ge plasma and ion extraction.

References

1. B. Chapman, "Glow Discharge Processes", John Wiley & Sons, New York, 1980.
2. W. Grimm, *Spectrochim. Acta, Part B* **23B**, 433 (1968).
3. P. W. J. M. Boumans, *Anal. Chem.* **44**, 1219 (1972).
4. D. S. Gough, *Anal. Chem.* **48**, 1926 (1976).
5. D. C. McDonald, *Anal. Chem.* **49**, 1336 (1977).
6. N. P. Ferreira and L. R. P. Butler, *Analyst* **103**, 607 (1978).
7. H. Hughes, *Analyst* **108**, 286 (1983).
8. J. B. Ko, *Spectrochim. Acta, Part B* **39B**, 1405 (1984).
9. K. Wagatsuma and K. Hirokawa, *Anal. Chem.* **56**, 908 (1984).
10. J. C. Woo, K. B. Lee, D. W. Moon and K. W. Lee, *Analytical Science* **1**, 32 (1988).
11. B. L. Bentz, C. G. Bruhn and W. W. Harrison, *Int. J. Mass Spectrom. Ion Phys.* **28**, 409 (1978).
12. N. Jakubowski, D. Stuewer and G. Toelg, *Int. J. Mass Spectrom. Ion Phys.* **71**, 183 (1986).
13. N. Jakubowski, D. Stuewer and W. Vieth, *Anal. Chem.* **59**, 1825 (1987).
14. T. J. Loving and W. W. Harrison, *Anal. Chem.* **55**, 1523 (1983).
15. T. J. Loving and W. W. Harrison, *Anal. Chem.* **55**, 1526 (1983).
16. M. Hecq, A. Hecq and M. Fontignies, *Analytica Chimica Acta* **155**, 191 (1983).
17. K. Robinson and E. F. H. Hall, *J. Metals* **39**, 14 (1987).
18. D. J. Hall and P. K. Robinson, *Am. Lab.* **19**, 74 (1987).
19. W. W. Harrison and B. L. Bentz, *Prog. Analyt. Spectrosc.* **11**, 53 (1988).
20. W. W. Harrison, K. R. Hess, R. K. Marcus and F. L. King, *Anal. Chem.* **58**, 341A (1986).
21. J. W. Coburn and W. W. Harrison, *Appl. Spec. Rev.* **17**, 95 (1981).
22. R. Pertel, *Int. J. Mass Spectrom. Ion Phys.* **16**, 39 (1975).
23. S. L. Tong and W. W. Harrison, *Anal. Chem.* **56**, 2028 (1984).
24. J. C. Huneke, *J. Res. Natl. Bur. Stand.* **93**, 392 (1988).
25. R. G. Wilson and G. R. Brewer, "Ion Beams: With Applications to Ion Implantation", Wiley, New York, 1973.
26. R. K. Marcus, F. L. King and W. W. Harrison, *Anal. Chem.* **58**, 972 (1986).

Study of Diffusion Controlled Reactions in Liquids: A Perturbation Series Solution and a Numerical Solution of the Smoluchowski Equations

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A general perturbation series solution of the Smoluchowski equation is applied to investigate the rate of recombination and the remaining probability of a pair of particles in liquids. The radiative boundary condition is employed and the convergence of the perturbation series is analyzed in terms of a convergene factor in time domain. The upper bound to the error introduced by the n-th order perturbation scheme is also evaluated. The long time behaviors of the rate of recombination and the remaining probability are found to be expressed in closed forms if the perturbtaion series is convergent. A new and efficient method of purely numerical integration of the Smoluhowski equation is proposed and its results are compared with those obtained by the perturbation method. For the two cases where the interaction between the particles is given by (i) the Coulomb potential and (ii) the shielded Coulomb potential, the agreement between the two results is found to be excellent.

Introduction

Diffusion-controlled reactions in liquids are commonly described by the Smoluchowski equation with an appropriate boundary condition.[1-4] The solution of the Smoluchowski equation is related to the physical quantity of interest such as the rate of recombination or the remaining probability of a pair of reacting particles. Many authors have attempted to solve the Smoluchowski equation in various ways. In the presence of a potential field only a few cases are solved exactly.[5,6] Otherwise one has to rely on some kinds of approximate method.

Some time ago Sibani and Pedersen[7] proposed a general perturbation scheme for the solution of the Smoluchowski equation in the weak potential region. In their approach the Smoluchowski equation is transformed into an equivalent integral equation and the solution is expressed in terms of a successive iteration series. The boundary condition employed in their work is the absorption boundary condition and the series expansion and the analysis of the convergence of the series is carried out in the Laplace transformed space.

The purpose of the present work is to apply their approach with the radiative boundary condition and to perform the perturbation series expansion and the convergence analysis in time domain. Also we propose a new efficient numerical method of integrating the Smoluchowski equation based

on a nonlinear transformation of the variable. This paper is organized as follows. First, in the following section, the general perturbation scheme in the integral equation approach is developed with the radiative boundary condition and the convergence of the series is analyzed in time domain. The long time behavior of the solution is also investigated and the rate of recombination and the remaining probability are evaluated explicitly. A new numerical method is then proposed and the applications of the two methods to the cases with the Coulomb and the shielded Coulomb potentials are presented.

Theory

The Smoluchowski equation in three–dimension with spherical symmetry is given by

$$\partial f(r, t)/\partial t = r^{-2}\frac{\partial}{\partial r}[r^2 D(\partial/\partial r + \beta\, dW/dr)]f(r, t) \quad (1)$$

where $f(r,t)$ is the probability distribution of finding a pair of reacting particles separated by a distance r at time t. D is the diffusion constant, W is the interaction potential between the particles, and β is the Boltzmann factor.

If we assume that the pair is created at the relative distance $r = r_o$ at time $t = 0$, the initial condition of Eq. (1) can be expressed as

$$f(r, t=0) = (4\pi r_0^2)^{-1}\delta(r - r_o). \quad (2)$$

The radiative boundary condition incorporating the reaction event of the pair of particles upon encounter is adopted here:

$$D[\partial/\partial r + \beta\, dW/dr]f(r, t) = hf(r, t) \text{ at } r = \sigma, \quad (3)$$

where σ is the contact distance and h is the measure of the intrinsic rate constant.

The physical quantity of interest in diffusion–controlled reactions is the rate of recombination of a reacting pair on the reaction surface which is defined by

$$R(t) = 4\pi\sigma^2 D[\partial f/\partial r + \beta\,(dW/dr)f]_{r=\sigma}$$
$$= 4\pi\sigma^2 hf(r=\sigma, t). \quad (4)$$

Another quantity of interest is the remaining probability given by

$$P(t) = \int f(r, t)\, d\vec{r}$$
$$= 1 - \int_0^t R(t')\, dt' \quad (5)$$

A. General Perturbation Scheme in the Integral Equation Approach. In the general perturbation scheme employed by Sibani and Pedersen,[7] the Smoluchowski equation is first transformed into an equivalent Fredholm integral equation of the second kind to give

$$\tilde\rho(x, s) = (1+x_o)^{-1}g(x, x_o, s)$$
$$+ \int_0^\infty dx'\, g(x, x', s)\, V(x')\rho(x, s) \quad (6)$$

where

$$\tilde\rho(x, s) = \int_0^\infty d\tau\rho(x, \tau)\exp(-s\tau) \quad (7)$$

$$V(x) = U''/2 - (U'/2)^2 + U'/(x+1) \quad (8)$$

The following transformations are introduced in obtaining Eq.(6):

$$\tau = tD/\sigma^2,\ x = (r/\sigma) - 1,\ x_o = (r_o/\sigma) - 1,\ U(r) = \beta W(r) \quad (9a)$$

$$\rho(x, \tau) = 4\pi\sigma^3(x+1)\exp\{[U(x) - U(x_o)]/2\}f(x, \tau) \quad (9b)$$

The free space Green's function, $g(x,x',s)$, satisfying the radiative boundary condition can be easily found as

$$g(x, x', s) = \{\exp[-s^{1/2}|x-x'|] - \exp[-s^{1/2}(x+x')]\}$$
$$/(2s^{1/2}) + (s^{1/2}+\eta)^{-1}\exp[-s^{1/2}(x+x')] \quad (10)$$

where

$$\eta \equiv 1 + \sigma h/D - (U'/2)_{x=0}$$

A formal solution of Eq.(6) can be obtained by an iterative procedure. We can write

$$\tilde\rho(x, s) = \sum_{n=0}^\infty \rho^{(n)}(x, s) \quad (11)$$

where

$$\tilde\rho^{(0)}(x, s) = (1+x_o)^{-1}g(x, x_o, s) \quad (12)$$

$$\tilde\rho^{(n)}(x, s) = \int_0^\infty dx'\, g(x, x', s)\, V(x')\tilde\rho^{(n-1)}(x', s)\ (n\geq 1) \quad (13)$$

Hence an approximate solution of Eq.(6) is given by truncating the above perturbation series if it is convergent. The convergence of the series will be discussed shortly.

However, if we are interested in only the rate of recombination and the remaining probability, we need not solve for a complete solution $\tilde\rho(x,s)$ for all x and our problem is much simplified. This can be seen by taking the Laplace transformations of these quantities:

$$\tilde R(z) = \int_0^\infty R(t)\exp(-zt)\, dt$$
$$= (4\pi\sigma^4 h/D)f(x=0, s) \quad (14)$$

$$\tilde P(z) = z^{-1}[1 - (4\pi\sigma^4 h/D)f(x=0, s)] \quad (15)$$

where $s = z\sigma^2/D$. As shown in Eqs.(14) and (15), the key quantity of interest is $f(x=0, s)$ or its inverse Laplace transformation $\tilde f(x=0, t)$ which is equivalent to $\rho(x=0, \tau)$.

Eq.(11) then shows that what we need are the values of $\tilde\rho^{(n)}$'s at $x = 0$. Unfortunately, to evaluate $\tilde\rho^{(n)}(0,s)$ we still need the values of $\tilde\rho^{(n-1)}(x,s)$ at all x as is obvious from Eq.(13). This persistent complexity can be relieved if we restrict ourselves to the case where $V(x)$ is a rapidly decreasing function which, in turn, restricts our choice of the interaction potential. If this is the case, the main contribution to the integral in Eq.(13) comes from the values of x near zero. We may then expand $\tilde\rho^{(n-1)}(x,s)$ in a Taylor series about $x = 0$.

$$\tilde{\rho}^{(n-1)}(x, s) = \tilde{\rho}^{(n-1)}(0, s) + \partial \tilde{\rho}^{(n-1)}/\partial x|_{x=0} x + O(x^2) \quad (16)$$

The derivative in the second term on the right hand side can be related to $\tilde{\rho}^{(n-1)}(0,s)$ by the radiative boundary condition to give

$$\partial \tilde{\rho}^{(n-1)}/\partial x|_{x=0} = \eta \tilde{\rho}^{(n-1)}(0, s). \quad (17)$$

where η is the constant given by Eq.(10). Then, Eq.(16) becomes

$$\rho^{(n-1)}(x, s) = (1+\eta x)\rho^{(n-1)}(0, s). \quad (18)$$

Substitution of Eq.(18) into Eq.(13) yields

$$\tilde{\rho}^{(n)}(0, s) = \int_0^\infty dx' g(0, x', s) V(x')(1+\eta x')\tilde{\rho}^{(n-1)}(0, s)$$

$$= [\int_0^\infty dx \zeta(x) g(0, x, s)]^n \tilde{\rho}^{(0)}(0, s) \quad (19)$$

where

$$\zeta(x) \equiv V(x)(1+\eta x) \quad (20)$$

From Eq.(11),(12), and (19), we can calculate $\tilde{\rho}(0,s)$ and, in turn, $\tilde{R}(z)$, and $\tilde{P}(z)$ from Eqs.(14) and (15).

In passing, we want to remark that requiring $V(x)$ to be short–ranged does not seem to be a serious limitation since, as can be seen from Eq.(8), if $U\sim r^{-n}$ as $r\to\infty$ then $V\sim x^{-(n+2)}$ as $x\to\infty$. Even for the Coulomb potential, which is the most long–ranged potential, we find $V\sim x^{-4}$ as $x\to\infty$ owing further to some cancellations (see Section IV).

B. Convergence of the Perturbation Series in Time Domain. We now consider the time domain solution which can be expressed as

$$\rho(0, \tau) = L^{-1}[\rho(0, s)] = \sum_{n=0}^\infty \rho^{(n)}(0, \tau) \quad (21)$$

where L^{-1} denotes the inverse Laplace transformation operator, and

$$\rho^{(n)}(0,\tau) = L^{-1}[\tilde{\rho}^{(n)}(0,s)]$$

$$= \int_0^\infty dx_1 \cdots \int_0^\infty dx_n \prod_{j=1}^n \zeta(x_j) L^{-1}[\tilde{\rho}^{(0)}(0, s)$$

$$\prod_{j=1}^n g(0, \tau)$$

$$= \int_0^\infty dx_1 \cdots \int_0^\infty dx_n \prod_{j=1}^n \zeta(x_j) \int_0^\tau d\tau_0 \rho^{(0)}(0, \tau - \tau_0)$$

$$\qquad (22)$$

$$\times \int_0^{\tau_0} d\tau_1 G(x_1, \tau_0 - \tau_1) \int_0^{\tau_1} d\tau_2 G(x_2, \tau_1 - \tau_2) \times \cdots$$

$$\times \int_0^{\tau_{n-1}} d\tau_n G(x_n, \tau_{n-1} - \tau_n)$$

In writing the last line of Eq.(22), we have applied the convolution theorem of the Laplace transformation repeatedly n times. $G(x_i, \tau)$ denotes the inverse Laplace transform of $g(0, x_i, s)$ in Eq.(10) and its explicit expression is

$$G(x_i, \tau) = L^{-1}[g(0, x_i, s)]$$

$$= (\pi\tau)^{-1/2} \exp(-x_i^2/4\tau) - \eta \exp(\eta^2 \tau + \eta x_i) \quad (23)$$

$$\times erfc(\eta \tau^{1/2} + x_i \tau^{-1/2}/2)$$

where $erfc(x)$ represents the complementary error function. $\rho^{(0)}(0,\tau)$ is the inverse Laplace transform of $\tilde{\rho}^{(0)}(0,s)$ in Eq. (12):

$$\rho^{(0)}(0, \tau) = L^{-1}[\tilde{\rho}^{(0)}(0, s)]$$

$$= (1+x_0)^{-1} G(x_0, \tau) \quad (24)$$

Applying the following inequality

$$|\int_a^b dy f(y)| \le \int_a^b dy |f(y)| \quad (25)$$

repeatedly, we find that the magnitude of $\rho^{(n)}(0,\tau)$ in Eq.(22) is bounded as

$$|\rho^{(n)}(0, \tau)| \le \int_0^\infty dx_1 \int_0^\infty dx_2 \cdots \int_0^\infty dx_n \prod_{i=1}^n |\zeta(x_i)|$$

$$\times \int_0^\tau d\tau_0 |\rho^{(0)}(0, \tau - \tau_0)| \int_0^{\tau_0} d\tau_1 |G(x_1, \tau_0 - \tau_1)| \quad (26)$$

$$\times \int_0^{\tau_1} d\tau_2 |G(x_2, \tau_1 - \tau_2)| \times \int_0^{\tau_{n-1}} dx_n |G(x_n, \tau_{n-1} - \tau_n)|$$

The last integral factor in this equation is further bounded as

$$\int_0^{\tau_{n-1}} d\tau_n |G(x_n, \tau_{n-1} - \tau_n)| = \int_0^{\tau_{n-1}} d\tau_n |G(x_n, \tau_n)|$$

$$\le \int_0^\tau d\tau_n |G(x_n, \tau_n)| \quad (27)$$

The last integral expression in this inequality depends no longer on τ_{n-1}, so that we can manipulate the second factor from the end in Eq.(26), involving the integration over τ_{n-1}, in a similar way. This procedure is repeated to yield the inequality

$$|\rho^{(n)}(0, \tau)| \le \int_0^\tau d\tau_0 |\rho^{(0)}(0, \tau_0)|$$

$$\times \prod_{i=1}^n \int_0^\infty dx_i |\zeta(x_i)| \int_0^\tau d\tau_i |G(x_i, \tau_i)|$$

$$= [K(\tau)]^n \int_0^\tau d\tau_0 |\rho^{(0)}(0, \tau_0)| \quad (28)$$

where

$$K(\tau) \equiv \int_0^\infty dx |\zeta(x)| \int_0^\tau d\tau' |G(x, \tau')|$$

$$= \int_0^\infty dx |\zeta(x)| L^{-1}[s^{-1} g(0, x, s)]$$

$$= \int_0^\infty dx |\zeta(x)| \eta^{-1}[erfc(x\tau^{-1/2}) - \exp(\eta^2\tau + \eta x)$$

$$\times erfc(\eta \tau^{1/2} + x\tau^{-1/2}/2)] \quad (29)$$

In passing from the first to the second line in this equation, we noted the positiveness of $G(x, \tau)$.

Since we have from Eqs.(21) and (28),

$$|\rho(0, \tau)| = \sum_{n=0}^\infty |\rho^{(n)}(0, \tau)| \le \int_0^\tau d\tau_0 |\rho^{(0)}(0, \tau_0)| \sum_{n=0}^\infty [K(\tau)]^n,$$

$$\qquad (30)$$

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we find that, as long as $\int_0^\tau d\tau_0 |\rho^{(0)}(0,\tau_0)|$ is finite, an absolute convergence of the series for $\rho(0,\tau)$ is assured if $K(\tau)$, the convergence factor, is less than unity. $K(\tau)$ increases with τ so that if $K(\infty) < 1$, we can be assured of the convergence of the series at all times. The factor $\int_0^\tau d\tau_0 |\rho^{(0)}(0,\tau_0)|$ can be evaluated explicity from Eq.(24) to give

$$\int_0^\tau d\tau_0 |\rho^{(0)}(0,\tau_0)| = (1+x_0)^{-1} \int_0^\tau d\tau_0 G(x_0,\tau)$$
$$= [\eta(1+x_0)]^{-1} [erfc(x\tau^{-1/2}/2) - \exp(\eta^2\tau + \eta x)$$
$$\times erfc(\eta\tau^{1/2} + x\tau^{-1/2}/2)] \tag{31}$$

which indeed is finite for all times of τ.

We now turn to the error analysis. The upper bound to the error introduced by the n-th order perturbation calculation is as follows:

$$E_n = |\rho(0,\tau) - \sum_{l=0}^n \rho^{(l)}| = \sum_{l=n+1}^\infty \rho^{(l)}$$
$$\leq \int_0^\tau d\tau_0 |\rho^{(0)}(0,\tau_0)| \sum_{l=n+1}^\infty [K(\tau)]^l \tag{32}$$
$$= [1-K(\tau)]^{-1} [K(\tau)]^{n+1} \int_0^\tau d\tau_0 |\rho^{(0)}(0,\tau_0)|$$

C. The Long Time Limit Behavior. With the help of Eq.(19), the infinite series in Eq.(11) may be expressed in a closed form, if the series is convergent, to give

$$\tilde\rho(0,s) = \tilde\rho^{(0)}(0,s) [1 - \int_0^\infty dx \zeta(x) g(0,x,s)]^{-1} \tag{33}$$

By substituting Eqs.(10) and (12) into Eq.(33), we obtain

$$\tilde\rho(0,s) = (1+x_0)^{-1} \exp(-s^{1/2}x_0)$$
$$\times [s^{1/2} + \eta - \int_0^\infty dx \zeta(x) \exp(-s^{1/2}x)]^{-1} \tag{34}$$

For small s (the long time limit) Eq.(34) can be reduced to

$$\tilde\rho(0,s) \approx [(1+x_0) A (s^{1/2} + B/A)]^{-1} \exp(-s^{1/2}x_0) \tag{35}$$

where

$$A \equiv 1 + \int_0^\infty dx \zeta(x) x \tag{36}$$

$$B \equiv \eta - \int_0^\infty dx \zeta(x). \tag{37}$$

Eq.(35) can be inverted analytically and we don't have to rely on the perturbation series solution in the long time limit.

D. The Rate of Recombination and the Remaining Probability. The rate of recombination given by Eq.(14) can be rewritten as

$$\tilde R(z) = x\alpha(x_0) \tilde\rho(x=0,s) \tag{38}$$

where

$$\alpha(x_0) = \exp\{[U(x_0) - U(0)]/2\}$$
$$x = h\sigma/D.$$

The perturbation series expression for the rate of recombina-

tion becomes

$$\tilde R(z) = x\alpha(x_0) \sum_{n=0}^\infty \tilde\rho^{(n)}(0,s) \tag{39}$$

which may be inverse Laplace transformed to give

$$R(t) = x\alpha(x_0) \sum_{n=0}^\infty \rho^{(n)}(0,t) \tag{40}$$

where

$$\rho^{(0)}(0,t) = (D^{1/2}/r_0) \{(\pi t)^{-1/2}\exp[-(r_0-\sigma)^2/4Dt]$$
$$- D^{1/2}\xi\exp[\xi(\xi Dt + r_0-\sigma)] erfc[\xi(Dt)^{1/2}$$
$$+ (r_0-\sigma)(Dt)^{-1/2}/2]\} \tag{41}$$

$$\rho^{(1)}(0,t) = (D/r_0\sigma) \int_0^\infty dx \zeta(x) \{[2\xi^2 Dt + (r_0-\sigma+\sigma x)\xi + 1]$$
$$\times \exp[\xi(\xi Dt + r_0 - \sigma + \sigma x)] erfc[\xi(Dt)^{1/2}$$
$$+ (r_0-\sigma+\sigma x)(Dt)^{-1/2}/2] - 2\xi(Dt/\pi)^{1/2}$$
$$\exp[-r_0-\sigma+\sigma x)^2/4Dt]\} \tag{42}$$

$$\rho^{(2)}(0,t) = -(D^{3/2}/r_0\sigma^2) \int_0^\infty dx_1 \int_0^\infty dx_2 \zeta(x_1) \zeta(x_2)$$
$$\times \{[2\xi^3 D^{3/2} t^2 + 2\xi^2 X D^{1/2} t + \xi(3D^{1/2}t$$
$$+ X^2 D^{-1/2}/2) + X D^{-1/2}] \times \exp[\xi(\xi Dt + X)]$$
$$erfc[\xi(Dt)^{1/2} + X(Dt)^{-1/2}/2]$$
$$- (2\xi^2 Dt + \xi X + 2)(t/\pi)^{1/2}\exp(-X^2/4Dt)\} \tag{43}$$

with $\qquad \xi = \eta/\sigma$ and $X = r_0 - \sigma + \sigma(x_1 + x_2)$.

The remaining probability given by Eq.(15) can be rewritten as

$$\tilde P(z) = z^{-1}[1 - x\alpha(x_0) \tilde\rho(x=0,s)] \tag{44}$$

which may be inverted to give

$$P(t) = 1 - x\alpha(x_0) L^{-1}[z^{-1}\tilde\rho(0,s)]$$
$$= 1 - x\alpha(x_0) \sum_{n=0}^\infty P^{(n)}(t) \tag{45}$$

where

$$P^{(0)}(t) = (r_0\xi)^{-1} \{erfc[(r_0-\sigma)(Dt)^{-1/2}/2]$$
$$- \exp[\xi(\xi Dt + r_0 - \sigma)]$$
$$\times erfc[\xi(Dt)^{1/2} + (r_0-\sigma)(Dt)^{-1/2}/2]\} \tag{46}$$

$$P^{(1)}(t) = (\sigma/r_0\eta^2) \int_0^\infty dx \zeta(x) \{erfc[Y(Dt)^{-1/2}/2]$$
$$- 2\xi(Dt/\pi)^{1/2} \times \exp(-Y^2/4Dt)$$
$$+ (2\xi^2 Dt + \xi Y - 1)\exp[\xi(\xi Dt + Y)]$$
$$\times erfc[\xi(Dt)^{1/2} + Y(Dt)^{-1/2}/2]\} \tag{47}$$

$$P^{(2)}(t) = (\sigma/r_0\eta^3) \int_0^\infty dx_1 \int_0^\infty dx_2 \zeta(x_1) \zeta(x_2)$$

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$$\{erfc[X(Dt)^{-1/2}/2]$$

$$+\xi(Dt/\pi)^{1/2}(2\xi^2 Dt+\xi X-2)\exp(-X^2/4Dt)$$

$$-[1-\xi X-\xi^2(Dt-X^2/2)+2\xi^4 D^2 t^2+2\xi^3 XDt]$$

$$\times\exp[\xi(\xi Dt+X)]erfc[\xi(Dt)^{1/2}+X(Dt)^{-1/2}/2]\} \quad (48)$$

with $Y=r_o-\sigma+\sigma x$ and $X=r_o-\sigma+\sigma(x_1+x_2)$.

In the long time limit, both quantities can be expressed in closed forms with the help of Eqs.(35)–(37). The results become

$$R(t)=P_1(4\pi D)^{-1/2}t^{-3/2} \quad (49)$$

$$P(t)=P_o+P_1(\pi Dt)^{-1/2} \quad (50)$$

where

$$P_o\equiv 1-\sigma x a(x_o)/r_o B \quad (51)$$

$$P_1\equiv \sigma x a(x_o)[(r_o-\sigma)+\sigma A/B]/r_o B. \quad (52)$$

Numerical Method

In order to assess the accuracy of the results from the present perturbation scheme we compare these with pure numerical results based on direct integration of the Smoluchowski equation using the Crank–Nicholson finite difference scheme.[8] However, direct application of the finite difference scheme to the Smoluchowski equation as expressed in Eq.(1) poses some problems. Since the diffusion space is partitioned into a set of discrete mesh points in the finite difference scheme the infinite outer boundary has to be truncated to a finite outer boundary. This causes non-negligible error due to the outer boundary condition of vanishing probability distribution function at infinity. If the spatial integration range is extended sufficiently, the outer boundary condition effect may be reduced but this costs a huge computer memory and a long cpu time.

The above situation can be enormously improved by introducing a nonlinear transformation of the spatial variable given by

$$q=\exp\{-\lambda[(r/\sigma)-1]\} \quad (53)$$

where λ is a positive parameter which may be optimized according to the shape of the potential curve.

The Smoluchowski equation in Eq.(1) is transformed into

$$D^{-1}(\sigma/\lambda)^2 \partial f/\partial t=q^2 f''+q[1+qU'-2(\lambda-\ln q)^{-1}]f'$$

$$+q[qU''+U'-2(\lambda-\ln q)^{-1}U']f \quad (54)$$

where the prime denotes the differentiation with respect to q. The radiative boundary condition, the outer boundary condition, and the initial condition are also transformed, respectively, to give

$$[f'+fU']_{q=1}=-(x/\lambda)f(q=1,t) \quad (55)$$

$$f(q=0,t)=0 \quad (56)$$

$$f(q,t=0)=[4\pi\sigma^2(1-\lambda^{-1}\ln q_o)^2]^{-1}$$

$$(\lambda/\sigma)q_o\delta(q-q_o) \quad (57)$$

Table 1. Convergence Factor and Error Estimates for the Coulomb Potential

$r_c(\times 10^{-9} M)$	$K(\infty)$	$E_2/H^a(\times 10^{-2})$
2.0	0.0437	0.01
4.0	0.1748	0.65
5.0	0.2732	2.81
5.7	0.3509	6.66
6.7	0.4857	22.28
7.0	0.5355	33.05
7.3	0.5877	49.22
7.7	0.6423	74.09

$^a H=\int_0^\tau d\tau_0|\rho^{(0)}(0,\tau_0)|$; See Eq. (31).

The spatial range of $\sigma<r<\infty$ is also transformed to $1>q>0$ and the common method of abrupt truncation of the outer boundary is no longer necessary.

Applications and Discussions

A. The Coulomb Potential. The Coulomb potential is given by

$$U(x)=-(r_c/\sigma)(x+1)^{-1} \quad (58)$$

where

$$r_c=\beta|Z_1 Z_2|e^2/\varepsilon$$

and ε is the dielectric constant of the medium. For this potential $V(x)$ defined in Eq.(8) is found to be a rapidly decreasing function and the approximation introduced in Eq.(16) may be justified.

$$V(x)=-(r_c/\sigma)^2/4(1+x)^4 \quad (59)$$

The convergence factor varying with the values of r_c are tabulated in Table 1 along with the upper bound to the error introduced by the n-th order perturbation calculation. Other parameter values taken in this calculation are $h=2.0$ M/s, $D=1.0\times 10^{-10}$ M^2/s, $r_o=5.0\times 10^{-9}$ M, $\sigma=2.0\times 10^{-9}$ M. In Figures 1 and 2 the remaining probability for the Coulomb potential is plotted. For the numerical calculation the optimum value of $\lambda=0.06$ is used. The agreement of the present perturbation calculation with the numerical result is excellent for the weak Coulomb potential ($r_c=5.0\times 10^{-9}$ M) as shown in Figure 1. The convergence factor in this case is $K(\tau=\infty)=0.2732$ and the second order perturbation calculation gives an excellent result for the full range of time. As the strength of the potential increases to $r_c=7.3\times 10^{-9}$ M the convergence deteriorates and the second order calculation is good only for short time region as shown in Figure 2. In both cases, the analytic long time limit expression in Eq. (50) agrees very well with the numerical results.

B. The Shielded Coulomb Potential. The Shielded Coulomb potential is given by

$$U(x)=\chi\exp[-(1+x)\gamma](1+x)^{-1} \quad (60)$$

where

$$\chi=e^2 Z_1 Z_2\beta\exp(\gamma)[\sigma\varepsilon(1+\gamma)]^{-1}$$
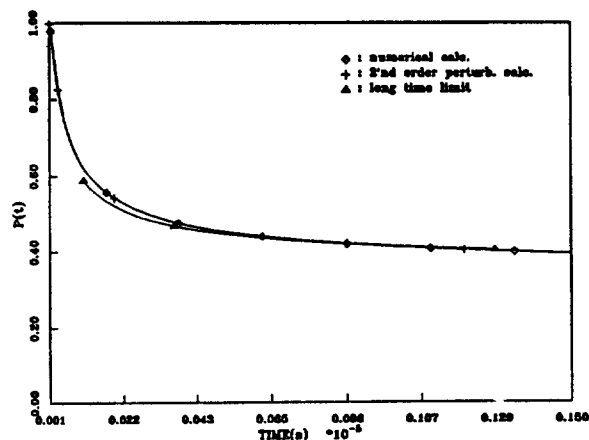
$$\gamma=\phi\sigma$$

Figure 1. Remaining probability for a weak Coulomb potential. $r_c = 5.0 \times 10^{-9}$ M.
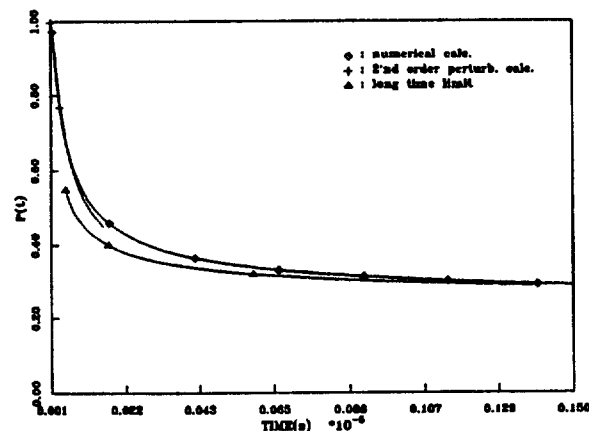

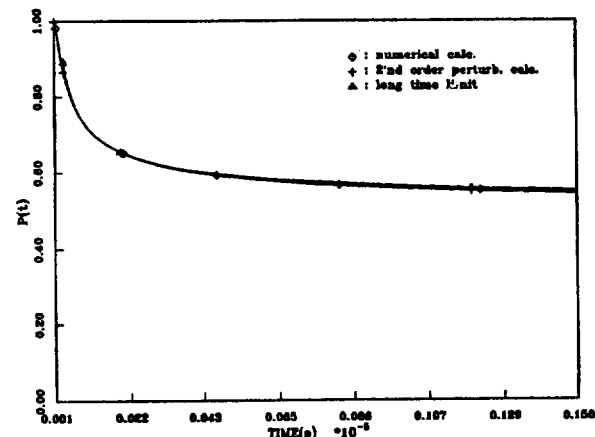**Figure 2.** Remaining probability for a strong Coulomb potential. $r_c = 7.3 \times 10^{-9}$ M.

Figure 3. Remaining probability for a weak shielded Coulomb potential. $X = -6.00 \times 10^{-9}$, $Y = 5.00 \times 10^8$.

Table 2. Convergence Factor and Error Estimates for the Shielded Coulomb Potential

X ($\times 10^{-9}$)	γ ($\times 10^8$)	$K(\infty)$	E_2/H^a ($\times 10^{-2}$)
-3.00	1.00	0.1244	0.22
	3.00	0.1571	0.46
	4.00	0.1480	0.38
	5.00	0.1331	0.27
	6.00	0.1169	0.18
	8.00	0.0867	0.07
-4.50	1.00	0.2450	1.95
	3.00	0.2660	2.56
	4.00	0.2431	1.90
	5.00	0.2143	1.25
	6.00	0.1853	0.78
	8.00	0.1347	0.28
-6.00	1.00	0.4048	11.14
	3.00	0.3952	10.21
	4.00	0.3523	6.75
	5.00	0.3051	4.09
	6.00	0.2603	2.39
	8.00	0.1859	0.79
-7.50	1.00	0.6037	55.50
	3.00	0.5448	35.53
	4.00	0.4757	20.52
	5.00	0.4057	11.23
	6.00	0.3421	6.08
	8.00	0.2401	1.82
-9.00	4.00	0.6132	59.60
	5.00	0.5160	28.39
	6.00	0.4305	14.01
	8.00	0.2975	3.75
-10.50	5.00	0.6361	70.75
	6.00	0.5257	30.63
	7.00	0.4337	14.40
	8.00	0.3579	7.14
	9.00	0.2958	3.68
-12.00	6.00	0.6275	66.35
	7.00	0.5139	27.92
	8.00	0.4215	12.95
	9.00	0.3466	6.37

$^a H$ has the same expression as in Table 1.

and ϕ is the reciprocal thickness of the ionic layer. The convergence factor varying with the values of X and γ are tabulated in Table 2. Other parameter values are the same as for the Coulomb potential except the optimum value of $\lambda = 0.10$ which appears in Eq. (54). The remaining probability for this potential is plotted for two different sets of the values of X and γ in Figure 3 and 4. Again the agreement with the nume-

rical result is excellent for the weaker potential (the smaller absolute value of X) for all times. In fact, for the same value of X the convergence factor decreases as the screening of the potential increases (the larger values of γ). In both cases, the analytic long time limit expression in Eq. (50) agrees very well with the numerical results.

Conclusion

In this work we applied the general perturbation schme proposed by Sibani and Pedersen[7] in time domain to evaluate the rate of recombination and the remaining probability of a pair of reacting particles in liquids in the presence of the Cou-
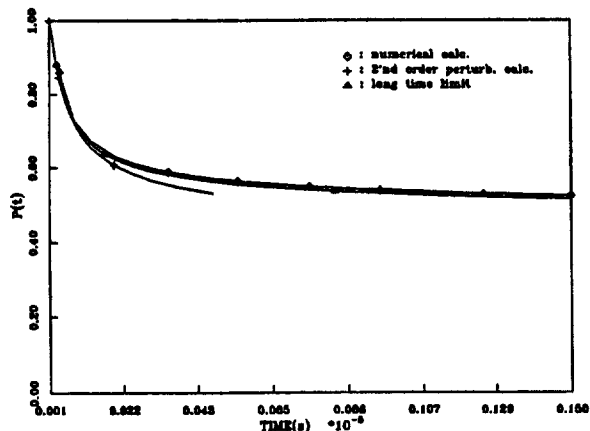
Chemisorption of CO on Rh/SiO₂

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Figure 4. Remaining probability for a strong shielded Coulomb potential. $\chi = -12.00 \times 10^{-9}$, $\gamma = 7.00 \times 10^{8}$.

lomb and the shielded Coulomb potentials. For both potentials the agreement with the numerical result is excellent and we need to consider only up to the second order perturbation term. This approach, however, is appropriate only for weak potentials since the potential parameter(s) representing the potential strength is related to the convergence of the perturbation series. Nevertheless, this approach may be applied to relatively strong potentials if we are interested only in the short time region. This fact is well illustrated in Figure 2 for the Coulomb potential and in Figure 4 for the shielded Coulomb potential. On the other hand, for the long time region

we can use the closed form solutions given by Eqs.(49) and (50).

The numerical method proposed in Section III saves both computing time and computer memory significantly once the parameter λ is optimized and it may be helpful for the future investigation of diffusion–controlled processes in liquids.

References

1. H. J. V. Tyrrell and K. R. Harris, *Diffusion in Liquids: A theoretical and experimental study* (Butterworths, London, 1981).
2. S. A. Rice, *Diffusion–Limited Reactions* (Elsevier, Amsterdam, 1985).
3. U. M. Goesele, *Prog. React. Kinet.* **13**, 63 (1984).
4. D. F. Calef and J. M. Deutch, *Ann. Rev. Phys. Chem.* **34**, 493 (1983).
5. K. M. Hong and J. Noolandi, *J. Chem. Phys.* **68**, 5163 (1978).
6. D. Y. Kim, S. Shin, and K. J. Shin, *Bull. Kor. Chem. Soc.* **4**, 271 (1986).
7. P. Sibani and J. B. Pedersen, *J. Chem. Phys.* **74**, 6934 (1981).
8. W. Press, B. Flannery, S. A. Teukolsky, and W. T. Vetterling *Numerical Recipes* (Cambridge Univ. Press, 1986).

A Study on the Chemisorption of Carbon Monoxide on Silica–Supported Rhodium

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We have investigated the infrared absorption spectra for carbon monoxide chemisorbed on reduced and oxidized Rh/SiO₂ with and without potassium coating within the frequency range of 1800–2200 cm⁻¹ at various Rh concentrations, CO pressures, and temperatures. In case of no potassium coating, only two bands at 2070 and 1900 cm⁻¹ appeared for CO adsorbed on reduced Rh/SiO₂ while for oxidized Rh/SiO₂ four bands were found at 2100, 2070, 2040, and 1900 cm⁻¹. We have successfully tried to explain the differences between our observations and those by other investigators who used the Rh/Al₂O₃ system instead of Rh/SiO₂ on the basis of the suggestions by Yates *et al.* Accordingly, we propose that the surface OH groups are deeply involved in producing the Rh⁺¹ sites which are responsible for the gem-dicarbonyl species. On coating with potassium all the IR bands for three carbonyl species were found to suffer red shift, the magnitude of which increased with increasing Rh/CO ratio.

Introduction

One of the current research topics of importance is the determination of the structures of molecules adsorbed on supported transition metal catalysts, and the elucidation of

the character (oxidation state, dispersed state, *etc.*) of the supported metals and the nature of support-metal interaction in such catalysts is no less important. Rhodium has been one of the more popular metals for such study, not merely because the supported rhodium catalysts are widely in use for industrial purposes but because it is relatively easy to prepare the rhodium in the Rh⁰ metallic state on a support such

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