4.8.1. Hydrogen in water.

From the linear relationship between D_{AB} and T/η_B it is possible to determine the diameter of the hydrogen molecule according to the Stokes-Einstein equation. For this radius we calculated a value of 70 pm. This is small compared with the value of about 120 pm published in the literature [101]. However, the correlation described in eqn (4-32) is the result of one of the two limiting cases of interest. In deriving this correlation, it is assumed that there is no tendency for the fluid to slip at the surface of the diffusing particle. Hence, eqn (4-32) can be used to describe the diffusion of larger spherical molecules. However, when there is no tendency for the fluid to stick at the surface of the diffusing molecule, eqn (4-32) becomes:

$$D_{AB} = kT/(4\pi\eta_B R_A) \tag{4-44}$$

It is plausible that the diffusion of hydrogen into water is an example of the second limiting case. Himmelblau [102] even suggested that for this system the factor 4 in the denominator of eqn (4-44) should be smaller. The radius of the hydrogen molecule calculated from eqn (4-44) is about 110 pm, which value is more in agreement with the experimental data.

For the molar volume of hydrogen we used the value of $14.3\ 10^{-6}\ m^3\ mol^{-1}$ also used by Wilke and Chang. Our results as well as the values obtained from the above-mentioned correlations are given in Fig. 4.11. and in Table 4.9.

Table 4.9. Comparison of the values of the diffusion coefficient of hydrogen in water from some predicting equations with our experimental results.

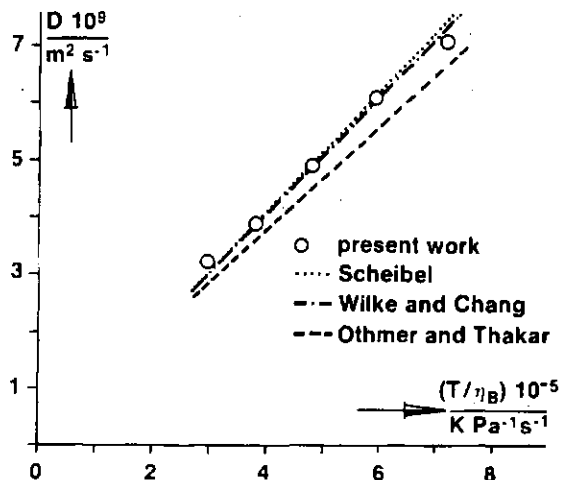|	predicting equations			experimental results
$T/°C$	Othmer and Thakar $D\ 10^9/(m^2\ s^{-1})$	Scheibel $D\ 10^9/(m^2\ s^{-1})$	Wilke and Chang $D\ 10^9/(m^2\ s^{-1})$	this work $D\ 10^9/(m^2\ s^{-1})$
20	2.8	3.0	3.0	3.2
30	3.6	4.0	3.9	3.9
40	4.5	5.0	4.9	4.9
50	5.5	6.1	6.1	6.1
60	6.6	7.4	7.3	7.1

Fig. 4.11. Diffusion coefficients of hydrogen in water.

Fairly good agreement is obtained with the Othmer-Thakar correlation. Values
calculated with this predicting method differ by less than 13 percent from our
experimental values.
Further, it can be concluded that both the Wilke-Chang and the Scheibel correla-
tion predict our experimental results better. A maximum difference of less than
7 percent is obtained at 20 °C.

4.8.2. Hydrogen in 1-propanol.
In Table 4.10. we compare our experimental results of the diffusion coefficient
of hydrogen in 1-propanol at 30 °C with the values predicted by the equations
mentioned above.

Table 4.10. Comparison of the experimental value of the diffusion coefficient
of hydrogen in 1-propanol with values calculated from predicting
equations at 30 °C.

	predicting equations			experimental result
$T/{}^\circ C$	Othmar and Thakar $D\ 10^9/(m^2\ s^{-1})$	Scheibel $D\ 10^9/(m^2\ s^{-1})$	Wilke and Chang $D\ 10^9/(m^2\ s^{-1})$	this work $D\ 10^9/(m^2\ s^{-1})$
30	1.4	1.3	2.0 ($\chi = 1.0$) 2.5 ($\chi = 1.5$)	8.0

It is obvious that all predicting equations give much lower values for the dif-
fusion coefficient of hydrogen in 1-propanol than our experimental values. Also
Sporka et al. find higher experimental values ($D = 11.9\ 10^{-9}\ m^2\ s^{-1}$) than those
obtained from the predicting equations (see section 4.6.4.).

4.8.3. Hydrogen in n-heptane.
The experimental value of the diffusion coefficient of hydrogen in n-heptane
is about $13\ 10^{-9}\ m^2\ s^{-1}$ at 30 °C. Again, this result is compared with values
obtained from predicting equations, in Table 4.11.
From Table 4.11. it is clear that the equation of Wilke and Chang predicts our
experimental result very well. The equations of Scheibel and Othmer and Thakar
predict values which are lower compared with our experimental result.

Table 4.11. Comparison of the experimental value of the diffusion coefficient
of hydrogen in n-heptane with values calculated from predicting
equations at 30 °C.

	predicting equations			experimental result
$T/{}^\circ C$	Othmer and Thakar $D\ 10^9/(m^2\ s^{-1})$	Scheibel $D\ 10^9/(m^2\ s^{-1})$	Wilke and Chang $D\ 10^9/(m^2\ s^{-1})$	this work $D\ 10^9/(m^2\ s^{-1})$
30	7.9	5.9	12.3	13

4.8.4. Hydrogen in an aqueous polyacrylamide solution.

In a number of publications, the diffusion of molecules in a dilute polymer solution has been investigated experimentally and theoretically [103-106]. However, the results are not in agreement with each other. The experimental value of the diffusion coefficient with increasing polymer concentration decreases or increases or shows a maximum value. Therefore, models have been developed which predict either an increase [104] or a decrease [106] or even an increase and a decrease [105] of the value of the diffusion coefficient with increasing polymer concentration.

Fig. 4.9. shows that our values decrease slightly with increasing polymer concentration. This behaviour is in agreement with the behaviour predicted by a model [106] in which the diffusion coefficient is given by the sum of the diffusion coefficient in the almost pure solvent and the diffusion coefficient in a highly concentrated polymer solution both with their own weight-factors. However, there is no publication in which the "zero-shear" viscosity of a polymer solution has been calculated or measured. There are some articles in which the diffusion coefficient of a gas in a liquid of which the viscosity has been increased by addition of a component has been investigated [107-110]. In these publications, the diffusion coefficient commonly decreases with increasing viscosity. In all these cases the results can be represented by the following equation:

$$D/D_w = (\eta/\eta_w)^{-n} \tag{4-45}$$

Also our experimental results can be represented very well by eqn (4-45). We have calculated the values of n according to eqn (4-45) from the results from the literature for some systems. In Table 4.12. the values of n and the ranges of viscosity and concentration are given.

From Table 4.12. we can conclude that in spite of the large differences in aqueous systems, the diffusion coefficient decreases with increasing viscosity and that the results can be represented very well by eqn (4-45) even at high viscosity.

Table 4.12. Comparison of our experimental results with values from the literature (aqueous solutions).

Addition	$c_a \, 10^{-3}$ mol m^{-3}	$\eta \, 10^{-3}$ Pa s	Gas	Number of experiments	n	σ_n	$\frac{T}{K}$	ref.
NaCl	0.0-3.776	0.893-1.37	CO_2	5	0.90	0.02	298	[107]
NaNO$_3$	0.0-3.602	0.893-1.32	CO_2	5	0.85	0.06	298	[107]
Na$_2$SO$_4$	0.0-0.898	0.893-1.33	CO_2	6	0.65	0.03	298	[107]
MgCl$_2$	0.0-1.262	0.893-1.49	CO_2	5	0.58	0.02	298	[107]
Mg(NO$_3$)$_2$	0.0-1.219	0.893-1.36	CO_2	4	0.38	0.01	298	[107]
MgSO$_4$	0.0-0.969	0.893-1.70	CO_2	7	0.57	0.03	298	[107]
Saccharose	0.0-1.96	0.856-14.8	O_2	5	0.70	0.01	301	[108]
Glycol	0.0-16.8	0.890-15.4	CO_2	7	0.56	0.02	298	[109]
Glycerine	0.0-8.27	0.890-19.2	CO_2	10	0.75	0.02	298	[109]
Glycerine	0.0-5.92	0.894-4.673	CO_2	6	0.68	0.01	298	[110]
Separan AP-30	0-2 wt %	1.002-2940*	H_2	5	0.029	0.002	293	this
Separan AP-30	0-2 wt %	1.002-2.80**	H_2	5	0.23	0.02	293	work

* "zero-shear" viscosity η_0
**"infinite-shear" viscosity η_∞

Furthermore, Table 4.12. shows different values of n for polymer solutions and non-polymer solutions. For polymer solutions, the value (n ≈ 0.03) is essentially less than for non-polymer solutions (0.38 < n < 0.90). From this it follows that the "zero-shear" viscosity of diluted polymer solutions influences the value of the diffusion coefficient of slightly soluble gases less than the viscosity of non-polymer solutions.
Further, the value of n for the relation between D/D_w and η_∞/η_w has been calculated. According to Table 4.12., n = 0.23.

4.8.5. Helium in water.
For the predicting equations, use was made of the value for the molar volume of hydrogen as calculated according to the method of LeBas.
According to this method one finds a value for the molar volume of hydrogen of 14.3 10^{-6} m^3 mol^{-1}. However, experimentally a value has been found which is about twice as high: 28.5 10^{-6} m^3 mol^{-1}. As a consequence, the predicting equations, based on the calculated molar volume, should be corrected by a factor $2^{1/3}$ (Scheibel) or $2^{0.6}$ (Wilke-Chang; Othmer and Thakar) when using the experimental value of the molar volume in these equations. The experimental value of the molar volume of helium is 31.9 10^{-6} m^3 mol^{-1} [102]. In the calculation of the diffusion coefficient of helium in water we used the corrected experimental value of the molar volume of helium being 16 10^{-6} m^3 mol^{-1}.
In Table 4.13. and Fig. 4.12. we compare our experimental results with the values calculated from the predicting equations.
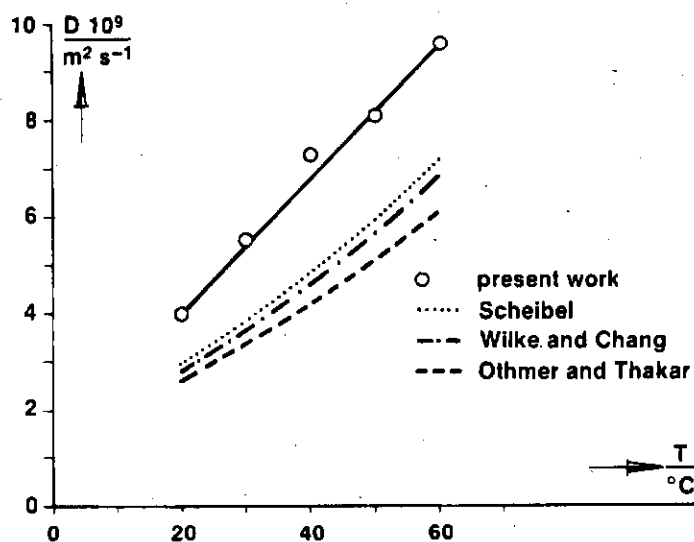

Fig. 4.12. Comparison of our experimentally determined values of the diffusion coefficient of helium in water with values calculated from predicting equations (see also Fig. 4.10.).

All predicting equations give somewhat lower values for the diffusion coefficient of helium in water than our experimental results. Furthermore, the values calculated from the predicting equations are all close together. Again, values calculated with the Scheibel correlation show little difference with those obtained from the Wilke-Chang equation. Our experimental values are about 30 percent higher than those calculated with the predicting equations.

Table 4.13. Comparison of our experimental results of the diffusion coefficient
of helium in water with values calculated from predicting
equations in the range 20 - 60 °C.

	predicting equations			experimental results
T/°C	Othmer and Thakar $D\ 10^9/(m^2\ s^{-1})$	Scheibel $D\ 10^9/(m^2\ s^{-1})$	Wilke and Chang $D\ 10^9/(m^2\ s^{-1})$	this work $D\ 10^9/(m^2\ s^{-1})$
20	2.6	2.9	2.8	4.0
30	3.4	3.8	3.6	5.5
40	4.2	4.8	4.6	7.3
50	5.1	5.9	5.7	8.1
60	6.1	7.2	6.9	9.6

4.9. Accuracy.

To investigate whether leakage of gas along the plunger of the needle occurs,
the micrometer thimble was turned only so far as to form a cap of gas on the
tip of the needle so that the gas-liquid interface was just visible.
The system was left to itself for 5 minutes. After that time, the micrometer
thimble was turned to such an extent that an equally small cap of gas was
formed on the tip of the needle.
The same procedure was carried out with a rest-time of 30 minutes. The dif-
ference in micrometer reading of the experiment of 5 minutes was subtracted from
that of the experiment of 30 minutes. This was done to eliminate the contribu-
tion owing to absorption of gas across the gas-liquid interface of the
small cap. In this way the pure leakage can be calculated when neglecting the
very small contribution from diffusion of gas across the circular gas-liquid
interface in the needle. It has been found that the leakage of hydrogen is
about 1 % of the flow rate of the gas absorbed in water under normal experi-
mental conditions. This decrease in volume of gas absorbed from the gas bubble
will lead to a diffusion coefficient value which is about 2 per cent lower
than that given in Table 4.2. It can therefore be concluded that no correction
for the leakage of the syringe is needed.

4.10. Conclusions.

It has been shown that application of the CBS-method leads to accurate values of
diffusion coefficients of gases in liquids provided that:
- no disturbances occur in the stagnant liquid phase in the environment of the
  gas bubble during the diffusion process;
- the method is carried out carefully according to the instructions described;
- the Henry number of the system is known;
- the Rayleigh number of the inner cell contents obeys Ra < 1800 to prevent free
  convection;
- the Bond number of the gas bubble obeys Bo < 0.01 to prevent that the local
  curvature of the bubble surface deviates by more than 1 percent from the
  average value;
- the surface tension $\sigma > 25\ 10^{-3}$ N m^{-1};
- the gas has been saturated with vapour of the solvent.
The values of the diffusion coefficients discussed in this chapter have been
determined by a pure diffusion process without free convection. The CBS-method
can be used to generate engineering data and to test predicting equations for
diffusion coefficients. The diffusion coefficients can be determined without
knowing the partial pressure of the gas in the bubble, provided that the Henry
number is independent of the partial pressure in the pressure range considered
and the gas has been saturated with vapour of the solvent.

4.11. Further research.

In this chapter the experimental results of the diffusion coefficient of slightly soluble gases in liquids have been discussed. It has been shown that measurement according to the CBS-method leads to accurate and reliable values of the diffusion coefficients when using the theory of section 4.2.

Another major consideration in developing this experimental method is to have a well-defined system (single spherical gas bubble with a well-defined gas-liquid interface) to perform absorption experiments of gas in liquids in which a chemical reaction takes place. In the liquid of the diffusion cell not only a homogeneous but also a heterogeneous reaction could occur. The theoretical treatment of the CBS-method presented in section 4.2. should therefore be extended to a chemically enhanced absorption.

Recently, Wimmers et al. [111] of our laboratory applied this method to three phase systems with chemically enhanced absorption on the gas-liquid surface. They have shown that addition of small active carbon particles does not influence the absorption rate. Further, they have shown that the gas absorption rate increases significantly if catalyst particles are added to the gas-liquid surface and a second reactant is available in the liquid.

As further research, experiments will be performed to determine gas absorption rates in three phase slurry systems at different temperatures to determine representative kinetic data.

When this procedure is successful, it is possible to design large scale slurry reactors from information obtained from accurate gas absorption measurements from a single spherical gas bubble in 3 cm^3 of process liquid in combination with reliable data on the hydrodynamic behaviour of representative slurry systems in vessels about 30 cm in diameter and 4 m long.

In Chapter 7, the influence of the relevant physical quantities on the gas absorption rate will be elucidated.

CHAPTER 5

MODELS FOR MASS TRANSFER IN SLURRY REACTORS

5.1. Introduction.
In this chapter, we will describe three models for the mass transfer of gas
from the dispersed gas phase to the active sites of the solid catalyst
particles suspended in the liquid of a slurry reactor. At the active sites,
the gas component, denoted as A', reacts with another chemical component B from
the liquid phase. We will discuss models in which the catalyst particles are
distributed homogeneously:
- in the bulk of the liquid only ($d_p > \delta$);
- in the liquid film only ($d_p \ll \delta$); particles tend to stay near gas-liquid
  interface;
- in both the bulk and the liquid film ($d_p < \delta$).
In this chapter we shall discuss models for zero-order and first-order reactions
in the gas component A.
For each model, the following assumptions are made:
- the catalyst particles are spherical;
- the active sites are distributed homogeneously in the catalyst particles;
- for the gas in the gas phase, there is no resistance to mass transfer;
- for the chemical component B and the product(s), there is no resistance to
  mass transfer, neither in the liquid film nor in the pores of the catalyst
  particle;
- the solubility of the gas in the liquid C_{A1} as well as the mass transfer
  coefficient k_L are not affected by the concentration of the catalyst.
This list of assumptions will be extended if necessary.

5.2. Catalyst particles in the bulk of the liquid only.
In Fig. 5.1., a steady-state concentration profile of the gas is represented
for the case that the catalyst particles are distributed homogeneously in the
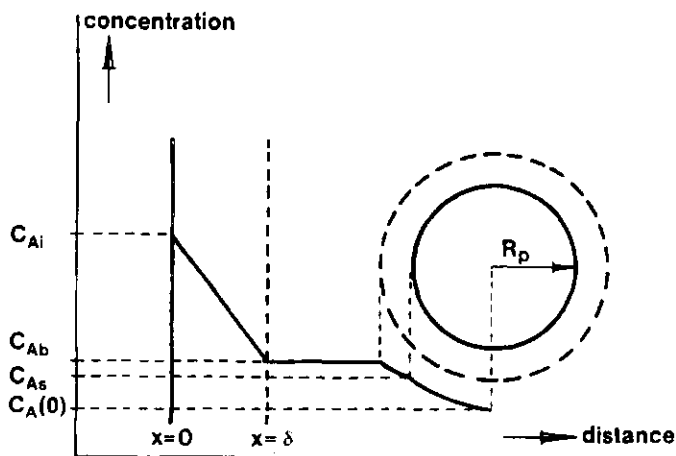bulk of the liquid only.

Fig. 5.1. Steady-state concentration profile of component A in the case that
the catalyst particles are distributed homogeneously in the bulk of
the liquid only.

5.2.1. Reaction of zero order in the gas component A.

For the zero-order reaction, the equation of diffusion for a porous spherical catalyst particle is given by:

$$D^* \frac{1}{r^2} \frac{d}{dr}\left(r^2 \frac{dC_A(r)}{dr}\right) = k_o C_B^m \qquad (5-1)$$

with the boundary conditions:

$$C_A(r) = C_{As} \quad \text{for} \quad r = R_p \qquad (5-2)$$

$$dC_A(r)/dr = 0 \quad \text{for} \quad r = 0 \qquad (5-3)$$

The solution of this problem is:

$$C_A(r) = C_{As} - k_o C_B^m (R_p^2 - r^2)/(6D^*) \qquad (5-4)$$

The rate of gas absorption for one catalyst particle is found from:

$$\Phi_A/n_p = 4\pi R_p^2 D^* dC_A(r)/dr \Big|_{r=R_p} = 4\pi k_o C_B^m R_p^3/3 \qquad (5-5)$$

The number of catalyst particles per unit volume of bulk liquid equals:

$$n_p = 3\overline{C}_p/(4\pi R_p^3 \rho_p (1 - a_L\delta)) \qquad (5-6)$$

so that the rate of gas absorption per unit volume of liquid is given by:

$$\Phi_A = k_o C_B^m \overline{C}_p/(\rho_p(1 - a_L\delta)) = k_o C_B^m \phi' \qquad (5-7)$$

in which:

$$\phi' = \overline{C}_p/(\rho_p(1 - a_L\delta)) \qquad (5-8)$$

gives the volume of the catalyst particles per unit volume of bulk liquid.

The ratio of the actual absorption to the maximum physical absorption of gas (i.e. $C_{Ab} = 0$) from the gas phase into the liquid phase is defined by:

$$E \equiv \Phi_A/(k_L a_L C_{Ai}) = k_o C_B^m \phi'/(k_L a_L C_{Ai}) \equiv \tfrac{1}{2}\Theta_o^2/(1 - a_L\delta) \qquad (5-9)$$

Eqn (5-9) is only valid when the effectiveness of the catalyst particle equals unity i.e. when there is no single active site in the pores of the catalyst particle at which the concentration of gas is zero.
This requirement can be expressed in the inequality:

$$C_A(0) = C_{As} - k_o C_B^m R_p^2/(6D^*) > 0 \qquad (5-10)$$

which results from eqn (5-4). Eqn (5-10) leads to:

$$C_{As} > k_o C_B^m d_p^2/(24D^*) \qquad (5-11)$$

Let us now introduce the quantity Λ_o, defined by:

$$\Lambda_o \equiv k_o C_B^m d_p^2/(24D^* C_{Ai}) \qquad (5-12)$$

From eqns (5-11) and (5-12) it can be deduced that the effectiveness is unity if:

$$C_{As}/C_{Ai} > \Lambda_o \qquad (5-13)$$

In the steady-state, the rate of gas absorption per unit volume of liquid from the gas phase to the active sites of the catalyst particles can also be expressed by:

$$\Phi_A = k_L a_L (C_{Ai} - C_{Ab}) = k_s a_s (C_{Ab} - C_{As})/(1 - a_L \delta) \tag{5-14}$$

Elimination of C_{Ab} gives for C_{As}:

$$C_{As} = C_{Ai} - \Phi_A \{(k_L a_L)^{-1} + (1 - a_L \delta)/(k_s a_s)\} \tag{5-15}$$

or

$$C_{As}/C_{Ai} = 1 - \Phi_A \{(k_L a_L)^{-1} + (1 - a_L \delta)/(k_s a_s)\}/C_{Ai} \tag{5-16}$$

Combination of eqns (5-9), (5-16) and (5-13) yields:

$$E < (1 - \Lambda_o)/(1/\Gamma' + 1) \tag{5-17}$$

with

$$\Gamma' = k_s a_s/(k_L a_L (1 - a_L \delta)) \tag{5-18}$$

Because $E = \frac{1}{2}\Theta_o^2/(1 - a_L \delta)$ when the effectiveness is unity, eqn (5-17) is rewritten as:

$$\Theta_o^2 < 2(1 - \Lambda_o)(1 - a_L \delta)/(1/\Gamma' + 1) \tag{5-19}$$

As long as the inequality of eqn (5-19) is valid, the effectiveness is unity. If the effectiveness is not unity, the boundary conditions of eqn (5-1) are:

$$C_A(r) = C_{As} \quad \text{for} \quad r = R_p \tag{5-20}$$

and

$$dC_A(r)/dr = 0 \quad \text{for} \quad r = R^* < R_p \tag{5-21}$$

For the boundary conditions of eqns (5-20) and (5-21), the solution of eqn (5-1) is given by:

$$C_A(r) = C_{As} - k_o C_B^m (R_p^2 - r^2)/(6D^*) + k_o C_B^m R^{*3}(r^{-1} - R_p^{-1})/(3D^*) \tag{5-22}$$
$$\text{for} \quad R^* < r < R_p$$

Further, we assume that:

$$C_A(r) = 0 \quad \text{for} \quad 0 < r < R^* \tag{5-23}$$

In this case, the ratio of the actual gas absorption rate to the maximum physical absorption of gas (i.e. $C_{Ab} = 0$) into the liquid is obtained from eqn (5-22):

$$E \equiv \Phi_A/(k_L a_L C_{Ai}) = \{1 - (R^*/R_p)^3\}k_o C_B^m \phi'/(k_L a_L C_{Ai}) = \tag{5-24}$$
$$= \frac{1}{2}\{1 - (R^*/R_p)^3\}\Theta_o^2/(1 - a_L \delta)$$

Because of the continuity of the function describing the gas concentration, substitution of $r = R^*$ into eqn (5-22) must lead to $C_A(R^*) = 0$. After this substitution, and using eqn (5-12), it is found that:

$$C_{As}/C_{Ai} = \Lambda_o\{1 - 3(R^*/R_p)^2 + 2(R^*/R_p)^3\} \tag{5-25}$$

It is obvious that the right-hand side of eqn (5-16) must be equal to the right-hand side of eqn (5-25):

$$1 - \Phi_A\{(k_L a_L)^{-1} + (1 - a_L\delta)/(k_s a_s)\}/C_{Ai} = \Lambda_o\{1 - 3(R^*/R_p)^2 + 2(R^*/R_p)^3\}$$

$$(5-26)$$

Further, from eqn (5-24) it follows that:

$$R^*/R_p = (1 - 2(1 - a_L\delta)E/\Theta_o^2)^{1/3} \qquad (5-27)$$

Substitution of the definitions of E and Γ' and of eqn (5-27) into eqn (5-26) gives the following function of E:

$$E\left(1 + 1/\Gamma' - 4(1 - a_L\delta)\Lambda_o/\Theta_o^2\right) - 3\Lambda_o\{(1 - 2(1 - a_L\delta)E/\Theta_o^2)^{2/3} - 1\} = 1$$

$$(5-28)$$

The next step is to find the value of E of eqn (5-28) for given values of Θ_o, Λ_o, Γ' and $a_L\delta$.

In Fig. 5.2. a diagram has been drawn for E as a function of $\frac{1}{2}\Theta_o^2/(1 - a_L\delta)$ for given values of Λ_o $(0 \leqslant \Lambda_o \leqslant 1)$ and $\Gamma'(0 \leqslant \Gamma' \leqslant \infty)$.
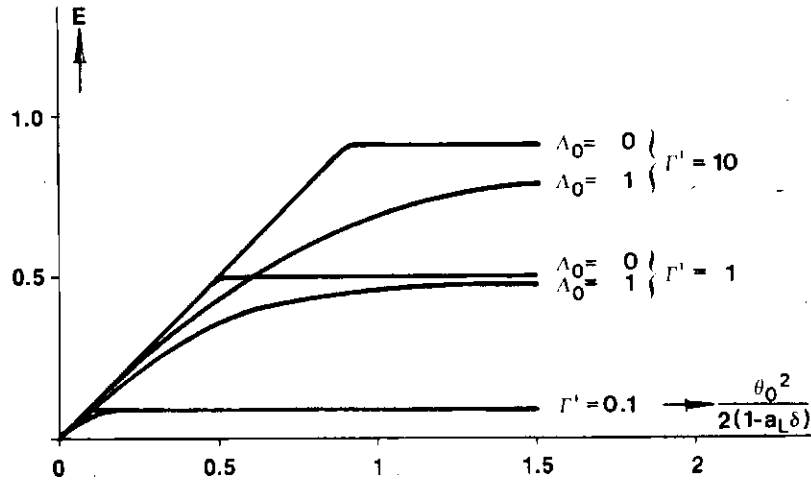

Fig. 5.2. Diagram of E as a function of $\frac{1}{2}\Theta_o^2/(1 - a_L\delta)$ in the case that the catalyst particles are distributed homogeneously in the bulk of the liquid only.

5.2.2. Reaction of first order in the gas component A.

For a first-order reaction, the equation of diffusion for a porous spherical catalyst particle is given by:

$$D^* \frac{1}{r^2} \frac{d}{dr}\left(r^2 \frac{dC_A(r)}{dr}\right) = k_1 C_A(r) C_B^m \qquad (5-29)$$

with the boundary conditions:

$$C_A(r) = C_{As} \quad \text{for} \quad r = R_p \tag{5-30}$$

and:

$$dC_A(r)/dr = 0 \quad \text{for} \quad r = 0 \tag{5-31}$$

The solution of this problem is:

$$C_A(r) = C_{As}R_p\sinh(\lambda'r)/(r\sinh(\lambda'R_p)) \tag{5-32}$$

with

$$\lambda' = (k_1C_B^m/D*)^{\frac{1}{2}} \tag{5-33}$$

The rate of gas absorption per unit volume of liquid is given by:

$$\Phi_A = \{(\lambda'R_p)\coth(\lambda'R_p) - 1\}3D*C_{As}\phi'/R_p^2 \tag{5-34}$$

It is known that for a first-order reaction the effectiveness is given by:

$$\eta_1 = 3\{(\lambda'R_p)\coth(\lambda'R_p) - 1\}/\{(\lambda'R_p)^2\} \tag{5-35}$$

When we define (see also eqn (5-12)):

$$\Lambda_n \equiv k_nC_B^md_p^2C_{Ai}^{n-1}(n+1)/(24D*) \tag{5-36}$$

it is found that:

$$\Lambda_1 = k_1C_B^md_p^2/(12D*) \tag{5-37}$$

With the eqns (5-33) and (5-37) it follows that:

$$\Lambda_1 = (\lambda'd_p)^2/12 \tag{5-38}$$

so that:

$$\lambda'R_p = (3\Lambda_1)^{\frac{1}{2}} \tag{5-39}$$

and the effectiveness is found from eqn (5-35):

$$\eta_1 = \{((3\Lambda_1)^{\frac{1}{2}})\coth((3\Lambda_1)^{\frac{1}{2}}) - 1\}/\Lambda_1 \tag{5-40}$$

The ratio of the actual absorption to the maximum physical absorption (i.e. $C_{Ab} = 0$) is determined from eqn (5-34):

$$E \equiv \Phi_A/(k_La_LC_{Ai}) = \eta_1k_1C_B^mC_{As}\phi'/(k_La_LC_{Ai}) = \eta_1\Theta_1^2C_{As}/(C_{Ai}(1 - a_L\delta)) \tag{5-41}$$

in which:

$$\Theta_1^2 = k_1C_B^m\phi''/(k_La_L) \tag{5-42}$$

In general, it is defined that:

$$\Theta_n^2 \equiv 2k_nC_B^mC_{Ai}^{n-1}D\phi/(k_L^2(n+1)) = Ha_n^2\phi \tag{5-43}$$

Substitution of eqn (5-15) and the definitions of E and Γ' into eqn (5-41) yields:

$$E = \eta_1\Theta_1^2\{1 - E(1/\Gamma' + 1)\}/(1 - a_L\delta) \tag{5-44}$$

from which it follows that:

$$1/E = 1 + (1 - a_L\delta)/(\eta_1\Theta_1{}^2) + 1/\Gamma' \tag{5-45}$$

With substitution of eqn (5-40) for the effectiveness, eqn (5-45) is written as:

$$1/E = 1 + \Lambda_1(1 - a_L\delta)\{\Theta_1{}^2\langle((3\Lambda_1)^{\frac{1}{2}})\coth((3\Lambda_1)^{\frac{1}{2}}) - 1)\}^{-1} + 1/\Gamma' \tag{5-46}$$

In Fig. 5.3., a diagram of E is given as a function of $\Theta_1{}^2/(1 - a_L\delta)$ and different values of the parameters η_1 $(0 < \eta_1 < 1)$ and Γ' $(0 < \Gamma' < \infty)$
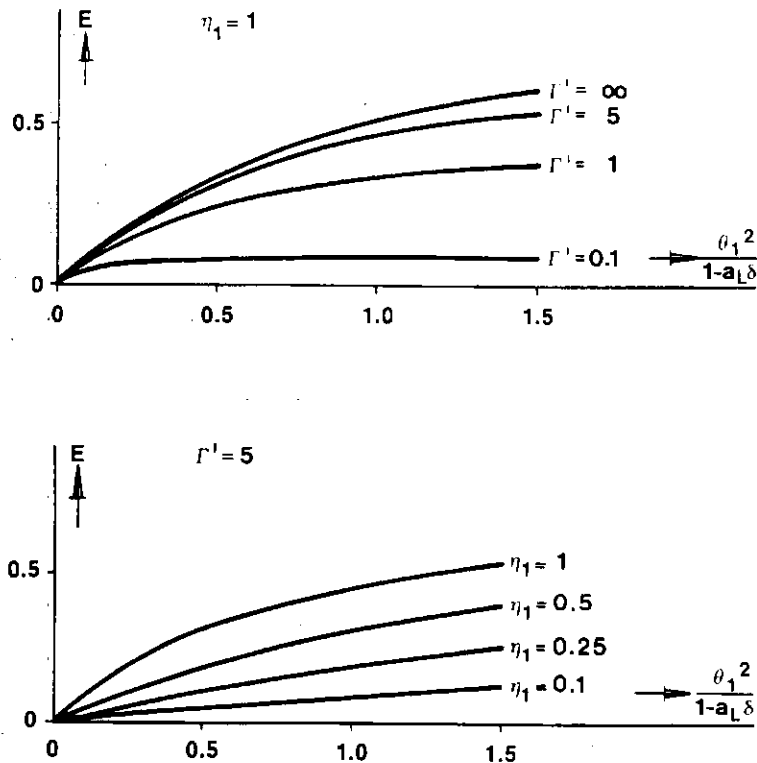
Fig. 5.3. Diagram of E as a function of $\Theta_1{}^2/(1 - a_L\delta)$, η_1 and Γ' in the case that the catalyst particles are distributed homogeneously in the bulk of the liquid only.

5.3. Catalyst particles in the liquid film only.

In the following model, it is assumed that the catalyst particles will be present in the liquid film only. The mass transfer into the bulk of the liquid is zero. The separate catalyst particles are distributed homogeneously in the liquid film.

The thickness of the liquid film is assumed to be:

$$\delta = D/k_L \tag{5-47}$$

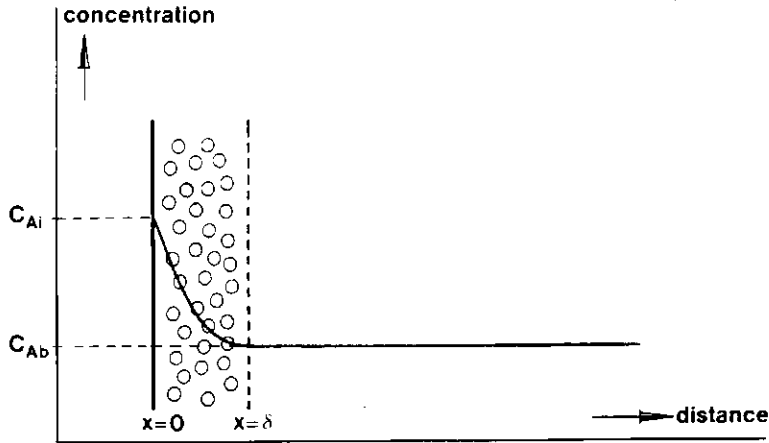This representation is given in Fig. 5.4.

88

Fig. 5.4. Steady-state concentration profile of component A in the case that the catalyst particles are distributed homogeneously in the liquid film only.

The total volume of catalyst particles per unit volume of liquid is:

$$v_p = \overline{C}_p / \rho_p \qquad (5-48)$$

Further,

$$a_L \delta = A_L \delta / V_L \qquad (5-49)$$

is the volume of the liquid film per unit volume of liquid.
The above-mentioned considerations lead to:

$$\phi = v_p / (a_L \delta) = \overline{C}_p / (\rho_p a_L \delta) \qquad (5-50)$$

The physical quantity ϕ is the volume of the catalyst particles per unit volume of liquid film.
The concentration of catalyst $\overline{C}_p$ is again based on the total volume of liquid.

5.3.1. Reaction of zero order in the gas component A.
The equation of diffusion for the liquid film is:

$$D \frac{d^2 C_A(x)}{dx^2} = k_o C_B^m \phi \qquad (5-51)$$

with:

$$\phi = \overline{C}_p / (\rho_p a_L \delta) \qquad (5-52)$$

With the boundary conditions:

$$C_A(x) = C_{Ai} \quad \text{for} \quad x = 0 \qquad (5-53)$$

and:

$$dC_A(x)/dx = 0 \quad \text{for} \quad x = \delta \tag{5-54}$$

the following solution is found:

$$C_A(x) = C_{Ai} + k_o C_B^m \phi x^2/(2D) - k_o C_B^m \phi x \delta/D \tag{5-55}$$

From this equation it follows that the ratio of the actual gas absorption to the maximum physical gas absorption is given by:

$$E \equiv \Phi_A/(k_L a_L C_{Ai}) = -Da_L dC_A(x)/dx \big|_{x=0} /(k_L a_L C_{Ai}) = k_o C_B^m \phi \delta/(k_L C_{Ai}) = \tag{5-56}$$
$$= \tfrac{1}{2}\Theta_o^2$$

This relation holds as long as:

$$C_{Ab} = C_A(\delta) \geqslant 0 \tag{5-57}$$

From eqn (5-55) it can be obtained that this requirement is fulfilled if:

$$C_{Ai} - k_o C_B^m \phi \delta^2/(2D) \geqslant 0 \tag{5-58}$$

By substituting $\delta = D/k_L$ and dividing both sides of the inequality (5-58) by C_{Ai} it is found that $C_{Ab} \geqslant 0$ if:

$$\Theta_o \leqslant 2 \tag{5-59}$$

When eqn (5-51) is solved with the boundary conditions

$$C_A(x) = C_{Ai} \quad \text{for} \quad x = 0 \tag{5-60}$$

and

$$dC_A(x)/dx = 0 \quad \text{for} \quad x = \delta* \leqslant \delta \tag{5-61}$$

the following solution is found:

$$C_A(x) = C_{Ai} + k_o C_B^m \phi x^2/(2D) - k_o C_B^m \phi \delta* x/D \quad \text{for} \quad x \leqslant \delta* \tag{5-62}$$

Further, we assume that:

$$C_A(x) = 0 \quad \text{for} \quad \delta* \leqslant x \leqslant \delta \tag{5-63}$$

From eqn (5-62) it can be deduced that the ratio of the actual absorption of gas to the maximum physical absorption is given by:

$$E \equiv \Phi_A/(k_L a_L C_{Ai}) = -Da_L dC_A(x)/dx \big|_{x=0} /(k_L a_L C_{Ai}) = k_o C_B^m \phi \delta*/(k_L C_{Ai}) = \tag{5-64}$$
$$= \tfrac{1}{2}\delta* \Theta_o^2/\delta$$

The concentration in the liquid film for $x \geqslant \delta*$ must be zero.
From eqn (5-62) it can be obtained that this requirement is fulfilled if:

$$\delta*/\delta = 2/\Theta_o \tag{5-65}$$

which after substitution in eqn (5-64) leads to:

$$E = \Theta_o \tag{5-66}$$

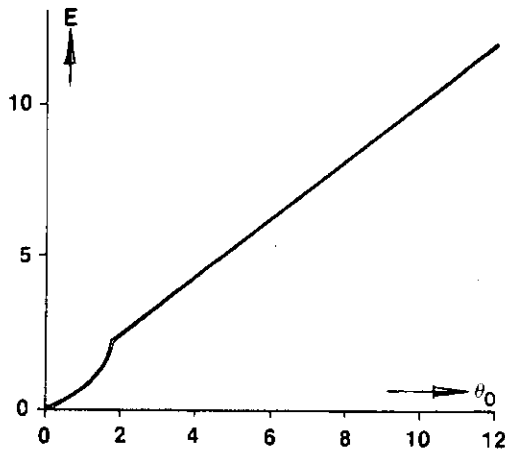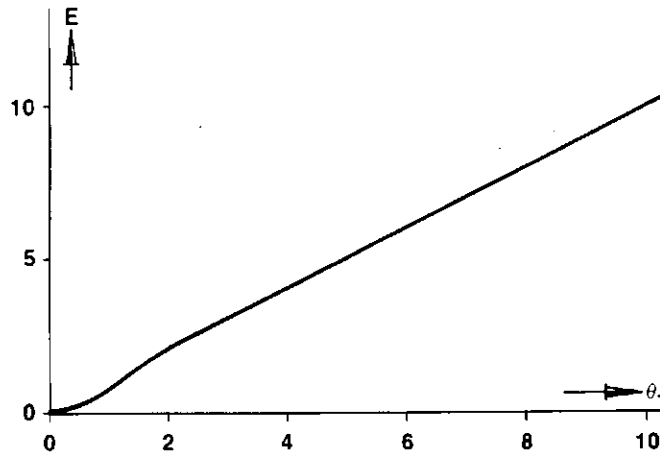In Fig. 5.5., a diagram is given of E as a function of Θ_o.

Fig. 5.5. Diagram of E as a function of Θ_0 in the case that the catalyst particles are distributed homogeneously in the liquid film only.

5.3.2. Reaction of first order in the gas component A.
The equation of diffusion for the liquid film reads:

$$D \frac{d^2C_A(x)}{dx^2} = k_1 C_A(x) C_B^m \phi \qquad (5-67)$$

with:

$$\phi = \overline{C}_p/(\rho_p a_L \delta) \qquad (5-68)$$

The boundary conditions are:

$$C_A(x) = C_{Ai} \quad \text{for} \quad x = 0 \qquad (5-69)$$

and

$$dC_A(x)/dx = 0 \quad \text{for} \quad x = \delta \qquad (5-70)$$

with which the following solution is found:

$$C_A(x) = C_{Ai} \cosh(\lambda(\delta - x))/\cosh(\lambda\delta) \qquad (5-71)$$

with:

$$\lambda = \{k_1 C_B^m \phi/D\}^{\frac{1}{2}} \qquad (5-72)$$

From eqn (5-71) it can be deduced that the rate of gas absorption per unit volume of liquid equals:

$$\Phi_A = -Da_L dC_A(x)/dx \big|_{x=0} = Da_L \lambda C_{Ai} \tanh(\lambda\delta) \qquad (5-73)$$

The ratio of the actual absorption to the maximum physical absorption is given by:

91

$$E \equiv \Phi_A/(k_{La_L}C_{Ai}) = (\lambda\delta)\tanh(\lambda\delta) \tag{5-74}$$

From eqn (5-72), it is found that:

$$\lambda\delta = \Theta_1 \tag{5-75}$$

From eqns (5-74) and (5-75) we obtain:

$$E = \Theta_1\tanh(\Theta_1) \approx \Theta_1 \text{ for large values of } \Theta_1 \text{ e.g. } \Theta_1 \geqslant 2. \tag{5-76}$$

In Fig. 5.6., a diagram of E as a function of Θ_1 is given for the case that the catalyst particles are distributed homogeneously in the liquid film only.

Fig. 5.6. Diagram of E as a function of Θ_1 in the case that the catalyst particles are distributed homogeneously in the liquid film only.

5.4. Catalyst particles homogeneously distributed in the liquid.
In this section, the model is described in which the concentration of catalyst particles in the liquid film and that in the bulk of the liquid are identical. For the catalyst particles in the bulk, the same procedure is followed as in section 5.2. The procedure of section 5.3. is followed for the catalyst particles in the liquid film. This model is represented in Fig. 5.7.

5.4.1. Reaction of zero order in the gas component A.
The equation of diffusion for the liquid film is:

$$D \frac{d^2C_A(x)}{dx^2} = k_0C_B^m\phi'' \tag{5-77}$$

in which

$$\phi'' = \overline{C}_p/\rho_p \tag{5-78}$$

denotes the volume of the catalyst particles per unit volume of liquid. For the boundary conditions:
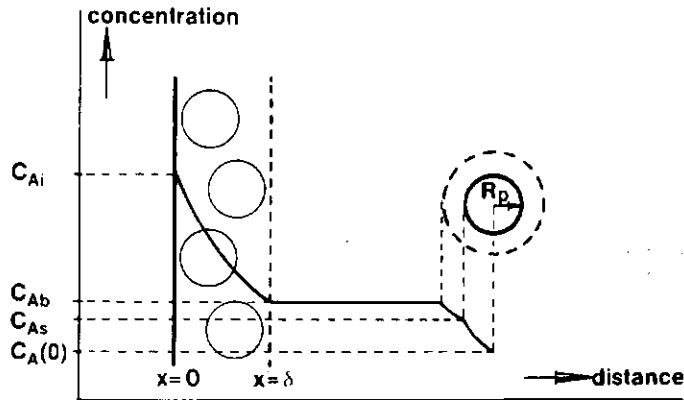
Fig. 5.7. Steady-state concentration profile of component A in the case that the catalyst particles are distributed homogeneously in both the bulk and film of the liquid.

$$C_A(x) = C_{Ai} \quad \text{for} \quad x = 0 \tag{5-79}$$

and

$$dC_A(x)/dx = -\{1 - (R*/R_p)^3\}k_oC_B^m(1 - a_L\delta)\phi''/(a_LD) \quad \text{for} \quad x = \delta \tag{5-80}$$

eqn (5-77) leads to:

$$C_A(x) = C_{Ai} + k_oC_B^m\phi''x^2/(2D) - \{\{1 - (R*/R_p)^3\}(1 - a_L\delta) + a_L\delta\}k_oC_B^m\phi''x/(a_LD) \tag{5-81}$$

so that the ratio of the actual gas absorption to the maximum physical gas absorption is given by:

$$E \equiv \Phi_A/(k_La_LC_{Ai}) = \{\{1 - (R*/R_p)^3\}(1 - a_L\delta) + a_L\delta\}k_oC_B^m\phi''/(k_La_LC_{Ai}) = \tag{5-82}$$

$$= \tfrac{1}{2}\{\{1 - (R*/R_p)^3\}(1 - a_L\delta) + a_L\delta\}\Theta_o^2$$

From eqn (5-11) it was found that $\eta_o = 1$ if:

$$C_{As} > k_oC_B^m d_p^2/(24D*) \tag{5-83}$$

If the effectiveness is unity, it is found that in the steady-state for the catalyst particles in the bulk:

$$k_oC_B^m\phi'' = k_sa_s(C_{Ab} - C_{As}) \tag{5-84}$$

Substitution of C_{As} from eqn (5-84) into eqn (5-83) yields:

$$C_{As} = C_{Ab} - k_oC_B^m\phi''/(k_sa_s) > k_oC_B^m d_p^2/(24D*) \tag{5-85}$$

from which it follows that:

$$C_{Ab}/C_{Ai} > \Lambda_o + \tfrac{1}{2}\Theta_o^2/\Gamma \tag{5-86}$$

93

Substitution of $x = \delta$ in eqn (5-81) for the concentration of gas in the bulk of the liquid gives:

$$C_{Ab}/C_{Ai} = 1 - \tfrac{1}{2}\Theta_o^2/(1 - a_L\delta/2) \tag{5-87}$$

Substitution of eqn (5-87) into eqn (5-86) gives:

$$\Theta_o < (1 - \Lambda_o)/(1/\Gamma + 1 - a_L\delta/2) \tag{5-88}$$

This result is comparable with eqn (5-19).
For the catalyst particles in the bulk it is found that when the effectiveness is not unity:

$$\{1 - (R*/R_p)^3\}k_o C_B^m\phi'' = k_s a_s(C_{Ab} - C_{As}) \tag{5-89}$$

from which the concentration C_{As} is found to be:

$$C_{As} = C_{Ab} - \{1 - (R*/R_p)^3\}k_o C_B^m\phi''/(k_s a_s) \tag{5-90}$$

Dividing eqn (5-90) by C_{Ai} and substitution of C_{Ab}/C_{Ai} from eqn (5-81) gives:

$$C_{As}/C_{Ai} = 1 - \tfrac{1}{2}\Theta_o^2\{\{1 - (R*/R_p)^3\}(1/\Gamma + 1 - a_L\delta) + \tfrac{1}{2}a_L\delta\} \tag{5-91}$$

The right-hand side of eqn (5-91) must be equal to the right-hand side of eqn (5-25):

$$1 - \tfrac{1}{2}\Theta_o^2\{\{1 - (R*/R_p)^3\}(1/\Gamma + 1 - a_L\delta) + \tfrac{1}{2}a_L\delta\} = \Lambda_o\{1 - 3(R*/R_p)^2 + 2(R*/R_p)^3\} \tag{5-92}$$

From eqn (5-82) it follows that:

$$(R*/R_p)^3 = 1 + (a_L\delta - 2E/\Theta_o^2)/(1 - a_L\delta) \tag{5-93}$$

Substitution of eqn (5-93) into eqn (5-92) gives:

$$\tfrac{1}{2}\Theta_o^2\{(2E/\Theta_o^2 - a_L\delta)(1/\Gamma + 1 - a_L\delta)/(1 - a_L\delta) + \tfrac{1}{2}a_L\delta\} +$$
$$+ \Lambda_o\{1 - 3(1 + (a_L\delta - 2E/\Theta_o^2)/(1 - a_L\delta))^{2/3} + \tag{5-94}$$
$$+ 2(1 + (a_L\delta - 2E/\Theta_o^2)/(1 - a_L\delta))\} = 1$$

From eqn (5-94), we have to find the value of E for given values of Γ, Λ_o, a_L and δ as a function of Θ_o.
By substituting $a_L\delta = 0$, eqn (5-94) is reduced to eqn (5-28)

The rate of gas absorption from the liquid film into the bulk of the liquid is zero if:

$$k_s a_s(C_{Ab} - C_{As}) = 0 \tag{5-95}$$

which will be true if $C_{Ab} = C_{As}$.
However, this condition will be reached only if $C_{Ab} = C_{As} = 0$ and consequently the effectiveness is zero.
When $R*/R_p = 1$ is substituted into eqn (5-82), it is found that:

$$E = \tfrac{1}{2}a_L\delta\Theta_o^2 \tag{5-96}$$

The value of Θ_o for which the effectiveness is zero can be found from eqn (5-91) by equating both the effectiveness and the left-hand side of this

equation to zero ($R*/R_p = 1$):

$$\Theta_o^2 = 4/(a_L\delta) \tag{5-97}$$

Combination of eqns (5-97) and (5-96) leads to:

$$E = 2 \tag{5-98}$$

From this point, the same procedure has to be followed as in section 5.3.
This means that eqn (5-77) must be solved with the boundary conditions:

$$C_A(x) = C_{Ai} \text{ for } x = 0 \tag{5-99}$$

and:

$$dC_A(x)/dx = 0 \quad \text{for } x = \delta* < \delta \tag{5-100}$$

The solution found is:

$$C_A(x) = C_{Ai} + k_o C_B^m \phi'' x^2/(2D) - k_o C_B^m \phi'' \delta* x/D \tag{5-101}$$

The ratio of the actual absorption of gas to the maximum physical absorption
is given by:

$$E \equiv \Phi_A/(k_L a_L C_{Ai}) = k_o C_B^m \phi'' \delta* a_L/(k_L a_L C_{Ai}) = \tfrac{1}{2} a_L \delta* \Theta_o^2 \tag{5-102}$$

The concentration in the liquid film for $x > \delta*$ must be zero. Substituting of
$x = \delta*$ and $C_A(x) = 0$ in eqn (5-101) and using the definition of Θ_o lead to:

$$\delta*^2 = 4\delta/(a_L \Theta_o^2) \tag{5-103}$$

Combination of eqns (5-102) and (5-103) results in:

$$E = (a_L\delta)^{\tfrac{1}{2}}\Theta_o \tag{5-104}$$

In Fig. 5.8., a diagram of E is given as a function of Θ_o for various values
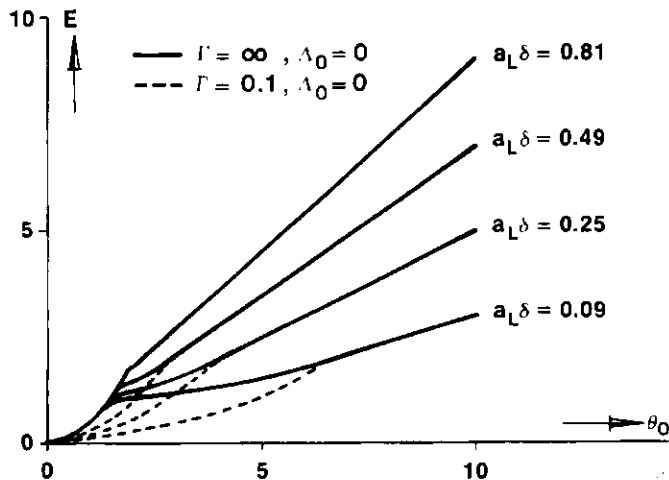of $a_L\delta$.

Fig. 5.8. Diagram of E as a function of Θ_o and $a_L\delta$ in the case that the
catalyst particles are distributed homogeneously in both film and
bulk of the liquid.

5.4.2. Reaction of first order in the gas component A.
The equation of diffusion for the liquid film reads:

$$D \frac{d^2 C_A(x)}{dx^2} = k_1 C_A(x) C_B^m \phi"$$

(5-105)

with the boundary conditions:

$$C_A(x) = C_{Ai} \quad \text{for} \quad x = 0$$

(5-106)

and

$$dC_A(x)/dx = -\eta_1 k_1 C_B^m C_{As} \phi"(1 - a_L\delta)/(a_L D) \quad \text{for} \quad x = \delta$$

(5-107)

The solution of this problem is:

$$C_A(x) = \left\{ C_{Ai}\cosh(\lambda"(\delta - x)) - \left(\eta_1\lambda"C_{As}(1 - a_L\delta)/a_L\right)\sinh(\lambda"x) \right\}/(\cosh(\lambda"\delta))$$

(5-108)

with

$$\lambda" = (k_1 C_B^m \phi"/D)^{\frac{1}{2}}$$

(5-109)

so that the ratio of the actual gas absorption to the maximum physical absorption is given by:

$$E \equiv \Phi_A/(k_L a_L C_{Ai}) = (\lambda"\delta)\tanh(\lambda"\delta) + \eta_1(\lambda")^2 C_{As}(1 - a_L\delta)\delta/(a_L C_{Ai}\cosh(\lambda"\delta))$$

(5-110)

In the steady-state, for the catalyst particles in the bulk, it is found that:

$$\eta_1 k_1 C_{As} C_B^m \phi" = k_s a_s(C_{Ab} - C_{As})$$

(5-111)

so that

$$C_{As} = C_{Ab}\left\{1 + \eta_1 k_1 C_B^m \phi"/(k_s a_s)\right\}^{-1} = C_{Ab}/(1 + \eta_1 \Theta_1^2/\Gamma)$$

(5-112)

Substitution of $x = \delta$ into eqn (5-108) gives for the concentration of gas in the bulk:

$$C_A(\delta) = C_{Ab} = C_{Ai}/(\cosh(\lambda"\delta)) - (\eta_1\lambda"(1 - a_L\delta)C_{As}/a_L)\tanh(\lambda"\delta)$$

(5-113)

From the eqns (5-112) and (5-113), it follows that:

$$C_{As}/C_{Ai} = 1/(\cosh(\lambda"\delta))\left\{(\eta_1\Theta_1^2(1 - a_L\delta)/(\lambda"\delta))\tanh(\lambda"\delta) + 1 + \eta_1\Theta_1^2/\Gamma\right\}^{-1}$$

(5-114)

Substitution of C_{As}/C_{Ai} from eqn (5-114) into eqn (5-110) gives:

$$E = (\lambda"\delta)\tanh(\lambda"\delta) +$$

(5-115)

$$\eta_1\Theta_1^2(1 - a_L\delta)/(\cosh^2(\lambda"\delta))\left\{(\eta_1\Theta_1^2(1 - a_L\delta)/(\lambda"\delta))\tanh(\lambda"\delta) + 1 + \eta_1\Theta_1^2/\Gamma\right\}^{-1}$$

in which

$$\lambda"\delta = (a_L\delta)^{\frac{1}{2}}\Theta_1$$

(5-116)

Substituting $a_L\delta = 0$, eqn (5-115) leads to eqn (5-45).
The rate of gas absorption from the liquid film into the bulk of the liquid
is zero if:

$$C_{Ab} = C_{As} = 0 \tag{5-117}$$

When eqn (5-105) is solved using the boundary conditions:

$$C_A(x) = C_{Ai} \text{ for } x = 0 \tag{5-118}$$

and

$$dC_A(x)/dx = 0 \text{ for } x = \delta \tag{5-119}$$

the following solution is found:

$$C_A(x) = C_{Ai}\cosh(\lambda''(\delta - x))/(\cosh(\lambda''\delta)) \tag{5-120}$$

The chemical enhancement factor is given by:

$$E \equiv \Phi_A/(k_L a_L C_{Ai}) = (\lambda''\delta)\tanh(\lambda''\delta) \tag{5-121}$$

Combination of eqns (5-116) and (5-121) results in:

$$E = (a_L\delta)^{\frac{1}{2}}\Theta_1\tanh\{(a_L\delta)^{\frac{1}{2}}\Theta_1\} = (a_L\delta)^{\frac{1}{2}}\Theta_1 \tag{5-122}$$

for high values of $(a_L\delta)^{\frac{1}{2}}\Theta_1$ e.g. $(a_L\delta)^{\frac{1}{2}}\Theta_1 > 2$.
Fig. 5.9. gives a diagram of E as a function of Θ_1 for various values of $a_L\delta$
for the case that the catalyst particles are distributed homogeneously in
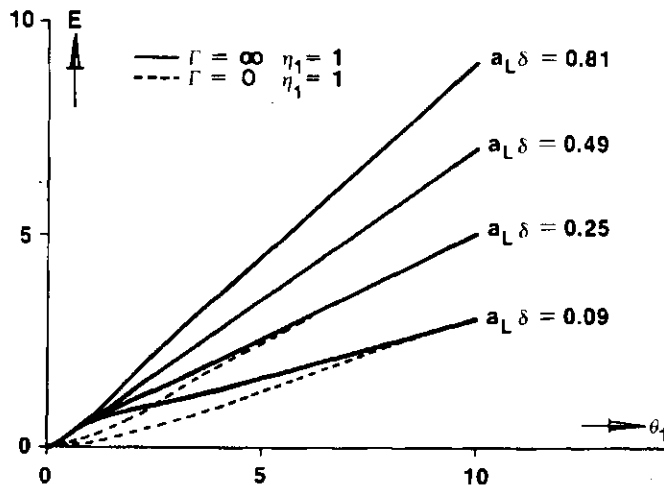both liquid film and bulk of the liquid.

Fig. 5.9. Diagram of E as a function of Θ_1 and $a_L\delta$ in the case that the
particles are distributed homogeneously in both film and bulk of
the liquid.