Model of the Effect of Chemical Reaction on Bulk-Phase Concentrations

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Mass transfer accompanied by an irreversible or reversible chemical reaction is a common process of high importance in chemical industry (Danckwerts, 1970; Shah, 1979; Charpentier 1981). Although there has been a significant amount of research on this topic, no general mathematical model is available which can be used to calculate bulk-phase concentration in the entire finite reaction rate regime including the effect of the surface renewal frequency in case of both irreversible and reversible reactions. For this purpose, the mass transfer rate of absorbed and product component through the interface boundary into the bulk absorbent phase (J_δ, J_E) has to be given (Nagy et al., 1982, 1983, 1986). J_δ and J_E give the mass transfer term of the differential mass balance equation of the bulk absorbent phase for the absorbed and product components, respectively, while the mass transfer rate at the interface (J) provides that of the gas phase for the absorbed component.

There is an essential difference between the role of irreversible and reversible reactions. In the case of irreversible reaction ($K \rightarrow \infty$), the absorbed material can be reacted completely in the boundary layer formed at the interface even at a relatively low reaction rate ($Ha > 3$) (Danckwerts, 1970; Charpentier, 1981). Using this "fast" reaction regime ($Ha > 3$, $J_\delta \rightarrow 0$ and $a_2^0 \rightarrow 0$) component concentrations were investigated by Mhaskar (1974) and, Shah and Paraskos (1975), as well as by Szeri et al. (1976). In the "slow" reaction rate regime ($Ha < 0.3$ and $J \approx J_\delta \approx J^0$), the effect of first-order irreversible reactions was studied by Pavlica and Olson (1970) by applying the axial dispersion model. Nagy et al. (1982, 1983) have given a general mathematical model using the film-theory for the case of irreversible first-order reactions. They have shown that the results obtained by this model for the "intermediate" rate regime ($0.3 < Ha < 3$) can differ strongly from that obtained by the Pavlica and Olson model for the "slow" rate regime.

The influence of reversible chemical reaction on bulk-phase concentrations has received much less attention in literature. According to Danckwerts (1970), it is because of the general acceptance that reacting components are in chemical equilibrium in the bulk phase. It is obvious that, in a fairly low reaction rate regime, this supposition is not fulfilled neither in the bulk phase nor in the interface boundary. The latter is justified by the fact that the absorption rate, accompanied by reversible reactions, is given in three different ways in literature. The components are:

1. in chemical equilibrium at every point of the interface boundary (Olander, 1960);
2. in equilibrium only at the inner edge of the interface boundary (Danckwerts, 1970. p. 123.); or
3. not necessarily in chemical equilibrium even in the bulk phase (Secor and Beutler, 1967). The question is how strongly the reaction rate necessary to achieve chemical equilibrium in the bulk phase depends on different mass transfer and hydrodynamic conditions.

Theoretical Studies

The mass transfer rates of absorbed components at the interface (J) are determined on the basis of mass transfer theories already published (Danckwerts, 1970; Huang and Kuo, 1963, 1965). The value of J_δ can be calculated from the concentration gradient at $x = \delta_2$ in the case of the film theory (Danckwerts, 1970, p. 163). As for unsteady-state mass transfer (e.g., film-penetration theory), J_δ can be given only if the amount of material reacted in the interface boundary ($\bar{\psi}$) is known. The average values of J, J_δ and ψ ($\bar{J}$, $\bar{J}_\delta$, $\bar{\psi}$) can be obtained by the Laplace transform of the concentration (Huang and Kuo, 1965; Danckwerts, 1970). For example, the average value of J_δ for reversible reaction $[Q(x, t) = k_1(a_2(x, t) - e_2(x, t)/K)]$ can be expressed as follows (Nagy, 1986):

$$\bar{J}_\delta = \bar{J} - \bar{\psi}\delta_2 = \bar{J} - \int_0^{\delta_2} k_1 s[\tilde{a}_2(x, s) - \tilde{e}_2(x, s)/K]\, dx \quad (1)$$

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$\bar{\mathbf{J}}_\delta$ *for irreversible first-order reaction:* $\mathbf{Q} = \mathscr{k}_1\mathbf{a}_2$

Applying the film-penetration theory $\bar{\psi}\delta_2$ was determined from the Laplace transform of the concentration (Huang and Kuo, 1963), and $\bar{J}_\delta$ was expressed as follows (Nagy, 1986):

$$\bar{J}_\delta = k_\delta(a_2^* - \alpha_0 a_2^0) \tag{2}$$

where

$$k_\delta = \sqrt{\frac{\mathscr{k}_1 D_{2A}}{1 + \frac{\tanh^2 \xi}{M^2}}\left[\frac{\frac{\tanh^2 \xi}{M^2}}{\tanh(\lambda_0 \xi)} + \frac{1}{\sinh(\lambda_0 \xi)}\right]} \tag{3}$$

$$\alpha_0 = \frac{\frac{1}{1 + \frac{\tanh^2 \xi}{M^2}}\left[\left(\frac{\tanh^4 \xi}{M^4} + 1\right)\cosh(\lambda_0 \xi) + \frac{2\tanh^2 \xi}{M^2}\right] - \xi^2 \frac{\sinh(\lambda_0 \xi)}{\lambda_0 \xi}}{\frac{\tanh^2 \xi}{M^2}\cosh(\lambda_0 \xi) + 1} \tag{4}$$

and

$$\lambda_0 = \sqrt{1 + \frac{M^2}{\tanh^2 \xi}} \tag{5}$$

The value of $\bar{J}_\delta$ can be obtained as a limiting case for the surface renewal theory ($\delta_2 \rightarrow \infty$) and for the film theory ($s \rightarrow 0$).

Values of $\bar{\mathbf{J}}_\delta$ *and* $\bar{\mathbf{J}}_E$ *for reversible reaction:* $\mathbf{Q} = \mathscr{k}_1(\mathbf{a}_2 - \mathbf{e}_2/\mathbf{K})$

In the case of reversible reactions, the mass flows of both the absorbing component A and the product E to the bulk phase (J_δ and J_E) should be given. As for steady-state mass transfer (film-theory), the transfer rate of the absorbing component is the following:

$$J_\delta = \bar{J}_\delta = -D_{2A}\left[\frac{da_2}{dx}\right]_{x=\delta_2}$$

$$= k_\delta\left\{a_2^* - \frac{1}{1+P}\left[\alpha_1\left(a_2^0 - \frac{e_2^0}{K}\right) + Pa_2^0 + \frac{e_2^0}{K}\right]\right\} \tag{6}$$

where

$$k_\delta = k_2^0 \frac{P + \frac{1}{\cosh R}}{P + \frac{\tanh R}{R}} \tag{7}$$

$$\alpha_1 = \frac{P\left(\frac{1}{\cosh R} + R\tanh R\right) + 1}{\frac{1}{\cosh R} + P} \tag{8}$$

The mass transfer rate of component E can be calculated from the equation $J_E = J - J_\delta$.

In the case of unsteady-state mass transfer (film-penetration theory), highly complicated multiterm equations can be obtained, as shown in the Supplementary Materials.

Mass balance equations of bulk phases

The use of the axial dispersion model is quite common. In the case of irreversible, first-order reactions, J is the mass transfer term of the gas phase (Phase 1) and J_δ is that of the absorbent phase (Phase 2). The actual volume of bulk liquid should be reduced by the volume of the interface boundary. (This is of importance when the volume of the interface boundary cannot be neglected.) The linear differential equation system obtained can be solved analytically (Nagy, 1986). In the case of reversible, first-order reactions, two mass-balance equations are necessary for the bulk absorbent phase. Considering the mass transfer resistance of Phase 1 (k_1^0), the following is derived:

$$\frac{1}{Pe_2}\frac{dA_2}{dY^2} - \frac{dA_2}{dY} + N_A\left\{A_1 - \frac{1}{\tau_1}\left[\tau_2(A_2 - E_2) + \tau_3 A_2 + E_2\right]\right\} - Da(A_2 - E_2) = 0 \tag{9}$$

$$\frac{1}{Pe_2}\frac{d^2E_2}{dY^2} - \frac{dE_2}{dY} + \frac{N_E}{K}\left\{A_1 - \frac{1}{\tau_1}\left[\tau_4(A_2 - E_2) + \tau_3 A_2 + E_2\right]\right\} + \frac{Da}{K}(A_2 - E_2) = 0 \tag{10}$$

where

$$N_\delta = \frac{k_{22}\mathcal{A}hH}{\hat{\epsilon}_2 U_2} \tag{11a}$$

$$N_E = \frac{k_E\mathcal{A}hH}{\hat{\epsilon}_2 U_2} \tag{11b}$$

$$Da = \frac{\mathscr{k}_1 h}{U_2} \tag{11c}$$

When the film-theory is used, $\tau_1 = 1 + P$, $\tau_2 = \alpha_2$ (Eq. 12a), $\tau_3 = P$ and $\tau_4 = \alpha_3$ (Eq. 12b) (For film-penetration theory, see the Supplementary Materials.)

$$\alpha_2 = \frac{\alpha_1 - \frac{k_{12}}{k_1^0\cosh R}}{1 - \frac{k_{12}}{k_1^0}} \tag{12a}$$

$$\alpha_3 = \frac{\dfrac{k_{12}}{\cosh R} - k_{22}\alpha_2}{k_{12} - k_{22}} \tag{12b}$$

The boundary conditions used for the solution of differential equations (Eqs. 9 and 10) are as follows:

$$\left.\begin{array}{l} A_2 - \dfrac{1}{Pe_2}\dfrac{dA_2}{dY} = 0; \quad E_2 - \dfrac{1}{Pe_2}\dfrac{dE_2}{dY} = 0 \quad \text{when } Y = 0 \\ \text{and} \\ \qquad \dfrac{dA_2}{dY} = \dfrac{dE_2}{dY} = 0 \quad \text{when } Y = 1 \end{array}\right\} \tag{13}$$

The differential equations (Eqs. 9 and 10) have to be completed with the balance equations of the absorbed component for Phase 1. The differential equations system of the three equations obtained cannot be solved analytically. In order to have an analytical solution, A_1 is assumed to be constant in the case of reversible reaction. Thus, the values of only A_2 and E_2 are investigated. This simplification can be allowed mainly because the E_2/A_2 ratio is of importance, and this simplification does not change the essential quantitative features of this ratio.

Results and Discussion

The results obtained from the model presented are compared to those calculated from models taken from literature.

Mass transfer accompanied by irreversible reactions

As for unsteady-state mass transfer, the value of $\bar{J}_\delta$ as the function of the reaction rate is influenced strongly by the surface renewal frequency and the film thickness. This effect can be represented by the function of $\bar{J}_\delta/\bar{J}$, or a_2^0/a_2^* vs. $\epsilon_2/\mathcal{A}\delta_2$, as shown in the Supplementary Material for perfectly-mixed phases. (For film theory, see, e.g., Trambouze, 1981.)

In the case of perfectly-mixed phases ($Pe_1 = Pe_2 \rightarrow 0$), the results obtained by Pavlica-Olson (1970) and Mhaskar (1974) are compared to the presented model in Figure 1. These models differ from each other by the mass transfer term. Pavlica and Olson apply the physical mass transfer in both mass balance equations $J^0 = k_{12}^0(a_1^0 - Ha_2^0)$, while in Mhaskar's model $a_2^0 = 0$ and $J = k_{12}a_1^0$, where $k_{12} = 1/(1/k_1^0 + H/\sqrt{(k_2^0)^2 + k_1 D_{2A}})$. Absorbent-phase concentrations obtained from the model of Pavlica-Olson for "slow" and "intermediate" reaction rate regimes are practically the same as those obtained from the authors, as shown in the right upper corner of Figure 1. This is to be expected, since the volume of the interface boundary was negligible compared to that of the bulk phase (Nagy, 1986). It should be noted that, if the volume of the interface boundary is comparable with the bulk-phase volume, the difference between the two models can be very large. This difference increases with the decrease of $\epsilon_2/\mathcal{A}\delta_2$. The change in the concentration of the gas phase (Figure 1) clearly shows the limitations of the model of Pavlica-Olson, as well as that of Mhaskar. The model proposed by the authors can be used throughout the entire reaction rate regime. It can be seen that the so-called intermediate reaction rate regime (indicated by the symbol □), for which the other two models do not give correct results, is relatively narrow.

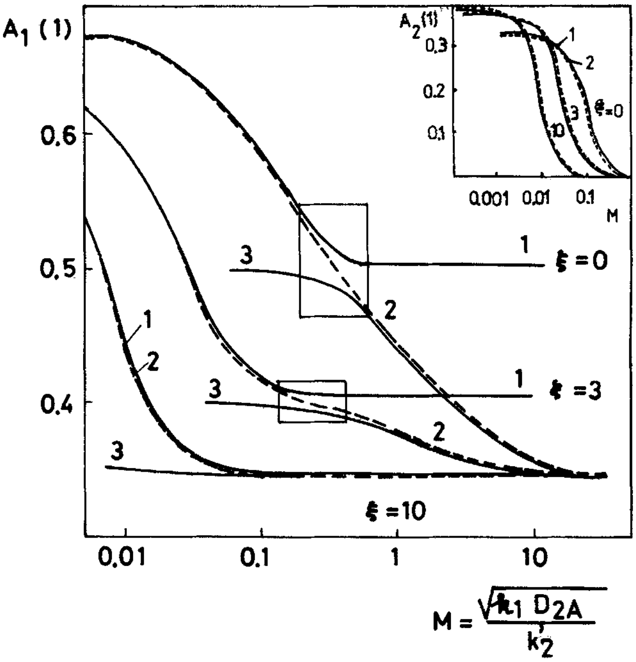

Figure 1. Comparison of the mathematical models: irreversible reaction.

$Pe_1 = Pe_2 \rightarrow 0$; $N_1^0 = 1$; $U_1H/U_2 = 1$, $k_1^0H/k_2^0 = 1$; □, "intermediate" rate regime
1 = Pavlica-Olson's model (1970)
2 = proposed model
3 = Mhaskar's model (1974)

Mass transfer accompanied by reversible reactions

It is generally accepted that the components are in chemical equilibrium ($A_2 = E_2$) in the bulk of Phase 2 (Danckwerts, 1970). In this case, the following axial dispersion model can be given for component A of the liquid phase:

$$\frac{1}{Pe_2}\frac{d^2A_2}{dY^2} - \frac{dA_2}{dY} + \frac{k_{12}\mathcal{A}hH}{\hat{\epsilon}_2U_2(1 + K)}(A_1 - A_2) = 0 \tag{14}$$

It is obvious that the components cannot be in chemical equilibrium at fairly low reaction rates. This reaction rate regime can be determined definitely by the equation system (Eqs. 9–10). For this purpose, the concentration of Phase 1 was supposed to be constant, and thus $A_1 = 1$ was chosen in the calculations. An analytical solution of equation system (Eqs. 9–10) with boundary conditions (Eq. 13) is possible (Nagy, 1986). Using the film theory ($\xi = 0$), concentrations calculated by means of the two models are compared in Figure 2 for a practically perfectly-mixed phase ($Pe_2 = 0.01$). The value of $\mathcal{A}$ was changed according to the value of $N_2^0 = k_{12}^0\mathcal{A}hH/\hat{\epsilon}_2U_2$.

Figure 2 shows that, at sufficiently high values of Ha, the components are indeed in the state of chemical equilibrium in the bulk absorbent phase, and the data of the two models are in good agreement. Decreasing the value of Ha, a reaction rate regime can be reached, where the components are not in chemical equilibrium, and thus the results obtained by the two models disagree. Concentrations obtained at $\xi = 0$ (film theory) and $\xi = 10$ (and $K = 10$) are also shown in the figure. The effect resulted in some 50% increase in concentration, although, in the calcu-

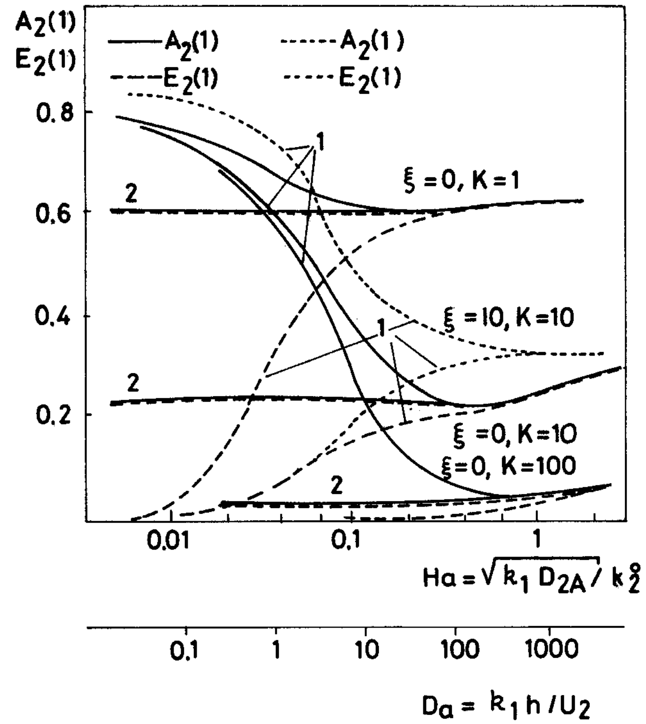

Figure 2. Comparison of the mathematical models: reversible reaction.
$N_2^0 = 3$; $k_1^0 H/k_2^0 = 1$; $Pe_2 = 0.01$
1 = presented model, Eqs. 9–10
2 = by Eq. 14
Values of the constant parameters for mass transfer accompanied by reversible reactions are: $\epsilon_2 = 0.5$; $H = 0.02$; $k_1^0 = 0.01$ m/s; $k_2^0 = 2 \times 10^{-4}$ m/s; $D_{2A} = D_{2E} = 2.8 \times 10^{-9}$ m²/s; $h = 0.24$ m; $U_2 = 0.01$ m/s

lation the volume of the interface boundary, it was negligible compared to that of the bulk.

The change of E_2/A_2 in axial direction at different values of Pe_2 is also of interest (Figure 3). At a given *Ha* number, the value of the E_2/A_2 ratio in axial direction depends strongly on the value of Pe_2. This has an influence on the ratio of the outlet concentrations as well. In reactors of high Pe_2 number, the value of the $E_2(1)/A_2(1)$ ratio can be approximately 20–50% higher than that of a perfectly-mixed reactor ($Pe_2 \rightarrow 0$). The reaction rate (i.e., the *Ha* number), required to reach chemical equilibrium, increases with the increasing values of *K* (Figure 4). (The components are regarded to be in chemical equilibrium—$e_2^0/Ka_2^0 \geq 0.99$—within the area above the curves.) According to the film theory ($\xi = 0$), if $Ha > 2$, the components in the bulk are practically in the state of chemical equilibrium under the experimental conditions occurring in practice. As to the film-penetration theory, however, the reaction rate required for chemical equilibrium increases depending on the value of ξ. In the case of the parameter values investigated—$\xi = 0$–10 and $K = 0.1$–100, the components can be regarded as in the state of chemical equilibrium in the bulk absorbent phase, only if $Ha > 6$. In extreme cases (e.g., when the volume of the bulk decreases compared to that of the interface boundary), the value of *Ha* required for equilibrium can even be higher. The reaction rate required for equilibrium in the interface boundary is shown in the left upper corner of Figure 4.

The modeling method presented can also be applied for reversible reactions of higher orders as well.

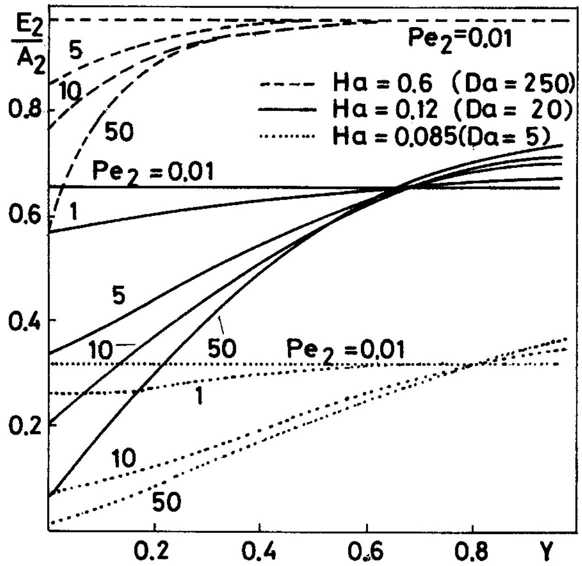

Figure 3. Change of the concentration ratio in the axial direction at various values of *Ha* and Pe_2.
$K = 10$; $N_2^0 = 2$; $k_1^0 H/k_2^0 = 1$; $\xi = 0$

Notation

a, e = concentrations of dissolved (A) and product (E) component, kmol/m³
$\tilde{a}, \tilde{e}$ = Laplace transform of the concentrations $a(x, t)$ and $e(x, t)$
$a(0)$ = inlet concentration of A, kmol/m³
A, E = concentrations of A and E, $A_1 = a_1^0/a_1(0)$, $A_2 = a_2^0 H/a_1(0)$, $E_2 = e_2^0 H/Ka_1(0)$
$A(1), E(1)$ = outlet concentrations of A and E
$\mathcal{A}$ = interfacial area per unit volume of reactor, m²/m³
D = diffusivity, m²/s
D_{ax} = axial dispersion coefficient, m²/s
Da = Damköhler number, $Da = k_1 h/U_2$
h = height of reactor, m
H = Henry's law constant, $H = a_1^*/a_2^*$
Ha = Hatta number, $Ha = \sqrt{k_1 D_{2A}}/k_2^0$

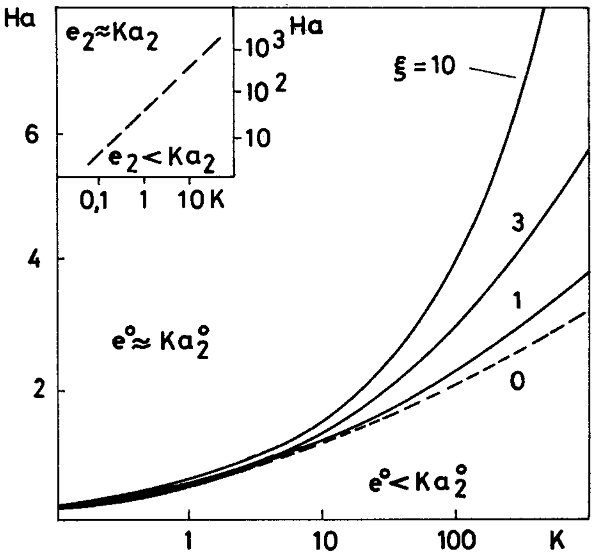

Figure 4. *Ha* number for reaching chemical equilibrium [$E_2(1)/A_2(1) \geq 0.99$] as a function of the chemical equilibrium constant at various values of ξ.
$N_2^0 = 3$; $k_1^0 H/k_2^0 = 1$; $Pe_2 = 0.01$

$J, \bar{J}$ = rate of chemical mass transfer for component A at interface ($\bar{J}$ is average value of J), kmol/m$^2 \cdot$ s
J_δ, J_E = rate of chemical mass transfer through the boundary layer into the bulk absorbent phase for A and E, kmol/m$^2 \cdot$ s
$\mathscr{k}_1$ = reaction rate constant, s^{-1}
k_2', k_2^0 = liquid-side mass transfer coefficients without chemical reaction according to the film penetration and film theory, $k_2' = k_2^0\xi/\tanh \xi$, $k_2^0 = D_{2A}/\delta_2$, m/s
k_2 = liquid-side mass transfer coefficient with chemical reaction for reversible reaction $k_2 = k_2^0(1 + P)/(P + (1/R) \tanh R)$
k_δ = mass transfer coefficient for $\bar{J}_\delta$ defined in Eqs. 3 and 7, m/s
k_{12} = overall mass transfer coefficient with chemical reaction, $k_{12} = 1/(1/k_1^0 + H/k_2)$, m/s
k_{22}, k_E = overall mass transfer coefficients for $\bar{J}_\delta$ and $\bar{J}_E$ $k_{22} = k_\delta k_{12}/k_2$, $k_E = k_{12} - k_{22}$, m/s
K = chemical equilibrium constant
$M = \sqrt{\mathscr{k}_1 D_{2A}}/k_2'$
N_1^0, N_2^0 = numbers of overall transfer units based on phase 1 and 2, $N_1^0 = k_{12}^0\, \mathcal{A}h/\hat{\epsilon}_1 U_1$, $N_2^0 = k_{12}^0 \mathcal{A}hH/\hat{\epsilon}_2 U_2$
$P = D_{2A}/D_{2E}K$
Pe = Peclet number, $= Uh/D_{ax}$
Q = rate of reaction of A per unit volume, kmol/m$^3 \cdot$ s
$R = Ha\sqrt{1 + P}$
s = fractional rate of surface renewal, s^{-1}
t = time, s
U = superficial velocity of phase, m/s
x = distance beneath liquid surface, m
Y = dimensionless axial coordinate

Subscript

A = component A
E = component E
1 = Phase 1
2 = absorbent phase

Superscript

0 = bulk phase or without reaction
* = at interface

Greek letters

δ = average thickness of a surface element or a film, m
ϵ = fractional volume of a phase
$\hat{\epsilon}$ = fractional volume of a bulk phase, $\hat{\epsilon}_2 = \epsilon_2 - \mathcal{A}\delta_2$
ψ = amount of reacted A in the boundary layer, kmol/m$^3 \cdot$ s
$\bar{\psi}$ = average value of ψ, kmol/m$^3 \cdot$ s
$\xi = \sqrt{s\delta_2^2/D_{2A}}$

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