# Surface Renewal and Penetration Models in the Transient State

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**The transient models for some interphase transport processes have been developed based on the transient age distributions derived from the population balance. These models appear to represent physical reality more accurately than do the steady state models during the start-up period of the transport processes.**

The penetration model of interphase mass transfer was introduced by Higbie (*1*) to formulate the gas absorption rate by a liquid when the exposure time is very short. Danckwerts (*2*) extended Higbie's model to the interphase mass transfer in a turbulent fluid-fluid system by incorporating the surface renewal concept. The two models may be jointly referred to as the surface renewal and penetration theory and have been further extended and modified in a variety of ways (*3* to *6*). While the theory appears to be sufficiently flexible for treating a variety of transport processes, its applications have been restricted mainly to fully developed stationary or macroscopic processes.

The purpose of this work is to develop the transient models of some transport processes based on the transient age distributions. These models appear to represent physical reality more accurately than do the steady state models during the start-up period of some interphase transport processes.

## GENERAL TRANSIENT AGE DISTRIBUTION FUNCTIONS

Consider the transport process between a fluid and another phase. Suppose that, at the onset of the process, the interface is occupied by the fresh fluid elements. In other words, at any time $t$ from the onset of the transport process, the oldest fluid elements at the interface must have the age of $t$. The fluid elements at the interface establish a certain steady state distribution function $\phi(\theta)$ for all $\theta$ less than $t$ as shown in Figure 1(A, B, and C). At time $t$ the application of the population balance (*7*, *8*) to ages of those fluid elements which are on the interface give rise to the transient age (contact time) distribution[*] which can be written in the form (*7*, *9*)

$$\phi(t,\theta) = \phi(\theta) + \left[1 - \int_0^t \phi(\theta)d\theta\right] \delta(\theta - t) \quad \text{for} \quad 0 \leqq \theta \leqq t \tag{1}$$

and

$$\phi(t,\theta) = 0 \quad \text{for} \quad \theta > t \tag{1a}$$

The first term on the right-hand side of Equation (1) represents the steady portion of the age distribution or the portion of ages contributed by the fluid elements which come into the interface after the onset of the process. The second term represents the contribution by the fluid elements originally at the interface. When $t$ approaches infinity, the magnitude of the second term will eventually approach zero and only the first term remains in the right-hand side of Equation (1). Therefore, $\phi(t, \theta)$ reduces to the steady state age distribution function $\phi(\theta)$ as $t \rightarrow \infty$. Equation (1) is the basic expression for the transient age distribution functions employed here.

Different transient distributions $\phi(\theta, t)$ can be obtained by direct substitution of different steady state age distributions $\phi(\theta)$ into Equation (1). In this way every steady state age distribution function may be generalized to a corresponding unsteady state age distribution function. For example, the substitutions of the multiple capacitance age distribution, the random age distribution, and the uniform age distribution functions into Equation (1) yield the following corresponding transient age distribution functions:

$$\left.\begin{aligned} \phi(t,\theta) &= se^{-ms}\left[\sum_{j=0}^{m-1} \frac{(ms\theta)^j}{j!}\right] + \delta(\theta - t) \\ &\qquad \left[\frac{e^{-mst}}{m} \sum_{j=0}^{m-1} \sum_{m=0}^{j} \frac{(mst)^n}{n!}\right] \\ &\qquad\qquad \text{for} \quad 0 \leqq \theta \leqq t \\ \phi(t,\theta) &= 0 \quad \text{for} \quad t < \theta, \end{aligned}\right\} \tag{2}$$

$$\left.\begin{aligned} \phi(t,\theta) &= se^{-s\theta} + e^{-st}\,\delta(\theta - t) && \text{for} \quad 0 \leqq \theta \leqq t, \\ \phi(t,\theta) &= 0 && \text{for} \quad t < \theta, \end{aligned}\right\} \tag{3}$$

and

$$\left.\begin{aligned} \phi(t,\theta) &= \frac{1}{\tau} + \left(1 - \frac{t}{\tau}\right) \delta(\theta - t) \\ & \qquad \text{for} \quad 0 \leqq \theta \leqq t \leqq \tau, \\ \phi(t,\theta) &= 0 \qquad \text{for} \quad t < \theta \leqq \tau, \\ \phi(t,\theta) &= 0 \qquad \text{for} \quad \tau < \theta \end{aligned}\right\} \tag{4}$$

Equation (3) agrees with the one derived by Tadaki and Maeda (*10*) based on physical reasoning. Figures 1*A*, 1*B*, and 1*C* show graphically the multiple capacitance, random, and uniform contact time distributions in the transient state, respectively.

It is worth noting that the uniform age distribution is fairly representative of the distribution of the absorbent contact time in a short wetted-wall column (where the

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[*] Note that $\phi(\theta)$ is the fully developed steady state age distribution function. Therefore in Equation (1) $[1 - \int_0^t \phi(\theta)d\theta]$ is numerically identical to $[\int_t^\infty \phi(\theta)d\theta]$.

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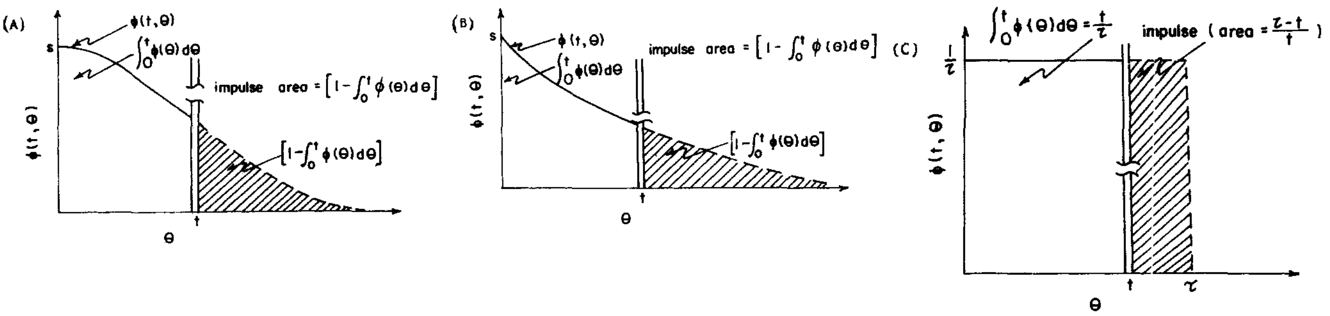

**Fig. 1. *Transient age distribution function at time t—modifications of multiple capacitance distribution (A), random age distribution (B), and uniform age distribution (C).***

absorbent liquid flows in a laminar flow) or in a absorption tower filled regularly and uniformly with single-size packing material (where an absorbent liquid flows slowly). The random age distribution may be realized in a well-stirred vessel. In an actual system in which an interphase transport process occurs, it is impossible to reproduce either one of these idealized age distributions. The multiple capacitance age distribution can be employed to represent approximately any situation between these two ideal cases.

## SURFACE RENEWAL AND PENETRATION MODELS IN THE TRANSIENT STATE

Based on the general transient contact time distributions derived in the preceding section, the surface renewal and penetration models for the transient state will be developed. Consider a transport system involving a fluid and another phase under the condition of no chemical reaction or heat generation. It is assumed that the transport process begins at the instant that the fluid is brought into contact with the interface. New fluid elements from the bulk stream are assumed to replace continually the old fluid elements on the interface. During the contact period with the other phase, the fluid elements on the interface are assumed to absorb heat (or mass) by conduction (or molecular diffusion).

Let $\psi_i(\theta)$ be the instantaneous transfer rate of those surface elements at the contact time $\theta$. If $\phi(t, \theta)$ is the age distribution function of the interface fluid elements, then at time $t$, from the onset of the transfer process, $\phi(t, \theta)d\theta$ is the fraction of fluid elements on the interface having a contact time between $\theta$ and $\theta + d\theta$. Under these conditions, the average local transport rate can be expressed as the summation of the individual contributions of fluid elements of all ages from zero to $t$ inclusive

$$\psi(t) = \int_0^t \phi(t,\theta)\ \psi_i(\theta)d\theta \tag{5}$$

Note that the upper limit of integration is $t$ instead of infinity because no fluid elements have ages greater than $t$. The magnitude of $\psi(t)$ changes with $t$. If $t$ approaches infinity, $\phi(t, \theta)$ reduces to $\phi(\theta)$, as can be seen from Equation (1). Then Equation (5) reduces to the familiar steady state expression for the transfer rate (*2, 3, 5, 7*)

$$\lim_{t\to\infty} \psi(t) = \psi = \int_0^\infty \phi(\theta)\psi_i(\theta)d\theta \tag{5a}$$

In Equation (5*a*), $\psi_i(\theta)$ is the instantaneous local transfer rate of the fluid elements and is a function of contact time $\theta$. $\psi(t)$ is the average local transfer rate at any given time $t$ before the steady state is reached; hence, it is a function of time $t$. $\lim\limits_{t\to\infty} \psi$ is the average local transfer rate under steady state condition, thus, it is no longer a function of $t$. At given time $t$ the local transport coefficient $H(t)$ is defined as

$$\begin{aligned} H(t) &= \frac{\psi(t)}{P_0 - P_b} \\ &= \frac{1}{P_0 - P_b}\int_0^t \phi(t,\theta)\psi_i(\theta)d\theta \end{aligned} \tag{6}$$

where $P_b$ is a transport potential (such as $\rho c_p T$ or $C$) of the fluid in the bulk stream, and $P_0$ is the potential of the fluid at the interface. Substituting Equation (1) into Equations (5) and (6), one obtains

$$\begin{aligned} \psi(t) &= \int_0^t \left\{ \left[\phi(\theta) + \delta(\theta - t)\int_t^\infty \phi(\theta)d\theta\right]\psi_i(\theta)\right\} d\theta \\ &= \int_0^t \phi(\theta)\psi_i(\theta)d\theta + \int_t^\infty \phi(\theta)d\theta \int_0^t \delta(\theta - t)\psi_i(\theta)\, d\theta \\ &= \int_0^t \phi(\theta)\psi_i(\theta)d\theta + \psi_i(t)\int_t^\infty \phi(\theta)\, d\theta \end{aligned} \tag{7}$$

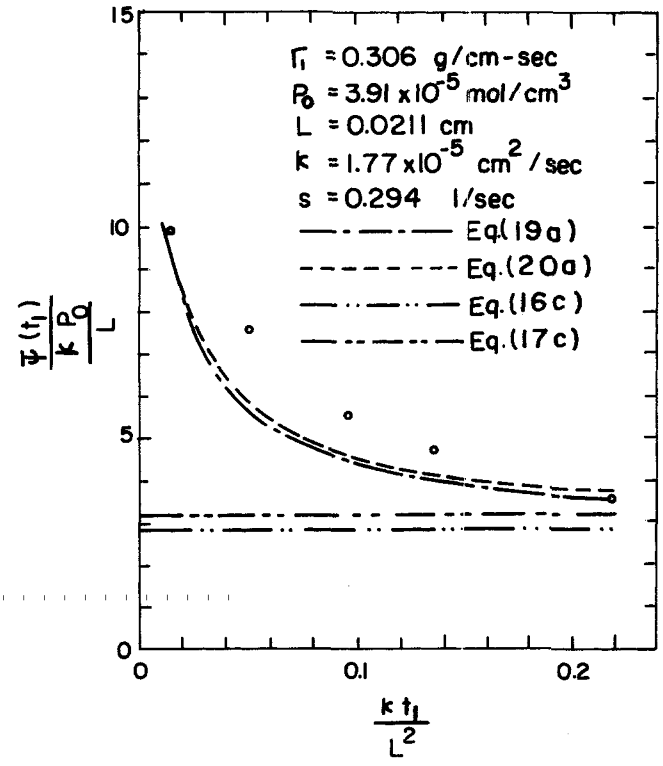

**Fig. 2. Comparison of experimental data with various equations.**

and

$$H(t) = \frac{1}{(P_0 - P_b)} \left[ \int_0^t \phi(\theta)\psi_i(\theta)d\theta + \psi_i(t) \int_t^\infty \phi(\theta)d\theta \right] \quad (8)$$

Equations (7) and (8) are, respectively, the basic formulations for the average local transport rate and the average local transport coefficient at given time $t$ based on the transient renewal-penetration model.

The instantaneous local transfer rate $\psi_i(\theta)$ of the fluid elements at the interface can be evaluated if the temperature or concentration profile of the fluid elements on the interface is known (*1* to *5*), that is,

$$\psi_i(\theta) = -\kappa \frac{\partial P}{\partial z} \bigg|_{z=0} \quad (9)$$

where the temperature or concentration profile of surface fluid elements may be found by solving the Fourier equation

$$\frac{\partial P}{\partial \theta} = \kappa \frac{\partial^2 P}{\partial z^2} \quad (10)$$

The solution of Equation (10) depends on the initial and boundary conditions stipulated. A set of general boundary conditions (*3*) may be written as

$$P = P_b \quad \text{for} \quad z \geqq 0, \quad \theta = 0 \quad (11)$$

$$P = P_b \quad \text{for} \quad z = l, \quad \theta \geqq 0 \quad (12)$$

$$\frac{\partial P}{\partial z} = \gamma(P_0 - P) \quad \text{for} \quad z = 0, \quad \theta > 0 \quad (13)$$

If the residence time of the fluid elements on the interface is very short, the depth of penetration becomes very small in comparison with the average thickness $l$ of the fluid elements. Therefore, $l$ may be assumed to be infinity. If the interfacial resistance is negligibly small, the interfacial transfer coefficient $h_s$ and hence $\gamma$ in the general boundary condition may be assumed to be infinity. It is seen that the other boundary conditions may be obtained by the process of allowing $l$ or $\gamma$ or both to approach infinity. The resulting four different expressions for the instantaneous transfer rate $\psi_i(\theta)$ under various boundary conditions are summarized in Table 1.

The evaluation of the average local transport coefficient or the transport rate during the transient state requires a knowledge of $\phi(\theta)$ in addition to $\psi_i(\theta)$; this requirement can be inferred from Equations (7) and (8). If the multiple capacitance contact time (or age) distribution $\phi(\theta)$ defined by

$$\phi(\theta) = se^{-ms\theta} \sum_{j=0}^{m-1} \frac{(ms\theta)^j}{j!}$$

is employed, one obtains the transport coefficient in the transient state as

TABLE 1. INSTANTANEOUS TRANSFER RATE AT THE INTERFACE FOR THE SYSTEMS WITHOUT CHEMICAL REACTION

| Interface boundary conditions | Boundary extent conditions | Instantaneous transfer rate at interface | Reference |
|---|---|---|---|
| With* interfacial resistance | Finite† extent | $\psi_{i1}(\theta) = (P_o - P_b)\frac{\kappa}{l} \left\{ \frac{\gamma l}{1 + \gamma l} + 2\gamma^2 l^2 \sum_{n=1}^{\infty} \frac{e^{-\frac{\beta_n^2 \kappa\theta}{l^2}}}{[\gamma l + \gamma^2 l^2 + \beta_n^2]} \right\}$ | 11 |
| | | or | |
| | | $\psi_{i1}(\theta) = (P_o - P_b)\kappa\gamma \left\{ e^{\kappa\gamma^2\theta} \operatorname{erfc} \gamma\sqrt{\kappa\theta} + 2 \sum_{n=1}^{\infty} \left[ e^{2nl\gamma + \kappa\theta\gamma^2} \operatorname{erfc} \left( \frac{nl}{\sqrt{\kappa\theta}} + \gamma\sqrt{\kappa\theta} \right) \right] \right\}$ | |
| | Infinite** extent | $\psi_{i2}(\theta) = (P_o - P_b)\kappa\gamma\, e^{\gamma^2\kappa\theta} \operatorname{erfc} \gamma\sqrt{\kappa\theta}$ | 3 |
| Without†† interfacial resistance | Finite extent | $\psi_{i3}(\theta) = (P_o - P_b)\sqrt{\frac{\kappa}{\pi\theta}} \left[ 1 + 2 \sum_{n=1}^{\infty} e^{-\frac{n^2 l^2}{\kappa\theta}} \right]$ | 4, 5 |
| | | or | |
| | | $\psi_{i3}(\theta) = (P_o - P_b)\frac{\kappa}{l} \left[ 1 + 2 \sum_{n=1}^{\infty} e^{-\frac{n^2\pi^2\kappa\theta}{l^2}} \right]$ | |
| | Infinite extent | $\psi_{i4}(\theta) = (P_o - P_b)\sqrt{\frac{\kappa}{\pi\theta}}$ | 1, 2 |

* $\gamma$ and $\gamma l$ are finite.
** $l$ approaches infinity.
† $l$ is finite.
†† $\gamma$ and $\gamma l$ approach infinity.
Note: $\gamma = h_s/\kappa$, $\beta_n$ are the consecutive roots of equation $\beta \cot \beta + \gamma l = 0$.

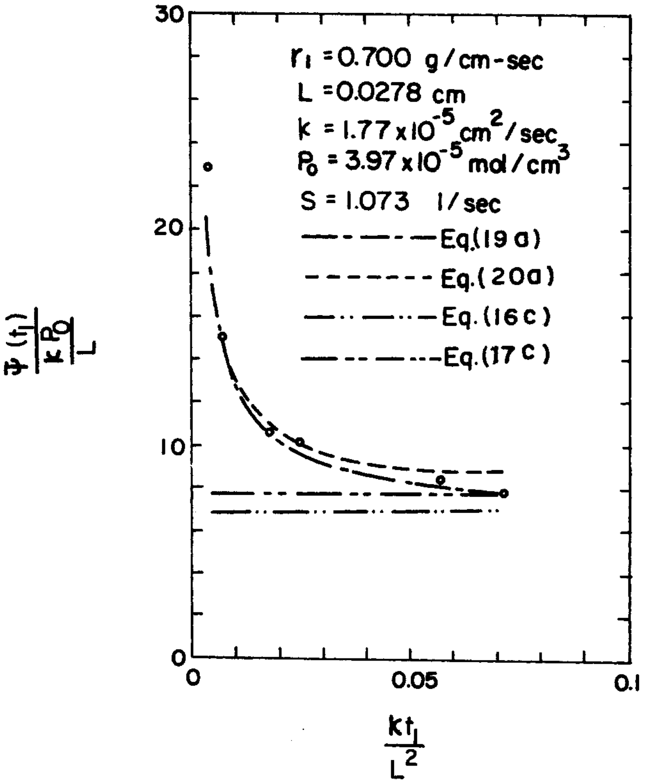

Fig. 3. Comparison of experimental data with various equations (see Figure 2).

$$H_m = \frac{1}{(P_0 - P_b)} \left\{ \int_0^t \psi_i(\theta) s e^{-ms\theta} \sum_{j=0}^{m-1} \frac{(ms\theta)^j}{j!} d\theta \right.$$

$$\left. + \psi_i(t) \int_t^\infty s e^{-ms\theta} \sum_{j=0}^{m-1} \frac{(ms\theta)^j}{j!} d\theta \right\} \quad (14)$$

or

$$H_m = \frac{1}{(P_0 - P_b)} \left\{ \sum_{j=0}^{m-1} \frac{(ms)^j}{j!} \int_0^t \psi_i(\theta) s e^{-ms\theta} \theta^j d\theta \right.$$

$$\left. + \frac{\psi_i(t) e^{-mst}}{m} \sum_{j=0}^{m-1} \sum_{n=0}^{j} \frac{(mst)^n}{n!} \right\} \quad (14a)$$

Equations (14) and (14a) are general expressions for the local transport coefficient in the transient state. For a given set of boundary conditions in Equation (10), $\psi_i(\theta)$ is fixed. The transient transport coefficient based on the different age distributions may be obtained by varying the value of $m$. When $m$ approaches infinity, the limiting value of $H_m$ is easier to obtain from Equation (14) than from Equation (14a). Taking the limit of Equation (14) and remembering that $s = 1/\tau$, one obtains

$$\lim_{m \to \infty} H_m = \frac{1}{(P_0 - P_b)} \left\{ \int_0^t \psi_i(\theta) s d\theta \right.$$

$$\left. + \psi_i(t) \left[ 1 - \int_0^t s d\theta \right] \right\}$$

$$= \frac{1}{(P_0 - P_b)} \left\{ \int_0^t \psi_i(\theta) s d\theta + \psi_i(t)(1 - st) \right\}$$

or

$$H_\infty = \frac{1}{(P_0 - P_b)\tau} \left\{ \int_0^t \psi_i(\theta) d\theta + \psi_i(t)(\tau - t) \right\} \quad (14b)$$

Equation (14*a*) is convenient for computation in the case of a finite number of capacitance while Equation (14*b*) is convenient for computation in the case of infinitely many capacitances (Higbie's uniform age distribution). If the age distribution function is chosen (that is, if $m$ is fixed), the transport coefficient in the transient state and hence, the expression for $\psi_i(\theta)$ may be found from Equations (14*a*) or (14*b*) under various boundary conditions. All of the limiting cases of Equation (14) corresponding to various age distributions (such as $m = 1$, $m \to \infty$) and under the different boundary conditions (such as $l \to \infty$ or $h_s \to \infty$ or both) of Equation (10) are obtained and are summarized in a table available elsewhere.* Two examples follow:

1. When $m = 1$ (random age distribution), $\gamma \to \infty$ (negligibly small interfacial resistance), and $l \to \infty$ (semi-infinite surface fluid elements). From Table 1, one finds that the corresponding $\psi_i(\theta)$ is

$$\psi_i(\theta) = (P_0 - P_b) \sqrt{\frac{\kappa}{\pi\theta}} \quad (15)$$

Equation (14*a*) thus reduces to

$$H_{1\gamma l}(t) = s \int_0^t \sqrt{\frac{\kappa}{\pi\theta}} e^{-s\theta} d\theta + e^{-st} \sqrt{\frac{\kappa}{\pi\tau}}$$

$$= \sqrt{\kappa s} \operatorname{erf} \sqrt{st} + e^{-st} \sqrt{\frac{\kappa}{\pi\tau}} \quad (16)$$

or

$$\psi_{1\gamma l}(t) = (P_0 - P_b) \left[ \sqrt{\kappa s} \operatorname{erf} \sqrt{st} + e^{-st} \sqrt{\frac{\kappa}{\pi t}} \right] \quad (16a)$$

Equation (16*a*) agrees with the transient mass transfer coefficient obtained by Tadaki and Maeda (*10*). When $t$ approaches infinity, Equation (16*a*) reduces to the steady state surface renewal model of Danckwerts (*2*):

$$\psi_{1\gamma l} = (P_0 - P_b)\sqrt{\kappa s} \quad (16b)$$

2. When $m \to \infty$ (uniform age distribution), $\gamma \to \infty$ (no surface resistance), and $l \to \infty$ (semi-infinite surface fluid elements), Equation (14) then reduces to Equation (14*b*). The latter, with the help of Equation (15), reduces to

$$H_{\infty\gamma l}(t) = \frac{1}{\tau} \left[ \int_0^t \sqrt{\frac{\kappa}{\pi\theta}} d\theta + \sqrt{\frac{\kappa}{\pi t}} (\tau - t) \right]$$

$$= \frac{1}{\tau} \sqrt{\frac{\kappa t}{\pi}} + \sqrt{\frac{\kappa}{\pi t}} \quad (17)$$

or

$$\psi_{\infty\gamma l}(t) = (P_0 - P_b) \left[ \frac{1}{\tau} \sqrt{\frac{\kappa t}{\pi}} + \sqrt{\frac{\kappa}{\pi t}} \right] \quad (17a)$$

It is seen that when $t \to \tau$, Equation (17*a*) reduces to the familiar steady state penetration model of Higbie (*1*),

$$\psi_\infty = 2(P_0 - P_b) \sqrt{\frac{\kappa}{\pi t}} \quad (17b)$$

The following procedure yields the time average transfer rate for any time interval, for example, from zero to $t_1$. Let the average transfer rate over the time interval $t_1$ be denoted by $\overline{\psi}(t_1)$, then

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$$\bar{\psi}(t_1) = \frac{1}{t_1}\int_0^{t_1} \psi(t)\,dt$$
$$= \frac{P_0 - P_b}{t_1}\int_0^{t_1} H(t)\,dt \tag{18}$$

From Equations (16) and (18), one obtains

$$\bar{\psi}_{1\gamma l}(t_1) = \frac{(P_0 - P_b)}{t_1}\int_0^{t_1} \left(\sqrt{\kappa s}\ \mathrm{erf}\ \sqrt{st} + e^{-st}\sqrt{\frac{\kappa}{\pi t}}\right) dt$$
$$= (P_0 - P_b)\sqrt{\frac{\kappa}{t_1}}\left\{\frac{e^{-st_1}}{\sqrt{\pi}} + \frac{1 + 2st_1}{2\sqrt{st_1}}\ \mathrm{erf}\ \sqrt{st_1}\right\}. \tag{19}$$

From Equations (17) and (18), one obtains

$$\bar{\psi}_{\infty\gamma l}(t_1) = (P_0 - P_b)\left[\frac{2}{3\tau}\sqrt{\frac{\kappa t_1}{\pi}} + 2\sqrt{\frac{\kappa}{\pi t_1}}\right]$$
$$= (P_0 - P_b)\left[\frac{2}{3\tau}\sqrt{\frac{\kappa t_1}{\pi}} + 2\sqrt{\frac{\kappa}{\pi t_1}}\right]$$
$$= (P_0 - P_b)\sqrt{\frac{\kappa}{t_1}}\,\frac{2}{\sqrt{\pi}}\left(1 + \frac{st_1}{3}\right), \qquad t_1 \leqq \tau \tag{20}$$

Equations (19) and (20) show that the average transfer coefficient over the time interval from 0 to $t_1$ is a function of $\sqrt{\kappa/t_1}$ and $st_1$. It must be noted that these two equations are valid only in the cases of short contact time and negligibly small interfacial resistance.

## DISCUSSION AND CONCLUSION

For many years the steady state operation has been considered as the ultimate goal in process industries. Recently, however, the unsteady state process has been drawing increasing attention. It has been noted that benefits can be obtained by deliberately operating a process in the unsteady state. As indicated by Schrodt (*12*), the capacity and efficiency of any operation may be improved by unsteady state processing. The transient model based on the renewal-penetration mechanism appears to provide strong support for this so far as heat and mass transport processes are concerned. Based on the transient surface renewal and penetration model presented here, it can be proved that the transient local heat or mass transfer rate is always greater than or at least equal to the steady state local transfer rate

$$\psi(t) \geqq \lim_{t\to\infty} \psi(t)$$

or from Equation (7)

$$\int_0^t \phi(\theta)\psi_i(\theta)\,d\theta + \psi_i(t)\left[1 - \int_0^t \phi(\theta)\,d\theta\right]$$
$$\geqq \lim_{t\to\infty}\left\{\int_0^t \phi(\theta)\psi_i(\theta)\,d\theta + \psi_i(t)\left[1 - \int_0^t \phi(\theta)\,d\theta\right]\right\} \tag{21}$$

Equation (21) is proved as follows. The instantaneous transfer rate always decreases as the time increases (see Table 1)

$$\psi_i(t) \geqq \psi_i(\theta)$$

for all values of $\theta$ between $t$ and infinity. Furthermore, by definition,

$$\phi(\theta) \geqq 0$$

Hence,

$$\lim_{a\to\infty}\left\{\int_t^a [\psi_i(t) - \psi_i(\theta)]\,\phi(\theta)\,d\theta\right\} \geqq 0$$

or

$$\lim_{a\to\infty}\left\{\int_t^a \psi_i(t)\,\phi(\theta)\,d\theta - \int_t^a \psi_i(\theta)\phi(\theta)\,d\theta\right\} \geqq 0$$

Adding and subtracting the term,

$$\int_0^t \phi(\theta)\psi_i(\theta)\,d\theta$$

to the left-hand side of the above expression, one obtains

$$\int_0^t \phi(\theta)\psi_i(\theta)\,d\theta + \int_t^\infty \psi_i(t)\phi(\theta)\,d\theta - \int_0^\infty \phi(\theta)\psi_i(\theta)\,d\theta \geqq 0$$

or

$$\int_0^t \phi(\theta)\psi_i(\theta)\,d\theta + \psi_i(t)\left[1 - \int_0^t \phi(\theta)\,d\theta\right] \geqq \lim_{t\to\infty}\int_0^t \phi(\theta)\psi_i(\theta)\,d\theta$$

or

$$\int_0^t \phi(\theta)\psi_i(\theta)\,d\theta + \psi_i(t)\left[1 - \int_0^t \phi(\theta)\,d\theta\right]$$
$$\geqq \lim_{t\to\infty}\left\{\int_0^t \phi(\theta)\psi_i(\theta)\,d\theta + \psi_i(t)\left[1 - \int_0^t \phi(\theta)\,d\theta\right]\right\}$$

This inequality relation shows that the transient effect al-

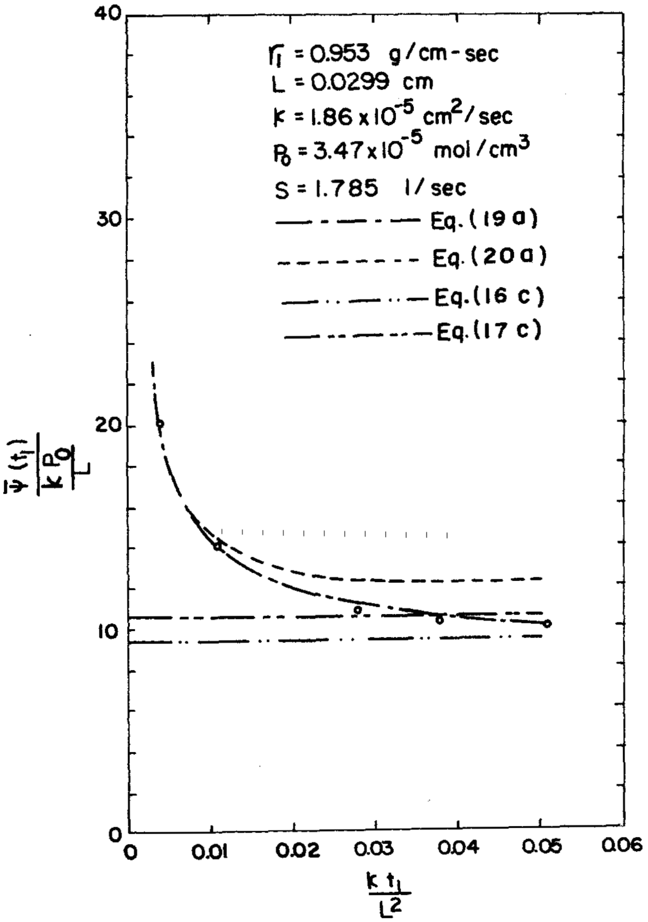

Fig. 4. Comparison of experimental data with various equations (see Figure 2).

ways tends to increase the rate of transport where the present model is applicable. More specifically, the local transport coefficients obtained in the two examples of the preceding section and given by Equations (16) and (17) can also be proved to be greater than or at least equal to the corresponding local transport coefficients under the condition

$$\left[\sqrt{\kappa s}\ \text{erf}\ \sqrt{st} + e^{-st}\sqrt{\frac{\kappa}{\pi}}\right] \geqq \sqrt{\kappa s} \quad (22)$$

and

$$\left[\frac{1}{\tau}\sqrt{\frac{\kappa t}{\pi}} + \sqrt{\frac{\kappa}{\pi t}}\right] \geqq \frac{2}{\sqrt{\pi}}\sqrt{\frac{\kappa}{\tau}}, \quad t \leqq \tau \quad (23)$$

The transient models given by Equations (19) and (20) are compared with the experimental data obtained by Fujita (*13*), Kamei (*14*), and Hikita (*15*). Their experimental data were also employed by Tadaki and Maeda (*10*) in experiments on mass transfer in the liquid film on a wetted-wall column; pure carbon dioxide was absorbed by the water while it was running down the inner wall of the outer tube. Their experimental results are compared here with the transient models given by Equations (19) and (20) and with the steady state models given by Equations (16*b*) and (17*b*). In dimensionless form, these four equations may be rewritten in the following way

$$\frac{\overline{\psi}(t_1)}{\frac{\kappa(P_0 - P_b)}{L}} = \frac{1}{\sqrt{\frac{\kappa t_1}{L^2}}}\left[\frac{1}{\sqrt{\pi}}e^{-st_1} + \frac{1 + 2st_1}{2\sqrt{st_1}}\ \text{erf}\sqrt{st_1}\right] \quad (19a)$$

$$\frac{\overline{\psi}(t_1)}{\frac{\kappa(P_0 - P_b)}{L}} = \frac{1}{\sqrt{\frac{\kappa t_1}{L^2}}}\left[\frac{2}{\sqrt{\pi}}\left(1 + \frac{st_1}{3}\right)\right] \quad (20a)$$

$$\frac{\overline{\psi}(t_1)}{\frac{\kappa(P_0 - P_b)}{L}} = \sqrt{\frac{s}{\kappa}}\,L \quad (16c)$$

$$\frac{\overline{\psi}(t_1)}{\frac{\kappa(P_0 - P_b)}{L}} = \sqrt{\frac{4s}{\pi\kappa}}\,L \quad (17c)$$

These equations represent in dimensionless form the time average transfer rates between the onset of the process and any moment $t_1$; they are compared to the experimental data in Figures 2 through 5. Note, however, that in Equations (16*c*) and (17*a*), the right-hand sides are independent of $t_1$ and the dimensionless time average transfer rates are also the instantaneous transfer rate because of the steady state condition. In each graph, the dimensionless term $\overline{\psi}(t_1)/(\kappa P_0/L)$ is plotted against the dimensionless term $\kappa t_1/L^2$. The bulk concentration $P_b$ is assumed to be negligibly small. Note that the mass flow rate of liquid per unit periphery $\Gamma_1$ and, hence, the mean frequency of renewal $s$ increases as the figure number increases.

The transient models predict results better than do the steady state models in the case of a short-time process. Furthermore, the transient models agree well with experimental data for large flow rates, but the analytically obtained predictions are smaller than the experimental results for small flow rates. Nevertheless, the deviations are expected in the case of small flow rates (long contact time) because, as mentioned previously, Equations (19) and (20) are valid under conditions of short contact time. The average contact times are 3.4 sec. (Figure 2), 0.93 sec. (Figure 3), 0.56 sec. (Figure 4) and 0.41 sec. (Figure 5). Agreement of the analytical results with the experimental data is expected to be improved if the transient film-penetration or film-renewal model is employed.* In these models, the average thickness $l$ of the fluid elements is assumed to be finite. It has been noted that transfer rate increases as $l$ decreases.

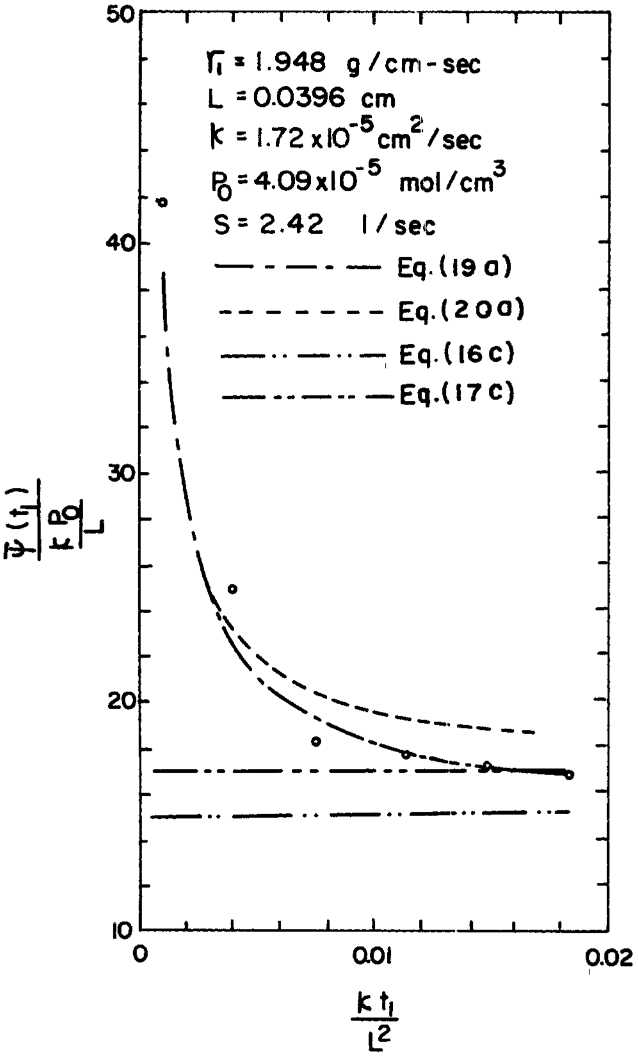

Fig. 5. Comparison of experimental data with various equations (see Figure 2).

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## NOTATION

$C$ = molar concentration, $M/L^3$

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* See footnote on p. 157.

$c_p$ = heat capacity at constant pressure, $L^2/t^2T$
$H$ = generalized local transport coefficient, $L^3/T$
$h_s$ = inverse of surface resistance, $L/t$
$l$ = thickness of stagnant film; average thickness of fluid elements, $L$
$L$ = thickness of liquid layer in wetted wall column, $L$
$m$ = number of capacitances or capacitors in multiple capacitances model, dimensionless
$P$ = potential, $\rho c_p\,T$ in $M/Lt^2$ or $C$ in $M/L^3$
$s$ = frequency or fractional rate of surface renewal, $t^{-1}$
$t$ = time of process on the macroscopic scale, $t$
$T$ = temperature, $T$
$z$ = distance from interfacial plan, $L$

**Greek Letters**

$\gamma$ = $h_s/\kappa$, $L^{-1}$
$\delta$ = impulse function, $t^{-1}$
$\theta$ = contact time or age, $t$
$\kappa$ = generalized molecular diffusivity, $L^2/t$
$\pi$ = 3.14159 . . ., dimensionless
$\rho$ = density of fluid or particles, $M/L^3$
$\tau$ = mean residence time, $t$
$\phi$ = contact time (or age) distribution function, $t^{-1}$
$\psi_i$ = instantaneous local transport rate, $ML^2/t^3$ or $M/t$
$\psi$ = average local transfer rate, $ML^2/t^3$ or $M/t$
$\overline{\psi}$ = average transfer rate for any time interval, $ML^2/t^3$ or $M/t$

**Subscripts**

$b$ = quantity evaluated at bulk stream
$l$ = infinite thickness of fluid elements
$0$ = quantity evaluated at interface
$\gamma$ = no surface resistance
$\infty$ = infinitely many capacitors

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# Studies of Singular Solutions in Dynamic Optimization: II. Optimal Singular Design of a Plug-Flow Tubular Reactor

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Although much attention has been given recently to the development of methods for the determination of the optimal control of a batch reactor or the best operating conditions for a tubular reactor, a number of difficulties and uncertainties still remain, especially when the analysis involves an exothermic reversible reaction. Several investigators (*1, 5, 8*) have been concerned with the establishment of the optimum temperature profile along a tubular reactor, from which the optimal control (heat removal rate) must then be obtained. Others (*2, 10* to *12*) have studied methods suitable for direct determination of the heat flux profile, some of which resulted in the possible appearance of singular control for a portion of the reactor length. The present authors have looked further into the occurrence of such singular problems during the application of the theory of optimal control and have developed an improved approach to the determination of the optimal heat transfer coefficient distribution along a tubular reactor (*6, 7*).

This paper presents the details of an application of the method of solution presented in the companion paper (*7*) to the optimal design of a tubular reactor. It is shown that, in general, if the reactor is "sufficiently long," the optimal

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