Non-isothermal gas absorption with reversible chemical reaction

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Abstract A fundamental description of non-isothermal mass transfer accompanied by a single reversible chemical reaction has been presented. The description is based on the Higbie penetration theory. Arrhenius type dependence of solubility, reaction rates and diffusivities on temperature has been assumed. Special emphasis has been paid to bimolecular irreversible reactions where depletion of the liquid phase reactant occurs. In addition, the mass transfer behavior in the infinite enhancement regime has also been presented. It has been shown that the Shah criterion fails under conditions where depletion of the liquid phase reactant occurs. In the infinite enhancement regime, the non-isothermal enhancement factor is dependent on the ratio of the diffusivities of the reactants, the ratio of the initial stoichiometric reactant concentrations and the activation energies of solubility and reactant diffusivity. These characteristics of the infinite non-isothermal enhancement factor have been reported earlier by Asai et al. (1985, A.I.Ch.E. J. 31, 1304-1312). Additionally, it has been shown that, for bimolecular irreversible reactions, the use of correlations for interfacial temperature rise that assume all heat to be released at the interface is not valid for systems with low Lewis numbers but also not for systems where depletion of the liquid phase reactant occurs. Further, the model has been used to study the effect of reversibility on bimolecular reactions. The effect of temperature dependence of the solubility of the gaseous component and diffusivities of the various species on the overall enhancement has been presented. Since the non-isothermal enhancement factor of bimolecular reversible reactions is dependent on various parameters, it is not possible to determine its value by analytical or via approximate techniques. One is forced to use numerical methods for this purpose instead. © 1997 Elsevier Science Ltd

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1. INTRODUCTION

Thermal effects are important in a number of gas-liquid processes involving chemical reactions in the liquid phase. Dissolution of gas into the liquid releases the heat of solution, ΔH_S, at the gas-liquid interface. In addition, the heat of reaction, ΔH_R, is released (assuming exothermic reaction) either within the penetration depth or the liquid bulk, depending on the reaction rate relative to the rate of mass transport. These heat effects can form a temperature gradient near the interface, which, in turn, affects the physico-chemical properties of the system. For the three main temperature dependent properties, a rise in temperature would increase the diffusion coefficient(s) and the reaction rate constant(s) while the solubility of the gas would decrease, respectively. Thus, it is clear that there are two counteracting phenomena affecting mass transfer within the liquid phase. The

complexity of the problem is increased as more complex reactions are considered. For such cases, one is forced to use numerical techniques to simultaneously solve the heat and mass transfer equations.

The models presented in literature may be classified depending on the use of the film or the penetration theory to describe simultaneous heat and mass transfer. In addition, for some models, two asymptotic values of the Lewis number are assumed. $Le = 1$ for the classical film theory and $Le \rightarrow \infty$ so that the heat and mass transfer equations may be decoupled. Table 1 gives an overview on some important literature on non-isothermal gas absorption.

The model presented in this paper uses the Higbie penetration theory and is similar to that used by Versteeg et al. (1989) which has been extended in order to incorporate heat production and transport. An Arrhenius type of temperature dependence has been used for all three physico-chemical properties. No limitations have been placed on the Lewis number. In addition, any reaction scheme can be

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Table 1. Overview of important literature on non-isothermal gas absorption

Author(s)	Year	Model	Temperature dependent properties	Dependence function	Reaction	Solution	Remarks
Danckwerts	1952, 1967	Penetration	None		First order	Analytical	
Brian et al.	1961	Penetration	None		Bimolecular	Analytical	Accounts for bulk flow
Chiang and Toor	1964	Penetration	Solubility	Linear		Analytical	
Clegg and Mann	1969	Penetration	Solubility	Linear	Unimolecular	Analytical	Convective cell model
	1972	Penetration	Solubility	Linear		Analytical	Chiang Toor model
Clegg and Kilgannon	1970	Penetration	None	—	—	Analytical	
Shah	1971	Penetration	Solubility, k	—	Consecutive	Numerical	
Cook and Moore	1972	Penetration	D, solubility, k	Linear	First order	Numerical	
Shah	1972	Penetration	Solubility	Arrhenius	First order	Numerical	Correlation based on ε_{eff}
Mann and Clegg	1975	Penetration	Solubility, k	Linear	Unimolecular 1st, 3rd, 7th order	Numerical	
Tamir et al.	1975	Penetration	Solubility	Arrhenius, Henry	First order	Numerical	Includes gaseous environment
Allan and Mann	1979	Film	D, solubility, λ	Hyperbolic approx.	-	Analytical	
Suresh et al.	1983	Penetration	D, solubility, k	Arrhenius	—	Analytical	
Asai et al.	1985	Penetration	Solubility, k	Arrhenius	First order, Instantaneous bimolecular	Analytical	Unusable for high ϕ_0
Bhattacharya et al.	1987	Film model	Solubility, k	Arrhenius	Bimolecular	Analytical	Iterative procedure
Chatterjee and Altwicker	1987	Penetration/film	None	Arrhenius	First order	Analytical	
Bhattacharya et al.	1988	Film model	D, solubility, k	Arrhenius	Consecutive	Analytical	
Cagnoli et al.	1991	Penetration	D, solubility, k	Arrhenius	Bimolecular	Numerical	Pseudo first order regime
Al-Ubaidi et al.	1990	Film model	D, solubility, k	Arrhenius	Bimolecular	Analytical	
Evans and Selim	1990	Penetration	D, solubility, k	Arrhenius	Bimolecular	Numerical	Pseudo first order regime
Frank et al.	1995	Maxwell–Stefan	D, solubility, k	Arrhenius	Bimolecular	Numerical/Analytical	

implemented, including reversibility and multiple-steps as long as power law kinetics hold.

2. MASS AND HEAT TRANSPORT EQUATIONS

The transport and production of a component l may be described as

$$\frac{\partial c_l(x,t)}{\partial t} = \frac{\partial}{\partial x}\left(D_l(T)\frac{\partial c_l(x,t)}{\partial x}\right) + \sum_j^{\#R} R_{l,j}(c,T) \quad (1)$$

while heat production and transport may be described as

$$\frac{\partial T(x,t)}{\partial t} = \frac{\partial}{\partial x}\left(a(T)\frac{\partial T(x,t)}{\partial x}\right)$$
$$+ \frac{1}{\rho(T)c_p(T)}\sum_j^{\#R} R_j(c,T)(-\Delta H_{R,j}(T)). \quad (2)$$

Initial conditions:

$$t = 0, \ \forall x: \quad \begin{array}{l} c_l(x,0) = c_{l,\text{bulk}}(t) \\ T(x,0) = T_{\text{bulk}}(t). \end{array} \quad (3)$$

Boundary conditions:

$$x \to \infty, \quad \forall t: \quad \begin{array}{l} c_l(x_\infty,t) = c_{l,\text{bulk}} \\ T(x_\infty,t) = T_{\text{bulk}}. \end{array} \quad (4)$$
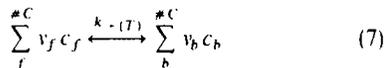
$x = 0, \ \forall t:$

$$-D_l(T)\frac{\partial c_l(0,t)}{\partial x} = k_G\left[\bar{c}_{l,G}(t) - \frac{c_l(0,t)}{m_l(T)}\right] \quad (5)$$

$$-\lambda(T)\frac{\partial T(0,t)}{\partial x} = h_G(\bar{T}_G(t) - T(0,t)) \quad$$

$$+ \sum_k^{\#C} -D_k(T)\frac{\partial c_k(0,t)}{\partial x}(-\Delta H_{S,k}(T)). \quad (6)$$

Production of chemical species and heat

Each reaction j is regarded as a single step reaction with power law kinetics

$$\sum_f^{\#C} v_f c_f \xrightleftharpoons{k_{\pm}(T)} \sum_b^{\#C} v_b c_b \quad (7)$$

$$p_{\pm j}(c,T) = k_{\pm j}(T)\prod_k^{\#C} c_k^{n_{\pm l,k}}. \quad (8)$$

The production of a component l can then be calculated with

$$R_{l,j}(c,T) = -v_{l,j}[p_{+j}(c,T) - p_{-j}(c,T)] \quad (9)$$

Assumptions and simplifications applied in the present study

- The liquid phase reaction is limited to the penetration depth. The bulk concentrations are assumed to be constant.
- For the liquid phase, it is assumed that, initially, no gaseous reactants and/or reaction products are present.

- Gas–liquid contact time is assumed to be independent of temperature and mass transfer phenomena.
- All liquid phase components are assumed to be non-volatile.
- The temperature dependence of thermal conductivity, specific heat, density, heat of reaction and heat of absorption has been neglected. Since these physical properties are, relatively, mild functions of temperature (Welty et al., 1969), using a fixed value for these parameters would not affect the overall results.
- Heat losses to the gas phase are ignored ($h_G = 0$).
- No mass transfer resistance is present in the gas phase.
- The heat of solution is released instantaneously at the interface.
- Bulk flow, Dufour and Soret effects are neglected. For a detailed explanation of these effects, see Bird et al. (1960).

A numerical code incorporating the mass and heat transport equations along with the assumptions mentioned above was developed in-house. For all simulations presented in this study, an initial temperature of 298.15 K has been used. In addition, the diffusivities of all species have been assumed to be equal at this initial temperature ($D_l = 10^{-9}$ m^2/s). Although simulations presented in this study are limited to neglecting heat loss to the gas phase, the numerical model can account for this type of heat loss. Details of the numerical scheme on which the code is based can be obtained from Versteeg et al. (1989).

3. VERIFICATION WITH MODEL SYSTEMS

Various analytical solutions for determining interfacial temperature rise and enhancement factors for simpler reaction stoichiometries are available in literature. Some comparisons of the present model with these previous solutions have been presented below.

3.1. First-order irreversible reactions
For reactions of the type

$$A(g) \to A(l) \quad (10a)$$

$$A(l) \xrightarrow{k_l} \text{products} \quad (10b)$$

various analytical and approximate solutions are available in literature. An overview of these solutions is presented in Table 1.

3.1.1. Danckwerts' solution.
Danckwerts (1952) provided an analytical solution to determine interfacial temperature rise for first-order irreversible reaction assuming all physico-chemical parameters to be temperature independent.

The solutions are given by the following expressions, involving the Bessel functions I_0 and I_1

$$\vartheta_D^{(S)} \frac{\rho c_p}{(-\Delta H_{S,A}) m_A c_{A,G}} \cdot \sqrt{\frac{a}{D_A}}$$
$$= e^{-k_1 t/2} [(1 + k_1 t) I_0(k_1 t/2) + k_1 t I_1(k_1 t/2)] \quad (11)$$

$$\vartheta_D^{(R)} \frac{\rho c_p}{(-\Delta H_R) m_A c_{A,G}} \cdot \sqrt{\frac{a}{D_A}}$$
$$= k_1 t e^{-k_1 t/2} [I_0(k_1 t/2) + I_1(k_1 t/2)] \quad (12)$$

where (S) and (R) are the contributions to the interfacial temperature by solution and reaction, respectively. The total temperature rise at the interface is given by the sum of the above contributions. Figure 1 compares results obtained using the model presented in this paper with the Danckwerts' solution. Here, the change in interfacial temperature as a function of gas–liquid contact time has been shown. At $t = 0$, no reaction occurs so that contribution of the reaction term is also zero. Due to the assumption of no gas and interfacial resistance there is an infinite mass transfer rate, resulting in a jump in the interfacial temperature on account of the heat of solution. As t increases, the extent of reaction in the liquid increases. This makes the contribution due to ΔH_R on the temperature rise greater. The enhancement of the absorption rate by the reaction also increases the contribution of ΔH_S on the interfacial temperature rise as is seen in Fig. 1. For large values of '$k_1 t$', the total temperature rise at the

interface is given by

$$\vartheta_D = \Psi_{EFF} 2\sqrt{\frac{k_1 t}{\pi}} \quad (13)$$

where

$$\Psi_{EFF} = \frac{\Psi}{\sqrt{Le}} \cdot \left(1 + \frac{1}{H}\right) \quad (14)$$

$$H = \frac{-\Delta H_{S,A}}{-\Delta H_R} \qquad \Psi = \frac{m_A c_{A,G}}{\rho c_p T_0} (-\Delta H_{S,A}) \quad (15)$$

Ψ_{EFF} is the dimensionless temperature rise of the interface under conditions of physical absorption and $H = \infty$. From the figure it can be seen that the agreement between the Danckwerts' solution and numerical results for the contribution of $\Delta H_{S,A}$ is exact, while the Danckwerts' solution slightly overestimates the contribution of ΔH_R. This is because the Danckwerts' solution assumes all heat to be released at the gas–liquid interface only, while in reality, heat release due to ΔH_R occurs over the entire penetration depth for mass. On account of the assumption that all heat release occurs at the gas liquid interface, validity of the Danckwerts' solution is limited to systems with high Le numbers or high values of H.

3.1.2. *The Shah criterion.* Shah (1972) extended the Danckwerts' solution to incorporate temperature dependent physico-chemical properties for first-order
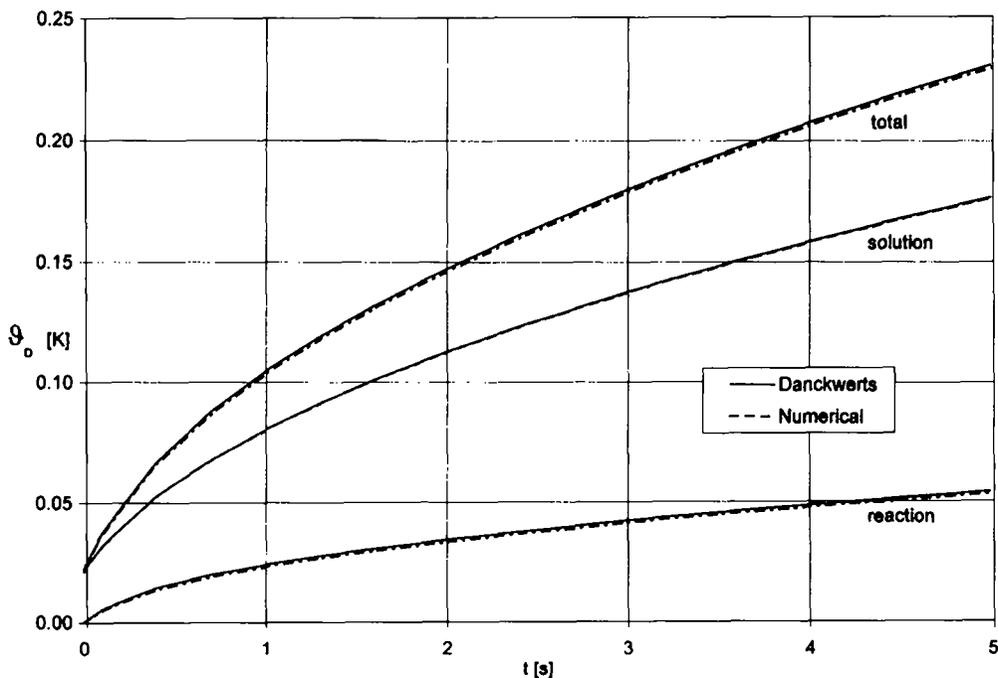

Fig. 1. Comparison between Danckwerts' and numerical solution. Interfacial temperature rise—first order irreversible reaction. Physico-chemical properties assumed independent of temperature. $H = 3.17$, $Le = 50.3$, $k_1 = 10 \text{ s}^{-1}$, $\Psi_{FFF} = 9.71 \times 10^{-5}$.

reactions. He assumed an Arrhenius type of dependence for solubility, diffusivity and the reaction rate represented as

$$X = X_0 \exp\left[-\varepsilon_x\left(\frac{T_0}{T} - 1\right)\right] \qquad \varepsilon_x = \frac{E_x}{RT_0}. \qquad (16)$$

Including these functions in eq. (13) results in an overall temperature dependence of the system, denoted as

$$\varepsilon_{EFF} = \varepsilon_S + \tfrac{1}{2}(\varepsilon_{D_A} + \varepsilon_R). \qquad (17)$$

The ε_{EFF} contains two counteracting phenomena - a reduction in solubility and an increase in diffusivity and reaction rate for a rise in temperature. An ε_{EFF} of zero indicates that these phenomena compensate each other perfectly, so that the system is insensitive to temperature rise and the Danckwerts' relation can be applied. For a unique value of ε_{EFF}, irrespective of the values of the individual parameters it contains, a unique temperature rise of the interface is observed. This is referred to as the Shah criterion. The model presented here was verified with this Shah criterion [see Fig. 2 of Shah (1972)] and an excellent match was observed for various values of ε_{EFF}.

3.1.3. The Asai extension of the Shah criterion. Shah
(1972) limited his study of non-isothermal behavior of first-order irreversible reactions to the interfacial temperature rise of the system. Asai et al. (1985) extended this analysis to include the non-isothermal enhancement factor, β, as well. The absorption flux for a first-order reaction [eq. (10b)] and for $Ha > 2$ is given by

$$J_A = \sqrt{k_1 D_A}\,(m_A\,c_{A,G}). \qquad (18)$$

The absorption behavior is characterized by the non-isothermal enhancement factor, β, defined as

$$\beta = \frac{\text{chemical flux, with heat effects}}{\text{physical flux, without heat effects}}. \qquad (19a)$$

The enhancement factor for the isothermal case is defined, similarly as

$$E_A = \frac{\text{chemical flux}}{k_L(m\,c_{A,G} - c_{A,bulk})} \qquad (19b)$$

over a range of non-isothermal Hatta numbers, ϕ_0. This is identical to the isothermal Hatta number by definition, but with an additional specification that the physico-chemical properties are defined at the initial liquid bulk temperature, T_0

$$\phi_0 = \sqrt{\frac{k_1(T_0)\,D_A(T_0)}{k_L^2}}. \qquad (20)$$

Inserting the temperature dependence of the parameters into eq. (18), the energies of activation can be combined to give the same ε_{EFF} as defined in eq. (17). Thus, for a unique value of ε_{EFF}, a unique mass flux can be expected. As a special case, for an ε_{EFF} of zero, the temperature effects of the system compensate each other and the isothermal flux expression may still be

used for mass transfer. Thus, for this case, the absorption behavior is not influenced by a temperature rise. For $\varepsilon_{EFF} > 0$, the value of β is higher than the isothermal enhancement at the same ϕ_0 number. Conversely, for $\varepsilon_{EFF} < 0$, β is lower than E_A at the same value of ϕ_0.

Asai et al. (1985), presented an approximate solution for the non-isothermal enhancement factor, β, based on a modified Danckwerts' solution. The physico-chemical properties were calculated using a time averaged interfacial temperature. The value of β was then calculated using the solution for the isothermal enhancement factor.

In Fig. 2, β, obtained using the model presented in this study, has been compared with the approximate solution of Asai, as a function of ϕ_0. The varying parameter is ε_{EFF}. The values of the individual energies of activation for each case are given separately in Table 2. Cases 3–5 have the same value of ε_{EFF} while the values of the individual energies of activation have been varied. However, the value of β is practically identical for all three cases, thus indicating that the use of the lumped parameter, ε_{EFF}, results in a unique non-isothermal enhancement factor. It is interesting to note that for high, positive values of ε_{EFF} (Case 6: $\varepsilon_{EFF} = 10$) and high ϕ_0 numbers, a deviation between the numerical model and the approximate solution is observed. This may be attributed to the simplification used by Asai et al. (1985), to approximate the
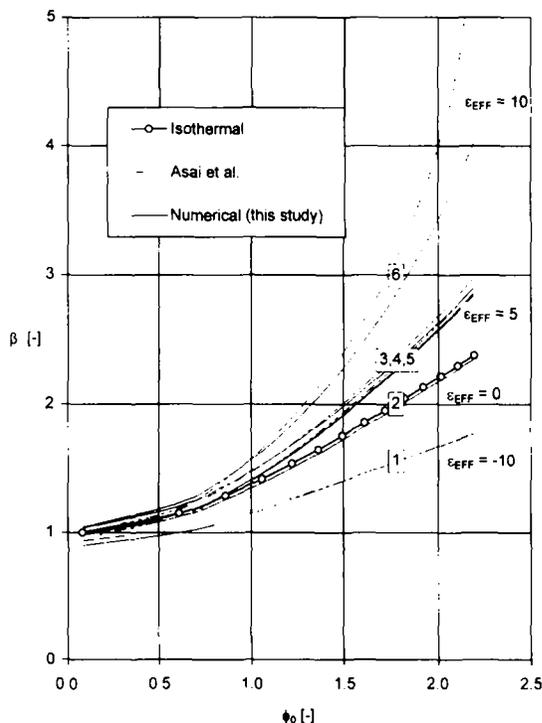

Fig. 2. Non-isothermal enhancement as a function of ϕ_0. First-order irreversible reaction. $H = 1$, $Le = 100$, $\Psi_{EFF} = 0.0206$. Line numbers refer to cases presented in Table 2.

Table 2. Energies of activation for cases presented in Fig. 2

| Case	ε_S	ε_R	ε_D	ε_{EFF}
1	-15	5	5	-10
2	-5	5	5	0
3	-10	15	15	5
4	-5	5	15	5
5	-5	15	5	5
6	-10	15	25	10

Arrhenius temperature dependence of the physicochemical properties. The Arrhenius function as defined in eq. (16) was approximated by Asai as

$$X = X_0 \left(\frac{T}{T_0}\right)^{\varepsilon_x}, \qquad \varepsilon_x = \frac{E_x}{RT_0}. \qquad (21)$$

For a rise in temperature of 10%, the difference in the value of X calculated by eq. (16) and eq. (21) may be as high as 6% for $\varepsilon_{EFF} = 10$.

4. BIMOLECULAR IRREVERSIBLE REACTION

Previous studies on this system (Evans and Selim, 1990; Cagnoli et al., 1991) are limited to high initial concentrations of the liquid phase reactant and low values of ϕ_0. Under these conditions, depletion of the liquid phase reactant does not occur and the system may be approximated by a pseudo first-order reaction. Bhattacharya et al. (1987), have considered depletion of the reactant but results have been presented at lower values of ϕ_0. Asai et al. (1985) provide both rigorous and approximate penetration theory solutions for the interfacial temperature rise and non-isothermal enhancement factor. The solutions are, however, limited to the instantaneous reaction regime. These limitations have been overcome in the present study where special emphasis has been paid to low initial concentrations of the liquid phase reactant and the gas absorption with bimolecular irreversible reaction in the infinite enhancement regime. The reaction stoichiometry considered is

$$A(g) \rightarrow A(l) \qquad (22a)$$

$$A(l) + B(l) \xrightarrow{k_{1,1}} \text{products.} \qquad (22b)$$
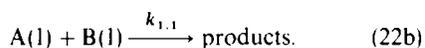
Additional parameters are required to describe the mass transfer behavior of bimolecular reactions. The Hatta number, ϕ_0 [eq. (20)], is modified to account for the concentration of the liquid phase reactant, B, as

$$k_1(T_0) = k_{1,1}(T_0) c_{B,0}. \qquad (23)$$

In addition, the ratio of the reactant concentrations is defined as

$$\chi = \frac{c_{B,0}}{m_A(T_0) c_{A,G}} \qquad (24)$$

and the diffusivity ratio defined as

$$r_A = \frac{D_A(T_0)}{D_B(T_0)}. \qquad (25)$$

The isothermal infinite enhancement factor, E_γ, is defined as

$$E_t = \sqrt{r_A} \left(1 + \frac{\chi}{r_A}\right). \qquad (26)$$

For an isothermal system, it is known that, for a system with a unique value of E_χ, a unique enhancement factor is obtained at a given Hatta number. This is not true for a non-isothermal system. In addition to the parameters r_A and χ, the value of β also depends on other parameters, namely

- the amount of heat released (Ψ);
- the heat ratio (H);
- the ratio of heat and mass transfer rates (Le);
- the temperature dependence of the physicochemical properties.

In order to gain a better understanding of the system, the diffusivity ratio, r_A, has been kept constant in this study.

4.1. Effect of Ψ_{EFF}

According to Danckwerts (1952), the parameters Ψ, H and Le may be lumped together into a single parameter, Ψ_{EFF}, defined by eq. (14) for a first-order irreversible reaction. At a given ϕ_0, the non-isothermal behaviour of the system could be completely described by Ψ_{EFF}. In order to see if this observation could be extended to bimolecular irreversible reactions, simulations were carried out with the model presented in this paper at various values of Ψ, H, χ and Le. It has been observed that, for all practical purposes, non-isothermal behaviour of bimolecular irreversible reactions can also be uniquely described by Ψ_{EFF}. Deviations are observed for special cases such as low Lewis numbers ($Le \sim 1$) and low values of χ. These deviations have been discussed in detail in Section 4.3.

4.2. Effect of physico-chemical properties

The effect of the different activation energies has been studied at two different values of χ.

Initial stoichiometric excess of B ($\chi = 10$). Simulation results for this case and high Lewis numbers ($Le = 100$) have been presented in Fig. 3. Activation energies for the cases presented in Fig. 3 are given in Table 3. It is observed that the influence of the physico-chemical properties on absorption behavior varies with the Hatta number. At low Hatta numbers (typically $\phi_0 < 10$), enhancement behavior is uniquely dependent on ε_{EFF} only so that the Shah criterion holds. As Hatta is increased, depletion of B occurs resulting in a decrease in the slope of the enhancement factor curve. The Shah criterion does not hold any
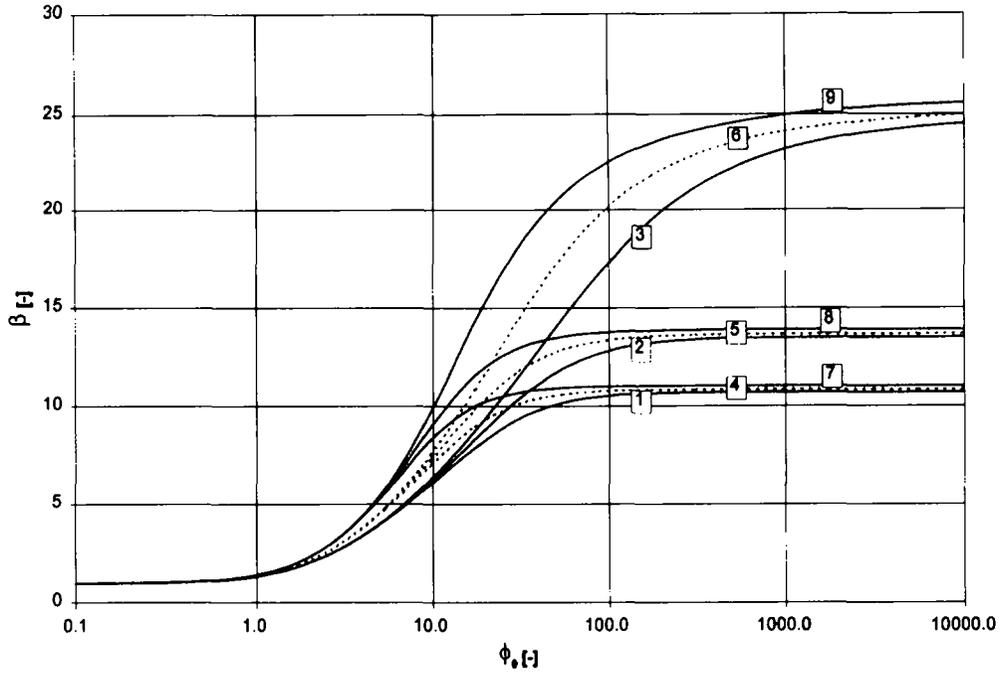
Fig. 3. Non-isothermal enhancement factor as a function of ϕ_0. Irreversible bimolecular reaction. $\chi = 10$, $Le = 100$, $H = 1$, $\Psi_{EFF} = 10^{-2}$. Line numbers refer to cases presented in Table 3.

Table 3. Activation energies for the cases presented in Fig. 3

Case	ε_{DA}	ε_R	ε_S	ε_{DB}	ε_{EFF}
1	4	6	-10	0	5
2	4	6	-10	4	5
3	4	6	-10	8	-5
4	4	11	-7.5	0	0
5	4	11	-7.5	4	0
6	4	11	-7.5	8	0
7	4	16	-5	0	5
8	4	16	-5	4	5
9	4	16	-5	8	5

longer as can be seen by comparing enhancement curves for cases 1-3. These cases have the same value of ε_{EFF} but β increases for a higher value of ε_{DB}. This is explained by the fact that depletion of B is occurring at these values of ϕ_0 so that a higher value of ε_{DB} increases the mobility of B towards the interface, which increases the reaction rate. This, in turn, increases the rate of absorption. However, at a given Hatta number and a fixed ε_{DB}, the value of β is higher for greater values of ε_{EFF}.

As ϕ_0 is increased further, the system enters the infinite enhancement regime where reaction rate is instantaneous with respect to mass transfer. As is observed from Fig. 3, in this regime, the deviation from isothermal case is mainly determined by ε_{DB}, rather than the values of ε_S or ε_{DA}. This is explained by the high concentration ratio, χ, used in these

simulations. Since B can be readily supplied from the bulk, an increase in its mobility with an increase in ε_{DB}, has a stronger effect on enhancement as the reaction plane shifts towards the interface. A similar effect would have been observed by a decrease in r_A. However, this ratio has been kept constant in the present study. The effect of ε_{DB} is found to be stronger for positive values of ε_{EFF} as this results in a higher temperature rise which, in turn, strengthens the effect of ε_{DB} on enhancement. For example, increasing ε_{DB} from 4 to 8 results in a greater increase in enhancement for $\varepsilon_{EFF} = 5$ (cases 8 and 9) than for $\varepsilon_{EFF} = -5$ (cases 2 and 3). An approximate solution for β, is available in literature (Asai et al., 1985) based on a modified form of the Danckwerts' solution. This approximate solution uses a simplification of the Arrhenius function [eq. (21)] which was found to cause significant deviations from numerical results for first-order irreversible reactions (see Section 3.1.3). Keeping this in mind, the approximate solution was not compared to values of β, obtained from the numerical model presented in this paper.

It is interesting to note that, for cases with the same value of ε_{EFF}, an increase in ε_{DB} results in infinite enhancement being observed at higher values of ϕ_0 (compare cases 7 and 9). Infinite enhancement occurs when the rate of reaction is instantaneous with respect to the rate of mass transfer. Greater the value of ε_{DB}, greater is the sensitivity of the mobility of B to rise in temperature. This increase in mobility of B results in a higher rate of mass transfer. Consequently, rate of reaction should increase in order to remain instantaneous with respect to mass transfer. This explains

the observation that the infinite enhancement factor is observed at higher Hatta numbers.

Initial stoichiometric amount of B ($\chi = 1$). Due to the low value of χ, the influence of chemical reaction on the absorption rate is small. As a result, the temperature rise is also low and, hence, the deviations from isothermal cases are also small. Simulations in the infinite enhancement regime show that, due to the lower concentrations of B, ε_{DB} has a smaller influence as compared to ε_S and ε_{DA}. In this case, maximum influence on enhancement is exerted by the solubility of A. If, however, the sum of the three parameters ($\varepsilon_{DA} + \varepsilon_{DB} + \varepsilon_S$) is close to zero, then the system can be approximated with an isothermal system.

4.3. *Limitations on the validity of* Ψ_{EFF}

As has been mentioned earlier in Section 4.1, unlike the case of first-order reactions, the use of Ψ_{EFF} to describe the interfacial temperature rise is not sufficient for certain extreme cases of bimolecular irreversible reactions (low Le numbers and low χ). In order to explain this discrepancy, two systems have been compared. One where $H = \infty$, so that all heat is released by solution only and the point of heat release in limited to the gas–liquid interface. The second, where $H = 0$, so that heat release occurs due to reaction only and the point of release is dependent on the region within the penetration depth in which reac-

tion occurs. For both systems, the physico-chemical properties have been assumed to be temperature independent so that the enhancement behavior of both systems is identical. A deviation in interfacial temperature rise, depending on the mode of heat release, can be defined as

$$\Delta \vartheta(\%) = \frac{\vartheta_{H=\infty} - \vartheta_{H=0}}{\vartheta_{H=\infty}} \cdot 100. \tag{27}$$

This is the relative difference in the interfacial temperature rise for a system where all heat release occurs due to solution only ($\vartheta_{H=\infty}$) and a system where all heat release occurs only due to reaction ($\vartheta_{H=0}$). Variation in $\Delta \vartheta$ as a function of ϕ_0 has been compared in Fig. 4(a) for a first-order irreversible and a bimolecular irreversible reaction.

For a first-order irreversible reaction, with an increase in ϕ_0, the reaction shifts towards the interface. Thus the point of heat release for the system with $H = 0$ also shifts towards the interface and the interfacial temperature rise for the two systems becomes identical and $\Delta \vartheta$ tends to zero. Hence, for first-order reactions, the assumption that all heat release occurs at the gas–liquid interface is increasingly valid at higher values of ϕ_0, even for low Lewis numbers.

In case of bimolecular irreversible reactions, in the instantaneous reaction regime, there is a formation of a reaction plane at which A and B react. For $H = 0$ [Fig. 4(b)], all heat release occurs at this reaction
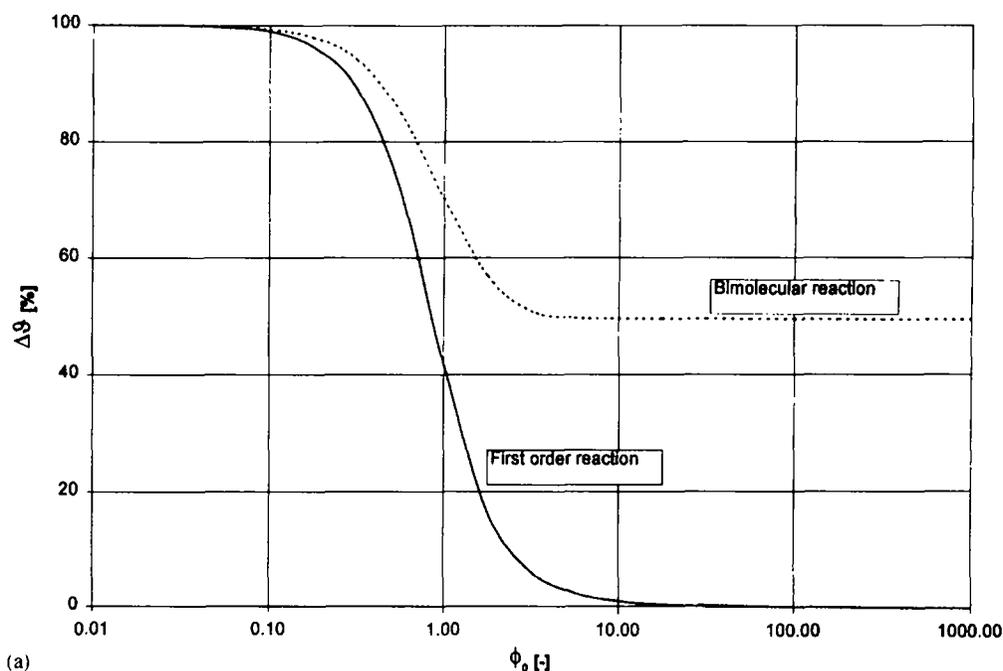

(a)

Fig. 4. (a) Influence of the heat ratio on the interfacial temperature rise. Comparison between a first-order and bimolecular reaction. Physico-chemical properties are assumed independent of temperature. $\chi = 1$, $Le = 1$, $\Psi_{EFF} = 10^{-2}$. (b) Concentration and temperature profiles. Bimolecular irreversible reaction—instantaneous reaction regime. $H = 0$, $\chi = 1$, $Le = 1$, $\Psi_{EFF} = 10^{-2}$, $\phi_0 = 10^3$. (c) Concentration and temperature profiles. Bimolecular irreversible reaction—instantaneous reaction regime. $H = \infty$, $\chi = 1$, $Le = 1$. $\Psi_{EFF} = 10^{-2}$, $\phi_0 = 10^3$.
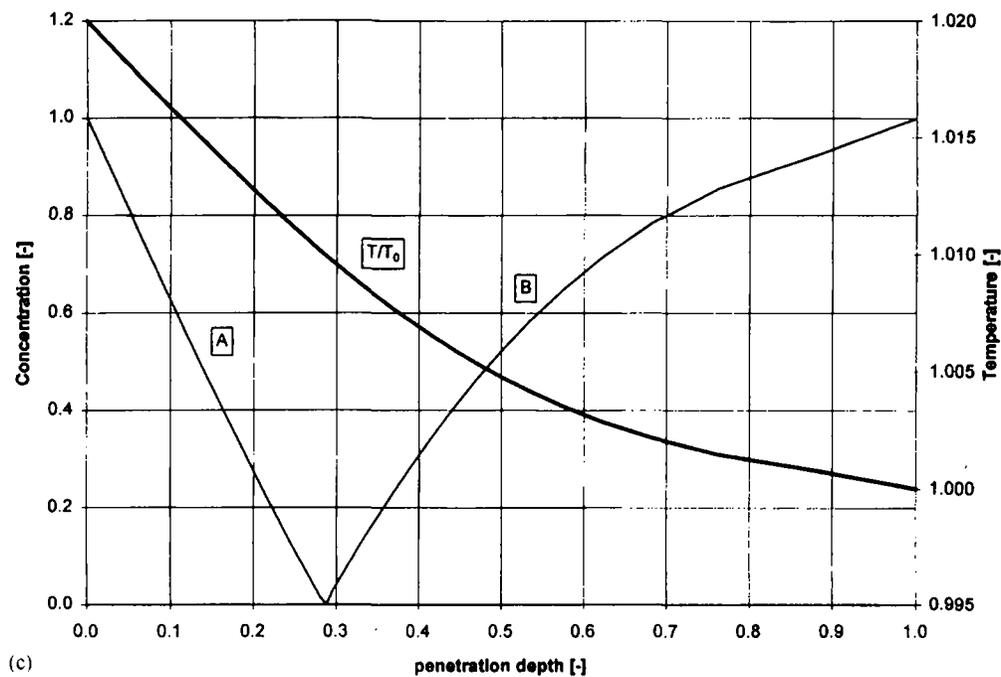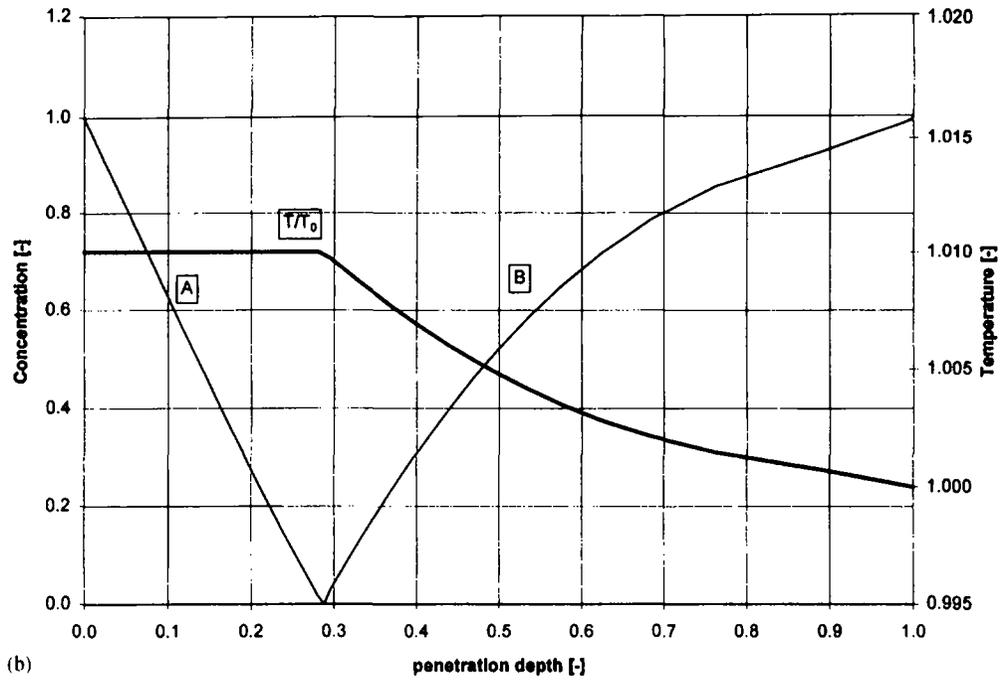
(b)

(c)

Fig. 4. Continued

plane only and there is no temperature gradient between the reaction plane and the interface. Since temperature independent physico-chemical properties have been assumed, the absorption rate is not influenced by temperature effects. Hence, the heat flux through the reaction plane for $H = \infty$ [Fig. 4(c)] is approximately the same as for the case of $H = 0$, except that the point of heat release is shifted to the interface for $H = \infty$. A temperature gradient must

exist between the interface and the reaction plane resulting in a higher interfacial temperature. As a result, the interfacial temperature rise for the two systems can never be identical and $\Delta\vartheta$ tends to a constant non-zero value.

The temperature difference that exists between the interface and the reaction plane is dependent on the value of χ, Le and r_A. An increase in Le reduces the slope of the temperature variation resulting in $\Delta\vartheta$

tending to zero. Since χ determines the position of the reaction plane from the interface, an increase in χ causes a shift towards the interface so that $\Delta\vartheta$ also tends to zero. A similar effect is observed for a lower diffusivity ratio, r_A. Conversely, a large difference in the interfacial temperature rise caused by the two types of heat release ($H = \chi$ and $H = 0$) would be observed for cases with low Le numbers, low χ, and high diffusivity ratios. For all these three cases, the use of the lumped parameter, Ψ_{EFF}, to characterize the thermal behavior of bimolecular irreversible reactions would fail.

5. BIMOLECULAR REVERSIBLE REACTION

All previous studies on bimolecular reactions are limited to the study of irreversible reactions. In order to overcome this limitation, the model presented in this paper has been used to study the behavior of non-isothermal bimolecular reversible reactions. The stoichiometry under consideration is

$$A(g) \rightarrow A(l) \tag{28a}$$

$$A(l) + B(l) \xleftarrow{\ k_{+1}, k_{-1}\ } C(l) + D(l) \tag{28b}$$
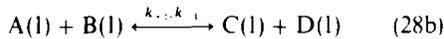
with the equilibrium constant defined as

$$K = \frac{k_{+1}(T_0)}{k_{-1}(T_0)} = \frac{c_C\, c_D}{c_A\, c_B}. \tag{29}$$

In order to understand various phenomena occurring during mass transfer, the temperature dependence of the solubility and the transport properties was varied independently to determine their effect on the overall

enhancement. The concentration ratio, χ, has been taken to be 100 for all simulations. The equilibrium constant was varied between three values -0.1, 10 and 100. For all simulations, for $K = 0.1$, a low enhancement was observed even at high Hatta numbers which is in agreement with results in literature for isothermal reactions (Versteeg *et al.*, 1989). As a consequence, the temperature rise was small as well and the effect of temperature dependence of the properties was weak.

5.1. Temperature dependence of solubility

Figure 5 gives the variation of β as a function of the ϕ_0 number for different values of ε_S. Input parameters for the simulations presented in Fig. 5 are given in Table 4. Cases 1 and 4 represent isothermal absorption for two different equilibrium constants. As is observed for any reversible bimolecular reaction, as K increases, the overall enhancement also increases.

The values of infinite enhancement factors, β_∞, for cases 1–6 in Fig. 5 have been presented in Table 5. From an observation of the values of β_∞, the following points need to be mentioned.

- At a fixed equilibrium constant, β_∞ reduces when the value of ε_S is made more negative. For example, changing ε_S from 0 to -5 at $K = 10$ (cases 1 and 2) reduces β_∞ by 20%. This is because, a lower ε_S makes the gas distribution coefficient, m, more sensitive to temperature changes. By the definition of the non-isothermal enhancement factor, β [eq. 19(a)], this change in the value of ε_S does not affect the denominator of
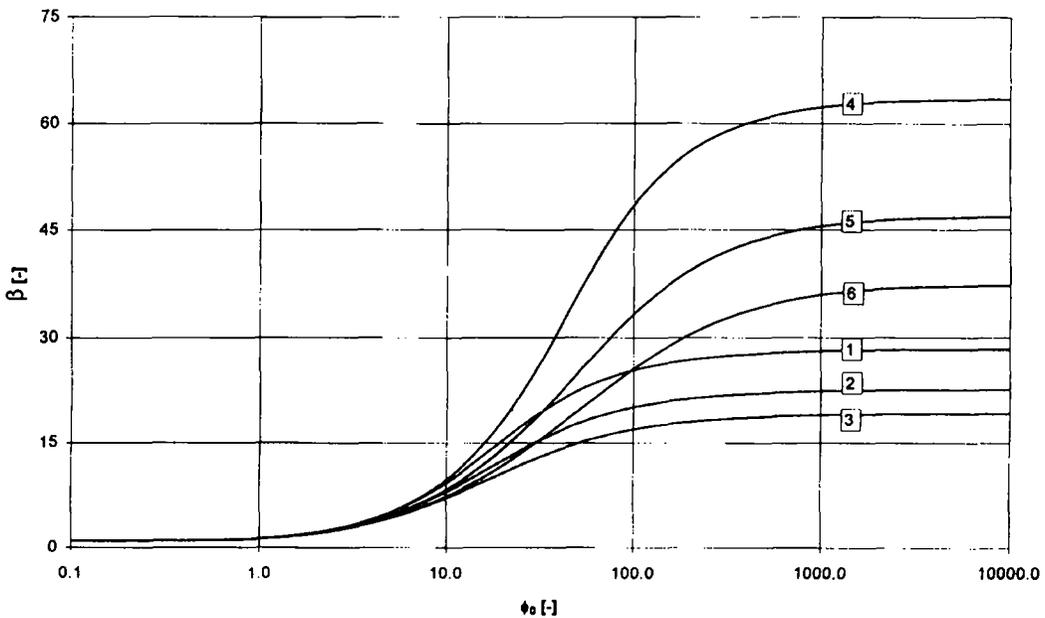

Fig. 5. Influence of temperature dependence solubility on β. Reversible bimolecular reaction. $\chi = 100$; $Le = 100$; $H = 1$; $\Psi_{FFF} = 5 \times 10^{-3}$. Line numbers refer to cases presented in Table 4.

Table 4. Input parameters for cases presented in Figs 5–9

Case	K	Fig. 5 ε_S	Fig. 6 ε_D	Fig. 7		Fig. 8		Fig. 9	
				ε_{DA}	$\varepsilon_{DB,C,D}$	ε_{DB}	$\varepsilon_{DA,C,D}$	$\varepsilon_{DA,B}$	$\varepsilon_{DC,D}$
1	10	0	0	0	0	0	0	0	0
2	10	5	4	4	0	4	0	4	0
3	10	−10	8	0	4	0	4	0	4
4	100	0	0	0	0	0	0	0	0
5	100	−5	4	4	0	4	0	4	0
6	100	−10	8	0	4	0	4	0	4

Table 5. Infinite enhancement factors, β_∞, for cases presented in Figs 5–9 for $\gamma = 100$; $Le = 100$; $H = 1$; $\Psi_{EFF} = 5 \times 10^{-3}$; $\phi_0 = 10^4$

Case	K	Fig. 5	Fig. 6	Fig. 7	Fig. 8	Fig. 9
1	10	28.3	28.3	28.3	28.3	28.3
2	10	22.6	41.0	28.8	29.4	29.9
3	10	19.2	3273.1	40.2	37.6	36.9
4	100	63.5	63.5	63.5	63.5	63.5
5	100	46.8	179.7	64.8	78.3	80.0
6	100	37.2	9067.8	174.2	85.4	83.4

eq. 19(a) as the physical flux is calculated in the absence of heat effects. The chemical flux, however, reduces due to the lower interfacial concentration of A. Thus, there is a reduction in the value of β. As the equilibrium constant is increased, this effect of ε_S on enhancement is more pronounced. For $K = 100$, a similar change in ε_S from 0 to −5 results in a 26% reduction in β_∞. At these high K values, the enhancement and, correspondingly, the temperature rise of the system is large. This results in a steeper drop in gas solubility than for the case of $K = 10$. Consequently, reduction in β_∞ is greater at higher values of the equilibrium constant.

• At a fixed equilibrium constant, if the value of ε_S is reduced in two equal steps (i.e. from 0 to −5 and further, from −5 to −10), then the reduction in β_∞ in the second step is found to be less than the reduction of β_∞ in the first step. For example, for $K = 10$, if ε_S is further reduced from −5 to −10 (cases 2 and 3) then an additional decrease in β_∞ of 15% is observed. For $K = 100$ (cases 5 and 6), a similar reduction of 21% is seen. This is because, as the value of ε_S is increased, its dependence on temperature reduces due to the assumption of an Arrhenius type of function.

5.2. Temperature dependence of diffusivity

5.2.1. Identical activation energies for all components.
Simulations with identical initial diffusivities of all components and with the same temperature

dependence (ε_D) have been presented in Fig. 6 for two values of the equilibrium constant. Input parameters for these simulations are given in Table 4. From the figure it is clear that, for a fixed value of the equilibrium constant, enhancement is higher for larger values of ε_D. An increase in temperature of the system, on account of gas absorption, increases the mobility of all the components equally. This rise in mobility will cause the reaction products, C and D, to be transferred faster away from the reaction zone to the bulk, while reactant B will move faster towards the reaction zone from the bulk. The average concentrations of C and D within the penetration depth will reduce while that of B will increase. In order to maintain the equilibrium limitation (the value of K does not change as it is a function of ε_R only), the concentration of A in the penetration depth will drop. Thus, the slope of the concentration curve of A near the interface increases and, correspondingly, results in a higher enhancement factor.

This rise in enhancement is found to exponentially rise with ε_D. For $K = 10$, an increase in ε_D from 0 to 4 (cases 1 and 2) results is an increase in β_∞ of 45% (see Table 5). An additional increase of ε_D by 4 (cases 2 and 3) results in a value of β_∞ that is far beyond the scale of Fig. 6. This is due to the enormous temperature rise that takes place. Due to the exponential form of the temperature dependence of diffusivity, a slight additional increase in temperature will result in a larger increase in the diffusivity for higher values of ε_D. This, in turn, increases enhancement which strengthens the temperature rise further.
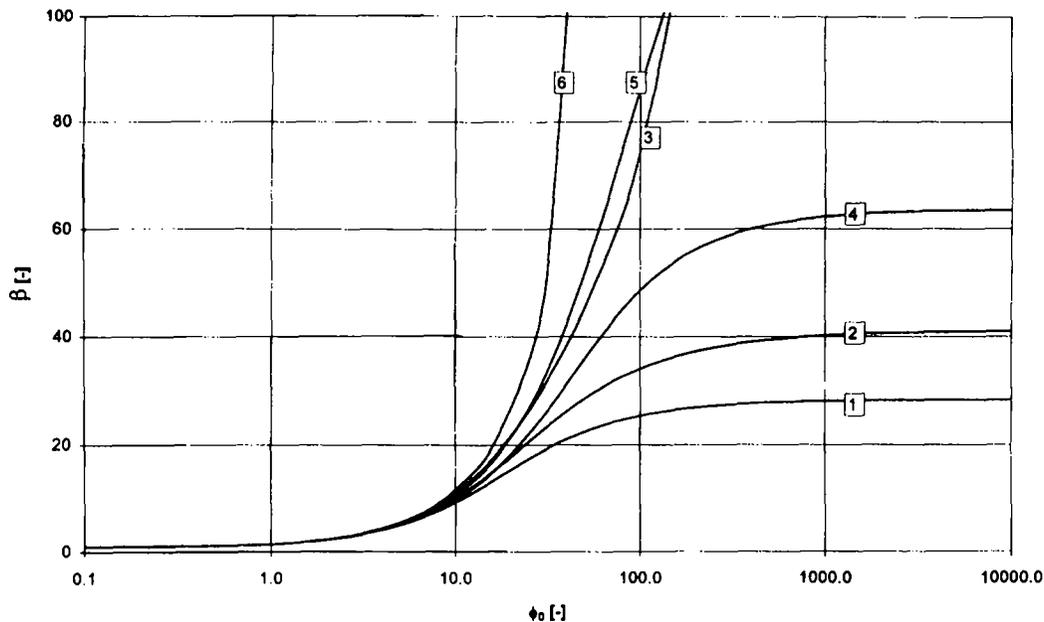
Fig. 6. Influence of temperature dependence of diffusivity of all components on β. Reversible bimolecular reaction. $\chi = 100$; $Le = 100$; $H = 1$; $\Psi_{EFF} = 5 \times 10^{-3}$. Line numbers refer to cases presented in Table 4.
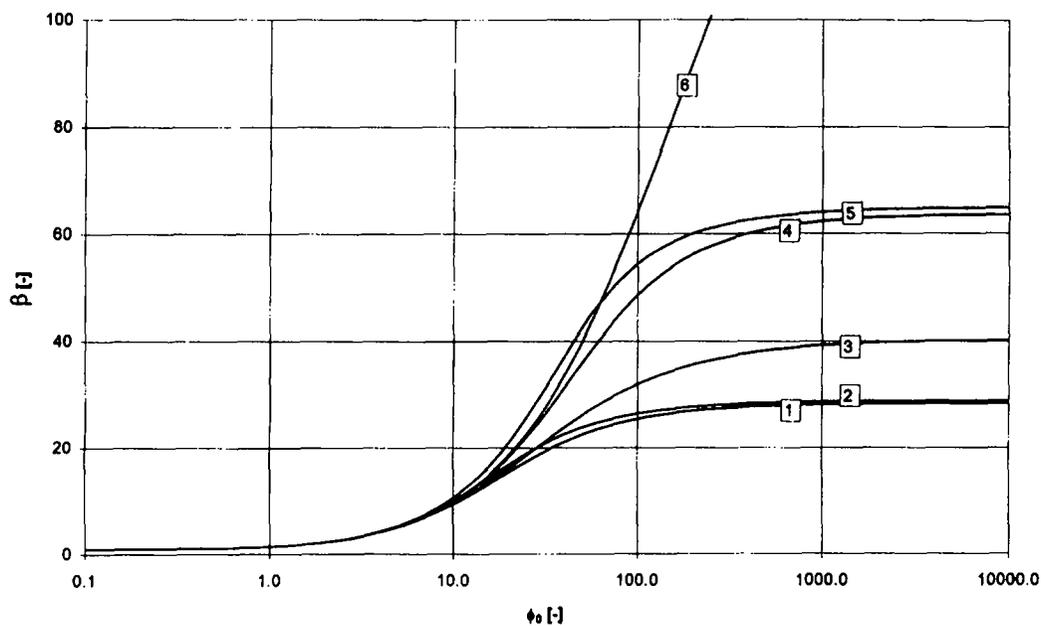

Fig. 7. Influence of temperature dependence of diffusivity of component A on β. Reversible bimolecular reaction. $\chi = 100$; $Le = 100$; $H = 1$; $\Psi_{EFF} = 5 \times 10^{-3}$. Line numbers refer to cases presented in Table 4.

5.2.2. *Variable activation energies of the components.* In order to study the effect of temperature dependence of the individual components, simulation have been carried out with varying the activation energies of A (Fig. 7), B (Fig. 8) and both A and B (Fig. 9). Input parameters for these simulations are presented in Table 4.

In Fig. 7, the temperature dependence of diffusivity of A is varied independently of the other three components. The following points are observed

• For an increase in ε_{DA} from 0 to 4 keeping temperature independent diffusivities of all other components (cases 1 and 2: $K = 10$ and cases
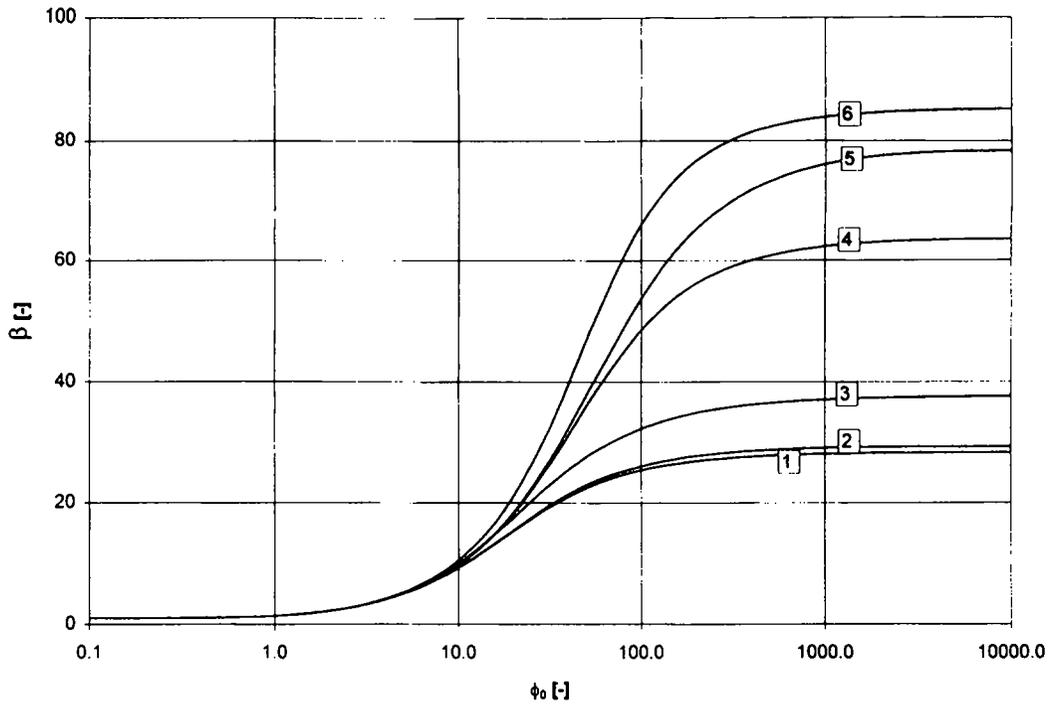
Fig. 8. Influence of temperature dependence of diffusivity of component B on β. Reversible bimolecular reaction. $\chi = 100$; $Le = 100$; $H = 1$; $\Psi_{EFF} = 5 \times 10^{-3}$. Line numbers refer to cases presented in Table 4.

Fig. 9. Influence of temperature dependence of diffusivity of components A and B on β. Reversible bimolecular reaction. $\chi = 100$; $Le = 100$; $H = 1$; $\Psi_{EFF} = 5 \times 10^{-3}$. Line numbers refer to cases presented in Table 4.
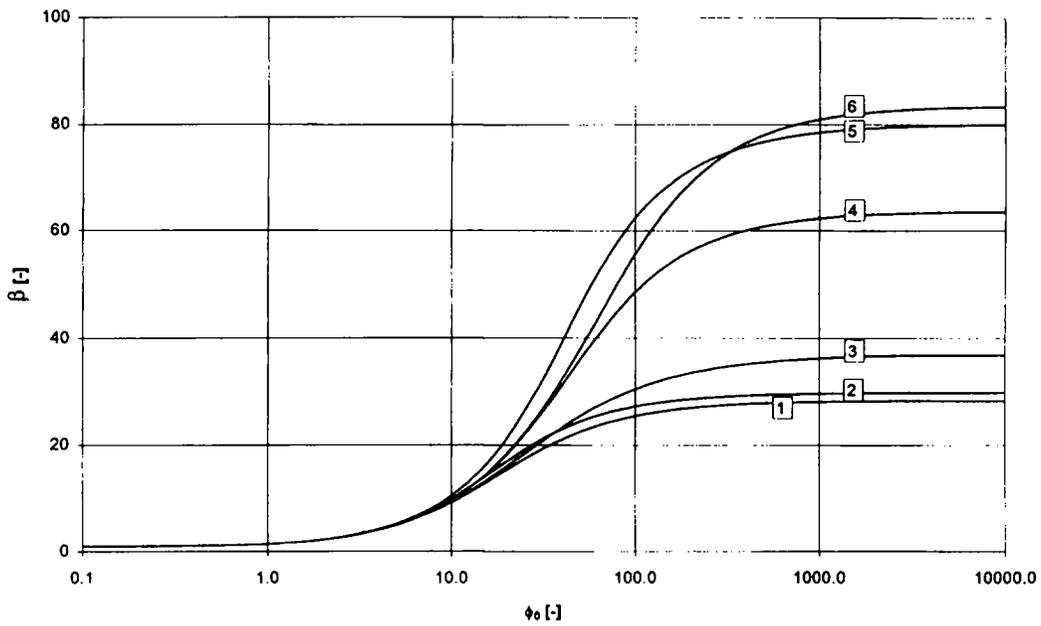
4 and 5: $K = 100$) results in a slightly higher value of β_∞. The explanation for this observation is similar to that seen for bimolecular irreversible reactions. Since χ for these simulations is large ($\chi = 100$), the value of β_∞ is mainly affected by ε_{DB} rather than the mobility of A. At lower

ϕ_0 numbers, a greater enhancement is observed for higher values of ε_{DA}. In this regime the rate of reaction is less than the rate of transfer of A into the penetration depth so that the concentration of A near the interface is high. Here, a change in ε_{DA}, and hence in the mobility of A, will

have a stronger effect as compared to that in the infinite enhancement regime.

• Keeping ε_{DA} at zero and increasing the other $\varepsilon_{Di\,(i=B,C,D)}$ to 4 has a much larger influence on the enhancement (compare cases 1 and 3: $K = 10$ and cases 4 and 6: $K = 100$).The explanation for this sharp increase in enhancement is the same as that in Section 5.2.1. Increase in mobility of C and D transports it faster into the liquid bulk while reactant B is transferred faster into the penetration depth. In order to maintain the equilibrium constraint, concentration of A in the penetration depth falls and, correspondingly, the enhancement increases. It is interesting to compare β_x for case 3 (Table 5) with the case when diffusivity of A is temperature dependent (Fig. 6; case 2). A slightly lower enhancement is observed for $\varepsilon_{DA} = 0$. For both cases, the physical flux under isothermal conditions will be identical. However, the greater mobility of A for $\varepsilon_{DA} = 4$ (Fig. 6; case 2) will result is a marginally higher chemical flux as compared with the case with $\varepsilon_{DA} = 0$. Thus, the value of β will be slightly higher for temperature dependent diffusivity of A.

The temperature dependence of diffusivity of component B is varied independently of the diffusivities of the other components in Fig. 8. Input parameters for the various cases are given in Table 4. The following points are of interest

• Keeping the diffusivities of all other components equal to zero an increase in the value of ε_{DB} results in an increase in enhancement. This increase is greater at higher values of the equilibrium constant (compare cases 1 and 2: $K = 10$ and cases 4 and 5: $K = 100$). As has been explained earlier, the increase in enhancement is due to the greater mobility of B at higher values of ε_{DB}. With an increase in the equilibrium constant, the reaction becomes more irreversible. Under these conditions and with a high initial stoichiometric concentration of B ($\chi = 100$), the enhancement is mainly determined by the mobility of B. Thus at higher values of K, ε_{DB} has a greater influence on enhancement.

• For both values of K, increasing the activation energy of all components while keeping $\varepsilon_{DB} = 0$ results in a higher value of β as compared to increasing the value of ε_{DB} only (compare cases 3 and 2: $K = 10$ and cases 6 and 5: $K = 100$). Making the diffusivities of components A, C and D dependent on temperature increases their mobility with temperature rise. C and D move faster from the penetration depth towards the bulk of the liquid, thereby reducing their average concentration in the penetration depth. This, in turn, reduces the rate of the backward reaction. The reduced backward reaction combined with a higher mobility of A result in higher values of β over the range of ϕ_0 numbers as compared to

the case when only the diffusivity of component B is temperature dependent. The influence of diffusivities of C and D on enhancement will be lower as the equilibrium constant is increased as the reaction becomes more irreversible in nature and the enhancement is mainly determined by the mobility of B. This is confirmed by comparing the values of β_x for $K = 10$ (Table 5: cases 2 and 3) with those for $K = 100$ (Table 5: cases 5 and 6).

In Fig. 9, the temperature dependence of diffusivities of both A and B are kept identical and are varied independent of the diffusivities of components C and D. The following points can be observed

• Increasing both ε_{DA} and ε_{DB} results in a slightly higher value of β_x as compared to the case when only ε_{DB} is increased (Table 5: compare case 2, Fig. 8 with case 2, Fig. 9). As explained earlier, this slight increase in the value of β is on account of the additional mobility of A caused by the temperature dependence of its diffusivity.

• Before infinite enhancement has been reached, the value of β is greater for the case when the diffusivities of only A and B are temperature dependent as compared to when only diffusivities of C and D are temperature sensitive (compare cases 2 and 3: $K = 10$ and cases 5 and 6: $K = 100$). Before infinite enhancement has been reached ($10 < \phi_0 < 100$), the overall mass transfer behavior is determined by the forward reaction, eq. (28b). The amount of components C and D formed in the penetration depth is not sufficient to cause the backward reaction [eq. (28b)] to influence mass transfer. Consequently, increasing the mobility of components A and B will have a stronger influence on the value of β than an increase in the mobility of C and D.

• Once infinite enhancement has been reached ($\phi_0 \geq 10^4$), the value of β_x is greater for the case when diffusivities of only C and D are temperature dependent, rather than for the case when only A and B are temperature dependent (Table 5: compare cases 2 and 3: $K = 10$ and cases 5 and 6: $K = 100$). Increasing the mobility of C and D causes the concentrations of these components in the penetration depth to reduce. In order to maintain the equilibrium constraint the concentration of A near the interface also reduces resulting in a higher value of β. The temperature dependence of C and D has a larger effect on the β_x than for temperature dependence of only A and B. This effect is smaller at higher equilibrium constants as the reaction becomes increasingly irreversible so that the effect of the diffusivity of the products on β reduces.

6. CONCLUSIONS

A fundamental description of non-isothermal mass transfer accompanied by reversible chemical reaction has been presented. The description is based on the

Higbie penetration theory. The temperature dependence of solubility, reaction rates and diffusivity has been assumed to be Arrhenius type of functions. The model has been verified by comparing the non-isothermal enhancement factor and interfacial temperature rise with analytical and numerical solutions available in literature for reactions of simpler stoichiometries.

For bimolecular irreversible reactions, it has been shown that the Shah criterion fails under conditions where depletion of the liquid reactant, B, occurs. The interfacial temperature rise and non-isothermal enhancement factor are no longer only dependent on the lumped parameter, ε_{EFF}, but also on the transport of B, determined by ε_{DB}. According to Evans and Selim (1990), the parameters ε_{EFF} and ε_{DB} are sufficient to describe the non-isothermal behavior of bimolecular irreversible reactions. This claim is true under conditions of high initial stoichiometric concentrations of B and low ϕ_0. In this regime, the reaction may be approximated as a pseudo first-order reaction. In the infinite enhancement regime, enhancement depends on the temperature dependence of solubility and the transport properties (in addition to the diffusivity ratio, r_A, and initial stoichiometric concentration ratio, χ). For a high χ, enhancement is a function of χ, r_A and ε_{DB} while for equimolar χ, enhancement is dependent on χ, r_A, ε_{DS}, ε_{DA} and ε_{DB}. These findings are similar to those reported by Asai et al. (1985). In addition, it has been shown that, for bimolecular irreversible reactions, solutions for interfacial temperature rise that assume all heat to be released at the interface are not valid for low Le numbers but also for systems with low concentration ratios, χ. For such systems, the interfacial temperature rise would depend on the heat ratio, H. However, the error in determining the enhancement factor, assuming that all heat is released at the interface, is negligible.

As observed in the case of isothermal reversible reactions, for the non-isothermal reactions, the enhancement and temperature rise over the penetration depth are higher for higher values of the equilibrium constant. Temperature dependent solubility causes the enhancement [as defined in eq. (19a)] to reduce with temperature rise. This reduction is found to be greater at higher K values. The infinite enhancement factor is dependent on the activation energies of solubility and diffusivities of all components. At lower values of K, the temperature dependence of the diffusivities of the products, C and D, has a greater influence on the value of β_i than at higher values of K where the irreversible character of the reaction is increased. It is not possible to use an analytical or approximate correlation to determine the value of the infinite enhancement factor for non-isothermal reversible bimolecular reaction and one has to take recourse of numerical techniques for this purpose.

NOTATION

a	thermal diffusivity, $m^2 s^{-1}$
c	concentration, $mol\ m^{-3}$
c_p	specific heat of the liquid phase, $J\ kg^{-1}\ K^{-1}$
$\#C$	number of components, dimensionless
D	diffusion coefficient, $m^2 s^{-1}$
E_A	isothermal enhancement factor, dimensionless
h_G	gas phase heat transfer coefficient, $W\ m^{-2}\ K^{-1}$
H	heat ratio, dimensionless
Ha	Hatta number (isothermal), dimensionless
ΔH_R	heat of reaction, $J\ mol^{-1}$
ΔH_S	heat of solution, $J\ mol^{-1}$
I_0, I_1	Bessel functions, dimensionless
J	absorption flux, $mol\ m^{-2}\ s^{-1}$
k_1	reaction rate constant (first-order), s^{-1}
$k_{1,1}$	reaction rate constant, $m^3\ mol^{-1}\ s^{-1}$
k_G	gas phase mass transfer coefficient, $m\ s^{-1}$
k_L	liquid phase mass transfer coefficient, $m\ s^{-1}$
Le	Lewis number (a/D), dimensionless
m	distribution coefficient, dimensionless
p_j	production rate by reaction j, $mol\ m^{-3}\ s^{-1}$
r_A	diffusivity ratio D_A/D_B, dimensionless
$\#R$	number of reactions, dimensionless
$R_{l,j}$	production rate of component l by reaction j, $mol\ m^{-3}\ s^{-1}$
t	time coordinate, s
T	temperature, K
x	place coordinate, m

Greek letters

β	non-isothermal enhancement factor, dimensionless
β_i	infinite non-isothermal enhancement factor, dimensionless
ε	energy of activation (dimensionless E/RT_0), dimensionless
ϑ	interface temperature rise, K
λ	thermal conductivity of the liquid phase, $J\ m^{-1}\ s^{-1}\ K^{-1}$
ν	stoichiometric constant, dimensionless
ρ	density of the liquid phase, $kg\ m^{-3}$
ϕ_0	Hatta number (non-isothermal), dimensionless
χ	concentration ratio, dimensionless
Ψ	dimensionless adiabatic temperature rise, dimensionless
Ψ_{EFF}	effective dimensionless adiabatic temperature rise, dimensionless

Subscripts

0	initial value
A, B, C, D	component A, B, C and D
b	backward
bulk	bulk value
D	Danckwerts' solution
EFF	effective value
f	forward
G	gas phase
j	reaction j
k	component k

ℓ	component ℓ
(R)	reaction
(S)	solution
X	physico-chemical property X

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