

## Simultaneous absorption of two gases in a reactive liquid, one gas reacting instantaneously

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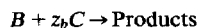
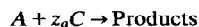
The case of simultaneous absorption and reaction of gases in a reactive medium, in which one of the gases reacts instantaneously, is of considerable industrial importance. A typical example is the selective removal of hydrogen sulfide out of gases, also containing carbon dioxide, by means of a solution of alkanol amines [10]. Hydrogen sulfide reacts in the liquid instantaneously, carbon dioxide has a finite rate.

Several authors [2-6] have dealt with the problem of finding expressions for the simultaneous mass transfer. A number of solutions are available, but they are all implicit or numerical.

In this contribution an explicit solution is added and a comparison is made between the different models.

### REACTION KINETICS AND MASS TRANSFER MODEL

We consider the simultaneous absorption of the gas phase components *A* and *B* in a liquid containing a non-volatile reagent *C*. The reactions proceed according to



The reaction rate of both reactions is of second order (first order in each component), with that of *A* being infinitely fast.

A film model of this system (Fig. 1) is extensively described by Goettler *et al* [2], Ouwerkerk [5] and Ramachandran *et al* [6] and will only be summarized here. According to Ramachandran [6] the film model gives (in dimensionless notation)

$$0 < \xi < \xi_p \quad \frac{d^2 a}{d\xi^2} = \frac{d^2 b}{d\xi^2} = 0 \quad (1)$$

$$\xi_p < \xi < 1 \quad \frac{d^2 c}{d\xi^2} = \frac{d^2 b}{d\xi^2} = bcM_b \quad (2)$$

with the boundary conditions

$$\xi = 0 \quad a = a_i, \quad b = b_i$$

$$\xi = \xi_p \quad a = 0, \quad b = b_\lambda, \quad c = 0$$

$$\xi = 1 \quad a = b = 0, \quad c = 1$$

The relationship between the enhancement factors for mass transfer of *a* and *b*,  $\phi_a$  and  $\phi_b$ , respectively, and the various fluxes are

$$-\left. \frac{da}{d\xi} \right|_{\xi=\xi_p} = \left. \frac{dc}{d\xi} \right|_{\xi=\xi_p} \quad (3)$$

$$\left. \frac{dc}{d\xi} \right|_{\xi=1} = \phi_b b_i + \phi_a a_i \quad (4)$$

$$\phi_a = - \left. \left( \frac{da}{d\xi} / a_i \right) \right|_{\xi=0} \quad (5)$$

$$\phi_b = - \left. \left( \frac{db}{d\xi} / b_i \right) \right|_{\xi=0} \quad (6)$$

where

$$b = \frac{z_b D_b B}{D_c C_0}, \quad b_i = \frac{z_b D_b B_i}{D_c C_0}, \quad b_\lambda = \frac{z_b D_b B_\lambda}{D_c C_0} \quad (7)$$

$$a = \frac{z_a D_a A}{D_c C_0}, \quad a_i = \frac{z_a D_a A_i}{D_c C_0} \quad (8)$$

$$c = \frac{C}{C_0} \quad (9)$$

$$\xi = \frac{x}{\delta}, \quad \xi_p = \frac{\lambda}{\delta} \quad (10)$$

$$\delta = \frac{D_b}{k_L} \quad (11)$$

$$M_b = k_b D_b C_0 / k_L^2 \quad (12)$$

The system can be transformed into

$$\xi_p < \xi < 1 \quad \frac{d^2 b}{d\xi^2} = bcM_b$$

with the boundary conditions

$$c(\xi_p) = 0$$

$$c(1) = 1 \quad (2')$$

$$\phi_b = - \left. \left( \frac{db}{d\xi} / b_i \right) \right|_{\xi=\xi_p} = \frac{b_i - b_\lambda}{b_i \xi_p} \quad (13)$$

see also [3], eqn (32)

$$\phi_a = 1/\xi_p \quad (14)$$

see also [6], eqn (23). Integration of the left parts of eqn (2) gives

$$b = (c - 1) + (1 + a_i + b_i)(1 - \xi) \quad (15)$$

see also [3], eqns (34) and (31)

$$(\phi_a - 1)a_i + (\phi_b - 1)b_i = 1 \quad (16)$$

see also [6], eqn (33)

Equations (2')-(16) cannot be solved analytically [6]. Goettler *et al* [2], Ouwerkerk [5] and we found an approximate solution by linearisation of the profile of *c*, instead of using relation (15), while Ramachandran *et al* [6] use a linear profile for *c* and, by maintaining eqn (15), also a linear profile for *b*.

For linearisation Goettler [2] and Ramachandran [6] used the boundary conditions of (2'), Ouwerkerk [5] evaluated the flux of *c* at  $\xi = \xi_p$  as to be the flux of *a*, while the present study matched this flux to be equal to the flux of *c* at  $\xi = 1$ .

Table 1 summarizes the different profile substitutions. In contrast to the other authors, who assume  $c = f(\xi)$  for  $\xi_p < \xi < 1$  and  $c = 0$  for  $\xi \leq \xi_p$ , Onda [4] assumes a constant value of *c* over the whole film  $0 \leq \xi \leq 1$ , analogous to Van Krevelen *et al* [7] and Hikita *et al* [8]. Figure 1 shows the approximate profiles.

### SOLUTIONS

The solutions of the differential equation (2'), using (13), for models 1, 2 and 3, result in [1]

$$\left( \frac{b_i - b_\lambda}{b_i} \right) \frac{1}{\xi_p} = \begin{cases} \frac{f(\lambda^{2/3} u)}{u} & \text{for } \lambda^{2/3}(1 - \xi_p) \leq 3 \end{cases} \quad (17a)$$

$$\begin{cases} 0.729 \lambda^{2/3} & \text{for } \lambda^{2/3}(1 - \xi_p) > 3 \end{cases} \quad (17b)$$

Table 1 The profile substitutions

Model	Profile equation	Profile number
1 Goettler	$c = (\xi - \xi_p)/(1 - \xi_p)$	1
2 Ouwerkerk	$c = a_i(\xi - \xi_p)/\xi_p$	2
3 Present model	$c = (1 + a_i + b_i)(\xi - \xi_p)$	3
4 Onda	$c = 1 + (1 - \phi_a)a_i + (1 - \phi_b)b_i$	4
5 Ramachandran	$\begin{cases} c = (\xi - \xi_p)/(1 - \xi_p) \\ b = b_\lambda(1 - \xi)/(1 - \xi_p) \end{cases}$	$\begin{cases} 1 \\ 5 \end{cases}$

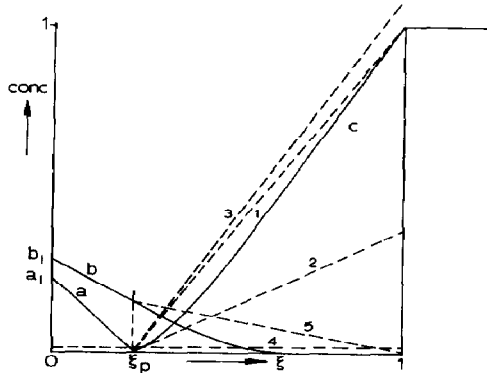


Fig 1 Film model of the simultaneous absorption of two gases, a and b, in a reactive liquid containing c, one gas (a) reacting infinitely fast Dashed approximate profiles for c, in solving the corresponding mathematical model 1, Goettler, 2, Ouwerkerk, 3, present model, 4, Onda, (1+5), Ramachandran (In fact, though not drawn, each linearisation method results in a different value of  $\xi_p$ )

where

$$\lambda^2 = \begin{cases} M_b(1 - \xi_p) & \text{for Goettler†} & (18) \\ M_b(a_i/\xi_p) & \text{for Ouwerkerk} & (19) \\ M_b(1 + a_i + b_i) & \text{for present model} & (20) \end{cases}$$

$$u = 1 - \xi_p \quad (21)$$

$$f(\lambda^{2/3}u) = \frac{1 + \frac{\lambda^2 u^3}{23} + \frac{\lambda^4 u^6}{2356} +}{1 + \frac{\lambda^2 u^3}{34} + \frac{\lambda^4 u^6}{3467} +} \quad (22)$$

In case  $a_i$  and  $b_i \ll 1$ , the criteria for (17a) and (17b) are equivalent with  $\sqrt{M_b} \leq 5$  and  $\sqrt{M_b} > 5$ , respectively Combination of eqns (14), (13) and (16) with eqn (17a,b) gives  $\phi_a$  and  $\phi_b$  (mostly an implicit system) For the other models  $\phi_a$  and  $\phi_b$  are also calculated from implicit equations Onda gives

$$\phi_a = \frac{\sqrt{cM_a}}{\tanh \sqrt{cM_a}} \quad (23)$$

and

$$\phi_b = \frac{\sqrt{cM_b}}{\tanh \sqrt{cM_b}} \quad (24)$$

with c given by eqn (4) in Table 1 Ramachandran calculates

$$\phi_b = \frac{b_\lambda}{b_i} \left( \frac{1}{1 - \xi_p} - \frac{M_b(1 - \xi_p)b_\lambda}{12} \right) \quad (25)$$

relating  $b_\lambda$ ,  $\xi_p$  and  $\phi_a$  by eqns (13)–(15)

#### EVALUATION OF THE MODELS

Starting with the model of Onda *et al* [4], it is evident that for  $M_a \rightarrow \infty$ , c will approach to zero, since  $\phi_a$  will be finite Thus the product  $cM_b$  will be  $\ll 1$  A series expansion of eqn (24) gives  $\phi_b = 1 + 1/3 cM_b = 1$  For  $M_a \gg M_b$  the assumption of a constant concentration profile over the whole film may give a non-realistic model approximation, resulting in  $\phi_b = 1$  over a great range of values for  $M_b$

For  $a_i$  and  $b_i \ll 1$ , the model of Ramachandran may also give big errors, because eqn (15) is used in approximating the profile of b Here, two functions of  $\xi$ , both of high magnitude, must be subtracted in order to obtain b, which is of low magnitude It can be shown mathematically that in some cases enhancement factors for b greater than  $\sqrt{M_b}$  may be calculated

From eqn (13)

$$b_\lambda = b_i(1 - \phi_b \xi_p) \quad (26)$$

Elimination of  $b_\lambda$  from (25) with eqn (26) gives

$$\phi_b = \frac{T}{1 + T\xi_p} \quad \text{with} \quad T = \frac{1}{1 - \xi_p} + \frac{M_b(1 - \xi_p)}{12} \quad (27)$$

As

$$\frac{a_i}{1 + a_i} \leq \xi_p \leq \frac{a_i + b_i}{1 + a_i + b_i} \quad (28)$$

$\phi_b$  is evaluated as

$$\phi_b \geq \left[ \frac{12(1 + a_i + b_i)}{M_b} + a_i + b_i \right]^{-1} \quad (29)$$

For  $M_b = 1600$  and  $a_i = b_i = 10^{-3}$  eqn (29) gives  $\phi_b > 105$ , which is greater than  $\sqrt{M_b}$  Figure 2 shows this once more For  $10 < \sqrt{M_b} < 120$  and  $a_i = b_i/2 = 2.50 \times 10^{-3}$  the calculated  $\phi_b$  exceeds  $\sqrt{M_b}$

Thus more b is predicted to be absorbed in the presence of a than without a This result is not in agreement with physical reality

For  $a_i = b_i$ , the solutions obtained with the models 1, 2 and 3 only differ a few percents from each other (see Fig 2) and correspond to the numerically calculated curves of Goettler *et al* [3]

Changing  $b_i/a_i$  to, e.g. the value of 20, however, shows that model 2 differs markedly (up to 25%) from the results of 1 and 3 (see Fig 3), especially for  $\sqrt{M_b} > 2$  and  $b_i$  and  $a_i \ll 1$

This could be expected from a too low assumed concentration profile of c, as discussed by Ouwerkerk and Goettler [9]

The present model also gives some deviations, but only for  $\phi_b < 2$  and  $b_i > 0.5$  For gas absorption this region is less important

An advantage of the present model over the others is that an explicit equation for  $\phi_b$  and  $\phi_a$  (via eqn (16)) for  $\sqrt{M_b} > 5$ , results by eliminating  $b_\lambda$

$$\phi_b = \frac{1 + a_i + b_i}{b_i} - \frac{a_i}{b_i} \left/ \left[ \frac{\xi_p \infty - S}{2} + \sqrt{\left( \frac{\xi_p \infty - S}{2} \right)^2 + \frac{Sa_i}{1 + a_i + b_i}} \right] \right. \quad (30)$$

with

$$\xi_p \infty = \frac{a_i + b_i}{1 + a_i + b_i} \quad (31)$$

$$S = 13717 / [(1 + a_i + b_i)M_b]^{1/3} \quad (32)$$

†Solution (17a) is an extension of the model of Goettler

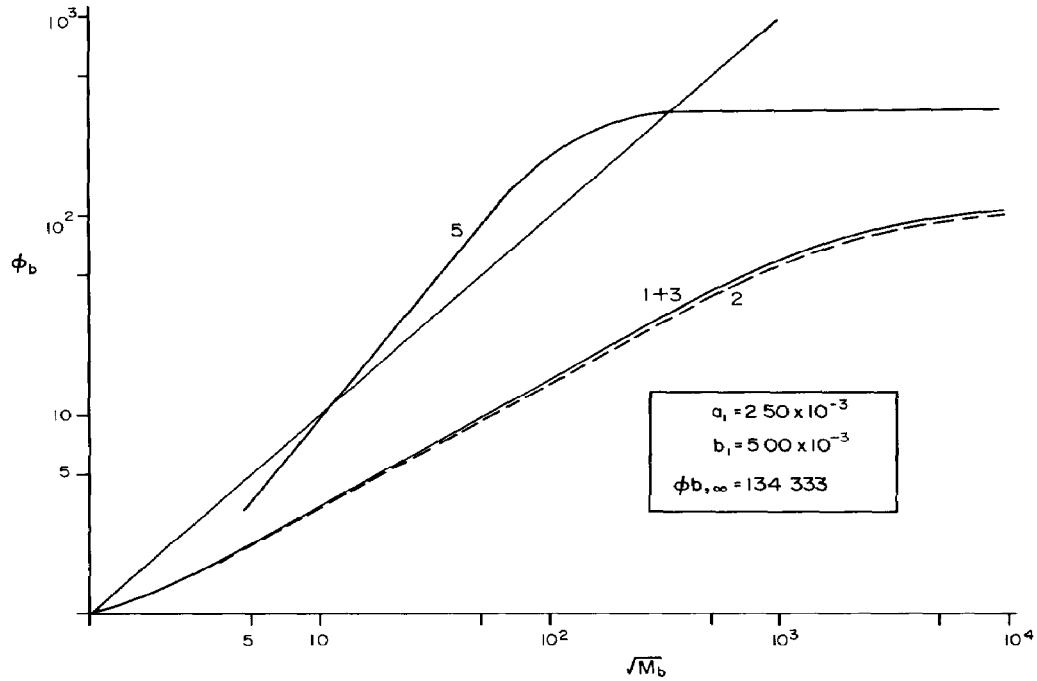


Fig 2 Plot of the enhancement factor of  $b$  ( $\phi_b$ ) vs  $\sqrt{M_b}$  for model 1 (Goettler), 2 (Ouwkerk), 3 (present model) and 5 (Ramachandran)

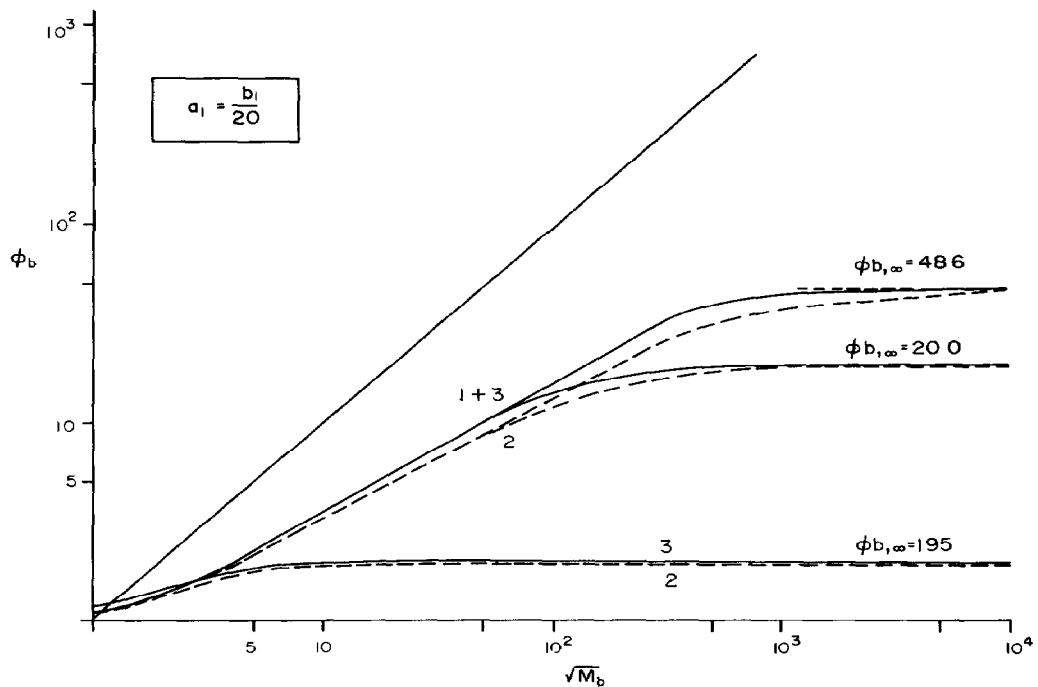


Fig 3 Plot of the enhancement factor of  $b$  ( $\phi_b$ ) vs  $\sqrt{M_b}$  for model 1 (Goettler), 2 (Ouwkerk) and 3 (present model)

### CONCLUSIONS

Several authors have described the simultaneous absorption of two gases, accompanied by irreversible chemical reaction, one of which is infinitely fast. Two of them, [4] and [6], derived equations for the enhancement factors, which are only valid in limiting conditions.

The models of Goettler *et al* [2], Ouwkerk [5] and the present model are closely related, but differ somewhat for  $a_1 \ll b_1$ .

For  $\sqrt{M_b} \geq 5$ , it is preferable to use our solution, which is the

only explicit one, and for  $\sqrt{M_b} < 5$  the presented extension of the Goettler model (eqn 18).

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## NOTATION

- $A$  concentration of the species entering the medium, in which instantaneous reaction occurs,  $\text{kmol/m}^3$   
 $a$  concentration of the species entering the medium, in dimensionless notation according to eqn (8)  
 $B$  concentration of the species entering the medium, in which reaction of finite rate occurs,  $\text{kmol/m}^3$   
 $b$  concentration of the species entering the medium, in dimensionless notation according to eqn (7)  
 $C$  concentration of the species in the liquid,  $\text{kmol/m}^3$   
 $c$  concentration of the species in the liquid, in dimensionless notation according to eqn (9)  
 $D$  diffusion coefficient,  $\text{m}^2/\text{sec}$   
 $f()$  function of  
 $k$  reaction rate constant, subscript indicating the reaction,  $\text{m}^3/(\text{kmol sec})$   
 $k_L$  physical mass transfer coefficient,  $\text{m/sec}$   
 $M_b$  diffusion-reaction modulus of species  $b$   
 $M_a$  diffusion-reaction modulus of species  $a$ ,  $(= k_a \delta^2 C_0 / D_a)$   
 $S$  dimensionless parameter defined by eqn (32)  
 $T$  dimensionless parameter defined by eqn (27)  
 $u$  dimensionless parameter defined by eqn (21)  
 $x$  distance in the direction of diffusion,  $\text{m}$   
 $z$  stoichiometric coefficient

## Greek symbols

- $\delta$  film thickness, defined by eqn (11),  $\text{m}$   
 $\phi$  enhancement factor

- $\lambda$  distance in the film where  $c = a = 0$ ,  $\text{m}$   
 $\xi$  dimensionless distance, defined by eqn (10)

## Subscripts

- $a, b, c$  of species  $A, B, C$ , respectively  
 $0$  in the bulk  
 $i$  at the interphase  
 $\lambda$  at  $x = \lambda$   
 $p$  at  $\xi = \frac{\lambda}{\delta}$   
 $\infty$  in the case the reactions of  $a$  and  $b$  are both instantaneous

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## An improved approach of simulating chemical reactions by a Markov-chain cell model

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As reported by Pippel and Philipp in a former publication [1] transport phenomena in chemical reaction systems can be approximately treated as stochastic processes with Markovian behaviour. Especially the Markov chains, which are discrete in space and time (cell model), give a favourable algorithm for numerical calculations. Based on these considerations a system of two matrix equations, representing the Markov approximation of the material and energy transport, was derived. However, the incorporation of kinetic expressions into these relations was done in a rather heuristic way by using a two-step procedure for each time interval  $\Delta t$ : (1) pure reaction step without transport and (2) transport step representing the Markov transition of matter and energy between the cells.

In this paper some additional information will be given about further possibilities of handling rate expressions without integration, on the basis of the material balance in a mixing cell similar to a CSTR

$$\frac{dn_k}{dt} + \lambda_i n_k = \lambda_i n_k^{in} + v_i r_k \quad (1)$$

with the transition intensity  $\lambda_i = v_i/v$

Equation (1) can be considered as a homogeneous differential equation (left part) with an inhomogeneous term  $\lambda_i n_k^{in} + v_i r_k$ . The general solution for an inflow mole number  $n_k^{in}$ , which is approximately constant during  $(t, t + \Delta t)$ , is

$$n_k(t + \Delta t) = n_k(t) \exp(-\lambda_i \Delta t) + n_k^{in}(t) [1 - \exp(-\lambda_i \Delta t)] + v_i \exp(-\lambda_i \Delta t) \int_0^{\Delta t} r_k(t+s) \exp(\lambda_i s) ds \quad (2)$$

The first two terms on the RHS of eqn (2) correspond to the transition probabilities of the Markov chains [1], similar expressions have been derived by means of the state-space method [2]. They are not of further interest here.

The third term in eqn (2) gives the mole number change as a result of a reaction  $\Delta n_k^R$

$$\Delta n_k^R = v_i \exp(-\lambda_i \Delta t) \int_0^{\Delta t} r_k(s+t) \exp(\lambda_i s) ds \quad (2a)$$

The integral cannot be solved generally because  $r_k$  is not explicitly given as a function of time  $t$ .

Some approaches have been published to calculate approximate solutions.

(i) As carried out in [2], the general way of utilizing the state-space method is to set  $r_k$  constant, i.e.  $r_k(t+s) = r_k(t)$ . In this case the solution of eqn (2a) is given by the expression

$$n_k^R(t, t + \Delta t) = \frac{v_i}{\lambda_i} r_k(t) [1 - \exp(-\lambda_i \Delta t)] \quad (3)$$

For small changes of the reaction rate this assumption may be used. However, if the rates increase considerably both changes in concentration and reaction should be taken into consideration.

The only way how to guarantee the mathematical stability of the algorithm is to perform the calculation with less time steps. It should be pointed out here that with eqn (3) the exact stationary states can be computed.

(ii) The two-step procedure described in [1]

$$\Delta n_k^R(t, t + \Delta t) = v_i \exp(-\lambda_i \Delta t) \int_0^{\Delta t} r_k(N(t), s) ds \quad (4)$$