The Process of Diffusion in a Centrifugal Field of Force. II

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The general equation for the settling of particles and molecules in a liquid suspension or ideal solution has been solved for the case of a cell with radial sides and two bounding cylindrical ends. A set of curves is given which shows the concentration at all points in the cell for different values of the time.

In a previous article[1] the equation for the settling of particles and molecules in a liquid suspension or ideal solution in a centrifugal field of force was solved for the case of a sector shaped cell extending to the center of the centrifuge. It is the object of the present paper to find a solution of this equation for the case of a cell with radial sides and two bounding cylindrical ends. It is of great practical importance to obtain the solution for a cell of this type since this is the kind most commonly used in experimental determinations of molecular weights by the use of the ultracentrifuge. A solution based on a perturbation method has recently been given,[2] but the perturbation imposes such severe restrictions upon the quantities involved that the results are of mathematical interest only and are of little importance for comparison with experimental results.

The equation to be considered is[3]

$$\frac{1}{r}\frac{\partial}{\partial r}\left\{\left(D\frac{\partial c}{\partial r}-\omega^2 rsc\right)r\right\}=\frac{\partial c}{\partial t}, \tag{1}$$

in which c is the concentration of the solution, s the sedimentation constant, D the diffusion constant, ω the angular velocity of the rotor, and r the distance from the center of rotation to any point in the cell. (For a more precise definition of the quantities involved the reader is referred to the previous article[1] mentioned above.) The solution of (1) will give the concentration c as a function of r and t.

An acceptable solution, $c(r, t)$, must satisfy the following boundary conditions; (i) the net flow of dissolved substance through each cylindrical bounding surface is zero. This condition may be expressed mathematically by saying that

$$\frac{\partial c}{\partial r}-\delta rc=0 \quad \text{for } r=\begin{cases} r_1 \\ r_2 \end{cases}, \tag{2}$$

where r_1 and r_2 are the coordinates of the inner and outer bounding surfaces, respectively, and where $\delta=\omega^2 s/D$. (ii) When $t=0$ the function $c(r, t)$ represents an arbitrary initial distribution of concentration which is assumed to be known.

It can be shown[1] that a particular solution, $c(r, t)$, of (1) is

$$c(r, t)=M(\alpha; 1; z)e^{(\alpha-1)\tau} \quad (\tau=2\omega^2 st), \tag{3}$$

where α is a constant which is to be determined from the boundary conditions, and where $M(\alpha; \gamma; z)$ is a solution of the differential equation

$$\frac{d^2M}{dz^2}+\left(\frac{\gamma}{z}-1\right)\frac{dM}{dz}-\frac{\alpha}{z}M=0 \quad \left(z=\frac{\delta r^2}{2}\right). \tag{4}$$

In the case of the cell extending to the center of the rotor only that solution of (4) which is bounded at the origin was required. However, for the type of cell under discussion here, the relation (2) must be satisfied for two different values of r. Consequently it will be necessary to use the complete solution of (4), and the usefulness of the final result will depend in great measure upon how successful we are in our search for a solution which possesses simple and convenient properties.

In terms of the new variable z the first boundary condition becomes

$$\frac{d}{dz}M(\alpha; 1; z)-M(\alpha; 1; z)=0 \quad \text{for } z=\begin{cases} \delta r_1^2/2=a \\ \delta r_2^2/2=b. \end{cases} \tag{5}$$

[1] Archibald, Phys. Rev. **53**, 746 (1938).
[2] S. Oka, Proc. Physico-Mat. Soc., Japan **19**, 1094 (1937).
[3] Lamm, Arkiv. Mat., Astron., Fysik **21B**, No. 2 (1929).

From the theory of differential equations

$$M(\alpha;\gamma;z)=AF(\alpha;\gamma;z)+BW(\alpha;\gamma;z), \quad (6)$$

where A and B are constants and where $F(\alpha;\gamma;z)$ and $W(\alpha;\gamma;z)$ are two independent solutions of Eq. (4). The solution, bounded at the origin, is the confluent hypergeometric series; *viz.*

$$F(\alpha;\gamma;z)=1+\frac{\alpha}{1\cdot\gamma}z+\frac{\alpha(\alpha+1)}{1\cdot 2\cdot\gamma(\gamma+1)}z^2+\cdots.$$

A list of recurrence formulae for this function have been given by Webb and Airey.[4]

Several methods are available for determining a second solution $W(\alpha;\gamma;z)$ but not all of them lead to forms which are useful. If possible we should like the function $W(\alpha;\gamma;z)$ to possess the same recurrence formulae as $F(\alpha;\gamma;z)$. Such a function may be found in the following manner:

$F(\alpha;\gamma;z)$ can be expressed as the sum of two contour integrals as follows[5] (γ is assumed to be a positive integer):

$$F(\alpha;\gamma;z)=W_1(\alpha;\gamma;z)+W_2(\alpha;\gamma;z),$$

where

$$W_1(\alpha;\gamma;z)=\frac{\Gamma(\gamma)}{2\pi i}\int_C\left(1-\frac{z}{t}\right)^{-\alpha}e^t t^{-\gamma}dt,$$

and the contour C is a path in the t plane which comes from $-\infty$, encircles the point $t=0$ once in a counter-clockwise direction and returns to $-\infty$. W_2 is given by the same integrand, and a path that comes from $-\infty$, encircles the point $t=z$ once in a counter-clockwise direction and returns to $-\infty$.

It can be shown[6] that W_1 and W_2 are two independent solutions of Eq. (4). Consequently we are at liberty to choose for our function $W(\alpha;\gamma;z)$ either W_1 or W_2 or a linear combination of them both. However, for the purpose in hand, we are restricted to a choice which will give a real value for $W(\alpha;\gamma;z)$ whenever z is real. Such a choice is the following:

$$W(\alpha;\gamma;z)=\pi\cot\pi\alpha W_1(\alpha;\gamma;z)-i\pi W_2(\alpha;\gamma;z). \quad (7)$$

[4] Webb and Airey, Phil. Mag. **36**, 129 (1919).
[5] Mott and Massey, *Atomic Collisions* (1933), p. 36.
[6] Whittaker and Watson, *Modern Analysis* (1927), p. 343.

It can be shown that $W(\alpha;\gamma;z)$ as defined in (7) shares with $F(\alpha;\gamma;z)$ the three properties listed below, the first two of which will be needed subsequently. The third has been very useful for purposes of computation.

$$(d/dz)F(\alpha;\gamma;z)=(\alpha/\gamma)F(\alpha+1;\gamma+1;z), \quad (8a)$$

$$\alpha F(\alpha+1;\gamma+1;z)=(\alpha-\gamma)F(\alpha;\gamma+1;z)+\gamma F(\alpha;\gamma;z), \quad (8b)$$

$$\alpha F(\alpha+1;\gamma;z)=(z+2\alpha-\gamma)F(\alpha;\gamma;z)+(\gamma-\alpha)F(\alpha-1;\gamma;z). \quad (8c)$$

The expression for $W(\alpha;\gamma;z)$ is[7]

$$W(\alpha;\gamma;z)=F(\alpha;\gamma;z)\{\log z+\psi(1-\alpha)-\psi(\gamma)+C\}+\sum_{n=0}^{\gamma-2}\frac{\Gamma(\gamma)\Gamma(n+\alpha-\gamma+1)\Gamma(\gamma-n-1)(-1)^{n+\gamma}}{\Gamma(\alpha)n!z^{\gamma-n-1}}+\sum_{n=1}^{\infty}P_nQ_nz^n,$$

where

$$P_n=\frac{\Gamma(n+\alpha)}{\Gamma(\alpha)}\cdot\frac{\Gamma(\gamma)}{\Gamma(n+\gamma)}\cdot\frac{1}{n!},$$

$$Q_n=\left(\frac{1}{\alpha}+\frac{1}{\alpha+1}+\cdots+\frac{1}{\alpha+n-1}\right)-\left(\frac{1}{\gamma}+\frac{1}{\gamma+1}+\cdots+\frac{1}{\gamma+n-1}\right)-(1+\tfrac{1}{2}+\cdots+1/n),$$

$$\psi(a)=\Gamma'(a)/\Gamma(a),$$

$$C=\text{Euler's constant}=0.5772\cdots.$$

(Extensive tables of the ψ function are available.[8]) It is the presence of the ψ functions in the expression for $W(\alpha;\gamma;z)$ which renders this solution a particularly suitable one. If they are omitted the expression is still a solution of Eq. (4) but the recurrence formulae (8) are no longer satisfied.

Consequently we choose (6) as the general solution of Eq. (4) where the functions F and W

[7] Cf. an article by the author to appear in a subsequent issue of Phil. Mag.
[8] Davis, *Tables of the Higher Mathematical Functions* (1933).

are defined above. If the expression for $c(r, t)$ given by Eq. (3) be substituted in the boundary condition (5) the following relations must hold:

$$\begin{aligned} &A\{F'(\alpha;1;a)-F(\alpha;1;a)\} \\ &\qquad +B\{W'(\alpha;1;a)-W(\alpha;1;a)\}=0, \\ &A\{F'(\alpha;1;b)-F(\alpha;1;b)\} \\ &\qquad +B\{W'(\alpha;1;b)-W(\alpha;1;b)\}=0. \end{aligned} \tag{9}$$

However, by virtue of (8a) and (8b)

$$F'(\alpha;1;a)-F(\alpha;1;a)=(\alpha-1)F(\alpha;2;a),$$

and

$$W'(\alpha;1;a)-W(\alpha;1;a)=(\alpha-1)W(\alpha;2;a).$$

These two equations enable (9) to be expressed in the simple form,

$$\begin{aligned} (\alpha-1)\{AF(\alpha;2;a)+BW(\alpha;2;a)\}=0, \\ (\alpha-1)\{AF(\alpha;2;b)+BW(\alpha;2;b)\}=0. \end{aligned} \tag{10}$$

Thus one permissible value of α is $\alpha=1$.

The system of Eqs (10) can have roots other than the trivial ones $A=0$, $B=0$ only if the determinant

$$\begin{vmatrix} F(\alpha;2;a), & W(\alpha;2;a) \\ F(\alpha;2;b), & W(\alpha;2;b) \end{vmatrix}$$

is equal to zero. Thus the permissible values of α (in addition to $\alpha=1$) are those values of α which satisfy the equation

$$\begin{aligned} &F(\alpha;2;a)W(\alpha;2;b) \\ &\qquad -F(\alpha;2;b)W(\alpha;2;a)=f(\alpha)=0. \end{aligned} \tag{11}$$

Consequently we may take as the complete solution of Eq. (1)

$$\begin{aligned} c(z,t)=\sum_{n=0}^{\infty}\{&A_nF(\alpha_n;1;z) \\ &+B_nW(\alpha_n;1;z)\}e^{(\alpha_n-1)\tau}, \end{aligned} \tag{12}$$

where the α_n's are the roots of the equation

$$(\alpha-1)f(\alpha)=0.$$

From Eq. (10) we have

$$B_n=-\frac{F(\alpha_n;2;a)}{W(\alpha_n;2;a)}A_n=-K_nA_n.$$

Thus (12) may be written as

$$c(z,t)=\sum_{n=0}^{\infty}A_nM(\alpha_n;1;z)e^{(\alpha_n-1)\tau}, \tag{13}$$

where $M(\alpha_n;1;z)=F(\alpha_n;1;z)-K_nW(\alpha_n;1;z)$.

The coefficients A_n are determined by the application of the second boundary condition. For $t=0$ we have

$$c(z,o)=\sum_{n=0}^{\infty}A_nM(\alpha_n;1;z),$$

where $c(z, 0)$ is the initial distribution of concentration which will be taken to be constant and equal to c_0. It can be shown[1] that the functions $M(\alpha;1;z)$ are orthogonal in the range $a\leqslant z\leqslant b$ with the weight factor e^{-z}. Thus the coefficient A_n is given by

$$A_n=\frac{c_0\int_a^b e^{-z}M(\alpha_n;1;z)dz}{\int_a^b e^{-z}\{M(\alpha_n;1;z)\}^2dz}.$$

The two integrals occurring in the above expression may be integrated by methods outlined in the previous article by the author.[1] However, only for the case of the integral occurring in the numerator does a simplification result from so doing. The other integral can be more easily evaluated by numerical integration. For the first integral we get

$$\begin{aligned} &\int_a^b e^{-z}M(\alpha_n;1;z)dz \\ &\qquad =(1/\alpha_n)\{be^{-b}M(\alpha_n;1;b)-ae^{-a}M(\alpha_n;1;a)\}. \end{aligned}$$

Thus the complete solution of Eq. (1) which satisfies the boundary conditions is

$$\begin{aligned} \frac{c}{c_0}=\sum_{n=0}^{\infty}\Bigg[&\frac{be^{-b}M(\alpha_n;1;b)-ae^{-a}M(\alpha_n;1;a)}{\alpha_n\int_a^b e^{-z}\{M(\alpha_n;1;z)\}^2dz} \\ &\times M(\alpha_n;1;z)\exp((\alpha_n-1)\tau)\Bigg]=\sum_{n=0}^{\infty}T_{\alpha_n}. \end{aligned} \tag{14}$$

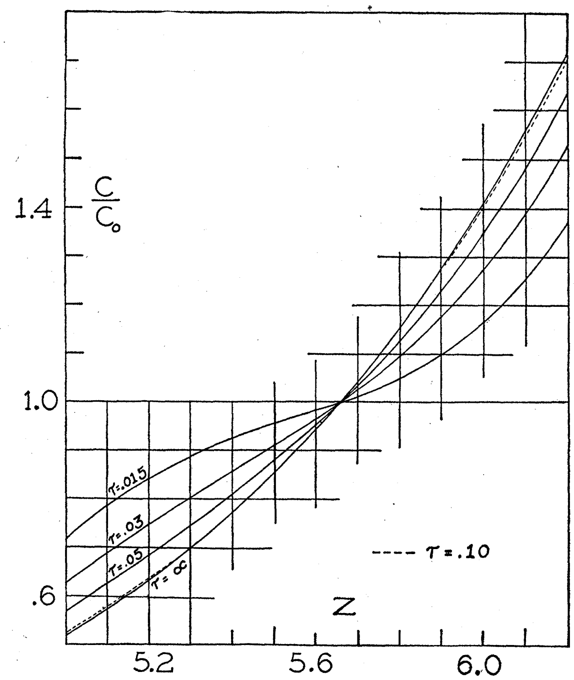

FIG. 1. Values of concentration change c/c_0 (c_0=initial constant concentration) as a function of position $z(=\omega^2sr^2/2D)$ for various values of $\tau(=2\omega^2st)$ when $a=5.0$ and $b=6.2$.

The term for which $\alpha=1$ can be greatly simplified. We have

$$M(1;1;z)=F(1;1;z)-\frac{F(1;2;a)}{W(1;2;a)}W(1;1;z)=e^z$$

since $W(1;2;a)=\infty$ and $F(1;1;z)=e^z$. Thus we may write (14) in the form

$$\frac{c}{c_0}=\frac{b-a}{e^b-e^a}e^z+\sum_{n=1}^{\infty}T_{\alpha_n}, \tag{15}$$

where the α_n's are the roots of Eq. (11).

In actual problems the constants a and b are rather large and z which lies between them is also large. Hence it would be advantageous to have asymptotic expansions for the functions $F(\alpha;\gamma;z)$ and $W(\alpha;\gamma;z)$. These expansions are available since it can be shown that[9]

$$W_1(\alpha;\gamma;z)\sim\frac{\Gamma(\gamma)}{\Gamma(\gamma-\alpha)}(-z)^{-\alpha}G(\alpha,\alpha-\gamma+1;-z),$$

$$W_2(\alpha;\gamma;z)\sim\frac{\Gamma(\gamma)}{\Gamma(\alpha)}e^z z^{\alpha-\gamma}G(1-\alpha,\gamma-\alpha;z),$$

where G denotes the semi-convergent series

$$G(p,q;z)=1+\frac{pq}{z1!}+\frac{p(p+1)q(q+1)}{z^2 2!}+\cdots.$$

The recurrence formula (8c) and the asymptotic expansions for the functions involved enable computations to be made from Eq. (15) in a straightforward and relatively simple manner. The series (15) converges so rapidly that two or three terms give good accuracy.

The curves in Fig. 1 were calculated from Eq. (15). The constants were chosen to correspond to an actual experiment described by Svedberg,[10] in which the dissolved substance was carbon-monoxide hemoglobin which has a molecular weight $M=68{,}000$ and a partial specific volume $V=0.749$ cm^3/g. For the cell used $r_1=4.16$ cm and $r_2=4.61$ cm. Also $\omega=290\pi$ and $T=293$°K. These data are sufficient to determine the two constants a and b. We have[1]

$$\begin{Bmatrix}a\\b\end{Bmatrix}=\frac{M(1-Vp)\omega^2}{2RT}\begin{Bmatrix}r_1^2\\r_2^2\end{Bmatrix}.$$

The numerical values are $a=5.0$ and $b=6.2$. The curves show that the concentration has reached its equilibrium value to a high degree of approximation when $\tau(=2\omega^2st)$ has the value 0.10. Since $s=5\times10^{-13}$ for carbon-monoxide hemoglobin this corresponds to a time of 33 hours. In the actual experiment an exponential distribution of concentration had been reached after a period of 39 hours. This indicates an excellent agreement between theory and experiment.

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[9] Mott and Massey, reference 5, p. 38.

[10] Svedberg, article in *Colloidal Chemistry, Theoretical and Applied*, edited by Alexander, Vol. 1, p. 851.