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

\[
A + z_a C \rightarrow \text{Products} \\
B + z_b C \rightarrow \text{Products}
\]

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)

\[
0 < \xi < \xi_r, \quad \frac{d^2 a}{d \xi^2} - \frac{d^2 b}{d \xi^2} = 0
\]

\[
\xi_r < \xi < 1, \quad \frac{d^2 c}{d \xi^2} - \frac{d^2 b}{d \xi^2} = bcM_b
\]

with the boundary conditions

\[
\xi = 0 \quad a = a_r, \quad b = b_r \\
\xi = \xi_r \quad a = 0, \quad b = b_r, \quad c = 0 \\
\xi = 1 \quad a = b = 0, \quad c = 1
\]

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

\[
\phi_a = -\left( \frac{da}{d \xi} \right)_{\xi=0} = \frac{dc}{d \xi} \bigg|_{\xi=\xi_r} \\
\phi_b = -\left( \frac{db}{d \xi} \right)_{\xi=0}
\]

where

\[
h = \frac{Z_b D_b B}{D_c C}, \quad h_r = \frac{Z_b D_b B}{D_c C}, \quad h_a = \frac{Z_b D_b B_a}{D_c C}
\]

The system can be transformed into

\[
\xi_r < \xi < 1, \quad \frac{d^2 b}{d \xi^2} = bcM_b
\]

with the boundary conditions

\[
c(\xi_r) = 0 \\
c(1) = 1
\]

Equations (2)–(16) cannot be solved analytically[6]. Goettler et al[2] and Ouwerkerk[5] 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 \( \xi = \xi_r \) 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 \( \xi_r < \xi < 1 \) and \( c = 0 \) for \( \xi < \xi_r \), Onda[4] assumes a constant value of \( c \) over the whole film \( 0 < \xi < 1 \), 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

\[
\left( \frac{b_r}{b} - 1 \right) \frac{1}{\xi_r} = \frac{f(\lambda) - \mu}{\lambda^2} \quad \text{for} \quad \lambda^2(1 - \xi_r) < 3
\]

\[
\lambda = 0.729 \cdot 10^2 \lambda^2 \quad \text{for} \quad \lambda^2(1 - \xi_r) > 3
\]
Table 1 The profile substitutions

<table>
<thead>
<tr>
<th>Model</th>
<th>Profile equation</th>
<th>Profile number</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Goettler</td>
<td>( c = \frac{(\xi - \xi_p)(1 - \xi_p)}{1 - \xi} )</td>
<td>1</td>
</tr>
<tr>
<td>2 Ouwerkerk</td>
<td>( c = a_1(\xi - \xi_p)\xi_p )</td>
<td>2</td>
</tr>
<tr>
<td>3 Present model</td>
<td>( c = (1 + a_1 + b_1)(\xi - \xi_p) )</td>
<td>3</td>
</tr>
<tr>
<td>4 Onda</td>
<td>( c = 1 + (1 - \phi_a)a_1 + (1 - \phi_b)b_1 )</td>
<td>4</td>
</tr>
<tr>
<td>5 Ramachandran</td>
<td>( \begin{cases} c = (\xi - \xi_p)(1 - \xi_p) \ b = b_1(1 - \xi)/(1 - \xi_p) \end{cases} )</td>
<td>5</td>
</tr>
</tbody>
</table>

\[ \phi_a = \frac{b_1}{\sqrt{cM_a}} \]  
\[ \phi_b = \frac{b_1}{\sqrt{cM_b}} \]

\[ \phi_b = b_1 \left( \frac{1}{1 - \xi_p} - \frac{M_b(1 - \xi_p)b_2}{12} \right) \]  
relating \( \phi_a, \xi_p \) and \( \phi_b \) 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 zero, since \( \phi_a \) will be finite. Thus the product \( cM_b \) will be \( \ll 1 \). A series expansion of eqn (24) gives

\[ \phi_b = 1 + 1/3cM_b - 1 \]  
For \( M_a > M_b \) 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 \( a_1 \) and \( b_1 \ll 1 \), 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)

\[ b_1 = b_1(1 - \phi_a \xi_p) \]  
Elimination of \( b_1 \) from (25) with eqn (26) gives

\[ \phi_b = \frac{T}{1 + T\xi_p} \quad \text{with} \quad T = \frac{1}{1 - \xi_p} + \frac{M_b(1 - \xi_p)}{12} \]  
As

\[ \phi_b = \frac{1}{1 + \phi_a} \leq \frac{a_1 + b_1}{1 + a_1 + b_1} \]  
(28)

\[ \phi_b \text{ is evaluated as} \]

\[ \phi_b = \left[ \frac{2(1 + a_1 + b_1)}{M_b} + a_1 + b_1 \right]^{-1} \]  
(29)

For \( M_b = 1600 \) and \( a_1 = b_1 = 10^{-3} \), 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 \( a_1 = b_1/2 = 2.50 \times 10^{-3} \), 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 \( a_1 = b_1 \), 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 \( b_1/a_1 \) 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 \( b_1 / a_1 = 1 \).

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 \( b_1 > 0.5 \). 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 \( b_1 \)

\[ \phi_b = \frac{1 + a_1 + b_1}{b_1} \left[ a_1 + b_1 \left( \frac{\xi_p - S}{2} + \sqrt{\left( \frac{\xi_p - S}{2} \right)^2 + \frac{S}{2}a_1 + b_1} \right) \right] \]  
with

\[ \xi_p = \frac{a_1 + b_1}{1 + a_1 + b_1} \]  
(31)

\[ S = 1 \times 1717/[1 + a_1 + b_1 M_b]^{1/3} \]  
(32)
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], Ouwerkerk [5] and the present model are closely related, but differ somewhat for $a_i \ll b_i$.

For $\sqrt{M_b} \gg 5$, 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, kmol/m³
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, kmol/m³
b concentration of the species entering the medium, in dimensionless notation according to eqn (7)
C concentration of the species in the liquid, kmol/m³
c concentration of the species in the liquid, in dimensionless notation according to eqn (9)
D diffusion coefficient, m²/sec
f(·) function of
k reaction rate constant, subscript indicating the reaction, m³/(kmol sec)
kₚ physical mass transfer coefficient, m/sec
Mₐ diffusion-reaction modulus of species b
Mₐ diffusion-reaction modulus of species a, ( = kₚδ²C₀ / Dₐ)
S dimensionless parameter defined by eqn (32)
T dimensionless parameter defined by eqn (27)
υ dimensionless parameter defined by eqn (21)
x distance in the direction of diffusion, m
z stoichiometric coefficient

Greek symbols

δ film thickness, defined by eqn (11), m
ϕ enhancement factor

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.

References

7. Van Krevelen D W and Hooyzer P J, Rec Trav Chim 1948 67 563