Chapter 1

NEW THEORETICAL APPROACHES TO CONTINUOUS PHASE MASS TRANSFER RATES
Chapter 3

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The present chapter is devoted to development of theoretical equations for continuous phase mass transfer rates during formation of fluid spheres and their travel when (i) the concentration change within the dispersed phase is comparatively insignificant, and (ii) when this change is large in magnitude. Two separate methods are used:

(A) A mass-balance integral method is employed for calculation of mass transfer rates during formation. This method is based on the integral techniques developed by Goodman (105) for transient non-linear heat transfer and useful in those cases in which exact methods are either not available or are cumbersome in application. Such situations may arise, for instance, when the exact model is basically and correctly represented by non-linear equations, but it is necessary to postulate assumptions which linearise them.

(B) The second method, which is employed for calculation of mass transfer rates during formation as well as travel is that of successive approximations. The method is based on theoretical tools developed by Walia (299) in similar cases, but incorporates some significant refinements which lead to more exact calculations.

For both methods it is further shown that some existing equations for mass transfer rates in the case of predominating
continuous phase resistance, e.g., the Baird equation (8) applicable to the formation period and the Higbie equation (132) applicable to the travel period, are special cases of general equations developed here. The nature of simplifying assumptions required to obtain these special cases indicates the range of their restricted applicability and, in particular, leads to the conclusion that assumption of negligible curvature of the surface of contact produces significant prediction inefficiencies. This becomes a serious limiting factor in prediction when the time of contact or diffusivity becomes large or the area of contact is small.

The two methods produce basically the same type of general equations which specify mass transfer efficiency during continuous phase mass transfer as a function of distribution coefficient $m$ (= solute concentration in continuous phase/solute concentration in dispersed phase at equilibrium) and dimensionless variable $D_0$ (= square root of time of contact and diffusivity, divided by diameter). Specifically for the formation period, for which both methods are employed, values of constants in the two functional relationships are somewhat different, but in predicting transfer efficiency the two relationships show only marginal variation. However, the second method is to be preferred because the general equation developed by it reduces exactly to the Baird equation which is theoretically acceptable under the assumption of a plane surface of contact equivalent to the curved area, while the general equation developed by the first method does so only approximately with $\sqrt{T}$ replaced by $\sqrt{3}$. 
Explicit assumptions

1. The general model is that of a fluid sphere growing in volume at a constant rate from an initial to a final radius. For the formation period, the initial radius is then zero; for the travel period, the initial and the final radii are identical, the constant volume growth rate being zero. In neither case does this assumption correspond exactly with reality, since the initial radius during formation depends on the nozzle size (and also on the size of the residual drop or bubble when one fluid sphere follows another); during formation as well as travel, transfer of solute produces some marginal volume changes.

2. Another simplifying assumption is that of a constant diffusion coefficient, a constant distribution ratio at equilibrium, and constant physical properties of the two phases despite time variant changes caused by the process of mass transfer.

3. During the formation stage, fluid sphere growth takes place by inflow of a solution of constant concentration.

4. The interfacial resistance is zero. Complications caused by uneven conditions at the surface due to distortion in shape, possible eruptive phenomena at the interface, etc., are ignored.

5. Dispersed phase resistance is assumed to be zero. This is equivalent to postulating a complete mixing within
the fluid sphere.

6. Except in the case of series type equations developed to take into account large concentration changes in the dispersed phase, it is assumed that the equilibrium concentration at the interface is constant at the initial level.

7. The continuous phase is assumed to be large in volume and its overall average concentration remains unaffected by transfer of comparatively small amounts of solute from the dispersed phase, by transfer in the reverse direction.

8. Growth of the sphere is assumed to be by even stretching of the entire surface, and the value of the mass transfer coefficient at any instant of time is assumed to be the same at all points of the surface. There is no tangential motion of the surface during growth. Such an assumption is not justifiable theoretically, nor should the effect of wake formation be ignored; it is postulated, however, that various inaccuracies introduced by such assumptions are positive as well as negative in magnitude and tend to cancel out one another.

9. During the travel period, it is assumed, following Highie (132), that the surface renews itself after travelling through a distance equal to the diameter of the sphere. While a surface renewal mechanism is not contrary to theoretical considerations, the time period
required for such renewal is more or less arbitrary in Higbie's approach and can be justified only to the extent of its correspondence with empirical reality.

10. The assumption that the boundary layer is not curved is discarded, but terms with exponent higher than 2 are neglected in the equation for radial velocity.

11. The differential equation applicable in the case when the area of contact has no curvature is:

\[ \frac{\partial C}{\partial \Theta} + \frac{\partial C}{\partial R} \cdot D \frac{\partial^2 C}{\partial R^2} = 0 \]  \hspace{1cm} (3.1)

When the curvature is to be taken into account, the differential equation is:

\[ \frac{\partial C}{\partial \Theta} + \frac{\partial C}{\partial R} \cdot D \frac{\partial^2 C}{\partial R^2} - \frac{2D}{R} \frac{\partial^2 C}{\partial R^2} = 0 \]  \hspace{1cm} (3.2)

In both cases, the influence of the motion of the fluid around the growing sphere is taken into consideration. The former equation is valid only when \( D_0 \ll 1 \); there is no such restriction on the latter equation.

With these assumptions, the final form of the equation for predicting transfer efficiency is of the type:

\[ \text{Transfer efficiency} = (\text{Constant})(m)(D_0) + (\text{Constant})(D_0)^2 \]  \hspace{1cm} (3.3)

provided that the concentration change within the dispersed phase is negligible. When the concentration change is large, this form gives rise to series type equations. Derivations from both
differential equations are described below.

\section{2 Integral mass-balance method: Formation period:}

\textbf{Constant driving force: Small }D_t \textbf{ values}

The basic approach here is that of postulating a penetration thickness, $\delta(t)$, such that for $R>\delta$ there is a negligible change in concentration; this concept is analogous to the boundary layer concept in the allied field of momentum transfer. The applicable differential equation (3.1 in the present case) is multiplied by $dR$ and integrated from $R_0$ to $R\rightarrow\infty$, where $r$ is the instantaneous radius of the fluid sphere. The concentration profile is redrawn to satisfy the resulting mass balance integral equation. The mass transfer equation is thereby only approximately satisfied. In the boundary layer theory, the corresponding analogous expression is provided by the momentum integral.

Without using the concept of the penetration thickness, equation (3.1) needs to be solved with the following initial and boundary conditions:

\begin{align*}
C &= C_0, \quad R < R < \infty, \quad t = 0 \quad (3.1 \text{ I}) \\
C &= C_0, \quad R = R, \quad t > 0 \quad (3.1 \text{ II}) \\
C &\rightarrow C_0, \quad R \rightarrow \infty, \quad t > 0 \quad (3.1 \text{ III})
\end{align*}

where (3.1 I) implies that the continuous phase is initially at a uniform concentration, (3.1 II) postulates equilibrium conditions at the interface, and (3.1 III) arises out of the assumed infinite extent of the continuous phase. No loss of generality is involved if $C_0$ is assumed to be zero, since it may easily be shown that the
transfer efficiency equation derived with this assumption is also valid for non-zero initial concentration in the continuous phase. (Transfer in the reverse direction may be shown to be governed by the same equation.) Hence the initial and boundary conditions for the case in which \( C_0 = 0 \) and the entire concentration change is assumed to occur within the boundary layer may be written as:

\[
\begin{align*}
C &= 0, & R < R < r + \delta, & \theta = 0 & (3.1 \text{ IV}) \\
C &= C_0, & R = r, & \theta > 0 & (3.1 \text{ V}) \\
C &= 0, & R = r + \delta, & \theta > 0 & (3.1 \text{ VI})
\end{align*}
\]

and since no solute penetrates beyond \( r^- \),

\[
\frac{\partial G}{\partial R} = 0, \quad R = r + \delta, \quad \theta > 0 \quad (3.1 \text{ VII})
\]

\( C_0 \) is constant if the concentration change within the dispersed phase is negligible.

Equation (3.1), it may be noted, is a simplified version of equation (3.2) and is obtained from the latter by omitting the term \((2D/R)(\partial C/\partial R)\). This is justified when the diffusion coefficient is small because, if \( x \) is given by the equation:

\[
R = r + x \quad (3.4)
\]

with the minimum value of \( x \) as zero and the maximum value as within the boundary layer, then with \( x \ll r \),

\[
\frac{\partial G}{\partial R} \approx \frac{\partial G}{\partial x} \quad (3.5)
\]

\[
\frac{1}{R} \frac{\partial G}{\partial R} \approx \frac{1}{r} \frac{\partial G}{\partial x} \quad (3.6)
\]
\[
\frac{\partial^2 c}{\partial x^2} = \frac{\partial^2 c}{\partial x^2} 
\]
(3.7)

Also

\[
\left\{ \frac{\partial^2 c}{\partial x^2} = \frac{c}{\partial x} \right\} \Rightarrow \left\{ \frac{1}{r} \frac{\partial c}{\partial x} = \frac{1}{r} \frac{c}{\delta} \right\} 
\]
(3.8)

Hence

\[
\frac{\partial^2 c}{\partial r^2} \Rightarrow \frac{2D}{r} \frac{\partial c}{\partial r} 
\]
(3.9)

and the term on the right-hand side of equation (3.9) may be neglected from equation (3.2) to produce equation (3.1) when \( D \) (and hence \( \delta \)) is small.

In the integral mass-balance method, we assume that, at any instant of concentration, \( c \) within the boundary layer may be represented in the form of a power-series function of \( r \). Thus:

\[
c = \sum_{n=0}^{\infty} \beta_n r^n 
\]
(3.10)

within the region \( r < R < r + \delta \). All \( \beta_n \) values are functions of \( \theta \). The concentration profile is nearly, though not exactly, parabolic. Therefore, we arbitrarily discard all \( \beta_n \) values for \( n > 2 \) as being very nearly 0, and obtain:

\[
c = \beta_0 + \beta_1 r + \beta_2 r^2 
\]
(3.11)

From the boundary condition (3.1 V),

\[
\beta_0 + \beta_1 r + \beta_2 r^2 = c_e 
\]
(3.12)

From the boundary condition (3.1 VI),

\[
\beta_0 + \beta_1 (r + \delta) + \beta_2 (r + \delta)^2 = 0 
\]
(3.13)
and from the boundary condition (3.1 VII),

\[ \beta_1 + 2 \beta_2 (r + \delta) = 0 \]  \hspace{1cm} (3.14)

Simultaneous solution of equations (3.12), (3.13) and (3.14) gives:

\[ \beta_0 = c_0 \left( \frac{r + \delta}{\delta} \right)^2 \]  \hspace{1cm} (3.15)

\[ \beta_1 = -2 c_0 \left( \frac{r + \delta}{\delta^2} \right) \]  \hspace{1cm} (3.16)

\[ \beta_2 = c_0 \frac{1}{\delta^2} \]  \hspace{1cm} (3.17)

Hence, from equation (3.11),

\[ C = c_0 \left\{ \left( \frac{r + \delta}{\delta} \right)^2 - 2 \left( \frac{r + \delta}{\delta^2} \right) R + \frac{1}{\delta^2} R^2 \right\} \]  \hspace{1cm} (3.18)

This value of \( C \) satisfies boundary conditions (3.1 V), (3.1 VI) and (3.1 VII). We require now the form of the function \( \delta(\theta) \) which satisfies equation (3.1) and initial condition (3.1 IV). To obtain this form, we multiply both sides of equation (3.1) by \( dR \) and integrate between \( R=R \) and \( R=r^+ \). Thus:

\[ \int_{r}^{r+\delta} \frac{dC}{d\theta} dR + \int_{R}^{r+\delta} V_R \frac{dC}{dR} dR - \int_{R}^{r+\delta} D \frac{d^2C}{dR^2} dR = 0 \]  \hspace{1cm} (3.19)

To evaluate the first term in equation (3.19), we note that

\[ \int_{r}^{r+\delta} \frac{C(R, \theta)}{d\theta} dR = \frac{d}{d\theta} \int_{r}^{r+\delta} C(R, \theta) dR - \int_{r}^{r+\delta} \frac{d(C(r+\delta, \theta))}{d\theta} \frac{C(r+\delta, \theta)}{d\theta} + \frac{dC}{d\theta} C(r, \theta) \]  \hspace{1cm} (3.20)
Further from the boundary conditions (3.1 V) and (3.1 VI),

\[ C(r, \theta) = 0 \quad (3.21) \]

\[ C(r + \delta, \theta) = 0 \quad (3.22) \]

and also noting that \( dr/d\theta \) signifies radical velocity at the periphery of the sphere, \( V_r \), and \( C(R, \theta) \) is given by equation (3.18), the first term in equation (3.19) equals:

\[ \int_{r}^{r+\delta} \frac{\partial C}{\partial R} dr = \frac{d}{d\theta} \int_{r}^{r+\delta} C \left( \frac{r+\delta - R}{\delta} \right)^2 dR \quad + \quad V_r C \quad (3.23) \]

It is easy to show that:

\[ \int_{r}^{r+\delta} \left( \frac{r+\delta - R}{\delta} \right)^2 dR = \frac{1}{3} \quad (3.24) \]

Hence

\[ \int_{r}^{r+\delta} \frac{\partial C}{\partial R} dr = \frac{1}{3} C \frac{d}{d\theta} \quad + \quad V_r C \quad (3.25) \]

To evaluate the second term in equation (3.19), we first write \( V_R \) in terms of \( V_r \):

\[ V_R = V_r \frac{L^2}{R^2} \quad (3.26) \]

and reduce this term to the form:

\[ \int_{r}^{r+\delta} V_R \frac{\partial C}{\partial R} dr = \frac{d}{dR} \int_{r}^{r+\delta} V_r \frac{L^2}{R^2} \frac{\partial C}{\partial R} dr \quad (3.27) \]
Next, since $C$ is given by equation (3.18),

$$\frac{\partial C}{\partial R} = -2 C_0 \left( \frac{r + \delta - R}{\delta^2} \right)$$  \hspace{1cm} (3.28)

it follows that

$$\int_{r}^{r+s} \frac{\partial C}{\partial R} \, dR = \frac{2 C_0 V_r r^2}{\delta^2} \int_{r}^{r+s} \left( \frac{1}{R^2} - \frac{F_{+\delta}}{R} \right) \, dR$$  \hspace{1cm} (3.29)

or

$$\int_{r}^{r+s} \frac{\partial C}{\partial R} \, dR = \frac{2 C_0 V_r r^2}{\delta^2} \left\{ \ln R + \frac{F_{+\delta}}{R} \right\}_{r}^{r+s}$$  \hspace{1cm} (3.30)

Obviously,

$$\left\{ \ln R + \frac{F_{+\delta}}{R} \right\}_{r}^{r+s} = \ln \left( 1 + \frac{\delta}{r} \right) - \frac{\delta}{r}$$  \hspace{1cm} (3.31)

The log term may be expanded in the usual series form:

$$\ln \left( 1 + \frac{\delta}{r} \right) = \frac{\delta}{r} - \frac{1}{2} \left( \frac{\delta}{r} \right)^2 + \frac{1}{3} \left( \frac{\delta}{r} \right)^3 - \frac{1}{4} \left( \frac{\delta}{r} \right)^4 + \ldots$$  \hspace{1cm} (3.32)

Substitution from equations (3.31) and (3.32) in equation (3.30) provides an expression for the second term of equation (3.19):

$$\int_{r}^{r+s} \frac{\partial C}{\partial R} \, dR = C_0 V_r \left\{ -1 + \frac{3}{2} \left( \delta/r \right) - \frac{1}{2} \left( \delta/r \right)^2 \ldots \right\}$$  \hspace{1cm} (3.33)

The third term in equation (3.19) is now to be evaluated. From equation (3.18):

$$\frac{\partial^2 C}{\partial R^2} = 2 C_0 \frac{1}{\delta^2}$$  \hspace{1cm} (3.34)
Hence
\[
\int_{r}^{r+d} \frac{2c}{R^2} \, dR = 2 \, D \, C_o \left( \frac{R}{\sqrt{2}} \right)^{r+d} = 2 \, D \, C_o \frac{1}{\delta} \quad (3.35)
\]
Substituting from equations (3.25), (3.33) and (3.35) in equation (3.19) after ignoring terms containing \((d/r)^2\), \((d/r)^3\) and terms with other high exponents, and dividing the resultant equation by \(1/3 \, C_o\), we get
\[
\frac{d\delta}{d\theta} + 2 \, v_r \, \frac{d}{d\theta} \frac{1}{\delta} = 0 \quad (3.36)
\]
The radius as a function of time is given by
\[
r = \left(\frac{3\mu}{4} \right)^{1/3} \, t^{1/3} = M^{1/3} \, t^{1/3} \quad (3.37)
\]
where \(\mu\) is the constant volume growth rate and \(M\) is hence a constant. Differentiating with respect to time, we get
\[
v_r = \frac{dr}{d\theta} = \frac{1}{\delta} \, M^{1/3} \, t^{-2/3} \quad (3.38)
\]
Therefore
\[
\frac{v_r}{r} = \frac{1}{3} \, \frac{1}{\theta} \quad (3.39)
\]
From equations (3.39) and (3.36),
\[
\frac{d\delta}{d\theta} + 2 \, \frac{d}{d\theta} \frac{1}{\delta} \frac{6\theta}{\delta} = 0 \quad (3.40)
\]
The solution of this equation which satisfies initial condition (3.1 IV) is
\[
\delta = \sqrt{\frac{36 D \theta}{7}} \tag{3.41}
\]

and the concentration profile in the boundary layer is hence given by

\[
C = \frac{7 C_e}{36 D \theta} \left( \frac{36 D \theta}{7} + r - R \right)^2 \tag{3.42}
\]

The expression for the concentration gradient at any point in the boundary layer is hence:

\[
\frac{\partial C}{\partial R} = - \frac{7 C_e}{18 D \theta} \left( \frac{36 D \theta}{7} + r - R \right) \tag{3.43}
\]

and at \( R = r \), that is, at the surface of the sphere it is:

\[
\left( \frac{\partial C}{\partial R} \right)_{R=r} = - C_e \sqrt{\frac{7}{9 D \theta}} \tag{3.44}
\]

The instantaneous rate of transfer at the surface, that is, from the sphere per unit time per unit area is given by:

\[
N = - D \left( \frac{\partial C}{\partial R} \right)_{R=r} = C_e \sqrt{\frac{7 D}{9 \theta}} \tag{3.45}
\]

The amount of solute transferred in time \( \theta_2 \) is:

\[
Q = \int_{0}^{\theta_2} 4\pi r^2 N \, d\theta
= \int_{0}^{\theta_2} 4\pi (M \theta)^{2/3} C_e \sqrt{\frac{7 D}{9 \theta}} \, d\theta
= \frac{8\pi C_e r^2}{7^{3/2}} (D \theta_2)^{3/2} \tag{3.46}
\]

and the fraction of equilibrium achieved after the drop has developed to its final radius \( r \) is:
\[ E_s = \frac{3 m_0}{4\pi r^3 c_s} \]
\[ = \frac{12 m_D}{r^7} \]  
\[ (3.47) \]

where \( D \) has been defined as \( \sqrt{D \theta_s/4 r^2} \).

1.1 Integral mass-balance method: Formation period:

Constant driving force; Large \( D \) values

The equation applicable in this case is the one in which curvature term also appears, that is equation (3.2). The required initial and boundary conditions are:

\[ C = 0, \quad R < R < \infty, \quad \theta = 0 \]  
\[ (3.2 \text{ I}) \]
\[ C = C_s, \quad R = r, \quad \theta > 0 \]  
\[ (3.2 \text{ II}) \]
\[ C \to 0, \quad R \to \infty, \quad \theta > 0 \]  
\[ (3.2 \text{ III}) \]

For the solution of this equation, the assumed concentration profile is:

\[ C = \frac{1}{R} \left( \beta_0 + \beta_1 R + \beta_2 R^2 \right) \]  
\[ (3.48) \]

where \( \beta_0, \beta_1 \) and \( \beta_2 \) are functions of \( \theta \). It may be noted that an extra \( R \) appears as a denominator in this equation as compared to the previous case. The justification for its inclusion lies in the fact that the steady-state concentration distribution for a spherical object is inversely proportion to \( R \).

Defining a boundary layer in the same way as before, the initial and boundary conditions to be satisfied are:
\[ C = 0, \quad R < R < r + \delta, \quad \theta = 0 \]  
\[ (3.2 \text{ IV}) \]
\[ C = C_e, \quad R = r, \quad \theta > 0 \]  
\[ (3.2 \text{ V}) \]
\[ C = 0, \quad R = r + \delta, \quad \theta > 0 \]  
\[ (3.2 \text{ VI}) \]

and with the requirement that no mass penetrates beyond \( R = r + \delta \),

\[ \frac{\partial C}{\partial R} = 0, \quad R = r + \delta, \quad \theta > 0 \]  
\[ (3.2 \text{ VII}) \]

Applying these conditions,

\[ \frac{1}{r} \left( \beta_0 + \beta_1 r + \beta_2 r^2 \right) = C_e \]  
\[ (3.49) \]

and

\[ \frac{1}{r+\delta} \left( \beta_0 + \beta_1 (r+\delta) + \beta_2 (r+\delta)^2 \right) = 0 \]  
\[ (3.50) \]

also

\[ -\frac{1}{(r+\delta)^2} \beta_0 + \beta_2 = 0 \]  
\[ (3.51) \]

Simultaneous solution of equations (3.49), (3.50) and (3.51) provides:

\[ \beta_0 = r \frac{C_e (r+\delta)^2}{\delta^2} \]  
\[ (3.52) \]

\[ \beta_1 = -2 r \frac{C_e (r+\delta)^2}{\delta^2} \]  
\[ (3.53) \]

\[ \beta_2 = r \frac{C_e}{\delta^2} \]  
\[ (3.54) \]

Therefore \( C \) is given by

\[ C = \frac{r C_e (r+\delta-R)^2}{R \delta^2} \]  
\[ (3.55) \]

If we define \( W = C R \), then we may write equation (3.2) in the manner:
$$\frac{\partial W}{\partial \theta} + V_R R \frac{\partial C}{\partial R} - D \frac{\partial^2 W}{\partial R^2} = 0 \quad (3.56)$$

Multiplying both sides of equation (3.56) by \(dR\) and integrating between \(r\) and \(r^+\), we get

$$\int_{r}^{r^+} \frac{\partial W}{\partial \theta} dR + \int_{r}^{r^+} V_R R \frac{\partial C}{\partial R} dR = \int_{r}^{r^+} D \frac{\partial^2 W}{\partial R^2} dR = 0 \quad (3.57)$$

For evaluation of the first term in equation (3.57), we note that

$$\int_{r}^{r^+} \frac{\partial W(r, \theta)}{\partial \theta} dR = \frac{d}{d\theta} \int_{r}^{r^+} W(r, \theta) dR = \frac{d}{d\theta} W(r^+, \theta) - W(r, \theta) \quad (3.58)$$

From boundary conditions (3.2 V) and (3.2 VI),

$$W(r, \theta) = r C,e \quad (3.59)$$

$$W(r^+, \theta) = 0 \quad (3.60)$$

The radial velocity \(V_r\) at the surface equals \(dr/d\theta\), and \(W(R, \theta)\) may be obtained from equation (3.55). Hence the first term in equation (3.57) equals:

$$\int_{r}^{r^+} \frac{\partial W}{\partial \theta} dR = \frac{d}{d\theta} \int_{r}^{r^+} r C,e \left(\frac{R}{r^+} - R\right)^2 dR + V_r r C,e \quad (3.61)$$

Writing the value of the integral on the right-hand side from equation (3.24),
\[
\int_{r}^{r+d} dR = \frac{1}{2} C_g \frac{d(r^2)}{dR} + v_r r_c
\]  

(3.62)

For the second term in equation (3.57), we first apply equation (3.26) for \( v_R \) to obtain:

\[
\int_{r}^{r+d} v_R R \frac{dC}{dR} dR = v_R r^2 \int_{r}^{r+d} \frac{1}{r} \frac{dC}{dR} dR
\]  

(3.63)

From equation (3.55)

\[
\frac{dC}{dR} = \frac{C_g}{d^2} \left\{ 1 - \frac{(r+d)^2}{R^2} \right\}
\]  

(3.64)

giving

\[
\int_{r}^{r+d} v_R R \frac{dC}{dR} dR = v_R \frac{r^3 C_g}{d^2} \int_{r}^{r+d} \left\{ \frac{1}{r} - \frac{(r+d)^2}{R^2} \right\} dR
\]

(3.65)

or

\[
\int_{r}^{r+d} v_R R \frac{dC}{dR} dR = v_R \frac{r^3 C_g}{d^2} \left\{ \ln R + \frac{(r+d)^2}{2 R^2} \right\}_{r}^{r+d}
\]  

(3.66)

Proceeding in the same manner in which equation (3.33) was derived the expression in the second term in equation (3.57) is hence evaluated as:

\[
\int_{r}^{r+d} v_R R \frac{dC}{dR} dR = C_g v_r r \left\{ -1 + \frac{1}{2} \left( \frac{r}{R} \right) - \frac{1}{4} \left( \frac{r}{R} \right)^2 + \ldots \right\}
\]  

(3.67)

In order to evaluate the third term in equation (3.57), we first write on the basis of equation (3.55),

\[
\frac{d^2 y}{dR^2} = 2 r C_g \frac{1}{d^2}
\]  

(3.68)
and then obtain:

\[ \int_{0}^{d} \frac{D}{dR^2} \frac{dR}{r} = 2 D \frac{C_e}{r} \left( \frac{R}{d^2} \right)^{F+d} \]

\[ = 2 D \frac{C_e}{r^2} \frac{1}{d} \]  (3.69)

With the completion of evaluation of all three terms, we substitute expressions from equation (3.62), (3.67) and (3.69) in equation (3.57), ignore terms containing \((d/r)^2\) and terms with other high exponents, and divide the resultant equation by \(1/3 \, C_e\). As a result,

\[ \frac{d}{d\theta} (r \, \varphi) + V_r \frac{d}{d\theta} - 6 D \frac{C}{d} = 0 \]  (3.70)

However,

\[ \frac{d}{d\theta} (r \, \varphi) = r \frac{d}{d\theta} + dV_r \]  (3.71)

Hence equation (3.69) may be written as:

\[ \frac{d}{d\theta} + 2 V_r \left( \frac{d}{r} \right) - \frac{6 D}{d} = 0 \]  (3.72)

Equation (3.72) is identical with equation (3.36) and hence an expression for \( \delta \) is provided by equation (3.41). Substituting this expression in equation (3.55), we obtain the concentration profile in the boundary layer:

\[ C = \frac{7 \frac{C_e}{36}}{D \, R \, 3} \left\{ \left( \frac{36 \, D \, G}{7} + R - R \right) \right\}^2 \]  (3.73)

For any point in the boundary layer, the concentration gradient is provided by the equation:
\[ \frac{\partial C}{\partial R} = \frac{7rC_0}{36D R^2 \theta} \left( R^2 - (r + \frac{75 D \theta}{2})^2 \right) \]  

(3.74)

At \( R = r \), that is, at the surface of the sphere, the concentration gradient is:

\[ \left\{ \frac{\partial C}{\partial R} \right\}_{R=r} = \frac{7rC_0}{36D r^2 \theta} \left( r^2 - (r + \frac{75 D \theta}{2})^2 \right) \]

\[ = -C_0 \sqrt{\frac{7}{9D \theta}} \left( 1 + \frac{9D \theta}{7r^2} \right) \]  

(3.75)

From this, it is easy to obtain the instantaneous rate of mass transfer from the sphere. The requisite equation is:

\[ N = -D \left\{ \frac{\partial C}{\partial R} \right\}_{R=r} = C_0 \sqrt{\frac{7D}{9 \theta}} \left( 1 + \frac{9D \theta}{7r^2} \right) \]  

(3.76)

Therefore, the total amount of mass transferred from the entire surface during \( \theta = 0 \) to \( \theta = \theta_2 \) may be calculated as before.

\[ Q = \int_{\theta=0}^{\theta_2} 4\pi r^2 N \, d\theta \]

\[ = \int_{\theta=0}^{\theta_2} 4\pi r^2 C_0 \sqrt{\frac{7D}{9 \theta}} \left( 1 + \frac{9D \theta}{7r^2} \right) \, d\theta \]

\[ = \int_{\theta=0}^{\theta_2} 4\pi M^{2/3} \theta^{2/3} C_0 \sqrt{\frac{7D}{9 \theta}} \left( 1 + \frac{9D \theta}{7M^{2/3} \theta^{2/3}} \right) \, d\theta \]  

(3.77)

or

\[ Q = \frac{2\pi}{7r} C_0 \sqrt{\frac{7}{9 \theta}} \left( D \theta \right)^{2/3} \left( 1 + \frac{3(D/4)^{1/3}}{\theta^{1/3}} \right) \]  

(3.78)

Hence the transfer efficiency is:

\[ E_2 = \frac{3M}{4\pi r^2 C_0} \]  

(3.79)
or \[ E_2 = \frac{12}{7} \alpha D_0 \left( 1 + \frac{2\gamma^3}{4} D_0 \right) \] (3.80)

Equation (3.80) shows that the effect of curvature of the boundary layer is to introduce at least one additional term in equation (3.47) which ignores this effect. (More additional terms are necessary if some simplifying assumptions, viz. omission of \( \beta_3^\prime \), \( \beta_4 \), etc., in equations (3.11) and (3.48), and omission of \((\delta / r)^2\), \((\delta / r)^3\), etc., in derivation of equations (3.35) and (3.70), are not made.) This additional term becomes insignificant if \( D_0 < 1 \), that is, when the diffusivity is not large, or the time of formation (\( \theta_2 \)) is very small, or the final radius is quite large.

3-4 The method of successive approximations: Constant driving force

Equation (3.2) is now solved by the method of successive approximations. To show that the results obtained by this method are valid, we assume that the initial radius of the sphere is \( r_0 \) and that it grows from this size to its final radius at a constant volumetric growth rate, \( u \). It will be proved that when \( u = 0 \), the result obtained in this manner for a non-growing sphere is identical with the corresponding equation derived by an exact method. The method will also be applied to the case of a forming sphere by setting \( r_0 = 0 \) and \( u = 0 \).

We first rewrite equation (3.2) and the requisite boundary conditions.

\[ \frac{\partial C}{\partial t} + \nu \frac{\partial C}{\partial R} = D \left( \frac{\partial^2 C}{\partial R^2} + \frac{2}{R} \frac{\partial C}{\partial R} \right) \] (3.2)
\[ C = 0, \quad R < R < \infty, \quad \theta = 0 \quad (3.2 \text{ I}) \]
\[ C = C_0, \quad R = r, \quad \theta > 0 \quad (3.2 \text{ II}) \]
\[ C \rightarrow 0, \quad R \rightarrow \infty, \quad \theta > 0 \quad (3.2 \text{ III}) \]

Since \( u \), the volumetric growth rate, is constant, \( M \) defined by the following equation is also a constant:

\[ M = \frac{2y}{4\pi} \quad (3.81) \]

It is easily shown that

\[ r = (M \theta + r_o^3)^{1/3} \quad (3.82) \]

\[ V_r = \frac{dr}{d\theta} = \frac{M}{3r^2} \quad (3.83) \]

Assuming a boundary layer of thickness \( \delta \) as before, we define distance \( x \) as

\[ R = r + x \quad (3.84) \]

with the minimum value of \( x \) as 0 and the maximum value as \( \delta \). The radial velocity \( V_r \) is given by:

\[ V_r = V_r (\frac{r + x}{r})^{-2} \]

\[ = \frac{M}{3r^2} - \frac{2Mx}{3r^3} + \frac{Mx^2}{r^4} - \ldots \quad (3.85) \]

we neglect higher terms than the last one in this equation, since \( x \ll r \).

The order of analysis technique is now applied for simplification of equation (3.2). At a distance \( R \), the concentration is a function of \( x \) and \( \theta \) only.
Hence,

\[ \left( \frac{\partial C}{\partial \theta} \right)_R = \left( \frac{\partial C}{\partial x} \right)_x \left( \frac{\partial x}{\partial \theta} \right) \]  
(3.86)

Also at a distance R, from equation (3.84),

\[ \frac{\partial x}{\partial \theta} = \frac{\partial r}{\partial \theta} \]  
(3.87)

From equations (3.83), (3.86) and (3.87),

\[ \left( \frac{\partial C}{\partial \theta} \right)_R = \left( \frac{\partial C}{\partial \theta} \right)_x - \frac{M}{3} \frac{\partial C}{\partial x} \]  
(3.88)

when \( x \) is small as compared to \( r \),

\[ \frac{\partial C}{\partial R} \approx \frac{\partial C}{\partial x} \]  
(3.89)

\[ \frac{1}{R} \frac{\partial C}{\partial R} \approx \frac{1}{r} \frac{\partial C}{\partial x} \]  
(3.90)

\[ \frac{\partial^2 C}{\partial R^2} = \frac{\partial^2 C}{\partial x^2} \]  
(3.91)

These values are substituted in equation (3.2), in which partial derivatives are in terms of variable \( R \), to produce the following equation in which partial derivatives are in terms of variable \( x \).

\[ \frac{\partial C}{\partial \theta} - \left( \frac{2 M x}{3 r^2} - \frac{M x^2}{3 r^4} + \frac{2 D}{r} \right) \frac{\partial C}{\partial x} = D \frac{\partial^2 C}{\partial x^2} \]  
(3.92)

In this equation, subscripts are dropped since no ambiguity is likely to be caused by their absence.

Equation (3.92) is now solved by the method of successive approximations. We write its solution as:
\[ C = C_1 + C_2 \] (3.93)

where \( C_1 \) is the solution of

\[ \frac{\partial C_1}{\partial \theta} - \left( \frac{2M}{3r} \right) \frac{\partial C_1}{\partial x} - D \frac{\partial^2 C_1}{\partial x^2} = \] (3.94)

and \( C_2 \) is a correction for the first approximation \( C_1 \) and is a solution of the equation:

\[ \frac{\partial C_2}{\partial \theta} - \left( \frac{2M}{3r} \right) \frac{\partial C_2}{\partial x} - D \frac{\partial^2 C_2}{\partial x^2} = \left( \frac{2D - M}{r} \frac{x^2}{r^4} \right) \frac{\partial C_1}{\partial x} \] (3.95)

To obtain a solution of equation (3.94) for \( C_1 \), we convert it into the standard form of diffusion equation by introducing two variables \( \varphi (x, \theta) \) and \( \tau (\theta) \) which are independently variable. We define \( \varphi \) and \( \tau \) as follows:

\[ \varphi = x r^2 = x (M \theta + r_0)^{3/2} \] (3.96)

\[ \tau = \frac{3D}{7M} \left( (M \theta + r_0)^{7/3} - r_0 \right) = \kappa (r^7 - r_0) \] (3.97)

where \( \kappa \) is a constant defined by

\[ \kappa = \frac{3D}{7M} \] (3.98)

By differentiating \( \tau \) with respect to \( \theta \) and simplifying,

\[ \frac{\partial \tau}{\partial \theta} = D r^4 \] (3.99)

Also it is easy to see that

\[ \left\{ \frac{\partial C_1}{\partial \theta} \right\}_x = \left\{ \frac{\partial C_1}{\partial \theta} \right\}_\varphi + 2 \frac{M}{3r} \left\{ \frac{\partial C_1}{\partial \varphi} \right\}_\theta \] (3.100)
\[
\frac{\partial C_4}{\partial x} = r^2 \frac{\partial^2 C_4}{\partial \phi^2} \tag{3.101}
\]
\[
\frac{\partial^2 C_4}{\partial x^2} = r^4 \frac{\partial^2 C_4}{\partial \phi^2} \tag{3.102}
\]

On substituting these in equation (3.94), which is in terms of variables \(x\) and \(\phi\), this equation is converted into the following one which is in terms of variables \(\phi\) and \(T\):

\[
\frac{\partial C_4}{\partial T} = \frac{\partial^2 C_4}{\partial \phi^2} \tag{3.103}
\]

(The subscripts have been dropped) The initial and boundary conditions for equation (3.103) are written as:

\[
\begin{align*}
C_4 &= 0, & \phi > 0, & T = 0 & \tag{3.103 I} \\
C_4 &= C_0, & \phi = 0, & T > 0 & \tag{3.103 II} \\
C_4 &\to 0, & 0 \to \infty, & T > 0 & \tag{3.103 III}
\end{align*}
\]

The solution of this equation presents no difficulty and is:

\[
C_4 = C_0 \text{erfc} \left( \frac{\phi}{2\sqrt{T}} \right) \tag{3.104}
\]

To solve equation (3.95) for \(C_2\), we write equations similar to (3.99) to (3.102) used for \(C_4\), and obtain:

\[
\frac{\partial C_2}{\partial T} - \frac{\partial^2 C_2}{\partial \phi^2} = \left( \frac{2}{r^2} - \frac{3x^2}{7r^5} \right) \frac{\partial C_1}{\partial \phi} \tag{3.105}
\]

We know, from equation (3.104), that

\[
\frac{\partial C_1}{\partial \phi} = C_0 \frac{e^{-x^2/4}}{\sqrt{\pi T}} \tag{3.106}
\]
Combining equations (3.96), (3.105) and (3.106), we get

\[
\frac{\partial c_2}{\partial \tau} - \frac{3 c_2}{3 \phi^2} = \frac{2 c}{r^2} \left\{ \frac{3 \phi^2}{14 \sigma^2} - 1 \right\} \sigma^2/4 \tau
\]  \hspace{1cm} (3.107)

The initial and boundary conditions for this equation are:

\begin{align*}
  c_2 &= 0, \quad \phi > 0, \quad \tau = 0 \quad (3.107 \text{ I}) \\
  c_2 &= 0, \quad \phi = 0, \quad \tau > 0 \quad (3.107 \text{ II}) \\
  c_2 &\to 0, \quad \phi \to \infty, \quad \tau > 0 \quad (3.107 \text{ III})
\end{align*}

The solution of this equation for \( c_2 \) which conforms to these conditions is obtained by finding a particular integral \( (c_3) \) and its complementary function \( (c_4) \), such that

\[
c = c_1 + c_2 = c_1 + (c_3 + c_4)
\]  \hspace{1cm} (3.108)

At this stage, it is more convenient to treat the two cases of formation stage and travel stage separately.

3-5 Formation period: Small change in Dispersed-phase concentration

Expressions for \( c_3 \) and \( c_4 \) will first be found for the case of a sphere which grows from an initial zero radius to its final size at a volumetric growth rate, \( u \). In this situation, \( r_0 = 0 \), and \( u > 0 \). From equations (3.96) and (3.97),

\[
\phi = x r^2 = x (M \theta)^{2/3}
\]  \hspace{1cm} (3.109)

\[
\sigma = r^7 = \frac{3}{7 M} (M \theta)^{7/3}
\]  \hspace{1cm} (3.110)

\( c_4 \) is defined by equation (3.104). Differential equation (3.107) for \( c_2 \) becomes:
\[ \frac{\delta^2 c_3}{\delta \varphi^2} - \frac{\delta^2 c_3}{\delta \varphi^2} = \frac{2 C_0}{\pi} \varphi^{3/7} e^{-\frac{\varphi^2}{4T}} \left( \frac{3}{14} \varphi^2 - \frac{27}{14} T - \frac{13}{14} \right) \]  

(3.111)

The particular integral \( (C_3) \) is then found by representing it in a series form:

\[ C_3 = \sum_{k} \sum_{n} a_{k,n} \frac{\varphi^n}{\tau^{k+b}} e^{-\frac{\varphi^2}{4T}} \]  

(3.112)

where \( b \) is a constant to which an arbitrary value may be arranged for a simple solution. By differentiating with respect to \( \varphi \) and \( T \),

\[ \frac{\delta c_3}{\delta T} - \frac{\delta^2 c_3}{\delta \varphi^2} = \sum_{k} \sum_{n} a_{k,n} \frac{\varphi^{n-2}}{\tau^{k+b+1}} e^{-\frac{\varphi^2}{4T}} \left[ \frac{\varphi^n}{\tau^{k+b+1}} - n(n-1) \frac{\varphi^{n-2}}{\tau^{k+b+1}} \right] \]  

(3.113)

For finding \( C_3 \), we equate right-hand sides of equations (3.111) and (3.113). In this case, we find that a simple solution results if \( b = -1/14 \). Substituting this value, and equating coefficients of terms containing \( -13/14 \), we get

\[ \frac{4}{7} a_{0,0} - 2 a_{1,2} = -\frac{2 C_0}{\pi} \varphi^{3/7} \]  

(3.114)

and equating coefficients of terms containing \( \varphi^2 - 27/14 \),

\[ \frac{11}{7} a_{1,2} - 12 a_{2,4} = \frac{3}{7} \frac{C_0}{\pi} \varphi^{3/7} \]  

(3.115)

For all other terms,

\[ (\frac{11}{7} - k + n) a_{k-1,n} = (n+1)(n+2) a_{k,n+2} \]  

(3.116)

Assigning an arbitrary value of zero to \( a_{2,4} \) gives:
$a_{0,0} = -\frac{28}{11^{1/2}} c_0 c^{3/7}$ \hspace{1cm} (3.117)

$a_{1,2} = \frac{3}{11^{1/2}} c_0 c^{3/7}$ \hspace{1cm} (3.118)

Other coefficients are all equated to zero. Substitution of these values in equation (3.112) provides:

$c_3 = \frac{1}{10} c_0 c^{3/7} \left\{ \frac{3}{11} \varphi^2 \tau^{-13/14} - \frac{28}{11} \tau^{1/14} \right\} e^{-\varphi^2/4\tau}$ \hspace{1cm} (3.119)

This equation may be shown to satisfy the following initial and boundary conditions:

$c_3 = 0, \quad \varphi > 0, \quad \tau = 0$ \hspace{1cm} (3.119 I)

$c_3 = -\frac{28}{11} c_0 c^{3/7} 1/14, \quad \varphi = 0, \quad \tau > 0$ \hspace{1cm} (3.119 II)

$c_3 \rightarrow 0, \quad \varphi \rightarrow \infty, \quad \tau > 0$ \hspace{1cm} (3.119 III)

A comparison with the conditions of $C_2$ shows that the complementary function $C_4$ should conform to the following initial and boundary conditions:

$c_4 = 0, \quad \varphi > 0, \quad \tau = 0$ \hspace{1cm} (3.120 I)

$c_4 = \frac{28}{11^{1/2}} c_0 c^{3/7} \tau^{-1/14}, \quad \varphi = 0, \quad \tau > 0$ \hspace{1cm} (3.120 II)

$c_4 \rightarrow 0, \quad \varphi \rightarrow \infty, \quad \tau > 0$ \hspace{1cm} (3.120 III)

The diffusion equation gives, for $C_4 = 1, \varphi = 0$, the expression for $C_4$ as follows:

$\frac{2}{11^{1/2}} \text{erfc} \left\{ \frac{\tau}{2^{1/2}} \right\}$
With the boundary condition as in equation (3.120 II),

Duhamel's theorem leads to the result:

\[ c_4 = \frac{56}{11\pi} C e^{3/7 - 1/14} \int_\varphi^{2\pi} \left( 1 - \frac{\varphi^2}{47\eta^2} \right)^{1/14} e^{-\eta^2} d\eta \]

(3.120)

Since, by equation (3.108), \( C \) equals the sum of \( C_1, C_2 \) and 

\( C_4 \), and the values of these are provided by equations (3.104),

(3.119) and (3.120), it is possible to write:

\[ c = C e \text{erfc} \left( \frac{\varphi}{2\pi} \right) \frac{1}{\sqrt{\pi}} C e^{3/7 \varphi^2 - 13/14 - 28/11} \]

\[ \int_1^{1/14} e^{-\varphi^2/47} + \frac{56}{11} C e^{3/7 - 1/14} \int_\varphi^{2\pi} \left( 1 - \frac{\varphi^2}{47\eta^2} \right)^{1/14} e^{-\eta^2} d\eta \]

whence

\[ \left\{ \frac{3C}{\partial \varphi} \right\} = - \frac{C}{\sqrt{\pi} \eta} \left( 1 + \frac{28}{11\pi} \Delta_1 \right) \alpha^{3/7 - 1/14} \]

(3.122)

in which

\[ \Delta_1 = \left\{ -2\varphi \frac{\partial}{\partial \varphi} \right\} \int_0^{2\pi} (1 - \frac{\varphi^2}{47\eta^2})^{1/14} e^{-\eta^2} d\eta \bigg|_{\varphi = 0} \]

\[ = \left\{ \int_0^{\Delta_1} \frac{dG}{28 \alpha^{13/14} (\alpha + 1)^{4/7}} \right\} \bigg|_{G = 0} \]

(3.123)

in which

\[ G = \frac{\Delta_1}{\varphi^2} - \frac{1}{4} \]

(3.124)

The value of the integral in equation (3.123) is determined 
numerically as 1.077 by Simpson's rule as well as Gauss formula.
From equation (3.109),
\[
\left( \frac{\partial C}{\partial x} \right)_{x=0} = (M \theta)^{2/3} \left( \frac{\partial C}{\partial \theta} \right)_{\theta=0} = (3.125)
\]

Using equations (3.98), (3.109) and (3.110) we have
\[
\left( \frac{\partial C}{\partial x} \right)_{x=0} = -\sqrt{\frac{7}{3 \pi D \theta}} \cdot C_0 \left\{ 1 + \frac{1.735}{1/2} \frac{D^{1/2} \theta^{1/6}}{M^{1/3}} \right\} = \left(3.126\right)
\]
The instantaneous rate of mass transfer per unit time per unit area is, hence,
\[
N = -D \left( \frac{\partial C}{\partial x} \right)_{x=0} = \sqrt{\frac{7 D}{3 \pi \theta}} \cdot C_0 \left\{ 1 + \frac{4 \pi}{7} \frac{D^{1/2} \theta^{1/6}}{M^{1/3}} \right\} = \left(3.127\right)
\]
The amount of solute transferred from the entire surface during time \( \theta = 0 \) to \( \theta = \theta_f \) is given by
\[
Q = \int_{0}^{\theta_f} 4\pi r^2 N \, d\theta = \int_{0}^{\theta_f} 4\pi (M \theta)^{2/3} N \, d\theta = \left(3.128\right)
\]
and the fraction of equilibrium achieved after the drop has developed to its final radius \( r \) is:
\[
E_f = \frac{3 \pi Q}{4 \pi r^3 C_0} = \frac{\frac{36 \pi}{121} \frac{M}{D} \left(1 + 1.772 \frac{D}{D_0} \right)}{\left(3.129\right)}
\]
where \( D_0 \) equals \( \sqrt{D \theta_f/4 \, r^2} \). It may be noted that the coefficient of the second term in equation (3.129) equals \( \pi \) numerically.
This term represents the effect of sphericity. On neglecting this term, the equation becomes identical with the Ilkovic-Baird
equation which assumes that the spherical surface may be approximated by a plane of contact of equal area. If we addi-
tionally divide the remaining expression by $\sqrt{7/3}$, which factor represents the influence of motion of fluid around the growing sphere, we obtain the Licht-Pansing equation. Also, the equation is valid only if $E_2$ is not very high, as otherwise $C_e$ cannot be treated as being substantially constant.

2-5 Travel period: Small change in Dispersed-phase concentration

Expressions for $C_2$ and $C_4$ will now be found for a non-
growing sphere in which $r_0$ is the constant radius of the sphere and $u=M=0$. For this case, from equation (3.96) and (3.97).

$$\phi = x r_0^2$$  \hfill (3.150)

$$T = \frac{L}{M} \left( \frac{3D}{M} \left( (M + r_0^3)^{7/3} - r_0^7 \right) \right)$$

$$= D \theta r_0^4$$  \hfill (3.151)

$C_4$ is defined by equation (3.104). Differential equation (3.107) for $C_2$ becomes:

$$\frac{\partial C_2}{\partial \theta} - \frac{2}{\partial \phi^2} C_2 - \frac{2}{r_0^3 \sqrt{\pi T}} C_e e^{-\phi^2/4T}$$  \hfill (3.152)

since $\phi \to \infty$ as $M \to 0$. The initial and boundary conditions for $C_2$ remain unaltered.

The particular integral ($C_2$) is again found by expressing $C_2$ in the series form given in equation (3.112) and writing differential equation (3.113). A simple solution results in this case if $b = -\frac{1}{4}$. A comparison of coefficients becomes possible if
the right-hand side of this equation and equation (3.132) are equated. Thus, with coefficients of terms containing $r^{-3}$,

$$a_{0,0} - 2a_{1,2} = \frac{2C_3}{r_0^3 \sqrt{\pi}}$$  \hspace{1cm} (3.133)

Since a complementary function is later to be found, it is permissible to assign arbitrary values to as many of these coefficients as is convenient. We assign an arbitrary value of zero to all coefficients except $a_{0,0}$, and obtain:

$$a_{0,0} = -\frac{2C_3}{r_0^3 \sqrt{\pi}}$$  \hspace{1cm} (3.134)

Hence $C_3$ is evaluated as:

$$C_3 = -\frac{2C_3}{r_0^3 \sqrt{\pi}} \tau^3 e^{-p^2/4\tau}$$  \hspace{1cm} (3.135)

This equation for $C_3$ satisfies the following initial and boundary conditions:

1. $C_3 = 0$, $\varphi > 0$, $\tau = 0$ \hspace{1cm} (3.135 I)
2. $C_3 = -\frac{2C_3}{r_0^3 \sqrt{\pi}} \tau^3$, $\varphi = 0$, $\tau > 0$ \hspace{1cm} (3.135 II)
3. $C_3 \to 0$, $\varphi \to \infty$, $\tau > 0$ \hspace{1cm} (3.135 III)

A comparison with conditions for equation (3.107) shows that the complementary function $C_4$ should satisfy the following conditions:

1. $C_4 = 0$, $\varphi > 0$, $\tau = 0$ \hspace{1cm} (3.136 I)
2. $C_4 = \frac{2C_3}{r_0^3 \sqrt{\pi}} \tau^3$, $\varphi = 0$, $\tau > 0$ \hspace{1cm} (3.136 II)
3. $C_4 \to 0$, $\varphi \to \infty$, $\tau > 0$ \hspace{1cm} (3.136 III)
If the boundary condition at \( \varphi = 0 \) had been \( C_4 = 1 \), the solution of the diffusion equation for \( C_4 \) would have been:

\[
\frac{2}{\sqrt{\pi}} \text{erfc} \left( \frac{\varphi}{2\sqrt{T}} \right)
\]

With boundary condition given by equation (3.136 II), we obtain by Duhamel's theorem,

\[
C_4 = \frac{4}{\pi r_0^3} \frac{1}{\sqrt{2\pi T}} \int_{\varphi/2\sqrt{T}}^{\infty} \left( 1 - \frac{\varphi^2}{4T\eta^2} \right)^{3/2} e^{-\eta^2} \, d\eta \quad (3.136)
\]

Separate solutions for \( C_4 \), \( C_3 \) and \( C_4 \) have now been obtained and are available in equations (3.104), (3.135) and (3.136), respectively. Hence by equation (3.105),

\[
C = C_0 \text{erfc} \left( \frac{\varphi}{2\sqrt{T}} \right) - \frac{2}{\pi} \frac{C_0}{r_0^3} \frac{\sqrt{T}}{2\pi} \int_{\varphi/2\sqrt{T}}^{\infty} \left( 1 - \frac{\varphi^2}{4T\eta^2} \right)^{3/2} e^{-\eta^2} \, d\eta
\]

we define \( C \) by the equation:

\[
C = \frac{\eta^2}{\varphi^2} - \frac{1}{4}
\]

and \( \Lambda_2 \) by the equation:

\[
\Lambda_2 = \left\{ \frac{-8}{3\pi} \right\} \int_0^{\infty} \left( 1 - \frac{\varphi^2}{4T\eta^2} \right)^{3/2} e^{-\eta^2} \, d\eta \quad (3.136)
\]

\[
= \left\{ \int_0^{\infty} \frac{d\varphi}{\varphi^2(\varphi^2+1)} \right\} \quad (3.139)
\]

The value of \( \Lambda_2 \) can be obtained by numerical integration using Simpson's rule and the Gauss formula and equals 6.283. We
differentiate equation (3.137) with respect to \( \phi \) and, after setting \( \phi = 0 \), find:

\[
\left\{ \frac{\partial C}{\partial \phi} \right\}_{\phi = 0} = - \frac{C_0}{\sqrt{\pi \tau}} \left[ 1 + \frac{2}{r_o^2} \sqrt{\frac{\tau}{\pi}} \right]
\]

(3.139)

Substituting the values of \( \phi \) and \( \tau \) in terms of \( x \) and \( \theta \) from equations (3.109) and (3.110), and the numerical value of \( \Delta_2 \), we get the instantaneous rate of mass transfer per unit time per unit area:

\[
N = -D \left\{ \frac{\partial C}{\partial x} \right\}_{x=0} = \frac{D C_0}{\sqrt{\pi} \Gamma D} \left[ 1 + 3.1415 \frac{D \Gamma}{\pi r_o^2} \right]
\]

(3.140)

The amount of solute transferred in time \( \theta_2 \) is given by

\[
Q = \int_{0}^{\theta_2} 4\pi r_o^2 N \, d\theta
\]

(3.141)

and the fraction of solute transferred in this period by

\[
E_t = \frac{3 \pi Q}{4\pi r_o^2 C_0}
\]

(3.142)

\[
= \frac{12 \pi}{\sqrt{\pi}} D_0 (1 + 1.772 D_0)
\]

(3.143)

The coefficient of the second \( D_0 \) term is again found to equal \( \frac{1}{\sqrt{\pi}} \) numerically. If this term is neglected, the resultant expression for \( E_t \) is identical with the one obtained by assuming the surface area of the sphere to be adequately represented by a plane surface of equal area.

The same results may be obtained by an exact method.

Defining \( W=RC \) equation (3.2) is written as:

\[
\frac{\partial W}{\partial \theta} = D \frac{\partial^2 W}{\partial R^2}
\]

(3.144)
with the initial and boundary conditions:

\[ W = 0, \quad \text{for } R > r_0, \quad \theta = 0 \quad (3.144 \text{ I}) \]
\[ W = r_0 C_e, \quad R = r_0, \quad \theta > 0 \quad (3.144 \text{ II}) \]
\[ W \to 0, \quad R \to \infty, \quad \theta > 0 \quad (3.144 \text{ III}) \]

The solution of equation (3.144) which satisfies these boundary conditions may be obtained by the method of Laplace transforms. Taking transforms of both sides and applying the initial condition, we get

\[ p \tilde{W} = D \frac{\partial^2 \tilde{W}}{\partial R^2} \quad (3.145) \]

This equation is satisfied by the following solution which remains finite as \( R \to \infty \),

\[ \tilde{W} = A e^{-qR} \quad (3.146) \]

where

\[ q = \sqrt{\frac{B}{D}} \quad (3.147) \]

and \( A \) is a constant the value of which may be determined from the boundary condition at \( R = r_0 \). Applying this condition,

\[ A = \frac{r_0 C_e}{p} e^{-q/r_0} \quad (3.148) \]

Hence

\[ \tilde{W} = \frac{1}{p} r_0 C_e e^{-q(R-r_0)} \quad (3.149) \]

which gives

\[ W = r_0 C_e \text{erfc} \left( \frac{R-r_0}{2\sqrt{D\theta}} \right) \quad (3.150) \]

and
\[ C = \frac{r GC}{R} \text{erfc} \frac{R-r_0}{2\sqrt{D \theta}} \quad (3.151) \]

From equation (3.151), the value of \( N \) is obtained as:

\[ N = -D \left\{ \frac{\partial C}{\partial R} \right\}_{R=r} = \frac{D C_0}{\sqrt{\pi D \theta}} \left\{ 1 + \frac{1}{r_0^2} \right\} \quad (3.152) \]

This equation is identical with equation (3.140) derived by the method of successive approximations, thus showing that this method provides results which have a very good correspondence with those obtained from exact methods.

\section*{3-7 Formation period: Variable driving force: Small \( D_0 \) values}

For small values of \( D_0 \), an equation of the type given by (3.80) or (3.129) reduces to

\[ E_x = \gamma m D_0 \quad (3.153) \]

where \( \gamma \) is a constant. Computationally, this equation can give values of \( E_x > 1 \), since \( m \) and \( D_0 \) have no upper limits. The reason for this error lies in assuming that \( C_s \) is constant. Actually, the process of mass transfer results in decreasing the concentration; the larger the decrease, the larger is the discrepancy in the calculated value of \( E_x \) which should theoretically lie within the limits \( 0 \leq E_x \leq 1 \).

This problem can be resolved by developing a series type equation for such situations in the manner described on pages 85 to 90 in Chapter 2A. Applied to the present case, this method provides,

\[ E_x = m D_0 - \frac{7(\gamma m D_0)^2}{(8)} + \frac{49(\gamma m D_0)^2}{(8)(9)} - \ldots \quad (3.154) \]

Equation (3.154) observes the required lower and upper limits.
for $E_x$ and is theoretically derived from mass balance considerations. It is pertinent to note that equation (3.154) is subject to all limitations arising out of assumptions made in derivation of equation (3.153) except the assumption regarding the constancy of $C_e$.

In practice, the usual procedure is to employ a logarithmic mean driving force, instead of a constant driving force, for calculation of average mass transfer coefficients. It can be demonstrated that this procedure is equivalent to assuming that

$$E_x = 1 - \exp(-\gamma m D_0)$$

$$= \gamma m D_0 - \frac{\left(\gamma m D_0\right)^2}{2} + \frac{\left(\gamma m D_0\right)^3}{6} - \ldots \quad (3.155)$$

$E_x$ obtained in this manner also falls within the required theoretical range. Though this value of $E_x$ represents a considerable improvement on that obtained from equation (3.153), it is only an approximation while equation (3.154) gives an exact value. The difference in calculated values is small when $E_x = 0.10$, but becomes progressively larger when higher transfer efficiencies are involved.

3-3 Formation period: Variable driving force: Large $D_0$ values

For large $D_0$, the second term in equation (3.80) or (3.143) is not negligible and may even exceed the first term. For this case, a series type equation for variable driving force may be derived in the following fashion: If the concentration in the dispersed phase is distinguished from the continuous phase concentration by using a prime as a superscript, then $C_e = m C'$ for $\theta > 0$ and $C_e = m C_0'$ for $\theta = 0$, where the subscript 0
denotes the constant concentration in the solution which flows at a constant volume rate \( u \) through the nozzle. Since we assume complete mixing within the dispersed phase, concentration throughout this phase is \( C' \) at \( \theta > 0 \). Let a change equal to \( dC' \) occur in time interval \( d\theta \) which elapses after concentration \( C' \) has been attained in time \( \theta \) from the start of the formation period. The change in amount of solute within the dispersed phase in time interval \( d\theta \) is \( d(u C' \theta) \). During the same time interval, solute inflow through the nozzle is \( u C'_0 d\theta \) and outflow into the continuous phase is \( d\theta \). Hence

\[
d(u C' \theta) = u C'_0 d\theta - d\theta
\]

(3.156)

\( N \), the instantaneous rate of mass transfer per unit time per unit area is provided by equation (3.76) by the mass-integral method and by (3.127) by the second method. From the latter,

\[
d\theta = 4\pi r^2 N d\theta
\]

\[
= 4 \sqrt{\frac{2\gamma}{M}} \quad C'_{\theta}^{2/3} \quad D^{1/2} \quad \theta^{1/6} \left\{ 1 + \frac{4}{\gamma} M^{-1/3} D^{1/2} \theta^{1/6} \right\}
\]

(3.157)

because \( r^3 = M \theta \). By substitution and simplification and using the relationships \( N = 3/4 \mu / \pi \), \( D_0 = 1/2 M^{-1/3} D^{1/2} \theta^{1/6} \), we obtain

\[
C'_0 = C' + u \frac{dC'}{d\theta} + \sqrt{\frac{2\gamma}{\pi}} \quad \mu D_0 \left\{ 1 + \frac{8\pi}{\gamma} D_0 \right\} C'
\]

(3.158)

Equation (3.158) is an ordinary differential equation of first order, and its solution may be obtained by expressing \( E_x \) as a polynomial function of the form:

\[
E_x = \frac{C'_0 - C'}{C'_0} = \sum_{k=0}^{\infty} \sum_{n=0}^{\infty} b_{k,n} \quad M^{k+n} \quad D_0^{k+2n}
\]

(3.159)
Through a single comparison of coefficients it may be shown that

\[ b_{k,n} = 2^n \left( \frac{84}{31} \right)^{3(k+n)} a_{k,n} \]

where

\[ a_{k,n} = \begin{cases} 0 & \text{for } k \text{ or } n < 0 \\ 1 & \text{for } k \text{ and } n = 0 \\ - \frac{a_{k,n-1} + a_{k-1,n}}{1 + \frac{k}{6} + \frac{n}{3}} & \text{otherwise} \end{cases} \]  

(3.160)

We have thus:

\[ E_t = \sum_{k=0}^{\infty} \sum_{n=0}^{\infty} a_{k,n} 2^n \left( \frac{84}{31} \right)^{3(k+n)} m^{k+n} \pi^{k+2n} \]  

(3.161)

on the basis of equation (3.127) derived by the method of successive approximations. A similar equation with somewhat different values of constants may be obtained from equation (3.76) which is derived from the mass–integral method and is analogous to equation (3.127).

3-9 Travel stage: Variable driving force

Equation (3.143) was derived for a constant driving force causing mass transfer to or from a non-growing stationary fluid sphere. We now postulate that the sphere is not stationary in the continuous phase but is in movement. Following Higbie (132), it is assumed that the surface is renewed every time the sphere travels through a distance equal to one diameter. In this simplified picture, one may hold the sphere as moving in i discrete steps, each step lasting for time t.
Let \( L \) = total distance travelled by the sphere
\( v \) = velocity of motion
\( \Theta \) = total time of travel = \( L/v \)
\( t \) = time of travel in each step = \( 2\pi/v \)
\( i \) = number of steps of duration \( t \) each = \( \Theta/t = L/2\pi \).

A comparatively simple but approximate solution is obtained if we assume that during the small time interval of each step the concentration at the surface is constant. Thus at the end of the first step equation (3.143) gives:

\[
1 - E_{t1} = 1 - \frac{12m}{\sqrt{\pi}} D_G (1 + \sqrt{\pi} D_G) \tag{3.162}
\]

where \( D_G \) is now redefined in terms of \( t \) as:

\[
D_G = \sqrt{\frac{D}{4 \pi r^2}} = \sqrt{\frac{\Theta}{\mu}} \sqrt{\frac{2\pi r V}{\text{Sc.Re}}} = \sqrt{\frac{1}{\text{Sc.Re}}} = \frac{1}{\sqrt{\text{Pe}}} \tag{3.163}
\]

At the end of the \( i \) th step, it is easily shown that

\[
1 - E_{ti} = \left(1 - \frac{12m}{\sqrt{\pi}} D_G (1 + \sqrt{\pi} D_G)\right)^i
= \left(1 - \frac{12m}{\sqrt{\pi} \text{Pe}} \left(1 + \sqrt{\frac{\pi}{\text{Pe}}} \right)\right)^i \tag{3.164}
\]

The average mass transfer coefficient over time \( \Theta \), per unit time per unit area is:

\[
k_o = \frac{F}{3 \pi \Theta} \left(1 - \frac{12m}{\sqrt{\pi} \text{Pe}} \left(1 + \sqrt{\frac{\pi}{\text{Pe}}} \right)\right) \tag{3.165}
\]

and

\[
Sh = \frac{\text{Pe}}{6 \pi i} \left(1 - \frac{12m}{\sqrt{\pi} \text{Pe}} \left(1 + \sqrt{\frac{\pi}{\text{Pe}}} \right)\right)^i \tag{3.166}
\]

A further approximation at the expense of accuracy may be
obtained by assuming that $n \ll 1$ or $Pe \gg 1$ for any reasonably large size of sphere. Then

$$\left(1 - \frac{12 \ln (1 + \sqrt{\frac{D}{Pe}})}{\ln Pe} \right)^i - \frac{12 \ln (1 + \sqrt{\frac{D}{Pe}})}{\sqrt{\ln Pe}} \right) \right)$$

(3.167)

and

$$Sh = 2\sqrt{\frac{D Pe}{\pi}} = 2 + 1.1284Sc^{\frac{1}{2}}Re^{\frac{3}{4}}$$

(3.168)

Equation (3.168) gives

$$k_c = \frac{D}{r} + 2\sqrt{\frac{D}{\pi t}}$$

(3.169)

which is strictly valid when $i=1$. Equation (3.169) thus assumes equality between $t$ and $\theta$. Error in calculation increases progressively as $i$ increases in value. In any case, even the parent equation (3.166) is not accurate enough as it is assumed in its derivation that concentration at the surface is constant during each step.

If the latter assumption is discarded, it is possible to obtain a solution of the diffusion equation (3.144) in terms of error functions. Proceeding as before and applying the initial condition and the requirement that the solution should remain finite as $x \to \infty$, we obtain:

$$w = A e^{-qx}, \quad x > 0$$

(3.170)

where the value of $A$ depends on the boundary condition of the interface. By material balance at the interface between the amount of material transferred towards the continuous phase, that is,

$$-4\pi r^2 \frac{DC}{dx} \bigg|_{x=0}$$

and the amount of material lost from the dispersed phase, that is,
\[-\frac{4}{3} \pi r^3 \frac{\partial C'}{\partial t} \text{ which equals } \frac{4}{3} \pi r^3 \left\{ \frac{\partial C}{\partial t} \right\}_{x=0}\]

we obtain the boundary condition written in terms of \( \dot{w} = R(C-C_0) \),

\[
\frac{\partial W}{\partial t} - \frac{3 m D}{r} \left\{ \frac{\partial W}{\partial x} - \frac{W}{r} \right\}, \quad x = 0
\]

(3.171)

and Laplace transforms of both sides:

\[
p\ddot{W} + (W e^{-\alpha t})_{t=0} = \frac{3 m D}{r} \left\{ \frac{\partial \bar{W}}{\partial x} - \frac{\bar{W}}{r} \right\}, \quad x = 0
\]

(3.172)

We note that the initial condition here is:

\[
\bar{W} = r \left( m C_0' - C_0 \right), \quad x = 0
\]

(3.173)

Where \( C_0' \) is the initial concentration in the dispersed phase at the beginning of a step. Hence,

\[
p\ddot{W} = r \left( m C_0' - C_0 \right) = \frac{3 m D}{r} \left\{ \frac{\partial \bar{W}}{\partial x} - \frac{\bar{W}}{r} \right\}, \quad x = 0
\]

(3.174)

The discontinuity at the interface disappears after the start of the diffusion process and hence equation (3.170) becomes valid for \( x > 0 \). Applying the boundary condition specified in equation (3.174) to this equation, we obtain:

\[
\bar{W} = \frac{r (m C_0' - C_0) e^{-\alpha x}}{D (q^2 + 3MQ/r + 3r^2)}
\]

(3.175)

The inverse transform is given by the expression:

\[
W = \frac{m C_0' - C_0}{\sqrt{9m^2 - 12m}} \left\{ \frac{h_2 \exp(h_2 x + Dt \ h_2^2) \ \erfc\left(\frac{x}{2 \sqrt{Dt}}\right) + h_2 \sqrt{Dt}}{2 \sqrt{Dt}} \right. \\
- \frac{h_4 \exp(h_4 x + Dt \ h_4^2) \ \erfc\left(\frac{x}{2 \sqrt{Dt}}\right) + h_4 \sqrt{Dt}}{2 \sqrt{Dt}} \right\}
\]

(3.176)

where \(-h_4\) and \(-h_2\) are the two roots of the equation:
\[ q^2 + \frac{2m}{r} q + \frac{2m}{r^2} = 0 \]  
(3.177)

At the interface, that is, at \( x=0 \)

\[
w = \frac{mc_g - c}{(9m^2 - 12m)} \left\{ \frac{h_2 \exp(Dt h_2^2) \text{erfc}(h_2/\sqrt{Dt})}{(9m^2 - 12m)} 
- \frac{h_1 \exp(Dt h_1^2) \text{erfc}(h_1/\sqrt{Dt})}{(9m^2 - 12m)} \right\} \tag{3.178}
\]

Noting that \( D_0 = 1/\sqrt{Pe} \), if the time considered is that of one step, we get

\[
1 - E_{t_1} = \frac{Pe}{2/(9m^2 - 12m)} \left\{ e^{z_2^2 \text{ierfc} z_2} - e^{z_1^2 \text{ierfc} z_1} \right\} \tag{3.179}
\]

in which

\[
z_1 = \frac{3m}{(9m^2 - 12m)} \tag{3.180}
\]

\[
z_2 = \frac{3m}{(9m^2 - 12m)} \tag{3.181}
\]

In \( i \) steps, the final equilibrium reached will be:

\[
E_{ti} = 1 - e^{-iF} \tag{3.182}
\]

where

\[
F(\text{Pe}, \text{m}) = -\ln \left\{ \frac{1}{z_1 - z_2} \left( e^{z_2^2 \text{ierfc} z_2} - e^{z_1^2 \text{ierfc} z_1} \right) \right\} \tag{3.183}
\]

\[
= -\ln \left\{ \sum_{n=0}^{\infty} \frac{(-1)^n}{\Gamma(3n+1)} \frac{z_1^{n+1} - z_2^{n+1}}{z_1 - z_2} \right\} \tag{3.184}
\]

If \( m < 4/3 \), \( z_1 \) and \( z_2 \) are conjugate complex numbers, but equation
(3.184) is still valid. It can be easily shown that the values of $F$ obtained are not complex even in such a case. A summation formula for $F$, convenient for computational purposes, is provided by

$$F = -\ln\left\{1 + \sum_{n=1}^{\infty} \frac{(\frac{3}{4}m)^n}{\sqrt{Pe} \Gamma(n+1)} \left\{ \sum_{k=1}^{k \leq (m+1)} n+1 \right\} c_{2k-1} \right\}$$

(3.185)

This formula is particularly useful when $m < 4/3$, while the alternative expression (3.184) is easier to compute when $m > 4/3$.

Table (3.1) shows some values of $F$ at certain levels of $m$ and $Pe$. A set of values of $Sh_0$ as a function of $m$ and $Pe$, with $i=1$, given in Table (3.2). If we take only two terms in the series expansion of $F$, we get

$$E_{ti} = \frac{12a}{\sqrt{\pi} Pe} \quad (3.186)$$

and

$$k_0 = 2\frac{D}{\sqrt{\pi} \xi} \quad (3.187)$$

This mass transfer coefficient is applicable when $Pe \gg 1$ or $m \ll 1$.

Equation (3.182) shows the form of dependence of $E_i$ and hence of $Sh_0$, on $i$, $m$ and $Pe$. The presence of $i$ in this equation permits only a graphical comparison with the empirical and semi-empirical equations listed in Tables (C-1) and (C-3) in Appendix. However, it is possible to show that many of these equations are special cases of equation (3.182) and are valid only for particular systems in restricted ranges of variables.
## TABLE 3.1

Dependence of $F$ on $m$ and $Pe$

<table>
<thead>
<tr>
<th>$m$</th>
<th>Value of $F \times 10^3$ at various $Pe$ levels</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$10^2$</td>
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<tr>
<td>0.01</td>
<td>7.954</td>
</tr>
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<td>606.3</td>
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<tr>
<td>Value of ( F \times 10^3 ) at various ( P_e ) levels</td>
<td></td>
</tr>
<tr>
<td>--------------------------------------------------</td>
<td></td>
</tr>
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<td>( m )</td>
<td>( 10^2 )</td>
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TABLE 3.2
Dependence of Continuous Phase $Sh$ on $m$ and $Pe$
For instance, for $i=1$, $m=21.3$, the new equation gives:

$$Sh = 126 + 1.13 Pe^{3} - \ldots$$

and if $Sc = 340$, the same result is given by the empirical equation:

$$Sh = 126 + 1.8 Re^{3} Sc^{0.42} - \ldots$$

This may be seen to be identical with equation (III.7) of Garner et al. (86) in Table (C-3). Similarly, for $i=1$, $m=30$, and $Sc = 1090$, the new equation provides the empirical expression:

$$Sh = 178 + 3.62 Re^{1/2} Sc^{1/3} - \ldots$$

which is identical with equation (III.23) of Thorsen and Terjesen (283) in the same Table. Empirical equations of this type are hence applicable when specific systems and certain variable ranges are used; they cannot be used for other systems, or even for the same systems in a different range of variables.

Equations of the type:

$$Sh = 2 + a Re^{b} Sc^{c}$$

are also empirical in nature and result primarily from an attempt to force the regression line through $Sh_{Pe=0} = 2$. Such is the case in equations of Froesling (80), Kinzer and Gunn (166), Ranz (235), Ranz and Marshall (235), Maxwell and Storrow (207), Hsu (139), Garner and Buckling (98), Garner and Tayeban (99), Griffith (106), Steinberger and Treybal (275), Yuge (321), Hughmark (143) and others. The usual value of 1/3 for the exponent of $Sc$ is, of course, based on the consideration that the ratio of the thickness of the velocity boundary layer to that of the concentration boundary layer equals $Sc^{1/3}$. 
At large values of $Pe$, the initial coefficient becomes almost insignificant as compared to the next term, and hence many empirical equations omit this coefficient. Examples of this form are found in Williams (311), Gamson, Thodos and Hougten (84), Wilke and Hougten (310), Maises and Sherwood (216), Insebo (149), Cary (41), Xenakis et al. (316), Garner and Keye (91), Hau and Sage (140), Steele and Geankoplis (274), Linton and Sherwood (198), Pasternak and Gauvin (225), Skelland and Cornish (267), Williamson et al. (312), etc.

A more serious error arises when a linear extrapolation of $Sh$ to $(Sh)_{Pe=0}$ is attempted in those cases in which experimental data have been obtained at large values of $Pe$. For example, assuming that data have been obtained in the range of $Pe$ from 10,000 to 50,000, linear extrapolation gives $(Sh)_{Pe=0} = 54$ when $m > 1$.

This may be compared with the value 44 obtained by Garner and Grafton (87) and 50 obtained by Garner and Tawabian (86) for approximately this range of $Pe$. It is evident that such equations have a negligible potential for extension to other systems and for describing data in different ranges of variables. For $i=1$, the new equation gives:

$$Sh = \frac{2}{\sqrt{\pi}} Pe^{3/2} - 2(3m-1) + \frac{16}{\sqrt{\pi}} \frac{m(m-2)}{3} Pe^{-3} - 12 m + (9 m^2 - 9 m + 1) Pe^{-1} + \frac{1152}{5 \sqrt{\pi}} m^2 (3m^2 - 4m + 1) Pe^{-3/2} - \ldots$$ (3.188)

For $m=0.01$, this simplifies to:

$$Sh = 1.1284 Pe^{3/2} + 1.94 - 0.1778 Pe^{-3} - 0.1093 Pe^{-1} + 0.01248 Pe^{-3/2} - \ldots$$ (3.189)

For $m=1$
\[ Sh = 1.1284 \, Pe^{\frac{1}{3}} - 4 + 9.027 \, Pe^{-\frac{1}{3}} - 12 \, Pe^{-1} + 0 - \ldots \]  
(3.190)

For \( m = 100 \),
\[ Sh = 1.1284 \, Pe^{\frac{1}{3}} - 599 + 269006 \, Pe^{-\frac{1}{3}} - 106921200 \, Pe^{-1} + 38478155190 \, Pe^{-3/2} - \ldots \]  
(3.191)

These equations show two characteristics which are worthy of note. Firstly, the dependence of \( Sh \) on \( m \) varies strongly with the absolute value of \( m \). When \( Pe \) is of the order of 10,000 and a system is chosen such that the equilibrium concentration in the continuous phase is about 1/100 of the concentration in the dispersed phase, the expected \( Sh_0 \) is 599 which is only 2 percent more than the expected \( Sh_0 \) for \( m = 1 \). If the two solvents are interchanged such that the continuous phase solvent becomes the dispersed phase solvent and vice versa, the expected \( Sh_0 \) is 122, that is, nearly 65 percent below the expected \( Sh_0 \) for \( m = 1 \). Thus, any attempt to correlate \( Sh \) data for different systems is apt to be unsuccessful unless the effect of \( m \) is considered, especially for systems in which the distribution coefficients are more favourable for the continuous phase. Secondly, for \( i = 1 \), moderate values of \( m \) and large values of \( Pe \), the equation reduces to the theoretical equation developed by Boussinesq (22) and used by Ruckenstein (246) and others:

\[ Sh = 1.1284 \, Pe^{\frac{1}{3}} \]

Many mass transfer equations have been developed by an analogy with heat transfer in which \( m = 1 \); however, use of such equations when \( m \gg 1 \), as in the case in many mass transfer situations, leads to erroneous results. Introduction of empirical correction
factors based on $\mu_0, \mu_d, \lambda_0$, etc., may sometimes result in a fortuitous concordance of experimental results with certain empirical forms, but a more suitable way is to recognise the role of the distribution coefficients in altering the values of coefficients of second and subsequent terms. The same remarks hold true when the value of coefficient of $\sqrt{\text{Pe}}$ is empirically altered, as in the equations used by Heertjes et al. (123), Garner and Tayeban (99), Griffith (106), Ward et al. (302), Bentwich et al. (16), Veronilin et al. (297), Chah and Tobias (44), Winnikow (313), Hirose and Moo-Young (133) and some other investigators; or when the dependence of $\text{Sh}$ and $\text{Pe}$ is sought to be expressed in the form:

$$\text{Sh} = a + b \text{Pe} + c \text{Pe}^2 + \ldots$$

as by Ward et al. (302), or in the form

$$\text{Sh} = a + b \text{Re}^c \text{Sc}^d + e \text{Re}^f \text{Sc}^g + \ldots$$

used by Kramers (170), Hughmark (144), Lee and Barrow (187), Estep and Smith (72) and others.

It may be concluded that the general equation (3.182) has a wide-ranging scope and, in fact, includes most empirical equations reported in literature as special cases for particular systems in specified variable ranges. Outside these ranges and for other systems, these are liable to produce erroneous results.