' vol. 13, p. 192.

‡ 'Phil. Trans.,' vol. 202, p. 243.

atmospheric pressure per square centimetre of surface per minute, not the slighest change could be detected in the value of the negative leak. This proves indubitably that the negative ionisation produced by hot platinum in air is not due to traces of absorbed hydrogen.

The apparatus used in this part of the investigation is shown in fig. 16. The

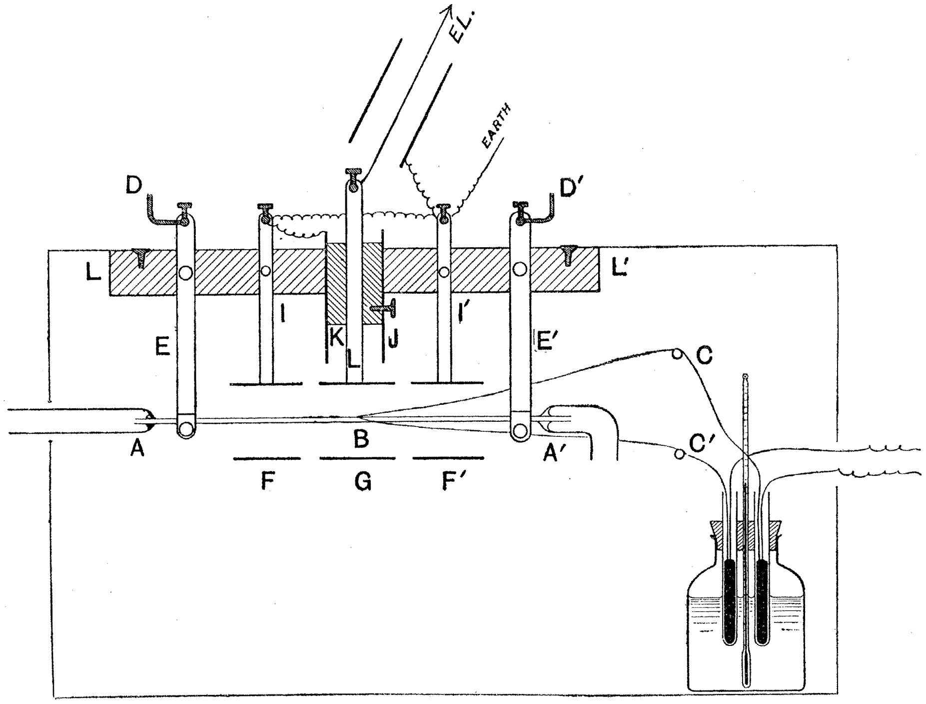

Fig. 16.

platinum tube ABA′ was about 15 centims. long, and its internal and external diameters were 0·05 and 0·10 centim. respectively. It was clamped at each end by the metal supports E, E′, and heated by means of a current let in at D, D′. The current of hydrogen or air inside the tube was let through by means of the glass tubes A, A′ sealed on at each end of the platinum tube. The temperature of the tube was measured by means of the thermocouple C, C′ of platinum and rhodioplatinum welded on to the middle point B. The wire was surrounded by three aluminium cylinders, F, G, and F′, to the middle one of which the leak was measured. The outer cylinders acted as guard rings and maintained a uniform field near the central uniformly heated part of the tube B. The dimensions of the middle cylinder were: length = 3 centims., diameter = 3·2 centims. The various supports E, I, I′, E′, could slide in holes cut in a slab of vulcanised fibre LL′, which was used because ebonite was found to buckle with the heat. When they had been adjusted in position they could be clamped by means of screws. The vulcanised fibre was not found to be sufficiently good insulating material, so the support L to the testing electrode was protected by an earth-connected tube J in which it was held by an ebonite cylinder K. The whole of this part of the apparatus was fixed in a wooden box covered with lead foil connected to earth.

In reducing the thermocouple readings to temperatures, the platinum temperature was first calculated by making use of the reading corresponding to the melting-point of potassium sulphate. This point was determined experimentally in the way already described. The platinum temperatures were then reduced to centigrade by means of the correction curve given by CALLENDAR.* The legitimacy of this process was tested by making an independent determination of the melting-point of sodium sulphate. The value found was 885° C., and is within 2° of that (883° C.) given by HEYCOCK and NEVILLE for this constant.

Sealed on to A′ were a mercury manometer, a glass bulb of about 300 cub. centims. capacity, and a glass tap. The last named was connected to the apparatus for delivering and purifying the hydrogen which was prepared, as described previously, by the action of pure zinc on hydrochloric acid. From experiments on the diffusion of the hydrogen through the walls of the platinum tube it is believed to have been exceptionally pure. The tube A was also sealed on to a three-way tap so that the hydrogen or air could be either sucked by means of a water pump or allowed to bubble through water. These arrangements made it easy (1) to test if the hydrogen was diffusing through the tube properly, (2) to replace the stream of hydrogen by air and *vice versâ*, and (3) to change the pressure inside the apparatus which regulated the rate of diffusion of the hydrogen through the walls of the tube.

It is convenient to consider first the effect of the hydrogen on the negative ionisation in air. Preliminary experiments showed that the current could not be saturated by the voltages at the writer's disposal, so the current with -80 volts was measured instead of the saturation current. This makes the absolute values of the currents considerably smaller than those previously obtained, more especially as the latter are probably greater than the normal on account of ionisation by collisions (see p. 23). The first test was made at 1200° C. After the tube had been heated for a long time with air both inside and outside, the current with -80 volts was found to be 21×10^{-14} ampère per square centimetre of surface. The tube was then allowed to cool, the air replaced by hydrogen inside, and the leak again measured. With hydrogen inside at a pressure of 115 millims. the leak under the same conditions was 26×10^{-14} ampère per square centimetre, and with hydrogen at atmospheric pressure 24×10^{-14} ampère per square centimetre. These numbers are all equal within the probable accuracy of the temperature regulation.

Another experiment was made at 1380° C. The current with -80 volts with hydrogen inside the apparatus at atmospheric pressure was found to be $3 \cdot 7 \times 10^{-11}$ ampère per square centimetre, and with the hydrogen at 65 millims. the current was $3 \cdot 6 \times 10^{-11}$ ampère per square centimetre. In the latter case the amount of hydrogen

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* 'Phil. Mag.' [5], vol. 48, p. 519.

diffusing through the wire would have been rather less than one-third of what it was in the former. A calculation based on the results of RICHARDSON, NICOL, and PARNELL* showed that the amount of hydrogen diffusing through each square centimetre of surface of the platinum per minute must have been equal to about 2 cub. centims. at 0° C. and 760 millims.

Since the platinum tube in these experiments was giving the small negative ionisations normally produced in air before the hydrogen was allowed to diffuse through, the above experiments prove indisputably that the negative ionisation produced by hot platinum in air and other gases is not due to residual traces of absorbed hydrogen. It appears to be possible to go further than this and to say that the effect, on the leak, of hydrogen inside the metal is not due to its direct action as hydrogen, but to some change it produces in the properties of the metal surface. This change appears to be inhibited when the metal is heated in an atmosphere of air or oxygen.

To substantiate this conclusion it is necessary to prove that there was enough hydrogen inside the outer surface of the wire during the experiment to have appreciably altered the value of the negative leak if it were exerting its full effect. This may be done by finding a minimum value of the external hydrogen pressure which would just stop the diffusion outwards for an instant. If the velocities of the escaped hydrogen molecules were suddenly reversed, the diffusion would stop momentarily, and the external pressure then occurring would give the minimum external pressure which would keep the hydrogen inside the surface layer in equilibrium. The equilibrium pressure might be greater than this, but could not be less. In the experiment the mass of hydrogen diffusing through 1 sq. centim. per second at 1380° C. = $2·65 \times 10^{-7}$ gramme. In free hydrogen at 1 centim. pressure the mass which is carried across an area of 1 sq. centim. per second = $2·3 \times 10^{-2}$ gramme at 1380° C. Hence the minimum value of the external pressure with which the hydrogen instantaneously present inside the surface layer could be in equilibrium is $1·15 \times 10^{-4}$ millim. It is necessary to show that a pressure of this amount of hydrogen would have produced an appreciable increase in the value of the leak. According to one table given by H. A. WILSON (*loc. cit.*, p. 265), at 1350° C. hydrogen at 6×10^{-4} millim. pressure increases the negative leak by a factor of 2500. The writer, however, is inclined to think that a more accurate comparison with the present experiments can be got by comparing the tables on pp. 260 and 269 of WILSON'S paper. These show that hydrogen at a pressure of 13×10^{-4} millim. increases the leak at 1375° C. by a factor of 8, so that $1·15 \times 10^{-4}$ millim. would cause an increase by a factor of not less than 1·6. The experiments recorded in the present paper (p. 52) also indicate an increase in the leak of about 100-fold at 1340° C. due to hydrogen at a pressure certainly less than 10^{-2} millim. On the assumption that the negative ionisation is nearly proportional to the pressure, this would give about the

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* 'Phil. Mag.' [6], vol. 8, p. 1.

same increase due to 10^{-4} millim. as that obtained above. Reasons have been adduced earlier in this paper (p. 52) for believing that the assumption that the negative ionisation is nearly proportional to the pressure of the hydrogen is incorrect. It has been retained in the present argument because it is the assumption which is most unfavourable to the view advocated. On the most unfavourable view, then, the hydrogen diffusing through the wire should have produced an increase of at least 60 per cent. in the leak. Allowing an experimental uncertainty of 20 per cent., no change could be detected in the leak due to the diffusion of hydrogen through the wire. This strongly supports the view, which also seems required on other grounds, that the hydrogen does not act *per se*, but produces some change in the platinum surface, and this change is prevented from taking place if the platinum is heated in air.*

In contrast to the negative ionisation, the positive ionisation produced by the hot platinum tube was found to be altered when hydrogen was allowed to diffuse through from inside. In fact, at constant temperature an additional amount of ionisation is caused thereby which is proportional to the amount of hydrogen diffusing through the tube.

At high temperatures the positive ionisation was found to be readily saturated. Thus at 1200° C. the leak with +80 volts was equal to 64 divisions, and with +400 volts 75 divisions with air inside the tube; with hydrogen diffusing through, the values under these voltages were 88 and 95 divisions respectively. These proportions were much the same, so the leak was generally measured with +80 volts, as higher voltages were not always available. On changing from a low to a high voltage, a big leak was often noticed at first, but this always fell away in a few minutes, until, approximately, the above ratio was obtained. Effects of this kind have already been described in detail (see § 9). At low temperatures the positive ionisation obtained with this apparatus seemed to be different in character, for it was

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[* *Note added September* 7, 1906.—It seems advisable to indicate the exact bearing of this argument more precisely. It is intended to confirm the conclusion, which has been drawn from direct experiment on page 52, that the high value of the negative ionisation in a vacuum containing traces of hydrogen is due to the fact that the hydrogen keeps the surface of the wire in a certain state, rather than that the wire contains a certain amount of hydrogen. The writer does not wish to create the impression that hydrogen never exerts a direct influence on the magnitude of the negative leak. The numbers on p. 53 show that the value of the ionisation, at constant temperature, increases with the pressure of the hydrogen at high pressures; so that it is probable that at high pressures there is a negative leak which is a definite function of the pressure of the hydrogen. This is also demanded by the fact that the constant ω_-, which enters into the temperature formula, is dependent on the pressure.

A comparison of the table at the top of page 53 with that on page 52 would seem to indicate that the ionisation in hydrogen at 1·9 millims. pressure is much greater than in a hydrogen vacuum. The writer considers, however, that these experiments are not comparable with one another, owing to the wires having been differently treated before the two experiments. The *direct* tests made on pp. 50 and 51 showed that decreasing the pressure from about 1 millim. to ·001 millim. only reduced the ionisation in hydrogen by about 40 per cent. of its value.]

impossible to saturate it. This is shown by the following numbers for the positive current under different voltages at 809° C. :—

Volts, +	0	4	10	20	40	80	400	960
Current (1 = $1 \cdot 8 \times 10^{-12}$ ampère per sq. centim.)	0	2·6	10	22	32	64	225	390

A number of experiments were made to find the cause of this anomalous behaviour at low temperature, but no satisfactory conclusion was arrived at. Fortunately, this does not matter much as far as the present investigation is concerned, for the experiments described below were all carried out at much higher temperatures, when saturation was very nearly attained with 80 volts.

Experiments on the variation of the positive ionisation with the rate at which hydrogen was diffusing through the walls of the tube were made at 1200° C. approximately. The rate of diffusion was varied by varying the pressure of the hydrogen inside the apparatus, since the quantity diffusing in a given time has been shown* to vary very nearly as the square root of the pressure inside. The way in which the saturation current varied with the pressure P of the hydrogen inside the tube is shown by the following numbers :—

P.	Current. (1 = $1 \cdot 8 \times 10^{-11}$ ampères per sq. centim.)	
	Found.	Calculated.
millims.		
0	42	42
30	51	52
60	56·3	55
172	64	65·6
780	90	92·4

The numbers in the last column were calculated by assuming that the current was equal to $a+bP^{\frac{1}{2}}$, a and b being constants. The agreement of the results shows that the leak consists of two parts, one independent of, and the other proportional to, the square root of the pressure of the hydrogen inside the tube. The effect of the hydrogen diffusing out of the platinum, therefore, is to produce an additional number of positive ions proportional to the amount of hydrogen diffusing out.

These results tend to indicate that the hydrogen inside the metal, which is known from other considerations to be in the atomic state, is positively charged. Only a small fraction (about 10^{-7}) of the hydrogen comes out in the ionic form, but on

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* Richardson, Nicol, and Parnell, *loc. cit.*

account of the electrostatic attraction the charged atoms might be expected to have greater difficulty in escaping from the metal. This would especially be the case at low temperatures, and may account for the hydrogen set free from palladium not being ionised. These considerations are also in agreement with the fact that electrolytic hydrogen, which is positively charged, is capable of diffusing into some metals—for instance iron—at ordinary temperatures.

Experiments were also made to see how the positive ionisation in air varied with the temperature, (1) when the tube had been heated for a long time in air and there was no hydrogen inside the tube, (2) with a constant pressure (atmospheric) of hydrogen inside. The results, which extend from 973° C. to 1331° C., are exhibited in fig. 17; the numbers in brackets denote the order in which the observations were taken. The upper curve represents the ionisation with hydrogen inside the tube, the lower one that without. The difference between corresponding ordinates represents the part of the ionisation which is due to the hydrogen diffusing through at any temperature. The values of the hydrogen part of the current ($1 = 1{\cdot}8 \times 10^{-12}$ ampère per square centimetre) at various temperatures are given in the following table:—

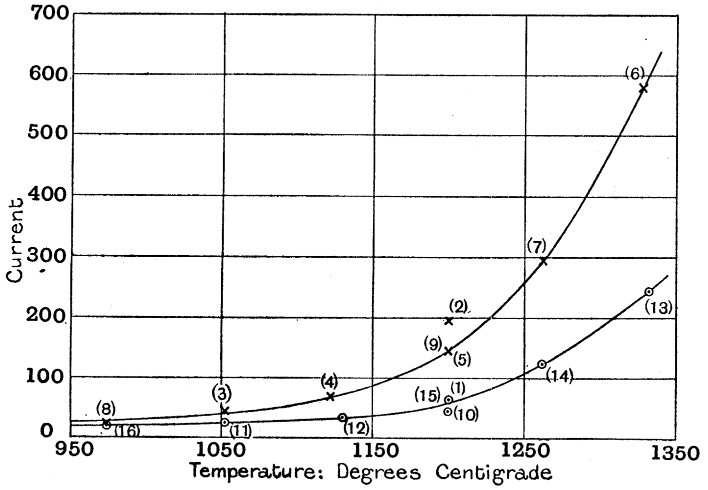

Fig. 17.

Temperature, ° C.	973	1052	1129	1200	1262	1331
Current	6	17	13	80	172	340

These numbers increase much more rapidly with the temperature than the quantities of hydrogen diffusing as given by RICHARDSON, NICOL, and PARNELL'S experiments. Hence the efficiency for producing positive ionisation of a given amount of hydrogen diffusing out of platinum increases rapidly with increasing temperature.

The fact that hydrogen diffusing out of a platinum wire produces a positive ionisation proportional to the amount of gas diffusing, taken in conjunction with the fact that the additional ionisation so produced, even when the amount of gas diffusing per minute is equal to 1 cub. centim. at 0° C. and 760 millims. per square centimetre, is only about equal to the positive leak when no hydrogen is apparently present, proves that the positive ionisation in oxygen and other gases as well as the negative is not due to residual traces of absorbed hydrogen. This position has already been shown to be highly probable by other considerations, the chief of which are:—(1) The constancy of the positive ionisation in oxygen with long-continued heating, (2) the agreement between different wires, (3) the fact that heating a wire in hydrogen seemed to produce a permanent decrease, and not an increase, when the steady ionisation it produced in oxygen was measured subsequently.

IX.—§ 16. SOME THEORETICAL CONSIDERATIONS.

The above experiments show that the steady positive ionisation produced by hot platinum in different gases, so far as its variation with temperature is concerned, obeys a formula first deduced by the writer* and shown to represent the negative corpuscular ionisation from hot platinum. That this would be the case was rendered highly probable by the fact established by the writer† some time ago that the temperature relations of the positive ionisation, when it is changing with time, were adequately expressed by the formula $C = A\theta^{\frac{1}{2}}e^{-Q/2\theta}$, A and Q being constants. The only theoretical conclusion which this temperature relation seems to warrant is that the liberation of an ion occurs when the dynamical system from which it is produced acquires a certain amount of energy, which is furnished, it may be indirectly, by the energy of thermal agitation of surrounding systems. It does not really afford any evidence as to whether the production of ions is, or is not, accompanied by chemical action.

It is interesting to compare the values of Q, which represent, on the assumption that equilibrium is possible, the amount of energy in calories associated with the production of 1 gramme equivalent of ions. The numbers which were obtained are given in the following table:—

Gas.	Pressure.	Q_+.	Q_-.	N_+.	N_-.
	millims.				
Oxygen	2	$3 \cdot 04 \times 10^4$	$13 \cdot 55 \times 10^4$	5×10^{10}	3×10^{23}
Air	760	$4 \cdot 92 \times 10^4$	$8 \cdot 97 \times 10^4$	5×10^{13}	10^{16}
Nitrogen	2·8	$7 \cdot 12 \times 10^4$	$11 \cdot 2 \times 10^4$	3×10^{16}	2×10^{21}
Hydrogen	1·9	$3 \cdot 58 \times 10^4$	$12 \cdot 0 \times 10^4$	10^{11}	10^{26}
Hydrogen	226	$5 \cdot 7 \times 10^4$	$5 \cdot 56 \times 10^4$	10^{15}	2×10^{14}

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* 'Camb. Phil. Proc.,' vol. 2, p. 286.

† 'B.A. Reports, Cambridge,' 1904, p. 472.

The only general conclusion which these numbers point to is that the work required to liberate a positive ion tends to be smaller than that required to liberate a negative ion. This is probably due to the fact that the negative ions are corpuscles, whereas the positive ions are associated with a certain amount of matter.

Throughout this paper, the view has been maintained with regard to the negative ionisation that it is due to the escape of corpuscles which are present in a more or less free condition inside the metal, the variations in the amount of negative ionisation caused by different gases being due to the effect the gases have on the amount of work necessary for a corpuscle to get through the surface. The positive ionisation, on the other hand, has been supposed to be caused entirely by traces of gas absorbed by the metal. There is, however, another view of the origin of the positive ionisation which cannot be lightly dismissed. This is that it is due to the escape of positive ions which are moving freely inside the metal in much the same way as the negative corpuscles have been supposed to be, and that the effects of different gases are simply due to the changes they produce in the surface. There are a number of considerations which make this hypothesis plausible at first sight. It would give an obvious explanation of why the positive obeyed the same temperature law as the negative ionisation, and would also account for the work necessary for a positive ion to escape being in general smaller than that for a negative ion. For since the particles at the surface of the metal are all at the same temperature, the energy of a moving ion will tend to become equalised with the average value for the metal at each collision, so that, to take an exaggerated case, an ion which had found its velocity reduced to nothing, owing to the work it had done in getting through a certain fraction of the surface, would get a fresh start if it made a collision. Thus the work function in question will be equal to the average amount of work to be done between the last collision inside the metal and a point outside; it will thus be greater for an ion with a long free path, such as a corpuscle, than for one with a short free path. On this view, the effects of different gases are to be explained by the changes they produce in the work required for an ion to escape from the surface layer. This might occur by the formation of an electrical double layer, or simply by a change in the physical properties of the bounding region, or by both. The former would act differentially on the positive and negative ionisations, whilst the latter might be expected to act in the same way, though not necessarily to the same extent, on both. A combination of the two could obviously be made to account for any observed simultaneous change in the two leaks. If we calculate the number of ions per cubic centimetre inside the metal from the ionisation in different gases according to the formula previously* given by the author, we get the numbers given in the columns N_+ and N_- in the last table. These numbers do not mean much, owing to the ignorance of other data which really enter into the calculation, but on the view at present discussed they should range

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* 'Camb. Phil. Proc.,' vol. 2, p. 286 *et seq.*

around the true value for the number of free ions per cubic centimetre. This would give for the positive ions 10^{13} and for the negative 10^{21}; thus the number of free positive ions would be insignificant compared with the number of free negative ions, and the theory would at once account for this small value for the amount of one metal transported into another by the electric current.*

To test this theory, which has both simplicity and elegance to recommend it, both the positive and negative ionisations were measured simultaneously in oxygen at low pressures. The very great increase in the positive ionisation, produced by small quantities of oxygen as compared with other gases, would indicate, if we accept the above view, that the effect was probably specific and caused by the formation of an electrical double layer. In this case, increasing the positive should decrease the negative leak. The results of this experiment, which are given on p. 22, show that although the oxygen altered the positive leak in a ratio of 10 to 1, the negative leak was not changed by 20 per cent. As it is very unlikely that some other effect of the oxygen would compensate so well as this, the writer considers that this experiment renders the above view very improbable. It is chiefly on account of this experiment that the view, that the positive ionisation is due to the absorbed gas, and only indirectly to the metal, has been adopted in describing the results obtained in this investigation.

X.—§ 17. Summary of the Principal Results.

The positive ionisation, *i.e.*, the number of positive ions produced by 1 sq. centim. of platinum surface per second, possesses a minimum value, which depends on temperature and pressure, in most gases. The positive ionisation in oxygen at a low pressure ($<$ 1 millim.) is much greater than in the other gases tried. In oxygen at low pressures, and temperatures below 1000° C., the ionisation varies as the square root of the pressure; at higher temperatures and low pressures it varies nearly directly as the pressure, whilst at higher pressures at all temperatures the variation with pressure is slower, so that at pressures approaching atmospheric the ionisation becomes practically independent of the pressure.

The variation with pressure in air is similar to that in oxygen. In nitrogen and hydrogen the ionisation appeared to increase more rapidly with the pressure at high pressures than in oxygen. In very pure helium at low pressures there was a positive ionisation which was a function of the pressure.

The experiments on ionisation by collisions indicate that the positive ions liberated by hot platinum in oxygen are of the same order of magnitude as those produced by the collisions. They are not great masses approximating to dust particles.

The positive leak in oxygen always oscillated round a certain value under specified

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* This view can easily be made to give a reasonable quantitative explanation of the change in the positive ionisation produced by oxygen at different pressures.

conditions. It was, therefore, never steady, so the minimum values were taken. This kind of effect was much less marked, if it occurred at all, in the other gases.

The minimum value of the positive ionisation was found to remain practically constant with a wire heated during three months at various times, for 150 hours altogether, in oxygen at 900° C. to 1000° C. Moreover, four different wires of different dimensions, after continued heating in oxygen, gave nearly the same value for the ionisations at the same temperatures and pressures.

The positive ionisation in air at constant temperature is smaller than that which would be obtained if the nitrogen were withdrawn, so as to leave only oxygen at a low pressure. The nitrogen, therefore, exerts an inhibiting effect on the oxygen.

The minimum value of the positive ionisation at a definite pressure in all gases appears to be connected with the temperature by the relation first deduced by the author for the negative ionisation. This relation may be written $i = A\theta^{\frac{1}{2}}e^{-Q/2\theta}$, where i is the ionisation, θ is the absolute temperature, and A and Q are constants. The value of the constant Q, which is a measure of the energy associated with the liberation of an ion, is in most cases smaller for the positive than for the negative ionisation.

These results refer to wires which have been heated in a vacuum and subsequently in the gas in question for a long time. New wires exhibit peculiar properties, especially in regard to their behaviour under different electromotive forces. Old wires also exhibit hysteretic effects with change of pressure and temperature.

The view is developed that the positive ionisation is caused by the gas adsorbed by the metal and the consequence examined of supposing the ionisation to be proportional to the amount of the adsorbed gas present. In the case of oxygen, by making the assumption that the rate of increase of the adsorbed gas is proportional jointly to the concentration of the external dissociated oxygen and to the area of unoccupied platinum surface, whilst the rate of breaking up is proportional to the amount present, a formula is obtained which agrees with the experimental results. This formula is that the ionisation $i = \frac{Ap}{B+p}$, where $p = (kP+\frac{1}{4}k^2)^{\frac{1}{2}}-\frac{1}{2}k$, P being the external pressure and k the dissociation constant of oxygen. A, B and k are constants depending on the temperature and are of the general form $a\theta^{\frac{1}{2}}e^{-b/\theta}$. Thus this view accounts for both the temperature and pressure variation.

The positive ionisation from the outer surface of a hot platinum tube in air is increased when hydrogen is allowed to diffuse through from inside the apparatus. The increase in the ionisation is proportional at constant temperature to the quantity of hydrogen escaping from the surface in unit time. For different temperatures the effect produced by a given quantity of hydrogen is greater the higher the temperature.

The negative ionisation from hot platinum in air is unaltered when hydrogen is allowed to diffuse out through the platinum.

These results show that neither the negative nor the positive ionisations usually observed with hot platinum heated in air or oxygen are due to residual traces of absorbed hydrogen.

Careful measurements were made to see if the negative ionisation in oxygen at low pressures varied with the pressure of the oxygen at constant temperature. Although the addition of oxygen increased the positive leak by a factor of ten, the change in the negative leak was constant within the experimental error, in agreement with the work of previous observers.

The negative ionisation was found to have very nearly the same absolute value and the same temperature variation for two wires of different dimensions when heated in oxygen.

A wire which has been heated in hydrogen furnishes a negative ionisation which is very big compared with that from a wire heated in oxygen at the same temperature. If the hydrogen is at a pressure of the order of 1 millim. the negative ionisation can be rapidly reduced to a much smaller value by applying a high negative potential to the wire. The wire subsequently recovers its ionising power if the potential is reduced again. Under these conditions the ionisation varies in an interesting way with the time. The reduction in the ionising power of the wire appears to be caused by the bombardment of the surface by positive ions produced by collisions.

Long-continued heating of a platinum wire, which has previously been allowed to absorb hydrogen, in a good vacuum so as to expel the gas does not appear to reduce its ionising power. The ionisation apparently is not a definite function of the quantity of gas absorbed by the wire. The amount of hydrogen which a platinum wire will absorb at a low pressure is much greater than is usually suspected.

These results indicate that the increase in the negative ionisation in hydrogen at a low pressure is not caused by the hydrogen directly, but is rather a result of some change it produces in the surface of the platinum.

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