University of Groningen

Microporous hollow fibre membrane modules as gas-liquid contactors. Part 2. Mass transfer with chemical reaction

Kreulen, H.; Versteeg, G.F.; Swaaij, W.P.M. van

Published in:
Journal of Membrane Science

DOI:
[10.1016/0376-7388\(93\)80002-F](https://doi.org/10.1016/0376-7388(93)80002-F)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1993

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Kreulen, H., Versteeg, G. F., & Swaaij, W. P. M. V. (1993). Microporous hollow fibre membrane modules as gas-liquid contactors. Part 2. Mass transfer with chemical reaction. *Journal of Membrane Science*, 78(3), 217-238. [https://doi.org/10.1016/0376-7388\(93\)80002-F](https://doi.org/10.1016/0376-7388(93)80002-F)

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Microporous hollow fibre membrane modules as gas–liquid contactors

Part 2. Mass transfer with chemical reaction

H. Kreulen*, C.A. Smolders, G.F. Versteeg** and W.P.M. van Swaaij

Faculty of Chemical Technology, University of Twente, P.O. Box 217, 7500 AE Enschede (The Netherlands)

(Received March 26, 1992; accepted in revised form November 20, 1991)

Abstract

Absorption determined by mass transfer in the liquid is described well with the Graetz–Léveque equation adapted from heat transfer. The influence of a chemical reaction on the mass transfer was simulated with a numerical model and tested on the absorption of CO₂ in a hydroxide solution. Absorption determined by mass transfer in the gas phase and the pores of the membrane was also analysed experimentally and numerically. It was found that the gas phase concentration profile is established at a very short distance from the entrance of the fibre. This results in a constant Sherwood number along the fibre. A module coated with a very thin silicone rubber layer showed absorption rates comparable to the uncoated membranes. If absorption liquids are used which wet the membranes, resulting in leaky membranes, such a coating can enlarge the application of microporous hollow fibre membrane module.

Keywords: mass transfer; microporous membranes; absorption; gas–liquid contactors

1. Introduction

Gas absorption can be carried out in a variety of reactors like bubble columns, packed towers, venturi scrubbers, sieve trays, etc. Each of these contactors has its specific advantages and disadvantages for the different absorption processes. A new type of gas absorber is the microporous hollow fibre membrane module presented in Part 1 [1] of this study. Until recently this membrane unit was only used for filtration purposes. Qi and Cussler [2,3] showed

that it could be used in gas absorption with the gas phase flowing through and liquid phase flowing around the fibres or *vice versa*.

Absorption processes accompanied by chemical reaction usually are very attractive. Firstly, the absorption capacity of the liquid is enlarged and a smaller liquid flow is required. Secondly, the mass transfer can be enhanced by the chemical reaction, which results in a smaller absorber.

Four experimental studies were published in open literature on absorption with chemical reaction in porous membrane systems. Qi and Cussler [2] studied gas–liquid mass transfer in a hollow fibre module with microporous non-wetted polypropylene membranes. Experi-

*Present address: AKZO Chemicals, P.O. Box 10, 7400 AA Deventer, The Netherlands.

**To whom correspondence should be addressed.

ments were carried out with the absorption of pure CO₂ in sodium hydroxide solutions. From the degree of OH⁻ conversion, liquid phase mass transfer coefficients were calculated. The influence of the chemical reaction on their results will be discussed in Appendix A.

Qi and Cussler [3] also measured overall mass transfer coefficients for the absorption of H₂S, CO₂, SO₂ and NH₃ from gas mixtures in aqueous solutions of NaOH, H₂SO₄ or alkanolamines with the same membranes. For the fast reacting systems: H₂S, SO₂ and NH₃, it was concluded that for their experimental conditions the mass transfer resistance of the membrane determined the mass transfer process. For slower reactions, CO₂ absorption in the various liquids, the mass transfer resistance of the liquid was also affecting the mass transfer rate. These observations seem consistent with absorptions in other gas absorbers.

Cooney and Jackson [4] studied the absorption of diluted SO₂ in a solution of NaOH with membranes made of cellulose acetate (CA). They concluded that in their modules the transport through the membrane and the transport in the liquid phase both were rate determining steps. It seems reasonable that the CA membrane adds to the mass transfer resistance because of its hydrophilicity. A dense CA film swells to give a significant increase of the membrane thickness.

Geuzens et al. [5] published data for CO₂ absorption in aqueous solutions of KOH and NaOH with flat porous teflon membranes, which are not wetted by these liquids. The absorption rate they measured was only determined by the membrane resistance.

In the present work the aspects of absorption accompanied by chemical reaction using hollow fibre membrane absorbers will be investigated both theoretically and experimentally. The experimental results from literature, mentioned above, will be discussed and compared with the results obtained in the present study.

2. Theory

In a module with porous non-wetted membranes, absorption is a three step process: transfer of component A from the gas phase to the membrane, through the membrane and into the liquid phase. It is assumed that in the liquid phase an irreversible reaction of A takes place with component B which is already present in the liquid.

The local flux can be expressed by eqn. (1):

$$J_A = K_{ov} \Delta C_A \quad (1)$$

K_{ov} , the overall mass transfer coefficient, can be related to the serial resistances against mass transfer in the three phases:

$$\frac{1}{K_{ov}} = \frac{1}{k_G} + \frac{1}{k_M} + \frac{1}{m k_L E} \quad (2)$$

The mass transfer coefficients of the gas and liquid phase, k_G and k_L , are determined by convection and diffusion. The mass transfer coefficient of the membrane depends on the molecular diffusion and the structure of the membrane. In the enhancement factor, E , the effect of the chemical reaction on the absorption is expressed. It is defined as the ratio of the chemical enhanced and the physical absorption flux at the same driving forces.

2.1. Mass transfer and chemical reaction in the liquid phase

In the hollow fibres used in this study the liquid is flowing lamarily through the lumen. With physical absorption at these conditions and a constant interface concentration mass transfer can be described analogous to the heat transfer problem solved by Graetz [6,7] and Lvque [8]. This was confirmed experimentally in Part 1 of this study [1]. However, this model for mass transfer is not easy to use in combination with chemical reaction.

For the general non-asymptotic situation and

assuming laminar flow in a tube, it is necessary to solve the differential mass balances describing the concentration profiles in the liquid (eqns. 3 and 4) in order to calculate the absorption fluxes.

A:

$$v_r \frac{\partial C_A}{\partial z} = D_A \left(\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_A}{\partial r} \right) \right) - k_{1,1} C_A C_B \quad (3)$$

B:

$$v_r \frac{\partial C_B}{\partial z} = D_B \left(\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_B}{\partial r} \right) \right) - \nu_B k_{1,1} C_A C_B \quad (4)$$

In these partial differential equations molecular diffusion in axial direction is neglected, which is in most cases allowed, see also part 1.

For flow through the long and small fibres only developed laminar flow needs to be considered. The radial velocity profile is given by:

$$v_r = 2 \bar{v} \left[1 - \left(\frac{r}{R} \right)^2 \right] \quad (5)$$

The following boundary conditions are imposed on the membrane system. At the membrane-liquid interface the flux of component A in the liquid phase is equal to the flux in the gas phase:

$$D_A \left(\frac{\partial C_A}{\partial r} \right)_{r=R} = k_{\text{ex}} (\bar{C}_{A,g} - C_{A,g,i}) \quad (6a)$$

in which:

$$k_{\text{ex}} = \frac{1}{\frac{1}{k_g} + \frac{1}{k_m}} \quad (7)$$

Moreover, it is assumed that component B is non-volatile:

$$\left(\frac{\partial C_B}{\partial r} \right)_{r=R} = 0 \quad (6b)$$

At the centerline of the tube, in view of symmetry, we may state that:

$$\left(\frac{\partial C_A}{\partial r} \right)_{r=0} = 0 \quad (6c)$$

$$\left(\frac{\partial C_B}{\partial r} \right)_{r=0} = 0 \quad (6d)$$

Initial conditions at $z=0$ are:

$$C_A = 0 \text{ and } C_B = C_{B0} \quad (6e)$$

This problem cannot be solved analytically and therefore a numerical technique is used which will be discussed in section 3.

2.2. Mass transfer in the gas phase

In some operations, the gas may flow through the porous non-wetted fibres while the liquid phase is flowing outside the fibres. To describe the mass transfer from the gas phase flowing laminarily through the fibres the Graetz-Léveque equation cannot be used because the assumption of a constant concentration along the fibre wall is not valid. In this case the concentration at the wall is influenced by the mass transfer resistance in the porous structure of the membrane and the varying flux along the fibre axis.

Mass transfer in the gas phase flowing through a fibre is described by a similar equation as eqn. (3), with the reaction term left out.

$$v_r \frac{\partial C_{A,G}}{\partial z} = D_{A,G} \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_{A,G}}{\partial r} \right) \right] \quad (8)$$

The following boundary conditions apply:

(a) At the membrane-gas interface the flux through the membrane is equal to the flux to the membrane interface:

$$D_{A,G} \left(\frac{\partial C_{A,G}}{\partial r} \right)_{r=R} = -k_M (C_{A,G,R} - C_{A,G,i}) \quad (9a)$$

(b) At the centre line of the fibre, because of symmetry:

$$\left(\frac{\partial C_{A,G}}{\partial r}\right)_{r=0} = 0 \quad (9b)$$

(c) The initial condition at the entrance of the fibre ($z=0$):

$$C_{A,G} = C_{A,G,0} \quad (9c)$$

With these boundary conditions, eqn. (8) was solved with the same numerical technique as the problem for the liquid phase, which will be discussed in the next section.

3. Numerical solution

The differential mass balances in eqns. (3) and (4) were made dimensionless by introducing the following dimensionless parameters:

$$\alpha = \frac{D_A}{k_{1,1} C_{B,0} R^2} \quad (10a)$$

Which is a reciprocal form of the square of the Hatta number.

$$\lambda = \frac{z k_{1,1} C_{B,0}}{2 \bar{v}} \quad (10b)$$

λ can be considered as a Damköhler number, denoting the number of reaction units

$$U = \frac{r}{R} \quad (10c)$$

$$C_A^* = \frac{C_A}{m C_{A,G}} \quad (10d)$$

$$C_B^* = \frac{C_B}{C_{B,0}} \quad (10e)$$

which gives:

$$(1-U^2) \frac{\partial C_A^*}{\partial \lambda} = \alpha \left[\frac{1}{U} \frac{\partial}{\partial U} \left(U \frac{\partial C_A^*}{\partial U} \right) \right] - C_A^* C_B^* \quad (11)$$

$$(1-U^2) \frac{\partial C_B^*}{\partial \lambda} = \alpha \frac{D_B}{D_A} \left[\frac{1}{U} \frac{\partial}{\partial U} \left(U \frac{\partial C_B^*}{\partial U} \right) \right] - \nu_B \frac{m C_{A,G}}{C_{B,0}} C_A^* C_B^* \quad (12)$$

In the present study the discretisation is carried out according to the discretisation scheme reported by Baker and Oliphant [9], leading to eqns. (13). This "T-molecule" scheme is also shown in Fig. 1.

$$\frac{\partial C}{\partial \lambda} = \frac{1}{2\Delta\lambda} (3C^{\psi+1} - 4C^\psi + C^{\psi-1}) \quad (13a)$$

$$\frac{\partial}{\partial U} \left(\frac{\partial C}{\partial U} \right) = \frac{1}{(\Delta U)^2} (C_{\xi-1} - 2C_\xi + C_{\xi+1}) \quad (13b)$$

This discretisation gives a set of $\Xi+1$ equations for each component at each axial coordinate and these equations are solved simultaneously. The solution is used to calculate the set of equations at the next axial coordinate.

The reaction term was linearised according to:

$$C_A^{\psi+1} C_B^{\psi+1} = C_A^{\psi+1} C_B^\psi + C_A^\psi C_B^{\psi+1} + C_A^\psi C_B^\psi \quad (14)$$

Because of this linearisation, iterations over each step in the axial direction were necessary to make the mass balances fit. Depending on the axial number of grid points more or less iterations are needed. Because $C_{\Xi+1}$ and $C_{\Xi-1}$ do

Fig. 1. Discretisation scheme used in the numerical model.

not exist in the discretisation scheme, eqns. (13) cannot be used to solve $C_{\bar{\varepsilon}}$ and C_0 , respectively. Therefore the following assumptions were made. $C_{\bar{\varepsilon}+1}$ is taken equal to $C_{\bar{\varepsilon}-1}$ because of symmetry around the fibre axis. To derive C_0 , C_1 is written as a second order Taylor expansion:

$$C_1 = C_0 + \Delta U \frac{\partial C}{\partial U} + \frac{(\Delta U)^2}{2} \frac{\partial^2 C}{\partial U^2} \quad (15)$$

The first order terms are taken from the boundary conditions for A and B (Eqns. 6a and 6b, respectively), while the second order derivatives are taken from the differential mass balances, eqns. (3) and (4).

According to eqn. (13a), $C^{\psi-1}$ is needed to start the calculation, although it is not incorporated in the discretisation scheme. Therefore $C^{\psi-1}$ is assumed to exist, located before the entrance of the mass exchanging area and taken equal to the initial condition, C^0 . This is consistent with the real physical situation as there is no mass exchange in the first part of the fibre because it is surrounded by the potting with which the fibres are glued in the module. Thus the liquid in this part of the fibre has the same composition as the liquid entering of the mass exchanging area.

Because the concentration gradients at the entrance of the mass exchanging area of the fibre and the region close to the wall are the steepest, it is desirable, in view of accuracy, to increase the concentration of grid points at these places. Therefore the following coordinate transformations were applied.

$$\lambda = g(l) = l \cdot l \quad (16)$$

$$U = f(x) = 1 - (0.01 x + 0.99 x^4) \quad (17)$$

The calculations were performed with a Pascal program on a 386 Personal Computer. To determine the accuracy of the numerical method in relation to the computer calculation time, different gridpoint concentrations were used in a standard calculation with $\alpha = 10^{-5}$, $D_B/$

TABLE 1

Calculated fluxes with different grid point concentrations

$\bar{\varepsilon} \times \Psi$ (-)	$J_{A,loc}$ (mol/m ² -sec)	$J_{A,mean}$ (mol/m ² -sec)
20 × 100	1.658×10^{-3}	2.312×10^{-3}
20 × 200	1.664×10^{-3}	2.328×10^{-3}
20 × 400	1.667×10^{-3}	2.336×10^{-3}
40 × 100	1.651×10^{-3}	2.301×10^{-3}
40 × 200	1.656×10^{-3}	2.317×10^{-3}
40 × 400	1.659×10^{-3}	2.326×10^{-3}
80 × 200	1.656×10^{-3}	2.316×10^{-3}
80 × 400	1.659×10^{-3}	2.325×10^{-3}

$D_A = 0.5$ and $\nu_B m C_{Ag}/C_{B0} = 0.04$. The calculated fluxes at $\lambda = 200$ are compared in Table 1. A grid of $\bar{\varepsilon} \times \Psi = 40 \times 200$ was chosen for other calculations to get reasonable calculation times with sufficient accuracy.

The model for the gas phase was solved in a similar way. However, since only one component had to be considered and no iterations because of the linearised reaction were needed, the calculation time was significantly reduced. The results can be compared to those of Yamané et al. [10] who used the discretisation scheme of Crank-Nicholson without coordinate transformations to describe mass transfer in the gas phase flowing through a porous tube.

4. Numerical results

4.1. Mass transfer with chemical reaction in a liquid flowing laminarly through a fibre with a gas permeable wall

Variation of reaction rate

The ratio of diffusion and reaction is expressed by α (eqn. 10). To illustrate the effect of its value on the calculated fluxes, different $k_{1,1}$ values were used in a standard case of which

the variables are given in Table 2. In the calculations no external mass transfer resistance is assumed which gives a constant gas phase concentration over the fibre length. The calculated local fluxes are presented in Fig. 2.

For $\alpha \rightarrow \infty$ ($k_{1,1} \rightarrow 0$) an asymptotic solution is obtained similar to physical absorption which can be used to verify the numerical model. The results coincide with the mass transfer analogy of the Graetz-Lévêque solution.

All the calculated fluxes for the different reaction rate constants show a decrease with the fibre length, see Fig. 2. For the large values of α this is caused by physical saturation of the liquid with A. Because hardly any A is consumed by the reaction, the liquid becomes saturated with A to some extent which reduces the

TABLE 2

Standard conditions for calculation of fluxes with different reaction rate constants

$C_{A,g}$	41.6 mol/m ³
D_A	1.0×10^{-9} m ² /sec
m	0.5
$C_{B,0}$	1000 mol/m ³
D_B	2.0×10^{-9} m ² /sec
ν_B	2
R	1.0×10^{-3} m
ν_L	0.1 m/sec
Z	0.4 m

Fig. 2. Simulated local flux as a function of fibre length for different reaction rate constants, other data see Table 2.

flux. For the intermediate values of α the flux is almost constant over the fibre length. Physical saturation does not occur because the chemical reaction takes away the transferred A. For intermediate α the concentration of B present is still that large that it is not depleted significantly. The reaction can be considered to be pseudo first order. At low values of α the reaction rate of A with B is very fast, diffusion of B from the center to the wall is rate determining. The flux decreases along the fibre length because of the consumption of B.

The enhancement factor, E , mentioned in eqn. (2), cannot be used to illustrate the effect of the chemical reaction on the absorption fluxes in fibre membranes because driving forces for the chemical and physical flux cannot be taken equal in a sensible way. Therefore a modified enhancement factor, E_{mod} , is defined as the chemical flux divided by the physical flux ($\alpha \rightarrow \infty$) at the same tube length, liquid flow, etc. These values are plotted in Fig. 3 for different reaction rate constants. Initially, with an increasing reaction rate, E_{mod} increases with fibre length because the chemical enhanced flux is almost constant while the physical flux decreases. For the fast reaction rates the E_{mod} shows a slight decrease with fibre

Fig. 3. Simulated modified local enhancement factor versus fibre length for different reaction rate constants. Asymptotic enhancement factors were calculated according to eqn. (3) (Ha) and eqn. (4) (E_{Lev}).

length. This is due to the consumption of B. The chemical enhanced flux is decreasing relatively more rapidly than the physical flux, which decreased only due to saturation of the liquid with A, see Fig. 2.

In the lower part of Fig. 3, the enhancement factor equal to the Hatta number:

$$E = Ha = \frac{\sqrt{k_{1,1} \bar{C}_B D_A}}{k_L} \quad (18)$$

for the slowest reaction rate used in the calculations, is presented. In this case the mixing cup concentration was used for the effective bulk concentration of B, while the mass transfer coefficient was taken from the physical flux ($\alpha \rightarrow \infty$). Although this calculated enhancement factor and E_{mod} from the numerical model coincide in Fig. 3, E_{mod} is slightly larger due to the definition difference of the enhancement factors. However, the degree of saturation in the physical absorption process is not very high resulting in only small differences between the two enhancement factors. For $\alpha \rightarrow 0$ the asymptotic solution of maximal enhancement is obtained, see eqn. (19).

$$E = E_{\infty} = \left(1 + \frac{D_B \bar{C}_B}{\nu_B D_A C_{A,i}} \right) \left(\frac{D_B}{D_A} \right)^n \quad (19)$$

In this case the reaction zone is located close to the fibre wall. In this small zone, the liquid velocity gradient of the laminar velocity profile can be considered as constant. This situation should resemble the Lvque model which assumes a constant velocity gradient in the boundary layer. The value of the enhancement factor according to the Lvque model, E_{Lev} , can be calculated by eqn. (19) with $n = 1/3$. In this equation a bulk phase concentration of B must be used. Because in the fibre the reaction zone is located close to the fibre wall the system can be looked upon as if a bulk phase is present from which B is supplied. Therefore the concentration of B at the centre of the fibre, which did

not decrease over the fibre length, was taken as the bulk concentration, C_B in eqn. (19), to obtain E_{Lev} .

In Fig. 3, it is shown that this enhancement factor, E_{Lev} , is somewhat larger than E_{mod} . Asymptotically, with fibre length going to zero, there two factors have the same value. This can be explained by the fact that the chemical and physical flux are obtained with the same driving force. Due to the saturation at longer fibre lengths the physical flux is no longer obtained with the same driving force as the chemical flux. This effect and the depletion of component B cause the deviation between E_{mod} and E_{Lev} . Nevertheless, the enhancement factor defined by the Lvque model provides a good estimate to calculate the influence of a fast chemical reaction on the absorption flux for practical fibre lengths.

For the intermediate reaction rates neither eqn. (3) nor eqn. (4) provided values of the enhancement factor corresponding to the numerical results. This is not surprising since the conditions for the validity of these equations are not satisfied, which is also the case in systems with a bulk phase present.

Absorption with external mass transfer resistance

The influence of a possible external mass transfer resistance on the absorption can be calculated in this numerical approach with the boundary condition of eqn. (8a). It must be mentioned that in the calculations the external resistance, $1/k_{\text{ex}}$, is not explicitly divided between the membrane and the gas phase part as in eqn. (2).

Two gas phase concentrations: 41.6 and 4 mol/m³ were used and the reaction rate constant $k_{1,1}$ was taken as 1 m³/(mol·sec). Other variables of these calculations are mentioned in Table 2. The results are plotted in Figs. 4(a) and 4(b) respectively, in which the mean flux over the fibre length is given versus the exter-

Fig. 4. Mean absorption fluxes over the fibre length and liquid interface concentrations simulated as a function of the external mass transfer coefficient. Gas phase concentration (a) 41.6 mol/m³, (b) 4 mol/m³.

nal mass transfer coefficient together with the interface concentration in the liquid phase. In both figures it can be seen that when k_{ex} is decreased mass transfer in the gas phase gets a more significant influence on the fluxes, as can be expected. With the same value of the external mass transfer coefficient, this effect is less pronounced with the higher gas phase concentration because then, the contribution of the liquid phase resistance is relatively larger.

4.2. Mass transfer in a gas flowing laminarly through a fibre with a gas permeable wall

The model for mass transfer in the gas phase was used to calculate absorption fluxes which

were completely determined by mass transfer in the gas and the membrane phase. This means the concentration at the gas–liquid interface, $C_{A,G,i}$, was assumed to be zero. The absorption flux is calculated as a function of gas phase velocity in a fibre with the same dimensions as the one used in the calculations for mass transfer in the liquid phase (Table 2) with a wall thickness of the membrane of 2×10^{-4} m. The results are presented in Fig. 5 as the overall mass transfer coefficient versus the gas phase velocity with the mass transfer coefficient of the membrane as a parameter.

In the limit of a negligible mass transfer resistance of the membrane ($k_m \rightarrow \infty$, indicated by $k_m = 100$), the results are similar to the results of the Graetz–Lévêque equation for mass transfer, in which a fixed wall concentration is assumed. The Graetz number in the numerical runs is smaller than 10. This means that the concentration profile is developed completely and therefore the mass transfer coefficient in the gas phase is not a function of gas velocity. The overall mass transfer coefficient is calculated from the flux at the gas–liquid interface. Therefore the outer diameter of the fibre must be taken to calculate the Sherwood number, which for $k_m = 100$ equals 3.67. This value co-

Fig. 5. Simulated overall mass transfer coefficients versus gas phase velocity in the fibres with the membrane mass transfer coefficient as a parameter.

incides with the Graetz-Lvque solution for this asymptotic case.

It can be concluded that because the mass transfer through the membrane wall is determined by diffusion only, the overall mass transfer coefficients are not a function of gas phase velocity.

5. Experimental

5.1. Set-up and modules

Experiments were carried out with the absorption of H_2S , CO_2 and N_2O in aqueous solutions of sodium hydroxide. Four different modules were used of which the specifications are given in Table 3. The membranes in modules A, B and C are made of microporous polypropylene (Accurel, AKZO). The fourth module, D, was supplied by Sempas and consists of microporous membranes with a thin ($0.7\ \mu\text{m}$) silicone rubber layer at the inside of the fibres.

The experimental set-up is shown in Fig. 6 and is a different one compared to that used in Part I. The gases were supplied from gas bottles and the compositions of the gas mixtures were adjusted with thermal mass flow controllers. Actual gas phase velocities in the fibres up to 3 m/sec could be applied.

The liquid was pumped from a storage vessel through the module and recycled. The liquid flow rate is measured with rotameters in the liquid stream. The hydroxide solution was re-

newed when 10% of the initial concentration of OH^- was converted. Liquid phase velocities through the modules up to 2 m/sec were applied. The experiments were performed at 293 K.

The reaction rate of CO_2 with OH^- is relatively fast. To study mass transfer with a slower reaction rate a solution of methyl-di-ethanolamine (MDEA) was applied. After a short time of operation severe leakage of the liquid through the membranes was observed. The combination of the vibrations induced by the pump and the low surface tension of the amine is suspected as the cause of this phenomenon but no hard proof could be found. However, the Sempas module with the coated membranes could supply a secure prevention of the leakage. To study whether the silicone rubber layer reduces the absorption rates the module was tested with N_2O and CO_2 absorption in the hydroxide solution in comparison to the membranes without coating.

5.2. Liquid phase mass transfer

Liquid phase mass transfer coefficients were measured with the absorption of N_2O . Pure N_2O was used to avoid a mass transfer resistance in the gas and membrane phase; k_L was derived from eqn. (19). The absorption flow Q_{Abs} was measured with a soap film meter.

TABLE 3

Specifications of the membrane modules used in the experiments

Module	$d_{\text{fibre,in}}$ ($10^{-3}\ \text{m}$)	$d_{\text{fibre,out}}$ ($10^{-3}\ \text{m}$)	d_{module} ($10^{-2}\ \text{m}$)	length (m)	nr. of fibres (—)	a_{Lin} (m^{-1})	a_{Lout} (m^{-1})	x_{fibres} (—)
A	2.2	2.6	1.0	0.21	8	704	832	0.54
B	2.2	2.6	1.4	0.59	14	370	438	0.48
C	0.6	1.0	1.4	0.24	85	817	1362	0.43
D	1.2	1.6	1.0	0.28	25	1200	—	0.64

Fig. 6. Experimental set-up.

$$k_L = -\frac{Q_{v,L}}{A} \ln\left(1 - \frac{C_z}{C_w}\right) \quad (20)$$

$$= -\frac{Q_{v,L}}{A} \ln\left(1 - \frac{Q_{Abs}}{m Q_{v,L}}\right)$$

To study the influence of chemical reaction on liquid phase mass transfer, pure CO₂ was absorbed. The absorption fluxes were measured similar to the experiments with N₂O.

5.3. Gas phase mass transfer

A diluted stream of H₂S in N₂ was mixed from two gas bottles via thermal mass flow controllers. One gas bottle contained a 2000 ppm mixture of H₂S with N₂, the other existed of pure N₂. The mixture was led through the reactor while in- and outlet concentrations were measured with a Varian 3400 gaschromatograph. For the analysis of sulfur it was equipped with a flame photometric detector (FPD). The slow ab- and desorption of H₂S by the stainless steel of the tubing in the set-up disturbed the signal in the outlet with H₂S gas phase concentration below 5 ppm.

Overall K_G values were calculated to eqn. (21).

$$K_G = -\frac{Q_{v,G}}{A} \ln\left(\frac{C_{G,in}}{C_{G,out}}\right) \quad (21)$$

5.4. Absorption from a gas mixture

A gas containing 15% of CO₂ (balance N₂) was taken to study both gas and liquid phase controlled absorption. Fluxes were determined with a soap film meter and a gas chromatograph which also contained a thermal conductivity detector (TCD) next to the FPD.

6. Experimental results

6.1. Liquid phase mass transfer by physical absorption

Physical mass transfer coefficients were measured as a function of liquid velocity. The dependency of k_L with the liquid velocity was also calculated with the numerical model with negligible reaction rates, which then in fact is the numerical solution of the Graetz–Léveque problem. The results are plotted in Fig. 7(a) in

Fig. 7. Experimental physical absorption of N_2O in an aqueous solution of NaOH in different modules. Gas around, liquid through the fibres. (a) Sherwood number as a function of the Graetz number compared to the theoretical relation according to Graetz-Léveque, (b) Sherwood number as a function of the Reynolds number.

the dimensionless Graetz and Sherwood numbers. At large Gz numbers the experimental values deviate from the theoretical values. This is attributed to the change from laminar to turbulent flow as can be seen from Fig. 7(b) in which the Sherwood number is plotted as a function of the Reynolds number. For Re between 1000 and 2000 an increase of the dependency of Sh with Re is observed.

In practical applications it may not be attractive, because of the power consumption, to create turbulent flow in membrane absorbers with narrow fibres in densely packed modules. Next to this economical reason it is also possi-

ble that due to the high liquid pressure the membranes become wetted with the absorption liquid. Mass transfer will then be greatly reduced because of the diffusion process in the stagnant liquid in the pores of the membrane. Therefore no further attention is paid to mass transfer in turbulent flows.

Wetting of the membranes was also observed with an aqueous solution of MDEA. Therefore module D, the membranes of which are coated with a thin silicone rubber layer, was tested with the hydroxide solutions to see whether the additional mass transfer resistance of the silicone layer reduced the mass transfer.

The permeability of N_2O in silicone rubber is given by Robb [11] to be 4350 barrer. This yields a mass transfer coefficient of 4.7×10^{-3} m/sec in the present silicone layer of 0.7×10^{-6} m, which, in terms of mass transfer resistance, is negligible compared to the mass transfer resistance in the liquid phase.

This conclusion is confirmed by the experimentally determined Sherwood numbers. When these are compared to the results of the membranes with the open pores no significant mass transfer reduction by the silicone layer can be observed (Fig. 7a).

6.2. Liquid phase mass transfer with chemical enhanced absorption

The absorption from a 100% CO_2 gas phase is presented in Fig. 8 as the mean flux over the fibre length versus the liquid velocity in the fibres for the three modules used in this study (Table 3). The influence of the fibre length on the absorption flux can be seen when the results of modules A and B are compared. In these modules the fibres have the same diameters. In the longer module B the mean flux is lower than in module A because the hydroxide is depleted to a larger extent and the saturation of the liquid with CO_2 is more pronounced.

The influence of fibre diameter on the ab-

Fig. 8. Experimental absorption flux of CO_2 in an aqueous solution of NaOH as function of liquid phase velocity in the fibres of three different modules.

sorption is shown with the results of module A and C, which have about the same fibre lengths but different fibre diameters. In Fig. 8, depending on the liquid velocity, either the absorption in module A or C is higher. Mass transfer in turbulent flow is generally larger than in laminar flow. Therefore the absorption with the larger liquid velocities in module A is higher than in module C, since with liquid velocities larger than 0.5 m/sec the flow in module A is turbulent (see also section 6.1), while the flow in module C is laminar over the whole range of liquid velocities used in the experiments.

For the liquid velocities below 0.5 m/sec the fluxes in module C are higher. From the numerical results (section 5.1) it can be concluded that with very fast reaction rates, which is the case for CO_2 reacting with OH^- , the chemical enhancement is not depending on the diameter of the fibres. Therefore the absorption fluxes in module A and C differ in terms of the physical mass transfer. From the Graetz-Lvque equation it follows that k_L is proportional to $d^{-0.33}$. With the difference in fibre diameter between modules A and C, k_L differs a factor 1.5, which is about the ratio between the measured fluxes.

To simulate the measured fluxes with the numerical model, actual physical constants are

needed, which were found in literature. They are given in Table 4. The rate constant of the reaction of CO_2 with OH^- was taken from Pohorecki and Moniuk [12]. The stoichiometric constant was taken equal to 2 which is valid in the range of pH used in the experiments (Danckwerts and Sharma [13]). The distribution coefficient was calculated from the $\text{N}_2\text{O}/\text{CO}_2$ analogy (Laddha et al. [14]). The relation of Joosten and Danckwerts [15] was used to correct the distribution and diffusion coefficient of N_2O for the ionic strength of the solution. The ratio of diffusion coefficients of OH^- and CO_2 was measured in a stirred cell, which is reported in Appendix B.

The simulated fluxes are compared with the experimental fluxes in Fig. 9. With the as-

TABLE 4

Physical and kinetic data used in the simulation of the experimental results

$C_{\text{CO}_2, \text{G}}$	40.6 mol/m ³ (100%)
$C_{\text{OH}^-, \text{L}}$	600 mol/m ³
D_{CO_2}	1.5×10^{-9} m ² /sec
D_{OH^-}	2.91×10^{-9} m ² /sec
m_{CO_2}	0.75
ν_B	2
$k_{1,1}$	8.4 m ³ /(mol·sec)

Fig. 9. Simulated versus experimental fluxes for the absorption of CO_2 in an aqueous solution of NaOH. Data used in simulations, see Table 4.

sumed parameters it is possible to predict the absorption fluxes within 20% from the experimental value. The experimental fluxes measured with module D, containing the silicone rubber coated membranes, can also be simulated fairly well with the numerical model. However, in this model the additional mass transfer resistance of the silicone layer is not taken into account. Obviously the layer does not influence the mass transfer rate significantly. This is also deduced from the permeability of the silicone film if translated into a mass transfer resistance for the present experimental system this equals 286 sec/m. This resistance is negligible compared to the mass transfer resistance of the liquid phase, $1/(m k_L E)$, which is about 6600 sec/m.

6.3. Gas phase mass transfer

In order to obtain gas phase determined mass transfer, diluted H_2S in N_2 was passed through the modules and analysed as mentioned in section 4.3. For the experiments with the gas flowing through the fibres the ratio of in- and outlet concentration of H_2S is presented in Fig. 10 as a function of the gas phase velocity. The experimentally determined values did not show a de-

Fig. 10. Absorption of H_2S from a mixture with N_2 in an aqueous solution of NaOH in three different modules, see Table 3. Comparison with results of a simulation model. Gas flowing through the fibres.

pendency on the liquid flow rate from which it may be concluded that the mass transfer is completely determined by the resistances in the gas and membrane phase. Thus a zero gas-liquid interface concentration was assumed in the numerical calculations. The results of these numerical calculations are also presented in Fig. 10 and show some discrepancies with the experimentally determined values, especially for the low gas flow rates. In this case the gas phase analysis was not accurate enough (section 5.3). The measurements show that removal of H_2S above 99% is not possible. However, due to the release of H_2S from the tubing the outlet signal of the module may be disturbed.

For higher gas phase velocities in module A and B the results of the simulation and the experiments agree quite well. From the simulations it follows that module C is the most effective for H_2S removal. However, the inaccuracy of the gas phase analysis does not permit a proper comparison of theory and practice at low gas phase velocities.

In experiments in which a higher velocity was applied small gas bubbles were formed in the liquid. This must be attributed to the pressure of the gas phase which became larger than the pressure in the liquid phase.

Fig. 11. Experimentally determined overall gas mass transfer coefficients as a function of gas phase velocity around the fibres for three different modules.

With gas flow around the fibres, K_G calculated from eqn. (20) is presented in Fig. 11 as a function of the gas phase velocity. In this situation it is less likely that the accuracy of the gas phase analysis is affecting the experimental results because the absorption of H_2S was less effective, outlet concentrations of H_2S were higher than 20 ppm. However, the maldistribution of the gas phase around the fibres can influence the removal of H_2S substantially. This was shown in a previous study on physical absorption, see Part 1 [1]. The non-uniformity of the gas flow is caused by different channel widths between the fibres in the module. Therefore, the experimental data do not allow general conclusions on gas phase mass transfer with gas flowing around the fibres. However they provide module specific data which can be used for the simulation of the data derived from absorption of CO_2 in a 15% mixture with nitrogen which will be discussed in the next section.

6.4. Absorption from a gas mixture

The results of absorption experiments from a CO_2/N_2 (15/85%) mixture flowing co- and countercurrently with the hydroxide solution are presented in Fig. 12 (module A). Hardly any difference is observed between these two cases

Fig. 12. Experimental absorption of CO_2 from a gas mixture in an aqueous solution of NaOH determined with co- and countercurrent flow of gas and liquid phase. Liquid through the fibres in module A, see Table 3. Gas phase velocity = 0.22 m/sec.

which can be attributed to the relatively short lengths of the fibre modules. This is in agreement with calculations carried out with the numerical model which showed that with the fibres used in the present study no significant difference between the absorption in co- and countercurrent flow can be observed.

In Fig. 13 the dependency of the absorption fluxes with liquid phase velocity is presented with different gas phase velocities. The liquid is flowing through the fibres. The absorption rate is only slightly influenced by the liquid

Fig. 13. Experimental absorption of CO₂ from a gas mixture in an aqueous solution of NaOH, dependency of gas and liquid flow rate in two modules with liquid through the fibres.

phase velocity, which could be attributed to a minor mass transfer resistance in the liquid phase. However, the problem of a non-uniform gas phase distribution (section 6.3) should also be considered.

The experiments were simulated with the numerical model. The simulated and experimental values are compared in Fig. 14. The kinetic and physical data used are the same as those used in section 6.2. The overall mass transfer coefficients of the gas phase were estimated from the experiments reported in section 6.3 with gas flowing around the fibres. The calculations show that with these module spe-

cific parameters the absorption can be simulated rather well.

7. Conclusions

Chemical enhanced absorption in liquids flowing laminarly through a hollow fibre membrane module has been studied with the absorption of carbon dioxide and hydrogen sulphide in solutions of sodium hydroxide. This process can be simulated with a numerical model assuming an irreversible second order reaction. The model calculations coincide with the analytical solution of the Graetz-Lvque problem at the limit of only physical absorption. In the case of low depletion of the liquid phase reactant the simple chemical enhancement factor for a pseudo first order reaction rate being equal to the Hatta number (eqn. 3) can be used to predict the chemical enhanced absorption flux in the fibre system. For instantaneous reactions the Lvque model provides also a good approximation of the enhancement factor for low liquid loadings.

With the same numerical technique, mass transfer from a gas phase flowing through the fibres was calculated. With a negligible membrane mass transfer resistance the numerical solution reduces to the analytical solution of the Graetz-Lvque problem. For practical conditions the concentration profile is developed

Fig. 14. Simulated versus experimental fluxes for the absorption of CO₂ from a gas mixture in an aqueous solution of NaOH. Liquid through the fibres. Data for simulation see Table 4.

completely at very short fibre lengths. Therefore the mass transfer coefficient in the gas phase is not expected to be depending on gas phase velocity or fibre length.

The data of the experimental absorption of pure carbon dioxide and nitrous oxide in the hydroxide solution were simulated within 20% by the numerical model for which physical and chemical parameters were taken from literature.

The microporous membranes may be wetted by the absorption liquid. To prevent this in a practical application it can be worthwhile to use membranes coated with a very thin permeable layer on the liquid side of the membrane. In the present study a module equipped with silicone rubber coated membranes was used. This very thin layer (0.7 μm) did not show a significant increase of the mass transfer resistance in comparison to an uncoated membrane. Especially if absorption liquids are being used which would wet the membranes because of their surface tension these kind of membranes could enlarge the field of application of the microporous hollow fibre membrane module in gas/liquid contacting.

In the case of gas flow through the fibres where mass transfer is nearly completely determined by the resistance in the gas phase and the membrane, the analysis of the gas phase was not accurate enough to compare the experimental with the simulated results.

Acknowledgements

These investigations were supported by TNO the Netherlands organization for applied scientific research. We also acknowledge G. Schorfhaar for the construction of the experimental setup, dr.ir. J.A.M. Kuipers for his sup-

port in the mathematical issues and E. Damhuis and C. Bootsvelde for their part in the experimental work.

List of symbols

A	membrane area (m^2)
C	liquid phase concentration (mol/m^3)
C	bulk liquid phase concentration (mol/m^3)
C_G	gas phase concentration (mol/m^3)
d	fibre diameter (m)
D	diffusion coefficient (m^2/sec)
E	enhancement factor (—)
Gz	Graetz number [$vd^2/(ZD)$]
Ha	Hatta number (eqn. 3) (—)
J	absorption flux [$\text{mol}/(\text{m}^2\text{-sec})$]
k	mass transfer coefficient (m/sec)
$k_{1,1}$	second order reaction rate constant [$\text{m}^3/(\text{mol}/\text{sec})$]
K	overall mass transfer coefficient (m/sec)
m	distribution coefficient (—)
M	radial number of grid points (—)
n	power value in eqn. (4) (—)
N	axial number of grid points (—)
Q_v	volumetric flow rate (m^3/sec)
r	radial coordinate (m)
R	fibre radius (m)
Re	Reynolds number ($\rho vd/\mu$)
Sc	Schmidt number [$\mu/(\rho D)$]
Sh	Sherwood number (kd/D)
t	time coordinate (sec)
U	dimensionless radial coordinate (—)
v	velocity (m/sec)
V	volume (m^3)
x	transformed dim. less radial coord. (—)
z	axial coordinate (m)
Z	fibre length (m)
α	dimensionless ratio of diffusion over reaction rate (—)
λ	dimensionless length coordinate (—)
μ	dynamic viscosity (Pa-sec)
ν	stoichiometric coefficient (—)

ρ	density (kg/m ³)
ξ	discrete radial coordinate number (–)
Ξ	number of radial grid points (–)
ψ	discrete axial coordinate number (–)
Ψ	number of axial grid points (–)

Indices

Abs	absorption
b	bulk
ex	external
exp	experimental
G	gas phase
i	gas/liquid-interface
in	inlet stream
L	liquid phase
Lev	acc. to Leveque model
M	membrane phase
mod	modified
out	outlet stream
ov	overall
r	radial
sat	saturated
sim	simulated
th	theoretical
tot	total
v	volumetric
w	at the wall of the fibre
0	initial/at entrance
∞	at infinite reaction rate
*	dimensionless concentration

References

- 1 H. Kreulen, C.A. Smolders, G.T. Versteeg and W.P.M. van Swaaij, Microporous hollow fibre membrane modules as gas–liquid contactors. Part I. Physical mass transfer processes. A specific application: Mass transfer in highly viscous liquids *J. Membrane Sci.*, 78 (1993) 197.
- 2 Qi, Z. and Cussler, E.L., 1985. Microporous hollow fibres for gas absorption, part I: Mass transfer in the liquid, *J. Membrane Sci.*, 23, 321.
- 3 Qi, Z. and Cussler, E.L., 1985b, Microporous hollow fibres for gas absorption, part II: Mass transfer across the membrane, *J. Membrane Sci.*, 23, 333.
- 4 Cooney, D.O. and Jackson, C.C., 1989, Gas absorption in a hollow fibre device, *Chem. Eng. Comm.*, 79, 153.
- 5 Geuzens, P., Froment, L., Leysen, R. and Vlasselaar, F., 1990, Gas absorption through membranes, in: *Gas separation technology*, ed: E.F. Vansant, R. Dewolfs, 405.
- 6 Graetz, L., 1883, Über die Wärmeleitungsfähigkeit von Flüssigkeiten, 1e Abhandlung, *Annalen der Physik und Chemie*, 18, 79.
- 7 Graetz, L., 1885, Über die Wärmeleitungsfähigkeit von Flüssigkeiten, 2e Abhandlung, *Annalen der Physik und Chemie*, 25, 337.
- 8 Lévêque, J., 1928, *Annls. Mines Carbur.*, Paris (Series 12), 201; idem *ibid*, 305; idem *ibid*, 381.
- 9 Baker, G.A. and Oliphant, T.A., 1960, An implicit numerical method for solving the two-dimensional heat equation, *Quart. Appl. Math.*, 17, 4, 361.
- 10 Yamané, T., Matsuda, M. and Sada, E., 1981, Application of porous teflon tubing method to automatic fed-batch culture of micro-organisms. I: Mass transfer through porous teflon tubing, *Biotechn. and Bioeng.*, 23, 2493.
- 11 Robb, W.L., 1968, Thin silicone membranes – their permeation properties and some applications, *Annals New York Acad. Sci.*, 146, 119.
- 12 Pohorecki, R. and Moniuk, W., 1988, Kinetics of reaction between carbon dioxide and hydroxyl ions in aqueous electrolyte solutions, *Chem. Eng. Sci.*, 43, 7, 1677.
- 13 Danckwerts, P.V. and Sharma, M.M., 1966, The absorption of CO₂ into solutions of alkalis and amines (with some notes on hydrogen sulphide and carbonyl sulphide), *The Chem. Eng.*, October, 244.
- 14 Laddha, S.S., Diaz, J.M. and Danckwerts, P.V., 1981, The N₂O analogy: the solubilities of CO₂ and N₂O in aqueous solutions of organic compounds, *Chem. Eng. Sci.*, 36, 228.
- 15 Joosten, G.E.H. and Danckwerts, P.V., 1972, Solubility and diffusivity of nitrous oxide in equimolar potassium carbonate – potassium bicarbonate solutions at 25°C and 1 atm., *J. of Chem. and Eng. Data*, 17, 4, 452.
- 16 Sieder, E.N. and Tate, G.E. 1936, Heat transfer and pressure drop of liquids in tubes, *Ind. Eng. Chem.*, 28, 1429.
- 17 Yang, M. and Cussler, E.L., 1986, Designing hollow-fibre contactors, *AIChE J.*, 32, 1910.
- 18 Nijssing, R.A.T.O., Hendriks, R.H. and Kramers, H., 1959, Absorption of CO₂ in jets and falling films of electrolyte solutions with and without chemical reactions, *Chem. Eng. Sci.*, 10, 88.
- 19 Glasscock, D.A. and Rochelle, G.T., 1989, Numerical simulation of theories for gas absorption with chemical reaction, *AIChE J.*, 35, 1271.

- 20 Littel, R., Filmer, B., Versteeg, G.F. and Van Swaaij, W.P.M., 1991, Modelling of simultaneous absorption of H₂S and CO₂ in alkanolamine solutions: the influence of parallel and consecutive reversible reactions and the coupled diffusion of ionic species, *Chem. Engng. Sci.*, 46, 2302.
- 21 Westerterp, K.R., van Swaaij, W.P.M. and Beenackers, A.A.C.M., 1984, *Chemical Reactor Design and Operation*, Wiley and Sons, New York.
- 22 Higbie, R., 1935, The rate of absorption of a pure gas into a still liquid during short periods of exposure, *Trans. Am. Inst. Chem. Engr.*, 35, 365.
- 23 Versteeg, G.F., Blauwhoff, P.M.M. and Van Swaaij, W.P.M., 1987, The Effect of Diffusivity on Gas-Liquid Mass Transfer in Stirred Vessel. Experiments at Atmospheric and Elevated Pressures, *Chem. Engng. Sci.*, 42, 1103.

Appendix A

Discussion of the results of Qi and Cussler [2]

In the introduction it was mentioned that Qi and Cussler [2] measured mass transfer coefficients in a liquid phase flowing through a non-wetted porous fibre with the reaction between OH⁻ ions and CO₂, transferred from the gas phase. It seems contradictory to determine liquid phase mass transfer coefficients in a chemically reacting system but Qi and Cussler claim it can be done with certain assumptions. With the numerical models developed in this study it is possible to check the validity of the approach of Qi and Cussler.

From the degree of OH⁻ conversion the liquid phase mass transfer coefficients for OH⁻ ions were calculated.

$$k_L = - \frac{\nu_L d}{4 Z} \ln \left(\frac{C_{\text{OH}^-} - C_{\text{OH}^-}_{\text{eq}}}{C_{\text{OH}^-} - C_{\text{OH}^-}_{\text{eq}}} \right) \quad (\text{A1})$$

Qi and Cussler concluded that the experimentally determined correlation of Sieder and Tate [16] for heat transfer in laminar pipe flow is also valid for mass transfer in their system.

$$Sh = 1.86 Gz^{1/3} \left(\frac{\mu}{\mu_w} \right)^{1/7} \quad (\text{A2})$$

However, Qi and Cussler did not take into account the ratio of bulk and wall viscosity as was originally proposed by Sieder and Tate [16]. The Sieder and Tate relation is a modified version of the theoretical solution derived by Graetz [6,7] and Lvque [8].

$$Sh = 1.62 Gz^{1/3} \quad (\text{A3})$$

In other studies (Yang and Cussler [17]) and in Part 1 of the present study [1] it was found that this relation describes the mass transfer process accurately.

One of the concepts of the Graetz-Lvque problem is that the heat is transported only through the wall of the tube, in case of cooling, with the boundary condition that the wall temperature is constant over the tube length. This means that for the application in the mass transfer analogon, mass should disappear in the liquid by reaction only at the position of the wall and that the transferred component must have a constant wall concentration. Qi and Cussler assumed that the hydroxyl ions were only consumed at the fibre wall because of the very fast reaction between CO₂ and OH⁻, giving a zero OH⁻ concentration at the wall and being constant along the fibre. Therefore, these authors concluded that the liquid phase mass transfer coefficient for the transport of OH⁻ deduced from their experiments (Fig. 3 in their paper) could be described with the relation of Sieder and Tate. However, they found that the mass transfer coefficient depended on the sodium hydroxide concentration, shown in Fig. 4 of their paper. This seems to indicate that the assumption of a negligible wall concentration may not be valid. However, also the similarity between the Graetz-Lvque problem and their experimental system should be reconsidered.

With the two numerical models developed in section 2 and 3 of the present study it is possible to simulate the experiments of Qi and Cussler and check whether the assumed zero wall concentration of hydroxyl ions is valid. With the first model, describing mass transport in the liquid phase with chemical reaction (section 2.1) the experimental work of Qi and Cussler can be simulated and from these simulations the mass transfer coefficient of OH^- can be derived. The second model, describing mass transfer in the gas phase flowing through the fibres (section 2.2), can be used to calculate the mass transfer of OH^- in a liquid phase flowing through the fibres according to the assumptions of the Graetz-Lvque problem. With this latter numerical model, it is assumed that OH^- is not consumed in the fibre but that it is transferred out of the fibre. The wall concentration of the transferred OH^- is set equal to zero. Therefore a very large k_m and a zero membrane/liquid interface concentration (eqn. 11a) were used in the calculations. In section 4.2 it was shown that in this case, the results are equal to the Graetz-Lvque solution.

The calculations with the two models were performed with a fibre of the dimensions used by Qi and Cussler, inner diameter = 4.13×10^{-4} m and exposed length = 0.15 m. The liquid velocity and the OH^- concentration were varied in the same range as used in the experiments, $0.01 < v_L < 0.32$ m/sec and $400 < [\text{OH}^-] < 2500$ mol/m³, respectively. The other variables needed in the calculations are taken from Table 4. It was assumed that the experiments of Qi and Cussler were carried out at room temperature at atmospheric pressures with a gas phase existing of pure carbon dioxide.

The results are given in Tables A-1 and A-2, L-model refers to the model with chemical reaction in the liquid phase, G-model refers to the model developed for mass transfer in the gas phase. Table A-1 shows that for an initial hydroxide concentration of 1000 mol/m³, the mass

transfer coefficients do not differ that much between the two models except for the lowest velocity. Because of the fast reaction rate between OH^- and CO_2 , hydroxide ions are removed only at the interface. If the supply of fresh hydroxide is reduced by lowering the liquid flow, CO_2 penetrates further into the liquid, which results in a relatively larger OH^- consumption compared to a situation in which CO_2 is not able to penetrate into the liquid phase. The mean dimensionless concentration of unreacted CO_2 in the liquid outlet of the module is an illustrative number in this case (Table A-1). However, the penetration of CO_2 in the liquid and the subsequent consumption of OH^- is not in agreement with the boundary condition for the Graetz-Lvque problem that the OH^- ions are only removed at the interface. The results of the G-model in Table A-2 do not show an influence of the hydroxide concentration on the mass transfer coefficient. This is consistent with the assumptions of this model. However, the results of the L-model show a decrease of the mass transfer coefficient with an increasing hydroxide concentration. When the initial hydroxide concentration is decreased, relatively more hydroxide is consumed in the liquid further from the interface because CO_2 was able to penetrate deeper into the liquid and react with hydroxide further from the interface. Table A-2 also shows that relatively small differences in hydroxide conversion cause considerable deviations in the calculated mass transfer coefficients.

The large dependency of the mass transfer coefficient on the hydroxide concentration found by Qi and Cussler in their Fig. 4 (an increase of the hydroxide concentration from 1.0 to 2.5 M reduces k_L from 4×10^{-5} to 10^{-5} m/sec), cannot be explained completely with these calculations. This may be attributed to the kinetic and physical constants which are depending on the hydroxide concentration (Joosten and Danckwerts [15], Pohorecki and Moniuk

TABLE A-1

Simulated results of experiments carried out by Qi and Cussler ([2], Fig. 3), variation of liquid phase velocity, $C_{\text{OH}^-} = 1000 \text{ mol/m}^3$

v_L (m/sec)	L-model			G-model	
	$C_{\text{OH}_2^-}/C_{\text{OH}_0^-}$ (-)	k_L (10^{-5} m/sec)	$C_{\text{CO}_2\text{L}}/m C_{\text{CO}_2\text{G}}$ (-)	$C_{\text{OH}_2^-}/C_{\text{OH}_0^-}$ (-)	k_L (10^{-5} m/sec)
0.01	4.76×10^{-4}	5.21	3.24×10^{-1}	1.69×10^{-2}	2.78
0.02	9.28×10^{-2}	3.24	2.43×10^{-2}	1.20×10^{-1}	2.92
0.04	2.93×10^{-1}	3.35	5.66×10^{-3}	3.10×10^{-1}	3.19
0.08	5.00×10^{-1}	3.78	2.66×10^{-3}	5.11×10^{-1}	3.70
0.16	6.63×10^{-1}	4.49	1.54×10^{-3}	6.65×10^{-1}	4.45
0.32	7.80×10^{-1}	5.43	9.57×10^{-4}	7.78×10^{-1}	5.52

TABLE A-2

Simulated results of experiments carried out by Qi and Cussler ([2], Fig. 4), variation of inlet hydroxide concentration, $v_L = 0.201 \text{ m/sec}$

$C_{\text{OH}_0^-}$ (mol/m ³)	L-model		G-model	
	$C_{\text{OH}_2^-}/C_{\text{OH}_0^-}$ (-)	k_L (10^{-5} m/sec)	$C_{\text{OH}_2^-}/C_{\text{OH}_0^-}$ (-)	k_L (10^{-5} m/sec)
400	0.689	5.15	0.708	4.78
800	0.704	4.86	0.708	4.78
1250	0.712	4.71	0.708	4.78
2500	0.724	4.46	0.708	4.78

[12]) which was not taken into account in the calculations.

The conclusion of the above presented simulations is that the conditions for measuring mass transfer coefficients with the CO_2/OH^- system are not always fulfilled completely because the reaction can influence the mass transfer process. Therefore a mathematical model is clearly needed to check the validity of the results measured with these conditions. However, the experimental values of Qi and Cussler do not differ very much from the values predicted by theory because of the velocities and the concentrations that were applied during the experiments.

Appendix B

Experimental determination of the diffusion coefficient of hydroxyl ions in a NaOH solution during carbondioxide absorption

For the simulation of the absorption experiments carried out in the membrane modules the diffusion coefficient of hydroxyl ions in the solution is needed. The absorption of CO_2 in an aqueous solution of NaOH is followed by a reaction between CO_2 and OH^- ions. Depending on pH the following reversible reactions take place (Nijsing et al. [18]):

Low pH: $\text{CO}_2 + \text{OH}^- \rightleftharpoons \text{HCO}_3^-$

High pH: $\text{CO}_2 + 2 \text{OH}^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}_2\text{O}$

The diffusion rate of the charged components present in the mixture is affected by the electrical forces in order to assure electroneutrality of the liquid phase which has not been taken into account in the present model. Therefore the transport of e.g. OH^- depends on the experimental conditions resulting in an apparent diffusion coefficient. Fundamental approaches of the coupled diffusion problem are given by Glasscock and Rochell [19] and Littel et al. [20].

However, in the present study the diffusion coefficient of OH^- was derived from the enhancement factor of CO_2 absorption in a stirred cell with an identical NaOH solution as was used in the experiments with the membrane module. If the experiments are carried out in the instantaneous reaction regime and the diffusion coefficient of CO_2 is known, the diffusion coefficient of OH^- can be calculated from the enhancement factor (Westerterp et al. [21]).

In a batchwise operated stirred cell the pressure decrease of pure CO_2 is a measure for the absorption rate:

$$V_G \frac{dP_{\text{CO}_2}}{dt} = -m k_L E \frac{P_{\text{CO}_2}}{R T} A \quad (\text{B1})$$

With the penetration model (Higbie [22]), which is generally used for this kind of experimental systems with a free gas/liquid interface (Westerterp et al. [21]) the enhancement factor, E , for very fast irreversible reactions is described by:

$$E = E_\infty = \left(1 + \frac{D_{\text{OH}} [\text{OH}^-]_b}{\nu D_{\text{CO}_2} [\text{CO}_2]_i} \right) \sqrt{\frac{D_{\text{CO}_2}}{D_{\text{OH}}}} \quad (\text{B2})$$

$$\text{if } E \ll Ha (= \sqrt{\frac{k_{1,1} [\text{OH}^-] D_{\text{CO}_2}}{k_L^2}})$$

With

$$1 \ll \frac{D_{\text{OH}} [\text{OH}^-]_b}{\nu D_{\text{CO}_2} [\text{CO}_2]_i} \ll Ha \quad (\text{B3})$$

which will be evaluated, the ratio of diffusion coefficients can be calculated directly from the pressure decrease with time:

$$\sqrt{\frac{D_{\text{OH}}}{D_{\text{CO}_2}}} = - \frac{dP_{\text{CO}_2}}{dt} \frac{\nu V_G}{k_L A [\text{OH}^-]_b R T} \quad (\text{B4})$$

The mass transfer coefficient, k_L , is a function of liquid stirrer speed and is measured from the absorption of N_2O in the same cell. This method is discussed by Versteeg et al. [23]. By means of the $\text{N}_2\text{O}/\text{CO}_2$ analogy (Laddha et al. [14]), k_L for CO_2 can be calculated.

The liquid, used in the absorption experiments with the membrane modules, was also used in these experiments which were carried out at 293 K. $[\text{OH}^-]_b$ was about 600 mol/m³. The stoichiometric constant, ν , was taken equal to 2, which is valid in the pH range of this solution (Nijsing et al. [18], Danckwerts and Sharma [13]). The interfacial area of the cell was $6.53 \times 10^{-3} \text{ m}^2$. The pressure was measured by an electronic pressure transducer with output on a recorder.

After filling the cell with the desired amount of CO_2 , the liquid stirrer was started and the pressure decrease was monitored. The pressure decreased linear in time for at least four min-

TABLE B-1

Experimental conditions

$P_{\text{CO}_2,0}$ (bar)	V_G (10^{-6} m^3)	k_L (10^{-5} m/ sec)	$[\text{OH}^-]_b$ (mol/m ³)	$(D_{\text{OH}}/D_{\text{CO}_2})^{0.5}$ (—)
0.8	628	1.56	653	1.37
0.8	669	1.70	649	1.23
1.0	627	1.47	561	1.49
1.0	670	1.52	546	1.53
0.6	634	2.00	656	1.36
0.6	671	2.10	661	1.29
1.0	640	1.60	680	1.44
1.0	681	1.55	680	1.43

utes. After this initial period, the pressure decreased less rapidly which may be caused by the influence of the reaction rate. Therefore eqn. (B-4) was evaluated from the initial constant slope.

The experimental conditions and results are presented in Table B-1. The mean of the experimental values in the last column was taken which gave a ratio of diffusion coefficients equal

to 1.94. This value is in accordance with Danckwerts and Sharma [13], who reported ratios between 1.7 and 2.1. The diffusion coefficient of CO_2 was estimated at $1.5 \times 10^{-9} \text{ m}^2/\text{sec}$ (section 6.2), which results in a diffusion coefficient for the hydroxyl ion of $2.91 \times 10^{-9} \text{ m}^2/\text{sec}$. The conditions in eqn. (B2) are fulfilled, $Ha = 160$ while $E_\infty = 17$ ($k_L = 1.7 \times 10^{-5} \text{ m/sec}$, $[\text{OH}^-] = 600 \text{ mol/m}^3$).