Lawrence Berkeley National Laboratory

Recent Work

Title

LONGITUDINAL DISPERSION III SOLVENT-EXTRACTION COLUMNS: MATHSMATICAL THEORY

Permalink https://escholarship.org/uc/item/30w522b9

Author Miyauchi, Terukatsu.

Publication Date 1957-08-15

UCRL 3911

UNIVERSITY OF CALIFORNIA



TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

BERKELEY, CALIFORNIA

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

UNIVERSITY OF CALIFORNIA

Radiation Laboratory Berkeley, California

Contract No. W-7405-eng-48

épse,

LONGITUDINAL DISPERSION IN SOLVENT-EXTRACTION COLUMNS: MATHEMATICAL THEORY

Terukatsu Miyauchi

E.

August 15, 1957

Printed for the U.S. Atomic Energy Commission

LONGITUDINAL DISPERSION IN SOLVENT-EXTRACTION COLUMNS: MATHEMATICAL THEORY

Terukatsu Miyauchi

Radiation Laboratory and Department of Chemical Engineering University of California, Berkeley, California

August 15, 1957

ABSTRACT

The influence of longitudinal dispersion of fluid in continuous countercurrent solvent-extraction columns has been analyzed theoretically, by application of a simplified model which utilizes mean diffusivities and mean velocities for both continuous and dispersed phases. From the mathematical treatment of the model, it has been found that the influence of the longitudinal dispersion on the extent of extraction can be expressed as a function of four dimensionless parameters. These parameters include, as variables, the rates of longitudinal dispersion, the over-all mass-transfer coefficient, the equilibrium partition ratio, and the rates of fluid flow. Solutions for various special cases of mixing behavior have been presented, which apply directly to specific types of apparatus.

The longitudinal dispersion has an undesirable effect, especially when a high degree of extraction is desired. The theory developed shows that there will be a maximum attainable extent of extraction, under any given pattern of longitudinal dispersion. This means that the extent of extraction is limited by this phenomenon, even if the over-all coefficient of mass transfer is increased to infinity. It is necessary to define three kinds of over-all HTU: two of these, used previously, include the effect of the longitudinal dispersion.

LONGITUDINAL DISPERSION IN SOLVENT-EXTRACTION COLUMNS: MATHEMATICAL THEORY

Terukatsu Miyauchi

-3-

Radiation Laboratory and Department of Chemical Engineering University of California, Berkeley, California

August 15, 1957

INTRODUCTION

In continuous countercurrent solvent-extraction columns, it is widely recognized that the effective coefficient of mass-transfer is lowered by longitudinal dispersion in either phase. This effect should be particularly large, in such apparatus as the Mixco column reported by Oldshue and Rushton,⁸ the rotating-disc column reported by Reman and Olney,⁹ and pulsed columns.^{10,11,14}

Attempts have already been made to obtain mass-transfer coefficients by measuring concentration distributions within an extractor. This approach should be more accurate than the alternative of using a logarithmic mean driving force computed only from the end concentrations of the incoming and outgoing streams. Recently, a theoretical approach that permits evaluation of local behavior of pulsed columns has been reported from this laboratory by Lane, Lehman, and Rubin, ¹⁴ and experimental measurements of dispersion in packed columns are now being made by Jacques and Vermeulen.

In order to interpret the behavior of continuous solvent-extraction columns, it is desirable to analyze the interrelation between such variables as the true coefficient of mass transfer, the rate of longitudinal dispersion of fluid in each phase, the flow rate of each stream, the partition ratio of the transferring component, and the extent of extraction. This paper has been developed so as to combine these variables with over-all behavior of continuous extraction columns. A simplified model of flow behavior has been used, similar to one assumed previously², 4, 5, 16</sup> in relation to one-dimensional homogeneous-phase flow systems.

For homogeneous systems with noticeable longitudinal dispersion, this model has already been found by Yagi and Miyauchi¹⁶ to give a better representation of the Mixco and related columns than the concept of "equivalent completely mixed stage" reported recently by Young.¹⁷

^{*}On leave from Department of Chemical Engineering, University of Tokyo, Tokyo, Japan.

BASIC EQUATIONS

Basic Differential Equations

For homogeneous continuous-flow systems Damköhler has given an equation of continuity,

$$\partial \tilde{c}_{i} / \partial \theta = - \operatorname{div} (-E_{i} \operatorname{grad} \tilde{c}_{i}) - \operatorname{div} (\overline{\tilde{u}_{i}} c_{i}) + \phi (c_{i}),$$

where u_i is the linear velocity of the fluid and c_i is the concentration of the ith component, at the point of interest.¹ For one-dimensional steadystate flow systems, in which a mean diffusivity and a mean velocity of the ith component are assumable, Damköhler's equation becomes

$$\mathbf{E}_{i} d^{2} \tilde{\mathbf{c}}_{i} / d\hat{\mathbf{z}}^{2} - \tilde{\mathbf{u}}_{i} d\tilde{\mathbf{c}}_{i} / d\mathbf{z} - \phi (\tilde{\mathbf{c}}_{i}) = 0$$

For one-dimensional countercurrent two-phase mass-transfer processes, this equation is modified as follows by introducing a void fraction ϵ for each phase, and substituting the mass-transfer term for $\phi(\hat{c}_i)$:

$$\left\{ \begin{array}{c} \epsilon_{\mathbf{x}} \mathbf{E}_{\mathbf{x}} d^{2} \tilde{\mathbf{c}}_{\mathbf{x}}^{2} / dz^{2} - \mathbf{F}_{\mathbf{x}} d\tilde{\mathbf{c}}_{\mathbf{x}}^{2} / dz - \mathbf{K}_{\mathbf{x}} a \left(\tilde{\mathbf{c}}_{\mathbf{x}} - \mathbf{m} \tilde{\mathbf{c}}_{\mathbf{y}} \right) = 0 \\ \epsilon_{\mathbf{y}} \mathbf{E}_{\mathbf{y}} d^{2} \tilde{\mathbf{c}}_{\mathbf{y}}^{2} / dz^{2} + \mathbf{F}_{\mathbf{y}} d\tilde{\mathbf{c}}_{\mathbf{y}}^{2} / dz + \mathbf{K}_{\mathbf{x}} a \left(\tilde{\mathbf{c}}_{\mathbf{x}} - \mathbf{m} \tilde{\mathbf{c}}_{\mathbf{y}} \right) = 0 \\ \end{array} \right\} , \quad (1)$$

where the direction of mass transfer is taken from phase X to phase Y, and a linear-distribution equilibrium (with m as the partition coefficient) is assumed; K_x represents the over-all mass-transfer coefficient relative to phase X, a is the interfacial area per unit volume, and F is the superficial velocity of the designated phase.

These equations are based on a simplified model which assumes that the two liquid phases flow in opposite directions, with each phase undergoing longitudinal dispersion, as shown in Fig. 1. Accordingly, the process of mass transfer is assumed to take place across the phase boundary, PQ. However, in an actual extractor, one phase is dispersed into the other as shown in Fig. 2.



x phase; u_x , ϵ_x , E_x y phase; u_y , ϵ_y , E_y

-5-

MU-14081

Fig. 1. Proposed model

MU-14082

Fig. 2. Actual situation in an extractor

-7-

MU-14083

Fig. 3. Concentration distribution in an extractor. Curve ABDE, actual distribution of c_x ; curve FGHK, same for c_y . Curve AD'E, apparent distribution of c_x assuming piston flow; curve FH'K, same for c_y .

5

If the droplets coalesce and break up so rapidly that there is no fluctuation in their concentration at any particular point, the two models become identical.

-8-

If not, the concentration variations between droplets at a section will reflect the gradient of average concentration under conditions of constant E_x and E_y . This point is discussed in Appendix 1; it is concluded that the simplified model provides a sound and workable approach.

Rearranging the equations into dimensionless form, we have

$$d^{2}C_{x}/dZ^{2} - P_{x}B \ dC_{x}/dZ - N_{ox}P_{x}B(C_{x}-mC_{y}) = 0$$

$$d^{2}C_{y}/dZ^{2} + P_{y}B \ dC_{y}/dZ + N_{oy}P_{y}B(C_{x}-mC_{y}) = 0$$
, (2)
where $C_{x} = c_{x}/c_{x}^{0}$, $C_{y} = c_{y}/c_{x}^{0}$, $P_{x} = u_{x}d/E_{x}$, $P_{y} = u_{y}d/E_{y}$, $N_{ox} = K_{x}aL/F_{x}$, $N_{oy} = K_{x}aL/F_{y}$, $B = L/d$, $u_{x} = F_{x}/\epsilon_{x}$, $u_{y} = F_{y}/\epsilon_{y}$, and $Z = z/L$.

Boundary Conditions

The rate of longitudinal dispersion in an extractor is assumed to be much higher than that in the incoming and outgoing streams away from the extractor. The suitable boundary conditions are given as follows. Integration of Eq. 1 for phase X, over an arbitrary length of column, ℓ , gives

$$\frac{\epsilon_{\mathbf{x}} \mathbf{E}_{\mathbf{x}}}{\ell} \left[\left(\frac{\mathrm{d} \mathbf{c}_{\mathbf{x}}}{\mathrm{d} \mathbf{z}} \right)_{\ell} - \left(\frac{\mathrm{d} \mathbf{c}_{\mathbf{x}}}{\mathrm{d} \mathbf{z}} \right)_{0} \right] - \mathbf{F}_{\mathbf{x}} (\mathbf{c}_{\mathbf{x}} \ell - \mathbf{c}_{\mathbf{x}0}) - \mathbf{n} = 0,$$

where $c_{x0} = (c_x)_{Z=0}$, $c_{x\ell} = (c_x)_{Z=\ell}$, and n is the total amount of component (in moles) transferred from phase X to phase Y between the point of interest and the X inlet.

At the X-inlet end of the column, the net flow is given in dimensionless terms by the sum

$$\frac{1}{\mathbb{P}_{\mathbf{x}}^{B}} \left(\frac{dC_{\mathbf{x}}}{dZ} \right)_{0} - C_{\mathbf{x} \ 0} \leq -1$$

-9-

Outside the column, the net flow is $-C_x^{(0)}$, or -1, because $P_x B \rightarrow \infty$ and $(dC_x/dZ)_0 \rightarrow 0$ for the model assumed. Equating the net flows, at Z = 0, gives

$$-\left(\frac{dC_{\mathbf{x}}}{dZ}\right)_{0} = P_{\mathbf{x}}B\left(1 - C_{\mathbf{x}}\right).$$
(3a)

At the X-outlet end, a comparison of the net flows inside and outside yields the relation \sim

$$\frac{1}{P_{\mathbf{x}}^{B}} \left(\frac{dC_{\mathbf{x}}}{dZ} \right)_{1} = \underbrace{C_{\mathbf{x}1} - C_{\mathbf{x}}}_{+}^{1},$$

where $C_{x1} = (C_x)_{Z=1}$, and C_x^{1} is the concentration of outgoing phase X.

The coefficient $1/P_x B$ is always positive or zero. At the boundary, the concentration gradient calculated from the left-hand term is opposite in sign to the gradient given by the right-hand term. Thus the only condition allowed by this equation is

$$C_{x1} = C_x^{1}, (dC_x/dZ)_{1} = 0.$$
 (3b)

Because the boundary region is small, mass transfer in this region is neglected, and the boundary condition becomes identical with the result given by Danckwerts.²

The boundary conditions for phase Y are derived from the similar consideration described above. Thus the boundary conditions for phase X and phase Y are

$$Z = 0: - (dC_x/dZ) = P_x B (1 - C_{x_1}), - (dC_y/dZ) = 0$$

$$Z = 1: - (dC_x/dZ) = 0, - (dC_y/dZ) = P_y B (C_{y_1} - C_y^{-1})$$
(4)

Solutions

-10 -

Eliminating the term C_y from Eq. (2) gives a single linear differential equation of fourth order,

$$d^{4}C_{x}/dZ^{4} - \alpha d^{3}C_{x}/dZ^{3} - \beta d^{2}C_{x}/dZ^{2} - \gamma dC_{x}/dZ = 0, \qquad (5)$$

where a, $\beta,$ and γ are constants independent of Z, as defined below. General Case

By solving Eq. (5) so as to satisfy the boundary conditions, one obtains the following solutions: 6

$$\frac{C_{x} - mC_{y}^{1}}{1 - mC_{y}^{1}} = A_{1}e^{\lambda_{1}Z} + A_{2}e^{\lambda_{2}Z} + A_{3}e^{\lambda_{3}Z} + A_{4}e^{\lambda_{4}Z}$$

$$\frac{m(C_{y} - C_{y}^{1})}{1 - mC_{y}^{1}} = a_{1}A_{1}e^{\lambda_{1}Z} + a_{2}A_{2}e^{\lambda_{2}Z} + a_{3}A_{3}e^{\lambda_{3}Z} + a_{4}A_{4}e^{\lambda_{4}Z}$$
(6)

where

$$A_1 = D_{A1}/D_A$$
, $A_2 = D_{A2}/D_A$, $A_3 = D_{A3}/D_A$, $A_4 = D_{A4}/D_A$;

$$D_{A} = D_{A1} - \begin{vmatrix} 1 - \frac{\lambda_{2}}{P_{x}B} & 1 - \frac{\lambda_{3}}{P_{x}B} & 1 - \frac{\lambda_{4}}{P_{x}B} \\ \lambda_{2}a_{2} & \lambda_{3}a_{3} & \lambda_{4}a_{4} \\ \lambda_{2}e^{\lambda_{2}} & \lambda_{3}e^{\lambda_{3}} & \lambda_{4}e^{\lambda_{4}} \\ (1 + \frac{\lambda_{2}}{P_{y}B}) & a_{2}e^{\lambda_{2}} & (1 + \frac{\lambda_{3}}{A_{3}}) & a_{3}e^{\lambda_{3}} & (1 + \frac{\lambda_{4}}{A}) & a_{4}e^{\lambda_{4}} \\ (1 + \frac{\lambda_{2}}{P_{y}B}) & a_{2}e^{\lambda_{2}} & (1 + \frac{\lambda_{3}}{A_{3}}) & a_{3}e^{\lambda_{3}} & (1 + \frac{\lambda_{4}}{A}) & a_{4}e^{\lambda_{4}} \\ \lambda_{3}e^{\lambda_{3}} & \lambda_{4}e^{\lambda_{4}} \\ \lambda_{3}e^{\lambda_{3}} & \lambda_{4}e^{\lambda_{4}} \\ \lambda_{3}e^{\lambda_{2}} & \lambda_{4}e^{\lambda_{4}} \\ \lambda_{2}e^{\lambda_{2}} & \lambda_{4}e^{\lambda_{4}} \\ \lambda_{2}e^{\lambda_{2}} & \lambda_{4}e^{\lambda_{4}} \\ \lambda_{2}e^{\lambda_{2}} & \lambda_{4}e^{\lambda_{4}} \\ \lambda_{2}e^{\lambda_{2}} & \lambda_{3}e^{\lambda_{3}} \\ \end{pmatrix}$$

$$(j = 1, 2, 3, and 4)$$

 $\begin{array}{l} \lambda_1 = 0 \\ \lambda_2 = a/3 + 2\sqrt{p}\cos(u/3) \\ \lambda_3 = a/3 + 2\sqrt{p}\cos(u/3 + 2\pi/3) \\ \lambda_4 = a/3 + 2\sqrt{p}\cos(u/3 + 4\pi/3) \end{array} \right\} ,$

(6.a)

where u is determined as an angle between 0 and π , such that

and

 $\cos u = q/p^{3/2};$

$$p = (\alpha/3)^{2} + \beta/3$$

$$q = (\alpha/3)^{3} + \alpha\beta/6 + \gamma/2$$

with

 $\left. \begin{array}{l} a = P_{x}B - P_{y}B \\ \beta = N_{ox}P_{x}B + P_{x}B P_{y}B + N_{ox}P_{y}B (\Lambda) \\ \gamma = N_{ox}P_{x}B P_{y}B (1 - \Lambda) \end{array} \right\}$

The solutions are obtained as Eq. (6) only for

$$q^2 - p^3 = \frac{1}{27} (a^3\gamma - a^2\beta^2/4 + 9 a\beta\gamma/2 - \beta^2 + 27\gamma^2/4) < 0.$$

This relation is satisfied for ordinary extraction operations, except when both phases are perfectly mixed. In this case, the relation becomes zero. The terminal values of C_x and mC_y are given as follows:

$$\frac{C_{x0} - mC_{y}^{1}}{1 - mC_{y}^{1}} = A_{1} + A_{2} + A_{3} + A_{4}$$

$$\frac{C_{x1} - mC_{y}^{1}}{1 - mC_{y}^{1}} = A_{1}e^{\lambda_{1}} + A_{2}e^{\lambda_{2}} + A_{3}e^{\lambda_{3}} + A_{4}e^{\lambda_{4}}$$

$$\frac{m(C_{y0} - C_{y}^{1})}{1 - mC_{y}^{1}} = a_{1}A_{1} + a_{2}A_{2} + a_{3}A_{3} + a_{4}A_{4}$$

$$\frac{m(C_{y1} - C_{y}^{1})}{1 - mC_{y}^{1}} = a_{1}A_{1}e^{\lambda_{1}} + a_{2}A_{2}e^{\lambda_{2}} + a_{3}A_{3}e^{\lambda_{3}} + a_{4}A_{4}e^{\lambda_{4}}$$

Result with Linear Extraction Coefficient.

For $\gamma = 0$ or $mF_x/F_y = \Lambda = 1$, the solution of Eq. (5) takes a different form:

$$\frac{C_{x} - mC_{y}^{1}}{1 - mC_{y}^{1}} = B_{1} + B_{2}Z + B_{3}e^{\mu_{3}Z} + B_{4}e^{\mu_{4}Z}$$
(7)

$$\frac{m(C_{y} - C_{y}^{1})}{1 - mC_{y}^{1}} = B_{1} + B_{2}/N_{ox} + B_{2}Z + b_{3}B_{3}e^{\mu_{3}Z} + b_{4}B_{4}e^{\mu_{4}Z},$$

where

$$B_{1} = D_{B1}/D_{B}, B_{2} = D_{B2}/D_{B}, B_{3} = D_{B3}/D_{B}, \text{ and } B_{4} = D_{B4}/D_{B},$$

$$b_{3} = 1 + \mu_{3}/N_{ox} - \mu_{3}^{2}/N_{ox}P_{x}B$$

$$b_{4} = 1 + \mu_{4}/N_{ox} - \mu_{4}^{2}/N_{ox}P_{x}B$$

$$\mu_{3} = \alpha/2 + \sqrt{(\alpha/2)^{2} + \beta}$$

$$\mu_{4} = \alpha/2 - \sqrt{(\alpha/2)^{2} + \beta}$$
and
$$\begin{bmatrix} -1/P_{x}B(1 - \mu_{3}/P_{x}B) (1 - \mu_{4}/P_{x}B) \\ 1 & \mu_{3}e^{\mu_{3}} & \mu_{4}e^{\mu_{4}} \\ 1 & \mu_{3}e^{\mu_{3}} & \mu_{4}e^{\mu_{4}} \\ 1 & \mu_{3}e^{\mu_{3}} & \mu_{4}e^{\mu_{4}} \\ \end{bmatrix}$$

$$D_{B1} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

$$B_{2} = -\begin{bmatrix} b_{3}\mu_{3} & b_{4}\mu_{4} \\ \mu_{3}e^{\mu_{3}} & \mu_{4}e^{\mu_{4}} \\ \mu_{3}e^{\mu_{3}} & \mu_{4}e^{\mu_{4}} \\ 0 & B_{3} = (e^{\mu_{4}} - b_{4})\mu_{4} \\ 0 & B_{4} = -(e^{\mu_{3}} - b_{3})\mu_{3} \end{bmatrix}$$

RELATION BETWEEN APPARENT AND TRUE HTU AND NTU

Definition of HTU

There should be three kinds of HTU (height of transfer unit), depending on the definition of the concentration driving force.

"True" values

By the original definition of HTU,³"true" HTU is the ratio of volumetric flow rate across a unit cross section to the true over-all coefficient of mass transfer:

$$H_{ox} = F_{x}/K_{x}a$$
 (8)

Likewise, the true number of over-all transfer units(NTU) is

$$N_{ox} = K_{x} a L/F_{x} .$$
 (8,a)

"Measured" values

When an extractor behaves in the same manner as the proposed model, the actual concentration distribution for the X phase in the extractor is given by curve ABDE of Fig. 3 and for the Y phase by curve FGHK. These two curves can be known by measuring the concentration distribution in the extractor. The number of transfer units defined from these measured values is

$$N_{oxM} = \int_{C_{x0}}^{C_{x1}} \frac{dC_x}{C_x - mC_y}$$
(9)

From this definition of NTU, an apparent HTU is derived at

$$H_{oxM} = L/N_{oxM}$$
 (9.2)

"Piston-flow" values

Another apparent NTU is defined in terms of the logrithmic-mean driving force computed from the exterior incoming and outgoing concentrations at both ends of the extractor:

UCRL-3911

(10)

$$N_{oxP} = \int_{1.0}^{C_{xI}} \frac{dC_{x}}{C_{xP} mC_{y}}$$

Integration of the right-hand side of this equation gives Eqs.(15) and (17). The corresponding apparent HTU is defined as

$$H_{oxP} = L/N_{oxP}.$$
 (10.a)

-15-

 H_{oiM} and H_{oiP} should include the effect of longitudinal dispersion of the transferring material. In general, one will find $H_{oiP} \ge H_{oiM} \ge H_{oi}$.

Relations Between
$$H_{ox}$$
, H_{oxM} , and H_{oxP}

 H_{ox} and H_{oxp} From Eq. (6.a), the outlet concentration C_{x1} is given as

$$\frac{C_{x1} - mC_y^1}{1 - mC_y^1} = \sum_{j=1}^{4} A_j b^{\lambda_j}; (j = 1, 2, 3, \text{ and } 4), \quad (11)$$

where A_i and λ_i are the functions of N_{ox} for given values of mF_x/F_y , P_xB , and P_yB and independent of C_y^1 . On the other hand, C_{x1} is given as follows from Eq. (15), * for the case in which the X- and Y-phases are assumed to follow piston flow:

$$\frac{C_{x1} - mC_y^1}{1 - mC_y^1} = \frac{(1 - \bigwedge)e^{\lambda}}{1 - \bigwedge e^{\lambda}}, \qquad (11.a)$$

where $\lambda = -N_{oxP}$ $(1 - \Lambda)$.

Comparison of Eqs.(11) and (11.a) gives an explicit relation between $N_{\rm ox}$ and $N_{\rm oxP}$,

*For \bigwedge = 1, use Eq. (17) instead of Eq. (15).

UCRL-3911

$$\sum_{j=1}^{4} A_j e^{\lambda_j} = \frac{(1-\Lambda)e^{\lambda}}{1-\Lambda e^{\lambda}}$$
(11,b)

-16-

This equation shows that the relation between N_{ox} and N_{oxP} is independent of C_y^1 . Accordingly, the ratio H_{oxP}/H_{ox} is determined only by P_x^B and P_y^B , and is not influenced by C_y^1 .

 H_{ox} and H_{oxM}

Equation 6 gives

$$C_{x} = mC_{y} = (1 - m C_{y}^{1}) \sum_{j=1}^{4} (1 - a_{j}) A_{j} e^{\lambda_{j} Z},$$

$$dC_{x} = (1 - m C_{y}^{1}) \sum_{j=1}^{4} A_{j} \lambda_{j} e^{\lambda_{j} Z} dZ.$$

Accordingly one has

$$N_{oxM} = \int_{0}^{1} \left[\sum_{j=1}^{4} A_{j} \lambda_{j} e^{\lambda_{j} Z} \int_{j=1}^{4} (1-a_{j}) A_{j} e^{\lambda_{j} Z} \right] dZ . (12)$$

This equation gives us the value of H_{oxM} . The ratio H_{oxM}/H_{ox} is equal to N_{ox}/N_{oxM} and is larger than 1. These ratios are also independent of C_y^1 , because A_j , λ_j , and a_j do not include C_y^1 .

** For $\Lambda = 1$, use Eq. (7) instead of Eq. (6).

Numerical Example

-17-

The following parameters can be considered for illustration: $\Lambda = 1$, $P_x B = P_y B = 4$, $N_{ox} = 5$, $C_y^1 = 0$. The concentration distribution is given by $C_x = 0.8110 - 0.5176 Z + 0.3862 \cdot 10^{-4} e^{7.49Z} + 0.0209 e^{-7.49Z}$ $mC_y = 0.7080 - 0.5176 Z - 1.168 \cdot 10^{-5} e^{7.49Z} - 0.0691 e^{-7.49Z}$

The resulting numerical values are shown in Table I.

Table I Calculated concentration distributions									
C _x	0.832	0.769	0.658	0.554	0.455	0.376	0.362		
mC _y	0.638	0.624	0.545	0.447	0.342	0.231	0.168		
$C_x - mC_y$	0.194	0.145	0.113	0.107	0.113	0.145	0.194		
$1/(C_x - mC_y)$	5.15	6.90	8.85	9.34	8.85	6.90	5.15		

Graphical integration gives

$$N_{oxM} = \int_{0.362}^{0.832} \frac{dC_x}{(C_x - mC_y)} = 3.87 .$$

Calculation from Eq. (17), below, gives

$$C_{x1} = (1 + N_{oxP})^{-1} = 0.362$$
, or $N_{oxP} = 1.76$.

Accordingly one finds

$$H_{ox}: H_{oxM}: H_{oxP} = N_{ox}^{-1}: N_{oxM}^{-1}: N_{oxP}^{-1}$$

= 1.0 : 1.29 : 2.84.

This result shows that H_{oxM} and H_{oxP} express apparent HTU values that include the effect of fluid mixing, while H_{ox} gives the true coefficient of mass transfer. As N_{ox} increases, the ratio of H_{oxP}/H_{ox} increases always more rapidly than the ratio of H_{oxM}/H_{ox} .

SOLUTIONS FOR SPECIAL CASES

Solutions for various special cases are obtained by simplification of the basic equations. Table II summarizes these cases and indicates the physical situations to which they correspond.

S	pecial s	olutions	corres	ponding to l	imiting values of the parameters			
P _x B	PB	Α	Case	Equation	Type of application			
finite	finite	<i>≠</i> 1	G	(6), (6, a)	Mixco, pulsed, rotating-disc, and			
•		= 1	G ₂	(7)	a long column with mechanical agitation.			
00	CO	$\neq 1$ -1	1 2	(14),(15) (16);(17)	Perfect countercurrent piston-flow operation			
0	0	all	3	(18)	Perfect mixing			
0 00	00	all all	4 5	(19) (20)	Large gas bubbles through a mixing tank [*]			
finite	ω	<u>≠ 1</u>	6	(21)	Dispersed phase in non-			
00	finite	\neq I = 1	8 9	(24) (25)	column, without mechanical agitation*			
0 finite	finite 0	all all	10 11	(26) (27)	Small gas bubbles through a mixing tank			

Table II

*See Appendix 1

Case 1.
$$P_x B \rightarrow \infty$$
, $P_y B \rightarrow \infty$; $\bigwedge \neq 1$.

From Eq. (2), we have

$$\frac{dC_x}{dZ + N_{ox}(C_x - mC_y) = 0}{dC_y} \frac{dZ + N_{oy}(C_x - mC_y) = 0}{dC_y}$$

and

$$C_{x0} = 1, \quad C_{y1} = C_y^1.$$

The solutions are

$$\frac{C_{x} - mC_{y}^{1}}{1 - mC_{y}^{1}} = \frac{e^{\lambda Z} - \Lambda e^{\lambda}}{1 - \Lambda e^{\lambda}}$$

$$\frac{m(C_y - C_y^1)}{1 - mC_y^1} = \frac{(e^{\lambda Z} - e^{\lambda})}{1 - (\Lambda) e^{\lambda}}$$

where

$$\lambda = -N_{ox} (1 - (\bigwedge)).$$

The terminal (product) values of C_x and C_y are given by

$$\frac{C_{x1} - mC_{y}^{1}}{1 - mC_{y}^{1}} = \frac{(1 - (\Lambda) e^{\lambda})}{1 - (\Lambda' e^{\lambda})}$$

$$\frac{m (C_{y0} - C_{y}^{1})}{1 - mC_{y}^{1}} = \frac{(1 - e^{\lambda}) (\Lambda')}{1 - (\Lambda' e^{\lambda})}$$

(13)

(14)

(15)

(16)

(17)

Case 2.
$$P_x B \rightarrow \infty$$
, $P_y B \rightarrow \infty$; $\Lambda = 1$.

From Eq. (13) we have

$$d^2 C_{\rm x}/dZ^2 = 0.$$

Solution of the equation so as to satisfy the boundary conditions yields

-21-

$$\frac{C_{x} - mC_{y}^{1}}{1 - mC_{y}^{1}} = \frac{1 + N_{ox}(1 - Z)}{1 + N_{ox}}$$

$$\frac{m (C_{y} - C_{y}^{1})}{1 - mC_{y}^{1}} = \frac{N_{ox} (1 - Z)}{1 + N_{ox}}$$

$$\frac{C_{x1} - mC_{y}^{1}}{1 - mC_{y}^{1}} = \frac{1}{1 + N_{ox}}$$

$$\frac{m (C_{y0} - C_{y}^{1})}{1 - mC_{y}^{1}} = \frac{N_{ox}}{1 + N_{ox}}$$

Equations (14) through (17) correspond to the well-known Kremser or Underwood equations for counter-current continuous operations.

Case 3. $P_x B \rightarrow 0; P_y B \rightarrow 0.$

In this case, both phases undergo perfect mixing. Equations (1) reduce to

$$u_x \epsilon_x (c_x^0 - c_{x1}) = u_y \epsilon_y (c_{y0} - c_y^1) =$$
 al $(c_{x1} - mc_{y0})$

or

(18)

(19)

$$C_{x1} = N_{ox}(C_{x1} - mC_{y0})$$
$$C_{y0} - C_{y}^{1} = N_{oy}(C_{x1} - mC_{y0})$$

These equations give, for C_{x1} and C_{y0} ,

$$\frac{C_{x1} - mC_{y}^{1}}{1 - mC_{y}^{1}} = \frac{1 + N_{ox}(\Lambda)}{1 + N_{ox}(1 + \Lambda)}$$
$$\frac{m(C_{y0} - C_{y}^{1})}{1 - mC_{y}^{1}} = \frac{N_{ox}}{1 + N_{ox}(1 + \Lambda)}$$

Case 4.
$$P_x B \rightarrow 0; P_y B \rightarrow \infty$$
.

The Basic equations are

$$dC_{y}/dZ + N_{oy} (C_{x1} - mC_{y}) = 0$$

$$C_{x1} = 1 - (F_{y}/F_{x}) (C_{y0} - C_{y1})$$

$$C_{y1} = C_{y}^{1}$$

The solutions is

$$\frac{C_{x1} - mC_{y}^{1}}{1 - mC_{y}^{1}} = \frac{\bigwedge}{(1 - e^{-\Lambda N_{ox}})_{+}} \bigwedge$$
$$\frac{m(C_{y0} - C_{y}^{1})}{1 - mC_{y}^{1}} \frac{(1 - e^{-\Lambda N_{ox}}) \bigwedge}{(1 - e^{-\Lambda N_{ox}})_{+}}$$

(20)

$$\frac{\text{Case 5. } P_x B \neq \infty; P_y B \neq 0.}{\text{The basic equations are}}$$

$$\frac{dC_x/dZ + N_{ox}(C_x - mC_{y0}) = 0}{C_{y0} = C_y^1 + (F_x/F_y)(1 - C_{x1})}$$

$$C_{x0} = 1$$

The solutions is

$$\frac{C_{x1} - mC_{y}^{1}}{1 - mC_{y}^{1}} = \frac{e^{-N_{ox}} + (1 - e^{-N_{ox}}) \cdot \Lambda^{*}}{1 + (1 - e^{-N_{ox}}) \cdot \Lambda^{*}}$$
$$\frac{m(C_{y0} - C_{y}^{1})}{1 - mC_{y}^{1}} = \frac{(1 - e^{-N_{ox}}) \Lambda^{*}}{1 + (1 - e^{-N_{ox}}) \Lambda^{*}}$$

Case 6. P_x^B finite; $P_y^B \rightarrow \infty; \bigwedge \neq 1$

The basic equations are

$$d^{2}C_{x}/dZ^{2} - P_{x}BdC_{x}/dZ - N_{ox}P_{x}B(C_{x} - mC_{y}) = 0$$

$$dC_{y}/dZ + N_{oy}(C_{x} - mC_{y}) = 0$$
(21)

The boundary conditions are

$$-(dC_{x}/dZ)_{Z = 0} = P_{x}B(1 - C_{x0})$$

-(dC_{x}/dZ)_{Z = 1} = 0 and C_{y1} = C_{y}^{1}

-23-

(21a)

The solution is

$$\frac{C_{x} - mC_{y}^{1}}{1 - mC_{y}^{1}} = F_{1}e^{\lambda_{1}Z} + F_{2}e^{\lambda_{2}Z} + F_{3}e^{\lambda_{3}Z} + F_{3}e^{\lambda_{3}Z} + F_{1}e^{\lambda_{1}Z} + F_{2}e^{\lambda_{2}Z} + F_{3}e^{\lambda_{3}Z} + F_{1}F_{1}e^{\lambda_{1}Z} + F_{2}F_{2}e^{\lambda_{2}Z} + F_{3}F_{3}e^{\lambda_{3}Z} + F_{1}F_{3}e^{\lambda_{3}Z} + F_{1}F_{3}e^{\lambda_{3}Z} + F_{2}F_{2}e^{\lambda_{3}Z} + F_{3}F_{3}e^{\lambda_{3}Z} + F_{3}F_{3}e^{\lambda_{3}Z}$$

with

$$F_{1} = D_{F1}/D_{F}, F_{2} = D_{F2}/D_{F}, \text{ and } F_{3} = D_{F3}/D_{F}$$

$$D_{F} = D_{F1} + \begin{vmatrix} 1 - \lambda_{2}/P_{x}B & 1 - \lambda_{3}/P_{x}B \\ \lambda_{2}e^{\lambda_{2}} & \lambda_{3}e^{\lambda_{3}} \end{vmatrix}$$

$$D_{F1} = \begin{vmatrix} \lambda_{2}e^{\lambda_{2}} & \lambda_{3}e^{\lambda_{3}} \\ \lambda_{2}e^{\lambda_{2}} & \lambda_{3}e^{\lambda_{3}} \\ f_{2}e^{\lambda_{2}} & f_{3}e^{\lambda_{3}} \end{vmatrix}, D_{F2} = \lambda_{3}e^{\lambda_{3}}$$

$$D_{F3} = -\lambda_{2}e^{\lambda_{2}}$$

and

$$f_{i} = 1 + \lambda_{i} / N_{ox} - \lambda_{i}^{2} / N_{ox} P_{x}B$$

(i = 1, 2, and 3)

$$\lambda_{1} = 0$$

$$\lambda_{2} = (a/2) + \sqrt{(a/2)^{2} + b}$$

$$\lambda_{3} = (a/2) - \sqrt{(a/2)^{2} + b}$$

$$a = P_{x}B + (\bigwedge)N_{ox}$$

$$b = (1 - \bigwedge)N_{ox}P_{x}B$$

(22)

Case 7.
$$P_x B$$
 finite; $P_y B \rightarrow \infty$; $\bigwedge = 1$

From Eq. (21a), the equation to be solved is

$$d^{3}C_{x}/dZ^{3}$$
 - a $d^{2}C_{x}/dZ^{2} = 0$.

The boundary conditions are the same as in Case (6). The suitable solutions are

-25-

$$\frac{C_{x} - mC_{y}^{1}}{1 - mC_{y}^{1}} = G_{1} + G_{2}Z + G_{3}e^{aZ}$$

$$\frac{m(C_{y} - C_{y}^{1})}{1 - mC_{y}^{1}} = G_{1} + G_{2}/N_{ox} + G_{2}Z - (N_{ox}/P_{x}B)G_{3}e^{aZ}$$

 $1 - mC_y^1$

$$a = P_x B + \Lambda N_{ox} = P_x B + N_{ox}$$

and

$$G_{1} = D_{G1}/D_{G}, \quad G_{2} = D_{G2}/D_{G}, \quad G_{3} = D_{G3}/D_{G}$$

$$D_{G} = D_{G1} + \begin{vmatrix} -1/P_{x}B - (N_{ox}/P_{x}B) \\ 1 & ae^{a} \end{vmatrix}$$

$$D_{G1} = \begin{vmatrix} 1 & ae^{a} \\ 1 + 1/N_{ox} - (N_{ox}/P_{x}B)e^{a} \\ 1 + 1/N_{ox} - (N_{ox}/P_{x}B)e^{a} \end{vmatrix}$$

$$D_{G2} = ae^{a}, \text{ and } D_{G3} = -1$$

in the second second

Case 8.
$$P_x B \rightarrow \infty$$
; $P_y B$ finite; $\bigwedge \neq 1$.

The basic equations are

$$dC_x/dZ + N_{ox}(C_x - mC_y) = 0$$

-26-

$$d^{2}C_{y}/dZ^{2} + P_{y}R dC_{y}/dZ + N_{oy}P_{y}B (C_{x} - mC_{y}) = 0$$

Dimensionless boundary conditions are

$$C_{x0} = 1$$
, $-(dC_y/dZ)_Z = 0 = 0$
 $-(dC_y/dZ)_Z = 1 = P_y B(C_{y1} - C_y^1)$

By a procedure similar to Case 7, the basic equations can be combined to give

$$d^{3}C_{x}/dZ^{3} + h d^{2}C_{x}/dZ^{2} + k dC_{x}/dZ = 0,$$
 (23)

where

$$\begin{array}{l} h = N_{ox} + P_{y}B \\ k = N_{ox}P_{y}B (1 - \bigwedge) \end{array} \right\}$$

The solutions depend upon whether $k \neq 0$ or k = 0. For $k \neq 0$ or $\bigwedge \neq 1$, the solution is

$$\frac{C_{x} - mC_{y}^{1}}{1 - mC_{y}^{1}} = H_{1}e^{\lambda_{1}Z} + H_{2}e^{\lambda_{2}Z} + H_{3}e^{\lambda_{3}Z}$$
(24)

$$\frac{m(C_{y} - mC_{y}^{1})}{1 - mC_{y}^{1}} = h_{1}H_{1}e^{\lambda_{1}Z} + h_{2}H_{2}e^{\lambda_{2}Z} + h_{3}H_{3}e^{\lambda_{3}Z}$$

3 (r. 5

where

$$H_1 = D_{H1}/D_H$$
, $H_2 = D_{H2}/D_H$, and $H_3 = D_{H3}/D_H$,

and

$$\begin{split} & D_{H} = D_{H1}^{c} + (\tilde{H}_{3}\lambda_{3} - h_{2}\lambda_{2}) \\ & D_{H1} = \begin{vmatrix} h_{2}\lambda_{2} & h_{3}\lambda_{3} \\ (1 + \lambda_{2}/P_{y}B)e^{\lambda_{2}}h_{2} & (1 + \lambda_{3}/P_{y}B)e^{\lambda_{3}}h_{3} \\ & D_{H2} = h_{3}\lambda_{3} & ; D_{H3} = -h_{2}\lambda_{2} & , \\ & h_{i} = 1 + \lambda_{i}/N_{ox} \\ & (i = 1, 2, \text{ and } 3) & , \\ & \lambda_{1} = 0 \\ & \lambda_{2} = -(h/2) + \sqrt{(h/2)^{2} - k} \\ & \lambda_{3} = -(h/2) - \sqrt{(h/2)^{2} - k} \\ & \lambda_{3} = -(h/2) - \sqrt{(h/2)^{2} - k} \\ & h = N_{ox} + P_{y}B \\ & k = N_{ox}P_{y}B (1 - \Lambda_{-}) \\ & \\ & Case 9. P_{x}B \rightarrow \infty; P_{y}B \text{ finite}; \Lambda = 1. \end{split}$$

Eq. (23) becomes

$$d^{3}C_{x}/dZ^{3} + h d^{2}C_{x}/dZ^{2} = 0$$
.

The final solution is

$$\frac{C_{x} - mC_{y}^{1}}{1 - mC_{y}^{1}} = J_{1} + J_{2}Z + J_{3}e^{-hZ}$$

$$\frac{m(C_{y} - C_{y}^{1})}{1 - mC_{y}^{1}} = J_{1} + J_{2}/N_{ox} + J_{2}Z + (1 - h/N_{ox}) J_{3}e^{-hZ},$$
(25)

where \mathbf{re}

and

$$J_1 = D_{J1}/D_J$$
, $J_2 = D_{J2}/D_J$, and $J_3 = D_{J3}/D_J$,
 $D_J = 1 + D_{J1}$

. . . [

$$D_{J1} = \begin{vmatrix} -1 & (1 - h/N_{ox}) h \\ (1 + 1/N_{ox} + 1/P_{y}B) & e^{-h} \end{vmatrix}$$

$$D_{J2} = (1 - h/N_{ox}) h$$
, and $D_{J3} = 1$.

Case 10. $P_x B = 0$; $P_y B$ finite.

The basic equations are

$$d^{2}C_{y}/dZ^{2} + P_{y}B dC_{y}/dZ + N_{oy}P_{y}B(C_{x1} - mC_{y}) = 0$$

 C_{x1} is constant throughout the column.

The boundary conditions are

$$- (dC_y/dZ)_Z = 0 = 0$$

-(dC_y/dZ)_Z = 1 = P_yB(C_{y1} - C_y^1)

The solutions are:

$$\frac{C_{x1} - mC_{y}^{1}}{1 - mC_{y}^{1}} = \frac{\Lambda}{\Lambda} + \frac{\lambda_{2} - \lambda_{1}}{\Lambda} + (1 + \frac{\lambda_{2} - \lambda_{1}}{D})$$

$$\frac{m(C_{y0} - C_{y}^{1})}{1 - mC_{y}^{1}} = \frac{\Lambda}{\Lambda} + \frac{\lambda_{2} - \lambda_{1}}{\Lambda} + (1 + \frac{\lambda_{2} - \lambda_{1}}{D})$$

$$\frac{m(C_{y} - C_{y}^{1})}{1 - mC_{y}^{1}} = \frac{\Lambda}{\Lambda} + \frac{\lambda_{2} e^{\lambda_{1} Z} - \lambda_{1} e^{\lambda_{2} Z}}{\Lambda} + (1 + \frac{\lambda_{2} - \lambda_{1}}{D})$$
(26)

)

(27)

where

$$D = (\lambda_1 e^{\lambda_2} - \lambda_2 e^{\lambda_1}) + (\frac{\lambda_1 \lambda_2}{P_y B}) (e^{\lambda_1} - e^{\lambda_2})$$
$$\lambda_1 = (\frac{P_y B}{2}) + (\frac{P_y B}{2}) + N_{ox} P_y B' \Lambda^*$$
$$\lambda_2 = -(\frac{P_y B}{2}) - (\frac{P_y B}{2}) + N_{ox} P_y B' \Lambda^*$$

Case 11. $P_x B$ finite; $P_y B = 0$.

The basic equations are

$$d^{2}C_{x}/dZ^{2} - P_{x}BdC_{x}/dZ - N_{ox}P_{x}B(C_{x} - mC_{y0}) = 0$$

 mC_{y0} is constant throughout the column. The boundary conditions are

$$-(dC_{x}/dZ)_{Z = 0} = P_{x}B(1 - C_{x0})$$
$$-(dC_{x}/dZ)_{Z=1} = 0$$

The solutions are

$$\frac{C_{x} - mC_{y}^{1}}{1 - mC_{y}^{1}} = 1 - \frac{1 - (\lambda_{2}e^{(\lambda_{2} + \lambda_{1}Z)} - \lambda_{1}e^{(\lambda_{1} + \lambda_{2}Z)})/D}{1 + \left\{1 + \frac{(\lambda_{1} - \lambda_{2})}{D} - e^{(\lambda_{1} + \lambda_{2})}\right\} \Lambda$$

$$\frac{C_{x1} - mC_{y}^{1}}{1 - mC_{y}^{1}} = 1 - \frac{1 + (\lambda_{1} - \lambda_{2}) e^{(\lambda_{1} + \lambda_{2})}/D}{1 + \left\{1 + \frac{(\lambda_{1} - \lambda_{2}) e^{(\lambda_{1} + \lambda_{2})}}{D} e^{(\lambda_{1} + \lambda_{2})}\right\}}$$

$$\frac{m(C_{y0} - C_{y}^{1})}{1 - mC_{y}^{1}} = 1 - \frac{1}{1 + \left\{1 + \frac{(\lambda_{1} - \lambda_{2})}{D} - e^{(\lambda_{1} + \lambda_{2})}\right\}} \wedge$$

UCRL-3911

where

$$D = (\lambda_2 e^{\lambda_2} - \lambda_1 e^{\lambda_1}) - \frac{\lambda_1 \lambda_2}{\lambda_1 + \lambda_2} (e^{\lambda_2} - e^{\lambda_1})$$
$$\lambda_1 = \left(\frac{P_x B}{2}\right) + \sqrt{\left(\frac{P_x B}{2}\right)^2 + N_{ox} P_x B}$$
$$\lambda_2 = \left(\frac{P_x B}{2}\right) - \sqrt{\left(\frac{P_x B}{2}\right)^2 + N_{ox} P_x B}$$

CHARACTERISTICS OF THE PROPOSED MODEL

Figures 4, 5, and 6 show the concentration distributions calculated for three particular sets of parameters. Comparison of Fig. 5 with Fig. 4 shows the effect of increasing N_{ox} . Comparison of Fig. 6 with Fig. 4 shows the effect of decreasing the extraction coefficient r_{y}/F_{y} .

From these figures, some particular characteristics are seen, as follows:

1. The concentration driving force between two phases is obviously lowered by back-mixing of fluid, but not so much as was expected. At both ends of an extractor, the concentration driving force becomes higher than that in piston flow for the same N_{ox} .

2. The concentration of incoming streams increases or decreases abruptly at the time the streams enter the extractor. In contrast, the concentration curve for outgoing streams becomes flat as they approach the outlet, and no discontinuity in concentration occurs at the exit.

3. When extraction is accompanied by back-mixing of fluid, the extent of extraction is lowered in comparison with the case of piston flow, especially at high values of N_{ox} and low values of $P_x B$ or $P_y B$. This lowering of the yield is attributable partly to the decrease of concentration driving force, and partly to back-mixing of the transferring component.

These characteristics are shown further in Figs. 7 through 10. Figure 7 shows the effects of $P_x B$ and N_{ox} on C_{x0} , the dimensionless concentration of phase X just inside the inlet.

As N_{ox} increases, C_{x0} gradually becomes insensitive to N_{ox} and is controlled by the Péclet group, $P_x \mathbb{B}$ (or $P_y B$).

Figure 8 shows the effect of N_{ox} and $P_x B$ on C_{x1} , the concentration of outgoing X phase. C_{x1} also becomes insensitive to N_{ox} . From these facts, an approximate value of $P_x B$ may be estimated by measuring C_{x1} and C_{x0} experimentally, if the effect of mass transfer at the phase boundary between heavier and lighter phases at settling sections is properly corrected for.

Figure 9 shows the influence of $P_x B$ and N_{ox} on the ratio of H_{toxP}/H_{ox} . These numerical values are computed from Eq. (11.b) at $mF_{x'}/F_y = 1$ and $P_x B = P_y B$. The ratio increases with decreasing Péclet group, and increasing N_{ox} .

MU-14084

Fig. 4. Concentration distribution: $P_x B = P_y B = 4$, $N_{ox} = 5$, / = 1

Fig. 5. Concentration distribution: $P_x B = P_y B = 4$, $N_{ox} = 100$, $\Lambda = 1$

MU-14086

1 1 Figure 10 illustrates local accumulation or depression of a transferring component in the X phase due to longitudinal dispersion, fluid flow, and mass transfer.

More complete numerical computations are in progress and will be presented in a later paper.

EXTENT OF EXTRACTION AT AN INFINITE MASS-TRANSFER COEFFICIENT

As is evident from Figs. 5 and 8, the extent of extraction approaches a certain value as N_{ox} or K increases, at given values of $P_x B$ and $P_y B$. It is interesting to examine how the extent of extraction is limited by the longitudinal dispersion of each phase, under the limiting condition of an infinite value of the true over-all coefficient of mass-transfer.

If the N_{ox} included in Eqs.(6) and (7) is increased to infinity, the following solutions are finally derived.

Case 12,
$$\bigwedge \neq 1$$
; $N_{ox} \rightarrow \infty$

For the solution given by Eq. (6), the ratio $q/p^{3/2}$ decreases to zero, and u approaches $\pi/2$. If q is positive, $q/p^{3/2}$ is also positive and u approaches $\pi/2$ in the first quadrant. (If q is negative, a similar end result is obtained.) The difference, $(\pi/2)$ -u, is positive and approaches zero. That is,

$$\cos u = \sin (\pi/2 - u) = q/p^{3/2} \rightarrow 0^+$$

On the other hand, one obtains

$$\sin (\pi/2 - u) = (\pi/2 - u), \text{ if } (\pi/2 - u) \le 1.$$

Accordingly, one obtains

$$\pi/2 - u = q/p^{3/2}$$

 $u/3 = (\pi/6 - q/3p^{3/2})$

or

Fig. 8. Variation of c_x at column outlet ($\bigwedge = 1$, $P_x B = P_y B$).

UCRL-3911

From this value of u,

$$\lambda_2 = a/3 + 2\sqrt{p}\cos(\pi/6 - q/3p^{3/2}),$$

with

$$\cos (\pi/6 - q/3p^{3/2}) = \cos (\pi/6) \cos (q/3p^{3/2}) + \sin (\pi/6) \sin(q/3p^{3/2})$$
$$= \sqrt{3/2} + (q/3p^{3/2})/2,$$
$$\therefore \lambda_2 = a/3 + q/3p + \sqrt{3p}.$$

Similarly, $\lambda_3 = a/3 + q/3p - \sqrt{3p}$,

$$a_4 = a/3 - 2(q/3p)$$
.

Substitution for a in these equations yields

$$\lambda_{1} = 0,$$

$$\lambda_{2} = \frac{1}{2} \left[\frac{(P_{x}B)^{2} - (\Lambda (P_{y}B)^{2})}{P_{x}B + (\Lambda (P_{y}B))} \right] + \sqrt{3p}$$

$$\lambda_{3} = \frac{1}{2} \left[\frac{(P_{x}B)^{2} - (\Lambda (P_{y}B)^{2})}{P_{x}B + (\Lambda (P_{y}B))} - \sqrt{3p},$$

$$\lambda_{4} = \frac{(\Lambda - 1)P_{x}BP_{y}B}{P_{x}B + (\Lambda P_{y}B)}$$

Substituting these roots into Eq. (6), and setting $N_{ox} \rightarrow \infty$, gives

$$a_1 = a_4 = 1$$

 $a_2 = a_3 = -' \land (P_x B/P_y B)$.

(29)

(30)

Introducing these values in Eq. (6), and eliminating negligible terms, we obtain finally

-41-

$$\frac{C_{x} - mC_{y}^{1}}{1 - mC_{y}^{1}} = \frac{\left(\bigwedge^{1} \left\{\bigwedge^{1} - \exp\left[\frac{(1 - \bigwedge^{1}) P_{x} B P_{y} B}{P_{x} B + (\bigwedge^{1} P_{y} B)}(1 - Z)\right]\right\}}{\left(\bigwedge^{1} 2 - \exp\left[\frac{(1 - \bigwedge^{1}) P_{x} B P_{y} B}{P_{x} B + (\bigwedge^{1} P_{y} B)}\right]}\right]$$

If Z = 1, Eq. (28) (below) results. From Eq. (28), Eq. (29) or (30) can be derived easily by setting $P_x B$ or $P_y B$ equal to infinity.

a. P_x^B finite, P_y^B finite:

$$\frac{C_{x1} - mC_{y}^{1}}{1 - mC_{y}^{1}} = \frac{i \bigwedge (\bigwedge (\bigwedge) 1)}{i \bigwedge (2 - exp \left[\frac{(1 - \bigwedge) P_{x} B P_{y} B}{P_{x} B + i \bigwedge (P_{y} B)} \right]}$$
(28)

b. P_x^B finite, $P_y^B \rightarrow \infty$:

$$\frac{C_{x1} - mC_y^1}{1 - mC_y^1} = \frac{\sqrt[3]{\Lambda} \cdot (\Lambda^{-1})}{\sqrt[3]{\Lambda} \cdot 2 - exp\left[\frac{(1 - \Lambda^{-1})P_x^B}{\Lambda}\right]}$$

c. $P_x^B \neq \infty$, P_y^B finite:

$$\frac{C_{x1} - mC_y^1}{1 - mC_y^1} = \frac{\sqrt{\Lambda (\Lambda_{-1})}}{\sqrt{\Lambda^2 - exp\left[(1 - \Lambda) P_yB\right]}}$$

(31)

(32)

(33)

1 Same States

Case 13.
$$\bigwedge = 1; N_{ox} \rightarrow \infty$$

For the solution given by Eq. (7), the final solutions can be derived from the following approximations:

$$\mu_{3} = a/2 + \sqrt{(a/2)^{2} + \beta} \neq \sqrt{\beta} \text{ when } N_{\text{ox}} \neq \text{infinity,}$$

$$\mu_{4} = a/2 - \sqrt{(a/2)^{2} + \beta} \neq \sqrt{\beta} \text{ when } N_{\text{ox}} \neq \text{infinity,}$$

$$\mu_{3} + \mu_{4} = a.$$

The solution is

$$\frac{C_{x} - mC_{y}^{1}}{1 - mC_{y}^{1}} = \frac{(P_{x}B + P_{y}B) + P_{x}B P_{y}B (1 - Z)}{2P_{x}B + P_{x}B P_{y}B + 2P_{y}B}$$

from which we can derive the following equations, setting Z = 1.

a. $P_x B$ finite, $P_y B$ finite:

$$\frac{C_{x1} - mC_y^1}{1 - mC_y^1} = \frac{P_xB + P_yB}{2P_xB + P_xBP_yB + 2P_yB}$$

b.
$$P_xB$$
 finite, $P_yB \rightarrow \infty$:

$$\frac{C_{x1} - mC_y^1}{1 - mC_y^1} = \frac{1}{2 + P_x^B}$$

c.
$$P_x B \rightarrow \infty$$
, $P_y B$ finite:

$$\frac{C_{x1} - mC_y^1}{1 - mC_y^1} = \frac{1}{2 + P_y^B}$$

- 1

Equations (28) through (33) are shown graphically in Figs. 11 through 13. As \bigwedge decreases, the extent of extraction approaches unity. This limiting case of $\bigwedge \rightarrow 0$ corresponds to the behavior of continuous-flow homogeneous-phase reactors with first-order reaction.

-43-

The limiting cases described in this section (Eqs.(28) through (33))are useful in estimating the suitability of a given extractor for a given separation requirement.

CONCLUSIONS

1. A general theoretical treatment based on the proposed model has been presented, so as to permit evaluation of the over-all behavior of countercurrent solvent-extraction columns, taking into consideration the effect of longitudinal dispersion of both fluids. The behavior is expressed as a function of four dimensionless parameters. Solutions for various special cases of the pattern of longitudinal dispersion have been presented and their actual applic ations are indicated.

2. Three kinds of over-all height of transfer unit have been distinguished, and the interrelation between them is shown. It is indicated that two of them, used in previous work, reflect the influence of longitudinal dispersion.

3. Illustrative numerical examples are given, which indicate that longitudinal dispersion produces an extremely undesirable effect when a high degree of extraction is desired, and that the lowering of the extent of extraction is attributable partly to a lowering of the concentration driving force and partly to longitudinal dispersion of the transferring component.

4. Finally, it is made clear that there is a maximum attainable extent of extraction under a given pattern of longitudinal dispersion. Solutions for this maximum extent of extraction have been derived by use of an infinite value for the true over-all mass-transfer coefficient.

Fig. 12. Limiting extent of extraction for $N = \infty$ (with $P_B = \infty$) as a function of P_B and \bigwedge (See Eqs. 30 and 33).

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Professor Theodore Vermeulen for his encouragement, suggestions, and discussions.

This work was done under the auspices of the U.S. Atomic Energy Commission while the author was working on a scholarship from the Japanese Atomic Energy Commission.

NOMENCLATURE

-49-

Interfacial area between two phases, per unit column volume (cm^2/cm^3) а В L/d (dimensionless) Concentration of a transferring component in i phase (mole/cm³) c; ° c_0 Initial concentration of the incoming x phase $(mole/cm^3)$ $(c_x)_z \rightarrow 0$ (mole/cm³) C_{x0} c_{v}^{L} Initial concentration of the incoming y phase $(mole/cm^3)$ $(c_v)_{z \rightarrow L} (mole/cm^3)$ c_{vl} d A representative length (cm) Equilibrium distribution coefficient of a transferring component m between \mathbf{x} and \mathbf{y} phase (dimensionless) F_i/ϵ_i ; True mean linear velocity of the i phase (cm/sec) u_i Distance along the mean flow (the x-phase inlet is taken as the original \mathbf{z} point) (cm) $C_i = c_i/c_x^0$ $C_x^0 = c_x^0/c_x^0 = 1$ $C_{x0} c_{x0} / c_x^0$ $C_y^1 = C_y^1/c_x^0$ $c_{v1} - c_{v1}/c_{x}^{0}$ ŧ^Ei Diffusivity of a transferring component in the direction of mean flow (cm^2/sec) Superficial volumetric flow rate of i phase across a unit cross section = $\mathbf{F}_{\mathbf{i}}$ $u_i \epsilon_i (cm^3/cm^2 \cdot sec)$ $H_{oi} + L/N_{oi} = F_i/K_x a = \tilde{u}_i \epsilon_i/K_x a$; True HTU (cm) HoiM: Apparent HTU based on the measured concentration distribution in an extractor = $L/N_{oiM}(cm)$ Apparent HTU based on terminal concentration values, assuming HoiP piston flow for x and y phase (cm)

Kx

Over-all coefficient of mass transfer (cm/sec)

L Effective length of an extractor in the direction of the mean flow (cm) $N_{oi} \qquad \text{@aL/F}_i = L/(H_t)_{oi} \text{ (dimensionless)}$

 $N_{oiM} = \int_{C_{x0}}^{C_{x1}} \frac{dC_{x}}{C_{x} - mC_{y}} \quad (dimensionless)$ $N_{oiP} = \int_{10}^{C_{x1}} \frac{dC_{x}}{C_{x} - mC_{y}} \quad (dimensionless)$

 P_i $u_i d/E_i$: Péclet Number (dimensionless) Z z/L (dimensionless)

 ϵ_i Void fraction of i-phase (dimensionless)

 $\phi(\mathfrak{E}_i)$ Volumetric rate of reaction (mole/cm³ · sec)

 \bigwedge Extraction factor, mF_x/F_y (dimensionless)

Subscripts x and y refer to x and y phase respectively and i to ith component or phase.

APPLICABILITY OF THE MODEL

The basic equations are derived from the simplified model shown in Fig. 1. In an actual extractor, however, one phase (Y) is dispersed into a second phase (X) as shown in Fig. 2.

The basic equation expressing the behavior of the continuous phase is reported 16 to be suitable for Mixco and similar type columns. There is more question as to the conditions under which the model fits the dispersed phase, because the basic equation requires that all droplets at a given cross section have the same concentration.

There are two typical mechanisms that may cause longitudinal dispersion of the dispersed phase. One is longitudinal back-mixing of liquid droplets caused by local eddy motion of the mixed phases; the other is an apparent dispersion caused by a velocity distribution for the droplets, without any accompanying back-mixing of droplets. In the following description, the former is named "the eddy mechanism", and the latter "the velocity-distribution mechanism". The mathematical treatment expressed by Eq. (1) is called "the apparent-diffusivity method".

Two criteria exist for the applicability of the model assumed here. One is the residence-time distribution and the other the extraction behavior. The former can be measured by transient behavior - e.g., the outlet response to a delta (or pulse) function introduced at the extractor inlet - and is determined only by the longitudinal dispersion of the droplets.

On the other hand, the extraction behavior is influenced both by mass transfer between the droplets and the continuous phase and by the residencetime behavior of each phase.

I. Eddy Mechanism

A mechanically agitated column is the typical example. All droplets are presumed to have the same mean diameter, which will depend on the mixing geometry and power input.

Residence-Time Behavior

If local eddy motion of the mixed phases is superimposed upon a rising (or descending) motion of droplets, the apparent-diffusivity method provides a satisfactory approximation for the eddy mechanism, because reasonable mean diffusivities can be assumed in each phase. In addition, E_y may be of the same order of magnitude as E_x and may remain nearly unchanged throughout the column. In the approach to the ideal case, P_yB is proportional to the column height.

Under mixing conditions that favor rapid coalescence and redispersion of droplets, the physical situation becomes susceptible to the apparentdiffusivity method, because the behavior of the dispersed phase approaches that of a second continuous phase through the equalization of all the droplets at any one level in the extractor.

Extraction Behavior

In the case of negligible coalescence and redispersion of the droplets, they behave independently of one another. The concentration of different droplets at any given cross section is, therefore, not the same.

There are four parameters, $P_x B$, $P_y B$, N_{ox} , and Λ , which determine the extraction behavior. The applicability of the apparent-diffusivity method can be discussed in terms of all these parameters, except $P_x B$, for the following cases:

(A) $P_B \approx 0$. Under this condition, the mean concentration of phase Y is constant throughout the column. Accordingly, the extraction behavior corresponds to that of the homogeneous-phase flow reactors with first-order Peaction.² The model is applicable for all values of $P_x B$, N_{ox} , and Λ .

(B) $P_{y}B \approx \infty$. In this case, there is negligible back-mixing of the dispersed phase. Therefore, the apparent-diffusivity method is applicable to all values of $P_{x}B$, N_{ox} , and Λ .

(C) $P_y B$ finite. Under this condition, the concentration driving force between a droplet and the continuous phase changes from time to time owing to eddy motion of the droplet. This change reflects the concentration distribution of phase X and the magnitude of N_{ox} (which is proportional to the mass-transfer rate).

There are three extreme cases under which the apparent-diffusivity method is applicable. The method probably remains valid under intermediate conditions, but this case needs further investigation.

(1) N_{ox} and K_x a very high. Owing to the high rate, the droplets are always nearly in equilibrium with the surrounding continuous phase. Hence there is little effect of back-mixing of droplets on the extraction behavior.

(2) N_{ox} and K_{x} a very low. Lengthwise gradient for the driving force is very small compared with the total driving force. So there is again little effect of back-mixing of the dispersed phase.

(3) $P_X B \approx 0$. Because the concentration distribution of phase X is constant throughout the column, the extent of extraction of each droplet is determined by the length of residence time. This comes from the assumption that the rate of extraction is expressed by a rate equation of the first order (2).

The extent of extraction of the dispersed phase may be calculated by the apparent-diffusivity method for any values of $P_v B$, N_{ox} , and Λ .

For moderate values of N_{ox} , there is a possibility that the calculations based on the apparent-diffusivity method deviate from the exact solution. When \wedge is around 1, this deviation may not be serious, because the concentration gradient in phase X and phase Y is fairly linear, and d^2C_y/dZ^2 is small. When coalescence and redispersion of droplets occur, the behavior of the dispersed phase becomes more favorable to the apparent-diffusivity method, for the reason described for residence-time behavior. There is a positive indication of coalescence and redispersion of liquid droplets for agitated liquid-liquid extractors.^{12,13}

In conclusion, the apparent-diffusivity method is applicable to the eddy mechanism except perhaps in the range where P_yB and N_{ox} are finite and Λ is not around 1. Further experimental or theoretical study is needed for this range. Even here, however, it is entirely permissible to apply the apparent-diffusivity method, if enough coalescence and redispersion occur.

II. Velocity-Distribution Mechanism

A typical example is noncoalescing free flow of the dispersed phase through a long column without mechanical agitation. The residence-time distribution depends on the velocity distribution of droplets, which is nearly constant throughout the column height; hence the superficial Peclet group $(P_yB)_u$ determined from transient behavior remains unchanged with changing column height.

Under the following restrictions, the extent of extraction in the case of the velocity-distribution mechanism can be computed from the apparent-diffusion method. 7

For $(P_vB)_u > 50$, and \bigwedge around 1,

a. when $(N_{ox})_u$ is smaller than 20, the extent of extraction is given by Eq. (6), using $P_x B$ and $(P_v B)_y$,

- b. when $(N_{ox})_u$ is greater than 20, the extent of extraction is given by the apparent diffusion method, using the measured P_B, and
 - an infinite value for $P_v B$ irrespective of the measured value of

 $(P_yB)_u$. For $(P_yB)_u \approx 50$, the apparent-diffusion method is not generally applicable without serious error.

When the eddy mechanism is superimposed on the velocity-distribution mechanism, the following treatment is recommended. 7

Contribution of the velocity-distribution mechanism to the over-all longitudinal dispersion effective to extraction is apparently expressed by a superficial mean diffusivity D_{yu} , for $(P_y B)_u > \sim 50$. Assuming additivity of the superficial diffusivities that came from the different mechanisms, one obtains the over-all diffusivity or the diffusivity E_{ym} measured experimentally by the transient method from

$$E_{ym} = E_y + D_{yu}$$

or

$$1/(P_yB)_m = 1/P_yB + 1/(P_yB)_u$$

where E_y and P_yB are the mean diffusivity and Péclet group of the eddy mechanism.

When $(P_yB)_m$ is measured as a function of column height, we may have such a relation as

$$(P_yB)_m \propto B^n \text{ for } 0 \le n \le 1,$$

because $(P_yB)_u$ remains unchanged with B, and P_yB is proportional to B. The possible values of n, giving the lowest limit under which the apparent diffusion method cannot be applied without serious error, are as follows:

$$(P_yB)_m$$
 10 20 30 40 50
n 0.8 0.6 0.4 0.2 0.0

For example, when $(P_yB)_m$ is around 30 and n is greater than 0.4, the extent of extraction may safely be calculated by the apparent-diffusion method, using $(P_yB)_m$ as the effective Péclet group for phase Y in the range of $(N_{ox})_u \leq 20$.

Note:

The special notations used here are as follows:

(N_{ox})_u = (Ka)_uL/F_y, (Ka)_u = over-all coefficient of mass transfer, when all droplets have an equal velocity, and pass through

a column in plug flow,

 $(P_yB)_u = (U_yd/D_{yu}) (L/d).$

To determine $(P_yB)_u$ from the transient behavior it is recommended that the width of the residence-time distribution curve be used (i.e., the outlet response to the delta function) at the mid-point of its maximum height.⁷

LITERATURE CITED

- G. Damköhler, "Der Chemie-Ingenieur" A. Eucken and M. Jakob, Akademische Verlagsgesellschaft M.B.H. (Leipzig) 3 pt. 1, 366 (1937).
- 2. P.V. Danckwerts, Chem. Eng. Sci. 2, 1 (1953).
- 3. T.H. Chilton and A.P. Colburn, Ind. Eng. Chem. 27, 255 (1935).
- 4. E.R. Gilliland and E.A. Mason, ibid, 44, 218 (1952).
- 5. H. Kramer and G. Alberda, Chem. Eng. Sci. 2, 173 (1953).
- 6. W. R. Marshall, Jr., and R. L. Pigford, <u>The Application of Differential</u> <u>Equations to Chemical Engineering Problems</u> (Univ. of Delaware, <u>Newark</u>, Del. 1947, p. 35.
- 7. T. Miyauchi and T. Vermeulen, (UCRL), Report in preparation.
- 8. J.Y. Oldshue and J.H. Rushton, Chem. Eng. Progr. 48, 297 (1952).
- 9. G.H. Reman and R.B. Olney, ibid. 51, 141 (1955).
- 10. G. Sege and F. W. Woodfield, ibid, Symposium Series, No. 13, <u>50</u>, 39 (1954)
- 11. J.D. Thornton, ibid., Symposium Series, No. 13, 50, 179 (1954).
- 12. J.H. Vanderveen, E. Fenech, G.E. Langlois, and T. Vermeulen, UCRL Report in preparation.
- 13. T. Vermeulen, G. M. Williams, and G. E. Langlois, Chem. Eng. Prog. <u>51</u>, 85 (1955).
- 14. Vermeulen, Lane, Lehman, and Rubin, Am. Inst. Chem. Engr. J. (in press).
- 15. H.G. Vogt, and C.J. Geankoplis, Ind. Eng. Chem. 46, 1763 (1954).
- 16. S. Yagi and T. Miyauchi, Chem. Eng. (Japan), <u>17</u>, 382 (1953); <u>19</u>, 507 (1955).
- 17. E.F. Young, Jr., Chem. Eng. 64, Feb., 241 (1957).