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Separative Diffusion in the Transient State. III. Diffusion of a Heavy Fluid in a Cone

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Abstract

Diffusion of a heavy fluid into a cone is approximately one-dimensional. This process can be calculated by the differential equation of diffusion with chemical reaction. Numerical computation was applied for the study of separative diffusion. Separation factors and output quantities were found for cone angles of +30, +5, and −5° and for double barrier thickness. A periodic quasi-steady-state process is proposed which yields a reasonable output with tenfold steady-state separation.

INTRODUCTION

A cone can be considered as a section of a sphere. When we have impermeable walls and no convection of the diffusing substance, the diffusion field shows the features of spherical diffusion. This can be demonstrated by diffusion of a dye from the bottom of a glass funnel into the cone of the funnel filled with a gel medium. The diffusion front, which is initially plane, turns during the diffusion process into curved spherical shells having their center in the tip of the cone. However, when we allow a solution of colored salt to diffuse at the same geometry into liquid water, the areas of constant concentration are not indicated by spherical shells but by plane layers. At low viscosity the curved areas are unstable and are leveled down by convection. The result is an approximately one-dimensional diffusion process.

ONE-DIMENSIONAL DIFFUSION PROCESS IN A CONE

For the calculation of the process we make the following assumptions (Fig. 1). The bottom of the cone is given by a circular area with radius $r_0 = 1$ at $z = 0$. In this area the concentration is always

$$c_0 = 1 = \text{constant} \tag{1a}$$

for all times t, while for

$$\left.\begin{aligned} &0 < z < Z_T \\ &c = 0 \text{ at } t = 0 \end{aligned}\right\} \tag{1b}$$

During the diffusion process the concentrations in the cone are constant for a certain z. Therefore the problem is solved when the diffusion process in the cylindrical column above the bottom area is known. We describe the process from a phenomenological view: Convection processes which establish continuously hydrostatic equilibrium at a microscopic scale do not appear in

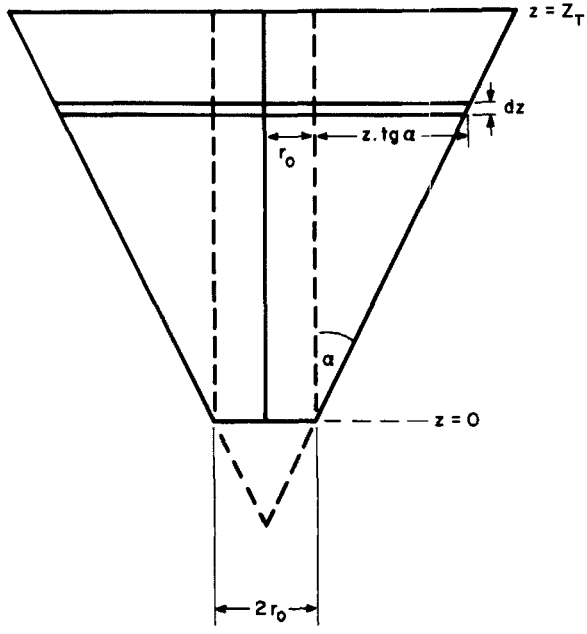

FIG. 1. Geometry of diffusion problems.

our evaluation because they act faster than diffusion, and diffusion remains the rate-determining process.

The effective phenomenological diffusion coefficient is found in the following way: The differential equation of the diffusion in the cylinder above the bottom area is the same as for a diffusion process in the course of which parts of the freely diffusing substance "disappear" or "become fixed" by an irreversible chemical reaction. In our case the "disappearance" is caused by horizontal spreading into layers which increase with z. Then, according to Crank (*1*), the diffusion is governed by the equation

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2} - \frac{\partial s}{\partial t} \tag{2}$$

where c is the concentration of the free solute and s is the concentration of the immobilized solute.

From Fig. 1 we find the ratio

$$R = s/c \tag{3a}$$

At a certain z the total amount of substance in a layer with thickness dz is

$$N_{(z)} = c(z)(r_0 + z \text{ tg } \alpha)^2\pi \, dz$$

while the amount of "free" substance is

$$C(z) = c(z)r_0^2\pi \, dz$$

The difference $N(z) - C(z) = S(z)$ is the "immobilized" substance which has disappeared from the volume $r_0^2\pi \, dz$.

As we refer both C and S to this same volume, we may replace C and S by c and s and get

$$R = \frac{2r_0 z \text{ tg } \alpha + z^2 \text{ tg}^2 \alpha}{r_0^2} \tag{3b}$$

With $s = Rc$, (2) becomes

$$\frac{\partial c}{\partial t} = \frac{D}{1+R}\frac{\partial^2 c}{\partial z^2}$$

$$= \frac{r_0^2}{r_0^2 + 2r_0 z \text{ tg } \alpha + z^2 \text{ tg}^2 \alpha} D\frac{\partial^2 c}{\partial z^2} \tag{4}$$

After having obtained an effective diffusion coefficient $D' = D/(1 + R)$, we may ignore the argumentation of eq. (2) and the conical geometry, and apply D' to the one-dimensional diffusion process occurring in the cylinder above the bottom section at $z = 0$. As D' depends on z, we write the differential equation

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z} D' \frac{\partial c}{\partial z} = \frac{\partial}{\partial z} \frac{r_0^2 D}{r_0^2 + 2r_0 z \operatorname{tg} \alpha + z^2 \operatorname{tg}^2 \alpha} \frac{\partial c}{\partial z} \tag{5}$$

For the solution we still need the boundary condition at the top of the conical medium at $z = Z_T = 5$ cm.

At first we consider the top boundary as impermeable:

$$\partial c/\partial z = 0 \text{ for } t \to \infty \text{ at } z = Z_t \tag{1c}$$

Numerical computation yielded the diffusion field at different times. The results are presented in Fig. 2 for the case $\alpha = 30°$. Comparison with the solution of the corresponding heat conductivity problem for the plate ($\alpha = 0$), given by Carslaw and Jaeger (*2*), shows a much slower process in our case. This can be expected because the effective diffusion constant strongly decreases with z.

SEPARATIVE DIFFUSION

Different α, Constant Barrier Thickness

We consider two substances, A and B, which have equal concentration:

$$c_0^A = c_0^B = 1 \text{ at } z = 0 \text{ for } t \to \infty \tag{1d}$$

and which diffuse as heavy fluids into the cone without disturbing each other. The diffusion constant D_B is assumed to be 1% higher than D_A:

$$D_B/D_A = 1.01$$

The solute arriving at Z_T is removed and collected. The boundary condition at the output side (1c) has to be changed for this procedure:

$$c_T^A = c_T^B = 0 \text{ for } t \to \infty \text{ at } z = Z_T \tag{1e}$$

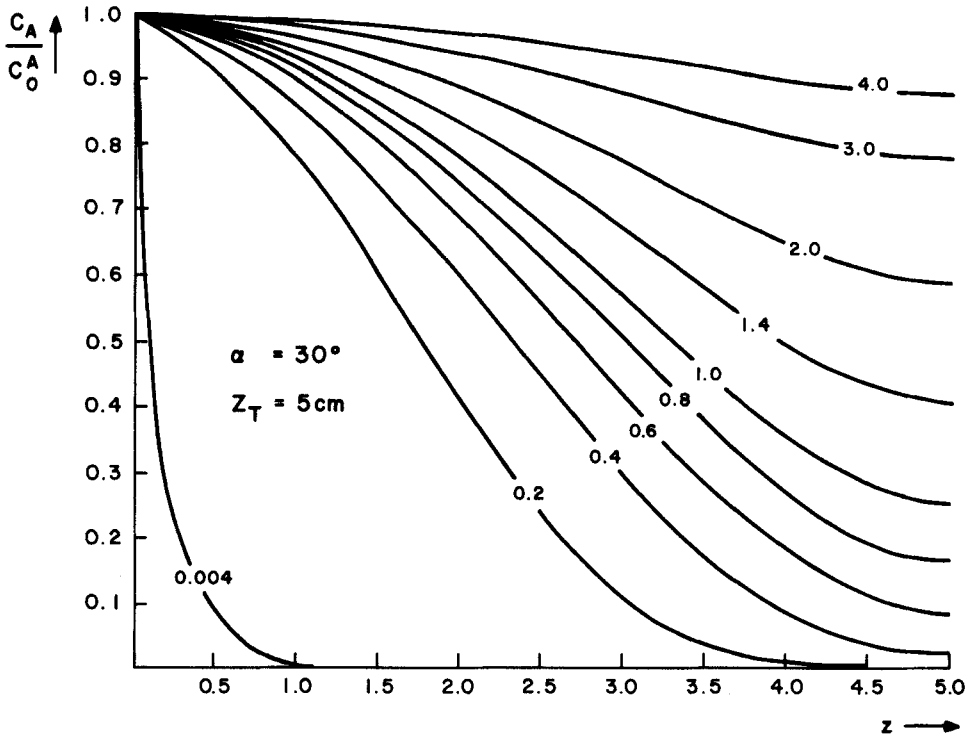

FIG. 2. Diffusion field in cone with impermeable top and different diffusion times $\tau = Dt/Z_T^2$.

The integrated outflows are

$$Q_{A,B} = \int_0^t D_{A,B} \text{ grad } c_{A,B} dt$$

and the separation factor S is defined here as

$$S = \frac{Q_B}{Q_A} \Big/ \frac{c_0^B}{c_0^A} \tag{6}$$

Equation (5) also holds for negative values of α; for $\alpha = 0$ we get normal one-dimensional diffusion as in the infinite plate. Computations were made for $\alpha = +30, +5, -5°$ and 0 at equal thickness $Z_T = 5$ cm. D_A was 10^{-5} cm^2/s.

The diffusion field at different dimensionless times $\tau = Dt/Z_t^2$ is presented in Fig. 3.

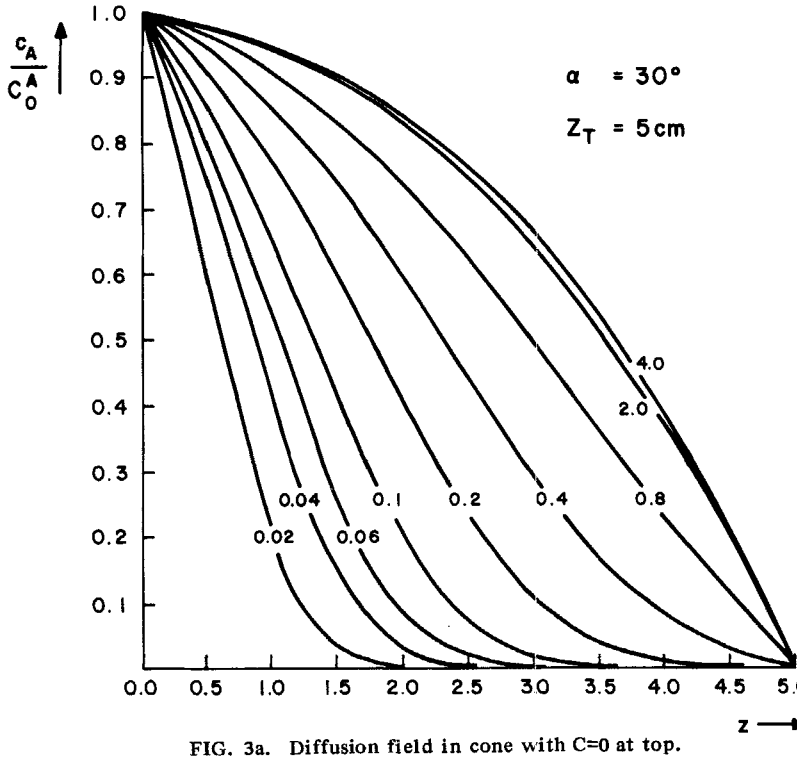

FIG. 3a. Diffusion field in cone with C=0 at top.

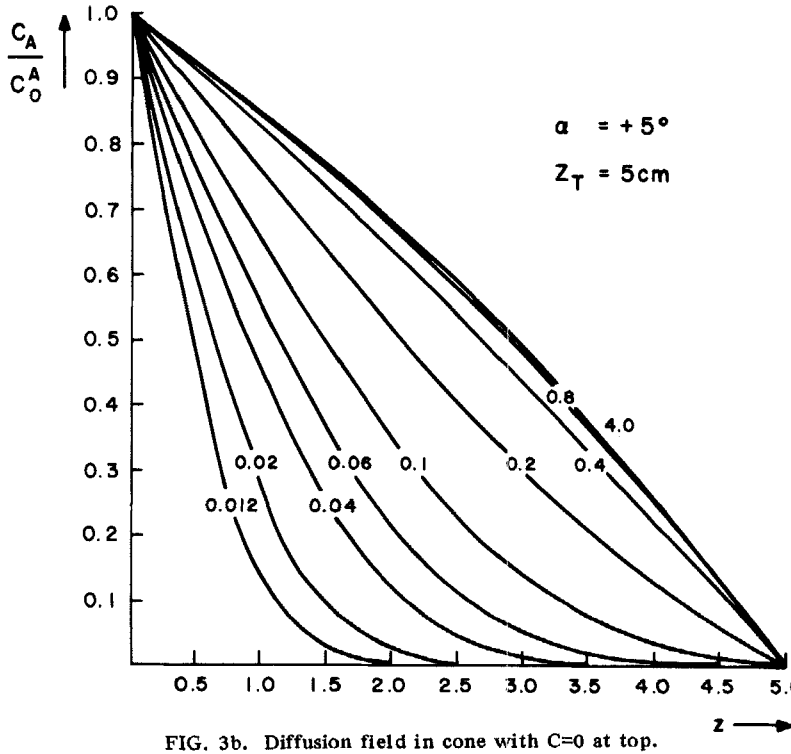

FIG. 3b. Diffusion field in cone with C=0 at top.

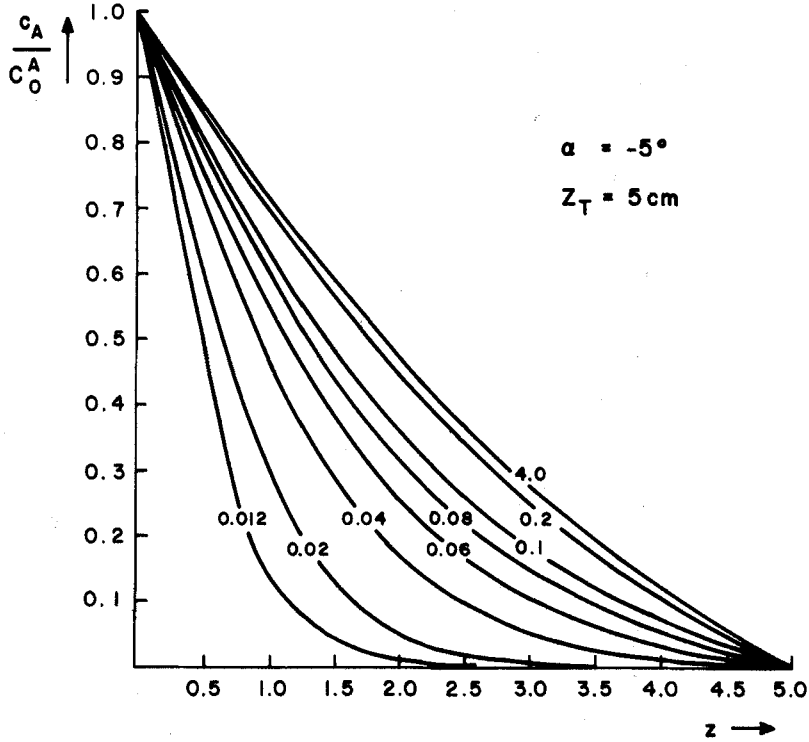

FIG. 3c. Diffusion field in cone with C=0 at top.

The curves of Fig. 3 cannot be generalized by changing the parameter Z_T. Therefore, on the abscissa the thickness of the medium is not indicated by dimensionless lengths $z/Z_T = 1$ as in Part I but by its absolute value $Z_T = 5$ cm (*3*).

The effect caused by increased Z_T is discussed below.

The computer results also yielded the separation factor S and the ratio ρ of integrated outflow to integrated inflow as time functions. These functions are presented in Figs. 4 and 5.

Both figures contain a check of the phenomenological method applied to the process. This check follows from a comparison of the curves for $\alpha = +5°$ and $\alpha = -5°$ with the curve for the plate ($\alpha = 0$) which was earlier obtained by the analytical method. This latter curve fits well between the two former ones, indicating a general reliability of the results. Deviations occur, however, in Fig. 4 in the range $\tau < 0.04$. It was earlier found that in this range the results are very sensitive against the choice of time intervals even for analytical solutions because of computer instability.

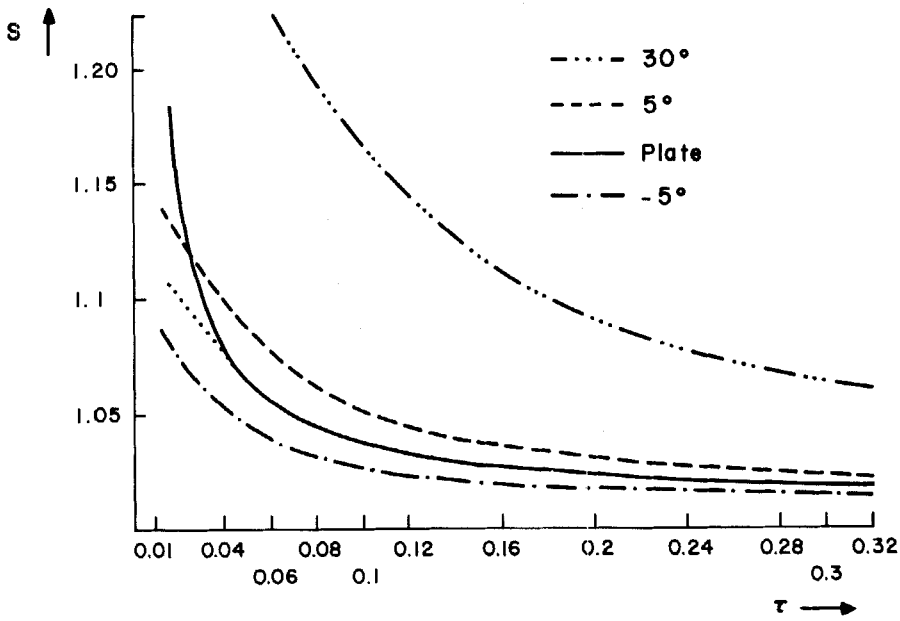

FIG. 4. Time function of separation factors of output.

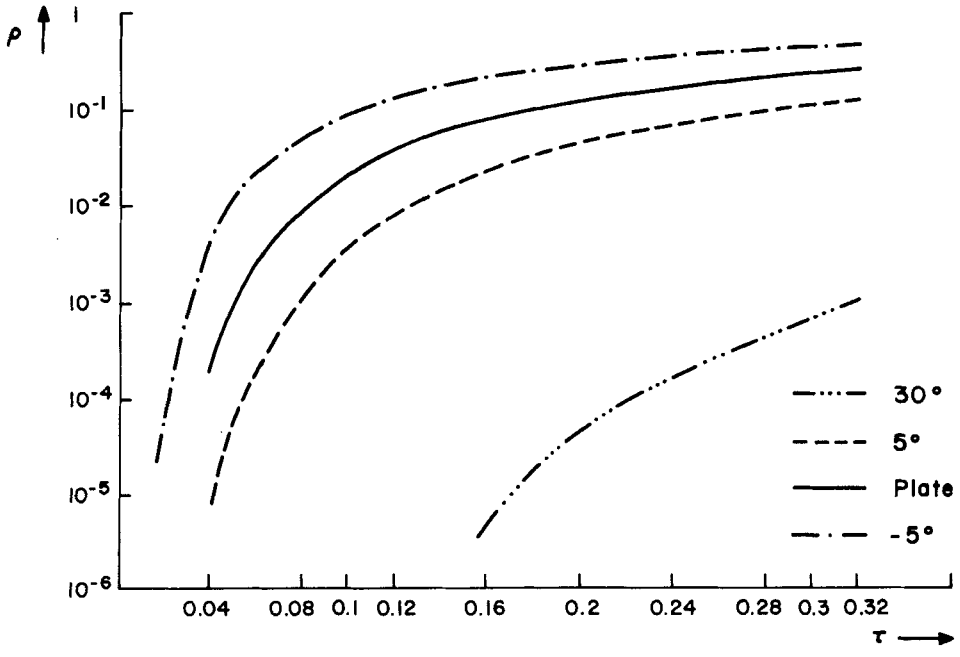

FIG. 5. Time function of quantity of output.

Doubled Thickness of Barrier

Numerical solutions were also computed for the same problem with $Z_T = 10$ cm while all other parameters remained unchanged. For the plate one can expect from the analytical solution that the output Q for a certain S increases linearly with the plate thickness while the diffusion time increases simultaneously with the square of the plate thickness (*3*). As we have no analytical solution for the present problem, we can only compare the computer results empirically.

Table 1 was compiled by finding approximately equal separation factors S in the results for the 5 and 10 cm barriers and by collecting the attached values for diffusion time and integrated output. It appears that the output is approximately doubled at not too short times. For the diffusion times, we find a strong increase with α as expected.

TABLE 1

S_5	S_{10}	t_{10}/t_5	Q_{10}/Q_5
	$\alpha = +30°$		
1.225	1.221	13.33	133
1.143	1.1476	10	1.928
1.111	1.112	10	2.056
1.091	1.091	10	2.0501
1.0605	1.0603	10	2.00
1.0503	1.050	10	1.981
	$\alpha = +5°$		
1.145	1.15	20	1.68×10^4
1.128	1.123	10	34.3
1.0665	1.0663	5.556	2.286
1.0386	1.0382	5.555	2.107
1.0286	1.0287	5.455	1.947
	$\alpha = -5°$		
1.0861	1.0888	3.33	32.35
1.0705	1.07044	2.333	4.925
1.0607	1.0604	2.125	2.813
1.0523	1.0529	2.0	1.9898
1.0488	1.04895	2.0	1.985
1.0457	1.0456	2.0	1.9735
1.0387	1.0383	2.0	2.0076

APPLICATION ON A PRODUCTION SCALE

The initial separation which can also be considered as "enrichment" at transient diffusion is higher than with any other basic process used in isotope separation, but the time in which this highly enriched very small amount of substance is produced by diffusion through a membrane is very short. This limitation has apparently discouraged any consideration of transient diffusion for production purposes. However, the following investigations, based on computer analysis, show the feasibility of the method for obtaining high enrichment together with a reasonable output in a quasi-stationary process.

First of all, one has to consider that not only the initial small output during the diffusion through a membrane is highly separated but also the substance within the barrier shows increasing separation toward the output side. Thin membranes are unsuitable for demonstration of this effect. We therefore

consider here a barrier presented by a 5-cm thick cone section with $\alpha = 30°$ as studied in the previous paragraphs.

The choice of the cone arose from the study of spherical diffusion. In Part II (*4*) we found that the ratio $\rho =$ output/input is highest for centrifugal spherical diffusion. This also holds for the diffusion from the tip of a cone.

Another useful feature of the cone is the following: We apply a hydrodynamic counterflow of the medium which is contrary to the diffusion flow. Because of mass conservation we obtain a distortion of the diffusion field with little displacement of the highly separated substance near the output area but with high "backlash" for the little separated substance in the input region. In other words, an additional spatial separation is produced. We thus arrive at the following transformation.

Counterflow in a Cone

The displacement H of substance from ζ to ζ' by shifting a volume v within the cone is found in the following manner (Fig. 6).

We have

$$\frac{\zeta - H}{\zeta} = \frac{b}{a}$$

$$\zeta = \frac{aH}{a-b} \quad \text{and} \quad \zeta - H = \frac{bH}{a-b}$$

A certain volume v, which is to be shifted, can be expressed by the parameters of the truncated cone:

$$v = \frac{\pi}{3}a^2\zeta - \frac{\pi}{3}b^2(\zeta - H) = \frac{\pi}{3}H\frac{a^3 - b^3}{a-b}$$

$$= \frac{\pi}{3}H(a^2 + ab + b^2)$$

Now we express a and b by tg α, ζ, and H:

$$\text{tg}\,\alpha = \frac{a}{\zeta} = \frac{b}{\zeta - H}$$

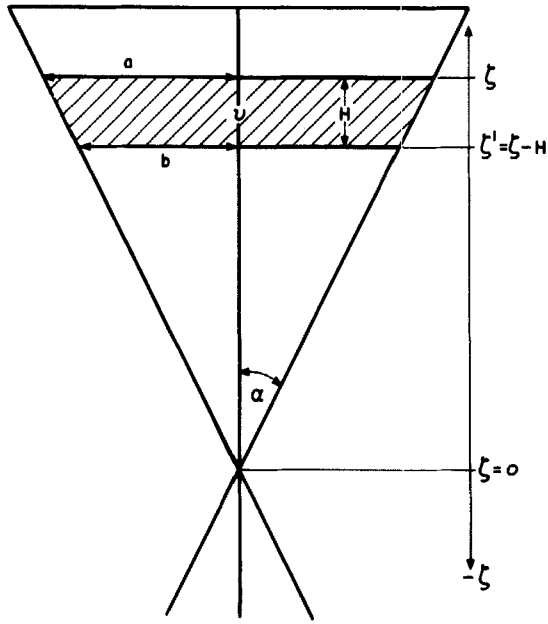

FIG. 6. Parameters for counterflow transformation.

and get

$$v = \frac{\pi H}{3}(\zeta^2 \operatorname{tg}^2 \alpha + \zeta(\zeta - H) \operatorname{tg}^2 \alpha + (\zeta - H)^2 \operatorname{tg}^2 \alpha)$$

$$= \frac{\pi \operatorname{tg}^2 \alpha}{3}(3\zeta^2 H - 3\zeta H^2 + H^3)$$

or

$$\frac{3v}{\pi \operatorname{tg}^2 \alpha} - \zeta^3 = (H - \zeta)^3$$

Thus the displacement H of substance at ζ by a shifted volume v is

$$H = \sqrt[3]{\frac{3v}{\pi \operatorname{tg}^2 \alpha} - \zeta^3} + \zeta$$

This formula also holds for $H > \zeta$. In this case H indicates the position beyond $\zeta = 0$ in the negative cone which is the downward continuation of our cone geometry. This region will not be considered here and we return to the coordinates of Fig. 1 which are linked to ζ by the relation

$$\zeta = z + r_0 \operatorname{cotg} \alpha$$

with $r_0 = 1$ and $\alpha = 30°$ we have $\zeta = z + \sqrt{3}$.

Enrichment by a Periodic Quasi-Stationary Process

We are trying to remove the fraction near the input area, which shows small separation, from our diffusion field and trying to build up the remaining fraction with higher separation to a concentration profile with a higher gradient and increased output.

For this purpose we select a curve from Fig. 3a, say $\tau = 0.04$. We remove all substances in the region $z < 1.5$ by pushing it back into the reservoir. This requires a volume shift of 9.97 mL. We assume that the concentration c_0 is not changed by this procedure: The reservoir may be very large and the injected solvent may be removed by a special process which does not concern us here.

Now we again allow diffusion to proceed from the reservoir for a duration of $\tau = 0.04$. After that we push a volume of 9.97 mL back again and repeat this cycle until a quasi-steady state is reached. This requires about 20 cycles.

The same procedure was performed by computation for $\tau = 0.08$ and $\tau = 0.12$ with the same volume shift and for $\tau = 0.04$ for a volume shift of 16.34 mL.

The quasi-steady-state profiles are presented in Figs. 7a and 7b and the outputs in Table 2. Columns 4 and 5 enable us to compromise between separation factor and output. The normal steady-state separation factor would be 1.01 in our case. Q^A of Column 5 still appears to be small, particularly for high S, but the values presented only represent the integrated output for a single cycle. It would appear that for a separation factor which is tenfold to steady-state separation ($S = 1.10$), a quasi-steady-state process of the kind described would be feasible.

The present example cannot be considered as optimal, and variations of the geometry and of the parameters of the cycles may yield substantial improvements. Working with a cone angle $\alpha < 30°$ raises the output quantity considerably, as Fig. 5 shows. For smaller angles the time parameters τ of the cycles will also be shorter and better suited for production purposes.

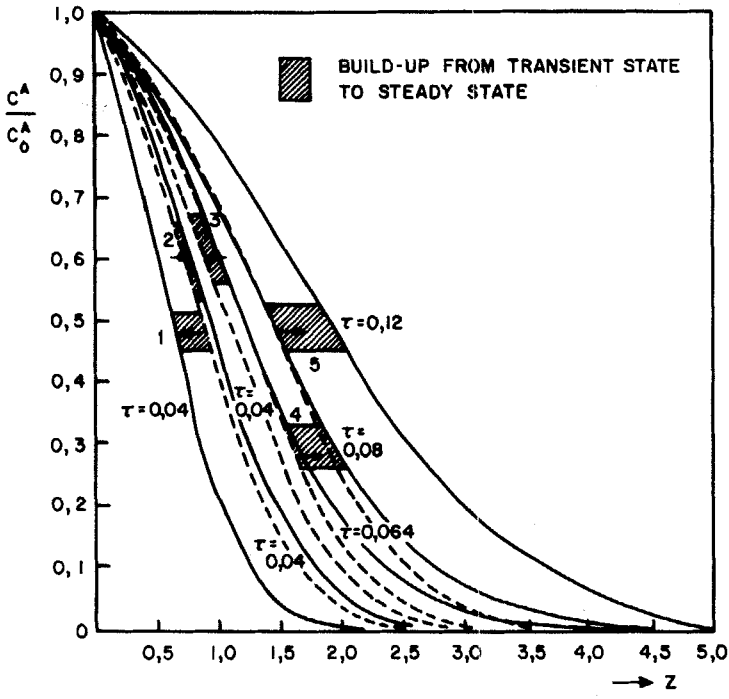

FIG. 7a. Quasi-steady-state concentration profiles (solid lines) with conjugated transient profiles (broken lines). Numbers refer to Table 2.

TABLE 2

No.	τ	Shifted volume (cm^3)	S	Q^A (per cycle)	$S_{transient}$	$Q^A_{transient}$
1	0.04	16.34	1.2192	0.94×10^{-9}	1.258	0.4×10^{-14}
2	0.04	9.97	1.1452	0.85×10^{-6}	1.258	0.4×10^{-14}
3	0.064	9.97	1.0875	0.15×10^{-3}	1.218	0.14×10^{-10}
4	0.08	9.97	1.0683	0.80×10^{-3}	1.193	0.6×10^{-9}
5	0.12	9.97	1.0436	0.73×10^{-2}	1.143	0.28×10^{-6}

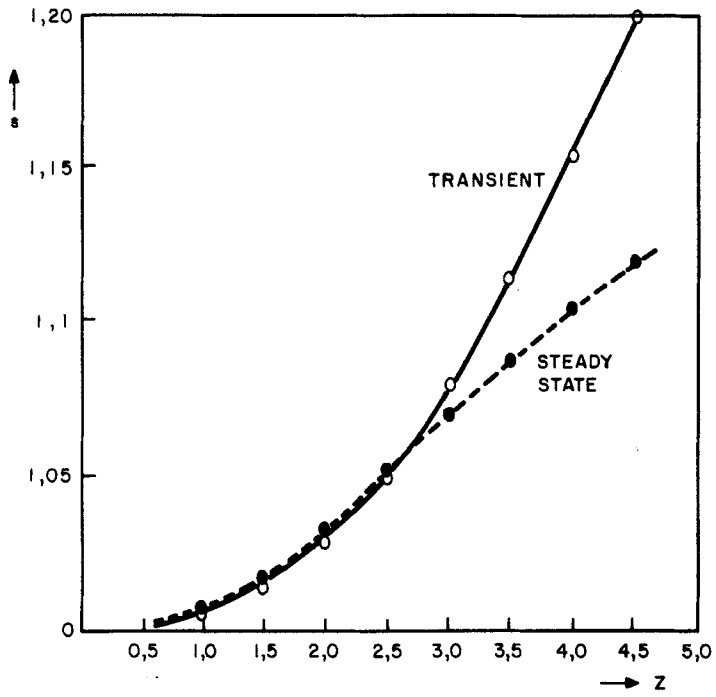

FIG. 7b. Profiles of separation factors for $\tau = 0.04$ and $v = 9.97$ cm^3 (Case 2 in Table 2).

Acknowledgments

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