matter with different binding character which suggests a similar behavior with regard to propagation and relaxation of defect charges as well as to the subsequent explosion.

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Exact Closed-Form Solution of the Generalized Debye-Smoluchowski Equation

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The first exact solution of the time-dependent Debye-Smoluchowski equation for diffusional drift under a general interaction in the presence of a reactive sink is presented. Associated time-dependent rates of chemical reactions in a dense gas are formulated and display the basic physical transition from reaction control to transport control as time progresses for a system initially in Boltzmann equilibrium.

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The number density $n^-(R,t)$ at time t of some species A (e.g., negative ions) drifting under interaction $V(R)$ across a sphere of radius R towards a central species B (positive ion) in a gas Z (or liquid) under the action of a reactive spherical sink of extent S from B is governed by the generalized Debye-Smoluchowski equation,

$$-\frac{dn^-(R,t)}{dt} = -\frac{\partial n^-(R,t)}{\partial t} + R^{-2}\frac{\partial}{\partial R}[R^2 j(R,t)] = \Gamma_3 n^-(R,t)\,\delta(R-S). \qquad (1)$$

Here Γ_3 is the speed of reaction (via ion-pair–gas collisions) for ions after being brought to S by the net inward diffusional-drift current,

$$j(R,t) = D\exp\left(\frac{-V}{kT}\right)\frac{\partial}{\partial R}\left[n(R,t)\exp\left(\frac{V}{kT}\right)\right], \qquad (2)$$

in terms of the diffusion coefficient D ($\mathrm{cm}^2\,\mathrm{s}^{-1}$) for relative diffusion of A and B in Z.

The number density N_i of all ion pairs AB with internal separation $R \geq S$ then decays at a rate,

$$-\frac{dN_i}{dt} = -\frac{d}{dt}\int_S^\infty 4\pi R^2 N^+ n^-(R,t)\,dR = -\frac{\partial N_i}{\partial t} + N^+[F_\infty - 4\pi S^2 j(S-\epsilon,t)] = 4\pi S^2\Gamma_3 n^-(S,t)N^+ = \alpha(t)N^+N^-, \qquad (3)$$

where F_∞ is the rate (s^{-1}) of generation of negative ions at infinity, and where α is the time-dependent rate ($cm^3\ s^{-1}$) of recombination appropriate to asymptotic ion densities $N^\pm$. If the ion current approaching S is absorbed by reaction within S, then $\lim_{\epsilon\to 0} j(S-\epsilon, t) \to 0$. In steady state, the rate $4\pi R^2 j(R,t)$ from (1) is constant for $R \geqslant S+\epsilon$ and equals the production rate F_∞ in (3).

Equation (1) automatically incorporates the boundary condition

$$\Gamma_3 n^-(S,t) = \lim_{\epsilon\to 0} j(S+\epsilon, t) \tag{4}$$

which follows on integration of (1) between $S\pm\epsilon$ and which equates the transported and absorbed currents at the boundary. At asymptotic R the correct solution of (1) tends to the Boltzmann distribution.

$$n^-(R\to\infty, t) = N^- \exp(-V/kT). \tag{5}$$

Equation (1) is of basic significance not only to ion-ion recombination in gases[1] and ionic solutions but also to chemical reactions in a dense medium, to coagulation of colloids, to medical radiology, to diffusion and field controlled reactions in metabolizing systems (as enzyme-substrate reactions in a cell[2]), and to diffusion across a membrane. While an exact time-dependent solution to (1) can be obtained[2] for the field-free ($V=0$) case, no exact solution has yet been determined for general V although a large body of literature exists on various approximate techniques[3] for the Coulomb case. We provide here the first analytical exact solution of (1) for general $V(R)$, subject to the condition that $n^-(R, t=0)$ is prepared as the Boltzmann distribution (5).

The following exact solution is based on the novel transformation from R to the variable

$$\tilde{R} = \left\{\int_R^\infty \exp[V(R)/kT] R^{-2}\, dR\right\}^{-1}; \qquad d\tilde{R}/dR = (\tilde{R}/R)^2 \exp(V/kT), \tag{6}$$

which is not without its physical significance. It is related[1] to the probability that an R-ion pair will further contract by diffusion under V, in the presence of an instantaneous sink at S. Let,

$$n_v(R,t) = n^-(R,t)\exp(V/kT) \tag{7}$$

such that (1) with (6) reduces to

$$\frac{\partial n_v(\tilde{R},t)}{\partial t} = \frac{\tilde{D}}{\tilde{R}^2}\frac{\partial}{\partial \tilde{R}}\left[\tilde{R}^2 \frac{\partial n_v(\tilde{R},t)}{\partial \tilde{R}}\right] \tag{8}$$

subject to (4). The transformed diffusion coefficient ($cm^2\ s^{-1}$) is

$$\tilde{D} = D\left(\frac{d\tilde{R}}{dR}\right)^2. \tag{9}$$

The form of this equation is, in the transformed $\tilde{R}$ representation, identical with that for the field-free case in the original R representation. Accordingly, introduce scaled quantities,

$$\tilde{r} = (\tilde{R}/\tilde{S}) - 1, \quad \tilde{\tau} = \tilde{D}t/\tilde{S}^2, \quad n' = (\tilde{R}/\tilde{S}) n_v(\tilde{R},t) \tag{10}$$

such that (8) reduces to

$$\partial n'(\tilde{r},\tilde{\tau})/\partial\tilde{\tau} = \partial^2 n'(\tilde{r},\tilde{\tau})/\partial \tilde{r}^2. \tag{11}$$

This can be now solved by the method of Laplace transformation which automatically incorporates the initial condition. The full solution of (1) appropriate to spontaneous reaction [$\Gamma_3 \to \infty$ in (4)] is then, after some analysis,

$$n^{(S)}(R,t) = N^- \exp\left(-\frac{V}{kT}\right)\left[1 - \frac{\tilde{S}}{\tilde{R}} \operatorname{erfc}\left\{\frac{(\tilde{R}-\tilde{S})}{2(DT)^{1/2}}\left(\frac{dR}{d\tilde{R}}\right)\right\}\right]. \tag{12}$$

The associated recombination rate is then

$$\alpha^{(S)}(t) = 4\pi S^2 j(S,t)/N^- = \alpha_{\mathrm{TRNS}}\left[1 + \frac{S^2 \exp[-V(S)/kT]}{\tilde{S}(\pi D t)^{1/2}}\right] \tag{13}$$

which tends at long time $t \gg S^2/D$ to the steady-state transport rate

$$\alpha_{\mathrm{TRNS}} = 4\pi S D = 4\pi D R_e/P(S), \tag{14}$$

where the natural unit of length R_e is (e^2/kT) and where

$$P(S) = R_e/\tilde{S} = R_e \int_S^\infty \exp(V/kT) R^{-2}\, dR. \tag{15}$$

Under condition of equilibrium with the field, the Einstein relation ($DR_e = Ke$) between D and the mobility K is valid. For a Coulombic attraction, the steady-state solution (14) is then

$$\alpha_{\mathrm{TRNS}}{}^{(S)} = 4\pi Ke/[1-\exp(-R_e/S)] \tag{16}$$

in accord with that of Bates.[4]

The boundary condition (4) for finite reaction under a field is,

$$\mathbf{\Gamma}_3(S) n^-(S,t) = D\exp\left[-\frac{V(S)}{kT}\right]\left\{\frac{\partial}{\partial R}\left[n(R,t)\exp\left(-\frac{V}{kT}\right)\right]\right\}_S \tag{17}$$

which yields, in the transformed representation (6),

$$n_v(S,t) = \frac{\tilde{D}}{\tilde{\Gamma}_3(S)}\left(\frac{dn_v}{d\tilde{R}}\right)_S, \tag{18}$$

where the transformed speed of reaction is

$$\tilde{\Gamma}_3 = \Gamma_3(d\tilde{R}/dR). \tag{19}$$

Hence, the full time-dependent solution obtained from Laplace transformation of (11) subject to the initial Boltzmann distribution is, for a general interaction, given by

$$n^-(R,t) = N^- \exp(-V/kT)\left[1 + \left(\frac{\tilde{\alpha}}{\tilde{\alpha}_D}\right)\left(\frac{\tilde{S}}{\tilde{R}}\right)\{\exp(2\tilde{\Omega}\,\tilde{\chi})\exp\tilde{\chi}^2\,\mathrm{erfc}(\tilde{\chi}+\tilde{\Omega}) - \mathrm{erfc}\,\tilde{\Omega}\}\right]. \tag{20a}$$

Here the associated quantities are defined as

$$\tilde{\chi}(t) = (1 + \tilde{\alpha}_3/\tilde{\alpha}_D)(\tilde{D}t)^{1/2}/\tilde{S}, \tag{20b}$$

$$\tilde{\Omega}(t) = (\tilde{R} - \tilde{S})/2(\tilde{D}t)^{1/2}, \tag{20c}$$

and

$$\tilde{\alpha} = \tilde{\alpha}_3\tilde{\alpha}_D/(\tilde{\alpha}_3 + \tilde{\alpha}_D), \tag{20d}$$

in terms of the transformed reaction and transport rates,

$$\tilde{\alpha}_3 = 4\pi\tilde{S}^2\tilde{\Gamma}, \quad \tilde{\alpha}_D = 4\pi\tilde{S}\tilde{D}. \tag{20e}$$

The ratio of these rates is, however, unchanged and given by

$$\frac{\tilde{\alpha}_3}{\tilde{\alpha}_D} = \frac{4\pi S^2\Gamma_3\exp[-V(S)/kT]}{\alpha_{\mathrm{TRNS}}} = \frac{\alpha_{\mathrm{RCTN}}}{\alpha_{\mathrm{TRNS}}}. \tag{21}$$

Here α_{RCTN} denotes the reaction rate which from (3) is the recombination rate that would pertain provided a Boltzmann distribution of ions were maintained as at low gas densities when j in (2) vanishes. The full time-dependent recombination rate is now given by (20a) in (2) as

$$\alpha(t) = 4\pi S^2\Gamma_3 n^-(S,t)/N^- = \alpha_\infty[1 + (\alpha_{\mathrm{RCTN}}/\alpha_{\mathrm{TRNS}})\exp\tilde{\chi}^2\,\mathrm{erfc}\,\tilde{\chi}], \tag{22a}$$

where $\tilde{\Omega}(R=S)$ in (20c) vanishes, $\tilde{\chi}$ in (20b) is, with the aid of (6), (9), and (21),

$$\tilde{\chi} = (1 + \alpha_{\mathrm{RCTN}}/\alpha_{\mathrm{TRNS}})[(Dt)^{1/2}/S]\exp[V(S)/kT]\left[S\int_S^\infty \exp(V/kT)R^{-2}\,dR\right]^{-1}, \tag{22b}$$

and where

$$\alpha_\infty = \alpha_{\mathrm{RCTN}}\alpha_{\mathrm{TRNS}}/(\alpha_{\mathrm{RCTN}} + \alpha_{\mathrm{TRNS}}) \tag{22c}$$

is the steady-state rate of recombination which is controlled by the rate limiting step of reaction versus transport and which exhibits a form[1] characteristic of physical mechanisms in series. At high gas densities N, $\alpha_{\mathrm{TRNS}} \ll \alpha_{\mathrm{RCTN}}$ such that $\alpha_\infty \to \alpha_{\mathrm{TRNS}}$, the transport rate. At low N, $\alpha_{\mathrm{TRNS}} \gg \alpha_{\mathrm{RCTN}}$ such that $\alpha_\infty \to \alpha_{\mathrm{RCTN}}$. As t increases from zero, then

$$\exp\chi^2\,\mathrm{erfc}\,\chi \to 1 - \frac{2}{\sqrt{\pi}}\chi + \chi^2 - \frac{4}{3\sqrt{\pi}}\chi^3 + \dots \tag{23}$$

such that

$$\alpha(t\to 0) = \alpha_{\mathrm{RCTN}}\left[1 - \frac{2}{\sqrt{\pi}}\left(\frac{\alpha_{\mathrm{RCTN}}}{\alpha_{\mathrm{TRNS}}}\right)\frac{(Dt)^{1/2}}{S}\exp[V(S)/kT]\left\{S\int_S^\infty \exp(V/kT)R^{-2}dr\right\}^{-1}\right] \tag{24}$$

decreases initially from the reaction rate α_{RCTN}. As $t \to \infty$,

$$\exp\chi^2\,\mathrm{erfc}\,\chi \to \frac{1}{\chi\sqrt{\pi}}\left(1 - \frac{1}{2\chi^2} + \frac{3}{4\chi^4}\cdots\right) \tag{25}$$

such that the long-time dependence is

$$\alpha(t\to\infty) = \alpha_\infty\left\{1 + \left(\frac{\alpha_\infty}{\alpha_{\mathrm{TRNS}}}\right)\frac{S\exp[-V(S)/kT]}{(\pi Dt)^{1/2}}\left[S\int_S^\infty \exp(V/kT)R^{-2}\,dR\right]\right\} \tag{26}$$

which tends eventually to the steady-state rate α_∞ for $t \gg (S^2/D)$.

The ion density (20a) tends to the steady-state limit

$$n^-(R, t\to\infty) = N^- \exp(-V/kT)\left[1-\left(\frac{\alpha_\infty}{\alpha_{\text{TRNS}}}\right)\frac{P(R)}{P(S)}\right] \tag{27}$$

which at low N is approximately Boltzmann but departs appreciably from Boltzmann at high N ($\alpha_\infty \sim \alpha_{\text{TRNS}}$) particularly in the region of the sink.

The full time dependence in (22a) for α is contained in (22b) for $\tilde{\chi}$ which, for a pure Coulomb attraction, varies as

$$\tilde{\chi}(\tau) = \left(1+\frac{\alpha_{\text{RCTN}}}{\alpha_{\text{TRNS}}}\right)^{1/2} \tau^{1/2}\left(\frac{R_e}{S}\right)^{1/2}\left[\exp\left(\frac{R_e}{S}\right)-1\right]^{-1}, \tag{28}$$

where the scaled time is

$$\tau = t/(S^2/D) \tag{29}$$

in the units of (S^2/D), the time approximately required for an ion to diffuse from the boundary to the center of the sink.

In Fig. 1 the time dependence is illustrated for the recombination rates $\alpha(t)$ resulting from (22) for various gas densities N (in units of N_L, the number density 2.69×10^{19} cm^{-3} at STP). The transport rate α_{TRNS} is given by (14) and the reaction rate α_{RCTN} for a fictitious (but representative) case of ions of equal mass (16 amu) and mobility 2 cm^2/V s recombining in an equal mass gas at 300 °K is obtained from a model[1,5] which yields the exact quasiequilibrium rates[6] at low N.

For high N, $\alpha(t)$ decreases initially from α_{RCTN}, which is $\gg \alpha_{\text{TRNS}}$, to its steady-state limit which is α_{TRNS}, i.e., for the assumed initial Boltzmann distribution, reaction first occurs spontaneously for the ions within S and then ion transport is initiated in an attempt to compensate for the resulting hole in the distribution. For low $N \lesssim N_L$ ($\equiv 1$ atm), a linear variation of $\alpha(t)$ with t is exhibited since the reaction rate $\alpha_{\text{RCTN}} \ll \alpha_{\text{TRNS}}$ is always the rate limiting step. Thus the transition from reaction to transport is best observed for dense gases. Also shown in Fig. 1 are the characteristic time scales (S^2/D) for diffusion across a sink of radius S which is compressible with N. This effect could therefore be detected by modern laser spectroscopic techniques based on rotational or vibrational transitions in molecular ions. The steady-state rates are of course independent of the initial condition.

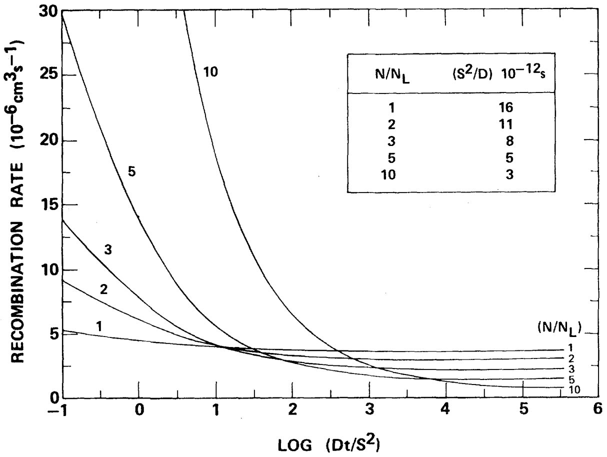

FIG. 1. Explicit time dependence of recombination rate $\alpha(t)$ at various gas densities, as indicated in units of Loschmidt's number N_L (2.69×10^{19} cm^{-3} at STP). Characteristic times (S^2/D) for diffusion are also indicated.

In summary, we have presented here the first exact closed-form analytical solution of the generalized Debye-Smoluchowski equation for diffusional drift in the presence of a reactive sink or source. The evolution of the rate of the overall process for an initial Boltzmann distribution exhibits the interesting phenomenon of control by reaction to control by transport, and illustrates the competition between these basic physical mechanisms as time progresses. This phenomenon is directly important to many areas as fluorescence quenching in solutions and in the disappearance rate of ionization tracks.

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