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Separative Diffusion in the Transient State. I. The Plate

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Abstract

For a single plate the separation factor S depends only on the dimension-less time $\tau = Dt/Z^2$ and the difference between the diffusion coefficients ΔD. The output for a certain S can be increased linearly with the plate thickness while simultaneously the diffusion time increases with the square of the plate thickness. For a cascade of 2 plates of equal thickness, the time scale for equal S is expanded by a factor 4 against the single plate. Simultaneously the output is increased by a factor 4β, where β is the efficiency coefficient for the transfer between the 2 plates.

INTRODUCTION

It is well known that the use of separative diffusion in the transient state involves a compromise: In a diffusion process of 2 components which are slightly different in their diffusion coefficients, the first fraction passing a barrier is more highly separated than any fraction present in the steady-state flux. But the higher the separation wanted, the smaller must be the quantity of the fraction. In precomputer times it was hardly possible to get a quantitative survey of these processes for obvious reasons. The transient state was assumed to be "very short" and this sometimes led to the belief that the steady state established itself earlier than it actually did. The uncritical use of "time lag" and "induction time" was perhaps misleading in the same direction. Thus it appeared worthwhile to analyze the transient state diffusion quantitatively for simple barriers such as the plate and the hollow cylinder. In this first part, separative diffusion through the plate is investigated.

The Single Plate

We consider the simple permeation problem for a standard substance A and a test substance B. Simultaneous one-dimensional diffusion proceeds through an infinite plate with thickness Z_1. No mutual interference between A and B is assumed.

The boundary conditions are for the concentrations $C^{A,B}$

$$C_A = C_B = 0, \qquad \text{at} \quad z = 0 \text{ for all } t \tag{1a}$$

$$C_A = C_B = C_1{}^{A,B}, \qquad \text{at} \quad z = Z_1 \text{ for all } t \tag{1b}$$

The initial condition is

$$C_A = C_B = 0, \qquad \text{at} \quad t = 0 \text{ for } 0 < z < Z_1 \tag{2}$$

The analytical solution of the differential equation

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2}, \qquad 0 < z < Z_1;\, t > 0 \tag{3}$$

is well known (*1*). We apply it for our substance A. With the above conditions (1a, b) it reads

$$C_A = \frac{C_1{}^A}{Z_1} z + \frac{2}{\pi}\sum_{n=1}^{\infty} \frac{C_1{}^A \cos n\pi}{n} \sin\frac{n\pi z}{Z_1} \exp\left(-\frac{n^2\pi^2 D_A t}{Z_1{}^2}\right) \tag{4}$$

The integrated in- and outfluxes can be obtained by formation of

$$Q^A = \int_0^t D_A \operatorname{grad} C_A \, dt \tag{5}$$

Thus the integrated outflux at $z = 0$ is

$$Q^A_{\text{out}} = \frac{D_A t}{Z_1} C_1{}^A + \frac{2Z_1}{\pi^2}\sum_{n=1}^{\infty} \frac{C_1{}^A \cos n\pi}{n^2}[1 - \exp(-D_A t n^2\pi^2/Z_1{}^2)] \tag{6a}$$

Using the fact that $\cos n\pi = (-1)^n$ and

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

then Eq. (6) reduces to

$$Q_{\text{out}}^{\text{A}} = C_1{}^{\text{A}}\left[\frac{D_{\text{A}}t}{Z_1} - \frac{Z_1}{6} - \frac{2Z_1}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp\left(-n^2\pi^2 D_{\text{A}}t/Z_1{}^2\right)\right] \tag{6b}$$

In an outflux–time diagram the asymptote to the output curve intercepts the time axis at a point $t = L$ which is known as the time lag. In Barrer's method for the determination of diffusion coefficients, L is found experimentally and D is calculated from the relation

$$L = Z_1{}^2/6D \tag{7}$$

The time lag is often interpreted as representative for the establishment of the steady state. It is obvious, however, from the definition of L that the system at $t = L$, which corresponds to a dimensionless time $\tau = Dt/Z_1{}^2 = 0.167$, is still far from the steady state.

A more severe criterion can be deducted from Fig. 1 which presents the concentration field within the plate at different dimensionless times. The figure was drawn according to Eq. (4). The steady state is indicated by the straight line $c(\tau \to \infty)$, and we can estimate its proximity by calculating the ratio of the concentrations $c(\tau)/c(\tau \to \infty)$, e.g., in the center of the plate. Table 1 presents the approach to steady state according to this criterion.

At $t = L$ only about 75% of the steady-state concentration is reached in the center of the plate. It is important to emphasize this difference because any estimate of the ratio $1/\alpha = D_{\text{B}}/D_{\text{A}}$ according to Eq. (8b) will be too high when steady-state diffusion is assumed after $t = L$.

After formulating the integrated outflux for B according to Eq. (6), we can introduce the separation factor

$$S = \frac{Q_{\text{out}}^{\text{B}}}{Q_{\text{out}}^{\text{A}}}\bigg/\frac{C_1{}^{\text{B}}}{C_1{}^{\text{A}}} \tag{8a}$$

which is defined here as quotient of the ratio of the emerging integrated fluxes and the ratio of the concentrations at the input side which is $C_1{}^{\text{B}}/C_1{}^{\text{A}} = 1$ according to Eq. (1b).

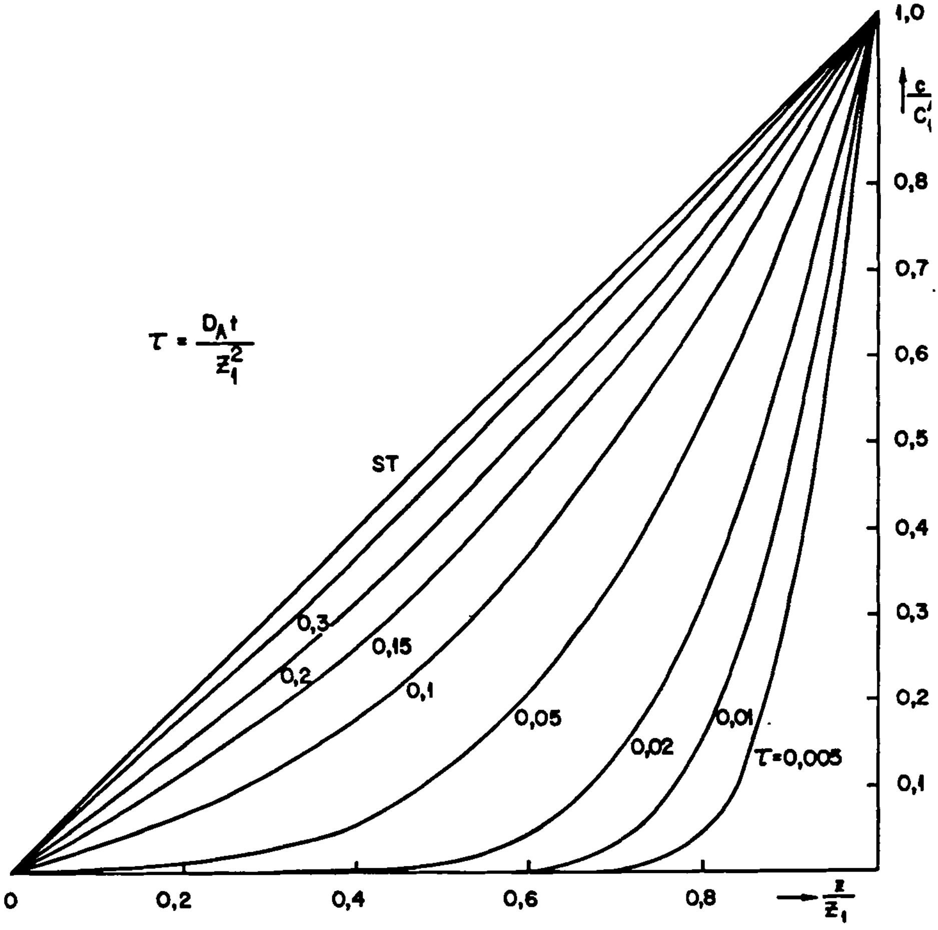

FIG. 1. Concentration field in the single plate.

TABLE 1

τ	0.1	0.15	0.16	0.17	0.2	0.4	0.6
$\frac{C(\tau, 0.5)}{C(\tau \to \infty, 0.5)}$	0.526	0.710	0.738	0.762	0.823	0.975	0.997

Introducing Eq. (6a) into Eq. (8), we obtain

$$S = \frac{\pi^2\tau_B + 2\sum\limits_{n=1} \frac{\cos n\pi}{n^2}[1 - \exp(1 - n^2\pi^2\tau_B)]}{\pi^2\tau_B\alpha + 2\sum\limits_{n=1} \frac{\cos n\pi}{n^2}[1 - \exp(-n^2\pi^2\tau_B\alpha)]} \tag{9}$$

In the steady state, as $t \to \infty$, we get

$$S = 1/\alpha = D_B/D_A \tag{8b}$$

It can be seen from Eq. (9) that S depends only on τ and α. The separation in the transient state can therefore be generalized for any combination of D_A, t, and Z_1 for a fixed α. Thus, when we have computed for a certain α the separation factor S for a certain set of D_A and Z_1 and for $0 < t < \infty$, we can use the results for finding S for any other combination of D_A and Z_1 for the same α. For checking the method, S was computed for 2 sets of constants:

(I) $D_A = 10^{-6}$, $D_B = 1.002 \times 10^{-6}$, $D_{B'} = 1.005 \times 10^{-6}$, $D_{B''} = 1.01 \times 10^{-6}$ cm²/sec, $Z_1 = 1$ cm
(II) $D_A = 10^{-5}$, $D_B = 1.002 \times 10^{-5}$, $D_{B'} = 1.005 \times 10^{-5}$, $D_{B''} = 1.01 \times 10^{-5}$ cm²sec, $Z_1 = 5$ cm

The outfluxes $Q_{\text{out}}{}^{A,B}$ according to Eq. (6) were computed with a IBM 360/65 computer using time steps $\Delta t = 10{,}000$ sec. S according to Eq. (8a) was then calculated with a desk calculator. Q was computed to 6 decimal places and agreement was found within the 6 decimal places of the numbers in Table 2. The data obtained from I and II suggest that for equal S the output quantity increases linearly with the ratio of the plate thicknesses while the diffusion time increases with the square of this ratio. We give a general proof of this relation.

Consider a plate of thickness kZ_1 where k is some constant. Then, at time k^2t, we have from Eq. (6b) that the total mass of a species which has diffused across the bottom of the plate ($z = 0$) is given by

$$Q_{\text{out}}^{(kZ_1)}(0,k^2t) = C_1\left[\frac{Dk^2t}{kZ_1} - \frac{kZ_1}{6} - \frac{2kZ_1}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp(-n^2\pi^2Dk^2t/k^2Z_1{}^2)\right]$$

or

$$\underset{\text{out}}{Q}\overset{(kZ_1)}{(0, k^2t)} = kC_1\left[\frac{Dt}{Z_1} - \frac{Z_1}{6} - \frac{2Z_1}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp(-n^2\pi^2Dt/Z_1{}^2)\right]$$

where the superscript refers to the plate thickness.

TABLE 2

τ	$D_B/D_A = 1.002$ S	$D_{B'}/D_A = 1.005$ S'	$D_{B''}/D_A = 1.01$ S''
0.012	1.045461	1.117194	1.246793
0.016	1.034611	1.088522	1.183925
0.02	1.028145	1.071643	1.147670
0.03	1.019557	1.049471	1.100897
0.04	1.015265	1.038492	1.078094
0.05	1.012681	1.031916	1.064551
0.06	1.010950	1.027526	1.055555
0.07	1.009707	1.024379	1.049131
0.08	1.008765	1.022009	1.044305
0.09	1.008035	1.020156	1.040540
0.10	1.007444	1.018665	1.037516
0.12	1.006549	1.016411	1.032951
0.14	1.005909	1.014781	1.029657
0.16	1.005409	1.013544	1.027161
0.18	1.005022	1.012571	1.025198
0.2	1.004708	1.011784	1.023611
0.4	1.003242	1.008108	1.016222
0.6	1.002751	1.006878	1.013757
0.8	1.002524	1.006310	1.012621
1.0	1.002400	1.005999	1.012000
1.8	1.002204	1.005510	1.011020

Thus, using Eq. (6b), we obtain

$$\underset{\text{out}}{\overset{(kZ_1)}{Q(0, k^2t)}} = k\underset{\text{out}}{\overset{(Z_1)}{Q(0, t)}} \tag{6c}$$

Also, using Eq. (6c) and the fact that the input concentrations are equal, the following relationship is obtained for the separation factors:

$$\overset{(kZ_1)}{S(k^2t)} = \overset{(Z_1)}{S(t)} \tag{8c}$$

Table 2 or the corresponding graph can be used for finding quantitatively a small difference between diffusion coefficients by one-dimensional diffusion similar to the method described for cylindrical diffusion (*2*). For a fast estimate of $S(\tau)$, this function may be approximated by the hyperbola

$$S = \frac{a}{\tau} + \frac{D_B}{D_A} \tag{10}$$

which yields relation Eq. (8b) for $\tau \to \infty$.

For $D_B/D_A = 1.01$ and $a = 2.7325 \times 10^{-3}$, S is well reproduced by

Eq. (10) in the range $0.02 < \tau < 0.2$, where the deviations from the computed values of $S - 1$ are $< 1\%$.

Cascade of Two Plates

With the goal of designing a still more sensitive tool for measuring small differences between diffusion coefficients, the transient state cascade for 2 plates of equal thickness was investigated. No withdrawal or recycling of the depleted fractions was considered. We resume the single plate geometry and add a second plate, of equal thickness Z_1, parallel to the first, and at a distance Z_2 below it. The interspace layer Z_2 contains initially pure solvent. Our interest is now focused on the second plate and we use a new coordinate system (Fig. 2) where $z = 0$ designates the bottom and $z = Z_1$ the top of the second plate. Between the two plates we assume a conveying mechanism for A and B which keeps the boundary condition (Eq. 1a) valid. Thus, in the new system

$$C_A = C_B = 0 \quad \text{at} \quad z = Z_1 + Z_2 \text{ for all } t \tag{1c}$$

We also assume proportionality between the differential outflux from

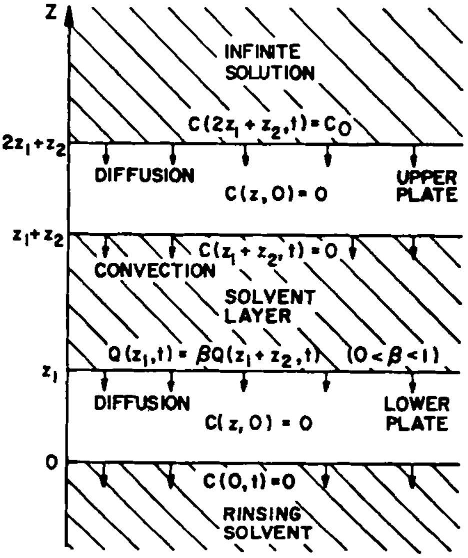

FIG. 2. Cascade of 2 plates.

plate 1 and the differential influx into plate 2:

$$\frac{\partial C(Z_1, t)}{\partial z} = \beta \frac{\partial C(Z_1 + Z_2, t)}{\partial z} \tag{11a}$$

Such a conveying mechanism is approximately given by the convection process which was used earlier (*3*) in qualitative experiments on liquid diffusion cascades: The substance emerging at $z = Z_1 + Z_2$ and entering the pure solvent layer by diffusion makes this layer gravitationally unstable and descends in small drops to the top of the second plate $z = Z_1$. Convection is much faster than diffusion, and convection times are negligible in comparison with diffusion times. Thus this transfer mechanism will result in an inhomogeneous concentration field within Z_2 with high concentration at the bottom and nearly zero concentration at the top. In the present case β depends on the extent of dilution within the solvent layer and would be in the range $0 < \beta < 1$. However, it is possible to make $\beta > 1$ by choosing a large area for the first plate and a small area for the second plate. The choice of β, which is arbitrary, will not affect the separation factor, as we will see. It will appear, however, as a factor of proportionality for the output quantity. At the bottom of plate 2 we assume zero concentration:

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

With these boundary conditions, Eqs. (11a) and (11b) and the initial condition

$$C(z, 0) = 0 \tag{12}$$

we have to solve the diffusion Eq. (3). Using the result of the single plate problem, the boundary condition (Eq. 11a) becomes

$$\frac{\partial C(Z_1, t)}{\partial z} = \frac{\beta C_1}{Z_1}\left[1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp(-n^2\pi^2 Dt/Z_1{}^2)\right] \tag{13}$$

Take the Laplace transform of Eq. (3) with respect to t, and let

$$c(z, s) = \mathscr{L}[C(z, t)]$$

Thus we obtain

$$sc - C(z, 0) = D\frac{d^2c}{dz^2} \tag{14}$$

Using Eq. (12), Eq. (14) reduces to

$$\frac{d^2c}{dz^2} - \frac{sc}{D} = 0, \qquad s > 0 \tag{15}$$

The general solution of Eq. (15) is

$$c(z, s) = A \exp(z\sqrt{s/D}) + B \exp(-z\sqrt{s/D}) \tag{16}$$

where A and B are constants of integration.

Transforming the boundary conditions (Eqs. 11a and 11b), we obtain

$$c(0, s) = 0 \tag{17}$$

$$\frac{\partial c(Z_1, s)}{\partial z} = \frac{\beta C_0}{\sqrt{D}} \frac{1}{\sqrt{s} \sinh(Z_1\sqrt{s/D})} \tag{18}$$

Now, from Eq. (16) the boundary condition (Eq. 17) implies that

$$A + B = 0 \tag{19}$$

and the boundary condition (Eq. 18) implies that

$$\sqrt{\frac{s}{D}}[A \exp(Z_1\sqrt{s/D}) - B \exp(-Z_1\sqrt{s/D})] = \frac{\beta C_1}{\sqrt{sD} \sinh(Z_1\sqrt{s/D})} \tag{20}$$

Solving for A and B from Eqs. (19) and (20), we obtain

$$A = -B = \frac{\beta C_1}{s \sinh(2Z_1\sqrt{s/D})} \tag{21}$$

Substituting Eq. (21) into Eq. (16) yields

$$c(z, s) = \frac{2\beta C_1 \sinh(z\sqrt{s/D})}{s \sinh(2Z_1\sqrt{s/D})} \tag{22}$$

Now we use the complex inversion formula to obtain $C(z, t)$. The final result is

$$C(z, t) = \beta C_1\left[\frac{z}{Z_1} + \frac{4}{\pi}\sum_{n=1}^{\infty} \frac{(-1)^n}{n} \exp(-n^2\pi^2 Dt/4Z_1^{\,2}) \sin\left(\frac{n\pi z}{2Z_1}\right)\right] \tag{23}$$

Figure 3 was drawn according to Eq. (23).

The differentical flux q is given by

$$q(z, t) = D\frac{\partial C}{\partial z}$$

From Eq. (23)

$$\frac{\partial C}{\partial z} = \frac{\beta C_1}{Z_1}\left[1 + 2\sum_{n=1}^{\infty}(-1)^n \exp(-n^2\pi^2 Dt/4Z_1^{\,2}) \cos\left(\frac{n\pi z}{2Z_1}\right)\right] \tag{24}$$

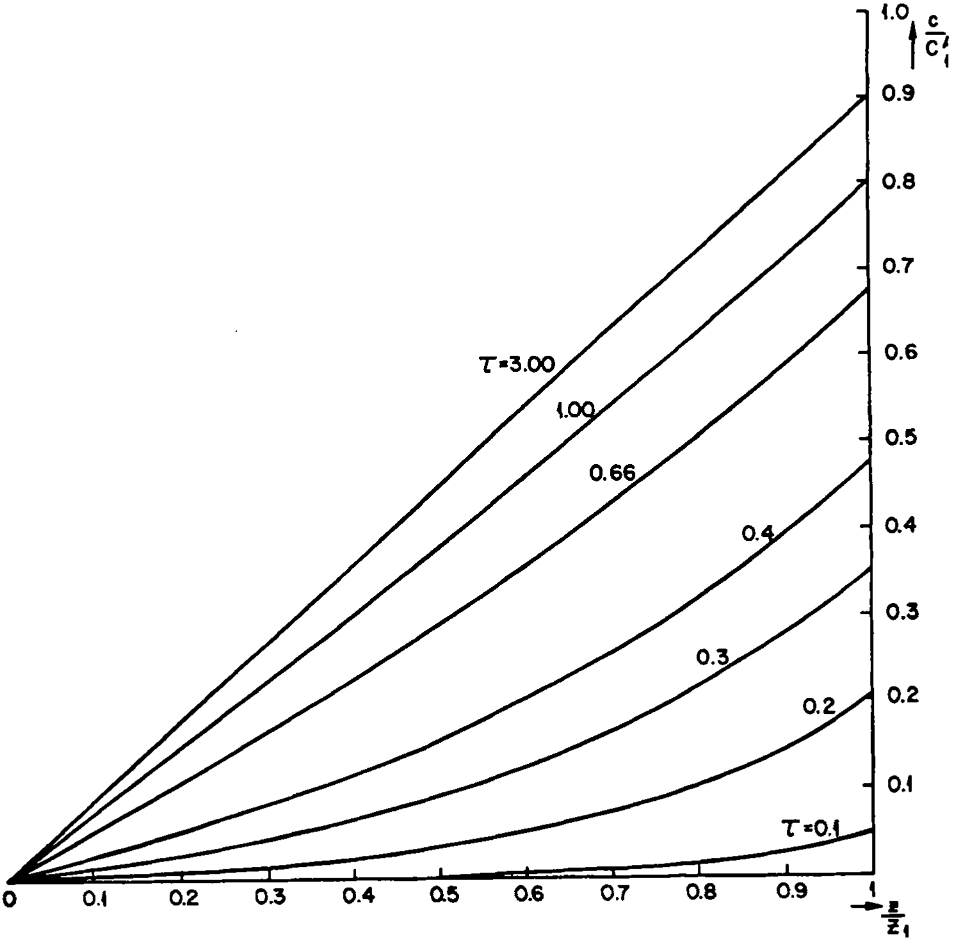

FIG. 3. Build-up of concentration in the second plate.

and hence

$$q(z, t) = \frac{\beta C_1 D}{Z_1}\left[1 + 2\sum_{n=1}^{\infty}(-1)^n \exp(-n^2\pi^2 Dt/4Z_1^2)\cos\left(\frac{n\pi z}{2Z_1}\right)\right] \tag{25}$$

In particular, the flux at the bottom of the lower plate ($z = 0$) is given by

$$q(0, t) = \frac{\beta C_1 D}{Z_1}\left[1 + 2\sum_{n=1}^{\infty}(-1)^n \exp(-n^2\pi^2 Dt/4Z_1^2)\right] \tag{26}$$

By setting $z = Z_1$ in Eq. (24), we recover the boundary condition (Eq. 13). The integrated flux Q is

$$Q(Z_1, t) = \int_0^t D\frac{\partial C}{\partial z}\, d\theta$$

Thus, up to time t, the total mass (per unit area of the plate) of a species which has diffused across the bottom of the lower plate ($z = 0$) is given by

$$Q(0, t) = \frac{\beta C_1 D}{Z_1}\int_0^t\left[1 + 2\sum_{n=1}^{\infty}(-1)^n \exp(-n^2\pi^2 D\theta/4Z_1^2)\right] d\theta$$

That is,

$$Q(0, t) = \frac{\beta C_1 D}{Z_1}\left[t - \frac{8Z_1^2}{\pi^2 D}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp(-n^2\pi^2 D\theta/4Z_1^2)\Big|_0^t\right]$$

$$= \frac{\beta C_1 D}{Z_1}\left[t - \frac{8Z_1^2}{\pi^2 D}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}(\exp(-n^2\pi^2 Dt/4Z_1^2) - 1)\right]$$

$$= \frac{\beta C_1 D}{Z_1}\left[t - \frac{2Z_1^2}{3D} - \frac{8Z_1^2}{\pi^2 D}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp(-n^2\pi^2 Dt/4Z_1^2)\right]$$

where we have used the fact that

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

Therefore

$$Q(0, t) = \beta C_1\left[\frac{Dt}{Z_1} - \frac{2Z_1}{3} - \frac{8Z_1}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp(-n^2\pi^2 Dt/4Z_1^2)\right] \tag{27}$$

RESULTS

Table 3 shows the separation factors at the bottom of the cascade for different diffusion coefficients. The outfluxes from the single plate and

TABLE 3

τ	$D_B/D_A = 1.002$ S_2	$D_B/D_A = 1.005$ S_2'	$D_B/D_A = 1.01$ S_2''
0.04	1.054037	1.140625	1.300130
0.05	1.043718	1.112557	1.236525
0.06	1.036773	1.094201	1.196248
0.07	1.031836	1.081260	1.168257
0.08	1.028146	1.071643	1.147670
0.09	1.025279	1.064214	1.131890
0.10	1.022989	1.058299	1.119404
0.12	1.019557	1.049471	1.100898
0.14	1.017105	1.043191	1.087826
0.16	1.015265	1.038491	1.078094
0.18	1.013830	1.034839	1.070560
0.20	1.012681	1.031917	1.064550
0.24	1.010950	1.027526	1.055555
0.28	1.009707	1.024379	1.049131
0.32	1.008769	1.022009	1.044305
0.36	1.008034	1.020156	1.040540
0.40	1.007444	1.018666	1.037516
0.80			1.023611
1.60			1.016222
4.00			1.011998

TABLE 4

τ	$\frac{Q_1 \text{ mass } (Z_1 = 1)}{\text{cm}^2}$	Q_2 ($\beta = 0.9, Z_1 = 1$)
0.02	0.427693D-08	
0.03	0.484192D-06	
0.04	0.574097D-05	
0.05	0.269342D-04	0.4367021D-11
0.06	0.785551D-04	0.158887D-09
0.07	0.173473D-03	0.213878D-08
0.08	0.320662D-03	0.153970D-07
0.10	0.788529D-03	0.256100D-06
0.12	0.148873D-02	0.174309D-05
0.14	0.240235D-02	0.707080D-05
0.16	0.350172D-02	0.206675D-04
0.18	0.475839D-02	0.484177D-04
0.20	0.614638D-02	0.969632D-04
0.40	0.237244D-01	0.283871D-02
0.60	0.433877D-01	0.105503D-01
0.80	0.633409D-01	0.221270D-01
1.00	0.833344D-01	0.361857D-01
1.80	0.163333	0.102859

from the cascade are presented in Table 4 for different times for the standard substance A with $D_A = 0.1 \times 10^{-5}$ cm^2/sec. It is assumed that $\beta = 0.9$.

Comparison between Tables 2 and 3 reveals the simple relation

$$S_1(\tau) = S_2(4\tau) \tag{28}$$

for every test substance B.

When we check the output quantity at equal S for the single plate and for the 2 plate cascade, using Table 4, we find

$$Q_2(4\tau) = 3.6Q_1(\tau)$$

Assuming $\beta = 0.8$, by computation we get $Q_2(4\tau)/Q_1(\tau) = 3.2$, suggesting the general relation

$$Q_2(4\tau)/Q_1(\tau) = 4\beta \tag{29}$$

This relation can be deduced from the analytical solution: Let $Q_1(z, t)$ and $Q_2(z, t)$ denote the integrated fluxes for the single plate and cascade, respectively. Now

$$\begin{aligned} Q_2(0, 4t) &= \beta C_1\left[\frac{4Dt}{Z_1} - \frac{2Z_1}{3} - \frac{8Z_1}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp\left(-4n^2\pi^2Dt/4Z_1^2\right)\right] \\ &= 4\beta C_1\left[\frac{Dt}{Z_1} - \frac{Z_1}{6} - \frac{2Z_1}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp\left(-n^2\pi^2Dt/Z_1^2\right)\right] \end{aligned}$$

Using Eq. (6b),

$$Q_2(0, 4\tau) = 4\beta Q_1(0, \tau)$$

Application of Eq. (8a) yields immediately Eq. (28).

Relations (28) and (29) can be generalized for transient state cascades of the same type with more than 2 barriers. It follows from Eq. (28) that for the steady state, $t \to \infty$, the separation for the cascade is equal to the separation of the single plate, in contrast to the steady-state cascades with which we are not concerned.

CONCLUSION

The present results render feasible the design of quantitative experiments for the detection of small differences between diffusion coefficients. A thick single plate as diffusion barrier will yield higher quantitative precision, albeit longer diffusion time, than the 2-plate cascade because of the uncertainty of β. A cascade with large β may be better suited for a quantitative estimate of a very small ΔD in a shorter time.

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