

**MASS TRANSFER ACROSS INTERFACE WITH A SIMULTANEOUS  
CHEMICAL REACTION IN BOTH PHASES;  
REACTION FACTOR FOR IRREVERSIBLE REACTIONS  
OF AN ARBITRARY ORDER**

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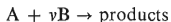
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Based on the film theory of mass transfer, relations were developed for determining the reaction factor in the case of an irreversible chemical reaction of an arbitrary order, when the mass transfer of reaction components proceeds countercurrently across the phase boundary. The relations make it possible to determine the rate of the process in a heterogeneous liquid system for the chemical reaction proceeding on both sides of the phase boundary.

Considerable attention has been devoted in the literature to the theory of mass transfer with a simultaneous chemical reaction and the results of numerous authors have been compiled in excellent monographs<sup>1,2</sup>. Theoretical solutions of the problem have been aimed mainly at applications on absorption with a chemical reaction and, consequently, only those cases have been studied when the reaction proceeds in one phase and when, followingly, unidirectional transport is involved of one or more reaction components across the interface. In two-phase liquid systems, a chemical reaction may proceed simultaneously in both phases and the transfer of reaction components between the phases occurs in both directions.

It is the purpose of this work to establish relations for the calculation of the rate of the process for an irreversible reaction



proceeding simultaneously in both phases with its rate in the homogeneous phase described by the kinetic equation

$$r_A = k_R c_A^p c_B^q \quad (1)$$

We assume that component A enters the system dissolved in phase (A) and component B in phase (B). A necessary condition for the reaction to proceed in phase (A) is a nonzero concentration of component B at the interface in phase (A),  $c_{BA}^+ > 0$ , which requires a certain non-

zero value of the solubility of component B in phase (A). The similar condition for the reaction in phase (B) is a nonzero concentration of component A at the interface in phase (B),  $c_{AB}^+ > 0$ , which necessitates a partial solubility of component A in phase (B). If these conditions are satisfied and the chemical reaction proceeds in both phases, mass transfer occurs of component A across the phase boundary into phase (B) and of component B into phase (A).

Mass transfer of component A may be expressed with the help of the reaction factor  $\Phi_{AB}$  by the relation

$$J_A^+ = \Phi_{AB} k_{AB} c_{AB}^+ \quad (2)$$

and, similarly, mass transfer of component B

$$J_B^+ = \Phi_{BA} k_{BA} c_{BA}^+ \quad (3)$$

and, simultaneously, Eqs (2) and (3) define the reaction factors  $\Phi_{AB}$  and  $\Phi_{BA}$  for the given case.

If  $\nu$  mol of component B react with one mol of component A in phase (B) during the reaction, we can express the total rate of the process by the amount of component A which reacts in a time unit and in a volume unit of the two-phase reaction mixture by the relation

$$r_A = \bar{a}(J_A^+ + \nu J_B^+) = \bar{a}(\Phi_{AB} k_{AB} c_{AB}^+ + \nu \Phi_{BA} k_{BA} c_{BA}^+). \quad (4)$$

Besides the mass transfer coefficients  $k_{AB}$ ,  $k_{BA}$  and the magnitude of the specific interfacial area  $\bar{a}$  it is necessary to know for evaluation of Eq. (4) the values of the reaction factors and concentrations at the interface.

As the choice of components A and B is arbitrary for a given reaction system and the relations describing the diffusion with a chemical reaction are analogous for both phases, it is sufficient to find the expression for only one of the reaction factors, *e.g.* for the reaction factor for component A in phase (B),  $\Phi_{AB}$ . The expression for the factor  $\Phi_{BA}$  is then obtained by interchanging the indices. In developing the relations for the factor  $\Phi_{AB}$ , which will be denoted from now on as  $\Phi$ , we will consider transport processes in phase (B) into which component A diffuses from the phase interface. For the sake of simplicity, the index of phase (B) will be deleted also for the remaining variables. As shown by Hikita and Asai<sup>3</sup> and Brian<sup>4</sup> for the solution of this problem in the case of the reaction in one phase, the results based on the film and penetration theories do not differ significantly from one another from a practical point of view. As the formulation of the problem in the film theory makes it possible to arrive at an approximate solution in a simpler way, this approach will be used here in developing working formulas. At the same time we will assume that the transport of reaction products inside the phase and across the phase interface does not affect the diffusion of reaction components.

## THEORETICAL

Mass transfer with a simultaneous chemical reaction whose rate is expressed by Eq. (1) is described by the differential equations

$$D_A(d^2 c_A/dx^2) = k_R c_A^p c_B^q, \quad (5)$$

$$D_B(d^2c_B/dx^2) = \nu k_R c_A^p c_B^q. \quad (6)$$

Boundary conditions are given by

$$x = 0, \quad c_A = c_A^+, \quad dc_B/dx = J_B^+/D_B, \quad (7)$$

$$x = \delta, \quad c_A = 0, \quad c_B = c_B^0. \quad (8)$$

A solution of this problem for a special case of  $J_B = 0$  was obtained by Hikita and Asai<sup>3</sup>. By using the transformation relations

$$a = c_A/c_A^+, \quad b = D_B c_B / \nu D_A c_A^+, \quad z = x/\delta \quad (9)-(11)$$

and after some manipulation, Eqs (5) and (6) assume the form of

$$d^2a/dz^2 = (M/Q^q) a^p b^q, \quad d^2b/dz^2 = d^2a/dz^2, \quad (12), (13)$$

where the dimensionless parameters  $M$  and  $Q$  are defined by

$$M = k_R (c_A^+)^p (c_B^0)^q \delta^2 / D_A c_A^+ = k_R (c_A^+)^{p-1} (c_B^0)^q D_A / k_A^2, \quad Q = D_B c_B^0 / \nu D_A c_A^+. \quad (14), (15)$$

If we introduce a further dimensionless parameter  $R$  denoting the ratio of the amounts of component B transferred across the phase interface and reacted in the reaction phase considered

$$R = J_B^+ / \nu J_A^+ \quad (16)$$

it is possible to express the boundary conditions in the transformed variables as

$$z = 0, \quad a = 1, \quad db/dz = R\Phi, \quad (17)$$

$$z = 1, \quad a = 0, \quad b = Q. \quad (18)$$

By combining the relation for the mass flux of component A across the phase interface

$$J_A^+ = -D_A (dc_A/dx)_{x=0}, \quad (19)$$

the definition of the reaction factor (2), the relation  $k_A = D_A/\delta$ , and transformations (9) and (11), we obtain the following expression for the reaction factor

$$\Phi = -(da/dz)_{z=0}. \quad (20)$$

Double integration of Eq. (13) with boundary conditions (17) and (18) combined with relation (20) leads to the following relation for the dimensionless concentrations of the reaction components

$$b = a + Q - \Phi(R + 1)(1 - z). \quad (21)$$

The maximum value of the reaction factor may reach

$$\Phi_{\max} = (Q + 1)/(R + 1) \quad (22)$$

as follows from Eq. (21) if we require that the value of  $b$  be positive also for  $z = 0$ . As the value of the reaction factor cannot be lower than unity, it is obvious from relation (22) that  $R$ , i.e. the ratio of the amounts of component B transferred between the phases and reacted in phase (B), cannot exceed the ratio  $Q$ , so that it holds

$$0 \leq R \leq Q. \quad (23)$$

Inserting  $b$  from Eq. (21) into Eq. (12) we obtain a nonlinear differential equation for variable  $a$

$$d^2a/dz^2 = Ma^p[(a + Q - \Phi(R + 1)(1 - z))/Q]^q \quad (24)$$

which generally does not possess the exact analytical solution.

Because a more direct and graphically expressible solution may be obtained from Eq. (24) for  $p = q = 1$ , e.g. for the special case of the reaction of the first order with respect to both components, we shall consider firstly this case.

*Special Case*  $r = k_R c_A c_B$

We search for an approximate solution of Eq. (24) in the form

$$a = \sinh [\Gamma(1 - z)]/\sinh \Gamma \quad (25)$$

which is formally identical with the exact solution of this equation for a reaction of the pseudofirst order when  $Q \rightarrow \infty$ . Differentiating function (25) and inserting into Eq. (20) we obtain a relation for the reaction factor

$$\Phi = \Gamma/\tanh \Gamma. \quad (26)$$

For determining the constant  $\Gamma$  we use the collocation method; by inserting function (25) and its second derivative into the differential equation (24) and solving for  $z = 0$  we get

$$\Gamma = \sqrt{\{M[1 + Q - \Phi(R + 1)]/Q\}}. \quad (27)$$

Eqs (26) and (27) enable an iterative calculation of the reaction factor  $\Phi$ . For  $R = 0$ , relation (27) reduces to the solution found by van Krevelen<sup>5</sup>.

For a rapid determination of  $\Phi$  we may use advantageously the graphical interpretation known from the solution for  $R = 0$ . Relation (27) can be namely formally transformed into the form corresponding to this case, *i.e.*

$$\Gamma = \sqrt{\{M_0[1 + Q_0 - \Phi]/Q_0\}}, \quad (28)$$

if we set

$$M_0 = M(1 - R/Q), \quad Q_0 = (Q - R)/(R + 1) = \Phi_{\max} - 1. \quad (29), (30)$$

The generalized graph for the calculation of reaction factor, which makes use of relations (29) and (30), is depicted in Fig. 1.

General Case  $r = k_R c_A^p c_B^q$

As shown by Hikita and Asai<sup>3</sup> for the solution of a similar problem for the transfer of one reaction component across the phase interface ( $R = 0$ ), the reaction factor

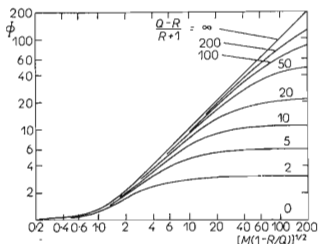


FIG. 1

Graph for the Determination of the Reaction Factor for  $p = q = 1$

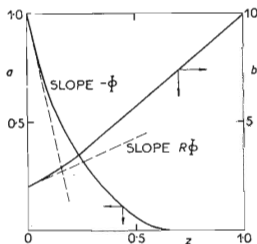


FIG. 2

Concentration Profiles in the Diffusional Film  $p = 1, q = 1, \sqrt{M} = 10, Q = 10, R = 1, \phi = 4.69$

may be well approximated by relation (26) even for this general form of the kinetic equation if the parameter  $\Gamma$  is expressed by

$$\Gamma = \Phi' \sqrt{(b(0)/b(1))^q} . \quad (31)$$

The effect of exponent  $p$  is included in the reaction factor for the limiting case of a fast reaction of the pseudo- $p$ th order,  $\Phi'$ , for which an exact relation may be found<sup>3</sup>

$$\Phi' = \sqrt{\{2M/(p + 1)\}} . \quad (32)$$

If the concentration ratio in Eq. (31) is expressed with the help of Eq. (21), we get for the special case of  $p = q = 1$  a relation identical with relation (27). This agreement entitles us to assume that the procedure can be used to approximate the reaction factor also in the general case for transfer of both reaction components across the phase interface and for exponents in the kinetic equation different from unity. By combining relations (21), (31) and (32) we get for the parameter  $\Gamma$  an expression

$$\Gamma = \sqrt{\{2M\{[1 + Q - \Phi(R + 1)]/Q\}^q/(p + 1)\}} \quad (33)$$

which, together with relations (26), makes it possible to calculate by an iterative procedure the magnitude of the reaction factor with a general form of the kinetic equation.

## DISCUSSION

The validity of proposed relations (26) and (33) has been verified numerically by solving the corresponding differential equations (12) and (13) on a Tesla 200 computer. The accuracy of the approximate expression for the reaction factor has been examined in the following range of variables:  $p(0 \div 3)$ ,  $q(0 \div 3)$ ,  $\sqrt{M}(2 \div 250)$ ,  $Q(2 \div 250)$ ,  $R(0 \div 25)$ . Characteristic concentration profiles of the reaction components in the diffusional film obtained from this numerical solution are illustrated in Fig. 2.

The values of the reaction factor calculated according to relations (26) and (33) in particular series of combinations of different exponents  $p$  and  $q$  were on the whole somewhat lower than those obtained from the numerical solution except for some series with exponent  $p$  lower than unity. The relative error  $\varepsilon$  for the determination of the reaction factor at given parameters  $\sqrt{M}$  and  $Q$  increases with increasing exponent  $q$  and in the region of  $\Phi$ -values far from  $\phi_{\max}$  also with increasing ratio  $Q$ , as the approximation implies a constant concentration of component  $b$  in the diffusional film equal to the value at the phase interface,  $b = b(0)$ . For  $R < 1$ , the relative error  $\varepsilon$  does not exceed the value of 6%; it is, however, always substantially lower in the region of higher values of  $\sqrt{M}$ . Largest deviations are found for the combina-

tion of exponents  $p = 0$  and  $q = 3$ ; in the most unfavourable case ( $R = 25$ ), *i.e.* for the reaction proceeding in the given phase only to a negligible extent, a deviation of 19% was established. Taking into account that the portion of the reacted amount in the given phase is  $1/(1 + R)$  of the total reacted amount in both phases, the relative error in the determination of the reaction factor will lead to a relative error of  $\varepsilon/(1 + R)$  in the total reacted amount, *i.e.* in the mentioned case to the error of only 0.7%. As the calculated values of  $\varepsilon/(1 + R)$  do not exceed in any case the limit of 10%, it is possible to conclude that the proposed relations enable to calculate the rate of the process in a two-phase system with sufficient accuracy. Simultaneously, it is to be expected that the reacted amount will be determined with a higher accuracy for that phase in which the reaction proceeds to a larger extent. It follows from a comparison with literature data<sup>3,6</sup> that the accuracy of the determination of the total reacted amount is comparable with that of the relations reported for systems with a reaction proceeding in one phase.

## LIST OF SYMBOLS

$a$	reduced concentration of component A (Eq. (9))
$\bar{a}$	specific interfacial area, $\text{m}^2/\text{m}^3$
$b$	reduced concentration of component B (Eq. (10))
$c$	concentration of the reaction component, $\text{kmol}/\text{m}^3$
$D$	diffusivity, $\text{m}^2/\text{s}$
$J$	mass flux, $\text{kmol}/\text{m}^2 \text{ s}$
$k$	mass transfer coefficient, $\text{m}/\text{s}$
$k_R$	reaction constant, $\text{k mol}^{1-p-q} \text{ m}^{3(p+q)}/\text{s}$
$M$	dimensionless parameter (Eq. (14))
$p, q$	exponents in the equation for the reaction rate
$Q$	dimensionless parameter (Eq. (15))
$r$	reaction rate, $\text{kmol}/\text{m}^3 \text{ s}$
$R$	dimensionless parameter (Eq. (16))
$x$	distance from the interface, $\text{m}$
$z$	reduced distance from the interface
$\delta$	thickness of the film, $\text{m}$
$\varepsilon$	relative error in the determination of the reaction factor
$\Phi$	reaction factor
$\nu$	stoichiometric coefficient

## Superscripts

$+$	at the interface
$0$	in the bulk of liquid

## Subscripts

A	component A
B	component B
AB	component A in phase (B)
BA	component B in phase (A)

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