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Separative Diffusion in the Transient State. II. The Hollow Cylinder and the Hollow Sphere

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Separative Diffusion in the Transient State. II. The Hollow Cylinder and the Hollow Sphere

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Abstract

For the hollow cylinder and the hollow sphere the separation factor S can be obtained, as for the plate, by generalization from the dimensionless time τ. Separation factors for the plate and the spherical shell are given by the same function of τ. The outfluxes, and accordingly the separation factor S, are equal for centrifugal and centripetal diffusion processes. With increasing outer radius R_2 and constant R_2/R_1, the equally separated output increases with the square of R_2 for the cylinder and with the cube of R_2 for the sphere, while the time for equal separation increases with the square of the barrier thickness in both cases.

INTRODUCTION

Diffusion into a hollow cylinder and into a hollow sphere means a focusing of the diffusion flux toward the center. This is desirable when early fractions of the transient state diffusion are to be collected. For this reason cylindrical barriers were chosen in an experimental method for the quantitative determination of a small difference between diffusion coefficients using separative diffusion in the transient state (9). In this work it was found empirically by numerical computer methods that the separation factor S can be generalized as a function of the dimensionless time $\tau = Dt/R^2$ for constant R_2/R_1 and constant D_B/D_A.

In the present paper this relation is deducted from the analytical solution, and further relations for the cylinder and the sphere are found by analytical methods.

The curves for the sphere were computed from the analytical solution. For the cylinder the inconvenience of computing Bessel functions was by-passed by using the numerical results.

In contrast to the focusing behavior of the centripetal diffusion, the reversed centrifugal diffusion process shows the property of fast dissipation. Thus it was surprising to find exactly equal output quantities in both cases. We are not aware that this identity has been explicitly stated in the standard textbooks on diffusion and heat conduction.

Cylindrical and spherical barriers can only be used in the absence of convection for solid-state and gel diffusion and not for fluid diffusion which is self-stabilizing by the density gradient only in a one-dimensional diffusion process. This advantage of one-dimensional diffusion can be combined with the higher yields of cylindrical or spherical diffusion by one-dimensional diffusion into a prism or into a cone. These problems will be dealt with elsewhere.

THE HOLLOW CYLINDER

Centripetal Diffusion with Constant D

The differential equation describing mass transport across a cylindrical wall is given by

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r}\frac{\partial C}{\partial r}\right) \tag{1}$$

where a constant diffusion coefficient has been assumed. The initial condition is zero concentration in the cylindrical wall

$$C(r, 0) = 0 \tag{2}$$

while the boundary conditions for the centripetal case are

$$C(R_1, t) = 0 \tag{3a}$$

$$C(R_2, t) = C_i \tag{3b}$$

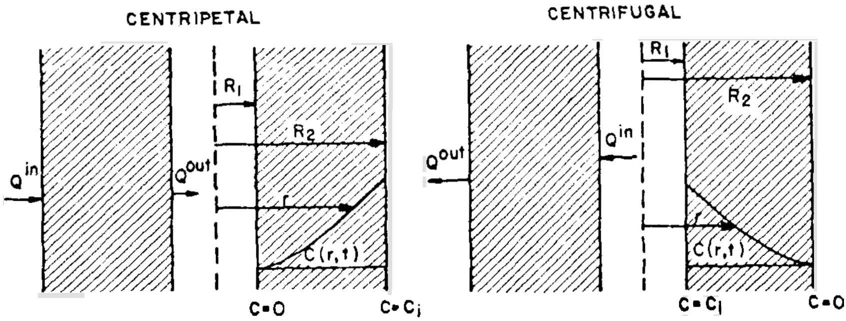

FIG. 1. Diffusion through the hollow cylinder.

The expression for the concentration distribution follows from the above set of equations as (*1*)

$$C(r, t) = \frac{C_i \ln r/R_1}{\ln (R_2/R_1)} - \pi C_i \sum_{n=1}^{\infty} \frac{J_0^2(\mu_n R_1) U_0(\mu_n r)}{J_0^2(\mu_n R_1) - J_0^2(\mu_n R_2)} \exp(-D\mu_n^2 t) \quad \text{(4a)}$$

where

$$U_0(\mu_n r) = J_0(\mu_n r) Y_0(\mu_n R_2) - J_0(\mu_n R_2) Y_0(\mu_n r)$$

and J_0, Y_0 are zeroth-order Bessel functions of the first and second kind, respectively. The μ_n are the positive roots of (*2*)

$$U_0(\mu_n R_1) = 0$$

Mass Fluxes across the Boundaries. The mass flux across a cylindrical area, radius r and unit length, in time t is

$$Q_t(r) = 2\pi D \int_0^t r \frac{\partial C}{\partial r} dt' \quad (5)$$

With

$$\frac{\partial C}{\partial r} = \frac{C_i/r}{\ln R_2/R_1} - \pi C_i \sum_{n=1}^{\infty} \frac{J_0^2(\mu_n R_1) U_0^1(\mu_n r)}{J_0^2(\mu_n R_1) - J_0^2(\mu_n R_2)} \exp(-D\mu_n^2 t)$$

where

$$U_0^1(\mu_n r) = \frac{\partial}{\partial r}\{U_0(\mu_n r)\}$$

we get for the integrated flux

$$Q_t^{cp}(r) = \pi C_i \left\{ \frac{2Dt}{\ln (R_2/R_1)} - 2\pi \sum_{n=1}^{\infty} \frac{J_0^2(\mu_n R_1)\{rU_0^1(\mu_n r)\}}{\mu_n^2\{J_0^2(\mu_n R_1) - J_0^2(\mu_n R_2)\}} \cdot [1 - \exp(-D\mu_n^2 t)] \right\} \tag{6a}$$

In particular we find for $r = R_1$(outflux)

$$[rU_0^1(\mu_n r)]_{r=R_1} = -\frac{2}{\pi \rho_n}$$

where (3)

$$\rho_n = \frac{J_0(\mu_n R_1)}{J_0(\mu_n R_2)} = \frac{Y_0(\mu_n R_1)}{Y_0(\mu_n R_2)}$$

The integrated outflux is therefore

$$Q_t^{cp}(R_1) = \pi C_i \left\{ \frac{2Dt}{\ln R_2/R_1} + 4 \sum_{n=1}^{\infty} \frac{J_0(\mu_n R_1) J_0(\mu_n R_2)}{\mu_n^2 [J_0^2(\mu_n R_1) - J_0^2(\mu_n R_2)]} \cdot [1 - \exp(-D\mu_n^2 t)] \right\} \tag{6b}$$

At the boundary $r = R_2$, $\rho_n = 1$ (3) so that the integrated influx is given by

$$Q_t^{cp}(R_2) = \pi C_i \left\{ \frac{2Dt}{\ln R_2/R_1} + 4 \sum_{n=1}^{\infty} \frac{J_0^2(\mu_n R_1)}{\mu_n^2 \{J_0^2(\mu_n R_1) - J_0^2(\mu_n R_2)\}} \cdot [1 - \exp(-D\mu_n^2 t)] \right\} \tag{6c}$$

The Separation Factor. The separation factor for substances A and B is defined by

$$S = \frac{Q_t(\mathrm{B})/C_i(\mathrm{B})}{Q_t(\mathrm{A})/C_i(\mathrm{A})} \tag{7a}$$

According to the above equations, S (at $r = R_1$) follows as

$$S = \frac{D_\mathrm{B}/D_\mathrm{A} + \frac{1}{\tau_\mathrm{A}} \left(\frac{\ln R_2/R_1}{2R_2^2} \right) \sum_{n=1}^{\infty} \Omega_n \left[1 - \exp\left(-\frac{D_\mathrm{B}}{D_\mathrm{A}} R_2^2 \mu_n^2 \tau_\mathrm{A} \right) \right]}{1 + \frac{1}{\tau_\mathrm{A}} \left(\frac{\ln R_2/R_1}{2R_2^2} \right) \sum_{n=1}^{\infty} \Omega_n [1 - \exp(-R_2^2 \mu_n^2 \tau_\mathrm{A})]} \tag{7b}$$

where $\tau_A = D_A t/R_2^2$ is a dimensionless time and

$$\Omega_n = 4\frac{J_0(\mu_n R_1)J_0(\mu_n R_2)}{\mu_n^2\{J_0^2(\mu_n R_1) - J_0^2(\mu_n R_2)\}}$$

For mathematical convenience, the substitution $\alpha_n = \mu_n R_1$ is introduced. Ω_n becomes

$$\Omega_n = R_1^2 \Omega_n^1$$

where

$$\Omega_n^1 = \frac{4J_0(\alpha_n)J_0\left(\alpha_n \frac{R_2}{R_1}\right)}{\alpha_n^2\left\{J_0^2(\alpha_n) - J_0^2\left(\alpha_n \frac{R_2}{R_1}\right)\right\}}$$

and the α_n are the positive roots of

$$U_0(\alpha_n) = J_0(\alpha_n)Y_0\left(\alpha_n \frac{R_2}{R_1}\right) - J_0\left(\alpha_n \frac{R_2}{R_1}\right)Y_0(\alpha_n) = 0$$

With $R_2/R_1 = \gamma$, S becomes

$$S = \frac{\frac{D_B}{D_A}\tau_A + \frac{\ln \gamma}{2\gamma^2}\sum_{n=1}^{\infty}\Omega_n^1\left[1 - \exp\left(-\frac{D_B}{D_A}\gamma^2\alpha_n^2\tau_A\right)\right]}{\tau_A + \frac{\ln \gamma}{2\gamma^2}\sum_{n=1}^{\infty}\Omega_n^1[1 - \exp(-\gamma^2\alpha_n^2\tau_A)]} \tag{7c}$$

which shows that S is a function only of D_B/D_A, γ, and τ_A. Thus when $S(\tau, D_B/D_A, \gamma)$ is found for a certain set of parameters D_A, R_2, it can be generalized for any other set of these parameters while D_B/D_A and γ are left constant.

As in Part I, S was computed for a standard substance A and three test substances B, B′ and B″ with

$$D_A = 1.000 \times 10^{-6}$$
$$D_B = 1.002 \times 10^{-6},$$
$$D_{B'} = 1.005 \times 10^{-6}$$
$$D_{B''} = 1.01 \times 10^{-6}$$

in cm^2/sec. The radii were $R_1 = 0.198$ cm, $R_2 = 2.35$ cm, giving $R_2/R_1 = 11.869$. The results are summarized in Table 1 for dimensionless times $\tau_A = D_A t/R_2^2$.

TABLE 1

Separation Factors

τ_A	$D_B/D_A = 1.002$ S	$D_{B'}/D_A = 1.005$ S	$D_{B''}/D_A = 1.01$ S
0.005	1.0495	1.1238	1.2476
0.01	1.0314	1.0786	1.1567
0.02	1.0294	1.0734	1.1468
0.03	1.0164	1.0418	1.0831
0.04	1.0152	1.0377	1.0750
0.06	1.0091	1.0232	1.0459
0.08	1.0078	1.0193	1.0387
0.10	1.0066	1.0170	1.0341
0.15	1.0052	1.0130	1.0257
0.20	1.0044	1.0111	1.0222
0.30	1.0036	1.0091	1.0178
0.50	1.0029	1.0069	1.0141
0.70	1.0026	1.0064	1.0127
1.00		1.0059	1.0118

Dependence of the Output Flux on Different Dimensions for Equal R_2/R_1 (i.e., γ) and Equal τ (or S). Consider two hollow cylinders having radii (R_1', R_2') and (R_1'', R_2''). The ratio of the outfluxes for these cylinders is from (6b)

$$\frac{Q_t^{cp}(R_1'')}{Q_t^{cp}(R_1')} = \left(\frac{R_1''}{R_1'}\right)^2 \frac{2\tau'' \dfrac{(\gamma'')^2}{\ln \gamma''} + \sum_{n=1}^{\infty} \Omega_n'('')\{1 - \exp[-\alpha_n^2(\gamma'')^2\tau'']\}}{2\tau' \dfrac{(\gamma')^2}{\ln \gamma'} + \sum_{n=1}^{\infty} \Omega_n'(')\{1 - \exp[-\alpha_n^2(\gamma')^2\tau']\}} \tag{8a}$$

where

$$\tau' = \frac{Dt'}{(R_2')^2}$$

$$\tau'' = \frac{Dt''}{(R_2'')^2}$$

$$\gamma' = \frac{R_2'}{R_1'}$$

$$\gamma'' = \frac{R_2''}{R_1''}$$

and $\Omega_n'('')$ and $\Omega_n'(')$ are respectively in terms of (R_1'', R_2'') and (R_1', R_2').

Consider now the case where $\tau'' = \tau'$ and $\gamma'' = \gamma'$, then

$$\frac{Q_t^{cp}(R_1'')}{Q_t^{cp}(R_1')} = \left(\frac{R_1''}{R_1'}\right)^2 = \left(\frac{R_2''}{R_2'}\right)^2 = \frac{t''}{t'} \tag{8b}$$

If an enlargement factor K is defined by $R_2'' = KR_2'$, then

$$\frac{Q_t^{cp}(R_1'')}{Q_t^{cp}(R_1')} = K^2 \tag{8c}$$

Centrifugal Diffusion with Constant D

The boundary conditions for centrifugal transport are

$$C(R_1, t) = C_i \tag{3c}$$

$$C(R_2, t) = 0 \tag{3d}$$

The initial condition (2) is retained and the solution of the diffusion equation is (*1*)

$$C(r, t) = \frac{C_i \ln R_2/r}{\ln R_2/R_1} + \pi C_i \sum_{n=1}^{\infty} \frac{J_0(\mu_n R_1) J_0(\mu_n R_2) U_0(\mu_n r)}{J_0^2(\mu_n R_1) - J_0^2(\mu_n R_2)} \exp(-D\mu_n^2 t) \tag{4b}$$

Figure 2 shows the concentration fields according to (4a) and (4b).

Mass Fluxes across the Boundaries. The general equation for the integrated mass flux for centrifugal transport across a cylindrical area of unit length and radius r is

$$Q_t^{cf}(r) = 2\pi D \int_0^t r\left(-\frac{\partial C}{\partial r}\right) d\tau \tag{6d}$$

The integrated flux across the input boundary at $r = R_1$ is found, as in the first subsection under The Hollow Cylinder, as

$$Q_t^{cf}(R_1) = \pi C_i \left\{ \frac{2Dt}{\ln(R_2/R_1)} + 4 \sum_{n=1}^{\infty} \frac{J_0^2(\mu_n R_2)}{\mu_n \{J_0^2(\mu_n R_1) - J_0^2(\mu_n R_2)\}} \cdot [1 - \exp(-D\mu_n^2 t)] \right\} \tag{6e}$$

The expression for the outflux (at the boundary $r = R_2$) is

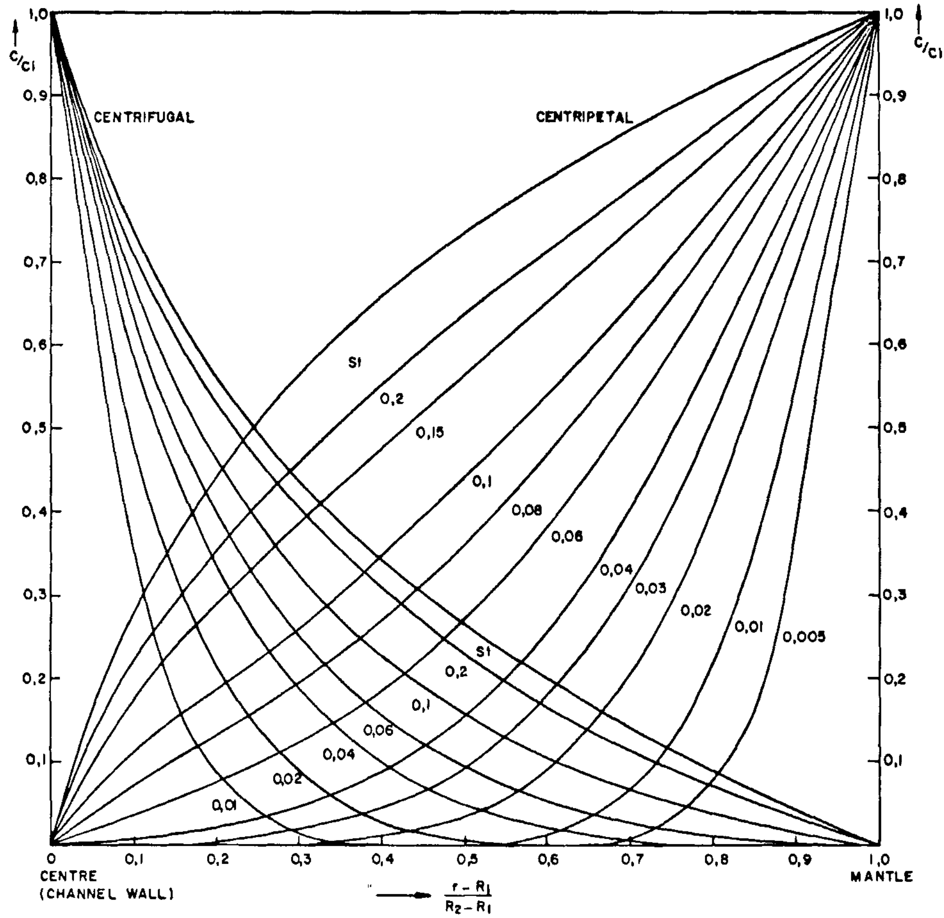

FIG. 2. Concentration fields in the cylindrical shell for centripetal and centrifugal diffusion. $R_2/R_1 = 9.4$.

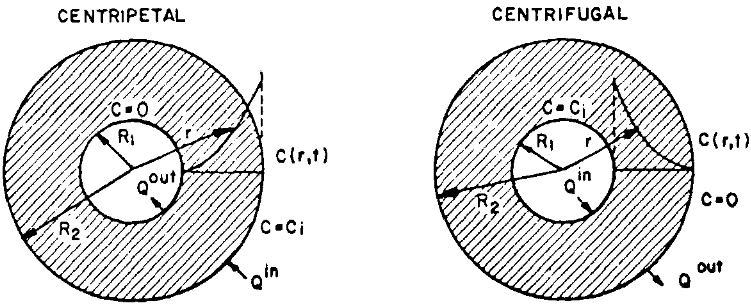

FIG. 3. Diffusion through the hollow sphere.

$$Q_t^{cf}(R_2) = \pi C_i \left\{ \frac{2Dt}{\ln(R_2/R_1)} + 4 \sum_{n=1}^{\infty} \frac{J_0(\mu_n R_1) J_0(\mu_n R_2)}{\mu_n^2 \{J_0^2(\mu_n R_1) - J_0^2(\mu_n R_2)\}} \cdot [1 - \exp(-D\mu_n^2 t)] \right\} \tag{6f}$$

Equations (6b) and (6f) are identical, thus

$$Q_t^{cp}(R_1) = Q_t^{cf}(R_2) \tag{9}$$

which means that centripetal and centrifugal outfluxes are the same. This result allows us to apply the results of the centripetal case to centrifugal diffusion.

THE HOLLOW SPHERE

The differential equation describing mass transport across the spherical shell is, for constant D,

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right) \tag{10}$$

The initial concentration will in all cases be assumed to be equal to zero

$$C(r, 0) = 0 \tag{11}$$

Centripetal Transport

The boundary conditions for centripetal transport are

$$C(R_1, t) = 0 \tag{12a}$$

$$C(R_2, t) = C_i \tag{12b}$$

so that the solution to the diffusion equation is given by (*4*)

$$C(r, t) = \frac{R_2(r - R_1)C_i}{r(R_2 - R_1)} + \frac{2R_2C_i}{\pi r} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin \frac{n\pi(r - R_1)}{R_2 - R_1} \cdot \exp\left[-\frac{Dn^2\pi^2 t}{(R_2 - R_1)^2}\right] \tag{13}$$

Mass Fluxes across the Boundaries. Corresponding to (5a), the mass flux across the spherical area is calculated from

$$Q_t^{cp}(r) = 4\pi D \int_0^t r^2 \frac{\partial C}{\partial r} dt' \tag{14a}$$

with

$$\frac{\partial C}{\partial r} = \frac{R_1 R_2 C_i}{r^2(R_2 - R_1)} - \frac{2R_2C_i}{\pi r^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin \frac{n\pi(r - R_1)}{(R_2 - R_1)} \exp\left[-D\frac{n^2\pi^2 t}{(R_2 - R_1)^2}\right] + \frac{2R_2C_i}{r(R_2 - R_1)} \sum_{n=1}^{\infty} (-1)^n \cos \frac{n\pi(r - R_1)}{(R_2 - R_1)} \exp\left[-D\frac{n^2\pi^2 t}{(R_2 - R_1)^2}\right]$$

At the boundary $r = R_1$, we get for the integrated outflux the expression (see also Ref. *4*)

$$Q_t^{cp}(R_1) = 4\pi R_1 R_2 C_i \left\{\frac{Dt}{R_2 - R_1} - \frac{R_2 - R_1}{6} - \frac{2(R_2 - R_1)}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp\left[-D\frac{n^2\pi^2 t}{(R_2 - R_1)^2}\right]\right\} \tag{14b}$$

where use has been made of

$$\sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} = -\frac{\pi^2}{12}$$

The expression for the influx at the boundary $r = R_2$ is

$$Q_t^{cp}(R_2) = 4\pi R_1 R_2 C_i \left\{\frac{Dt}{R_2 - R_1} + \frac{R_2(R_2 - R_1)}{3R_1} - \frac{2R_2(R_2 - R_1)}{\pi^2 R_1} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left[-D\frac{n^2\pi^2 t}{(R_2 - R_1)^2}\right]\right\} \tag{14c}$$

in which the sum

$$\sum_{n=1}^{\infty} \frac{1}{n^2} = \frac{\pi^2}{6}$$

has been used.

The Separation Factor. The separation factor for the transient state follows as

$$S = \frac{\frac{D_B}{D_A}\tau_A - \frac{1}{6} - \frac{2}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2} - \exp\left(-\frac{D_B}{D_A}n^2\pi^2\tau_A\right)}{\tau_A - \frac{1}{6} - \frac{2}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp(-n^2\pi^2\tau_A)} \tag{15}$$

This shows that, for the hollow sphere, the separation is a function only of D_B/D_A and τ_A, the dimensionless time.

$$\tau_A = \frac{D_A t}{(R_2 - R_1)^2}$$

Computation of S according to Eq. (15) yielded exactly the same result as for the plate and Eq. (15) can be shown to be identical with Eq. (9) of Part I. Thus Table 2 of Part I and the approximate formula, Eq. (10) of Part I, are also valid for the sphere and are not reproduced here.

The analytical determination of the ratio of the separation factors of the cylinder and the plate or sphere is difficult due to different mathematical forms, but it is shown however in Fig. 5 (and by comparison of Table 1 of this paper with Table 2 of Part I) that the separating power of the hollow cylinder is less than that of the other two geometries.

Dependence of the Output Flux on Different Dimensions for Equal R_2/R_1 and Equal τ. The ratio of the output fluxes for two hollow spheres having radii (R_1', R_2') and (R_1'', R_2'') is

$$\frac{Q_t^{cp}(R_1'')}{Q_t^{cp}(R_1')} = \frac{R_1''}{R_1'}\frac{R_2''}{R_2'}\frac{R_2'' - R_1''}{R_2' - R_1'}\frac{\tau'' - \frac{1}{6} - \frac{2}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp(-n^2\pi^2\tau'')}{\tau' - \frac{1}{6} - \frac{2}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp(-n^2\pi^2\tau')} \tag{16a}$$

For $\tau'' = \tau'$ and $\gamma'' = R_2''/R_1'' = \gamma' = R_2'/R_1'$ this reduces to

$$\frac{Q_t^{cp}(R_1'')}{Q_t^{cp}(R_1')} = \left(\frac{R_2''}{R_2'}\right)^2 \left(\frac{R_2'' - R_1''}{R_2' - R_1'}\right)$$

In terms of the enlargement factor $K = R_2''/R_2'$ this becomes

$$\frac{Q_t^{cp}(R_1'')}{Q_t^{cp}(R_1')} = K^3 \tag{16b}$$

or

$$\frac{Q_t^{cp}(R_1'')}{Q_t^{cp}(R_1')} = \left(\frac{t''}{t'}\right)^{3/2} \tag{16c}$$

in terms of t.

Centrifugal Transport with Constant D

The boundary conditions for centrifugal transport are

$$C(R_1, t) = C_i \tag{17a}$$

$$C(R_2, t) = 0 \tag{17b}$$

With $C(r, 0) = 0$ as the initial condition, the solution to the diffusion equation follows as (see Ref. *4*)

$$C = \frac{R_1 C_i (R_2 - r)}{r(R_2 - R_1)} - \frac{2R_1 C_i}{\pi r} \sum_{n=1}^{\infty} \frac{1}{n} \sin \frac{n\pi(r - R_1)}{(R_2 - R_1)} \exp\left[-D\frac{n^2\pi^2 t}{(R_2 - R_1)^2}\right] \tag{18}$$

The concentration fields according to Eqs. (13) and (18) are shown in Fig. 4.

Mass Fluxes across the Boundaries. The mass flux for centrifugal transport is calculated from the equation

$$Q_t^{cf}(r) = 4\pi D \int_0^t r^2 \left(-\frac{\partial C}{\partial r}\right) dt' \tag{19a}$$

with

$$\left(\frac{\partial C}{\partial r}\right) = -\frac{R_1 R_2 C_i}{r^2(R_2 - R_1)} + \frac{2R_1 C_i}{r^2 \pi} \sum_{n=1}^{\infty} \frac{1}{n} \sin \frac{n\pi(r - R_1)}{(R_2 - R_1)} \exp\left[-D\frac{n^2\pi^2 t}{(R_2 - R_1)^2}\right]$$
$$- \frac{2R_1 C_i}{r(R_2 - R_1)} \sum_{n=1}^{\infty} \cos \frac{n\pi(r - R_1)}{(R_2 - R_1)} \exp\left[-D\frac{n^2\pi^2 t}{(R_2 - R_1)^2}\right]$$

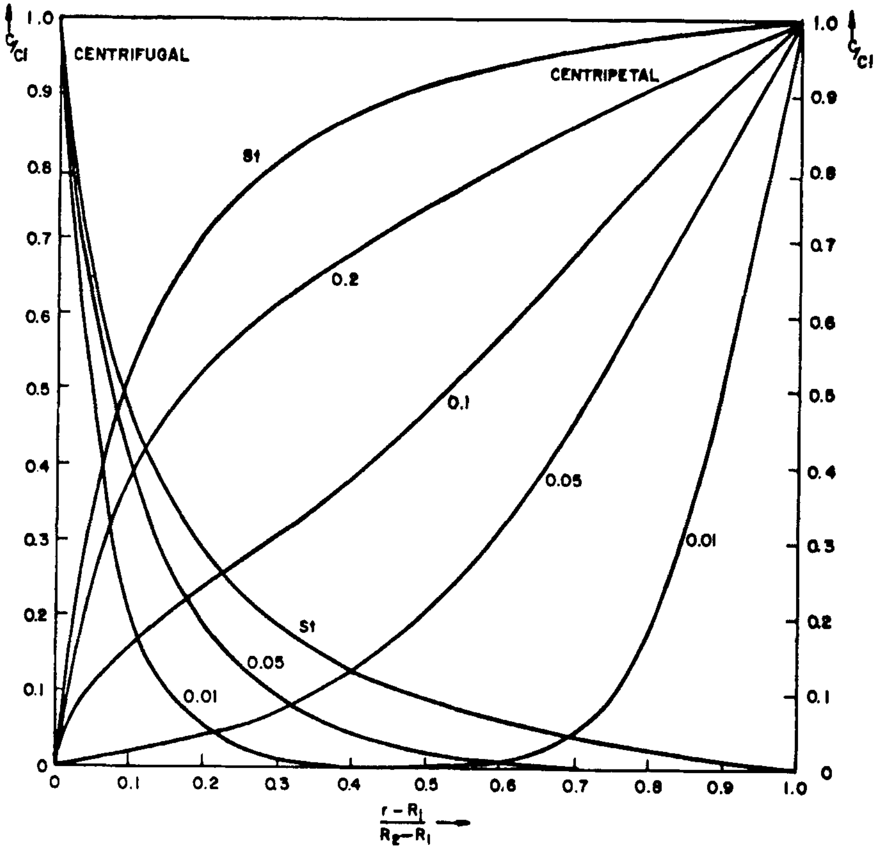

FIG. 4. Concentration fields in the spherical shell for centripetal and centrifugal diffusion. $R_2/R_1 = 10$.

The integrated influx (at $r = R_1$) now follows as

$$Q_t^{cf}(R_1) = 4\pi R_1 R_2 C_i \left\{ \frac{Dt}{R_2 - R_1} - \frac{R_1(R_2 - R_1)}{6R_2} \right.$$

$$\left. - \frac{2R_1(R_2 - R_1)}{\pi^2 R_2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp\left[-D \frac{n^2 \pi^2 t}{(R_2 - R_1)^2} \right] \right\} \quad (19b)$$

The expression for the outflux at the boundary $r = R_2$ is identical to that for the centripetal case, i.e., as for the hollow cylinder,

$$Q_t^{cp}(R_1) = Q_t^{cf}(R_2) \quad (20)$$

Again the conclusions from the centripetal case can be applied for centrifugal diffusion.

COMPARISON BETWEEN PLATE, CYLINDER, AND SPHERE

Comparison of Time Lags

The time lag is defined by the intercept on the time axis of the extrapolation of the straight line portion of the Q_t vs t curve. The straight line portion of the Q_t vs t curve corresponds to t-values large enough for the neglect of exponential terms in t—this in turn allows for the derivation of simple analytical expressions for time lags (5–7) which are used in experimental methods for the determination of D.

From the equality of outfluxes in centripetal and centrifugal diffusion it follows that the time lags are also equal for diffusion in each direction. For the sphere the time lag is the same as for the plate, and for the cylinder it is slightly higher, depending on R_2/R_1, as can be seen from Table 3.

It was shown in Part I that the diffusion process in the plate is still far from the steady state at $\tau = \tau_L$. Again, there is no justification to consider the steady state to be established at $\tau = \tau_L$ in the case of the cylinder and the sphere.

TABLE 2

Time Lags

Geometry	Time lag (dimensionless)
Plate	$\tau_L = \frac{Dt_L}{d^2} = \frac{1}{6}$ (d = thickness of plate)
Cylinder	$\tau_L = \frac{Dt_L}{(R_2 - R_1)^2} = \frac{(R_2^2 - R_1^2) - (R_2^2 + R_1^2)\ln R_2/R_1}{4(R_2 - R_1)^2 \ln R_1/R_2}$
Sphere	$\tau_L = \frac{Dt_L}{(R_2 - R_1)^2} = \frac{1}{6}$

TABLE 3

Time Lags—The Hollow Cylinder

	R_2/R_1				
	2	5	10	20	100
τ^L	0.167983	0.17325	0.17903	0.18546	0.1997

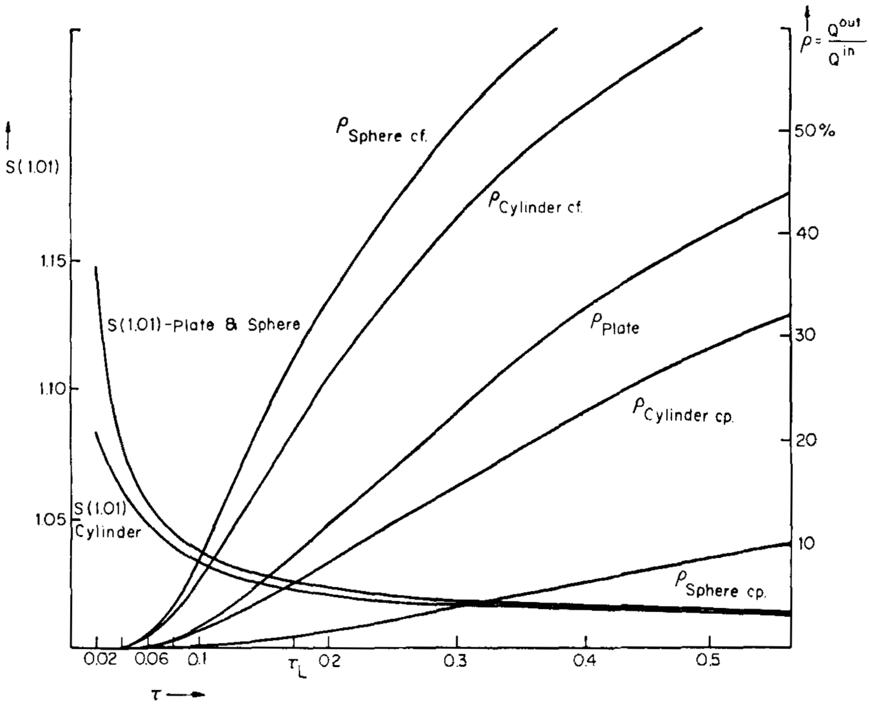

FIG. 5. Percentage of output relative to input for different separations with $D_B/D_A = 1.01$.

This is strikingly shown in Fig. 5 where the ratios $\rho = Q^{out}/Q^{in}$ are plotted against τ. At the steady state ρ should be constant but the curves show that ρ is strongly increasing at $\tau = \tau_L$.

Comparison of Outfluxes

The outfluxes for the three geometries are compared in Table 4. The table shows that the outflux for the cylinder depends upon both R_2/R_1 and one of R_1, R_2 while that for the plate depends only upon the thickness l. The outflux for the sphere depends upon the thickness and also on the factor $4\pi R_1 R_2$. For $R_1 \approx R_2$, i.e., a thin shell or for $R_2 - R_1 \ll R_1, R_2$, i.e., when the shell thickness is small compared with the diameter, $4\pi R_1 R_2$ is approximately equal to the area of the sphere. If this approximation holds,

TABLE 4

Comparison of Outfluxes

Plate[a]	$Q_t = C_i\left\{\frac{Dt}{l} - \frac{l}{6} - \frac{2l}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp(-Dn^2\pi^2t/l^2)\right\}$
Sphere	$Q_t = 4\pi R_1R_2C_i\left\{\frac{Dt}{(R_2-R_1)} - \frac{(R_2-R_1)}{6} - \frac{2(R_2-R_1)}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2} \cdot\exp[-Dn^2\pi^2t/(R_2-R_1)^2]\right\}$
Cylinder	$Q_t = 2\pi C_i\left\{\frac{Dt}{\ln(R_2/R_1)} + 2\sum_{n=1}^{\infty}\frac{J_0(\mu_nR_1)J_0(\mu_nR_2)}{\mu_n^2\{J_0^2(\mu_nR_1)-J_0^2(\mu_nR_2)\}} \cdot[1-\exp(-D\mu_n^2t)]\right\}$

[a] See Part I (*8*).

$$\frac{Q_t(\text{sphere})}{Q_t(\text{plate})} \approx \text{area of sphere}$$

for similar thicknesses of spherical shell and plate.

In Fig. 5 the relative outfluxes $\rho = Q_t^{\text{out}}/Q_t^{\text{in}}$ and the separation factors for the three geometries are presented. The graph yields the percentage of the input which is available at a certain separation $S(\tau)$.

Obviously this fraction is much higher for centrifugal than for centripetal diffusion. Thus centrifugal diffusion has to be preferred—in spite of the higher dilution of the output—when only a small amount of substance is available. This also holds for any preparative application.

Comparison of Output Quantities and Diffusion Times for Similar Enlargement of Boundaries

In Table 5 the outputs are compared for two hollow plates of thickness l', l'', two cylinders of radii (R_1', R_2'), (R_1'', R_2''), and for two spheres of radii (R_1', R_2'), (R_1'', R_2'').

TABLE 5

Comparison of Outfluxes for Similar Enlargement of Boundaries

Plate[a] [Part I, (6b), (8b)]	Cylinder[b] (8b)	Sphere[c] (16b), (16c)
$\frac{Q_t(l'')}{Q_t(l')} = K = \left(\frac{t''}{t'}\right)^{1/2}$	$\frac{Q_t(R_1'')}{Q_t(R_1')} = K^2 = \frac{t''}{t'}$	$\frac{Q_t(R_1'')}{Q_t(R_1')} = K^3 = \left(\frac{t''}{t'}\right)^{3/2}$

[a] $K = l''/l'$, $\tau'' = Dt''/(l'')^2 = \tau' = Dt'/(l')^2$

[b] $K = R_2''/R_2'$, $\tau'' = Dt''/(R_2'')^2 = \tau' = Dt'/(R_2')^2$, $R_2'/R_1' = R_2''/R_1''$.

[c] $K = R_2''/R_2'$, $\tau'' = Dt''/(R_2''-R_1'')^2 = \tau' = Dt'/(R_2'-R_1')^2$, $R_2'/R_1' = R_2''/R_1''$.

This table shows that the amount of equally separated output increases linearly (with barrier thickness) for the plate with the square for the cylinder, and with the cube for the sphere, while if diffusion times are considered the amount of substance increases in proportion to the square root of the time for the plate, linearly for the cylinder, and with the power 3/2 for the sphere. It is interesting to note that, for $\tau' = \tau''$, i.e., $S' = S''$, for all three geometries, $K^2 = t''/t'$.

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