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## THE COURSE OF CONSECUTIVE REACTIONS INSIDE A NONISOTROPIC CATALYST PARTICLE, AFFECTED BY INTERNAL DIFFUSION

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A system of differential equations for consecutive reactions inside a nonisotropic catalyst particle under conditions of internal diffusion is solved. The system of diffusion equations for the spherical geometry of the catalyst grain is numerically solved by using the collocation method. The solution is sought for various radial activity profiles across the catalyst particle and for various values of Thiele's modulus for the two consecutive reactions. The effect of the reaction orders with respect to the reactants on the degree of utilization of the internal catalyst surface and on the reaction selectivity is examined.

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In technical practice the desired products of catalytic reactions frequently undergo additional, unwanted changes. The processes then bear typical features of consecutive reactions. For increasing the throughput of the equipment, hence, the rate of the reaction leading to the product, active catalysts are conveniently employed. However, increase in the catalyst activity results not only in an increased reaction rate but also in an increased effect of the internal diffusion. When seeking for the optimum yield, it is necessary to assess the effect of the various parameters on the selectivity of the consecutive reactions involved.

The objective of this work was a study of the influence of the radial activity profile, rates of the consecutive reactions, and the internal diffusion on the degree of utilization of the internal catalyst surface effectiveness factor and on the selectivity of the consecutive reactions. A simpler problem has been treated previously<sup>1</sup> for a single irreversible reaction of the first or zeroth order.

Catalyst particles often have a nonisotropic character. A nonuniform distribution of the active component, leading to the occurrence of a radial activity profile across the particle, frequently develops during the impregnation of the inert support with the active component solution<sup>1,2</sup>, or it can also result from the process of gradual deactivation of the catalyst<sup>3</sup>.

### THEORETICAL

For the mathematical modelling purposes the substance is assumed to move through the grain looked upon as a homogeneous material, and Fick's law with a constant

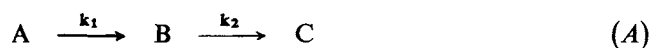
diffusion coefficient of the reaction components is used for the description of the diffusion behaviour<sup>4</sup>. The radial concentration profile of the active component across the catalyst particle is represented by a power function<sup>5</sup>. The reaction rate constant then is dependent on the particle radius as

$$k = k_0 R^\alpha . \quad (1)$$

Different distribution profiles of the rate constant across the catalyst particle then can be modelled by varying the inhomogeneity parameter  $\alpha$ . According to Eq. (1), the profile is nearly uniform for low inhomogeneity parameters ( $\alpha \approx 0.1$ ); for high  $\alpha$  values ( $\alpha \approx 10$ ), on the other hand, the activity profile corresponds to a situation where the active component is located within a thin surface layer near the outer surface of the catalyst grain.

The shape of the concentration profile of the active component across the support is an important property of a support catalyst. By choosing a catalyst with a suitable distribution of the active component, the catalyst activity in the reaction of interest can be improved considerably<sup>6</sup>. For instance, for a fast reaction, where the reaction course is markedly affected by internal diffusion, it is convenient if the active component is as close to the outer grain surface as possible, whereas for a slow reaction, *i.e.*, a reaction with a fast transport of the reaction components, a uniform distribution of the metal across the catalyst grain can be more advantageous<sup>6</sup>.

A system of differential equations describing the system of consecutive reactions



under conditions of internal diffusion is solved in this work for a spherical geometry of the catalyst particle, using the collocation method<sup>1</sup>.

The diffusion of the reaction components for consecutive reactions of the  $n$ -th and  $m$ -th order, respectively, is described by a system of differential equation<sup>5,7</sup> formulated for dimensionless concentrations and radial coordinate  $R$  (see List of Symbols) as

$$(1/R^2)(d/dR)[R^2(dC_A/dR)] = \Theta_A^2 C_A^n R^\alpha \quad (2)$$

$$(1/R^2)(d/dR)[R^2(dC_B/dR)] = \Theta_B^2 (K C_B^m - C_A^n) R^\alpha . \quad (3)$$

The boundary conditions are

$$dC_A/dR = dC_B/dR = 0 \quad (R = 0) \quad (4)$$

$$C_A = 1, \quad C_B = 0 \quad (R = 1) . \quad (5)$$

Thiele's moduli for components A and B can be written<sup>7</sup> as

$$\Theta_A^2 = R^2 k_1 / D_A \quad (6)$$

$$\Theta_B^2 = R^2 k_2 / D_B \quad (7)$$

In this treatment, the two diffusion coefficients will be put mutually equal ( $D_A = D_B$ ).

## CALCULATIONS

### *Concentration Profile of Component A*

Suppose that the first reaction,  $A \rightarrow B$ , is first order. The collocation method is based on the assumption that the concentration profile across the catalyst particle can be solved in a polynomial form. Due to the spherical symmetry of the particle, the solution of the equation can be expected to be an even function; hence, a polynomial with even powers of coordinate  $R$  can be considered. For instance, for component A we have

$$C_A(R) = A_0 + A_2 R^2 + A_4 R^4 + A_6 R^6 + A_8 R^8, \quad (8)$$

which satisfies the diffusion equation in four chosen collocation points within the interval  $R_i \in \langle 0; 1 \rangle$ . The polynomial chosen also meets the two boundary conditions. The coefficients,  $A_0, A_2, \dots, A_8$ , are to be determined. Let us substitute the  $C_A(R)$  polynomial in differential equation (2):

$$(1/R^2) [2R(dC_A/dR) + R^2(d^2C_A/dR^2)] = \Theta_A^2 R^\alpha C_A \quad (9)$$

The residue of the differential equation be  $Q(R)$ :

$$Q(R) = (d^2C_A/dR^2) + (2/R)(dC_A/dR) - \Theta_A^2 R^\alpha C_A \quad (10)$$

Now, suppose that  $C_A(R)$  is the exact solution of the differential equation in a finite number of selected points characterized by coordinates  $R$ ; then the residue must be zero for all the  $R$  values, hence, in all collocation points.

Applying the collocation method to our problem we demand that residue (10) of the differential equation be zero in the preselected points with the coordinates  $R_1 = 0.2, R_2 = 0.4, R_3 = 0.6, R_4 = 0.8$ . Four linear equations of the form

$$Q(R_i) = 0 \quad (i = 1 \text{ through } 4) \quad (11)$$

follow from this for the determination of the coefficients  $A_0$  through  $A_8$ . The fifth

equation for the unknown coefficients of the polynomial,

$$A_0 + A_2 + A_4 + A_6 + A_8 = 1 \quad (12)$$

follows from boundary condition (5).

By solving this system of linear equations, the  $A$ 's, and thus an approximate solution of Eq. (2), are obtained.

Polynomial (8) can be readily differentiated:

$$(dC_A/dR) = 2A_2R + 4A_4R^3 + 6A_6R^5 + 8A_8R^7 \quad (13)$$

$$(d^2C_A/dR^2) = 2A_2 + 12A_4R^2 + 30A_6R^4 + 56A_8R^6. \quad (14)$$

Substituting Eqs (13), (14) in differential equation (9) we obtain the general system of linear equations (11) in the form

$$\begin{aligned} &(-\Theta_A^2 R_i^\alpha) A_0 + (6 - \Theta_A^2 R_i^{2+\alpha}) A_2 + (20R_i^2 - \Theta_A^2 R_i^{4+\alpha}) A_4 + \\ &+ (42R_i^4 - \Theta_A^2 R_i^{6+\alpha}) A_6 + (72R_i^6 - \Theta_A^2 R_i^{8+\alpha}) A_8 = 0 \quad (i = 1 \text{ through } 4). \end{aligned} \quad (15)$$

This, together with the boundary condition (12), forms a system of five linear equations for the collocation points chosen.

#### Concentration Profile of Component B

The concentration profile for substance B across the catalyst particle will be approximated by the same polynomial as for substance A,

$$C_B(R) = B_0 + B_2R^2 + B_4R^4 + B_6R^6 + B_8R^8. \quad (16)$$

Its first and second derivatives are

$$dC_B/dR = 2B_2R + 4B_4R^3 + 6B_6R^5 + 8B_8R^7 \quad (17)$$

$$d^2C_B/dR^2 = 2B_2 + 12B_4R^2 + 30B_6R^4 + 56B_8R^6. \quad (18)$$

Substituting these derivatives and the solution for the concentration profile for component A in Eq. (3), we obtain the following system of linear equations in  $B_0, B_2, \dots, B_8$  for the two consecutive 1st order reactions:

$$\begin{aligned} &(\Theta_B^2 R_i^\alpha K) B_0 + (\Theta_B^2 R_i^{2+\alpha} K - 6) B_2 + (\Theta_B^2 R_i^{4+\alpha} K - 20R_i^2) B_4 + \\ &+ (\Theta_B^2 R_i^{6+\alpha} K - 42R_i^4) B_6 + (\Theta_B^2 R_i^{8+\alpha} K - 72R_i^6) B_8 = \Theta_B^2 R_i^\alpha C_A(R_i). \end{aligned} \quad (19)$$

This equation is solved for the chosen collocation points together with the boundary condition (5), from which the supplementary equation (20) follows:

$$B_0 + B_2 + B_4 + B_6 + B_8 = 0. \quad (20)$$

In this manner a system of linear equations is obtained, describing the concentration profile of component B across the catalyst particle for consecutive 1st order reactions.

Now, assume that the first reaction is zeroth order and the second reaction is first order; then, substituting  $n = 0$  and  $m = 1$  in the system of equations (2) and (3), the numerical form of the equations is

$$6A_2 + 20R_1^2 A_4 + 42R_1^4 A_6 + 72R_1^6 A_8 = \Theta_A^2 R_1^\alpha \quad (21)$$

$$\begin{aligned} & (\Theta_B^2 R_1^\alpha K) B_0 + (\Theta_B^2 R_1^{2+\alpha} K - 6) B_2 + (\Theta_B^2 R_1^{4+\alpha} K - 20R_1^2) B_4 + \\ & + (\Theta_B^2 R_1^{6+\alpha} K - 42R_1^4) B_6 + (\Theta_B^2 R_1^{8+\alpha} K - 72R_1^6) B_8 = \Theta_B^2 R_1^\alpha. \end{aligned} \quad (22)$$

Similarly, for the reaction order combination  $n = 1$ ,  $m = 0$  the collocation method leads to a system of equations of which the first is described by a relation identical with Eq. (15), the second can be written in a general form as

$$6B_2 + 20R_1^2 B_4 + 42R_1^4 B_6 + 72R_1^6 B_8 = \Theta_B^2 R_1^\alpha (K - C_A(R_1)). \quad (23)$$

If both consecutive reactions are zeroth order, the solution of the diffusion equations simplifies appreciably. Relations describing the linear equations system for the unknown  $A$ 's and  $B$ 's, in a general collocation point  $R_i$ , can be written as

$$6A_2 + 20R_1^2 A_4 + 42R_1^4 A_6 + 72R_1^6 A_8 = \Theta_A^2 R_1^\alpha \quad (24)$$

$$6B_2 + 20R_1^2 B_4 + 42R_1^4 B_6 + 72R_1^6 B_8 = \Theta_B^2 R_1^\alpha (K - 1). \quad (25)$$

In this work, all the systems of linear algebraic equations obtained by solving the system of diffusion equations (2) and (3) for zeroth and first order reactions, including the boundary conditions (4) and (5) (*i.e.*, supplemented by Eqs (12) and (20)) were solved by the matrix inversion method.

#### *Effectiveness and Selectivity Factors*

By finding all  $A$ 's in polynomial (8) and all  $B$ 's in polynomial (16), the concentration profiles of reactants inside a catalyst particle can be determined and used for the calculation of the effectiveness factor<sup>4</sup>,

$$\eta = r/r_{\text{kin}} = (3 + \alpha) \int_0^1 (C_A - KC_B) R^{2+\alpha} dR. \quad (26)$$

Analytical expression of this integral leads to a finite algebraic equation,

$$\eta = (A_0 - B_0K)/(3 + \alpha) + (A_2 - B_2K)/(5 + \alpha) + (A_4 - B_4K)/(7 + \alpha) + (A_6 - B_6K)/(9 + \alpha) + (A_8 - B_8K)/(11 + \alpha). \quad (27)$$

The selectivity for the reaction pathway (A) is defined as <sup>7,8</sup>

$$S = \int_0^1 (C_A - KC_B) R^{2+\alpha} dR / \int_0^1 C_A R^{2+\alpha} dR; \quad (28)$$

in this expression, the integrals can be evaluated and the equation can be rearranged in the form

$$S = [(A_0 - B_0K)/(3 + \alpha) + (A_2 - B_2K)/(5 + \alpha) + (A_4 - B_4K)/(7 + \alpha) + (A_6 - B_6K)/(9 + \alpha) + (A_8 - B_8K)/(11 + \alpha)] / [A_0/(3 + \alpha) + A_2/(5 + \alpha) + A_4/(7 + \alpha) + A_6/(9 + \alpha) + A_8/(11 + \alpha)]. \quad (29)$$

The diffusion equations system (2), (3) was solved numerically on a Hewlett-Packard 9835A computer for various combinations of Thiele's modulus  $\Theta_A$ , inhomogeneity parameter  $\alpha$ , rate constant ratio  $K$ , and reaction orders  $m$  and  $n$ .

## RESULTS

### *Conditions of Solvability of the Problem*

The solvability of the system of diffusion equations for the reaction pathway (A) involving first and zeroth order reactions is constrained by certain input data values which were determined empirically. The constraints given by the use of the collocation approach are lowest for first order reactions. The system of diffusion equations is solvable for the entire region of  $K$  within which the solution was sought,  $0.001 \leq K \leq 100$ . There are some limitations for the combinations of  $\alpha$  and  $\Theta_A$ : at  $\alpha < 0.5$  the system is solvable up to  $\Theta_A = 20$ , and at  $\alpha > 0.5$  the system can be solved for  $\Theta_A < 50$ .

For the two reactions of zeroth order, the system of diffusion equations is solvable within the limited region of Thiele's modulus values of  $\Theta_A < 5$ . An additional restriction was found for the rate constant ratio  $K$ ; the collocation method is only applicable at  $K \leq 1$ , the concentration profile of substance B being zero and selectivity, unity at  $K = 1$ .

For solving the system of diffusion equations describing the consecutive reactions with  $n = 0$ ,  $m = 1$ ,  $K$  can be chosen within the entire region examined,  $0.001 \leq K \leq$

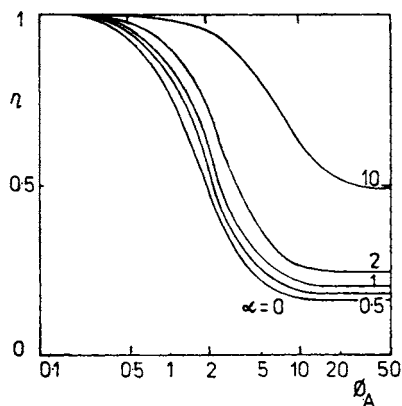


FIG. 1

Effect of the inhomogeneity parameter on the dependence of the effectiveness factor on Thiele's modulus for  $K = 2$ ,  $m = 1$ ,  $n = 1$

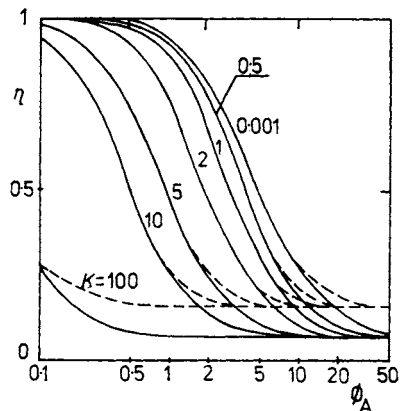


FIG. 2

Effect of the rate constant ratio and number of collocation points on the dependence of the effectiveness factor on Thiele's modulus;  $\alpha = 0$ ,  $m = 1$ ,  $n = 1$ . Solution for 9 collocation points (—) and for 4 collocation points (-----)

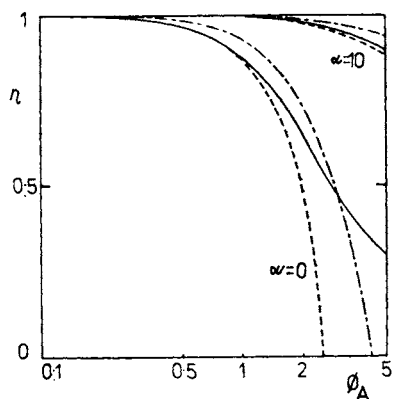


FIG. 3

Effect of the reaction orders on the dependence of the effectiveness factor on Thiele's modulus at  $K = 1$ . -----  $n = 0$ ,  $m = 1$ ; - · - · -  $n = 1$ ,  $m = 1$ ; · · · ·  $n = 0$ ,  $m = 0$

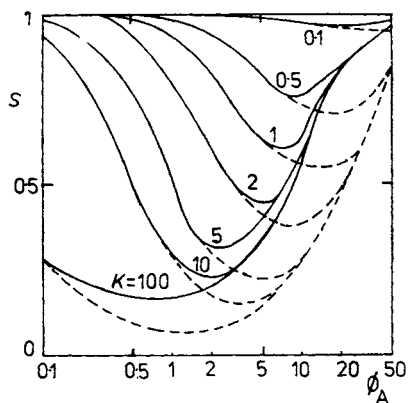


FIG. 4

Effect of the rate constant ratio and number of collocation points on the dependence of selectivity on Thiele's modulus;  $\alpha = 0$ ,  $m = 1$ ,  $n = 1$ . Solution for 9 collocation points (—) and for 4 collocation points (-----)

$\leq 100$ . Reasonable values, however, are only obtained for low Thiele's modulus values,  $\Theta_A < 5$ , similarly as in the preceding case.

The combination  $n = 1, m = 0$  is not tractable by the collocation method as used in this work.

### Effect of Parameters on the Effectiveness Factor

Fig. 1 shows the dependence of the catalyst effectiveness factor,  $\eta$ , on Thiele's modulus  $\Theta$  for various values of the particle inhomogeneity parameter  $\alpha$ . The rate constant ratio for the two 1st order reactions was chosen  $K = 2$ . The nonuniform distribution of the active component inside the catalyst particle, expressed by Eq. (1), affects significantly the relationship between the effectiveness factor and Thiele's modulus. With increasing inhomogeneity of the particle, which corresponds to a situation where the catalyst activity increases in the direction from the particle centre towards the outer surface, the factor increases. This result is consistent with the concept of a better utilization of the active component if the latter is applied in the surface shell of the catalyst particle.

Fig. 2 shows the dependence of the effectiveness factor,  $\eta$ , on Thiele's modulus for various ratios of the rate constants of the two 1st order reactions, calculated for an isotropic spherical particle ( $\alpha = 0$ ). The solutions for four or nine collocation points are also shown; this comparison was made for estimating the effect of the degree of the polynomial on the solution. The internal diffusion effectiveness factor decreases with increasing rate constant ratio  $K$ , whose high values correspond to a si-

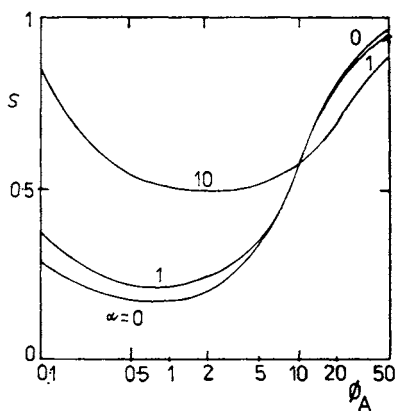


FIG. 5  
Effect of the inhomogeneity parameter on the dependence of selectivity on Thiele's modulus;  $n = 1, m = 1, K = 100$

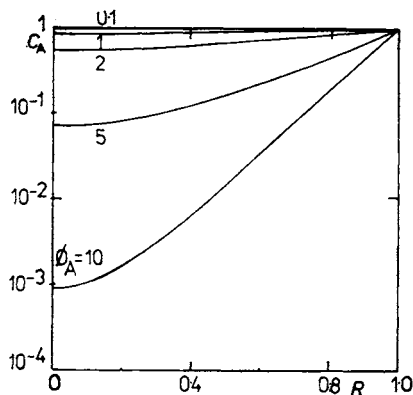


FIG. 6  
Concentration profile of component A across the catalyst grain in dependence on Thiele's modulus;  $\alpha = 0, n = 1, m = 1, K = 10$



tuation where the second reaction in the consecutive reaction chain is preferred. The sensitivity of the  $\eta = f(\Theta_A)$  dependence to the parameter  $K$  is highest at  $\alpha = 0$  and decreases slightly with increasing  $\alpha$ . Fig. 2 also shows that increase in the number of collocation points, chosen symmetrically on the radial coordinate of the catalyst particle, leads to a better fit of the numerical solution to the theory at low values of the effectiveness factor  $\eta$ . For  $\eta > 0.3$ , the solution was found independent of the number of collocation points used.

The character of the dependences discussed is similar for the first and zeroth orders of the consecutive reactions. The effect of the reaction orders on the  $\eta = f(\Theta_A)$  dependence is illustrated by Fig. 3. This dependence is highly susceptible to the reaction order particularly in the region of a strong effect of the internal diffusion on the rate of the process under study. Taking into account the solvability conditions (see above), the effect of the reaction orders  $m, n$  was examined at  $\Theta_A < 5$ . For  $n = 0$  and at  $\Theta > 3$ , the internal diffusion effectiveness factor  $\eta$  decreases to negative values lacking physical meaning; this is due to the error of the method used.

#### *Effect of Parameters on the Consecutive Reactions Selectivity*

In addition to the internal diffusion effectiveness factor, the effect of the various parameters on the selectivity of the consecutive reactions, defined by Eq. (28), was also investigated. The effect of Thiele's modulus on the selectivity is shown in Fig. 4. This dependence is parametrically highly sensitive to the rate constant ratio  $K$ ; it decreases rapidly with increasing  $K$ . The effect of  $K$  on the selectivity is comparable

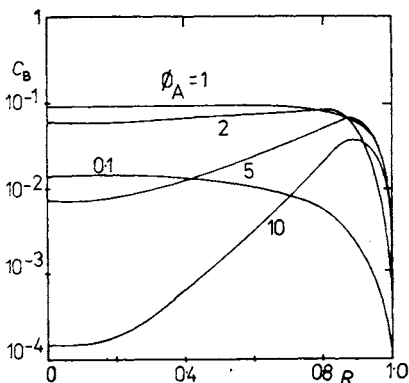


FIG. 7

Concentration profile of component B across the catalyst grain in dependence on Thiele's modulus;  $\alpha = 0, n = 1, m = 1, K = 10$

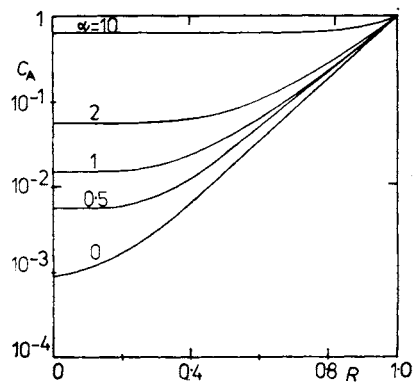


FIG. 8

Effect of the inhomogeneity parameter on the concentration profile of component A;  $\Theta_A = 10, n = 1, m = 1, K = 10$

to that of  $K$  on the dependence  $\eta = f(\Theta_A)$ , plotted in Fig. 2. The effect of increased number of collocation points on the accuracy of the numerical calculation of the effectiveness factor and the selectivity is approximately the same. This effect is appreciable particularly in the region of the strong influence of the internal diffusion. It appeared that the  $\Theta_A K$  product is important for the numerical solution of the diffusion equation system by the method used. Distorted effectiveness factor and selectivity values are obtained at  $\Theta_A K > 10$ ; it is unreasonable from the physical point of view that the dependence of the selectivity on Thiele's modulus should not be monotonically decreasing.

The effect of different activity profiles across the particle on the selectivity is illustrated by Fig. 5; catalysts with a steeper activity profile near the particle surface ( $\alpha \approx 10$ ) provide a higher selectivity of the consecutive reactions.

#### Concentration Profiles of the Reaction Components Across the Catalyst Particle

The concentration differences inside the catalyst particle depend on the ratio of the chemical reaction rate to the diffusion rate. A significant parameter, affecting the concentration profiles of the reaction components, thus is Thiele's modulus  $\Theta_A$  and the related modulus  $\Theta_B$  (the diffusion coefficients  $D_A$  and  $D_B$  are assumed mutually equal). Examples of the effect of Thiele's modulus on the concentration profiles of substances A and B, for 1st order reactions, are shown in Figs 6 and 7, respectively; the concentration gradients are seen to increase with increasing Thiele's modulus values, *i.e.*, with increasing effect of internal diffusion on the reaction process.

The concentration distribution of the starting substance A and the intermediate product B across the catalyst grain is affected markedly by the concentration differences of the active component, expressed by the inhomogeneity parameter  $\alpha$  (Figs 8 and 9); the concentrations increase and the concentration differences for compounds A and B level out as the inhomogeneity parameter increases.

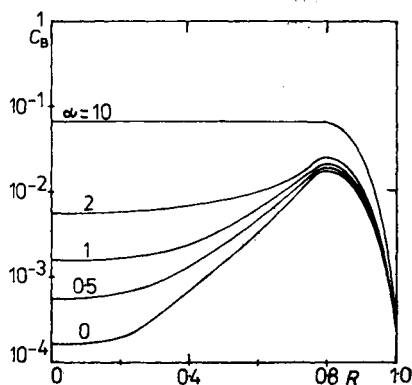


FIG. 9

Effect of the inhomogeneity parameter on the concentration profile of component B;  $\Theta_A = 10$ ,  $n = 1$ ,  $m = 1$ ,  $K = 10$

## CONCLUSIONS

The results obtained show that catalysts with steeper activity profiles near the catalyst particle surface layer exhibit higher values of the effectiveness factor and selectivities for consecutive reactions; the concentration of the reaction components in these catalysts is also higher. The ratio of the rate constants of the two consecutive reactions acts against the effect of the inhomogeneity parameter. In the internal diffusion region both the effectiveness factor and the selectivity in dependence on Thiele's modulus are parametrically highly sensitive to the reaction orders of the consecutive reactions.

This theoretical treatment should now be followed by consecutive reactions selectivity experiments using catalysts with different radial distribution of activity or the active component.

## LIST OF SYMBOLS

$A_i$	coefficients of polynomial (8)
$B_i$	coefficients of polynomial (16)
$c$	concentration ( $\text{mol m}^{-3}$ )
$c_0$	concentration outside particle ( $\text{mol m}^{-3}$ )
$C$	dimensionless concentration
$C(R)$	concentration profile
$d_p$	catalyst grain diameter (m)
$D$	effective diffusion coefficient ( $\text{m}^2 \text{s}^{-1}$ )
$k$	rate constant
$k_0$	rate constant at $R = 1$
$K$	rate constant ratio
$m$	reaction order with respect to component B
$n$	reaction order with respect to component A
$r$	reaction rate ( $\text{mol kg}^{-1} \text{s}^{-1}$ )
$r_{\text{kin}}$	reaction rate in kinetic regime ( $\text{mol kg}^{-1} \text{s}^{-1}$ )
$R$	dimensionless particle radius
$R_i$	collocation point coordinate
$S$	selectivity
$\alpha$	inhomogeneity parameter
$\eta$	internal diffusion effectiveness factor
$\Theta$	Thiele's modulus, $d_p(k_0 C^{n-1}/D)^{0.5}$

subscripts:

A	reaction component A
B	reaction component B

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