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A Note on the Theory of Diffusion Controlled Reactions with Application to the Quenching of Fluorescence

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The principles of Smoluchowski's collision theory of reactions in solution are outlined. This theory is applicable to reactions which occur immediately on the collision of two reactant particles; that is, diffusion controlled reactions. The rate of such reactions depends on the collision frequency of reactants. In this paper an expression for the collision frequency is derived as a function of time when initially there is a Boltzmann distribution of particles around any particular reactant molecule. Both the Brownian motion of and the forces between reactant molecules are considered in the calculation. The general results are applied to the theory of quenching of fluorescence. It is shown that the quenching constant, k_q , defined by

$$\left(\frac{I_0}{I} - 1\right) / n_q = k_q,$$

(where I_0 is the intensity of fluorescence in the absence of quencher and I the intensity in the presence of quencher of concentration n_q) can be expressed as a sum of two terms, one proportional to the reciprocal of the viscosity of the solvent and the other to the reciprocal of the square root of the viscosity.

RECENTLY there has been a renewal of interest in Smoluchowski's collision theory of reaction rates in solutions. This theory,¹ which is applicable to those reactions which occur instantaneously upon collision of two molecules or ions (diffusion controlled reactions) was originally developed to explain the process of coagulation of colloids. It assumes that any pair of colloidal particles adhere to each other after they collide and behave as a single larger particle. Thus, after many collisions giant coagulated particles are formed. The collision frequency calculations required for this theory were shown to be equivalent to the calculation of the rate of diffusion of particles into the sphere of influence of a single particle in the solution. In Smoluchowski's work the effect of forces between particles was neglected. Zsigmondy² and Tuorila³ obtained reasonable experimental agreement with Smoluchowski's theory. Some deviation was to be expected because of the assumptions that were made to avoid the complications caused by the

wide variety of shapes of coagulated particles formed by collisions.

In 1935 Sveshnikoff⁴ developed a theory of quenching of fluorescence using Smoluchowski's methods. Qualitatively the explanation of quenching is based on the idea that a molecule or ion in solution which has been excited by the absorption of a photon returns to its ground state by the emission of light (fluorescence) or by collision with a foreign particle called a quencher. An increase in quencher concentration causes more collisions, lowering the intensity of fluorescence. Sveshnikoff derived an expression for the collision frequency of excited particles with quencher from a study of the diffusion of quencher into the sphere of influence of the excited particles. Usually one assumes that this sphere has a radius equal to the sum of the radii of the two colliding particles.

Frequently the excited particles and quencher are ions, in which case Coulomb forces interfere with the normal diffusion process. Debye⁵ has evaluated the influence of these forces on the steady-state collision frequency. As will be discussed later in this paper, the transient collision frequency (collision frequency before the steady

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¹ M. Smoluchowski, *Physik. Zeits.* **17**, 557, 585 (1916); *Zeits. f. physik. Chemie* **92**, 129 (1917).

² R. Zsigmondy, *Zeits. f. physik. Chemie* **92**, 600 (1917).

³ Tuorila, *Kolloid-Chem. Beihefte* **22**, 191 (1926).

⁴ B. Sveshnikoff, *Acta Physicochimica U.S.S.R.* **3**, 257 (1935).

⁵ P. Debye, *Trans. Electrochem. Soc.* **82**, 265 (1942).

state is achieved) is important in describing some reactions; for example, quenching of fluorescence in the photo-stationary state. A first attempt at this transient problem has been made by Umberger and LaMer.⁶

The purpose of this paper is to outline the principles of Smoluchowski's collision theory of reactions in solution, and to use it to derive formulae for collision frequency as a function of time in dilute solutions. The results will be applied to the theory of quenching of fluorescence.

I. GENERAL THEORY

Let us consider a solution containing two kinds of particles as solute, and suppose that a reaction occurs when a particle of one kind enters the "sphere of influence" of one of the other kind; that is, when their centers are separated by a distance R (usually assumed to be the sum of the radii of the two particles). Under this assumption the reaction rate is a function of the number of collisions per unit time. In general, the collision frequency depends on the Brownian motion of the particles. We base our collision frequency calculations on Smoluchowski's differential equation for the probability of finding a particle in a given region of space while it is experiencing a Brownian motion in the force field of another particle. The solution of this differential equation enables us to determine the probability of a collision between two particles in a given time interval. Assuming the independence of collisions, we see that the product of this probability by the number of particles of each type in the system during the collision interval gives the total number of collisions in the interval. Thus we are able to calculate the reaction rate at that time.

Smoluchowski's equation:⁷

$$\partial w_B / \partial t = D_2 \operatorname{div} \{ \operatorname{grad} w_B - (\mathbf{F} w_B / kT) \} \quad (1)$$

describes the motion of a particle "B" in the force field of a stationary particle "A" separated from it by a distance r . Here $w_B(r, t)$ is defined

so that $4\pi r^2 w_B(r, t) dr$ is the probability of finding the two particles separated by a distance between r and $r + dr$ at time t . k is Boltzmann's constant, T the absolute temperature, and D_2 the diffusion constant of particles of kind B in the solution. If the force \mathbf{F} can be derived from a potential U ,

$$\mathbf{F} = -\operatorname{grad} U, \quad (2)$$

(1) becomes

$$\partial w_B / \partial t = D_2 \{ \nabla^2 w_B + (w_B / kT) \nabla^2 U + (1/kT) (\partial w_B / \partial r) (\partial U / \partial r) \}. \quad (1a)$$

When A also experiences a Brownian motion, one must replace D_2 by $D = D_1 + D_2$, where D_1 is the diffusion constant for particles of kind A in the solution. It is convenient to introduce a new function $\alpha(r, t)$ defined by

$$\alpha(r, t) = w_B \exp \{ U(r) / kT \}, \quad (3)$$

for after this substitution (1a) becomes (assuming the diffusion field to be spherically symmetrical)

$$\frac{\partial \alpha}{\partial t} = D \left\{ \frac{\partial^2 \alpha}{\partial r^2} + \frac{\partial \alpha}{\partial r} \left(\frac{2}{r} - \frac{1}{kT} \frac{\partial U}{\partial r} \right) \right\}. \quad (4)$$

This equation has also been derived in a somewhat different manner by Umberger and LaMer.⁶

To calculate the collision frequency we use the initial condition:

at time $t=0$, particles of kind B are arranged in a Boltzmann distribution about one of kind A , thus

$$w_B(r, 0) = n_B(0) \exp \{ -U(r) / kT \}, \quad (5a)$$

where $n_B(0)$ is the mean concentration in particles per cc of B 's exterior to the sphere $r = |R|$. In terms of $\alpha(r, t)$ this is equivalent to

$$\alpha(r, 0) = n_B(0) = n_B; \quad (5b)$$

and Smoluchowski's boundary conditions:

(a) Very far from the particle A the concentration of B 's remain at their initial value

$$w_B(\infty, t) = n_B \quad (6a)$$

or

$$\alpha(\infty, t) = n_B. \quad (6b)$$

This is strictly true only in the case where $n_B(0) \gg n_A(0)$, so that while the supply of A 's is exhausted by the reaction the concentration

⁶ J. Umberger and V. LaMer, J. Am. Chem. Soc. 67, 1099 (1945).

⁷ M. Smoluchowski, Ann. d. Physik 48, 1103 (1915). See also S. Chandrasekhar, Rev. Mod. Phys. 15, 1 (1943). This paper also contains a short exposition of Smoluchowski's theory of coagulation of colloids.

of B 's is but slightly affected. Thus, while $n_B(t) \simeq n_B$ for all t , $n_A(t) \rightarrow 0$ as $t \rightarrow \infty$.

(b) The concentration of particles of kind B on the sphere of influence of an A is zero before a reaction involving that particular A occurs

$$w_B(R, t) = 0 \quad (7a)$$

or

$$\alpha(R, t) = 0. \quad (7b)$$

Under conditions (a) and (b), Eq. (1) is equivalent to the equation describing the diffusion of particles into a spherical hole of radius R from a spherically symmetrical steady source a large distance away.

The solution of (4) under these conditions enables one to calculate⁶ the rate $I(t)$ at which particles of kind B arrive at the surface $|r| = R$ at time t :

$$\begin{aligned} I(t) &= 4\pi r^2 D \left(\frac{\partial w_B}{\partial r} + \frac{w_B}{kT} \frac{\partial U}{\partial r} \right)_{r=R} \\ &= 4\pi D R^2 \exp \{ -U(R)/kT \} (\partial \alpha / \partial r)_{r=R} \end{aligned} \quad (8)$$

and the collision frequency $\nu(t)$ at time t from

$$\nu(t) = I(t) n_A(t). \quad (9)$$

II. COLLISION FREQUENCY IN GENERAL FORCE FIELD

In this section we shall solve the differential Eq. (4),

$$\frac{\partial \alpha}{\partial t} = D \left\{ \frac{\partial^2 \alpha}{\partial r^2} + \frac{\partial \alpha}{\partial r} \left(\frac{2}{r} - \frac{1}{kT} \frac{\partial U}{\partial r} \right) \right\}, \quad (4)$$

under the initial condition (5b),

$$\alpha(r, 0) = n_B, \quad (5b)$$

and the boundary conditions (6b) and (7b):

$$\alpha(\infty, t) = n_B, \quad (6b)$$

$$\alpha(R, t) = 0. \quad (7b)$$

The steady-state solution of (4) (that corresponding to $\partial \alpha / \partial t = 0$) has been obtained by Debye⁵ and is, as can be verified by direct substitution into (4), (6b), and (7b)

$$\alpha(r) = n_B \{ 1 - [S(r)/S(R)] \}, \quad (10)$$

where

$$S(r) = \int_r^\infty z^{-2} \exp \{ U(z)/kT \} dz. \quad (11)$$

To obtain the transient solution of (4) we introduce a new function $f(r, t)$ defined by

$$\alpha(r, t)/n_B = 1 + [S(r)/S(R)] [f(r, t) - 1]. \quad (12)$$

By substituting (12) into (4), (5b), (6b), and (7b) we see that $f(r, t)$ satisfies

$$\frac{\partial f}{\partial t} = D \left\{ \frac{\partial^2 f}{\partial r^2} + \frac{\partial f}{\partial r} \left[\frac{2S'(r)}{S(r)} + \left(\frac{2}{r} - \frac{1}{kT} \frac{\partial U}{\partial r} \right) \right] \right\}, \quad (13)$$

$$f(R, t) = 0, \quad f(r, 0) = 1, \quad \text{and} \quad f(\infty, t) < \infty, \quad (13a)$$

where

$$S'(r) = \partial S / \partial r = -r^{-2} \exp \{ U(r)/kT \}. \quad (14)$$

The transformation (12) is useful because in the range of large r the coefficient of $(\partial f / \partial r)$ becomes negligible, while in the range of medium r 's corresponding to close approach of two particles, forces of the Coulomb type $U(r) \sim a/r$ cause the term $2S'(r)/S(r)$ to cancel the remainder of the coefficient of $\partial f / \partial r$, leaving a coefficient of lower order than that of $\partial \alpha / \partial r$ in (4). This is apparent if we write

$$S(r) \simeq \int_r^\infty z^{-2} (1 + a/zkT + a^2/2(zkT)^2 + \dots) dz,$$

from which we obtain

$$2S'(r)/S(r) \simeq -2/r - a/r^2 kT - O(1/r^3);$$

thus, leaving terms of $O(1/r^3)$ when added to

$$\left(\frac{2}{r} - \frac{1}{kT} \frac{\partial U}{\partial r} \right) \simeq 2/r + a/kTr^2.$$

We shall on this account neglect the term involving $\partial f / \partial r$ in (15), waiting until the next section to estimate the error caused by this simplification. The solution of the approximate $f(r, t)$ equation $\partial f / \partial t = D \partial^2 f / \partial r^2$ under the conditions (13a) is

$$f(r, t) = \text{erf} \{ (r - R) / 2(Dt)^{1/2} \}, \quad (15)$$

where

$$\text{erf } y = 2\pi^{-1/2} \int_0^y \exp(-v^2) dv. \quad (15a)$$

Therefore,

$$\begin{aligned} \alpha(r, t)/n_B - 1 &\simeq S(r)/S(R) \\ &\times \{ -1 + \text{erf} [(r - R) / 2(Dt)^{1/2}] \}, \end{aligned} \quad (16)$$

and from (8) the collision frequency $\nu(t)$ at time t is

$$\nu(t) = I(t)n_A(t) \simeq 4n_B n_A(t) \pi D \times \left\{ \frac{1}{S(R)} + \frac{R^2 \exp[-U(R)/kT]}{(\pi D t)^{1/2}} \right\}, \quad (17)$$

where $S(R)$ is given by (11). In the absence of interparticle forces, $U(R)=0$ and $S(R)=1/R$, reducing (17) to the classical Smoluchowski expression

$$\nu(t) = 4\pi n_B n_A(t) D R \{1 + R/(\pi D t)^{1/2}\}. \quad (17a)$$

III. COLLISION FREQUENCY WHEN $U(r)$ IS COULOMB POTENTIAL

The potential function of particular interest for studying reaction rates in very dilute solutions is the Coulomb potential

$$U(r) = z_A z_B e^2 / \mathfrak{D} r, \quad (18)$$

where ez_A = charge on particle of kind A and ez_B = charge on particle of kind B .

It is convenient to define a length L as

$$L = z_A z_B e^2 / \mathfrak{D} k T. \quad (19a)$$

L is positive when both kinds of particles have the same type of charge, and negative otherwise. With a Coulomb potential

$$S(r) = \int_r^\infty z^{-2} \exp(L/z) dz = (e^{L/r} - 1)/L, \quad (19b)$$

so that (13) becomes

$$\frac{\partial f}{\partial t} = D \left\{ \frac{\partial^2 f}{\partial r^2} + \frac{1}{L} \frac{\partial f}{\partial r} \left(\frac{2L}{r} - \frac{L^2}{r^2} \coth \frac{L}{2r} \right) \right\}. \quad (20)$$

It is to be noted that the coefficient of $(\partial f / \partial r)$ can be written as

$$\frac{1}{L} \left\{ \frac{2L}{r} - \left(\frac{L}{r} \right)^2 \coth \frac{L}{2r} \right\} \simeq (1/L) \left\{ -\frac{1}{6} (L/r)^3 + \frac{1}{360} (L/r)^5 + \dots \right\}$$

which for most values of L/r of interest is small. The boundary conditions (13a) are still valid.

Let $f(r, t)$ be divided into two parts

$$f(r, t) = f_1(r, t) + f_2(r, t), \quad (21)$$

such that $f_1(r, t)$ satisfies

$$\partial f_1 / \partial t = D(\partial^2 f_1 / \partial r^2), \quad (22)$$

the boundary conditions

$$f_1(R, t) = 0 \quad \text{and} \quad f_1(\infty, t) < \infty, \quad (23a)$$

and the initial condition

$$f_1(r, 0) = 1. \quad (23b)$$

Then f_2 satisfies the initial and boundary conditions

$$f_2(R, t) = f_2(\infty, t) = f_2(r, 0) = 0. \quad (24)$$

By introducing the Laplace transform of $f_1(r, t)$:

$$F_1(r, s) = \int_0^\infty f_1(r, t) \exp(-st) dt, \quad (25)$$

one can reduce (22) to an ordinary equation

$$d^2 F_1 / dr^2 - (s/D) F_1 = -1/D,$$

with the boundary conditions $F_1(R, s) = 0$ and $F_1(\infty, s) < \infty$. The solution of this equation is

$$F_1(r, s) = (1/s) \{1 - \exp[-(r-R)(s/D)^{1/2}]\}. \quad (26)$$

Inverting the Laplace transform, we have⁸

$$f_1(r, t) = \text{erf}[(r-R)/2(Dt)^{1/2}], \quad (27)$$

and as a first approximation

$$\alpha(r, t) / n_B \simeq 1 + \left(\frac{e^{L/r} - 1}{e^{L/R} - 1} \right) \left\{ -1 + \text{erf} \left(\frac{r-R}{2(Dt)^{1/2}} \right) \right\}, \quad (28)$$

which agrees with (16).

The determination of $f_2(r, t)$ is somewhat more complicated. Except in the region of very small r , (20) reduces to (22), so one could expect f_1 to be the main contribution to f , and to be quite larger than f_2 . Then, substituting (21) into (20), remembering (22) and neglecting the product of the two small quantities, df_1/dr and that following (20), we have

$$\frac{\partial f_2}{\partial t} = D \left\{ \frac{\partial^2 f_2}{\partial r^2} + \frac{\partial f_1}{L \partial r} \left(\frac{2L}{r} - \frac{L^2}{r^2} \coth \frac{L}{2r} \right) \right\}. \quad (29)$$

⁸ Cf. the table of transforms in Churchill, *Modern Operational Mathematics in Engineering* (McGraw-Hill Book Company, Inc., New York, 1944), p. 295.

The initial and boundary values of f_2 are given by (20). This equation is solved in the appendix where it is shown that

$$f_2(r, t) = -\frac{2}{(\pi Dt)^{\frac{1}{2}}} \left\{ \int_R^\infty \exp [-(r-3R+2y)^2/4Dt] \log \left(\frac{y}{L} \sinh \frac{L}{2y} \right) dy \right. \\ \left. - \int_r^\infty \exp [-(2y-R-r)^2/4Dt] \log \left(\frac{y}{L} \sinh \frac{L}{2y} \right) dy \right\}, \quad (30)$$

$$= -\frac{2}{(D\pi t)^{\frac{1}{2}}} \left\{ \quad \right\}.$$

Thus,

$$-1 + \alpha(r, t)/n_B \simeq \left(\frac{e^{L/r} - 1}{e^{L/R} - 1} \right) \left[-1 + \operatorname{erf} \left(\frac{r-R}{2(Dt)^{\frac{1}{2}}} \right) - \frac{2}{(\pi Dt)^{\frac{1}{2}}} \left\{ \quad \right\} \right].$$

We are now able to calculate the rate at which particles arrive at the surface $|r| = R$ from (8)

$$I(t) = 4\pi DR^2 \exp \{ -U(R)/kT \} (\partial \alpha / \partial r)_{r=R}.$$

Since

$$\log \{ (R/L) \sinh (L/2R) \} = \frac{2}{Dt} \int_R^\infty (y-R) \log \{ (R/L) \sinh (L/2R) \} \exp [-(y-R)^2/Dt] dy, \quad (31)$$

we have

$$\left[\frac{1}{n_B} \frac{\partial \alpha}{\partial r} \right]_{r=R} = \frac{Le^{L/R}}{R^2(e^{L/R} - 1)} + (\pi Dt)^{-\frac{1}{2}} + \frac{4\pi}{(\pi Dt)^{\frac{1}{2}}} \int_R^\infty (y-R) \exp [-(y-R)^2/Dt] \log \left(\frac{y \sinh L/2y}{R \sinh L/2R} \right) dy \quad (31a).$$

and

$$I(t) = 4\pi Dn_B \left\{ \frac{L}{e^{L/R} - 1} + \frac{R^2 e^{-L/R}}{(\pi Dt)^{\frac{1}{2}}} + \frac{4\pi R^2 e^{-L/R}}{(\pi Dt)^{\frac{1}{2}}} \right. \\ \left. \times \int_R^\infty (y-R) \exp [-(y-R)^2/Dt] \log \left(\frac{y \sinh L/2y}{R \sinh L/2R} \right) dy \right\}. \quad (32a)$$

Integrating the right-hand term by parts, we obtain

$$I(t) = 4\pi DRn_B \left\{ \frac{L/R}{e^{L/R} - 1} + \frac{Re^{-L/R}}{(\pi Dt)^{\frac{1}{2}}} + \frac{Re^{-L/R}}{(\pi Dt)^{\frac{1}{2}}} \int_R^\infty \left(\frac{2}{y} - \frac{L}{y^2} \coth \frac{L}{2y} \right) \exp [-(y-R)^2/Dt] dy \right\}. \quad (32b)$$

The integral

$$J(L/R, Dt/R^2) = \frac{R}{(\pi Dt)^{\frac{1}{2}}} \int_R^\infty \left(\frac{2}{y} - \frac{L}{y^2} \coth \frac{L}{2y} \right) \exp \left\{ -\frac{(y-R)^2}{Dt} \right\} dy \quad (33)$$

is evaluated in Appendix II. The value of the third term in the bracket in (32b) is tabulated in Table I as a function of $\tau = Dt/R^2$ and is compared with the sum of the first two terms. Four typical ratios 3, 2, 1, and -1 have been chosen. According to Umberger and LaMer⁶ $L/R=3$ corresponds approximately to the self-quenching of fluorescein and $L/R=2$ to the quenching of a fluorescein ion by an iodide ion. It is to be noted that over the entire time scale the perturbation term (33) gives a very small percentage contribution to the collision frequency $n_A(t)I(t)$ and for most purposes may be neglected, leaving

$$\nu(t) = n_A(t)I(t) \simeq 4\pi n_A(t)n_B DR \left\{ \frac{L/R}{e^{L/R} - 1} + \frac{Re^{-L/R}}{(\pi Dt)^{\frac{1}{2}}} \right\}. \quad (34)$$

TABLE I. Comparison of the sum of the two main terms in the bracket of (32b) with correction term, Δ , given by the integral in the same bracket.

L/R	$\frac{\pi Dt}{R^2}$	10^{-4}	10^{-3}	10^{-2}	10^{-1}	1	10	10^2	10^3	10^4	∞
3.0	approx. 5.13 correction, Δ -.03	1.73	.655	.314	.207	.174	.162	.158	.157	.157	
		-.03	-.03	-.025	-.02	-.02	$-.02 < \Delta < 0$	$-.02 < \Delta < 0$	0	.0007	0
2.0	approx. 13.8 correction -.04	4.59	1.67	.741	.448	.356	.327	.317	.314	.313	
		-.04	-.04	-.035	-.02	-.01	-.004	-.002	-.0003	0	
1.0	approx. 37.4 correction -.03	12.2	4.26	1.74	.950	.698	.619	.594	.586	.582	
		-.03	-.03	-.025	-.02	-.015	-.015	-.01	-.004	0	
0	approx. 101 correction 0	32.6	11.0	4.16	2.00	1.32	1.10	1.03	1.01	1.00	
		0	0	0	0	0	0	0	0	0	
-1.0	approx. 273 correction -.22	87.5	28.8	10.2	4.30	2.44	1.85	1.67	1.61	1.58	
		-.22	-.20	-.17	-.13	-.10	-.09	-.08	-.02	0	

The results in Table I confirm our original assumption that f_2 in (21) is small compared to f_1 , so that (32a) can be accepted as a complete expression for $I(t)$.

IV. COLLISION FREQUENCY FOR SCREENED COULOMB POTENTIAL

The results of the last section are valid only for solutions so dilute that there are very few ions per unit distance between an arbitrarily selected pair. As the concentration increases the number of intermediate ions increases, screening the effect of one ion on another distant one. In this case, according to the Debye-Hückel theory of strong electrolytes

$$U(r) = -\frac{1}{2} \left\{ \frac{\exp(\kappa R_2/2)}{1 + \frac{1}{2}\kappa R_1} + \frac{\exp(\kappa R_1/2)}{1 + \frac{1}{2}\kappa R_2} \right\} \frac{z_1 z_2 e^2 e^{-\kappa r}}{\mathcal{D}r}, \quad (35)$$

where R_1 and R_2 are radii of the two particles and κ the ionic strength of the solution. Following Debye,⁵ if we let

$$\gamma = -\frac{1}{2} \left\{ \frac{\exp(\frac{1}{2}\kappa R_2)}{1 + \frac{1}{2}\kappa R_1} + \frac{\exp(\frac{1}{2}\kappa R_1)}{1 + \frac{1}{2}\kappa R_2} \right\}, \quad (35a)$$

$$\kappa^2 = (4\pi e^2 / \mathcal{D}kT) \sum n_i z_i^2, \quad (35b)$$

$S(r)$ becomes (from (11)):

$$S(r) = \int_r^\infty z^{-2} \exp\{(\gamma L/z)e^{-\kappa z}\} dz.$$

When κ is small,

$$S(r) \simeq \int_r^\infty z^{-2} \exp\{(\gamma L/z)(1 - \kappa z + \dots)\} dz, \\ = e^{-\kappa \gamma L} (e^{L\gamma/r} - 1) / L\gamma.$$

Thus, the collision frequency is, from (17),

$$\nu(t) \simeq 4\pi n_B n_A(t) D \left\{ \frac{\gamma L \exp(\kappa L \gamma)}{(e^{L\gamma/R} - 1)} + \frac{R^2 \exp[-(\gamma L/R)e^{-R\kappa}]}{(\pi Dt)^{1/2}} \right\}. \quad (36)$$

On the basis of the numerical work discussed in the last section, we neglect the contribution of the perturbation terms to (36).

V. APPLICATION TO QUENCHING OF FLUORESCENCE

In the absence of a quencher fluorescence is a simple first-order reaction. When a solution of a

dye such as fluorescein is irradiated with light of the proper wave-length, it is excited into a higher energy state. After the light source is removed the excited molecules return to their normal states with the emission of radiation. This emission occurs in such a manner that if $n_A(t)$ is the number of excited molecules at time t , their rate of return to a normal state is proportional to the number excited at that time; that is,

$$dn_A(t)/dt = -n_A(t)/\tau_0,$$

where τ_0 is the rate constant for the reaction. Clearly

$$n_A(t) = n_A \exp(-t/\tau_0), \quad (37)$$

where $n_A = n_A(0)$ = number of excited molecules when light source is removed at time $t=0$.

If potassium iodide is added to the fluorescein solution at the moment the exciting radiation is removed, it is found that the light emitted by the excited molecules as they return to their ground state is not as intense as in the absence of the KI. This quenching effect can be explained by assuming that when an iodide ion collides with an excited fluorescein molecule it absorbs the excess energy of the fluorescein, returning it to its ground state. Thus, an excited fluorescein molecule loses its excess energy either by collision or through fluorescence.

The number of collisions in time dt at time t is (17a):

$$\begin{aligned} \nu(t)dt &\simeq 4n_B n_A(t) \pi D \\ &\times \left\{ \frac{1}{S(R)} + \frac{R^2 \exp[-U(R)/kT]}{(\pi D t)^{\frac{1}{2}}} \right\} dt \\ &= n_B n_A(t) \{ \beta + \epsilon t^{-\frac{1}{2}} \} dt. \end{aligned} \quad (38)$$

Thus, if each collision removes energy from an excited fluorescein molecule,

$$dn_A(t)/dt = -\{ (1/\tau_0) + \beta n_B + \epsilon n_B t^{-\frac{1}{2}} \} n_A(t),$$

or at time t :

$$n_A(t) = n_A(0) \exp \{ -t(\beta n_B + 1/\tau_0) - 2\epsilon n_B t^{\frac{1}{2}} \}. \quad (39)$$

In the case of a Coulomb potential

$$\beta = \frac{4\pi(L/R)(D_1 + D_2)(R_1 + R_2)}{(e^{L/R} - 1)} \quad (40a)$$

and

$$\epsilon = 4R^2 e^{-L/R} [\pi(D_1 + D_2)]^{\frac{1}{2}}. \quad (40b)$$

Employing Einstein's relation between viscosity of solvent and diffusion constant

$$D_j = kT/6\pi\eta R_j,$$

we have

$$\beta = \frac{2kT[2 + (\dot{R}_1/R_2) + (R_2/R_1)]}{3\eta(R/L)(e^{L/R} - 1)} \quad (41a)$$

and

$$\epsilon = 4R^2 e^{-L/R} \left\{ \frac{kT}{6\eta} \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \right\}^{\frac{1}{2}}. \quad (41b)$$

The mean life of an excited fluorescein ion is, in the absence of quencher, τ_0 , for

$$(1/n_A) \int_0^\infty n_A(t) dt = \int_0^\infty \exp(-t/\tau_0) dt = \tau_0. \quad (42)$$

In the presence of quencher it is

$$\begin{aligned} \tau^* &= \int_0^\infty \exp \left\{ -t \left(\beta n_B + \frac{1}{\tau_0} \right) - 2\epsilon n_B t^{\frac{1}{2}} \right\} dt \\ &= \frac{\tau_0 \exp x^2}{(1 + \beta n_B \tau_0)} \int_0^\infty \exp [-(u^{\frac{1}{2}} + x)^2] du, \end{aligned}$$

where

$$x = n_B \epsilon \{ \tau_0 / (1 + \beta n_B \tau_0) \}^{\frac{1}{2}}. \quad (42a)$$

By an obvious transformation

$$\begin{aligned} \tau^* &= \frac{2\tau_0 \exp x^2}{1 + \beta n_B \tau_0} \int_x^\infty (y-x) \exp[-y^2] dy \\ &= \frac{\tau_0}{1 + \beta n_B \tau_0} \{ 1 - x\pi^{\frac{1}{2}} (\exp x^2) (1 - \operatorname{erf} x) \}; \end{aligned} \quad (43a)$$

and when x is small,

$$\begin{aligned} \tau^* &\simeq \frac{\tau_0}{1 + n_B \beta \tau_0} (1 - x\pi^{\frac{1}{2}}) \\ &= \frac{\tau_0}{1 + \beta n_B \tau_0} \{ 1 - n_B \epsilon [\pi \tau_0 / (1 + \beta n_B \tau_0)]^{\frac{1}{2}} \}. \end{aligned} \quad (43b)$$

As $n_B \rightarrow 0$

$$\left(\frac{\tau_0}{\tau^*} - 1 \right) \rightarrow n_B \beta \tau_0 + n_B \epsilon (\pi \tau_0)^{\frac{1}{2}}. \quad (44)$$

Since the process of fluorescence is a very rapid one ($\tau_0 \sim 10^{-8}$ second), it is quite difficult to follow the decrease in $n_A(t)$ with time. One usually studies quenching of fluorescence in the *photo-stationary* state; that is, in a state in which the particles in the solution are kept excited by a constant source of light and in which the intensity of fluorescence remains constant. In any small time interval the same number of dye molecules become excited as lose their excess energy by either radiation or collision. It can be shown that under these conditions the ratio of the intensity of fluorescence in an unquenched solution to that in a quenched solution containing the same concentration of dye is equal to the ratio of the mean lives of the excited dye molecules in each of the solutions^{3, 6}

$$I_0/I = \tau_0/\tau^*.$$

The quenching constant, k_Q , defined by

$$[(I_0/I) - 1]/n_B = k_Q$$

is, in the range of low quencher concentration, therefore (from (44)),

$$k_Q = \beta\tau_0 + \epsilon(\pi\tau_0)^{1/2}. \quad (45a)$$

In particular, in the presence of Coulomb forces between particles, we obtain from⁹ (41)

$$k_Q = \frac{2kT\tau_0 \left(2 + \frac{R_1}{R_2} + \frac{R_2}{R_1} \right)}{3\eta(R/L)(e^{L/R} - 1)} + 4R^2 e^{-L/R} \left(\frac{kT\pi\tau_0}{6\eta} \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \right)^{1/2}. \quad (45b)$$

This expression differs from the classical one by the appearance of a term inversely proportional to the square root of the viscosity of the solvent. A similar expression can be obtained in the case of screened Coulomb forces by evaluating β and ϵ from (36) and (38).

Many experimental curves of k_Q plotted as a function of the reciprocal of the viscosity of the solvent have been collected in a paper of Davis

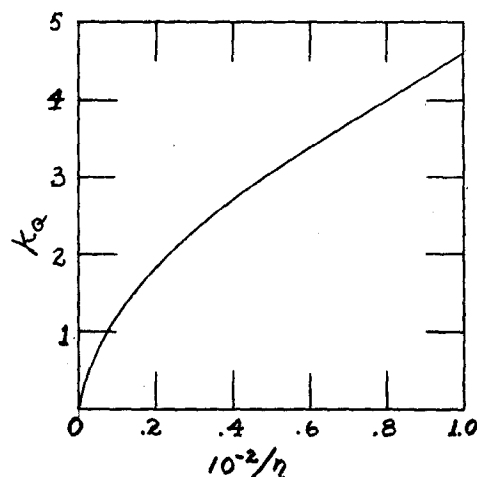


FIG. 1. Quenching of fluorescence of fluorescein by potassium iodide. Solvent is sucrose or glycerol solution. The volume molar concentration scale was used in determining k_Q (data from Sveshnikoff).

and LaMer.¹⁰ An example (see Fig. 1) is that obtained for the quenching of fluorescence of fluorescein by potassium iodide (original data from Sveshnikoff). It appears from (45) that two possible causes of the curvature in the experimental curves are

- a significant fraction of the collisions between quencher and newly excited particles occur before a steady collision rate is achieved,
- change in dielectric constant of solvent with change in viscosity.

Classically¹⁰ the quenching constant curve should be a straight line. As was pointed out to the author by Dr. J. Q. Umberger, the first of the above two causes of the curvature is implicit in the theory of Sveshnikoff.⁴ There an expression for τ^* is derived which is identical to (43) in the absence of forces between particles. However, in calculating the limiting low concentration expression for the quenching constant analogous to (45a) Sveshnikoff omitted the term corresponding to ϵ and therefore did not obtain the $\eta^{-1/2}$ component.

In conclusion the author wishes to thank Dr. J. Q. Umberger for his many informative discussions concerning quenching of fluorescence.

⁹ In this special case k_Q was obtained previously by J. Q. Umberger (private communication).

¹⁰ H. Davis and V. LaMer, J. Chem. Phys. **10**, 585 (1942).

APPENDIX I

Solution of the Differential Eq. (29)

From (29)

$$\frac{\partial f_2}{\partial t} = D \left\{ \frac{\partial^2 f_2}{\partial r^2} + \frac{\partial f_1}{L \partial r} \left[\frac{2L}{r} - \frac{L^2}{r^2} \coth \frac{L}{2r} \right] \right\},$$

where

$$f_1(r, t) = \operatorname{erf} [(r-R)/2(Dt)^{1/2}]$$

and

$$f_2(R, t) = f_2(\infty, t) = f_2(r, 0) = 0.$$

Let us introduce the Laplace transform of $f_1(r, t)$ and $f_2(r, t)$,

$$F_j(r, s) = \int_0^\infty f_j(r, t) e^{-st} dt,$$

and use the expression (22b) for $F_1(r, s)$. Then (25) is transformed into the ordinary equation

$$\frac{d^2 F_2}{dr^2} - \frac{s F_2}{D} = -\frac{1}{L(Dt)^{1/2}} \left\{ \frac{2L}{r} - \frac{L^2}{r^2} \coth \frac{L}{2r} \right\} \exp \{ -(r-R)(s/D)^{1/2} \},$$

and the boundary conditions become

$$F_2(R, s) = F_2(\infty, s) = 0.$$

By direct substitution one can verify that

$$F_2(r, s) = -2(sD)^{-1/2} \exp \{ (r-R)(s/D)^{1/2} \} \left[\int_R^r \log \left(\frac{y}{L} \sinh \frac{L}{2y} \right) \exp (-2(y-R)(s/D)^{1/2}) dy \right. \\ \left. - (1 - \exp (-2(r-R)(s/D)^{1/2})) \int_R^\infty \log \left(\frac{y}{L} \sinh \frac{L}{2y} \right) \exp (-2(y-R)(s/D)^{1/2}) dy \right].$$

Since the inverse Laplace transform of

$$F(r, s) = \int_0^\infty f(r, t) e^{-st} dt = s^{-1} \exp (-ks^{1/2})$$

is

$$f(r, t) = (\pi t)^{-1/2} \exp (-k^2/4t),$$

one has immediately

$$f_2(r, t) = -\frac{2}{(\pi Dt)^{1/2}} \left\{ \int_R^\infty \exp (-(r-3R+2y)^2/4Dt) \log \left(\frac{y}{L} \sinh \frac{L}{2y} \right) dy \right. \\ \left. - \int_r^\infty \exp (-(2y-R-r)^2/4Dt) \log \left(\frac{y}{L} \sinh \frac{L}{2y} \right) dy \right\}$$

as is given by (30) in the text.

APPENDIX II

Integration of $J(L/R, Dt/R^2)$

According to (33), $J(L/R, Dt/R^2)$ is defined by

$$J(L/R, Dt/R^2) = \frac{2R}{(\pi Dt)^{1/2}} \int_R^\infty \left\{ \frac{1}{y} - \frac{L}{2y^2} \coth \frac{L}{2y} \right\} \exp \left\{ -\frac{(y-R)^2}{Dt} \right\} dy.$$

Letting $\tau = Dt/R^2$ and $\mu = L/2R$, we have by an obvious transformation

$$J(2\mu, \tau) = 2(\tau\pi)^{-\frac{1}{2}} \int_0^\infty \left(\frac{\mu}{1+v} - \frac{\mu^2}{(1+v)^2} \coth \frac{\mu}{1+v} \right) \exp(-v^2/\tau) dv.$$

At early times (as $\tau \rightarrow 0$) the main contribution to the integral comes from the interval of small values of v , thus:

$$J(2\mu, \tau) \sim (1 - \mu \coth \mu) - (\tau/\pi)^{\frac{1}{2}} (1 - 2\mu \coth \mu + \mu^2 \operatorname{csch}^2 \mu) + (\tau/2)(1 - 3\mu \coth \mu + 3\mu^2 \operatorname{csch}^2 \mu - \mu^3 \operatorname{csch}^2 \mu \coth \mu).$$

At late times (as $\tau \rightarrow \infty$)

$$J(2\mu, \tau) \rightarrow 2(\pi\tau)^{-\frac{1}{2}} \int_0^\infty \left(\frac{1}{1+v} - \frac{\mu}{(1+v)^2} \coth \frac{\mu}{(1+v)} \right) dv = -2(\pi\tau)^{-\frac{1}{2}} \log \left(\frac{1}{\mu} \sinh \mu \right).$$

At intermediate times it seems convenient to substitute the series

$$x^2 \coth x = x + x^3/3 + x^5/45 - 2x^7/945 + x^9/4725 + \dots$$

into $J(2\mu, \tau)$. Then, after integrating term by term one obtains

$$J(2\mu, \tau) = -2(\pi\tau)^{-\frac{1}{2}} \left(\frac{1}{3} \mu^2 I_3 + \frac{\mu^4}{45} I_5 - \frac{2\mu^6}{945} I_7 + \frac{\mu^8}{4725} I_9 + \dots \right),$$

where

$$I_n = \int_0^\infty \frac{1}{(1+v)^n} \exp(-v^2/\tau) dv.$$

By integrating by parts one can show that I_5, I_7 , etc. can be calculated from I_3 . Thus for values of τ of interest one need only integrate I_3 numerically in order to determine $J(2\mu, \tau)$ completely.