Nonisothermal Gas Absorption with Chemical Reaction

The temperature rise at a gas-liquid interface due to heat evolution and the relevant enhancement factor for gas absorption rate are analyzed for absorption, with an instantaneous irreversible reaction and with a first-order irreversible reaction allowing for the temperature dependence of the major physicochemical properties. The analysis reveals that, unlike isothermal absorption, the film theory solutions with the replacement of any system parameters do not give a reasonable approximation to the realistic penetration theory solution, except in the case of the physical absorption regime. However, the modified Danckwerts analysis, in which the physicochemical properties are evaluated at the time-averaged interface temperature, is shown to be useful in obtaining the approximate penetration theory solutions with satisfactory accuracy.

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SCOPE

In physical absorption of a highly soluble gas, or in chemical absorption, the temperature of the liquid phase, especially near the gas-liquid interface, rises due to heat generated by the heats of solution and reaction. Consequently, it may become essential to take into account the variation of the physicochemical properties with temperature in determining the gas absorption rate. The importance of such nonisothermal effects has been demonstrated for several absorption systems, as illustrated in a previous paper (Suresh et al., 1983). Nonisothermal effects on the gas absorption rate, therefore, must be understood for the reasonable design of industrial absorbers and gas-liquid reactors for reactions accompanied by a considerable evolution of heat.

Assuming constant properties, Danckwerts (1953, 1967, 1970) presented analytical expressions for the interface temperature rise based on the film theory, penetration theory, and his surface renewal theory for a few absorption schemes. However, his expressions may not be justified in view of the assumption of constant properties when the interface temperature rise is substantial. Numerous studies on the interface temperature rise and relevant enhancement factor have been since conducted, taking into account the temperature dependence of the physicochemical properties for the absorption with a first-order or, more generally, a *m*th order irreversible reaction in terms either of the film theory or the penetration theory (Kobayashi and Saito, 1965; Clegg and Mann, 1969; Hiraoka and Tanaka, 1969; Onda et al., 1969; Cook and Moore, 1972; Bentwich, 1973; Tripathi et al., 1974; Mann and Clegg, 1975; Tamir et al., 1975; Mann and Moyes, 1977; Allan and Mann, 1979). However, previous workers assumed constant diffusivity of dissolved gas and mostly a linear dependence of gas solubility and reaction rate constant on temperature. Owing to the assumptions of such temperature dependence of the relevant physicochemical properties, the applicability of previous analytical results might be limited to the case without significant temperature rise. Shah (1972) assumed Arrhenius variation of such properties with temperature in his penetration theory analysis for a first-order irreversible reaction and obtained numerical solutions for the interface temperature rise. He also presented an empirical approximate solution, based on his numerical solution, for the interface temperature rise. However, no solution for the enhancement factor has been reported. As regards absorption with instantaneous irreversible reaction, on the other hand, the Danckwerts analysis has been extended only to the case with bulk flow (Onda et al., 1969; Ikemizu et al., 1978a, b), without allowance for the temperature dependence of the physical properties.

The aim of the present work is to analyze the interface temperature rise and relevant enhancement factor for absorption with an instantaneous irreversible reaction and with a first-order irreversible reaction, assuming reasonable temperature dependence of the physicochemical properties, such as gas solubility, diffusivities of the relevant species, and reaction rate constant, and to present methodology to obtain approximate solutions applicable over a wide range of temperature variations.

CONCLUSIONS AND SIGNIFICANCE

The interface temperature rise and relevant enhancement factor have been analyzed for absorption with an instantaneous irreversible reaction and with a first-order irreversible reaction, allowing for the temperature dependence of the properties.

The modified Danckwerts analysis, called the modified

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Danckwerts model (MDM) below, in which the physicochemical properties are evaluated at the integrally time-averaged interface temperature or reaction plane temperature, has been shown to be useful in obtaining the approximate solutions of the interface temperature rise and enhancement factor, with satisfactory accuracy. This procedure may be expected to be applicable for other reaction schemes, provided that the interface temperature rise based on the conventional Danckwerts model and isothermal enhancement factor can be analyzed.

It is well known that under isothermal conditions, the enhancement factor for the film theory with the replacement of the diffusivity ratio r by $\sqrt{r}$ approximates closely the penetration theory solution for most reaction schemes. Such an analogy, however, does not hold in general under nonisothermal conditions, even with the simultaneous substitution of some other system parameters. For physical absorption, on the other hand, the modified film theory solutions with the Lewis number Le replaced by $\sqrt{Le}$ are in almost complete agreement with the rigorous penetration theory solutions for both the interface temperature rise and relevant enhancement factor.

ASSUMPITONS

In the subsequent analysis the following assumptions are made:

1. Properties other than gas solubility, diffusivities of the relevant species in the liquid phase, and reaction rate constant are invariant with temperature.
2. Gas phase mass transfer resistance is negligible.
3. Solvent is nonvolatile.
4. Heat transfer to gas phase through the interface is negligible.
5. Bulk flow and Dufour, Soret, Marangoni, and Rayleigh effects are negligibly small.

The variation of thermal conductivity with temperature was not included, since it is generally less than 10% per 30°C of temperature change and it is much smaller than that of the above-mentioned temperature-dependent properties. Bulk flow effect might be appreciable for highly soluble gases, especially near physical absorption regime characterized by the small values of concentration ratio $q(=B_0/\nu A_{i0})$ for an instantaneous irreversible reaction, and by the small values of dimensionless time k_0t for a first-order irreversible reaction, as discussed by Ikemizu et al. (1978a, b) and Tamir et al. (1975), respectively. Since the purpose of this work is of methodological nature and we wish to avoid mathematical complexity, this effect is not taken into account here, although the proposed approximate analytical procedure could be extended to allow for the bulk flow effect.

The temperature dependence of the properties may be reasonably expressed over a wide range of temperature as

$$Q = Q_0 \exp[\epsilon\theta/(1+\theta)]\ (Q = A_i, D_A, D_B \text{ and } k) \tag{1}$$

where

$$\theta = \frac{T - T_0}{T_0}, \quad \epsilon = \frac{E}{RT_0} \tag{2}$$

In subsequent analysis, however, this Arrhenius type of temperature dependence is approximated using the expansion

$$\exp[\theta/(1+\theta)] \simeq 1 + \theta \tag{3}$$

as follows:

$$Q = Q_0(1+\theta)^{\epsilon} \tag{4}$$

An approximate expansion given by Eq. 3 will only be in error by 0.4% even for $\theta = 0.1$, which corresponds to the temperature rise in the liquid phase of about 30°C when the liquid bulk is kept at room temperature. It seems impractical to consider higher values of θ, since some of the foregoing assumptions might not be satisfied.

INSTANTANEOUS IRREVERSIBLE REACTION

Rigorous Solutions

Let us consider the case where a solute gas A dissolves into a liquid and then reacts irreversibly and instantaneously with a reactant B, which is already present in the liquid phase, according to the following reaction:

$$A + \nu B \rightarrow C \tag{a}$$

Differential equations and revelant initial and boundary conditions for the diffusions of species A and B and of heat are given by

For region I$(0 < x < x')$

$$\frac{\partial a}{\partial t} = D_{A0}\frac{\partial}{\partial x}\left[(1+\theta)^{\epsilon_{DA}}\frac{\partial a}{\partial x}\right] \tag{5}$$

$$\frac{\partial \theta}{\partial t} = \alpha\frac{\partial^2\theta}{\partial x^2} \tag{6}$$

For region II $(x' < x < \infty)$

$$\frac{\partial b}{\partial t} = D_{B0}\frac{\partial}{\partial x}\left[(1+\theta)^{\epsilon_{DB}}\frac{\partial b}{\partial x}\right] \tag{7}$$

$$\frac{\partial \theta}{\partial t} = \alpha\frac{\partial^2\theta}{\theta x^2} \tag{8}$$

$$x > 0, \quad t = 0; \quad b = 1 \tag{9}$$

$$x = 0, \quad t > 0; \quad a = (1+\theta_i)^{\epsilon_S}, \quad \theta = \theta_i,$$

$$-\lambda T_0\frac{\partial\theta}{\partial x} = -D_{A0}A_{i0}(1+\theta_i)^{\epsilon_{DA}}(-\Delta H_S)\frac{\partial a}{\partial x} \tag{10}$$

$$x = x', \quad t > 0; \quad a = 0, \quad b = 0, \quad \theta = \theta',$$

$$-\lambda T_0\left(\frac{\partial\theta}{\theta x}\right)_{II} = -\lambda T_0\left(\frac{\partial\theta}{\partial x}\right)_{I} - D_{A0}A_{i0}(1+\theta')^{\epsilon_{DA}}(-\Delta H_R)\frac{\partial a}{\partial x},$$

$$-D_{A0}A_{i0}(1+\theta')^{\epsilon_{DA}}\frac{\partial a}{\partial x} = \frac{D_{B0}B_0}{\nu}(1+\theta')^{\epsilon_{DB}}\frac{\partial b}{\partial x} \tag{11}$$

$$x = \infty, \quad t \geq 0; \quad b = 1, \quad \theta = 0 \tag{12}$$

where

$$a = \frac{A}{A_{i0}}, \quad b = \frac{B}{B_0} \tag{13}$$

Subscripts I and II refer to the values when x approaches x' from region I and from region II, respectively. The solutions of Eqs. 5–8 are given by

For region I $(0 < \eta < \eta')$

$$a = (1+\theta_i)^{\epsilon_S}\left[1 - \frac{G_2(\eta)}{G_2(\eta')}\right] \tag{14}$$

$$\theta = \theta_i - (\theta_i - \theta')\frac{\operatorname{erf}(\eta/\sqrt{Le})}{\operatorname{erf}(\eta'/\sqrt{Le})} \tag{15}$$

For region II ($\eta' < \eta < \infty$)

$$b = 1 - \frac{G_3(\eta)}{G_3(\eta')} \tag{16}$$

$$\theta = \theta' \frac{\mathrm{erf}c(\eta/\sqrt{Le})}{\mathrm{erf}c(\eta'/\sqrt{Le})} \tag{17}$$

where

$$Le = \frac{\alpha}{D_{A0}}, \quad \eta = \frac{x}{2\sqrt{D_{A0}t}} \tag{18}$$

Applying boundary conditions Eqs. 10 and 11 to Eqs. 14–17, we obtain

$$\frac{\theta'}{\theta_i - \theta'} = \frac{\mathrm{erf}c(\eta'/\sqrt{Le})}{\mathrm{erf}(\eta'/\sqrt{Le})} \left[1 + \frac{1}{P}\exp\left(\frac{\eta'^2}{Le}\right) G_1(\eta')\right] \tag{19}$$

$$\frac{1}{2}\sqrt{\frac{\pi}{Le}}\,\frac{\psi(1 + \theta_i)^{\epsilon_{DA} + \epsilon_S}}{\theta_i - \theta'}\,\mathrm{erf}\left(\frac{\eta'}{\sqrt{Le}}\right) = G_2(\eta') \tag{20}$$

$$rq = (1 + \theta_i)^{\epsilon_{DA} + \epsilon_S} \frac{G_1(\eta')G_3(\eta')}{G_2(\eta')} \tag{21}$$

where

$$G_1(y) = \exp\left[\frac{-2}{(1 + \theta_i)^{\epsilon_{DA}}} \int_0^y \frac{z\,dz}{\left\{1 - \dfrac{\theta_i - \theta'}{1 + \theta_i}\dfrac{\mathrm{erf}(z/\sqrt{Le})}{\mathrm{erf}(\eta'/\sqrt{\mathrm{Le}})}\right\}^{\epsilon_{DA}}}\right] \tag{22}$$

$$G_2(\eta) = \int_0^{\eta} \frac{G_1(y)\,dy}{\left[1 - \dfrac{\theta_i - \theta'}{1 + \theta_i}\dfrac{\mathrm{erf}(y/\sqrt{Le})}{\mathrm{erf}(\eta'/\sqrt{\mathrm{Le}})}\right]^{\epsilon_{DA}}} \tag{23}$$

$$G_3(\eta) = \int_{\eta}^{\infty} \frac{\exp\left[-\dfrac{2}{r}\displaystyle\int_{\eta'}^{y} \frac{z\,dz}{\left\{1 + \theta'\dfrac{\mathrm{erf}c(z/\sqrt{Le})}{\mathrm{erfc}(\eta'/\sqrt{Le})}\right\}^{\epsilon_{DB}}}\right]}{\left[1 + \theta'\dfrac{\mathrm{erf}c(y/\sqrt{Le})}{\mathrm{erf}c(\eta'/\sqrt{Le})}\right]^{\epsilon_{DB}}}\,dy \tag{24}$$

$$P = \frac{\Delta H_S}{\Delta H_R}, q = \frac{B_0}{\nu A_{i0}}, r = \frac{D_{B0}}{D_{A0}}, \psi = \frac{\alpha A_{i0}(-\Delta H_S)}{\lambda T_0} \tag{25}$$

Equations 19–24 may be solved numerically to obtain simultaneously the values of the interface temperature rise θ_i, the location of reaction plane η', and the temperature rise at reaction plane θ'. It should be noted that the interface temperature rise θ_i is invariant with time for $t > 0$, as has been assumed implicitly in the above derivation.

The average absorption rate during contact time t is obtained from

$$N_A = \frac{1}{t}\int_0^t - D_{A0}A_{i0}(1 + \theta_i)^{\epsilon_{DA}} \left(\frac{\partial a}{\partial x}\right)_{x=0} dt \tag{26}$$

The enhancement factor β, which is defined as the ratio of the actual average absorption rate to the average physical absorption rate without heat effects evaluated at initial or liquid bulk temperature, is given by

$$\beta = \frac{N_A}{2A_{i0}\sqrt{D_{A0}/\pi t}} = \frac{\sqrt{Le}}{\psi}\,\frac{\theta_i - \theta'}{\mathrm{erf}(\eta'/\sqrt{Le})} \tag{27}$$

For physical absorption, being a limiting case of $q = 0$, the solution is simplified as

$$\int_0^{\infty} [1 + \theta_i\,\mathrm{erf}c(y/\sqrt{Le})]^{-\epsilon_{DA}} \times \exp\left[-2\int_0^y \frac{z\,dz}{\{1 + \theta_i\,\mathrm{erf}c(z/\sqrt{Le})\}^{\epsilon_{DA}}}\right] dy = \frac{\psi}{2\theta_i}\sqrt{\frac{\pi}{Le}}\,(1 + \theta_i)^{\epsilon_S} \tag{28}$$

$$\beta = \frac{\sqrt{Le}}{\psi}\,\theta_i \tag{29}$$

Approximate Solutions

Since the numerical evaluations of Eqs. 22–24 are troublesome, we proceed to get approximate analytical solutions by making the following approximations in these equations:

$$1 - \frac{\theta_i - \theta'}{1 + \theta_i}\,\frac{\mathrm{erf}(w/\sqrt{Le})}{\mathrm{erf}(\eta'/\sqrt{Le})} \simeq 1 \tag{30}$$

$$1 + \theta'\,\frac{\mathrm{erf}c(w/\sqrt{Le})}{\mathrm{erf}c(\eta'/\sqrt{Le})} \simeq 1 + \theta' \tag{31}$$

where $w = z$ or y.

The solutions obtained are equivalent to those derived from the Danckwerts analysis (Danckwerts 1970), which corresponds to $\epsilon_S = \epsilon_{DA} = \epsilon_{DB} = 0$ in Eqs. 19–24 and 27,by substituting $Le(1 + \theta_i)^{-\epsilon_{DA}}$, $q(1 + \theta_i)^{-\epsilon_S}$, $r(1 + \theta_i)^{-\epsilon_{DA}}(1 + \theta')^{\epsilon_{DB}}$, $\beta(1 + \theta_i)^{-\epsilon_S-(1/2)\epsilon_{DA}}$, $\eta'(1 + \theta_i)^{-\epsilon_{DA}/2}$, and $\psi(1 + \theta_i)^{\epsilon_S}$ for Le, q, r, β, η', and ψ, respectively. The approach using this approximation, in which the gas solubility and diffusivity of the dissolved gas are evaluated at the interface temperature and the diffusivity of the reactant is evaluated at reaction plane temeprature, is termed below the modified Danckwerts model (MDM), while the conventional Danckwerts analysis, in which the physical properties are evaluated at initial or liquid bulk temperature, is called the ordinary Danckwerts model (ODM).

The MDM solutions are given by

$$\theta'_{MD} = \theta_{MD,i} - \frac{\psi}{\sqrt{Le}}(1 + \theta_{MD,i})^{\epsilon_{DA}/2+\epsilon_S} \times \frac{\mathrm{erf}(\eta'_{MD}/\sqrt{Le})}{\mathrm{erf}[\eta'_{MD}(1 + \theta_{MD,i})^{-\epsilon_{DA}/2}]} \tag{32}$$

$$\theta_{MD,i} = \frac{\psi}{\sqrt{Le}}\,\frac{(1 + \theta_{MD,i})^{\epsilon_{DA}/2 + \epsilon_S}}{\mathrm{erf}[\eta'_{MD}(1 + \theta_{MD,i})^{-\epsilon_{DA}/2}]} \times \left[1 + \frac{1}{P}\exp\left\{\frac{\eta'^2_{MD}}{Le} - \frac{\eta'^2_{MD}}{(1 + \theta_{MD,i})^{\epsilon_{DA}}}\right\}\mathrm{erfc}\left(\frac{\eta'_{MD}}{\sqrt{Le}}\right)\right] \tag{33}$$

$$q\sqrt{r} = \frac{(1 + \theta_{MD,i})^{\epsilon_{DA}/2+\epsilon_S}}{(1 + \theta'_{MD})^{\epsilon_{DB}/2}} \times \exp\left[\left(\frac{1}{r(1 + \theta'_{MD})^{\epsilon_{DB}}} - \frac{1}{(1 + \theta_{MD,i})^{\epsilon_{DA}}}\right\} \times \eta'^2_{MD}\right] \times \mathrm{erf}c\left[\frac{\eta'_{MD}}{\sqrt{r}(1 + \theta'_{MD})^{\epsilon_{DB}/2}}\right] \Big/ \mathrm{erf}\left[\frac{\eta'_{MD}}{(1 + \theta_{MD,i})^{\epsilon_{DA}/2}}\right] \tag{34}$$

$$\beta_{MD} = \frac{\sqrt{Le}}{\psi}\,\frac{\theta_{MD,i} - \theta'_{MD}}{\mathrm{erf}(\eta'_{MD}/\sqrt{Le})} \tag{35}$$

For physical absorption, Eqs. 32–35 reduce to

$$\theta_{MD,i} = \frac{\psi}{\sqrt{Le}}(1 + \theta_{MD,i})^{\epsilon_{\mathrm{eff}}} \tag{36}$$

$$\beta_{MD} = \frac{\sqrt{Le}}{\psi}\,\theta_{MD,i} \tag{37}$$

where ϵ_{eff} is concerned with the combined activation energy of the solution and diffusion for the isothermal physical absorption rate, $N_A = 2A_{i0}\sqrt{D_{A0}/\pi t}$ and given by

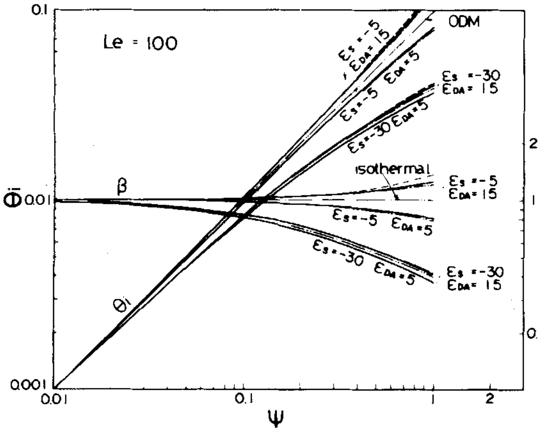

Figure 1. Interface temperature rise θ_i and enhancement factor β for physical absorption based on penetration theory. —— Rigorous solutions, Eqs. 28 and 29. - - - - - MDM solutions, Eqs. 36 and 37. —··— Solutions for Le = 1 (Suresh et al., 1983) --- Modified film theory solutions, Eqs. 39 and 40.

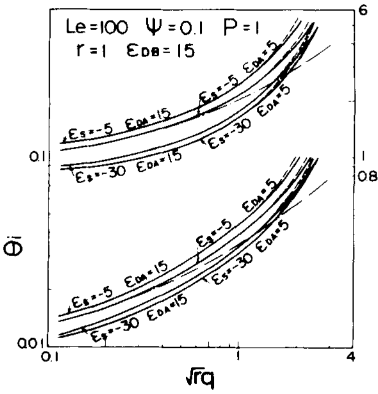

Figure 3. Interface temperature rise θ_i and enhancement factor β for absorption with instantaneous irreversible reaction based on penetration theory. —— Rigorous solutions, Eqs. 19-24 and 27. - - - - - MDM solutions, Eqs. 32-35. -·- Same as in Figure 2.

$$\epsilon_{\text{eff}} = \epsilon_S + \frac{\epsilon_{DA}}{2} \tag{38}$$

Results and Discussion

First of all, physical absorption is considered as a limiting case of $q = 0$. This problem is analyzed and discussed for the penetration theory in a previous paper (Suresh et al., 1983). Thus only the relation between the analytical results obtained from the penetration theory and film theory is briefly discussed here.

The corresponding rigorous solution for the film theory, in which equal film thickness both for mass transfer and for heat transfer is assumed (similar to the ODM), can be easily obtained. The qualitative behavior of the interface temperature rise θ_i and enhancement factor β in the film theory with respect to any system parameter is very similar to that in the penetration theory. As pointed out by Danckwerts (1970) for his ODM solution, however, the penetration theory predicts a much higher interface temperature rise θ_i. Further, the penetration theory predicts substantially higher or lower enhancement factor β, in dependence on the values of ϵ_S and ϵ_{DA}. However, comparison of the film theory solution with the penetration theory solution reveals the similarity of β, with the only difference in terms $\sqrt{Le}$ and Le. Thus one may expect that the film theory solution with the replacement of Le by $\sqrt{Le}$ may approximate closely the rigorous penetration theory solution, Eqs. 28 and 29. Such modified solution is given by

$$(1 + \theta_i)^{1-\epsilon_{DA}} + \frac{\psi}{\sqrt{Le}}(1 + \theta_i)^{\epsilon_S}(\epsilon_{DA} - 1) = 1 \tag{39}$$

$$\beta = \frac{\sqrt{Le}}{\psi}\theta_i \tag{40}$$

Figure 1 shows the rigorous penetration theory solutions compared with the above modified film theory solutions, as well as with the MDM solutions, Eqs. 36 and 37, and with the solutions for Le

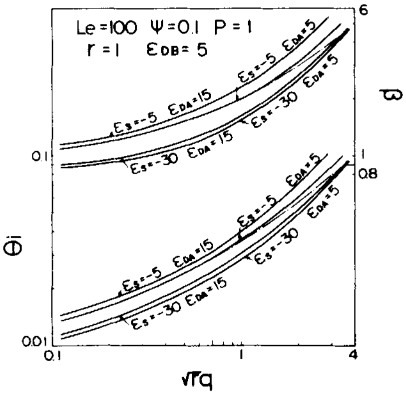

Figure 2. Interface temperature rise θ_i and enhancement factor β for absorption with instantaneous irreversible reaction based on penetration theory. —— Rigorous solutions, Eqs. 19-24 and 27, and MDM solutions, Eqs. 32-35. -·- ODM solution for θ_i and isothermal enhancement factor, corresponding to MDM solutions with $\epsilon_S = \epsilon_{DA} = \epsilon_{DB} = 0$.

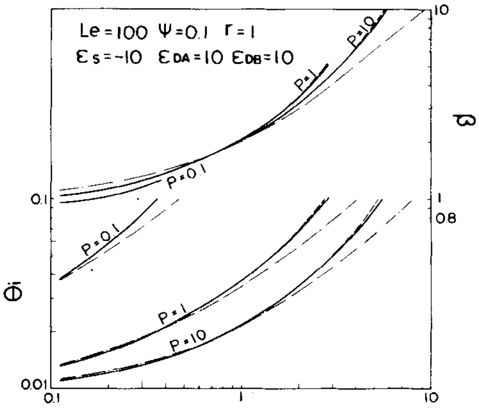

Figure 4. Interface temperature rise θ_i and enhancement factor β for absorption with instantaneous irreversible reaction based on penetration theory. Lines same as in Figure 3.

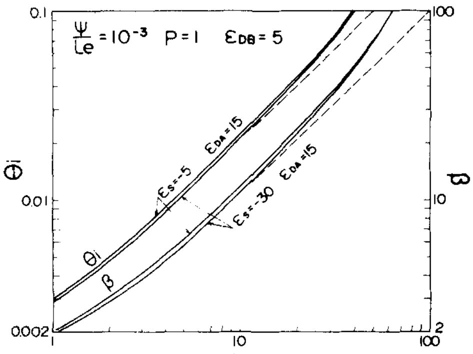

Figure 5. Interface temperature rise θ_i and enhancement factor β for absorption with instantaneous irreversible reaction based on film theory. —— Rigorous solutions, Eqs. 41–43. - - - - - ODM solution for θ_i and isothermal enhancement factor, corresponding to rigorous solutions with $\epsilon_S = \epsilon_{DA} = \epsilon_{DB} = 0$.

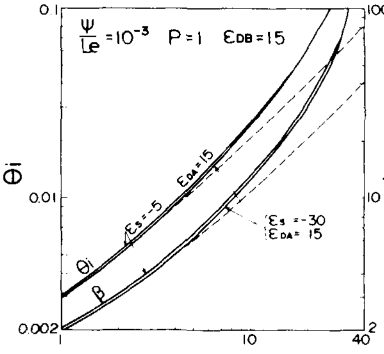

Figure 6. Interface temperature rise θ_i and enhancement factor β for absorption with instantaneous irreversible reaction based on film theory. Lines same as in Figure 5.

= 1 (Suresh et al., 1983). In general, the modified film theory solutions approximate indistinguishably the penetration theory solutions for any combination of ϵ_S and ϵ_{DA}. The MDM solutions also approximate closely the rigorous solutions, while the previous solutions for $Le = 1$ deviate greatly from the rigorous solutions in the region of large values of ψ for the combination of $\epsilon_S = -5$ and $\epsilon_{DA} = 15$. The good agreement of the modified film theory solutions with the rigorous penetration theory solutions was also observed for othe values of Le. Therefore the modified film theory solutions can be recommended, for the prediction of the interface temperature rise θ_i and of the relevant enhancement factor β, as being both accurate and much simpler in expression.

Representative illustrations of the rigorous penetration theory solutions for an instantaneous irreversible reaction are presented in Figures 2 to 4, together with those based on the MDM and ODM. The MDM solutions always result in satisfactory accuracy. It should be noted from Figures 2 and 3 that the temperature rise θ_i and enhancment factor β depend on the combinations of ϵ_S, ϵ_{DA}, and ϵ_{DB}. Further, it may be seen from Figure 4 that the variation of the enhancement factor with P is significantly small compared with the variation of the interface temperature rise. Such behavior was also observed for any system parameter, such as Le and ψ.

The film theory solution was also rigorously analyzed and compared with the penetration theory solution. The solution is given by

$$(1+\theta_i)^{1-\epsilon_{DA}} + \frac{\psi}{Le}(1+\theta_i)^{\epsilon_S}(\epsilon_{DA}-1) = \left[1 - \frac{\psi rq(\epsilon_{DB}-1)(P+1)}{PLe}\right]^{(\epsilon_{DA}-1)/(\epsilon_{DB}-1)} \quad (41)$$

$$\theta' = \left[1 - \frac{\psi rq(\epsilon_{DB}-1)(P+1)}{PLe}\right]^{1/(1-\epsilon_{DB})} - 1 \quad (42)$$

$$\beta = \frac{N_A}{D_{A0}A_{i0}/x_f} = \frac{Le}{\psi}\left(\theta_i - \frac{\theta'}{1+P}\right) \quad (43)$$

Some of the results calculated for the film theory are shown in Figures 5 and 6, together with the ODM solution for the interface temperature rise and isothermal enhancement factor, which are equivalent to the solution of $\epsilon_S = \epsilon_{DA} = \epsilon_{DB} = 0$. The lines for $-\epsilon_S = \epsilon_{DA} = 5$ and $-\epsilon_S = 6\epsilon_{DA} = 30$, which fall between the lines for $\epsilon_S = -5$ and $\epsilon_{DA} = 15$ and for $\epsilon_S = -30$ and $\epsilon_{DA} = 15$, have been omitted for clarity. As seen in Figures 5 and 6, the interface temperature rise θ_i and relevant enhancement factor β depend greatly on ϵ_{DB} and to a small extent on ϵ_S and ϵ_{DA}. This behavior might be expected from the fact that the reaction plane approaches the gas-liquid interface with an increase of rq and then the diffusion of reactant B to the interface becomes rate-determining. On the other hand, the different behavior for the penetration theory shown in Figures 2 and 3 is due to the fact that heat effects for the penetration theory are much larger than those for the film theory and consequently the substantial influence of heat generation emerges at much smaller values of q, in other words, nearer the physical absorption regime where ϵ_S and ϵ_{DA} are controlling factors. Therefore the film theory solutions with the replacement of Le by $\sqrt{Le}$ and of r by $\sqrt{r}$, as expected from the analogies for nonisothermal physical absorption discussed above and for isothermal absorption with an instantaneous irreversible reaction, respectively, do not give a reasonable approximation to the penetration theory solutions. Thus the analysis based on the film theory does not serve as a quantitative guide to the solution for the realistic penetration theory except in the case of the physical absorption regime.

The analytical results for the interface temperature rise and relevant enhancement factor are summarized in Table 1.

FIRST-ORDER IRREVERSIBLE REACTION

We consider the case in which a dissolved gas A reacts irreversibly according to the following reaction scheme:

$$A \rightarrow C \quad \text{(b)}$$

TABLE 1. ANALYTICAL RESULTS

Solution	No Reaction	Instantaneous Irreversible Reaction	First-Order Irreversible Reaction
Rigorous or numerical	Eqs. 28 and 29	Eqs. 19–24 and 27	Shah (1972) for θ_i
Approximate (recommended for use)	Eqs. 39 and 40 or Eqs. 36 and 37	Eqs. 32–35	Eqs. 53, 54, and 56

This reaction is assumed to be first order with respect to a solute gas A, although the extension to a mth order reaction might be done easily using the well-known Hikita-Asai (1963) approximation.

The diffusion equations for a dissolved gas and for heat and the relevant initial and boundary conditions are

$$\frac{\partial a}{\partial t} = D_{A0}\frac{\partial}{\partial x}\left[(1+\theta)^{\epsilon_{DA}}\frac{\partial a}{\partial x}\right] - k_0(1+\theta)^{\epsilon_R}a \tag{44}$$

$$\frac{\partial \theta}{\partial t} = \alpha\frac{\partial^2\theta}{\partial x^2} + \frac{k_0A_{i0}(1+\theta)^{\epsilon_R}(-\Delta H_R)}{\rho C_p T_0}a \tag{45}$$

$$x > 0,\ t = 0;\quad a = 0, \theta = 0 \tag{46}$$

$$x = 0,\ t > 0;\ a = (1+\theta_i)^{\epsilon_S},\ \theta = \theta_i,$$

$$-\lambda T_0\frac{\partial\theta}{\partial x} = -D_{A0}A_{i0}(1+\theta_i)^{\epsilon_{DA}}(-\Delta H_S)\frac{\partial a}{\partial x} \tag{47}$$

$$x = \infty,\ t \geq 0;\quad a = 0, \theta = 0 \tag{48}$$

This problem has been solved numerically by Shah (1972) for the interface temperature rise, but the enhancement factor has not been reported. In what follows, we consider approximate solutions based on MDM. Then the MDM solution for the interface temperature rise is compared with Shah's numerical solutions and the solution for the enhancement factor is presented.

Approximate Solutions

The interface temperature rise based on the ODM is given by the following expressions (Danckwerts, 1953, 1967,1970):

$$\theta_{OD,i} = \frac{\psi}{\sqrt{Le}}\exp\left(-\frac{2\gamma^2}{\pi}\right)\left[\left\{1+\frac{4\gamma^2}{\pi}\left(1+\frac{1}{p}\right)\right\}I_0\left(\frac{2\gamma^2}{\pi}\right) + \frac{4\gamma^2}{\pi}\left(1+\frac{1}{P}\right)I_1\left(\frac{2\gamma^2}{\pi}\right)\right] \tag{49}$$

where

$$\gamma = \frac{\sqrt{\pi k_0 t}}{2} \tag{50}$$

Le, P, and ψ are defined by Eqs. 18 and 25. It should be noted here that $\theta_{OD,i}$ is a function of contact time t through the definition of γ, different from the case of an instantaneous irreversible reaction. As respresentative properties during the absorption processes, therefore, we assume it to be reasonable to use the properties evaluated at time averaged interface temperature.

Defining $\overline{\theta_{OD,i}}$ by

$$\overline{\theta_{OD,i}} = \frac{1}{t}\int_0^t \theta_{OD,i}dt \tag{51}$$

and integrating after the substitution of Eq. 49 result in

$$\overline{\theta_{OD,i}} = \frac{\psi}{\sqrt{Le}}\exp\left(-\frac{2\gamma^2}{\pi}\right)\left[\left\{1+\frac{8\gamma^2}{3\pi}\left(1+\frac{1}{P}\right)\right\}I_0\left(\frac{2\gamma^2}{\pi}\right) + \frac{1}{3}\left\{1-\frac{2}{P}+\frac{8\gamma^2}{\pi}\left(1+\frac{1}{P}\right)\right\}I_1\left(\frac{2\gamma^2}{\pi}\right)\right] \tag{52}$$

In Eqs. 49 and 52, we replace A_{i0}, D_{A0}, and k_0 included in the definitions of Le, γ, and ψ by $A_{i0}(1+\overline{\theta_{MD,i}})^{\epsilon_S}$, $D_{A0}(1+\overline{\theta_{MD,i}})^{\epsilon_{DA}}$ and $k_0(1+\overline{\theta_{MD,i}})^{\epsilon_R}$, respectively, without changing the original definitions of Le, γ, and ψ, and we simultaneously change $\theta_{OD,i}$ and $\overline{\theta_{OD,i}}$ to $\theta_{MD,i}$ and $\overline{\theta_{MD,i}}$, respectively. This substitution gives rise to the following MDM solution for the temperature rise at the interface:

$$\begin{aligned}\theta_{MD,i} = {} & \frac{\psi}{\sqrt{Le}}(1+\overline{\theta_{MD,i}})^{(\epsilon_{DA}/2+\epsilon_S)}\exp\left[-\frac{2\gamma^2}{\pi}(1+\overline{\theta_{MD,i}})^{\epsilon_R}\right] \\ & \times\left[\left\{1+\frac{4\gamma^2}{\pi}\left(1+\frac{1}{P}\right)(1+\overline{\theta_{MD,i}})^{\epsilon_R}\right\}I_0\left\{\frac{2\gamma^2}{\pi}(1+\overline{\theta_{MD,i}})^{\epsilon_R}\right\}\right. \\ & \left.+\frac{4\gamma^2}{\pi}\left(1+\frac{1}{P}\right)(1+\overline{\theta_{MD,i}})^{\epsilon_R}I_1\left\{\frac{2\gamma^2}{\pi}(1+\overline{\theta_{MD,i}})^{\epsilon_R}\right\}\right]\end{aligned} \tag{53}$$

$$\begin{aligned}\overline{\theta_{MD,i}} = {} & \frac{\psi}{\sqrt{Le}}(1+\overline{\theta_{MD,i}})^{(\epsilon_{DA}/2+\epsilon_S)}\exp\left[-\frac{2\gamma^2}{\pi}(1+\overline{\theta_{MD,i}})^{\epsilon_R}\right] \\ & \times\left[\left\{1+\frac{8\gamma^2}{3\pi}\left(1+\frac{1}{P}\right)(1+\overline{\theta_{MD,i}})^{\epsilon_R}\right\}I_0\left\{\frac{2\gamma^2}{\pi}(1+\overline{\theta_{MD,i}})^{\epsilon_R}\right\}\right. \\ & +\frac{1}{3}\left\{1-\frac{2}{P}+\frac{8\gamma^2}{\pi}\left(1+\frac{1}{P}\right)(1+\overline{\theta_{MD,i}})^{\epsilon_R}\right\} \\ & \left.\times I_1\left\{\frac{2\gamma^2}{\pi}(1+\overline{\theta_{MD,i}})^{\epsilon_R}\right\}\right]\end{aligned} \tag{54}$$

The enhancement factor can be derived from the isothermal solution (Danckwerts 1950)

$$\beta_{IS} = \left(\gamma + \frac{\pi}{8\gamma}\right)\operatorname{erf}\left(\frac{2\gamma}{\sqrt{\pi}}\right) + \frac{1}{2}\exp\left(-\frac{4\gamma^2}{\pi}\right) \tag{55}$$

with the similar replacement to yield finally

$$\begin{aligned}\beta_{MD} = {} & (1+\overline{\theta_{MD,i}})^{\epsilon_{eff}}\left[\left\{\gamma+\frac{\pi}{8\gamma}(1+\overline{\theta_{MD,i}})^{-\epsilon_R}\right\}\right. \\ & \times\operatorname{erf}\left\{\frac{2\gamma}{\sqrt{\pi}}(1+\overline{\theta_{MD,i}})^{\epsilon_R/2}\right\} \\ & \left.+\frac{1}{2}(1+\overline{\theta_{MD,i}})^{-\epsilon_R/2}\exp\left\{-\frac{4\gamma^2}{\pi}(1+\overline{\theta_{MD,i}})^{\epsilon_R}\right\}\right]\end{aligned} \tag{56}$$

where the effective activation energy ϵ_{eff} is defined by

$$\epsilon_{eff} = \epsilon_S + \frac{\epsilon_{DA}+\epsilon_R}{2} \tag{57}$$

and represents that for the isothermal limiting absorption rate with $\gamma \gg 1$, i.e., $N_{A,IS} = A_{i0}\sqrt{k_0D_{A0}}$.

Results and Discussion

Equations 53 and 54, giving the interface temperature rise based on the MDM, are compared in Figures 7 and 8, corresponding to $P = 1$ and 10, respectively, with the numerical solutions solved by

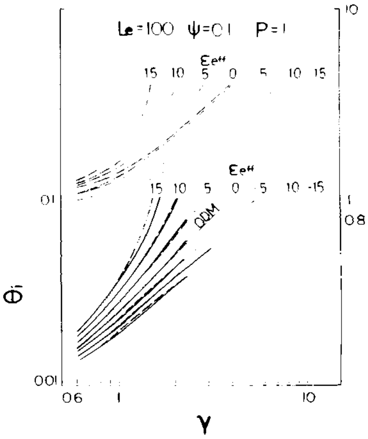

Figure 7. Interface temperature rise θ_i and enhancement factor β for penetration theory. —— Numerical solutions (Shah, 1972). - - - - - MDM solutions, Eqs. 53, 54, and 56. -·- Isothermal enhancement factor, Eq. 55.

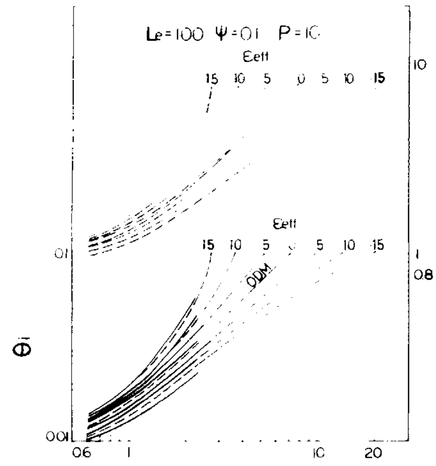

Figure 8. Interface temperature rise θ_i and enhancement factor β for penetration theory. Lines same as in Figure 7.

Shah (1972) for several values of ϵ_{eff}. Similarly to the numerical solutions, the MDM solutions also show no appreciable difference in both interface temperature rise θ_i and enhancement factor β for any combination of the individual value of ϵ, as long as ϵ_{eff} remains constant. Further, the values corresponding to $\epsilon_{eff} = 0$ agree well with the temperature rise based on the ODM, Eq. 49, and the isothermal enhancement factor, Eq. 55. The approximate solution of the interface temperature rise for any value of ϵ_{eff} can be seen to agree remarkably with numerical solutions with an error of only a few percent for most cases, justifying the use of the physicochemical properties evaluated at the time-averaged interface temperature. An alternative approximate solution for the interface temperature rise was presented by Shah (1972). However, his expression does not suggest the general analytical procedure for any other reaction schemes.

The corresponding enhancement factor β_{MD} is also shown in Figures 7 and 8. The numerical solutions for β have not been available to compare with β_{MD}, but the accuracy might be expected to parallel that of $\theta_{MD,i}$, since β_{MD} is a counterpart concerned intimately with $\theta_{MD,i}$. As both figures show, the behavior of the enhancement factor with regard to ϵ_{eff} is very similar to that of θ_i.

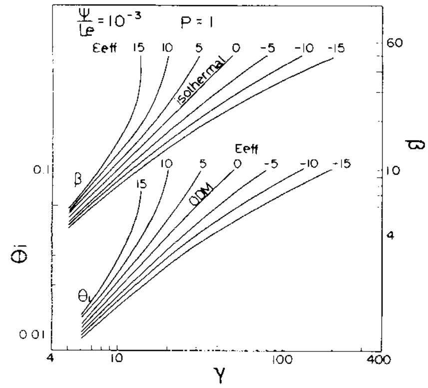

Figure 9. Interface temperature rise θ_i and enhancement factor β for film theory. —— Rigorous solutions, Eqs. 58 and 59 or 60.

Next, a comparison of the present penetration theory solution with the film theory solution is made to test the analogy between the theories. The approximate film theory solutions for interface temperature rise and for enhancement factor, which are substantially rigorous, are obtained by solving simultaneously the following equations 58 and 59 or 60 (see appendix):

$$\beta = \frac{N_A}{D_{A0}A_{i0}/x_f} = \frac{\theta_i[(\epsilon_{DA}-1)(1+\theta_i)^{\epsilon_S} + LeP\{1-(1+\theta_i)^{1-\epsilon_{DA}}\}/\psi]}{(P+1)[1-(1+\theta_i)^{1-\epsilon_{DA}}]} \tag{58}$$

For $\epsilon_{DA} \leq 1$

$$\beta = (1+\theta_i)^{\epsilon_{eff}}\,\gamma\,\frac{I_{p-1}(\Phi_1)I_{-p}(\Phi_2) - I_{1-p}(\Phi_1)I_p(\Phi_2)}{I_p(\Phi_1)I_{-p}(\Phi_2) - I_{-p}(\Phi_1)I_p(\Phi_2)} \tag{59}$$

For $\epsilon_{DA} > 1$

$$\beta = (1+\theta_i)^{\epsilon_{eff}}\,\gamma\,\frac{I_{p+1}(\Phi_1)I_{-p}(\Phi_2) - I_{-(p+1)}(\Phi_1)I_p(\Phi_2)}{I_p(\Phi_1)I_{-p}(\Phi_2) - I_{-p}(\Phi_1)I_p(\Phi_2)} \tag{60}$$

where

$$p = \frac{|\epsilon_{DA}-1|}{\epsilon_R - \epsilon_{DA} + 2}, \quad \gamma = x_f\sqrt{\frac{k_0}{D_{A0}}}$$

$$\Phi_1 = \frac{2\gamma(1+\theta_i)^{(\epsilon_R-\epsilon_{DA}+2)/2}}{(\epsilon_R-\epsilon_{DA}+2)\theta_i}, \quad \Phi_2 = \frac{2\gamma}{(\epsilon_R-\epsilon_{DA}+2)\theta_i} \tag{61}$$

One illustrative result is shown in Figure 9 for $P = 1$. The interface temperature rise and enhancement factor were unique functions of ϵ_{eff}, similarly to the penetration theory, independently of the individual value of ϵ. From a comparison of Figures 9 and 7, it should be noted that the behavior in the penetration theory is analogous to that in the film theory except that of β in the small region of γ, but the nonisothermal effects emerge at much smaller values of γ for the penetration theory. Similarly to an instantaneous irreversible reaction, for the present reaction scheme also, the film theory solutions with the replacement of Le by $\sqrt{Le}$ do not approximate closely the penetration theory solutions. Thus the film theory solutions cannot be used as a substitution of the penetration theory solutions, unlike isothermal absorption with the present reaction scheme.

The analytical results for the interface temperature rise and relevant enhancement factor are summarized in Table 1.

NOTATION

A = concentration of dissolved gas A
A_i = solubility of gas A
a = dimensionless concentration of dissolved gas, A/A_{i0}
B = concentration of reactant B in liquid phase
b = dimensionless concentration of reactant B, B/B_0
C_p = specific heat of liquid
D = diffusivity
E = activation energy
k = reaction rate constant
Le = Lewis number, α/D_{A0}
N = average absorption rate
P = $\Delta H_S/\Delta H_R$
p = parameter defined by Eq. 61
Q = temperature-dependent property (A_i, D_A, D_B, and k)
q = concentration ratio, $B_0/\nu A_{i0}$
R = gas constant
r = diffusivity ratio, D_{B0}/D_{A0}
T = thermodynamic temperature
t = exposure time of liquid with gas

x = distance from interface into liquid
x_f = effective film thickness

Greek Letters

α = thermal diffusivity, $\lambda/\rho C_p$
β = enhancement factor
γ = dimensionless parameter, $x_f\sqrt{k_0/D_{A0}}$ for film theory and $\sqrt{\lambda k_{0t}}/2$ for penetration theory
ΔH_R = enthalpy change due to reaction
ΔH_S = enthalpy change due to solution
ϵ = activation energy group, E/RT_0
η = dimensionless independent variable, $x/2\sqrt{D_{A0}t}$
θ = dimensionless temperature rise, $(T - T_0)/T_0$
λ = thermal conductivity of liquid
ν = number of moles of reactant B reacting with one mole of dissolved gas A
ρ = liquid density
Φ_1, Φ_2 = variables defined by Eq. 61
ψ = $\alpha A_{i0}(-\Delta H_S)/\lambda T_0$

Subscripts

A = dissolved gas
B = reactant in liquid phase
D = diffusion
eff = effective value
i = gas-liquid interface
IS = isothermal condition
MD = modified Danckwerts model
OD = ordinary Danckwerts model
R = reaction
S = solution
0 = initial or liquid bulk condition
I = region I $(0 < x < x')$
II = region II $(x' < x < \infty)$

Superscripts

= reaction plane
— = time-averaged value

APPENDIX: APPROXIMATE FILM THEORY SOLUTIONS FOR A FIRST-ORDER IRREVERSIBLE REACTION

The approximate differential equations for the film theory are given by Eqs. 44 and 45 with $\partial a/\partial t = \partial\theta/\partial t = 0$. The relevant boundary conditions are equivalent toEqs. 47 and 48 with the replacement of $x = \infty$ by $x = x_f$. Here the same film thickness is assumed for the transport of both mass and heat in accordance with the ODM. The basic equations cannot be analytically solved, since they are coupled nonlinear differential equations. Therefore we proceed to get the approximate solutions.

Eliminating the reaction term from Eqs. 44 and 45 and integrating the resulting equation twice with respect to x under the boundary conditions, with the help of the following expression for the absorption rate N_A

$$N_A = -D_{A0}A_{i0}(1 + \theta_i)^{\epsilon_{DA}}\left(\frac{da}{dx}\right)_{x=0} \tag{A1}$$

there results

$$D_{A0}A_{i0}(-\Delta H_R)(1 + \theta_i)^{\epsilon_S} + \frac{\lambda T_0}{1 - \epsilon_{DA}}[(1 + \theta_i)^{1-\epsilon_{DA}} - 1]$$

$$= -N_A(\Delta H_R + \Delta H_S)\int_0^{x_f}\frac{dx}{(1 + \theta)^{\epsilon_{DA}}} \tag{A2}$$

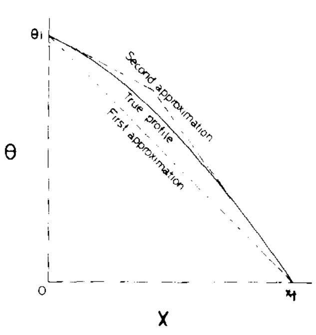

Figure A1. Assumed temperature profile in liquid film.

The integration on the righthand side of this equation cannot be yet ready for evaluation, since the functional relation between θ and x is unknown. It can be seen from Eq. 45 with $\partial\theta/\partial t = 0$ that $d^2\theta/dx^2$ is negative for exothermic reaction ($\Delta H_R < 0$). Therefore the plot of θ against x becomes concave downward, as shown by the solid line in Figure A1. Two approximate solutions have been derived. The first approximate solution is based on the assumption that θ varies linearly with respect to x, as shown by the broken line. The second one is based on the assumption that θ varies with x along two straight lines, which are drawn as tangent lines at $x = 0$ and $x = x_f$, as shown by chain lines. However, these two approximate solutions for θ_i, between which the rigorous solutions lie, have been proved to result in the almost same values of θ_i. This fact indicates that both of these approximate solutions may be regarded substantially as rigorous solutions. Thus much simpler approximate solutions based on the first approximation are presented here.

The temperature profile in the liquid film for this model can be written as

$$\theta = \theta_i\left(1 - \frac{x}{x_f}\right) \tag{A3}$$

Substitution of Eq. A3 in Eq. A2 and subsequent integration lead to Eq. 58 in the text. On the other hand, the substitution of Eq. A3 in Eq. 44 with $\partial a/\partial t = 0$ and integration with the relevant boundary conditions provide the concentration of the dissolved gas A and the evaluation of N_A by Eq. A1 leads to the expression for the enhancement factor given by Eq. 59 or 60 in the text.

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