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On the bulk-liquid reaction in isothermal reactive gas absorption

A.A. Shaikh *, U.A. Al-Mubaiyedh

Department of Chemical Engineering, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

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Abstract

A generalized film model is used to describe isothermal reactive gas absorption without limitation on the reaction regime. The model is applied to analyze the effect of the liquid phase, bulk-side, reaction on gas absorption accompanied by a general (m,n)-th-order reaction involving a volatile liquid reactant. A computational analysis is performed in order to examine criteria given in the literature for the condition(s) under which the contribution of the bulk reaction can be significant. It is shown that the Hatta number is not the only indicator by which the importance of this contribution should be assessed. Other parameters reflecting reactor type, operating conditions, reaction orders, and extent of liquid mixing are shown to play an important role in determining the significance of the bulk-liquid reaction in the slow- and moderately fast-reaction regimes. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Bulk-liquid reaction; Reactive gas absorption; Hatta number

1. Introduction

The effect of chemical reaction on the rate of gas absorption has been studied extensively. In the present communication, we are interested in the role that the bulk-liquid-side reaction (henceforth called the bulk reaction) plays in isothermal gas absorption accompanied by chemical reaction. Our interest has been stimulated by the sometimes conflicting accounts in the literature regarding the contribution of the bulk reaction. In many instances, inconsistent criteria have been given in terms of *specific* values of the Hatta number, M, at which the bulk reaction would be negligible. Indeed, some workers (see, e.g., Alper [1]) have argued that in reactive gas absorption, the slow-reaction regime, wherein concentration of the dissolved gaseous reactant is not negligible in the bulk-liquid, is rather uncommon in practice. While it is well-known that a number of important industrial reactions (e.g., in natural gas treating) are very fast, there are other industrial reactions, such as nitrations, sulfonations, and chlorinations, which are slow or moderately fast (see, e.g., Barona [2]). As significantly, but perhaps less obviously, is the possibility in gas–liquid reactors of a shift from one regime to another upon variation of operating conditions (say, in agitated-tank reactors) or along the reactor itself. Examples of the former were demonstrated by Ding et al. [3] and of the latter by Shaikh and Zarook [4].

Table 1
Criteria for the fast-reaction regime in gas absorption with irreversible second-order reaction

Criterion	Hatta number range
Barona [5]	$M^2 \geq (E_i - E)/(E_i - 1)$
Kramers–Westerterp [6]	$M > 2$
Coulson–Richardson [7]	$M > 2$
Charpentier [8,9]	$M > 3$
Westerterp et al. [10]	$M > 2$, or $(\alpha' - 1)\ M^2 \gg 1$
Ozturk–Shah [11]	$M > 0.2$
Trambouze et al. [12]	$M > 5$
Zarzycki–Chacuk [13]	$M \gg 1$

The case of irreversible, second-order, reactions involving a nonvolatile liquid reactant has received most attention in the literature, as different criteria have been reported for this case to specify conditions under which concentration of the dissolved gas in the bulk-liquid could be negligible. A sample of those criteria is given in Table 1. Note that Barona's criterion [5] contains the enhancement factor, E, and therefore, it is somewhat less useful, as one needs to know the regime before selecting the applicable enhancement-factor expression. The criteria of Kramers–Westerterp [6], Coulson–Richardson [7] and Charpentier [8,9] are consistent with the fact that fast reactions are generally associated with relatively high Hatta numbers. The criterion of Westerterp et al. [10] appears to be rooted in a quantitative analysis of the pseudo-first-order reaction case. Note, however, that the

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* Corresponding author. Tel.: +966-3-860-2205; fax: +966-3-860-4234; e-mail: aashaikh@dpc.kfupm.edu.sa

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criteria of Ozturk–Shah [11] and Trambouze et al. [12] are incompatible.

To be sure, recognition of the contribution of the bulk reaction goes back to the classic treatise of Sherwood and Pigford [14], where it was shown that, for pseudo-first-order reactions, the bulk reaction could be significant at relatively high Hatta number values (i.e., $M > 0.2$). More recently, Haynes [15] and Hallaile and Merchuk [16] analyzed the pseudo-first-order kinetics case and showed that reactor operating variables could also affect the magnitude of the dissolved gas concentration in the bulk-liquid. It appears that the only quantitative analysis of the more common bimolecular reaction case is that of Haynes [15]. However, Haynes' analysis does not directly address the importance of the bulk-liquid reaction, but deals with whether the well-known van Krevelen–Hoftijzer [17] approximate enhancement factor is applicable in the slow-reaction regime. It is worth noting here that Haynes has apparently overlooked the work of Teramoto et al. [18] in which the van Krevelen–Hoftijzer analysis was extended to cover the slow-reaction regime.

In the present communication, we shall consider the problem of gas absorption with a general (m,n)-th-order reaction involving a volatile liquid reactant without a priori restrictions on the reaction regime. We aim to analyze in detail, contribution of the bulk reaction, and to investigate applicability of the criteria reported in the literature (i.e., those summarized in Table 1). Although our analysis will be based on the admittedly somewhat simplistic film model, it is now commonly accepted that this model provides a satisfactory vehicle for analysis, because of its reasonably accurate predictions of the effect of reaction on gas absorption (at least in the case of single reactions) in addition to its relative mathematical tractability.

2. Model equations and analysis

Consider an irreversible (m,n)-th-order reaction between dissolved gaseous species A (m-th-order) and volatile liquid species B (n-th-order) that proceeds according to the following stoichiometry: $A_{(G\rightarrow L)} + \nu\, B_{(L)} \rightarrow \mathrm{Products}_{(L)}$. The dimensionless film-model equations are:

$$\frac{d^2A}{dX^2} - M^2A^mB^n = 0 \tag{1}$$

$$\frac{d^2B}{dX^2} - SM^2A^mB^n = 0 \tag{2}$$

subject to the following boundary conditions:

$$X=0:\ A=1, \tag{3a}$$

$$\frac{dB}{dX} = \mathrm{Bi_m}(B - B_G) \tag{3b}$$

$$X=1:\ B=1, \tag{4a}$$

$$\frac{dA}{dX} = M^2(\alpha' - 1)A^mB^n + \beta'(A - A_0). \tag{4b}$$

Note that the preceding model equations reduce to those of Shaikh and Varma [19] when $m=n=1$, however, in contrast to the case considered in Ref. [19], the boundary condition given by Eq. (4b) now accounts for the possible presence of species A in the liquid feed stream. Once $A_0 = 0$, Eq. (4b) reduces to the case considered by those authors. Note also that the classic van Krevelen–Hoftijzer film model [17] is a subcase of Eqs. (1)–(4); it will be obtained likewise when $m=n=1$, and when $\mathrm{Bi_m}=0$ and $A(1)=0$. Similarly, the model equations reduce to those of Westerterp et al. [10] when $m=1, n=0, \mathrm{Bi_m}=0$, and $\beta'=0$. It should be noted that α' in Eq. (4b) is identical to the 'Hinterland ratio' in Ref. [10].

3. Results and discussion

Clearly, concentration of the dissolved gas in the bulk-liquid, $A(1)$, is dependent on the Hatta number M, reaction orders, and the set of parameters $\{A_0, \mathrm{Bi_m}, S, \alpha', \beta'\}$. As the concentration ratio S is typically small in gas–liquid systems, we shall concentrate our attention on the effect of the other four parameters on the concentration of species A in the bulk-liquid. Eqs. (1)–(4) therefore have been solved numerically using the orthogonal-collocation code COLNEW to investigate the behavior of $A(1)$ as these parameters vary.

3.1. Parameter sensitivity analysis

The parameter α' defines the ratio of total liquid volume to film volume; by definition, then $\alpha' > 1$. The magnitude of α' depends on the gas–liquid reactor in question (and indirectly on operating conditions). For example, using the typical parameter ranges reported by Charpentier [20] for agitated-tank reactors, and a typical diffusion coefficient value of 10^{-5} cm^2/s, we find $\alpha' \in [3,3800]$. Likewise, for bubble column reactors (in which the liquid phase is frequently modelled as being perfectly mixed), we find $\alpha' \in [100,7840]$.

Fig. 1a demonstrates that, for small α', $A(1)$ can be appreciable up to $M=3$. While in Fig. 1b, in which the reaction is not linear in the gaseous species, it is shown that $A(1)$ can be appreciable even up to $M=10$. This clearly does not agree with the criteria given in Table 1 save for that of Zarzycki and Chacuk [13]. By contrast, note that in Fig. 1a and for large α', $A(1)$ can be negligible for $M<1$. In this case, the Ozturk–Shah criterion is valid; whereas, all the others in Table 1 are too conservative. However, when the reaction is second-order in the gaseous species, this is not the case and $A(1)$ can be appreciable for Hatta number values beyond $M=1$.

The next parameter β' is related to the liquid residence time and mass-transfer characteristics of the gas–liquid reactor. Thus, it can have values $\gg 1$ or $\ll 1$, depending on reactor type and operating conditions. Fig. 2a and b show quite remarkable effects of β' on $A(1)$. It is clear in Fig. 2a

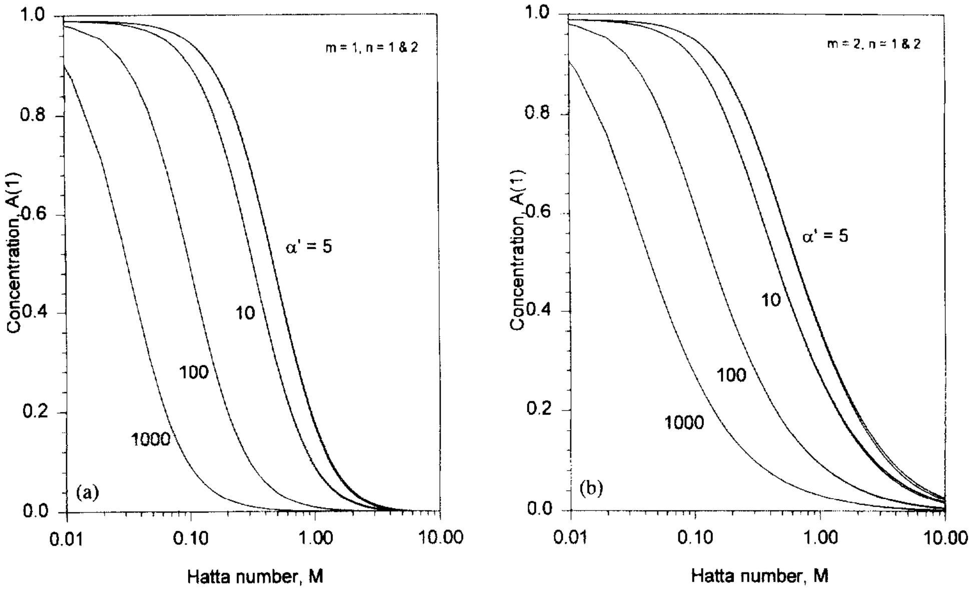

Fig. 1. Effect of ratio of total liquid volume to film volume on the dissolved gaseous reactant concentration in the bulk-liquid ($A_0=0$, $B_G=0$, $\mathrm{Bi}_m=1.5$, $S=0.1$, $\beta'=0.01$).

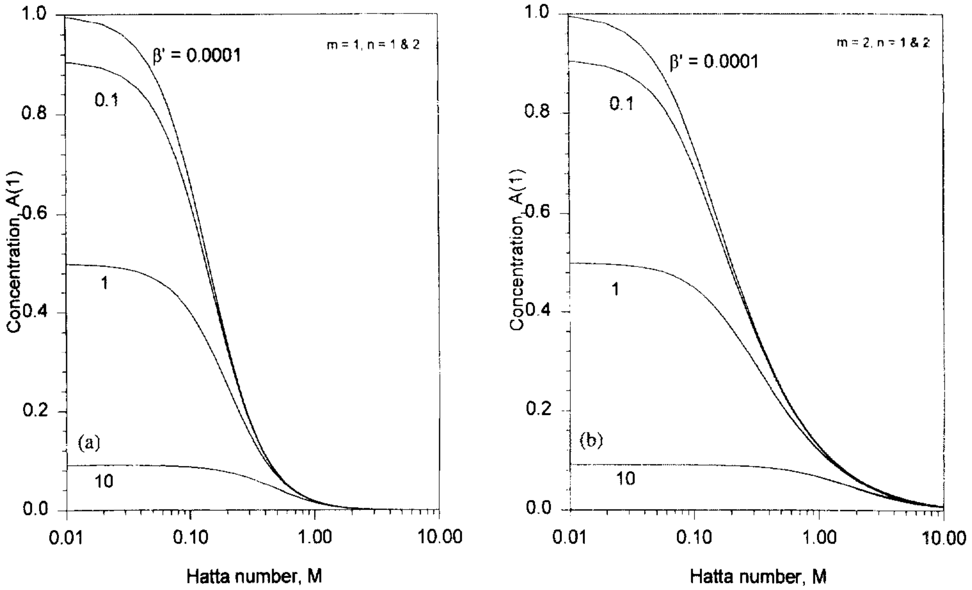

Fig. 2. Effect of β' on the dissolved gaseous reactant concentration in the bulk-liquid ($A_0=0$, $B_G=0$, $\mathrm{Bi}_m=1.5$, $S=0.1$, $\alpha'=50$).

that $A(1)$ can be appreciable when $M>0.2$. More interestingly, however, we note that at high values of β', $A(1)$ can be very low even at low values of M. One can observe that $A(1)\rightarrow 0$ as β' increases, and this happens even at *very low* values of Hatta number. For instance, when $M=0.01$ and $\beta'=10$, Fig. 2a shows that $A(1)=0.09$. This means that while the system is in the slow-reaction regime (i.e., the regime commonly characterized in the literature by $M\ll 1$), concentration of the dissolved gaseous reactant in the bulk-liquid does not necessarily become high. In that region, then, this concentration can be *appreciable or negligible* depending on the value of the parameter β'. The latter normally results from relatively large values of β'; in a given reactor, such values of β' are practically associated with relatively low liquid residence times. Therefore, we may conclude that $M<2$ or $M<3$ (cf. Table 1) are necessary, but not sufficient, conditions for the concentration of the dissolved gaseous reactant to be appreciable. We should mention that the effect of β' has been studied by Hallaile and Merchuk [16] in the limiting case of pseudo-first-order reactions. However, because of the range of values used, it was not possible to show that $A(1)$ can be negligible at large values of β', although this conclusion can be deduced from their theoretical analysis.

The parameter Bi_m reflects volatility of the liquid reactant; when $\mathrm{Bi}_m=0$, the problem reduces to the case where the liquid reactant is nonvolatile. As Bi_m appears in the boundary condition given by Eq. (3b), one might expect that Bi_m will not have a significant effect on concentration of the dissolved gaseous reactant in the bulk-liquid except in the fairly uncom-

Table 2
Effect of Biot number on concentration of dissolved gaseous reactant in the bulk-liquid ($A_0=0$, $B_G=0$, $m=1$, $n=1$, $S=0.001$, $\alpha'=50$, $\beta'=0.01$)

$\mathrm{Bi_m}\rightarrow$ $M\downarrow$	3.75 $A(1)$	0.75 $A(1)$	0.15 $A(1)$	0.0 $A(1)$
0.01	0.9853	0.9853	0.9853	0.9853
0.1	0.6648	0.6645	0.6642	0.6641
0.5	0.0732	0.0726	0.0721	0.0719
1.0	0.0180	0.0175	0.0171	0.0169
1.5	0.0072	0.0068	0.0064	0.0063
2.0	0.0034	0.0031	0.0029	0.0028

mon case of high S. A summary of the model solutions in this case is given in Table 2. We observe here that $A(1)$ is indeed rather insensitive to the magnitude of $\mathrm{Bi_m}$ except at relatively high Hatta number values. However, in this limit $A(1)\rightarrow 0$, and thus, it may be concluded that this parameter does not significantly affect contribution of the bulk reaction. This result is supported by the work of Shaikh and Varma [19] in which it was shown that the influence of liquid reactant volatility is essentially restricted to the fast-reaction regime.

Normally, the liquid feed stream does not contain appreciable dissolved gaseous reactant, but there might be cases in which a small amount of A is present or when a cascade of reactors is used. Fig. 3a and b show that the effect of A_0 is restricted to Hatta numbers <1. These figures also show that higher A_0 values lead to higher $A(1)$ values as expected. Note though that in general, the effect of A_0 in the slow-reaction regime is not as pronounced as those of α' and β'. Note also that, if the reaction is fast enough, no dissolved gas will appear in the liquid effluent stream—at least for the parameter ranges considered.

The computations presented in Figs. 1–3 also demonstrate the effect of reaction orders m and n. We observe that over the Hatta number range considered, the concentration of A in the bulk-liquid is more sensitive to the reaction order in A and less sensitive to the reaction order in B. It is also possible to observe in these figures that as m increases, $A(1)$ becomes appreciable even up to $M=10$. By contrast, the effect of the reaction order in B is rather insignificant; this is mainly due to the value of the parameter S used in the computations.

3.2. Effect of liquid mixing

The question of whether the mixing state of the liquid phase in gas–liquid reactors can influence the reaction regime is worthwhile. While the assumption of a perfectly-mixed liquid in, say, agitated-tank reactors is plausible, its extension to other reactors is not always valid. Indeed, in other contactors employed for slow or moderately-fast reactions, such as bubble column reactors, the liquid typically is partially mixed [21].

In the case of a partially-mixed liquid, Eqs. (1)–(4a) are still applicable, however, boundary condition (4b) needs to be modified. For heuristic purposes, we shall next consider a pseudo-first-order reaction taking place in a counter-current bubble column reactor of length $y=H$ under steady-state conditions, where the liquid phase leaves the column at $y=0$. The axial-dispersion model can be used to describe the mixing state of the liquid phase. Therefore, the boundary condition for the film model at the edge of the film can be expressed in dimensionless form as: $X=1$, $A=A_b$. Accordingly, the change of the concentration in the bulk-liquid phase along the axis of the reactor is described by the following dimensionless differential equation and the well-known Danckwerts' boundary conditions:

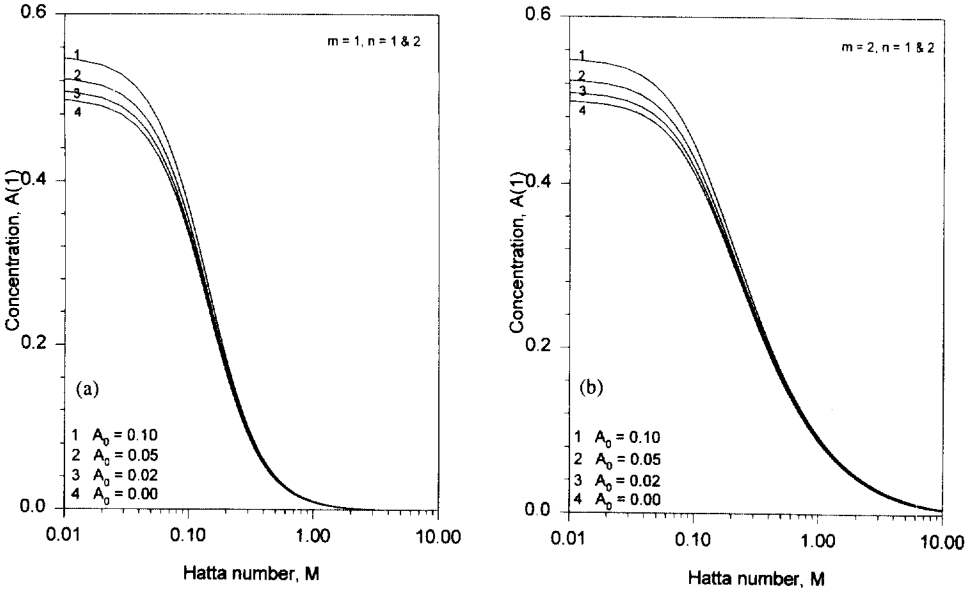

Fig. 3. Effect of the presence of dissolved gaseous reactant in liquid feed ($B_G=0$, $\mathrm{Bi_m}=1.5$, $S=0.1$, $\alpha'=100$, $\beta'=1$).

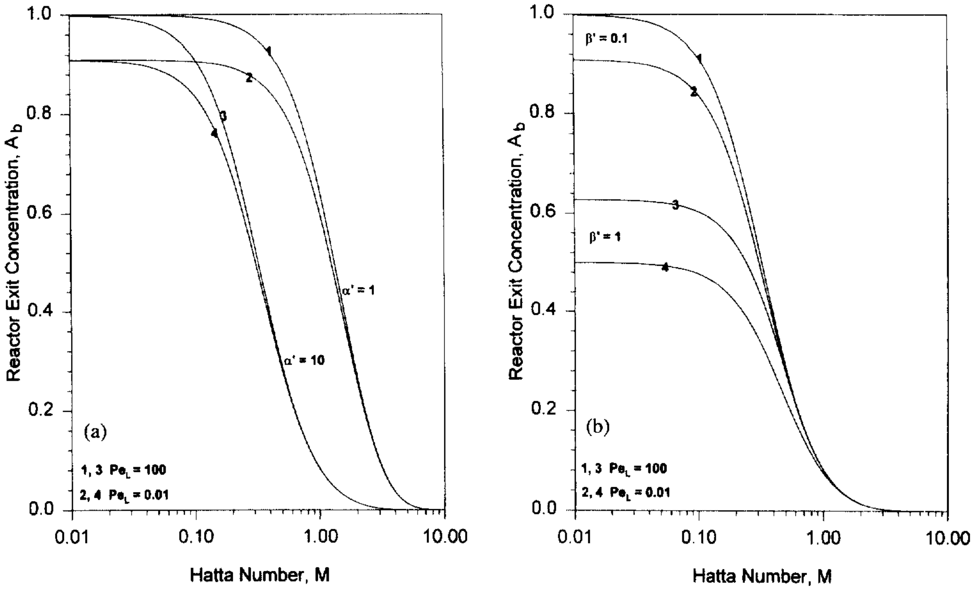

Fig. 4. Effect of the mixing state of the liquid phase on the dissolved gaseous reactant concentration in the liquid effluent (pseudo-first-order kinetics).

$$\frac{1}{\mathrm{Pe_L}}\frac{\mathrm{d}^2A_b}{\mathrm{d}Y^2}+\frac{\mathrm{d}A_b}{\mathrm{d}Y}=\frac{1}{\beta'}\left[\left(\frac{\mathrm{d}A_b}{\mathrm{d}X}\right)_{X=1}+M^2(\alpha'-1)A_b\right] \tag{5}$$

$$Y=0:\ \frac{\mathrm{d}A_b}{\mathrm{d}Y}=0 \tag{6a}$$

$$Y=1:\ -\frac{1}{\mathrm{Pe_L}}\frac{\mathrm{d}A_b}{\mathrm{d}Y}=(A_b-A_0). \tag{6b}$$

The solution of the film model can be combined with Eqs. (5) and (6) to yield a closed-form, albeit rather involved, solution that gives variation of the concentration along the reactor axis. We have used this solution to produce the results shown in Fig. 4a and b in terms of $A_b(0)=f(M;\ \mathrm{Pe_L},\alpha')$ and $A_b(0)=f(M;\ \mathrm{Pe_L},\beta')$, respectively. Note that the mixing extremes are represented by large and small $\mathrm{Pe_L}$ values. Thus, the lower value of $\mathrm{Pe_L}$ corresponds to the case analyzed by Westerterp et al. [10]; i.e., well-mixed bulk-liquid. Fig. 4a and b demonstrate not unexpectedly that the mixing state of the liquid could also significantly affect concentration of the dissolved gas in the bulk-liquid. On the basis of these results, it is possible to envisage a gas–liquid reaction system that may be characterized by the slow-reaction regime in one reactor, and by the fast-reaction regime in another type of reactor even under virtually the same operating conditions.

4. Concluding remarks

In this work, we have presented numerical solutions of a general film model describing the effect of an (m,n)-th-order reaction on gas absorption. The solutions have been used to analyze importance of the bulk-liquid reaction through assessing dependence of the dissolved gas concentration in that region on the physicochemical parameters of the problem. We have attempted to demonstrate that this concentration should not be determined a priori solely in terms of the Hatta number. It has been shown that concentration of the dissolved gas could be appreciable at relatively high values of Hatta number, and could also be negligible at relatively low values of Hatta number. We have also shown that reactor type, operating conditions, and macromixing state of the liquid phase could all play a role in determining the magnitude of the dissolved gas concentration in the bulk-liquid. It has been demonstrated that, contrary to some reports in the literature, cases characterized by Hatta numbers <3 do not necessarily imply appreciable concentrations of the dissolved gas in the bulk-liquid. Hence, it is advisable to account for contribution of the bulk reaction in modelling the performance of gas–liquid reactors and kinetics of gas–liquid reactions.

In closing, it is worth mentioning that when sizing, optimizing, or analyzing the performance of gas–liquid reactors, the Hatta number, on the whole, is an unknown parameter. Therefore, the advantage of using generalized enhancement-factor expressions, such as those of [18] and [22] in the development of reactor models is evident.

5. Nomenclature

A	dimensionless concentration of gaseous reactant, C_A/C_{Ai}
a	interfacial area per unit reactor volume
B	dimensionless concentration of liquid reactant, C_B/C_{BL}
B_G	dimensionless concentration, C_{BG}/C_{Bi}
$\mathrm{Bi_m}$	Biot number for mass transfer, $(D_A k_{GB} K_B / D_B k_L)$
C_A	concentration of gaseous reactant in liquid phase
C_B	concentration of liquid reactant in liquid phase
C_{BG}	concentration of liquid reactant corresponding to its bulk-gas partial pressure
D_j	diffusion coefficient for species j, $j=$ A or B

D_L	dispersion coefficient of the liquid phase
E	enhancement factor
E_i	enhancement factor for instantaneous reaction, $(1+1/S)$
F_L	volumetric flow rate of liquid phase
H	reactor height
k	reaction rate constant
k_{GB}	gas-side mass transfer coefficient for species B
k_L	liquid-side mass transfer coefficient
K_B	equilibrium constant for species B
M	Hatta number, $(kD_A C_{BL})^{1/2}/k_L$
m	reaction order with respect to gaseous reactant
n	reaction order with respect to liquid reactant
Pe_L	Peclet number for liquid phase, $u_L H/D_L$
S	dimensionless parameter, $\nu D_A C_{Ai}/D_B C_{BL}$
u_L	superficial velocity of liquid phase
V_L	total volume of liquid phase
X	dimensionless distance, x/δ
x	distance inside liquid film
Y	dimensionless distance along reactor, y/H
y	distance along reactor

Greek letters

α'	ratio of total liquid volume to film volume, $\varepsilon_L/a\delta$
β'	dimensionless parameter, $1/\tau_L a k_L$
δ	thickness of liquid-side film
ε_L	liquid hold-up
ν	stoichiometric coefficient
τ_L	liquid residence time

Subscripts

b	bulk-liquid
G	gas phase
i	gas–liquid interface
L	liquid phase
0	liquid feed

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