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FOR TWO-PHASE AXIAL DISPERSION

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DIFFUSION AND BACK-FLOW MODELS FOR TWO-PHASE AXIAL DISPERSION

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ABSTRACT

Two-phase flow operations are described by a generalized model which assumes back flow, superimposed on the net flows through a column, with perfectly mixed stages in cascade. The diffusion model, which is used extensively to describe longitudinal dispersion, is derived as an extreme case of the back-flow model. The perfectly mixed stage (or cell) model is derived as another extreme. It is shown that the dispersed phase for these models may be treated as a second continuous phase. The nature of the longitudinal-dispersion coefficient is also examined.

Introduction

Axial-mixing effects in agitated countercurrent equipment may be described by a detailed analysis of back flows between discrete segments of the "cascade", frequently with greater rigor than by assuming a differentially-continuous diffusion model with a constant axial-dispersion coefficient for each phase. For single-phase operations, the relations between a multicompartment (or mixing-cell) nonequilibrium model and the diffusion model have been explored widely, although usually without considering back flow. For two-phase operations, relative to the diffusion model, the cell model is underdefined if back flows are neglected and it is overdefined if they are specified for both phases. Thus we find it worth while to explore the mathematical relation between these models in some detail.

An added justification for this work is the one of providing adequate background for design calculations that can take into account the axial-dispersion effects in countercurrent operations. For overall calculations under conditions of constant mass-transfer coefficients and linear equilibrium, integrated solutions based on the diffusion model are now available to describe the system. If, however, the parameters are not held constant, a stepwise numerical calculation must be undertaken which inherently resembles the cell-model treatment.

Figure 1 shows the "back-flow" model schematically. It consists of n_p perfectly mixed stages with stage height L_0, each having the same volume. Exchange of material between two adjacent stages is due to (a) net flows, $\overline{F}_x$ and $\overline{F}_y$, of main streams, and

(b) an additional back flow F of the mixed phases, which occurs in each direction and is the sum of individual-phase back flows of F_x and F_y. Thus the total flows between adjacent stages are $(\overline{F}_x + F_x + F_y)$ and $(\overline{F}_y + F_y + F_x)$.

For the limiting case of $F(= F_x + F_y) \longrightarrow 0$, this system reduces to a "stage model" (of perfectly mixed cells in cascade) typified by the usual mixer-settler extractor. For another limiting case, with $n_p >> 1$, it will be shown later that the system reduces to the "diffusional model" which assumes mean diffusivities and mean velocities for both continuous and dispersed phases (16,21).

A particular case of this model has been utilized by Hill (7) for calculations on salt-metal extraction processes. Sherwood and Jenny (20) and Colburn (2) have utilized a similar concept to treat the effect of entrainment on tray efficiency. For single-phase flow Latinen and Stockton (9) have discussed the relation between the model and the diffusion model. Sleicher (22) has developed a similar treatment for a mixer-settler extractor with interstage entrainment.

DISPERSED-PHASE BEHAVIOR

For two-phase flow operations in a perfectly mixed stage, one phase is usually dispersed into the other in the form of bubbles or droplets. If enough coalescence and redispersion take place, the concentration of each droplet is the same, and the dispersed phase may be considered as a second continuous phase. If not, the overall rate process in the stage should be treated on the basis of the residence-time distribution of droplets and

of their concentration distribution as they enter.

To formulate the rate process, phase X is taken as continuous and phase Y as dispersed. The direction of mass transfer is from phase X to phase Y. (The final conclusion is independent of these arbitrary choices.) We consider first the limiting case of no concentration variation from droplet to droplet in a given stage; and later, in less detail, the case of no coalescence (and hence no redispersion) between droplets.

Calculation Using a Mean Concentration

This case is consistent with the assumption that the dispersed phase behaves as a second continuous phase. When the equilibrium relation is linear (that is, $x^* = b + my$), the material balance and the rate equation taken for the jth stage give the following dimensionless relations:

$$\left.\begin{aligned} (1 + \alpha_x)(x_{j-1} - x_j) - \alpha_x(x_j - x_{j+1}) &= N_{oxO}[x_j - (b + m\bar{y}_j)] \\ (1 + \alpha_y)(\bar{y}_j - \bar{y}_{j+1}) - \alpha_y(\bar{y}_{j-1} - \bar{y}_j) &= N_{oyO}[x_j - (b + m\bar{y}_j)] \end{aligned}\right\} \quad (1)$$

where $\alpha_x = F_x/\bar{F}_x$, $\alpha_y = F_y/\bar{F}_y$, $N_{oxO} = k_{ox}aL_O/\bar{F}_x$, $N_{oyO} = k_{ox}aL_O/\bar{F}_y$; $\bar{y}_j$ is the mean concentration of dispersed phase Y in (or leaving) the jth stage (the mean concentration is taken on a volume basis); and $k_{ox}a$ is assumed constant throughout the column.

Behavior Without Coalescence and Redispersion

For this case, in any given stage, the concentration of each droplet is different; depending on the time it has been in the stage, its size, and its entering concentration. The

equations developed here (See Appendix) are a generalization of previous work (11,15).

Uniform Drop Size

Consider the jth stage, under a steady continuous operation with flow rates of $\overline{F}_x + F$, and $\overline{F}_y + F$, where the contents are mixed perfectly, with a uniform drop diameter d_p, and a uniform volume fraction ϵ_y for the dispersed phase. Assume further that the partition coefficient m is constant, and that the overall coefficient of mass transfer is a constant. As shown in the Appendix, any assumed concentration distribution in a stage will determine the mean concentration, and integration of the changes that occur in the input concentration-distribution leads to an output distribution which conforms to Equation 1 . If some coalescence and redispersion do occur, as has been observed for agitated liquid-liquid systems (12,24,25), it may be possible to relax some of the restrictions just stated, and still apply Equation 1 . These conclusions apply even for the stage model ($\alpha_y = \alpha_x = 0$). Thus, if the foregoing conditions are satisfied, it is entirely permissible to treat the dispersed phase as if it were a second continuous phase.

TWO-PHASE FLOW SYSTEMS

Countercurrent Back-Flow Model

From the assumption that the dispersed phase can be characterized by mean concentration values, and from a material balance around the jth stage as diagrammed in Figure 1, the basic rate equation has the form of Equation 1 . Solving this equation is

tedious, as the solution contains five variable parameters: α_x, α_y, n_p, N_{ox0} and Λ. A machine computation and an approximate calculation method have been presented by Sleicher (22). Here, however, instead of the equations being solved, they will be used to develop the diffusion model and to show that the model is applicable to the behavior of the dispersed phase (with some restrictions) even without coalescence and redispersion of liquid droplets.

Diffusion Model

The diffusion-model equations (16,21) utilize the assumption that the dispersed phase can be treated as a second continuous phase. Since this assumption has been found reasonably satisfactory for the back-flow model, its use in the diffusion model will be particularly justifiable if the latter model can be derived from the general back-flow case. Such a derivation will be shown in this section.

The diffusion-model equations in dimensionless form are as follows:

$$\left.\begin{aligned} (1/P_xB)\ d^2x/dZ^2 - dx/dZ - N_{ox}\left[x - (b + my)\right] &= 0 \\ (1/P_yB)\ d^2y/dZ^2 + dy/dZ + N_{oy}\left[x - (b + my)\right] &= 0 \end{aligned}\right\} \qquad (2)$$

where $N_{ox} = k_{ox}aL/\overline{F}_x$ and $N_{oy} = k_{ox}aL/\overline{F}_y$. If lowest-order central differences are used, Equation 2 becomes, for phase X,

$$(1/P_xB)(x_{j+1} - 2x_j + x_{j-1})\Big/(\Delta Z)^2 - (x_{j+1} - x_{j-1})\Big/(2\Delta Z) = N_{ox}\left[x - (b + my)\right] \qquad (3)$$

with another similar equation for phase Y. For a total number

of segments, n_p, the size of each segment (ΔZ) is equal to $1/n_p$. With this equality, Equation 3 is transformed to

$$\left[(n_p/P_xB) + (1/2)\right](x_{j-1} - x_j) - \left[(n_p/P_xB) - (1/2)\right](x_j - x_{j+1})$$
$$= N_{oxO}\left[x_j - (b + my_j)\right] \qquad (4)$$

This equation is seen to be essentially the same as Equation 1, when the following equality is satisfied for phase X (and also for phase Y; i = x or y):

$$\frac{1}{P_iB} = \frac{1}{2n_p} + \frac{\alpha_i}{n_p}$$

or

$$\lim_{n_T \longrightarrow \infty} (P_iB) = n_p / \alpha_i \qquad (5)$$

The boundary conditions (16,21) at the two ends of the column, for solving Equation 2, are derived from the end conditions for the back-flow model, by putting $\Delta Z \longrightarrow 0$.

For single-phase flow with $n_p \gg 1$, Latinen and Stockton (9) have derived Equation 5 from Einstein's "random walk" diffusion equation (5,18), and they thus relate a longitudinal-dispersion coefficient to the rate of change of a series of discrete fluid displacements. For a finite number of stages they adopt the following form for both physical transients and homogeneous first-order reaction:

$$\frac{1}{PB} = \frac{1}{[2(n_p - 1)]} + \frac{\alpha}{(n_p - 1)} \qquad (6)$$

Use of the term $2(n_p - 1)$ is based upon Kramers and Alberda's treatment for the cell model (8).

Equations 5 or 6 also serve to carry out the reverse reduction of Equation 1 into Equation 3, which is then converted into Equation 2 with a sufficiently large number of segments ($n_p \gg 1$); this procedure justifies applying the diffusion model to the dispersed phase, and also renders the diffusion model applicable to a stagewise system. Nevertheless, these two models are basically different from each other; hence the conversion relation will vary somewhat, depending upon what basis is taken for comparison. We note that Equation 5 applies only for $n_p \gg 1$. The question of obtaining more accurate conversion relations is discussed below in three special cases, to examine the conditions under which the two models behave identically.

CONVERSION RELATION FOR TRANSIENT BEHAVIOR

One workable and representative link between the two models is provided by comparing the variance for residence-time distribution of fluid elements. The procedure used by Van der Laan (23) gives the variance σ_{Di}^2 of residence times, for phase i, based on the diffusion model:

$$(1/2)\ \sigma_{Di}^2 = 1/P_iB - (1/P_iB)^2(1 - e^{-P_iB}) \qquad (7)$$

with i = x or y.

The basic transient equations for the back-flow model are written without difficulty for phase i from the material balance taken for each stage. The variance σ_{Bi}^2 of residence times, for phase i, is then given by solving the transient equations in a similar manner:

$$\frac{1}{2}\,\sigma_{Bi}^{2} = \frac{1}{2n_p} + \frac{\alpha_i}{n_p} - \left[\left(\frac{1}{2n_p} + \frac{\alpha_i}{n_p}\right)^2 - \left(\frac{1}{n_p}\right)^2\right]\left[1 - \exp\left\{-\frac{f_\sigma}{(1/2n_p) + (\alpha_i/n_p)}\right\}\right] \tag{8}$$

where

$$f_\sigma = \left(\frac{1}{2} + \alpha_i\right)\cdot\ln\left(1 + \frac{1}{\alpha_i}\right) = 1 + \sum_{k=1}^{\infty} \frac{1}{(2k+1)(2\alpha_i+1)^{2k}}$$

As a matter of definition, the mean residence time θ_{Ti} for phase i is $\theta_{Ti} = L/(\overline{F}_i/\epsilon_i)$ in the foregoing treatment.

The conversion relation for phase i, based on the variances, is obtained by setting $\sigma_{Di}^{2} = \sigma_{Bi}^{2}$. The following simple empirical equations express the equality almost exactly for the entire range of n_p, α_x, and α_y:

$$\frac{1}{P_i B} = \frac{1}{2(n_p - 1)(1 + 1/2n_p)} + \frac{\alpha_i}{(n_p - 1/2)} \tag{9}$$

For $n_p \gg 1$, Equation 8 reduces to Equation 5 as expected.

CONVERSION RELATION FOR TWO-PHASE MASS TRANSFER

Another workable link between the two models is provided by equating the extents of mass-transfer for countercurrent flow at infinite N_{ox}. With this limiting condition the diffusion-model solution, as given by Miyauchi and Vermeulen (16), is

$$X \equiv \frac{x_L - (b + my_F)}{x_F - (b + my_F)} = \frac{\Lambda - \Lambda^2}{\exp\left[(1 - \Lambda)P_{oy}B\right] - \Lambda^2} \tag{10}$$

with

$$\frac{1}{P_{oy}B} \equiv \frac{\Lambda}{P_x B} + \frac{1}{P_y B}$$

and the back-flow model solution by Sleicher (21), originally

obtained for a multistage mixer-settler extractor with entrainment, and with each stage at equilibrium, rearranges to the form:

$$X \equiv \frac{x_L - (b + my_F)}{x_F - (b + my_F)} = \frac{\Lambda - \Lambda^2}{\beta^{-(n_p-1)} - \Lambda^2} \qquad (11)$$

with $\beta \equiv 1 - (1 - \Lambda) / (\Lambda\alpha_x + \alpha_y + 1)$,

and $\alpha_i = F_i / \overline{F}_i$

Equating the above two relations, the exact conversion relation for phase i (= x or y) is

$$\frac{1}{P_i B} = \frac{1}{2(n_p - 1)f_T} + \frac{\alpha_i}{(n_p - 1)f_T} \qquad (12)$$

where

$$f_T = \left(\frac{1}{2} + \psi\right) \ln\left(1 + \frac{1}{\psi}\right) = 1 + \sum_{k=1}^{\infty} \frac{1}{(2k + 1)(2\psi + 1)^{2k}}$$

with

$$\psi = \left[\Lambda + \left(\Lambda\alpha_x + \alpha_y\right)\right] / (1 - \Lambda)$$

The correction factor f_T is seen to have essentially the same form as f_σ, and is shown in Figure 2 as a function of Λ and $\Lambda\alpha_x + \alpha_y$. With $(\Lambda\alpha_x + \alpha_y) > 0.5$, f_T is nearly equal to 1 irrespective of Λ.

Equation 12 may be used to compute the countercurrent-diffusion-model solution with the back-flow-model result, at finite values of N_{ox}. For this comparison, calculations were made at the relatively severe conditions of $n_p = 2$, over the range of variables of $1 < N_{ox} < \infty$, $0.56 < (\Lambda\alpha_x + \alpha_y) < 32$, and $0.0625 < \Lambda < 16$. Under these conditions, the fraction unextracted usually agreed to well within ±5% in its absolute value. At increasing n_p, α_i, and N_{ox}, the

approximation improves rapidly.

Agreement to within ± 10% was obtained under the same conditions by taking $f_T = 1$ throughout.

Application to Liquid Extraction

We take as an example the operation of pulsed perforated-plate columns; a similar treatment should be applicable to rotating-shaft equipment such as the RDC or Mixco extractors.

Now we let ω, ℓ, and ϵ_i be respectively the pulse frequency, pulse amplitude, and volume-fraction of phase i in the column. The rate of interstage mixing F_i may be considered equal to a pulse velocity $\omega\ell\epsilon_i$. According to experimental observations, a given stage is seen to behave as β perfectly mixed stages in series, and hence the total effective number of stages may be taken as βn_p as a first approximation. Since n_p is usually at least eight to ten stages, Equation 9 (or Equation 12 with $f_T = 1$) is applicable to give a longitudinal-dispersion coefficient. The following equation is obtained for "emulsion-type operation" in the sense of Sege and Woodfield (19); we introduce $\alpha_i = \omega\ell\epsilon_i / \overline{F}_i$, and βn_p as the total effective number of stages, and neglect the terms $(1/n_p)$ and $(1/2)$ in comparison with n_p; in Equation 9:

$$\frac{E_i}{\omega\ell\epsilon_i L_0} = \frac{\overline{F}_i / \omega\ell\epsilon_i}{2\beta - (1/n_p)} + \frac{1}{\beta} \qquad (13)$$

For ideal "mixer-settler" operation, the restriction $\omega\ell = \overline{F}_i$ is needed to give steady flow of each phase through the column. This may be written in its alternative form of $\omega\ell\epsilon_i / \overline{F}_i = \epsilon_i < 1$.

Introducing $\alpha_1 = 0$, with the actual number of stages as n_p, E_1 is obtained as follows:

$$\frac{E_1}{\omega \ell \epsilon_1 L_0} = \frac{\bar{F}_1 / \omega \ell \epsilon_1}{2 - (1/n_p)} \tag{14}$$

Figure 3 compares Equations 13 and 14 with experimental continuous-phase data calculated from extraction runs by Eguchi and Nagata (4) (open circles), and from physical-transient runs by Oya (17). Curve MM' is for the "mixer-settler" operation, Equation 14 ; and curves BB' ($\beta = 1$) and CC' ($\beta = 2$) are for "emulsion-type" operation, Equation 13 . Point P is the upper limit for the former, and point Q the lower limit for the latter. The ideal-pass curve should be along MPQB' for $\beta = 1$, but the actual pass seems to be along MPQ'B'; this suggests that the flow-mechanism changes gradually from the mixer-settler type to the emulsion type. Experimental values of β are commonly between 1 and 2; further investigations are needed before β can be adequately correlated, particularly for the behavior of the dispersed phase.

CONVERSION RELATION FOR HOMOGENEOUS REACTION

In single-phase systems, chemical reaction may provide a source or sink for the individual components which is analogous to the effect of having a second phase. It is therefore of interest to examine such systems here. The conversion relation is derived on the basis of obtaining the same extent of reaction for the two models. For a diffusion-model reactor in which isothermal q^{th}-order homogeneous reaction occurs,

mathematical solutions are available for $q = 1$ (3,26), and $q = 0.5$ and 2 (6,10). The basic rate equation for the back-flow model is given by Equation 1, if the parameters x, α_x and N_{oxo} are replaced by c, α ($= F/\bar{F}$), and N_{qo} ($= N_q/n_p$) respectively; here $N_q = k_q c_F^{(q-1)} L/\bar{F}$.

The analytical solution for $q = 1$ is:

$$X \equiv \frac{c_L}{c_F} = (\gamma_1 - \gamma_2)(1 + 1/\alpha)^{n_p} \Big/ (g_1 h_2 - g_2 h_1) \tag{15}$$

where

$$g_k = \alpha(\gamma_k - 1); \; h_k = (\gamma_k - 1)\gamma_k^{n_p} \quad (k = 1 \text{ and } 2)$$

$$\gamma_1 = r + \sqrt{r^2 - (1 + 1/\alpha)} \; ; \quad \gamma_2 = r - \sqrt{r^2 - (1 + 1/\alpha)}$$

$$r = 1 + [(1 + N_{1,o})/2\alpha]; \quad N_{1,o} = k_1 L/\bar{F} n_p = k_1 L_o \Big/ \bar{F}$$

For arbitrary reaction-order, the back-flow-model solution can be obtained numerically, starting from the outlet concentration c_L, and continuing stage by stage to reach the feed concentration c_F.

Equating the diffusion-model X with the back-flow-model X, the following empirical relation is found for $q = 0.5$, 1, and 2.

$$\frac{1}{PB} = \frac{1}{2(n_p - 1)[1 - (1/n_p)]} + \frac{\alpha}{n_p + 1 - q} \tag{16}$$

Under the most severe conditions tested, $n_p = 2$ with various α, and $\alpha = 0$ with various n_p; in both cases the fraction unreacted covers $X > 0.007$ for $q = 2$, $X > 0.0007$ for $q = 1$, and $X > 0.59$ for $q = 0.5$. The fraction unreacted agrees to within $\pm$ 10 percent in its absolute value when calculated from Equation 16, even at the lowest α and n_p.

DISCUSSION

Further Properties of the Relations

When the contribution of back flow entirely dominates longitudinal dispersion, the conversion relations give the following simple formula for higher values of n_p:

$$P_i B = n_p/\alpha_i \quad \text{or} \quad E_i = F_i L_0 \quad (i = x \text{ or } y) \tag{17}$$

where the relation $L = n_p L_0$ is utilized. Equation 17 simplifies further when $F_i = \epsilon_i F$, where F is the superficial rate of interstage mixing of the mixed phases:

$$E_x/\epsilon_x = E_y/\epsilon_y = FL_0 \tag{18}$$

When the contribution of the cell model entirely dominates longitudinal dispersion, the following two equations are obtained from Equations 9 and 16, depending upon the situation treated: For physical-transient behavior,

$$P_i = \overline{F}L_0/E_i = 2[1 - (1/n_p)][1 + (1/2\ n_p)] \tag{19}$$

and, for homogeneous chemical reaction,

$$P_i = \overline{F}L_0/E = 2[1 - (1/n_p)]^2 \tag{20}$$

Furthermore Equations 10 and 12 give the following exact conversion relations for the equilibrium-stage model and the equilibrium-diffusion model:

$$P_x B = P_y B = (\Lambda + 1)\left(\frac{\ln \Lambda}{\Lambda - 1}\right)(n_p - 1) \tag{21}$$

$$P_{oy} B = \frac{\ln \Lambda}{\Lambda - 1} \cdot (n_p - 1) \tag{22}$$

These two simple equations show clearly how the number of equilibrium stages and the extent of longitudinal dispersion behave as the limiting factors for mass transfer in counterflow column operations.

Mathematically Equivalent Systems

Once the conversion equation is selected, we can in principle equate a staged cascade described by n_p, α_x, α_y, Λ, and N_{ox} to a differentially continuous column described by P_xB, P_yB, and the same Λ and N_{ox}. No ambiguity is involved if the physical system is staged, the α's have been measured in some way, and we wish to use column mathematics (14,16). If stepwise calculation of a column is required, however, there is a relatively free choice of cascades.

A useful model is obtained by letting the stream with the larger PB correspond to $\alpha = 0$. It will provide the simplest scheme for numerical computation, but will tend to describe a column less accurately, always with the restriction of $n_p = PB/2$. Selection arbitrarily of larger n_p's, in succession, used with the convergence equation, can be expected to show a convergence to concentration profiles that are insensitive to the particular choice.

When packed beds are operated in the fully turbulent region, as may sometimes occur in gas absorption (1,13), the equivalent stage height L_0 can be taken equal to ηd_p. Equations 19 and 20 are then easily modified to formulas based on d_p, where n_p is given by $L/\eta d_p$. Figure 4 shows P or P_i ($= \overline{F}L_0/E_i$) as a function of L/L_0, in this case.

LITERATURE CITED

1. Aris, R., Amundsen, N. R., A.I.Ch.E. Journal 3, 280 (1957).
2. Colburn, A. P., Ind. Eng. Chem. 28, 526 (1936).
3. Danckwerts, P, V., Chem. Eng. Sci. 2, 1 (1953).
4. Eguchi, W., Nagata, S., Chem. Eng. (Japan) 23, 146 (1959).
5. Einstein, H. A., Dissertation, Eidgenössische Technische Hochschule, Zürich (1937).
6. Fan, L. T., Bailie, R. C., Chem. Eng. Sci. 13, 63 (1960).
7. Hill, F. B., Brookhaven National Laboratory, unpublished work, 1957.
8. Kramers, H., Alberda, G., Chem. Eng. Sci. 2, 173 (1953).
9. Latinen, G. A., Stockton, F. D., paper presented at A.I.Ch.E. National Meeting, St. Paul, Minnesota (September 1959).
10. Levenspiel, O., Ind. Eng. Chem. 51, 1431 (1959).
11. Mattern, R. V., Bilous, O., and Piret, E. L., A.I.Ch.E. Journal 3, 497 (1957).
12. Madden, A. J., Damerell, G. L., A.I.Ch.E. Journal 8, 233 (1962).
13. McHenry, K. W. Jr., Wilhelm, R. H., A.I.Ch.E. Journal 3, 83 (1957).
14. McMullen, A. K., Miyauchi, T., Vermeulen, T., U.S. At. Energy Comm. Rept. UCRL-3911-Suppl. (1958).
15. Miyauchi, T., Ph.D. Dissertation, Univ. of Tokyo (1956).
16. Miyauchi, T., and Vermeulen, T., Ind. Eng. Chem. Fundamentals 2, 113 (1963).
17. Oya, H., M.S. Thesis in Chem. Eng., Univ. of Tokyo (1960).
18. Rifai, M. N. E., "Dispersion Phenomena in Laminar Flow through Porous Media", Ph.D. Dissertation, Univ. of California, Berkeley, Calif., 1956.

19. Sege, G., Woodfield, F. W., Chem. Eng. Progr. Symp. Series, No. 13, 50, 39 (1954).

20. Sherwood, T. K., Jenny, F. J., Ind. Eng. Chem. 27, 265 (1935).

21. Sleicher, C. A. Jr., A.I.Ch.E. Journal 5, 145 (1959).

22. Sleicher, C. A. Jr., A.I.Ch.E. Journal 6, 529 (1960).

23. Van der Laan, E. T., Chem. Eng. Sci. 7, 187 (1958).

24. Vanderveen, J. H., U.S. At. Energy Comm. Rept. UCRL-8733 (1960).

25. Vermeulen, T., G. M. Williams, and G. E. Langlois, Chem. Eng. Progr. 51, 85 (1955).

26. Yagi, S., and T. Miyauchi, Chem. Eng. (Japan) 19, 507 (1955).

NOMENCLATURE

a specific interfacial area of mixed phases (cm^2/cm^3)

b Intercept value for partition equilibrium, in the relation $x^* = b + my$ (g or mole/cm^3)

B L/d (dimensionless)

c concentration of reactant (g or mole/cm^3)

d representative length (cm)

d_p packing-particle diameter (cm)

E longitudinal-dispersion coefficient (cm^2/sec)

f concentration-distribution function based on number of droplets

f_σ correction factor, Equation 8

f_T correction factor, Equation 12

F volumetric rate of interstage mixing (cm^3/cm^2-sec)

$\overline{F}$ mean volumetric flow rate of main (through) flow (cm^3/cm^2-sec)

g,h constants in Equation 15

k integer, index in series summation (dimensionless)

k_{oi} overall coefficient of mass-transfer based on phase i (cm/sec)

k_q rate coefficient for q^{th}-order reaction (g or mole/cm^3)$^{1-q}$ $(sec)^{-1}$

ℓ pulse amplitude (cm)

L height of column (cm)

m equilibrium partition coefficient, in the relation $x^* = b + my$ (dimensionless)

n_o total number of droplets per unit volume of dispersed phase ($1/cm^3$)

n_p total number of stages (dimensionless)

N	number of transfer units or reaction units (dimensionless)
N_q	$k_q c_F^{q-1} L / \overline{F}$ (dimensionless)
P	Peclet number for single phase ($\overline{F} d / E$); or for phase i ($\overline{F}_i d / E_i$) dimensionless)
q	reaction-order (dimensionless)
r	constant, in Equation 15
V_0	volume of a single stage (cm^3)
v_o	mean volume per droplet (cm^3)
x,y	concentration of transferring component in phases X and Y respectively (g or mole/cm^3)
X	ratio of X-phase concentrations out and in, Equation 10
z	axial distance measured from the phase-X inlet (cm)
Z	z/L (dimensionless)
α	$F / \overline{F}$ (dimensionless)
β	factor in Equation 11
γ_1,γ_2	constants, Equation 15 (dimensionless)
ϵ_i	volume fraction of phase i (dimensionless)
η	L_0 / d_p (dimensionless)
θ	mean residence time (sec)
Λ	extraction factor ($= m\overline{F}_x / F_y$) (dimensionless)
ξ	traveling variable for ϕ (dimensionless)
σ^2	variance of residence times (dimensionless)
τ	elapsed time (sec); τ_{TOi} = superficial mean holding time of phase i; $\tau_{Ti} = \epsilon_i \tau_{TOi} / (1 + 2\alpha_i)$, net mean holding time of phase i.
ϕ	time ratio τ/τ_{Ty}, Equation A-1
ψ	factor in Equation 12
ω	pulse frequency (cycles/sec) (dimensionless)

Subscripts

B	Back-flow model value
C	Continuous-phase value
D	Diffusion-model value
F	Feed-end value
i	Phase i
j	Stage j
k	Index in summation
L	outlet-end value
o	Over-all
p	Plates or stages; particle (in d_p)
T	Total; two-phase
x	Phase x
y	Phase y
6	Transient-behavior value
0	Single-stage value

* (superscript) equilibrium value

APPENDIX

We consider the jth stage under steady continuous operation with flow rates of $\overline{F}_x + F$ and $\overline{F}_y + F$ (with $F = F_x + F_y$), where the contents are mixed perfectly, with a uniform drop size d_p for the dispersed phase. The operational condition is the same as shown in Figure 1. Let y_j be the concentration of a droplet in the jth stage, $\overline{y}_j$ the mean value for all the droplets in that stage, and n_o the total number of droplets per unit volume of the dispersed phase. With these notations, the number of droplets per unit time is given as follows for each stream:

$$\begin{cases} \text{From } (j-1)^{th} \text{ to } j^{th}: n_o(\overline{F}_y + F_y) \\ \text{From } (j+1)^{th} \text{ to } j^{th}: n_o F_y \end{cases} \quad \begin{cases} \text{From } j^{th} \text{ to } (j-1)^{th}: n_o F_y \\ \text{From } j^{th} \text{ to } (j+1)^{th}: n_o(\overline{F}_y + F_y) \end{cases}$$

The fraction of droplets leaving the jth stage during any time interval from τ to $\tau + d\tau$ (with τ measured from the time of their introduction), relative to the number of droplets introduced in this stage during the interval $\tau = 0 \sim 0 + d\tau$, is given by

$$n_o\left[(\overline{F}_y + F_y) + F_y\right] e^{-\phi}\, d\phi \cdot d\tau \qquad \text{(A-1)}$$

where $\phi = \tau/\tau_{Ty} = \tau(1 + 2\alpha_y) \big/ \epsilon_y \tau_{TOy}$;

$$\tau_{Ty} = \epsilon_y V_\theta \big/ (\overline{F}_y + 2F) = \epsilon_y V_\theta \big/ \overline{F}_y(1 + 2\alpha_y) = \epsilon_y \tau_{TOy} \big/ (1 + 2\alpha_y);$$

and $\alpha_y = F_y / \overline{F}_y$.

For the droplets coming in from the $(j-1)^{th}$ stage, the concentration distribution may be quite random in y^1 (feed concentration of phase Y) and y_{jT}^* (concentration of droplets in equilibrium with phase X at the final or $j_T{}^{th}$ stage) as their

lower and upper limits respectively, as shown in Fig. 5. This condition is a natural result of the back flow. We define this concentration distribution for the droplets from the $(j-1)^{th}$ stage as $f_{j-1}(y_{j-1})$, such that

$$\int_{y^1}^{y^*_{jT}} f_{j-1}(y_{j-1})dy_{j-1} = 1 \qquad \text{(A-2)}$$

Then the fraction of the dispersed phase leaving from the jth stage, which originally had a concentration between y_{j-1} and $y_{j-1} + d(y_{j-1})$, is given in the time interval τ to $\tau + d\tau$ after the lapse of time by

$$n_o(\overline{F}_y + F_y)\ e^{-\phi}\ f_{j-1}(y_{j-1})d\phi\ dy_{j-1} \cdot d\tau \qquad \text{(A-3)}$$

The concentration of this fraction changes from the initial value y_{j-1} to the final value $(y_j)_{j-1}$ during travel through the jth stage. Since the stage is mixed perfectly, the rate of total solute leaving the jth stage (accompanied by the dispersed phase from the $(j-1)^{th}$ stage) is given by

$$n_o(\overline{F}_y + F_y)\int_{y^1}^{y^*_{jT}} f_{j-1}(y_{j-1})dy_{j-1}\int_0^{\infty} (y_j)_{j-1}\exp(-\phi)d\phi \qquad \text{(A-4)}^*$$

This amount of solute returns partly to the original $(j-1)^{th}$ stage, and the rest of it goes to the $(j+1)^{th}$ stage.

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* The integral with respect to time is written exactly as

$$\int_{-\infty}^{\phi} (y_j)_{j-1}\ \exp\left[-(\phi-\xi)\right]d\xi$$

(footnote continued)

The rate of droplets leaving the jth stage, corresponding to the same stream, is

$$n_o(\overline{F}_y + F_y) \int_{y^1}^{y^*_{jT}} f_{j-1}(y_{j-1})dy_{j-1} \int_0^{\infty} \exp(-\phi)d\phi \qquad \text{(A-5)}$$

where the double integral is obviously equal to 1.

For the droplets, entering from the $(j+1)^{th}$ stage and departing from the jth stage to the $(j+1)^{th}$ and $(j-1)^{th}$ stages, a similar consideration gives Equation A-6 corresponding to Equation A-4, and simply $n_o F_y$ in place of Equation A-5. Thus,

$$n_o F_y \int_{y^1}^{y^*_{jT}} f_{j+1}(y_{j+1})\, dy_{j+1} \int_0^{\infty} (y_j)_{j+1} \exp(-\phi)d\phi \qquad \text{(A-6)}$$

where $f_{j+1}(y_{j+1})$ is the concentration distribution for the droplets from the $(j+1)^{th}$ stage.

The mean concentration $\overline{y}_j$ for the dispersed phase going from the jth stage to the upper and lower stages is given by Equation A-7. The total rate of solute leaving is the sum of Equations A-4 and A-6; the total flow rate is $n_o(\overline{F}_y + F_y) + n_o F_y$;

(footnote)

However, this expression is formally equivalent to the integral used in Eq.(A-4). The same formal simplification is utilized in the following steps.

and the stage is mixed perfectly.

$$\bar{y}_j = \left(\frac{\bar{F}_y + F_y}{\bar{F}_y + 2F_y}\right) \int_{y^1}^{y^*_{jT}} f_{j-1}(y_{j-1})\, dy_{j-1} \int_0^{\infty} (y_j)_{j-1} \exp(-\phi)\, d\phi$$

$$+ \left(\frac{F_y}{\bar{F}_y + 2F_y}\right) \int_{y^1}^{y^*_{jT}} f_{j+1}(y_{j+1})\, dy_{j+1} \int_0^{\infty} (y_j)_{j+1} \exp(-\phi)\, d\phi \qquad \text{(A-7)}$$

where, as indicated before, $(y_j)_{j-1}$ is the concentration of droplets leaving the jth stage at $\phi = \phi$, after introduction from the $(j-1)^{th}$ stage at $\phi = 0$. Also, $(y_j)_{j+1}$ is a similar concentration, relative to the $(j+1)^{th}$ stage.

To express $\bar{y}_j$ as an explicit function of N_{oyO}, y^*_j, $\bar{y}_{j-1}$, and $\bar{y}_{j+1}$, further relations are needed to combine $(y_j)_{j-1}$ and $(y_j)_{j+1}$ with ϕ, y_{j-1}, and y_{j+1}. Consider a single droplet with the concentration y_{j-1}, introduced from the $(j-1)^{th}$ stage to the jth stage at $\tau = 0$. Its concentration y_j changes during travel through the jth stage, according to the relation:

$$v_o\, dy_j \big/ d\tau = k_{oy} a_o (y^*_j - y_j) \qquad \text{(A-8)}$$

with the conditions that $y_j = y_{j-1}$ at $\tau = 0$, and $y_j = (y_j)_{j-1}$ at $\tau = \tau$. Integration of the equation under the given conditions yields

$$(y_j)_{j-1} = y^*_j - (y^*_j - y_{j-1}) \exp\left\{-\left[N_{oyO} \big/ (1 + 2\alpha_y)\right] \phi\right\} \qquad \text{(A-9)}$$

where N_{oyO} is equal to $\epsilon_y (a_o / v_o) k_{oy} \tau_{Toy}$. It is easily shown to be equivalent to N_{oyO} given in Equation 1, except for a slight modification. Similarly, for $(y_j)_{j+1}$ we get the equation:

$$(y_j)_{j+1} = y_j^* - (y_j^* - y_{j+1}) \exp\left\{-\left[N_{oyO}/(1 + 2\alpha_y)\right]\phi\right\} \qquad \text{(A-10)}$$

To derive Equations A-9 and A-10, k_{oy} is assumed to remain constant.

Integration of Equation A-7, introducing Equations A-9 and A-10 into it, yields exactly Equation 1, where the following obvious relations have been utilized.

$$\overline{y}_{j-1} = \int_{y^1}^{y^*_{jT}} y_{j-1}\, f_{j-1}(y_{j-1})\, dy_{j-1} \;;$$

$$\overline{y}_{j+1} = \int_{y^1}^{y^*_{jT}} y_{j+1}\, f_{j+1}(y_{j+1})\, dy_{j+1}$$

Thus it has been proved entirely permissible and exact to treat the dispersed phase as a second continuous phase, in so far as the following four conditions are satisfied: (a) drop-size is uniform; (b) overall coefficient of mass transfer is constant; (c) volume-fraction (holdup) of the dispersed phase is constant throughout the column; and (d) a linear equilibrium holds.

These restrictions may be relaxed, depending upon how fast coalescence and redispersion of the dispersed phase take place in the system. There is a positive indication of coalescence and redispersion of liquid droplets for agitated liquid-liquid systems, making the restrictions less necessary in such instances.

Since for the limiting case of $\alpha_y \longrightarrow 0$ the back-flow model is reduced to the stage model, the statement given above is also

true even for this model. For example, it is permissible to say that the dispersed phase in mixer-settler extractors can be treated as a second continuous phase. In addition, it is not necessary that the dispersed droplets be separated into a homogeneous phase before entering the next stage.

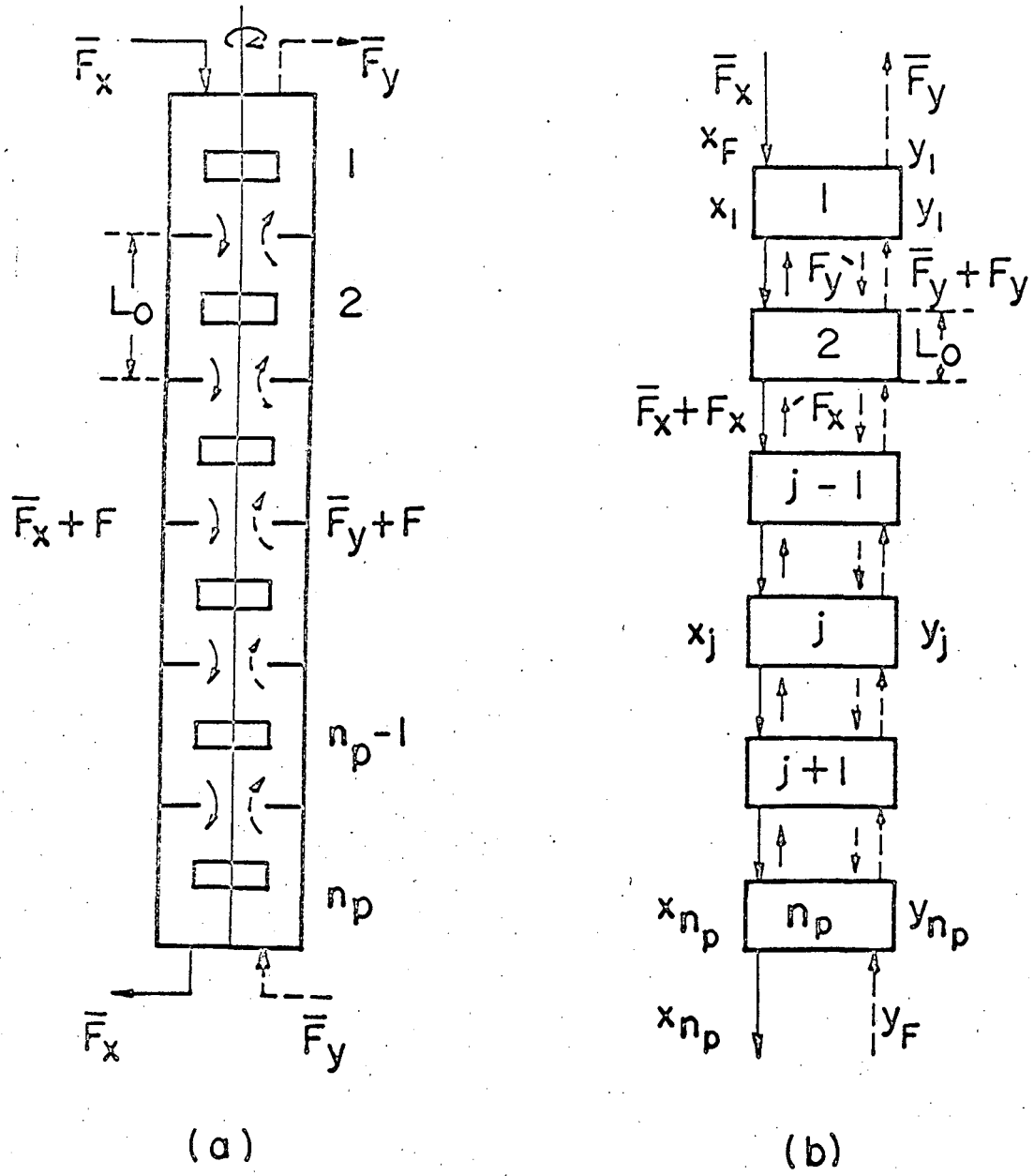
The basic relation for the stage model, corresponding to Equations A-7 and A-9, is

$$\overline{y}_j = \int_{y^1}^{y_j^*} f_{j-1}(y_{j-1})\, dy_{j-1} \int_0^{\infty} y_j \exp(-\phi)\, d\phi \qquad \text{(A-11)}$$

with

$$y_j = y_j^* - (y_j^* - y_{j-1}) \exp(-N_{oyO}\phi) \qquad \text{(A-12)}$$

As stated before, Equation A-12 is derived under the premise of a constant N_{oyO}.



1. Back-flow model for countercurrent operation--
(a) Multicompartment contactor; (b) Identification of flows, with internal flow $F = F_x + F_y$.

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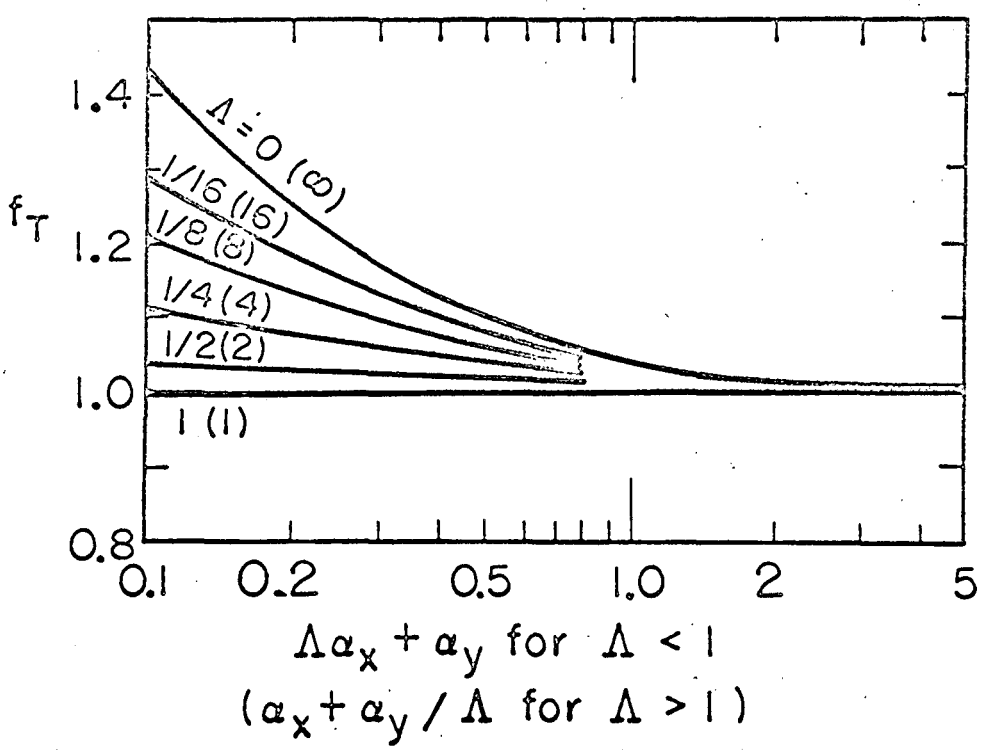

2. Correction factor f_T in Equation 12, computed from $N_{ox} \longrightarrow \infty$.

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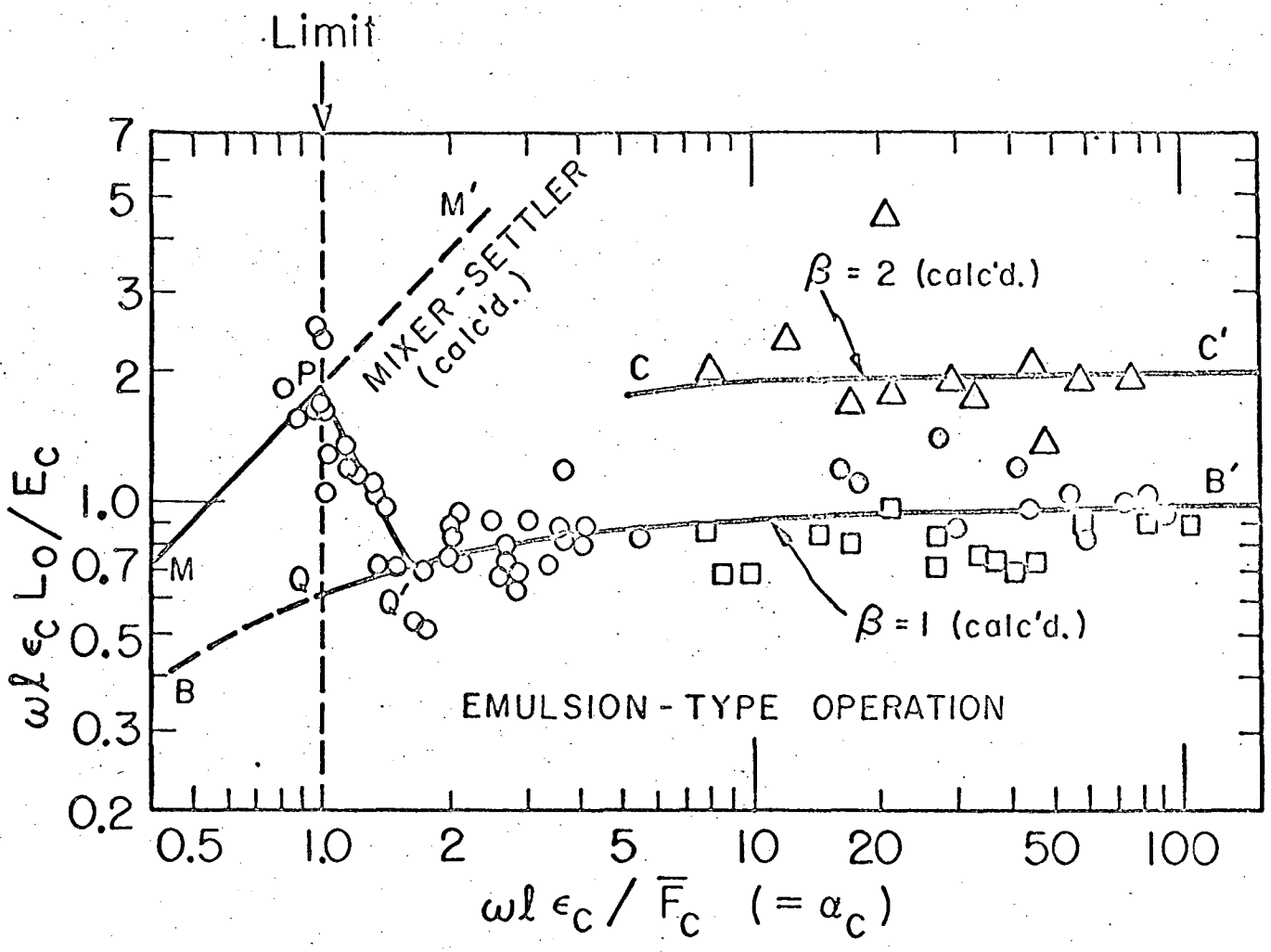
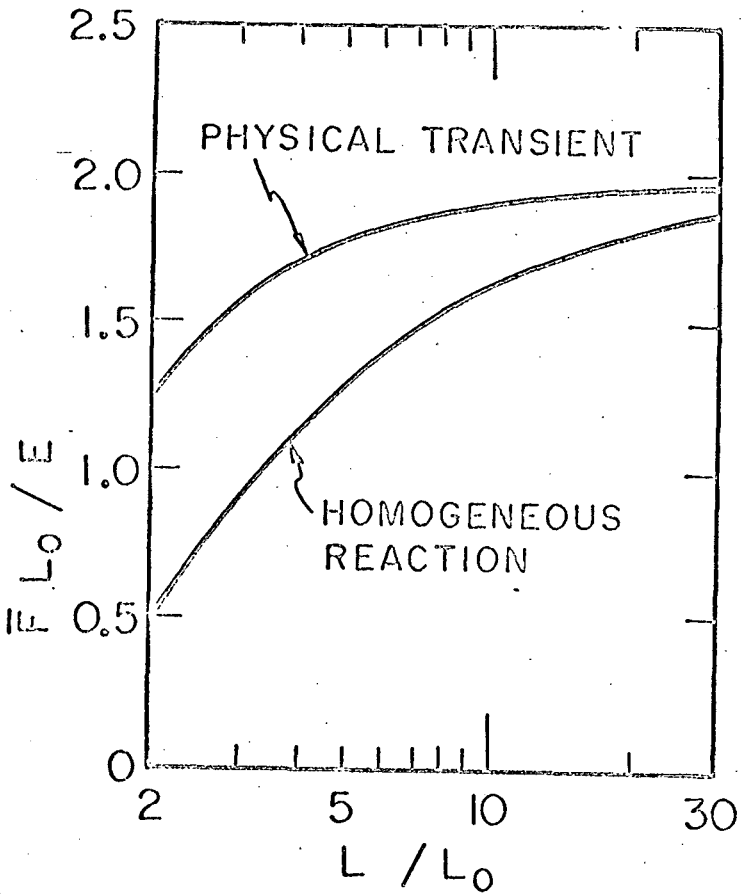
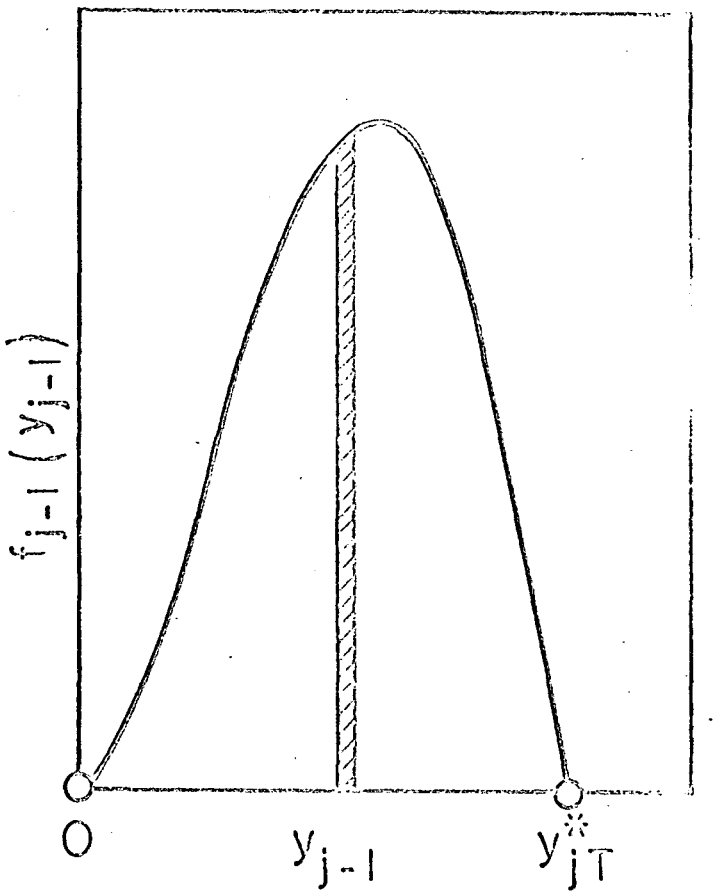


3. Longitudinal-dispersion coefficient for the continuous phase, in pulsed sieve-plate columns.



4. Longitudinal-dispersion coefficient for packed beds under turbulent flow.



5. Concentration-distribution function.

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