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Mass transfer with complex chemical reaction in gas–liquid systems—I. Consecutive reversible reactions with equal diffusivities

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Abstract

A fundamental description of gas–liquid mass transfer with reversible consecutive reaction has been derived. The Higbie penetration theory has been used and numerical simulations were carried out for isothermal absorption. Although the model can be adapted to reactions of general stoichiometric and kinetic orders, results in this paper have been limited to unit orders only. The model has been applied for a wide range of process conditions to investigate the effect of reversibility of both reaction steps and the effect of the use of (partially) loaded solutions on the mass transfer characteristics. For consecutive reactions with both steps irreversible, the approximate solutions of Onda (1970, 1972) have been found to be sufficiently accurate (maximum deviation of 4.3% for the penetration theory solution). It has also been shown that the overall enhancement factor can be regarded as the summation of the enhancement factors of the individual reaction steps. This has been quantitatively shown for the case where the first step is irreversible while the second is reversible. Finally, an approximate technique to determine infinite enhancement factors for reversible consecutive reactions has been given. This approximation is based on the method described by DeCoursey (1982). Deviations from numerical calculations for both loaded and unloaded solutions were found to be less than 1.3%. Part I of this paper deals with the case of equal diffusivities of the chemical species involved whereas the effect of unequal diffusivities on the overall absorption rate and enhancement will be dealt with in Part II. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Gas absorption; Consecutive reactions; Modelling; Mass transfer

1. Introduction

Consecutive chemical reactions play an important role in the process industry. Industrial examples are, among others, alkylation and substitution chlorination of organic compounds. For a summary of consecutive reaction systems one is referred to Doraiswamy and Sharma (1984).

One of the first studies into consecutive reactions was limited to homogeneous systems (Rodiguin and Rodiguina, 1964). However, industrially, these reactions usually occur as heterogeneous processes. Therefore, an additional phenomenon occurs — mass transfer with simultaneous chemical reaction.

The consecutive reaction stoichiometry for heterogeneous processes is described by (1a)–(1c)

A number of researchers have dealt with the problem of heterogeneous gas–liquid mass transfer with consecutive reaction in the liquid phase. Except for two studies, which have been mentioned at the end for this section, all work on consecutive reaction systems is based on the isothermal and irreversible case. Pioneering work on consecutive reactions was done by van de Vusse (1966 a, b), who used the chlorination of *n*-decane as a model system. This work was limited to the effect of diffusion on selectivity and yield of the intermediate products. Chlorination of *n*-decane, however, generates a large number of

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side products, thereby complicating the fundamental analysis of such a system. Hence, it was found necessary to seek model systems with a limited number of reaction paths. With this, the mass transfer phenomena could be investigated more thoroughly. Inoue and Kobayashi (1968) suggested the use of chlorination of *p*-cresol dissolved in carbon tetrachloride since this system consists of only two reactions. They also measured rate constants for both the reaction steps involved. This experimental system was also used by Hashimoto et al. (1968) and Teramoto et al. (1969, 1970), who presented an approximate method for estimating the yield of the intermediate product at a given reaction time. This was validated experimentally with chlorination experiments in a stirred cell. Further work on the effect of mass transfer on the selectivity of the intermediate product was done by Pangarkar and Sharma (1974). They derived approximate solutions for selectivity of the intermediate, based on the film theory, which were then validated experimentally with the chlorination of *p*-cresol. Special emphasis was placed on the case where depletion of the liquid reactive species occurs and for instantaneous consecutive reaction. Darde et al. (1983, 1984a, b) incorporated the consecutive reaction scheme using the film theory into a model for an ideal CSTR and the results were found to agree with experiments on chlorination of *p*-cresol carried out in a bubble column (modelled as a cascade of CSTRs).

Some work that had appeared in literature was focused on approximations to determine selectivity and yield of the intermediate without actual experimental validation. Kubota and Lee (1973) gave an analytical approximation for selectivity based on the method of van Krevelen and Hoftijzer. Kastánek and Fialová (1982) elaborated this method by proposing simple empirical criteria for the safe application of the approximate solutions and compared the analytical approximations with numerical solutions of the film theory. Approximate solutions for the enhancement factor have been provided by Onda et al. (1970, 1972), who derived semi-analytical solutions for the film and penetration theory for the case where both reaction steps may be considered irreversible. A more detailed description of the absorption rate for the case presented by Onda (1970, 1972) was provided by Huang et al. (1980), who presented quantitative values of enhancement factors over a range of Hatta numbers using both film and penetration theory solutions. They observed that the difference in the enhancement factors obtained from the two theories was always less than 2%.

It is only the work of Kuo and Huang (1973) that studies the effect of reversibility on consecutive reactions. However, this study was conducted for a simplified reaction stoichiometry (see Section 4.4.5). The authors showed that the effect of reversibility was to reduce the absorption rate and, thereby, the enhancement as com-

pared to the irreversible reaction scheme. In the case of non-isothermal absorption, an analysis of exothermic irreversible consecutive reaction was made by Bhat-tacharya et al. (1988). The authors provided approximate analytical solutions for the interfacial temperature rise and the enhancement factor as a function of the Hatta number.

The limitation of irreversibility of consecutive reactions has been overcome in the present study. However, isothermal absorption has still been assumed. The Higbie penetration theory has been used for this study. Further, an analysis of gas absorption into loaded solutions has been presented. The results obtained have then been compared to available literature after making necessary simplifications. For an overview of the existing literature on reactions with simplified stoichiometries, the reader is referred to the review by van Swaaij and Versteeg (1992) on the subject. Part I of the study is limited to the case of equal diffusivities of all chemical species involved whereas Part II focuses on the effect of unequal diffusivities on the absorption rate and its corresponding effect on the overall enhancement factor.

2. Theory

2.1. Species conservation equations

The reaction stoichiometry under consideration is given by reactions (1a)–(1c). The numerical description, however, considers general stoichiometric and kinetic orders of the different chemical species.

Based on the penetration theory, the unsteady-state species conservation equations may be written as

$$\frac{\partial A}{\partial t} = D_A \frac{\partial^2 A}{\partial x^2} - R_{A1} - R_{A2} \quad (2a)$$

$$\frac{\partial B}{\partial t} = D_B \frac{\partial^2 B}{\partial x^2} - R_{A1} \quad (2b)$$

$$\frac{\partial C}{\partial t} = D_C \frac{\partial^2 C}{\partial x^2} + R_{A1} - R_{A2} \quad (2c)$$

$$\frac{\partial D}{\partial t} = D_D \frac{\partial^2 D}{\partial x^2} + R_{A1} \quad (2d)$$

$$\frac{\partial E}{\partial t} = D_E \frac{\partial^2 E}{\partial x^2} + R_{A2} \quad (2e)$$

$$\frac{\partial F}{\partial t} = D_F \frac{\partial^2 F}{\partial x^2} + R_{A2}. \quad (2f)$$

It is assumed that the kinetic expressions can be described by simple power-law expressions (3a) and (3b), as

they are usually accurate enough for estimation of local reaction rates

$$R_{A1} = k_{1,1}AB - k_{1,2}CD \quad (3a)$$

$$R_{A2} = k_{2,1}AC - k_{2,2}EF. \quad (3b)$$

The species conservation equations have been solved with the following initial (4a) and boundary conditions (4b)–(4d):

initial:

$$t = 0, \quad x \geq 0 \Rightarrow A = A_0, \quad B = B_0, \quad C = C_0,$$

$$D = D_0, \quad E = E_0, \quad F = F_0 \quad (4a)$$

boundary:

$$t > 0, \quad x = 0 \Rightarrow k_G(A_G - A_{i,G}) = -D_A \left(\frac{\partial A}{\partial x} \right)_{x=0} \quad (4b)$$

$$t > 0; x = 0 \Rightarrow$$

$$\begin{aligned} \left(\frac{\partial B}{\partial x} \right)_{x=0} &= \left(\frac{\partial C}{\partial x} \right)_{x=0} = \left(\frac{\partial D}{\partial x} \right)_{x=0} = \left(\frac{\partial E}{\partial x} \right)_{x=0} \\ &= \left(\frac{\partial F}{\partial x} \right)_{x=0} = 0 \end{aligned} \quad (4c)$$

$$t > 0, x \rightarrow \infty \Rightarrow A = A_0, B = B_0, C = C_0, D = D_0,$$

$$E = E_0, F = F_0. \quad (4d)$$

Under conditions where the liquid is already loaded with the gas-phase component, the bulk equilibrium of all chemical species needs to be considered. A loading factor, α is defined as

$$A_T = \alpha B_T \quad (5a)$$

where A_T and B_T are the total bulk concentrations of A and B in all forms. These are defined as

$$A_T = A_0 + D_0 + E_0 \quad (5b)$$

$$B_T = B_0 + D_0. \quad (5c)$$

Here, B_T is the initial amount of B added to the solution before equilibrium. The equilibrium concentrations of all the species at a given solute loading is determined by solving Eqs. (5a) and (5b) along with the equilibrium definitions and mass balances.

$$K_1 A_0 B_0 - C_0 D_0 = 0 \quad (5d)$$

$$K_2 A_0 C_0 - E_0 F_0 = 0 \quad (5e)$$

$$D_0 - C_0 - E_0 = 0 \quad (5f)$$

$$E_0 - F_0 = 0. \quad (5g)$$

Here, K_1 and K_2 are defined as the equilibrium constants for reactions (1b) and (1c), respectively. The equilibrium reactions (5d)–(5g) are sufficient to describe the reaction stoichiometry under consideration. However, for ap-

Table 1
Program input parameters

Variable	Value	Units
A_i	10	mol m^{-3}
B_T	1000*, 40	mol m^{-3}
k_L	10^{-4} – 10^{-7}	m s^{-1}
$k_{1,1}$	0.25 – 2.6×10^5	$\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$
K_1	0.01–100	—
K_2	0.01–100	—
K_{R2}	10^{-5} – 10^2	—
α	10^{-3} –0.999	—
D_B	10^{-9}	$\text{m}^2 \text{s}^{-1}$

*Initial concentration of B when both reactions are irreversible.

plications to practical systems, it is usually necessary to consider additional equilibria. For example, aqueous equilibria and/or electroneutrality would have to be considered if electrolytic systems are studied.

2.2. Numerical model

The set of partial differential equations (2a)–(2f) subject to initial and boundary conditions (4a)–(4d) was solved using a technique similar to that described by Versteeg et al. (1989). The numerical code has been implemented in PASCAL.

The set of equilibrium Eqs. (5a)–(5g) were solved separately using a Newton–Raphson algorithm for a given value of B_T , K_1 and K_2 to obtain the initial bulk concentrations of all species at different loading factors, α .

The variables used in the present simulations are given in Table 1.

3. Validation

By varying the process parameters and/or conditions such as stoichiometric and kinetic orders, kinetic rate constants and mass transfer coefficients, it is possible to simplify the generalised stoichiometry given by reactions (1a)–(1c) to simpler systems for which analytical and semi-analytical solutions are available. The enhancement factors calculated as a function of the corresponding Hatta number are compared with the results available in open literature.

The systems used to validate the numerical code and the corresponding results obtained are given in Table 2. The results obtained are well within the inherent deviations to be expected when comparing the numerical results with approximate or semi-analytical solutions used for the validation. These deviations could be on account of the use of the film theory or linearisation based on the Hikita–Asai or van Krevelen–Hoftijzer approximation. This confirms the accuracy of the numerical

Table 2
Reaction stoichiometries considered for the validation of the numerical code together with the maximum and average deviations found in the numerical computations

Case	Kinetic expression	Maximum deviation (%)	Average deviation (%)	Number of points	Validation literature
First-order irreversible	$k_{1,0}$ A	0.73	0.11	24	Higbie (1935)
Second-order irreversible	$k_{1,1}$ AB	3.72	0.94	24	DeCoursey (1974)
Second-order reversible	$k_{1,1}$ AB – $k_{1,2}$ CD	5.36	1.67	80	Yeramian et al. (1970)
Second-order reversible with unequal diffusivities	$k_{1,1}$ AB – $k_{1,2}$ CD $D_A \neq D_B$	5.90	1.0	124	DeCoursey and Thring (1989)
Second-order reversible with loaded solutions	$k_{1,1}$ AB – $k_{1,2}$ CD $A_T = \alpha B_T$	6.00	2.1	144	DeCoursey and Thring (1989)

$$\text{Deviation defined as: dev} = \frac{|E_{\text{Numerical}} - E_{\text{Analytical}}|100}{E_{\text{Analytical}}}.$$

$$\text{Average deviation is defined as: avgdev} = \frac{E_{\text{dev}}}{\text{Number of points}}.$$

code used for the mass transfer flux calculations with consecutive chemical reaction.

4. Consecutive reactions

4.1. Both reactions irreversible

The simplest form of consecutive reactions with unit stoichiometric and kinetic orders has been studied earlier by Onda and co-workers (1970, 1972). The same system was numerically investigated by Huang et al. (1980).

Results obtained from simulations, carried out with the model described in this paper, are presented in Fig. 1(a) as enhancement factor, E_A , defined as

$$E_A = \frac{N_A}{k_L(A_i - A_0)} \quad (6a)$$

which is the ratio of chemical to physical flux under identical concentration driving force, over a range of Hatta numbers, Ha , defined as

$$Ha = \frac{\sqrt{k_{1,1}B_0D_A}}{k_L}. \quad (6b)$$

From Eq. (6b), it is clear that the Hatta number, used in this study, is defined on the basis of the first reaction (1b).

The Hatta numbers were varied by changing, either the liquid mass transfer coefficient, k_L , or the kinetic rate constants. The varying parameter in the graph, K_{R2} , is defined as the ratio of the forward rate constants

$$K_{R2} = \frac{k_{2,1}}{k_{1,1}}. \quad (6c)$$

The following points need to be noted:

(a) The reactions show a characteristic two-step increase in the enhancement factor. Each step can be seen

as a contribution by the individual reactions to the total enhancement. If reaction (1c) is slower than reaction (1b), then, at lower Ha , the absorption of A is determined by reaction (1b) only. Consequently, the enhancement factor increases, as is observed for a single irreversible reaction, to its asymptotic value called the *intermediate asymptotic enhancement factor* ($E_{\infty 1}$). However, at higher Ha , sufficient intermediate C is produced within the penetration depth so that reaction (1c) can also influence the absorption of A. As a result, the enhancement factor further increases from the intermediate asymptotic value ($E_{\infty 1}$) to its final value. This value has been called the *final infinite enhancement factor* (E_{∞}). In addition, the point at which one observes the additional enhancement provided by the second reaction has been defined as the ‘kick-in’ point. A typical ‘kick-in’ point for one case ($K_{R2} = 10^{-5}$) is shown in Fig. 1(a).

(b) At extremely high Ha ($Ha > 10^6$), both reactions (1b) and (1c) are instantaneous with respect to mass transfer. Under these conditions the overall reaction scheme simplifies to:

The infinite enhancement factor E_{∞} , for the stoichiometry given above and equal diffusivities, is defined as

$$E_{\infty} = 1 + \frac{2B_0}{A_i}. \quad (8)$$

It is observed that all reactions, irrespective of K_{R2} , finally converge to the same E_{∞} .

(c) The value of K_{R2} is indicative of the reactivity of the intermediate C with A. At very low values of K_{R2} (typically 10^{-5}), the reaction between A and C is noticeable only at very high Hatta numbers. For such a case, a clear intermediate asymptotic enhancement

Fig. 1. (a) Effect of K_{R2} on enhancement factor. Irreversible consecutive reaction. Distinct two-step increase in enhancement observed with the 'kick-in' point indicated for $K_{R2} = 10^{-5}$. $K_{R2} = (k_{2,1}/k_{1,1})$. (b) Deviation between Onda's solutions and results from present model. Relative deviation

$$\% = \frac{(E_{\text{Numerical}} - E_{\text{Approximation}})100}{E_{\text{Numerical}}}$$

factor is observed. This intermediate value is equal to the infinite enhancement factor for a single irreversible reaction (1b). For conditions of equal diffusivity, the value of $E_{\infty 1}$ for $K_{R2} = 10^{-5} = (1 + B_o/A_i)$. This corresponds to the value of 101 seen in Fig. 1(a). With an increase in K_{R2} , the 'kick-in' point shifts to lower Hatta numbers. A higher value of K_{R2} indicates higher reaction rates of C with A so that reaction (1c) can influence the absorption of A at increasingly lower Ha . Consequently, this means that the final infinite enhancement factor is also achieved at increasingly lower Hatta numbers. For $K_{R2} > 1$, reaction (1c) is instantaneous over the entire range of Hatta numbers so that any intermediate C formed is immediately consumed by reactions (1c). No intermediate plateau in enhancement is seen and the value of E_A rises to

its final infinite value directly. The overall reaction stoichiometry is then represented by reaction (7) resulting in a value of E_{∞} as defined in Eq. (8). This corresponds to the value of 201 as seen in Figure 1(a). For intermediate values of K_{R2} , the value of $E_{\infty 1}$ varies within these two asymptotes.

4.1.1. Comments on Onda et al. (1970, 1972)

Onda and co-workers have provided semi-analytical solutions for enhancement factor as function of Hatta number for irreversible consecutive reaction. The enhancement factors have been obtained by linearising the set of non-linear differential species conservation Eqs. (2a)–(2c) using the Hikita–Asai technique. The resulting approximate solutions can be applied to consecutive

reactions of general kinetic orders. The flux description presented in this paper has been compared with the Onda solution for film theory (1970) and penetration theory (1972). For the case of equal diffusivities and unloaded solutions, the film theory solution of Onda results in an enhancement factor that is obtained by solving Eqs. (9a)–(9e) simultaneously.

$$E_A = \frac{\sqrt{M_1}}{\tanh \sqrt{M_1}} \quad (9a)$$

where

$$M_1 = Ha^2(\beta + K_{R2}\gamma). \quad (9b)$$

In order to determine the value of M_1 , Onda et al., assume that the concentration profiles of species B and the ratio C/B may be expressed as quadratic functions of the dimensionless film thickness, z .

$$\frac{B}{B_0} = (1 - \beta)z^2 + \beta \quad (9c)$$

$$\frac{C}{B} = \frac{\gamma}{\beta}(1 - z^2). \quad (9d)$$

Substituting the above expressions for the concentration profiles of B and C in the linearised species conservation equation results in a relationship between the interfacial concentrations of B and C, as follows:

$$\gamma = \frac{(1 - \beta)}{1 + \frac{5}{6}K_{R2}((1 - \beta)/\beta)}. \quad (9e)$$

As an extension to the film theory solution, Onda et al. (1972) presented a method to calculate the enhancement factor based on the penetration theory. This method, however, is limited to equal diffusivities of the chemical species. The value of E_A , is given by solving Eqs. (10a)–(10c) simultaneously.

$$E_A = \left(\sqrt{M_1} + \frac{\pi}{8\sqrt{M_1}} \right) \operatorname{erf} \left(2\sqrt{\frac{M_1}{\pi}} \right) + \frac{1}{2} \exp \left(-\frac{4M_1}{\pi} \right) \quad (10a)$$

$$E_A = 1 + 2\frac{B_0}{A_i}(1 - \beta) - \frac{B_0}{A_i}\gamma \quad (10b)$$

$$\gamma = \frac{(1 - \beta)}{1 + K_{R2}((1 - \beta)/\beta)}. \quad (10c)$$

In actual calculations Eq. (10a) was simplified to

$$E_A = \left(\sqrt{M_1} + \frac{\pi}{8\sqrt{M_1}} \right). \quad (10d)$$

This simplification is valid for higher Hatta numbers (typically $Ha > 3$). The error function contribution then reduces to unity and the exponential part reduces to zero.

The deviations between the Onda solutions and the present numerical data are given in Fig. 1(b). The error

curve for the film theory has a double-peak shape with minimum errors at the intermediate asymptotic enhancement and the final infinite enhancement. Maximum error is observed at very low Hatta numbers (for $E_A = 1.2$; relative deviation = 6%). This can be attributed to the use of the penetration theory for the numerical calculations while the Onda solution is based on the film theory. It is known that the difference in the two theories, for the case of equal diffusivities, is negligible at infinite enhancement and is more pronounced at lower Hatta numbers (Huang et al., 1980). Another reason for the deviation is the assumption of the concentration profile of B made by Onda et al. on which the value of B_i is based. The value of β obtained with the flux description presented here was compared with that obtained using the Onda approximation. It was found that at a $Ha = 90.5$ (relative deviation = 3.9%), the value of β obtained by the Onda approximation = 0.4 while that obtained numerically was = 0.29. Conversely, at the intermediate asymptotic value ($Ha = 1450$, deviation = 0.23%), the value of β from both methods was similar.

The overall performance of Onda's penetration theory solution is slightly better. It is observed that the highest error occurs at a relatively high Hatta number ($> 10^4$). The maximum deviation here is 4.3%. However, the average deviation when compared with numerical data is 1.6% for the penetration theory solution and 1.9% for the film theory solution. It needs to be noted that while the film theory tends to over-estimate the enhancement, the penetration theory under-estimates it and vice versa. Both solutions generate negligible deviations at the intermediate asymptotic enhancement factor.

4.1.2. Comments on Huang, et al. (1980)

Huang et al. (1980) studied the influence of consecutive irreversible second-order reactions on liquid phase mass transfer. They described this system using, both, the film and penetration theory. The resulting set of (partial) differential equations were then solved using orthogonal collocation. Due to the small size of the graphs of Huang et al. (1980), it was difficult to compare the results with any degree of accuracy. However, the authors also derived an analytical approximation for E_A at short contact times (corresponding to low values of Ha). Under these conditions, it can be assumed that $B = B_0$ throughout the penetration depth and $C/B_0 \rightarrow 0$. The species conservation equation for A is then solved to obtain the enhancement factor.

$$E_{A,t \rightarrow 0} = \left(Ha + \frac{\pi}{8Ha} \right) \operatorname{erf} \left(\frac{2Ha}{\sqrt{\pi}} \right) + \frac{2Ha}{\pi} \times \exp \left(-\frac{4Ha^2}{\pi} \right). \quad (11)$$

Expression (11) is similar to that obtained for a pseudo-first-order reaction. This approximation was compared

Fig. 2. Effect of K_2 on enhancement factor. Consecutive (irr)–(rev) reaction.

with the presently obtained numerical results for low Hatta numbers ($Ha < 3$). A maximum deviation of 5.8% was seen for the lowest Hatta number ($Ha = 1$) while for higher Hatta numbers the agreement was much better.

4.2. First reaction irreversible–second reaction reversible

The results from the simulation for the above case are given in Fig. 2 for $K_{R2} = 10^{-4}$. As may be observed, the initial part of the curve is similar to a second order irreversible reaction and can be described with available techniques (e.g. DeCoursey, 1974) till the curve reaches the intermediate asymptotic enhancement value. For the case of equal diffusivities, the value of $E_{\infty 1}$ corresponds to the quantity $(1 + B_0/A_i)$. As Ha increases further, the first reaction becomes instantaneous with respect to mass transfer so that, now, further enhancement is essentially provided by the second reaction.

4.2.1. Effect of K_2

From Fig. 2 it is clear that the value of K_2 influences the final infinite enhancement factor. For very low K_2 (typically $< 10^{-2}$) practically no further enhancement is provided by the second reaction. This is obvious as at such low K_2 , the net production of E and F is very low; the effect of the forward reaction reaction (1c) is overruled by the comparatively fast backward reaction of reaction (1c) resulting in negligible additional absorption of A. With an increase in K_2 , the rate of the forward reaction (1c) increases, resulting in greater absorption of A and a higher enhancement factor. However, the value of E_{∞} cannot exceed the value for the case where both reactions are irreversible (8). This corresponds to a value of $E_A = 9$ for the initial concentrations used in the simulations presented in Fig. 2.

4.2.2. Final infinite enhancement factor, E_{∞}

It is observed that the final infinite enhancement factor, E_{∞} , can be described by the following equation:

$$E_{\infty} = E_{\infty 1} + E_{\infty 2} - 1 \quad (12)$$

where $E_{\infty 1}$ and $E_{\infty 2}$ are the contributions of reactions (1b) and (1c) to the final infinite enhancement factor. For irreversible chemical reaction and equal reactant diffusivities, $E_{\infty 1}$ is given by

$$E_{\infty 1} = 1 + \frac{B_0}{A_i} \quad (13)$$

The value of $E_{\infty 2}$ may be obtained from standard techniques for infinite enhancement factors for single reversible reactions (e.g. DeCoursey and Thring, 1989; Secor and Beutler, 1967). However, in order to use these techniques, the value of the initial concentration of the intermediate C is required. Since at these Hatta numbers, Eq. (1b) is instantaneous with respect to mass transfer, it can be assumed that all B present initially is completely converted to C. In other words, one may assume that the initial concentration of C is the same as the initial concentration of B. Table 3 compares the approximate final infinite enhancement factor from Eq. (12) to those obtained numerically. The DeCoursey and Thring (1989) technique has been used for evaluating $E_{\infty 2}$. As can be observed, the differences in the values are negligible.

4.3. First reaction reversible–second reaction irreversible

The results for the above case are presented in Fig. 3 for $K_{R2} = 10^{-3}$. The results may be explained on the basis of the following parameters:

4.3.1. Effect of K_1

K_1 affects the intermediate asymptotic enhancement factor, which increases with a rise in K_1 as observed in any single-step reversible reaction. However, for all cases, the value of $E_{\infty 1}$ cannot exceed the corresponding value for a single irreversible reaction. For the results presented in Fig. 3, this upper limit on $E_{\infty 1}$ corresponds to $E_A = 5$. In addition, K_1 affects the ‘kick-in’ point. At lower K_1 values, the ‘kick-in’ point is observed at higher Hatta numbers. This can be explained by the fact that, at lower K_1 values, the concentration of intermediate species, C, is lower. Due to this the reaction (1c) starts influencing mass transfer only at a higher Hatta number. The value of the intermediate asymptotic enhancement factor may be calculated with a standard method for reversible reactions (e.g. DeCoursey and Thring, 1989).

4.3.2. Effect of irreversibility of the second reaction

The irreversibility of reaction (1c) results in the equilibrium of reaction (1b) being shifted to the side of the products. As a result, at very high Hatta numbers, where both reactions behave instantaneously with respect to

mass transfer, the stoichiometry is once again described by reaction (7). The value of E_{∞} is then given by Eq. (8), corresponding to the value of $E_A = 9$ in Fig. 3.

4.4. First reaction reversible–second reaction reversible

Typical results for this type of reaction are presented in Fig. 4(a) and (b). The reaction may be studied under the following cases:

- Both K_1 and K_2 are very high (typically K_1 and $K_2 > 100$).
The problem reduces to both reactions being irreversible and simulations give results similar to that in Section 4.1.
- Both K_1 and K_2 are very low (typically K_1 and $K_2 < 0.01$).
The problem reduces to that of physical diffusion of A into a liquid as given by Eq. (1a). Simulations gave an enhancement factor of unity as expected.
- Intermediate values of K_1 and K_2 (typically $K_1 > 0.1$ and $K_2 < 100$).

The simulations are explained on the basis of the following parameters:

4.4.1. Effect of K_1

At a fixed K_2 [Fig. 4(a)], the following remarks need to be mentioned:

- K_1 affects the value of the intermediate asymptotic enhancement factor, which reduces at lower values of K_1 .
- K_1 affects the ‘kick-in’ point of the second reaction. The explanation to this is similar to that provided in Section 4.3.1.

Table 3
Consecutive (irr)–(rev) reaction. Comparison of approximate and numerical values of E_{∞}

K_2	$E_{\infty 1}$	$E_{\infty 2}$	E_{∞} Approx.	E_{∞} Numerical	Deviation (%)*
0.01	5	1.19	5.19	5.20	0.20
0.1	5	1.58	5.58	5.59	0.18
1	5	2.56	6.56	6.56	0.00
10	5	4.06	8.06	8.06	0.00
100	5	4.85	8.85	8.85	0.00

*Deviation defined as: $\text{dev} = \frac{|E_{\text{Numerical}} - E_{\text{Approximation}}|100}{E_{\text{Approximation}}}$.

Fig. 3. Effect of K_1 on the enhancement factor. Consecutive (rev)–(irr) reaction.

- K_1 affects the value of the final infinite enhancement factor. This may be explained by comparing two cases—with equilibrium constants $K_1 = K_2 = 0.01$, an enhancement of 1.3 was observed in the present calculations, while for a case where $K_1 = 100$, K_2 remaining 0.01, an enhancement of 5.1 was obtained. The additional enhancement of the second reaction remains more or less the same, while the enhancement by the first reaction is changed. This phenomenon is qualitatively explained in Section 4.4.4.

4.4.2. Effect of K_2

At a fixed K_1 [Fig. 4(b)], the following remarks need to be mentioned.

- K_2 affects the value of the final infinite enhancement factor; the lower the K_2 , the lower is the enhancement factor.

- K_2 does not affect the ‘kick-in’ point for the second reaction as well as the intermediate asymptotic enhancement factor.

4.4.3. Effect of K_{R2}

The effect of K_{R2} is similar to that observed in Section 4.1. It has no effect on the intermediate asymptotic enhancement factor, or the final infinite enhancement factor.

4.4.4. Additional enhancement and infinite enhancement

As can be seen in Fig. 4(a), the infinite enhancement is influenced by K_1 . The enhancement provided by the first reaction is a function of K_1 only. However, the additional enhancement provided by the second reaction is influenced by both K_1 and K_2 . For a given K_2 value, the additional enhancement of the second reaction

Fig. 4. (a) Effect of K_1 on the enhancement factor. Consecutive (rev)-(rev) reaction. (b) Effect of K_2 on enhancement factor. Consecutive (rev)-(rev) reaction.

$(E_{\infty} - E_{\infty 1})$ is not a constant value. At a fixed K_2 , the additional enhancement provided by the second reaction increases with increasing K_1 and then decreases again as K_1 is increased further.

Due to the different phenomena occurring simultaneously in the penetration depth, it is difficult to clarify the exact reason for the behaviour mentioned in the earlier paragraph. One possible way to explain this is to see the effect of K_1 on the concentration of the intermediate, C, in the penetration depth. As K_1 is increased initially, additional C is formed by reaction (1b). Due to the higher availability of C, the rate of the forward reaction of reaction (1c) is also increased, thereby increasing the absorption of A causing the observed additional enhancement.

At very high values of K_1 , the forward reaction (1c) will cause the enhancement to rise sharply. However, beyond a point, there is no further increase as the concentrations of E and F also rise. This makes the backward reaction of reaction (1c) reduce the overall enhancement. For reactions with higher K_1 values, this effect is observed at comparatively lower Hatta numbers as compared to the case of low K_1 values. This can explain the observed reduction in additional enhancement caused by the second reaction at very high values of K_1 .

4.4.5. Comments on Kuo and Huang (1973)

Kuo and Huang studied the influence of consecutive reversible chemical reactions of type $A + B \xrightleftharpoons[k_{2,1}/k_{2,2}]{k_{1,1}/k_{1,2}} E \xrightleftharpoons[k_{2,1}/k_{2,2}]{k_{2,1}/k_{2,2}} P$ on liquid phase mass transfer behaviour at a gas–liquid interface using the film theory. The numerical code described in this paper was modified to simulate the reaction scheme of Kuo and Huang in order to validate reversibility of consecutive reactions. Calculations

were done for reaction conditions comparable with that of Kuo and Huang. The highest deviation occurs for very low Hatta numbers (6.7%), but decreases with the increasing Hatta number. This can be accounted for by the different mass transfer theories used.

Fig. 5 shows a parity plot for the given system.

5. Effect of solute loading on reversible–reversible reactions

Calculations were done to study the influence of solute loading on mass transfer behaviour. For a given solute loading, α , and initial concentration B_T , the bulk concentrations of the other components were calculated (see Section 2.1). Calculations were done for K_1 and K_2 values from 0.01 to 100 and for values of α ranging from 0.1 to 0.999.

Typical results comparing corresponding values for unloaded solutions are given in Figs. 6(a) and (b). The following points need to be noted:

- In general, all other parameters remaining the same, the enhancement factor for a loaded solution is lower than that for an unloaded solution. This is obviously due to the reduced driving force on account of the presence of A in the liquid bulk.
- Unlike the case of unloaded solutions, K_2 affects the intermediate asymptotic enhancement factor, $E_{\infty 1}$. The value of $E_{\infty 1}$ is lower for higher values of K_2 . This can be explained by observing the concentration profiles for species C and D as a function of K_2 [Fig. 6(c)]. It can be seen that, with an increase in K_2 , there is an increase in $D_0 - C_0$ (D_0 increases while C_0 decreases). However, the product $C_0 \times D_0$

Fig. 5. Parity plot; comparison of enhancement factor as obtained from Kuo and Huang approximation (1973) with results from present model. $K_1 = K_2 = 0.1$.

(a)

(b)

(c)

Fig. 6. (a) Consecutive (rev)-(rev) reaction, enhancement factor as a function of Hatta number. Influence of loading as a function of K_2 . $K_1 = 0.1$. (b) Consecutive (rev)-(rev) reaction, enhancement factor as a function of Hatta number. Influence of solute loading as a function of K_2 . $K_1 = 100$. (c) Concentration profiles of components C and D for loaded solutions ($\alpha = 0.1$) as a function of K_2 . Dashed lines for $K_2 = 10^{-2}$ while whole lines for $K_2 = 10^2$.

remains constant due to the equilibrium constraint (5d) as K_1 , A_0 and B_0 are fixed. The value for $E_{\infty 1}$ can be reduced in case of loaded solutions if there is an increase in the rate of the backward reaction of reaction (1b). It shall be shown, by means of the following analysis that this reduction in $E_{\infty 1}$ does actually occur. The effect of solute loading on the backward reaction of reaction (1b) can be represented as

$$\bar{r} = k_{1,2}[C_0 + x][D_0 + x] \quad (13a)$$

where C_0 and D_0 represent the initial concentrations and 'x' the addition to the concentration as a result of production by the forward reaction of (1b).

Expanding eq. (13a) gives

$$\bar{r} = k_{1,2}[C_0 D_0 + x(C_0 + D_0) + x^2]. \quad (13b)$$

The reaction equation can be written as three separate additions to the reaction rate. The product $C_0 \times D_0$ is constant and if we can neglect the effect of solute loading on x^2 then the addition to the backward reaction due to solute loading can be described as

$$\bar{r} = k_{1,2}[x(C_0 + D_0)]. \quad (13c)$$

Since $C_0 \times D_0 = \text{constant}$ we can write eq. (13c) as

$$f(C_0, D_0) = x(C_0 + D_0) = \left(\frac{\text{const}}{D_0} + D_0 \right) x. \quad (13d)$$

Differentiating the right-hand side with respect to D_0 gives

$$\frac{\partial f(D_0)}{\partial (D_0)} = \left(1 - \frac{\text{const}}{D_0^2} \right) x. \quad (13e)$$

This function equals zero at $D_0 = \sqrt{\text{const}}$. This means that the backward reaction is minimum at $D_0 = C_0$ and is higher for unequal amounts of C_0 and D_0 . Correspondingly, the addition to the backward reaction rate of the first reaction increases with the difference $D_0 - C_0$ (higher K_2), thus reducing the value of $E_{\infty 1}$.

- It is interesting to note that in Fig. 6(a), results are presented for an $\alpha = 0.5$ ($K_2 = 100$) and $\alpha = 0.45$ ($K_2 = 0.01$) as these correspond to cases where A_0 is slightly less than A_i . For values of α above those presented, the initial concentration of A in the liquid phase is greater than the interfacial value. Consequently, desorption of A from the liquid phase occurs for values of α greater than those reported in Fig. 6(a).

6. Approximate technique to determine E_{∞} of reversible consecutive reactions

A technique for calculating E_{∞} of reversible consecutive reactions with equal diffusivities of all chemical spe-

cies has been derived based on the method described by DeCoursey (1982). DeCoursey developed this method for single reversible chemical reactions based on the Danckwerts' model of mass transfer. He used the approximation technique of van Krevelen and Hoftijzer for linearising the reaction terms of the species conservation equations. However, since DeCoursey used an unsteady state theory, the concentrations of the reactants from the liquid phase were approximated by a time-mean value and assumed independent of time. Variation of these concentrations with distance from the interface was neglected as well. The liquid bulk was assumed to be at equilibrium at all times. In addition, it was assumed that at any point within the liquid phase, equilibrium could be expressed in terms of the time-mean concentrations.

For the situation described in this paper, time-mean concentrations are obtained from the instantaneous concentrations by taking 's-multiplied' Laplace transforms of Eq. (2a) under initial condition (4a). Similar exercise is carried out for all the other species. Bridging equations for each reaction species are then obtained by eliminating the reaction terms on manipulation of the component mass balances.

The bridging equations are

$$D \frac{\partial^2}{\partial x^2} (\bar{B} - \bar{A} - \bar{E}) - s(\bar{B} - \bar{A} - \bar{E}) + s(B_0 - A_0 - E_0) = 0 \quad (14a)$$

$$D \frac{\partial^2}{\partial x^2} (\bar{C} + \bar{A} + 2\bar{E}) - s(\bar{C} + \bar{A} + 2\bar{E}) + s(C_0 + A_0 + 2E_0) = 0 \quad (14b)$$

$$D \frac{\partial^2}{\partial x^2} (\bar{D} + \bar{A} + \bar{E}) - s(\bar{D} + \bar{A} + \bar{E}) + s(D_0 + A_0 + E_0) = 0 \quad (14c)$$

$$D \frac{\partial^2}{\partial x^2} (\bar{E} + \bar{A} - \bar{B}) - s(\bar{E} + \bar{A} - \bar{B}) + s(E_0 + A_0 - B_0) = 0 \quad (14d)$$

$$D \frac{\partial^2}{\partial x^2} (\bar{F} + \bar{A} - \bar{B}) - s(\bar{F} + \bar{A} - \bar{B}) + s(F_0 + A_0 - B_0) = 0 \quad (14e)$$

where the overhead bars define time-averaged values.

These equations are then solved along with the transformed species transport equation for A.

$$D \frac{\partial^2}{\partial x^2} \bar{A} - s(\bar{A} - A_0) - \bar{R}_{A1} - \bar{R}_{A2} = 0. \quad (14f)$$

To do this, the equations are rewritten in a manner similar to that described by DeCoursey (1982) and implementing

the given dimensionless parameters. The equations reduce to

$$\beta = 1 - \frac{(E_{\infty} - 1)}{q} + \varepsilon - \Gamma_3 \quad (15a)$$

$$\gamma = \Gamma_1 + \frac{(E_{\infty} - 1)}{q} - 2\varepsilon + 2\Gamma_3 \quad (15b)$$

$$\delta = \Gamma_2 + \frac{(E_{\infty} - 1)}{q} - \varepsilon + \Gamma_3 \quad (15c)$$

$$\zeta = \varepsilon \quad (15d)$$

with

$$\beta = \frac{\bar{B}_i}{B_0}, \gamma = \frac{\bar{C}_i}{B_0}, \delta = \frac{\bar{D}_i}{B_0}, \varepsilon = \frac{\bar{E}_i}{B_0} \quad \text{and} \quad \zeta = \frac{\bar{F}_i}{B_0}.$$

These equations can be substituted in the relations for K_1 and K_2 , which in turn can be substituted in the equation for θ , defined as

$$\theta = \frac{\bar{A}_{ei} - A_0}{A_i - A_0} \quad (16a)$$

where A_{ei} is the time-averaged equilibrium interfacial concentration.

This results in two equations for θ (one for each equilibrium constraint)

$$\theta_1 = \frac{q(\Gamma_1 + (E_{\infty} - 1)/q - 2\varepsilon + 2\Gamma_3)(\Gamma_2 + (E_{\infty} - 1)/q - \varepsilon + \Gamma_3)}{K_1(1 - (E_{\infty} - 1)/q + \varepsilon - \Gamma_3)} - q \frac{A_0}{B_0} \quad (16b)$$

Fig. 7. (a) Parity plot; comparison of DeCoursey approximation (1982) with numerical values for E_{∞} . Consecutive (rev)–(rev) reaction—unloaded solutions. (b) Parity plot; comparison of DeCoursey approximation (1982) with numerical values for E_{∞} . Consecutive (rev)–(rev) reaction—loaded solutions.

Table 4

Selection of enhancement factors at different Hatta numbers. Further parametric values given in Table 1 and the respective figures

Fig.	k_L	$k_{1,1}$	Ha	E_A		
				$K_{R2} = 10^{-5}$	$K_{R2} = 10^{-2}$	$K_{R2} = 1$
1(a)	1.00×10^{-4}	1.00×10^{-2}	1	1.4	1.4	1.4
	7.81×10^{-7}	1.00×10^{-2}	128	73.4	74.5	104.5
	9.77×10^{-8}	1.00×10^{-2}	1024	100.2	143.8	195.9
	3.05×10^{-9}	5.12×10^0	741,460	201.0	201.0	201.0
2				$K_2 = 10^{-2}$	$K_2 = 1$	$K_2 = 10^2$
	1.00×10^{-4}	2.50×10^{-1}	1	1.36	1.36	1.36
	7.81×10^{-7}	2.50×10^{-1}	128	5.10	5.18	5.18
	9.77×10^{-8}	2.50×10^{-1}	1024	5.18	6.27	7.79
	9.77×10^{-8}	1.31×10^5	741,460	5.20	6.56	8.85
4(a)				$K_1 = 10^{-1}$	$K_1 = 1$	$K_1 = 10$
	1.00×10^{-4}	2.50×10^{-1}	1	1.29	1.35	1.36
	7.81×10^{-7}	2.50×10^{-1}	128	1.69	2.78	4.35
	9.77×10^{-8}	2.50×10^{-1}	1024	3.03	4.99	6.81
	9.77×10^{-8}	1.31×10^5	74,1460	3.78	5.90	7.57
Loaded solutions						
6(a)	k_L	$k_{1,1}$	Ha	$K_2 = 0.01; \alpha = 0.45$		
	1.00×10^{-4}	2.98×10^{-1}	1		1.15	
	7.81×10^{-7}	2.98×10^{-1}	128		1.28	
	9.77×10^{-8}	2.98×10^{-1}	1024		1.33	
	9.77×10^{-8}	1.77×10^5	788,200		1.34	
				$K_2 = 100; \alpha = 0.9$		
	1.00×10^{-4}	4.21×10^{-1}	1		1.09	
	7.81×10^{-7}	4.21×10^{-1}	128		1.14	
	9.77×10^{-8}	4.21×10^{-1}	1024		1.57	
	9.77×10^{-8}	2.21×10^5	741,450		3.95	

$$\theta_2 = \frac{q\varepsilon^2}{K_2(\Gamma_1 + (E_\infty - 1)/q - 2\varepsilon + 2\Gamma_3)} - q \frac{A_0}{B_0} \quad (16c)$$

with

$$\Gamma_1 = \frac{C_0}{B_0}, \Gamma_2 = \frac{D_0}{B_0}, \Gamma_3 = \frac{E_0}{B_0} \quad \text{and} \quad q = \frac{B_0}{A_i - A_0}.$$

The above set of equations can be solved for both loaded and unloaded solutions. The only difference being that for unloaded solutions the initial concentrations of all the chemical species is taken as zero.

For instantaneous reversible consecutive reaction, $Ha \rightarrow \infty$ and $\theta = 1$. With this simplification E_∞ and ε can be calculated simultaneously from Eq. (16b) and (16c). This was carried out using commercially available software (MAPLE V). The results are presented as parity plots with respect to numerical obtained values [Fig. 7(a) and (b)]. The figures show that the match between the approximate technique and numerical values is very close with maximum deviation of 1.3% for unloaded solutions and 0.3% for loaded solutions with an α of 0.1.

7. Conclusions

A numerical model based on the Higbie penetration theory for isothermal reversible consecutive chemical re-

action has been presented in this paper. The model has been successfully validated for simpler reaction stoichiometries.

It has been shown that, although the Onda technique (Onda et al., 1970, 1972) for enhancement factors of irreversible consecutive reactions is useful in determining the intermediate asymptotic enhancement factor and the final infinite enhancement factor, there is some deviation from numerical results for the intermediate enhancement factor (max. 6% for film theory and 4.3% for penetration theory).

For reversible consecutive reactions, it has been shown that the final infinite enhancement (E_∞) can be seen as a contribution of the infinite enhancement of the first reaction ($E_{\infty 1}$) along with the additional enhancement provided by the second reaction ($E_{\infty 2}$). This was quantitatively shown for irreversible–reversible reactions.

For the case of solute loading, enhancement factors obtained are lower than that for the unloaded case. Unlike unloaded solutions, the value of K_1 affects the intermediate asymptotic enhancement value for the case of loaded solutions. Finally, an approximate technique to determine final infinite enhancement factors based on the method of DeCoursey (1982) has been presented for consecutive reversible reactions with equal diffusivities. The match with numerically obtained values is very good for both loaded and unloaded solutions.

The vigorous numerical analysis that has been presented in this work serves to archive the effect of reversibility and solute loading on consecutive reactions in gas–liquid systems. In order to facilitate further numerical and approximate analysis on this reaction system, a selection of results have been presented in Table 4.

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Notation

A	component A, concentration of component A, mol m^{-3}
B	component B, concentration of component B, mol m^{-3}
C	component C, concentration of component C, mol m^{-3}
D	component D, concentration of component D, mol m^{-3}
D_{sub}	diffusivity, sub: component $\text{m}^2 \text{s}^{-1}$
E	component E, concentration of component E, mol m^{-3}
E_A	enhancement factor defined by Eq. (6a), dimensionless
E_{∞}	final infinite enhancement factor defined by Eqs. (8) and (12), dimensionless
$E_{\infty 1}$	intermediate asymptotic enhancement factor, dimensionless
$E_{\infty 2}$	enhancement provided by reaction (1c), dimensionless
$f(C_0, D_0)$	function defined by Eq. (13d), $\text{mol m}^{-3} \text{s}^{-1}$
F	component F, concentration of component F, mol m^{-3}
Ha	Hatta number, defined by Eq. (6b), dimensionless
$k_{\text{sub1,sub2}}$	reaction rate constant, sub1: reaction number, sub2: reaction direction, $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$
k_G	gas side mass transfer coefficient, m s^{-1}
k_L	liquid side mass transfer coefficient, m s^{-1}
K_{sub}	equilibrium constant sub: reaction number, dimensionless
K_{R2}	$k_{2,1}/k_{1,1}$, dimensionless
M_1	constant defined by Eq. (9b), dimensionless
N_A	gas flux, $\text{mol m}^{-2} \text{s}^{-1}$
q	parameter defined by DeCoursey (1982), dimensionless
$\tilde{r}$	backward reaction rate, $\text{mol m}^{-3} \text{s}^{-1}$

$R_{\text{sub1,sub2}}$	reaction rate, sub1: component, sub2: reaction number $\text{mol m}^{-3} \text{s}^{-1}$
s	Laplace time variable, s^{-1}
t	time variable, s
x	place variable, m
$\bar{x}$	additional concentration defined in Eq. (13a), mol m^{-3}
z	dimensionless film thickness ($= x/\text{film thickness}$), dimensionless
$\overline{\text{CAP}}$	time-average concentration, cap: component, mol m^{-3}

Greek letters

α	loading factor defined by Eq. (5a), dimensionless
β	dimensionless interface concentration ($= \bar{B}_i/B_0$), dimensionless
γ	dimensionless interface concentration ($= \bar{C}_i/B_0$), dimensionless
Γ	dimensionless initial concentration of component, dimensionless
δ	dimensionless interface concentration ($= \bar{D}_i/B_0$), dimensionless
ε	dimensionless interface concentration ($= \bar{E}_i/B_0$), dimensionless
ζ	dimensionless interface concentration ($= \bar{F}_i/B_0$), dimensionless
θ_{sub}	dimensionless driving force, sub: reaction number, dimensionless

Subscripts

0	bulk condition
ei	equilibrium value at interface
G, g	gas phase
i	liquid-phase interface
i, G	gas-phase interface
L, l	liquid phase
T	total

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