# A supporting formulation for introducing gas–liquid reactions

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## C.D. Luzi [a,b,*], S.P. Bressa [a,b], G.D. Mazza [c,d], G.F. Barreto [a,b]

[a] *Programa de Investigación y Desarrollo en Ingeniería de Reactores (PROIRQ), Departamento de Ingeniería Química, Facultad de Ingeniería, Universidad Nacional de La Plata, Argentina*
[b] *Centro de Investigación y Desarrollo en Ciencias Aplicadas "Dr. J.J. Ronco" (CINDECA), CCT La Plata, Consejo Nacional de Investigaciones Científicas y Técnicas, Universidad Nacional de La Plata, Calle 47 N° 257, B1900AJK La Plata, Argentina*
[c] *Instituto Multidisciplinario de Investigación y Desarrollo de la Patagonia Norte (IDEPA), Consejo Nacional de Investigaciones Científicas y Técnicas, Universidad Nacional del Comahue, Argentina*
[d] *Departamento de Ingeniería Química, Facultad de Ingeniería, Universidad Nacional del Comahue, Buenos Aires 1400, Neuquén 8300, Argentina*

## A B S T R A C T

In spite of the widespread industrial application of non-catalytic or homogeneously catalyzed gas–liquid reactions (GLRs), many undergraduate chemical engineering curricula do not include this subject and heterogeneous catalysis provides the only example of a heterogeneous chemical reaction system.

Textbooks dealing with GLRs describe and formulate separately the different processes affecting the rate of chemical absorption, without providing a clear picture of the overall problem, which is highly desirable for the identification of effects and understanding of their interplay.

As an attempt to provide a different alternative for teaching GLRs, a general approximate formulation for the transport/reaction problem, in terms of a global enhancement factor (GEF) for a single chemically absorbed species, including all possible effects on the basis of the two-film model is presented here.

This contribution includes the development of the approximation for the GEF, an analysis of different regimes, which in part can be directly adopted for teaching, and an evaluation of the precision of the GEF estimation, mainly devoted to the lecturer.

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## 1. Introduction

Gas–liquid reactions (GLRs), either non-catalytic or homogeneously catalyzed, are employed in many important industrial processes, as it has been summarized in specialized books (*e.g.* Astarita et al., 1983; Danckwerts, 1970; Doraiswamy and Sharma, 1984; Kaštánek et al., 1993) and chemical reaction engineering textbooks (*e.g.* Froment et al., 2011; Westerterp et al., 1984). Frequent uses of GLRs concern the purification of a gas stream by absorption of undesirable species enhanced by chemical reaction, but many applications include the synthesis of more valuable products or the purification of liquid streams.

In spite of the practical significance of GLRs and of their specific features, many undergraduate chemical engineering curricula do not include this subject and heterogeneous

catalysis provides the only example of a heterogeneous chemical reaction system. Actually, GLRs is not a short subject to deal with, as it involves a reference to different models for describing the transport/reaction process at a local level (i.e. film, penetration or surface-renewal models), the formulation and solution of the problem with one of these models and its application for design, analysis and selection of several possible types of gas–liquid contactors.

In comparison to heterogeneously catalyzed reactions, GLRs introduces two distinct features, as regards the local transport/reaction problem. On one hand, there are two reaction domains for a reactant A transferred from the gas. Fast reactions start, and frequently end, taking place close to the gas–liquid interface, where diffusion still govern mass transfer, and slower reactions proceed mainly in the liquid bulk. On the other hand, when reaction occurs close to the interface, the liquid reactant (says B) has to diffuse towards the interface, i.e. in direction opposite to that of A. As the reader acquainted with the subject should know, these features introduce distinct operation regimes, and formulation for the overall rate of chemical absorption becomes more complex than the counterpart in heterogeneous catalysis.

Available textbooks dealing with GLRs describe and formulate separately the different processes affecting the rate of chemical absorption. Perhaps the most important point to remark is the almost independent treatment of *slow* and *fast* reaction regimes. Different stages are also used for linear and non-linear kinetics and for cases limited or not by mass transfer resistance in the gas phase. Although this approach presents the merit of a gradual introduction of topics, it is our impression that a rather lengthy description arises without providing an overall picture of the problem, which is highly desirable for the identification of effects and understanding of their interplay.

An opposite alternative for the description of the transport/reaction process in GLRs is to present a unified treatment including simultaneously all significant effects. Then, the description of any conceptual or practical issue can be backed up by the available general formulation. It can be argued that developing a general formulation may not be appealing from a didactic point of view, particularly for a subject that, as discussed before, presents a significant degree of complexity. However, if heterogeneous catalysis is lectured before, the situation is different, as the basic notion of coupling between mass transport and chemical reaction would be already introduced, along with conservation equations and some approximations used for their solution. In our teaching experience, the background from heterogeneous catalyzed reactions greatly facilitates the presentation of a general solution for GLRs.

It is the objective of this contribution to develop a general approximate formulation for the transport/reaction problem in GLRs and show how it could be employed to present the different possible regimes and their significance. To be specific in outlining the scope of the formulation, we point out that the film model is employed for both sides of the gas–liquid interface (two-film model) under the assumptions of a single isothermal irreversible reaction of the type $A_{(G)} + bB_{(L)} \rightarrow$ products, with irreversible kinetics $r = kC_A^m C_B^n$ ($m$, $n \geq 0$), reactant B being non-volatile and constant transport and phase equilibrium properties. A general picture of the situation to be evaluated on the basis of the two-film model is given in Fig. 1, where local values of partial pressure of A in the gas stream ($p_{AG}$) and liquid bulk concentrations ($C_{BL}$ and
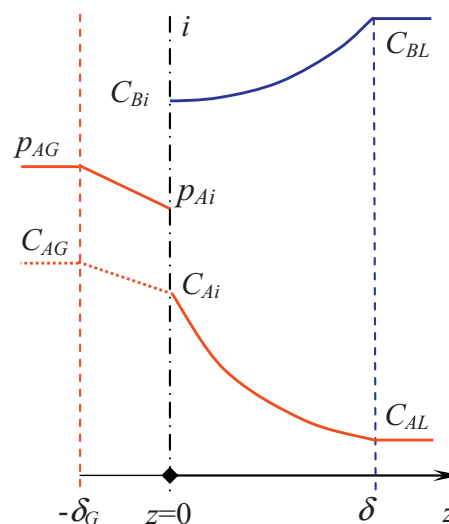


**Fig. 1 – Generic profiles of the gas and liquid reactants, A and B respectively, through the gas and liquid films.**

$C_{AL}$) are assumed to be known. Evaluating the flux of A at the interface, $\mathcal{N}_{Ai}$, is the main target. The processes defining the flux $\mathcal{N}_{Ai}$ are: mass transfer of A in both films, mass transfer of B in the liquid film, chemical reaction in the liquid film under variable concentrations $C_B$ and $C_A$, and chemical reaction in the liquid bulk under uniform concentrations $C_{BL}$ and $C_{AL}$. The simultaneous effect of these processes will be analyzed along with the kinetic features represented by reaction orders $m$, $n$.

The manuscript is organized as follows. Section 2 summarizes some basic definitions, mainly concerned with physical absorption of A. An approximated solution for the problem of absorption with chemical reaction is presented in Section 3. A significant concept, neglecting the accumulation rate of A in the liquid stream, is introduced in Section 3.1. The different regimes of operation are described in Sections 4–7. While a large part of the material presented in Sections 2–7 can be directly employed for teaching, Sections 8–10 are more specialized and mainly directed to teachers: Section 8 accounts for the magnitude and relevance of errors from the approximated formulation, Section 9 presents a criterion for acceptance of the hypothesis of negligible rate of accumulation of A in the liquid stream for the analysis of gas–liquid contactors and Section 10 extends the analysis of Section 3 to a more generalized kind of irreversible kinetics. Finally, Section 11 mainly intends to summarize the relevant aspects of the present formulation in teaching GLRs.

## 2. Physical transport on both sides of the interface

It will be assumed for the analysis at a given position of a gas–liquid contactor that transport properties, including mass transfer coefficients, and the solubility in the liquid of reactant A are not composition dependent. This is in practice the case for a diluted system concerning species A and B. Also, local thermal equilibrium is assumed. At these conditions, the quoted transport and thermodynamic properties can be estimated beforehand.

Either for physical or chemical absorption, $\mathcal{N}_{Ai}$ can be expressed as the flux through the gas film,

$$\mathcal{N}_{Ai} = k_{GA}^0 \; (p_{AG} - p_{Ai}), \tag{1}$$

where $k_{GA}^0$ is the mass transfer coefficient for $A$ at low mass transfer rates, $p_{AG}$ and $p_{Ai}$ are the partial pressures of $A$ in the local gas bulk and at the interface, respectively. In practice, the volumetric absorption rate of $A$, $a\mathcal{N}_{Ai}$, is frequently the magnitude of importance, being $a$ the interfacial area per unit volume of gas–liquid contactor.

The thermodynamic equilibrium condition at the interface (suffix $i$) in terms of Henry's law is written:

$$p_{Ai} = H_A C_{Ai}. \tag{2}$$

Defining $C_{AG}$ as the molar concentration of $A$ in the liquid that would be at equilibrium with $p_{AG}$, we can write from Henry's law

$$p_{AG} = H_A C_{AG} \tag{3}$$

Using Eqs. (2) and (3) in Eq. (1) leads to

$$\mathcal{N}_{Ai} = k_{GA}^0 H_A (C_{AG} - C_{Ai}) \tag{4}$$

If any local value $p_A$ in the gas film is divided by $H_A$, an equilibrium profile of molar concentration in the liquid phase can be drawn, allowing a continuous description of $C_A$ all along both films (Fig. 1).

Fick's law is used for the flux of $A$ in the liquid film,

$$\mathcal{N}_A = -D_{AL} \frac{dC_A}{dz} \tag{5}$$

When there is no reaction in the liquid film, *i.e.* physical transfer of $A$ in the liquid film, $\mathcal{N}_A = \mathcal{N}_{Ai}$ and Eq. (5) can be integrated in $0 \le z \le \delta$ to express

$$\mathcal{N}_{Ai} = k_A (C_{Ai} - C_{AL}), \tag{6}$$

where the liquid mass transfer coefficient $k_A$ is defined by

$$k_A = \frac{D_{AL}}{\delta}. \tag{7}$$

Using Eqs. (4) and (6) to eliminate $C_{Ai}$:

$$\mathcal{N}_{Ai} = k_A^T (C_{AG} - C_{AL}), \tag{8}$$

where the overall mass transfer coefficient of $A$ is defined by

$$k_A^T = \left( \frac{1}{k_{GA}^0 H_A} + \frac{1}{k_A} \right)^{-1}. \tag{9}$$

It should be borne in mind that Eq. (8) is only valid for the case of physical transfer of $A$ in the liquid film. The corresponding concentration profile is depicted in Fig. 2.

The Biot number is defined by

$$Bi = \frac{k_{GA}^0 H_A}{k_A}. \tag{10}$$

The physical meaning of $Bi$ is recalled in expression (T1.1) given in Table 1. Values of $Bi$ strongly vary with the affinity of $A$ for the liquid solution. Frequently, $Bi \gg 1$ (*i.e.* large values of $H_A$), but for gases such as $SH_2$, $Cl_2$ or $NH_3$ in water $Bi$ values can be of the order of unity or smaller. The $Bi$ number will be used to remove the explicit appearance of $k_{GA}^0 H_A$ in the
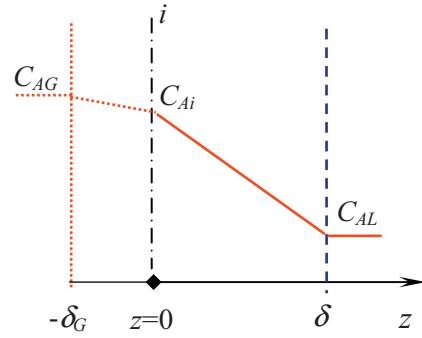


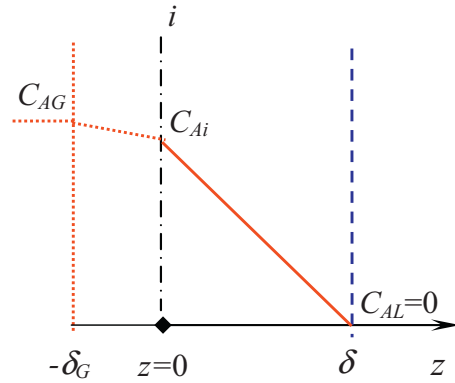**Fig. 2 – Concentration profile for physical absorption of A.**



**Fig. 3 – Concentration profile for physical absorption of A when $C_{AL} = 0$ (maximum physical flux).**

formulation to be presented below. Thus, the global coefficient $k_A^T$, Eq. (9), becomes expressed as

$$k_A^T = \frac{Bi}{1+Bi} k_A \tag{11}$$

The maximum physical flux, denoted $\mathcal{N}_{Ai}^0$, takes place when $C_{AL} = 0$ (see Fig. 3) and can be written in two useful ways:

$$\mathcal{N}_{Ai}^0 = k_A^T C_{AG}, \tag{12}$$

and

$$\mathcal{N}_{Ai}^0 = k_A C_{Ai}^0 \tag{13}$$

**Table 1 – Physical meaning of non-dimensional parameters.**

| | |
|---|---|
| $Bi = \dfrac{k_{GA}^0 H_A}{k_A} \; : \; \dfrac{\text{specific transfer rate of A in the gas film}}{\text{specific transfer rate of A in the liquid film}}$ | (T1.1) |
| $\Omega = \dfrac{D_{BL} C_{BL}}{b D_{AL} C_{AG}} \; : \; \dfrac{1}{b} \left( \dfrac{\text{characteristic diffusion rate of B in the liquid film}}{\text{characteristic diffusion rate of A in the liquid film}} \right)$ | (T1.2) |
| $\gamma^2 = \dfrac{a\delta[k C_{Ai}^{0m} C_{BL}^n]}{a k_A C_{Ai}^0} \; : \; \dfrac{\text{characteristic reaction rate in the liquid film}}{\text{characteristic transfer rate of A in the liquid film}}$ | (T1.3) |
| $\dfrac{\gamma^2}{\Omega} \; : \; b \left( \dfrac{\text{characteristic reaction rate in the liquid film}}{\text{characteristic transfer rate of B in the liquid film}} \right)$ | (T1.4) |
| $\kappa = \dfrac{\varepsilon}{a\delta} \; : \; \dfrac{\text{total liquid volume}}{\text{liquid-film volume}}$    (Hinterland ratio) | (T1.5) |
| $(\kappa - 1)\gamma^2 \; : \; \dfrac{\text{characteristic reaction rate in the liquid bulk}}{\text{characteristic transfer rate of A in the liquid film}}$ | (T1.6) |
| $\kappa \gamma^2 \; : \; \dfrac{\text{characteristic reaction rate in the liquid phase}}{\text{characteristic transfer rate of A in the liquid film}}$ | (T1.7) |

where $C_{Ai}^0$ is the interfacial concentration of $A$ when the physical flux is maximum (see Fig. 3), and is readily obtained from Eqs. (11) to (13):

$$C_{Ai}^0 = \frac{Bi}{1+Bi} C_{AG} \tag{14}$$

The flux $\mathcal{N}_{Ai}^0$ and concentration $C_{Ai}^0$ will be useful magnitudes of reference to deal with the problem including chemical reaction. Note that both can be directly evaluated once $C_{AG}$ and the mass transfer coefficients are defined.

## 3. Mass transfer with chemical reaction in the liquid phase

The flux $\mathcal{N}_{Ai}$ when $A$ undergoes a chemical reaction in the liquid phase will be expressed in dimensionless terms as

$$\phi^T = \frac{\mathcal{N}_{Ai}}{\mathcal{N}_{Ai}^0}, \tag{15}$$

where $\phi^T$ is named *Global Enhancement Factor* (GEF).

There are some other ways to express the effect of a chemical reaction on the absorption rate of $A$, as discussed, *e.g.* in the textbook of Froment et al. (2011). We will restrict our analysis to the GEF defined in Eq. (15).

As regards the profiles in Fig. 1, we note that the interfacial concentration $C_{Ai}$ will have to be evaluated simultaneously with $\phi^T$. However, a simple relationship between them is obtained by using Eq. (4) for $\mathcal{N}_{Ai}$ and alternatively Eq. (12) or (13) for $\mathcal{N}_{Ai}^0$,

$$C_{Ai} = \left( \frac{1+Bi-\phi^T}{1+Bi} \right) C_{AG} \tag{16}$$

$$C_{Ai} = \left( \frac{1+Bi-\phi^T}{Bi} \right) C_{Ai}^0 \tag{17}$$

In most textbooks and literature papers, the analysis to evaluate the flux $\mathcal{N}_{Ai}$ starts by assuming that $C_{Ai}$ is known and therefore it is used as the reference concentration for $A$. In a second stage, the mass transfer resistance is taken into account and continuity of fluxes at the interface allows the final evaluation of $C_{Ai}$. The formulation proposed here introduces $C_{Ai}$ as an unknown quantity from the outset, a feature consistent with the definition of $\phi^T$ based upon the global reference flux $\mathcal{N}_{Ai}^0$.

### 3.1. Solution of mass conservation equations in the liquid film

The flux of $B$ in the liquid film is also expressed by means of Fick's law, $\mathcal{N}_B = -D_{BL} dC_B/dz$. The steady state mass conservation equations corresponding to a generic compound "$j$" is

$$\frac{d\mathcal{N}_j}{dz} = \alpha_j r, \tag{18}$$

where $\alpha_j$ is the stoichiometric coefficient of "$j$". Now, introducing the Fick's expressions in Eq. (18) for species $A$ and $B$ yields

$$D_{AL} \frac{d^2 C_A}{dz^2} = r, \tag{19}$$

$$D_{BL} \frac{d^2 C_B}{dz^2} = br \tag{20}$$

The boundary conditions associated with Eqs. (19) and (20) are

at $z = 0 : \mathcal{N}_{Ai} = -D_{AL} dC_A/dz,\, dC_B/dz = 0$   ($B$ is non-volatile)

$$\tag{21a}$$

at  $z = \delta : C_A = C_{AL}, C_B = C_{BL}.$ $\tag{21b}$

The first step in dealing with Eqs. (19)–(21) is finding a relationship between $C_A$ and $C_B$ at a generic point $z$. This can be achieved by eliminating $r$ between Eqs. (19) and (20) and the result integrated twice on $z$, with the help of Eqs. (21). Using $k_A = D_{AL}/\delta$, as defined in Eq. (7) and introducing the dimensionless coordinate $z^* = z/\delta = z k_A/D_{AL}$, it is obtained:

$$C_B - C_{BL} = \frac{b D_{AL}}{D_{BL}} \left[ C_A - C_{AL} - \frac{\mathcal{N}_{Ai}}{k_A}(1 - z^*) \right] \tag{22}$$

Eq. (22) formally allows working with a single conservation equation, for which Eq. (19) is chosen. Note that we are introducing the still unknown flux $\mathcal{N}_{Ai}$ in Eq. (22). This is not the major inconvenience in seeking a solution, but the essential limitation is the nonlinearity of the reaction rate expression $r = kC_A{}^m C_B{}^n$. Actually, finding an analytical solution is only possible if $r$ is linear on $C_A$, a case limited to $m=1$ and when $B$ is far more concentrated than $A$. In the general case, a simplification introduced first by van Krevelen and Hoftijzer (1948) and generalized later by Hikita and Asai (1964), should be used for obtaining an approximate solution: the factor $C_B^n$ in the rate expression is assumed uniform throughout the liquid film and evaluated at the interface, $C_{Bi}^n$. Furthermore, the factor $C_A^m$ should be also conveniently linearized. Following again Hikita and Asai (1964), this can be done by substituting $C_A^m$ by $[2/(m+1)] C_{Ai}^{m-1} C_A$. This approximation can be better justified in a later stage (see Section 5). Then, the key approximation is written as

$$r = kC_A^m C_B^n \cong k \left( \frac{2}{m+1} C_{Ai}^{m-1} C_A \right) C_{Bi}^n \tag{23}$$

Approximation of Eq. (23) leads to reasonably precise results if $A$ is the limiting reactant in the liquid film. Therefore, the use of Eq. (23) is constrained to

$$\frac{D_{BL} C_{BL}}{b D_{AL} C_{Ai}} > 1 \tag{24}$$

The restriction defined by Eq. (24) will be fulfilled in many practical applications. An exception can be the case in which the process is intended for purifying a liquid stream by reaction of an undesirable compound $B$. In this case, $C_{BL}$ will probably have to be reduced to a small tolerable value, for which Eq. (24) may not be sustained.

To proceed with the use of Eq. (23), we find an expression for $C_{Bi}$ from Eq. (22) evaluated at $z^* = 0$:

$$C_{Bi} - C_{BL} = \frac{b D_{AL}}{D_{BL}} \left( C_{Ai} - C_{AL} - \frac{\mathcal{N}_{Ai}}{k_A} \right) \tag{25}$$

Using Eq. (17) for $C_{Ai}$, the definition of $\phi^T$ (Eq. (15)) to express $\mathcal{N}_{Ai}$, Eq. (13) for $\mathcal{N}_{Ai}^0$, and taking into account the relationship between $C_{Ai}^0$ and $C_{AG}$ in Eq. (14), we obtain:

$$\frac{C_{Bi}}{C_{BL}} = C_{Bi}^* = \frac{\Omega + 1 - \phi^T - (Bi/(1+Bi)) C_{AL}^*}{\Omega}, \tag{26}$$

where the first equation defines the dimensionless concentration $C_{Bi}^*$. Besides,

$$C_{AL}^* = \frac{C_{AL}}{C_{Ai}^0}, \tag{27}$$

and

$$\Omega = \frac{D_{BL}C_{BL}}{bD_{AL}C_{AG}}. \tag{28}$$

Parameter $\Omega$ will play an important role in the formulation, as it relates the diffusion capacities of $A$ and $B$ in the liquid film (see expression (T1.2) in Table 1).

Replacing $C_{Bi}$ in Eq. (23), the resulting expression for $r$ in the conservation equation of $A$, Eq. (19), and using again $z^* = z \, k_A/D_{AL}$:

$$\frac{d^2 C_A}{(dz^*)^2} = \frac{2}{m+1} \gamma^2 C_{Bi}^{*n} C_{Ai}^{*m-1} C_A, \tag{29}$$

where (using Eq. (17)):

$$C_{Ai}^* = \frac{C_{Ai}}{C_{Ai}^0} = \frac{1 + Bi - \phi^T}{Bi}, \tag{30}$$

and

$$\gamma^2 = \frac{D_{AL} k (C_{Ai}^0)^{m-1} C_{BL}^n}{k_A^2}. \tag{31}$$

Parameter $\gamma$ is known as Hatta number and $\gamma^2$ relates characteristic rates of reaction and diffusion of $A$ in the liquid film, as expression (T1.3) in Table 1 discloses more clearly. We also note in Table 1 (expression (T1.4)) the meaning of the ratio $\gamma^2/\Omega$.

Solving Eq. (29), with boundary conditions $C_A = C_{Ai}$ at $z^* = 0$ and $C_A = C_{AL}$ at $z^* = 1$, it is obtained

$$C_A = \frac{C_{Ai} \sinh[M\gamma'(1 - z^*)] + C_{AL} \sinh(M\gamma' z^*)}{\sinh(M\gamma')}, \tag{32}$$

where:

$$M = \left(\frac{2}{m+1}\right)^{1/2}; (\gamma')^2 = \gamma^2 (C_{Bi}^*)^n (C_{Ai}^*)^{m-1} \tag{33}$$

It must be noted that Eq. (32) and formulations derived from it have been used in the textbooks of Santamaría et al. (2002) and Trambouze and Euzen (2004) for the specific case $m = n = 1$ and $Bi \to \infty$.

The derivative $dC_A/dz^*$ from Eq. (32) is easily expressed as:

$$\frac{dC_A}{dz^*} = \varXi(M\gamma') \left\{ \frac{-C_{Ai} \cosh[M\gamma'(1 - z^*)] + C_{AL} \cosh(M\gamma' z^*)}{\cosh(M\gamma')} \right\}, \tag{34}$$

where the function $\varXi(x) = x/\tanh(x)$ has been introduced.

Eq. (34) is the starting point to obtain the formulation for the fluxes at $z^* = 0$ and $z^* = 1$.

However, we should first revise the procedure made up to this point. In essence, the approximation of Hikita and Asai (1964) for the rate expression has been adopted to obtain Eq. (34), but two distinct aspects have been considered with respect to their work: introducing the definition of the GEF to account for the gas phase resistance and considering the

general case $C_{AL} \neq 0$. While the first aspect does not modify the validity of Hikita and Asai (1964) approximation, the second one does. Their approximation turns out to be highly precise (this will be revised later on) for their assumed condition $C_{AL} = 0$, a case warranted by a high enough liquid hold-up (e.g. bubble columns or stirred tanks). Nonetheless, certain types of gas–liquid contactors, as wetted-wall reactors, spray columns and even packed towers, present liquid hold-ups much smaller than bubble columns or stirred tanks. Because of this fact and also because of didactic reasons, our concern here is to deal with the general case $C_{AL} \neq 0$. Within this frame, Eq. (34) presents some undesirable features, as a consequence of the reaction rate linearization, Eq. (23). Therefore, a pair of modifications will be now introduced. Consider substitution of $\gamma'$ from Eq. (33) into Eq. (34). Then,

(a) the factor $[M C_{Bi}^{*n/2}]$ is removed from the arguments of the three hyperbolic cosines in Eq. (34),
(b) the factor $C_{Bi}^{*n/2}$ is removed from the argument of the hyperbolic tangent of function $\varXi$ in Eq. (34).

Modification (a) allows obtaining the correct limiting values of $\mathcal{N}_{Ai}$ at very low and very high values of $\gamma$, in the case of low liquid hold-ups. This feature will be discussed more specifically in Sections 5.1 and 8.2. Modification (b) is introduced to improve the overall level of precision for predicting $\mathcal{N}_{Ai}$, as discussed in Section 8.2. Then, Eq. (34) becomes

$$\frac{dC_A}{dz^*} = \varXi(M\gamma_i) C_{Bi}^{*n/2} \left\{ \frac{-C_{Ai} \cosh[\gamma_i(1 - z^*)] + C_{AL} \cosh(\gamma_i z^*)}{\cosh(\gamma_i)} \right\}, \tag{35}$$

where $\gamma_i = \gamma C_{Ai}^{*((m-1)/2)}$.

From Eq. (35), the fluxes at the interface, $\mathcal{N}_{Ai}/k_A = (-dC_A/dz^*)_{z^*=0}$, and at the film ending, $\mathcal{N}_{A\delta}/k_A = (-dC_A/dz^*)_{z^*=1}$, can be evaluated. Using Eq. (15) for $\mathcal{N}_{Ai}$ and Eq. (13) for $\mathcal{N}_{Ai}^0$, we obtain:

$$\phi^T = \varXi(M\gamma C_{Ai}^{*(m-1)/2}) C_{Bi}^{*n/2} \left[ C_{Ai}^* - \frac{C_{AL}^*}{\cosh\left(\gamma C_{Ai}^{*(m-1)/2}\right)} \right], \tag{36}$$

$$\frac{\mathcal{N}_{A\delta}}{k_A C_{Ai}^0} = \varXi(M\gamma C_{Ai}^{*(m-1)/2}) C_{Bi}^{*n/2} \left[ \frac{C_{Ai}^*}{\cosh(\gamma C_{Ai}^{*(m-1)/2})} - C_{AL}^* \right]. \tag{37}$$

Given $C_{BL}$, $C_{AG}$ and $C_{AL}$ (and values of kinetic and transport properties), Eq. (36) can be solved iteratively to evaluate $\phi^T$. To this end, Eqs. (26) and (30) should be used for $C_{Bi}^*$ and $C_{Ai}^*$. After evaluating $\phi^T$, $\mathcal{N}_{A\delta}$ will follow directly from Eq. (37).

Before ending this section, we recall the basic Eq. (24), which can be checked before the evaluation of $\phi^T$, because it will be fulfilled if $\Omega > 1$. If not, a posteriori check can be done by using Eq. (16) for $C_{Ai}$, which allows writing Eq. (24) as $\Omega > (1 + Bi - \phi^T)/(1 + Bi)$.

### 3.2. Accumulation of A in the liquid bulk

For a given contactor, mass conservation equations of $A$ in the gas stream and of $B$ in the liquid stream will define point values of $C_{BL}$ and $C_{AG}$. In general, it will be also necessary to write a conservation equation for $A$ in the liquid stream to specify $C_{AL}$. For example, if the plug flow assumption can be applied for the liquid phase (e.g. in packed or bubble columns),

the following mass balance equation arises for $A$ in the liquid stream:

$$q_L \frac{dC_{AL}}{dV} = a\mathcal{N}_{A\delta} - (\varepsilon - a\delta)\, k C_{AL}^m C_{BL}^n \tag{38}$$

where $\varepsilon$ is the liquid hold-up in the contactor.

Therefore, mass balance equations for $A$ in the gas stream and for $A$ and $B$ in the liquid stream, along with Eqs. (36) and (37), complete the mathematical description of a given problem.

However, from an educational point of view, before attacking the solution of the problem as a whole, it is most advisable to analyze how the different dimensionless parameters affect the dimensionless transfer rate $\phi^T$. In this regards, the status of $C_{BL}$ and $C_{AG}$ is quite different to that of $C_{AL}$. While it is conceivable to choose rather arbitrary values for $C_{BL}$ and $C_{AG}$ (they will be related to concentrations of $B$ and $A$ in the liquid and gas inlet streams), the liquid feed will be normally devoid of $A$, i.e. $C_{AL,0} = 0$. Then, the field of $C_{AL}$ will be a result of the actual operation, rather than being an independent input (actually, it will be normally desirable that $C_{AL} \cong 0$, as this means complete conversion of the amount of $A$ transferred to the liquid phase).

A reasonable way to circumvent this issue is by assuming that the rate of accumulation of $A$ in the liquid stream, $q_L dC_{AL}/dV$, is negligible in Eq. (38) (e.g., as a consequence of a small value of $q_L$). This has been considered in some textbooks (e.g. Kramers and Westerterp, 1963). Then, taking $q_L dC_{AL}/dV = 0$ in Eq. (38),

$$a\mathcal{N}_{A\delta} = (\varepsilon - a\delta)\, k C_{AL}^m C_{BL}^n, \tag{39}$$

which expressed in dimensionless form renders

$$\frac{\mathcal{N}_{A\delta}}{k_A C_{Ai}^0} = (\kappa - 1)\,\gamma^2 (C_{AL}^*)^m \tag{40}$$

In Eq. (40) $\kappa = \varepsilon/(a\delta)$ is the ratio of total liquid and liquid film volumes and is known as the Hinterland ratio. Table 1 recalls the meaning of $\kappa$ and that of the product $(\kappa - 1)\gamma^2$ in Eq. (40).

Replacing $\mathcal{N}_{A\delta}$ from Eq. (37) in Eq. (40):

$$\Xi\,(M\gamma C_{Ai}^{*(m-1)/2})\,C_{Bi}^{*n/2}\left[\frac{C_{Ai}^*}{\cosh(\gamma C_{Ai}^{*(m-1)/2})} - C_{AL}^*\right] = (\kappa - 1)\,\gamma^2 C_{AL}^{*m}. \tag{41}$$

Now, a *local* problem can be stated in the following way. Given $C_{BL}$ and $C_{AG}$, Eqs. (36) and (41) allows evaluating $\phi^T$ and $C_{AL}$. In this way, the dependence of $\phi^T$ upon the different dimensionless parameters becomes $\phi^T = \phi^T(\gamma, \Omega, \kappa, Bi, m, n)$.

Assumption $q_L dC_{AL}/dV = 0$ changes the dependency of $\phi^T$ with $C_{AL}^*$ to that with $\kappa$. The value of $\kappa$ is primarily associated with the type of gas–liquid contactor and also to specific operating conditions, but not to the concentration fields.

It can be important to bear in mind that in practice the liquid stream will be accumulating $A$ ($q_L dC_{AL}/dV > 0$) from the inlet until a point where $C_{AL}$ has risen to a level at which the flux ($a\mathcal{N}_{A\delta}$) can be balanced by chemical consumption (i.e. to virtual satisfaction of Eq. (39)). Hence, it can be concluded that using Eq. (41) at any point in the contactor will result in an upper bound for the true value of $C_{AL}$.

The use of $q_L dC_{AL}/dV = 0$, as stated, facilitates the analysis of the parametric dependence of $\phi^T$. Besides, in studying the

behaviour of packed or bubble columns, disregarding the differential equation Eq. (38) removes the need to solve a system of differential equations and the design formulation can be just expressed in terms of the familiar HTU-NTU concept.

In the following paragraphs we will assume valid the use of Eqs. (36) and (41). An analysis for verifying if $q_L dC_{AL}/dV = 0$ can be adopted with reasonable precision will be given in Section 9.

## 4.  Different regimes in the liquid phase

Eqs. (36) and (41) allow quantifying the transfer rate of $A$ from a source (the gas stream) to a chemical sink (the liquid phase) limited by two physical resistances, the gas film (for $A$) and the liquid film (for $A$ and $B$), and by finite reaction rates in both, the (unmixed) liquid film and the (mixed) liquid bulk. All of these processes are represented by the dimensionless parameters listed in Table 1. For didactic reasons and also from a practical point of view, special cases in which the slower processes will control the transfer rate of $A$ from its source should be identified.

A convenient starting point to this end is assuming large values for some parameters, which are likely to be so in practice. Thus, large values of $Bi$, $\kappa$ and $\Omega$ are assumed in the cases depicted in Fig. 4.

As the gas film resistance is physically in series with all the other processes in the liquid phase, $Bi \to \infty$ means that $C_{Ai} \cong C_{AG}$.

Condition $\kappa \gg 1$ in Fig. 4 means that for some range of $\gamma$ values satisfying

$$\gamma^2 \ll 1, \tag{42}$$

the value of $\kappa$ is such that the product $(\kappa - 1)\gamma^2$ will span from very low ($\ll 1$) to very large ($\gg 1$) values. Recalling the meaning of parameter $\gamma^2$ (Table 1), the restriction expressed by Eq. (42) defines cases in which, because of negligible reaction in the liquid film, the only relevant processes in the liquid phase will be mass transfer of $A$ in the liquid film in series with reaction in the liquid bulk. Thus, the regimes identified as I–III in Fig. 4 arise as $\gamma$ increases within the limit imposed by Eq. (42).

For large values of $\gamma$, no longer satisfying Eq. (42), regimes IV–VII in Fig. 4 will progressively arise.

For the subset of regimes III–VII (the inclusion of regime III should be remarked), all the processes occurring in the liquid film can be eventually significant, while reaction in the liquid bulk is potentially high enough (more specifically, $(\kappa - 1)\gamma^2 \gg 1$, following the meaning in Table 1) to set $C_{AL} \cong 0$. Then, reaction in the bulk liquid is not controlling and parameter $\kappa$ will not enter in the definition of the GEF.

For regimes IV and V, a value $\Omega \gg 1$ means that a flat profile of $C_B$ holds, i.e. $\gamma^2/\Omega \ll 1$. Thus, both regimes are characterized by the simultaneous control of diffusion of $A$ and reaction in the liquid film. In regime IV ($\gamma^2 \sim 1$), the flux of $A$ towards the liquid bulk is not negligible and thus reaction takes place in the liquid film (participating in control) and in the liquid bulk (not controlling). In regime V, on the other hand, when $\gamma^2 \gg 1$, reaction in the film is fast enough to prevent $A$ from reaching the end of the film. Note that this case will take place irrespective of the value of $\kappa$.

In regime VI, the three processes in the liquid film (diffusion of $A$ and $B$ and reaction) control simultaneously the overall rate of transfer.
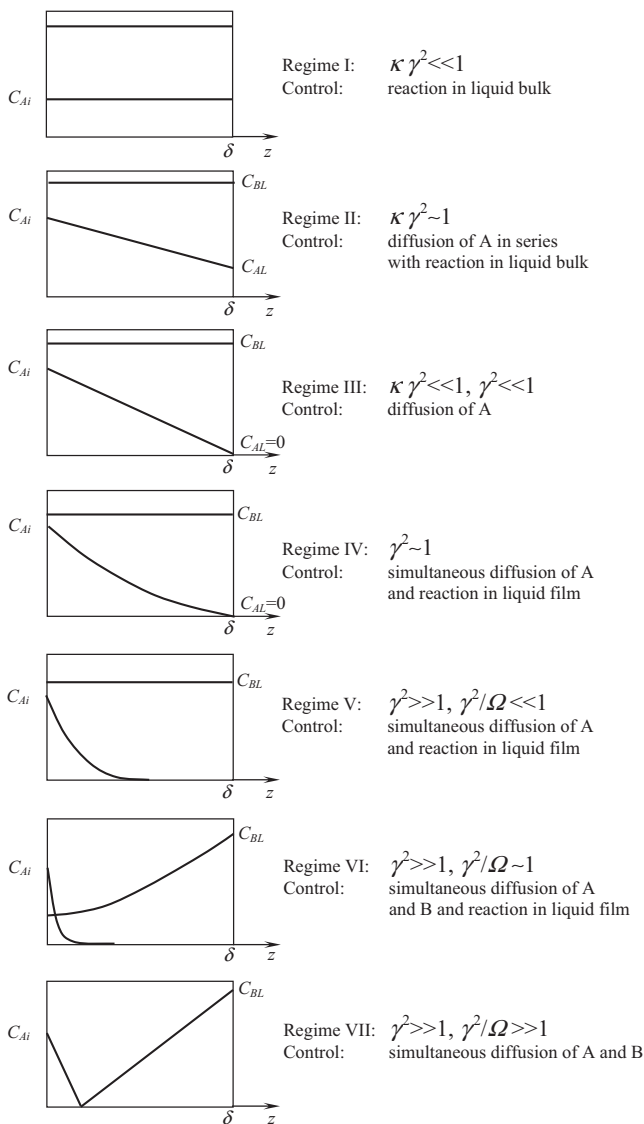
**Fig. 4 – Regimes occurring in the liquid phase. Values $Bi \to \infty$, $\Omega \gg 1$, $\kappa \gg 1$ are assumed. Parameter $\gamma$ increases from regime I to VII. The $C_B$ scale is assumed shorter than that of $C_A$.**

Finally, a limiting situation is reached in regime VII, in which reaction rate has raised to a point that coexistence of $A$ and $B$ in the liquid film is impeded by strong diffusion limitations of both reactants, $A$ and $B$, and the reaction zone virtually collapses into a plane.

Before closing this section, it is convenient to discuss what happens when assumptions $Bi \to \infty$, $\Omega \gg 1$ and $\kappa \gg 1$ are not applicable.

First, it is noted that the different regimes identified in Fig. 4 will also hold for finite values of $Bi$. Although in general $C_{Ai}$ will be lower than $C_{AG}$ for finite values of $Bi$, the occurrence of any of the seven regimes will depend on the values of the remaining parameters ($\gamma$, $\kappa$ and $\Omega$).

Relatively small values of $\Omega$ can avoid the occurrence of regime V, as the relationships $\gamma^2 \gg 1$ and $\gamma^2/\Omega \ll 1$ may not hold simultaneously. Then, when $\gamma^2 \sim \gamma^2/\Omega \sim 1$, a variant of regime VI will be found, with simultaneous control of diffusion of $A$ and $B$ and chemical reaction, but with part of the reaction taking place in the liquid bulk at $C_{AL} \cong 0$ (if the assumption $\kappa \gg 1$ is kept), as a result of a finite flux of $A$ at the limit of the

liquid film. This case will be henceforth identified as regime IV/VI.

Finally, removing the assumption $\kappa \gg 1$ will open the possibility for a different regime, in which reaction can take place in both the liquid film and liquid bulk at finite values of $C_{AL}$. This case (named Regime VIII) will be further considered in Section 7.

## 5. The GEF for regimes I–VII

Expressions of $\phi^T$ for regimes I–VII just discussed are given in Table 2. The effect of finite values of $Bi$ is included. They have been divided into two groups, *slow* (regimes I–III) and *fast* (III–VII) reactions, and Eqs. (T2.1) and (T2.2) are the general expressions for each group.

General restrictions for each group are given in Table 2. They have been derived by comparing the results from Eqs. (T2.1) and (T2.2) with those from the general Eqs. (36) and (41). These general restrictions are chiefly expressed in terms of parameter $\gamma$ and they guarantee that $\phi^T$ will be evaluated within a precision of 5%. It should be mentioned that tighter conditions are possible to write, but at the expense of more complex expressions, as more parameters will be involved. For example, condition stated as $\gamma > 3$ (a sufficient condition for fast reactions) can be more precisely stated as $\gamma > [5(\Omega + 1)/\Omega]^{1/2}$, when parameter $\Omega$ is accounted for.

Other important features of the formulation in Table 2 are discussed below.

### 5.1. Slow reactions, regimes I–III

Recalling the explanation given in Section 4, we can easily formulate the case of regimes I–III independently of the general expressions defined in Eqs. (36) and (41). Consider first regime II (see Fig. 4). As mass transfer in the gas film, in the liquid film and chemical reaction in the liquid bulk are in series, we can write:

$$a\mathcal{N}_{Ai} = ak_{GA}^0 H_A(C_{AG} - C_{Ai}) = ak_A(C_{Ai} - C_{AL}) = (\varepsilon - a\delta)kC_{AL}^m C_{BL}^n \tag{43}$$

For high enough values of $(ak_A)$, when $C_{AL} \cong C_{Ai}$, regime I is reached and it follows from Eq. (43) that $a\mathcal{N}_{Ai} = (\varepsilon - a\delta)kC_{Ai}^m C_{BL}^n$. This expression clearly neglects reaction in the film, a fact consistent with the assumption in Section 4, $\varepsilon \gg a\delta$ (i.e. $\kappa \gg 1$). However, in general we like to include cases in which $\kappa$ is small and, therefore, the general expression for regime I is $(a\mathcal{N}_{Ai}) = \varepsilon k C_{Ai}^m C_{BL}^n$. Eq. (43) can be modified to undertake this situation by using $\varepsilon$ instead of $(\varepsilon - a\delta)$ in the last term. If in addition the overall mass transfer coefficient $k_A^T$ (Eq. (11)) is introduced, we rewrite Eq. (43) in the form:

$$ak_A^T(C_{AG} - C_{AL}) = a\mathcal{N}_{Ai} = \varepsilon k C_{AL}^m C_{BL}^n \tag{44}$$

which in dimensionless terms becomes

$$1 - \left(\frac{Bi}{1+Bi}\right)C_{AL}^* = \phi^T = \kappa\gamma^2(C_{AL}^*)^m. \tag{45}$$

Eq. (T2.1) in Table 2 arises by combining the two equalities in Eq. (45). Eq. (T2.1) can be employed when $\gamma < 0.25^c$, where the exponent $c$ depends on $m$ (the reaction order of $A$) and is given in Table 2 ($c = 1$ for the "typical" value $m = 1$).

| Table 2 – Specific expressions for GEF. $\Xi(x) = x/\tanh(x)$, GF regime: gas film regime. | | | |
|---|---|---|---|
| **Slow reactions**: Regimes I–III | | | |

General restriction: $\gamma < 0.25^c$, $c = \begin{cases} (m+1)/2, & \text{if } m \geq 0.5 \\ 0.85 - m/5, & \text{if } m < 0.5 \end{cases}$

$\phi^T = \kappa \gamma^2 C_{AL}^{*m}$  (T2.1)

$C_{AL}^* = \left(\frac{1+\text{Bi}}{\text{Bi}}\right)(1 - \phi^T)$

**Fast reactions**: Regimes III–VII, GF

General restriction ($C_{AL} \approx 0$): $\gamma > 3$ or $(\kappa - 1)\gamma^2 > 20^m$

$\phi^T = \Xi(M\gamma) C_{Ai}^{*(m+1)/2} C_{Bi}^{*n/2}$  (T2.2)

$C_{Ai}^* = \frac{1 + \text{Bi} - \phi^T}{\text{Bi}}, \quad C_{Bi}^* = \frac{1 + \Omega - \phi^T}{\Omega}$

**Specific cases for fast reactions**

**Without Bi effect**

Specific restrictions:

| | | | |
|---|---|---|---|
| $\text{Bi} > 10(m+1)(\phi_\Omega^T - 1)$: $\phi_\Omega^T = 1 + \frac{\Omega[\Xi(M\gamma) - 1]}{[(1+\Omega)^\beta + \Xi^\beta(M\gamma)]^{1/\beta} - 1}; \quad \beta = \left(\frac{2}{n}\right)^{0.65}$ | Regimes III–VII | $\phi^T = \Xi(M\gamma) C_{Bi}^{*n/2}$ | (T2.3) |
| $\Xi(M\gamma) < 1 + \frac{1}{10}\left(\frac{m+1}{\text{Bi}} + \frac{n+0.1}{\Omega}\right)^{-1}$: | Regimes III–V | $\phi^T = \Xi(M\gamma)$ | (T2.4) |
| $\text{Bi} > \Omega; \Xi(M\gamma) > (1+\Omega)\left(\frac{20\Omega}{1+\Omega}\right)^{n/2}\left(\frac{\text{Bi}}{1+\text{Bi}-0.95(1+\Omega)}\right)^{(m+1)/2}$: | Regime VII | $\phi^T = 1 + \Omega$ | (T2.5) |

**Without $\Omega$ effect**

Specific restrictions:

| | | | |
|---|---|---|---|
| $\Omega > (10n+1)(\phi_{\text{Bi}}^T - 1)$: $\phi_{\text{Bi}}^T = 1 + \frac{\text{Bi}[\Xi(M\gamma) - 1]}{[(1+\text{Bi})^\beta + \Xi^\beta(M\gamma)]^{1/\beta} - 1}; \quad \beta = \left(\frac{2}{m+1}\right)^{0.65}$ | Regimes III–V, GF | $\phi^T = \Xi(M\gamma) C_{Ai}^{*(m+1)/2}$ | (T2.6) |
| $\Omega > \text{Bi}; \Xi(M\gamma) > (1+\text{Bi})\left(\frac{20\text{Bi}}{1+\text{Bi}}\right)^{(m+1)/2}\left(\frac{\Omega}{1+\Omega-0.95(1+\text{Bi})}\right)^{n/2}$: | GF regime | $\phi^T = 1 + \text{Bi}$ | (T2.7) |

Note the difference between the restrictions defined by Eq. (42), stated on a qualitative basis for regimes I–III to occur, and $\gamma < 0.25^c$, which establishes a definite upper limit $\gamma = 0.25^c$ for regimes I–III. The same comment applies for the other restrictions in Fig. 4 (stated either with the symbol "$\gg$" or "$\ll$") and in Table 2 (in terms of either ">" or "<").

It should be noted at this point that Eq. (T2.1) is not formally obtained from the general formulation, Eqs. (36) and (41). Instead, when $\gamma < 0.25^c$, it follows that

$$\phi^T = \gamma^2[(\kappa - 1)C_{AL}^{*m} + C_{Ai}^{*m}] \qquad (46)$$

with $C_{AL}^* = [(1+\text{Bi})/\text{Bi}](1 - \phi^T)$ and $C_{Ai}^*$ from Eq. (30). However, close to the upper limit $\gamma = 0.25^c$, Eq. (46) and (T2.1) only differ slightly and virtually the same results are obtained for lower values of $\gamma$. Eq. (T2.1) is to be preferred, as it can be derived easily and is somewhat simpler to use than Eq. (46).

Once $\phi^T$ is evaluated from Eq. (T2.1), $C_{AL}$ can be calculated from Eqs. (14) and (45):

$$C_{AL} = C_{AG}(1 - \phi^T). \qquad (47)$$

Note also that explicit expressions for $\phi^T$ can be obtained from Eq. (T2.1) when $m = 0.5$, 1 or 2. For $m = 1$,

$$\phi^T = \frac{\kappa \gamma^2}{\text{Bi}/(1+\text{Bi}) + \kappa \gamma^2}.$$

Regime I is defined when $C_{AL} \cong C_{Ai}$. If in addition we require no effect of the gas film, $C_{AL} \cong C_{Ai} \cong C_{AG}$. Then, with errors less than $\approx 5\%$, imposing $(C_{AL}/C_{AG})^m > 0.95$,

$$\kappa \gamma^2 < \frac{1}{1 + 20m}\left(\frac{\text{Bi}}{1+\text{Bi}}\right)^m \Rightarrow \text{Regime I}: \phi^T = \kappa \gamma^2 \left(\frac{1+\text{Bi}}{\text{Bi}}\right)^m. \qquad (48)$$

Although $\phi^T$ depends on Bi, the flux $\mathcal{N}_{Ai} = \phi^T \mathcal{N}_{Ai}^0$ does not. Thus, using Eq. (48)

$$a\mathcal{N}_{Ai} = \varepsilon k(C_{AG})^m C_{BL}^n \qquad (49)$$

is obtained, without any effect of mass transfer resistances.

We recall at this point that in reaching Eq. (35) the factor $M = \sqrt{2/(m+1)}$ was removed from the arguments of the hyperbolic cosines (modification (a) in Section 3.2). If $M$ is retained, for conditions leading to Eq. (48), $\phi^T = (\kappa - 1 + M^2)\gamma^2[(1+\text{Bi})/\text{Bi}]^m$ will be obtained, which does not match the correct Eq. (48) when $m \neq 1$.

In practice, we can require for defining regime III that $C_{AL}^* < 0.05$. Then,

$$\kappa \gamma^2 > 20^m \Rightarrow \text{Regime III}: \phi^T = 1. \qquad (50)$$

It should be stressed that Eqs. (48)–(50) are further restricted by the general condition $\gamma < 0.25^c$.

### 5.2. Fast reactions, regimes III–VII

The group of regimes III–VII, "*fast reactions*" in Table 2, arises when $C_{AL} \cong 0$. This condition, as discussed before, may be accomplished when the characteristic diffusion rate of A is very low, either respect to reaction rate in the film or respect

to reaction rate in the liquid bulk. The general restriction for $C_{AL} \cong 0$ is either $\gamma > 3$ or $(\kappa - 1)\gamma^2 > 20^m$ (see Table 2), respectively. By taking $C_{AL} = 0$ in Eq. (36), we obtain the expression of $\phi^T$ for regimes III–VII. If as a matter of simplification, with practically no loss of precision, the factor $C_{Ai}^{*(m-1)/2}$ is removed from the argument of the hyperbolic tangent in function $\Xi$, Eq. (T2.2) is obtained.

Table 2 also includes several specific expressions, Eqs. (T2.3)–(T2.7), obtained from Eq. (T2.2) and restrained to certain regimes. Each of them is subject to a specific restriction that, in general, should be fulfilled *in addition* to the general restriction for the group $[\gamma > 3$ or $(\kappa - 1)\gamma^2 > 20^m]$. Eqs. (T2.3)–(T2.5) in Table 2 are specifically considered next, while Eqs. (T2.6) and (T2.7) will be discussed in Section 6.

### 5.2.1. *Regimes III–VII without Bi effect*

Values of $\phi^T$ from any of Eqs. (T2.3) to (T2.5) do not depend on Bi number through the term $C_{Ai}^{*(m+1)/2}$ in the general Eq. (T2.2). Each specific restriction in Table 2 can be regarded as defining a minimum value of Bi to this end.

Eq. (T2.3) is the general expression to evaluate $\phi^T$ in regimes III–VII, and arises when in Eq. (T2.2) the factor $C_{Ai}^{*(m+1)/2}$ can be taken as 1 within a precision of 5%. To test if this condition can be accomplished an estimation of $\phi^T$ is needed, for which $\phi_\Omega^T$ defined in Table 2 is proposed. If the restriction is fulfilled, $\phi_\Omega^T$ approximates $\phi^T$ with a deviation less than around 8%, and the iterative procedure that in general is required by Eq. (T2.3) can be avoided.

Eq. (T2.4) for regimes III–V is the specific case of Eq. (T2.2) when the product $[C_{Bi}^{*n/2} C_{Ai}^{*(m+1)/2}]$ can be taken as 1 within a precision of 5%. For further discrimination among regimes III–V, according to the value of $\gamma$, the following expressions are obtained from Eq. (T2.4):

$$M\gamma < 0.3 \Rightarrow \text{Regime III} : \phi^T = 1 \tag{51a}$$

$$M\gamma > 2 \Rightarrow \text{Regime V} : \phi^T = M\gamma. \tag{51b}$$

As noted in Section 4, regime III is the bridge between slow (regimes I–III) and fast reactions (III–VII) and as such, it can be obtained as a limiting case from both groups. The fact that slow and fast reactions are subject to different general restrictions is reflected in the different specific restrictions expressed in Eqs. (50) and (51a) for regime III to apply.

Regime V is defined (see Fig. 4) when $C_B = C_{BL}$ is uniform in the liquid film and both $dC_A/dz = 0$ and $C_A = 0$ at $z = \delta$. Eq. (19) at these conditions can be easily solved (see *e.g.* Froment et al., 2011) for the flux at the interface:

$$\mathcal{N}_{Ai} = \sqrt{\frac{2}{m+1} k D_{AL} C_{Ai}^{m+1} C_{BL}^{n}} \tag{52}$$

As Eq. (51b) involves $C_{Ai}^0 \approx C_{Ai}$, the value $\mathcal{N}_{Ai}$ obtained from Eq. (51b) is the same as that in Eq. (52). For fast reactions, regime V can be readily shown to be the most sensitive one to the order $m$. Hence, the linearization of the term $C_A^m$ in the reaction rate expression (see Eq. (23)) was actually chosen with the aim of achieving the correct evaluation of $\phi^T$ in regime V.

For regime VII, Eq. (T2.5) in Table 2 ($\phi^T = 1 + \Omega$) holds. Eq. (T2.5) arises when $C_{Bi}^* \rightarrow 0$ in Eq. (T2.2), as a consequence of a large enough value of the product $[\Xi(M\gamma)C_{Ai}^{*(m+1)/2}]$. This condition may be satisfied even for values of $C_{Ai}^*$ significantly less
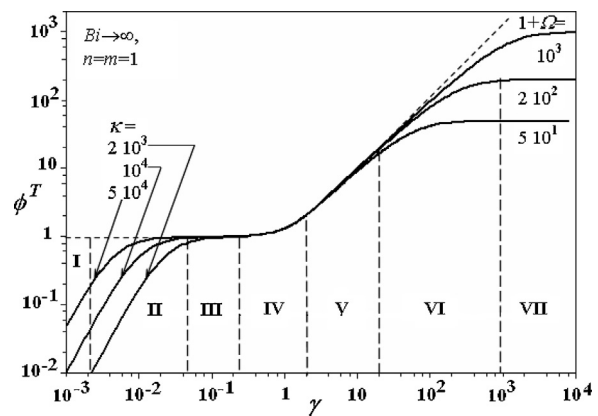


Fig. 5 – $\phi^T$ vs. $\gamma$ for Bi $\rightarrow \infty$, $n = m = 1$ ($\kappa = 2 \times 10^3$, $10^4$, $5 \times 10^4$; $1 + \Omega = 50$, 200, 1000). The vertical dashed lines bounding regimes I–II, II–III, V–VI, VI–VII hold for $\kappa = 10^4$ and $1 + \Omega = 200$.

than one. Hence, the specific restriction of Eq. (T2.5) in Table 2 can be fulfilled for lower values of Bi than required for the restriction of the more general Eq. (T2.3).

Eq. (T2.5) can also be easily obtained by equating the flux of A to b times that of B towards the reaction plane.

### 5.3. *Overall behaviour of $\phi^T$ as a function of $\gamma$*

Fig. 5 shows a plot of $\phi^T$ for conditions in Fig. 4, i.e. Bi $\rightarrow \infty$ and values of $\kappa$ and $\Omega$ large enough to obtain the sequence of regimes I–VII as $\gamma$ increases.

It is remarked that for regimes I–III $\phi^T$ is independent of $\Omega$ and it is independent of $\kappa$ for regimes III–VII.

For illustrating the effect of orders $m$ and $n$, a plot similar to that in Fig. 5, but with ($M\gamma$) as the abscissa, can be drawn. Then, for given values of $\Omega$ and $\kappa$, a family of curves depending on $n$ will arise just in regime VI and another set depending on $m$ will appear in regimes I and II (see expressions in Table 2).

For any pair ($m, n$) the regimes II and those represented by straight lines (the odd ones, I, III, V, VII) are exactly represented by equations in Table 2. Instead, expressions for regimes IV and VI are, in general, approximations (an exception is the case $m = 1$ in regime IV), due to the linearization of the reaction rate in Eq. (23). However, the errors are definitely tolerable, as will be further discussed in Section 8.1.

The sensitivity of the volumetric mass transfer rate $a\mathcal{N}_{Ai}$ with the contactor characteristic variables ($k_A$, $a$, $\varepsilon$), specific rate constant ($k$) and bulk concentration of $B(C_{BL})$ are listed in Table 3 for the situation in Fig. 5: Bi $\rightarrow \infty$, $r = kC_AC_B$ ($n = m = 1$), large $\kappa$ and $\Omega$. The sequence from top to bottom in Table 3 may be associated with a continuous temperature increase (i.e. raising $\gamma$). Table 3 shows how the effect of some variables ($k$, $k_A$, $C_{BL}$) fluctuates as the sequence of the different regimes proceeds. This is a consequence of the different processes participating in the control of the overall process. Besides, as it is desirable to obtain values of $a\mathcal{N}_{Ai}$ as high as possible, Table 3 indicates the suitable variable to modify (e.g. by the choice of operating condition, contactor type or design) for a given set of starting conditions.

Examples of regime identification and numerical evaluation of $\phi^T$ and $\mathcal{N}_{Ai}$ are given in the Appendix. Case (a) deals with situations in which Bi $\rightarrow \infty$ is assumed.

| Table 3 – Effect of different variables on $(a\mathcal{N}_{Ai})$, for $r = k\,C_A\,C_B$ (i.e. $n = m = 1$), $Bi \to \infty$, and large values of $\kappa$ and $\Omega$. The effect of a generic variable $v$ is expressed as $d[\ln(a\mathcal{N}_{Ai})]/d[\ln(v)]$. | | | | | | |
|---|---|---|---|---|---|---|
| Regime | $a\mathcal{N}_{Ai}$ | $k$ | $k_A$ | $a$ | $\varepsilon$ | $C_{BL}$ |
| I | $\varepsilon k C_{AG}\,C_{BL}$ | 1 | 0 | 0 | 1 | 1 |
| II | $\varepsilon k C_{AG} C_{BL}/(1 + \kappa\gamma^2)$ | 1–0 | 0–1 | 0–1 | 1–0 | 1–0 |
| III | $a k_A C_{AG}$ | 0 | 1 | 1 | 0 | 0 |
| IV | $a C_{AG}\sqrt{k D_{AL} C_{BL}}/\tanh(\gamma)$ | 0–0.5 | 1–0 | 1 | 0 | 0–0.5 |
| V | $a C_{AG}\sqrt{k D_{AL} C_{BL}}$ | 0.5 | 0 | 1 | 0 | 0.5 |
| VI | $a C_{AG}\sqrt{k D_{AL} C_{BL} C_{Bi}^*}$ | 0.5–0 | 0–1 | 1 | 0 | 0.5–1 |
| VII | $a k_A[C_{AG} + C_{BL} D_{BL}/(b D_{AL})]$ | 0 | 1 | 1 | 0 | 0.5–1 |

## 6. Effect of the gas side mass transfer resistance (Bi effect)

We discuss in this section the effect of $Bi$ as originated by a change of $k_{GA}^0$, rather than $k_A$ that is assumed to remain invariable. In the end, the interface flux is the magnitude of interest $\mathcal{N}_{Ai} = k_A^T C_{AG}\phi^T$, but as the evaluation of $\phi^T$ (Table 2) is far more complex than $k_A^T = k_A Bi/(1 + Bi)$, in Section 5.2.1 we have mainly made reference to the effect of $Bi$ on $\phi^T$. An effect of $Bi$ on $\mathcal{N}_{Ai}$ or $\phi^T$ does not imply an effect on the other. For example, when Eqs. (48 and 49) apply (regime I), $\phi^T$ may be affected while $\mathcal{N}_{Ai}$ is not. Just the opposite happens in regime III ($\phi^T = 1$) or VII ($\phi^T = 1 + \Omega$).

As discussed in Section 2, $Bi$ numbers are frequently high (larger than the unity). Therefore, the effect of $Bi$ is expected to be more significant for fast reactions (regimes IV–VII), which will be specially considered in the remainder of this section.

A point to remark concerns the evaluation of $\phi^T$ for the set of specific cases "*without Bi effect*" in Table 2. The effect of $Bi$ through $C_{Ai}^*$ was considered in establishing the restrictions for Eqs. (T2.3)–(T2.5) in Table 2. However, when $m \neq 1$ parameter $\gamma$ also depends on $Bi$, through $(C_{Ai}^0)^{(m-1)/2}$, i.e. $\gamma \propto [Bi/(1 + Bi)]^{(m-1)/2}$, and the following question can be raised. If for a given finite value $Bi_0$ a value $\gamma_0$ arises and the value $\phi^T = \phi_0^T$ can be evaluated from any of Eqs. (T2.3)–(T2.5) (i.e. the companion restriction is satisfied), will $\phi_0^T$ hold (with a tolerance of ~5%) for any value $Bi > Bi_0$? The answer is not obvious, but calculations show that for any practical purpose $\phi_0^T$ can still be accepted all the way from $Bi_0$ to $Bi \to \infty$, in spite of the changes in $\gamma$ from the original value $\gamma_0$. In further describing the effect of $Bi$, this observation allows us to focus on the term $C_{Ai}^*$ rather than on $C_{Ai}^0$.

The general expression for fast reaction, Eq. (T2.2), clearly allows identifying in a separate way the effects of the three significant processes for fast reactions (see Table 2): the effect of chemical reaction quantified by $\Xi(M\gamma)$, the limitation imposed by the liquid film to the transport of B, $C_{Bi}^*$, and the limitation imposed by the gas film to the transport of A, $C_{Ai}^*$. When $\Xi(M\gamma)$ is high enough, $\phi^T$ will be ultimately restrained either by $C_{Bi}^* \to 0$ or by $C_{Ai}^* \to 0$, whichever happens first according to the smaller value between $\Omega$ and $Bi$.

When $C_{Ai}^* = 0$ can be assumed for practical purposes, $\phi^T = 1 + Bi$ arises as a specific case from Eq. (T2.2). It is included in Table 2 as Eq. (T2.7) along with its specific restriction. The resulting value of the flux $\mathcal{N}_{Ai}$ when $\phi^T = 1 + Bi$ is

$$\mathcal{N}_{Ai} = k_{GA}^0 H_A C_{AG}. \tag{53}$$

When Eq. (53) applies, we say that the *Gas Film regime* (GF regime) holds, as the whole process becomes controlled by the gas film resistance, i.e. we find the maximum possible effect of

the product $(k_{GA}^0 H_A)$, or equivalently of $Bi$. As in general $\mathcal{N}_{Ai} = k_{GA}^0 H_A(C_{AG} - C_{Ai})$, the GF regime involves in practice that $C_{Ai}$ reaches a negligible value respect to $C_{AG}$ (say, $C_{Ai}/C_{AG} < 0.05$). Actually, the GF regime can be accompanied by any of the regimes IV–VI in the liquid phase. Yet, if $Bi$ is assumed to be very small (because of very low values of $H_A$), the GF regime can be still established along with regimes I–III or VIII (see Section 7 for the latter). In any case, as the flux is given by Eq. (53), the discrimination of the regime in the liquid phase is of little practical consequence.

Invoking again the usually large values of $Bi$ in practice, the establishment of the GF regime will require large values of $\gamma$. Fig. 6 depicts a sequence of profiles that arise by increasing $C_{BL}$ (i.e. increasing $\Omega$) and assuming that $\gamma$ is very high.

The left scheme of Fig. 6 corresponds to the starting situation, in which a relatively high value of $Bi$ is also assumed, such that $Bi > \Omega$. $C_{Bi}^* = 0$ has been virtually reached, i.e. regime VII holds and $\phi^T = 1 + \Omega$.

For higher values of $\Omega$, as $C_{BL}$ increases, the reaction plane will shift towards the interface. The middle scheme corresponds to the point when $Bi = \Omega$ just holds and the reaction plane has reached the interface, with both $C_{Bi}^*$ and $C_{Ai}^*$ being simultaneously $\cong 0$.

A further increase of $\Omega$ will render the right scheme of Fig. 6, in which $\Omega > Bi$, $\phi^T = 1 + Bi$, $C_{Bi}^* > 0$ and the reaction plane remains at the interface. Although very small, a finite value of $C_{Ai}$ and a decaying profile of $C_A$ in the liquid film could be still identified if the right scheme of Fig. 6 were conveniently zoomed in. This case actually corresponds to regime VI, recalling that $C_{Bi} < C_{BL}$.

Another specific case of Eq. (T2.2) arises when $\Omega$ is large enough for approximating $C_{Bi}^{*n/2} \approx 1$, but the gas film resistance leads to values $C_{Ai}^* < 1$. This case corresponds to regimes III–V in the liquid side, and is formulated by Eq. (T2.6) in Table 2, along with the corresponding restriction. If the restriction is fulfilled, $\phi_{Bi}^T$ can approximate $\phi^T$ with a deviation less than around 8%, and the iterative procedure that in general is required by Eq. (T2.6) can be avoided.

Further discrimination between the regimes can be made (cfr. Eqs. (51a) and (51b)):

$$M\gamma < 0.3 \Rightarrow \text{Regime III}: \phi^T = 1 \tag{54a}$$

$$M\gamma > 2 \Rightarrow \text{Regime V}: \phi^T = (M\gamma)C_{Ai}^{*(m+1)/2} \tag{54b}$$

It is noted that the pairs of Eqs. (T2.6)/(T2.7) and Eqs. (T2.3)/(T2.5) are equivalently derived from Eq. (T2.2) by exchanging the role of $\Omega$ and $Bi$.

Fig. 7 illustrates de effect of $Bi$ in Eq. (T2.2) for $\Omega = 9$. For $Bi = 20$ and 100, $\phi^T$ is limited by $\Omega$, $\phi^T|_{\gamma\to\infty} = 1 + \Omega$. For $Bi = 9$, both $\Omega$ and $Bi$ fix the limiting value of $\phi^T$, while for $Bi = 4$, $\phi^T|_{\gamma\to\infty} = 1 + Bi$.
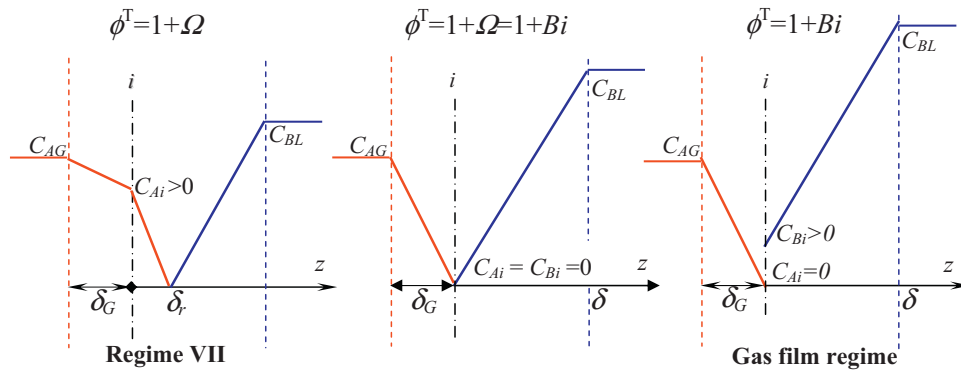
**Fig. 6 – Solution of Eq. (T2.2) for very large values of $\gamma$. $C_{BL}$ increases from left to right.**

The value $\Omega = 9$ used in Fig. 7 is low enough to prevent regime V from developing, i.e. regime VI follows directly from regime IV as $\gamma$ increases. Except for small values of $\gamma$ in Fig. 7, values of $Bi$ in the range $4 < Bi < 20$ exert a noticeable effect on $\phi^T$.

Case (b) in the Appendix illustrates the identification of regimes and evaluation of $\phi^T$ and $\mathcal{N}_{Ai}$ for a finite value of $Bi$.

## 7.     Regime VIII

Regime VIII is said to take place when reaction in the liquid film is significant and simultaneously $C_{AL}$ is significantly larger than 0. This case will arise when the rates of diffusion of $A$ in the liquid film, reaction in the liquid film and reaction in the liquid bulk are comparable. The profile of $C_A$ in the liquid phase is as depicted in Fig. 1. The conditions for regimen VIII arise when none of the general conditions for slow and fast reactions in Table 2 are fulfilled. In terms of the dimensionless parameters, such conditions are

$$0.25^c < \gamma < 3 \quad \text{and} \quad (\kappa - 1)\gamma^2 < 20^m. \tag{55}$$

As regards the remaining processes, transfer of $A$ in the gas film and transfer of $B$ in the liquid film, they may either be or not be relevant in regime VIII. When both are significant, we will have the general picture outlined in Fig. 1.

Quantification of regime VIII is seldom addressed in textbooks. Looking at conditions defined by Eq. (55), the range $0.25^c < \gamma < 3$ spans over one decade of $\gamma$ values. In terms of the kinetic coefficient $k$, $(\gamma^2 \propto k)$, regimes VIII will span over two decades of $k$ values. Then, there is a clear chance that $\gamma$
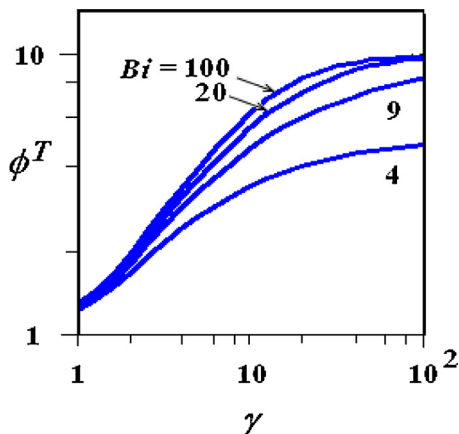
will lie in the range $0.25^c < \gamma < 3$. Some justification for bypassing the treatment of regime VIII in textbooks can be found if only relatively large values of $\kappa$ are conceived. Then, Eq. (55), $(\kappa - 1)\gamma^2 < 20^m$, can be taken from granted. However, to appraise how large should be $\kappa$ to avoid situations pertaining to regime VIII, we note that the order $m$ plays a significant role. Thus, for $m = 2$ and values $\gamma \cong 1$, values of $\kappa > 400$ will have to be involved to that end.

Following the approach of the present contribution, i.e. deriving the analysis from a unified formulation, the evaluation of GEF for regime VIII just corresponds to considering the basic Eqs. (36) and (41) without further simplification. Note that for $C_{Bi}^*$ the general Eq. (26) should be employed, rather than the one given in Table 2 for fast reactions, which sets $C_{AL} = 0$.

Values of $\phi^T$ in regime VIII can be visualized in Fig. 8 for the case $m = 2$, $n = 1$ and $Bi \to \infty$. The main role is played by parameter $\kappa$. On the other hand, the effect of $\Omega$ is only moderate when $\gamma$ is larger than about 1, and it is negligible if $\gamma < 1$. Relatively low values of $Bi$ will also show some effect (not shown in Fig. 8), while the reaction order of $B$ ($n$) will present only a weak effect, associated with small values of $\Omega$.

While for high or very high values of $\kappa$ regime III was regarded as a bridge between low and fast reactions (see Fig. 5), for moderate to low values of $\kappa$ regime VIII constitutes a *region* of paths between both sets of cases.

A standard multidimensional root solver can be used to evaluate $\phi^T$ and $C_{AL}^*$ from Eqs. (36) and (41). A nested iteration (manually or automatically driven) can also be safely
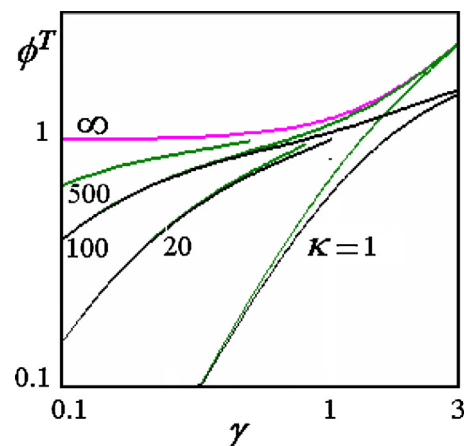


**Fig. 7 – Values of $\phi^T$ for $n = m = 1$, $\Omega = 9$ and different $Bi$ numbers.**



**Fig. 8 – Regime VIII for $m = 2$, $n = 1$, $Bi \to \infty$ and different values of $\kappa$. For $\kappa = 1, 20, 100$ black curves correspond to $\Omega = 1$ and green curves to $\Omega \to \infty$. For $\kappa = 500$ and $\kappa \to \infty$ only the curves for $\Omega \to \infty$ are shown.**

employed by guessing $C_{AL}^*$, solving Eq. (36) for $\phi^T$, and repeating until Eq. (41) can be closed with the right guess of $C_{AL}^*$.

If $m = 1$ and $\Omega \to \infty$ (pseudo-first order case, $r = kC_A C_{BL}^n$), Eqs. (36) and (41) can be explicitly solved:

$$\phi^T = \Phi(\gamma, \kappa) \frac{Bi + 1}{Bi + \Phi(\gamma, \kappa)}, \tag{56}$$

where: $\Phi(\gamma, \kappa) = \gamma^2 \left[1 + (\kappa - 1)\Xi(\gamma)\right] / \left[\Xi(\gamma) + (\kappa - 1)\gamma^2\right]$.

Eq. (56) covers regimes I–V and VIII, but it is particularly useful for regime VIII. To check if $\Omega$ is large enough for using Eq. (56), the same restriction of Eq. (T2.6) in Table 2 can be used. Note in Table 2 that when $m = 1$, $\phi_{Bi}^T = \Xi(\gamma)(1 + Bi)/(\Xi(\gamma) + Bi)$.

In the Appendix, Case (c) provides an example of operating conditions corresponding to regime VIII.

# 8. Precision of GEF evaluation

As discussed in Section 5, the evaluation of $\phi^T$ in regimes I–III does not introduce any error. Therefore, the discussion here will be focused on fast reactions (regimes III–VII), with $\phi^T$ evaluated from Eq. (T2.2) in Table 2 and regime VIII, with $\phi^T$ evaluated from the general Eqs. (36) and (41).

The error in evaluating $\phi^T$ will be appraised by comparison with the numerical solution of the conservation equations of A and B, i.e. Eqs. (19)–(21), without making any approximation for the reaction rate, $r = kC_A^m C_B^n$ and neglecting accumulation of A in the liquid bulk, i.e. using Eq. (39). Given values of the set $(\Omega, \kappa, Bi, m, n)$, the procedure employed was based on sweeping variable $\gamma$ to find the maximum value of the relative error modulus. This maximum modulus is denoted by $|e_\gamma|$ and the corresponding error by $e_\gamma$. As the approximation guarantees exact values for $\gamma \to 0$ and $\gamma \to \infty$, $|e_\gamma|$ takes place for some intermediate value of $\gamma$.

In general, the ranges $\Omega \geq 1$, $Bi > 0$, $\kappa \geq 1$, $0 \leq m \leq 2$, $0 \leq n \leq 2$ have been explored.

Since low values of $m$ are relevant for determining the largest level of errors, it can be worth explaining how the present formulation can be modified to evaluate $\phi^T$ just for $m = 0$ and/or $n = 0$. We should note that a zero order reaction is actually a step function of a given reactant concentration (say $C_A$) and, hence, it can take any value from 0 to 1 when $C_A \to 0$.

When $n = 0$, the procedure is simple: $C_{BL}^n$ and $C_{Bi}^{*n/2}$ are replaced by 1 and $\phi^T$ is evaluated. If $\phi^T \leq 1 + \Omega$, the value is accepted. Otherwise, $\phi^T = 1 + \Omega$ should be adopted. This procedure is valid for Eqs. (36) and (41) and also for Eq. (T2.2) (when $C_{AL} = 0$ is fixed).

When $m = 0$, if $C_{AL} = 0$ has been fixed, Eq. (T2.2) can be solved without further care.

When using Eqs. (36) and (41) with $m = 0$, the limiting case $\kappa = 1$ presents no trouble. In this case $C_{AL}^*$ can be easily eliminated between both equations and the following expression arises for evaluating $\phi^T$:

$$(m = 0, \kappa = 1) : \phi^T = \Xi(\gamma\sqrt{2}/\sqrt{C_{Ai}^*}) \tanh^2(\gamma/\sqrt{C_{Ai}^*}) C_{Ai}^* C_{Bi}^{*n/2} \tag{57}$$

When $\kappa > 1$ and $m = 0$, Eqs. (36) and (41) can be solved for $\phi^T$ and $C_{AL}$ by taking $C_{AL}^m = 1$ in the right hand side of Eq. (41). If $C_{AL} \geq 0$ results, the evaluation is accepted. Otherwise, $C_{AL} = 0$ is fixed and Eq. (36) is solved to obtain the final value of $\phi^T$.

## 8.1. Precision of Eq. (T2.2)

The precision of Eq. (T2.2) has been evaluated by Yeramian et al. (1970) for values $\Omega > 2$ and $Bi \to \infty$. We have extended the evaluation up to the lower limit $\Omega = 1$ and finite values of $Bi$. The more significant errors are found in regime IV when $m \neq 1$ and for the case defined previously as regime IV/VI. On the other hand, errors are definitely low in regime VI, typically 1–2%, and no error is introduced in regimes V and VII. The global maximum of $|e_\gamma|$ for Eq. (T2.2) corresponds to $e_\gamma\% = -7.8$ in regime IV/VI: $\gamma \approx 1.7$, $\Omega = 1$, $m = n = 2$ and $Bi \to \infty$. Also, a significant local maximum is found in regime IV: $e_\gamma\% = 6.6$ at $\gamma \approx 0.91$, $\Omega \to \infty$, $m = 0$ and $Bi \approx 3.4$.

It is recalled that in writing Eq. (T2.2) the terms $C_{Bi}^{*n/2}$ and $C_{Ai}^{*(m-1)/2}$ were removed from the argument of tanh in function $\Xi$ (modification (b) in Sections 3.1 and 5.2). The removal of the former was performed to gain precision in regime VIII (see Section 8.2), while the latter was removed to obtain a more conceptual formulation showing separate effects of the different mechanisms acting in the liquid and gas films (Section 5). It is interesting to discuss what happens if these terms are restored in the argument of tanh for the present case of fast reactions. The following expression is obtained for $\phi^T$:

$$\phi^T = \Xi(M\gamma C_{Ai}^{*(m-1)/2} C_{Bi}^{*n/2}) C_{Ai}^*. \tag{58}$$

Expression (58) for $C_{Ai}^* = 1$, $\phi^T = \Xi[M\gamma(C_{Bi}^*)^{n/2}]$, was first proposed by Hikita and Asai (1964). On one hand, Eq. (58) exactly accounts for the effect of the gas film resistance (i.e. the effect of $Bi$). However, in this sense, differences with respect to Eq. (T2.2) of no more than around 2% are found when $m \neq 1$, and they are confined to a certain range of $Bi$ (depending on $m$) around 1. Slightly more relevant is the effect of keeping $C_{Bi}^{*n/2}$ in the argument of function $\Xi$, as Eq. (58) is about 3% more precise than Eq. (T2.2) in regime IV/VI. The maximum $|e_\gamma|$ for the approximation expressed by Eq. (58) is $e_\gamma\% = 6.13$, and takes place in regime IV at $\gamma = 1$ for $m = 0$, $\Omega \to \infty$ and $Bi \to \infty$. It was already reported by Hikita and Asai (1964).

## 8.2. Precision of Eqs. (36) and (41) in regime VIII

Finite $Bi$ numbers involve that the gas-side mass transfer resistance will have a share of the overall process control. As no simplification was made to account for the effect of $Bi$ in Eqs. (36) and (41), it can be expected that this formulation will become more precise as $Bi$ decreases. In fact, it can be demonstrated that a maximum value $|e_\gamma|$ will result when $Bi \to \infty$, provided that $m \geq 0$ and that the modulus $|e_\gamma|$ for $Bi \to \infty$ is sufficiently smaller than the unity (as effectively happens). Then, $Bi \to \infty$ will be assumed in this section to assess the precision of Eqs. (36) and (41) in regime VIII.

If we consider $\kappa = 1$ (i.e. $\mathcal{N}_{A\delta} = 0$ from Eqs. (37) and (41)) and $\Omega \to \infty$, chemical absorption of A becomes the same as the problem of catalytic reaction of A in a slab of half-thickness equal to the liquid film thickness. Most frequently in textbooks, the evaluation of the effective reaction rate of the catalytic reaction (or the *effectiveness factor*) is approximated by using the so-called generalized Thiele modulus (see e.g. Froment et al., 2011) along with the solution for a first order reaction. This approach is completely similar to the linearization of the reaction rate expression made here, Eq. (23), as regards reactant A. It is known that the precision of such approximation deteriorates at low orders $m$. The maximum

error for the effectiveness factor in a catalytic slab arises for $m = 0$ and amounts $-18.3\%$.

In terms of our problem here, the error $e_\gamma\% = -18.3$ takes place for $\Omega \to \infty$, $\kappa = 1$ and $m = 0$ at $\gamma = \sqrt{2} \approx 1.41$. At this value of $\gamma$, $C_{AL} = 0$ is just reached at the end of the liquid film. A plot of the true $\phi^T$ against $\gamma$ presents the slope broken at $\gamma = \sqrt{2}$. Linearization, on the contrary, produces a smooth profile.

Comparing the maximum errors at $m = 0$ and $(\Omega, Bi) \to \infty$ obtained for $\kappa = 1$, $e_\gamma\% = -18.3$, with that for $\kappa \to \infty$, which using Eq. (58) is $e_\gamma\% = 6.13$ (in regime IV), it can be concluded that linearization of the term $C_A^m$ in the reaction rate expression introduces larger errors as $C_{AL}$ increases, recalling that $\kappa = 1$ (i.e. $\mathcal{N}_{A\delta} = 0$) implies a maximum value of $C_{AL}$, as opposed to $C_{AL} = 0$ when $\kappa \to \infty$ (maximum $\mathcal{N}_{A\delta}$).

Clearly, for regime VIII the maximum $|e_\gamma|$ will be at least of 18.3%. To identify the actual maximum, we investigated cases when $C_{Bi}^* < 1$ (i.e. finite values of $\Omega$), different values of order $n$ and also values $m > 0$, because of possible interaction between effects. For given values of the set $(\Omega, n, m)$, the effect of $\kappa$ was neat: the higher the value of $\kappa$ the lower $|e_\gamma|$.

The maximum of $\left|e_\gamma\right|$ was found for $m = 0$, $n = 1/2$, $\Omega = \kappa = 1$: $e_\gamma = -21\%$ at $\gamma \approx 1.6$ (note that this error is not far from the value $-18.3\%$ for $\Omega \to \infty$). On the other hand, high reaction orders introduce positive errors, the maximum of which was found for $\Omega = 1$, $m = n = 2$ and $\kappa = 1$: $e_\gamma = 17.7\%$ at $\gamma \approx 1.5$.

Both, negative and (in particular) positive errors $e_\gamma$ decrease in modulus fairly rapid as $\kappa$ increases. Then, it is interesting to find out if restricting the value of $\kappa$ in some extent can restore the level of errors obtained when $\kappa \to \infty$, i.e. $C_{AL} = 0$ (we recall that $e_\gamma = -7.8\%$ corresponded to the maximum modulus quoted in Section 8.1 for approximation T2.2). Order $m = 0$ imposes the minimum value of $\kappa$, which should be larger than about 6 for that purpose. A probable more useful way of bounding the errors is by simultaneously restricting the value of $m$. Thus, restraining $\kappa$ and $m$ in the way $\kappa \geq 2$ and $m \geq 0.2$ allows $|e_\gamma|$ to keep below 7.5% in regime VIII, irrespective of values of $\Omega$ and $n$.

Altogether, it can be concluded that precision provided by Eqs. (36) and (41) in general and by expressions in Table 2 in particular, is quite satisfactory, especially as a confident tool for teaching purposes.

When accumulation of A in the liquid stream is to be considered, $C_{AL}$ will be determined by including the mass balance equation of A in the liquid stream (Section 3.2). The value of $C_{AL}$ will be most frequently lower than that evaluated from neglecting the accumulation of A (i.e. using Eq. (41)), since the liquid stream acts as an additional sink for A, other than chemical reaction. Recalling the discussion at the beginning of this section about the effect of $C_{AL}$ on errors, it can be expected that $|e_\gamma|$ when using Eqs. (36) and (37) will be lower than for Eqs. (36) and (41). This has been proved to be true for a number of cases, although an exhaustive analysis was not carried out.

When $C_{Bi}^{*n/2}$ is maintained in the argument of the tanh in function $\Xi$ (recall modification (b) in Section 3.1), the maximum $|e_\gamma|$ for the critical value $m = 0$ is similar to those from Eqs. (36) and (41): $e_\gamma = -19\%$ at $\gamma \approx 1.6$, for $n = 1/2$ and $\Omega = \kappa = 1$. However, also at low $\kappa$ and $\Omega$ values, $|e_\gamma|$ increases strongly as $m$ and $n$ increase. The maximum identified error was $e_\gamma = 33\%$ at $\gamma \approx 1.5$ for $\Omega = \kappa = 1$, $m = n = 2$. This was the reason for removing $C_{Bi}^{*n/2}$ from the argument of function $\Xi$ in Eqs. (36), (37) and (41) (modification (b) in Section 3.1).

Finally, it is recalled that $C_{Bi}^{*n/2}$ was also removed from the argument of cosh in Eq. (34) (modification (a) in Section 3.1).

Errors when $C_{Bi}^{*n/2}$ is maintained in the arguments of both functions, $\Xi$ and cosh, have been also evaluated. Very high errors for low orders $m$ arise. The maximum $|e_\gamma|$ detected corresponds to $e_\gamma = -43\%$ at $\gamma \approx 1.9$, for $m = 0$, $n = 1$, $\Omega = 1$ and $\kappa = 1$. In part, the large errors are due to the fact that maintaining $C_{Bi}^{*n/2}$ in the argument of cosh avoids obtaining for $\kappa = 1$ the right asymptote $\phi^T = 1 + \Omega$ as $\gamma \to \infty$. For example, for $\Omega = 1$, the asymptote is 1.67 irrespective of orders $m$ and $n$.

In order to summarize the reasons for modification (a) in Section 3.1, we recall that the term $\cosh(M\gamma C_{Ai}^{*(m-1)/2} C_{Bi}^{*n/2})$ in Eq. (34) was replaced by $\cosh(\gamma C_{Ai}^{*(m-1)/2})$, a modification that allows obtaining a consistent approximation for $\phi^T$ at the extremes values $\gamma \to 0$ and $\gamma \to \infty$ for any value of the parameters ($\kappa$, $\Omega$, $Bi$, $m$, $n$). Thus, removal of $M$ leads to the right expression (48) as $\gamma \to 0$ (Section 5.1) and removal of $C_{Bi}^{*n/2}$ allows obtaining $\phi^T \to (1 + \Omega)$ as $\gamma \to \infty$, as discussed just above.

## 9. Test for validation of negligible accumulation of A in the liquid stream

The assumption of negligible accumulation of A in the liquid stream (hereafter referred in short as "the assumption") can be checked *a posteriori* of employing the general formulation, Eqs. (36) and (41), for solving the mass conservation equations in a given contactor. This task will be required when most of the operation is conducted in regimes in which $C_{AL} \neq 0$, i.e. regimes I, II or VIII.

For assessing the assumption, we will consider the global amount of A chemically converted. As using Eqs. (36) and (41) implies that at a local level the amount of A transferred to the liquid reacts chemically, the same will happen in the whole reactor. Then, if $R_A$ is the number of moles of A converted *per unit* time within the whole reactor volume, the assumption implies that $R_A = F_{A0} - F_{AS}$, where $F_{A0}$ and $F_{AS}$ are the molar flow rates of A in the inlet and outlet gas streams. We will fix 5% as a suitable level of tolerance in the estimation of $R_A$.

From the evaluation of the reactor operation using the assumption, a value for the concentration of A in the exit liquid stream, $C_{AL,S}$, will be available either from Eq. (41) or Eq. (47). Although in general this is not the actual value, if the assumption works correctly the molar flow rate of A in the exit liquid stream can be estimated as $q_L C_{AL,S}$, where $q_L$ is the volumetric liquid flow. Defining

$$\tau_Q = \frac{F_{A0} - F_{AS}}{q_L C_{AL,S}}, \tag{59}$$

it seems reasonable to set as a criterion for accepting the assumption that

$$\tau_Q \geq 20. \tag{60}$$

Actually, Eq. (60) behaves most of the times as a sufficient condition (we will discuss later on an exception), but it turns to be too stringent. To visualize why, we can consider the case of a slow reaction, regime I, carried out in a contactor that presents a large number of physical mass transfer units with respect to the liquid phase,

$$\tau_L = \frac{a k_A^T V}{q_L} \tag{61}$$

where $V$ is the total volume of the contactor.

As $\tau_L$ is assumed to be large and chemical reaction slow, in most of the contactor the liquid stream will be nearly saturated with $A$, i.e. $C_{AL} \cong C_{AG}$ will locally apply, as the extent of the contactor needed to increase $C_{AL}$ from zero (in the liquid feed) to the saturation value will be negligible respect to the total volume. Then, the correct local reaction rate per unit volume of contactor can be estimated as $(\varepsilon k C_{AG}^m C_{BL}^n)$; i.e. the same as evaluated from the assumption of negligible accumulation. Consequently, $\tau_Q$ (evaluated from Eq. (59)) will be small (much less than 20), but $R_A$ correctly evaluated. From this example, it seems clear that both $\tau_Q$ and $\tau_L$ play some role in assessing if the assumption is correct or not.

If the way in which $\tau_Q$ and $\tau_L$ interact is found out, it will be possible to correct the basic criterion expressed by Eq. (60). To this end, we have considered a very simple case consisting in a slow reaction (regimes I–III), reactant $B$ in large excess ($C_{B0} = C_{BS}$), liquid feed without reactant $A$, reaction order $m = 1$ and perfect mixing assumed in the gas and liquid phases. The mass balances for $A$ in both phases, accounting for the accumulation of $A$ in the liquid stream, are

$$\text{gas stream}: q_G(C_{AG,0} - C_{AG,S}) = Vak_A^T(C_{AG,S} - C_{AL,S}), \qquad (62)$$

$$\text{liquid stream}: q_L C_{AL,S} = Vak_A^T \left[ (C_{AG,S} - C_{AL,S}) - \frac{1+Bi}{Bi} \kappa\gamma^2 C_{AL,S} \right] \qquad (63)$$

The volumetric flow rates $q_L$ and $q_G$ of both phases are assumed to be independent of mass transfer and reaction rates. In the gas phase, a pseudo-liquid volumetric flow rate has been used, $q_G = F_{A0}/C_{AG,0}$ (i.e. the hypothetical volumetric liquid flow rate that can convey the inlet molar flow rate $F_{A0}$ at concentration $C_{AG,0}$).

When the accumulation of $A$ in the liquid phase is neglected, Eq. (62) still holds and the right hand side of Eq. (63) is set to zero. In either case, the solution for $C_{AL,S}$ and $C_{AG,S}$ is very simple, as the assumptions made lead to a linear problem for $C_{AL,S}$ and $C_{AG,S}$. It is obtained for $C_{AL,S}$

$$C_{AL,S} = \frac{C_{AG,0}}{1 + \left[ ((1+Bi)/Bi)\kappa\gamma^2 + 1/\tau_L \right] (1+\tau_G)}$$

(considering accumulation) $\qquad (64a)$

$$C_{AL,S} = \frac{C_{AG,0}}{1 + \left[ ((1+Bi)/Bi)\kappa\gamma^2(1+\tau_G) \right]}$$

(neglecting accumulation) $\qquad (64b)$

where the number of physical mass transfer units with respect to the gas phase is defined as

$$\tau_G = \frac{ak_A^T V}{q_G} \qquad (65)$$

In this example, it can be expressed $R_A = ((1+Bi)/Bi)\kappa\gamma^2 Vak_A{}^T C_{AL,S}$. Using Eqs. (64a) and (64b) and denoting $(R_A)_{corr}$ the number of moles of $A$ converted *per unit* time when the accumulation of $A$ is accounted for, it is obtained

$$(R_A)_{corr} = R_A \left( \frac{\tau_Q + \Delta}{\tau_Q + \Delta + 1} \right), \qquad (66)$$

where $\tau_Q$ is evaluated from Eq. (59) using the properties calculated with the assumption, which in the present case results $\tau_Q = ((1+Bi)/Bi)\kappa\gamma^2\tau_L$, and $\Delta$ is defined as

$$\Delta = \frac{\tau_L}{1 + \tau_G}. \qquad (67)$$

It follows from Eq. (66) that for $R_A$ to differ from $(R_A)_{corr}$ in no more than 5%,

$$\tau_Q + \Delta \geq 20. \qquad (68)$$

Eq. (68) is the modified criterion for the specific case dealt with above, which as expected includes both parameters $\tau_Q$ and $\tau_L$, but also adds the effect of $\tau_G$. Actually, it can be reasoned that if $\tau_G$ is large, composition in the gas phase will rapidly change and will retard the saturation of the liquid stream.

A similar analysis, i.e. subject to a linear system, can be made for other type of contactors. However, if the plug flow is appropriate for both streams, as in the case of a packed tower, the relationship involving the set of parameters ($\tau_Q$, $\tau_L$ and $\tau_G$) to keep valid the assumption is substantially more complicated than Eq. (68), and it will depend on whether the gas and liquid streams are counter or co-current. Combining plug flow and perfect mixing for each stream also introduces specific relationships. In this way, a catalogue of restrictions would be obtained, depending on the specific flow model of the contactor. Note also that any analytical criterion derivable for the different combination of flow models is only possible for a linear system, excluding the chance of accounting for non-linear features, as when $m \neq 1$ and/or $C_{BL}$ is variable.

Therefore, for any type of contactor we propose employing Eq. (68) as a criterion for accepting the assumption of neglecting accumulation of $A$ in the liquid stream, with $\tau_Q$, $\tau_L$, $\tau_G$ and $\Delta$ evaluated from Eqs. (59), (61), (65) and (67). Besides, the use of Eq. (66) to correct $R_A$ and obtain an improved estimation $(R_A)_{corr}$ is suggested.

To check the criterion expressed by Eq. (68), a long list of variables arises, which concerns the types of gas and liquid flows in the contactor, conditions of the gas and liquid inlet streams and all parameters that define $\phi^T$.

We have not made a fully systematic test for Eq. (68), i.e. including every combination of variables, but a number of evaluations have been performed to investigate the following effects:

- *regarding flow pattern*: plug flow in both streams (co and countercurrent cases), plug flow in the liquid and perfect mixing in the gas, perfect mixing in both phases in either continuous operation or fed-batch operation (liquid batch/continuous gas feeding);
- *regarding feed conditions*: different $C_{B0}$ (concentration of B at the liquid feed) to span conditions from stoichiometric defect up to a large excess of B, and different values of the ratio $q_G/q_L$;
- *regarding parameters affecting $\phi^T$*: transport and reaction parameters [$\kappa$, $\gamma_r$ (a reference value for $\gamma$), $m$, $n$, Bi] leading to regimes I, II, VIII.

The co-current and counter-current operations were analyzed more intensively. The tests were mostly conducted in the following way. Once conditions for a given problem

were defined, each set of equations including and neglecting accumulation of $A$ in the liquid stream was solved for a size of the contactor such that $\tau_Q + \Delta = 20$ when neglecting accumulation. Then, $R_A$ (using the assumption) was evaluated, corrected according to Eq. (66) and the relative error with respect to the actual value considering accumulation was evaluated.

The main conclusions are listed below.

- Values of $C_{B0}$, Bi and reaction orders $m$, $n$ were not found to have a significant impact on the level of error introduced by the assumption.
- For countercurrent operation in particular, and in general for the remaining types of contactors, except co-current operation, the errors were considerable lower than 5% (for the largest part, because of correction given by Eq. (66)) and in many instances of about 1%.
- The maximum errors arose for regime I, low values of $q_G/q_L$ and co-current operation. Actually, in some instances, the error exceeded significantly 5%. To account for this discrepancy, it is required that in addition to Eq. (68) it should be verified for co-current operation and regime I that:

$$\frac{q_G}{q_L} = \frac{\tau_L}{\tau_G} \geq 3. \tag{69}$$

The numerical comparison carried out reveals that criterion expressed by Eq. (68) (along with Eq. (69) for co-current operation) is safe to check the assumption; however, instances have been detected when in spite of Eq. (68) or (69) not being fulfilled, the assumption leads to small errors. For example, for co-current operation and very low reaction rates, errors less than 5% after employing the correction in Eq. (66) arise, even for $(\tau_Q + \Delta)$ as low as 2–4.

We recall that neglecting accumulation of $A$ in the liquid stream brings some important advantages for an introduction to GLRs, mainly because all possible regimes can be described as a continuous sequence from very low to very fast reactions. The fact that the assumption can also be realistic when the operation of gas–liquid contactors is analyzed, including very slow reactions, and that a simple tool (as defined by Eqs. (68) and (69)) is available to test its validity, provides a strong support for adopting the assumption.

## 10. Extension to other irreversible kinetics

The treatment carried out throughout this contribution for irreversible power-law kinetics can be generalized for other types of irreversible reactions.

Approximations for reversible rate expressions have been proposed, although they need further considerations than for irreversible kinetics. For the film model, a classical approximation is that of Onda et al. (1970), but it has been found to be inconsistent for an important number of cases (see *e.g.* van Swaaij and Versteeg, 1992).

The treatment in this section includes cases in which more than one non-volatile liquid species participate in the reaction with $A$. For example, we can consider the reaction $A + bB + dD \rightarrow$ products, where $B$ and $D$ are non-volatile. At a given point in the contactor, assume that out of $B$ and $D$ the limiting reactant in the liquid film is $B$ (the one with the minimum value of $D_{jL}C_{jL}/(-\alpha_J)$). A stoichiometric relation between

the fluxes of $B$ and $D$ will hold within the liquid film. In terms of molar concentrations, it can be written as:

$$C_D = C_{DL} + \left(\frac{d}{b}\right)\left(\frac{D_{BL}}{D_{DL}}\right)(C_B - C_{BL}). \tag{70}$$

For a reaction rate expression of the form $r = r(C_A, C_B, C_D)$, replacing $C_D$ from Eq. (70) allows expressing $r$ in the liquid film as dependent only on $C_A$ and $C_B$, $r = r(C_A, C_B)$. The same result will follow for any number of non-volatile liquid reactants.

As for power-law kinetics, the general expression $r = r(C_A, C_B)$ should be linearized to solve analytically the conservation equations in the liquid film. Using the auxiliary function

$$u(C_{Ai}, C_B) = \frac{2\int_0^{C_{Ai}} r(C_A, C_B)dC_A}{C_{Ai}^2}, \tag{71}$$

the expression equivalent to Eq. (23) is $r \cong u(C_{Ai}, C_{Bi})C_A$, for which restriction of Eq. (24) also applies.

Following similar steps as in Section 3.1, including corrections (a) and (b) for passing from Eq. (34) to Eq. (35), the formulation corresponding to Eqs. (36), (37) and (41) is obtained:

$$\phi^T = \frac{\Gamma_{ii}}{\tanh(\Gamma_{iL})}\left[C_{Ai}^* - \frac{C_{AL}^*}{\cosh(\gamma_{iL})}\right] \tag{72}$$

$$\frac{\mathcal{N}_{A\delta}}{k_A C_{Ai}^0} = \frac{\Gamma_{ii}}{\tanh(\Gamma_{iL})}\left[\frac{C_{Ai}^*}{\cosh(\gamma_{iL})} - C_{AL}^*\right] = (\kappa - 1)\gamma_{LL}^2 C_{AL}^* \tag{73}$$

where the first equality in Eq. (73) is equivalent to Eq. (37) and the second one to Eq. (41). The parameters introduced in Eqs. (72) and (73) are defined as

$$\Gamma_{ii}^2 = \frac{D_{AL}u(C_{Ai}, C_{Bi})}{k_A^2}, \tag{74a}$$

$$\Gamma_{iL}^2 = \frac{D_{AL}u(C_{Ai}, C_{BL})}{k_A^2} \tag{74b}$$

$$\gamma_{iL}^2 = \frac{D_{AL}r(C_{Ai}, C_{BL})}{k_A^2 C_{Ai}}, \tag{75a}$$

$$\gamma_{LL}^2 = \frac{D_{AL}r(C_{AL}, C_{BL})}{k_A^2 C_{AL}} \tag{75b}$$

For Eqs. (74) and (75), $C_{Bi}$ and $C_{Ai}$ are expressed from Eqs. (26) and (30) and all dimensionless concentrations are defined as in Section 3.

Precision obtained from employing Eqs. (72) and (73) is expected to be similar to that for power-law kinetics, provided that a normal kinetic behaviour holds for expression $r = r(C_A, C_B)$, *i.e.* that the effective reaction orders, $\partial \ln(r)/\partial \ln(C_A)$ and $\partial \ln(r)/\partial \ln(C_B)$ are positive for the range of concentrations $C_A$ and $C_B$ of interest ($0 < C_A < C_{AG}, 0 < C_B < C_{BL}$).

It should be emphasized that the same regimes in the liquid phase described for power law expressions can be identified for the general kinetic expression $r = r(C_A, C_B)$. Also, it is not difficult to assign to each regime the corresponding expression for $\phi^T$ from the general Eqs. (72) and (73), by making a similar analysis as for power law expressions. However, two important distinct aspects arise.

First, the specific expressions for $\phi^T$ will be, in general, significantly more difficult to interpret. Note, in this respect, that

although Eqs. (72) and (73) are written in a relatively compact way, they involve four Hatta numbers ($\Gamma_{ii}, \Gamma_{iL}, \gamma_{iL}, \gamma_{LL}$) that can not be related to each other in a general manner. Instead, only a single Hatta number ($\gamma$) was enough for power law expressions.

Second, the precise restrictions which *a priori* define the different regimes will not be those given in Table 2 (and the more specific ones discussed in Sections 5 and 6). A set of restrictions could be written for each type of kinetic expression, but it can be foreseen that they will be frequently difficult to derive and use.

It can be concluded that a general type of kinetic expression strongly impairs the possibility to describe the physical situations and corresponding quantitative analysis within a didactically appropriate frame, as allowed by power law expressions.

## 11.  Conclusions

The approximated formulation proposed in this contribution on the basis of the two-film model is basically given by Eqs. (36) and (37). They allowed expressing the total flux $\mathcal{N}_{Ai}$ of reactant $A$ absorbed with chemical reaction and the residual flux $\mathcal{N}_{A\delta}$ reaching the bulk of the liquid stream. The concept of a global enhancement factor (GEF) $\phi^T$ was used for expressing the flux $\mathcal{N}_{Ai}$. The initial step for obtaining Eqs. (36) and (37) is the linearization of the generic power-law rate expression (Eq. (23)), following the approach of Hikita and Asai (1964) when the concentration of $A$ in the liquid bulk is nil, $C_{AL} = 0$. However, for a general description including low values of the Hinterland ratio $\kappa$ in the general case with $C_{AL} \neq 0$ (*i.e.* when relatively slow reactions are involved), the linearization approach should be modified in order to obtain a formulation consistent with the true behaviour at very low and very high Hatta numbers. This was easily achieved by introducing modification (a) explained in Section 3.1. A second modification (b) was also included to gain in overall precision.

Eqs. (36) and (37) incorporates the effects of all processes on the rate of absorption with chemical reaction, including the gas side resistance. A conceptual purpose of the proposed formulation is to describe the specific regimes that arise according to the relative magnitudes of the effects, and associate to each of them an expression of $\phi^T$. This goal is further facilitated by the assumption of negligible accumulation of $A$ in the liquid stream, which allows introducing the Hinterland ratio $\kappa$ as a parameter, while eliminating the concentration $C_{AL}$ as an input variable. This modification leads to replace Eq. (37) by Eq. (41).

In this way, eight regimes associated with the liquid side have been identified and conveniently described as the Hatta number is varied from very low to very large values. Each of them can be associated to a specific expression for $\phi^T$ (Table 2). Sections 4–7 provide a way to undertake such description. Some details given there for the sake of completeness can be surely avoided in actual teaching practice and some different strategies can also be appropriated for the same purpose.

The precision of the proposed approximated formulation was evaluated in Section 8. The maximum level of errors is associated with very low values of $\kappa$, reaching around 20% for reaction order $m = 0$. This level is regarded as being tolerable, especially as a didactic tool, for an approximation describing simultaneously the effects of six dimensionless parameters. On the other hand, errors rapidly diminish when

order $m$ and parameter $\kappa$ are raised slightly above 0 and 1, respectively.

A criterion is presented in Section 9 for accepting the assumption of negligible accumulation of $A$ in the liquid. The analysis was based on the overall behaviour of gas–liquid contactors. The criterion is simple and a corrective expression is also proposed. The criterion was tested for a very large set of conditions. No instance in which the criterion was satisfied while the assumption was proved to be incorrect was found. Also, it was concluded that the assumption is suitable for a large variety of cases, including very slow reactions. The significance of the results described in Section 9 is that the assumption does not only provide a proper frame for describing the features of GLRs, but it is also a good approximation for evaluating the performance of gas–liquid contactors.

Finally, an extension to a more general type of irreversible kinetics is discussed in Section 10.

## Acknowledgements

## Appendix.

### *A numerical example of regime identification and calculation of GEF and interfacial flux*

Assume the kinetics of the liquid-phase reaction between reactant $A$ from a gas stream and reactant $B$ in a liquid stream, $A_{(G)} + B_{(L)} \rightarrow$ products, has been studied in the temperature range 15–75 °C. An irreversible power-law expression is available:

$$r = k_0 \exp\left[-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] C_A^2 C_B \qquad (A1)$$

Some preliminary calculations, as defined by points (a) to (c) below, for the reference levels $p_{AG} = 1\,\text{atm}$ and $C_{BL} = 2\,\text{kmol}\,\text{m}^{-3}$, will be undertaken to evaluate the performance of a given gas–liquid contactor, for which values $\kappa = 100$ and $k_A = 8 \times 10^{-5}\,\text{m}\,\text{s}^{-1}$ were estimated. Values of kinetic parameters and physical properties are given in Table A1

(a) The operation regimes, global enhancement factors ($\phi^T$), and fluxes at the interface ($\mathcal{N}_{Ai}$) for the extremes of the given temperature range are first evaluated under the assumption of a very high value of $Bi$ (*i.e.* $Bi \rightarrow \infty$).

(b) In a second step, the mass transfer coefficient of $A$, $k_{GA}^0$, was estimated and the value of $Bi = 20$ was obtained. The calculations made in point (a) are repeated, but considering now such value of $Bi$.

(c) The same answers are required for a final case considering the reaction carried out at the middle temperature of the studied interval, $T = 45\,°C$, and $Bi = 20$ (as in point b).

Case (a) ($Bi \rightarrow \infty$)
$T = 15\,°C$

| | |
|---|---|
| $k_0 = 0.27 \, \text{kmol}^{-2} \, \text{m}^6 \, \text{s}^{-1}$ | $D_{AL} = 2 \times 10^{-9} \, \text{m}^2 \, \text{s}^{-1}$ |
| $\frac{E}{R} = 12,800 \; \text{K}$ | $D_{BL} = 1 \times 10^{-9} \, \text{m}^2 \, \text{s}^{-1}$ |
| $T_0 = 288 \, \text{K}$ | $H_A = 30 \, \text{atm} \, \text{kmol}^{-1} \, \text{m}^3$ |

From $p_{AG} = 1 \, \text{atm}$ and $H_A$ in Table A1, $C_{AG} = 3.33 \times 10^{-2}$ kmol m$^{-3}$ arises, and the reaction rate coefficient is $k = 0.27 \, \text{kmol}^{-2} \, \text{m}^6 \, \text{s}^{-1}$ at $T = 15\,^{\circ}\text{C}$ (Eq. (A1)). From Eq. (31) and considering $C_{Ai}^0 \cong C_{AG}$ ($Bi \to \infty$), $\gamma = 0.075$ is obtained. This value of $\gamma$ fulfils the restriction of Eq. (T2.1) in Table 2 ($c = 1.5$ for $m = 2$), indicating that conditions correspond to a "slow reaction". Then, with $\kappa\gamma^2 = 0.563$, it can be verified that *regimen II* holds, as none of the restrictions accompanying Eqs. (48) and (50) is satisfied. Then, $\phi^T$ is to be evaluated from Eq. (T2.1), which for $m = 2$ can be written in an explicit way:

$$\phi^T = \beta - \sqrt{\beta^2 - 1}; \beta = 1 + \frac{1}{2\kappa\gamma^2} \qquad (A2)$$

It follows that $\phi^T = 0.286$, and from Eqs. (13) and (15), $\mathcal{N}_{Ai} = 7.64 \times 10^{-7}$ kmol m$^{-2}$ s$^{-1}$.

$T = 75\,^{\circ}\text{C}$

At this temperature we obtain $k = 575 \, \text{kmol}^{-2} \, \text{m}^6 \, \text{s}^{-1}$ and $\gamma = 3.46$. The general restriction of Eq. (T2.2) is fulfilled, and a "fast reaction" case now applies. As a consequence, $\kappa$ shows no effect on $\phi^T$, but parameter $\Omega$ can. From Eq. (T1.2) and the data in Table A1, $\Omega = 30$ is obtained. As $\Omega$ is considerably larger than $\gamma$, we can try if $C_{Bi}^{*n/2}$ can be taken as 1. In effect, the restriction of Eq. (T2.4) is satisfied (note that $M = \sqrt{2/(m+1)} = 0.816$), meaning that one of the regimes III–V applies. As $(M\gamma) = 2.83 > 2$, it is concluded that *regimen V* is established with $\phi^T$ given in Eq. (52). Then $\phi^T = 2.83$ and $\mathcal{N}_{Ai} = 7.53 \times 10^{-6}$ kmol m$^{-2}$ s$^{-1}$.

Case (b): $Bi = 20$

The procedure in this case is quite similar to the case when $Bi \to \infty$, but values of $\gamma$, $\phi^T$ and $\mathcal{N}_{Ai}$, should be recalculated.

$T = 15\,^{\circ}\text{C}$

With $Bi = 20$, $C_{Ai}^0 = 3.17 \cdot 10^{-2}$ kmol m$^{-3}$ from Eq. (14). It follows that $\gamma = 0.073$, from which it is concluded again that *regimen II* holds. From Eq. (T2.1) we obtain now:

$$\phi^T = \beta - \sqrt{\beta^2 - 1}; \beta = 1 + \frac{(1 + 1/Bi)^2}{2\kappa\gamma^2} \qquad (A3)$$

Replacing the parameter values, $\phi^T = 0.294$ and $\mathcal{N}_{Ai} = 7.43 \times 10^{-7}$ kmol m$^{-2}$ s$^{-1}$.

It should be noted that although the value of $\phi^T$ for $Bi = 20$ is slightly greater than the value for $Bi \to \infty$, $\mathcal{N}_{Ai}$ is lower, consistently with the existence of an additional mass transfer resistance (*i.e.* the gas film resistance). Nonetheless, all differences show little significance at this value $Bi = 20$.

$T = 75\,^{\circ}\text{C}$

From the value $C_{Ai}^0 = 3.17 \times 10^{-2}$ kmol m$^{-3}$ calculated above, $\gamma = 3.38$ is obtained, which corresponds again to a "fast reaction" case for $T = 75\,^{\circ}\text{C}$. Thus, bearing in mind the results for $Bi \to \infty$, it seems reasonable to try if the product $[C_{Ai}^{*(m+1)/2} C_{Bi}^{*n/2}]$ can be taken as 1, according to the restriction of Eq. (T2.4). It is easily proved that such restriction is not fulfilled,

what most probably means that $Bi$ exerts a significant effect on $\phi^T$ through the factor $C_{Ai}^{*(m+1)/2}$. In fact, the restriction of Eq. (T2.3) is not satisfied either. It can be reasoned that again $\Omega = 30$ cannot constrain the value of $\phi^T$, and hence Eq. (T2.6) can be employed. This is actually verified, as the restriction of Eq. (T2.6) in Table 2 is fulfilled ($C_{Bi}^{*n/2}$ can be taken as 1). As $(M\gamma) = 2.76 > 2$, Eq. (54b) can be used to evaluate $\phi^T$, and *regimen V* applies. Evaluating $\phi^T$ iteratively from Eq. (54b), there results $\phi^T = 2.46$, and $\mathcal{N}_{Ai} = 6.25 \times 10^{-6}$ kmol m$^{-2}$ s$^{-1}$. These values are around 20% less than those for $Bi \to \infty$.

Case (c): $T = 45\,^{\circ}\text{C}$ and $Bi = 20$

At $T = 45\,^{\circ}\text{C}$ we obtain $k = 17.9 \, \text{kmol}^{-2} \, \text{m}^6 \, \text{s}^{-1}$, and $C_{Ai}^0 = 3.17 \cdot 10^{-2}$ kmol m$^{-3}$ (as in Case b). Then $\gamma = 0.596$ and $(\kappa - 1)\gamma^2 = 35.1$. These values satisfy both restrictions of Eq. (55) and hence the system corresponds to *regime VIII*. As Eq. (56) cannot be used in this case, because $m = 2$, Eqs. (36) and (41) should be employed. To simplify the calculations, we can take $C_{Bi}^{*n/2} = 1$, as it was checked in Case (b) that this assumption is correct even for a faster reaction at 75 °C. Using a nested iteration for Eqs. (36) and (41), as suggested in Section 7, the following results are obtained: $C_{AL}^* = 0.147$, $\phi^T = 0.947$, $\mathcal{N}_{Ai} = 2.41 \times 10^{-6}$ kmol m$^{-2}$ s$^{-1}$.

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