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Conjugate mass transfer to a spherical drop accompanied by a second-order chemical reaction inside the drop

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Abstract

Conjugate mass transfer between a drop and a surrounding fluid flow with second-order (inclusive the particular case – pseudo-first-order), irreversible chemical reaction in the dispersed phase has been analyzed. The dispersed phase reactant is insoluble in the continuous phase and its complete depletion is allowed. Two sphere models were considered: the rigid sphere and the fluid sphere with internal circulation. For each sphere model two hydrodynamic regimes were employed: creeping flow and moderate *Re* numbers. Slow and fast chemical reactions were analyzed. A single, constant value was considered for *Pe*, $Pe = 100$. The influence of the diffusivity ratio on the particle average concentrations, total mass transferred and enhancement factor is studied. The values obtained for the enhancement factor of the pseudo-first-order chemical reaction are compared with solutions provided by published predictive equations. The chemical reaction enhances the mass transfer rate even for values of the modified Hatta modulus smaller or considerably smaller than one. For the flow patterns and sphere models considered in this work, the enhancement factor is independent on hydrodynamics. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Conjugate; Droplet; Mass transfer

1. Introduction

The phenomena of momentum, heat and mass transport between a translating sphere and its surrounding fluid have been investigated intensively due to a wide range of industrial and scientific applications. The problem is classified as:

> "external" – if the transfer resistance is assumed negligible inside the sphere as compared to that of continuous phase;
> "internal" – if the transfer resistance is assumed negligible in the continuous phase as compared to that inside the sphere, and
> "conjugate" – if the transfer resistance in both phases is comparable to each other.

Clift et al. [1], Brauer [2], Brounshtein and Shegolev [3] and Sadhal et al. [4] review the literature in this area. In comparison with the external and internal problems, the conjugate transfer is the subject of relatively few theoretical and experimental studies. The physical conjugate mass and/or heat transfer from a sphere was studied theoretically in:

(a) [5,6] – the stagnant phases case;
(b) [7–16] – the creeping flow regime;
(c) [14,17,18] - the moderate *Re* numbers domain.

Only Kleinman and Reed [19,20] and Juncu [21–23] theoretically analyzed the conjugate transfer from a fluid sphere in the presence of a chemical reaction, from our knowledge. Kleinman and Reed [19,20] studied the mass transfer between a drop and an infinite medium where an isothermal chemical reaction takes place. The main aspect investigated is the validity of the addition rule for mass transfer resistances function of the diffusivity ratio, the distribution coefficient and the Damkoehler number. The analysis made in [20] is completed by one of its asymptotic solutions (values of the diffusivity ratio considerably greater than one) in [21]. Juncu [22]

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Nomenclature

A	dimensionless concentration of reactant initially in continuous phase, $C_{a2}/C_{a\infty}$ or $HC_{a1}/\ C_{a\infty}$
B	dimensionless concentration of reactant soluble only in the dispersed phase, C_b/C_{b0}
C	concentration
$D_{x,i}$	diffusion coefficient of species x ($x = a$ or $x = b$) in phase i
E	enhancement factor
E_C	conjugate enhancement factor
FOR	pseudo-first-order irreversible reaction
H	distribution coefficient (Henry's law constant)
Ha	modified Hatta modulus, $Ha^2 = kr_0^2 C_{b0}/D_{a,1}$
Ha'	Hatta modulus, $Ha' = \sqrt{kD_{a,1}C_{b0}}/k_L$
k	chemical reaction rate constant
k_L	mass transfer coefficient
Pe_i	Peclet number, $2Ur_0/D_{a,i}$
r	dimensionless radial distance in spherical coordinate system
r_0	radius of the sphere
Re	particle Reynolds number, $2Ur_0/\nu$
R_C	dimensionless group, $\kappa C_{a\infty}/C_{b0}$
R_D	diffusivity ratio, $D_{b,1}/D_{a,1}$
Sh_i	Sherwood number, $2k_L r_0/D_{a,i}$
SOR	second-order irreversible reaction
t	time
U	free stream velocity
z	transformed r-coordinate

Greek symbols

Φ_D	diffusivity ratio, D_{a1}/D_{a2}
κ	stoichiometric coefficient
ν	kinematic viscosity
θ	polar angle in spherical coordinate system
ρ	density
τ_i	dimensionless time, $D_{a,i}t/r_0^2$

Subscripts

a	refers to reactant A
b	refers to reactant B
0	initial condition
1	dispersed phase
2	continuous phase
∞	large distance from the sphere

analyses the conjugate heat and mass transfer between a rigid sphere and an infinite medium in the presence of a nonisothermal first-order irreversible chemical reaction. The chemical reaction takes place inside the particle. The investigation is focussed on the influence of the physical properties (thermal conductivity, volume heat capacity and diffusivity) ratios on the particle average temperature and concentration, the effectiveness factor and interphase heat and mass transfer coefficients. Conjugate mass transfer between a sphere and a surrounding fluid flow in the presence of an isothermal, first-order irreversible chemical reaction occurring either in the continuous or in the dispersed phase has been analyzed in [23]. Two sphere models, the sphere with rigid interface and the sphere with mobile interface and internal circulation, have been studied in creeping flow. The influence of the Henry number and diffusivity ratio is studied at intermediate *Pe* numbers for slow, intermediate and fast chemical reaction.

Mass transfer involving an isothermal chemical reaction inside the drop was investigated theoretically, in the framework of the internal problem, in [24–26] for different cases of a first-order reaction, and in [27,28] for a second-order reaction. It must be mentioned that Brounshtein et al. [28], for fast chemical reaction, take into consideration the mass transfer in the continuous phase by a steady macroscopic mass balance equation that describes the sphere surface boundary condition. Ruckenstein et al. [29] analyzed the mass transfer from a drop in the presence of a first-order chemical reaction. The mass transfer resistance is localized (limited) only in the continuous phase. One of the studied cases is that of binary drop with uniform concentration and chemical reaction inside the drop.

The reactive extraction from a single drop was investigated experimentally in [30–32]. The quantity employed to describe the process is the enhancement factor. Experimentally determined values of the enhancement factor are compared to those provided by the film theory.

This paper is dedicated to the study of conjugate mass transfer accompanied by chemical reaction inside the sphere. To round the analysis which began in [23], the chemical reaction is considered second-order irreversible (note that the second-order reaction was not analyzed in any of the references [19–23]; from our knowledge, this is the first study that investigates the conjugate mass transfer in the presence of a second-order, irreversible, chemical reaction). Some new results are depicted for the pseudo-first-order chemical reaction. The rigid sphere and the fluid sphere with internal circulation are analyzed in two hydrodynamics regimes: creeping flows and moderate *Re* numbers (in [23] only creeping flow was considered). Values of the modified Hatta number smaller and greater than 1 are considered. The quantities employed to express the mass transfer in the presence of chemical reactions are the sphere average concentrations, the total mass transferred and the enhancement factor. For the second-order irreversible chemical reaction, the main aspect analyzed is the influence of the diffusivity ratio on mass transfer phenomenon. For both reactions, i.e., second-order and first-order, the influence of the hydrodynamics on the enhancement of the mass transfer rate due to the presence of the chemical reaction is investigated. The enhancement of the mass transfer rate by a slow chemical reaction is one of the aspects this work is focused (in [23] this aspect is only mentioned).

2. Model equations

Consider a fluid sphere, of radius r_0, moving into an unbounded volume of another immiscible fluid. Inside the sphere takes place the second-order irreversible chemical reaction that follows the stoichiometric relation

$$A + \kappa B \rightarrow \text{ Products.} \tag{1}$$

The reactant A diffuses into the sphere from the continuous phase. The reactant B is soluble only within the dispersed phase. The heat of reaction is low enough so that heat effects are negligible and do not cause variations in any of the physical properties of the two phases (isothermal system). Also, the solutions are dilute so that the flow and diffusion equations are uncoupled. The following supplementary assumptions are also considered valid:

(i) the fluids are Newtonian;
(ii) the flows are steady, axisymmetric and laminar;
(iii) the volume of the sphere remains constant;
(iv) the induced Marangoni and surface-active agent effects are negligible.

Under these assumptions, the dimensionless mathematical model equations, expressed in spherical coordinate system (r, θ), are:

Dispersed phase mass balance equations

$$\frac{\partial A_1}{\partial \tau_1} + \frac{Pe_1}{2}\left(V_{R,1}\frac{\partial A_1}{\partial r} + \frac{V_{\theta,1}}{r}\frac{\partial A_1}{\partial \theta}\right) = \Delta A_1 - Ha^2 A_1 B, \tag{2a}$$

$$\frac{\partial B_1}{\partial \tau_1} + \frac{Pe_1}{2}\left(V_{R,1}\frac{\partial B}{\partial r} + \frac{V_{\theta,1}}{r}\frac{\partial B}{\partial \theta}\right) = R_D \Delta B - (R_C Ha^2/H) A_1 B, \tag{2b}$$

where

$$V_{R,1} = -\frac{1}{r^2 \sin\theta}\frac{\partial \Psi_1}{\partial \theta}, \quad V_{\theta,1} = \frac{1}{r \sin\theta}\frac{\partial \Psi_1}{\partial r}$$

and

$$\Delta = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial}{\partial \theta}\right).$$

Continuous phase mass balance equation

$$\frac{\partial A_2}{\partial \tau_2} + \frac{Pe_2}{2e^z}\left(V_{R,2}\frac{\partial A_2}{\partial z} + V_{\theta,2}\frac{\partial A_2}{\partial \theta}\right) = \frac{1}{e^{2z}}\left(\frac{\partial^2 A_2}{\partial z^2} + \frac{\partial A_2}{\partial z} + \frac{\partial^2 A_2}{\partial \theta^2} + \cot\theta \frac{\partial A_2}{\partial \theta}\right), \tag{2c}$$

where

$$V_{R,2} = -\frac{1}{e^{2z}\sin\theta}\frac{\partial \Psi_2}{\partial \theta}, \quad V_{\theta,2} = \frac{1}{e^{2z}\sin\theta}\frac{\partial \Psi_2}{\partial z}.$$

In Eq. (2c) the transformation $r = \exp z$ was applied. The boundary conditions to be satisfied are:

- sphere center ($r = 0$)

$$A_1, B = \text{finite}, \tag{3a}$$

- interface ($r = 1, z = 0$)

$$A_1 = A_2, \quad \frac{\Phi_D}{H}\frac{\partial A_1}{\partial r} = \frac{\partial A_2}{\partial z}, \quad \frac{\partial B}{\partial r} = 0, \tag{3b}$$

- free stream ($z = \infty$)

$$A_2 = 1.0, \tag{3c}$$

- symmetry axis ($\theta = 0, \pi$)

$$\frac{\partial A_i}{\partial \theta} = \frac{\partial B}{\partial \theta} = 0, \quad i = 1, 2. \tag{3d}$$

The initial conditions are:

$$\tau_{1(2)} = 0.0, \quad A_1 = 0.0, \quad A_2 = 1.0, \quad B = 1.0. \tag{4}$$

The mathematical model previously presented describes the conjugate mass transfer with second-order, irreversible, chemical reaction in a fluid sphere with internal circulation. In this paper there are also analyzed the rigid sphere model and the pseudo-first-order reaction. The rigid sphere mathematical model is described by the same equations with $V_{R,1} = V_{\theta,1} = 0$. The pseudo-first-order reaction mathematical model is formed by Eqs. (2a) and (2c) with $B \equiv 1$ in Eq. (2a).

3. Quantities of interest

The conjugate transfer is detailed described by the evolution of the concentration field inside and outside the sphere. However, the concentration field contains too much information to be a quantity useful for practical purposes. In practice, quantities which can describe globally and accurate the process with a minimum of information are required.

Brunson and Wellek [27] consider the total mass transferred as "the most important dependent variable for use in comparing theoretical results with experimental data or for use in designing reactor – contactors". The dimensionless total mass transferred is the geometric average of the dimensionless concentration of component A present in the sphere in the reacted and unreacted states. The relation used for the computation of the total mass transferred is [27]:

$$\overline{A} = \overline{A}_1 + (1 - \overline{B})/R_C, \tag{5}$$

where $\overline{A}_1$, $\overline{B}$ are the dimensionless average sphere concentration of the species A and B, respectively. $\overline{A}_1$, $\overline{B}$ are computed with the relations:

$$\overline{A}_1(\overline{B}) = \frac{3}{2}\int_0^1 r^2\left(\int_0^\pi A_1(B)\sin\theta\,\mathrm{d}\theta\right)\mathrm{d}r. \tag{6}$$

The dimensionless overall mass transfer coefficient is another quantity commonly used to characterize the mass transfer rate even in the presence of the chemical reaction [20,29]. Eq. (7) gives the dimensionless overall mass transfer coefficient, ($Sh_{1(2)}$ if $\Phi_D/H < (\geqslant)1$)

$$Sh_{2(1)} = \frac{\left(\frac{H}{\Phi_D}\right)\int_0^\pi \frac{\partial A_2}{\partial z}\big|_{z=0}\sin\theta\,\mathrm{d}\theta}{1 - \overline{A}_1}. \tag{7}$$

Other dimensionless mass transfer coefficients used in this work are the "internal" Sh number, Sh_{in}, and the "external" Sh number, Sh_{ex}. Sh_{in} and Sh_{ex} are calculated by the relations

$$Sh_{\mathrm{in}} = \frac{\int_0^\pi \frac{\partial A_1}{\partial r}\big|_{r=1}\sin\theta\,\mathrm{d}\theta}{\overline{A}_{1,s} - \overline{A}_1}, \tag{8}$$

$$Sh_{\mathrm{ex}} = \frac{\int_0^\pi \frac{\partial A_2}{\partial z}\big|_{z=0}\sin\theta\,\mathrm{d}\theta}{1 - \overline{A}_{1,s}}, \tag{9}$$

where $\overline{A}_{1,s}$ is the dimensionless surface average concentration of species A,

$$\overline{A}_{1,s} = \frac{1}{2}\int_0^\pi A_1|_{r=1}\sin\theta\,\mathrm{d}\theta. \tag{10}$$

Reaction (1) was probably the most studied case in reactive extraction and gas–liquid reactions. Well-known monographs in this domain are [33–35]. Using the classical mass transfer models (i.e., film, penetration, surface renewal) the goal of the studies dedicated to this subject was to work out an expression for the enhancement factor. The enhancement factor is defined as

$$E = \frac{Sh(Ha \neq 0)}{Sh(Ha = 0)}. \tag{11}$$

In this paper, the chemical reaction takes place only in the dispersed phase. For this reason, the enhancement factor, E, is calculated using the internal Sh number, Sh_{in}. For the parameter values used in this work (see Section 5), only the dynamics of the second-order reaction deserve to be analyzed. In order to have a representative graphical presentation about the influence of the chemical reaction on the overall rate of the process, a second enhancement factor, E_C, named conjugate enhancement factor, was used. E_C was computed using in relation (11) the overall Sh numbers. In order to compute the enhancement factors, only the values of the Sh numbers obtained in conjugate mass transfer were used. The time variation of E and E_C was calculated using the transient values of the conjugate Sh numbers. The asymptotic values of E were calculated using the asymptotic values of Sh_{in}. Other quantities of interest used in this paper are the average concentrations $\overline{A}_1$, $\overline{B}$, $\overline{A}$.

4. Method of solution

The mass balance equations were solved numerically. The numerical methods used in this article for solving the mass balance equations are those employed and presented in [22]. For this reason it is not necessary to repeat here all the details mentioned in [22]. The continuous phase equation was discretized on a uniform grid with equal step sizes in both radial and angular directions. Inside the sphere, a uniform mesh with unequal step sizes in the radial and angular directions was used. The parabolic multigrid algorithm solved the time dependent model. The time step was variable and changed from the start of the computation to the final stage. A particular case studied is the pseudo-first-order reaction. The pseudo-first-order reaction leads, in this case, to a real steady state solution. The mathematical model of the steady state pseudo-first-order reaction is a linear elliptic equation. This linear elliptic equation was solved by the elliptic multigrid method. In creeping flow, the Stokes velocity profiles and the Hadamard–Rybczynski velocity profiles, [1], were used. The investigation performed at moderate Re numbers needs the numerical solving of the Navier–Stokes equations in order to obtain the velocity profiles. Juncu and Mihail [36] present the algorithm used to solve the Navier–Stokes equations for the flow past a rigid sphere. The algorithm developed in [37] solves the flow past a fluid sphere with internal circulation.

To verify the computer coding, the physical transfer case, i.e., $Ha = 0$, was first simulated. The agreement with the results presented in [10,12–16] was excellent. Also, during the simulation, the average concentration of the reactant B was constant and equal to one.

All computations were performed on a HP-9000 series 715 workstation in HP FORTRAN double precision.

5. Results

We consider useful to present at the beginning of this section the reasons on which the investigation strategy of this article is based. Two sphere models, i.e., the rigid sphere and the fluid sphere with internal circulation, were analyzed. For each sphere model two hydrodynamic regimes were taken into consideration: creeping flow and moderate *Re* numbers.

The dimensionless parameters of the mathematical model equations were selected in order to investigate new possible phenomena and not to insist on easy foreseeable aspects. For each sphere model and hydrodynamic field the same parameters values were chosen.

The internal, external or conjugate problems, with or without chemical reaction, show a similar effect of the *Pe* number on the mass transfer rate. For this reason we cancel the idea of an analysis of the *Pe* numbers influence. In all computations a single, fixed value of *Pe* was used: for the rigid sphere model $Pe_2 = 100$; for the fluid sphere model $Pe_2 = 100$ if $\Phi_D \geqslant 1$ and $Pe_1 = 100$ if $\Phi_D < 1$.

The parameters R_C and R_D appear only in the mass balance equation of reactant *B*. In the framework of internal problem, Brunson and Wellek [27] and Brounshtein et al. [28] shown that the increase in R_D and the decrease in R_C reduce the consumption of reactant *B* and preserves the chemical reaction life. The same effects are expected for a conjugate problem. Some tests made confirmed these assumptions. For these reasons, the influence of R_C and R_D on the process is not analyzed.

The parameters that characterize the coupling feature of the conjugate mass transfer are the diffusivity ratio (Φ_D) and the distribution coefficient (*H*). The results obtained in [23] show that when the chemical reaction takes place inside the sphere, the influence of the distribution coefficient on the mass transfer rate is not significant. Under these conditions, without loosing the generality, we can consider the distribution coefficient equal to one, $H = 1$. The variation domain of Φ_D used in this work, $0.01 \leqslant \Phi_D \leqslant 100$, covers the cases of practical interest.

The modified Hatta number, *Ha*, defines the kinetic regime. It is well-known that a chemical reaction can be diffusion limited. The existence of a limiting value of the *Ha* number beyond which mass transfer is not further enhanced is a first interest problem with practical implications. Varying the *Ha* number usually solves this problem. In this work it was preferred to study the influence of the diffusivity ratio on the kinetic regime for a given value of the *Ha* number. The values selected correspond to the slow chemical reaction and to the fast chemical reaction. To summarize, the results presented in this section were obtained for the following sets of variable dimensionless parameters:

$$Ha^2 = 10^{-4}, 10^{-2}, 0.1, 10, 100; \quad \Phi_D \in [0.01, 100].$$

Two chemical reactions, considered boundary cases, were analyzed: (1) the second-order reaction (SOR) with pseudo-equal participation of the two reactants, i.e., $R_C = R_D = 1$, and (2) the pseudo-first-order reaction (FOR). Due to the depletion of reactant *B*, the asymptotic behavior of SOR is not interesting. For this reason, the transients of SOR are presented in this section. For FOR we present the asymptotic, steady state solutions. The results are presented distinctly for each sphere model.

5.1. Rigid sphere

The velocity profiles at moderate *Re* number were computed for $Re = 100$. The flow separation is fully developed for the flow past a rigid sphere at $Re = 100$. Thus, the flow field at moderate *Re* number is different, not only quantitatively, from the creeping flow.

From the beginning, it must be mentioned that the influence of the exterior flow field on the mass transfer rate can be considered unimportant. There are quantitative differences (relatively low) but new phenomena or qualitative changes do not occur. Figs. 1–5 show the time evolution of average sphere concentrations, total mass transferred and enhancement factors for SOR, $Ha^2 = 10$, and creeping flow. The transient evolution of the sphere average concentrations, total mass transferred and enhancement factors of SOR for $Ha^2 = 0.1$ and $Re = 100$ are plotted in Figs. 6–10. The influence of the diffusivity ratio on asymptotic steady state values of the enhancement factor, *E*, for FOR, is presented in Table 1. The first row in each cell of Table 1 shows the value of the enhancement factor in creeping flow. The second row of each cell shows the value of the enhancement factor obtained at $Re = 100$. The third row of each cell shows the value of the enhancement factor computed with the film theory relation

$$E = \frac{Ha'}{\operatorname{tgh} Ha'}, \quad Ha' = 2\frac{Ha}{Sh_{\text{in}}(Ha = 0)}. \tag{12}$$

For a (pseudo) first-order reaction the relations used to compute the enhancement factor by classical theories, i.e., film, penetration and surface renewal, lead to the same numerical value. For a second-order, the comparison made in [38] between the enhancement factors provided by a full sphere model, the boundary layer approximation [39], and the film theory leads to the same conclusion. The assumptions used in [38] correspond to the external problem.

Fig. 1(a) shows that for a fast chemical reaction and $\Phi_D \leqslant 1$ the diffusion inside the sphere controls the process. The time evolution of $\overline{A}_1$ has the same aspect as in the case of physical transfer. The increase in Φ_D delays the transfer of species *A* from the continuous phase. This

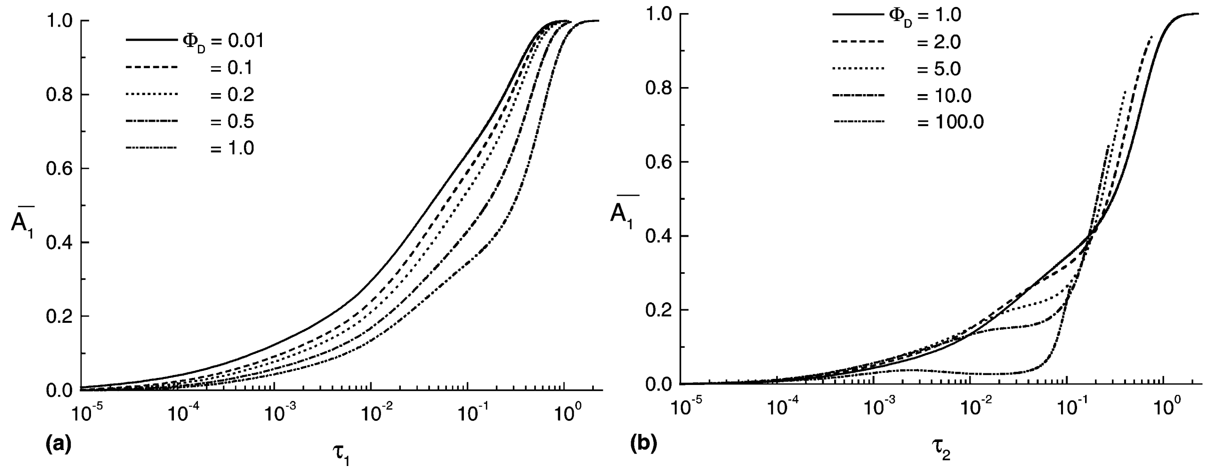

Fig. 1. Evolution of the transferring species average particle concentration at $Pe_2 = 100$, $Ha^2 = 10$ and creeping flow.

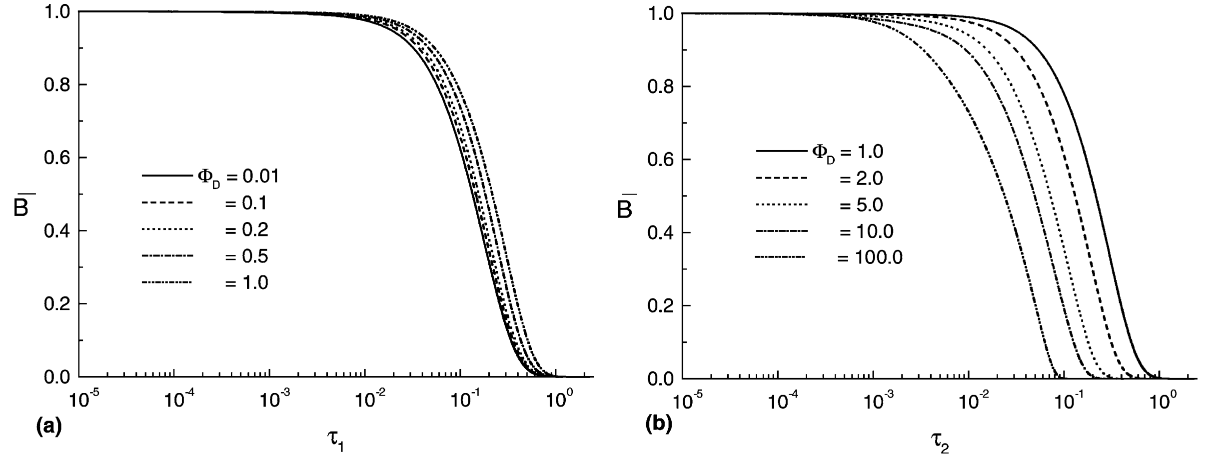

Fig. 2. Time variation of the average particle concentration of the dispersed phase reactant at $Pe_2 = 100$, $Ha^2 = 10$ and creeping flow.

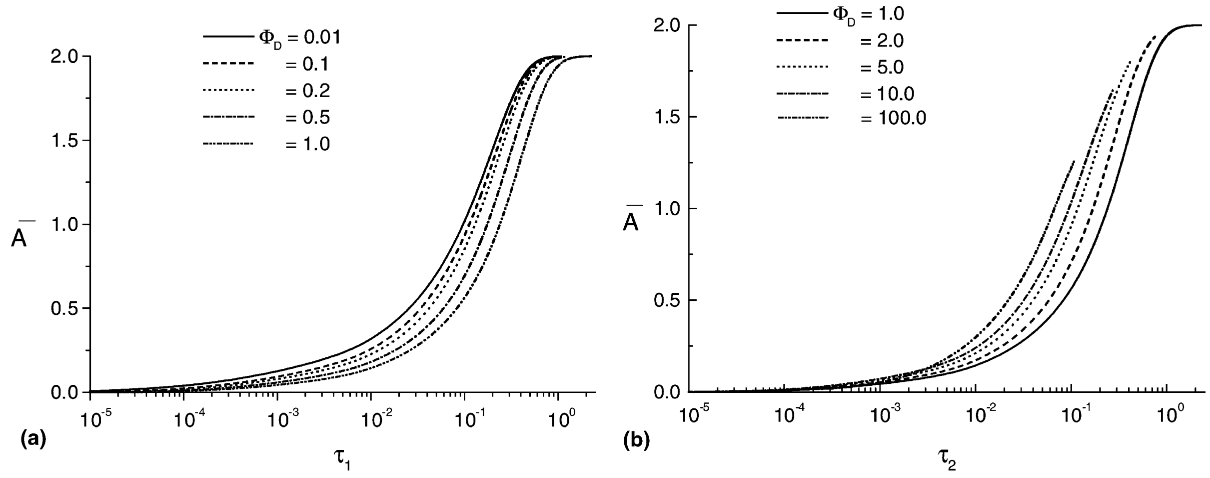

Fig. 3. Total mass transferred as a function of dimensionless time showing the effect of the diffusivity ratio at $Pe_2 = 100$, $Ha^2 = 10$ and creeping flow.

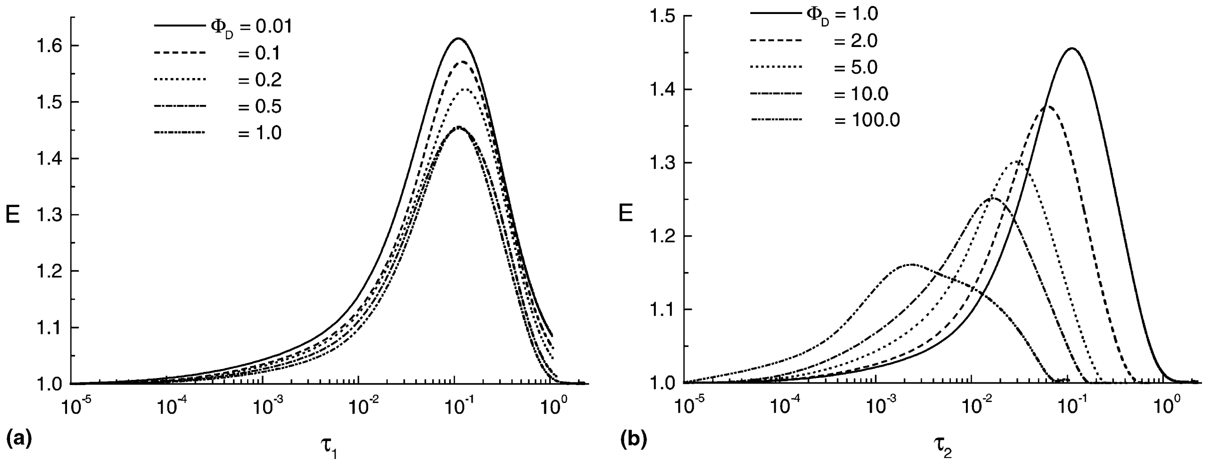

Fig. 4. Variation of E with dimensionless time at $Pe_2 = 100$, $Ha^2 = 10$ and creeping flow.

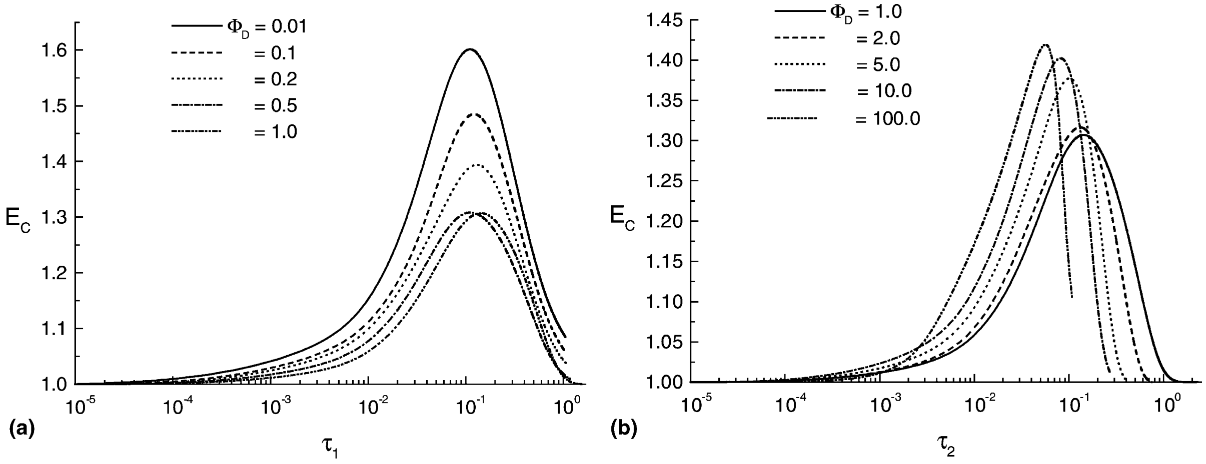

Fig. 5. Time evolution of E_C at $Pe_2 = 100$, $Ha^2 = 10$ and creeping flow.

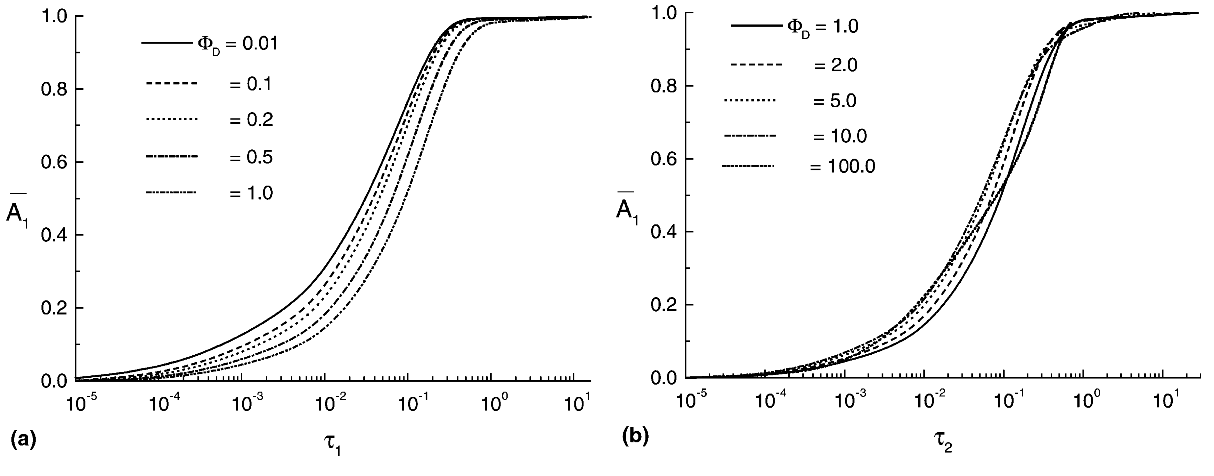

Fig. 6. Time evolution of $\overline{A}_1$ at $Pe_2 = 100$, $Ha^2 = 0.1$ and $Re = 100$.

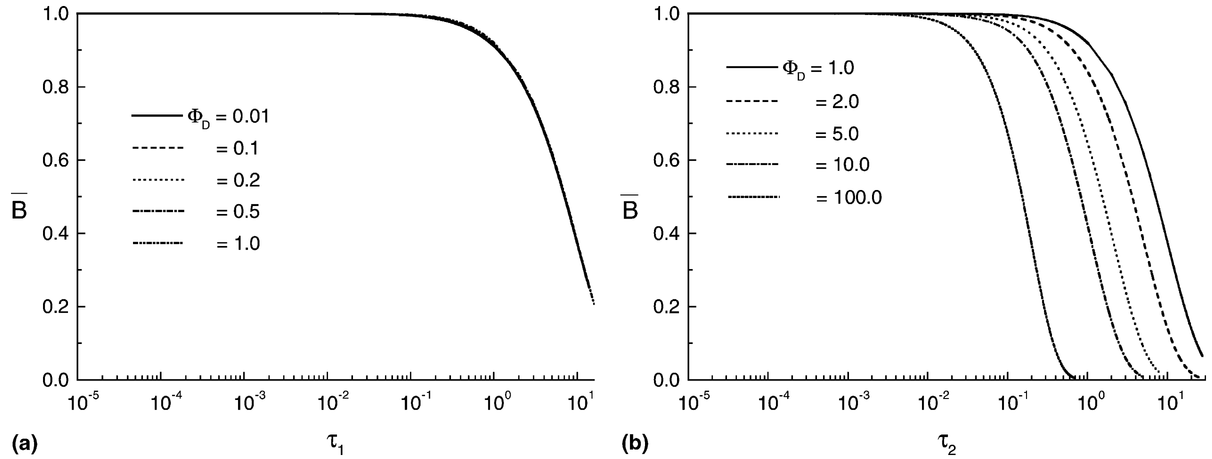

Fig. 7. Time variation of the average particle concentration of reactant B at $Pe_2 = 100$, $Ha^2 = 0.1$ and $Re = 100$.

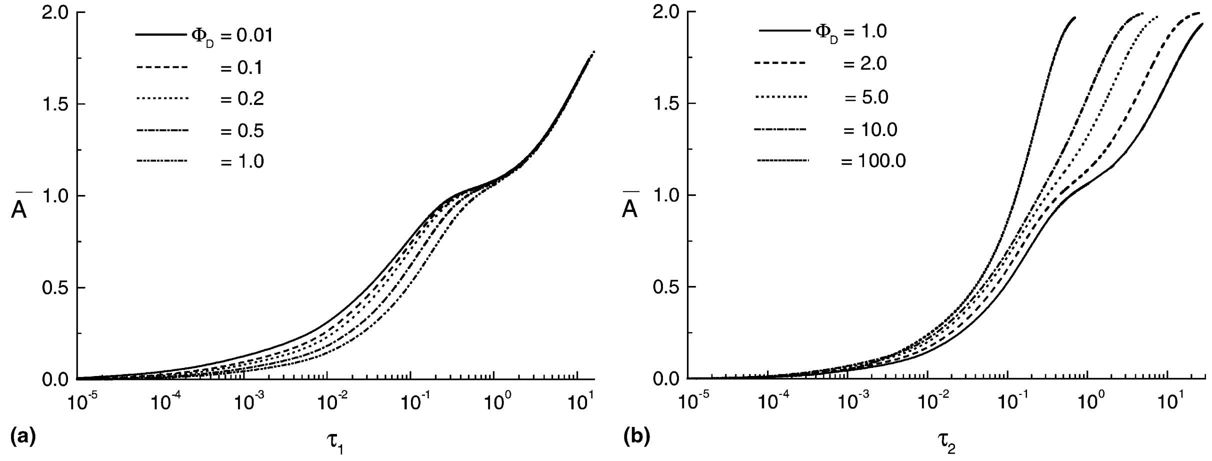

Fig. 8. Total mass transferred as a function of dimensionless time showing the effect of the diffusivity ratio at $Pe_2 = 100$, $Ha^2 = 0.1$ and $Re = 100$.

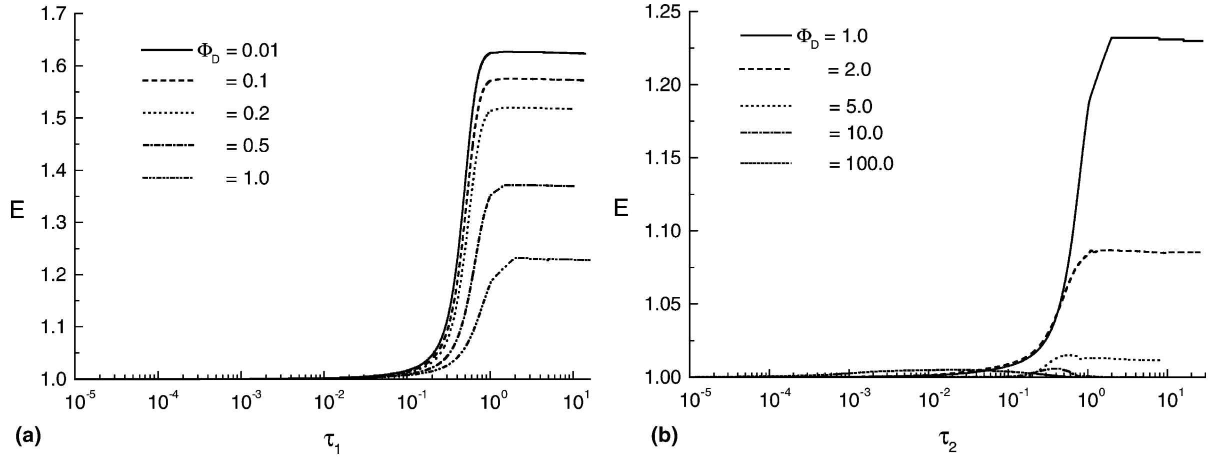

Fig. 9. Variation of enhancement factor with dimensionless time at $Pe_2 = 100$, $Ha^2 = 0.1$ and $Re = 100$.

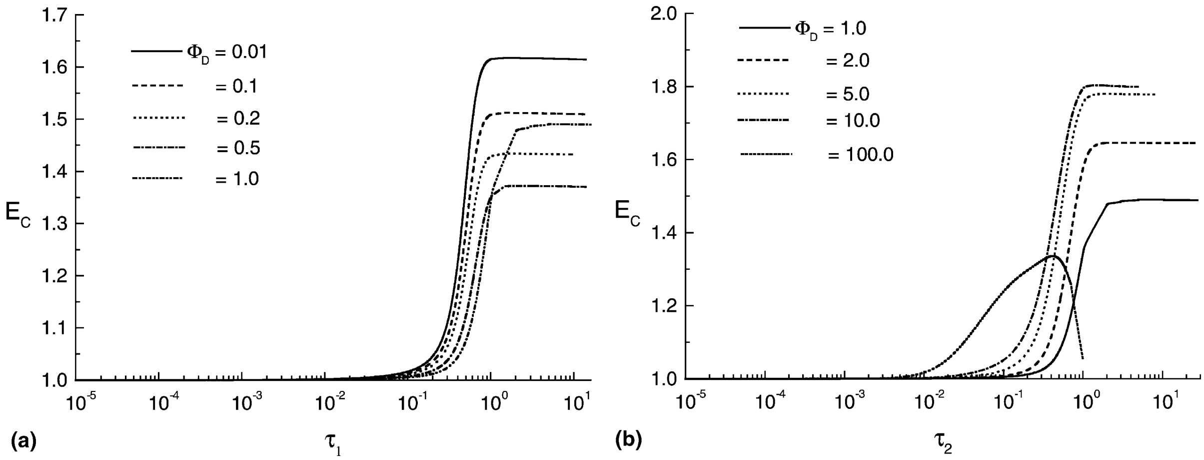

Fig. 10. Time evolution of E_C at $Pe_2 = 100$, $Ha^2 = 0.1$ and $Re = 100$.

Table 1
E values of FOR for rigid sphere model

Φ_D	Ha^2				
	10^{-4}	10^{-2}	10^{-1}	10	100
0.01	1.50[a]	1.51[a]	1.51[a]	1.87[a]	3.60[a]
	1.51[b]	1.51[b]	1.52[b]	1.90[b]	3.64[b]
	1.0[c]	1.0[c]	1.0[c]	1.30[c]	3.10[c]
0.1	1.44[a]	1.45[a]	1.45[a]	1.80[a]	3.46[a]
	1.45[b]	1.46[b]	1.46[b]	1.84[b]	3.52[b]
	1.0[c]	1.0[c]	1.0[c]	1.28[c]	2.98[c]
0.2	1.39[a]	1.39[a]	1.39[a]	1.72[a]	3.31[a]
	1.40[b]	1.41[b]	1.41[b]	1.74[b]	3.39[b]
	1.0[c]	1.0[c]	1.0[c]	1.23[c]	2.86[c]
0.5	1.25[a]	1.25[a]	1.26[a]	1.55[a]	2.99[a]
	1.26[b]	1.27[b]	1.27[b]	1.58[b]	3.10[b]
	1.0[c]	1.0[c]	1.0[c]	1.21[c]	2.59[c]
1.0	1.14[a]	1.14[a]	1.14[a]	1.42[a]	2.72[a]
	1.15[b]	1.15[b]	1.15[b]	1.44[b]	2.75[b]
	1.0[c]	1.0[c]	1.0[c]	1.18[c]	2.38[c]
2.0	1.06[a]	1.07[a]	1.07[a]	1.32[a]	2.55[a]
	1.08[b]	1.08[b]	1.08[b]	1.34[b]	2.60[b]
	1.0[c]	1.0[c]	1.0[c]	1.15[c]	2.24[c]
5.0	1.02[a]	1.02[a]	1.03[a]	1.27[a]	2.44[a]
	1.03[b]	1.03[b]	1.03[b]	1.29[b]	2.46[b]
	1.0[c]	1.0[c]	1.0[c]	1.14[c]	2.16[c]
10.0	1.01[a]	1.01[a]	1.01[a]	1.25[a]	2.41[a]
	1.02[b]	1.02[b]	1.02[b]	1.26[b]	2.43[b]
	1.0[c]	1.0[c]	1.0[c]	1.14[c]	2.13[c]
100.0	1.0[a]	1.0[a]	1.0[a]	1.24[a]	2.39[a]
	1.0[b]	1.0[b]	1.0[b]	1.24[b]	2.41[b]
	1.0[c]	1.0[c]	1.0[c]	1.14[c]	2.12[c]

[a] Present results, creeping flow.
[b] Present results, $Re = 100$.
[c] Film theory.

implies a reduced consumption of reactant B (see Fig. 2(a)) and a smaller value of the total mass transferred (Fig. 3(a)). The influence of Φ_D on the total mass transferred (Fig. 3(a)) can be viewed as an average between the influences of Φ_D on the particle average concentrations of the two reactants (Figs. 1(a) and 2(a)). Fig. 3(a) also shows that the total mass transferred tends to the asymptotic value $1 + 1/R_C$.

At $\Phi_D > 1$ the continuous phase controls the mass transfer while the chemical reaction takes place in the dispersed phase. In Fig. 1(b) it can be seen that if $\Phi_D > 2$ there is a time period for which the mass of reactant A transferred from the continuous phase is equal to that consumed by the chemical reaction (the rate of "external diffusion" is equal to the rate of chemical reaction). The value of $\overline{A}_1$ remains practically constant during this time interval. Fig. 1(a) shows that the increase in Φ_D increases this time interval. In the same time interval takes place the depletion of reactant B (Fig. 2(b)). After the complete depletion of reactant B a pure physical transfer of A takes place. Because the physical transfer is not interesting for this work, the time integration was stopped when $\overline{B} \leqslant 10^{-4}$. For this reason, some of the curves plotted in Figs. 1(b) and 3(b) do not reach their asymptotic value. Fig. 3(b) shows that the total mass transferred time evolution practically hide these phenomena. However, the transients of $\overline{A}$ indicate the presence of diffusion control.

Figs. 4 and 5 show that the physical transfer dominates the process at very short contact times. After an ignition time, the chemical reaction starts and the enhancement factors increase fast. The increase in the chemical reaction rate increases the depletion of reactant B. This implies the decrease in chemical reaction rate and implicitly the decrease in enhancement factors. It can be seen in Figs. 4 and 5 that the diffusivity ratio influences the enhancement factors. The variation of the two enhancement factors versus diffusivity ratio is different. E decreases with the increase in Φ_D. For $\Phi_D \in [0.01, 1.0]$, E_C decreases with the increase in the diffusivity ratio. For $\Phi_D > 1$, E_C increases with the increase in Φ_D. The influence of Φ_D on E and E_C is similar to that observed at FOR. For a FOR, the influence of the diffusivity ratio on mass transfer rate is analyzed in detail in [23]. For this reason, we do not focus on this aspect in this section. However, it must be mentioned that the increase in E_C with the increase in Φ_D, if $\Phi_D > 1$, is caused by the disappearance of mass wake due to the presence of the chemical reaction. For this reason, some aspects must be mentioned concerning the mass wake phenomenon, [16]. For the values of the Pe numbers and the velocity profiles employed in this work, mass wake accompanied the physical mass transfer. In all simulations made in this work, independent of the modified Hatta modulus values, the mass wake was not present when the chemical reaction takes place. As example, for SOR at $Ha^2 = 0.1$, at the beginning of the process, when the physical mass transfer is the dominant phenomenon, mass wake occurs. When the chemical reaction starts, mass wake disappears. After the depletion of reactant B, when the process becomes again a pure physical one, mass wake reappears.

The results presented in Figs. 6–10 show the existence of two distinct situations: one valid for $\Phi_D \leqslant 10$ and the other valid for $\Phi_D = 100$. The results obtained at $\Phi_D \leqslant 10$ lead to the following remarks:

- The process consists of two distinct phenomena that display in series; the physical mass transfer is the phenomenon which the process begins; chemical reaction practically starts when $\overline{A}_1$ becomes greater than 0.5.
- The influence of the diffusivity ratio on $\overline{B}$ is negligible if $\Phi_D \leqslant 1$; at $\Phi_D > 1$, sub-figures (b) show that the diffusivity ratio influences $\overline{B}$ and implicitly the total mass transferred even in the stage of the process controlled by the chemical reaction; however, it must be underlined that in sub-figures (b) τ_2 is the independent variable; viewed from the continuous phase, the chemical reaction rate is $\Phi_D\, Ha^2 AB$.
- During the chemical transformation, the enhancement factors have a constant value greater than 1; this value depends on Φ_D; the influence of the diffusivity ratio on enhancement factors is similar to that encountered in the case of fast chemical reaction.

Figs. 6–10 show that the case $\Phi_D = 100$ belongs to another world. The system has a transient behavior similar to that observed in Figs. 1–5. This behavior is not a consequence of using τ_2 as independent variable. If the curves obtained at $\Phi_D = 100$ are plotted again versus τ_1 the same behavior is present.

The behavior of the system at $Ha^2 = 10^{-2}$, 10^{-4} is similar for $\Phi_D \leqslant 10$. The transient evolution is not so sharp and the integration time is longer, or considerably longer at $Ha^2 = 10^{-4}$. The change of the system behavior at $\Phi_D = 100$ is not present. However, this change was the main reason in selecting the case $Ha^2 = 0.1$ for presentation.

For a first-order irreversible chemical reaction that takes place inside the sphere, the influence of H and Φ_D on mass transfer rate is presented in [23]. For this reason, in this work, the discussion is focused on two aspects that are not discussed in [23], i.e.,

- the influence of the hydrodynamics on E;
- the behavior of the system at $Ha < 1$.

Table 1 shows that the velocity profiles influence insignificantly the enhancement factor. As in classical theories, the enhancement factor can be considered independent on hydrodynamics. The differences that occur may be explained by the numerical errors. It must be mentioned that at $Re = 100$ the velocity profiles were calculated numerically.

Table 1, as Fig. 9, shows that in a slow reaction system the values of the enhancement factor are greater than 1. The decrease in Ha^2 from 0.1 to 10^{-4} does not change the values of E. This result contradicts the predictions of the classical theories. As example, the film theory considers the process as one of physical diffusion in the film followed by chemical reaction in the bulk. Both phenomena unfold in series with equal rates. The enhancement factor takes the value 1. Brunson and Wellek [27] consider that the range of dimensionless time important in many liquid extraction applications is $\tau < 10^{-3}$. Fig. 9 shows that for $\tau_{1(2)} < 10^{-3}$ E may be considered equal to one. However, for environmental processes, as examples, the contact time between phases is considerably longer.

The enhancement of the mass transfer rate at small and very small values of Ha is one of the important new results obtained in this work. Based only on the present results one cannot extrapolate this statement to other systems. For the case analyzed here, the chemical reaction takes place in a closed domain. The total mass transferred tends to the asymptotic value $1 + 1/R_C$. This asymptote cannot be reached only by physical mass transfer. The presence of the chemical reaction makes possible the attainment of this limit. The start of the chemical reaction implies the enhancement of the mass transfer rate.

Table 1 shows that the values of the enhancement factor provided by film theory at $Ha < 1$ agree with the present calculations only for $\Phi_D \gg 1$. For $\Phi_D \ll 1$ the relative error between the two values is approximately equal to 50%. For $Ha > 1$ the E values computed in this work are higher than those provided by film theory. Halwachs and Schuegerl [30] obtained experimental values of enhancement factor greater than those provided by film theory. It must be mentioned that for the computation of the Hatta modulus, Ha', the values Sh_{in} ($Ha = 0$) obtained in conjugate mass transfer were used.

5.2. Fluid sphere

In creeping flow, the viscosity ratio of the Hadamard–Rybczynski velocity profiles is considered equal to 1. At moderate Re numbers, the velocity profiles were computed for $Re = 50$, viscosity and density ratios equal to one. It must be mentioned that at $Re = 50$, viscosity and density ratios equal to one, flow separation is not present and break-up of internal circulation [40] does not occur.

The time evolution of average particle concentrations and total mass transferred at $Ha^2 = 0.1$ and 10, creeping flow and $Re = 50$, have the same characteristics as those encountered at rigid sphere. The process is faster for a sphere with internal circulation but the curves have the same shape and show the same phenomena. The time evolution of Sh number exhibits oscillations in both cases $Ha = 0$ and $Ha \neq 0$. The oscillations corresponding to the two Sh numbers used to compute the enhancement factors have not the same frequency. For this reason, the transients of E and E_C exhibit small oscillations. However, these oscillations do not change the salient features of E and E_C time evolution. For the FOR, the influence of the Φ_D and H on mass transfer rate was analyzed in [23]. Also, the behavior of the system for $Ha^2 < 0.1$ reproduces that presented in the previous section. Under these conditions, the discussion in this section is focused mainly on the influence of the hydrodynamics on the mass transfer rate of the first-order reaction. Also, the comparison between the E values obtained at two sphere models is presented.

Table 2 shows the E values computed in creeping flow (first line of each cell) and $Re = 50$ (second line of

Table 2
E values of FOR for fluid sphere with internal circulation

Φ_D	Ha^2		
	0.1	10	100
0.01	1.172[a] 1.23[b] 1.0[c]	1.36[a] 1.36[b] 1.125[c]	2.41[a] 2.38[b] 2.04[c]
0.1	1.147[a] 1.20[b] 1.0[c]	1.32[a] 1.32[b] 1.12[c]	2.35[a] 2.28[b] 2.02[c]
0.2	1.141[a] 1.19[b] 1.0[c]	1.296[a] 1.29[b] 1.119[c]	2.32[a] 2.24[b] 2.0[c]
0.5	1.12[a] 1.165[b] 1.0[c]	1.259[a] 1.25[b] 1.113[c]	2.27[a] 2.19[b] 1.96[c]
1.0	1.10[a] 1.12[b] 1.0[c]	1.226[a] 1.20[b] 1.111[c]	2.22[a] 2.14[b] 1.94[c]
2.0	1.159[a] 1.14[b] 1.0[c]	1.398[a] 1.37[b] 1.17[c]	2.75[a] 2.67[b] 2.32[c]
5.0	1.139[a] 1.10[b] 1.0[c]	1.44[a] 1.39[b] 1.18[c]	2.79[a] 2.74[b] 2.38[c]
10.0	1.09[a] 1.04[b] 1.0[c]	1.39[a] 1.35[b] 1.16[c]	2.76[a] 2.69[b] 2.30[c]
100.0	1.03[a] 1.01[b] 1.0[c]	1.29[a] 1.25[b] 1.14[c]	2.54[a] 2.47[b] 2.11[c]

[a] Present results, creeping flow.
[b] Present results, $Re = 100$.
[c] Film theory.

each cell). The third row of each cell shows the value of the enhancement factor provided by film theory. As in the case of rigid sphere, the influence of Ha^2 on E for $Ha^2 < 0.1$ can be considered negligible. For this reason, Table 2 presents only the values of E at $Ha^2 = 0.1$, 10.0, 100. In the previous section, at the rigid sphere model, the change of the hydrodynamic regime takes place only in the continuous phase where there is no chemical reaction. For a fluid sphere, the passing from creeping flow to intermediate Re numbers, influences the convection inside the sphere. However, at small viscosity ratios and intermediate Re numbers, the internal flow is similar to Hill's spherical vortex [40]. Under these conditions, dramatic changes in E are not expected.

Table 2 shows that the hydrodynamic regime does not influence significantly the enhancement factor. The relative differences between the creeping flow and intermediate Re values are smaller than 5%. These differences may be explained by numerical errors. As for the previous sphere model, the velocity profiles at intermediate Re numbers were computed numerically.

The E values depicted in Table 2 are smaller than those of Table 1. In both cases, i.e., $Ha = 0$ and $Ha \neq 0$, the values of the Sh number for the sphere with internal circulation are higher in comparison with the values provided by the rigid sphere. However, the increase in Sh ($Ha \neq 0$) is not high enough to assure the increase in enhancement factors. The convection inside the sphere has the tendency to equalize the concentration field inside the sphere. For this reason, the enhancement of mass transfer is not so great as expected.

The comparison between the present results and those computed with relation (12) leads to the same remark as in the case of rigid sphere. The values obtained in this work for the enhancement factor are higher than those provided by film model.

6. Conclusions

Conjugate mass transfer from an ambient fluid to a sphere in which a chemical reaction occurs has been investigated numerically. Second-order and pseudo-first-order irreversible chemical reactions were simulated. For the case of second-order, the total depletion of the reactant present initially inside the sphere and insoluble in the continuous phase was allowed. The influence of the diffusivity ratio, Φ_D, on the conjugate mass transfer rate was analyzed under the following conditions:

- rigid sphere and fluid sphere with internal circulation;
- creeping flow and moderate Re number;
- dimensionless reaction rate constant (named here modified Hatta modulus) varying from 10^{-4} to 100;
- moderate values of Pe numbers ($Pe = 100$).

The numerical results presented in the previous section show that the diffusivity ratio influences strongly the mass transfer rate. For Ha values smaller than 1 (slow chemical reaction), the enhancement factors take values greater than 1. The enhancement of the mass transfer due to the presence of the chemical reaction is greater for a rigid sphere. The values obtained in this work for the enhancement factor are higher than those provided by film theory.

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