
**MASS TRANSFER ACCOMPANIED BY AN IRREVERSIBLE
AND A CONSECUTIVE EQUILIBRIUM REACTION**

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Based on the film theory and by means of linearization of the principal differential balance equation an approximate expression has been derived for the enhancement of transfer of species A from the interface by the following reaction with the components B and C: $A + m B \rightarrow n C + p P$ and $A + C \rightleftharpoons D$. The former of these reactions is irreversible while the second is an equilibrium one. The asymptotic behaviour of the derived relationships has been verified and an error has been estimated of the prediction of the enhancement factor due to the linearization.

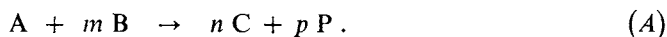
Many industrially important absorption or extraction processes take place under the conditions of transfer of the active component from the interface into the bulk of the phase being enhanced by one or more reactions of this component with the active components of this enriched phase. If these reactions are fast as to take place predominantly in the diffusional film adhering to the interface it is advantageous to express the enhancement of the mass transfer rate by the so called enhancement factor. For the case of simple reactions there are numerous solutions available, summarized *e.g.* in ref.¹. These solutions express the dependence of the enhancement factor on concentration variables and system parameters. Mass transfer accompanied by a set of reactions, however, has been investigated only for some particular cases. The rate of mass transfer of a species A, accompanied by reactions $A + B \rightleftharpoons C$, $C + B \rightleftharpoons E$, has been studied in ref.²⁻⁴. Onda⁵⁻⁷ and coworkers have derived an approximate expression for the enhancement factor for the case of consecutive irreversible reactions $A + m B \rightarrow n C$, $A + p C \rightarrow E$ and have submitted solutions for certain types of reversible reactions. Considerable attention has been paid to the effect of mass transfer on selectivity in a system of consecutive reactions⁸⁻¹².

The aim of this work has been to provide a solution for the enhancement factor of a species A when two consecutive reactions of the type $A + m B \rightarrow n C + p P$, $A + C \rightleftharpoons D$ take place simultaneously while the former may be regarded as an irreversible and the latter as an equilibrium one, *i.e.* instantaneous and reversible. An example of such a system is oxidation of potassium ferrocyanide in the water phase by iodine transferred from the organic phase. The rate of transfer of iodine in this case is affected not only by the redox reaction, which may be regarded over

a wide range of concentrations as an irreversible reaction, but also by the reaction of iodine with iodide ions, this latter being a reversible and instantaneous reaction.

FORMULATION OF THE MODEL

Species A diffuses from the interface into the phase containing species B while simultaneously reacting, following the scheme



The rate of this reaction is given by

$$dc_A/dt = -k_R c_A c_B \quad (1)$$

and is sufficiently high so that the reaction (A) takes place thoroughly in the diffusional film adhering to the interface. Simultaneously with this reaction there is another reaction taking place in the diffusional film of the component A with the component C appearing as a product of the reaction (A):



This reaction is practically instantaneous and reversible with the equilibrium constant

$$K = c_D / (c_A c_C). \quad (2)$$

The rates of formation of individual components, r_i , are constrained by the following relationships

$$m r_A - r_B + m r_D = 0 \quad (3)$$

$$n r_B + m r_C + m r_D = 0 \quad (4)$$

$$r_B = -m k_R c_A c_B. \quad (5)$$

Since the only component, transferred across the interface, is the component A, one can, in accord with Eqs (1) and (3)–(5), write down the balances of the fluxes of the components through the diffusional film in the form of the following differential equations

$$D_A (dc_A/dx) - (D_B/m) (dc_B/dx) + D_D (dc_D/dx) = -J_A^* \quad (6)$$

$$n D_B (dc_B/dx) + m D_C (dc_C/dx) + m D_D (dc_D/dx) = 0 \quad (7)$$

and the balance of the species B in the form

$$D_A(d^2c_A/dx^2) - D_C(d^2c_C/dx^2) = (n + 1)k_Rc_Ac_B. \quad (8)$$

The set of differential Eqs (6)–(8), with the boundary conditions

$$x = 0, \quad c_A = c_A^*, \quad dc_B/dx = 0 \quad (9)$$

$$x = \delta, \quad c_A = 0, \quad c_B = c_B^0, \quad c_C = c_C^0 \quad (10)$$

and the equilibrium condition (2) define the concentration profiles of individual components in the diffusional film sketched in Fig. 1a.

For the purpose of obtaining an approximate solution of the set (6)–(10) it is convenient to introduce the following dimensionless variables

$$z = x/\delta \quad (11)$$

$$y_i = c_i/c_A^* \quad (12)$$

$$q_i = D_i/D_A \quad (13)$$

$$\kappa = q_D K c_A^* \quad (14)$$

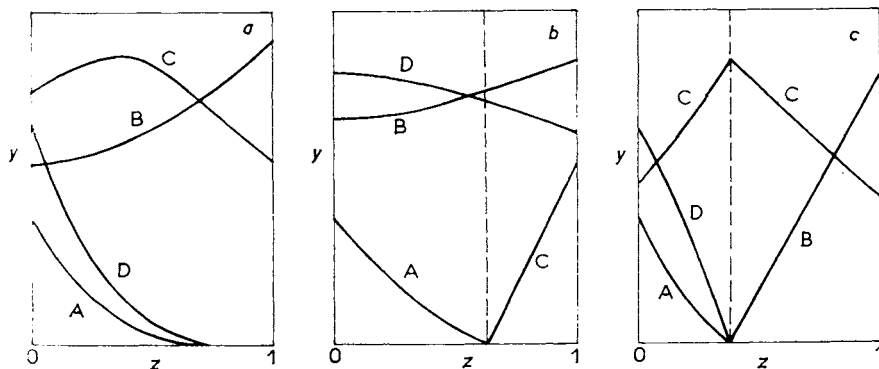


FIG. 1

Concentration profiles of the reaction components in the diffusional film, a) general case, b) $\kappa \rightarrow \infty$, both reactions irreversible, c) $M \rightarrow \infty$, both reactions instantaneous

$$\Phi = J_A^* \delta / (D_A c_A^*) \quad (15)$$

$$M = k_R \delta^2 c_B^0 / D_A \quad (16)$$

Integration of the differential Eqs (6) and (7) with the boundary conditions (9) and (10) may be expressed with the aid of Eqs (11)–(15) in the form of relationships between the dimensionless concentrations of species in the diffusional film

$$y_C = \{n[\Phi(1-z) - y_A] + q_C y_C^0\} / [q_C + (n+1)\kappa y_A] \quad (17)$$

$$y_B = y_B^0 + m[(q_C + \kappa y_A) y_C - q_C y_C^0] / (n q_B) \quad (18)$$

After rendering the differential equation (8) dimensionless by using expressions (11)–(15) and after elimination of $d^2 y_C / dz^2$ with the aid of Eq. (17) a differential equation is obtained in the form

$$d^2 y_A / dz^2 - [(U+V)/W] (dy_A / dz)^2 + (U/W) \Phi (dy_A / dz) - Z y_A = 0, \quad (19)$$

where

$$U = 2n\kappa q_C \quad (20)$$

$$V = 2(n+1)\kappa^2 q_C y_C \quad (21)$$

$$W = [q_C + (n+1)\kappa y_A] [q_C + \kappa(y_A + q_C y_C)] \quad (22)$$

$$Z = \frac{q_C + (n+1)y_A}{q_C + \kappa(y_A + q_C y_C)} M \frac{y_B}{y_B^0} \quad (23)$$

$$\Phi = -[1 + q_C \kappa y_C^* / (q_C + \kappa)] (dy_A / dz)_{z=0} \quad (24)$$

Solution of the differential equation (19) with the boundary conditions

$$y_A(0) = 1, \quad y_A(1) = 0 \quad (25)$$

determines for given values of the quantities y , q_i , M and κ the value of the enhancement factor Φ .

Since the differential Eq. (19) does not have an exact analytical solution, the enhancement factor must be found either through a numerical solution of the above boundary value problem or from an approximate solution.

In the following we shall derive an approximate solution for the enhancement factor and estimate its accuracy from comparison with numerically obtained solutions.

APPROXIMATE EXPRESSION FOR THE ENHANCEMENT FACTOR

In seeking a suitable approximation for the enhancement factor we shall require that the resulting expressions reduce to the accurate solutions for asymptotic cases for which such solutions exist. It turns out that the course of the concentration profiles near the interfacial surface is little affected by the second and the third term of the differential equation (19). These terms completely vanish for the special case of $\kappa = 0$ and $\kappa \rightarrow \infty$. In order to obtain an approximate solution let us linearize the differential equation by neglecting the above two terms and putting the variable Z equal its value at the interface, Z^* .

Integration of the obtained linearized equation

$$d^2 y_A / dz^2 - Z^* y_A = 0 \quad (26)$$

with the boundary conditions

$$y_A = (0), \quad y_A(\xi) = 0 \quad (27)$$

yields an expression for the gradient of the dimensionless concentration of the species A at the interface, $(dy_A/dz)_{z=0}$. Its substitution into Eq. (24) yields in turn an expression for the enhancement factor

$$\Phi = \frac{\sqrt{Z^*}}{\operatorname{tgh}(\xi \sqrt{Z^*})} [1 + q_c \kappa y_C^* / (q_c + \kappa)], \quad (28)$$

where

$$Z^* = \frac{q_c + (n + 1) \kappa}{q_c + \kappa(1 + q_c y_C^*)} M \frac{y_B^*}{y_B^0}. \quad (29)$$

The quantity ξ represents the dimensionless penetration depth of species A from the interface into the diffusional film.

If $\kappa \rightarrow \infty$, *i.e.* if both reactions are irreversible, the reaction zone, where the reaction (A) takes place, reduces to a reaction plane, its dimensionless distance from the interface being fixed by ξ , see Fig. 1b. For this asymptotic case this distance may be expressed from the condition of equality of the fluxes of reacting species using van Krevelen's solution¹³ for the flow of the species A through the reaction zone of the reaction (E). The stipulation that the approximate solution reduces to this asymptotic case for $\kappa \rightarrow \infty$, while simultaneously satisfying also the exact solution is met by the following function for the dimensionless distance ξ :

$$\xi = 1 - \left(\frac{\kappa}{q_c + \kappa} \right)^2 \frac{q_c y_C^0}{\sqrt{(\Phi^2 - Z^*)}}. \quad (30)$$

The expressions (28)–(30), together with the equations expressing the dimensionless concentrations of species B and C at the interface, following from Eqs (17) and (18)

$$y_C^* = [n(\Phi - 1) + q_C y_C^0] / [q_C + (n + 1)\kappa] \quad (31)$$

$$y_B^* = y_B^0 - m[(q_C + \kappa) y_C^* - q_C y_C^0] / (nq_B) \quad (32)$$

implicitly define the enhancement factor Φ .

If the variables M or κ assume their limiting values the above relationships for the calculation of $\Phi = \Phi(M, \kappa)$ significantly simplify.

If $M = 0$, there is only one equilibrium reaction (B) taking place in the system. From Eq. (29) then follows $Z^* = 0$ and as a limit of the right hand side of Eq. (28) for $Z^* \rightarrow 0$ we obtain the following relationship

$$\Phi(0, \kappa) = [1 + q_C \kappa y_C^* / (\kappa + q_C)] / \xi. \quad (33)$$

Upon elimination of y_C and ξ from Eqs (30), (31) and (33) there follows for the enhancement factor that

$$\Phi(0, \kappa) = 1 + \kappa q_C y_C^0 / (\kappa + q_C) \quad (34)$$

which is the exact expression derived by Olander¹⁴ for the equilibrium reaction (B).

If $M \rightarrow \infty$ we have a system of two instantaneous reactions. From Eqs (31) and (32) then there follows for the dimensionless concentration of the component B at the interface that

$$y_B^* = y_B^0 - (m/(nq_B)) \{(\kappa + q_C) [n(\Phi - 1) + q_C y_C^0] / [q_C + (n + 1)\kappa - q_C y_C^0]\}. \quad (35)$$

Taking the limit $M \rightarrow \infty$ there follows from Eq. (28) that $y_B^* \rightarrow 0$. Substituting this into Eq. (35) we obtain for the enhancement factor the following relationship

$$\Phi(\infty, \kappa) = 1 + q_B y_B^0 / m + \kappa [(m/n) q_B y_B^0 + q_C y_C^0] / (\kappa + q_C). \quad (36)$$

The concentration profiles of the reaction components for this case are sketched in Fig. 1c. Both reactions take place in the reaction plane $z = \xi$ splitting the diffusional film into two diffusional zones. By integration of the differential equations (6) and (7) for both these zones separately and elimination of the unknown distance of the reaction plane and the unknown concentrations of the species C and D in this plane it may be shown that Eq. (36) is an exact solution.

If $\kappa = 0$ there is only one reaction (A) taking place in the system and Eq. (28) reduces to

$$\Phi(M, 0) = \sqrt{(M y_B^* / y_B^0)} / \operatorname{tgh} \sqrt{(M y_B^0 / y_B^*)} \quad (37)$$

which is the familiar expression derived by Van Krevelen and Hoftijzer¹³ for an irreversible second-order reaction (A).

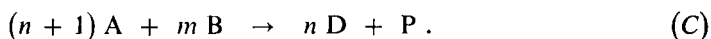
If $\kappa \rightarrow \infty$ we have a system of two irreversible reactions. From Eq. (31) there follows for this case that $y_C^* \rightarrow 0$ and as a limit of Eqs (28), (30) and (32) we obtain

$$\Phi(M, \infty) = \sqrt{(My_B/y_B^0)/\operatorname{tgh} [\xi \sqrt{(My_B^*/y_B^0)}]} \quad (38)$$

$$\xi = 1 - q_C y_C^0 / \sqrt{(\Phi^2 - My_B^*/y_B^0)} \quad (39)$$

$$y_B^* = y_B^0 - m(\Phi - 1)/nq_B. \quad (40)$$

The concentration profiles of the reaction components in the diffusional film are shown in Fig. 1b. The plane $z = \xi$ separates the diffusional films into the reaction zone ($0 < z \leq \xi$) and the diffusional zone ($\xi < z \leq 1$). In the reaction zone both reactions take place simultaneously while the component C, appearing at a finite rate by the reaction (A), is instantaneously consumed by the reaction (B). In this zone thus the transported component A reacts according to an overall reaction scheme



In reaction plane an instantaneous reaction (B) takes place which maintains the concentrations of species A and C at a zero level. In the diffusional zone we have pure diffusion of the species C and B from the bulk phase toward the reaction plane and of the reaction products D and P into the bulk phase only. It may be shown that Eqs (38)–(40) are identical with the results obtained as a combination of Van Krevelen's solution for the reaction zone with the relations describing diffusion of the components in the diffusional zone. If the concentration of C in the bulk phase vanishes, $y_C = 0$, then, according to Eq. (39), $\xi = 1$, i.e. the reaction plane coincides with the edge of the film and Eqs (38) and (40) reduce to Van Krevelen's solution for the transport of species A accompanied by the chemical reaction (C).

DISCUSSION

In order to assess the reliability of the proposed approximate solutions and for the purpose of the determination of their practical applicability it is important to estimate the error introduced into the solution by linearization of Eq. (19). For this purpose it is convenient to plot the region of the real solution as a dependence of the enhancement factor on the variables $M, \kappa/(\kappa + q_C)$ for given concentration and diffusivity conditions. Fig. 2 shows that the region of the real solution in this map is delimited by four lines representing the asymptotic solutions for the limiting values of parameters M and κ .

As it has been shown in the preceding paragraphs, for the asymptotic situations $M \rightarrow 0$ and $M \rightarrow \infty$ the approximation changes into the exact expressions (34) and (36). If $\kappa = 0$, the approximation reduces to that of Van Krevelen, the accuracy of which has been discussed in detail, for instance, in refs^{15,16} and appears quite sufficient for practical needs. Expression of the enhancement factor for the asymptotic case $\kappa \rightarrow \infty$ by Eqs (38)–(40) changes, for a finite value of the reaction modulus M , for $y_C^0 = 0$ also to Van Krevelen's solution, except that the stoichiometry changes to that of the reaction (C). It may be shown that the accuracy of the proposed approximation increases in this case with increasing value of y_C^0 and that the error is thus always less or at most equal to the error of Van Krevelen's approximation of the enhancement factor for a second-order reaction.

The accuracy of the approximation in the general case was estimated from comparison of the results with the numerical solution of the set (19)–(25). For purpose of the numerical solution the second-order differential equation (19) was transformed into a set of two first-order differential equations with the initial conditions

$$z = 0, \quad y_A = 1, \quad (dy_A/dz) = -\Phi/[1 + q_C y_C^* \kappa / (\kappa + q_C)], \quad (41)$$

where y_C^* was given by Eq. (31).

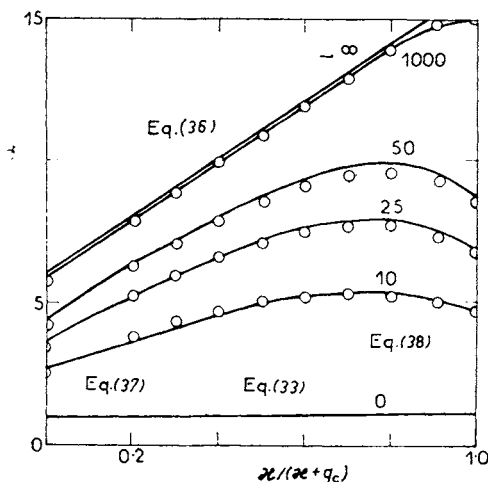


FIG. 2

Comparison of accurate and approximate values of the enhancement factor (points represent values computed from approximate relations). $y_B = 10$, $y_C = 0.1$, $q_1 = 1$, $m = n = 2$

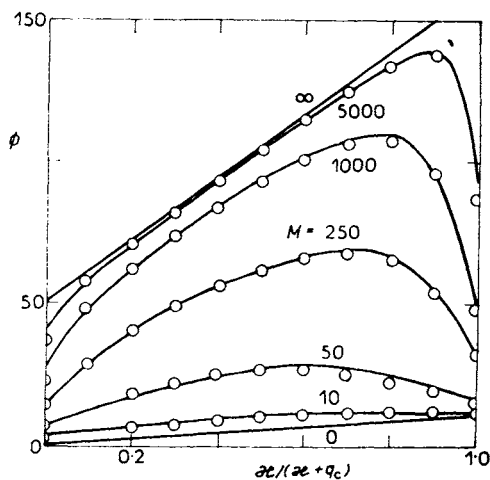


FIG. 3

Comparison of accurate and approximate values of the enhancement factor. $y_B = 100$, $y_C = 10$, $q_1 = 1$, $m = n = 2$

Since the value of Φ for the initial conditions was not known, an iterative approach was employed while the accuracy of the estimate was checked by testing the validity of the boundary condition (25).

A comparison of the exact solution of the asymptotic cases with their numerical solution has shown that the employed integration method yields results with an accuracy better than 0.1% in determining the value of Φ . The set of equations (19)–(25) was solved numerically in the following range of parameters:

$$10^1 < M < 10^3, \quad 10^{-2} \leq \kappa \leq 10^2, \quad 10^1 \leq y_B^0 \leq 10^2, \quad 10^{-1} \leq y_C^0 \leq 10^2,$$

for $q_i = 1$, $m = n = 2$.

A comparison of the obtained results with the proposed approximate solution has shown that the proximate solution yields in the investigated ranges of variable values of the enhancement factor with an accuracy better than 8%. The comparison of both solutions for selected values of variables is illustrated in Fig. 2 and 3.

It has been found that similarly as in the illustrated case the dependence of the enhancement factor on the variable $\kappa/(\kappa + q_C)$ and thus on κ displays in the majority of cases a maximum. In a given system thus the transfer of the species A may be enhanced more if one of the reactions is reversible than if both reactions are irreversible. This rather unexpected dependence may be explained by the fact that the flux of the component A, according to Eqs (6) and (9) is a sum of two terms proportional to the concentration gradient of the species A and D at the interface. The gradient of the species A at the interface vanishes for limiting values of κ . If $\kappa = 0$ the reaction (B) does not take place and since the component D does not cross the interface nor is it produced here, its concentration gradient is zero. If $\kappa \rightarrow \infty$ the reaction (B) takes place in the reaction plane, the component C does not exist at the interface and hence the component D cannot be produced here while its concentration gradient approaches zero. As has been shown by numerical calculations the concentration gradient of the species D at the interface in dependence on κ passes through a maximum. For this reason it is apparent that the enhancement factor need not have a monotonous course in dependence on the variable κ and may display maxima.

It may be concluded that the proposed approximation describes well the enhancement factor for the whole range of variables M and κ . Its error does not exceed that of Van Krevelen's solution for a second-order reaction which is an accuracy satisfactory for engineering calculations of the rate of mass transfer across the interface.

LIST OF SYMBOLS

- c concentration
 D diffusivity

J	flux of species
k_R	rate constant of reaction (B)
K	equilibrium constant of reaction (B)
M	reaction modulus, Eq. (16)
m	stoichiometric coefficient
n	stoichiometric coefficient
p	stoichiometric coefficient
q	dimensionless diffusion coefficient, Eq. (13)
r	rate of formation of a species by reaction
t	time
x	longitudinal coordinate
y	dimensionless concentration, Eq. (12)
z	dimensionless longitudinal coordinate, Eq. (11)
Z	dimensionless parameter, Eq. (23)
δ	thickness of the diffusional film
κ	dimensionless parameter, Eq. (14)
ϕ	enhancement factor, Eq. (16)
ξ	dimensionless length, Eq. (30)

Subscripts

i	reaction component generally
A, B, C, D,	reaction components A, B, C, D

Superscripts

o	in the bulk
$*$	at the interface

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