FREE PATH FORMULAE FOR THE COEFFICIENT OF DIFFUSION AND VELOCITY OF DRIFT OF ELECTRONS IN GASES

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Summary

Free path methods are used to derive formulae for the coefficient of diffusion and the drift velocity of electrons in weakly ionized gases in the general case in which the collisional cross section is a function of the speed of an electron and the law of scattering of electrons in single collisions with molecules is not restricted to a few specific cases. It is found that the results are, in effect, the same as those derived by means of the methods of Maxwell and Boltzmann.

The significance of the investigation for the interpretation of laboratory measurements of electronic diffusion and drift is also discussed.

I. Introduction

It is commonly supposed that formulae derived by the method of free paths are of necessity restricted in generality and less precise than those derived by the rigorous, but analytically more complex, methods introduced by Maxwell and Boltzmann. In what follows it is shown that both methods lead to equivalent formulae for the diffusion and drift of electrons in gases. It may be inferred therefore that the supposed limitations of the method of free paths is in this context in many instances attributable to imperfections of application rather than to those of principle.

II. Simple Formulae for Diffusion and Drift in Weakly Ionized Gases

As was first put in evidence by Townsend, a group of electrons moving among the molecules of a gas in the presence of a steady and uniform electric field **E** acquires a steady state of motion comprising a random agitational motion in which the speeds c of the electrons are distributed, superimposed upon a velocity of drift **W** of the centroid of the group. The mean agitational energy $Q=\frac{1}{2}m\overline{c^2}$ of the electrons exceeds Q_0, that of the gas molecules, and the speed W is, usually, a few per cent. only of the mean agitational speed $\bar{c}$.

The energy Q, the speed W, and the law of distribution of the speeds c, are all functions of the ratio E/N of the electric field strength to the molecular concentration N. The group of electrons also diffuses relative to its centroid with a coefficient of diffusion D.

In deriving formulae for D and W it is supposed that the paths of electrons are rectilinear segments terminated by encounters with molecules that produce

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abrupt changes of direction in the electron velocity $\mathbf{c}$, that is to say, the proportion of the time during which the velocities c of the electrons receive appreciable modification during encounters is very small compared with the time spent in rectilinear motion between encounters. It is also supposed that the directions of the velocities $\mathbf{c}$, that is of the free paths, are isotropically distributed throughout the group.

In addition to this basic picture of the motion it is necessary to know or to postulate :

(*a*) The law of scattering of electrons in single encounters with molecules ; that is to say, the distribution of directions of the speeds c' after single encounters relative to the speed c before these encounters.

(*b*) The dependence of the collisional cross section $A(c)$ of the molecules upon the speed c of the colliding electron.

(*c*) Moreover, because of the small proportion of its energy lost in a collision, an electron makes a number of collisions successively at effectively the same speed c.

The simplest case, that usually treated by the method of free paths, is that in which law of scattering (*a*) is that of isotropic scattering, all directions of motion after an encounter being equally probable, and the collisional cross section A is postulated to be constant. The molecular model consistent with these assumptions is the massive, smooth, and perfectly elastic sphere of fixed diameter.

The formulae for D and W in this special case are, as is well known,

$$\left.\begin{aligned} D &= \tfrac{1}{3} l \bar{c}, \\ W &= \tfrac{2}{3}(Ee/m) l \,.\, \overline{c^{-1}}, \end{aligned}\right\} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

in which $\bar{c}$ and $\overline{c^{-1}}$ are the mean speed and the mean of the reciprocals of the speeds respectively and $l = 1/NA$ is the mean free path.

In practice, the usefulness of these formulae is greatly increased by removing the restrictive nature of the assumptions implicit in them. In what follows, generalizations of these formulae are sought, by the method of free paths, to include (i) an arbitrary law of scattering, and (ii) an arbitrary dependence of the collisional cross section $A(c)$ upon c.

III. Formulae when the Collisional Cross Section depends upon the Speed c

It is still assumed that the scattering at an encounter is isotropic. It proves to be the case that the formula (**1**) for the diffusion coefficient should now be written

$$D = \tfrac{1}{3}(\overline{lc}), \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

but that the same modification of the formula for W is invalid, although it has often been considered correct in the literature. To find the correct formula proceed as follows.

Consider a group of electrons travelling either radially or in a parallel beam, from a common origin. Let n_0 be the number at the origin, $x=0$, and n_1 the number that reach distance x without collision, it being supposed that they all possess the same speed c.

If the number that collide in the interval between x and $x+\mathrm{d}x$ is $\mathrm{d}n_1$, then the differential equation for n_1 is

$$\mathrm{d}n_1 = -NA(c)n_1\mathrm{d}x. \qquad (3)$$

Suppose that because of the action of the electric field the speed of the electron changes along its trajectory so that at distance x it is $c+\Delta c(x)$. Consequently, at distance x the collisional cross section is $A(c)+(\mathrm{d}A/\mathrm{d}c)\Delta c(x)$, neglecting terms in larger powers of $\Delta c(x)$.

It follows from (3) that the proportion of the group in which collisions occur at distances greater than x is

$$n_1/n_0 = \exp\,[-NAx - N\int(\mathrm{d}A/\mathrm{d}c)\Delta c(x)\mathrm{d}x]. \qquad (4)$$

When A is constant this reduces to the usual expression $n_1/n_0=\exp\,(-x/l)$, where $l=1/NA$.

The proportion that collides between x and $x+\mathrm{d}x$ is

$$\mathrm{d}n_1/n_0 = [NA+N(\mathrm{d}A/\mathrm{d}c)\Delta c(x)]\mathrm{d}x\,.\,\exp\,[-NAx-N\int(\mathrm{d}A/\mathrm{d}c)\,.\,\Delta c(x)\mathrm{d}x]. \qquad (5)$$

When $\Delta c(x)/c$ is a small quantity this expression is approximately the same as

$$\begin{aligned}\mathrm{d}n_1/n_0 &= [NA+N(\mathrm{d}A/\mathrm{d}c)\Delta c(x)][1-N\int(\mathrm{d}A/\mathrm{d}c)\Delta c(x)\mathrm{d}x]\mathrm{d}x\,.\,\exp\,(-NAx)\\ &\simeq [NA-N(\mathrm{d}A/\mathrm{d}c)\{NA\int\Delta c(x)\mathrm{d}x-\Delta c(x)\}]\mathrm{d}x\,.\,\exp\,(-NAx).\end{aligned} \qquad (6)$$

In terms of the mean free path $l=1/NA$ this becomes

$$\mathrm{d}n_1/n_0 = \exp\,(-x/l)[1/l+(1/l^2)(\mathrm{d}l/\mathrm{d}c)\{\int\Delta c(x)\mathrm{d}x/l-\Delta c(x)\}]\mathrm{d}x. \qquad (7)$$

Consider a group of n electrons moving in a steady state of motion in a gas and let the number whose agitational speeds lie within the limits c and $c+\mathrm{d}c$ be

$$\mathrm{d}n_c = nf(c)\mathrm{d}c.$$

The displacement of the centroid of the group $\mathrm{d}n_c$ in time $\mathrm{d}t$ is given by the product of $c\mathrm{d}t/l$, which is the average number of free paths traversed by each member of the group, and the mean displacement in the direction of **E** along these free paths. It is therefore necessary to calculate this mean displacement.

Assume isotropic scattering and consider those electrons that make their next collisions after travelling distances lying between x and $x+\mathrm{d}x$ in the direction θ. In this distance they are given deflections $\frac{1}{2}(Ee/m)(x/c)^2 \sin\theta$ by the field at right angles to the direction θ so that on this account they are advanced a distance $\frac{1}{2}(Ee/m)(x/c)^2 \sin^2\theta$ in the direction of the force Ee.

In addition they travel a distance $x\cos\theta$ in the direction of E in the course of their free flight. The increment of speed $\Delta c(x)$ along the free path x is $(Ee/m)(x/c)\cos\theta$, consequently the proportion of those setting out in direction θ that collide between x and $x+\mathrm{d}x$ is given by substituting this value of $\Delta c(x)$ in equation (**7**).

It follows that the mean displacement of a particle of the group $\mathrm{d}n_c$ taken over all directions θ and free paths x is

$$\begin{aligned}\tfrac{1}{2}\int_0^\pi\int_0^\infty &[(Ee/2m)(x/c)^2\sin^2\theta+x\cos\theta]\exp(-x/l)\left[1/l+\frac{1}{l^2}\frac{\mathrm{d}l}{\mathrm{d}c}\left(\frac{x}{2l}-1\right)x\cos\theta\,.\,\frac{Ee}{mc}\right]\\ &\times\sin\theta\,\mathrm{d}\theta\,\mathrm{d}x\\ &=\tfrac{2}{3}\frac{Ee}{m}(l/c)^2+\tfrac{1}{3}\frac{Ee}{m}\left(\frac{l}{c}\right)\frac{\mathrm{d}l}{\mathrm{d}c}\\ &=\tfrac{1}{3}\left(\frac{Ee}{m}\right)\left(\frac{l}{c}\right)\cdot\frac{1}{c^2}\frac{\mathrm{d}}{\mathrm{d}c}(lc^2). \qquad (8)\end{aligned}$$

The number of collisions made by the group $\mathrm{d}n_c$ in time $\mathrm{d}t$ is $(c/l)\mathrm{d}n_c\mathrm{d}t$, so that the sum of the displacements in the direction of $\mathbf{E}e$ experienced by the group in time $\mathrm{d}t$ is obtained by multiplying expression (**8**) by $(c/l)\mathrm{d}n_c\mathrm{d}t$, giving

$$s\mathrm{d}t=\tfrac{1}{3}\left(\frac{Ee}{m}\right)\frac{1}{c^2}\frac{\mathrm{d}}{\mathrm{d}c}(lc^2)\mathrm{d}t\mathrm{d}n_c.$$

The displacement of the centroid of the whole group is

$$\mathrm{d}t\left(\int s\,.\,\mathrm{d}n_c\right)/n=\mathrm{d}t\int sf(c)\mathrm{d}c.$$

Consequently the drift velocity of the centroid is

$$\begin{aligned}\mathbf{W}=\int sf(c)\mathrm{d}c&=(\mathbf{E}e/3m)\left[\overline{c^{-2}\frac{\mathrm{d}}{\mathrm{d}c}(lc^2)}\right]\\ &=[\mathbf{E}e/3mN]\left[\overline{c^{-2}\frac{\mathrm{d}}{\mathrm{d}c}(c^2/A)}\right]. \qquad (9)\end{aligned}$$

When l is independent of c this expression reduces to that in equation (**1**).

In terms of the mean free time of flight $T=l/c$ along free paths traversed at speed c equation (**9**) becomes

$$\mathbf{W}=(\mathbf{E}e/m)\,.\,\overline{\mathrm{d}(c^3T)/\mathrm{d}c^3}. \qquad (10)$$

In the special case in which electrons and molecules repel according to an inverse fifth power law of their separation, it is known that $l=ac$, where a is a constant. In that case, $T=l/c=a=$constant and

$$\mathbf{W}=(\mathbf{E}e/m)T, \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (\mathbf{11})$$

which agrees with a formula given by Pidduck (1913, 1915).

In treatments of drift based on the Maxwell-Boltzmann procedure it is supposed, following Lorentz, that the distribution function in the presence of the electric field $\mathbf{E}$, here supposed directed along Ox, takes the form of a chief term representing the isotropic motion and a correction term; thus,

$$f=f_0(c)+uf_1(c), \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (\mathbf{12})$$

where u is the x component of $c(u, v, w)$ and $f_0(c)$ is so defined that

$$\iiint_{-\infty}^{\infty} f_0(c)\mathrm{d}u\mathrm{d}v\mathrm{d}w=4\pi\int_0^{\infty} f_0(c)c^2\mathrm{d}c=1.$$

The drift velocity W then becomes $\int u^2f_1(c)\mathrm{d}u\mathrm{d}v\mathrm{d}w$, the problem being to determine the form of $f_1(c)$ in relation to $f_0(c)$.

We here investigate the form of $f_1(c)$ required to make $\int u^2f_1(c)\mathrm{d}u\mathrm{d}v\mathrm{d}w$ the same as expression (**9**).

Put

$$f=f[\{(u-\Delta u)^2+v^2+w^2\}^{\frac{1}{2}}]\simeq f[c-u\Delta u/c],$$

and suppose that $u\Delta u/c\ll 1$. Then

$$f=f_0(c)-(u\Delta u/c)\mathrm{d}f_0/\mathrm{d}c.$$

The mean drift velocity W of the whole group is

$$\int fu\mathrm{d}u\mathrm{d}v\mathrm{d}w=4\pi\int f_0(c)c^2u\mathrm{d}c-4\pi\int\Delta u(u^2/c)(\mathrm{d}f_0/\mathrm{d}c)c^2\mathrm{d}c$$

averaged over all values of the component u. Consequently,

$$W=-\frac{4\pi}{3}\int\Delta uc^3\frac{\mathrm{d}f_0}{\mathrm{d}c}\mathrm{d}c=\frac{4\pi}{3}\left\{\Big[-\Delta uc^3f_0\Big]_0^{\infty}+\int f_0\frac{1}{c^2}\ \frac{\mathrm{d}}{\mathrm{d}c}(\Delta u\ .\ c^3)c^2\mathrm{d}c\right\}.$$

Thus, since the first term in the brackets vanishes at both limits,

$$W=(1/3c^2)\{\mathrm{d}(\Delta uc^3)/\mathrm{d}c\}.$$

Whence, on comparison with equation (**9**),

$\Delta u=(Ee/m)(l/c)$ and in equation (**12**) $f_1=(-Ee/m)(l/c^2)(\mathrm{d}f_0/\mathrm{d}c)$,

which is essentially the form given by Chapman and Cowling (1952, p. 348). Formula (**9**) was first derived explicitly by Davidson (1954) by a method different from that followed here.

IV. Formulae when the Scattering is Non-isotropic. Coefficient of Diffusion

Consider the diffusion of a group of electrons in a coordinate system moving with its centroid. The coefficient of diffusion, as is well known, is related to the mean rate of increase of the squares of the distances from the origin, as follows:

$$\mathrm{d}\overline{r^2}/\mathrm{d}t=6D. \qquad (13)$$

Of a large group n of particles and a subgroup of them at the vector position $\mathbf{r}_0$ at $t=0$, consider those particles of the subgroup whose speeds lie within the limits c and $c+\mathrm{d}c$. In time t each particle will traverse on the average ct/l free paths s so that the vector position of a particle at time t is

$$\mathbf{r}_c=\mathbf{r}_0+\sum_{m=1}\mathbf{s}_m. \qquad (14)$$

However, since the centroid of the subgroup does not change, the mean value of $\Sigma\mathbf{s}_m$, for the subgroup, is zero.

From equation (**14**) it follows that

$$r_c^2=r_0^2+2\mathbf{r}_0\,.\,\Sigma\mathbf{s}_m+\Sigma\mathbf{s}_m\,.\,\Sigma\mathbf{s}_m.$$

Whence the mean value of $r^2-r_0^2$ for the subgroup is

$$\begin{aligned}\overline{r_c^2-r_0^2}&=\overline{\sum_{m=1}\mathbf{s}_m\,.\,\sum_{m=1}\mathbf{s}_m}\\&=\sum_{m=1}\overline{s_m^2}+2\sum_{m=1}\overline{s_m(s_{m+1}\cos\theta_{1m}+s_{m+2}\cos\theta_{2m}+.\ .\ .+)}\\&=(ct/l)[2l^2+2l^2\,(\overline{\cos\theta_1}+\overline{\cos\theta_2}+\overline{\cos\theta_3}+.\ .\ .)]\\&=2clt[1+\overline{\cos\theta_1}+\overline{\cos\theta_2}+.\ .\ .].\end{aligned}$$

It is assumed that ct/l is a large number and that $\overline{\cos\theta_m}$ diminishes not too slowly with m, so that the content of the bracket is the same for all except the last few free paths. A term $\overline{\cos\theta_n}$ is the mean value of the cosine of the angle between a free path s_m and the nth subsequent free path s_{m+n} of the same particle.

Thus for the subgroup at $\mathbf{r}_0$ at $t=0$ and moving with speeds c,

$$\mathrm{d}\overline{r_c^2}/\mathrm{d}t=\overline{r^2-r_0^2}/t=2cl[1+\overline{\cos\theta_1}+\overline{\cos\theta_2}+.\ .\ .].$$

Since the expression on the right-hand side is independent of r_0 it follows that $\mathrm{d}\overline{r_c^2}/\mathrm{d}t$ for all electrons with speed c in the whole group n is given by the same expression. On averaging over all speeds c it follows that

$$D=\tfrac{1}{6}\mathrm{d}\overline{r^2}/\mathrm{d}t=\tfrac{1}{3}[lc(1+\overline{\cos\theta_1}+\overline{\cos\theta_2}+.\ .\ .]. \qquad (15)$$

According to a theorem established in Appendix I, these mean cosine terms are related as follows:

$$\overline{\cos\theta_n}=(\overline{\cos\theta_1})^n,$$

consequently the contents of the bracket on the right-hand side of equation (**15**) form a geometrical progression and this equation becomes

$$D=\tfrac{1}{3}[\overline{lc/(1-\overline{\cos\theta_1})}]$$
$$=\tfrac{1}{3}[\overline{l_{eq}c}]. \qquad (\mathbf{16})$$

Thus, when the scattering in single collisions is not isotropic $\overline{\cos\theta_1}$ is not zero. Nevertheless, formula (**1**) for D retains its form but with an equivalent mean free path $l_{eq}=l/(1-\cos\theta_1)$ as if the molecules scattered electrons isotropically.

(*a*) *Formula for Drift Velocity*

$\overline{\cos\theta_1}$ is, in general, not zero and additional terms appear in expression (**8**) for the mean displacement along a free path traversed at speed c.

When the scattering is isotropic any preferred direction in the velocities c before impact are obliterated by the encounter, but this is not the case when the scattering is not isotropic. The mean velocity parallel to $\mathbf{E}e$ acquired along single free paths is $(Ee/m)(l/c)$. Of this the velocity $(Ee/m)(l/c)\,\overline{\cos\theta_1}$ remains after a collision with a molecule.

The total mean velocity parallel to $\mathbf{E}e$ at the start of each free path, that has accumulated from previous free paths, is

$$(Ee/m)(l/c)[\overline{\cos\theta_1}+(\overline{\cos\theta_1})^2+\ldots]=(Ee/m)(l/c)\,\overline{\cos\theta_1}/(1-\overline{\cos\theta_1}).$$

This gives an additional displacement normal to the free path x of amount $(Ee/m)(l/c)\{\overline{\cos\theta_1}/(1-\overline{\cos\theta_1})\}(x/c)\sin\theta$ with a resolved part parallel to $\mathbf{E}e$ equal to $(Ee/m)(l/c)\{\overline{\cos\theta_1}/(1-\overline{\cos\theta_1})\}(x/c)\sin^2\theta$. This term when included in the first bracket of the integrand in expression (**8**) produces a term $\frac{2}{3}(Ee/m)(l/c)^2\{\overline{\cos\theta_1}/(1-\overline{\cos\theta_1})\}$ in the integral that combines with the term $\frac{2}{3}(Ee/m)(l/c)^2$ to give a single term

$$\tfrac{2}{3}(Ee/m)(l/c)^2[1/(1-\overline{\cos\theta_1})].$$

The residual velocity $(Ee/m)(l/c)\{\overline{\cos\theta_1}/(1-\overline{\cos\theta_1})\}$ also adds to $\Delta c(x)$ in equation (**7**) a term

$$(Ee/m)(l/c)\{\overline{\cos\theta_1}/(1-\overline{\cos\theta_1})\}\cos\theta.$$

The end result is that the term $\frac{1}{3}(Ee/m)(l/c)\mathrm{d}l/\mathrm{d}c$ in equation (**8**) becomes replaced by

$$\tfrac{1}{3}(Ee/m)(l/c)(\mathrm{d}l/\mathrm{d}c)\{1/(1-\overline{\cos\theta_1})\}.$$

The final term in equation (**8**) becomes $\frac{1}{3}(Ee/m)(l/c)(1/c^2)\mathrm{d}(l_{eq}c^2)/\mathrm{d}c$, where $l_{eq}=l/(1-\cos\theta_1)$ and is the same equivalent free path as is defined in the modified expression for the coefficient of diffusion, equation (**16**).

The expression for the drift velocity follows, and equation (**9**) becomes

$$\mathbf{W}=(\mathbf{E}e/3m)[\overline{c^{-2}\mathrm{d}(l_{eq}c^2)/\mathrm{d}c}]$$
$$=(\mathbf{E}e/m)[\overline{d(c^3T_{eq})/\mathrm{d}c^3}], \qquad (\mathbf{17})$$

where $T_{eq}=l_{eq}/c$.

Thus in the formulae for D and for W when the scattering is not isotropic the actual gas may be replaced by a model gas in which the scattering is isotropic but with a modified mean free path $l_{eq}=l/[1-\overline{\cos\theta_1}]$. In what follows l and l_{eq} will be regarded as synonymous except in specific discussions where the distinction is required.

V. Special Molecular Models

(a) *Hard Spherical Molecule*

Here the collisional cross section is independent of c but the scattering may not be isotropic. Formulae (**1**) are valid with l replaced by l_{eq}.

(b) *Point Centre of Force*

Neglect all encounters beyond a distance of closest approach σ. The deviation θ is a function of the impact parameter b and the proportion of encounters for which $b<\sigma$ and b lies between b and $b+\mathrm{d}b$ is $2b\mathrm{d}b/\sigma^2$. Consequently the mean values of quantities such as $\theta(b)$ and $\cos\theta(b)$ are

$$\overline{\theta(b)}=(2/\sigma^2)\int_0^\sigma \theta(b)b\mathrm{d}b\ ;\quad \overline{\cos\theta(b)}=\overline{\cos\theta_1}=(2/\sigma^2)\int_0^\sigma \cos\theta(b)b\mathrm{d}b.$$

When the law of force between an electron (mass m_1) and a molecule (mass m_2) is $P=k_{12}/r^\nu$, the angle $\theta(b)$ is given by (Chapman and Cowling 1952, p. 171)

$$\theta(b)=\pi-2\int_0^{v_{00}}\left\{1-v^2-\frac{2}{\nu-1}\left(\frac{v}{v_0}\right)^{\nu-1}\right\}^{-\frac{1}{2}}\mathrm{d}v=\pi-2\varphi(b) \qquad \ldots\ldots \quad (\mathbf{18})$$

where v_{00} is the real positive root of $1-v^2-\{2/(\nu-1)\}(v/v_0)^{\nu-1}=0$ and $v_0=b\{m_1m_2c^2/(m_1+m_2)k_{12}\}^{1/(\nu-1)}$.

The expression for l_{eq} in equations (**16**) and (**17**) is equivalent to

$$\begin{aligned}1/l_{eq}&=(1-\overline{\cos\theta_1})/l=N\pi\sigma^2\,.\,(2/\sigma^2)\int_0^\sigma[1-\cos\theta(b)]b\mathrm{d}b\\ &=2\pi N\int_0^\sigma[1-\cos\theta(b)]b\mathrm{d}b, \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (\mathbf{19})\end{aligned}$$

in which σ may now be made infinite provided the integral converges.

Equation (**19**) transforms to

$$1/l_{eq}=2\pi N\,.\left[\frac{(m_1+m_2)k_{12}}{m_1m_2}\right]^{2/(\nu-1)}\cdot\frac{1}{c^{4/(\nu-1)}}A_1(\nu)=\frac{2\pi NBA_1(\nu)}{c^{4/(\nu-1)}}, \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (\mathbf{20})$$

where $A_1(\nu)=\int_0^\infty(1-\cos\theta)v_0\mathrm{d}v_0$. It follows that, when $\nu=5$, $l_{eq}\propto c$.

Values of $A_1(\nu)$ for several values of ν are given by Chapman and Cowling (1952, p. 172); for instance, $A_1(5)=0\cdot422$. The formulae for D and W appropriate to these " point centres of force " models are

$$\left.\begin{aligned} D&=\tfrac{1}{3}[\overline{cl_{eq}}]=\tfrac{1}{3}[\overline{c^{(\nu+3)(\nu-1)}/2\pi NBA_1(\nu)}],\\ \mathbf{W}&=(\mathbf{E}e/3m)\left[\overline{c^{-2}\frac{\mathrm{d}}{\mathrm{d}c}\{c^{2(\nu+1)/(\nu-1)}/2\pi NBA_1(\nu)\}}\right].\end{aligned}\right\} \quad \ldots\ldots\ldots \quad (21)$$

In practice the general formulae (**16**) and (**17**) which do not relate to specific models prove to be more useful for interpreting the experimental measurements of D and $\mathbf{W}$ of electrons in gases.

VI. Applications to Laboratory Measurements of D and $\mathbf{W}$

In the methods devised by Townsend for investigating the motions of electrons in gases, the macroscopic quantities that are measured directly are the drift velocity $\mathbf{W}$ as a function of E/N (that is to say, E/p, where p is the pressure of the gas at a fixed temperature) and the ratio W/D. Consequently both $\mathbf{W}$ and D are obtained from the measurements.

(*a*) *The Ratio* W/D

According to equations (**16**) and (**17**), with l written for l_{eq},

$$\frac{W}{D}=\frac{Ee}{m}\,\frac{[\overline{c^{-2}\mathrm{d}(lc^2)/\mathrm{d}c}]}{(\overline{lc})}. \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (22)$$

In the " weak field " case in which W is small in comparison with the mean thermal speed of the molecules a condition of approximate equipartition of energy prevails and the electronic speeds are distributed according to Maxwell's law.

In equation (**22**) the factor $\overline{c^{-2}\mathrm{d}(lc^2)/\mathrm{d}c}$ is

$$\frac{4}{\alpha^3\sqrt{\pi}}\int_0^\infty \frac{\mathrm{d}}{\mathrm{d}c}(lc^2)\exp(-c^2/\alpha^2)\,.\,\mathrm{d}c.$$

When this expression is integrated by parts it is seen to be equivalent to $(3/\overline{c^2})(\overline{lc})$. Consequently equation (**22**) reduces to the well-known Nernst-Townsend relationship which is independent of any particular molecular model, since l is eliminated,

$$\begin{aligned} W/D&=Ee/(\tfrac{1}{3}m\overline{c^2})=Ee/kT\\ &=(3/2)(Ee)/(\tfrac{1}{2}m\overline{c^2}), \end{aligned} \quad \ldots\ldots\ldots\ldots\ldots \quad (23)$$

where k is Boltzmann's constant and T the absolute temperature of the gas.

In the " high field " case W greatly exceeds the mean speed of the molecules and the speeds c of the electrons are no longer distributed according to Maxwell's formula. The earliest general investigation of the law of distribution of the speeds c appears to be that made by Pidduck (1915) and the subject has been frequently discussed. The law of distribution for the case of elastic losses has been given in a convenient general form by Chapman and Cowling (1952, p. 350) and in what follows their formulation is adopted. In the notation of the present paper the distribution function in the " high field " case is

$$f_0(c)c^2\mathrm{d}c=\text{const.}\left[\exp\left(-\int\frac{3m^3c^2\mathrm{d}c}{M(Eel)^2}\right)\right].\,c^2\mathrm{d}c, \quad \ldots\ldots \ (\mathbf{24})$$

in which l is, in general, a function $l(c)$ of c.

It may be seen that in the " high field " cases, where the law of distribution is no longer that of Maxwell, equation (**22**) does not reduce to the form (**23**), but becomes

$$\left.\begin{array}{c} W/D=C\,.\,Ee/\tfrac{1}{2}m\overline{c^2}, \\ \text{where } C \text{ is the dimensionless factor} \\ \overline{c^2}\,.\,[\overline{c^{-2}\mathrm{d}(lc^2)/\mathrm{d}c}]/2(\overline{lc}), \end{array}\right\} \quad \ldots\ldots\ldots\ldots \ (\mathbf{25})$$

the value of which depends on the nature of the dependence of l upon c and is in general appreciably different from the value 3/2 that occurs in equation (**23**).

It is evident that, when equation (**25**) is used to deduce the value of the electronic mean energy $Q=\frac{1}{2}m\overline{c^2}$, it is necessary to know the value of C if accuracy is required. When l is constant the distribution function approximates to that of Druyvesteyn, namely,

$$f(c)c^2\mathrm{d}c=(4/\alpha^3\sqrt{\tfrac{3}{4}})\exp(-c^4/\alpha^4)c^2\mathrm{d}c.$$

The factor then becomes

$$C=\overline{c^2}\,.\,\overline{c^{-1}}/\bar{c}=1{\cdot}312\,; \quad W/D=1{\cdot}312\,.\,Ee/(\tfrac{1}{2}m\overline{c^2}).$$

When $l=g/c$, where g is a constant, the law of distribution tends to the form

$$f(c)c^2\mathrm{d}c=(6/\alpha^3\sqrt{\pi})\exp(-c^6/\alpha^6)c^2\mathrm{d}c,$$

and $C=\frac{1}{2}\overline{c^2}\,.\,\overline{c^{-2}}=1$.

If l is proportional to c then $C=3/2$, whatever the law of distribution of the speeds c, as in equation (**23**).

These examples show, as already remarked, that, in general, in order to derive the mean kinetic energy of the electrons Q from equation (**25**) it is necessary to know the dependence of $l(c)$ upon c. For instance, in nitrogen over a range of values of the parameter E/p (p=gas pressure) the coefficient of diffusion D is constant. Since $D=\frac{1}{3}(\overline{lc})$ it follows that $l=g/c$ and, as shown above, that $C=1$.

VII. Formula for a Gaseous Mixture

It is easy to extend the theorem of Appendix I to a gas, such as air, comprising molecules of several kinds and to show that $N/l_{eq}=\Sigma N_k(l_{eq})_k$, where $N=\Sigma N_k$ and l_{eq} is the equivalent free path in the mixture, N_k and $(l_{eq})_k$ being the partial concentrations of the kth component, the corresponding equivalent free path in it alone. This result is the same as that for a gas comprising a mixture of molecules of different kinds, all of which scatter isotropically.

A companion paper dealing with drift in a magnetic field and in an alternating electric field will appear in the next issue of this journal.

VIII. Acknowledgment

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Appendix I

Theorem

Let a large number of particles all travelling in the same direction enter a system of scattering centres. Let $\overline{\cos\theta_1}$, $\overline{\cos\theta_2}$, . . ., $\overline{\cos\theta_n}$, . . . etc. be the mean values of the cosines of the angles between the directions of entry of particles into the scattering system and those of the free paths traversed by the particles following their first, second, . . ., nth, . . . scattering within the system. If the law of scattering at single encounters is symmetrical about the direction of approach of a particle to a scattering centre and the law of scattering remains unchanged in successive encounters, then $\overline{\cos\theta_n}=(\overline{\cos\theta_1})^n$.

Proof

Let a group of P particles move into the system along parallel trajectories and suppose that the distribution of directions over the unit sphere of the free paths following the first collision of each particle is given by $\mathrm{d}P/P=-2\pi F(\theta)\sin\theta\mathrm{d}\theta$, or alternatively in terms of the cosines of the angles θ

$$\mathrm{d}P/P=s(\mu)\mathrm{d}\mu,$$

where $\mu=\cos\theta$.

It follows that

$$\int_{-1}^{+1}s(\mu)\mathrm{d}\mu=1. \qquad \text{(A1)}$$

Assume that $s(\mu)$ may be expanded in a series of Legendre coefficients, thus,

$$s(\mu)=a_0+\sum_1^\infty a_nP_n(\mu),$$

where

$$a_n=(n+\tfrac{1}{2})\int_{-1}^{+1}s(\mu)P_n(\mu)\mathrm{d}\mu. \qquad \text{(A2)}$$

It follows from (**A1**) and (**A2**) that $a_0=\frac{1}{2}$.

In order to find the distribution of the directions of the second, third, etc. free paths over the unit sphere use is made of a formula in the theory of spherical harmonics (MacRobert 1947).

Let (θ, φ) and (θ', φ') be points on the unit sphere and γ the angle between their radii; then

$$\cos\gamma = \cos\theta\cos\theta' + \sin\theta\sin\theta'\cos(\varphi - \varphi').$$

Let $Y_m(\theta, \varphi)$ be a spherical harmonic of degree m, then

$$\int_0^{2\pi}\int_{-1}^{+1} Y_m(\theta, \varphi) P_n(\cos\gamma)\,\mathrm{d}\mu\,\mathrm{d}\varphi = \{4\pi/(2n+1)\} Y_n(\theta', \varphi'). \quad .. \quad \textbf{(A3)}$$

The free paths following the first collisions comprise a number of elementary beams within solid angles $\mathrm{d}\omega = -\mathrm{d}\mu\,\mathrm{d}\varphi$ with strengths $Ps(\mu)\mathrm{d}\omega/2\pi$.

These elementary beams are scattered in the second encounters about the directions of their axes according to the same law as prevailed in the first. The number of representative points at any point on the unit sphere is comprised of contributions from the elementary beams scattered in the second encounters. It follows that the number of free paths within solid angle $\mathrm{d}\omega'$ in the direction (θ', φ') immediately following on the second collision is

$$\begin{aligned}\mathrm{d}P' &= -P\int_{(\theta,\varphi)} [s(\mu)\mathrm{d}\mu\,\mathrm{d}\varphi/2\pi][s(\cos\gamma)/2\pi]\mathrm{d}\omega' \\ &= -P[\mathrm{d}\omega'/(2\pi)^2]\int_0^{2\pi}\int_{-1}^{+1}[\tfrac{1}{2} + \Sigma a_n P_n(\mu)][\tfrac{1}{2} + \Sigma a_n P_n(\cos\gamma)]\mathrm{d}\mu\,\mathrm{d}\varphi,\end{aligned}$$

whence, using equation (**A3**),

$$\mathrm{d}P' = -P(\mathrm{d}\omega'/2\pi)[\tfrac{1}{2} + 2\Sigma\{a^2_n/(2n+1)\}P_n(\mu')],$$

where $\mu' = \cos\theta'$.

It can be seen that, after m collisions of each particle, the distribution of the directions of the free paths over the unit sphere is given by

$$\mathrm{d}P/P = -(\mathrm{d}\omega'/2\pi)[\tfrac{1}{2} + \sum_1^{\infty}\{2^{m-1}a_n^m/(2n+1)^{m-1}\}P_n(\mu')].$$

Consequently the mean value of $\cos\theta_m \equiv \overline{\cos\theta_m}$ is

$$\begin{aligned}\overline{\cos\theta_m} &= (1/4\pi)\int_0^{2\pi}\int_{-1}^{+1}[\tfrac{1}{2} + \Sigma\{2^{m-1}a_n^m/(2n+1)^{m-1}\}P_n(\mu')]\mathrm{d}\mu\,\mathrm{d}\varphi \\ &= (\tfrac{2}{3}a_1)^m = (\overline{\cos\theta_1})^m,\end{aligned}$$

which was to be proved.