

KINETICS OF GAS-LIQUID REACTIONS*

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Summary

The paper reviews the basic models for mass transport accompanied by chemical reaction in the perspective of using these theories in elucidating the kinetics of gas-liquid reactions. The application to data on the adsorption of COS in aqueous solutions of NaOCl and NaOH in a wetted wall contactor is discussed.

Introduction

Gas-liquid reactions are very important industrial operations. They are carried out in a variety of equipment, like packed columns, bubble columns, plate columns, and for different purposes, like removal of noxious and toxic gases, or the production of chemicals. The system encountered consists of a liquid phase which is contacted with the gas. That gas dissolves into the liquid, diffuses through the liquid through molecular diffusion and/or forced convection due to turbulence and reacts with a component dissolved in the liquid phase.

Several models have been proposed to describe these phenomena. Attention will be focussed only on the simple two-film model and on the more elaborated penetration model. Surface renewal models with non-uniform exposure time distributions are not considered because they offer no advantage for interpreting data obtained in a wetted-wall contactor.

Film model

In the two-film model (Fig. 1) a stagnant film is assumed at both sides of the interface and all resistance to mass transport is localized in these two films. This means that concentration gradients will only develop in these films. It is

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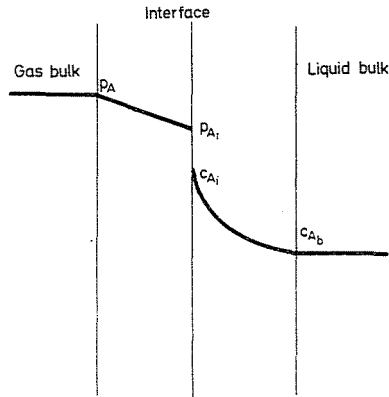
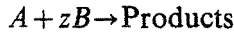


Fig. 1. The two film model

further assumed that no resistance to transport occurs at the interface itself, so that the interface concentration of the gaseous component in the solution is related to the interfacial partial pressure by Henry's law:

$$p_{A_i} = H e C_{A_i} \quad (1)$$

If a reaction



is carried out, the following continuity equations in the liquid film for both reactants hold [1—3]:

$$D_A \frac{d^2 C_A}{dy^2} = r \quad r = k C_A^m C_B^n \quad (2)$$

$$D_B \frac{d^2 C_B}{dy^2} = zr$$

with boundary conditions

$$\begin{aligned} C_A &= C_{A_i} & \text{at } y=0 \\ \frac{dC_B}{dy} &= 0 \\ C_A &= 0 & \text{at } y=\delta \\ C_B &= C_{B_b} \end{aligned} \quad (3)$$

These equations cannot be integrated analytically except for the limiting cases of a pseudo-first order reaction and for an instantaneous reaction. In the case of a pseudo-first order reaction, the reaction is first order in the gaseous component, A , and the concentration of the B species is uniform throughout the film. This allows to drop the continuity equation for B , resulting in the simplified model

$$D_A \frac{d^2 C_A}{dy^2} = (k C_{B_b}^n) \cdot C_A = k' C_A \quad (4)$$

with boundary conditions

$$\begin{aligned} C_A &= C_{A_i} & \text{at } y &= 0 \\ C_A &= 0 & \text{at } y &= \delta \end{aligned}$$

Introducing the dimensionless variables

$$Y = \frac{y}{\delta} = \frac{y}{\frac{D_A}{k_L}}$$

$$A = \frac{C_A}{C_{A_i}} \quad M = \frac{k' D_A}{k_L^2}$$

transforms Eq. (4) into

$$\frac{d^2 A}{dY^2} = MA \quad (5)$$

with boundary conditions

$$\begin{aligned} A &= 1 & \text{at } Y &= 0 \\ A &= 0 & \text{at } Y &= 1 \end{aligned}$$

Eq. (5) is readily integrated, yielding the dimensionless concentration profile as a function of the dimensionless depth in the film:

$$A = \frac{\sin h[\sqrt{M}(1-Y)]}{\sin h\sqrt{M}} \quad (6)$$

The absorption flux per unit area is obtained from Fick's law:

$$N_A = -D_A \left. \frac{dC_A}{dy} \right|_{y=0} = -k_L C_{A_i} \left. \frac{dA}{dY} \right|_{Y=0} \quad (7)$$

A convenient quantity related to this flux of absorption is the enhancement factor, which is defined as the ratio of the flux of absorption in the

presence of chemical reaction to the flux of pure physical absorption. The latter is defined by

$$\tilde{N}_A = k_L C_{A_i} \quad (8)$$

The enhancement factor thus defines the number of times the physical absorption flux is enhanced by the chemical reaction. From Eqs (7) and (8):

$$E = \frac{N_A}{\tilde{N}_A} = - \frac{D_A \left. \frac{dC_A}{dy} \right|_{y=0}}{k_L C_{A_i}} = - \left. \frac{dA}{dY} \right|_{Y=0} \quad (9)$$

or

$$E = \frac{\sqrt{M}}{\tan h \sqrt{M}} \quad (10)$$

When E is plotted as a function of \sqrt{M} , Fig. 2-a is obtained. When $\sqrt{M} > 3$, Eq. (10) reduces to

$$E = \sqrt{M}$$

This region is called the fast pseudo-first order regime. When $\sqrt{M} < 3$ the reaction is in the slow pseudo-first order regime.

The other limiting case is the instantaneous or infinitely fast reaction, in which the two reaction partners cannot coexist. The reaction must take place in a front where the concentration of both species is zero. This front is located at a certain depth y^* beneath the interface. In the region between the interface and the reaction plane, only A can be present and no B . In the region between the reaction plane and the liquid bulk, only B can exist and no A . This must result in a kind of concentration profiles like shown in Fig. 3. In these circumstances, the reaction is completely diffusion controlled: the rate of disappearance is completely determined by the rate with which both components diffuse towards the reaction front.

The appropriate equations and boundary conditions read [1—3]:

$$\begin{aligned} D_A \frac{d^2 C_A}{dy^2} &= 0 & \text{for } 0 < y < y^* \\ D_B \frac{d^2 C_B}{dy^2} &= 0 & \text{for } y^* < y < \delta \end{aligned} \quad (11)$$

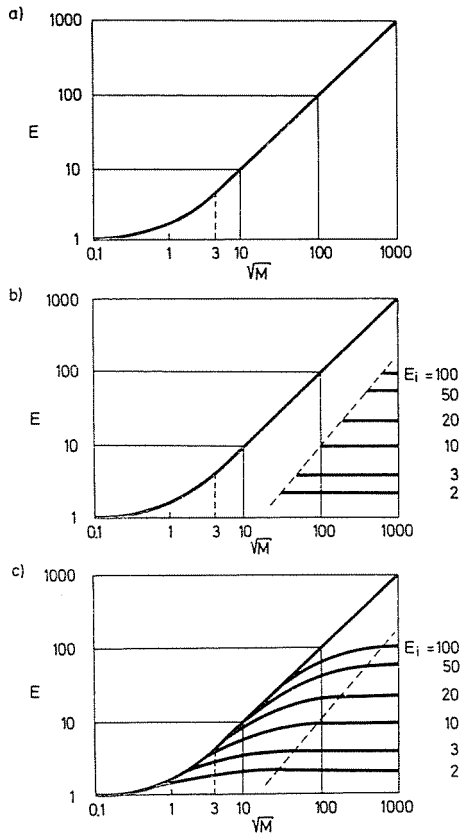


Fig. 2. Enhancement factor vs. Hatta number for a second order reaction

Boundary conditions:

$$\begin{aligned}
 C_A &= C_{A_i} & \text{at } y=0 \\
 C_A &= 0 & \text{at } y=y^* \\
 C_B &= 0 & \text{at } y=y^* \\
 C_B &= C_{B_b} & \text{at } y=\delta \\
 -D_A \frac{dC_A}{dy} &= \frac{1}{z} D_B \frac{dC_B}{dy} & \text{at } y=y^*
 \end{aligned}
 \tag{12}$$

The concentration profile is readily obtained,

$$C_A = C_{A_i} - \frac{(D_B C_{B_b} + z D_A C_{A_i}) k_L}{z D_A^2} y
 \tag{13}$$

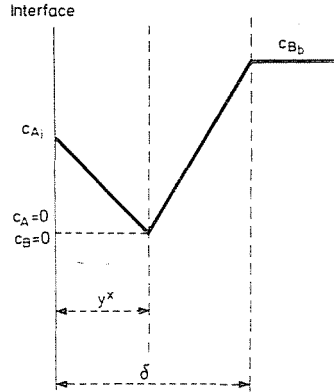


Fig. 3. Instantaneous reaction

and the enhancement factor is given by

$$E_i = 1 + \frac{1}{z} \frac{C_{B_b}}{C_{A_i}} \frac{D_B}{D_A} \quad (14)$$

The enhancement factor for an instantaneous reaction is independent of k_L , and thus of the film thickness δ , or the so-called hydrodynamic conditions. This provides a convenient means to verify experimentally whether or not the reaction is taking place in the instantaneous regime. Adding this result to Fig. 2-a yields Fig. 2-b where various $E = E_i$ curves with E_i as parameter are inserted in the appropriate range for \sqrt{M} . The region to the right of the dotted line is the domain of instantaneous reaction.

The region between the pseudo-first order curve and this instantaneous domain corresponds to the intermediate case where partial depletion of the liquid reactant occurs (Fig. 4). Physically the situation can be depicted as if the reaction took place in a zone in which depletion of the reactant B is caused, resulting in a non-uniform B concentration profile in that zone. For not too rapid reactions, the depletion will be moderate and the B profile will remain rather flat. With increasing rate, the depletion will become more severe and pronounced B profiles will develop. The limiting case of the instantaneous regime is reached when B becomes fully depleted at the interface. The set of equations for a second order reaction reads:

$$\begin{aligned} D_A \frac{d^2 C_A}{dy^2} &= k C_A C_B \\ D_B \frac{d^2 C_B}{dy^2} &= z k C_A C_B \end{aligned} \quad (15)$$

and appropriate boundary conditions as given in relations (3). There is no analytical solution for Eqs (15), and a rigorous analytic expression for the enhancement factor cannot be given. However the enhancement factor can be obtained from numerical integration of the set of Eqs. (15). This is facilitated by reshaping these equations into dimensionless form. Introducing the dimensionless variables

$$\begin{aligned}
 A &= \frac{C_A}{C_{A_i}} & B &= \frac{C_B}{C_{B_b}} \\
 Y &= \frac{y}{\delta} = \frac{y}{\frac{D_A}{k_L}} & M &= \frac{k'D_A}{k_L^2} \\
 E_i &= 1 + \frac{1}{z} \frac{C_{B_b}}{C_{A_i}} \frac{D_B}{D_A}
 \end{aligned} \tag{16}$$

the general Eqs. (15) are transformed into

$$\begin{aligned}
 \frac{d^2 A}{dY^2} &= M \cdot A \cdot B \\
 \frac{d^2 B}{dY^2} &= \frac{M}{E_i - 1} A \cdot B
 \end{aligned} \tag{17}$$

with boundary conditions

$$\begin{aligned}
 A &= 1, \quad \frac{dB}{dY} = 0 \quad \text{at } Y=0 \\
 A &= 0, \quad 2B=1 \quad \text{at } Y=1
 \end{aligned} \tag{18}$$

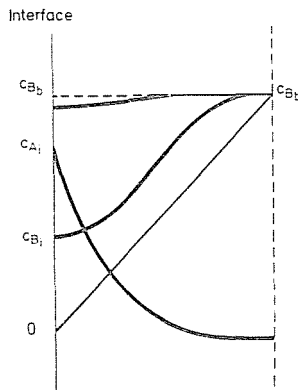


Fig. 4. Intermediate regime with partial depletion of the liquid reactant B

The set of equations is now integrated numerically for a series of values for the two parameters E_i and M and the enhancement factor evaluated as well.

Alternatively, in order to evaluate the enhancement factor, the A -concentration profile must be known accurately only in the vicinity of the interface. In this region, the B -concentration gradient is zero so that C_B is practically constant and equal to its (unknown) value at the interface, C_{B_i} . Under these conditions, the general model Eqs. (15) simplify to [4]

$$D_A \frac{d^2 C_A}{dy^2} = k C_{B_i} C_A \quad (19)$$

with boundary conditions as specified for Eq. (4). The enhancement factor is given by an expression like Eq. (10) in which the squared Hatta number M is replaced by N :

$$N = \frac{k C_{B_i} D_A}{k_L^2} \quad (20)$$

To relate C_{B_i} upon C_{B_b} , the reaction term is eliminated from Eq. (15):

$$D_A \frac{d^2 C_A}{dy^2} = \frac{1}{z} D_B \frac{d^2 C_B}{dy^2} \quad (21)$$

Integrating twice

$$C_{B_i} = C_{B_b} \left[1 + \frac{z D_A}{D_B} \frac{C_{A_i}}{C_{B_b}} \left(1 + \frac{\left. \frac{dC_A}{dy} \right|_{y=0}}{\frac{k_L C_{A_i}}{D_A}} \right) \right] \quad (22)$$

Substituting Eq. (9) and Eq. (14) in Eq. (22) yields

$$C_{B_i} = C_{B_b} \frac{E_i - E}{E_i - 1} \quad (23)$$

Substituting this relation in Eq. (20) for N finally yields an implicit equation for the enhancement factor [4]:

$$E = \frac{\sqrt{M \frac{E_i - E}{E_i - 1}}}{\tan h \sqrt{M \frac{E_i - E}{E_i - 1}}} \quad (24)$$

Eq. (24) is of the same form as Eq. (10), except that the Hatta number is multiplied by a correction factor which itself is dependent upon the enhance-

ment factor. Eq. (24) simplifies to

$$E = \sqrt{M \frac{E_i - E}{E_i - 1}} \quad (25)$$

when the right hand side of Eq. (25) exceeds 3, so that E is explicitly given by

$$E = \frac{-M + \sqrt{M^2 + 4ME_i(E_i - 1)}}{2(E_i - 1)} \quad (26)$$

It is easily shown that Eq. (25) and thus Eq. (24) degenerates into the previously treated limiting cases $E = E_i$ for large \sqrt{M} and $E = \frac{\sqrt{M}}{\tan h \sqrt{M}}$ when $E \ll E_i$.

Equation (24) is easily solved for E for given values for \sqrt{M} and E_i . When these results are inserted in Fig. 2-b, Fig. 2-c is obtained. For a given value of E_i and small enough values for \sqrt{M} there is no depletion yet and the curve coincides with that for the pseudo-first order reaction with a uniform B profile. When \sqrt{M} increases, depletion starts and magnifies and the curve gradually shifts from the pseudo-first order curve. Finally, for a large enough value of \sqrt{M} (approximately $10 E_i$) the curve shades off into the asymptote $E = E_i$. Increasing further \sqrt{M} does no longer influence the enhancement factor since the reaction has entered the instantaneous regime.

In summary:

- I. $\sqrt{M} > 10 E_i$, $E = E_i$ and the reaction is in the instantaneous regime.
- II. $\sqrt{M} < \frac{1}{2} E_i$, the E/\sqrt{M} curve lies sufficiently close to the curve for the pseudo-first order regime so that it may be safely assumed that the reaction is taking place in that regime.
If further:
 - $3 < \sqrt{M} < \frac{1}{2} E_i$, $E = \sqrt{M}$, and the reaction is in the fast pseudo-first order regime.
 - $3 > \sqrt{M} < \frac{1}{2} E_i$, E is close to 1 and the reaction takes place in the slow pseudo-first order regime which is almost comparable to physical absorption.
- III. $\frac{1}{2} E_i < \sqrt{M} < 10 E_i$ the reaction is in the intermediate regime with partial depletion of B and the enhancement factor is given by Eq. (24).

From these results it is clear that a reaction can move from one regime into another when the Hatta number varies over a sufficiently wide range as e.g. in industrial large scale absorbers.

For a general (m, n) -th order reaction, described by Eqs. (2) and (3) an approximate solution may be obtained by approximating the reaction term in the vicinity of the interface by

$$kC_A^m C_B^n = \left(\frac{2}{m+1} kC_{A_i}^{m-1} C_{B_i}^n \right) C_A \quad (27)$$

The enhancement factor is then approximately given by [5]

$$E = \frac{\sqrt{Q}}{\tan h \sqrt{Q}} \quad (28)$$

where Q is defined as

$$Q = M \left[\frac{E_i - E}{E_i - 1} \right]^n \frac{2C_{A_i}^{m-1}}{m+1} \quad (29)$$

Penetration model

A more elaborated and more realistic model is the penetration model which accounts also for concentration changes in the liquid as a function of time. This model is extremely well suited to describe the wetted-wall reactor where a liquid film flows downward in laminar motion over a rod thus being exposed to the gas for a certain period of time. For a convenient application the penetration depth of the gas should not extend beyond the flat region of the laminar, parabolic, velocity profile in the falling film.

When a thin slice of liquid between the distances y and $y + dy$ from the interface is considered (Fig. 5), the following continuity equations for a second order reaction, can be written [1—3]:

$$\begin{aligned} D_A \frac{\partial^2 C_A}{\partial y^2} &= \frac{\partial C_A}{\partial t} + kC_A C_B \\ D_A \frac{\partial^2 C_B}{\partial y^2} &= \frac{\partial C_B}{\partial t} + zkC_A C_B \end{aligned} \quad (30)$$

The boundary conditions read:

$$\begin{aligned} C_A &= C_{A_i} \\ \frac{\partial C_B}{\partial y} &= 0 \end{aligned} \quad \text{at } y=0, \text{ all } t$$

$$\begin{aligned} C_A &= 0 \\ C_B &= C_{B_b} \end{aligned} \quad \text{at } t=0, \text{ all } y \quad (31)$$

$$\begin{aligned} C_A &= 0 \\ C_B &= C_{B_b} \end{aligned} \quad \text{at } y=\infty, \text{ all } t$$

As with the film model, equations (30) do not possess an analytical solution, except for the limiting cases of pseudo-first order reactions and infinitely fast reactions.

For pseudo-first order reactions, the instantaneous absorption flux at time t is given by [6]

$$N_A(t) = C_{A_i} \sqrt{D_A k'} \left(\operatorname{erf} \sqrt{k't} + \frac{e^{-k't}}{\sqrt{\pi k't}} \right) \quad (32)$$

This flux is changing from point to point at the interface and cannot be measured experimentally. What can be measured is the average absorption flux over the entire contact time \bar{t} . This flux is defined by

$$\bar{N}_A(\bar{t}) = \frac{1}{\bar{t}} \int_0^{\bar{t}} N_A(t) dt \quad (33)$$

For a pseudo-first order reaction [6]:

$$\bar{N}_A(\bar{t}) = C_{A_i} \sqrt{k' D_A} \left[\left(1 + \frac{1}{2k'\bar{t}} \right) \operatorname{erf} \sqrt{k'\bar{t}} + \sqrt{\frac{1}{\pi k'\bar{t}}} e^{-k'\bar{t}} \right] \quad (34)$$

For sufficiently large $k'\bar{t}$ values (> 10) the average flux becomes practically independent of the hydrodynamic conditions, i.e. the contact time \bar{t} and \bar{N}_A is

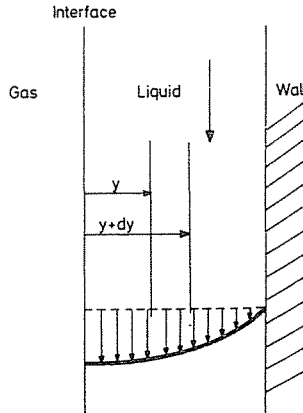


Fig. 5. Penetration model applied to a laminar falling film

given by

$$\bar{N}_A \cong C_{A_i} \sqrt{D_A k'} \quad (35)$$

For not too slow reactions, the wetted wall reactor operates in the horizontal region of the curve, since contact times realized are in the range of 0.1—1 sec.

This regime thus easily allows to determine the rate coefficient provided the solubility and the diffusivity are known. Defining M as before and noting that for the penetration model

$$k_L = 2 \sqrt{\frac{D_A}{\pi t}} \quad (36)$$

one obtains

$$M = \frac{k' D_A}{k_L^2} = \frac{\pi}{4} k' \bar{t} \quad (37)$$

and the enhancement factor is given by [6]

$$E = \sqrt{M} \left[\left(1 + \frac{\pi}{8M} \right) \operatorname{erf} 2 \sqrt{\frac{M}{\pi}} + \frac{1}{2\sqrt{M}} e^{-\frac{4M}{\pi}} \right] \quad (38)$$

For $\sqrt{M} \gg 1$, the enhancement factor again simplifies to

$$E = \sqrt{M}$$

In the case of an instantaneous reaction, the average flux is given by [7]

$$\bar{N}_A(\bar{t}) = \frac{2C_{A_i}}{\operatorname{erf}(\beta/\sqrt{D_A})} \sqrt{\frac{D_A}{\pi t}} \quad (39)$$

where β is a constant defined by

$$e^{\beta^2/D_B} \operatorname{erfc}(\beta/\sqrt{D_B}) = \frac{C_{B_b}}{zC_{A_i}} \sqrt{\frac{D_B}{D_A}} e^{\beta^2/D_A} \operatorname{erf}(\beta/\sqrt{D_A}) \quad (40)$$

and independent of the hydrodynamic conditions. The average flux is steadily decreasing as contact time is increasing. It is to be noticed that the flux is independent of the rate constant so that data from this regime are not well suited to eluci the kinetics of the reaction. As with the film model, the enhancement factor, given by

$$E_i = \frac{1}{\operatorname{erf}(\beta/\sqrt{D_A})} \quad (41)$$

is independent of the hydrodynamic conditions. For sufficiently large E_i , Eq. (41) simplifies to

$$E_i = \sqrt{\frac{D_A}{D_B}} + \frac{C_{Bb}}{zC_{Ai}} \sqrt{\frac{D_B}{D_A}} \left(= E_{i\text{film}} \cdot \sqrt{\frac{D_A}{D_B}} \right) \quad (42)$$

For the intermediate regime with partial depletion of the reactant B , the behaviour of $\bar{N}_A(\bar{t})$ vs \bar{t} will range between these two limiting types. Introducing the dimensionless variables (42) and

$$\begin{aligned} A &= \frac{C_A}{C_{Ai}} & B &= \frac{C_B}{C_{Bb}} \\ Y &= \frac{y}{\frac{D_A}{k_L}} & T &= \frac{t}{t} = \frac{t}{\frac{4}{\pi} \frac{D_A}{k_L^2}} \\ M &= \frac{k'D_A}{k_L^2} & q &= \frac{D_A}{D_B} \end{aligned} \quad (43)$$

the Eq. (30) can be recasted in dimensionless form:

$$\begin{aligned} \frac{\partial^2 A}{\partial Y^2} &= \frac{\pi}{4} \frac{\partial A}{\partial T} + M \cdot A \cdot B \\ \frac{\partial^2 B}{\partial Y^2} &= \frac{\pi}{4} q \frac{\partial B}{\partial T} + \frac{\sqrt{q}M}{E_i - \sqrt{q}} A \cdot B \end{aligned} \quad (44)$$

These equations have been solved numerically by Perry and Pigford [8], by Brian et al. [9] and by Pearson [10] for various values of the parameters q , E_i and M . The dependence of E on \sqrt{M} for various values of E_i is almost identical with that obtained with the film model. Further on, E appears to be only weakly dependent upon q [9]. Hence, the enhancement factor for the penetration model is reasonably well approximated by the result for the film model, Eq. (24).

Hikita and Asai [5] proposed an approximating expression for the enhancement factor of identical form as Eq. (38), where M is to be replaced by $M \frac{E_i - E}{E_i - 1}$.

For a general (m, n) -th order reaction, Hikita and Asai arrived again at the same approximating expression, Eq. (38), for the enhancement factor except that M is to be replaced by Q , defined in Eq. (29). They showed that this approximation was slightly superior over Eq. (28).

In summary, the enhancement factors for both models and different types of kinetics can be casted in general form as displayed in Table 1.

Table 1
Enhancement factors for film and penetration models for different types of kinetics

Film model

$$E = \frac{\sqrt{M\alpha}}{\tan h\sqrt{M\alpha}}; \quad M = \frac{kD_A C_{B_b}^n}{k_L^2}$$

Penetration model

$$E = \left(\sqrt{M\alpha} + \frac{\pi}{8\sqrt{M\alpha}} \right) \operatorname{erf} 2 \sqrt{\frac{M\alpha}{\pi}} + \frac{1}{2} e^{-\frac{4M\alpha}{\pi}}; \quad M = \frac{\pi}{4} kC_{B_b}^n \bar{t}$$

Value of α for both models and different types of rate equations

Pseudo-first-order reaction

$$\alpha = 1$$

Second order reaction

$$\alpha = \frac{E_i - E}{E_i - 1}$$

(m, n) -th order reaction

$$\alpha = \frac{2C_{A_i}^{m-1}}{m+1} \left(\frac{E_i - E}{E_i - 1} \right)^n$$

Absorption of COS in caustic hypochlorite solutions

These principles will now be applied in studying the kinetics of absorption of carbonyl sulfide in aqueous solutions of sodium hypochlorite and sodium hydroxide. The experiments were carried out in a wetted wall contactor where the contact time \bar{t} could be varied by varying the height of the column and the volumetric liquid flow rate (Fig. 6). The major advantage of such an apparatus is that the exchange surface between gas and liquid is exactly known. This is of vital importance for studies of this type.

Equipment

Fig. 6 is a schematic representation of the equipment. The liquid is introduced from a tank at a few meters of altitude through a thermostat and metered by a rotameter. The flow of the inlet gases, COS and N₂, is controlled by flow controllers and metered by rotameters. The outlet gas is sent to a gas chromatograph for quantitative analysis.

Solubility and diffusivities

The physical properties required for the analysis can, in principle, be measured in the wetted wall contactor.

To determine the diffusion coefficient for the gaseous species in water or non-reactive liquids, physical absorption experiments are carried out.

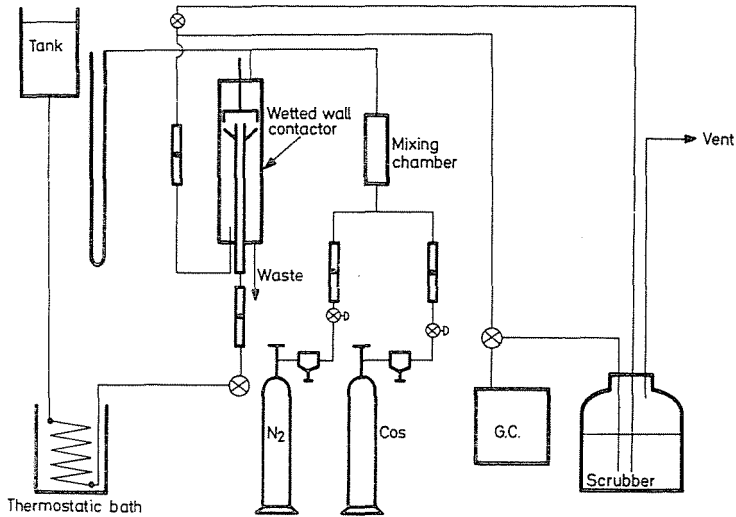


Fig. 6. Experimental unit

According to the penetration model the physical absorption flux is given by

$$\bar{N}_A(\bar{t}) = 2C_{A_i} \sqrt{\frac{D_A}{\pi \bar{t}}} \quad (45)$$

Substituting the contact time, given by

$$\bar{t} = \frac{2h}{3} \left(\frac{3\mu}{g\rho} \right)^{1/3} \left(\frac{\pi d}{v} \right)^{2/3} \quad (46)$$

in the absorption flux equation (45) yields

$$\tilde{N}_A(\bar{t}) = \sqrt{6} \left(\frac{g\rho}{3\pi\mu} \right)^{1/6} \left(\frac{1}{d} \right)^{1/3} C_{A_i} \sqrt{D_A} \frac{v^{1/3}}{\sqrt{h}} \quad (47)$$

Plotting $\tilde{N}_A(\bar{t})$ vs. $v^{1/3}h^{-1/2}$ should therefore give a straight line through the origin. From its slope, D_A can be determined provided C_{A_i} is known. For an undiluted gas dissolving in water, the solubility is given by Henry's law:

$$p_{A_i} = p_A = HeC_{A_i} \quad (48)$$

or can be determined experimentally by specially conceived equipment. The solubility in ionic solutions is different from that in water. It is computed by updating the solubility in water according to the method of Van Krevelen and Hoftijzer [11].

Determining the kinetics of a chemical reaction always involves experiments with varying driving force for the gaseous component, i.e. by

diluting the reactive gas with an inert diluent like N_2 which is not being absorbed in the liquid. However, eventual resistance to mass transfer in the gas film resulting in a gas film concentration drop, may complicate the data analysis considerably. To check experimentally whether there is a significant pressure drop over the gas film or not, physical absorption experiments with varying dilution ratios can be carried out under identical conditions for the gas flow rate through the equipment as in the experiments with chemical absorption (same gas film thickness!). For any dilution, the appropriate C_{A_i} may be calculated from the physical absorption flux Eq. (45), provided D_A is known.

The diffusivity of the dissolved liquid reactant or reactive ion, D_B , may be determined from absorption experiments with chemical reaction, provided the conditions are chosen in such a way that the reaction is diffusion controlled, i.e. that it is taking place in the instantaneous regime. The specific average absorption flux is then given by Eq. (39). A plot of $\bar{N}_A(\bar{t})$ vs. $\sqrt{\frac{1}{t}}$ should give a straight line, its slope being given by

$$\text{Slope} = \frac{2C_{A_i}}{\text{erf}(\beta/\sqrt{D_A})} \sqrt{\frac{D_A}{\pi}} \quad (49)$$

According to Eq. (40) β is a function of D_B only when the solubility C_{A_i} and the diffusivity D_A are known.

The value for D_B is such that after solving Eq. (40) for β , the slope Eq. (49) is satisfied.

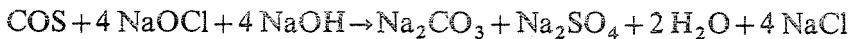
When E_i is large, E_i is given by Eq. (42) and the procedure is simplified substantially, since

$$\text{Slope} = 2C_{A_i} \sqrt{\frac{D_A}{\pi}} \cdot \left(\sqrt{\frac{D_A}{D_B}} + \frac{C_{B_b}}{zC_{A_i}} \sqrt{\frac{D_B}{D_A}} \right) \quad (50)$$

D_B is now readily found from Eq. (50) without having to solve the transcendental function (40) for β .

Kinetics

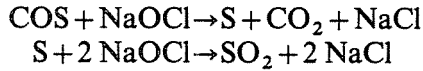
The overall reaction can be written as



and an empirical rate equation of the form

$$r = k C_{\text{COS}}^p C_{\text{NaOCl}}^m C_{\text{NaOH}}^n \quad (51)$$

can be proposed. NaOH is added primarily to remove the gaseous reactants CO_2 and SO_2 which are irreversibly formed by the oxidation of COS by NaOCl:



To investigate the effect of the various reactants, a series of experiments with varying COS, NaOCl and NaOH concentrations was set up according to the scheme of Fig. 7. Experimental data consist of average specific absorption fluxes $\bar{N}_A(\bar{t})$ as a function of contact time \bar{t} . Fig. 8 presents a sample of such

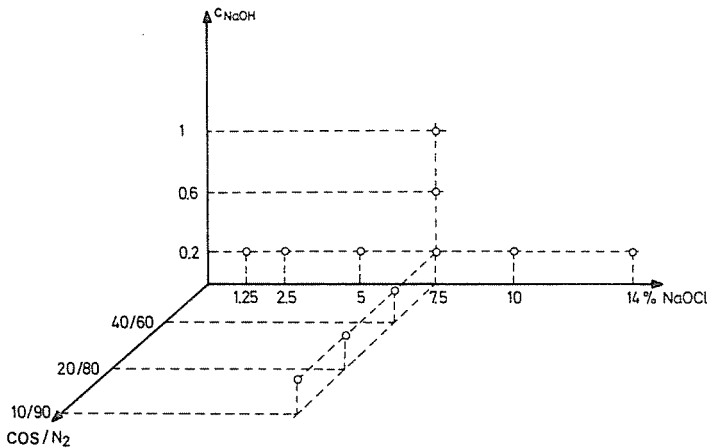


Fig. 7. Experimental region

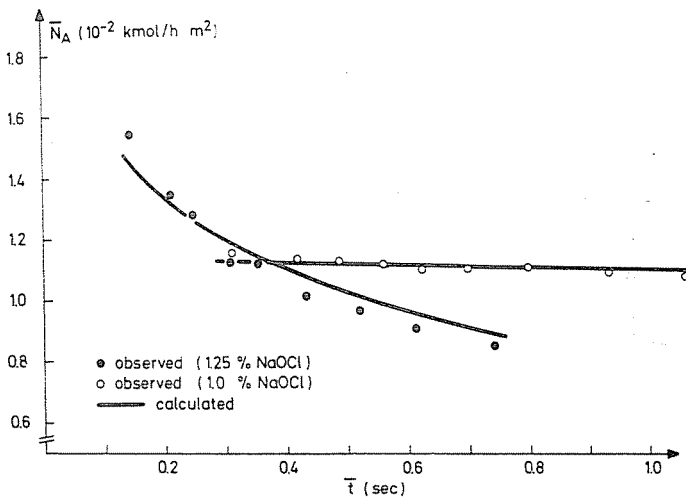


Fig. 8. Absorption rates as a function of contact time for different NaOCl concentrations

results for a gas consisting of pure COS and different NaOCl concentrations. The curvature in the low NaOCl concentration clearly demonstrates that under these conditions, i.e. high gas driving forces and low liquid reactant concentrations, the liquid reactant is seriously depleted and the reaction is not taking place in the fast pseudo-first order regime. Whether the reaction is instantaneous or takes place in the intermediate regime with partial depletion of NaOCl, is checked by calculating the experimental enhancement factor for a number of runs of absorption with chemical reaction and physical absorption pairwise under identical conditions. The non-constant figures of Table 2 indicate that the reaction is taking place in the intermediate regime. When the

Table 2
Experimental enhancement factors for 1.25%
NaOCl

<i>t</i> (sec)	0.2	0.3	0.4	0.5	0.6
<i>E</i>	1.83	1.9	1.97	2.02	2.06

liquid reactant concentration is drastically increased, the picture changes and the average specific absorption flux becomes virtually independent of contact time, indicating pseudo-first order behaviour. The same regime is indicated when the gas driving force is drastically reduced by feeding diluted mixtures of COS in N₂. The effect of NaOH on the absorption rate is shown to be inversely proportional with its concentration (Fig. 9). In the following analysis it is assumed that the partial orders are +1 with respect to COS and NaOCl and -1 with respect to NaOH.

The rate coefficient is most easily determined from the data pertaining to the fast pseudo-first order regime. According to Eq. (35):

$$k = \left(\frac{\bar{N}_A}{C_{A_i}} \right)^2 \frac{1}{D_A C_{B_b}} \quad (52)$$

When the dissolved reactant is depleted, use can be made of Fig. 2-c when *E* is known, for instance from experimental determinations: the abscissa value of the intersection of the horizontal line $E = E_{\text{observed}}$ with the curve E/\sqrt{M} corresponding to the particular E_i value is, the appropriate Hatta number at the current contact time *t*. *k* is then determined from $M = \frac{\pi}{4} k C_{B_b} \bar{t}$. Of course, the figure must be drawn on a sufficiently detailed scale to allow to extract *k* with sufficient precision. Alternatively the transcendental Eq. (24) can be solved for *M*, provided *E* is known. This is very efficiently achieved with any of the modern one-dimensional search strategies like e.g. the method suggested by Shacham and Kehat [12].

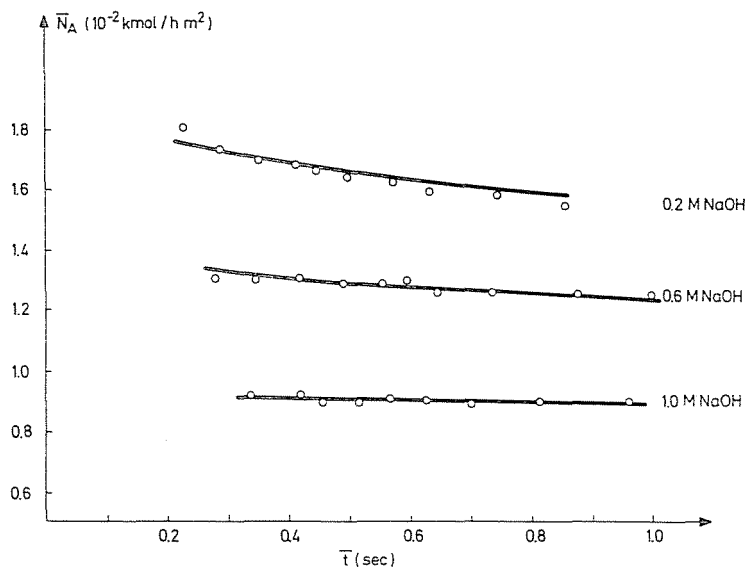


Fig. 9. Effect of NaOH on the absorption rate

The solid lines in Figs 8 and 9 are computed absorption fluxes with the so-obtained k values. The agreement with observed values is good and never exceeds 10%. The slight trend in the deviations might be explained:

- 1) by inaccuracies in the solubilities and diffusivities
- 2) by the analysis via Eq. (24) which is only approximate in the sense that it is based on an approximate solution of the continuity equations, that it does not account fully for the effect of the different diffusivities D_A and D_B , and that it is valid only for second order reactions
- 3) by the fact that the reaction orders are possibly not exactly 1.

Work is presently going on to refine the analysis and to establish the effect of the ionic strength on the rate coefficient.

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Notation

- A, B dimensionless concentrations of species A and B
 C_A, C_B concentrations of species A and B [kmol/m³]
 C_{Bb} concentration of dissolved liquid reactant B in the bulk of the liquid [kmol/m³]

C_{A_i}, C_{B_i}	interfacial concentrations of species A and B [kmol/m ³]
d	diameter of wetted tube [m]
D_A, D_B	diffusivities of species A and B [m ² /h]
E	enhancement factor
E_i	enhancement factor for an instantaneous reaction
g	gravity acceleration [m/h ²]
h	height of wetted tube [m]
He	Henry coefficient [bar m ³ /kmol]
k	rate coefficient
k_L	liquid side mass transfer coefficient [m/h]
k'	pseudo-first-order rate coefficient, defined as $kC_{B_0}^n$
m, n	partial reaction orders with respect to components A and B , respectively
M	squared Hatta number, defined as $kC_{B_0}^n D_A/k_L^2$
N_A	specific absorption flux in the presence of chemical reaction (film model) [kmol/m ² h]
$N_A(t)$	instantaneous specific absorption flux at time t (penetration model) [kmol/m ² h]
$\bar{N}_A(\bar{t})$	average specific absorption flux over time \bar{t} (penetration model) [kmol/m ² h]
\tilde{N}_A	physical (average) specific absorption flux, defined by $k_L C_{A_i}$ [kmol/m ² h]
p_{A_i}	interfacial partial pressure of gaseous component [bar]
q	diffusivity ratio D_A/D_B
Q	quantity defined in (29)
r	reaction rate [kmol/m ³ h]
t	time [h]
T	dimensionless time
t	contact time [h]
v	volumetric flow rate over wetted tube [m ³ /h]
y	distance from interface in liquid phase [m]
Y	dimensionless distance from interface in liquid phase
y^*	depth of reaction front [m]
z	number of moles of B reacting per mole of A

Greek symbols

α	multiplier, defined in Table 1
β	constant defined by equation (40)
δ	film thickness [m]
ρ	density of liquid [kg/m ³]
μ	viscosity of liquid [kg/m h]

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