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XIII. *The Electrical Conductivity Imparted to a Vacuum by Hot Conductors.*

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Introduction.

The experimental part of the present paper is an investigation of the electrical conductivity of the space surrounding hot surfaces of platinum, carbon, and sodium at low pressures. A preliminary account of some of the experiments on platinum was read before the Cambridge Philosophical Society on November 25th, 1901.*

The conductivity produced by hot metals has been the subject of a great number of researches by different authors. The phenomena are, however, very complicated; for the quantity and sign of the ionisation is found to vary in the most remarkable manner with the nature, temperature, and previous history of the metal, with the nature and pressure of the surrounding gas, and with small changes in the state of the metal surface. The present investigation was undertaken with the idea that in the negative ionisation at high temperatures the conductivity produced by metals took its simplest form. This idea is supported by the observation of Professor McClelland,† that the negative current is to a great extent independent of the nature of the gas, and is independent of its pressure over a range from ·04 to ·004 millim.

The chief problem which is here attacked experimentally is the way in which the saturation current from the hot metal surface to a neighbouring electrode varies with the temperature of the metal. The value of the saturation current corresponds to the total number of ions which are produced by the surface per second. Incidentally it was found necessary to examine, in addition to the above, the relation between the current and the electromotive force for the conductivity produced by the three above-mentioned conductors at various pressures.

The theory, by which it is proposed to explain the phenomena, is based on the

* 'Proc. Cambr. Phil. Soc.,' vol. 11, p. 286.

† 'Proc. Cambr. Phil. Soc.,' vol. 10, p. 241, and vol. 11, p. 296.

hypothesis of conduction in metals by corpuscles which has been elaborated by Professors DRUDE* and J. J. THOMSON.† According to that theory a metal is to be regarded as a sponge-like structure of molecules and comparatively large fixed positive ions, with small negative ions or corpuscles moving freely with great velocity throughout the mass. Since the corpuscles do not all leave the metal when they strike the surface, it is evident that there must be a surface discontinuity of potential which prevents their escape. If now we raise the temperature of the metal we increase the average velocity of the corpuscles, and, provided the energy required to take an ion through the surface does not increase with the temperature, many more of the ions which strike the surface will pass through than before. In this way we can calculate the way in which the number of corpuscles shot off from unit area of a metal surface varies with the temperature. The formula so obtained involves two new constants, viz., the number of ions in unit volume of the metal and the work done by an ion in passing through the surface.

It may be permissible to state in anticipation that almost the whole of the experimental results are in striking agreement with the theory. In particular the theoretical formula makes the saturation current increase enormously rapidly with the temperature of which it is an exponential function. The experiments show that this is actually the case, and the saturation current has been followed over the following ranges of values for the three conductors examined:

For platinum from 10^{-10} to 10^{-3} ampère per sq. centim.
,, carbon ,, 10^{-8} ,, 2 ,, ,, ,,
,, sodium ,, 10^{-11} ,, 2×10^{-2} ,, total current.

The corresponding ranges of temperature for platinum and sodium are roughly from 1000° C. to 1600° C., and from 100° C. to 450° C. respectively.

Perhaps the most surprising result of the investigation is the relatively enormous currents which have been obtained. The biggest leak measured was ·4 ampère from a carbon filament to an electrode placed near it; this corresponded to a current of 2 ampères per sq. centim. of the carbon surface, the potential on the wire being — 60 volts. In this case the gas pressure was only $\frac{1}{600}$ millim. of mercury, so that the ionisation produced by collisions was negligible. In all cases care was taken that the field which was put on the filaments was insufficient either to start a discharge or to maintain one when started.

The smaller currents with sodium were measured by means of a quadrant electrometer: the largest (·04 ampère) was registered on a Weston ammeter.

It is evident from these experiments that a metal if placed in a vacuum and heated to a sufficiently high temperature makes the space around it an extremely

* 'DRUDE'S Annalen,' vol. 1, p. 566.

† 'Rapports présentés au Congrès International de Physique,' Paris, 1900.

good conductor of electricity. The results show that in the case of an incandescent lamp, heated to the highest temperature it will stand, the specific conductivity of the surrounding space is comparable with that of the filament.

In the case of a hot conductor the current across the intervening space to the electrode will, of course, only go in one direction. The current when the hot metal is charged positively, and the electrode put to earth, is vanishingly small in comparison with the current when the wire is charged negatively.

The remainder of the present paper is divided up as follows :—

A.—*Theoretical Investigation.*

I. Calculation of the saturation current.
II. Equilibrium of corpuscles near a hot plane of infinite area.

B.—*Experimental Investigation.*

I. Experiments with platinum.
II. ,, ,, carbon.
III. ,, ,, sodium.

C.—*Conclusion.*

A.—Theoretical Investigation.

I. *Calculation of the Saturation Current*

§ 1. The application of the kinetic theory of gases to the equilibrium of the free negative electrons or corpuscles inside a metal scarcely needs justification here, since it has already been made use of by Professor Drude.* It may, however, be permissible to point out some results which show that the similarity between a corpuscle in a metal and a molecule in a gas under ordinary conditions is very close indeed. Professor Thomson† has shown, from the change of resistance of bismuth in a magnetic field, that the mean free path of a corpuscle in that metal has the value 10^{-4} centim.; while a series of experiments by Mr. Patterson‡ indicate that for platinum, gold, tin, silver, copper, zinc, cadmium, mercury, and carbon the mean free path has values which lie between $5{\cdot}9 \times 10^{-7}$ and $4{\cdot}1 \times 10^{-6}$ centim. The mean free path for a nitrogen molecule in air under standard conditions is 10^{-5} centim.; so that the mean free path of a corpuscle in bismuth is the same as that of a molecule in air at $\frac{1}{10}$th of an atmosphere pressure, whereas for other metals the mean free path is the same as that in air at about 10 atmospheres pressure. The free time is,

* 'Drude's Annalen,' vol. 1, p. 572, &c.

† 'Rapports présentés au Congrès International de Physique,' Paris, 1900, vol. 3, p. 138.

‡ 'Phil. Mag.' (6), vol. 3, p. 655.

of course, only about one-hundredth that of an air molecule possessing the same free path, owing to the great velocity of agitation of the corpuscles. Nevertheless we are quite justified in assuming that the time during which the corpuscles are moving freely is great compared with that during which they are colliding. In fact this assumption follows at once if we are to attach any definite meaning to the ideas of free paths and collisions.

If, in addition to neglecting the number of corpuscles which are colliding at any moment in comparison with those which are not, we assume that the atoms of the metal and the positive ions oscillate about fixed centres and are subject to forces of restitution which are functions of their displacements only, we obtain at once, by the application of the ordinary analysis of the kinetic theory, the distribution of velocity among the corpuscles. This is found to be the same as that for an equal number of similarly constituted gas molecules. Thus the number of corpuscles ($N_u N_v N_w$) which have velocity components in three mutually perpendicular directions between u and $u + du$, v and $v + dv$, and w and $w + dw$ respectively are given by

$$\left.\begin{aligned} N_u &= N\left(\frac{km}{\pi}\right)^{\frac{1}{2}} e^{-km(u-\alpha)^2}\, du \\ N_v &= N\left(\frac{km}{\pi}\right)^{\frac{1}{2}} e^{-km(v-\beta)^2}\, dv \\ N_w &= N\left(\frac{km}{\pi}\right)^{\frac{1}{2}} e^{-km(w-\gamma)^2}\, dw \end{aligned}\right\} \quad \ldots\ldots\ldots (1),$$

and

where N is the total number of corpuscles considered, m is the mass of a corpuscle, α, β, and γ are the impressed velocity components of the corpuscles in the direction of u, v, and w respectively, whilst $\frac{3}{4}k$ is the average energy of translation of a corpuscle, and is equal to that of a gas molecule at the same temperature as the metal considered. The velocities α, β, γ are connected with the components q, r, s of the current density according to the relation

$$(q, r, s) = n(\alpha, \beta, \gamma)\epsilon,$$

where ϵ is the charge on a corpuscle, and n is the number per cub. centim.

§ 2. If we suppose the impressed velocities to be nil or to be negligible compared with the velocities of agitation, the number of molecules in unit volume having velocity components between u and $u + du$, v and $v + dv$, and w and $w + dw$ becomes

$$n\left(\frac{km}{\pi}\right)^{\frac{3}{2}} e^{-km(u^2+v^2+w^2)}\, du\, dv\, dw \quad \ldots\ldots\ldots (2),$$

whilst the number with these velocity components which hit unit area perpendicular to u per second is

$$n\left(\frac{km}{\pi}\right)^{\frac{3}{2}} u e^{-km(u^2+v^2+w^2)}\, du\, dv\, dw \quad \ldots\ldots\ldots (3).$$

If we suppose the surface of the hot conductor to be perpendicular to the axis of u, then the total number of corpuscles which hit unit area of the surface per second is

$$\int_0^\infty \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} n \left(\frac{km}{\pi}\right)^{\frac{3}{2}} u e^{-km(u^2+v^2+w^2)}\, du\, dv\, dw.$$

We now suppose that there is a discontinuity in the electrostatic potential at the surface of the metal which is great enough to prevent the escape of the corpuscles at low temperatures. If the work done by an ion in passing through the surface layer is Φ, then the discontinuity in the potential is Φ/ϵ, where ϵ is the charge on an ion. We have further, by symmetry,

$$\frac{1}{\epsilon}\frac{\partial \Phi}{\partial y} = \frac{1}{\epsilon}\frac{\partial \Phi}{\partial z} = 0,$$

the surface being perpendicular to the axis of x.

Moreover $$m\dot{u} = -\frac{\partial \Phi}{\partial x}, \quad \text{whence} \quad u_0 = \sqrt{u^2 - \frac{2}{m}\Phi} \quad . \quad . \quad . \quad . \quad . \quad (4),$$

where u_0 is the normal component of the velocity of the corpuscle after it has escaped from the metal.

It is evident from this that not all the corpuscles which strike the surface of the metal escape from it, but only those which have a normal velocity component which is $\equiv \sqrt{\frac{2}{m}\Phi}$. Hence, to get the total number which pass through the surface layer, we have to integrate expression (3) with respect to du not from 0 to ∞, but from $\sqrt{\frac{2}{m}\Phi}$ to ∞. Thus the total number which escape per second from unit area is given by

$$\mathrm{N} = \int_{\sqrt{\frac{2}{m}\Phi}}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} n \left(\frac{km}{\pi}\right)^{\frac{3}{2}} u e^{-km(u^2+v^2+w^2)}\, du\, dv\, dw \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$= \frac{n}{2}(km\pi)^{-\frac{1}{2}} e^{-2k\Phi} = n\sqrt{\frac{\mathrm{R}\theta}{2m\pi}}\, e^{-\Phi/\mathrm{R}\theta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6),$$

since k is connected with θ, the absolute temperature, by the relation $k = (2\mathrm{R}\theta)^{-1}$, R being the gas constant for a single corpuscle. The saturation current being equal to the quantity of electricity carried by the ions which are shot off from the surface in one second, is given by

$$\mathrm{C} = \mathrm{N}\epsilon\mathrm{S} = n\epsilon\mathrm{S}\sqrt{\frac{\mathrm{R}\theta}{2m\pi}}\, e^{-\Phi/\mathrm{R}\theta}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7),$$

where S is the area of the metal surface and ϵ, as before, the charge on an ion.

§ 3. When the ions are removed by an external electric field as quickly as they are

set free at the surface of the metal, as in the case of the experiments to be described later, the metal must be continually losing energy owing to the emission of the corpuscles. This energy is composed of two parts: the first being represented by the work done by the corpuscles in passing through the surface layer, while the second is equal to the energy of translation which they possess when they have reached the outside of the metal. The sum of the two is easily calculated, since it is equal to the energy of translation which the corpuscles that have passed through the surface layer possessed while they were inside the metal. We have therefore merely to multiply the number of corpuscles which strike the surface by the energy each possesses and integrate between limits which embrace all values that pass through the surface layer. The total loss of energy per second is therefore

$$\mathrm{T} = \frac{n}{2}\left(\frac{km}{\pi}\right)^{\frac{3}{2}}\int_{\sqrt{\frac{2}{m}\Phi}}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} m\,(u^2+v^2+w^2)\,u e^{-km(u^2+v^2+w^2)}\,du\,dv\,dw \quad . \quad . \quad (8),$$

$$= \frac{n\,(1+k\Phi)\,e^{-2k\Phi}}{\pi^{\frac{3}{2}}m^{\frac{1}{2}}k^{\frac{3}{2}}} = n\left(1+\frac{\Phi}{2\mathrm{R}\theta}\right)\sqrt{\frac{2\mathrm{R}^3\theta^3}{\pi m}}\,e^{-\Phi/\mathrm{R}\theta} \quad . \quad . \quad . \quad . \quad . \quad . \quad (9).$$

Now the work done in a second by the corpuscles passing through the surface layer is obviously $= \mathrm{N}\Phi$, so that the part of the energy lost by the hot metal per second which appears in the form of the translational energy of the corpuscles, is given by

$$\mathrm{T} - \mathrm{N}\Phi = \frac{n\ e^{-2k\Phi}}{2\,\pi^{\frac{1}{2}}m^{\frac{1}{2}}k^{\frac{3}{2}}} = n\left(\frac{2\mathrm{R}^3\theta^3}{m\pi}\right)^{\frac{1}{2}}e^{-\Phi/\mathrm{R}\theta} \quad . \quad . \quad . \quad . \quad . \quad . \quad (10).$$

This calculation of the rate of emission of energy only applies, of course, to the case where the ions are removed by an external field as fast as they are formed. If there is no external field and the ions are allowed to remain, we soon arrive at a steady state when as many corpuscles possessing a given amount of energy enter the surface of the metal in a given time as leave it; so that in this case there is no loss of energy due to this cause.

The following proof of formula (6), which is due to Professor J. J. Thomson, is interesting, since it does not involve the methods of the kinetic theory of gases. Suppose we have a closed space which is bounded by a surface of hot metal, then the corpuscles will be given off from the metal until a steady state is reached. In this steady state as many corpuscles will pass through the bounding surface from the vacuum to the metal as from the metal to the vacuum, but the pressure will not be the same on both sides of the surface owing to the forces which tend to retain the corpuscles in the metal. There will thus be a discontinuity in the pressure at the surface of separation, and Φ being the work done on an ion when taken through the surface, we have

$$\int_1^2 p\,dv = \Phi,$$

where 1 refers to the metal and 2 to the neighbouring space, p being the pressure and v the volume occupied by a corpuscle at any point. Substituting for p its value $\mathrm{R}\theta/v$ from the gas equation, we get

$$\log v_2 - \log v_1 = \Phi/\mathrm{R}\theta\,;$$

whence, if n_2 be the number of corpuscles per unit volume outside and n_1 the number per unit volume inside the metal, we have

$$n_2 = n_1 e^{-\Phi/\mathrm{R}\theta}.$$

Now the number of corpuscles shot off from the surface per second is not equal to the number per unit volume of the space, but is equal to this multiplied by the average velocity perpendicular to the surface. So that, in the steady state, $\mathrm{N} = n_1 u$, where

$$u = \left(\frac{km}{\pi}\right)^{\frac{1}{2}} \int_0^\infty u e^{-kmu^2}\, du = \sqrt{\frac{\mathrm{R}\theta}{2m\pi}}\,; \quad \text{whence} \quad \mathrm{N} = n\sqrt{\frac{\mathrm{R}\theta}{2m\pi}}\, e^{-\Phi/\mathrm{R}\theta},$$

which is the same formula as has been deduced above without postulating the existence of a steady state.

By following up the analogy between the emission of corpuscles and evaporation, the preceding formulæ, connecting the corpuscular pressure with the temperature, can be obtained thermodynamically in a manner involving still fewer assumptions.

II. *The Equilibrium of Corpuscles near a Plane Surface of Hot Metal of Infinite Extent.*

§ 4. Both this problem and the corresponding problem in spheres are of considerable importance, not only in connection with experiments in vacuum tubes, but also with regard to the behaviour of hot celestial bodies in space. For instance, the aurora borealis and allied phenomena indicate that large quantities of ions continually reach the earth from some extraneous source, while certain variations of the earth's magnetic field and other meteorological phenomena seem to be intimately connected with events which take place at the surface of the sun. The present paper does not attempt to solve these questions, but the above facts indicate that the subject of the ionisation produced by hot bodies is not without importance in regard to meteorology.

The problem under consideration may be specified in the following terms:—Given an infinite quantity of hot metal bounded on one side by a plane surface of infinite extent which is maintained at a given potential, find the charge on unit area of the metal surface and the potential at any point in the space outside the metal when the steady state has been attained.

Let us take the surface of separation perpendicular to the axis of x, and let the suffix 1 refer to points inside the metal, the suffix 2 referring to points in the

neighbouring empty space. There is, as we have seen already, a discontinuity in the pressure of the corpuscles at the surface of the metal, and by the conservation of energy

$$\int_1^2 p\,dv = w \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11),$$

where w is the work done in taking unit-mass of the corpuscles through the surface layer, p is the pressure, and v the volume of unit mass of the corpuscles at any point. Similarly, in order to obtain the equations satisfied by the corpuscles outside the metal when the equilibrium stage has been reached, we use the principle that the work along any path extending from a point a to a point b due to expansion is equal to the work done by the electric forces. This gives

$$\int_b^a p\,dv + \int_b^a nve_0 \frac{d\mathrm{V}}{dx}\,dx = 0,$$

V being the electrostatic potential, e_0 the charge on a corpuscle, and n the number of corpuscles in unit volume, since everything is independent of y and z. Now $nv = \mathrm{N}_0$ the number of corpuscles in unit mass, whence

$$\frac{\mathrm{R}\theta}{v}\frac{dv}{dx} + \mathrm{N}_0 e_0 \frac{d\mathrm{V}}{dx} = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12).$$

In addition to this the electrostatic potential has to satisfy Poisson's equation, which takes the form

$$\frac{d^2\mathrm{V}}{dx^2} = -4\pi\zeta = \frac{4\pi \mathrm{N}_0 e_0}{v},$$

e_0 being the numerical value of the negative charge.

The equation to be satisfied is therefore

$$\mathrm{R}\theta \frac{d^2(\log v)}{dx^2} + 4\pi \frac{\mathrm{N}_0^2 e_0^2}{v} = 0$$

$$\text{or} \quad \frac{d^2v}{dx^2} - \frac{1}{v}\left(\frac{dv}{dx}\right)^2 + \mathrm{C} = 0, \quad \text{where} \quad \mathrm{C} = \frac{4\pi \mathrm{N}_0^2 e_0^2}{\mathrm{R}\theta} \quad . \quad . \quad (13).$$

A first integral of this equation is

$$\frac{d(\log v)}{dx} = \left(\mathrm{B} + \frac{2c}{v}\right)^{\frac{1}{2}}$$

B being an integration constant.

Now when v is infinite $\dfrac{d\log v}{dx} = 0$, and therefore $\mathrm{B} = 0$, so that

$$\sqrt{2c}\,dx = v^{-\frac{1}{2}}\,dv,$$

whence

$$v = \tfrac{1}{4}(\sqrt{2c}\,x - \mathrm{A})^2,$$

A being a second integration constant.

We have the further conditions:

$$\left.\begin{aligned} v &= \infty \quad \text{when} \quad x = \infty \\ v &= v_1 e^{w/\mathrm{R}\theta} \quad \text{when} \quad x = 0 \end{aligned}\right\}$$

which are satisfied if $\mathrm{A}^2 = 4v_1 e^{w/\mathrm{R}\theta}$.

Taking the positive root for v_1 (since negative values are inadmissible) and putting $v_1 = \mathrm{N}_0/n_1$ we obtain

$$v^{\frac{1}{2}} = \left(\frac{2\pi}{\mathrm{R}\theta}\right)^{\frac{1}{2}} \mathrm{N}_0 e_0 x + \left(\frac{\mathrm{N}}{n_1}\right)^{\frac{1}{2}} e^{\frac{1}{2}w/\mathrm{R}\theta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14).$$

This equation gives the concentration (v^{-1}) of the corpuscles at any distance x from the plane when the temperature is maintained at $\theta°$ absolute.

Returning to equation (12) we see that integration and substitution for v yield the electrostatic potential V in the form

$$\mathrm{V} = -2\frac{\mathrm{R}\theta}{\mathrm{N}_0 e_0} \log\left\{\left(\frac{2\pi}{\mathrm{R}\theta}\right)^{\frac{1}{2}} \mathrm{N}_0 e_0 x + \left(\frac{\mathrm{N}_0}{n_1}\right)^{\frac{1}{2}} e^{\frac{1}{2}w/\mathrm{R}\theta}\right\} + \gamma.$$

If $\mathrm{V} = \mathrm{V}_0$ for $x = 0$, the integration constant γ is determined as

$$\gamma = \mathrm{V}_0 + 2\frac{\mathrm{R}\theta}{\mathrm{N}_0 e_0} \log\left\{\left(\frac{\mathrm{N}_0}{n_1}\right)^{\frac{1}{2}} e^{\frac{1}{2}w/\mathrm{R}\theta}\right\},$$

so that V is finally to be obtained from

$$\mathrm{V} = \mathrm{V}_0 - 2\frac{\mathrm{R}\theta}{\mathrm{N}_0 e_0} \log\left\{1 + \left(\frac{2\pi n_1 \mathrm{N}_0}{\mathrm{R}\theta}\right)^{\frac{1}{2}} e_0 e^{-\frac{1}{2}w/\mathrm{R}\theta} x\right\} \quad . \quad . \quad . \quad . \quad (15).$$

The electric intensity at any point x is given by

$$-\frac{d\mathrm{V}}{dx} = \frac{2\left(2\pi\mathrm{R}\theta\,\dfrac{n_1}{\mathrm{N}_0}\right)^{\frac{1}{2}}}{1 + \left(\dfrac{2\pi n_1 \mathrm{N}_0}{\mathrm{R}\theta}\right)^{\frac{1}{2}} e_0 e^{-\frac{1}{2}w/\mathrm{R}\theta} x} e^{-\frac{1}{2}w/\mathrm{R}\theta} \quad . \quad . \quad . \quad . \quad . \quad (16),$$

and the charge on unit area of the radiating plane by

$$\sigma = -\frac{1}{4\pi}\left(\frac{d\mathrm{V}}{d\mathrm{X}}\right)_{\mathrm{X}=0} = \left(\frac{n_1 \mathrm{R}\theta}{2\pi \mathrm{N}_0}\right)^{\frac{1}{2}} e^{-\frac{1}{2}w/\mathrm{R}\theta} \quad . \quad . \quad . \quad . \quad . \quad . \quad (17),$$

the volume density ζ at any point x being

$$\zeta = -\frac{1}{4\pi}\frac{d^2V}{dx^2} = -\frac{n_1 e_0 e^{-w/R\theta}}{\left\{1 + \left(\frac{2\pi n_1 N_0}{R\theta}\right)^{\frac{1}{2}} e_0 e^{-\frac{1}{2}w/R\theta}\, x\right\}^2} \quad . \quad . \quad . \quad . \quad (18).$$

It is evident that $\int_0^\infty \zeta\, dx = \sigma$, since $dV/dx = 0$ for $x = \infty$. Thus, as we should expect, the charge on the surface is equal and opposite to the total charge in the space outside the metal.

As a numerical illustration we may calculate the potential at a point distant 10 centims. from a plane surface of platinum which is put to earth and maintained at a temperature of, say, 1500° absolute. Taking the number of molecules in a cubic centimetre at 0° and 760 millims. as 2×10^{19}, the charge on an ion as $6{\cdot}5 \times 10^{-10}$ and the value of w/R, which has been determined experimentally, to be $4{\cdot}93 \times 10^4$, we find the potential at a point 10 centims. from the surface to be 1·5 volts, while at a point 1 centim. distant it would be about 1·2 volts.

The experiments in the sequel were not intended to test this part of the theory, but they show, as we should expect, that practically the whole of the current is stopped by a fall of potential of the order of one volt when it tends to drive the corpuscles back to the hot metal.

It will be seen by inspection of formula (15) that even at the highest temperatures we can attain the potential differences at small distances from the hot surface never become very great. For instance, at the temperature of the sun (6000° C.) the difference of potential between the surface and a point 1 centim. distant from it would be only about sixteen times its value at 1300° C. On the other hand, the surface density increases very quickly with the temperature, as will be seen from formula (17). In the case of carbon at 6000° C., taking 10^{24} as a probable maximum value of n and $7{\cdot}8 \times 10^4$ as the value of w/R, we find that σ has the enormous value of 300 electrostatic units, whereas at 1300° C. σ would have been less than this in the ratio of 1 to 3×10^8.

These numbers are to be taken as purely illustrative. It is not supposed that any conductor could possibly exist in a vacuum at 6000° C.

It will be noticed that the preceding theory of the equilibrium of corpuscles near a surface where they are being emitted is quite independent of any hypothesis as to the nature of the mechanism by which they are set free. The results are therefore of interest even if the hypothesis, that the negative ions from hot conductors are the same as those which carry the current inside the metal, is ultimately found to be untrue.

B.—Experimental Investigation.

I. *Experiments with Platinum.*

§ 1. *Description of the Apparatus.*

The ultimate object of the experiments was to determine the way in which the saturation current from a hot platinum wire to a surrounding electrode, both placed in a vacuum, varied with the temperature of the wire. For this purpose the type of bulb shown in fig. 1 was found to be most convenient.

The wire to be heated was in the form of a spiral, with its axis passing centrally along the length of the tube; the current through the wire was supplied by means of the two thick leads AA_1 and BB_1. The electrode to which the current was measured was an aluminium cylinder which surrounded the hot part of the wire. The cylinder was supported by a stout aluminium wire E, sealed through the side tube D by means of platinum. The end E was connected to the electrometer or galvanometer which served to measure the current. The side tube F connected the bulb with the pump and McLeod gauge.

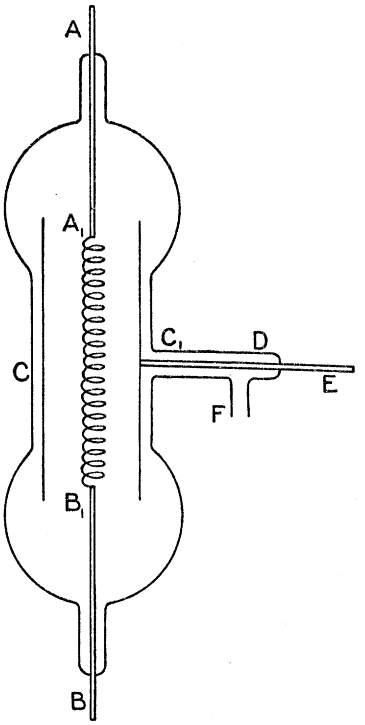

Fig. 1.

In the earlier experiments, trouble was experienced owing to loose contacts appearing at A_1 and B_1 when the platinum wire had been heated. In the final form of the tube this was obviated by making the leads AA_1 and BB_1 of platinum wire 1 millim. thick, to which the ends of the platinum spiral A_1B_1 were welded electrically. This made the platinum quite continuous through the tube. The support E of the electrode CC_1 was insulated outside the tube at D by means of sealing wax. Inside the tube there was only glass insulation, which, however, is very good at low pressures.

The temperature of the platinum wire was obtained by measuring its resistance. The arrangement of apparatus which was used to do this and to measure the current from the surface of the wire is indicated in fig. 2. The whole of the apparatus below AFK_2 is the part which was used to determine the resistance and was insulated on paraffin blocks. It could be charged to any desired potential up to 400 volts by means of the battery B_1 through the key K_1 and water resistance A. The potential was measured by the volt-meter W. In this way any desired potential could be maintained on the hot wire F. The cylindrical electrode C was put to earth through the galvanometer G_1, which thus served to measure the current. In some of the

experiments a Thomson galvanometer, of 4058 ohms resistance, which gave a deflection of 1 scale division for 7×10^{-10} ampère, was used, but this was replaced later by a less sensitive D'Arsonval galvanometer. The sensitiveness of the galvanometer deflections could be lowered at will by means of the shunt resistances, R_5 and R_6.

The resistance of the hot wire was determined by placing it in one arm of a Wheatstone's bridge, the other three arms being the resistances R_2, R_3, and R_4. The battery B_2, which worked the bridge, also supplied the current necessary to heat F. As there was a current of up to 1·5 ampères continually running through the arm F_1, the corresponding arm R_2 had to be constructed so as to carry this current

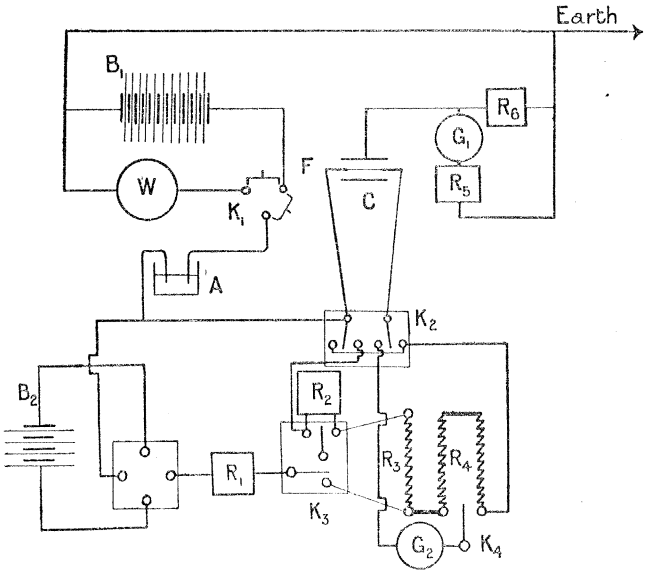

Fig. 2.

without heating. A German silver rheostat of very thick wire mounted on an iron frame and having a resistance of 1·7 ohms was found to fulfil the required conditions. The arm R_3 had a resistance of 1000 ohms, and plugs were taken out of the box R_4 till a balance was obtained in the galvanometer G_2. The maximum current which flowed through the arms R_3 and R_4 was thus about $\frac{1}{700}$th of that flowing through R_2 and F. There was therefore no danger of R_3 and R_4 being heated by the currents used. The adjustable resistance R_1 served to regulate the heating current. By means of the keys, K_2, K_3, K_4, the battery could be put on between the two resistances R_3 and R_4 at the one end, and R_2 and F at the other. In this way the currents flowing through the various arms could be made small, F would not become heated, and, by making the proper connections for the galvanometer G_2, the resistance of the arm F at the ordinary temperature could be determined. In the earlier experiments an arrangement was used which enabled the same galvanometer to be employed both for the resistance and leakage circuits; but it was found to be more convenient to use two galvanometers.

§ 2. *Variability of the Current.*

As some unsteadiness had been observed in the galvanometer readings for the leak during the earlier observations, a series of experiments was made in order to examine if the current from the wire varied when the conditions were kept as steady as possible. When the current was passed through the wire the tube became hot and gas was given off from the walls and from the hot wire, so that it was impossible to keep the pressure absolutely constant. However, by continuously pumping out the gas the pressure was kept practically constant, the limits of variation being very small. A constant current was run through the wire so that its temperature and resistance were invariable except in so far as they depended on the pressure of the gas in the apparatus.

Since the rate of escape of heat from the wire is determined largely by the gas pressure, the temperature of the wire is a function of the pressure. In fact, the galvanometer spot was a far more sensitive indicator of the pressure than the McLeod gauge. By carefully watching the galvanometer and pumping accordingly, the variations of both pressure and temperature were kept very small indeed.

Under these conditions it was hoped that the rate of leak from the wire with a constant voltage would remain approximately constant. It was found, however, that it varied in the most haphazard manner, oscillating irregularly between the limits of 10^{-6} and 10^{-4} ampère. The current did not become any steadier with continuous heating. Readings taken every three or four minutes for the space of three hours showed the same continuous irregular periodicity. The irregularities were quite independent of the potential that was or had been applied to the wire, and also seemed to have no relation to the rate at which gas was given off. There was no measurable falling off with time.

It ought, perhaps, to be mentioned that the tube used for this experiment seemed far more variable than those used for the temperature experiments, though they were never examined systematically. The platinum wire used for this tube was the purest obtainable.

These results are taken to indicate that the negative ionisation depends to a great extent on small changes in the condition of the surface of the hot wire. We should expect this to be the case on the view that the phenomena are due to the escape of corpuscles from the metal, since an alteration of 14 per cent. in the work done by an ion in going through the surface would multiply the current by 100.

Further experiments showed that fairly steady readings were obtained if the heating current was stopped and the tube allowed, as it were, to recover itself between each observation. The initial value of the current was almost constant, it then began to decrease slowly and afterwards varied in the irregular manner described above. The following readings taken with constant voltage, temperature, and pressure at the times stated, indicate the sort of agreement which is observed :—

Time of observation.	Current observed (in scale divisions).
12.18 P.M.	183
12.34 „	191
12.43 „	201
12.56 „	218
1.15 „	205
3.16 „	208
3.48 „	193
11.5 A.M. (next day)	193

This mode of observation is practically that followed in § 5, where the current is observed immediately after the temperature of the wire has been increased by a given amount.

§ 3. *Experiments with Alternating Currents.*

A mode of observation which is especially well calculated to show the relation between the positive and negative ionisation produced by hot platinum in a vacuum is to heat the wire by putting it on a 200-volt alternating circuit and to observe the current to the cylindrical electrode. The ions of both signs are alternately driven away from and attracted to the hot wire owing to the alternating field between the wire and the cylinder. The cylinder is connected to one quadrant of an electrometer, the other quadrant being put to earth. The direction of the current, which is indicated by the direction in which the spot of the electrometer moves, is determined by the sign of the ions which reach the cylinder in greatest quantity under the alternating electromotive force. At low temperatures all the ions produced by the wire are positive, so that the current is necessarily in the positive direction. At higher temperatures negative ions are also produced in gradually increasing quantity, so that at one temperature the same number of positive and negative ions reach the cylinder in a given time. At this temperature, which may be called the transition temperature, there is no current from the hot wire to the surrounding electrode under the given alternating field. At still higher temperatures, owing to the rapid rate at which the negative ionisation increases with the temperature, the current is always negative.

In these experiments the temperature of the wire was not determined, but a rough idea of it can be obtained from the resistance. This was determined with the apparatus indicated in fig. 2, except that the galvanometer G was replaced by a telephone. The following table gives corresponding values of the leak and the resistance of the wire ;—

Resistance of wire.	Current from wire to cylinder in ampères.
ohms	
3·20	$+1·38 \times 10^{-12}$
3·30	$+3·7 \times 10^{-12}$
3·48	$+3·7 \times 10^{-12}$
3·78	$+1·6 \times 10^{-12}$
4·00	$-7·2 \times 10^{-12}$
4·22	$-7·5 \times 10^{-11}$
4·42	$-6·8 \times 10^{-10}$
4·56	$-2·5 \times 10^{-9}$

It will be seen from these experiments and those to be described later that the negative ionisation increases very rapidly with the temperature, and becomes enormous compared with the positive. The transition temperature for platinum at low pressures is about 900° C.

§ 4. *The Relation between the Current and the Applied Electromotive Force.*

As the ultimate object of these experiments was to measure the saturation current from the wire, it was thought advisable to investigate the relation between the current and the potential applied. A large number of current-E.M.F. curves for hot platinum have been given by Professor McClelland.* As, however, my apparatus, though similar, was not quite the same as, and the currents employed were much greater than, in the case investigated by Professor McClelland, it was considered necessary to make new experiments on the subject.

As the absolute value of the current was continually varying in the way previously described, the current was continually referred to its value with a given potential on the wire. This "standard" potential was — 41 volts. The current with 41 volts on the wire was measured both before and after taking a reading with any assigned potential: the ratio of this reading to the mean of the readings with 41 volts was taken to be what the ratio of the current under the given voltage to the current at 41 volts would have been if the state of the tube had remained constant. In this way the variability of the hot wire could be satisfactorily eliminated.

In these experiments the value of the saturation current was about 3×10^{-6} ampère, and was probably about ten thousand times as big as the current used by Professor McClelland. In making the observations readings of the current were taken for every 6 or 7 volts up to 80, and afterwards at intervals of 40 volts up to 400. The numbers so obtained are plotted in the following curve (fig. 3), the value of the current with — 41 volts on the wire is fixed arbitrarily as unity. The voltages refer to the positive end of the wire.

The current rises to about one-third its final value with ten volts on the wire but

* 'Cambr. Phil. Proc.,' vol. 11, p. 296.

does not become saturated till about 160 volts. It will be seen that this curve is very similar to the one given by Professor McClelland for the same pressure (·1 millim.). The similarity of the two leads to the conclusion that the form of the current E.M.F. curve is largely independent of the amount of ionisation produced by

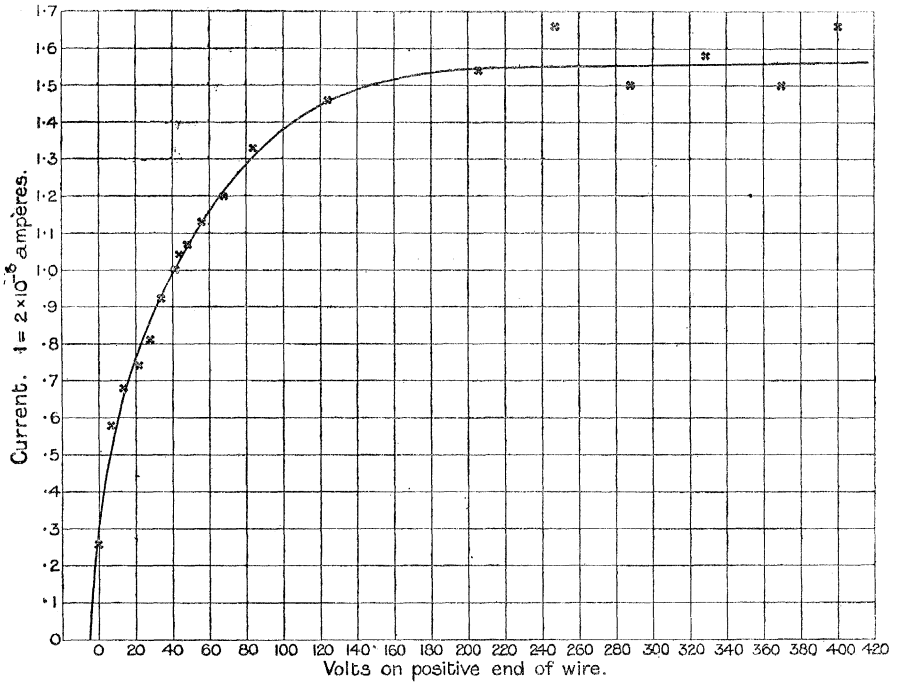

Fig. 3.

the wire. In many of the experiments on the variation of the current with the temperature the pressure was considerably less than ·1 millim., but we should expect that a voltage which would saturate the current at a given pressure would saturate it at any lower pressure. At any rate, the experiments to be described later show that this is true for the negative ionisation produced by hot carbon. Another set of experiments on platinum showed that at ·008 millim. the current was saturated by less than 80 volts.

§ 5. *The Relation between the Saturation Current and the Temperature of the Wire.*

The temperature of the wire was obtained from its resistance, and in order to determine this the apparatus indicated in fig. 2 was employed in the manner already described. During each observation it was found that the temperature of the wire, which was run at constant voltage, fell slightly, owing to the gas given off from the walls of the tube and elsewhere. A reading for the resistance was therefore taken immediately before and after the reading for the current, and the mean of the two resistances was taken to be that which corresponded to the current reading. The wire was heated for a long time and the tube constantly pumped out previous to

making the observations, in order to reduce the evolution of gas as far as possible. When the tubes were heated at first large quantities of gas came off, but after a time further heating and pumping did not seem to effect much reduction in the rate of evolution of gas. Despite constant pumping the pressure always rose slightly in the McLeod gauge; the increase was, of course, more marked the higher the temperature of the wire.

To obtain the temperature from the resistance measurements use was made of the determinations of the melting points of potassium and sodium sulphates of Messrs. Heycock and Neville.* The wire was set up in air and its resistance determined, first at the ordinary temperature and afterwards when the smallest possible grain of potassium sulphate placed on it just melted. In this way the resistance for two temperatures differing by about 1000° was obtained, and the temperature corresponding to any other resistance reading could be got by interpolation from the curves given by Professor Callendar.† To test the method the melting point of sodium sulphate was determined and no determination was more than 20° from the true value (883° C.). This agreement was held to be quite good enough for the purpose. The temperature as found from the resistance in this way is the average temperature of the wire whereas what is required is the temperature at the surface. A calculation showed, however, that the temperature at the centre of the hot wire only differed from that at the circumference by 4° C., a quantity which is negligible compared with the experimental error.

In the experiments on platinum a potential of 120 volts was maintained on the wire; this was more than enough to saturate the current at practically all the pressures which occurred. It was found afterwards that at pressures greater than ·09 millim. the current was not saturated by this potential but the deviation from the saturation value due to this cause is smaller for the observations taken than the error due to unavoidable irregularities.

The values of the pressures are given in the tables for comparison. Two numbers are inserted in each case in the resistance column, these are the resistances as determined immediately before and after the value of the saturation current was read. The difference between the two numbers is a measure of the rate at which the temperature of the wire was changing and, therefore, of the rate at which the pressure of the gas in the tube was increasing.

The following table gives the results which were obtained at temperatures below 1450° C.

* 'Jour. Chem. Soc.,' vol. 67, p. 160.

† 'Phil. Mag.,' vol. 48, p. 519.

Pressure of gas in millims. of mercury.	Resistance of hot wire in ohms.	Current from wire to cylinder, 1 = ampère $\times 10^{-9}$.	Temperature of wire in ° C.
·023	8·338 8·335	2·52	1031
·025	8·438 8·430	8·28	1058
·021	8·642 8·625	30·6	1105
·025	8·795 8·782	100·5	1146
·024	8·894 8·875	188	1170
·028	8·969 8·950	300	1190
·028	9·106 9·088	728	1224
·032	9·163 9·131	858	1243
·032	9·263 9·230	1,414	1269
·037	9·381 9·350	2,600	1298
·044	9·472 9·445	4,025	1323
·063	9·603 9·574	11,320*	1354
·063	9·925 9·883	11,740*	1445

The next table gives another series of observations extending over a higher range of temperature. Owing to the greater unsteadiness of the tube at the higher temperatures the points do not fall quite so accurately on the curve. The current at 1600° was the biggest measured and corresponded to $1{\cdot}03 \times 10^{-3}$ ampère per sq. centim. of platinum surface.

* The current became rather unsteady here.

Pressure in millims. of mercury.	Resistance of wire in ohms.	Saturation current, 1 = ampère × 10^{-7}.	Temperature in ° C.
·024	9·725 9·718	1·04	1194
·044	10·16 10·14	13·62	1298
·091	10·63 10·61	116	1419
·106	10·79 10·75	578	1449
·152	10·95 10·91	1370	1490
·180	11·13 11·07	1730	1533
·162	11·35 11·355	4180	1599

The relation between the saturation current and the temperature is shown graphically in fig. 4. The ordinates give the value of the saturation current, the

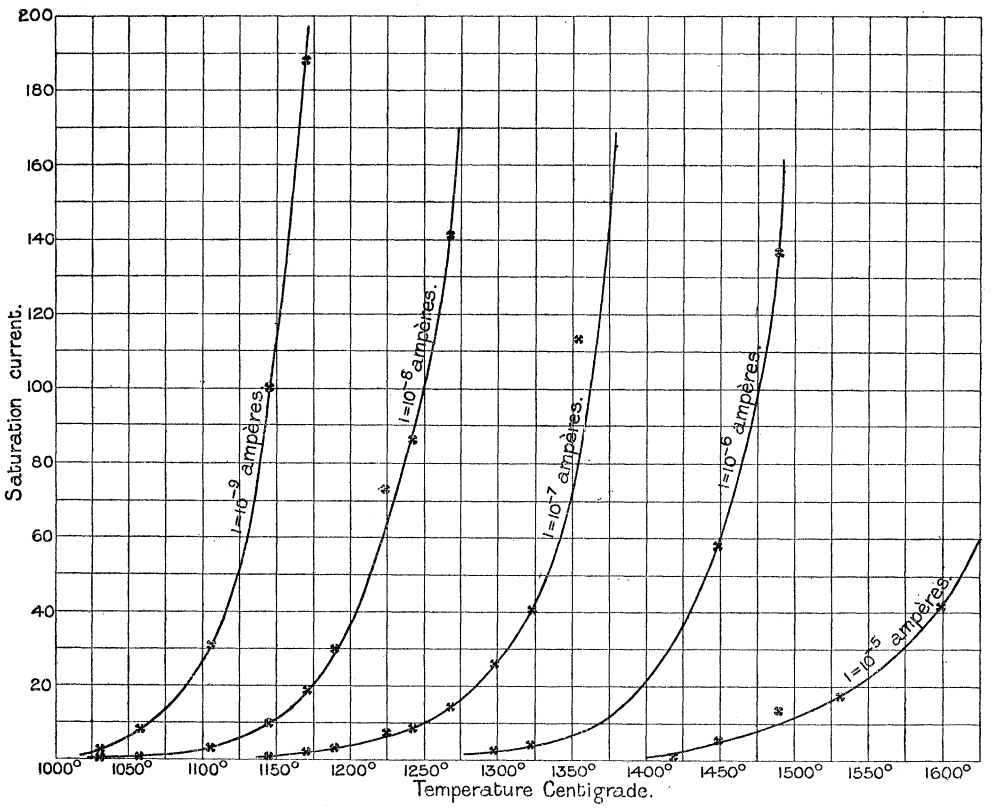

Fig. 4.

abscissæ being temperatures in °C. In the first curve, starting from the left of the diagram, each unit of the ordinate represents 10^{-9} ampère; in each succeeding curve as we pass to the right the value of the ordinate is successively multiplied by ten, so that in the last curve each unit is equal to 10^{-5} ampère. To obtain the saturation current per unit-area the values on the curve have to be multiplied by 2·5.

The curves show that the negative ionisation increases very rapidly with the temperature of the wire (in fact the saturation current varies roughly as the 70th power of the absolute temperature). It will be seen that the current never vanishes absolutely, but only in an asymptotic manner, so that it should be observable at any temperature provided sensitive enough instruments are employed. As a matter of fact at low temperatures it would of course be masked by other effects, which become large by comparison. The curves seem also to tend continuously to an infinite value of the saturation current; but the theory indicates that at higher temperatures the current would increase much more slowly with the temperature. This falling off of the rate of increase has not yet been observed with any of the conductors which have been examined.

We are now in a position to apply formula (7) to the reduction of the experimental results. For the sake of convenience we may write for the number of corpuscles shot off from unit area of the metal per second

$$N = (C/\epsilon S) = A\theta^{\frac{1}{2}}e^{-b/\theta},$$

where $A = n\,(R/2m\pi)^{\frac{1}{2}}$ and $b = \Phi/R$. The saturation current C is here to be measured in electrostatic units. In order to test the formula we may write the above equation in the form:

$$\log_{10} C - \log_{10} \epsilon S = \log_{10} A + \tfrac{1}{2}\log_{10}\theta - \frac{b}{2{\cdot}303\theta}.$$

If we put, for convenience, $\log_{10} C - \frac{1}{2}\log_{10}\theta - \log_{10} 3 + 1{\cdot}5 = y$ and $\theta^{-1} = x$, we may write our equation

$$y = \alpha - b_0 x_0,$$

so that plotting the values of y against those of θ^{-1} should give a straight line. In the accompanying graph the ordinates are the values of $\log_{10} C - \frac{1}{2}\log_{10}\theta$, the abscissæ being $\theta^{-1} \times 10^5$. The curve got is very approximately indeed a straight line; though any variation from strict rectilinearity might be explained by the variation with temperature of the coefficient A, that is, if our theory is correct, of n the number of corpuscles per cubic centimetre of platinum. We may therefore say with certainty that the main features of the phenomenon are to be represented by a formula of the type $A\theta^{\frac{1}{2}}e^{-b/\theta}$.

Interesting conclusions are also to be drawn from the actual values of the constants

themselves. From the constant A we obtain the number n of free corpuscles in a cubic centimetre of solid platinum, since we have the relation $n = \left(\frac{2m\pi}{R}\right)^{\frac{1}{2}} A$. A is obtained by putting corresponding values of θ and C in the equation

$$\log_{10} A = \log_{10} C - \tfrac{1}{2} \log_{10} \theta - \log_{10} \cdot 788 + 9 \cdot 523 + (2 \cdot 24 \times 10^4)\, \theta^{-1}.$$

At θ (absolute) $= 1542°$ this gives $A = 1 \cdot 51 \times 10^{26}$. The various constants in the logarithmic equation come from the area of the wire, which was ·394 sq. centim., and the value of the charge on an ion, which was taken to be 6×10^{-10} electrostatic unit. The value of m/R (m being the mass of, and R the gas-constant for, one corpuscle) was found to be $= 1 \cdot 204 \times 10^{-11}$. Putting this in the expression for n, we find $1 \cdot 3 \times 10^{21}$ free negative ions in a cubic centimetre of platinum at 1542° absolute. An independent value of n has been obtained by Mr. Patterson* from experiments on the change of resistance of platinum in a magnetic field. This when calculated by the method given by Professor Thomson† yields $n = 1 \cdot 37 \times 10^{22}$. The agreement of the value found above with this is really very good, when one considers the numerous sources of error to which the measurements are liable, and that an error of 7 per cent. in the absolute temperature, among other things, would multiply the value of n by ten.

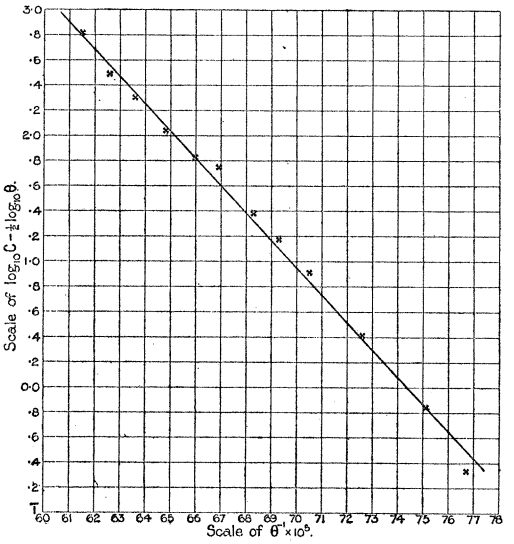

Fig. 5.

It was thought that possibly some regular change in the value of n with the temperature might be found if values were calculated for different temperatures. It was found, however, that n oscillated in an irregular manner between $\cdot 43 \times 10^{21}$ and $2 \cdot 0 \times 10^{21}$, so that the experiments yielded no evidence of any detectable variation of n. This method of obtaining n is extremely inaccurate, so that the agreement between the above numbers is really better than would be expected.

The signification of the constant $b = \Phi/R$ which occurs in the exponential factor is equally important, since Φ is the work done by an ion in passing through the surface layer. We obtain b from the equation

$$b = \frac{\log_e C/C' - \frac{1}{2} \log_e \theta/\theta'}{\theta'^{-1} - \theta^{-1}},$$

where C, C′ and θ, θ' are corresponding currents and absolute temperatures.

* 'Phil. Mag.' (6), vol. 3, p. 643.

† J. J. Thomson, 'Rapports présentés au Congrès International de Physique,' vol. 3, p. 138, Paris, 1900.

Substituting the values of C and C′ for $\theta = 1571$, $\theta' = 1378$ respectively, we get the average value of b from 1378° to 1571° absolute as $4{\cdot}93 \times 10^4$. If we assume that all the work done by the corpuscles in passing through the surface is electrical, we can calculate from this the discontinuity in the potential. Since R is equal to $\left(\frac{2}{1{\cdot}204}\right) \times 10^{-16}$, we have $\Phi = 4{\cdot}93 \times \frac{2}{1{\cdot}204} \times 10^{-12} = \epsilon\delta\phi$, where ϵ is the charge on an ion and $\delta\phi$ is the discontinuity in the potential at the surface of the metal. From this we obtain

$$\delta\phi = 1{\cdot}365 \times 10^{-2} \text{ electrostatic unit} = 4{\cdot}1 \text{ volts.}$$

The further discussion of these results will be postponed until the experiments on sodium and carbon have been considered. (See additional Note at end of this paper.)

II. *Experiments with Carbon.*

§ 1. *Description of Apparatus.*

In order to detect and examine the negative leak from carbon, the hot wire previously employed was replaced by a filament from an ordinary incandescent lamp. The thick filaments from small 8 or 12-volt lamps were found to be most suitable. In the form of apparatus which was used to investigate the relation between the negative leak and the resistance of the carbon (see fig. 6) the filament was allowed to remain inside the lamp. The lamps were opened up by snipping off the glass point at the top with a pair of pliers. The wide tube A was then fixed on by drawing it out at the end which was to be joined and blowing the junction out until it was wide enough to allow the aluminium electrode E to be introduced. This process required some care, as the lamps are liable to crack when hot. It was found that air leaks due to small cracks in the part of the lamp which is covered with plaster of Paris could be effectually stopped by embedding the whole lamp in melted paraffin wax. The tube L, into which the electrode was fixed with sealing-wax, was joined to a bulb C, which was somewhat wider than A, into which it was inserted, the joints being made air-tight by means of sealing-wax. The side tube D led to the pump and McLeod gauge. The filament F could be charged either positively or negatively, and the leak from it to the electrode E was measured in exactly the same way as has already been described in the case of platinum.

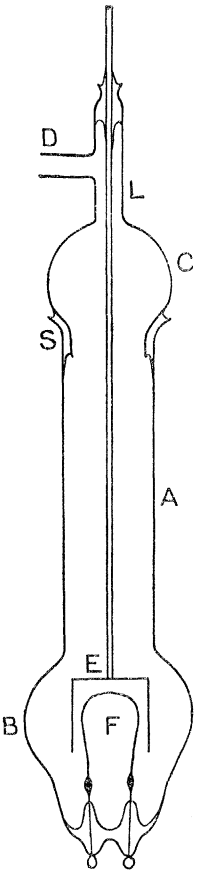

Fig. 6.

This form of apparatus was found to be quite satisfactory for investigating the connection between the current from the carbon on the one hand and the electromotive force, the resistance of the filament, and the

current required to heat it, respectively, on the other. The variation of the saturation current with the resistance gives an approximation to its variation with the temperature of the filament. It was thought that a better estimate might be obtained if the temperature of the incandescent filament were determined by means of a thermocouple. With this object a second form of tube was set up, which we shall proceed to describe.

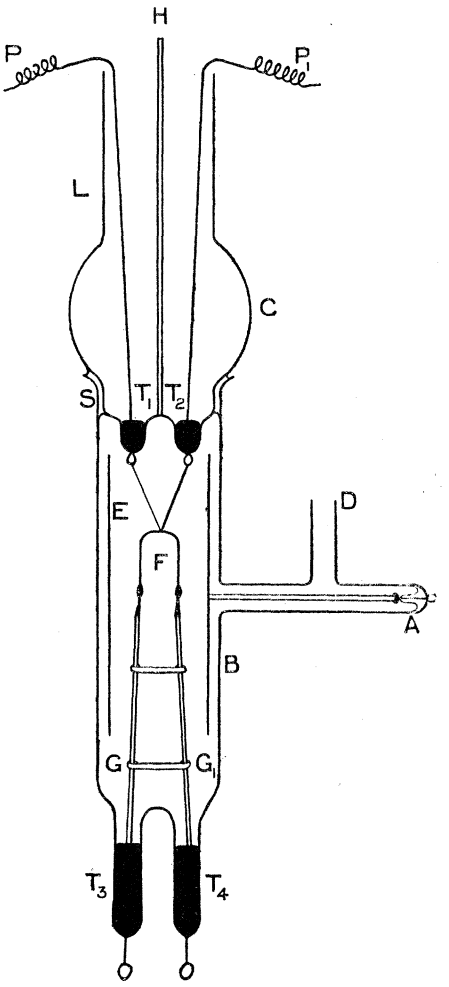

Fig. 7.

In this case the filament F, together with the platinum wires which support it (see fig. 7), was cut out of the original lamp and fastened to two stout copper wires G and G_1. This was done by placing the platinum and copper wires alongside, wrapping them round closely with fine copper wire and then soldering the whole. The filament was thus supported on two long copper legs; the rigidity of the structure was ensured by melting on two cross-pieces of blue glass in the positions shown in the figure. The ends of the copper terminals rested in the small tubes, T_3 and T_4, which contained mercury, and which were fused in to the end of the large tube B. The current which heated the filament entered by platinum wires, which were melted into the tubes T_3 and T_4. The electrode, to which the current was measured, was a long narrow aluminium cylinder E, which practically surrounded the hot filament. The cylinder was supported by a stout wire let in through the side-tube A. The tube D was connected with the pump and McLeod gauge.

The thermocouple was of platinum and iridio-platinum, the wires being the finest obtainable. The pure platinum wire was ·0025 centim. in diameter, whilst the 10 per cent. iridium alloy had a diameter of ·0035 centim. The wires were tied together on to the filament by means of a slip-knot, so as to make good contact but not to increase the diameter of the filament materially. They were then suspended from platinum wires let in to the tubes T_1 and T_2, which were inserted in the tube LC in exactly the same way as T_3 and T_4 were fixed in to B. The wires P and P_1, which were prevented from touching by the cardboard partition H, connected the mercury cups T_1 and T_2 with the rest of the thermocouple circuit. The tubes B and C were connected by a sealing-wax joint S just as in the former apparatus.

In the first experiments with carbon the apparatus shown in fig. 2 was used, just as for platinum, except that the tube with the incandescent platinum wire (fig. 1)

was replaced by the tube shown in fig. 6. In commencing an experiment the apparatus was exhausted to ·001 millim., so that the gas which was afterwards in the tube was all given off from the hot filament and the walls of the tube. The observations were generally taken so as to keep the tube as cool as possible, but by letting it get hot enough pressures up to a millimetre could be registered on the McLeod gauge, even with constant pumping. The first experiments were made to determine the way in which the leak varied with the applied electromotive force, other conditions being, so far as possible, kept constant.

§ 2. *Relation between the Current and the Applied E.M.F.*

In all cases there was no current which would show a deflection in the galvanometers used when the filament was charged positively. The positive leak from hot wires in a vacuum, though large when measured by an electrometer, is always negligible compared with the currents measured in these experiments. Some of the subjoined current E.M.F. curves were obtained by using the apparatus in fig. 6, others by using that in fig. 7. As we should expect the curves to vary considerably with the shape and position of the electrodes, the apparatus from which the curves were obtained will be definitely specified in each case. As an abbreviation for the "apparatus shown in fig. 6" we shall write "apparatus 6," and so on.

The relation between the current and the electromotive force depends largely on the pressure of the gas in the apparatus. It may also depend on the value of the maximum current which can be obtained, *i.e.*, on the temperature of the wire. At very low pressures (below, say, ·02 millim.) the current rises very rapidly with the E.M.F. till it reaches a certain value, after which it becomes practically independent of the E.M.F. This "saturation current" generally increased slightly with the electromotive force, the increase being attributable to the extra ions produced by collisions with the gas molecules. The following curve, given by apparatus 7, shows the phenomenon of saturation very clearly. The flow of the heating current was accompanied by a P.D. of 3·8 volts between the two ends of the filament, so that it is important to state which end of the filament the voltages refer to. There was found to be no current when the negative end of the filament was earthed, the whole of the filament being then positive to the surrounding earthed electrode. The values are the means of a considerable number of observations. This curve (fig. 8) is for a pressure of ·003 millim.; the voltage given is that of the negative end of the filament.

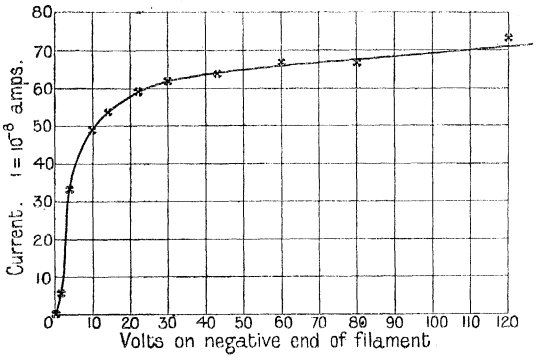

Fig. 8.

From the preceding curve it will be seen that the current was practically saturated by a potential of about 15 volts. With higher pressures of gas in the apparatus, the

saturating potential might become much greater, as is shown by the following curve, taken, also with apparatus 7, at a pressure of ·02 millim. In this case the current is not saturated till a potential of about 280 volts is reached. During this experiment the temperature of the filament, as indicated by the deflection produced by the thermo-couple, was kept constant.

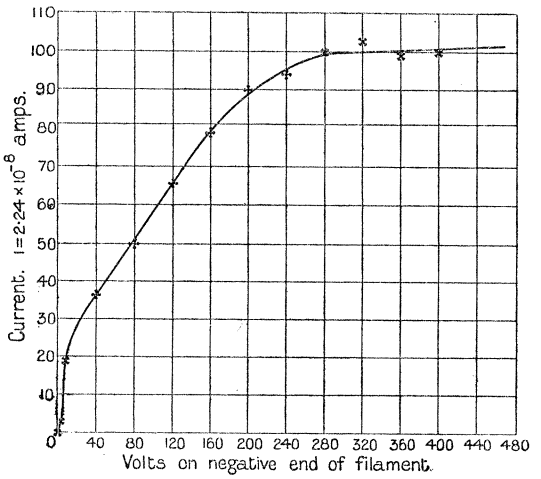

Fig. 9.

The bend in the curve at about 20 volts seems to indicate that a sort of saturation occurs here. The subsequent increase of current would then be explained by the ions produced by collisions as the electromotive force was increased. On this supposition, when we again reach the flat part of the curve at 280 volts we must suppose that every collision possible at this pressure produces ions. Similar considerations explain the gradual slope of the curve in fig. 8 after saturation. Owing to the peculiar shape of the electrodes it was not possible to calculate the magnitude of the effects.

With this curve it is interesting to compare one obtained at a slightly lower pressure (·013 millim.) with the other form of apparatus. In this case the current used to heat the filament was kept constant while its resistance decreased in the ratio of 1·025 to 1 during the observations. This does not imply that the temperature altered, since heating a carbon filament steadily decreases its resistance when cooled and measured again at the original temperature. The absolute value of the current is also some twenty times as great as that in the preceding curve. It will be seen that in this case saturation was reached with about 160 volts.

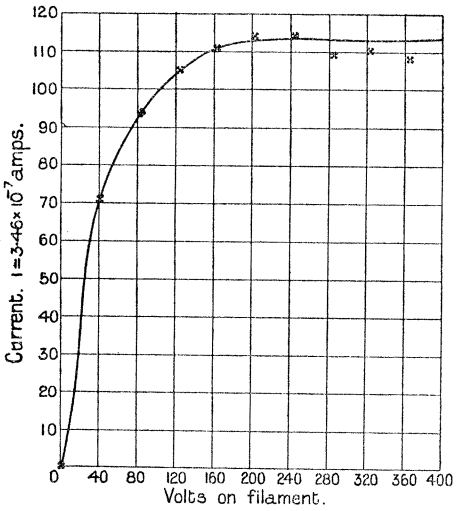

Fig. 10.

It is evident that in this case the bend at 20 volts does not appear. This may be due to the greater magnitude of the current and smaller pressure, which makes the Townsend effect less by comparison. With still higher pressures the current for low voltages is small and increases more rapidly as the voltage is raised than it would if it were proportional to the potential difference. The curve then passes through a singular point, the current increasing less and less rapidly with the voltage until the saturation value is reached. The current afterwards remains stationary for some time until it begins to increase

again as the voltage is raised. This increase is doubtless due to new ions produced by the collisions of the negative ions, since it is in all respects similar to the effects described by Professor Townsend.* All these characteristics are shown by the upper curve in fig. 11, which was obtained with apparatus 6. In this case the pressure increased from ·65 to ·85 millim. during the experiment; the heating current was maintained constant and equal to 1·07 ampères.

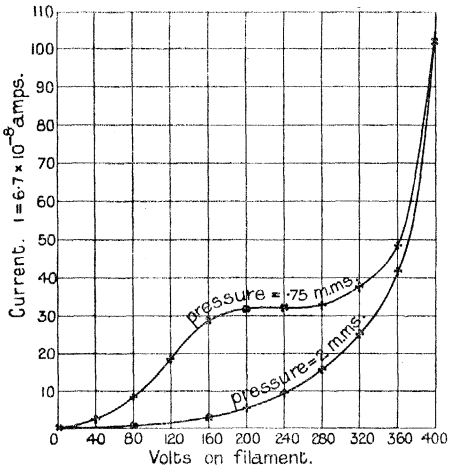

Fig. 11.

When the pressure of the gas is raised further, the current at low voltages becomes still smaller than before, the current E.M.F. curve being always concave to the axis of current. In this case the current never becomes saturated, owing to the collision effect coming in before the saturating potential is reached. Under these circumstances the current increases more and more rapidly with the potential as the latter is raised. These characteristics are very well shown by the lower curve in fig. 11, which was taken with apparatus 6 at a pressure of 2 millims. The filament was heated by a constant current.

It will be noticed that several of these curves are very similar to those obtained with hot platinum wires by Professor McClelland.†

In all these cases it was found that in retracing the observations backwards, the curves never quite coincided with those obtained first. These effects, which were of the nature of hysteresis, were partly attributable to change in the conditions while the observations were being made. Such changes were, for example, increase of pressure due to gas given off from the walls, change in the temperature of the carbon heated by a constant current owing to the permanent alteration of the resistance of a carbon filament produced by heating, &c. Even when such disturbances were eliminated as far as possible, the curve could never be made to return on its outward path. The form of the curve was always the same, but the value of the current on the return curve was invariably smaller than on the outward one; in a particular case, when the pressure increased from 2·4 to 2·6 millims., the current with about 200 volts was reduced to one-third its value on the return journey.

After having investigated in some detail the connection between the current and the electromotive force when the filament was maintained at a constant temperature, the connection between the saturation current and the other conditions was next examined. The experiments to be described are therefore concerned with the relation between the saturation current and

* Townsend, 'Phil. Mag.,' Feb., 1902.

† 'Camb. Phil. Proc.,' vol. 11, p. 296.

(1) The resistance of the filaments;
(2) The currents used to heat the filaments; and
(3) The temperature of the carbon surface, respectively.

In what follows a section will be devoted to each of the above headings.

§ 3. *The Relation between the Saturation Current and the Resistance of the Filament.* This was investigated in the same manner and with the same apparatus (fig. 2) as in the case of platinum. In all cases the apparatus which has already been described and is shown in fig. 6 was employed. The thick German silver resistance R (fig. 2), which served as an intermediate standard, had now a resistance of 1·62 ohms. The smaller currents were measured with the sensitive Thomson galvanometer. For the larger currents a D'Arsonval galvanometer, which gave a deflection of 1 millim. for a current of $3{\cdot}46 \times 10^{-7}$ ampère, was employed, owing to its greater convenience. As the resistance of the filament decreased slightly during the observations, a reading was taken both before and after each observation of the leak, the mean of the two readings being taken as the value of the resistance which corresponded to the reading for the current. Resistance readings were taken over a range of saturation current extending from $2{\cdot}8 \times 10^{-7}$ to 6×10^{-3} ampère per sq. centimetre of surface. The corresponding range of the value of the ratio of the resistance of the filament to its resistance at 11° C. at the commencement of the experiment was from ·610 to ·567. In other words, while the resistance of the filament only alters in the ratio of 610 to 567, the negative leak has become twenty thousand times as big as it was at first. It is evident, therefore, that, as in the case of platinum, the number of negative ions produced at the surface increases with enormous rapidity as the temperature rises. It will be shown later that, over a much greater range of temperature than this, there is no perceptible falling off in the rate at which the current increases.

The corresponding values which were obtained for the saturation current and the resistance of the carbon filament are given in the following table. The resistances are expressed as fractions of the resistance which the filament possessed at 10° C. before it was heated.

Saturation current in ampères.	Resistance as a fraction of initial resistance.
$3{\cdot}9 \times 10^{-8}$	·609
$9{\cdot}43 \times 10^{-8}$	·604
$3{\cdot}25 \times 10^{-7}$	·600
$8{\cdot}55 \times 10^{-7}$	·594
$19{\cdot}04 \times 10^{-7}$	·588
$4{\cdot}32 \times 10^{-6}$	·581
$13{\cdot}3 \times 10^{-6}$	·571
$3{\cdot}53 \times 10^{-5}$	·560
$7{\cdot}80 \times 10^{-5}$	·547
$2{\cdot}47 \times 10^{-4}$	·528
$3{\cdot}95 \times 10^{-4}$	·509
$9{\cdot}05 \times 10^{-4}$	·48

These numbers when plotted against one another on squared paper yield curves very like the current temperature curves for platinum (fig. 4). They have not, however, been inserted, since they are much the same as the current-temperature curves for carbon (fig. 13, p. 526), which have been plotted from the same observations.

Just as in the former experiments, the current was never found to be a function of the electromotive force alone, so also here the cooling curves never exactly coincided with those obtained as the temperature of the filament was raised. This was partly due to the permanent change in the resistance of carbon produced by heating.* It was attempted to correct for this by taking, instead of the ratio of the resistance at moment to the original resistance at 11° C. before commencing the experiment, the ratio to the resistance which the filament would possess if at a temperature of 11° C. at that moment. The permanent change in the resistance was assumed to be proportional to the rate at which the resistance changed during an experiment, the conditions being kept, as far as possible, constant. In this way it was possible to obtain by extrapolation the resistance which the filament would possess if allowed to cool down to 11° C. at any stage during the experiments. That this process brings the two curves more nearly into coincidence will be seen at once on comparing the numbers in columns I., VI., and VII. of the following table. In this case the potential on the filament was — 204 volts, and the heating current was run at constant voltage. The results of these corrections are shown in the accompanying table :—

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Saturation current, $1 = 10^{-7}$ ampère.	Heating current, ampères.	Initial resistance proportional to	Amount resistance decreased during experiment.	Corrected zero resistance 11° C., proportional to	Ratio of resistance to corrected zero resistance.	Ratio of resistance to original zero resistance.	Pressure, millim.
1·7	·59	1755	0	2910	·604	·604	—
5·2	·64	1726	0	2910	·594	·594	·003
20·7	·69	1698	0	2907	·584	·584	—
46·5	·735	1682	1	2901	·580	·578	·008
118	·78	1664	2	2889	·576	·572	—
294	·83	1645	2	2877	·573	·566	·02
735	·89	1624	2	2865	·567	·559	—
310	·87	1637	2	2853	·574	·563	·035
145	·84	1646	3	2835	·581	·566	—
72	·81	1654	2	2823	·586	·568	·04
34·6	·79	1665	1	2817	·592	·572	—
17·3	·76	1675	1	2811	·596	·576	·035
8·3	·72	1687	1	2805	·602	·580	·03

* Le Châtelier, 'Journal de Phys.,' ser. 3, vol. 1, p. 185.

In order to illustrate the magnitude of these changes, the numbers in columns I. and III. have been plotted in the accompanying curve (fig. 12).

The chief objects of these experiments on the relation between the negative current from and the resistance of, a carbon filament, was to determine the dependence of the former in the temperature. Le Châtelier,* using an optical method, has given numbers connecting the temperature of a carbon filament with its resistance. If we plot a curve from these numbers between the temperature of the filament and the ratio of its resistance at that temperature to its resistance at 15° C., we can use this to obtain the temperature of any other filament from its resistance. In this case we have again to face the uncertainty caused by the permanent change in the resistance of the filaments when heated. I have attempted to correct for this in the same manner as has been described above. Le Châtelier states that in his experiments there was a permanent lowering of the resistance of the filament amounting to about 10 per cent. This change has been distributed among the observations in such a way that the observations at the highest temperatures are responsible for the greater part of the alteration. The corrected curve thus coincides with the original one up to about 1000° C., after which it branches off, the divergence between the two becoming gradually greater, until finally at about 2000° it ends 10 per cent. higher than the one plotted from Le Châtelier's numbers.

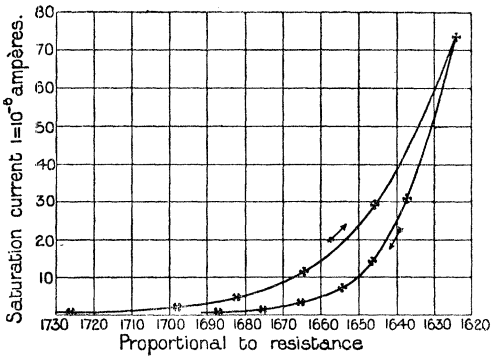

Fig. 12.

The numbers in the table on p. 523, when treated in this manner, yield the following :—

I.	II.	III.
·39	·610	1250
·943	·606	1265
3·25	·602	1285
8·55	·599	1305
19·04	·595	1325
43·2	·592	1345
133·4	·589	1365
353	·586	1380
780	·582	1400
2475	·577	1430
3950	·572	1460
9050	·567	1490

I. = Saturation current, unit being 10^{-7} ampère.

II. = Ratio of resistance to corrected resistance at 11° C.

III. = Temperature in degrees Centigrade.

* 'Journal de Phys.,' *loc. cit.*

The numbers in columns I. and III., when plotted against one another, yield the following curves (fig. 13) for the variation of the negative leak from carbon with the temperature. The various curves represent successively greater units of current as in the case of the curves for platinum (fig. 4).

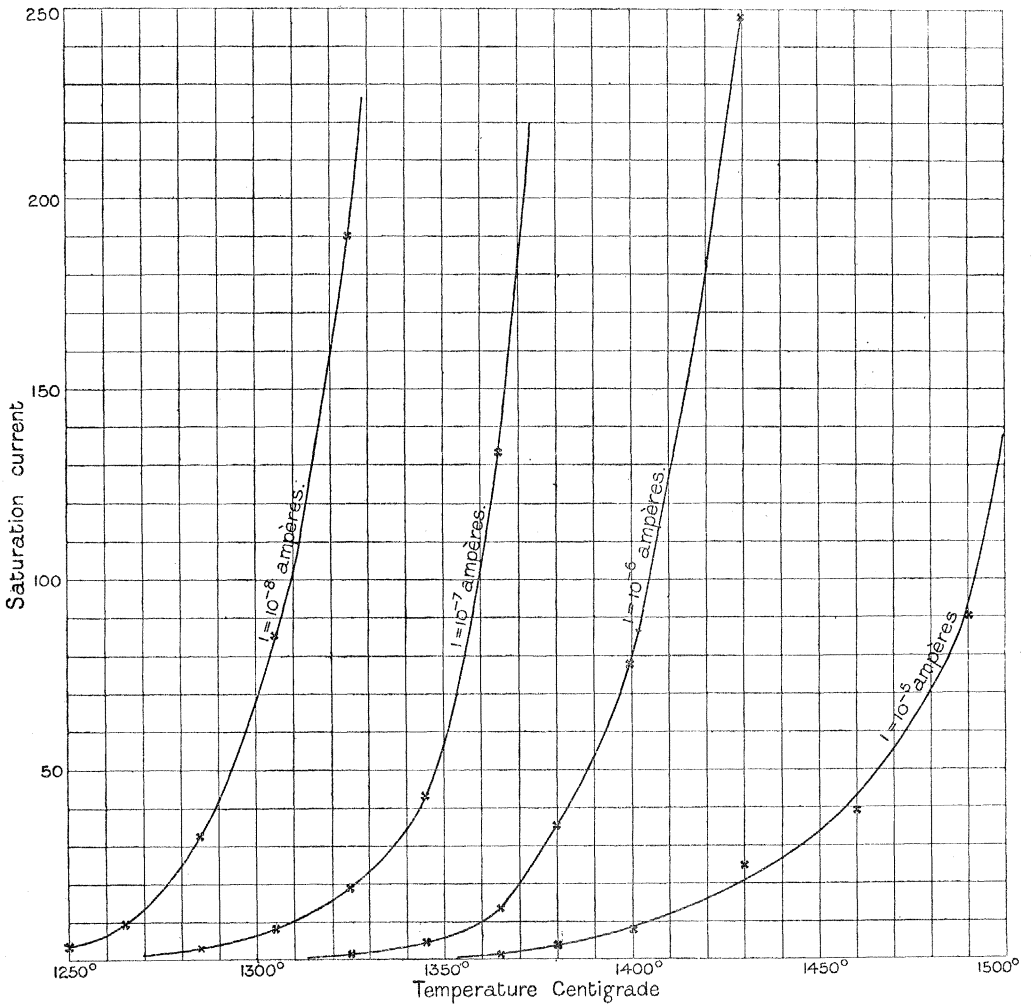

Fig. 13.

The further consideration of these results on the temperature variation of the negative leak from carbon will be postponed till § 5.

§ 4. *The Relation between the Negative Leak and the Current used to Heat the Filaments.*

A series of experiments was made in which the saturation current and the corresponding current required to heat the filament were measured; since it was thought that these measurements would be of especial interest at temperatures so high that they could not be determined, at any rate by the methods used in the present paper. In these experiments the portion of the apparatus used to measure the leak was unchanged, while the whole of the arrangement used to measure the

resistance was removed. The only part of the heating circuit which remained was the battery of twelve storage cells and the adjustable resistance used to regulate the current. The magnitude of the latter was determined by means of a small vertical ammeter, reading up to 4 ampères, which was inserted in the circuit.

The first experiments were made with the apparatus shown in fig. 6, and were pushed to very high temperatures. In fact, THE MAXIMUM CURRENT FROM THE FILAMENT TO THE ALUMINIUM ELECTRODE REACHED THE ENORMOUS VALUE OF 1·5 AMPÈRE PER SQUARE CENTIMETRE OF CARBON SURFACE. These experiments were made with a lamp which possessed a small air leak that had been stopped by embedding in paraffin in the manner already described. When the greatest currents were put on the lamp became hot so that the paraffin melted and the pressure inside the apparatus rose to 1 millim. During the course of the experiments the pressure was therefore not constant, but increased gradually from ·006 millim. to 1 millim. The potential on the filament was — 250 volts, and was sufficient to saturate the current at all the pressures concerned. The results of these observations are shown graphically in the accompanying diagram (fig. 14). The values of the ordinates are successively multiplied by ten as we move to the left from one curve to the next.

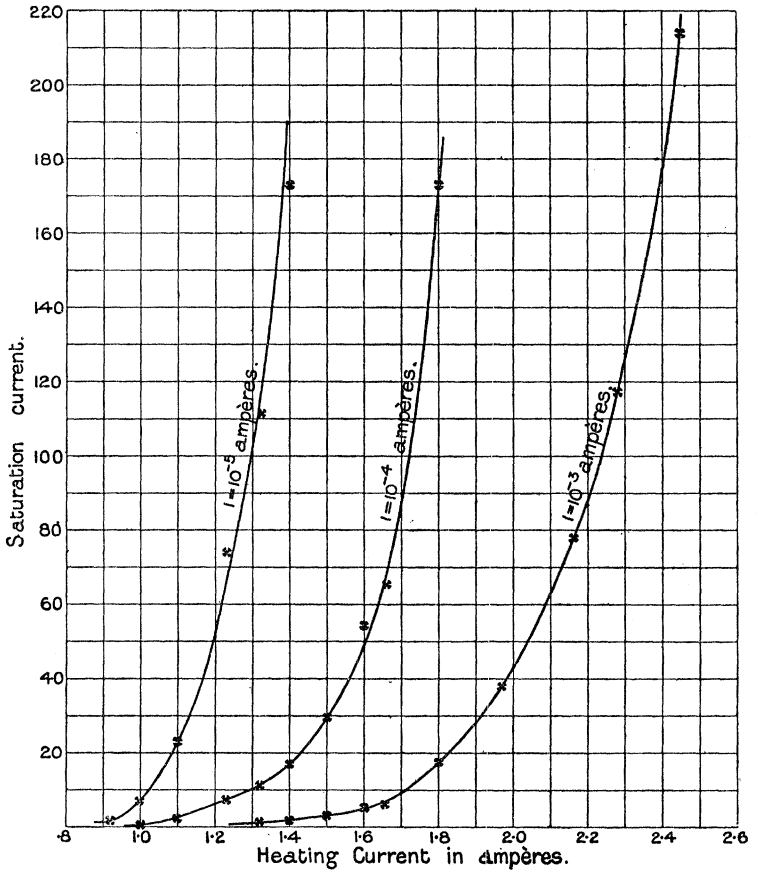

Fig. 14.

It will be noticed that there is a great similarity between fig. 14 and the curves connecting the saturation current with the resistance and temperature respectively. This is merely due to the rate of variation of the saturation current being so rapid that the differences in the alteration of resistance, temperature, and heating current becomes insignificant in comparison.

Since in the last experiments the big currents were always accompanied by a high pressure of gas in the apparatus, it might be thought that part of the increased current was due to the gas present. To investigate this point a series of experiments was made with the apparatus shown in fig. 7, so that the gas pressure could be kept down to a very low value. By heating the filament for a short time only and taking the observations very quickly, it was found that the temperature of the bulb and electrode could be prevented from rising perceptibly. Under these conditions it was found that the amount of gas given off was greatly diminished, the highest pressure recorded during the observations being ·006 millim. A reading of the McLeod gauge was taken between each reading of the galvanometer deflection for the saturation current. The potential on the filament was — 80 volts, this being more than enough to saturate the current (*cf.* fig. 8). The numbers which were obtained are given in the accompanying table:

Heating current, ampères.	Saturation current, 1 = ampère × 10^{-8}.	Pressure, millims. of Hg.
1·49	2·1	·002
1·59	10·5	·002
1·70	35	·0025
1·84	143	·0025
2·0	540	·003
2·26	2·24 × 10^3	·003
2·43	10·1 × 10^3	·005
2·68	42 × 10^3	·005
2·92	122 × 10^3	·006
3·45	760 × 10^3	·006
3·65	1640 × 10^3	·005

The greatest observed value of the saturation current is not given in the above table, since the corresponding reading of the ammeter was not taken. This enabled the reading to be taken much more quickly, so that the pressure only changed from ·0022 to ·0025 millim. The corresponding saturation current was ·04 ampère; in other words, a square centimetre of surface would have given a current of ·28 ampère across a vacuum at $\frac{1}{400}$th millim. pressure.

In the preceding series of experiments the highest possible value of the temperature had not been reached, so that further experiments were instituted to determine the maximum current which could be obtained from a square centimetre of a carbon filament when the temperature was pushed to the highest limit, *i.e.*, just before the

filament melted. The arrangement of the apparatus was altered somewhat, the leak being measured by a Weston ammeter instead of a galvanometer as before; in other respects the arrangement was unchanged. The pressure was kept very low and a potential of about — 60 volts was maintained on the filament, the surrounding cylinder being earthed.

With this apparatus it was found possible to maintain an actual current of ·4 ampère (corresponding to 2 AMPÈRES per square centimetre of filament surface) at a pressure of less than $\frac{1}{600}$ millim. The current could not be made to surpass this value since the filament melted on raising it to a slightly higher temperature. The fact that such large currents can be produced at such low pressures has an important bearing on the theory of the mechanism by which the corpuscles are produced, which will be considered later.

§ 5. *The Relation between the Saturation Current and the Temperature.*

From the experiments on the variation of the saturation current with the resistance we have been able to give numbers which indicate, roughly at any rate, the way in which the former depends on the temperature. It was thought that a more reliable estimate might be obtained if the temperature of the filament were determined by means of a thermal junction of platinum and iridio-platinum. With this object the following experiments were made:—

The tube employed was that shown in fig. 7, and already described. The filament in this tube was in the form of a simple U and had the following linear dimensions: length = 1·2 centim., diameter = ·0376 centim., and total area of surface = ·142 sq. centim. For these experiments the apparatus shown in fig. 2 had to be altered, the portions below AFK_2 being entirely reconstituted. The apparatus used for measuring the saturation current was unchanged, the only alterations being made in the portion used to measure the temperature. The thermocouple circuit was completed by taking the lead P_1 (fig. 7) to the cold junction, which was placed in a test-tube immersed in water at 12° C.; the other wire from the cold junction passed through a resistance box to a D'Arsonval galvanometer, and thence through P (fig. 7) to the hot junction. The adjustable resistance R_1 (fig. 2) still served to regulate the current which was used to heat the filament.

In order to standardise the thermocouple the melting-point of potassium sulphate was again taken as the fixed point. A junction of the same wire as that used during the experiments was fixed on to a stout platinum wire, which was clamped horizontally in the hottest part of a Bunsen burner. The Bunsen was arranged to burn vigorously with a bright green inner cone and was carefully protected from draughts. Very small portions of the salt were then placed on the stout wire on the side of the flame opposite to the thermocouple, and matters were so arranged that when the salt just melted it was exactly the same distance from the edge of the flame on the one side as the thermocouple on the other. The reading of the galvanometer was then

taken to correspond to the melting-point of the salt. The method was then tested by placing a small portion of salt on the thermocouple itself and observing when it began to melt. This was found to agree with the previous observations. The greatest difference between the observations taken was less than 3 per cent. A further test was supplied by determining the melting-point of sodium sulphate; the value found was within 20° of that given by Messrs. Heycock and Neville.* This agreement was considered to be quite good enough for the purpose in hand. The thermocouple was finally found to give an electromotive force of 17·7 millivolts when its junctions were at 1067° C. and 12° C. respectively.

The platinum temperatures given by the galvanometer readings have been corrected to the air thermometer scale by means of the curves given by Professor Callendar.†

The thermocouple method possesses one great advantage over the resistance method of determining the temperature of hot wires, in that the observations can be taken much more quickly, and so the wire has to be heated for a much shorter time. In this way the apparatus need never get hot, and far less gas is given off, so that the readings generally are much steadier.

The accompanying table represents a series of observations with this apparatus. The pressure was always less than $\frac{1}{500}$th of a millimetre of mercury, while the potential on the wire was — 44 volts, this being more than enough to saturate the current. The platinum temperatures are given under the column headed Pt, the numbers under t are the temperatures (degrees Centigrade) reduced to the air thermometer scale.

Scale-divisions of thermocouple.	Pt.	t.	Leak, $1 = 10^{-8}$ ampère.	Pressure.
				millims.
108·5	1122	1110	3·7	·001
110·8	1145	1129	8·2	—
112·8	1165	1145	25	—
114·8	1186	1162	39	·001
117	1209	1180	78	—
119	1229	1197	167	·0015
120·6	1245	1209	295	—
121·5	1254	1216	662	—
119·2	1231	1199	266	·0015
117·3	1212	1183	110	—
116·3	1202	1173	79	—
113	1168	1148	37	—
110·7	1144	1128	16·5	—
109	1127	1115	7·5	—
107	1107	1097	3·7	—
104·1	1077	1075	1·5	·0016

It will be noticed here again that the current for a given temperature is smaller as the temperature is being increased than when it is falling.

* 'Chem. Soc. Journal,' vol. 67, p. 160.

† 'Phil. Mag.,' vol. 48, p. 519.

The following table represents a series of observations taken with the thermocouple apparatus at somewhat higher temperatures. The potential on the filament was here $= -87$ volts.

Reading for thermocouple.	Pt.	t.	Saturation current $1 = 10^{-8}$ ampère.	Pressure in millims.
114·6	1184	1160	9	·003
117	1209	1180	60	·005
123	1270	1227	346	·007
131·3	1354	1290	2700	·007
138·5	1428	1359	22000	·007

The temperatures given by the thermocouple method are on the average about 120° lower than those obtained from the resistance for the same current. The temperature registered by the couple would be lower than that of the more remote parts of the filament for several reasons, the chief one being the conduction of heat away locally by the leads of the thermocouple itself. It is difficult to say whether we should expect this difference to amount to 120° C.

We are now in a position to test whether the experimental results are in agreement with the theoretical formula for the saturation current, viz. :—

$$C/\epsilon S = n\sqrt{\frac{R}{2m\pi}}\,\theta^{\frac{1}{2}}e^{-\Phi/R\theta} = A\theta^{\frac{1}{2}}e^{-b/\theta},$$

using the notation employed before. If we take, as in the case of platinum, $y = \log_{10}C - \frac{1}{2}\log_{10}\theta$ and $x_0 = \theta^{-1}$, the above equation reduces, as before, to the straight line

$$y = a - b_0x_0.$$

The following curve (fig. 15) has been plotted in this manner from the numbers

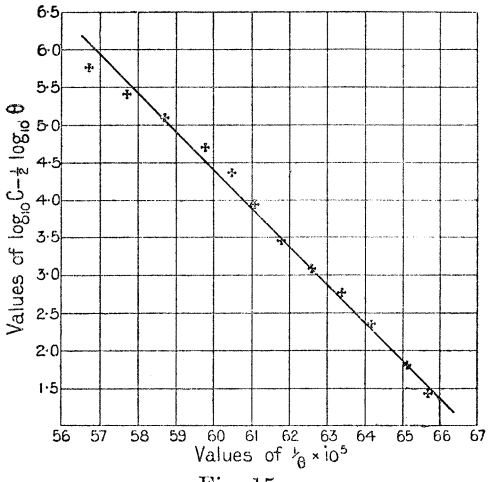

Fig. 15.

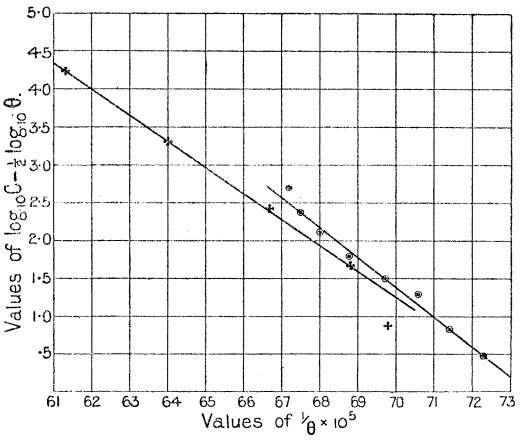

Fig. 16.

given in the table on p. 525. The ordinates are values of $\log_{10}C - \frac{1}{2}\log_{10}\theta$, while the abscissæ are values of $\theta^{-1} \times 10^5$.

The numbers on pp. 530 and 531 yield the curves in fig. 16. The straight line on the right is drawn from the observations on p. 530, and corresponds to lower temperatures than the other. The experimental points for this curve are denoted by ⊙. The other curve from the observations on p. 531 refers to somewhat higher temperatures. The experimental points for this curve are indicated thus : ×.

All these three curves are fairly close approximations to a straight line ; it is therefore quite evident that the observations are represented very closely by assigning to the saturation current a formula of the type $C/\epsilon S = A\theta^{\frac{1}{2}} e^{-b/\theta}$.

When we come to the actual values of the constants in the above formula, the agreement with the simple theory is not so good as in the case of platinum, though possibly this is partly due to the greater difficulty of the experiments. The curves in figs. 15 and 16 give for the value of b

$$11{\cdot}9 \times 10^4,\ 9{\cdot}7 \times 10^4, \text{ and } 7{\cdot}8 \times 10^4 \text{ respectively.}$$

In order that the differences of the values of b should be proportional to the contact E.M.F. between carbon, platinum, and other metals, b for carbon should be $5{\cdot}2 \times 10^4$, since its value for platinum is $4{\cdot}93 \times 10^4$. The difference between this and the above numbers does not appear to be very great, but the effect of a small error in b is enormous when we come to calculate from it the value of n, the number of corpuscles in a cub. centim. of carbon.

If we take $7{\cdot}8 \times 10^4$ as the best value of b, and $C = 2180$ at 1515° absolute as being the mean of the two series of temperature measurements, we find A is of the order 10^{34} and n is of the order 10^{29}. Now, Mr. PATTERSON* finds that at ordinary temperatures $n = 10^{19}$. The effect of temperature on the resistance of carbon indicates that the concentration of the corpuscles would be at least ten times as great at 1000° as at 0° C., so that we should expect to find n of the order 10^{20}. As a matter of fact, if we take $b = 5{\cdot}2 \times 10^4$ instead of $7{\cdot}8 \times 10^4$, we find $n = 5 \times 10^{21}$ instead of 10^{29}.

Reasons which might make this method of determining n give values which are too large, will be considered at some length after the experiments on sodium have been described.

III. *Experiments with Sodium.*

§ 1. *Nature of Problem.*

Sodium was selected as the next metal to be investigated on account of its strong electropositive character. Since this implies a great attraction for positive electricity, we should expect its power of retaining the negative corpuscles to be much smaller than that of the conductors hitherto examined. If the foregoing theory is correct the corpuscles ought to escape from the alkali metals at a much lower temperature than

* 'Phil. Mag.,' 6, III., 655.

from metals which are low down in the volta series. In fact, assuming (1) that the difference in the discontinuity of potential at a platinum vacuum and sodium vacuum surface is equal to the contact difference of potential for sodium and platinum (taken roughly to be equal to two volts), (2) that the value of the discontinuity (4·1 volts) previously obtained for platinum is correct, (3) that the concentration of the corpuscles for sodium is of the same order of magnitude as for copper, and (4) the correctness of the present theory, a preliminary calculation showed that currents of the order of some 10^{-6} ampère per square centimetre ought to be obtained at as low a temperature as 500° C.

The problem we have to face in the case of sodium is not quite the same as in the case of non-volatile substances such as carbon and platinum. For in this case the metal has an appreciable vapour pressure at the temperature at which the experiments are carried out, and part of the conductivity present is doubtless due to the spontaneous ionisation of the metal vapour. A second inconvenience, which is more of a practical nature, is caused by the distillation of the metal from the hotter to the colder parts of the tube, causing the state of the latter to continually vary. For the same reason some of the sodium condenses on the electrode which is supposed to be free from it, so that both electrodes emit negative ions.

We have seen that in the case of platinum and carbon no current was obtained when the hot conductor was positively charged; in other words, the conductivity was perfectly unipolar. In the case of sodium, owing to the spontaneous ionisation of the vapour and the condensation of the metal on the inserted electrode, we should expect to get a current in both directions. In the following experiments the first effect must have been small, owing to the low vapour-pressure at the temperatures employed, while the effect of the second was made small by using an electrode with a very small superficial area (a thin platinum wire). It will be seen that in every case the current when the sodium surface was negative was more than twenty times its value when the surface was positive.

The apparatus which was used to detect and measure the negative leak from sodium will now be described.

§ 2. *Description of Apparatus.*

After a great number of trials of various forms of glass apparatus, all of which came to an untimely end owing to the joints not being able to stand the continued heating or otherwise, the metal apparatus shown diagrammatically in fig. 17 was set up. The weldless steel tube ABDC was 76 centims. long and 3·2 centims. in diameter, and was kept at zero potential by means of the earth wire shown. The straight platinum wire A_1B_1 was insulated with sealing-wax at each end and could be charged positively or negatively to any desired potential. It formed the electrode mentioned above. The whole tube was placed in a small combustion furnace, by means of which the central portions could be heated to any desired temperature. The

temperature was determined by means of a copper-nickel thermocouple, C_1D_1, attached to a hollow semicircular cylinder of brass, E, placed at the middle point of the line CD. The brass piece E was cut from a tube which before the operation fitted easily

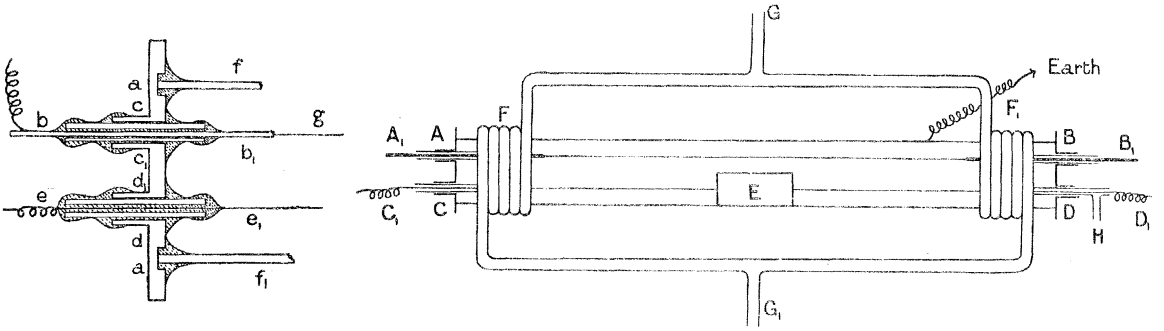

Fig. 17.

into ABCD, so that when the copper and nickel wires were tied round it, it fitted quite tightly. The spirals FF_1 were made of composition tubing wound tight round ABDC; they served to keep the ends of the tube cool and thus prevent the sealing-wax joints from softening. They were fed with cold water at G_1 and emptied at G. The side-tube H from DD_1 led to the pump and McLeod gauge.

The manner in which the wires A_1B_1 and C_1D_1 were fixed in at the ends is shown more clearly in the enlarged diagram on the left of the figure. The shaded parts represent the distribution of the sealing-wax which was used to make the joints. The ends ff_1 of the tube ABDC fitted into an annular depression on the brass plate aa. The platinum wire A_1B_1 was soldered at each end on to a stout copper wire, bb_1, which fitted fairly tight in a glass tube passing through the brass tube cc_1. The whole was fixed in air-tight by means of sealing-wax. One of the leads from the thermocouple was fixed in exactly the same way into the brass tube dd_1.

The sodium was originally placed in the form of small cubes on and around E, and it was considered that after heating for a short time in a vacuum a fairly uniform distribution of sodium over the central portions of the steel tube would be obtained. This was certainly what happened in the case of the glass apparatus which had been tried previously and in which the effect could be observed. The leak from the hot sodium to the platinum wire electrode A_1B_1 was then measured, according to its magnitude, either by an electrometer or by a galvanometer. At the lower temperatures where the quadrant electrometer was employed, one of the quadrants was connected to the case of the instrument which was insulated. The other quadrant was connected with a standard condenser and, by means of a wire passing axially on sealing-wax supports along a brass tube, with the electrode A_1B_1. The outside of the brass shielding-cylinder was connected with the case of the electrometer. In making an experiment the whole of the electrometer system was charged to a given potential, and the time required for the spot to move over a given number of scale divisions was noted. This measured the current from the insulated electrode

A_1B_1 to the surrounding earthed tube ABDC. By altering the capacity of the condenser a suitable rate of movement of the spot of the electrometer could be obtained each time.

In using the galvanometer the arrangement was practically the same as that employed before. One end of the battery was put to earth while the other was connected through the galvanometer to A_1B_1. The battery was capable of supplying any number of volts up to 420, the potential being measured by the Weston voltmeter used previously. A D'Arsonval galvanometer giving 1 millim. deflection for 2×10^{-8} ampère, and having a resistance of 500 ohms, was used.

With the exception of the change in the materials of the couple the thermoelectric circuit was exactly the same as that employed in the experiments on carbon. To reduce the galvanometer readings to temperatures use was made of the recent observations of Mr. E. P. Harrison.* Only one fixed point was determined, viz., that of the boiling-point of sulphur. The electromotive force at that temperature was found to correspond to 22·7 microvolts per degree over the whole range, a result which agrees very accurately with that given by Mr. Harrison. The relation between electromotive force and temperature was not assumed to be linear, but corresponding values for intermediate points were calculated from Mr. Harrison's curves. From these figures a curve was plotted which gave temperatures in terms of galvanometer readings directly. The galvanometer employed gave 1 millim. deflection for $1{\cdot}39 \times 10^{-7}$ ampère, and the total resistance of galvanometer and thermoelectric circuit with no resistance out of the box was 19·7 ohms.

In the various forms of glass apparatus previously tried it was found that considerable currents were obtained at ordinary temperatures when the sodium was charged negatively. This was ultimately found to be due to the photoelectric effect produced by the light present in the room, since it disappeared when the experiments were made in the dark. The steel tube finally used in the experiments had the great advantage that it could easily be made absolutely light-tight. In order to make sure that no light reached the sodium, the glass tubes through which the wires were let in at each end of the steel tube were painted over with black enamel. The leak was then tested and found to be small and the same in both directions; so that it was all due to imperfections in the insulation.

§ 3. *The Relation between the Current and the Electromotive Force.*

After testing the insulation and pumping down the apparatus experiments were first made to see how the current varied with the direction of the electromotive force. The first measurements showed that, at a temperature of about 300° C., the current when the wire was at a potential of + 40 volts was 3500 times its value when the wire was charged to − 40 volts. The value of the current when the wire was positive was $1{\cdot}5 \times 10^{-6}$ ampère. Later experiments showed, however, that the

* 'Phil. Mag.,' (6), vol. 3, p. 177.

positive current was invariably about 30 times as big as the negative. This was probably due to sodium having condensed on the wire electrode. For, although the wire had a surface per unit-length of less than one-hundredth that of the steel tube, the surface ionisation would be far easier to saturate; so that we should expect the currents in the two directions under a given voltage to have a ratio considerably less than 100 to 1. The above high value of the ratio obtained initially would correspond to the stage when no sodium had condensed on the wire.

In making these experiments the apparatus was first pumped down to a pressure of about ·1 millim., but it was found that on heating the steel tube a considerable amount of gas was given off. At first the amount of gas evolved was so great that the pressure in the apparatus, the volume of which was very considerable, rose to several centimetres of mercury. This evolution of gas was noticed in every case when sodium was heated, but by continued heating it usually became very small. In this particular instance, even after heating for several days, on pumping the apparatus out and heating again it was found that the pressure rapidly rose to about 5 millims. It was thought that the gases from the furnace might perhaps diffuse through the steel tube. To prevent this the latter was covered with a layer of soluble glass, which was carefully dried on; this seemed to have the desired effect, for it was found that afterwards there was no difficulty in keeping the pressure below a millimetre even when the tube was heated to 450° C.

Experiments were next made to investigate the way in which the current varied with the potential when the wire A_1B_1 was charged positively. It was found that the current E.M.F. curves were markedly different from those previously obtained with carbon and platinum. The current was small at first and increased much more rapidly with the voltage than if the two were proportional. In fact, the general shape of the current E.M.F. curves was much like that of the curves for current and temperature obtained with carbon and platinum. There was no indication of saturation at any potential.

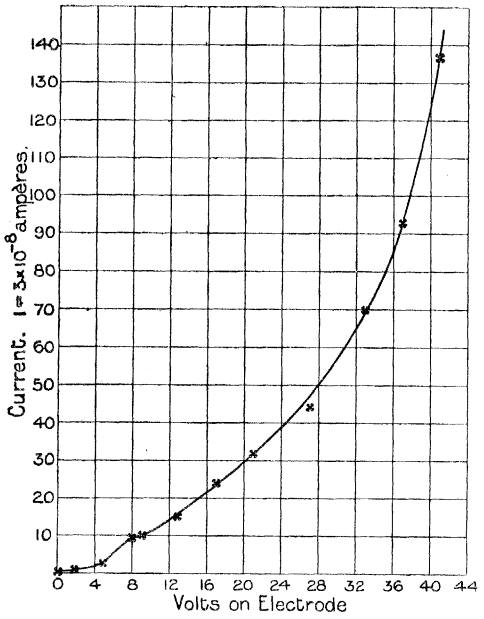

Fig. 18.

These differences are to be attributed to the difference in the experimental conditions and especially in the shape of the electrodes. In the case of sodium we have a large ionisation produced at the inner surface of a wide tube, and it is a well known fact that it is difficult to saturate the current to a wire inside the tube in such a case, owing to the weakness of the electric field near the surface.

The accompanying curve (fig. 18) gives the relation between the current and the

electromotive force for voltages in the wire electrode between 0 and + 40. The pressure was about 5 millims. The sudden increase in the current between 4 and 8 volts was obtained every time and did not seem to be due to experimental error.

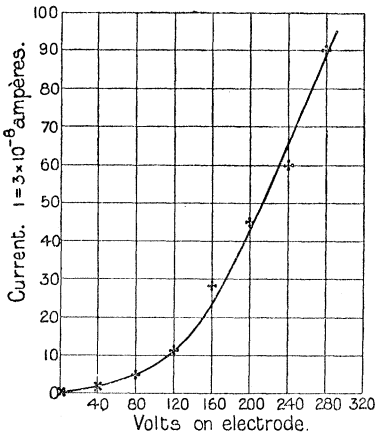

Fig. 19.

The current E.M.F. curve from 40 to 240 volts is very similar to that in fig. 18, except that it approximates very closely to a straight line between 160 and 240 volts. It is given in fig. 19.

When the voltage was increased above 240 it was found that the current rose rapidly to several thousand times its previous value. The increased current was quite steady at 320 volts, but at 280 volts it seemed to be in a very unstable state, since all kinds of intermediate readings could be obtained. Above 320 volts the current increased in a linear manner with the voltage. The experimental numbers are given below.

Volts on wire	200	240	280	280	320	360	400
Currents. Ampères $\times 10^{-7}$ . . .	3·6	5·7	93·6	155·4	7750	14350	20250

These numbers seem to indicate that with potentials greater than 240 volts an ordinary vacuum discharge took place at some point or points in the tube; in the following experiments care was therefore taken never to use potentials greater than 80 volts

§ 4. *Relation between the Current under a given Voltage and the Temperature.*

In the case of sodium, owing to the fact that the current could not be saturated, its value *under a given electromotive force* was measured at different temperatures.

This comes to practically the same thing as measuring the saturation current, since we should expect, *ceteris paribus*, the current with a given electromotive force always to be proportional to the number of ions liberated at the metal surface. In order to be sure of not getting a discharge, a potential of about 80 volts between the wire A_1B_1, and the cylinder was always employed. The following table represents a series of observations of current and temperature ranging from 217° C. to 427° C. It will be seen that the corresponding range of current is from 10^{-9} to 10^{-2} ampère; in other words, raising the temperature of the metal from 217° to 427° increases the current to ten million times its original value. The currents below 10^{-7} ampère were measured with the electrometer. In this series of experiments very low values of the currents were not measured; in a later series the current was taken nearly

down to 10^{-12} ampère. In that case it was found that the leak increased less rapidly with the temperature below than above about 180°, so that presumably the ionisation present below 180° is not due to the emission of corpuscles from the metal surface. In the series of experiments which gave the numbers in the following table the pressure of the gas was about 1·5 millims.

Reading of thermocouple.	Temperature, centigrade.	Current, ampères.	Reading of thermocouple.	Temperature, centigrade.	Current, ampères.
	°			°	
170	427	$1\cdot39\times10^{-2}$	139	334	$5\cdot14\times10^{-6}$
165	410	$8\cdot34\times10^{-3}$	136	327	$3\cdot06\times10^{-6}$
160	393	$8\cdot34\times10^{-4}$	132	317	$1\cdot53\times10^{-6}$
158	387	$3\cdot61\times10^{-4}$	129	310	$5\cdot56\times10^{-7}$
156	381	$1\cdot65\times10^{-4}$	123	296	$1\cdot39\times10^{-7}$
152	370	$6\cdot34\times10^{-5}$	122	284	$6\cdot25\times10^{-8}$
145	350	$1\cdot39\times10^{-5}$	102	248	$9\cdot72\times10^{-9}$
143	345	$1\cdot11\times10^{-5}$	89	217	$1\cdot8\times10^{-9}$
140	337	$7\cdot0\times10^{-6}$	—	—	—

Corresponding values of current and temperature have been plotted on the accompanying curve (fig. 20) in order to facilitate comparison with the results obtained for carbon and platinum. It will be seen that the general appearance of the curves is much the same as before. The unit of current is successively multiplied by ten as we pass to the right from one curve to the next.

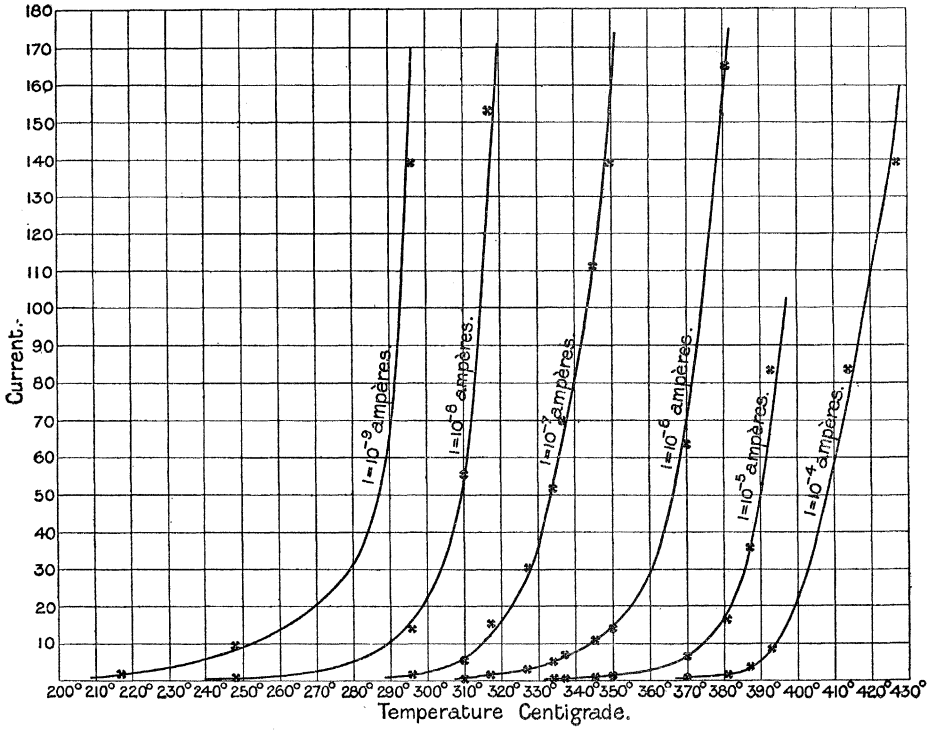

Fig. 20.

We now come to the application of the theoretical formula

$$C/\epsilon S = n\sqrt{\frac{R}{2m\pi}}\,\theta^{\frac{1}{2}}\,e^{-\Phi/R\theta}$$

to the reduction of these results. This equation may be written as before

$$y = \log_{10}C - \tfrac{1}{2}\log_{10}\theta = a + b_0 x_0,$$

where $x_0 = \theta_1^{-1}$, θ being the absolute temperature. To test the theory, values of y have been plotted against values of $\theta^{-1} \times 10^4$ in the following curve (fig. 21).

It will be seen that all the points fall very nearly on a straight line except the first two. They are all, however, fairly accurately represented by the dotted curve shown. As the two lowest points correspond to a low temperature, it is possible that some other effect is coming in here which would account for their deviation from rectilinearity.

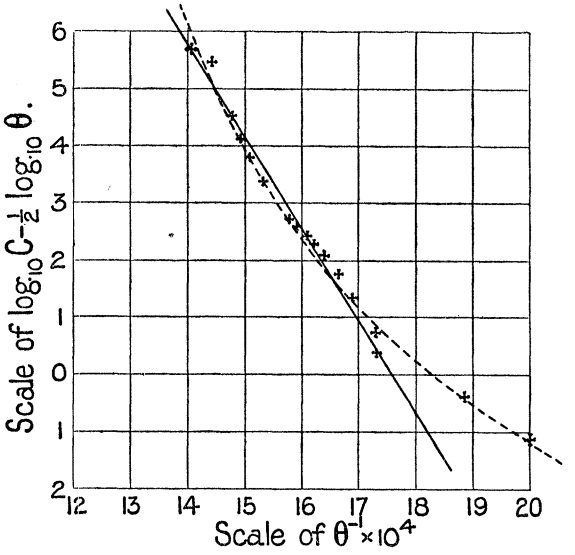

Fig. 21.

In calculating the value of $b\,(=\Phi/R)$ we may either confine our attention to the straight part of curve 4, and neglect the two first observations, or we may take the average over the whole range of the experiments. The two values differ by about 24 per cent.; if we take the mean we find $b = 3{\cdot}16 \times 10^4$. This gives, for the discontinuity of potential at the surface, the value 2·63 volts, and would therefore give 1·47 volt as the difference of its values for sodium and platinum.

The above value of the difference, which is approximately equal to the contact electromotive force for sodium and platinum, forms a strong confirmation of the theory; but when we come to calculate n, the number of free corpuscles in a cubic centimetre of sodium, the agreement is not so good. In fact, we find from the experimental results that for $\theta = 628$, $\log_{10} C - \frac{1}{2}\log_{10}\theta = 2{\cdot}615$; whence, putting in an estimated value of the area of the sodium surface, we get $n = 10^{26}$ about. The value of n has not been determined for sodium by any other method, but we should expect it to be not greatly different from that for copper, which is given by Mr. Patterson as 3×10^{22}. The value given by this method is thus far too great, for it is hard to imagine that the corpuscles can have a pressure of ten million atmospheres. I believe the discrepancy here is greater than can be explained by errors of experiment, although that was possible in the case of the high values found for carbon.

A further series of current measurements was made, using the quadrant electrometer, in order to investigate the leak at somewhat lower temperatures. It was also thought desirable to measure the currents under a given voltage in each of the two possible directions and to see if there was any relation between them. The experiments also served to test whether the current temperature curve, obtained when the tube was cooling, followed the same path as that obtained with rising temperature. It was scarcely to be expected that the two curves would coincide, even approximately, owing to the continual distillation of the sodium from the hotter parts of the tube to the cooler.

The results of the experiments are given in the accompanying table. In making the observations readings were generally taken with the wire electrode alternately positive and negative, a potential of 84 volts being used. In taking each reading the capacity was adjusted so as to give a convenient rate of movement of the electrometer spot. It was attempted to take corresponding positive and negative readings at as near the same temperature as possible, the gas furnace being adjusted after each pair of readings had been taken. The pressure in the apparatus varied from ·25 to ·4 millim.

Volts on wire = +84.		Volts on wire = −84.		Volts on wire = +84.		Volts on wire = −84.	
Temperature Centigrade.	Current 1 = ampère $\times 10^{-12}$.	Temperature Centigrade.	Current 1 = ampère $\times 10^{-12}$.	Temperature Centigrade.	Current 1 = ampère $\times 10^{-12}$.	Temperature Centigrade.	Current 1 = ampère $\times 10^{-12}$.
°		°		°		°	
10	2·4	10	2·2	306	$3{\cdot}24 \times 10^{4}$	—	—
92·5	23·4	92	6·65	325	$2{\cdot}12 \times 10^{5}$	323	890
104	31·6	97	6·3	340	$3{\cdot}66 \times 10^{5}$	338	$1{\cdot}01 \times 10^{4}$
131	247	—	—	340	$11{\cdot}4 \times 10^{5}$	340	$3{\cdot}26 \times 10^{4}$
141	318	—	—	311	$1{\cdot}96 \times 10^{5}$	314	$7{\cdot}1 \times 10^{3}$
146	352	145	16·4	289	$3{\cdot}66 \times 10^{4}$	290	228
183	1210	182	49·6	241	$2{\cdot}7 \times 10^{3}$	242	14·6
202	$2{\cdot}26 \times 10^{3}$	204	76	226	372	228	20·2
235	$5{\cdot}12 \times 10^{3}$	237	161	195	27	197·5	4·4
270	$8{\cdot}3 \times 10^{3}$	272	373	123·5	8·7	—	—
296	$3{\cdot}3 \times 10^{4}$	296	733				

The meaning of these numbers is best expressed graphically. In fig. 22 the logarithm of the current has been plotted against the temperature. The unit of current is 10^{-12} ampère. Curves 1 and 2 were taken with the wire charged positively, 3 and 4 with the wire charged negatively. The observations for curves 1 and 3 were made simultaneously with the temperature of the tube rising, whereas the curves 2 and 4 correspond to the second set of observations with the temperature falling.

The various marks refer to observational points for the different curves as follows:—○ to No. 1, ∗ to No. 2, ⊙ to No. 3, and · to No. 4.

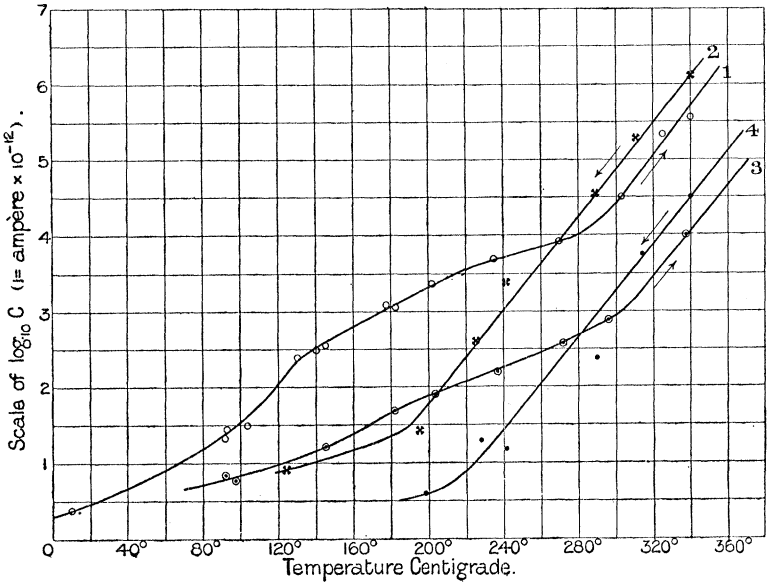

Fig. 22.

It will be noticed that the two curves belonging to any one set of observations become parallel above about 180°. The constant distance apart of the curves, which is approximately the same for the two sets of observations when measured along the vertical ordinate, has an average value of about 1·6. This shows that the ratio of the currents in opposite directions remains constant and independent of the temperature (above 180°) and is equal to about 40 to 1. The point of inflexion at about 280° on the up curves probably indicates an accidental change in the sodium surface, since it was not repeated on cooling.

C.—Conclusion.

§ 1. *The Determination of the Number of Ions in a Cubic Centimetre of Metal.*

The preceding results show that the number of negative ions produced by one square centimetre of surface of platinum, carbon, and sodium at temperature θ can be represented with fair accuracy by the formula $N = A\theta^{\frac{1}{2}}e^{-b/\theta} = A_1 n\theta^{\frac{1}{2}}e^{-b/\theta}$, where A and b are assumed to be definite constants for each metal. As an empirical result we find A and b have the values given in the following table :—

Conductor.	A.	b.
Platinum	10^{26}	$4{\cdot}93 \times 10^4$
Carbon	10^{34}	$7{\cdot}8 \times 10^4$
		$9{\cdot}7 \times 10^4$
		$11{\cdot}9 \times 10^4$
Sodium	10^{31}	$3{\cdot}16 \times 10^4$

The value of A is determined from that of b and so depends very largely on the value selected for b. An error of 10 per cent. in b multiplies A by about 100, whilst if b were determined wrongly to one part in three, A would be multiplied by 3×10^7. For this reason only the order of magnitude of A has been given in the table.

If we can assume that A and b are constants independent of the temperature, we obtain the value of n, the number of free corpuscles per cubic centimetre of the conductor, at once from the theory by dividing A by 10^5. Treating the values of A in this way, we find that the value of n for platinum agrees satisfactorily with that obtained by Mr. PATTERSON. On the other hand, the values (10^{29}) for carbon and (10^{26}) for sodium are greater than the maximum possible value. Moreover, the error in each case seems greater than can be accounted for by experimental uncertainties.

This error is probably due in part to the assumption that A and b are constants, whereas it is evident that they must both be functions of the temperature. It is possible on the preceding theory to say something about the forms of these functions which indicate that they both vary with the temperature.

With regard to the number n of corpuscles per cubic centimetre of metal, we suppose they are formed by decomposition of the neutral atoms in much the same way as in any case of chemical dissociation. If C_1 be the number of positive and C_2 of negative ions per cubic centimetre ($C_1 = C_2 = C$ as a rule), C_m being the number of undissociated atoms per cubic centimetre, and $C_0 (= C_m + C)$ being the value which C_m would possess if there were no dissociation, then:

$$C^2 \equiv C_1 C_2 = k C_m \equiv k (C_0 - C),$$

since the number of re-combinations per second is proportional to $C_1 C_2$, whilst the number of dissociations is proportional to C_m, and these two must be equal in the steady state.

Now VAN 'T HOFF* has shown that for all re-actions of this type the quantity k varies with the temperature according to the equation

$$\frac{d}{d\theta} (\log k) = q/2\theta^2,$$

q being the heat evolved when two ions re-combine, whence

$$k = A e^{-q/2\theta}.$$

A must be very large, for when $\theta = \infty$, $k = (A)$ must be great compared with C_0. We may write C in the form

$$C = \sqrt{(\tfrac{1}{4}k^2 + k C_0)} - \tfrac{1}{2}k,$$

whence we see that when $\theta = 0$, $k = 0$, and $C = 0$; when $\theta = \infty$, k is large compared with C_0 and $C = C_0$.

We see from the nature of the above function that the value of k would decrease

* 'Lectures on Phys. Chem.,' vol. 1, p. 141.

with enormous rapidity in the neighbourhood of the absolute zero; so that, although the resistance of metals decreases steadily with decreasing temperature down to the lowest temperatures yet reached, it is quite possible that it becomes infinite again at the absolute zero. The fact that the resistance of pure metals is proportional to the absolute temperature over a wide range, together with the high values of n which prevail at ordinary temperatures, seems to indicate that for most metals k has practically reached its maximum value, where it varies only slightly with θ.

For this reason we are led to the conclusion that the discrepancies of n are not due so much to disturbances produced by its temperature-variation (except, perhaps, in the case of carbon) as to the fact that the exponential coefficient b is a function of θ. We have seen that $b = \Phi/\mathrm{R}$, where Φ is the work done by a corpuscle in escaping from the metal, and R is the gas constant for a single corpuscle. Now $\mathrm{R} = \frac{5}{2}\frac{5}{7}\frac{5}{3} \times 10^{-14}$ roughly, and $b = 5 \times 10^{-4}$ for platinum, so that Φ is approximately equal to 10^{-11}.

A second approximation to the value of Φ is obtained when we consider the nature of the forces which retain the corpuscles inside the metal. These are a sort of integrated effect of the attractions of the positive and negative ions scattered about in the metal near the corpuscle. The field would thus be much the same as if the corpuscles were surrounded by a perfect spherical conductor of molecular dimensions. The quantity Φ is therefore of the same order as the energy required to remove a corpuscle from inside such a charged sphere, which is $\frac{1}{2}e^2/\zeta$, where e is the charge on an ion and ζ is the radius of an atom. Taking $\zeta = 2 \times 10^{-8}$ centim., this gives $\Phi = 9 \times 10^{-12}$.

If this view is correct—it hardly seems likely that the above numerical agreement is entirely a coincidence—we should expect the value of b to decrease as the temperature is raised owing to the greater distance of the atoms apart. We should therefore expect b to decrease in much the same way as the linear dimensions of the metal increase with the temperature. It is probable, therefore, that b can be represented with sufficient accuracy as a function of the temperature of the form $b = \alpha_1 - \alpha_2\theta$. Writing the equation at the beginning of this section in the form

$$\log \mathrm{C} = \log \mathrm{A}_1 + \tfrac{1}{2} \log \theta + \log n - b/\theta,$$

we see that the first three terms (with the possible exception of $\log n$, which we are not considering) vary extremely slowly with θ, if at all, so that we may use as an approximation

$$\log \mathrm{C} = \alpha_3 - b/\theta,$$

where $\alpha_3 = \log \mathrm{A}_1 + \frac{1}{2} \log \theta + \log n$. If now we put $b = \alpha_1 - \alpha_2\theta$, we see that $\log \mathrm{C} = \alpha_3 + \alpha_2 - \alpha_1/\theta$. So that, as we found in the experiments, $\log \mathrm{C}$ is a linear function of $1/\theta$, but the constant A from which n is determined is much larger than it ought to be, owing to part of b having become added to it.

As a numerical example, we may give to b the value $5 \times 10^4 - 7\theta$, which corresponds to a temperature coefficient of ·00014 per degree, and would change the value of b by 20 per cent. in a range of 1400°. On calculating out we find that this small temperature coefficient would leave b practically unaltered, but would make the apparent value of n one thousand times its true value, whilst doubling the coefficient would square the error in n, and so on. It is therefore evident that the temperature variation of b is quite adequate to explain the large values of n which have been found. Moreover, owing to the peculiar nature of the functions, it is impossible to arrive at the true values of n by this method.

The value of A found in these experiments are therefore not irreconcileable with the values of n given by Mr. PATTERSON, but the two values of n can be made identical by assigning to b a small temperature coefficient. The coefficients necessary have been calculated, and, together with corresponding orders of magnitude of A and of n, are given in the following table.

Conductor.	Order of A.	Order of n.	Value of b with temperature coefficient to give value of n in last column.
Platinum	10^{26}	10^{21}	$4 \cdot 93 \times 10^4$
Carbon	10^{34}	10^{20}	$7 \cdot 8 \times 10^4 (1 - \cdot 00027\theta)$*
Sodium	10^{31}	10^{23}	$3 \cdot 16 \times 10^4 (1 - \cdot 00022\theta)$†

From the values of b we can calculate the work done by an ion in passing through the surface, and hence the discontinuity of potential between the metal and the surrounding space. For the case of platinum this has already been done, the value obtained being 4·1 volts. For carbon and sodium, taking into account the temperature coefficients given above, we find for the discontinuity at 15° C. the values 6·1 and 2·45 volts respectively. It will be noticed that these numbers follow the same order as the Volta series, though their differences (at any rate for carbon and platinum) are not equal to the corresponding contact electromotive force.

§ 2. *The work done by a Corpuscle in passing through the Surface Layer.*

It has been shown on p. 543 that the value of Φ is of the same order of magnitude as $\frac{1}{2} e^2/\zeta$, where e is the charge on an ion and ζ is the radius of a molecule; it is therefore also of the same order of magnitude as the energy set free when two ions of opposite sign re-combine, and as the work required to produce an ion by collision. Theoretical considerations, in conjunction with the experimental results, render it probable that Φ may be represented very approximately as a linear function of the

* θ is the absolute temperature.

† It is noteworthy that this number ·00022 is practically equal to the coefficient of cubical expansion of sodium (·000204).

temperature, whilst the numbers given on p. 544 show that the temperature coefficient of Φ is of the same order of magnitude as the coefficient of linear expansion of the corresponding solid conductor.

These facts render it probable that Φ is a function of the size and distance apart of the molecules of which the conductor consists. If we consider ζ in the formula $\Phi = \frac{1}{2} e^2/\zeta$ as the distance apart of the centres of the molecules in the solid state, it will be proportional to the cube root of the atomic volume. We should therefore expect the work done by a corpuscle in passing through the surface layer of different metals to be approximately equal to a constant divided by the cube root of the atomic volume. Up to the present Φ has been determined only for sodium, platinum and carbon, but fortunately these three elements furnish a considerable range of atomic volume. As a matter of fact, carbon has the smallest atomic volume of all elements, whilst that of sodium is only exceeded by the alkali metals of greater atomic weight.

In the accompanying table values of the atomic volume and the inverse of its cube root are given in the first two columns. The third contains the surface discontinuity in the potential $\delta\phi$, which is proportional to Φ; whilst the numbers in the last column are the ratios of those in the second and third. In the case of carbon there is some doubt as to what the value of the atomic volume should be, since the density has different values for the different allotropic forms. Thus for charcoal the density is 1·9, for graphite 2·2, and for diamond 3·5.

Element.	At. vol.	(At. vol.)$^{-\frac{1}{3}}$.	$\delta\phi$ [volts].	(At. vol.)$^{-\frac{1}{3}}/\delta\phi$.
Sodium.	23	·35	2·45	·14
Platinum	9·3	·476	4·1	·12
Carbon charcoal.	6·3	·55	6·1	·09
„ diamond	3·46	·66	—	·11

It will be seen that the numbers in the last column are not quite constant; but they only change by about 40 per cent., whilst the atomic volume changes in the ratio of 6 to 1, and the atomic weight varies from 12 to 195. It seems therefore fair to conclude that the work done by a corpuscle in passing through the surface layer is, to a first approximation, inversely proportional to the cube root of the atomic volume of the element.

§ 3. *The Effect of Gas on the Current.*

The negative leak from a hot platinum wire surrounded by air at atmospheric pressure is always much smaller under a given voltage than at low pressures, when the wire is maintained at the same temperature in both cases. In one case, when the wire was giving a current of 3×10^{-6} ampère at a pressure of ·05 millim., air

was let into the apparatus and the current again measured under atmospheric pressure at the same temperature. It was found that there was no detectable leak till a temperature of 60° higher was reached, when one division of the galvanometer scale (3×10^{-8} ampère) was obtained with the wire at a potential of — 200 volts. The small value of the currents at atmospheric pressure is probably due to the difficulty of saturating them.

It was thought conceivable that the ionisation at low pressures might be due to the gas molecules hitting the hot wire and becoming ionised thereby. If we assume that the maximum current would correspond to each molecule producing one ion, we can calculate its value in any given case. If we take the number of molecules in a cubic centimetre of gas at 0° C. and 760 millims. to be 2×10^{19}, then the number which hit unit area of the wire per second is $\frac{1}{6}u \times 2 \times 10^{19}$ approximately, where u (the square root of the mean velocity square) may be taken as 5×10^4 centims. per second for air. The number which strike unit area of the wire per second at 1 millim. pressure is therefore $2{\cdot}2 \times 10^{20}$, which gives a saturation current of $14{\cdot}3 \times 10^{10}$ electrostatic units, or 47·3 ampères per square centimetre. At a pressure ·0016 this current would become ·08 ampère per square centimetre. As a matter of fact, during the experiments, a current of 2·0 ampères per square centimetre was obtained at ·0016 millim. pressure. This is twenty-five times the maximum value obtained by supposing each molecule to produce one ion; so that it is highly improbable that any considerable part of the conductivity investigated is due to ions produced in this way.

Another way of considering this question is to calculate the number of times each molecule of air inside the cylindrical electrode must collide with the filament per second to produce the observed current, assuming that each collision sets free one corpuscle. In the experiments in question the cylinder had a volume of about 1 cub. centim., so that each molecule present would have to pass backwards and forwards between the filament and the cylinder some 10^5 times each second. This seems to be an impossible feat for an uncharged molecule.

Both these points of view lead to the conclusion that the corpuscles are not produced by a dynamical action between the molecules of the surrounding gas and the surface of the metal. In fact, all the experimental results seem to point to the view that the corpuscles are produced from the metal by a process similar to evaporation. The effect of the surrounding gas, of impurities in the wire, and of its previous history are to be regarded as due to alterations in the property of the metal which corresponds to latent heat in the theory of evaporation.

§ 4. *The Edison Effect.*

It will readily be seen that the results which have been obtained furnish a complete explanation of the phenomenon known as the Edison effect. Edison first discovered this effect by connecting an insulated electrode, which was symmetrically

placed between the ends of the filament of an incandescent lamp, through a galvanometer to the positive end of the filament. A current was then observed which amounted in some cases to several milliampères, although there was no current when the electrode was joined to the negative terminal. Evidently the current was carried by corpuscles passing from the negative portions of the hot carbon to the relatively positive electrode; and, on this view, we should expect the current to vanish by comparison when the electrode was negative with respect to the filament.

This observation was confirmed and extended by Professor Fleming,* who showed, by using cylindrical electrodes which he placed round various parts of the filament, that the current only came from the negative end. He also found, in agreement with the results of the present paper, that a platinum filament likewise gave an effect. This was in the same direction as, but greater in magnitude than, that given by carbon. Finally, the Edison effect was found to increase rapidly with the temperature of the filament, which confirms its identification with the phenomena here investigated.

§ 5. *The Energy Emitted.*

It is of interest to compare the energy lost by a hot body owing to the emission of corpuscles with the energy given off in the form of electro-magnetic radiation. The recent measurements of F. Kurlbaum† show that the energy radiated in 1 second from 1 sq. centim. of the surface of an absolutely black body at 1° absolute is

$$S = 2{\cdot}12 \times 10^{-4} \frac{\text{erg}}{\text{centim. sec. deg.}^4},$$

whilst we have seen that the total rate of loss of energy of a conductor owing to the emission of corpuscles at temperature θ absolute is

$$E_\theta = n\{1 + \Phi/2R\theta\}\sqrt{\frac{2R^3\theta^3}{\pi m}}\, e^{-\Phi/R\theta}.$$

Since the quantities Φ and n in this formula have now been determined for carbon and platinum, we can calculate E at any temperature for these substances. The first term in brackets represents the part of the energy due to the motion of translation of the emitted corpuscles, and is less than 5 per cent. of the second term at all temperatures at which experiments have been carried out. We may therefore leave it out to a first approximation and calculate only the second term, which is equal to the work done by the corpuscles in passing through the surface layer. This is obviously equal to $N\Phi$

$$= C_0\delta\Phi,$$

* 'Phil. Mag.' [5], vol. 42, p. 52.

† 'Wied. Ann.,' vol. 65, p. 759.

where $\delta\Phi$ is the discontinuity in the potential, and C_0 is the saturation current per unit area.

Calculating in this way we find that for platinum at $\theta = 1900$ $E = 8 \times 10^4$ ergs/centim. sec. The value of S_{1900} is a much larger quantity, viz., $2{\cdot}75 \times 10^9$ ergs/centim. sec. The largest experimental values of E were obtained with carbon. Since the greatest value of the saturation current attained was $C_0 = 1{\cdot}5$ ampère $= 4{\cdot}5 \times 10^9$ electrostatic units per square centimetre and $\delta\Phi = 6$ volts, we have the rate at which energy is lost by the wire $= 9 \times 10^7$ ergs/centim. sec. The temperature corresponding to this current was not measured, but was certainly greater than 2000° absolute. The energy radiated from an absolutely black body at 2000° absolute would have been $3{\cdot}36 \times 10^9$ ergs/centim. sec.

We see then that at all the temperatures at which experiments were made the loss of energy due to the escape of the corpuscles is much less than that due to the emission of ordinary electromagnetic radiation; on the other hand, it increases much more rapidly with the temperature, so that, in the case of carbon at any rate, it would become first equal to, and finally great compared with, the electromagnetic radiation, at temperatures not much above 2000° C. It must not be forgotten that for this calculation the hot conductor is supposed to be placed in a vacuum and surrounded by an electric field which removes the ions; otherwise all the ions diffuse back to the metal and there is no loss of energy due to this cause.

In all these experiments we are a long way from the region where an appreciable fraction of the total number of ions which strike the surface of the conductor pass through. This is easily seen if we calculate the value of the saturation current per unit area on the supposition that every corpuscle which hits the surface escapes. Let us take $n = 10^{22}$ as a probable maximum for the number of corpuscles in a cubic centimetre of, say, carbon; then, at 2730° absolute $\frac{1}{6}nu = 3 \times 10^{28}$, so that the saturation current would be 18×10^{18} electrostatic units or 6×10^9 ampères per square centimetre. As the largest current which has been yet obtained is 2·0 ampères per square centimetre, it is evident that we are still a long way from the limit. This calculation seems to indicate that the region on the current temperature diagram when the current begins to be proportional to the square root of the absolute temperature is much higher than any temperature which can be reached in the ordinary way.

The magnitude of the currents which have been obtained with low voltages indicate that a vacuum bounded by a hot conductor is, at any rate under certain circumstances, an extremely good conductor of electricity. In fact, it seems probable that such a vacuum is capable of becoming the best conductor that can possibly be obtained. The conductivity of metals is limited by the shortness of the mean free path of the ions, whereas the mean free path of a corpuscle in an atmosphere of corpuscles is probably very large. All that is necessary, therefore, to produce a big current is to supply the ions quickly enough at the hot surface, that is, to raise the

temperature of the hot conductor to a sufficient extent. The experiments also seem to show that as far as electrical conductivity is concerned, the boundary of a hot conductor is an indefinite term; since so many of the corpuscles pass freely to the outside of the metal it is evident that at high enough temperatures quite an appreciable fraction of the current along a wire must be carried by the ions in the surrounding space.

In conclusion, I wish to thank Professor THOMSON for his never-failing advice and encouragement during the course of these experiments, which were carried out in the Cavendish Laboratory.

[*Note, added June* 30, 1903.—Since the present paper was written Mr. H. A. WILSON has made some experiments on the conductivity produced by hot platinum at low pressures, in which he finds that by carefully treating the wire the current can be reduced to about one two hundred thousandth of the value found by the author at the same temperature. Mr. WILSON also shows that the current is greatly increased by admitting hydrogen into the apparatus, and concludes that the high values found in this paper are due to hydrogen absorbed by the wire, which is only given off very slowly, if at all, by mere heating.

These results are not, however, inconsistent with the view that the effects are due to electrons shot out of the metal. To obtain the observed facts we have only to suppose that the occlusion of hydrogen diminishes the work which a corpuscle has to do in escaping from the surface. Mr. WILSON's own results are in agreement with this theory, for he finds that raising the pressure of hydrogen from 0 to 133 millims. reduces the value of the work in question in the ratio of 155 to 36. It might be thought that on this view the constant A which determines the number of ions per cub. centim. of platinum should be independent of the pressure of the hydrogen outside. The numbers found by Mr. WILSON do not support this supposition, but the numerous practical and theoretical difficulties demand that little weight should be attached to the difference.

It is possible that Mr. WILSON's process of removing hydrogen from a wire by oxidation may, as it were, overshoot the mark by leaving an electrical double layer with negatively charged oxygen on the outside. Such a double layer would increase the work for the corpuscles to get out and so would reduce the leak in the manner observed.]