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The Mobility of Negative Ions at Low Pressures.
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FROM the experiments made by Franck and Pohl on the mobility of the negative ions in argon and nitrogen carefully freed from oxygen, and also from the very interesting investigation on the mobility of the negative ions in air, recently published by Wellisch *, it seems clear that the electron can traverse in a free state distances which are large compared with the mean free path. In a recent communication to the Cambridge Philosophical Society, I showed that this result would explain many of the peculiarities shown by the negative ion at low pressures, such, for example, as its abnormally large mobility and the lack of proportionality between its velocity and the electric force acting upon it. In this paper I wish to find expressions for the magnitude of effects due to this cause and the factors on which they depend.

The case considered is when the charged particles are moving under a uniform electric field through gas enclosed by two parallel plates at right angles to the lines of electric force: this corresponds to the conditions under which the mobility of the negative ion is usually investigated. All the negative ions are supposed to begin as electrons, though some of them ultimately unite with the molecules of the gas and become negative ions. It is probable that when

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once the electron has become attached to a molecule it stays so for a time which is large compared with its life as a free electron; for the sake of simplicity we shall suppose that when once the electron is attached to a molecule it reaches one of the parallel plates and is removed from the field before it gets free again.

Let X be the electric force between the plates, k_1 the mobility of the electron, then k_1X is the velocity of drift of the electron: we assume that this is small compared with V, the velocity of the electron due to thermal agitation. We shall suppose that when an electron collides with a molecule the chance of its uniting with it and forming a negative ion is $1/n$.

We shall first calculate the expectation of an electron traversing a distance x parallel to the electric force without becoming attached to a molecule.

The time taken by the electron to traverse this distance is x/k_1X, and in this time, since V is assumed to be large compared with k_1X, it passes over a space which is approximately Vx/k_1X. We shall write α for V/k_1X, so that this space is equal to αx.

The expectation of the electron travelling over this space without a collision is $\epsilon^{-\alpha x/\lambda}$, where λ is the mean free path of the electron, and this is the expectation that it should pass over this space without making a collision and without uniting with a molecule and becoming a negative ion. The expectation that it makes one collision, but no more, in passing over the space x may be found as follows. The expectation that it passes over a distance ξ without a collision is $\epsilon^{-\alpha\xi/\lambda}$; the expectation that it should make a collision between ξ and $\xi+d\xi$ is $\alpha d\xi/\lambda$; and the expectation that it should make the rest of the journey without a collision is $\epsilon^{-\alpha(x-\xi)/\lambda}$. Hence the expectation that it makes but one collision, and that between ξ and $\xi+d\xi$, is

$$\epsilon^{-\alpha\xi/\lambda}(\alpha d\xi/\lambda)\epsilon^{-\alpha(x-\xi)/\lambda} \text{ or } \frac{1}{\lambda}\epsilon^{-\alpha x/\lambda}\alpha d\xi.$$

Hence the expectation that it makes one and only one collision in the whole journey is

$$\int_0^x \epsilon^{-\alpha x/\lambda}\frac{\alpha d\xi}{\lambda} \text{ or } \epsilon^{-\alpha x/\lambda}\alpha x/\lambda.$$

The expectation that this collision does not result in recombination is $(n-1)/n$. Hence the expectation of the one-collision electron traversing x without becoming a negative ion is

$$\epsilon^{-ax/\lambda}\left(\frac{n-1}{n}\right)\frac{\alpha x}{\lambda}.$$

The expectation that the electron makes two collisions and no more is

$$\int_0^x \epsilon^{-a\xi/\lambda}\frac{\alpha\xi}{\lambda}\cdot\frac{\alpha d\xi}{\lambda}\cdot\epsilon^{-a(x-\xi)/\lambda};$$

for $\epsilon^{-a\xi/\lambda}(\alpha\xi/\lambda)$ is the expectation that it should have made one, and only one, collision before reaching ξ; $\alpha d\xi/\lambda$, the expectation that it should make a collision between ξ and $\xi+d\xi$; and $\epsilon^{-a(x-\xi)/\lambda}$, the expectation that it should not make a collision in the rest of its journey. The value of the integral is

$$\tfrac{1}{2}\epsilon^{-ax/\lambda}\left(\frac{\alpha x}{\lambda}\right)^2.$$

The expectation that neither of the collisions should result in union is $((n-1)/n)^2$. Hence the expectation for a two-collision electron without recombination is

$$\epsilon^{-ax/\lambda}\frac{1}{2}\left(\frac{n-1}{n}\frac{\alpha x}{\lambda}\right)^2.$$

Similarly the expectation for a three-collision electron without union is

$$\epsilon^{-ax/\lambda}\frac{1}{2\,.\,3}\left(\frac{n-1}{n}\frac{\alpha x}{\lambda}\right)^3,$$

and so on. Hence, since any electron must have made collisions varying in number from nought to infinity, the expectation of the electron traversing the distance x in a free state is

$$\epsilon^{-ax/\lambda}\left\{1+\frac{n-1}{n}\frac{\alpha x}{\lambda}+\frac{1}{2}\left(\frac{n-1}{n}\frac{\alpha x}{\lambda}\right)^2+\frac{1}{2\,.\,3}\left(\frac{n-1}{n}\frac{\alpha x}{\lambda}\right)^3+\dots\right\}$$
$$=\epsilon^{-ax/\lambda}\ \epsilon^{(n-1)ax/n\lambda}=\epsilon^{-ax/n\lambda}.$$

Thus if N electrons start from $x=0$ the number which traverse x without recombination is $N\epsilon^{-ax/n\lambda}$.

In experiments on the mobility of ions the quantity measured is, in many cases, the charge of electricity received by one plate during an interval T when a layer of gas close to the other plate has been ionized at the beginning of the interval by a flash of Röntgen rays. If d is the distance between the plates, it is evident that no charge at all will be received until $T=d/k_1X$, and that apart from the loss by recombination all the negative ions will have reached the plate when $T=d/k_2X$, where k_2 is the mobility of the negative ion, k_1 that of the electron, and X the electric force between the plates. When T is between these limits the charge which reaches the plates can be readily calculated by the aid of the preceding expression. Let us consider the case of a negative particle which takes the whole time T to get across, travelling through a distance x as an electron and $d-x$ as a negative ion. We have

$$\frac{x}{k_1X}+\frac{d-x}{k_2X}=T,$$

$$x=\frac{d-k_2XT}{(1-k_2/k_1)}.$$

All the molecules which reach this distance x without combining will be in time to give up their charge to the plate, while those which combine before reaching this distance will be too late. Thus the charge Q received by the plate will be the charge carried by those electrons which travel this distance without combining, and this by the preceding expression is equal to

$$Ne\,\epsilon^{-\frac{a}{n\lambda}\frac{(d-k_2XT)}{(1-k_2/k_1)}},$$

where e is the charge on an electron and $\alpha=V/k_1X$.

We see that Q is a function of T, of the electric force, of the distance between the plates, of the pressure (since λ and the k's vary inversely as the pressure), and of the temperature through V.

Let us consider how Q varies when any one of these quantities changes, the others remaining constant.

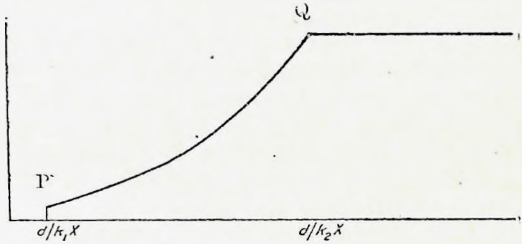
Variation of Q *with* T.—Considered as a function of T, Q is zero until $T=d/k_1X$ and becomes constant when T equals d/k_2X; between these limits it varies as $\epsilon^{\mu T}$, where $\mu=Vk_2/n\lambda(k_1-k_2)$.

The graph representing the relation between Q and T is shown in fig. 1. By means of the points P and Q we can determine k_1 and k_2, while μ can be determined by the equation

$$\log(Q_1/Q_2)=\mu(T_1-T_2),$$

where Q_1 and Q_2 are the values of Q corresponding to the intervals T_1 and T_2. When k_1, k_2, and μ are known we can determine the value of $n\lambda$.

Fig. 1.

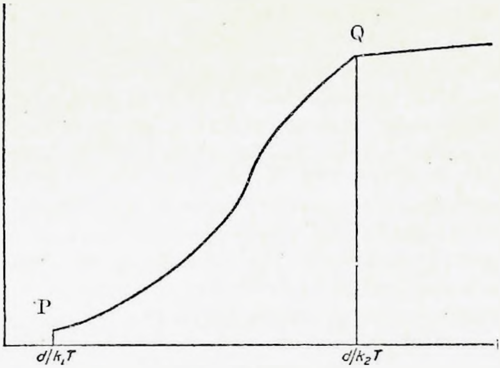


Variation of Q *with* X.—Considered as a function of X, Q varies as $\epsilon^{-\frac{\mu d}{k_2 X}}$. The smallest value of X which can send any charge to the plate is d/k_1T, and when $X=d/k_2T$, Q reaches the maximum value Ne. The Q and X graph has a point of inflexion when

$$X=\mu d/2k_2=Vd/2n\lambda(k_1-k_2).$$

The shape of the graph is shown in fig. 2. From the

Fig. 2.



points P and Q the values of k_1 and k_2 can be determined, and μ, and therefore $n\lambda$ by means of the equation

$$\log(Q_1/Q_2)=\frac{\mu d}{k_2}\left(\frac{1}{X_2}-\frac{1}{X_1}\right),$$

where Q_1 and Q_2 are the values corresponding to X_1 and X_2 respectively.

Variation of Q *with the pressure.*—Since k_1, k_2, and λ are all inversely proportional to the pressure p, Q will be of the form $\epsilon^{-\beta p(p-\gamma)}$. Q will therefore be very small until p diminishes so as to be comparable with $\beta^{-\frac{1}{2}}$. At this stage it will rapidly increase as the pressure diminishes, and there will be be an appreciable number of ions crossing with a mobility greater than k_2, and thus possessing an abnormally large mobility. Since β is proportional to d/X, the abnormality will set in at higher and higher pressures, as d is diminished and X increased. The apparent mobility will thus depend on the electric force, and also it will no longer be inversely proportional to the pressure.

Considered as a function of d, Q varies as $\epsilon^{-\frac{Vd}{n\lambda(k_1-k_2)}}$ and thus diminishes exponentially with d. Since V varies as $\theta^{\frac{1}{2}}$ where θ is the absolute temperature, Q will vary as $\epsilon^{-f\theta^{\frac{1}{2}}/n}$. It is probable that the electron would more readily escape from a molecule against which it struck when its kinetic energy is large than when it is small, so that we should expect n to depend upon θ; n and θ increasing together.

It will be seen from the preceding results that the mobility of a negative particle, as measured by its average velocity over a given distance when acted on by unit electric force, is not a definite quantity; some particles have one mobility, others another, and particles can be found possessing any given mobility, provided this is between k_1 and k_2. When, however, the conditions are such that $dV/n\lambda k_1X$ is large, as it will be unless the pressure is so low that $n\lambda$ is comparable with d, the number of particles having mobilities appreciably greater than k_2 is exceedingly small, so that in this case the mobility of the negative particle is substantially definite.

The number of ions which have a mobility greater than some given value K can easily be calculated as follows. If the electron travels a distance at least equal to x before uniting with a molecule to form a negative ion, the time taken to traverse the distance d will not be greater than

$$\frac{x}{k_1X}+\frac{d-x}{k_2X}.$$

The average speed will therefore not be less than

$$\frac{dX}{x/k_1+(d-x)/k_2};$$

so that K the mobility will not be less than

$$\frac{d}{x/k_1+(d-x)/k_2}.$$

The value of x which makes this expression equal to K is given by the equation

$$x=\frac{d(1-k_2/K)}{(1-k_2/k_1)}.$$

The number of particles which have a mobility not less than K is the same as the number of electrons which travel a distance x without uniting with a molecule, and by the preceding expression is equal to

$$N\epsilon^{-\frac{d}{n\lambda}\frac{(1-k_2/K)}{(1-k_2/k_1)}\frac{V}{k_1X}}.$$

If we take as a measure of the mobility of the negative particles a mobility such that half the particles have mobilities greater and half less than this value, then K must make this expression equal to N/2, and therefore

$$\frac{d(1-k_2/K)}{(1-k_2/k_1)}\frac{V}{Xk_1n\lambda}=\cdot 693,$$

or

$$\frac{K-k_2}{K}=\cdot 693\,\frac{n\lambda}{d}\,.\,\frac{X(k_1-k_2)}{V}.$$

Since Xk_1/V is the ratio of the speed parallel to x to the total speed of the electron, it is never greater than unity, so that K will not differ appreciably from k_2 until $n\lambda$ is comparable with d. When $n\lambda$ is large compared with d, and Xk_1 smaller than V, K will increase with X, and in this case the mobility of the negative ion will increase with the electric force.

We have supposed that there was a flash of ionization at the beginning of the interval T. If, however, the ionization is continuous over this time and if q electrons are produced per second, the number reaching the plate will, if T is less than d/k_2X, be equal to

$$\int_0^{T-d/k_1X} q\,\epsilon^{-v(d-k_2X(T-t))}\,dt$$

or

$$\frac{q}{v}\left(\epsilon^{-v(d-k_2T)}-\epsilon^{-vd\left(1-\frac{k_2}{k_1}\right)}\right)\quad\ldots\ldots\quad(a)$$

where

$$v=V/k_1Xn\lambda(1-k_2/k_1).$$

If T is greater than d/k_2X, then all the ions emitted from

$t=0$ to $t=\mathrm{T}-\dfrac{d}{k_2\mathrm{X}}$ reach the plate, so that the total number reaching the plate is

$$q\left(\mathrm{T}-\frac{d}{k_2\mathrm{X}}\right)+\int_{\mathrm{T}-d/k_2\mathrm{X}}^{\mathrm{T}-d/k_1\mathrm{X}} q\epsilon^{-v(d-k_2\mathrm{X}(\mathrm{T}-t))}\,dt$$

$$=q\left(\mathrm{T}-\frac{d}{k_2\mathrm{X}}\right)+\frac{q}{v}\left(1-\epsilon^{-vd\left(1-\frac{k_2}{k_1}\right)}\right) \quad . \quad . \quad . \quad (\beta)$$

If we regard T as constant, then Q the quantity reaching the plate will be represented by (a) from $\mathrm{X}=d/k_1\mathrm{T}$ to $\mathrm{X}=d/k_2\mathrm{T}$ and for greater values of X by (β). The graph representing the relation between Q and X will differ from that represented in fig. 2, in that it will start from zero when $\mathrm{X}=d/k_1\mathrm{T}$ and will not reach a constant value when $\mathrm{X}=d/k_2\mathrm{T}$, but will asymptotically approach the constant value $q\mathrm{T}$.

In comparing the preceding theory with experiment it is necessary to remember that we have supposed all the negative particles to leave one plate as electrons; we could not directly apply it to such a case as that tried by Mr. Wellisch, when the gas was ionized behind the plate by polonium and the negative ions driven through holes in this plate by a small electric field. With this arrangement some of the electrons may unite with the molecules before they get through the plate, and so start on their journey as ions and not as electrons; it is possible too that some methods of ionization may produce negative ions initially as well as electrons. It would be necessary to test the theory to produce the electrons at the surface of the plate, either by incandescent metal or by allowing ultra-violet light to fall on the plate.

We have at present, except in the case of flames, no direct determinations of k_1 the mobility of an electron: these, however, would be of very great value and would enable us to settle many points in connexion with the theory of the mobility of ions which are at present uncertain. The advantage possessed by the electron is that there is no uncertainty as to its nature: it is the same whatever may be the nature, temperature, or pressure of the gas. The ion, on the other hand, whether positive or negative may vary with each or all of these conditions. This uncertainty as to the size of the ion makes the evidence as to the nature of the action between ions and molecules, afforded by such phenomena as the variation of their mobility with temperature, pressure, and the nature of the gas, ambiguous.