
**THE EFFECT OF INTERFACIAL TURBULENCE
ON MASS TRANSFER ACCOMPANIED BY CHEMICAL REACTION**

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Relations have been derived for the reaction factor of an irreversible instantaneous reaction and a first-order reaction. Davies' theory has been used to express the effect of interfacial turbulence and the transfer of turbulence across the interface on mass transfer. Numerical solution has been compared with an approximation based on the film theory.

Interfacial mass transfer, under simple conditions prevailing at the interface as described¹ by the film, penetration and the surface renewal theory, accompanied by a chemical reaction has been dealt with by numerous authors. Solution for typical cases have been summarized in the monograph by Danckwerts². The solutions are usually presented in the form of the reaction factor. The reaction factor is defined as the chemical-reaction-enhanced mass transfer rate divided by the rate of the physical transfer at the same concentration of the transferred solute at the interface and identical hydrodynamic conditions. This work is an attempt to attack the problem of mass transfer accompanied by a chemical reaction under more complicated conditions of the transfer taking place in the presence of interfacial turbulence and turbulence transfer between the two phases. The aim was to find whether the concept of the reaction factor is applicable also in the presence of interfacial turbulence and the turbulence transfer. Further we wanted to assess the effect of these two phenomena on the magnitude of the reaction factor. Davies' model of the zone of damped turbulence³, taking into account the rate of energy transfer from the other phase as well as the interfacial turbulence, was used to calculate the rate of the physical mass transfer. According to this model the forces damping the motion of the vortices arriving from the bulk of the phase are most effective in the immediate vicinity of the interface — in the zone of damped turbulence. We examined those systems in which a chemical reaction occurs in the zone of damped turbulence. As a typical example we took an instantaneous irreversible reaction of the transferred solute and an irreversible first-order reaction.

THEORETICAL

Let us assume that a solute A is dissolved in phase 1 and transfers into phase 2 to react irreversibly with a dissolved solute B according to the scheme



The proposed models shall describe systems with a flat interface across which the turbulence transfer between mixed phases takes place.

The mass flux of the transferred solute shall be formally expressed in terms of the reaction factor, ϕ , introduced by

$$j_A = \phi k_A c_A^* \quad (1)$$

Physical Transfer

In order to express the rate of physical transfer Davies' model of the zone of damped turbulence is used. The mass flux of the transferred solute in phase 2 is given by

$$j(y) = -(D + \varepsilon(y)) \cdot dc/dy \quad (2)$$

According to Davies the interface works against the motion of the vortices arriving at the interface from the bulk of the phase in such a way that the coefficient of turbulent diffusivity, ε , decreases toward the interface. Davies reports that the coefficient of turbulent diffusivity decreases in the zone of damped turbulence with the decreasing component of the fluctuation velocity, $v_{y,2}$, according to the expression

$$\varepsilon(y) = \alpha v_{y,2} y \quad (3)$$

Further it is assumed that the fluctuations due to the transport of turbulence from the other phase and the interfacial turbulence cause the fluctuation velocity component, $v_{x,2}$, to increase in an additive fashion. From the equation of continuity Davies derived for the fluctuation component $v_{y,2}$ that

$$v_{y,2} = (y/\lambda) \cdot (v_2 + v_1 + v_\sigma - y(v_1 + v_\sigma)/\lambda) \quad (4)$$

Substitution of the last expression into Eqs (3) and (2) leads to the following expression for the mass flux

$$j(y) = -(D + (\alpha y^2/\lambda) \cdot (v_2 + v_1 + v_\sigma - y(v_1 + v_\sigma)/\lambda)) \cdot dc/dy \quad (5)$$

Introducing the dimensionless variables

$$\begin{aligned} Z &= y/\lambda, \quad T = (v_1 + v_\sigma)/v_2, \quad P = \lambda v_2 \alpha / D, \\ C &= (c - c^0)/(c^* - c^0), \quad J = j\lambda/(D(c^* - c^0)) \end{aligned} \quad (6)$$

Eq. (5) changes to

$$J = -(1 + P(1 + T)Z^2 - PTZ^3) \cdot (dC/dZ). \quad (7)$$

By integrating Eq. (7) with the boundary conditions

$$Z = 0, \quad C = 1; \quad Z = 1, \quad C = 0; \quad (8)$$

the dimensionless mass flux, J , may be expressed as

$$J^{-1} = \int_0^1 (1 + P(1 + T)Z^2 - PTZ^3)^{-1} dZ, \quad (9)$$

enabling the coefficient of physical transfer to be expressed by

$$k = (D/\lambda) \cdot J. \quad (10)$$

Irreversible Instantaneous Reaction

If the reaction rate constant of the chemical reaction (A) is large enough for the reaction to take place instantaneously and completely after the species A and B have met, the reaction occurs thoroughly in the zone of damped turbulence on the reaction plane where the concentrations of both reacting components vanish.

Integration of Eq. (7) with the boundary conditions (11), expressing the conditions at the interface and the reaction plane

$$Z = 0, \quad C_A = 1; \quad Z = Z_R, \quad C_A = 0, \quad (11)$$

leads to an expression for the dimensionless mass flux of the component A in dependence on the parameter P_A and T .

$$J_{A,r}^{-1} = \int_0^{Z_R} (1 + P_A \cdot (1 + T)Z^2 - P_A T Z^3)^{-1} dZ. \quad (12)$$

In analogy, integration of Eq. (7) with the boundary conditions for the component B

$$Z = Z_R \quad C_B = 1, \quad Z = 1 \quad C_B = 0 \quad (13)$$

leads to

$$J_{B,r}^{-1} = \int_{z_R}^1 (1 + P_B \cdot (1 + T) Z^2 - P_B T Z^3)^{-1} dZ. \quad (14)$$

The position of the reaction plane is implicitly determined by the mass balance

$$J_{A,r} = J_{B,r} R (c_B^0 / (z c_A^*)), \quad \text{where } R = D_B / D_A \quad (15)$$

and by Eqs (12) and (14).

The reaction factor is thus determined by Eqs (1), (9), (10) and (12) as the ratio

$$\phi = J_{A,r} / J_A. \quad (16)$$

Irreversible First-Order Reaction

If a first-order chemical reaction is sufficiently fast a reaction zone forms within the zone of damped turbulence adhering to the interface. Thus $c_A^0 = 0$. The mass flux of species A across the interface is defined by Eq. (2) for the concentration gradient prevailing at the interface, *i.e.* at $y = 0$. In order that we may be able to calculate this gradient it is necessary that we know the concentration profile of A in the reaction zone. That follows from the mass balance of A over a differential slice of the reaction zone.

$$dj_A/dy + k_R c_A = 0. \quad (17)$$

Changing over to the dimensionless form and using the variables defined by Eq. (6) and the dimensionless reaction rate constant

$$H = k_R \lambda^2 / D_A \quad (18)$$

there results

$$dJ_A/dZ + H C_A. \quad (19)$$

Numerical solution of the set (19) and (7) together with the boundary conditions

$$Z = 0 \quad C_A = 1, \quad Z = 1 \quad C_A = 0 \quad (20)$$

yields the concentration profile of the component A enabling the calculation of the mass flux.

APPROXIMATE RELATIONS

The calculation of mass fluxes from the above derived relations is complicated and requires numerical integration. Moreover, the effect of the turbulence transported

from the interface (*i.e.* the effect of the parameter T) on the fluxes is hard to estimate. Accordingly, we explored the possibility of using approximate relations utilizing Eq. (7) and the relations for the reaction factor based on the film theory. The expressions for the reaction factor following from the film theory were arranged into the form expressing the dependence on the coefficients of physical transfer of reacting species. It was assumed that an acceptable approximation is obtained if the coefficients of the physical transfer, incorporating the effect of turbulence transferred from the interface, are substituted into the just obtained expressions.

In case of the instantaneous reaction we may write according to the film theory

$$\phi_a = 1 + k_B c_B^0 / (z k_A c_A^*) . \quad (21)$$

Substituting k_A and k_B as they follow from Eqs (9) and (10) an approximation of the reaction factor is obtained for the selected concentration ratio.

If the experimental data on k_A and k_B are not available the next possible approximation is to try to analytically integrate Eq. (9). It may be shown that there exists such a $\beta = \beta(P, T)$ for which holds accurately for J^{-1} defined by Eq. (9) that

$$\begin{aligned} J^{-1} &= \int_0^1 (1 + P(1 + \beta T) Z^2)^{-1} dZ = \\ &= \text{arctg} (P(1 + \beta T))^{1/2} / (P(1 + \beta T))^{1/2} . \end{aligned} \quad (22)$$

This equation can be further simplified to

$$J = (2/\pi) \cdot (P(1 + \beta T))^{1/2} , \quad (23)$$

as it can be shown that $(P(1 + \beta T))^{1/2} \gg 1$ and hence $\text{arctg} (P(1 + \beta T))^{1/2} = (\pi/2)$. It suffices that also $P \gg 1$ and $(1 + \beta T) > 1$. Thus it is true that $P = (\alpha v_2 \lambda / \nu) \cdot Sc$. For all real liquid systems $Sc \gg 1$. For α Davis reports³ that based on analogy with the variation of turbulent diffusivity for the flow in a tube $\alpha = 0.4$. It is assumed that λ is greater than the size of the smallest vortices and v_2 greater than their velocity. Because for the smallest Kolmogorov's vortices the Reynolds number equals unity³⁻⁵, we have always $v_2 \lambda / \nu > 1$. It is thus proven that $P \gg 1$. In order to have $(1 + \beta T) > 1$ it suffices that simultaneously $\beta > 0$ and $T > 0$. As follows from Eq. (22), β can plausibly range between zero and unity. T is the ratio of positive numbers. Hence $(k + \beta T) > 1$.

Because $\beta = \beta(P, T)$ it is apparent that β satisfying Eq. (22) depends on diffusivity because on the latter depends P . It was assumed that the error committed by the assumption of equal β shall be small

$$\beta_A = \beta_B = \beta . \quad (24)$$

Substituting the last equation into Eq. (23) and (21) we obtain

$$\phi_a = 1 + R^{1/2}(c_B^0/(zc_A^*)) \quad (25)$$

For the case of an irreversible first-order reaction Hatta⁵ has derived using the film theory the following expression

$$\phi_a = M^{1/2} \operatorname{tgh}(M)^{1/2} \approx (M + 1)^{1/2}, \quad (\text{for } M > 1) \quad \text{where } M = D_A k_R / k_A^2. \quad (26)$$

For the calculation of ϕ_a from Eq. (26) one can use the experimental value of k_A or for a numerical verification use the value of k_A defined by Eqs (9) and (10). In that case

$$M = H/J_A^2. \quad (27)$$

RESULTS AND DISCUSSION

The approximate relations enable straight forward calculation of reaction factors from the coefficients of physical transfer. Its justification, however, needs a proof. For this reason we evaluated for the case of an instantaneous reaction and various values of Z_R the integrals (12) and (14) and calculated corresponding ratios $(c_B/(zc_A))$ from Eq. (15). Further we evaluated the integral (9) for *a*) the solute A and from Eq. (16) the reaction factor ϕ and *b*) for components A and B while the values k_A , k_B computed from Eq. (10), were substituted into Eq. (21) together with the ratio (c_B/zc_A) which had been used to evaluate the approximate reaction factor. These data served to compute the ratio ϕ/ϕ_a as a function of $(1 - 1/\phi_a)$ for R ranging between 0.4 and 3,

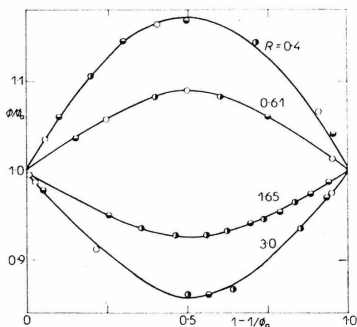


FIG. 1

ϕ/ϕ_a as a Function of $(1 - 1/\phi_a)$ for an Irreversible Instantaneous Reaction

T : ● 20; ○ 10; ■ 5; ● 1.

for T between 1 and 20 and P equal 10^5 . From the plot in Fig. 1 it is apparent that ϕ_a equals about 2. On the other hand it is almost independent of T .

Fig. 2 shows the reaction factor for an irreversible first-order reaction plotted versus the dimensionless criterion T . Solid line indicates numerical solution of the set (19) and (7) with the boundary conditions (20) scaled, according to Eq. (16), by the integral (9). The points indicate the approximate solution according to Eq. (26) with the aid of Eqs (9) and (10). In these calculations H ranged between $3.7 \cdot 10^6$ and $4 \cdot 10^9$ and P was put equal 10^5 .

The utility of the proposed approximation has been confirmed also experimentally. Rychnovský and Rod⁶ published the transfer rates of the reacting species for extraction of copper(II) ions from aqueous phase by chloroform solution of 8-hydroxyquinoline in a mixed cell with flat interface. They proved that concentration dependence of the transfer rate of the reaction species may be described by a model based on the film theory of mass transfer and an instantaneous reaction in the aqueous phase. No interfacial turbulence occurred in the system. The data point at independence of the reaction factor on the ratio of rpm of the impeller in both the organic and the aqueous phase in the range between 0.4 and 2.

The independence of the reaction factor on the turbulence transfer for an irreversible pseudo-first-order reaction was studied experimentally in a diffusion cell with flat interface using the n-butyl formate-aqueous solution of sodium hydroxide system. The ratio of the speed of revolution of the impeller, n_1/n_2 , was varied between 0.04 and 1. The reaction of sodium hydroxide with n-butyl formate may be regarded pseudo-first-order with respect to the ester provided the concentration of sodium hydroxide does not vary appreciably. The reaction rate constant for the pseudo-

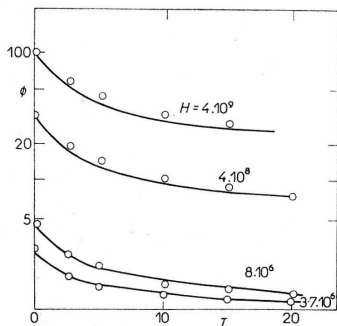


FIG. 2
The Reaction Factor for an Irreversible First-Order Reaction as a Function of the Criterion T
— numerical solution of Eqs (7), (19), (20), (16) and (9); \circ approximation, Eqs (26), (9) and (10).

-first-order reaction then depends on mean concentration of hydroxide by

$$k_R = k_{RII}c_B. \quad (28)$$

Combining this expression with Eq. (1) and the approximation (26) gives the following relationship for the mass flux

$$j_A = c_A^*(D_A k_{RII} c_B + k_A^2)^{1/2}. \quad (29)$$

The values of the mass flux, j_A , were evaluated numerically from the experimental time dependence of the concentration of hydroxide. Fig. 3 is a plot of $(j_A/c_A^*)^2$ versus mean concentration of hydroxide for various ratios of rpm of impellers in the organic and the water phase.

From the figure it is apparent that the experimental data suit Eq. (29) in the whole range of rpm's used. Dividing the slope of these straight lines by the diffusivity of ester in water ($D_A = 8.28 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$) the following value is obtained for the second-order reaction rate constant, $k_{RII}(25^\circ\text{C}) = 22.3 \text{ m}^3/(\text{kmol s})$. This value is in good agreement with the data of other authors, *e.g.* Sharma⁷ who found $21.8 \text{ m}^3/(\text{kmol s})$.

The intercepts represent the square of the transfer coefficients. The data obtained from Fig. 3 are summarized in Table I. In the calculation of the criterion T the values of the kinematic viscosity used were as follows: $\nu_1 = 0.735 \cdot 10^{-6} \text{ m}^2 \text{ s}^{-1}$, $\nu_2 = 1.02 \cdot 10^{-6} \text{ m}^2 \text{ s}^{-1}$. The reaction factor was calculated according to Eq. (26) for $M > 1$.

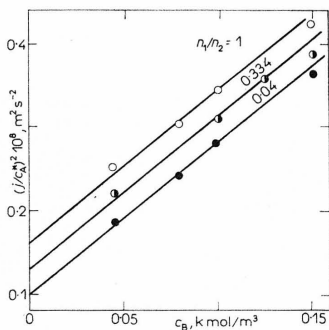


FIG. 3
 $(j/c_A^*)^2$ as a Function of Concentration c_B
 ○ $n_1/n_2 = 1$; ◐ $n_1/n_2 = 0.334$; ● $n_1/n_2 = 0.04$.

Even though the influence of the transfer of turbulence on the reaction factor is not marked Eqs (9), (10) indicate that the mass transfer coefficients do depend on the transport of turbulence from the interface.

The approximate relations for the calculation of mass transfer coefficients may be compared with the published experimental data in cells with a flat interface. For such a comparison, however, the variables defined by Eqs (6) and (18) must be related to quantities accessible to experimental measurements. This is the case of the definition of v_2 and λ . Davies' approach, assuming the transfer to depend primarily on Prandtl's vortices carrying maximum energy, was not used as it leads to a high value of the exponents (1.5) over the frequency of revolution of the impeller in the expressions for the mass transfer coefficients. We shall assume that from the view point of mass transfer of maximum importance are small vortices whose size is comparable with the Kolmogorov's vortices. The extent of the zone of damped turbulence is determined from the relations of Kolář⁴, Bulička and Procházka¹

$$\lambda \sim (v^3/\epsilon)^{1/4}, \quad v \sim (\epsilon\nu)^{1/4}. \quad (30)$$

For the special case of a cell with a flat interface mechanically stirred by identical impellers in both phases one can compute the velocities v_2 and v_1 from the known frequencies of revolution of the impellers. Substituting the relation

$$\epsilon \sim n^3 d^2 \quad (31)$$

into Eq. (28) one obtains expressions for v and λ .

$$v = (n^3 d^2 \cdot \lambda)^{1/4} = (\lambda^3 / (n^3 d^2))^{1/4}. \quad (32)$$

Substituting these expressions into Eqs (23) and (10) an expression is obtained for the

TABLE I
Dependence of the Reaction Factor on the Criterion T

n_1, s	n_2, s	T	$k_A \cdot 10^4$ ms^{-1}	ϕ
5	5	0.7	0.40	1.6
1.67	5	0.06	0.36	1.5
0.2	5	0.0005	0.32	1.4

mass transfer coefficient in dependence on the frequency of revolution of the impellers

$$k_{A,2} \sim d^{1/2} v_2^{-3/4} D_A^{1/2} n_2^{3/4} (1 + \beta((n_1/n_2)^{3/4} \cdot (v_1/v_2)^{1/4} + (v_a/n_2^{3/4} d^{1/2} v_2^{1/4})))^{1/2} . \quad (33)$$

A comparison of the numerical solution of Eqs (9) and (10) with Eq. (23) revealed that for the values of the parameter T from the interval 1–10 it suffices that a mean value of the correction factor $\beta = 0.78$ is used. According to Eq. (33) and in the absence of the transfer of turbulence from the interface the mass transfer coefficient depends on the frequency of revolution of the impellers by the following formula

$$k \sim n^{3/4} . \quad (34)$$

The ratio of the transfer coefficients for the reacting species in the same phase ($k_{A,2}/k_{B,2}$) is independent, according to Eq. (33), of the ratio of rpms of the impellers. These findings are in agreement with experimental data published by Procházka¹, and Rychnovský and Rod⁶. Eq. (33) predicts that the ratio of the transfer coefficients depends on the ratio of the frequency of revolution of the impellers. This dependence has not been unambiguously proven experimentally. Although data published by Rychnovský and Rod⁶ do suggest a dependence of (k_{A1}/k_{B2}) on the ratio of frequencies of revolution, an evaluation of a great deal more extensive set of data has lead Bulička and Procházka¹ to an opposite conclusion.

It may be concluded that even under the transfer of turbulence across the interface and in the presence of interfacial turbulence one may use the concept of the reaction factor to estimate the mass transfer rate. The reaction factor may be calculated from the knowledge of the transfer coefficients valid for physical transfer with the aid of the film model of mass transfer and the kinetics of the reaction involved.

LIST OF SYMBOLS

c	concentration of species in the reaction phase, kmol/m ³
C	dimensionless concentration in the reaction phase, Eq. (6)
d	impeller diameter, m
D	molecular diffusivity, m ² /s
e	rate of energy dissipation per unit mass, m ² /s ³
j	mass flux of species, kmol/m ² /s
J	dimensionless mass flux, Eq. (6)
H	dimensionless reaction rate constant, Eq. (18)
k	coefficient of physical mass transfer, m/s
k_R	first-order reaction rate constant, s ⁻¹
k_{RII}	second-order reaction rate constant, m ³ /kmol/s
M	dimensionless parameter, Eq. (26)

n	frequency of revolution of impeller, s^{-1}
P	dimensionless parameter, Eq. (6)
R	ratio of molecular diffusivities in the reaction phase D_B/D_A
$Sc = v/D$	Schmidt number
T	dimensionless parameter, Eq. (6)
v	characteristic velocity of turbulence, m/s
y	distance from interface, m
z	stoichiometric coefficient, Eq. (A)
Z	dimensionless distance from interface
α	constant in Eq. (3)
β	correction factor, Eq. (22)
ϵ	turbulent diffusivity, m^2/s
λ	thickness of the zone of damped turbulence, m
ν	kinematic viscosity, m^2/s
Φ	reaction factor

Subscripts

a	approximate
A	species A
B	species B
r	accompanied by chemical reaction
R	reaction plane
x	parallel to the interface
y	perpendicular to the interface
σ	due to interfacial turbulence
1	phase 1
2	phase 2

Superscripts

*	at the interface
0	in the bulk phase

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