THE DISTRIBUTION OF IONS FORMED BY ATTACHMENT OF ELECTRONS MOVING IN A STEADY STATE OF MOTION THROUGH A GAS

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Summary

The distribution of ions formed by attachment of electrons diffusing through a gas is solved exactly, and the results compared with an approximate calculation given earlier by Huxley. The corrections to the approximate results are inside the present experimental error, and so confirm the satisfactory agreement with experiment already obtained.

I. Introduction

The distribution of electrons and ions in a stream from a pole source and drifting and diffusing in a gas when the processes of ionization by collision and attachment to molecules are active, has been discussed in another paper (Huxley 1959), where an exact solution is given for the distribution of the electrons and an approximate solution for that of the ions. It was apparent that under conditions where the mean energy of agitation of an electron was as great as 20 times that of a gas molecule, or greater, the approximation to the exact solution was close and that the theory could provide the basis of an accurate method for measuring the coefficients of attachment of electrons as a function of mean energy of agitation in a given gas.

This expectation has been justified by the application of the method to oxygen in which self-consistent and accurate measurements of attachment coefficients were made (Huxley, Crompton, and Bagot 1959).

It is important, however, to extend the measurements to the range of small energies of agitation of the electrons from approximate thermal equilibrium to about 20 times this value, and for this purpose an exact solution of the problem is required. This solution is given in what follows.

II. Distribution of Electrons

Consider a pole source of electrons placed at the origin of coordinates in a gas and emitting electrons at constant rate of S per second. Let W be the drift speed of electrons through the gas in a constant and uniform electric field E and let D be the coefficient of diffusion of the electrons. Suppose that the processes of ionization by collision and electron attachment are both operative with coefficients α_i and α_a respectively. If the positive direction of the axis Oz

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be chosen to be that of W, the differential equation satisfied by concentration n of electrons in the stream is (Huxley 1959)

$$\nabla^2 n = 2\lambda \partial n/\partial z + 2\lambda\alpha n, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where

$$2\lambda = W/D\ ; \quad \alpha = \alpha_a - \alpha_i.$$

The solution of equation (1) appropriate to the pole source at the origin is (Huxley 1959)

$$n(x,y,z) = (S/4\pi Dr)\exp(\lambda z - \mu r), \quad \ldots\ldots\ldots\ldots \quad (2)$$

where

$$\mu^2 = \lambda^2 + 2\lambda\alpha\ ; \quad r^2 = x^2 + y^2 + z^2.$$

The distribution n' due to a pole source of strength $S\exp(2\lambda h)$ placed at the point $(0,0,2h)$ is

$$\begin{aligned} n'(x,y,z) &= \{S\exp(2\lambda h)/4\pi Dr'\}\exp\{\lambda(z-2h)-\mu r'\} \\ &= (S/4\pi Dr')\exp(\lambda z - \mu r'), \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3) \end{aligned}$$

where

$$r' = \{x^2 + y^2 + (z-2h)^2\}^{\frac{1}{2}}.$$

It follows from equations (2) and (3) that the solution of equation (1) that represents the distribution $n(x,y,z)$ in a stream of electrons emitted at the rate S from a pole source at the origin and drifting and diffusing to a metal electrode coinciding with the plane $z=h$, over which n is now everywhere equal to zero, is (Huxley 1959)

$$n = (S/4\pi D)\exp(\lambda z)\cdot\{\exp(-\mu r)/r - \exp(-\mu r')/r'\}, \quad z \leqslant h,$$
$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

since $r = r'$ over the plane $z = h$.

III. Distribution of Ions

Consider the distribution of negative ions formed by attachment of electrons to molecules in the stream of electrons from the isolated pole source represented by equation (2). Let $N(x,y,z)$ be the concentration of the negative ions. The differential equation satisfied by N is,

$$\nabla^2 N = 2\lambda_1 \partial N/\partial z - (\alpha_a W_1/D_1)n, \quad \ldots\ldots\ldots\ldots \quad (5)$$

where

$$2\lambda_1 = W_1/D_1,$$

and W_1 and D_1 are the drift speed and the coefficient of diffusion respectively of the negative ions. The ratio λ/λ_1 is approximately (or, with a Maxwellian distribution of agitational speeds, exactly) equal to the ratio of the energies of agitation of ions and electrons respectively.

It is required to find the particular solution of equation (5) given that n is a solution of equation (1).

Put

$$P=C\exp(-kz)\int_{-\infty}^{z}\exp(kz')\cdot n\,dz', \qquad \ldots\ldots\ldots\ldots \quad (6)$$

in which C and k are constants.

It follows that

$$\left.\begin{aligned}\partial P/\partial z&=-kP+Cn,\\ \partial^2P/\partial z^2&=k^2P-Ckn+C\partial n/\partial z.\end{aligned}\right\} \qquad \ldots\ldots\ldots\ldots \quad (7)$$

and

Also, consider

$$I=C\exp(-kz)\int_{-\infty}^{z}\exp(kz')\frac{\partial^2 n}{\partial z'^2}dz', \qquad \ldots\ldots\ldots\ldots \quad (8)$$

and let $\exp(kz')\partial n/\partial z$ and $\exp(kz')n$ both approach zero as z' tends to $-\infty$. After two successive integrations by parts and comparison with equation (7) it can be seen that

$$I=\partial^2P/\partial z^2,$$

and also

$$\nabla^2P=C\exp(-kz)\int_{-\infty}^{z}\exp(kz')\nabla'^2n\,dz'. \qquad \ldots\ldots\ldots\ldots \quad (9)$$

To solve equation (5) substitute the value $N=P$ in equation (5) and use equations (7), (8), (9), and (1), to find

$$C\int_{-\infty}^{z}\exp(kz')\{2\lambda\partial n/\partial z'+2\lambda\alpha n+2\lambda_1kn\}dz'+(\alpha_aW/D_1-2\lambda_1C)n\exp(kz)=0.$$

On differentiating this equation with respect to z and collecting terms, it reduces to

$$(2\lambda\alpha C+\alpha_aWk/D_1)n+\{\alpha_aW/D_1-2(\lambda_1-\lambda)C\}\partial n/\partial z=0,$$

whence

$$\left.\begin{aligned}C&=\frac{\alpha_aW}{2(\lambda_1-\lambda)D_1}=\frac{\lambda\alpha_a}{(\lambda_1-\lambda)}\frac{D}{D_1},\\ k&=-\lambda\alpha/(\lambda_1-\lambda).\end{aligned}\right\} \qquad \ldots\ldots\ldots\ldots \quad (10)$$

Thus

$$N=\frac{\lambda\alpha_a}{(\lambda_1-\lambda)}\frac{D}{D_1}\exp\left(\frac{\lambda\alpha}{\lambda_1-\lambda}z\right)\int_{-\infty}^{z}\exp\left(-\frac{\lambda\alpha}{\lambda_1-\lambda}z'\right)n\,dz'. \qquad \ldots \quad (11)$$

When the solution of equation (1), $n=S\exp(\lambda z-\mu r)/4\pi Dr$, is adopted, then

$$N=\frac{S\alpha_a\lambda}{4\pi D_1(\lambda_1-\lambda)}\exp\left(\frac{\lambda\alpha}{\lambda_1-\lambda}z\right)\int_{-\infty}^{z}\exp\left\{\left(1-\frac{\alpha}{\lambda_1-\lambda}\right)\lambda z'-\mu r'\right\}dz'/r'.$$

$$\ldots\ldots\ldots\ldots \quad (12)$$

The distribution of electrons from a source at the origin and its image at $(0,0,2h)$ is given in equation (**4**) and the corresponding distribution of ions is

$$N=\frac{S\alpha_a\lambda}{4\pi D_1(\lambda_1-\lambda)}\exp\left(\frac{\lambda\alpha}{\lambda_1-\lambda}z\right)\int_{-\infty}^{z}\exp\left(1-\frac{\alpha}{\lambda_1-\lambda}\right)\lambda z'$$
$$\times\left\{\frac{\exp(-\mu r')}{r'}-\frac{\exp(-\mu r'')}{r''}\right\}\mathrm{d}z', \qquad z\leqslant h, \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (\mathbf{13})$$

where $r'=(\rho^2+z'^2)^{\frac{1}{2}}$, $r''=\{\rho^2+(z-2h)^2\}^{\frac{1}{2}}$, and $\rho^2=x^2+y^2$.

The current density J at a point (ρ,h) on the receiving electrode is $J=(\varepsilon N W_1)_{z=h}$ and when $\lambda_1\gg\lambda$ this expression becomes essentially the same as that derived by Huxley (1959, equation (**25**)).

An alternative solution of equation (**5**), namely,

$$N=-\frac{S\lambda\alpha_a}{4\pi D_1(\lambda_1-\lambda)}\exp\left(\frac{\lambda\alpha}{\lambda_1-\lambda}z\right)\int_{z}^{\infty}\exp\left(1-\frac{\alpha}{\lambda_1-\lambda}\right)\lambda z'$$
$$\times\left\{\frac{\exp(-\mu r')}{r'}-\frac{\exp(\mu r'')}{r''}\right\}\mathrm{d}z'$$

is inadmissible since in it N does not vanish at $z=-\infty$.

Equation (**13**) does not make $N=0$ at $z=h$, and so does not represent the exact solution. If a suitable solution of the homogeneous equation corresponding to (**5**) is added then this boundary condition can be satisfied. The resulting expression is rather complicated and can be evaluated only approximately. The physical basis of the approximation may be represented as follows : suppose a uniform stream to approach a plane electrode at right angles to the stream, the concentration at a large distance from the electrode being N_0.

At a distance s from the electrode, the concentation is

$$N=N_0\{1-\exp(-2\lambda_1 s)\}$$

and the flux of ions to an area $\mathrm{d}S$ of the electrode is

$$\left(D_1\frac{\mathrm{d}N}{\mathrm{d}S}\right)_{s=0}\mathrm{d}S=2\lambda_1 D_1 N_0\mathrm{d}S=W_1N_0\mathrm{d}S,$$

which is the flux across an element $\mathrm{d}S$ of a geometrical plane normal to the undisturbed stream.

In an ionic stream $2\lambda_1=W_1/D_1\simeq 40E$, where E is the electron field strength in volt cm^{-1} and W_1 and D_1 are expressed respectively in cm sec^{-1} and cm^2 sec^{-1}.

If $E=1$ V cm^{-1}, it follows that $N\simeq\frac{2}{3}N_0$ at a distance of $0\cdot5$ mm from the electrode.

It follows that the distribution in the stream of ions of equation (**13**) in the vicinity of the electrode at $z=h$ is given closely by $N\{1-\exp-2\lambda_1(2h-z)\}$ and that the flux to the surface element $\mathrm{d}S$ of the electrode at a point (ρ,h) is $NW_1\mathrm{d}S$, where N is given by equation (**13**) with $z=h$. This, as explained above, is the procedure that was adopted in practice.

The exact mathematical treatment is most conveniently expressed in terms of Fourier Bessel transforms. The approximate solution (**13**) can be written in the alternative form

$$N=\frac{\alpha_a WS}{8\pi DD_1}e^{\lambda z}\int_0^\infty kdk\frac{J_0(k\rho)}{\sqrt{(\mu^2+k^2)}}\left\{\frac{\exp (z-2h)\sqrt{(\mu^2+k^2)}}{\alpha\lambda+(\lambda-\lambda_1)\{\lambda+\sqrt{(\mu^2+k^2)}\}}\right.$$
$$\left.-\frac{\exp\{-z\sqrt{(\mu^2+k^2)}\}}{\alpha\lambda+(\lambda-\lambda_1)\{\lambda-\sqrt{(\mu^2+k^2)}\}}\right\}. \quad \ldots\ldots\ldots\ldots \quad (\mathbf{13'})$$

The expression (**13′**) is defined for $z\geqslant 0$. For $z<0$, the second term inside the bracket must be replaced by $\exp\{z\sqrt{(\mu^2+k^2)}\}/[\alpha\lambda+(\lambda-\lambda_1)\{\lambda+\sqrt{(\mu^2+k^2)}\}]$. The two parts of the solution so obtained do not join up smoothly at $z=0$. But suitable choice of the complementary function for $z<0$ will ensure that the solution is continuous and satisfies the correct boundary condition at $z=-\infty$. So strictly speaking (**13′**) is not equivalent to (**13**) but rather to

$$\bar{N}=-\frac{S\alpha_a\lambda}{4\pi D_1(\lambda_1-\lambda)}\exp\left(\frac{\alpha\lambda z}{\lambda_1-\lambda}\right)\left\{\int_z^\infty dz'\exp\left(1-\frac{\alpha}{\lambda_1-\lambda}\right)\lambda z'\frac{\exp(-\mu r')}{r'}\right.$$
$$\left.+\int_{-\infty}^z dz'\exp\left(1-\frac{\alpha}{\lambda_1-\lambda}\right)\lambda z_1\frac{\exp(-\mu r'')}{r''}\right\}$$
$$=N^+ + N^-. \quad \ldots\ldots\ldots\ldots \quad (\mathbf{13''})$$

It can be verified that the following choice of complementary function is suitable :

$$N_c=-\frac{\alpha_a WS}{8\pi DD_1}\int_0^\infty kdk\frac{J_0(k\rho)}{\sqrt{(\mu^2+k^2)}}$$
$$\times\exp[(z-h)\{\lambda_1+\sqrt{(\lambda_1^2+k^2)}\}+h\{\lambda-\sqrt{(\mu^2+k^2)}\}]$$
$$\times\left[\frac{1}{\alpha\lambda+(\lambda-\lambda_1)\{\lambda+\sqrt{(\mu^2+k^2)}\}}-\frac{1}{\alpha\lambda+(\lambda-\lambda_1)\{\lambda-\sqrt{(\mu^2+k^2)}\}}\right].$$
$$\ldots\ldots\ldots\ldots \quad (\mathbf{14})$$

The ion current at the anode is now

$$-D_1\frac{\partial}{\partial z}(N+N_c)\Big|_{z=h}.$$

From (**13**),

$$-D_1\frac{\partial N}{\partial z}\Big|_{z=h}=-\frac{\lambda\alpha D_1}{\lambda_1-\lambda}N\Big|_{z=h}.$$

The calculation of $\partial N_c/\partial z\,|_{z=h}$ can be carried out approximately if $\lambda_1\gg\mu$ or $\lambda_1\simeq\mu$. The integrand contains a factor $\lambda_1+\sqrt{(\lambda_1^2+k^2)}$ on differentiating with respect to z, and then putting $z=h$. If $\lambda_1\gg\mu$, we write $\lambda_1+\sqrt{(\lambda_1^2+k^2)}=\lambda_1+\sqrt{\{(\lambda_1^2-\mu^2)+(\mu^2+k^2)\}}$, and expand in powers of $(\mu^2+k^2)/(\lambda_1^2-\mu^2)$. To the first order we have

$$\lambda_1+\sqrt{(\lambda_1^2+k^2)}=\lambda_1+\sqrt{(\lambda_1^2-\mu^2)}+\frac{\mu^2+k^2}{\sqrt{(\lambda_1^2-\mu^2)}}-\frac{(\mu^2+k^2)\sqrt{(\lambda_1^2+k^2)}}{\sqrt{(\lambda_1^2-\mu^2)}\{\sqrt{(\lambda_1^2+k^2)}+\sqrt{(\lambda_1^2-\mu^2)}\}}.$$

Neglecting the last term, this gives the approximate expression

$$-D_1\frac{\partial N_c}{\partial z}\bigg|_{z=h}=D_1\{\lambda_1+\sqrt{(\lambda_1^2-\mu^2)}\}N\bigg|_{z=h}+\frac{D_1}{\sqrt{(\lambda_1^2-\mu^2)}}\frac{\partial^2}{\partial z^2}\mathrm{e}^{-\lambda z}N\bigg|_{z=h}$$

$$\simeq 2\lambda_1 D_1 N\bigg|_{z=h}+\frac{D_1}{\lambda_1}\left(\frac{\partial^2}{\partial z^2}\mathrm{e}^{-\lambda z}N\bigg|_{z=h}-\tfrac{1}{2}\mu^2 N\bigg|_{z=h}\right), \quad \ldots \quad (\mathbf{15})$$

agreeing with the physical argument given earlier.

If $\lambda_1 \simeq \mu$, we write

$$\lambda_1+\sqrt{(\lambda_1^2+k^2)}=\lambda_1+\sqrt{(\mu^2+k^2)}+\frac{\lambda_1^2-\mu^2}{2\sqrt{(\mu^2+k^2)}}$$

$$+\frac{(\lambda_1^2-\mu^2)^2}{2\sqrt{(\mu^2+k^2)}}\,\frac{1}{\{\sqrt{(\mu^2+k^2)}+\sqrt{(\lambda_1^2+k^2)}\}^2}.$$

This is an expansion in powers of $(\lambda_1^2-\mu^2)/(\mu^2+k^2)$, and, to the first order, we can neglect the last term. Then, with the notation introduced above,

$$-D_1\left(\frac{\partial N_c}{\partial z}\right)_{z=h}=\lambda_1 D_1 N\bigg|_{z=h}-D_1\frac{\partial}{\partial z}\mathrm{e}^{-\lambda z}(N^+ + N^-)\bigg|_{z=h}$$

$$+\tfrac{1}{2}D_1(\lambda_1^2-\mu^2)\left(\int_h^\infty \mathrm{d}z' N^+ - \int_{-\infty}^h \mathrm{d}z' N^-\right). \quad \ldots\ldots\ldots\ldots \quad (\mathbf{15'})$$

The expressions (**15**), (**15′**) can be calculated numerically without too much difficulty.

IV. References

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