# EFFECT OF SURFACE DIFFUSION RETARDATION ON A PROCESS IN A POROUS CATALYST

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The course of a highly exothermic reaction in a porous catalyst depends to a great extent on the conditions under which the reactant is supplied to the surface of the catalyst and particularly on the resistance to heat removal. Consequently, it is of interest to study the conditions for an exothermic reaction employing the widest boundary conditions, which take account of the surface diffusion restrictions and resistance to heat removal. An attempt has been made to take the latter factor into account [1] but the error permitted in the calculations led to a number of incorrect conclusions.

For a first-order reaction the concentration and temperature distributions in a porous layer of thickness $2l$ are represented by the equations:

$$D\,d^2C/dx^2 - k(T)C = 0, \tag{1}$$

$$\lambda\,d^2T/dx^2 + Qk(T)C = 0, \tag{2}$$

where D is the effective diffusion coefficient in the porous catalyst; $\lambda$ is the thermal conductivity; C is the concentration; T is the temperature; Q is the heat of reaction; k(T) is the rate constant of the reaction.

The following boundary conditions are imposed on the concentration and temperature

$$dC/dx|_{x=l} = 0, \quad dT/dx|_{x=l} = 0; \tag{3}$$

$$D\,dC/dx|_{x=0} = \beta(C_0 - C_\infty), \quad \lambda\,dT/dx|_{x=0} = \alpha(T_0 - T_\infty), \tag{4}$$

where $\beta$ and $\alpha$ are the coefficients for mass and heat transfer from the external medium to the surface of the porous catalyst, the subscript 0 indicates the values of the variables at the surface (at x = 0) and the subscript $\infty$ indicates their values in the external medium.

Using (4), an estimate may be made of the conditions under which a marked drop in concentration and temperature occurs between the catalyst surface and the external medium. Since $\beta = D_m/\delta$, where $D_m$ is the molecular diffusion coefficient of the reactant and $\delta$ is the thickness of the diffusion layer at the surface of the catalyst, and $dC/dx \sim C_0\sqrt{k_0/D}$, where $\sqrt{D/k}$ is the effective depth to which the reaction penetrates into the porous layer [2], then

$$\frac{C_\infty - C_0}{C_0} \sim \frac{D}{D_m}\delta\sqrt{\frac{k_0}{D}} = \frac{D}{D_n}\frac{\delta}{l}\Psi_0, \tag{5}$$

where $\Psi = l\sqrt{k/D}$ is the Thiele modulus. As $D \leqslant D_m$ and $\delta \ll 1$, it is seen from (5) that a surface drop in concentration may be comparable with an internal one only for $\Psi_0 \gg 1$ (or $\sqrt{D/k} \ll l$), i.e., when the porous layer is functioning under internal diffusion conditions. However, if the reaction on the porous catalyst is taking place under kinetic or mixed conditions ($\Psi_0 \leqslant 1$), a surface drop in concentration is far less than an internal one, and, consequently, surface diffusion retardation hardly affects the process at all. To estimate the drop in temperature

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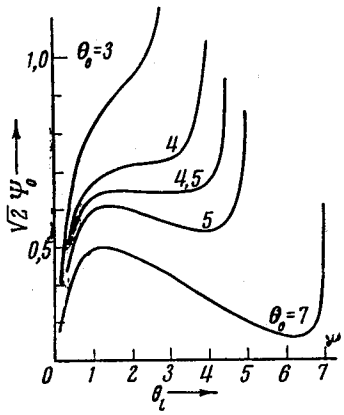


Fig. 1. Curves of the function $f(\theta_l, \Theta_0)$.

we use the relationship

$$\lambda(T - T_0) = DQ(C_0 - C), \tag{6}$$

which follows from Eq. (1) and (2). A drop in temperature between the central and outer surface of the catalyst is represented conveniently by the dimensionless quantity $\omega = E(T_0 - T_\infty)/RT_0^2$. Taking into account that $\alpha = \lambda_m/\delta \approx D_m\gamma/\delta$ for a gaseous medium (where $\gamma$ is the heat capacity per unit volume of gas), and using (4)-(6) we have

$$\omega = \frac{E}{RT_0^2}\frac{\lambda}{\alpha}\left(\frac{dT}{dx}\right)_0 = \frac{E}{RT_0^2}\frac{\lambda}{\alpha}\frac{DQ}{\lambda}\left(\frac{dC}{dx}\right)_0 \approx \frac{\delta}{l}\frac{\lambda}{\gamma D_m}\Theta_0\Psi_0, \tag{7}$$

where $\Theta_0 = C_0EQD/\lambda RT_0^2$ is the maximum internal heating; E is the activation energy; R is the gas constant. Since the transfer of heat in a porous catalyst occurs chiefly through the solid phase $\lambda/\gamma D_m \gg 1$. For a highly exothermic reaction the parameter $\Theta_0 \sim 1 \div 10$. Therefore, the value of $\omega$, which characterizes the effect of the surface resistance to heat removal, may be substantial ($\omega \sim 1$) for comparatively low values of $\Psi_0$, where the surface diffusion resistance is still not affecting the process.

Using the relationship (6) we obtain from (2) an equation for the dimensionless temperature $\theta = E(T - T_0)/RT_0^2$

$$d^2\theta/d\xi^2 + \Psi_0^2(\Theta_0 - \theta)\exp\theta = 0, \tag{8}$$

where $\xi = x/l$ is a dimensionless coordinate. The Frank-Kamenetskii transformation $k(T) = k(T_0)\exp.\,\theta$ [2] has also been carried out in (8).

Integrating (8) with regard to (3) we obtain the equation for determining the dimensionless temperature at the center of the layer $\theta_l$

$$\sqrt{2}\,\Psi = \int_0^{\theta_l}\left[\int_{\theta_1}^{\theta_l}(\Theta_0 - \theta_2)\exp\theta_2\,d\theta_2\right]^{-1/2} d\theta_1 \equiv f(\theta_l, \Theta_0). \tag{9}$$

Plots of the function $f(\theta_l, \Theta_0)$ for several values of $\Theta_0$ are shown in Fig. 1, from which it is seen that for $\Theta_0 > 4{,}5$ the $\theta_l - \Psi_0$ relationship becomes ambiguous which corresponds to the appearance of intermediate unstable conditions in a problem with known values of $C_0$ and $T_0$. At the maximum $f(\theta_l, \Theta_0)$ the conditions change stepwise from kinetic to diffusional and the minimum $f(\theta_l, \Theta_0)$ corresponds to the reverse transition.

The boundary conditions (4) are transformed:

$$M = \sqrt{2}\exp(\omega/2)\left[\int_0^{\theta_l}(\Theta_0 - \theta)\exp\theta\,d\theta\right]^{1/2} \Big/ \omega, \tag{10}$$

$$\Theta_0 = (\Theta_\infty - \omega/\mu), \tag{11}$$

where $M = (\alpha/\lambda)\sqrt{D/k_\infty} = \mathrm{Bi}/\Psi_\infty$ is a dimensionless heat transfer parameter $\mathrm{Bi} = \alpha l/\lambda$ is the Biot number; $\Theta_\infty = C_\infty EQD/\lambda RT_\infty^2$ и $\mu = \lambda\beta/D\alpha \gg 1$. We may note that the existence of the greatest possible surface heating $\Omega = \Theta_\infty\mu$ follows from (11).

Let us investigate the region $\Omega \gg \omega \sim 1$ in which the surface diffusion retardation can be neglected (the surface kinetic region). Under these conditions $\omega/\mu \ll 1$ and $\Theta_\infty = \Theta_0$. The dimensionless surface heating $\omega$ is determined by solving the system of Eqs. (9) and (10), where $\Psi_0$ varies with $\omega$ and is connected with $\Psi_\infty$ by $\Psi_0 = \Psi_\infty\exp\omega/2$.

Assuming that $\theta_l \ll \Theta_0$: in (9), we obtain in the internal kinetic region,

$$M = \Psi_\infty\Theta_0\exp\omega/\omega. \tag{12}$$

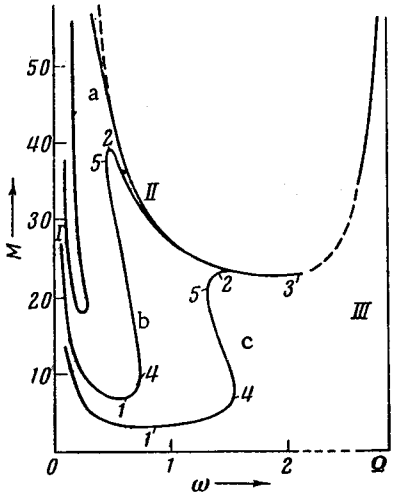


Fig. 2. Relationship between M and $\omega$ for $\Theta_\infty = 5$, and $\Psi_\infty = 0.37$ (a), 0.3 (b), and 0.2 (c).

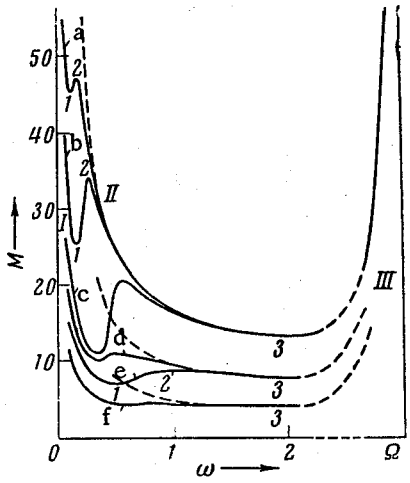


Fig. 3. Relationship between M and $\omega$ for $\Theta_\infty = 4$, $\Psi_\infty = 0.47$ (a), 0.45 (b), 0.4 (c); $\Theta_\infty = 3$, $\Psi_\infty = 0.5$ (d), 0.45 (e), $\Theta_\infty = 2$, $\Psi_\infty = 0.53$ (f).

In the internal diffusion region it may be considered that $\theta_l \simeq \Theta_0$. in (10). From this we obtain:

$$M = \frac{\exp \omega/2}{\omega} \sqrt{2(\exp \Theta_0 - 1 - \Theta_0)}. \qquad (13)$$

The right hand side of Eq. (12) has a minimum equal to $e\Psi_\infty\Theta_0$ at $\omega = 1$ and the minimum for Eq. (13) is reached at $\omega = 2$. Figures 2 and 3 show the paths of the $M(\omega)$ curves in the region $\omega \sim 1$ for several values of $\Theta_\infty$ and $\Psi_\infty$. The family of curves corresponding to a single value of $\Theta_\infty$ and different values of $\Psi_\infty$ fall in the internal diffusion region on the asymptotic curve determined by Eq. (13). The values of $\omega$ at which $dM/d\omega = 0$ (points 1-3 on Figs. 2 and 3) separate the alternating regions of stable and unstable conditions. Points 4 and 5 (Fig. 2), where $|dM/d\omega| = 0$, corresponds to the values of the parameter $\Psi_0 = \Psi_\infty \exp \omega/2$, at which a jump occurs between the internal regimes in a problem with given $C_0$, $T_0$. These points fall everywhere in the region of unstable conditions, which separates the internal kinetic and internal diffusion regions. Thus, the presence of a resistance to heat removal on the external surface of the catalyst leads to a broadening of the region of unstable states. This fact also appears in the production of an unstable region for those values of $\Theta_\infty$ where a problem without surface resistance does not generally have unstable conditions. The stepwise transitions to internal conditions may be observed right up to $\Theta_\infty = 2$ as is seen from Fig. 3.

For values of the heat transfer parameter M less than the absolute minimum of the $M(\omega)$ function (Figs. 2 and 3), regimes having low external heatings do not exist over the range considered $0 \leq \omega \leq 2$, and the process enters surface diffusion conditions ($\omega \sim \Omega$). Under surface diffusion conditions the drop in concentration at the surface of a grain becomes substantial and it therefore becomes necessary to take account of the dependence of $\Theta_0$ on $\omega$ in (11). Since the reaction is localized here in a narrow layer near the surface of the catalyst, the path of the $M(\omega)$ curve under surface diffusion conditions can be obtained from Eq. (13), taking account of the relationship (11). For $\mu >> 1$ the $M(\omega)$ function has a very high maximum at $\omega \sim \Omega$ and at $\omega = \Omega$ it drops rapidly to zero. As $\mu$ decreases the maximum drops; for low $\mu$ the maximum disappears and the transition into the surface diffusion region takes place smoothly.

The possible regimes for the process at $\Theta_\infty > 4{,}5$ and $\mu >> 1$, as well as the transitions between them with changes in the hydrodynamic conditions are shown in Table 1, where $\sqrt{2}\Psi^+$ is the value of $f(\theta_l, \Theta_0)$ at the maximum (Fig. 1); $\sqrt{2}\Psi^-$ is the value of $f(\theta_l, \Theta_0)$ at the minimum; I is the internal kinetic regime; II is the internal diffusion regime; III is the surface diffusion regime. At $4.5 > \Theta_\infty > 2$ the regimes are the same as in case 3 in the table.

To investigate the transitions between the regimes arising from a change in flow temperature, it is convenient to use the curves in the coordinates $\Psi_\infty$ and $\theta_l$ for different values of the parameters Bi and $\Theta_\infty$. In the region

TABLE 1

| | | Decrease in M (decrease in gas velocity) | Increase in M (increase in gas velocity) |
|---|---|---|---|
| 1 | $\Psi_\infty > \Psi^+$ | II → III | III → II * |
| 2 | $\Psi^- < \Psi_\infty < \Psi^+$ | a) I → II → III | III → II |
| | | b) I → II | III → II |
| 3 | $\Psi_\infty < \Psi^-$ | c) I → II → III | III → I |
| | | d) I → III | III → I† |

*In case 1 regime I is absent.

†In case 3b it is impossible to reach regime II with a change in the single parameter M.

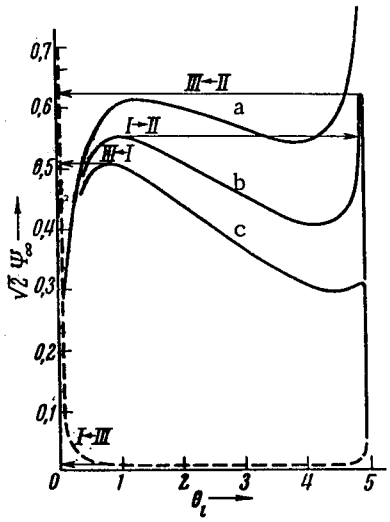


Fig. 4. The relationship between $\Psi_\infty$ and $\theta_l$ for $\Theta_\infty = 5$ and Bi = ∞ (a), 20 (b) and 10 (c).

where surface diffusion resistance is absent ($\omega < 2$) we obtain from (9) and (10)

$$\sqrt{2}\Psi_\infty = f(\theta_l, \Theta_0) \exp \left\{ -f(\theta_l, \Theta_0) \left[ \int_0^{\theta_l} (\Theta_0 - \theta) \exp \theta \, d\theta \right]^{1/2} \Big/ 2\mathrm{Bi} \right\}. \quad (14)$$

Figure 4 shows the relationship defined by Eq. (14). The subsequent path of the curve ($2 < \omega < \Omega$) may be found from (10) and (11)

$$\sqrt{2}\Psi_\infty = \frac{\mu \, \mathrm{Bi} (\Theta_\infty - \theta_l) \exp [(\theta_l - \Theta_\infty)\mu]}{\sqrt{\exp \theta_l - 1 - \theta_l}}. \quad (15)$$

For $\mu \gg 1$ the curve drops sharply to extremely low values for $\theta_l \simeq \Theta_\infty$ and rises along the ordinate axis for $\theta_l \ll 1$.

The transitions between the regimes for changes in $\Psi_\infty$ (a change in temperature) depend on the relative height of the maxima on the $\Psi_\infty^+(\theta_l)$ curve. For $\mathrm{Bi} > e\sqrt{\Psi^+(\exp \Theta_\infty - 1 - \Theta_\infty)}/\sqrt{2}$ the transitions follow the scheme I → II → III with an increase in $\Psi_\infty$ and III → I with a decrease in $\Psi_\infty$. For $\mathrm{Bi} < e\sqrt{\Psi(\exp \Theta_\infty - 1 - \Theta_\infty)}/\sqrt{2}$ the transitions follow the schemes I → III and III → I, respectively, and regime II does not appear. We may note that for $\mu \gg 1$ in the first case it is also impossible to reach regime II from regime III.

Thus, this investigation has shown that the presence of resistances to mass and heat transfer towards the external surface of the catalyst leads to the appearance of additional regimes in the process. Consequently, the conditions under which the reactions take place within a porous catalyst are altered substantially, the boundaries of the regions in which steady state conditions exist are displaced, and the region of unstable conditions is expanded.

## LITERATURE CITED


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2. D. A. Frank-Kamenetskii, Diffusion and Heat Transfer in Chemical Kinetics, Izd. Akad. Nauk SSSR (1947).