By starting at the boundary condition of $H = 1$ at $R = 0$, as indicated by Equation (8), the value of B_{DL} is determined by numerical integration. Deryagin and Levi (*1*) report

$$B_{DL} = 0.204 \ldots \qquad \text{(A20)}$$

Matching B_{DL} and B_{SL} by using Equations (A10) and (A20), we get

$$0.204\,(3N_{Ca})^{4/3} = D_0^2\,(1 - \cos\alpha) \qquad \text{(A21)}$$

Rearrangement of Equation (A21) leads to the plug flow theory, which may be written as

$$N_{Ca} = \frac{D_0^{3/2}\,(1 - \cos\alpha)^{3/4}}{3(0.204)^{3/4}} \qquad \text{(A22)}$$

There is a slight difference in constants between Equation (A22) and Equation (17) owing to the slight difference in results of numerical integration. The difference can be shown by evaluation of H''_{DL} from Equation (A19) and (A20). Thus

$$H''_{DL} = (2B_{DL})^{1/2} = (0.408)^{1/2} = 0.636$$

The comparable result used in Equations (12), (16), and (17) was the 0.642 value of White and Tallmadge (*8*). This 1% difference is not important for the discussion under consideration.

Comparison of the B value method with C value method indicates that:

1. The B value places flow parameters into the static term, whereas the C value does not.
2. The B value does not have a direct physical significance, whereas the C value signifies the curvature.
3. The B value is a complicated function of H'', whereas C is simply equal to L''.
4. The B value method appears to be longer and less direct.
5. The C value provides for an analytical but approximate expression for the effect of D_0 (or β).
6. The B value provides for an exact but numerical expression for the effect of D_0 without approximation.

The only apparent advantage of the B method is noted in reason 6. The C value method was selected for use in deriving Equation (16) mainly because an analytical solution (reason 5) was desired, but also in order to present the simpler and more direct derivation (reasons 1 and 4).

Zeroth-Order Reactions in Heterogeneous Catalysis

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The simultaneous zeroth-order reaction and diffusion in porous catalyst appeared in the classical paper of Wheeler (*1*). Successive influence of volume change on catalyst effectiveness has been discussed by Weekman and Gorring (*2*); selectivity under diffusion limitation has been reported by Van de Vusse (*3*), and effectiveness functions have been used to describe selectivity and poisoning (*4*). The zeroth-order reactions are special cases of power law kinetics (*5, 6*) and particular types of the Langmuir-Hinshelwood reactions, the treatment of which, in presence of diffusion limitation, has been given by Roberts and Satterfield (*7*).

In the cited references the diffusion during reaction is characterized by an experimentally determined diffusivity, or a simple pore structure is assumed (single-pore model). This model (*8, 9*) has been extended by Mingle and Smith (*10*) and Carberry (*11, 12*) to a more complex model (macro-micropore model) representing catalyst pills containing macropores created via pelletting of porous microspheres. The last may be visualized by a cylindrical pore (macropore) from which micropores branch along the length and at right angle to the macropore; Knudsen diffusion and molecular diffusion may be considered prevailing in the micropores and in the macropore, respectively. The macro-micropore effectiveness factor has been derived for isothermal irreversible and reversible first-order reactions (*10, 11*) and irreversible second-order reactions (*13*). In the last case, a generalized Thiele modulus has been introduced by which the functions effectiveness factor vs. Thiele modulus follow one another very closely.

The present paper pertains to the problem of reaction and diffusion for a zeroth-order kinetic law in the macro-micropore model. The derivations that follow are based upon the following assumptions:

1. The catalyst pellet is at uniform temperature.
2. The irreversible zeroth-order reaction occurs without volume change.
3. Significant reaction occurs only in the micropores; that is, the surface of the macropore is assumed entirely covered by micropores.

CATALYTIC EFFECTIVENESS

The controlling regime for zeroth-order reactions may be assumed as chemical if the effectiveness factor η_0 is unity; it happens for values of the micropore diffusion-reaction/modulus along the macropore length that

$$\mu \equiv \left[\frac{2\,K_0 C^{-1}}{r\,D}\right]^{1/2} \qquad l < \sqrt{2}.$$

On the other hand, the strong pore diffusion regime occurs when the reactant concentration drops to zero at the micropore and macropore end. In these conditions, because the micropore effectiveness factor is $\sqrt{2}/\mu$, and the number of micropores per unit area of macropore wall is $1/\pi r^2$, a balance over the macropore gives

$$\frac{d^2y}{d\rho^2} = 2\,\sqrt{2}\;m_0\;\theta^2\;y^{1/2} \qquad (1)$$

or

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$$\frac{d}{dy}\left[\frac{dy}{d\rho}\right]^2 = 4\sqrt{2}\; m_0\; \theta^2\; y^{1/2} \tag{2}$$

subject to the boundary conditions

$$\begin{aligned} &y = 1 \qquad && \frac{dy}{d\rho} = \left[\frac{dy}{d\rho}\right]_{\rho=0} \\ &y = 0 \qquad && \frac{dy}{d\rho} = 0 \end{aligned} \tag{3}$$

where $m_0 \equiv \left[\frac{2\,K_0\,C_0^{-1}}{rD}\right]^{1/2} l$ is the micropore diffusion-reaction modulus at the macropore mouth and $\theta \equiv \left[\frac{D}{D^+}\;\frac{l^{+2}}{r^+\,l}\right]^{1/2}$ is the geometric modulus of the macro-micropore model. The micropore diffusivity/macropore diffusivity ratio may be related to the micropore and macropore radius by the Wheeler's equation (*14*):

$$\text{diffusivity} = D^0\,[1 - e^{-2(\text{pore radius})/\lambda}]$$

where D^0 is the ordinary diffusivity for bulk gas. Hence, from Equation (2) and boundary conditions (3), we obtain

$$\left[\frac{dy}{d\rho}\right]_{\rho=0} = -\left[\frac{8\sqrt{2}}{3}\right]^{1/2} m_0^{1/2}\,\theta \tag{4}$$

and the effectiveness factor in the diffusion-limited regime becomes

$$\eta_0 = \frac{2^{3/4}}{3^{1/2}\, m_0^{3/2}\, \theta} \tag{5}$$

From Equation (5), a normalized Thiele modulus Ω_0 can be introduced so that the effectiveness factor becomes asymptotically Ω_0^{-1} for large Ω_0 (*15* to *17*):

$$\Omega_0 \equiv \frac{3^{1/2}\, m_0^{3/2}\, \theta}{2^{3/4}} \tag{6}$$

The chemical regime stops and the mixed regime, intermediate between the chemical and the diffusion-limited one, starts when the micropore diffusion reaction modulus at the macropore end becomes $\mu_{\rho=1} = \sqrt{2}$, that is, at values of the Thiele modulus given by

$$\Omega_0^* = \frac{3^{1/2}\,\theta}{(1 + 2\,\theta^2)^{3/4}} \tag{7}$$

Therefore, in the intermediate regime, the macropore is divided into two zones, the first starting at the macropore mouth and extending $\rho^* l^+$ into the macropore ($\mu < \sqrt{2}$), the second extending from $\rho^* l^+$ to l^+ ($\mu > \sqrt{2}$).

The material balance equation in the first zone is:

$$\frac{d^2y}{d\rho^2} = \frac{4}{3^{2/3}}\, \Omega_0^{4/3}\, \theta^{2/3} \tag{8}$$

and in the second one, Equation (1), holds, which by Equation (6) becomes

$$\frac{d^2y}{d\rho^2} = \frac{4}{3^{1/3}}\, \Omega_0^{2/3}\, \theta^{4/3}\, y^{1/2} \tag{9}$$

TABLE 1. EFFECTIVENESS FACTOR VS. NORMALIZED THIELE MODULUS

Normalized Thiele modulus	Effectiveness factor					
	Zeroth-order reaction			First-order reaction		
	$\theta =$ 100	$\theta = 500$	$\theta =$ 1000	$\theta =$ 100	$\theta =$ 500	$\theta = 1{,}000$
0.01	1	1	1	0.981	0.947	0.918
0.02	1	1	1	0.953	0.877	0.821
0.03	1	1	1	0.923	0.809	0.733
0.05	1	0.947	0.751	0.861	0.692	0.597
0.07	1	0.756	0.600	0.801	0.600	0.502
0.1	1	0.596	0.473	0.721	0.499	0.407
0.2	0.642	0.376	0.298	0.530	0.327	0.260
0.3	0.490	0.287	0.227	0.420	0.250	0.199
0.5	0.349	0.204	0.162	0.304	0.178	0.141
1	0.219	0.128	0.102	0.192	0.112	0.089
2	0.138	0.081	0.064	0.121	0.071	0.056
3	0.105	0.062	0.049	0.092	0.054	0.043
5	0.075	0.044	0.035	0.065	0.038	0.031
10	0.047	0.028	0.022	0.041	0.024	0.019

In these conditions, the effectiveness factor is given by

$$\eta_0 = \rho^* + \frac{3^{2/3}\left[-\frac{dy}{d\rho}\right]_{\rho=\rho^*}}{4\,\Omega_0^{4/3}\,\theta^{2/3}} \tag{10}$$

The system of differential Equations (8) and (9) involves the following boundary conditions:
Equation (8) $(0 \leqq \rho \leqq \rho^*)$:

$$\begin{aligned} &\rho = 0 \qquad && y = 1 \\ &\rho = \rho^* \qquad && y = \frac{\Omega_0^{4/3}}{3^{2/3}\,\theta^{4/3}} \end{aligned} \tag{11}$$

Equation (9) $(\rho^* \leqq \rho \leqq 1)$:

$$\begin{aligned} &\rho = \rho^* \qquad && y = \frac{\Omega_0^{4/3}}{3^{2/3}\,\theta^{4/3}} \\ &\rho = \rho^* \qquad && \frac{dy}{d\rho} = \frac{\Omega_0^{4/3}}{3^{2/3}\,\theta^{4/3}}\,\frac{1}{\rho^*} - \frac{1}{\rho^*} + \frac{2}{3^{2/3}}\,\Omega_0^{4/3}\,\theta^{2/3}\,\rho^* \\ &\rho = 1 \qquad && \frac{dy}{d\rho} = 0 \end{aligned} \tag{12}$$

The system of Equations (8) and (9) has been solved by the IBM 7090 digital computer, and the values of η_0 have been reported in Table 1 against the generalized Thiele modulus for different values of θ. The effectiveness factor for zeroth-order reactions is compared with the effectiveness factor for first order reactions. In the last case, the effectiveness factor is

$$\eta_I = \frac{\left[\tanh\left(\frac{\Omega_I^2}{2\theta^2}\right)^{1/3}\right]^{1/2} \tanh\left\{(2\Omega_I\,\theta^2)^{1/3}\left[\tanh\left(\frac{\Omega_I^2}{2\theta^2}\right)^{1/3}\right]^{1/2}\right\}}{\Omega_I} \tag{13}$$

where $\Omega_I \equiv 2^{1/2}\, m_I^{3/2}\, \theta$, with $m_I \equiv \left(\frac{2\,K_I}{r\,D}\right)^{1/2} l$.

Elsewhere (*13*), values of effectiveness factor vs. normalized Thiele modulus for first- and second-order reactions have been compared and the greatest difference between the two functions has been found to be about

10% for $\theta > 50$ in the intermediate regime between the chemical and the strong pore diffusion one. From Table 1 it results that also the functions $\eta(\Omega)$ for zeroth- and first-order reactions follow one another fairly closely, and the greatest difference, which falls in the mixted regime, is about 40% for $\theta = 100$, 36% for $\theta = 500$, and 26% for $\theta = 1{,}000$.

APPARENT KINETICS

The apparent kinetics consists of the apparent activation energy and order of process, which are defined as

$$E_{\text{app}} \equiv -\frac{\partial \ln \Phi}{\partial (1/Rg\, T)} \tag{14}$$

and

$$n_{\text{app}} \equiv \frac{\partial \ln \Phi}{\partial \ln C_0} \tag{15}$$

where Φ is the rate of disappearing of the reactant per unit catalyst surface, given by

$$\Phi = K_0\, \eta_0 \tag{16}$$

From Equation (16), we obtain

$$\frac{E_{\text{app}}}{E_0} = 1 + \frac{3}{4}\left[1 - \frac{E_d}{E_0}\right] \frac{\partial \ln \eta_0}{\partial \ln \Omega_0} \tag{17}$$

and

$$n_{\text{app}} = -\frac{3}{4}\,\frac{\partial \ln \eta_0}{\partial \ln \Omega_0} \tag{18}$$

where E_0 is the reaction activation energy from the Arrhenius law, and E_d is the diffusion activation energy (the temperature dependence of D/D^+ is assumed negligible).

By substituting $\frac{3}{4}\,\frac{\partial \ln \eta_0}{\partial \ln \Omega_0}$ from Equation (17) into Equation (18), for $E_d/E_0 \neq 1$ (practically $E_d/E_0 << 1$), the equation common to isothermal zeroth-order reaction processes is obtained (*18, 19*):

$$n_{\text{app}} = \left[1 - \frac{E_{\text{app}}}{E_0}\right] \Big/ \left[1 - \frac{E_d}{E_0}\right] \tag{19}$$

The strong pore diffusion regime ($\eta_0 = \Omega_0^{-1}$) is characterized by the simple relations

$$\frac{E_{\text{app}}}{E_0} = \frac{1}{4} + \frac{3}{4}\,\frac{E_d}{E_0} \tag{20}$$

and

$$n_{\text{app}} = \frac{3}{4} \tag{21}$$

In the diffusion-limited regime, the macro-micropore model gives, for $E_d/E_0 \simeq 0$, a lower value of the apparent activation energy and a higher value of the apparent order of process if compared with the single-pore model. In the last case we have

$$\frac{\left[\begin{array}{c}\text{apparent activation}\\ \text{energy of process}\end{array}\right]}{E_0} = \frac{1}{2} + \frac{1}{2}\,\frac{E_d}{E_0} \tag{22}$$

and

$$\text{apparent order of process} = \frac{1}{2} \tag{23}$$

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NOTATION

C = concentration of reactant in macropore
C_0 = concentration of reactant at macropore mouth
D = diffusivity of reactant in micropore
D^+ = diffusivity of reactant in macropore
E_{app} = apparent activation energy of process
E_d = diffusion activation energy
E_0 = reaction activation energy
K_0 = zeroth-order reaction rate constant
K_I = first-order reaction rate constant
l = micropore length
l^+ = macropore length
m_0 = micropore diffusion-reaction modulus at macropore mouth for zeroth-order reactions
m_I = micropore diffusion-reaction modulus for first-order reactions
n_{app} = apparent order of process
r = micropore radius
r^+ = macropore radius
Rg = gas constant
T = absolute temperature
y = concentration of reactant in macropore/concentration of reactant at macropore mouth

Greek Letters

η_0 = effectiveness factor for zeroth-order reactions
η_I = effectiveness factor for first-order reactions
λ = mean free path of gaseous molecule
μ = micropore diffusion-reaction modulus along the macropore length
θ = macro-micropore model geometric modulus
ρ = macropore coordinate/macropore length
ρ^* = reduced extension of the macropore zone with $\mu < \sqrt{2}$ in the mixed regime
Φ = rate of disappearing of reactant per unit catalyst surface
Ω_0 = normalized Thiele modulus for zeroth-order reactions
Ω_0^* = normalized Thiele modulus at which the mixed regime starts
Ω_I = normalized Thiele modulus for first order reactions

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