Numerical Simulation of Theories for Gas Absorption with Chemical Reaction

Steady- and unsteady-state theories for interfacial mass transfer are used to model gas absorption with second-order, reversible reaction and the absorption of CO_2 into aqueous MDEA (methyldiethanolamine). The latter case represents a system of industrial interest, having both finite rate and equilibrium reactions. Steady-state theories studied are film theory, simplified eddy diffusivity theory, and an approximation to surface renewal theory. Higbie's penetration and Danckwert's surface renewal theories are the unsteady-state theories reviewed. The Nernst-Planck equations for diffusion and reaction in ionic systems are solved numerically using orthogonal collocation on finite elements. Comparisons are made between the absorption enhancement factor obtained for all theories. The applicability of approximate methods of solution for absorption with chemical reaction is also discussed.

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Introduction

Absorption with simultaneous chemical reaction is used widely to remove acid gases such as CO_2 and H_2S from hydrocarbon and inert mixtures. The chemical reaction can significantly increase the solubility of a gas, reducing the required solvent flow rate for a given removal specification. Furthermore, if the chemical reaction is fast enough, it increases the rate of absorption, thus increasing the overall liquid-phase mass transfer coefficient and subsequently reducing the size of the required absorption column. If the solvent is reactive preferably toward one particular gas in a mixture, it can be used for selective removal. An example of this process is the selective removal of H_2S, when CO_2 and H_2S mixtures are passed through a column using aqueous MDEA (methyldiethanolamine), which reacts instantaneously with H_2S and relatively slowly with CO_2 (Astarita et al., 1983).

The effect of chemical reaction in absorption processes has often been taken into account using empirically determined tray efficiencies (Dow Chemical, 1987). We can do much better, however, using a predictive model, if we know sufficient physico-chemical property data. Since the exact nature of the hydrodynamics at a free gas-liquid interface is still unknown, we must make simplifying assumptions for the proposed behavior of the absorption and reaction processes. These assumptions take the form of the well-known film, penetration and surface renewal theories, as well as some lesser known theories. The solution of these models for general reaction schemes requires solving coupled, nonlinear ordinary or partial differential equations describing multicomponent diffusion and reaction. Currently, film theory with chemical reaction is being used in contactor modeling for acid gas treating process design (Katti and Wolcott, 1987; Sardar and Weiland, 1985; Lindner, 1988; Lindner et al., 1988).

In this paper, we would like to compare the predicted effect of chemical reaction on the absorption process for some of the "rigorous" models, as well as an approximate method. The results will be presented in terms of the enhancement factor, which is defined as the rate of absorption with chemical reaction to that without chemical reaction under the same conditions. The first reaction scheme considered will be a second-order, reversible reaction. Since we are interested in acid gas treating processes, we will choose the absorption of CO_2 into aqueous MDEA as another model system. We will not only take into account the multiple reactions that occur in this system, but also the diffusion of ionic species. It is the purpose here to determine if there are any relevant differences in the predictions of these models over a range of conditions encountered experimentally and industrially.

Mass Transfer Models: an Overview

The oldest of the mass transfer theories studied is the film theory (Lewis and Whitman, 1924). In this theory, it is proposed that a stagnant film of liquid rests at the gas-liquid interface,

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and mass transfer from the gas to the liquid phase occurs by molecular diffusion only through this stagnant film. Below this film, the composition is uniform due to turbulence. By nature, film theory is a steady-state theory and requires the solution of ordinary differential equations to determine concentration profiles in the boundary layer at a gas-liquid interface.

Penetration theory was introduced as more realistic alternative to film theory (Higbie, 1935). Higbie proposed that elements of fluid rise from the bulk of the liquid to the interface, remain at the interface for a period of time known as the contact time, and are then swept back into solution. Danckwerts furthered this concept by assuming that the time of contact is not the same for all elements, but provided by a distribution of times (Danckwerts, 1951). His theory is known as surface renewal theory and is characterized by the fraction of surface renewed per unit time. In practice, surface renewal theory provides more tractable analytical solutions for the absorption rate; however, penetration theory is faster to solve numerically. Both penetration and surface renewal theories are unsteady-state theories, hence the description of these theories involves the solution of partial differential equations. These theories are generally accepted as being more accurate than film theory for mass transfer at turbulent gas-liquid interfaces (Danckwerts, 1970), at the expense of additional computation time.

In all of the previously-mentioned theories, the mass transfer occurs by diffusion through a laminar boundary layer, analogous to diffusion in a solid. In turbulent flow, however, a more realistic approach is the eddy diffusivity theory (King, 1966). Here, the diffusion coefficient is modified to allow for the effect of turbulent, as well as diffusive, transport in the boundary layer. We will use a simplified form of the eddy diffusivity theory (Prasher and Fricke, 1974) to reduce the number of unknown parameters. Eddy diffusivity theory can be treated as a unsteady-state theory; however, we choose to treat it as a steady-state alternative to film theory, and it will be shown that the steady-state eddy diffusivity theory, which involves the solution of ordinary, not partial, differential equations, is an excellent approximation to the unsteady-state surface renewal theory. The comparison is so good, in fact, that the use of an unsteady-state theory is not necessary for the reaction schemes considered in this paper.

Approximate methods for several reaction schemes are also available. Specifically, the algebraic methods of DeCoursey (1982) and Onda et al. (1970) are both available for second-order, reversible reactions. These methods are of limited use, however, for complex reaction schemes and will not be presented in comparison. Another type of approximation is due to Chang and Rochelle (1982), in which film theory is corrected to approximate surface renewal theory. This is done by adjusting the diffusion coefficients of all species (except for the diffusing gas). The details and justification of this method will be discussed later.

The mass transfer models can be discriminated by observing the predicted effect of the diffusion coefficient on the mass transfer coefficient. This is difficult experimentally, however, since diffusion coefficients of gases in liquids vary over only a small range. Film theory predicts a linear dependence. Penetration and surface renewal theories predict a dependence to the one-half power, and the dependence for the eddy diffusivity model varies, depending on parameter values. The general range for the experimentally-determined diffusion coefficient dependence is 0.5 to 0.75, depending on the mass transfer equipment (Kozinski and King, 1966). This dependence, however, can increase with the addition of surface-active agents (Davies, 1980).

In a recent work, Seo and Lee (1988) measured the turbulence at a gas-liquid interface directly using a hot-wire anemometer and interpreted the data assuming a two-dimensional eddy model (Luk and Lee, 1986). This is significant since the interfacial behavior is measured directly and not inferred from absorption data. An interesting analysis is provided based upon an assumed gamma distribution of contact times of elements at the gas-liquid interface (Bullin and Dukler, 1972). This model has, as limits, the surface renewal and Higbie penetration theories. It is shown that, for the stirred-tank system studied, the true residence time distribution lies between the two models.

Throughout the discussion, the effect of gas-phase resistance to mass transfer will be neglected. This effect can be important for absorption from mixtures of gases with accompanying high absorption rates. Neverthless, taking the gas-phase resistance into account is straightforward in numerical simulation and not pertinent to this work. Interfacial equilibrium is also assumed in the calculations. This has been demonstrated to be valid for uncontaminated surfaces during the physical absorption of slightly soluble gases (Scriven and Pigford, 1958). This assumption, however, has been called into question for systems with high absorption enhancement due to reaction (Asolekar et al., 1985). The nonionic diffusion process is assumed to obey Fick's law, except when turbulence is taken into account empirically with an eddy diffusivity model. Therefore, the only coupling of the diffusion fluxes is through electrical potential gradients and chemical reaction. For a discussion of complicating effects not covered here, the reader is referred to the papers of Krishna (1987), and Krishna and Standart (1979).

Film theory

Since film theory is a steady-state process, an ordinary differential equation describing the diffusion of each species can be written in the usual manner. For electrolyte solutions, we include the effect of the electrical potential on ion diffusion. In doing so, we shall assume the validity of the Nernst-Einstein equation to relate ionic conductances to diffusion coefficients (Newman, 1973). This assumption leads to the Nernst-Planck equation (Krishna, 1987):

$$D_i \nabla^2 C_i - Z_i D_i \frac{F}{kT} \nabla (C_i \nabla \Phi) = r_i[\underline{C}(x)] \quad i = 1, \ldots, n \qquad (1)$$

where ∇ and ∇^2 represent the first and second derivatives with respect to one spatial dimension. Assuming dynamic electroneutrality, $\Sigma Z_i J_i = 0$ (Krishna, 1987), where J is the flux of each species, we can calculate the electrical potential gradient explicitly in terms of ion concentrations and concentration gradients by use of the Henderson formula (Mills et al., 1985):

$$\nabla \Phi = \frac{kT}{F} \frac{\sum_{i=1}^{n} Z_i D_i \nabla C_i}{\sum_{i=1}^{n} Z_i^2 D_i C_i} \qquad (2)$$

The Henderson formula can be considered a multicomponent extension of the common formula for binary diffusion of ionic species (Vinograd and McBain, 1941).

This paper will consider the case of only one absorbing species, denoted by Component 1. The rate of absorption at the gas-liquid interface is proportional to the concentration gradient of the nonionic absorbing species:

$$R = -D_1 \nabla C_1 \big|_{x=0} \qquad (3)$$

We solve the set of coupled differential equations assuming that the absorbing gas is the only volatile species and that there is no gas-phase or interfacial resistance to mass transfer:

$$\begin{aligned} \text{at } x = 0: \quad & C_1 = C_1^* \\ & J_i = 0 \qquad i = 2, \ldots, n \\ \text{at } x = \delta: \quad & C_i = C_i^o \qquad i = 1, \ldots, n \end{aligned} \qquad (4)$$

Since ionic species in electrolyte solution do not diffuse independently, we replace Eq. 1 for one of the ionic species by an algebraic charge balance:

$$\sum_{i=1}^{n} Z_i C_i = 0 \qquad (5)$$

Furthermore, we approximate equilibrium reactions by using a very large rate constant. Reversible reactions are treated by assuming that the reverse rate constant is equal to the forward rate constant divided by the equilibrium constant. The resulting equations (Eqs. 1 and 5), along with the boundary conditions, are solved by numerical methods described in detail later.

Solving Eq. 1 for the physical absorption of a nonionic species, we obtain the relationship between the physical mass transfer coefficient and the film thickness δ. As noted earlier, the mass transfer coefficient is proportional to the diffusion coefficient to the first power:

$$k_1^o = \frac{D_1}{\delta} \qquad (6)$$

In order to compare the mass transfer theories, a physical mass transfer coefficient is chosen, and then the film thickness (or the characteristic parameter for any of the theories) is used in the calculations. The enhancement factor, defined as the ratio of absorption with chemical reaction to that without, is calculated using the results of the numerical solution:

$$E = \frac{R}{R_{\text{phys}}} = \frac{R}{k_1^o (C_1^* - C_1^0)} \qquad (7)$$

Penetration and surface renewal theories

For the penetration and surface renewal theories, we write the unsteady-state form of Eq. 1:

$$D_i \nabla^2 C_i - Z_i D_i \frac{F}{kT} \nabla (C_i \nabla \Phi) = \frac{\partial C_i}{\partial t} + r_i \, [\underline{C}(x, t)] \qquad i = 1, \ldots, n \qquad (8)$$

The same boundary conditions are used as for film theory, except that the spatial domain, x, is on $[0, \infty)$ instead of $[0, \delta]$(i.e., the fluid element depth is infinite with respect to the penetration depth during the contact time). We now need the initial conditions, which are assumed to be the same as the boundary conditions at infinity, since the fluid element is initially of uniform composition. For both penetration and surface renewal theories, the equations are integrated and the concentration gradient of the absorbing gas is obtained as a function of time.

The physical mass transfer coefficients for penetration and surface renewal theories are shown below (Danckwerts, 1970):

$$k_1^o = 2\sqrt{\frac{D_1}{\pi\theta}} \qquad (9)$$

$$k_1^o = \sqrt{D_1 s} \qquad (10)$$

The parameter θ is the contact time of the element at the interface, and s is the fraction of surface renewed per unit time.

The expressions for the enhancement factor for penetration and surface renewal theories are shown in Eqs. 11 and 12, respectively:

$$E = \frac{1}{k_1^o \theta (C_1^* - C_1^o)} \int_0^\theta R(t)\, dt \qquad (11)$$

$$E = \frac{1}{k_1^o (C_1^* - C_1^o)} \int_0^\infty s e^{-st} R(t)\, dt \qquad (12)$$

For surface renewal theory, the exponential term is the fraction of the surface with a contact time between t and $t + dt$ (Danckwerts, 1951):

$$\phi = s e^{-st} dt \qquad (13)$$

Numerically, the integration is carried out until the fraction of surface left is negligible.

As done by Versteeg (1986), the infinite x domain is mapped onto a finite domain using a time-dependent spatial transformation. Normally, there exists an infinite gradient in the gas concentration profile at the initial time, since the interfacial concentration is not the same as the bulk concentration. This transformation compresses the spatial domain so that there is no such gradient at the initial time in r space:

$$r = \operatorname{erf}\left(\frac{x}{\sqrt{D_1 \pi t}}\right) \qquad (14)$$

This transformation is based upon the solution for physical absorption, and consequently the computed solution is a straight line in r space in the limit of no reaction.

Eddy diffusivity theory

For eddy diffusivity theory, we provide the following addition to the diffusion coefficient, as suggested by King (1966):

$$\nabla[(D_i + ax^m)]\nabla C_i] - Z_i D_i \frac{F}{kT} \nabla (C_i \nabla \Phi) = \frac{\partial C_i}{\partial t} + r_i \, [\underline{C}(x, t)] \qquad i = 1, \ldots, n \qquad (15)$$

with $0 \leq x < \infty$. To solve this model, we must know at least three parameters, a, m, and at least one parameter describing a residence time distribution. We first simplify this theory to a steady-state theory, and then, following the suggestion of Prasher and Fricke (1974) we assume a value of 2 for m. This provides the following relationship for the physical mass transfer coefficient:

$$k_l^o = \frac{2}{\pi}\sqrt{aD_1} \qquad (16)$$

In this manner, we have obtained a steady-state theory with the dependence of the mass transfer coefficient to the one-half power of the diffusion coefficient. The expression for the enhancement factor is the same as for film theory, using Eq. 16 for the mass transfer coefficient. As in the unsteady-state theories, we map the infinite domain onto a finite domain for computation:

$$r = \frac{2}{\pi}\tan^{-1}\left(x\sqrt{\frac{a}{D_1}}\right) \qquad (17)$$

This transformation is based on the solution for physical absorption, and the concentration profile is a straight line in r space for physical absorption.

Approximate film theory

Chang and Rochelle (1982) noted that film theory could be modified to approximate surface renewal theory, if the diffusion coefficient of each species is corrected by a square root ratio of the species diffusion coefficient to the species on which the mass transfer coefficient is based; in this case, the absorbing gas:

$$D_{i,\text{corr}} = D_i\sqrt{\frac{D_1}{D_i}} \qquad (18)$$

This approximation can be qualitatively justified by comparing the analytical solution of film and surface renewal theories for an instantaneous, irreversible, second-order reaction, $A + B \Longrightarrow C$, in the limit of high enhancement factors (Danckwerts, 1970):

$$E_{\text{surf}} = \sqrt{\frac{D_a}{D_b}} + \frac{C_{b,\text{bulk}}}{C_{a,\text{int}}}\sqrt{\frac{D_b}{D_a}} \qquad (19)$$

$$E_{\text{film}} = 1 + \frac{C_{b,\text{bulk}}}{C_{a,\text{int}}}\frac{D_b}{D_a} \qquad (20)$$

Applying the correction factor will make the film theory solution quantitatively similar to surface renewal theory.

Numerical Solution

For each theory, a set of coupled, nonlinear differential equations must be solved. This is accomplished first by using orthogonal collocation on finite elements in the spatial dimension (Villadsen and Stewart, 1967; Villadsen and Michelson, 1978; Finlayson, 1980). The method is only briefly outlined here; the cited references contain all the necessary background information. We first divide the domain into elements, and within each element the concentration of each species is approximated by a polynomial. The criterion for choosing the coefficients of the approximating polynomials is that the residuals of the differential equations, shown for film theory in Eq. 21 as an example, are zero at certain points, known as collocation points:

$$\text{Residual} = D_i\nabla^2 C_i - Z_i D_i \frac{F}{kT}\nabla(C_i\nabla\Phi) - r_i\,[\underline{C}(x)] = 0 \qquad i = 1, \ldots, n \qquad (21)$$

The residual for each component is satisfied at the collocation points, but not necessarily in between. Note that, although the residual of the differential equation is satisfied at a collocation point, the solution, C, is not necessarily correct at that point. In our case, orthogonal collocation is being used, and the collocation points are the zeroes of a series of shifted Legendre polynomials on [0, 1] mapped into each element. In practice, however, we do not solve for the polynomial coefficients, but for the concentrations themselves. Consider the concentration of each species at any point in the element in terms of a Lagrange polynomial interpolated solution:

$$C_i = \sum_{k=1}^{p} C_{ik} l_k \qquad (22)$$

The first and second derivatives can be expressed as a summation of derivative weights and the species concentration within each element:

$$\nabla C_{ij} = \sum_{k=1}^{p} C_{ik} A_{jk} \qquad (23)$$

$$\nabla^2 C_{ij} = \sum_{k=1}^{p} C_{ik} B_{jk} \qquad (24)$$

where the A_{jk} and B_{jk} are the derivatives of the Lagrange interpolation polynomial at the collocation point, j. The derivative weights are obtained from code based upon the routines in Villadsen and Michelsen (1978). Several elements are usually used, with the condition that at each element boundary, the first *derivative is continuous:*

$$\nabla C_i|_{x^+} = \nabla C_i|_{x^-} \qquad (25)$$

where x^+ and x^- denote the approach to the element boundary from the right and left sides, respectively.

For the steady-state theories, the equations are subsequently transformed into a larger set of coupled, nonlinear algebraic equations. For the unsteady-state theories, the spatial discretization on results in a set of coupled ordinary differential/algebraic equations which are integrated through time by DASSL (Petzold, 1982), a FORTRAN package which solves equations of the following form:

$$\underline{F}(\underline{y}, \underline{y}', t) = \underline{0} \qquad (26)$$

This program uses backward differentiation formulas to integrate the differential equations. It can perform numerical differencing for a Jacobian approximation, and takes advantage of banded Jacobians to reduce computation time (both of these features are utilized in this work). It is important to note that the algebraic and ordinary differential equations can be interspersed, and no extra work is required of the user than already required for packages which solve only ordinary differential equations.

This technique of transforming the partial differential equations into ordinary differential equations, and then using a general-purpose program to solve the resulting set of equations, is known as the method of lines. It is a semidiscrete method, contrasted to a fully-discretized method, in which the time derivatives are replaced by a finite difference approximation. The method of lines is, in general, not as efficient computationally as the fully-discretized methods (Kurtz et al., 1978), but it is easier to set up, and more importantly, to change problems. For some problems, the method of lines is less likely to fail due to the sophisticated convergence checking algorithms used in state-of-the-art integrating packages, such as DASSL.

The steady-state theories result in a set of coupled nonlinear algebraic equations. The solution to these equations is not trivial, especially when the nonlinear, complicating effect of the potential gradient coupling is included. MINPACK (Moré et al., 1980) was used with some success in solving the equations. This, however, was not always successful for fast reaction rates using reasonable initial guesses. Therefore, the steady-state equations were also solved using a parametric continuation method (e.g., Vickery et al., 1988). In this method, we vary a parameter continuously from a problem for which we know the solution to a problem for which we need the solution. Let us take, for example, the film theory equations, and multiply each of the rate terms by a parameter, t:

$$D_i\nabla^2 C_i - Z_i D_i \frac{F}{kT}\nabla(C_i\nabla\Phi) = t r_i[\underline{C}(x,t)] \quad i = 1,\ldots,n \qquad (27)$$

When t is 0, the problem reduces to that of physical diffusion, and the solution is trivial. As t is advanced to 1, the solution changes from the trivial problem to a nontrivial problem that we wish to solve. There are many methods for tracking the solution (Watson and Scott, 1987). We choose to let DASSL integrate the equations and have found no problems associated with this method. It is interesting to note that, with this method, we actually solve many real problems as we are proceeding along the path from $t = 0$ to $t = 1$. If Eq. 1 is put in dimensionless form, one sees that the effect is analogous to varying the mass transfer coefficient from infinity (no enhancement) to the finite value:

$$r = \frac{x}{\delta} \qquad (28)$$

$$\begin{aligned} d_i\nabla_r^2 C_i - Z_i d_i \frac{F}{kT}\nabla_r(C_i\nabla_r\Phi) &= \frac{\delta^2}{D_1} r_i[\underline{C}(x,t)] \quad i = 1,\ldots,n \\ &= \frac{D_1}{k_1^{o2}} r_i[\underline{C}(x,t)] \qquad (29) \end{aligned}$$

where ∇_r denotes differentiation with respect to r, instead of x, and d_i is the dimensionless diffusion coefficient. This method is also analogous to varying the rate constant for systems with a single reaction.

It seems unreasonable that the steady-state problem can be solved more easily as an unsteady-state problem, but this phenomenon has been noted by others (Wayburn and Seader, 1987). There is, however, one advantage that can be taken. Unlike the unsteady-state theories, the solution for $t < 1$ does not have to be very accurate. Therefore, we use a low-order approximation in space (e.g., one element), solve this problem until $t = 1$, and then interpolate the solution, using Lagrange polynomials, to a new, more dense spatial grid. We solve this problem using MINPACK with the good initial guess. This general technique has been suggested before (Allgower and Georg, 1980), and it has proved to be the most reliable method we used to solve the boundary value problems. Furthermore, it has resulted in a significant reduction in computation time for the steady-state, as opposed to the unsteady-state, theories.

For the penetration and surface renewal theories, we must integrate the concentrate gradient through time. (See Eqs. 11 and 12). Since, in general, the solution will be available at variable time steps, we must use an integration method that does not require function evaluations at regular time intervals. Furthermore, we need a method that is accurate, since it would be wasteful to use smaller time steps in evaluating a set of perhaps 100 or more differential/algebraic equations in order to evaluate a single integral accurately. To solve this problem, we interpolate the gradient piecewise through time, and then we use Gaussian quadrature to evaluate the integral. This technique allows both high accuracy and does not restrict the point of function evaluation.

All computations are performed on a Cray X-MP/24 vector processor machine, using only one of the two processors available. The code has been written to perform efficiently on a vector processor, and the problems solved here can be completed in a matter of seconds on this machine. Typical times are one-half second for a steady-state theory and four seconds for an unsteady-state theory, although the times vary greatly depending on the error tolerance, spatial resolution, rate constants, and reaction mechanisms. However, one can draw the conclusion that, with the increasing availability of powerful computers, the solution of boundary layer equations in process design, experimental data interpretation, and sensitivity analysis is certainly not prohibitive. Furthermore, the steady-state theories typically require much less computation time than the unsteady-state theories.

Since the equations for the mass transfer theories are similar, we use the same collocation code to solve all of the problems. We can neglect time derivatives for the steady-state theories, apply the appropriate transformation for each theory, and modify the diffusion coefficients for the eddy diffusivity theory. In this manner, a number of theories can be compared easily.

Results

Second-order, reversible reaction

Before proceeding to discussion of the MDEA system, it is appropriate to compare the mass transfer theories for a simple case. We chose the bimolecular, reversible reaction:

$$A + B \Longleftrightarrow C + D$$

The rate expression used for this reaction is shown in Eq. 30:

$$r_i = \vartheta_i k_2 \left\{ C_A C_B - \frac{1}{K_{eq}} C_C C_D \right\} \qquad (30)$$

The stoichiometric coefficients, ϑ_i, are +1 for products and −1 for reactants. Numerical results are already available in the literature for this reaction for both penetration (Secor and Beutler, 1967; Versteeg, 1986) and film theories (Onda et al., 1970). We will, however, present our own results for completeness. In this simple case, we will neglect potential gradient coupling and assume the diffusion coefficients for all species except the absorbing gas as the same. We will also consider only the case where the diffusion coefficient ratio is different from unity. In Figure 1, the enhancement factor is presented as a function of the dimensionless rate constant, M:

$$M = \frac{D_1 k_2 C_{B^o}}{k_1^{o2}} \tag{31}$$

The primary difference between the theories occurs at the highest enhancement factors, where the gradients in the liquid-phase species concentrations are largest. This region corresponds to the instantaneous upper limit.

Figure 2 shows the ratio of the enhancement factor of each of the four other theories to surface renewal theory. There are two regions where the theories are significantly different. The major difference is at the highest enhancement factors, where film theory deviates approximately 30%. This deviation would not be as large if the diffusion coefficients were the same and would be larger if the diffusion coefficient ratio was greater. We note that the large difference at the instantaneous limit can be predicted by taking the ratio of the enhancement factors from Eqs. 19 and 20 for irreversible surface renewal and film theories.

The approximate method of Chang and Rochelle (1982) modifies only the diffusion coefficients of the nonvolatile reactants. When the approximate and film theory solutions are the same, the diffusion of liquid-phase reactants is unimportant, corresponding to a pseudofirst-order reaction condition (Danckwerts, 1970). Upon examining Figure 2 for the low enhancement factors, one finds that there are differences in the models even when liquid-phase reactant diffusion is unimportant, reflecting the fact that the models are different even for the simple case of the first-order reaction scheme. This difference is demonstrated in Figure 3, where the results are shown for a simple first-order reaction scheme. At low enhancement factors, the theories have the largest deviation; but, at high enhancement

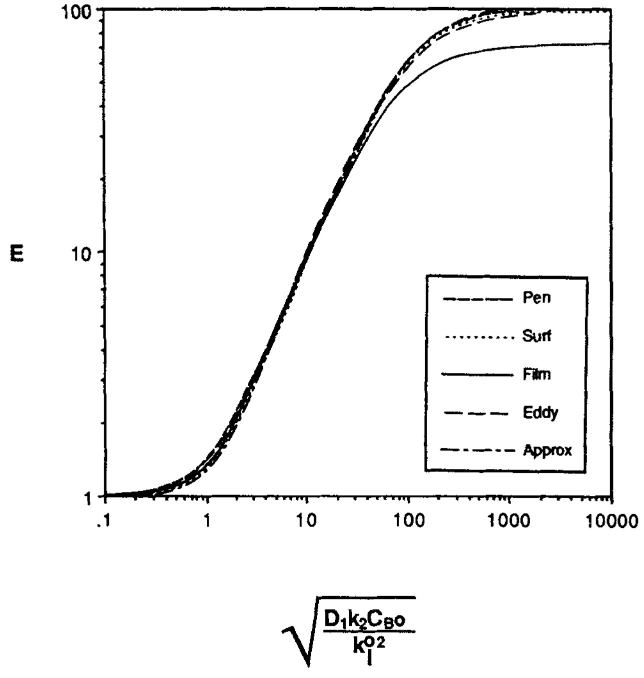

Figure 1. Enhancement factor for a second-order, reversible reaction, $A + B \Longleftrightarrow C + D$.
$K_{eq} = 350$; $D_B = D_C = D_D = 0.5D_A$; $C_{B,\text{bulk}}/C_{A,\text{int}} = 200$; $C_{A,\text{bulk}} = C_{B,\text{bulk}} = C_{C,\text{bulk}} = 0$

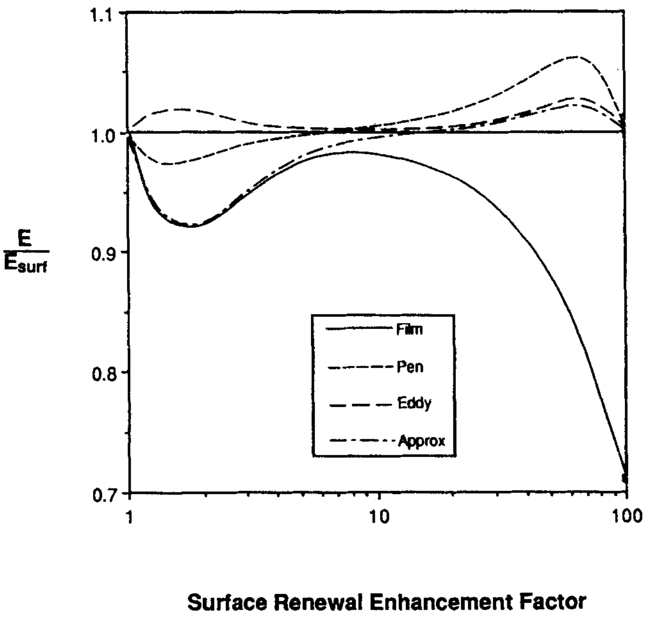

Figure 2. Comparison of mass transfer theories for a second-order, reversible reaction, $A + B \Longleftrightarrow C + D$.
$K_{eq} = 350$; $D_B = D_C = D_D = 0.5D_A$; $C_{B,\text{bulk}}/C_{A,\text{int}} = 200$; $C_{A,\text{bulk}} = C_{B,\text{bulk}} = C_{C,\text{bulk}} = 0$

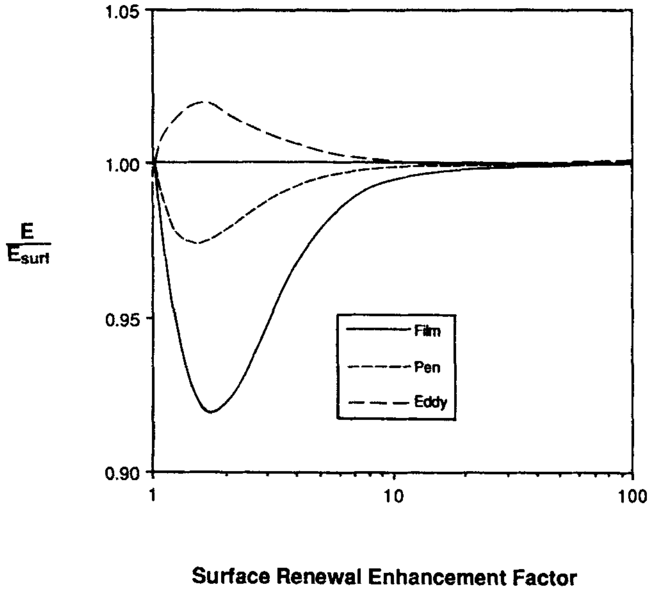

Figure 3. Comparison of mass transfer theories for a first-order, irreversible reaction.

factors, all of the theories approach the same limit:

$$E = \sqrt{M} \tag{32}$$

This result has been demonstrated from the analytical solutions for penetration, film and surface renewal theories by Danckwerts (1970), and we have verified this relation numerically for the eddy diffusivity theory.

Figures 4 and 5 show similar results for a second-order reaction at conditions studied by Chang (1979), the equilibrium constant is lower, and the interfacial concentration of the absorbing gas is higher. At both sets of conditions, high and low enhancement factors, the eddy diffusivity theory provides a good approximation to the unsteady-state theories, while the approximate method does best at higher enhancement factors. It appears, therefore, that both eddy diffusivity and the approximate model can be used to obtain the enhancement factor for the simple reaction case. The differences from the presumably more accurate unsteady-state models are, in fact, negligible compared to the uncertainty in the actual mass transfer mechanism.

CO_2 absorption into aqueous MDEA

Four reactions are considered for the absorption of CO_2 into aqueous MDEA solutions (Critchfield and Rochelle, 1987):

$$CO_2 + MDEA{:}H_2O \overset{K_1}{\Longleftrightarrow} MDEAH^+ + HCO_3^-$$

$$HCO_3^- \overset{K_2}{\Longleftrightarrow} CO_2 + OH^-$$

$$CO_3^= + H_2O \overset{K_3}{\Longleftrightarrow} HCO_3^- + OH^-$$

$$MDEA + H_2O \overset{K_4}{\Longleftrightarrow} MDEAH^+ + OH^-$$

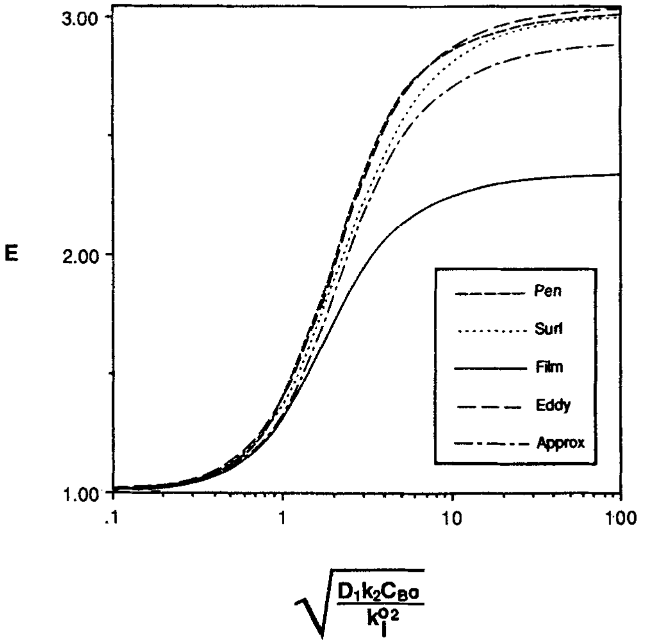

Figure 4. Enhancement factor for a second-order, reversible reaction, $A + B \Longleftrightarrow C + D$.
$K_{eq} = 1$; $D_B = D_C = D_D = 0.5D_A$; $C_{B,bulk}/C_{A,int} = 10$; $C_{A,bulk} = C_{B,bulk} = C_{C,bulk} = 0$

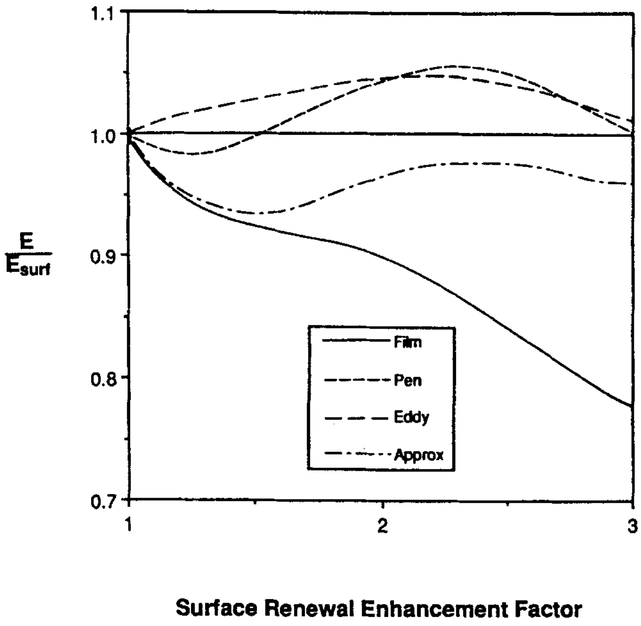

Figure 5. Comparison of mass transfer theories for a second-order, reversible reaction, $A + B \Longleftrightarrow C + D$.
$K_{eq} = 1$; $D_B = D_C = D_D = 0.5D_A$; $C_{B,bulk}/C_{A,int} = 10$; $C_{A,bulk} = C_{B,bulk} = C_{C,bulk} = 0$

The first two reactions are finite rate reactions; the second two reactions involve only a proton transfer and will be considered instantaneous with respect to mass transfer. Neglecting water as a species, we have six simultaneous diffusion equations to solve. The water dissociation reaction is neglected, since the concentration of the hydronium ion is very low at the conditions of the simulation and not needed in the reaction rate expressions. (The equilibrium constant for the water dissociation is implicitly represented in the buffer equilibrium constants, K_3 and K_4.)

Table 1. Model Parameters for MDEA System at 45°C

Parameter	Value	Source
K_1	132	Critchfield and Rochelle, 1987
K_2	4.18×10^{-8} kmol · m^{-3}	Critchfield and Rochelle, 1987
K_3	5.96×10^{-4} kmol · m^{-3}	Critchfield and Rochelle, 1987
K_4	Not Independent	
k_{MDEA}	10 m^3 · kmol^{-1} · s^{-1}	Critchfield and Rochelle, 1987
k_{OH^-}	3.47×10^4 m^3 · kmol^{-1} · s^{-1}	Astarita et al., 1983
H_{CO_2}	50 atm · m^3 · kmol^{-1}	Critchfield and Rochelle, 1987
D_{N_2O}	1.7×10^{-9} m^2 · s^{-1}	Versteeg, 1986
D_{DEA}	0.75×10^{-9} m^2 · s^{-1}	Versteeg, 1986*
$D_{HCO_3^-}$	0.94×10^{-9} m^2 · s^{-1}	Kigoshi and Hashitani, 1963*
$D_{CO_3^=}$	0.7×10^{-9} m^2 · s^{-1}	Kigoshi and Hashitani, 1963*
D_{OH^-}	4.5×10^{-9} m^2 · s^{-1}	Newman, 1973*
CO_2 Loading	0.005 kmol/kmol MDEA	
Total MDEA	1.0 kmol · m^{-3}	

*Modified

Since this is an ionic system, we replace the diffusion equation for bicarbonate with an algebraic charge balance equation and use the Henderson formula to correct for the ionic effects on diffusion. The instantaneous reactions are treated by making the rate constants large enough so that the reactions are in equilibrium everywhere in the boundary layer. This assumption is easily checked using the calculated concentration profiles. The finite rate reactions are treated in the same manner as the reversible, bimolecular reaction, discussed previously.

The resulting set of equations are solved with the model parameters shown in Table 1. The equilibrium data used are the same as in Critchfield and Rochelle (1987) for 45°C. Since the equilibrium constant for the CO_2-MDEA reaction is correlated as a function of ionic strength, a mean value of 0.1 kmol/m^3 is assumed in all calculations. The rate constant for hydroxide is taken from Astarita et al. (1983), evaluated at an ionic strength of 0.1 kmol/m^3. The N_2O analogy is used to estimate the diffusion coefficient of CO_2 in 2 kmol/m^3 MDEA, using the data of Versteeg (1986). The diffusion coefficient of MDEA is assumed to be the same as DEA. All of the liquid-phase reactant diffusion coefficients are adjusted using the modified Stokes-Einstein relationship and the viscosity data of Versteeg (1986). Also, the diffusion coefficient of MDEAH$^+$ is assumed to be the same as MDEA, although it is most likely smaller.

In the results, we wish not only to compare the mass transfer theories, but also to establish the importance of the additional reaction of hydroxide with CO_2 and the equilibrium reactions. This is accomplished readily in a numerical model by simply "turning off" the rate constants for all reactions except for the primary reaction of CO_2 with MDEA; the equilibrium concentrations in the bulk are still the same, however. Figure 6 shows the enhancement factor, now as a function of the interfacial concentration of CO_2 for both the true reaction case and the "simplified" reaction scheme at an equivalent contact time of 10 seconds, which corresponds to a mass transfer coefficient of 1.46 × 10^{-5} m/s. At low CO_2 concentrations, corresponding to low CO_2 partial pressures, the enhancement factor is highest, since there is no depletion in the boundary layer of the MDEA and hydroxide. This condition corresponds to the pseudofirst-order reaction regime. At this point, the hydroxide reaction has its largest effect and must be taken into account in predicting the enhancement factor. As the partial pressure is increased, the hydroxide becomes depleted in the boundary layer, the MDEA becomes the primary contributor to the adsorption enhancement, and the enhancement factors become the same for both cases. This depletion effect is demonstrated explicitly in Figures 7 and 8, where boundary layer concentration profiles are shown for two selected CO_2 partial pressures using film theory. Figure 7 shows the results with a low CO_2 partial pressure, resulting in nearly pseudofirst-order conditions. (There is a small gradient in hydroxide.) The contribution of each reactant, MDEA and hydroxide, can be obtained by taking the product of the concentration and the rate constant, to obtain a pseudofirst-order enhancement factor:

$$k_1 = k_{OH^-}[OH^-] + k_{MDEA}[MDEA] \qquad (33)$$

For these conditions, a pseudofirst-order rate constant of 39 s^{-1} is obtained (using the interfacial concentration of hydroxide), and hydroxide contributes to about half of this value. The conditions shown in Figure 8, corresponding to a higher CO_2 concentration, show that the hydroxide is depleted at the interface, and its contribution to the enhancement factor is now less than 10%.

Figure 9 shows an expanded comparison of the mass transfer theories for the MDEA system (with hydroxide and the equilibrium reactions included in the simulation). Surface renewal the-

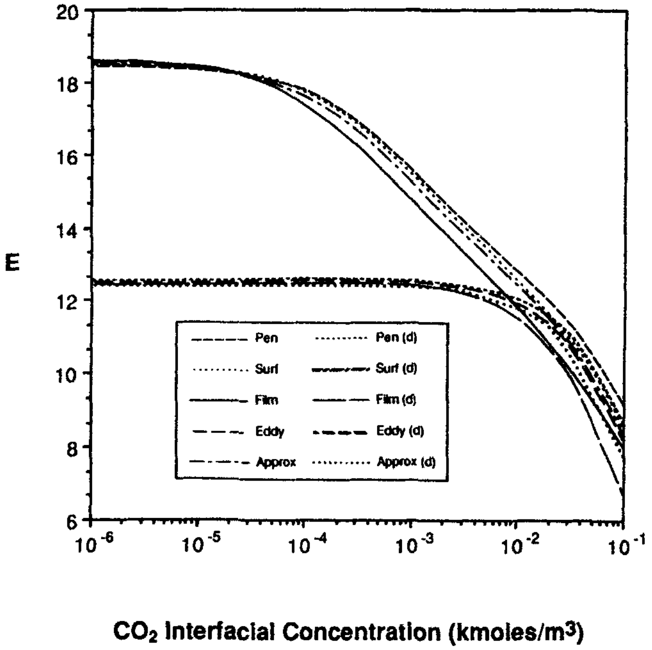

Figure 6. Effect of CO_2 interfacial concentration and hydroxide reaction for the MDEA system.

k_l^o = 1.46 × 10^{-5} m/s; T = 45°C; CO_2 loading = 0.005; (d) = numerical solution with the hydroxide reaction "deactivated"

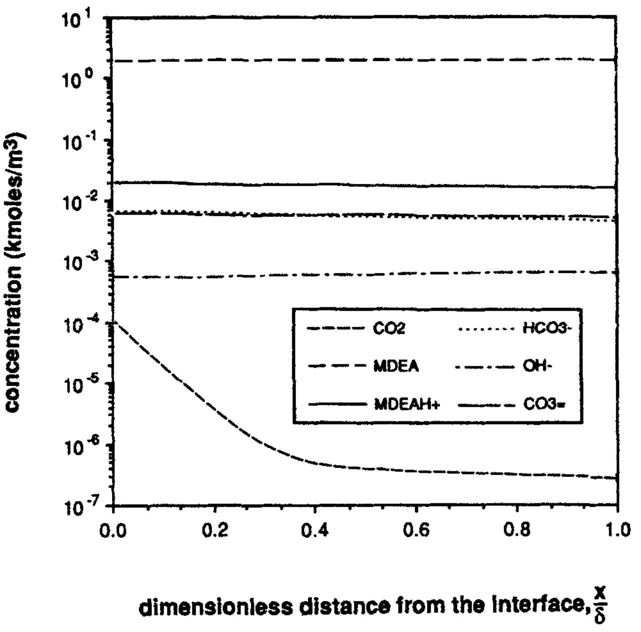

Figure 7. Concentration profiles for the MDEA system with the film theory solution.

k_l^o = 1.46 × 10^{-5} m/s; T = 45°C; CO_2 loading = 0.005; $CO_{2,int}$ = 1 × 10^{-4} kmol/m^3; enhancement factor = 17.5

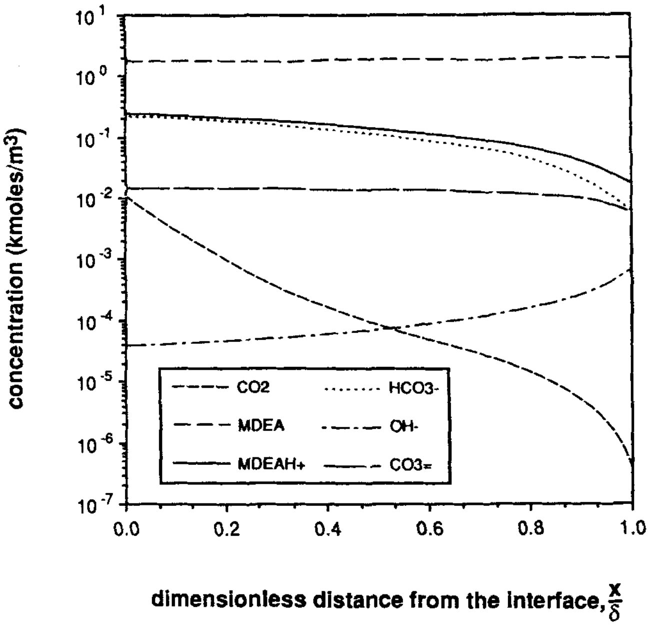

Figure 8. Concentration profiles for the MDEA system with the film theory solution.

$k_l^o = 1.46 \times 10^{-5}$ m/s; $T = 45°C$; CO_2 loading = 0.005; $CO_{2,int} = 1 \times 10^{-2}$ kmol/m³; enhancement factor = 11.9

ory is assumed to be the "correct" theory and serves as the basis for comparison. Film theory deviates the most in this case, with both of eddy diffusivity theory and the approximate theory providing solutions similar to surface renewal.

The same type of data is shown in Figure 10 for the MDEA and the "simplified" MDEA system, except now at an equivalent contact time of 0.1 s ($k_l^o = 1.46 \times 10^{-4}$ m/s). The hydroxide reaction again contributes significantly to the absorption enhancement, until the partial pressure of CO_2 is large enough to cause boundary layer depletion. Now, however, the primary deviation in the models results from the differences in the theories for a pseudofirst-order reaction. This region corresponds to a small value of M, shown in Figure 3 for a first-order reaction.

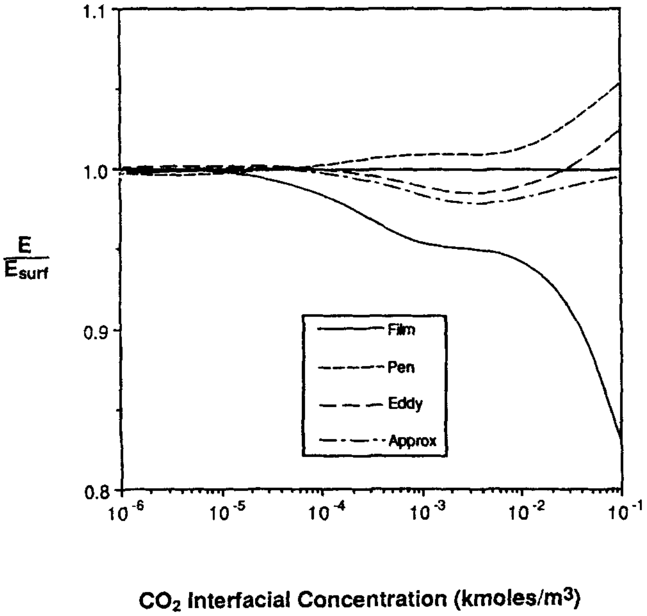

Figure 9. Comparison of mass transfer theories for the MDEA system.

$k_l^o = 1.46 \times 10^{-5}$ m/s; $T = 45°C$; CO_2 loading = 0.005

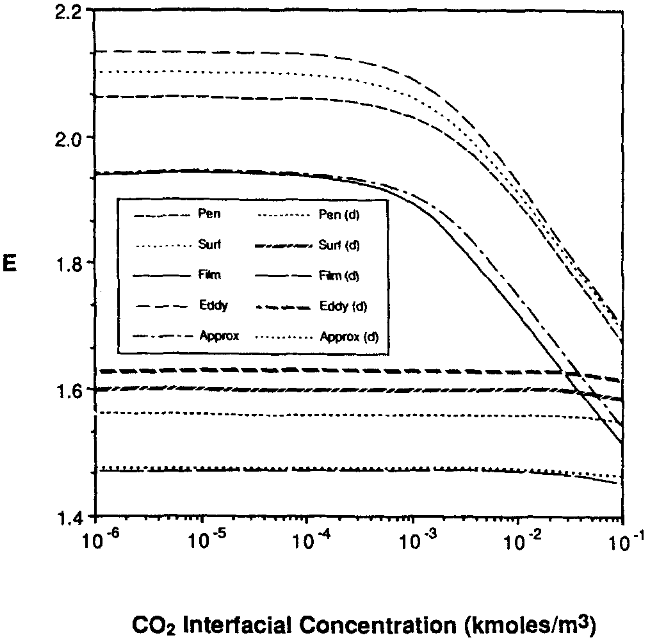

Figure 10. Effect of CO_2 interfacial concentration and hydroxide reaction for the MDEA system.

$k_l^o = 1.46 \times 10^{-4}$ m/s; $T = 45°C$; CO_2 loading = 0.005; (d) = numerical solution with the hydroxide reaction "deactivated"

It should be noted that Carta and Pigford (1983) found significant differences between penetration theory and film theory for the case of NO absorption into aqueous nitric acid solution. The distinguishing feature of this example is that the reaction is autocatalytic. Therefore, for the case of autocatalytic reactions, one must use caution in determining the appropriate mass transfer model.

Conclusions

Four "rigorous" mass transfer theories were compared. It has been demonstrated that eddy diffusivity theory and the approximate method of Chang and Rochelle provide an excellent approximation to the surface renewal theory, generally considered to be more accurate than film theory. These results have been demonstrated for a second-order, reversible reaction and for a more complicated system of industrial interest. In light of the shorter computation time involved for the steady-state theories and the inherent uncertainty at the present time in the actual mass transfer mechanism at a gas-liquid interface, a steady-state model is most useful for experimental data interpretation and acid gas treating process design. Furthermore, since numerical implementation of the eddy diffusivity theory differs little from film theory, we prefer the eddy diffusivity theory.

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Notation

$\underline{\underline{A}}$ = matrix of first derivative collocation weights
a = eddy diffusivity parameter
$\underline{\underline{B}}$ = matrix of second derivative collocation weights
C = concentration, kmol · m^{-3}
C_{ij} = concentration of ith species at point j, kmol · m^{-3}
D = diffusion coefficient, $m^2 \cdot s^{-1}$
d = dimensionless diffusion coefficient, D/D_1
E = enhancement factor, R/R_{phys}
erf = error function
F = Faraday's constant, 9.6485×10^{-4} C · $kmol^{-1}$
i = current flux, C · $m^{-2} \cdot s^{-1}$
J = flux for species, i, kmol · $m^2 \cdot s^{-1}$
K = equilibrium constant
k = Boltzmann's constant, 1.381×10^{-23} J · K^{-1} (V · C · K^{-1})
k_1 = first-order rate constant, s^{-1}
k_2 = second-order rate constant, $m^3 \cdot kmol^{-1} \cdot s^{-1}$
k_1^o = mass transfer coefficient, $m^2 \cdot s^{-1}$
l = Lagrange polynomial
m = distance exponent for eddy diffusivity
n = number of components
p = number of collocation points in an element, including end points
R = absorption rate, kmol · $m^{-2} \cdot s^{-1}$
r = dimensionless spatial distance
r_i = reaction term for species i, kmol · $m^{-3} \cdot s^{-1}$
R_{phys} = absorption rate with no chemical reaction, kmol · $m^{-2} \cdot s^{-1}$
s = surface renewal rate, s^{-1}
T = temperature, K
t = time, s
x = distance from interface, m
Z = charge number

Greek letters

δ = film thickness, m
Φ = electrical potential, V
ϕ = fraction of surface area, defined in Eq. 13
θ = contact time, s
ϑ = stoichiometric coefficient
∇ = one-dimensional differentiation operation $\partial/\partial x$
∇^2 = one-dimensional Laplacian operator, $\partial^2/\partial x^2$

Subscripts

1 = absorbing chemical species
= = matrix notation
– = vector notation
i = species designation
o = corresponds to a bulk-phase concentration

Superscripts

′ = time derivative
* = corresponds to an interface concentration
o = corresponds to a bulk-phase concentration

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