Nonisothermal Gas Absorption Accompanied by a Second-Order Irreversible Reaction

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Most past theories of gas absorption accompanied by chemical reaction have assumed isothermal conditions (Danckwerts, 1970). There exist, however, a large number of industrially-important gas-liquid reactions which are accompanied by large heat effects. These are usually encountered in the absorption of highly-soluble gases or in the production of organic chemicals such as in the sulfonation and chlorination of liquid hydrocarbons.

For exothermic reactions, the temperature rise caused by the heats of solution and reaction may give rise to two important, but opposing, contributions. In heating the liquid, the rates of reaction and diffusion are increased, further steepening the concentration gradient near the gas-liquid interface. But, it also decreases the solubility of the solute gas in the liquid, thereby reducing the absorption driving force. Thus, the rate of absorption is enhanced or inhibited depending on the relative influence of temperature on the reaction rate constant, diffusivity and solubility of the absorbing gas.

Several theoretical analyses of absorption with a first-order exothermic reaction have been made. These were largely 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 general case involving a second-order reaction was solved recently by Bhattacharya et al. (1987). These authors adopted the Mann and Moyes film model ($\delta_H/\delta_M = \sqrt{Le}$) and derived approximate expressions for the enhancement factor and the interfacial temperature rise without limitation on the reaction regime. Although these expressions are valid for all Hatta numbers, the accuracy of these expressions are not known. Furthermore, the analysis of Bhattacharya et al. was mainly concerned with the multiplicity behavior of the system. While steady-state multiplicity was shown to be possible, no attempt was made to determine criteria for this phenomenon. This is not surprising considering the large number of parameters involved in this problem.

The present work, however, follows a different approach. Our goal is to examine the effect of the various parameters on the absorption behavior and identify the important parameters, or combination thereof, which are relevant to the understanding of the impact of local heat effects on contactor performance. To this end, the nonlinear film theory equations are solved without approximation using B-spline collocation, and a parametric study is made. The parametric study is used to determine the proper parameter combinations that characterize the importance of heat effects in the system. In addition, the effect of the ratio δ_H/δ_M on the interfacial temperature rise and the enhancement factor is thoroughly investigated.

Film Theory Equations

The problem to be considered is that in which a gas component, A, is absorbed into the 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:

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

A schematic diagram of the film model with concentration and temperature profiles is shown in Figure 1. The mathematical model is based on the following assumptions:

1. Mass transfer resistance 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.

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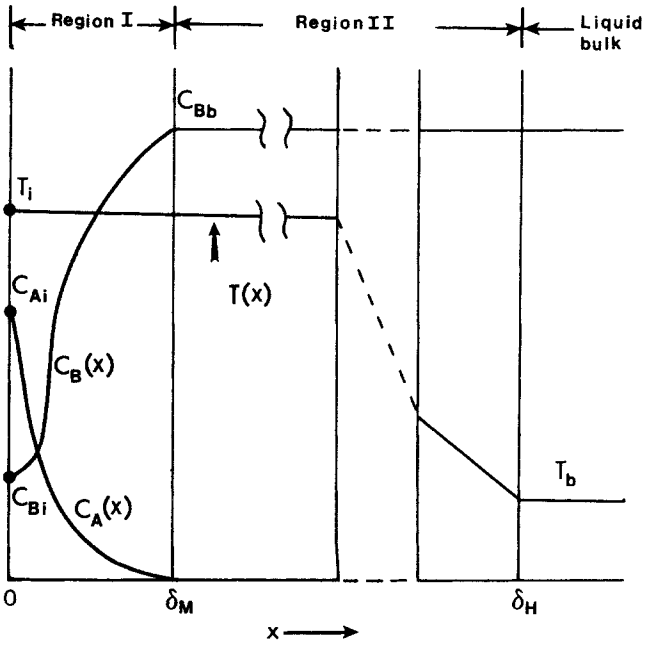

Figure 1. Film model with concentration and temperature profiles.

3. The reaction in the liquid phase is essentially completed within the film.

4. The liquid phase consists of nonvolatile components so that there is no material or energy losses due to evaporation. This limits the analysis to systems with low temperature rise.

5. Heat transfer to the gas phase, due to convection at the interface, is 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, Dufour, Soret, and Rayleigh effects are negligible.

8. Appropriate Arrhenius-type expressions are assumed for the temperature dependence of the diffusivities, solubility, and reaction rate constant.

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:

$$-K\frac{dT}{dx} = -K\frac{T_b - T}{\delta_H - \delta_M} \quad \text{at} \quad x = \delta_M. \tag{2}$$

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

The nonisothermal enhancement factor is defined as the ratio of the actual rate of chemical gas absorption with heat effects to the rate of physical absorption with no heat effects:

$$E_{\text{non}} = \frac{-D_A(T_i)\left[\dfrac{dC_A}{dx}\right]_{x=0}}{k_l^{\circ}C_{Aib}} \tag{3}$$

where C_{Aib} is the interfacial concentration of the dissolved gas evaluated at the bulk temperature T_b.

In order to determine the importance of heat effects in nonisothermal gas absorption, an additional enhancement factor is defined as:

$$E_H = \frac{\text{Rate of Chemical Gas Absorption and Heat Effects}}{\text{Isothermal Rate of Chemical Gas Absorption}}. \tag{4}$$

Based on this definition, it is clear that the absorption rate will be reduced, enlarged or become independent of heat effects, if E_H is less than, larger than or equal to unity, respectively.

The differential equations describing the reaction and heat transfer in nondimensional form are:

$$\frac{d}{dX}\left[e^{\epsilon_{DA}}\frac{\theta}{1+\theta}\frac{dA}{dX}\right] - Me^{\epsilon_R}\frac{\theta}{1+\theta}\,AB = 0 \tag{5}$$

$$\frac{d}{dX}\left[e^{\epsilon_{DB}}\frac{\theta}{1+\theta}\frac{dB}{dX}\right] - MSe^{\epsilon_R}\frac{\theta}{1+\theta}\,AB = 0 \tag{6}$$

$$\frac{d^2\theta}{dX^2} + \beta_R Me^{\epsilon_R}\frac{\theta}{1+\theta}\,AB = 0 \tag{7}$$

with the boundary conditions at:

$X = 0$:

$$A = e^{-\epsilon_S}\frac{\theta}{1+\theta} \tag{8a}$$

$$\frac{dB}{dX} = 0 \tag{8b}$$

$$\beta_S e^{\epsilon_{DA}}\frac{\theta}{1+\theta}\frac{dA}{dX} = \frac{d\theta}{dX}, \quad \theta = \theta_i \tag{8c}$$

$X = 1$:

$$A = 0 \tag{9a}$$

$$B = 1 \tag{9b}$$

$$\left(\frac{\delta_H}{\delta_M} - 1\right)\frac{d\theta}{dX} + \theta = 0 \tag{9c}$$

The ratio of δ_H/δ_M

Inspection of Eqs. 5 through 9 reveals that the ratio δ_H/δ_M needs to be specified before a solution can be obtained. Three choices are available: 1. $\delta_H/\delta_M = Le^0$; 2. $\delta_H/\delta_M = Le^{1/2}$; 3. $\delta_H/\delta_M = Le^{1/3}$. The first choice ($\delta_H/\delta_M = Le^0$) is in accordance with the classical film model and was previously adopted by Danckwerts (1970), Asai et al. (1987), and Chatterjee and Altwicker (1987). The second choice ($\delta_H/\delta_M = Le^{1/2}$) is in accordance with the penetration theory and was proposed first by Mann and Moyes (1977). The third choice ($\delta_H/\delta_M = Le^{1/3}$) is in accordance with boundary-layer theory and the Chilton-Colburn analogy.

In the present study, we adopt all three choices and investigate the effect of the ratio of δ_H/δ_M on the absorption behavior. The set of Eqs. 5–9 define a nonlinear boundary value problem involving three coupled second-order ordinary differential equa-

tions. The present problem was solved using B-spline collocation. A detailed description of the numerical solution and a Fortran computer program are available (Al-Ubaidi, 1988).

Approximate Solution

An approximate solution to a similar problem was presented recently by Bhattacharya et al. (1987). The approximate solution was based on the van Krevelen-Hoftijzer approximation and the simplifications introduced by Mann and Moyes (1977). The same approach may be used to develop an approximate solution to the system of Eqs. 5–9. Details for the derivation of this solution are available (Al-Ubaidi, 1988). The final result consists of the following three equations for the interfacial concentration of the liquid reactant C_{Bi}, the interfacial temperature rise θ_i, and the nonisothermal enhancement factor E_{non}:

$$\frac{C_{Bi}}{C_{Bb}} = 1 - S_{non}[E_{non} - E^{o}_{non}] \tag{10}$$

$$\theta_i = \left[\frac{\beta_R + \beta_S}{\tanh(\zeta\eta_{non}\sqrt{M})} - \frac{\beta_R}{\sinh(\zeta\eta_{non}\sqrt{M})}\right] \cdot \left\{\frac{\delta_H}{\delta_M}\right\} \eta_{non}\sqrt{M}e^{\epsilon_{eff}}\frac{\theta_i}{1+\theta_i} \tag{11}$$

$$E_{non} = \frac{\eta_{non}\sqrt{M}}{\tanh(\zeta\eta_{non}\sqrt{M})} e^{\epsilon_{eff}}\frac{\theta_i}{1+\theta_i} \tag{12}$$

where

$$S_{non} = Se^{-\epsilon_{DB}}\frac{\theta_i}{1+\theta_i}$$

$$E^{o}_{non} = e^{(\epsilon_{DA}-\epsilon_S)}\frac{\theta_i}{1+\theta_i}$$

$$\zeta = \exp\left[\frac{1}{2}\{\epsilon_R - \epsilon_{DA}\}\frac{\theta_i}{1+\theta_i}\right]$$

$$\epsilon_{eff} = \frac{1}{2}\{\epsilon_R + \epsilon_{DA}\} - \epsilon_S$$

$$\eta_{non} = \sqrt{\frac{C_{Bi}(\theta_i)}{C_{Bb}}}.$$

Equations 10, 11 and 12 constitute a set of nonlinear algebraic equations for the three unknowns C_{Bi}/C_{Bb}, θ_i, and E_{non}, respectively. These were solved numerically using the Newton-Raphson method. When $\sqrt{M} > 3$, these equations simplify to:

$$\frac{C_{Bi}}{C_{Bb}} = 1 - S_{non}(E_{non} - E^{o}_{non}) \tag{13}$$

$$\theta_i = (\beta_R + \beta_S)\left(\frac{\delta_H}{\delta_M}\right)\eta_{non}\sqrt{M}e^{\epsilon_{eff}}\frac{\theta_i}{1+\theta_i} \tag{14}$$

$$E_{non} = \eta_{non}\sqrt{M}e^{\epsilon_{eff}}\frac{\theta_i}{1+\theta_i}. \tag{15}$$

The accuracy of the approximate solution presented above was tested by comparison with the numerical solution obtained by B-spline collocation. A maximum deviation of about 12% for the interfacial temperature rise and 7% for the nonisothermal enhancement factor were found. These deviations decrease significantly when the power of the Lewis number increases from 1/3 to 1/2, i.e., when the ratio δ_H/δ_M increases. It may, therefore, be concluded that the present approximate solution can be used with satisfactory accuracy for design evaluations. Furthermore, the close agreement between both solutions supports the

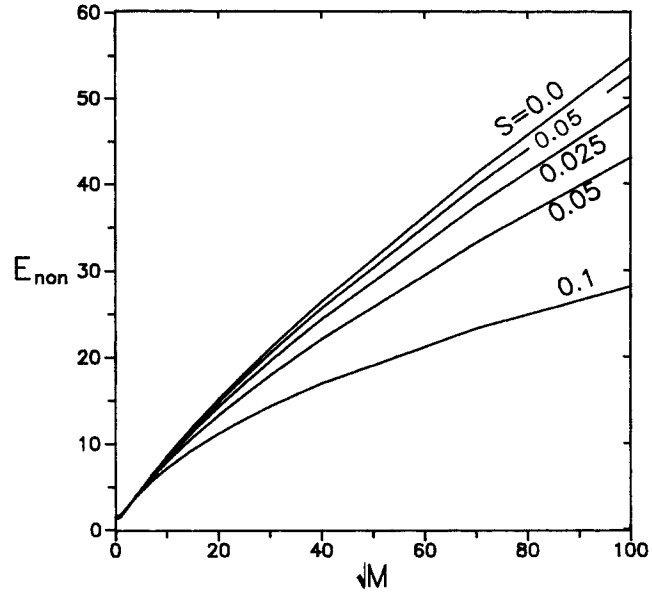

Figure 2. Variation of the nonisothermal enhancement factor E_{non} with Hatta number $\sqrt{M}$.

$\beta_R = 0.005$; $\beta_S = 0.001$; $\epsilon_R = 10$; $\epsilon_{DA} = \epsilon_{DB} = 3$; $\epsilon_S = 7.5$; $\delta_H/\delta_M = Le^{1/3}$; and $Le = 100$

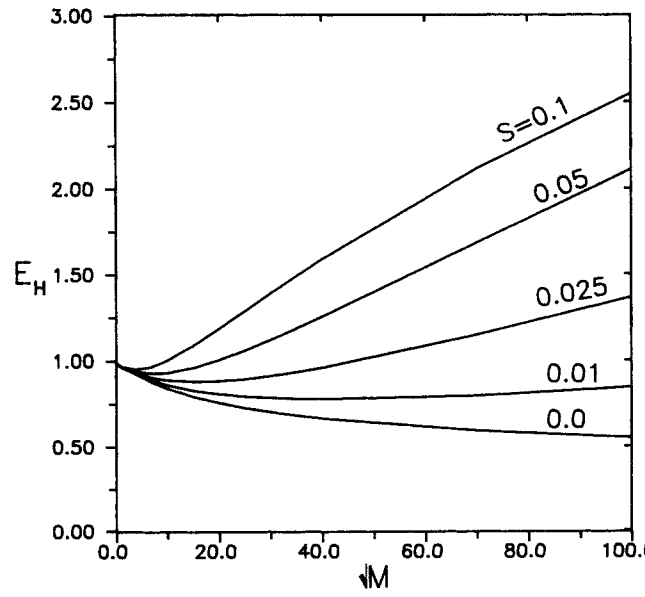

Figure 3. Variation of the enhancement factor due to heat effects, E_H, with Hatta Number $\sqrt{M}$.

$\beta_R = 0.005$; $\beta_S = 0.001$; $\epsilon_R = 10$; $\epsilon_{DA} = \epsilon_{DB} = 3$; $\epsilon_S = 7.5$; $\delta_H/\delta_M = Le^{1/3}$; and $Le = 100$

validity of the results obtained previously by Bhattacharya et al. (1987) for $\sqrt{M} > 1$.

Results and Discussion

The enhancement factor

Figure 2 shows the nonisothermal enhancement factor E_{non} as a function of Hatta number $\sqrt{M}$ for different values of S. The similarity between this figure and the familiar van Krevelen-Hoftijzer plot for isothermal absorption is apparent. For a given S, the enhancement factor tends to reach an asymptotic value which is determined by the instantaneous reaction regime. Figure 3 shows the corresponding plot for the enhancement factor E_H. It is clear from this figure that the departure of E_H from unity is strongly dependent on $\sqrt{M}$ and S.

The effective activation energy

Figure 4 shows the enhancement factor E_H for $S = 0$ (pseudo-first-order reaction) for different values of ϵ_{eff}. It is clear from the figure that:

$$E_H = \begin{cases} >1, \text{ for } \epsilon_{eff} > 0 \\ =1, \text{ for } \epsilon_{eff} = 0 \\ <1, \text{ for } \epsilon_{eff} < 0 \end{cases}$$

which agrees with that of Asai et al. (1985), and Chatterjee and Altwicker (1987). This criterion, herein after called the Shah-Asai criterion, was found to apply for a wide range of the pertinent parameters provided that the reaction is a pseudofirst-order reaction.

Figures 5 and 6 show the enhancement factor E_H for $S = 0.1$ (second-order reaction) for $\epsilon_{DB} = 0$ and $\epsilon_{DB} = 3$, respectively. A careful examination of these figures shows that the Shah-Asai criterion is only partially satisfied, namely,

$$E_H = \begin{cases} >1, \text{ for } \epsilon_{eff} > 0 \text{ and all values of } \sqrt{M}, S, \text{ and } \epsilon_{DB} \\ \simeq 1, \text{ for } \epsilon_{eff} = 0, \epsilon_{DB} = 0 \text{ and all values of } \sqrt{M} \text{ and } S \\ >1, \text{ for } \epsilon_{eff} = 0, \epsilon_{DB} > 0 \text{ and all values of } \sqrt{M} \text{ and } S \\ >1 \text{ or } <1, \text{ for } \epsilon_{eff} < 0 \text{ (greater or less than unity depending on } \sqrt{M}, S, \text{ and } \epsilon_{DB}). \end{cases}$$

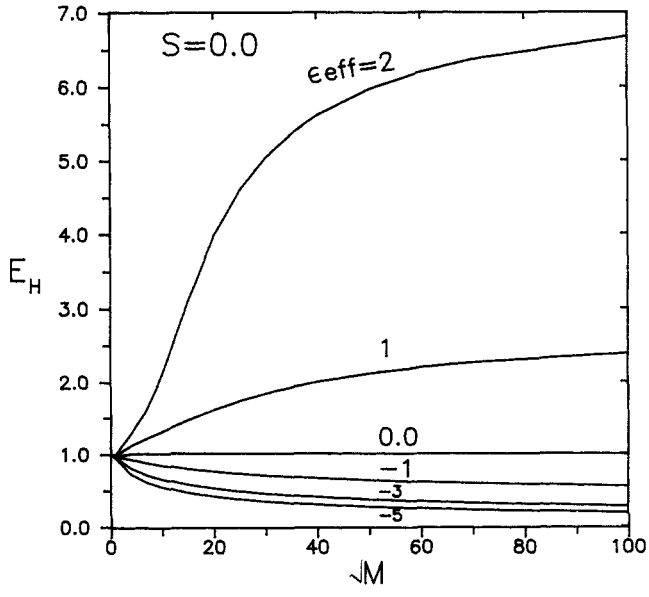

Figure 4. Effect of the activation energies on the enhancement factor for a pseudofirst-order reaction.

$\beta_R = 0.005$; $\beta_S = 0.001$; $\delta_H/\delta_M = Le^{1/3}$; and $Le = 100$

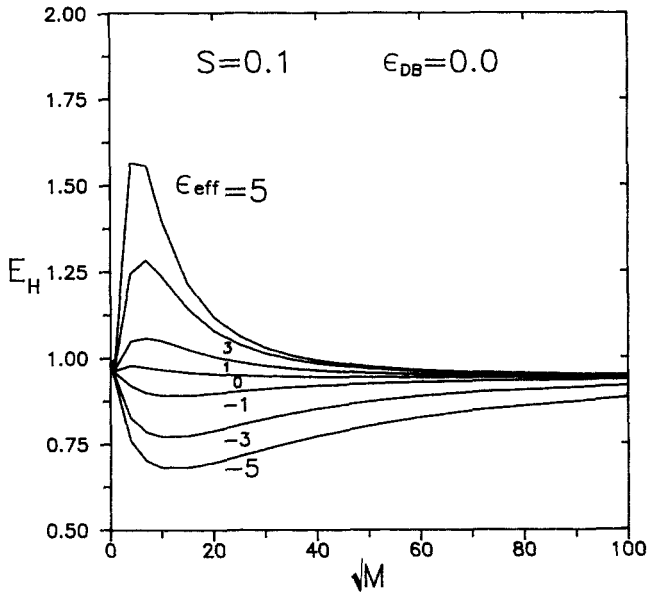

Figure 5. Effect of the activation energies on the enhancement factor for a second-order reaction.

$\epsilon_{DB} = 0.0$; $\beta_R = 0.005$; $\beta_S = 0.001$; $\delta_H/\delta_M = Le^{1/3}$; and $Le = 100$

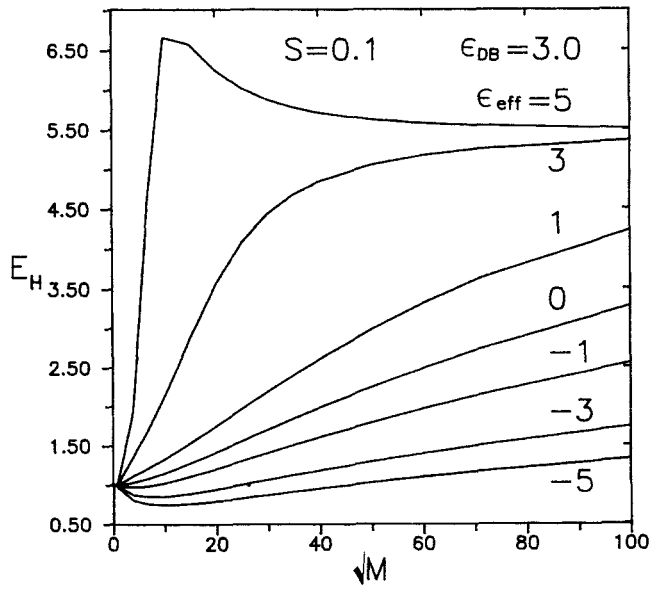

Figure 6. Effect of the activation energies on the enhancement factor for a second-order reaction.

$\epsilon_{DB} = 3.0$; $\beta_R = 0.005$; $\beta_S = 0.001$; $\delta_H/\delta_M = Le^{1/3}$; and $Le = 100$

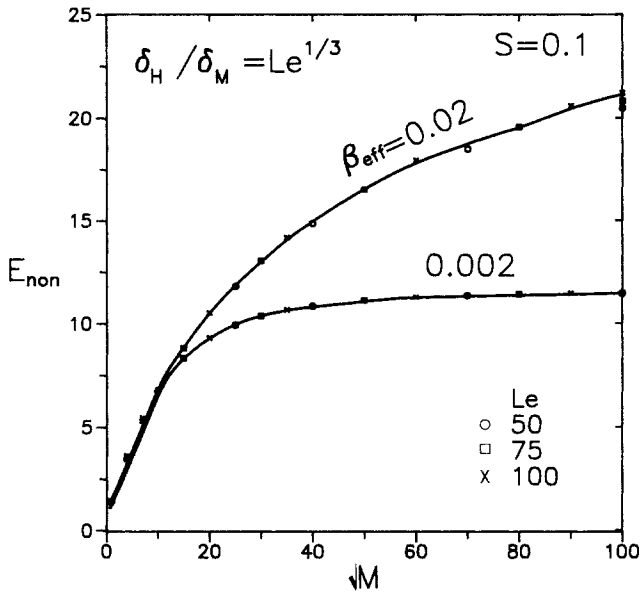

Figure 7. Effect of the heat of generation on the enhancement factor.

$S = 0.1$, $\epsilon_R = 10$, $\epsilon_{DA} = \epsilon_{DB} = 3$, and $\epsilon_S = 7.5$.

Figures 5 and 6 also show that E_H increases with increasing ϵ_{DB}. Higher values of ϵ_{DB} leads to an increase in the diffusional rate of the liquid reactant and hence the rate of absorption. We may also note that all the curves in these figures approach asymptotic values which correspond to the instantaneous reaction regime.

The effective heat of generation

Inspection of Eqs. 10, 11 and 12 reveals that the enhancement factor E_{non} and the interfacial temperature rise θ_i depend on the quantity $(\beta_R + \beta_S)\ \delta_H/\delta_M$, rather than the individual values. This hypothesis was tested extensively for a wide range of the pertinent parameters. Sample results are shown in Figure 7. In this figure, two curves are shown with $\beta_{eff} = 0.002$ and $\beta_{eff} = 0.02$ where

$$\beta_{eff} = (\beta_R + \beta_S)\delta_H/\delta_M.$$

The individual values of β_R, β_S, and Le are listed in Table 1. It is clear from the figure that the hypothesis is valid.

The effect of δ_H/δ_M

The effect of the ratio δ_H/δ_M on the absorption behavior was studied extensively for a wide range of the pertinent parameters. Table 2 gives the percentage deviation for the interfacial temperature rise and the nonisothermal enhancement factor for $\delta_H/\delta_M = Le^0$ and $\delta_H/\delta_M = Le^{1/3}$ from the solution with $\delta_H/\delta_M = Le^{1/2}$. Further comparisons for different values of β_{eff}, ϵ_{DB} and ϵ_{eff} are available (Al-Ubaidi, 1988). These comparisons indicate that changing the Lewis number power from 1/3 to 1/2 has a minor effect on the results. On the other hand, the results with $\delta_H/\delta_M = Le^0$ deviate considerably from those with $\delta_H/\delta_M = Le^{1/3}$ and $Le^{1/2}$. For instance, with $\delta_H/\delta_M = Le^0$, deviations as high as 100% in the interfacial temperature rise and the enhancement factor may be obtained for $\epsilon_{eff} > 0$. This compares with deviations of about 11% for the interfacial temperature rise and 3% for the enhancement factor with $\delta_H/\delta_M = Le^{1/3}$ under similar conditions.

Realizing that the physical model with $\delta_H/\delta_M = Le^0$ is not realistic on physical grounds, it is doubtful that results based on this model will be supported by experiment. The Lewis number power of 1/3 was experimentally verified in analogous systems involving heat effects. The Lewis number power of 1/2 is theoretically rooted with the penetration theory. However, since results with $Le^{1/3}$ and $Le^{1/2}$ are basically identical, it is hard to discriminate between the two models.

Table 1. Heat of Reaction and Solution, and Lewis Number for Figure 7

β_R	β_S	Le	$\delta_H/\delta_M = Le^{1/3}$	β_{eff}
0.00033	0.0001	100	4.6345	0.002
0.00037	0.0001	75	4.2111	0.002
0.00044	0.0001	50	3.6792	0.002
0.0033	0.001	100	4.6345	0.02
0.0037	0.001	75	4.2111	0.02
0.0044	0.001	50	3.6792	0.02

Notation

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

Table 2. Effect of δ_H/δ_M on Temperature Rise and Enhancement Factor*

		$S = 0.01$			
$(\beta_{eff}, \delta_H/\delta_M)$	$\sqrt{M}$	E_{non}	% Dev.**	θ_i	% Dev.
	2	2.0828	−1.02	0.0032	11.11
	4	4.0602	1.01	0.0071	11.25
	6	6.1485	1.12	0.0113	8.13
	8	8.2815	1.21	0.0156	6.59
$(0.002, Le^0)$	10	10.4577	1.31	0.0199	5.69
	20	22.0056	2.30	0.0430	4.23
	40	48.4579	8.30	0.0959	9.19
	60	78.1781	26.68	0.1554	27.08
	2	2.0927	−1.50	0.0032	11.11
	4	4.0948	0.17	0.0077	3.75
	6	6.2088	0.02	0.0121	1.63
	8	8.3700	0.15	0.0164	1.80
$(0.002, Le^{1/3})$	10	10.5797	0.16	0.0209	0.95
	20	22.4686	0.25	0.0447	0.45
	40	52.3791	0.88	0.1047	0.85
	60	102.3777	3.98	0.2050	3.80
	2	2.0618	0.00	0.0036	0.00
	4	4.1018	0.00	0.0080	0.00
	6	6.2184	0.00	0.0123	0.00
	8	8.3829	0.00	0.0167	0.00
$(0.002, Le^{1/2})$	10	10.5967	0.00	0.0211	0.00
	20	22.5239	0.00	0.0449	0.00
	40	52.8446	0.00	0.1056	0.00
	60	106.6213	0.00	0.2131	0.00

*$\epsilon_{DB} = 5.0$, $\epsilon_{eff} = 5$, $Le = 100$

**% Deviation $= \dfrac{Le^{1/2}\text{ Result} - Le^0 \text{ or } Le^{1/3}\text{ Result}}{Le^{1/2}\text{ Result}} \times 100$

E_H = enhancement factor due to heat effects
E_{non} = nonisothermal enhancement factor
E^o_{non} = nonisothermal enhancement factor for physical absorption
k^o_l = liquid mass transfer coefficient for physical absorption = D_A/δ_M for film theory
Le = Lewis number = α/D
$\sqrt{M}$ = Hatta number = $\sqrt{(\delta_M k_{2b} C_{Bb})/D_{Ab}}$
S = diffusional rate of A to B, $(\nu D_{ab} C_{Aib})/(D_{Bb} C_{Bb})$
T = absolute temperature
X = dimensionless thickness, x/δ_M

Greek letters

α = thermal diffusivity of liquid phase, $K/\rho C_p$
β_{eff} = effective heat of generation, $(\beta_R + \beta_S)\delta_H/\delta_M$
β_R = dimensionless heat of reaction, $(-\Delta H_R) D_{Ab} C_{Aib}/KT_b$
β_S = dimensionless heat of solution, $(-\Delta H_S) D_{Ab} C_{Aib}/KT_b$
δ_H = heat transfer film thickness
δ_M = mass transfer film thickness
$(-\Delta H_R)$ = heat of reaction
$(-\Delta H_S)$ = heat of solution
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 liquid phase reaction, E_R/RT_b
ϵ_S = dimensionless activation energy of solution, $(-\Delta H_S)/RT_b$
θ = dimensionless liquid temperature, $T - T_b/T_b$
ν = stoichiometric coefficient

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