APPARENT KINETICS OF BIMOLECULAR REACTIONS IN STRONG DIFFUSION REGION

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The problem of apparent reaction orders of bimolecular reactions in the presence of strong effect of internal mass transport is discussed. Relations are derived, allowing to calculate the apparent reaction orders in the region of strong diffusion in dependence on the ratio of concentrations and effective diffusivities of reacting components.

With heterogeneously catalyzed chemical reactions on porous catalysts, the influence of mass transport plays a more or less important role. Internal diffusion not only diminishes the effectivity factor but also changes the apparent reaction orders with respect to individual reaction components as well as the overall reaction order. Problems concerning the effectivity factor of bimolecular reactions were discussed by several authors[1-3]. The influence of internal diffusion on the monomolecular reaction order was studied by Satterfield and Sherwood[4] and Tartarelli and Morelli[5]. The influence of internal diffusion and various forms of poisoning of the catalyst on the bimolecular reaction order was analyzed by us[6]. The apparent kinetics of second-order bimolecular reaction on a macro-microporous catalyst was studied by Tartarelli and coworkers[7].

The aim of the present work was the analysis of apparent orders with respect to individual reaction components during a reaction of two compounds in a strong diffusion region, where an asymptotic solution can be used and certain relationships can be expressed analytically.

THEORETICAL

We shall consider a chemical reaction of the type A + B → products without a change of the number of mol, which proceeds isothermally in a catalyst particle in the form of an infinite plate. We assume that the reaction kinetics can be described by the power equation $R = k p_A^\alpha p_B^\beta$ and that the concentration and temperature gradients between the bulk phase and catalyst surface can be neglected. The course of the chemical reaction is then described by the differential equation of mass balance in the dimensionless form

$$\mathrm{d}^2\psi/\mathrm{d}\xi^2 - \Phi^2 \mathrm{f}(\psi, G) = 0, \qquad (1)$$

where $G = p_{A0} D_A / p_{B0} D_B$ and $\Phi = L(\varrho_k R T k p_{A0}^{\alpha-1} p_{B0}^\beta / D_A)^{1/2}$. The boundary condi-

tions are $\xi = 1, \psi = 1; \xi = 0, \mathrm{d}\psi/\mathrm{d}\xi = 0$. The partial pressures p_A and p_B are related to each other by the mass balance $p_B = p_{B0} + (D_A/D_B)(p_A - p_{A0})$ so that the term $\mathrm{f}(\psi, G)$ in Eq. (1) can be expressed as

$$\mathrm{f}(\psi, G) = \psi^\alpha [1 + G(\psi - 1)]^\beta . \tag{2}$$

The nonlinear differential equation (1) must be solved in the general case numerically. An asymptotic solution for the case of a strong influence of internal diffusion can be found by an analogous method as used by Petersen[8]. To determine the concentration gradient at the catalyst surface and from this the effectivity factor, the knowledge of the dimensionless partial pressure ψ_0 in the center of the plate is needed. This can be determined from the asymptotic solution for the case of a strong influence of internal diffusion, where the rate of chemical reaction in the center of the plate drops to zero owing to exhaustion of one of the reaction components. Then $\Phi^2 \mathrm{f}(\psi, G) = 0$, whence

$$\psi_0 = 0 \quad \text{for} \quad G \leqq 1, \quad \psi_0 = (G - 1)/G \quad \text{for} \quad G \geqq 1 . \tag{3}$$

The asymptotic value of the effectivity factor in the strong diffusion region can be expressed as

$$\eta = -\Phi^{-2}(\mathrm{d}\psi/\mathrm{d}\xi)_{\xi=1} = (\sqrt{2}/\Phi)[\mathrm{F}(G)]^{1/2} . \tag{4}$$

As was shown in the work[6], the apparent orders with respect to individual reaction components under the influence of internal diffusion are

$$\bar{\alpha} = \alpha + \tfrac{1}{2}(\alpha - 1)(\partial \ln \eta/\partial \ln \Phi)_G + (\partial \ln \eta/\partial \ln G)_\Phi ,$$
$$\bar{\beta} = \beta + \tfrac{1}{2}\beta(\partial \ln \eta/\partial \ln \Phi)_G - (\partial \ln \eta/\partial \ln G)_\Phi . \tag{5}$$

Since

$$(\partial \ln \eta/\partial \ln G)_\Phi = \tfrac{1}{2}\mathrm{d} \ln \mathrm{F}(G)/\mathrm{d} \ln G = \tfrac{1}{2}[G/\mathrm{F}(G)]\,\mathrm{F}'(G) \tag{6}$$

and in a strong diffusion region $\partial \ln \eta/\partial \ln \Phi \to -1$, then

$$\bar{\alpha} = \tfrac{1}{2}(\alpha + 1) + \tfrac{1}{2}(\mathrm{d} \ln \mathrm{F}/\mathrm{d} \ln G) ,$$
$$\bar{\beta} = \tfrac{1}{2}\beta - \tfrac{1}{2}(\mathrm{d} \ln \mathrm{F}/\mathrm{d} \ln G) . \tag{7}$$

The function $\mathrm{F}(G)$ is obtained by integration of the rate term (2)

$$\mathrm{F}(G) = \int_{\psi_0}^{1} \psi^\alpha [1 + G(\psi - 1)]^\beta \, \mathrm{d}\psi , \tag{8}$$

where $\psi_0 = 0$ for $G \leqq 1$ and $\psi_0 = (G - 1)/G$ for $G \geqq 1$. The integral (8) can be

expressed analytically by elementary functions if any of the numbers α, β and $\alpha + \beta$ is an integer; in other cases it has to be calculated numerically[9]. The same applies for differentiation of the function $F(G)$.

Analytical expressions for $F(G)$ and its derivative for $\beta = 1$ and 2 (α arbitrary) are in Table I. From known values of $\partial \ln F/\partial \ln G$, the apparent orders for the case of a strong influence of internal diffusion and for a given G value can be determined with the aid of Eq. (7).

DISCUSSION

The apparent reaction orders $\bar{\alpha}$ and $\bar{\beta}$ for $\beta = 1$ and 2 in dependence on G for various values of α are plotted in Figs 1 and 2. The parameter G involves the influence of the ratio of partial pressures of the substances A and B in the bulk phase as well as the influence of their different effective diffusivities. It is equal to the ratio of maximum possible rates of diffusion transport of both reaction components into the catalyst

TABLE I

Analytical Expressions for Function $F(G)$ and its Derivative

$F(G)$	$\partial \ln F/\partial \ln G$
$\beta = 1 \quad G \leqq 1$	
$\dfrac{\alpha + 2 - G}{(\alpha + 1)(\alpha + 2)}$	$-\dfrac{1}{2}\dfrac{G}{\alpha + 2 - G}$
$\qquad G \geqq 1$	
$\dfrac{\alpha + 2 - G - (G - 1)^{\alpha + 2}/G^{\alpha + 1}}{(\alpha + 1)(\alpha + 2)}$	$\dfrac{G}{2}\dfrac{-1 + (\alpha + 1 + G)(G - 1)^{\alpha + 1}/G^{\alpha + 2}}{\alpha + 2 - G + (G - 1)^{\alpha + 2}/G^{\alpha + 1}}$
$\beta = 2 \quad G \leqq 1$	
$\dfrac{2G^2 - G(6 + 2\alpha) + \alpha^2 + 5\alpha + 6}{(\alpha + 1)(\alpha + 2)(\alpha + 3)}$	$\dfrac{G(2G - 3 - \alpha)}{2G^2 - G(6 + 2\alpha) + \alpha^2 + 5\alpha + 6}$
$\qquad G \geqq 1$	
$\dfrac{2G^2 - G(6 + 2\alpha) + \alpha^2 + 5\alpha + 6 - 2(G - 1)^{\alpha + 3}/G^{\alpha + 1}}{(\alpha + 1)(\alpha + 2)(\alpha + 3)}$	$\dfrac{G[2G - 3 - \alpha - (\alpha + 2G + 1)(G - 1)^{\alpha + 2}/G^{\alpha + 2}]}{\alpha^2 + \alpha(5 - 2G) + 2G^2 - 6G + 6 - 2(G - 1)^{\alpha + 3}/G^{\alpha + 1}}$

particle. Since the ratio of effective diffusivities is determined by the reacting substances, the value of G can be changed practically only by changing the ratio of partial pressures of both substances in the bulk phase. When G approaches unity, the apparent orders are most sensitive to an excess of any reaction component, this excess causing a decrease of the corresponding reaction order. Since the overall order in the strong diffusion region practically does not change and approaches the value of $\frac{1}{2}(\alpha + \beta + 1)$, the decrease of the apparent order with respect to one component is compensated by an increase of the order with respect to another one. With increasing excess of one component, the corresponding order approaches asymptotically one half of its original value in the kinetic region.

The reaction orders for hydrogenation of benzene in the kinetic and strong diffusion regions found experimentally[10] and calculated from our equations are:

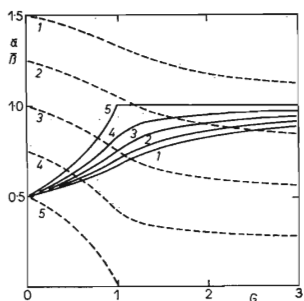| Order	Kinetic region	Strong influence of internal diffusion	
		calculated	found
C_6H_6	0·64	0·82	0·73 — 0·77
H_2	1·00	0·50	0·33

Fig. 1

Dependence of Apparent Orders $\bar{\alpha}, \bar{\beta}$ in Strong Diffusion Region on Parameter G for $\beta = 1$

·········· Apparent order $\bar{\alpha}$, ——— apparent order $\bar{\beta}$. α: *1* 2, *2* 1·5, *3* 1, *4* 0·5, *5* 0·005.
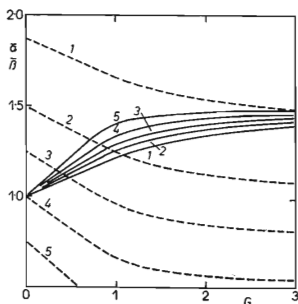

Fig. 2

Dependence of Apparent Orders $\bar{\alpha}, \bar{\beta}$ in Strong Diffusion Region on Parameter G for $\beta = 2$

·········· Apparent order $\bar{\alpha}$, ——— apparent order $\bar{\beta}$. α: *1* 2·75, *2* 2, *3* 1·5, *4* 1, *5* 0·5.

The experiments[10] were performed with an excess of hydrogen and the value of G was 0·016. The agreement between the calculated and measured values of reaction orders is good with benzene but only rough with hydrogen. However, the number of mol undergoes change during the hydrogenation reaction and also adsorption can play a role here, factors which were not considered in our theory. Moreover, our model is based on a simple porous structure of the catalyst.

The equations derived for a plate-shaped catalyst particle apply in the case of a strong influence of internal diffusion also for other geometries since in the strong diffusion region the solution takes asymptotically the form valid for a plate[11]. The results obtained can serve for the purpose of orientation even in the case of a weak influence of internal diffusion where the asymptotical solution of Eq. (1) cannot be used and the accurate determination of apparent orders would require relatively tedious numerical calculations.

In calculations and modelling of chemical reactors, formal kinetic equations obtained from data measured under the influence of internal diffusion are used frequently. However, it has to be taken into account that the results can be distorted owing to a change of apparent orders with changing reaction conditions (especially the ratio of concentrations of the reacting substances). Only when the parameter G is very small or larger than 3 (*i.e.* one substance is in a large excess or the effective diffusivities differ widely from one another), the apparent orders do not change appreciably with the reaction conditions.

LIST OF SYMBOLS

D_i	effective diffusivity of i-th component
G	parameter of Eq. (1) equal to $p_{A0}D_A/p_{B0}D_B$
$f(\psi, G)$	rate term of Eq. (1)
$F(G)$	integral function defined by Eq. (8)
L	thickness of catalyst plate
p_{0i}	partial pressure of i-th component in bulk phase
R	reaction rate
R	gas constant
T	absolute temperature
α, β	orders with respect to components A and B in kinetic region
$\bar{\alpha}, \underline{\beta}$	apparent orders with respect to A and B in diffusion region
ψ	dimensionless partial pressure equal to p_A/p_{A0}
ξ	dimensionless coordinate equal to x/L
ϱ_k	catalyst density
Φ	modified Thiele module (Eq. (1))

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