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Shorter Communications

Selectivity of consecutive—zero order followed by first order—reaction sequence

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In a recent paper[1], Blackmore *et al.* have considered the selectivity of reaction schemes of type II and III (Wheeler's classification) in which one of the reactions takes place by a zero order reaction mechanism. Their analysis of the reaction scheme

$$A \xrightarrow{k_0} B \xrightarrow{k_1} C \tag{1}$$

where species A reacts by a zero order mechanism and species B by a first order mechanism is subject to a conceptual error. While they correctly recognise the possibility of the concentration of A reducing to zero at some position x_s within the catalyst slab (see Fig. 2 of [1]), they exclude the possibility of B reacting to produce C in the interval $0-x_s$; there is of course no reason why B should not react in this zone. It is the purpose of this communication to present a correct analysis of the reaction scheme (1) taking into account both intra and inter-particle diffusional resistances. Blackmore *et al.* only take account of intraparticle diffusion effects and have analysed the flab slab geometry; here both the flat slab and the spherical pellet are considered. The problem has been analysed conveniently in terms of non-dimensional variables.

ANALYSIS OF REACTION IN A FLAT SLAB

Consider the reaction sequence (1) taking place in a flat slab of half thickness L. The process of diffusion with chemical reaction can be characterised by the following differential equations, written in dimensionless form,

$$\frac{d^2a}{d\xi^2} = \phi_0^2 \qquad |\lambda \leqq \xi \leqq 1| \tag{2}$$

$$\frac{d^2a}{d\xi^2} = 0 \qquad |0 \leqq \xi \leqq \lambda| \tag{3}$$

$$\frac{d^2b}{d\xi^2} = -\phi_0^2 + \phi_1^2 b \qquad |\lambda \leqq \xi \leqq 1| \tag{4}$$

$$\frac{d^2b}{d\xi^2} = \phi_1^2 b \qquad |0 \leqq \xi \leqq \lambda| \tag{5}$$

where the following dimensionless variables have been defined

$$a = A/A_b; \quad b = B/A_b; \quad c = C/A_b; \quad \xi = x/L; \quad \lambda = x_s/L;$$

$$\phi_0^2 = \frac{k_0 L^2}{D_e A_b}; \quad \phi_1^2 = \frac{k_1 L^2}{D_e}. \tag{6}$$

The boundary conditions are

$$\text{at } \xi = 0, \qquad \frac{db}{d\xi} = \frac{dc}{d\xi} = 0 \tag{7}$$

and

$$\text{at } \xi = 1, \qquad \frac{da}{d\xi} = Sh(1-a); \quad \frac{db}{d\xi} = Sh(b_b - b);$$

$$\frac{dc}{d\xi} = Sh(c_b - c) \tag{8}$$

where $Sh = k_m L/D_e$.

The concentration of A will fall to zero at some position within the slab when the modulus ϕ_0 exceeds a critical value given by (the derivation of this relationship is given by Ramachandran and Krishna[2])

$$\phi_{0c} = \left(\frac{2}{1+2/Sh}\right)^{1/2}. \tag{9}$$

The position λ at which the concentration of A falls to zero is then obtained as ([2])

$$\lambda = 1 + 1/Sh - [1/(Sh)^2 + 2/\phi_0^2]^{1/2}, \quad |\phi_0 \geqq \phi_{0c}|. \tag{10}$$

At the position λ we must have the condition

$$\text{at } \xi = \lambda, \quad a = 0 \quad \text{and} \quad \frac{da}{d\xi} = 0 \tag{11}$$

but the composition gradients of B and C will not be zero, as assumed by Blackmore *et al.*; we must have

$$\left.\frac{db}{d\xi}\right|_{\xi=\lambda-} = \left.\frac{db}{d\xi}\right|_{\xi=\lambda+}; \quad \left.\frac{dc}{d\xi}\right|_{\xi=\lambda-} = \left.\frac{dc}{d\xi}\right|_{\xi=\lambda+} \tag{12}$$

where we match the composition gradients at the plane $\xi = \lambda$. We must have in addition, of course, matching of compositions at this plane:

$$b|_{\xi=\lambda-} = b|_{\xi=\lambda+}; \quad c|_{\xi=\lambda-} = c|_{\xi=\lambda+}. \tag{13}$$

Solution of the differential eqns (2)–(5) with the boundary conditions (7) and (8) and the additional conditions at the plane $\xi = \lambda$, eqns (11)–(13), yields the following composition profiles and gradients for species A, B and C:

Concentration profile for species A

$$a = \frac{\phi_0^2}{2}(\xi - \lambda)^2 \quad |\lambda \leqq \xi \leqq 1| \tag{14}$$

$$a = 0 \qquad |0 \leqq \xi \leqq \lambda| \tag{15}$$

$$\left.\frac{da}{d\xi}\right|_{\xi=1} = \phi_0^2(1-\lambda). \tag{16}$$

Concentration profile for species B

$$b = \beta \sinh(\phi_1\lambda)\sinh(\phi_1(\xi-\lambda)) + \left(\beta\cosh(\phi_1\lambda) - \frac{\phi_0^2}{\phi_1^2}\right) \times \cosh(\phi_1(\xi-\lambda)) + \frac{\phi_0^2}{\phi_1^2}, \quad |\lambda \leqq \xi \leqq 1| \tag{17}$$

and

$$b = \beta\cosh(\phi_1\xi) \quad |0 \leqq \xi \leqq \lambda| \tag{18}$$

where

$$\beta = \frac{b_b - \dfrac{\phi_0^2}{\phi_1^2}\left(1 - \cosh(\phi_1(1-\lambda)) - \dfrac{1}{Sh}\phi_1\sinh(\phi_1(1-\lambda))\right)}{\cosh(\phi_1) + \dfrac{1}{Sh}\phi_1\sinh(\phi_1)}. \tag{19}$$

The concentration gradient at the surface of the slab is obtained as

$$\left.\frac{db}{d\xi}\right|_{\xi=1} = \beta\phi_1 \sinh(\phi_1) - \frac{\phi_0^2}{\phi_1^2}\phi_1 \sinh(\phi_1(1-\lambda)). \tag{20}$$

Concentration profile for species C

For the reaction sequence (1) the total molar concentration remains constant and therefore the concentration of species C at any position is obtained from

$$c = 1 + b_b + c_b - a - b \tag{21}$$

and the concentration gradient at the surface is

$$\left.\frac{dc}{d\xi}\right|_{\xi=1} = -\left.\frac{da}{d\xi}\right|_{\xi=1} - \left.\frac{db}{d\xi}\right|_{\xi=1}. \tag{22}$$

For a particular set of values of the parameters $Sh = 50$; $\phi_0 = 3$; $\phi_1 = 3$; $b_b = 0$; $c_b = 0$, the concentration profiles for A, B and C are as shown in Fig. 1. The concentration of A falls to zero at a position $\lambda = 0.5482$, calculated from eqn (10). The important thing to note is that reaction of B to produce C can take place in the zone $0-\lambda$ (contrast Fig. 1 with Fig. 2 of Ref. [1]).

The selectivity of the reaction scheme can be obtained from eqns (16), (20) and (22). Thus the selectivity with respect to B may be calculated from the definition

$$S_B = \frac{\dfrac{db}{d\xi}}{\left.\dfrac{dc}{d\xi}\right|_{\xi=1}}. \tag{23}$$

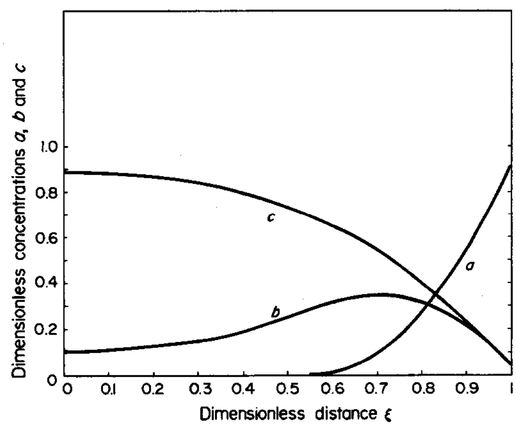

Fig. 1. Concentration profiles for flat plate. $Sh = 50$; $\phi_0 = 3$; $\phi_1 = 3$; $\lambda = 0.5482$; $b_b = 0$; $c_b = 0$.

ANALYSIS OF REACTION IN A SPHERICAL PELLET

The analysis of reaction within a sphere of radius R can be carried out in an analogous manner. The dimensionless variables characterising the diffusion behaviour are:

$$a = A/A_b;\quad b = B/A_b;\quad c = C/A_b;\quad \xi = r/R;\quad \lambda = r_s/R;$$

$$\phi_0^2 = \frac{k_0 R^2}{D_e A_b};\quad \phi_1^2 = \frac{k_1 R^2}{D_e};\quad Sh = \frac{k_m R}{D_e}. \tag{24}$$

The critical value of the modulus ϕ_0, for which the concentration of A falls to zero at the centre of the sphere, is obtained as (see [2] for the derivation)

$$\phi_{0c} = \left(\frac{6}{1 + 2/Sh}\right)^{1/2}. \tag{25}$$

For values of the modulus $\phi_0 \geqq \phi_{0c}$, the concentration of A will fall to zero at some finite position λ within the pellet. This position is determined by the condition (11) and the value of λ is given implicitly by the eqn

$$\frac{\phi_0^2}{6}(1 - 3\lambda^2 + 2\lambda^3) = 1 - \frac{1}{Sh}\frac{\phi_0^2}{3}(1-\lambda^3). \tag{26}$$

The concentration profiles and concentration gradients are obtained as for the flat slab; the results are summarized below.

Concentration profile for species A

$$a = \frac{\phi_0^2}{6}(\xi^2 - 3\lambda^2 + 2\lambda^3/\xi) \quad |\lambda \leqq \xi \leqq 1| \tag{27}$$

and

$$a = 0 \quad |0 \leqq \xi \leqq \lambda|. \tag{28}$$

The concentration gradient of species A at the surface of the pellet is given by

$$\frac{da}{d\xi} = \frac{\phi_0^2}{3}(1-\lambda^3). \tag{29}$$

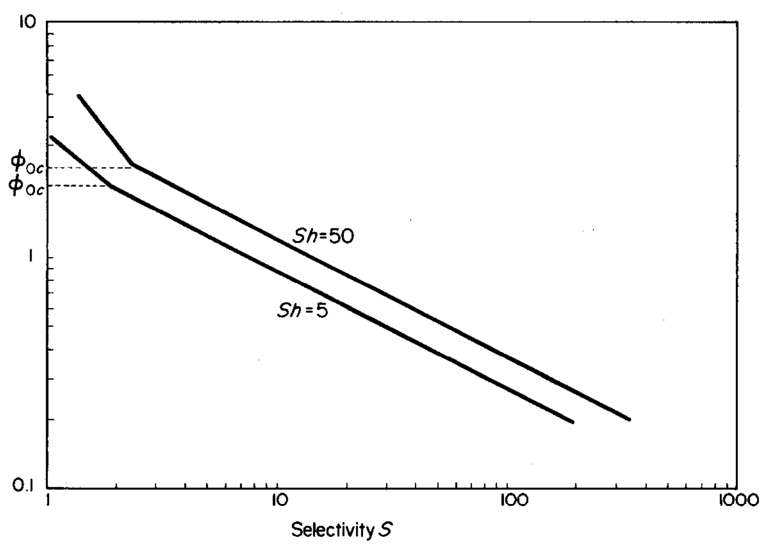

Fig. 2. Effect of Thiele parameter ϕ_0 and external mass transfer parameter Sh on the selectivity of consecutive reaction scheme for sphere. $\phi_0/\phi_1 = 1.0$.

Concentration profile for species B

$$b = \frac{\alpha}{\xi}\sinh(\phi_1\xi) + \frac{\phi_0^2}{\phi_1^2}\left(1 - \frac{\sinh(\phi_1(\xi-\lambda))}{\phi_1\xi} - \frac{\lambda\cosh(\phi_1(\xi-\lambda))}{\xi}\right)$$
$$|\lambda \leqq \xi \leqq 1| \quad (30)$$

and

$$b = \frac{\alpha}{\xi}\sinh(\phi_1\xi) \quad |0 \leqq \xi \leqq \lambda| \quad (31)$$

where α is obtained from

$$\alpha\left(\sinh\phi_1 + \frac{1}{Sh}(\phi_1\cosh\phi_1 - \sinh\phi_1)\right)$$
$$= b_b - \frac{\phi_0^2}{\phi_1^2}\left[1 - \frac{\sinh(\phi_1(1-\lambda))}{\phi_1} - \lambda\cosh(\phi_1(1-\lambda)) - \frac{1}{Sh}\{(1-\lambda)\cosh(\phi_1(1-\lambda)) + \phi_1(\lambda - 1/\phi_1^2)\sinh(\phi_1(1-\lambda))\}\right]. \quad (32)$$

The concentration gradient of B at the surface of the pellet is given by

$$\left.\frac{db}{d\xi}\right|_{\xi=1} \times \left(\sinh\phi_1 + \frac{1}{Sh}(\phi_1\cosh\phi_1 - \sinh\phi_1)\right)$$
$$= b_b(\phi_1\cosh\phi_1 - \sinh\phi_1) - \frac{\phi_0^2}{\phi_1^2}(\phi_1\cosh\phi_1 - \sinh\phi_1 + \sinh\phi_1\lambda - \phi_1\lambda\cosh\phi_1\lambda). \quad (33)$$

The concentration profile and concentration gradient for component C can be obtained by use of eqns (21) and (22) and the selectivity determined from eqn (23).

Figure 2 shows the effect of the zero order Thiele modulus on the selectivity of reaction scheme (1) for a spherical pellet. There is a sharp transition in the selectivity at the critical Thiele modulus ϕ_{0c}. Below the critical value ϕ_{0c}, the selectivity increases in favour of B. Small spherical pellets and large bulk concentrations of A therefore favour the production of B. The effect of external mass transfer resistance, characterised by the modified Sherwood number Sh, is also obtained in Fig. 2; this figure shows that the external mass transfer resistance plays a very important role in determining the selectivity of zero order reactions, especially for values of $\phi_0 \leqq \phi_{0c}$.

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NOTATION

- a dimensionless concentration of species A, $a = A/A_b$
- A concentration of species A inside catalyst
- A_b bulk concentration of species A
- b dimensionless concentration of species B, $b = B/A_b$
- b_b dimensionless concentration of species B in bulk solution, $b_b = B_b/A_b$
- B concentration of species B inside catalyst
- B_b concentration of species B in bulk solution
- c dimensionless concentration of species C, $c = C/A_b$
- c_b dimensionless concentration of species C in bulk solution, $c_b = C_b/A_b$
- C concentration of species C inside catalyst
- C_b concentration of species C in bulk solution
- D diffusion coefficient of species A, B and C in bulk solution, assumed equal for the three species
- D_e effective diffusion coefficient for species A, B and C inside the catalyst particle
- k_0 zero order rate constant
- k_1 first order rate constant
- k_m mass transfer coefficient of species A, B and C in the bulk solution
- L half thickness of flat slab
- r radial distance inside spherical pellet
- r_s distance inside the spherical particle at which the concentration of A falls to zero
- R radius of spherical particle
- S_B selectivity of species B
- Sh modified Sherwood number, $Sh = k_mL/D_e$ for flat slab and $= k_mR/D_e$ for spherical pellet
- x distance from centre of flat slab
- x_s distance from centre of flat slab at which the concentration of A falls to zero

Greek symbols

- α, β arbitrary constants
- ξ dimensionless distance, $\xi = x/L$ for flat slab and $= r/R$ for spherical pellet
- λ dimensionless position, $\lambda = x_s/L$ or $= r_s/R$
- ϕ_0 characteristic Thiele modulus for zero order reaction
- ϕ_1 characteristic Thiele modulus for first order reaction
- ϕ_{0c} critical Thiele modulus for zero order reaction

REFERENCES

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[2] Ramachandran P. A. and Krishna R., Influence of external and internal diffusion on zero order reactions, *J. Appl. Chem. Biotechnol.* to be published.

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Diffusional mass transfer to a growing bubble

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In a supersaturated gaseous solution an initiated bubble will grow as material diffuses from the surroundings to the bubble. At first the growth of the bubble depends very strongly on the inertia, viscosity and surface tension of the surrounding liquid. However, the growth sooner or later becomes limited by the rate at which material can diffuse to the bubble surface. A solution of the diffusion equation alone will then fully describe the growth rate of the bubble. Of the several attempts (see, e.g. Refs. [1–3]) which have been made to obtain a solution, Scriven's[4] similarity solution is the most appropriate and has been recently found[5] to be accurate and applicable.

The asymptotic diffusional bubble growth theory of Scriven and