Role of Liquid Reactant Volatility in Gas Absorption with an Exothermic Reaction

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A film-theory model is presented for nonisothermal gas absorption with a second-order exothermic reaction. The model accounts for the volatility of the liquid reactant and heat transfer from the liquid surface to the gas phase. The pertinent equations were solved numerically using B-spline collocation. Results from this solution show that for intermediate values of Hatta number the liquid-reactant volatility is detrimental to the enhancement of gas absorption. As Hatta number approaches zero or infinity, however, the effect of liquid-reactant volatility becomes minor. Heat losses to the gas phase drastically reduce the interfacial temperature rise, which in turn enhances or inhibits the absorption rate depending on the effective activation energy being larger or less than zero, respectively. Approximate expressions for the enhancement factor and the interfacial temperature rise were also developed. Comparisons with the "exact" numerical solution verified the accuracy of these expressions over a reasonable spectrum of parameter values. The model developed was applied to two cases representing real conditions: the chlorination of toluene and the sulfonation of dodecylbenzene. Volatility effects are shown to be important for the former system, while the relatively nonvolatile dodecylbenzene served as a counter example.

Introduction

Many industrially important gas-liquid reactions, such as oxidation, sulfonation, nitration, halogenation, and alkylation, are highly exothermic in nature. In these processes, two types of heat are generated: the heat of solution that is generated at the gas-liquid interface; the heat of reaction that is generated within the mass transfer film near the interface for fast reactions or within the bulk liquid for slow reactions. The release of the heat of solution and reaction during absorption may result in significant temperature increase at the interface, which in turn affects the absorption rate behavior. Thus, in heating the liquid, it increases the rate of reaction and diffusion further steepening the concentration gradient near the gas-liquid interface and thereby increasing the absorption driving force. But it also decreases the solubility of the gas in the liquid, thereby decreasing the absorption driving force. Hence, the overall rate of absorption is a result of the combination of these two opposing effects.

Such an interfacial temperature rise has been observed by several investigators. For instance, Mann and Clegg (1975) and Mann and Moyes (1977) indirectly measured temperature rises up to 53°C for chlorination and 58°C for sulfonation using a laminar jet technique, whereas Ponter et al. (1974) measured the interfacial temperature rise directly by an infrared technique and found a 20°C rise for sulfonation. Increases of this magnitude will significantly affect the solubility; hence, this phenomenon needs to be understood for the design of absorption-reaction systems.

For first-order reactions, the interfacial temperature rise and the relevant enhancement factor have been analyzed theoretically by several investigators. These were mainly carried out using either the film or the penetration models (Danckwerts, 1953; Shah, 1972; Mann and Moyes, 1977; Asai et al., 1985; Chatterjee and Altwicker, 1987). The more general case involving a second-order bimolecular reaction was analyzed using the film theory by Bhattacharya et al. (1987) and more recently by Al-Ubaidi et al. (1990). A penetration theory analysis of the same case was also attempted by Evans and Selim (1990).

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A major shortcoming exists with these analyses. Thus, all these researchers completely neglected evaporation of the liquid reactant into the gas phase. In many practical systems, especially in laboratory reactors, evaporation from the liquid may drastically reduce the interfacial temperature rise, and the nonisothermal effects predicted by the above theoretical work may be completely obscured. The importance of evaporation of the liquid reactant during nonisothermal gas absorption was emphasized by Stockar and Wilke (1977) and, more recently, by Villadsen (1988). Furthermore, previous studies on gas absorption with chemical reaction under isothermal conditions have shown that the volatility of the liquid reactant can be detrimental to the enhancement of gas absorption (Pangarkar, 1974; Shah and Sharma, 1976; Shaikh and Varma, 1984; Ozturk and Shah, 1986). Therefore, for exothermic gas absorption with chemical reaction, the volatility of the liquid is expected to give rise to complex possibilities for the enhancement factor and the relevant temperature rise.

The increase in the interfacial temperature is also likely to result in heat dissipation from the liquid surface to the gas phase. Heat losses to the gas phase reduce the interfacial temperature rise and, under certain conditions, thermal effects may become less relevant. In this article, the effects of the liquid reactant volatility and heat losses to the gas phase on the rate of chemical absorption under nonisothermal conditions are investigated.

Film Model

Film-theory equations

The problem considered is the situation in which a gas component, A, is absorbed into a liquid phase and then reacts irreversibly with component B which is already present in the liquid phase. Product P is produced as a result of the liquid-phase reaction according to the following stoichiometry:

$$A(g) + \nu B(l) \rightarrow P(l) \tag{1}$$

The kinetic equations for A and B are:

$$R_A = -k_2 C_A B_B \tag{2}$$

$$R_B = -\nu k_2 C_A C_B \tag{3}$$

A schematic diagram of the film model with concentration and temperature profiles for the case involving a volatile liquid reactant is shown in Figure 1. The mathematical model is based on the following assumptions:

1. Mass transfer resistance of the solute gas A in the gas phase is negligible relative to resistance in the liquid phase.
2. The interfacial mass transfer resistance at the gas-liquid interface is negligible.
3. The reaction in the liquid phase is essentially completed within the film.
4. The liquid phase consists of a volatile liquid reactant B so that there is material and energy losses due to evaporation.
5. Heat transfer to the gas phase, due to convection at the interface, is *not* negligible.
6. The physical properties of the liquid phase, such as density, heat capacity, and thermal conductivity, are independent of temperature and conversion.
7. Bulk flow, Dufort, Soret, and Rayleigh effects are negligible.
8. The temperature dependence of the diffusivities, solubility, and chemical rate constant may be reasonably expressed over a wide concentration range as:

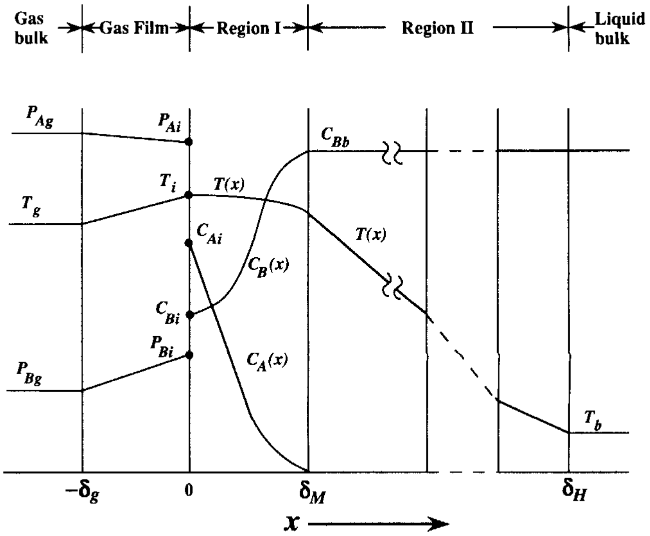

Figure 1. Film model with concentration and temperature profiles.

$$D_A(T) = D_{Ab}\exp\left[-\frac{E_{DA}}{R}\left(\frac{1}{T}-\frac{1}{T_b}\right)\right] \tag{4}$$

$$D_B(T) = D_{Bb}\exp\left[-\frac{E_{DB}}{R}\left(\frac{1}{T}-\frac{1}{T_b}\right)\right] \tag{5}$$

$$C_{Ai}(T) = C_{Aib}\exp\left[+\frac{(-\Delta H_S)}{R}\left(\frac{1}{T}-\frac{1}{T_b}\right)\right] \tag{6}$$

$$k_2(T) = k_{2b}\exp\left[-\frac{E_R}{R}\left(\frac{1}{T}-\frac{1}{T_b}\right)\right] \tag{7}$$

where the heat of solution $(-\Delta H_S)$ and the activation energies E_{DA}, E_{DB}, and E_R are independent of temperature and composition.

The first assumption that ignores the gas-side resistance associated with the transfer of the solute gas A in the gas film is equivalent to the validity of the following inequality for species A: $k_g \gg Hk_\ell$, where k_g is the gas-side mass-transfer coefficient for species A, H is Henry's law constant, and k_ℓ is the liquid side mass-transfer coefficient. This inequality implies that either pure gas A is used $(k_g \rightarrow \infty)$ or that gas A has very low solubility $(H \ll 1)$. A similar inequality, however, has not been assumed for species B. That is, the terms in the inequality are considered to be of the same order of magnitude for species B implying that the gas-side resistance for this species is not negligible. This assumption was first adopted by Pangarkar (1974), and later used by Hikita et al. (1979) and Shaikh and Varma (1984).

Since no reaction takes place beyond the mass transfer film, the temperature profile in the region $\delta_M < x < \delta_H$ is linear and the heat flux at the edge of the mass transfer film is given by:

$$-K_\ell \frac{dT}{dx} = -K_\ell \frac{T_b - T}{\delta_H - \delta_M} \quad \text{at } x = \delta_M \tag{8}$$

We, therefore, need only consider the equations in the mass transfer film.

The film-theory equations describing simultaneous diffusion and reaction with heat effects in the mass transfer film ($0 < x < \delta_M$) for the case of a volatile liquid reactant are given by:

$$\frac{d}{dx}\left[D_A(T)\,\frac{dC_A}{dx}\right] - k_2(T)C_AC_B = 0 \tag{9}$$

$$\frac{d}{dx}\left[D_B(T)\,\frac{dC_B}{dx}\right] - \nu k_2(T)C_AC_B = 0 \tag{10}$$

$$\frac{d^2T}{dx^2} + \frac{(-\Delta H_R)}{K_\ell}\,k_2(T)C_AC_B = 0 \tag{11}$$

with the boundary conditions:

$$x = 0\text{:} \quad C_A = C_{Ai}(T), \quad T = T_i \tag{12a}$$

$$D_B(T)\,\frac{dC_B}{dx} = k^o_{gB}(P_B - P_{Bg}), \; P_B = P_{Bi} \tag{12b}$$

$$(-\Delta H_S)\left[-D_A(T)\,\frac{dC_A}{dx}\right] = -K_\ell \frac{dT}{dx}$$

$$+ h_g(T - T_g) + (+\Delta H_V)\left[D_B(T)\,\frac{dC_B}{dx}\right] \tag{12c}$$

$$x = \delta_M\text{:} \quad C_A = 0 \tag{13a}$$

$$C_B = C_{Bb} \tag{13b}$$

$$-K_\ell \frac{dT}{dx} = -K_\ell \frac{T_b - T}{\delta_H - \delta_M} \tag{13c}$$

The first term on the right side of Eq. 12c represents heat conduction into the liquid phase, the second term represents heat losses due to convection to the gas phase, and the third term represents energy consumed in the evaporation of the liquid-phase reactant B. Boundary condition (Eq. 13a) implies that the reaction is essentially completed in the liquid film. This is generally the case for Hatta number $\sqrt{M}$ greater than 3. For $\sqrt{M} < 3$, the dissolved gas concentration in the bulk liquid becomes nonzero and the reaction may take place mainly in the bulk (slow reaction regime). This regime requires the consideration of global reactor behavior and will be treated elsewhere. It should be remembered, however, that the fast reaction regime where $\sqrt{M} > 3$ is frequently encountered in practice (Danckwerts, 1970).

If it is further assumed that a linear distribution law governs the phase equilibrium of the liquid reactant, B, then Eq. 12b can be written as:

$$D_B(T)\,\frac{dC_B}{dx} = k^o_{gB}H_B(T)\,(C_B - C_{Bg}), \; C_B = C_{Bi} \tag{14}$$

where $H_B(T)$ is given by:

$$P_B = H_{Bb}\exp\left[-\frac{(+\Delta H_V)}{R}\left(\frac{1}{T} - \frac{1}{T_b}\right)\right]C_B$$

Integration of Eqs. 9 through 11 with given boundary conditions leads to the temperature distribution $T(x)$ and the concentration profiles $C_A(x)$ and $C_B(x)$ in the liquid film. The rate of absorption of dissolved gas across unit area of the interface is then readily computed from:

$$\overline{R} = -D_A(T_i)\,\frac{dC_A}{dx}\bigg|_{x=0}$$

For the present problem, a nonisothermal enhancement factor may be defined as:

$$E^*_{\text{non}} = \left[\frac{\text{rate of chemical absorption with heat \& volatility}}{\text{rate of physical absorption without heat \& volatility}}\right]$$

$$= \frac{-D_A(T_i)\left[\dfrac{dC_A}{dx}\right]_{x=0}}{k^o_\ell C_{Aib}} \tag{15}$$

Accordingly, the rate of absorption of gas A becomes:

$$\overline{R} = E^*_{\text{non}}k^o_\ell C_{Aib}$$
$$= k_\ell\, C_{Aib}$$

In order to ascertain the importance of heat effects and volatility on the rate of absorption, two additional enhancement factors are defined as:

$$E_{HV} = \left[\frac{\text{rate of chemical absorption with heat \& volatility}}{\text{rate of isothermal chemical absorption}}\right]$$

$$= \frac{E^*_{\text{non}}}{E} \tag{16}$$

$$E_V = \left[\frac{\text{rate of chemical absorption with heat \& volatility}}{\text{rate of chemical absorption with heat effects alone}}\right]$$

$$= \frac{E^*_{\text{non}}}{E_{\text{non}}} \tag{17}$$

The definition of E_{HV} accounts for heat and volatility effects on the absorption rate; the absorption rate is enhanced or reduced depending on the value of E_{HV} being larger than or less than unity, respectively. On the other hand, the definition of E_V accounts for the effects of volatility alone on the absorption rate.

It is convenient to define the following dimensionless variables:

$$X = \frac{x}{\delta_M}, \; A = \frac{C_A}{C_{Aib}}, \; B = \frac{C_B}{C_{Bb}}, \; \theta = \frac{T - T_b}{T_b}, \tag{18}$$

and the following dimensionless parameters:

$$\epsilon_{DA}=\frac{E_{DA}}{RT_b},\ \epsilon_{DB}=\frac{\mathrm{E}_{DB}}{RT_b},\ \epsilon_S=\frac{(-\Delta H_S)}{RT_b},\ \epsilon_R=\frac{E_R}{RT_b},\ \epsilon_V=\frac{(+\Delta H_V)}{RT_b}$$

$$S=\frac{\nu D_{Ab}C_{Aib}}{D_{Bb}C_{Bb}},\ M=\frac{\delta_M^2 k_{2b}C_{Bb}}{D_{Ab}},\ \beta_R=\frac{(-\Delta H_R)D_{Ab}C_{Aib}}{K_\ell T_b},$$

$$\beta_S=\frac{(-\Delta H_S)D_{Ab}C_{Aib}}{K_\ell T_b},\ \beta_V=\frac{(+\Delta H_V)D_{Bb}C_{Bb}}{K_\ell T_b} \qquad (19)$$

The problem then runs as follows:

$$\frac{d}{dX}\left[\exp\left(\epsilon_{DA}\frac{\theta}{1+\theta}\right)\frac{dA}{dX}\right]-M\exp\left(\epsilon_R\frac{\theta}{1+\theta}\right)A\ B=0 \qquad (20)$$

$$\frac{d}{dX}\left[\exp\left(\epsilon_{DB}\frac{\theta}{1+\theta}\right)\frac{dB}{dX}\right]-M\ S\exp\left(\epsilon_R\frac{\theta}{1+\theta}\right)A\ B=0 \qquad (21)$$

$$\frac{d^2\theta}{dX^2}+\beta_R\ M\exp\left(\epsilon_R\frac{\theta}{1+\theta}\right)A\ B=0 \qquad (22)$$

with the boundary conditions:

$$X=0\text{: } A=\exp\left(-\epsilon_S\frac{\theta}{1+\theta}\right),\ \theta=\theta_i \qquad (23a)$$

$$\exp\left(\epsilon_{DB}\frac{\theta}{1+\theta}\right)\left[\frac{dB}{dX}\right]=Bi_M\exp\left(\epsilon_V\frac{\theta}{1+\theta}\right)(B-B_g) \qquad (23b)$$

$$\beta_S\exp\left(\epsilon_{DA}\frac{\theta}{1+\theta}\right)\left[\frac{dA}{dX}\right]=\left[\frac{d\theta}{dX}\right]-Bi_H(\theta-\theta_g)$$
$$-\beta_V Bi_M\exp\left(\epsilon_V\frac{\theta}{1+\theta}\right)(B-B_g) \qquad (23c)$$

$$X=1\text{:}\quad A=0 \qquad (24a)$$

$$B=1 \qquad (24b)$$

$$\left(\frac{\delta_H}{\delta_M}-1\right)\left[\frac{d\theta}{dX}\right]+\theta=0 \qquad (24c)$$

where Bi_H and Bi_M are the Biot numbers for heat and mass transfer given by:

$$Bi_H=\frac{h_g\delta_M}{K_\ell}$$

$$Bi_M=\frac{k_{gB}^o H_{Bb}\delta_M}{D_{Bb}}$$

When $Bi_M=Bi_H=0$, the above system of equations reduces to the case of a nonvolatile liquid reactant with no convection heat losses to the gas phase. This case was analyzed previously by Al-Ubaidi et al. (1990), in which they neglected not only evaporation of the liquid reactant but also convection heat losses to the gas phase. Both restrictions are lifted in this analysis. We also should bear in mind that in evaluating the right side of Eq. 17, the Biot number Bi_H (which is not necessarily equal to zero) must be the same for both the numerator and the denominator.

Method of solution

The set of Eqs. 20-24 defines a nonlinear two-point boundary-value problem involving three coupled second-order ordinary differential equations. Of the currently available numerical codes for the solution of this class of boundary-value problems, COLSYS (Ascher et al., 1978, 1979, 1981) has proved to be competitive with other robust general-purpose codes and is effective particularly for solving difficult problems (Davis and Fairweather, 1981; Denison et al., 1983; Ho, 1983; Davis, 1984). This code is basically a one-dimensional finite element method using *B*-spline collocation at Gaussian points. The code has many excellent features such as versatility, adaptive mesh selection, reliable error estimates, and robust convergence. Because of these advantages, the present problem was solved using COLSYS.

Approximate solution

A basic requirement in the modeling of gas-liquid reactors is the accurate simulation of interface mass transfer. For the modeling of nonisothermal gas-liquid reactors, the interface mass transfer process is highly complicated by the need for solving the nonisothermal diffusion-reaction problem in the liquid film as given by the nonlinear system of Eqs. 9 through 14. For this reason, approximate solutions of these equations which reduce the problem to a system of nonlinear algebraic equations are highly desirable. With this in mind, an approximate solution to the present problem is developed and its accuracy relative to the exact numerical solution is ascertained.

To start, Mann and Moyes (1977) introduced two simplifications in the film model: since $\delta_M \ll \delta_H$, the temperature across the reaction zone is essentially constant and equal to the unknown interfacial temperature T_i; the heat generation due to reaction may be treated as an interfacial heat flux. Using these approximations, Eqs. 9-11 simplify to:

$$D_A(T_i)\frac{d^2C_A}{dx^2}-k_2(T_i)C_AC_B=0\quad 0<x<\delta_M \qquad (25)$$

$$D_B(T_i)\frac{d^2C_B}{dx^2}-\nu k_2(T_i)C_AC_B=0\quad 0<x<\delta_M \qquad (26)$$

$$\frac{d^2T}{dx^2}=0\qquad 0<x<\delta_H \qquad (27)$$

Equations 25-27 imply that while the temperature is approximately constant across the mass transfer film ($\approx T_i$), the temperature profile $T(x)$ must be linear across the heat transfer film $0<x<\delta_H$. The unknown temperature T_i is obtained from the following overall heat balance over the mass transfer film:

$$(-\Delta H_S)\left[-D_A(T_i)\frac{dC_A}{dx}\bigg|_{x=0}\right]+$$
$$(-\Delta \mathrm{H}_R)\left[-D_A(T_i)\frac{dC_A}{dx}\bigg|_{x=0}-\left(-D_A(T_i)\frac{dC_A}{dx}\bigg|_{x=\delta_M}\right)\right]=$$

$$-K_\ell \frac{dT}{dx}\bigg|_{x=\delta_M} + h_g(T_i - T_g) + (+\Delta H_V) k^o_{gB} H_B(T_i)(C_B - C_{Bi}) \tag{28}$$

This heat balance is exact and can be easily derived by first eliminating the reaction terms between Eqs. 9 and 11 and integrating the resulting equation across the mass transfer film.

The conduction heat flux at $x=\delta_M$, which appears on the right side of Eq. 28, is obtained from the solution of Eq. 27 as:

$$-K_\ell \frac{dT}{dx}\bigg|_{x=\delta_M} = -K_\ell \frac{T_b - T_i}{\delta_H} \tag{29}$$

Moreover, the temperature T_M at the edge of the mass transfer film is taken equal to T_i in accordance with Mann's first approximation.

Next, we eliminate the kinetic terms of Eqs. 25 and 26 to obtain:

$$\frac{d^2}{dx^2}\left[C_A - \frac{D_B(T_i)}{\nu D_A(T_i)} C_B\right] = 0 \tag{30}$$

Integrating this equation twice under the appropriate boundary conditions, we obtain the following relation between $C_A(x)$ and $C_B(x)$:

$$\frac{C_B(x)}{C_{Bb}} = 1 + S_{\text{non}} E^o_{\text{non}} \frac{C_A(x)}{C_{Ai}(T_i)} - \left[1 + S_{\text{non}} E^o_{\text{non}} - \frac{C_{Bi}}{C_{Bb}}\right]\left[1 - \frac{x}{\delta_M}\right] \tag{31}$$

where

$$S_{\text{non}} = S \exp\left(-\epsilon_{DB} \frac{\theta_i}{1+\theta_i}\right)$$

$$E^o_{\text{non}} = \exp\left[(\epsilon_{DA} - \epsilon_S) \frac{\theta_i}{1+\theta_i}\right]$$

Substituting Eq. 31 into Eq. 25, the following differential equation is obtained:

$$D_A(T_i) \frac{d^2 C_A}{dx^2} - k_2(T_i) C_A(x) C_{Bb}\left[1 + S_{\text{non}} E^o_{\text{non}} \frac{C_A(x)}{C_{Ai}(T_i)} - \left(1 + S_{\text{non}} E^o_{\text{non}} - \frac{C_{Bi}}{C_{Bb}}\right)\left(1 - \frac{x}{\delta_M}\right)\right] = 0 \tag{32}$$

The concentration profile $C_A(x)$ of the solute gas A in the mass transfer film can be approximated by:

$$C_A(x) = C_{Ai}(T_i) + \frac{dC_A}{dx}\bigg|_{x=0} x = C_{Ai}(T_i) - \frac{D_{Ab}}{D_A(T_i)} C_{Aib} \overset{*}{E}_{\text{non}} \frac{x}{\delta_M} \tag{33}$$

This linearized concentration profile has been used successfully in previous work by Hikita et al. (1977, 1979). Rearranging Eq. 33, we obtain:

$$\frac{x}{\delta_M} = \frac{D_A(T_i)}{D_{Ab}}\left[\frac{C_{Ai}(T_i)}{C_{Aib}} - \frac{C_A(x)}{C_{Aib}}\right] \frac{1}{\overset{*}{E}_{\text{non}}} \tag{34}$$

Substitution of this expression into Eq. 32 leads to:

$$D_A(T_i) \frac{d^2 C_A}{dx^2} - k_2(T_i) C_{Bb}(\Gamma_1 C_A^2 - \Gamma_2 C_A) = 0 \tag{35}$$

where

$$\Gamma_1 = \frac{\Lambda}{C_{Ai}(T_i)} \qquad \Gamma_2 = \Lambda - \frac{C_{Bi}}{C_{Bb}}$$

$$\Lambda = \left[S_{\text{non}} E^o_{\text{non}} - \frac{E^o_{\text{non}}}{\overset{*}{E}_{\text{non}}}\left(1 + S_{\text{non}} E^o_{\text{non}} - \frac{C_{Bi}}{C_{Bb}}\right)\right] \tag{36}$$

Here, we linearize Eq. 35 by making the following approximation:

$$C_A^2 = \frac{2}{3} C_{Ai}(T_i) C_A(x) \tag{37}$$

This approximation was originally suggested by Hikita and Asai (1964) in the analysis of gas absorption accompanied by an irreversible $(m,n)th$-order reaction and has been used widely with sufficient accuracy to linearize nonlinear differential equations in other chemical absorption problems (Onda et al., 1970, 1972; Shah and Kenney, 1972). Substituting Eq. 37 into Eq. 35, we obtain:

$$D_A(T_i) \frac{d^2 C_A}{dx^2} - k_2(T_i) C_{Bb}\left(\frac{C_{Bi}}{C_{Bb}} - \frac{\Lambda}{3}\right) C_A(x) = 0 \tag{38}$$

The equation now reduces to a form that can be solved analytically for $C_A(x)$. The solution is given by:

$$\frac{C_A(x)}{C_{Ai}(T_i)} = \frac{\sinh[\xi \overset{*}{\eta}_{\text{non}} \sqrt{M}\,(1 - x/\delta_M)]}{\sinh[\xi \overset{*}{\eta}_{\text{non}} \sqrt{M}]} \tag{39}$$

where

$$\overset{*2}{\eta}_{\text{non}} = \frac{C_{Bi}(\theta_i)}{C_{Bb}} - \frac{1}{3}\left[S_{\text{non}} E^o_{\text{non}} - \frac{E^o_{\text{non}}}{\overset{*}{E}_{\text{non}}}\left(1 - \frac{C_{Bi}(\theta_i)}{C_{Bb}} + S_{\text{non}} E^o_{\text{non}}\right)\right]$$

$$\xi = \exp\left[0.5(\epsilon_R - \epsilon_{DA}) \frac{\theta_i}{1+\theta_i}\right]$$

Next, we derive an exact expression for the interfacial concentration of the liquid reactant, $C_{Bi}(\theta_i)$. Eliminating the kinetic terms from Eqs. 25 and 26 and integrating the resulting equation twice across the film, we obtain the following expression for $C_{Bi}(\theta_i)$:

$$\frac{C_{Bi}(\theta_i)}{C_{Bb}}=\frac{1-S_{\rm non}(E^*_{\rm non}-E^o_{\rm non})+Bi_M\exp\left[(\epsilon_V-\epsilon_{DB})\dfrac{\theta_i}{1+\theta_i}\right]B_g}{1+Bi_M\exp\left[(\epsilon_V-\epsilon_{DB})\dfrac{\theta_i}{1+\theta_i}\right]} \tag{40}$$

Expressions for the mass fluxes of the solute gas A at $x=0$ and $x=\delta_M$ are now readily obtained through the differentiation of Eq. 39. Substitution of the mass fluxes into Eq. 28 and 15 gives the following equations for the interfacial temperature θ_i and the nonisothermal enhancement factor $E^*_{\rm non}$:

$$\theta_i=\left[\frac{\beta_R+\beta_S}{\tanh(\eta^*_{\rm non}\sqrt{M}\xi)}-\frac{\beta_R}{\sinh(\eta^*_{\rm non}\sqrt{M}\xi)}\right]$$

$$\times\,\eta^*_{\rm non}\sqrt{M}\exp\left[\epsilon_{\rm eff}\frac{\theta_i}{1+\theta_i}\right]\frac{(\delta_H/\delta_M)}{1+Bi_H(\delta_H/\delta_M)}+\frac{Bi_H(\delta_H/\delta_M)}{1+Bi_H(\delta_H/\delta_M)}\theta_g$$

$$-\frac{\beta_V Bi_M\exp\left(\epsilon_V\dfrac{\theta_i}{1+\theta_i}\right)(\delta_H/\delta_M)}{1+Bi_H(\delta_H/\delta_M)}(B_i-B_g) \tag{41}$$

$$E^*_{\rm non}=\frac{\eta^*_{\rm non}\sqrt{M}}{\tanh(\eta^*_{\rm non}\sqrt{M}\xi)}\exp\left(\epsilon_{\rm eff}\frac{\theta_i}{1+\theta_i}\right) \tag{42}$$

where

$$\epsilon_{\rm eff}=0.5(\epsilon_R+\epsilon_{DA})-\epsilon_S$$

Equations 40 through 42 constitute a set of nonlinear algebraic equations for the three unknowns C_{Bi}/C_{Bb}, θ_i, and $E^*_{\rm non}$. These were solved numerically using the Newton-Raphson method. For $\sqrt{M}\geq 3$, these equations simplify to:

$$\frac{C_{Bi}(\theta_i)}{C_{Bb}}=\frac{1-S_{\rm non}(E^*_{\rm non}-E^o_{\rm non})+Bi_M\exp\left[(\epsilon_V-\epsilon_{DB})\dfrac{\theta_i}{1+\theta_i}\right]B_g}{1+Bi_M\exp\left[(\epsilon_V-\epsilon_{DB})\dfrac{\theta_i}{1+\theta_i}\right]} \tag{43}$$

$$\theta_i=(\beta_R+\beta_S)\eta^*_{\rm non}\sqrt{M}\left[\frac{(\delta_H/\delta_M)}{1+Bi_H(\delta_H/\delta_M)}\right]\exp\left(\epsilon_{\rm eff}\frac{\theta_i}{1+\theta_i}\right)+$$

$$\frac{Bi_H(\delta_H/\delta_M)}{1+Bi_H(\delta_H/\delta_M)}\theta_g-\frac{\beta_V Bi_M\exp\left[\epsilon_V\dfrac{\theta_i}{1+\theta_i}\right](\delta_H/\delta_M)}{1+Bi_H(\delta_H/\delta_M)}(B_i-B_g) \tag{44}$$

$$E^*_{\rm non}=\eta^*_{\rm non}\sqrt{M}\exp\left(\epsilon_{\rm eff}\frac{\theta_i}{1+\theta_i}\right) \tag{45}$$

Several limiting cases may be discerned from these equations. For instance, when $Bi_M\to\infty$, the gas-phase resistance for the volatile liquid reactant becomes negligible, and Eq. 43 reduces to $C_{Bi}=C_{Bg}$. Similarly, when $Bi_H\to\infty$, no gas-phase resistance to heat transfer exists, and Eq. 44 reduces to $\theta_i=\theta_g$. On the other hand, when $Bi_H=Bi_M=0$, Eqs. 40-42 reduce to Al-Ubaidi et al. (1990) equations for the case of a nonvolatile liquid reactant with no convection heat losses to the gas phase.

When heat effects are negligible, $\beta_R=\beta_S=\beta_V=\epsilon_{DA}=\epsilon_{DB}=\epsilon_R=\epsilon_S=\epsilon_V=0$, Eqs. 40-42 reduce to:

$$\frac{C_{Bi}}{C_{Bb}}=\frac{1-S(E^*-1)+Bi_MB_g}{1+Bi_M} \tag{46}$$

$$\theta_i=0 \tag{47}$$

$$E^*=\frac{\eta^*\sqrt{M}}{\tanh(\eta^*\sqrt{M})} \tag{48}$$

where

$$\eta^*=\sqrt{\frac{C_{Bi}}{C_{Bb}}-\frac{1}{3}\left[S-\frac{1}{E^*}\left(1-\frac{C_{Bi}}{C_{Bb}}+S\right)\right]}$$

which apply to the case of a volatile liquid reactant under isothermal conditions (Hikita et al., 1979). These equations reduce to the van Krevelen-Hoftijzer solution for isothermal absorption with a nonvolatile liquid reactant when $Bi_M=0$.

Thus the general Eqs. 43-45 reduce to the correct expressions under various limiting conditions.

Accuracy of the approximate solution

The accuracy of the approximate solution for the case of a volatile liquid reactant was compared with the numerical solution obtained by B-spline collocation. Table 1 gives the percentage deviation for the interfacial temperature rise and the nonisothermal enhancement factor for various combinations of Bi_H and Bi_M for $\delta_H/\delta_M=Le^{1/2}$. As seen from this table, the maximum deviation is about 13% for the interfacial temperature and 4% for the enhancement factor. It may, therefore, be concluded that Eqs. 40-42 provide an accurate approximate solution for the case of nonisothermal gas absorption with a volatile liquid reactant and convection heat losses to the gas phase.

Results and Discussion

Concentration and temperature profiles

Figure 2 compares the concentration and temperature profiles in the mass transfer film for the two cases of a volatile (solid lines) and nonvolatile (dashed lines) liquid reactant. As can be seen from the figure, when Bi_M increases from zero to 0.8, the liquid reactant is depleted in the neighborhood of the surface due to evaporation and the interfacial concentration falls from $B_i=0.88$ to $B_i=0.57$. In addition, the heat consumed in the evaporation of B causes the interfacial temperature to be reduced from $\theta_i=0.16$ to $\theta_i=0.1$. Clearly, the reduction in temperature causes the rate constant k_2 to decrease; but it also causes the solubility of the dissolved gas to increase from $A_i=0.35$ to $A_i=0.5$, as shown in the figure. The absorption rate, however, is reduced by about 40% in spite of the increased solubility of the dissolved gaseous species. This behavior is

Table 1. Percentage Deviation of Approximate Solution from Numerical Solution[†]

		%Deviation[‡]					
		S					
(Bi_H, Bi_M)		0.01		0.05		0.1	
	$\sqrt{M}$	E^*_{non}	θ_i	E^*_{non}	θ_i	E^*_{non}	θ_i
(0.015, 0.15)	2	0.64	−3.62	0.72	−2.03	0.81	0.08
	4	0.33	−2.67	0.42	−2.71	0.55	−2.73
	6	0.05	−0.96	0.05	−0.97	0.08	−0.98
	8	−0.04	−0.66	−0.11	−0.73	−0.17	−0.80
	10	−0.08	−0.47	0.21	−0.61	−0.34	−0.74
(0.075, 0.75)	6	1.78	−1.55	1.96	−0.20	2.19	1.11
	8	1.02	0.07	1.17	0.67	1.41	1.29
	10	0.56	−0.01	0.67	0.31	0.87	0.82
	15	0.01	−0.16	−0.04	−0.08	0.02	0.09
	20	−0.22	−0.24	−0.41	−0.35	−0.53	−0.37
	30	−0.37	−0.30	−0.77	−0.61	−1.26	−1.04
(0.15, 1.5)	8	2.89	9.41	3.10	9.08	3.39	9.81
	10	2.14	3.30	2.38	4.37	2.72	5.49
	15	0.89	1.16	1.19	1.72	1.58	2.55
	20	0.35	0.49	0.47	0.82	0.82	1.43
	30	−0.26	−0.03	−0.39	−0.05	−0.23	0.19
	40	−0.51	−0.26	−0.88	−0.53	−1.00	−0.59
(0.375, 3.75)	15	3.70	13.81	4.08	12.56	4.58	13.35
	20	2.80	5.42	3.26	6.42	3.91	8.18
	30	1.55	2.26	2.10	3.36	2.98	5.12
	40	0.75	1.23	1.28	2.00	2.32	3.80
	50	0.21	0.65	0.65	1.29	1.82	2.99
	60	−0.71	0.24	0.14	0.65	1.41	2.38
	70	−0.46	−0.05	−0.30	0.20	1.07	1.90

[†] $\beta_R=0.005$, $\beta_S=0.001$, $\beta_V=0.05$, $B_g=0.0$, $\theta_g=0.0$, $\epsilon_{DA}=3$, $\epsilon_{DB}=5$, $\epsilon_R=10$, $\epsilon_S=7.5$, $\epsilon_V=2$, $\delta_H/\delta_M=Le^{1/2}$, $Le=100$

[‡] $\%\ \text{deviation} = \dfrac{\text{numerical} - \text{approximate}}{\text{numerical}} \times 100$

based on the physical reasoning that the depletion of B and the accompanying decrease in the rate constant k_2 more than offset the increase in the reactant concentration A, so that the local rate of reaction is reduced, leading to a reduction in the absorption rate.

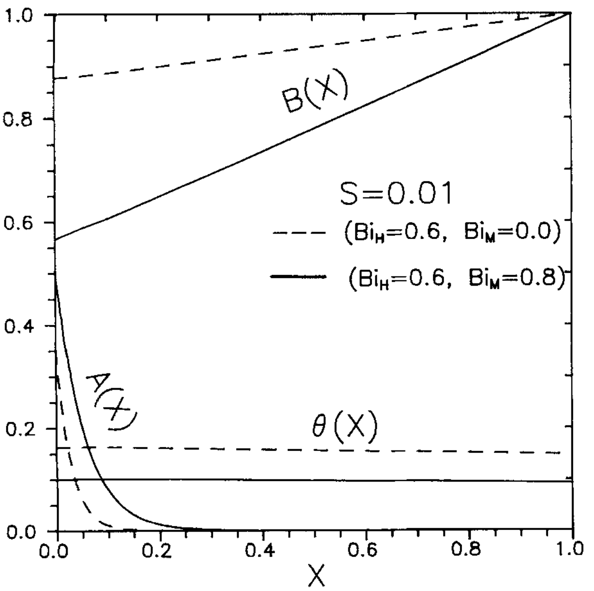

Figure 2. Effect of Bi_M on the concentration and temperature profiles in the film region.

$\beta_R=0.005$, $\beta_S=0.001$, $\beta_V=0.005$, $\epsilon_R=22$, $\epsilon_{DA}=3$, $\epsilon_{DB}=5$, $\epsilon_S=7.5$, $\epsilon_V=2$, $B_g=\theta_g=0$, $\sqrt{M}=10$, $\delta_H/\delta_M=Le^{1/2}$, and $Le=100$.

Figure 3 shows the effect of the Biot number for heat transfer, Bi_H, on the concentration and temperature profiles. When Bi_H increases from 0.45 to 0.75, the heat loss to the gas phase increases, leading to a significant reduction in the temperature throughout the film region. Thus, as can be seen from this figure, the interfacial temperature decreases from $\theta_i=0.15$ to $\theta_i=0.07$, a 55% reduction. This reduction causes the solubility of A to increase from $A_i=0.37$ to $A_i=0.63$, a 60% increase. The concentration of the liquid reactant B, however, is reduced only slightly. However, the decrease in the rate constant k_2, caused by a substantial temperature drop throughout the film, more than offsets the increase in the solubility of A, and the absorption rate is thereby reduced. That is the effect of the reaction rate constant, and diffusivity is dominant over the solubility enhancement.

It should also be noted in Figures 2 and 3 that the temperature $\theta(x)$ changes by only 5% from its maximum at the gas-liquid interface to its lower value at the edge of the mass-transfer film. This small difference supports the approximations of Mann and Moyes (1977) who considered the temperature to be essentially constant throughout the reaction zone.

Figure 4 shows the effect of Bi_M on the dimensionless interfacial concentration B_i. The figure clearly indicates that B_i is greatly influenced by the parameter Bi_M, especially at low values of Hatta number. The effect starts to diminish as the instantaneous reaction regime is approached. We may also note

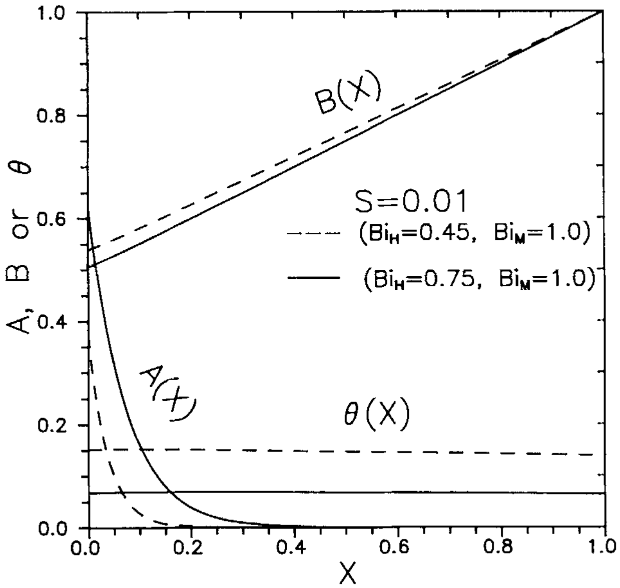

Figure 3. Effect of Bi_H on the concentration and temperature profiles in the film region.

$\beta_R=0.005$, $\beta_S=0.001$, $\beta_V=0.005$, $\epsilon_R=22$, $\epsilon_{DA}=3$, $\epsilon_{DB}=5$, $\epsilon_S=7.5$, $\epsilon_V=2$, $B_g=\theta_g=0$, $\sqrt{M}=10$, $\delta_H/\delta_M=Le^{1/2}$, and $Le=100$.

that the curves in Figure 4 approach the asymptotic value of $B_i=0$ as Hatta number becomes large. This asymptote corresponds to the case of an infinitely rapid reaction where the reaction takes place beneath the surface and the concentration of B is zero at the interface.

Figures 5 and 6 show the effect of Bi_M and Bi_H on the interfacial temperature rise θ_i. As expected, higher values of Bi_M or Bi_H lead to a decrease in the interfacial temperature rise. We may also note that the curves in Figure 5 approach a single horizontal asymptote as Hatta number becomes large. This asymptote corresponds to the case of a nonvolatile liquid reactant in the instantaneous reaction regime. In this regime, the reaction is confined to a plane situated beneath the interface and the liquid reactant B does not reach the gas-liquid interface. Accordingly, the interfacial temperature rise becomes independent of the volatility magnitude as this regime is approached. A similar behavior is also obtained in Figure 6, except that in this case each curve reaches its own asymptote as Hatta number becomes large. The asymptotes correspond to the instantaneous reaction regime for the indicated values

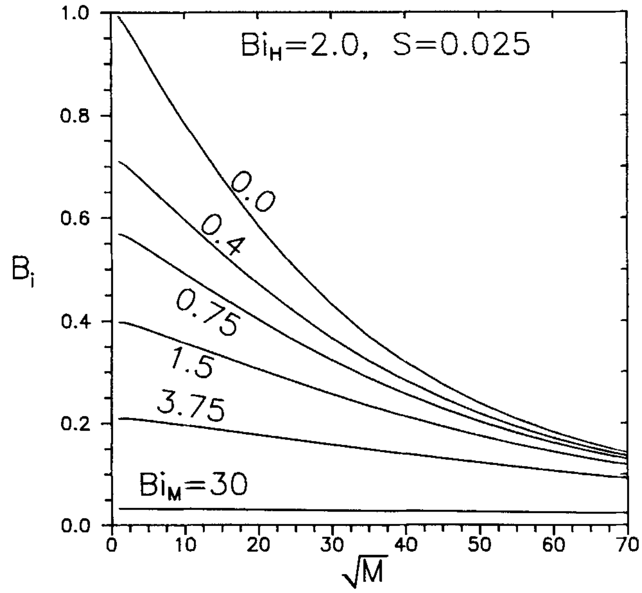

Figure 4. Effect of Bi_M on the interfacial concentration of the liquid reactant.

$\beta_R=0.005$, $\beta_S=0.001$, $\beta_V=0.005$, $\beta_R=22$, $\epsilon_{DA}=3$, $\epsilon_{DB}=5$, $\epsilon_S=7.5$, $\epsilon_V=2$, $B_g=\theta_g=0$, $\sqrt{M}=10$, $\delta_H/\delta_M=Le^{1/2}$, and $Le=100$.

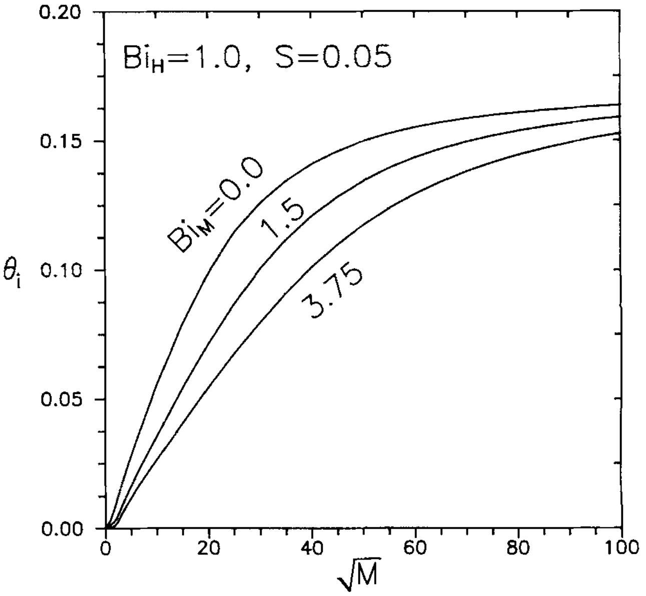

Figure 5. Effect of Bi_M on the surface temperature rise.

$\beta_R=0.005$, $\beta_S=0.001$, $\beta_V=0.005$, $\epsilon_R=22$, $\epsilon_{DA}=3$, $\epsilon_{DB}=5$, $\epsilon_S=7.5$, $\epsilon_V=2$, $B_g=\theta_g=0$, $\sqrt{M}=10$, $\delta_H/\delta_M=Le^{1/2}$, and $Le=100$.

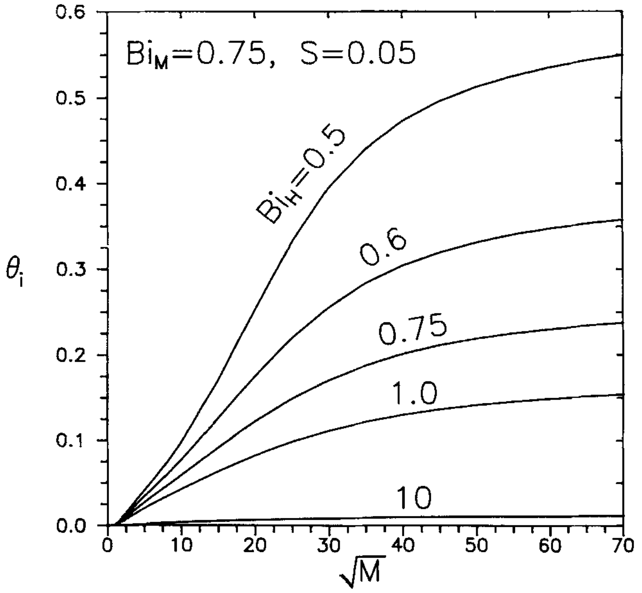

Figure 6. Effect of Bi_H on the surface temperature rise.

$\beta_R=0.005$, $\beta_S=0.001$, $\beta_V=0.005$, $\epsilon_R=22$, $\epsilon_{DA}=3$, $\epsilon_{DB}=5$, $\epsilon_S=7.5$, $\epsilon_V=2$, $B_g=\theta_g=0$, $\sqrt{M}=10$, $\delta_H/\delta_M=Le^{1/2}$, and $Le=100$.

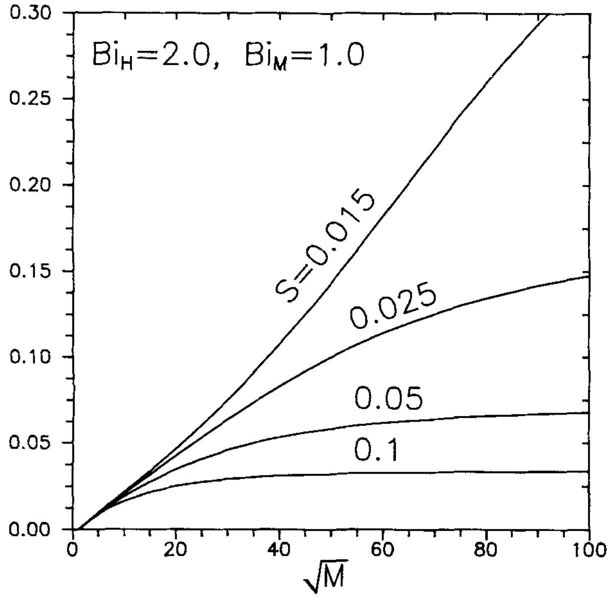

Figure 7. Effect of S on the surface temperature rise.

$\beta_R=0.005$, $\beta_S=0.001$, $\beta_V=0.005$, $\epsilon_R=22$, $\epsilon_{DA}=3$, $\epsilon_{DB}=5$, $\epsilon_S=7.5$, $\epsilon_V=2$, $B_g=\theta_g=0$, $\sqrt{M}=10$, $\delta_H/\delta_M=Le^{1/2}$, and $Le=100$.

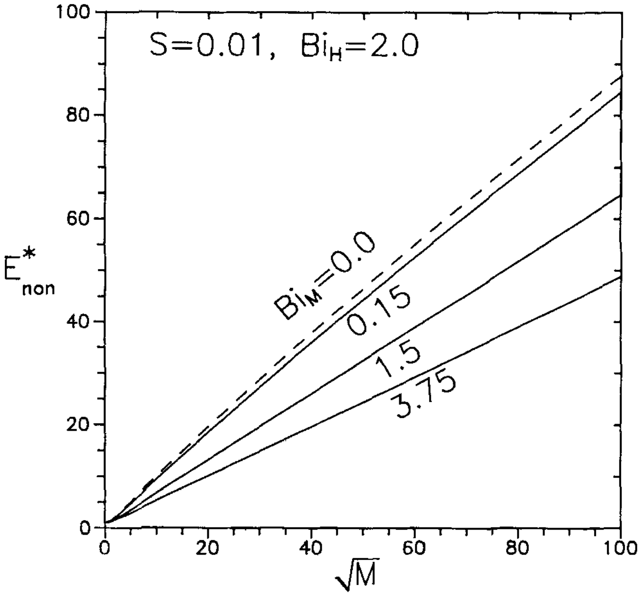

Figure 8a. Effect of Bi_M on the enhancement factor for $S=0.01$.

$\beta_R=0.005$, $\beta_S=0.001$, $\beta_V=0.005$, $\epsilon_R=14$, $\epsilon_{DA}=3$, $\epsilon_{DB}=5$, $\epsilon_S=7.5$, $\epsilon_V=2$, $B_g=\theta_g=0$, $\delta_H/\delta_M=Le^{1/2}$, and $Le=100$.

of Bi_H. As Bi_H increases, the asymptotes are reached at much smaller values of $\sqrt{M}$. At $Bi_H=10$, the interfacial temperature rise is essentially negligible for all values of $\sqrt{M}$ so that little error is introduced by assuming $Bi_H=\infty$ in this case.

The effect of the parameter S on the interfacial temperature rise θ_i is shown in Figure 7. The figure reveals that lower values of S lead to an increase in the interfacial temperature rise θ_i. This behavior is based on the following physical reasoning. At low values of S, the bulk concentration of the liquid reactant is relatively large enough or it diffuses toward the surface fast enough to prevent the reaction or evaporation causing substantial depletion there. The concentration of B is therefore relatively large throughout the film and the local rate of reaction is accordingly high. As a result the heat generated due to reaction is high and so leads to a substantial temperature rise. On the other hand, at large values of S, the concentration of the liquid reactant is relatively small throughout the film leading to a low rate of reaction. The heat generated due to reaction is accordingly low and the temperature rise is relatively small.

Enhancement factor

Figures 8a and 8b show the nonisothermal enhancement factor E^*_{non} as a function of Hatta number $\sqrt{M}$ for different values of Bi_M. In Figure 8a $S=0.01$, and in Figure 8b $S=0.05$. Higher values of Bi_M increase the magnitude of the liquid reactant concentration gradient at the interface and so lead to a decrease in the enhancement of gas absorption. Conversely, if Bi_M is sufficiently small due to a small value of k^o_{gB} such that the liquid concentration gradient at the interface approaches zero, then it can be safely assumed that E^*_{non} will not be appreciably different from the value of the corresponding nonvolatile case ($Bi_M=0$). We also observe that the curves in each figure approach the horizontal asymptote correspondings to $Bi_M=0$ as Hatta number becomes large. Thus, the effect of volatility on E^*_{non} diminishes as $\sqrt{M}$ approaches the diffusion-controlled limit. Furthermore, comparing the results in both figures, we notice that the effect of increasing S is to cause the asymptotic condition to emerge at smaller values of $\sqrt{M}$.

The effect of the Biot number for heat transfer, Bi_H, on the nonisothermal enhancement factor E^*_{non} is shown in Figures 9a and 9b. In Figure 9a, where $\epsilon_{eff}=5$, we observe that E^*_{non} decreases as Bi_H increases. As alluded to earlier, when Bi_H is increased, the temperature throughout the reaction zone is

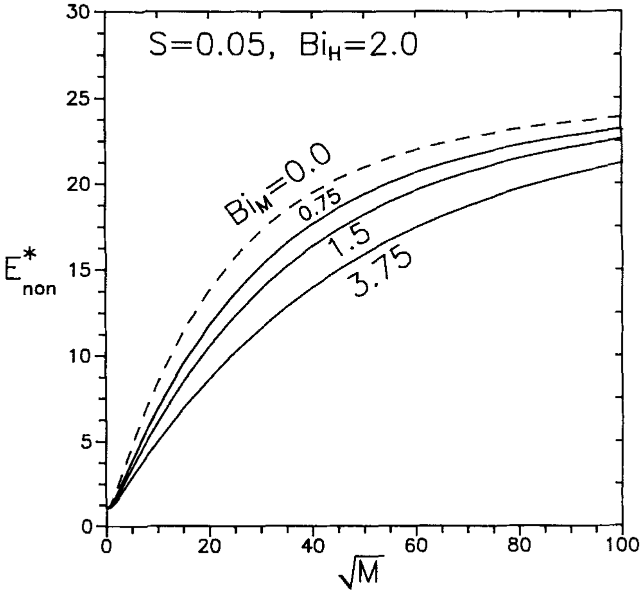

Figure 8b. Effect of Bi_M on the enhancement factor for $S=0.05$.

$\beta_R=0.005$, $\beta_S=0.001$, $\beta_V=0.005$, $\epsilon_R=14$, $\epsilon_{DA}=3$, $\epsilon_{DB}=5$, $\epsilon_S=7.5$, $\epsilon_V=2$, $B_g=\theta_g=0$, $\delta_H/\delta_M=Le^{1/2}$, and $Le=100$.

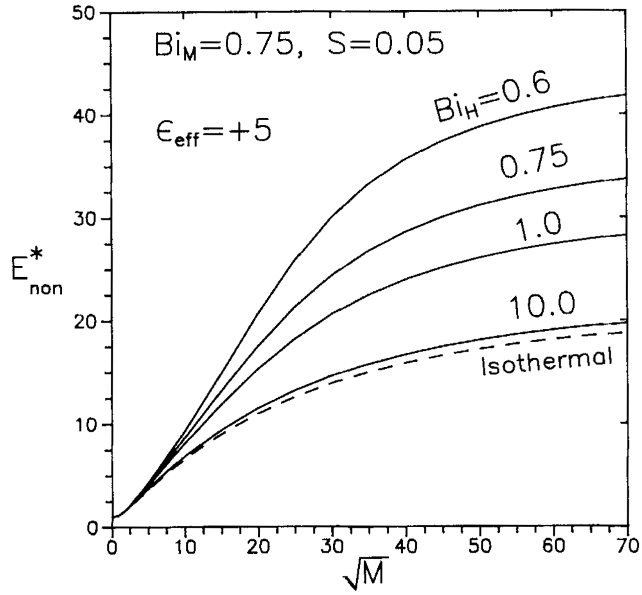

Figure 9a. Effect of Bi_H on the enhancement factor for $\epsilon_{eff} = +5$.

$\beta_R = 0.005$, $\beta_S = 0.001$, $\beta_V = 0.005$, $\epsilon_R = 22$, $\epsilon_{DA} = 3$, $\epsilon_{DB} = 5$, $\epsilon_S = 7.5$, $\epsilon_V = 2$, $B_g = \theta_g = 0$, $\delta_H/\delta_M = Le^{1/2}$, and $Le = 100$.

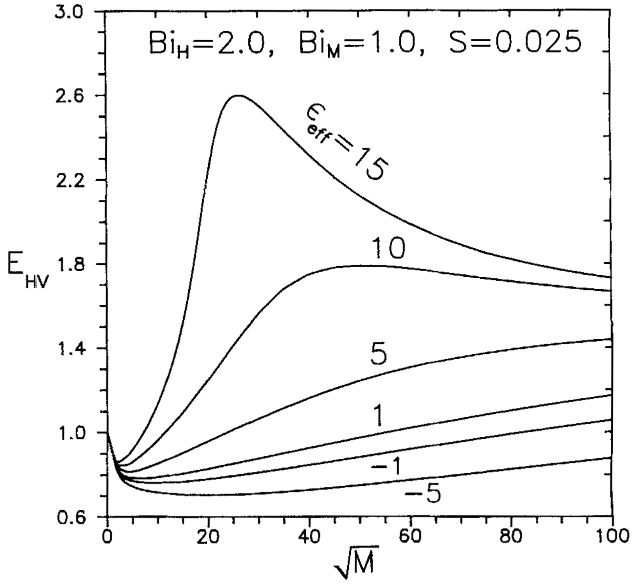

Figure 10. Effect of the effective activation energy, ϵ_{eff}, on the enhancement factor E_{HV}.

$\beta_R = 0.005$, $\beta_S = 0.001$, $\beta_V = 0.005$, $\epsilon_{DA} = 3$, $\epsilon_{DB} = 5$, $\epsilon_S = 7.5$, $\epsilon_V = 2$, $B_g = \theta_g = 0$, $\delta_H/\delta_M = Le^{1/2}$, and $Le = 100$.

reduced. The drop in temperature causes the rates of reaction and diffusion to decrease, thereby reducing the absorption rate. But, it also increases the solubility of the solute gas and in turn the absorption rate. Thus, the rate of absorption is reduced or enhanced depending on the relative influence of temperature on the reaction rate constant, diffusivity, and solubility of the absorbing gas. When ϵ_{eff} is larger than zero, the activation energies due to reaction and diffusion exceed that due to solubility so that the effect of temperature on reaction and diffusion becomes dominant over its effect on solubility. The net effect is that the absorption rate is reduced as the temperature is decreased. This situation is realized in Figure 9a. When ϵ_{eff} is sufficiently negative, however, the effect of temperature on solubility becomes dominant and the absorption rate is enhanced as the temperature is increased. This situation is shown in Figure 9b.

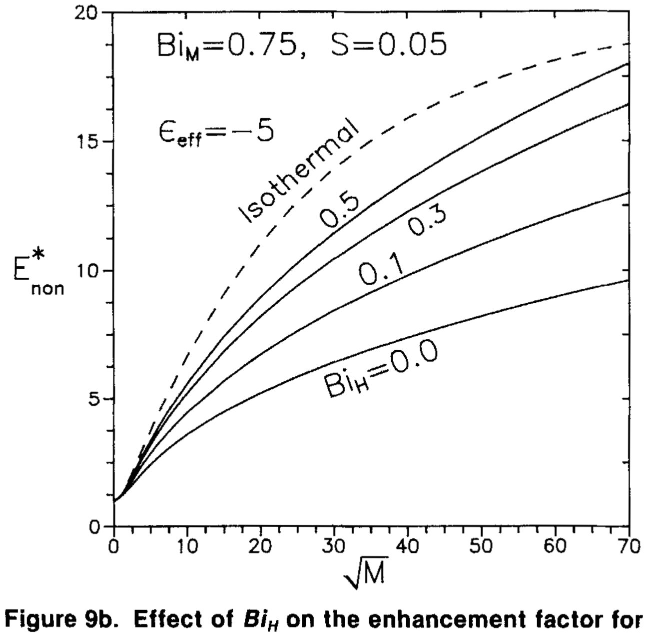

Figure 9b. Effect of Bi_H on the enhancement factor for $\epsilon_{eff} = -5$.

$\beta_R = 0.005$, $\beta_S = 0.001$, $\beta_V = 0.005$, $\epsilon_R = 22$, $\epsilon_{DA} = 3$, $\epsilon_{DB} = 5$, $\epsilon_S = 7.5$, $\epsilon_V = 2$, $B_g = \theta_g = 0$, $\delta_H/\delta_M = Le^{1/2}$, and $Le = 100$.

We may also observe that as Hatta number becomes large, the curves in Figures 9a and 9b approach horizontal asymptotes that correspond to the instantaneous reaction regime. Furthermore, as Bi_H becomes large, E^*_{non} approaches the isothermal asymptote that corresponds to isothermal chemical absorption with a volatile liquid reactant.

The effect of ϵ_{eff} on the absorption behavior is further brought out in Figure 10. The figure depicts the enhancement factor E_{HV} vs. Hatta number with ϵ_{eff} as parameter. The factor E_{HV} represents the extent to which heat effects and volatility increase or decrease the rate of chemical absorption compared to chemical gas absorption with no heat effects on volatility. It is clear from this figure that the departure of E_{HV} from unity depends strongly on the effective activation energy, ϵ_{eff}, and Hatta number $\sqrt{M}$. For large Hatta numbers, the curves eventually reach horizontal asymptotes that correspond to the instantaneous reaction regime. The asymptotic values depend to a large extent on the individual values of the activation energies ϵ_{DA}, ϵ_{DB}, and ϵ_S, rather than their combination ϵ_{eff}. Though not shown, when $\epsilon_{DB} = 0$, the asymptotes combine closely to a single asymptote that is approximately equal to the isothermal asymptote ($E_{HV} = 1$). This was previously shown in Al-Ubaidi et al. (1990) for the nonvolatile case.

Figure 11 depicts the effect of volatility alone on the rate of gas absorption. The figure shows E_V as a function of Hatta number for different values of S. As Hatta number approaches zero, that is, when gas absorption becomes chemical-reaction controlled, the volatility of the liquid reactant as well as the

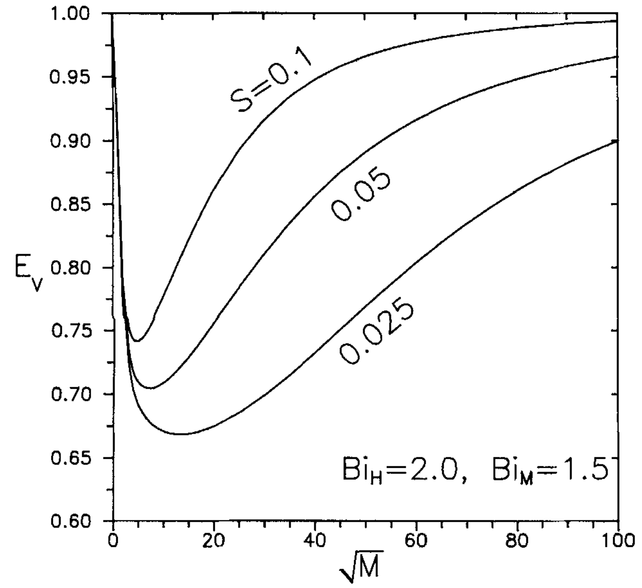

Figure 11. Effect of the parameter S on the enhancement factor E_V.

$\beta_R=0.005$, $\beta_S=0.001$, $\beta_V=0.005$, $\epsilon_{DA}=3$, $\epsilon_{DB}=5$, $\epsilon_S=7.5$, $\epsilon_V=2$, $B_g=\theta_g=0$, $\delta_H/\delta_M=Le^{1/2}$, and $Le=100$.

quantity S do not materially influence the absorption rate. Similarily, as Hatta number becomes large, that is, when gas absorption becomes mass-transfer-controlled, E_V approaches unity indicating that the absorption rate becomes independent of the volatility magnitude. On the other hand, for intermediate values of Hatta number, the liquid reactant volatility is always detrimental to gas absorption. The actual influence of volatility depends on the relative magnitudes of $\sqrt{M}$ and S. For instance, when $S=0.025$ and $\sqrt{M}=20$, the nonisothermal enhancement factor is about 33% lower than the corresponding value for the nonvolatile case. As S increases to 0.1, however, the enhancement factor is only 14% lower than the corresponding value for a nonvolatile liquid.

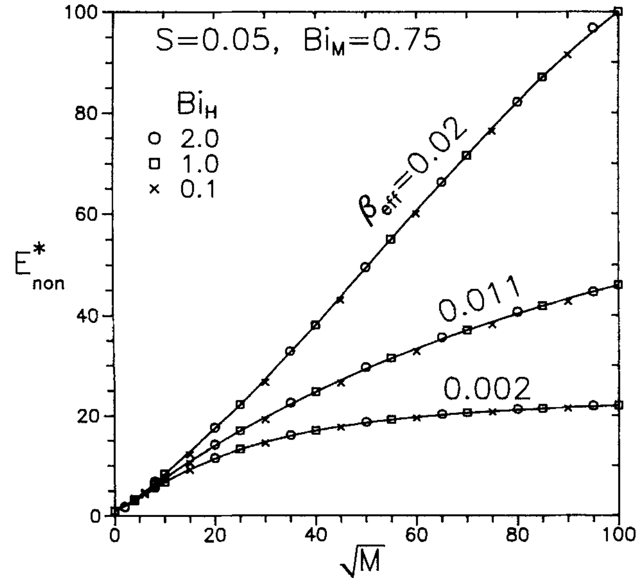

Figure 12. Effect of the heat of generation, β_{eff}, on the enhancement factor E_V.

$\beta_V=0.005$, $\epsilon_R=14$, $\epsilon_{DA}=3$, $\epsilon_{DB}=5$, $\epsilon_S=7.5$, $\epsilon_V=2$, $B_g=\theta_g=0$, $\delta_H/\delta_M=Le^{1/2}$, and $Le=100$.

Table 2. Dimensionless Heat of Reaction, Heat of Solution, Lewis Number, and Bi_H for Figure 12

β_R	β_S	Le	Bi_H	β_{eff}
0.0035	0.0007	100	2.0	0.002
0.00184	0.00036	100	1.0	0.002
0.000335	0.000065	100	0.1	0.002
0.0199	0.004	100	2.0	0.011
0.0184	0.0036	100	1.0	0.011
0.00335	0.00056	100	0.1	0.011
0.035	0.007	100	2.0	0.02
0.0184	0.0036	100	1.0	0.02
0.00335	0.00065	100	0.1	0.02

Effective heat of generation

The approximate solution (Eqs. 40–42) indicates that the temperature rise, θ_i, and the nonisothermal enhancement factor, E^*_{non}, depend on the quantity $(\beta_R+\beta_S)Bi_H(\delta_H/\delta_M)/[1+Bi_H(\delta_H/\delta_M)]$, rather than the individual values provided that (δ_H/δ_M) is fixed. This hypothesis was tested extensively by solving the original differential equations (Eqs. 20–24) for a wide range of the pertinent parameters. Sample results are shown in Figure 12. In this figure, three curves are shown with $\beta_{eff}=0.02$, 0.011, and 0.002 where

$$\beta_{eff}=(\beta_R+\beta_S)\,\frac{Bi_H(\delta_H/\delta_M)}{1+Bi_H(\delta_H/\delta_M)}$$

The individual values of β_R, β_S, Bi_H, and Lewis number are listed in Table 2. It is clear from this figure that the hypothesis is valid.

Application to real systems

The model developed above was applied to two practical systems: the chlorination of toluene and the sulfonation of dodecylbenzene. Data for these systems were taken from Mann and Clegg (1975) and Mann and Moyes (1977), as shown in Table 3. These data give $\beta_R=0.022$, $\beta_S=0.0055$, $\beta_V=0.031$, $\epsilon_R=30.0$, $\epsilon_S=17.0$, $\epsilon_V=3.4$, and $\epsilon_{DB}=6.4$ for the SO_3-dodecylbenzene system, and $\beta_R=0.022$, $\beta_S=0.0039$, $\beta_V=0.039$, $\epsilon_R=27.0$, $\epsilon_S=9.0$, $\epsilon_V=1.4$, and $\epsilon_{DB}=4.4$ for the Cl_2-toluene system. In addition, $\epsilon_{DA}=3.0$ and $\theta_g=B_g=0.0$ for both systems. Figures 13 and 14 show the nonisothermal enhancement factor, E^*_{non} and the temperature rise θ as a function of Hatta number, $\sqrt{M}$, for both systems. In Figure 13, evaporation was assumed negligible for the SO_3-dodecylbenzene system, and the Biot number for mass transfer, Bi_M, was taken equal to zero. The calculated interfacial temperature rise varies between $\theta_i=0.0046$ ($T_i=299.4$ K) to $\theta_i=0.085$ ($T_i=323.4$ K) as $\sqrt{M}$ increases from 4 to 100. Because the vapor pressure of dodecylbenzene is negligibly small throughout this temperature range, our assumption of $Bi_M=0$ (negligible evaporation of the liquid reactant) is justified. On the other hand, taking $Bi_M=0$ for the Cl_2-toluene system, Figure 14 shows a temper-

Table 3. Data for Sulfonation of Dodecylbenzene and Chlorination of Toluene

	SO_3-Dodecylbenzene	Cl_2-Toluene
$(-\Delta H_R)$, J/kmol	1.68×10^8	1.26×10^8
$(-\Delta H_S)$, J/kmol	4.2×10^7	2.31×10^7
$(+\Delta H_V)$, J/kmol	8.4×10^6	3.36×10^6
K_ℓ, J/(s·m·K)	0.0322	0.1494
α, m^2/s	2.0×10^{-8}	1.05×10^{-7}
D_{Ab}, D_{Bb}, m^2/s	10^{-9}	3.5×10^{-9}
C_{Aib}, $kmol/m^3$	1.273	2.18
C_{Bb}, $kmol/m^3$	35	150
T_b, K	298	298
E_R, J/kmol	7.44×10^7	6.72×10^7
E_{DA}, J/kmol	7.56×10^6	7.56×10^6
E_{DB}, J/kmol	1.58×10^7	1.08×10^7
Le	20	30

ature rise of $\theta_i=0.0045$ ($T_i=299.3$ K) to $\theta_i=0.282$ ($T_i=382$ K) as $\sqrt{M}$ increases from 4 to 80. Throughout this temperature range, however, the vapor pressure of toluene is fairly high, and evaporation of the liquid reactant cannot be neglected. On the other hand, calculations with $Bi_M=3.75$ show a lower temperature rise and correspondingly reduced enhancement that reflect the effect of evaporation.

Conclusions

Nonisothermal gas absorption accompanied by a second-order exothermic reaction has been analyzed for the case of a volatile liquid reactant. Heat transfer and liquid-reactant evaporation from the liquid surface to the gas phase were taken into account through lumped heat and mass transfer coefficients. A film-theory model was developed and the governing equations were solved numerically for a reasonable spectrum of parameter values. In addition, approximate expressions for the interfacial temperature rise and the enhancement factor were developed. Comparisons with "exact" numerical solutions verified the accuracy of these expressions over a wide range of the system parameters.

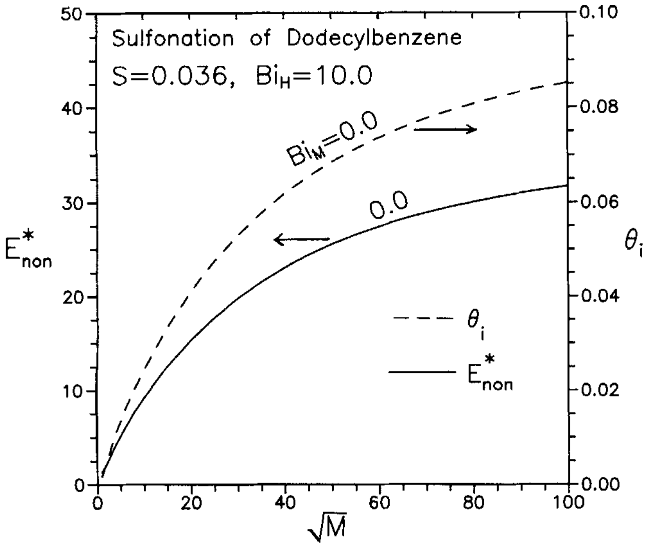

Figure 13. Enhancement factor and interfacial temperature rise for the sulfonation of dodecylbenzene.

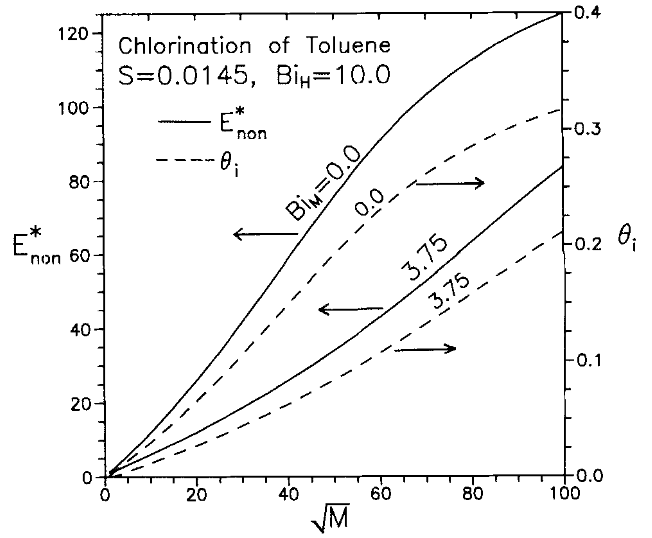

Figure 14. Enhancement factor and interfacial temperature rise for the chlorination of toluene.

The liquid reactant volatility is shown to have a detrimental influence on the enhancement of gas absorption by reaction. The extent of this deleterious effect is found to depend largely on the Hatta number $\sqrt{M}$ and the dimensionless parameter $S(=\nu D_{Ab}C_{Aib}/D_{Bb}C_{Bb})$. It is found that as $\sqrt{M}\rightarrow0$ and $\sqrt{M}\rightarrow\infty$, the effect of liquid reactant volatility is minor; it becomes more significant for intermediate values of Hatta number. The effect becomes more pronounced as S decreases due to the depletion of the liquid-reactant concentration near the gas-liquid interface.

The effect of heat losses to the gas phase is found to enhance or decrease the absorption rate depending on the effective activation energy, ϵ_{eff}, being positive or negative, respectively. As ϵ_{eff} approaches zero, the nonisothermal effect becomes less significant.

The model developed was applied to the two cases that represent real conditions. These included the chlorination of toluene and the sulfonation of dodecylbenzene. Volatility effects are shown to be important for the former system, while the relatively nonvolatile dodecylbenzene served as a counter example. We should note that the present model of nonisothermal behavior does not include aqueous systems where the solvent water is likely to be more volatile than the liquid reactant. Such systems will be treated elsewhere.

The results obtained in this work are essential for the proper design of gas-liquid reactors. These results address the microscale phenomena taking place close to the gas-liquid interface. As such, they may be incorporated into the design models by Pandya (1983), De Leye and Froment (1986), Yu and Astarita (1987), Fu et al. (1988), Tontiwachwuthikul et al. (1989), and Carey et al. (1991).

Notation

A = dimensionless concentration of dissolved gas A in the liquid phase, C_A/C_{Aib}
B = dimensionless concentration of the liquid reactant B in the liquid phase, C_B/C_{Bb}

B_i = dimensionless interfacial concentration of the liquid reactant B, C_{Bi}/C_{Bb}
Bi_H = Biot number for heat transfer, $h_g \delta_M / K_\ell$
Bi_M = Biot number for mass transfer, $k^o_{gb} H_{Bb} \delta_M / D_{Bb}$
C_A, C_B = concentrations of A, B in liquid film
C_{Ai}, C_{Bi} = interfacial concentrations of A, B at prevailing interfacial temperature T_i
C_{Aib}, C_{Bib} = interfacial concentrations of A, B evaluated at the bulk temperature T_b
C_{Bb} = concentration of B in the bulk liquid
C_{Bg} = concentration of B in the bulk gas
D_A, D_B = diffusion coefficients of A, B in the liquid film
D_{Ab}, D_{Bb} = diffusion coefficients of A, B in liquid film evaluated at the bulk temperature T_b
E = isothermal enhancement factor for chemical absorption of A
E^* = isothermal enhancement factor for chemical absorption of A with volatility
E_{non} = nonisothermal enhancement factor for chemical absorption of A without volatility
E^o_{non} = nonisothermal enhancement factor for physical absorption of A (defined in Eq. 31)
E^*_{non} = nonisothermal enhancement factor for chemical absorption of A with volatility
E_D = activation energy of diffusion
E_{HV} = enhancement factor due to heat and volatility effects, E^*_{non}/E
E_R = activation energy of liquid reaction
E_V = nonisothermal enhancement factor due to volatility, $E^*_{\mathrm{non}}/E_{\mathrm{non}}$
H_{Bb} = distribution constant for the liquid reactant B evaluated at the bulk temperature T_b,P_B/C_B
h_g = heat transfer coefficient in the gas phase
K_ℓ = thermal conductivity in the liquid phase
k = reaction rate constant
k^o_{gB} = gas mass transfer coefficient for physical desorption of B,D_B/δ_g
k^o_ℓ = liquid mass-transfer coefficient for physical absorption of A,D_A/δ_M
k_ℓ = liquid mass-transfer coefficient for chemical absorption of A
Le = Lewis number, α / D_{Ab}
$\sqrt{M}$ = Hatta number, $\delta_M \sqrt{k_{2b} C_{Bb} / D_{Ab}}$
P = pressure
$\underline{R}$ = universal gas constant
R = rate of absorption of A per unit interfacial area
S = diffusional rate of A relative to B, $\nu D_{Ab} C_{Aib} / D_{Bb} C_{Bb}$
S_{non} = nonisothermal value of S defined in Eq. 31
T = absolute temperature, K
T_i = temperature of gas-liquid interface
x = distance from the interface into the liquid phase
X = dimensionless thickness, x/δ_M

Greek letters

α = thermal diffusivity of liquid phase, $K_\ell/\rho C_p$
β_{eff} = effective heat of generation, $(\beta_R + \beta_S) B_{iH} (\delta_H/\delta_M) / [1 + B_{iH}(\delta_H/\delta_M)]$
β_R = dimensionless heat of reaction, $(-\Delta H_R) D_{Ab} C_{Aib} / K_\ell T_b$
β_S = dimensionless heat of solution, $(-\Delta H_S) D_{Ab} C_{Aib} / K_\ell T_b$
β_V = dimensionless heat of vaporization, $(+\Delta H_V) D_{Bb} C_{Bb} / K_\ell T_b$
$(-\Delta H_R)$ = heat of reaction
$(-\Delta H_S)$ = heat of solution
$(+\Delta H_V)$ = heat of vaporization of liquid reactant
δ_H = heat transfer film thickness
δ_M = mass transfer film thickness
ϵ_D = dimensionless activation energy of diffusion, E_D/RT_b
ϵ_{eff} = effective activation energy, $0.5(\epsilon_R + \epsilon_{DA}) - \epsilon_S$
ϵ_R = dimensionless activation energy of reaction, E_R/RT_b
ϵ_S = dimensionless activation energy of solution, $(-\Delta H_S)/RT_b$
ϵ_V = dimensionless activation energy of evaporation, $(+\Delta H_V)/RT_b$
θ = dimensionless liquid temperature, $(T - T_b)/T_b$
θ_i = dimensionless temperature at the gas-liquid interface, $(T_i - T_b)/T_b$
ν = stoichiometric coefficient

Subscripts

2 = second order reaction
A = dissolved gas
b = evaluated at bulk liquid temperature, T_b
B = liquid reactant
g = gas phase
i = gas-liquid interface
ℓ = liquid
non = nonisothermal

Superscripts

o = physical absorption
$*$ = volatility effect

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