APPARENT KINETICS OF A BIMOLECULAR CATALYTIC REACTION IN THE REGION OF INFLUENCE OF THE EXTERNAL MASS TRANSFER

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The effect of the external mass transfer on the apparent kinetics of a bimolecular heterogeneous catalytic reaction is studied on a theoretical model. It was found that the over-all reaction order changes due to the external mass transfer from its original value in the kinetic region towards the value of unity in the region of a strong influence of the external mass transfer. Relations are given which make it possible to calculate apparent reaction orders in different regions of influence of the external mass transfer from the orders in the kinetic region, the ratio of the mass transfer coefficients and the ratio of concentrations of both components in the bulk phase. The effect of the external diffusion on values of apparent orders is illustrated graphically.

During kinetic measurements on laboratory equipments, the effect of an imperfect external mass transfer can confound the results. The external mass transfer slows down the total rate and changes both the apparent orders with respect to single reactants and the over-all reaction order. This study deals with a derivation of relations for calculating apparent orders of a bimolecular catalytic reaction in the region of influence of the external mass transfer. The authors are not aware of any literature work on this problem. Thematically, this work starts from a former communication[1], which dealt with the apparent kinetics of a bimolecular catalytic reaction under a strong influence of the internal mass transfer.

THEORETICAL

Let us suppose that we have a heterogeneous catalytic chemical reaction without any change in the number of mol, A + B = products, proceeding isothermally on the surface of a non-porous catalyst. Let us further suppose that the reaction may be described by a power-law kinetic equation of the form

$$r = k p_{As}^\alpha p_{Bs}^\beta , \qquad (1)$$

where p_{As} and p_{Bs} are the concentrations of components A and B on the catalyst surface. The mass transfer rate from the bulk phase to the catalyst surface is determined by the relation

$$r_d = k_{gA}(p_A - p_{As}) = k_{gB}(p_B - p_{Bs}) \qquad (2)$$

and in a steady state it is equal to the reaction rate. The apparent reaction orders are

defined by the expressions:

$$\bar{\alpha} = (\partial \ln r / \partial \ln p_A)_{p_B} = (p_A/r)(\partial r / \partial p_A)_{p_B}, \tag{3}$$

$$\bar{\beta} = (\partial \ln r / \partial \ln p_B)_{p_A} = (p_B/r)(\partial r / \partial p_B)_{p_A}.$$

With respect to the fact that $r = r[p_{As}(p_A, p_B), p_{Bs}(p_A, p_B)]$, we have

$$(\partial r / \partial p_A)_{p_B} = (\partial r / \partial p_{As})_{p_{Bs}}(\partial p_{As} / \partial p_A)_{p_B} + (\partial r / \partial p_{Bs})_{p_{As}}(\partial p_{Bs} / \partial_A)_{p_B}. \tag{4}$$

After a substitution into Eq. (3) it is possible to obtain an expression for the apparent order with respect to component A

$$\bar{\alpha} = \alpha(\partial \ln p_{As} / \partial \ln p_A)_{p_B} + \beta(\partial \ln p_{Bs} / \partial \ln p_A)_{p_B} \tag{5}$$

and analogically for the apparent order with respect to component B

$$\bar{\beta} = \alpha(\partial \ln p_{As} / \partial \ln p_B)_{p_A} + \beta(\partial \ln p_{Bs} / \partial \ln p_B)_{p_A}. \tag{6}$$

The relation between the surface concentrations p_{As}, p_{Bs} is described by mass balance Eqs (1), (2). With the help of Eq. (2) we can express p_{Bs} as a function of p_{As}. After introducing the dimensionless quantities $\psi = p_{As}/p_A$, $G = p_A k_{gA}/p_B k_{gB}$, $\Phi = k p_A^{\alpha-1} p_B^{\beta}/k_{gA}$ and rearranging we obtain an expression for the dimensionless concentration from Eqs (1), (2)

$$\psi = 1 - \Phi\psi^\alpha[1 - G(1 - \psi)]^\beta. \tag{7}$$

The dimensionless concentration ψ is defined as the ratio of partial pressures of component A on the catalyst surface and in the bulk phase. Parameter G is given by the product of the ratios of the mass transfer coefficients and the bulk phase partial pressures of components A and B. Parameter Φ is an analogue of the Thiele modulus for the internal diffusion and it is defined as the ratio of the rate of the chemical reaction in the bulk phase and the maximum possible rate of the diffusion transfer of component A from the bulk phase to the catalyst surface. In the case when the key component A is present in excess or for $k_{gA}/_{gB} > 1$, the partial pressure p_{Bs} would be negative for p_{As} resp. ψ approaching zero, which would not correspond to the physical basis of the process. Therefore we must realize that the definition region of the dimensionless concentration depends on the value of parameter G:

$$\psi \in \langle 0; 1 \rangle \quad \text{for} \quad G \leqq 1, \quad \psi \in \langle (G - 1)/G; 1 \rangle \quad \text{for} \quad G > 1. \tag{8}$$

After performing the derivatives according to relations (5)—(6), we get expressions for the apparent orders

$$\bar{\alpha} = (\alpha/\psi)/\{1 + \alpha\Phi\psi^{\alpha-1}[1 - G(1 - \psi)]^\beta + \beta G\Phi\psi^\alpha[1 - G(1 - \psi)]^{\beta-1}\} =$$
$$= \alpha/\{\psi + \alpha(1 - \psi) + \beta G\psi(1 - \psi)/[1 - G(1 - \psi)]\}, \tag{9a}$$

$$\bar{\beta} = \beta/[1 - G(1 - \psi)]/\{1 + \alpha\Phi\psi^{\alpha-1}[1 - G(1 - \psi)]^\beta +$$
$$+ \beta G\Phi\psi^\alpha[1 - G(1 - \psi)]^{\beta-1} = \beta/\{[1 - G(1 - \psi)] [1 + \alpha(1 - \psi)/\psi] +$$
$$+ \beta G(1 - \psi)\} \qquad (9b)$$

and for the apparent over-all reaction order

$$\bar{m} = \{\alpha/\psi + \beta/[1 - G(1 - \psi)]\}/\{1 + \alpha\Phi\psi^{\alpha-1}[1 - G(1 - \psi)]^\beta +$$
$$+ \beta G\Phi\psi^\alpha[1 - G(1 - \psi)]^{\beta-1} \qquad (10)$$

where the dimensionless concentration ψ on the catalyst surface is calculated from Eq. (7).

RESULTS AND DISCUSSION

The extent to which the course of a bimolecular chemical reaction is influenced by the external mass transfer is determined by values of two parameters, Φ and G. Parameter Φ represents the ratio of maximum rates of the chemical reaction and the diffusion mass transfer of component A. Parameter G may be interpreted as the ratio of maximum possible values of the diffusion rates of components A and B through the stagnant film surrounding a catalyst particle. In contrast to a monomolecular reaction, the value of parameter $\Phi \to 0$ (resp. $\Phi \to \infty$) does not guarantee that the kinetic (resp. diffusion) region has been reached. The extent of influence of the external diffusion must be always judged on the basis of the values of both the Φ- and G-parameters. Their product can be used only for the definition of limiting regions. The kinetic region is defined by a value of the product $\Phi G \to 0$; it means that the rate of the diffusion transfer of any of components A, B is much higher than that of the chemical reaction. The diffusion region is determined by a value of the product $\Phi G \to \infty$, which signifies that at least one of the diffusion transfers of components A, B is much slower than the reaction rate.

For calculating the apparent reaction orders, it was at first necessary to calculate the dependence of the dimensionless concentration ψ on the kinetic orders and parameters Φ and G according to Eq. (7). Eq. (7), which is generally an implicit one, was solved numerically by the Newton method. The apparent orders were calculated from Eqs (9) and (10). Now, it will be useful to analyze limiting cases. For the kinetic region it follows from Eq. (7) that the dimensionless surface concentration ψ approaches the value of unity. After a substitution into the relations for the apparent orders we get $\bar{\alpha} = \alpha$, $\bar{\beta} = \beta$, $\bar{m} = \alpha + \beta$. In the diffusion region, the reaction rate is much higher than the diffusion rate and hence $\Phi G \to \infty$. It follows then from Eq. (7) that it must hold either $\psi = 0$ or $1 - G(1 - \psi) = 0$. In the first case, the rela-

tion $G \leqq 1$ must be satisfied according to conditions (8). If $G < 1$, we obtain the values of $\bar{\alpha} = 1$, $\bar{\beta} = 0$, $\bar{m} = 1$; if $G = 1$, then $\bar{\alpha} = \alpha/(\alpha + \beta)$, $\bar{\beta} = \beta/(\alpha + \beta)$, $\bar{m} = 1$.
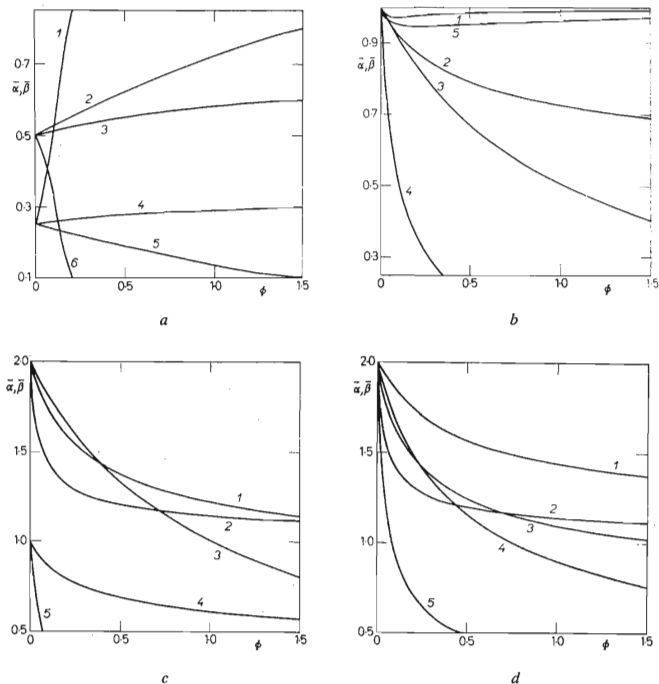

FIG. 1

Dependence of the Apparent Reaction Orders with Respect to the Single Components on Parameter Φ for Different True Values of the Reaction Orders (α, β) in the Kinetic Region

a) $\alpha = 0.5$, $\beta = 0.25$. 1 $\bar{\beta}$, $G = 10$, 2 $\bar{\alpha}$, $G = 0.01$, 3 $\bar{\alpha}$, $G = 1$, ₅ $\bar{\beta}$, $G = 1$, 5 $\bar{\beta}$, $G = 0.01$, 6 $\bar{\alpha}$, $G = 10$.

b) $\alpha = 1$, $\beta = 1$. 1 $\bar{\beta}$, $G = 10$, 2 $\bar{\alpha} = \bar{\beta}$, $G = 1$, 3 $\bar{\beta}$, $G = 0.01$, 4 $\bar{\alpha}$, $G = 10$, 5 $\bar{\beta}$, $G = 5$. It holds $\alpha \approx 1$ for $G = 0.01$ in the whole range of Φ-values.

c) $\alpha = 1$, $\beta = 2$. 1 $\bar{\beta}$, $G = 1$, 2 $\bar{\beta}$, $G = 10$, 3 $\bar{\beta}$, $G = 0.01$, 4 $\bar{\alpha}$, $G = 1$, 5 $\bar{\alpha}$, $G = 10$. It holds $\alpha \approx 1$ for $G = 0.01$ in the whole range of Φ-values.

d) $\alpha = 2$, $\beta = 2$. 1 $\bar{\alpha}$, $G = 0.01$, 2 $\bar{\beta}$, $G = 10$, 3 $\bar{\alpha} = \bar{\beta}$, $G = 1$, 4 $\bar{\beta}$, $G = 0.01$, 5 $\bar{\alpha}$, $G = 10$.

In the second case, *i.e.* for $1 - G(1 - \psi) = 0$, it also holds $G \geqq 1$ and $\psi = (G - 1)/G$. For the apparent orders we then get $\bar{\alpha} = 0$, $\bar{\beta} = 1$, $\bar{m} = 1$. From this, it is obvious that the apparent over-all reaction order approaches unity in the diffusion region; the apparent order with respect to the component which is in excess on the catalyst surface decreases to zero, while that with respect to the deficient component approaches unity. Dependences of the apparent reaction orders with respect to the single components on parameter Φ are illustrated in Fig. 1 for different values of parameter G. The change in the apparent order due to the external mass transfer of a component which is on the catalyst surface in excess compared to the second component is the smaller, the lower is the value of this order in the kinetic region. Analogically, the change in the order of the deficient component is the smaller, the more the kinetic order with respect to this component approaches unity. Values of parameter G greater than unity indicate that component B is the deficient one, values less than unity correspond to the case of component B being in excess. At the value of parameter G equal to unity, the ratio of the apparent orders does not change due to the external diffusion. At these conditions, a greater change due to the external transfer is observed for the order which exhibits the higher value in the kinetic region.

An interesting effect is the occurrence of an extreme on the dependence of the apparent order on parameter Φ as shovn in Fig. 1*b*. This extreme may appear only
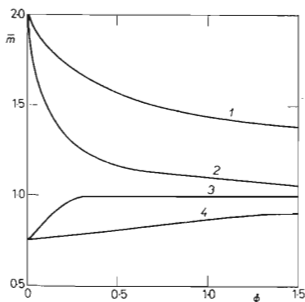

Fig. 2

Dependence of the Over-All Apparent Reaction Order $\bar{m}$ on Parameter Φ

1 $\alpha + \beta = 0\cdot5 + 0\cdot25 = 0\cdot75$; $G = 1$. *2* $\alpha + \beta = 0\cdot5 + 0\cdot25 = 0\cdot75$; $G = 10$. *3* $\alpha + \beta = 1 + 1 = 2$; $G = 10$. *4* $\alpha + \beta = 1 + 1 = 2$; $G = 1$.
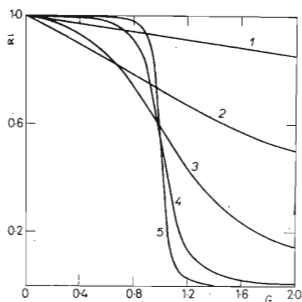
Fig. 3

Dependence of the Apparent Reaction Order with Respect to Component A on Parameter G

True value of the orders in the kinetic region $\alpha = 1$, $\beta = 1$. Φ: *1* $0\cdot1$, *2* 1, *3* 10, *4* 150, *5* 1000.

if both components are not present in the same amount on the catalyst surface ($G \neq 1$). With increasing influence of the external transfer, both the over-all reaction rate tends to change towards the value of unity and the disproportionality between the reactants on the catalyst surface increases steadily, which leads in the pure diffusion region to the first order with respect to the deficient component. A minimum on the dependence of the apparent order on parameter Φ may appear only for the surficially deficient component at an over-all order greater than unity. Similarly, an occurrence of a maximum can be expected only at an over-all order less than unity and only for the component being in excess on the catalyst surface. The more the value of parameter G approaches unity, the more the location of the extreme shifts towards higher values of parameter Φ and its shape becomes shallower until it disappears totally at $G = 1$. It is interesting to note that at the first-order over-all rate in the kinetic region and at $G = 1$, the orders with respect to the single components are constant in the whole region of values of parameter Φ.

It follows from Fig. 2 that due to the imperfect external transfer, the over-all order approaches unity. From Fig. 3 we may deduce that in the strong diffusion region, a transition from the region of values $G < 1$ into that of $G > 1$ results in a jump change in the apparent orders. Practically it means that there exists a limiting interval of the ratio of concentrations of components A, B, in which the apparent orders change very rapidly under influence of the external diffusion. This interval becomes narrower as the diffusion region is approached. This transition manifests itself in the diffusion region by a break on the dependence of the reaction rate on the concentration of one component at a constant concentration of the other component. From the given facts it follows that it is necessary to eliminate the influence of the external mass transfer on the rate of a chemical reaction during determining the reaction kinetics. In the opposite case, the kinetics found is only an apparent one, it holds only in the given region of influence of the external transfer and the results obtained cannot be applied to another type of apparatus except that in which they were determined.

REFERENCES

1. Hlubuček V., Pašek J.: This Journal *37*, 1599 (1972).

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