

aggregative behaviour, but in the present work particulate fluidisation was obtained over the whole range of voidages

The technique will now be used to permit a more extensive study of segregation and pressure fluctuations, together with the effect on heat transfer to small immersed surfaces

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NOTATION

d effective particle diameter, L
 e bed voidage
 g acceleration due to gravity, LT^{-2}
 h height above distributor, L
 n slope of plot of $\log u_c$ vs $\log e$
 P pressure at height h due to solids, $ML^{-1}T^{-2}$
 u_c Fluidisation velocity, LT^{-1}

u_{mf} minimum fluidising velocity, LT^{-1}
 u_0 free falling velocity of particles, LT^{-1}

Greek symbols

ρ liquid density, ML^{-3}
 ρ_s solid density, ML^{-3}

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On the effect of a diffusing catalyst on the rate of absorption with a catalytic chemical reaction

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Recently da Silva and Danckwerts[1] presented a contribution in which the effect of a diffusing catalyst on the rate of mass transfer with chemical reaction is analyzed both theoretical and experimentally

Specifically they studied the simultaneous absorption of CO_2 with small amounts of Cl_2 or Br_2 in a buffer liquid solution of $KHCO_3$ and K_2CO_3 . The ClO^- (or BrO^-) formed acts as a catalyst in the reaction of CO_2 with H_2O while this reaction is negligible in the absence of the catalytic species. Their experimental results were compared with theoretical predictions based on the well known film model. Under same assumption da Silva[2] presented a theoretical analysis for penetration theory but no attempt was made to compare its predictions with experimental results.

The purpose of this contribution is to show that some of the restrictions imposed are not necessary and that a rather simple solution can be obtained to predict the rate of absorption of CO_2 under their experimental conditions. In fact our results would be in close agreement with da Silva and Danckwerts[1] predictions if their system of equations were properly solved. It can be shown that their final result of the rate of mass transfer in terms of the Airy functions is incorrect. Nevertheless it will be shown that, under their experimental conditions and same assumptions, a simple expression to predict the rate of mass transfer can be obtained which is identical with ours which will be deduced under less restrictive assumptions.

The main point is concerned with catalytic species (in this case ClO^-) profile. Da Silva and Danckwerts[1], and also da Silva[2], assumed that Cl_2 absorption takes place through an instantaneous reaction. Thus the concentration profile of the catalyst will be governed by a differential mass balance for pure physical diffusion (i.e. for the film model a linear function from the interface). However this is truly valid from the reaction plane inward since the non-permeability condition of ClO^- through the interface must be taken into account. Moreover if the reaction were instantaneous the OH^- concentration would decay to zero at the reaction plane and the overall model should be one of simultaneous absorption with instantaneous reactions. Since in their experiments OH^- source was the buffer CO_3^{2-}/CO_3H^- system it seems appropriate the assumption that CO_2 absorption takes place with the sum of a pseudo first order reaction with

OH^- and the second order catalyzed reaction mentioned above. So, even if Cl_2 reaction with OH^- is very rapid it cannot be considered as instantaneous in such a buffer system and specially under experimental conditions where Cl_2 partial pressure was very low. However in our theoretical development there is no need to assume any order for Cl_2 reaction with OH^- . Moreover it will be shown that, under these conditions, the ClO^- concentration profile is not important in determining the rate of CO_2 absorption but interfacial value is fundamental.

APPROXIMATE THEORY

Assuming valid film model (of thickness δ) the following system of differential equations will describe the mass balance for each species

$$\frac{d^2a}{dx^2} = D_1(1 + \beta(C/C_s))a \quad (1)$$

$$\frac{d^2b}{dx^2} = (r_B\delta^2/B_S D_B) \quad (2)$$

$$m \frac{d^2c}{dx^2} = -(r_B\delta^2/B_S D_B) \quad (3)$$

where the following dimensionless variables were defined

$$a = (A/A_S), \quad b = (B/B_S), \quad c = (C/B_S), \quad x = (X'/\delta), \\ \beta = (k_c C_S/k_1), \quad D_1 = k_1\delta^2/D_A, \quad m = D_C/D_B \quad (4a-g)$$

A , B and C being the dimensional concentrations of CO_2 , Cl_2 and ClO^- respectively, k_1 and k_c the pseudo first order and second order catalytic reaction constants, D the diffusivity coefficient, R_B the rate of reaction of Cl_2 per unit volume and the subindexes A , B , C and S stand for CO_2 , Cl_2 , ClO^- and interfacial value respectively.

The equation system (1), (2) and (3) is subject to the following boundary conditions

$$a = 1, \quad b = 1, \quad (dc/dx) = 0 \quad \text{at } x = 0 \quad (5a)$$

$$a = 0, \quad b = 0, \quad c = 0 \quad \text{at } x = 1 \quad (5b)$$

From eqns (2) and (3) it results

$$\frac{d^2(b+mc)}{dx^2} = 0 \quad (6)$$

So after using conditions (5a) for b and c it can be found

$$c_s = \left\{ \frac{R_B}{k_{LA}^0 B_S} - 1 \right\} (1/m) \quad (7)$$

R_B being the rate of absorption of Cl_2 in the reactive film and k_{LA}^0 the mass transfer coefficient of Cl_2 in the absence of chemical reaction R_B was measured in the work of da Silva and Danckwerts[1] while the rate of Cl_2 physical absorption ($k_{LA}^0 B_S$) can be estimated for each run. Clearly if the reaction factor for Cl_2 were much greater than 1, the approximate expression

$$C_s \approx \frac{R_B}{k_{LA}^0 m (D_B/D_A)} \quad (8)$$

proposed by da Silva and Danckwerts[1] would be correct. In eqn (8) k_{LA}^0 is the mass transfer coefficient for CO_2 pure physical absorption which was measured in Ref [1]. However it can be shown that in most of the experimental runs expression (8) does not give a good approximation of C_s . Thus in this work eqn (7) will be used to predict C_s .

Before solving approximately eqn (1) two facts should be taken into account. First, the reported value of the reaction factor (E), for CO_2 absorption, reported in Ref [1], even in the absence of the catalytic species, suggests that a valid solution can be obtained with the asymptotic form for a very rapid first order reaction. Second, due to the interfacial boundary condition for the catalytic species a valid asymptotic approximation for c profile (up to terms of order x^2 after an expansion from the interface) is $C = C_s$. Thus a simple approximate solution of eqn (1) in terms of reaction factor can be written in the following form

$$\frac{E_c}{E_{Nc}} = (1 + \beta)^{1/2} \quad (9)$$

E_c and E_{Nc} being the reaction factors with and without the diffusing catalytic species respectively.

It can be shown, using as perturbation parameter $(D_1)^{-1/2}$, that the linear c profile suggested by da Silva and Danckwerts[1] would produce the following approximate solution

$$\frac{E_c}{E_{Nc}} = (1 + \beta)^{1/2} \left\{ 1 - \frac{D_1^{-1/2}}{4(1 + \beta)^{3/2}} \right\} \quad (10)$$

In the most adverse situation of experimental conditions reported in Ref [1] it can be shown that the term in the bracket is at least 0.95 and in most cases is 0.99. This is to prove that under experimental conditions the form of c profile is immaterial to predict the ratio E_c/E_{Nc} . However its interfacial value plays an important role since it affects β linearly (see eqn 4e).

In Fig 1 theoretical predictions are plotted as continuous curves of E_c/E_{Nc} as a function of R_B .

The upper curve was calculated with the reported value of $k_1 = 4.18 \text{ sec}^{-1}$ and the lower curve with $k_1 = 6.18 \text{ sec}^{-1}$ since according with simple calculations it appears to be more consistent with experimental value of E_{Nc} reported in Ref [1]. Experimental values of E_c/E_{Nc} are also shown in the same figure as dispersed points. Numerical differences among experimental and theoretical values of E_c/E_{Nc} were calculated for $k_1 = 6.18 \text{ sec}^{-1}$. The maximum observed deviation is of the order of 30% but for most of the tabulated values in Ref [1] it is below 20%.

It should be noted that E_c/E_{Nc} must be a unique function of β while it is expected that a plot of E_c/E_{Nc} as a function of R_B

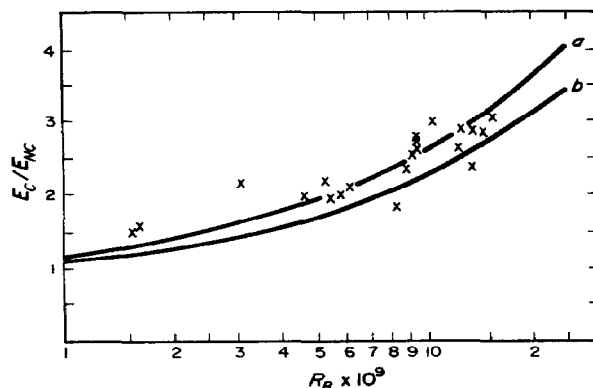


Fig 1 Effect of R_B on the ratio of reaction factors E_c/E_{Nc} . Curves (a), calculated with $k_1 = 4.18 \text{ sec}^{-1}$ and (b), with $k_1 = 6.18 \text{ sec}^{-1}$.

should show the influence of the Cl_2 partial pressure. However within the range of partial pressure investigated it gives a unique curve.

In performing β calculations expression (7) was used to estimate C_s . The following data were taken

(a) According to Sherwood and Pigford[3] B_s was estimated as

$$B_s = 0.4H(p_B/2) \quad (11)$$

Cl_2 partial pressure (p_B) was divided by 2 since in all experimental runs the outlet value of p_B was almost zero. $H = 6.247 \times 10^{-3} \text{ gml/cm}^3 \text{ atm}$ at 25°C . The coefficient 0.4 is to correct the Cl_2 solubility due to the effect of ionic strength (which in this case equals 4). The value of this coefficient was obtained graphically from Fig 7 of the work of Hikita *et al* [4].

(b) Ratio

$$m = \frac{D_c}{D_B} = 0.786$$

from data given in Ref [4]. Assuming that the ratio of diffusivity coefficient is not affected by ionic strength from data given in Refs [1, 4]

$$\frac{D_B}{D_A} = \frac{1.48 \times 10^{-5} \text{ cm}^2/\text{sec}}{1.95 \times 10^{-5} \text{ cm}^2/\text{sec}} = 0.76$$

(c) $k_c = 6670 \text{ l/gmol sec}$, $k_{LA}^0 = 4.13 \times 10^{-3} \text{ cm/sec}$ from Ref [1].

It can be concluded that experimental values of Ref [1] can be fairly well correlated by our simple expression (9) while C_s must be estimated by its exact value (eqn 7). Nevertheless it should be noted that this system is essentially unsteady since the interfacial ClO^- concentration is a growing function of time. Thus in our simple model only a rough average value can be estimated with eqn (7) of this work. Thus it would be of great interest the analysis of the unsteady state system of equations also to explore the theoretical possibility that the rate of mass transfer of CO_2 (in this case) would increase with time.

Finally in this contribution the reported results of CO_2 and Br_2 absorption were not considered due to the uncertain value of k_c for this system.

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NOTATION

a	dimensionless CO_2 concentration (A/A_S)
A	dimensional CO_2 concentration, gmol/l
b	dimensionless Cl_2 concentration, (B/B_S)
B	dimensional Cl_2 concentration, gmol/l
c	dimensionless ClO^- concentration (C/B_S)
C	dimensional ClO^- concentration, gmol/l
D_1	dimensionless kinetics parameter ($k_1\delta^2/D_A$)
D	diffusivity coefficient, cm^2/sec
E_c	reaction factor with the catalytic reaction
E_{Nc}	reaction factor without the catalytic reaction
H	Henry constant for Cl_2 , gmol/ cm^3 atm
k_1	first order rate constant for the reaction between CO_2 and OH^- , sec^{-1}
k_c	catalytic rate constant for the reaction between CO_2 and H_2O , l/gmol sec
k_L^0	liquid-film mass transfer coefficient for pure physical absorption, cm/sec
m	diffusivity ratio (D_c/D_B)
p_B	Cl_2 partial pressure, atm
r_B	reaction rate for Cl_2 , gmol/l sec
R_B	rate of absorption of Cl_2 , gmol/ cm^2 sec

X	dimensionless distance from the interface
X'	dimensional distance from the interface, cm

Greek symbols

β	dimensionless parameter ($k_c C_S/k_1$)
δ	film thickness, cm

Subindexes

A	refers to CO_2
B	refers to Cl_2
C	refers to ClO^-
S	interfacial value

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Analysis of an axially irradiated cylindrical photoreactor—I. Plug flow model

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The kinetic studies of photochemical reactions using transversely irradiated reactor (TIR), encounters uncertainties regarding incident radiation intensity distribution, for analyzing the data [1-3]. In this communication, axially irradiated reactor (AIR), with two configurations, PFI and PFII, depending on the directions of flow and irradiation, being either identical or opposite, (Fig 1) is analyzed.

The analysis of AIR is carried out (i) to test its efficacy in kinetic studies, (ii) to test the effect of mixing and levelling of intensity gradient in axial direction and compare it with beneficial effect [4] of levelling of concentration and intensity gradient in

transverse direction in TIR and (iii) to compare the performance of the two configurations cited.

ANALYSIS

The analysis is restricted to the following assumptions (i) uniform, monochromatic incident radiation, perpendicular to reactor cross-section, (ii) power-law type rate expression, (iii) complete lateral mixing for absorbing and reacting species over the entire reactor length and (iv) idealized boundary conditions at $z=0$ and/or $z=L$. This would involve simultaneous solution of two ordinary differential equations describing mass and radiation balances. Two broad classes of photochemical reactions are considered below.

Sensitizer absorption (SA)

For this class of photochemical reactions where some substances which absorbs the irradiation and pass the energy to the actual reactant, remains, usually, unchanged in concentration, the mass and radiation balances are decoupled. Symbolically



where s is the absorbing sensitizer. The corresponding rate law is given by

$$r = k[I_a]^p c^n$$

where volumetric rate of absorption of radiation, I_a is given by

$$\begin{aligned} I_a &= \mu I_0 e^{-\mu z} && \text{for PFI} \\ &= \mu I_0 e^{\mu(z-L)} && \text{for PFII} \\ &= \frac{I_0}{L}(1 - e^{-\mu L}) && \text{for MF} \end{aligned}$$

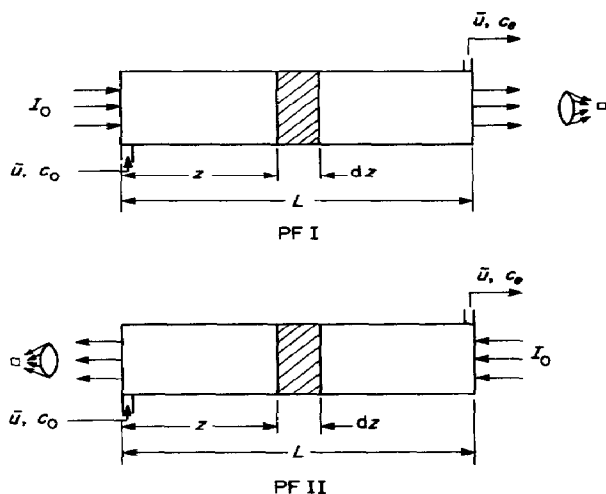


Fig 1 Basic features of the plug flow model of an axially irradiated photo reactor