

ON THE FLOW AND EXCHANGE DIFFUSION OF ELECTRONS AND NEGATIVE IONS FORMED BY MOLECULAR ATTACHMENT*

By W. G. KAUMAN†

Formation of negative ions by attachment of electrons to molecules was first recognized by Thomson (1916). Huxley (1959) recently discussed the steady-state structure of a stream of electrons and ions drifting and diffusing in a gas, taking account of ionization by molecular attachment.

In general, there is a finite probability of de-ionization by detachment of electrons, particularly at high ratios of applied field to pressure or when attachment results in a short-lived excited state (Loeb 1955). With detachment non-negligible, the process may be considered as an example of "exchange diffusion"‡ (Kauman 1959) and treated by a method developed for electrodiffusion (Bak and Kauman 1958, 1959). In the present communication we shall show that this method permits separation of the rates of ionization and de-ionization and may be readily applied to non-steady states, alternating fields, and systems with a variety of boundary conditions.

Using Huxley's notation but putting k_1 (instead of $f\nu$) for the rate of ionization and k_2 for the rate of de-ionization, assuming first-order reactions, and neglecting, for simplicity, paired production of positive ions and electrons, we have

$$\partial n / \partial t = D_n \nabla^2 n - \vec{W}_n \cdot \nabla n - k_1 n + k_2 N, \quad \dots \dots \dots (1)$$

$$\partial N / \partial t = D_N \nabla^2 N - \vec{W}_N \cdot \nabla N - k_2 N + k_1 n, \quad \dots \dots \dots (2)$$

where n = number of electrons per unit volume,
 N = number of negative ions per unit volume,
 D_i = diffusion coefficient ($i = n, N$),
 $W_i = em_i E$ = drift velocity,
 e = electronic charge,
 m_i = mobility,
 E = electric field (antiparallel to z -axis).

* Manuscript received December 23, 1959.

† Division of Forest Products, C.S.I.R.O., Melbourne.

‡ "Exchange diffusion" occurs when two species of particles (M_1, M_2), reacting according to $M_1 \rightleftharpoons M_2$, diffuse in an external force field.

The system (1), (2) may be solved by first calculating the result for an instantaneous point source of electrons at $R=0$, $t=0$ and then integrating with respect to time to convert to a continuous source of strength s (electrons per unit time) at the origin (cf. Crank 1956). Neglecting small transient terms and terms above the second order in E , the non-steady-state solution for $\lambda^2 \mathcal{D}_z t \ll 1$ and $\tilde{\lambda}^2 \tilde{\mathcal{D}}_z t \ll 1$ is

$$n \approx \frac{s}{4\pi\kappa} \left[\frac{k_2}{\mathcal{D}^{3/2}} e^{\lambda z} \left\{ \frac{1}{R} \operatorname{erfc} R/2\sqrt{t} - \frac{\lambda^2 \mathcal{D}_z R}{4\sqrt{\pi}} \Gamma(-\tfrac{1}{2}, R^2/4t) \right\} \right. \\ \left. + \frac{k_1}{\tilde{\mathcal{D}}^{3/2}} e^{\tilde{\lambda} z} \left\{ \frac{1}{\tilde{R}} \operatorname{erfc} \tilde{R}/2\sqrt{t} - \frac{\tilde{\lambda}^2 (\tilde{\mathcal{D}}_z + \kappa) \tilde{R}}{4\sqrt{\pi}} \Gamma(-\tfrac{1}{2}, \tilde{R}^2/4t) \right\} \right], \quad \dots (3)$$

where

$$\begin{aligned} \mathcal{D}^3 &= \mathcal{D}_x \mathcal{D}_y \mathcal{D}_z, & \tilde{\mathcal{D}}^3 &= \tilde{\mathcal{D}}_x \tilde{\mathcal{D}}_y \tilde{\mathcal{D}}_z, \\ \mathcal{D}_x &= \mathcal{D}_y = [k_2 D_n + k_1 D_N]/\kappa, & \tilde{\mathcal{D}}_x &= \tilde{\mathcal{D}}_y = [k_1 D_n + k_2 D_N]/\kappa, \\ \mathcal{D}_z &= \mathcal{D}_x + \mathcal{D}(E), & \text{with } \mathcal{D}(E) &= [(m_n - m_N) e E]^2 k_1 k_2 / \kappa^3, \\ \tilde{\mathcal{D}}_z &= \tilde{\mathcal{D}}_x - \mathcal{D}(E), & & \\ R^2 &= x^2/\mathcal{D}_x + y^2/\mathcal{D}_y + z^2/\mathcal{D}_z, & \tilde{R}^2 &= x^2/\tilde{\mathcal{D}}_x + y^2/\tilde{\mathcal{D}}_y + z^2/\tilde{\mathcal{D}}_z, \\ \lambda &= [k_1 m_N + k_2 m_n] e E / 2 \mathcal{D}_z \kappa, & \tilde{\lambda} &= [k_1 m_n + k_2 m_N] e E / 2 \tilde{\mathcal{D}}_z \kappa, \\ \kappa &= k_1 + k_2. \end{aligned}$$

In the steady state, the solution is

$$n = \sum_{r=0}^{\infty} a_r z^r R^{-(r+\frac{1}{2})} K_{r+\frac{1}{2}}(\lambda R \sqrt{\mathcal{D}_z}) \\ + \sum_{r=0}^{\infty} b_r z^r \tilde{R}^{-(r+\frac{1}{2})} K_{r+\frac{1}{2}}\{\tilde{\lambda} \tilde{R} \sqrt{(\tilde{\mathcal{D}}_z + \kappa/\tilde{\lambda}^2)}\}, \quad \dots (4)$$

where $K_{r+\frac{1}{2}}$ are modified Bessel functions of the second kind of order $r+\frac{1}{2}$. The first terms of the series in (4) are

$$n = \frac{s}{4\pi\kappa} \left[\frac{k_2}{\mathcal{D}^{3/2} R} \exp \lambda(z - R \sqrt{\mathcal{D}_z}) + \frac{k_1}{\tilde{\mathcal{D}}^{3/2} \tilde{R}} \exp \tilde{\lambda}\{z - \tilde{R} \sqrt{(\tilde{\mathcal{D}}_z + \kappa/\tilde{\lambda}^2)}\} \right]. \\ \dots (5)$$

The solutions for N are similar to the above, except that in the absence of a source of negative ions, the sign of the term in $\exp(\tilde{\lambda} z)$ is negative and k_2 in the leading term is replaced by k_1 , with corresponding changes in the coefficients in (4). Assuming an appropriate image source (cf. Huxley 1959), we can make $n=N=0$ at $z=h$ by subtracting from each term in (3), (4), (5) a similar term with z replaced by $2h-z$.

The electronic current to an infinite plane electrode at $z=h$ is, to a first approximation,

$$i_{n\infty} = \frac{eS}{\chi} [k_2 + k_1 \exp \tilde{\lambda} h \{1 - \sqrt{1 + \chi/\tilde{\lambda}^2 \tilde{\mathcal{D}}_z}\}]. \quad \dots \quad (6)$$

If $W \gg 4D_n k_1$, $k_1 \gg k_2$, and $m_n \gg m_N$, (5) and (6) reduce to Huxley's equations (9) and (11).

If the applied field alternates with frequency $\omega/2\pi$, the results are of the same form as above, but the series terms are more complicated and depend also on ω , and $\mathcal{D}(E)$ (cf. equation (3)), averaged over a cycle, is

$$\bar{\mathcal{D}}_i(E) = -\frac{E_0^2}{8\chi} \left\{ \frac{4\omega^2 m_i^2}{\omega^2 + \chi^2} - (m_n + m_N)^2 \left(1 - \frac{(k_1 - k_2)^2}{\omega^2 + \chi^2} \right) \right\}, \quad \dots \quad (7)$$

where $E_0/\sqrt{2}$ = root-mean-square field. Further, $\lambda = [(m_n + m_N)eE_0 \cos \omega t]/2\mathcal{D}_z$, and similarly for $\tilde{\lambda}$.

The general equations (1) and (2) may also be solved with finite boundary conditions, for instance $n(0, t) = N(0, t) = \frac{1}{2}C_0$, $n(h, t) = N(h, t) = \frac{1}{2}C_h$, $(C_0 - C_h)/h = g \ll C_0$. The one-dimensional steady-state solution for $k_1 = k_2 = k$, $|m_n - m_N| \ll k$ is then of the form

$$\begin{aligned} n \approx \frac{1}{2}g(h-z) + \frac{1}{2}C_h + \frac{gmeE}{4k} \{1 - e^{-\Lambda z} - e^{\Lambda(z-h)}\} \\ + \frac{gm^2e^2E^2}{4k\sqrt{2kD}} \left\{ \frac{2z}{h} - 1 + e^{-\Lambda z} - e^{\Lambda(z-h)} \right\} + 0[(m_n - m_N)/k], \quad \dots \quad (8) \end{aligned}$$

where $\Lambda \sim meE/D$ and D, m are mean values.

It is important to note that in the systems described, the divergence of the electric field is finite, and the drift velocity of the particles therefore is not constant. For instance, the electric field corresponding to the system described by equation (8) is of the order

$$E \approx E_a + (e/\epsilon)C_h(\frac{1}{2}h - z), \quad \dots \quad (9)$$

where E_a = applied field, ϵ = permittivity. The effect of the divergence of E may be taken into account by perturbation procedures. In the presence of a species of positive ions not taking part in the exchange diffusion, the divergent term of the field is, to a first approximation, $\{eE_a(C_0 - C_h)/2h(C_0 + 3C_s)\}(z - \frac{1}{2}h)$, where C_s is the concentration of the positive ions. The electric current in this case is

$$I \approx -e^2 \frac{m_n + m_N}{2} \left\{ 2C_s + C_0 - \frac{ge(m_n - m_N)E_a}{2k} \right\} E_a. \quad \dots \quad (10)$$

With an alternating field, I is the form $I(\text{alt.}) = I_0 + I_1 \sin \omega t + I_2 \cos 2\omega t$, where I_0 and I_2 are independent of C_s but depend on k, m , and ω with a cut-off frequency given by $\omega = 2k$ (Kauman and Bak 1959).

The present method not only permits a complete description of the behaviour of electrons and ions formed by molecular attachment, but is also amenable to the treatment of other electronic exchange processes, for instance transport of carriers in semiconductors (cf. van Roosbroeck 1950; Shockley 1950). It may be extended to more than two ionic species by iteration procedures.

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