

On the Second Order Reactions in Heterogeneous Catalysis

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Isothermal second order reactions of the type $\nu A \rightarrow$ products and $A + B \rightarrow$ products are investigated in the macro-micro-pore catalyst model. Effectiveness factors, calculated by a computer, are reported and related to a generalized Thiele modulus. Equations concerning the falsification of activation energy and order of process under diffusion effect conditions are given.

INTRODUCTION

The second order isothermal reactions and the related importance of intraparticle diffusion in porous catalyst appeared in the classical paper of Thiele (1). Successively, the influence of volume change on the kinetics has been discussed by Weekman and Goring (2), nonisothermal cases have been solved by Tinkler and Metzner (3), Carberry (4), and Petersen (5) and a second order reaction involving two reactants has been treated by Maymo' and Cunningham (6). The second order reactions are, moreover, 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 catalysis is characterized by an experimentally determined diffusivity and a simple pore structure is assumed (single-pore model). The present paper pertains to the problem of simultaneous reaction and diffusion for a second order kinetic law in the macro-micro-pore model. The last has been introduced to represent catalyst pills containing macropores created via pelleting of porous microspheres and may be visualized

by a cylindrical pore of radius r^+ (macropore) from which micropores of radius $r < r^+$ branch along the length and at right angle to the macropore (8-10). Knudsen diffusion and molecular diffusion may be considered prevailing in the micropores and in the macropore respectively.

In the macro-micro-pore model the catalytic effectiveness and selectivity have been analyzed by Mingle and Smith (8), Carberry (9, 10) and Tartarelli and Morelli (11) for first order reactions, Tartarelli *et al.* (12) for zero order reactions; the falsification of activation energy and order of process under diffusion effect conditions has been given by Tartarelli *et al.* (13-16) for second order reactions.

The derivations that follow are based upon the following assumptions:

1. The catalyst pellet is at uniform temperature.
2. The irreversible second order reactions $\nu A \rightarrow$ products and $A + B \rightarrow$ products occur without volume change.
3. Significant reaction occurs only in the micropores, i.e., the surface of the macropore is assumed entirely covered by micropores.

NOTATION

a	Reduced concentration of reactant A in micropore, $[A]/[A]_0$
a^+	Reduced concentration of reactant A in macropore, $[A]^+/[A]_0$
$[A]_0$	Concentration of reactant A at gas-catalyst interface
b	Reduced concentration of reactant B in micropore, $[B]/[A]_0$
b^+	Reduced concentration of reactant B in macropore, $[B]^+/[A]_0$
b_0	Reduced concentration of reactant B at gas-catalyst interface, $[B]_0/[A]_0$
$[B]_0$	Concentration of reactant B at gas-catalyst interface
D_A, D_B	Diffusivity of reactants A, B in micropore
D_A^+, D_B^+	Diffusivity of reactants A, B in macropore
E'_{app}, E''_{app}	Apparent activation energy of process
E_d	Diffusion activation energy
E_r	Reaction activation energy
K	Reaction rate constant
l	Micropore length
l^+	Macropore length
m	Micropore diffusion-reaction modulus for second order reactions
\mathbf{m}	Micropore diffusion-reaction modulus for first order reactions
$n'_{A,app}, n''_{A,app}$	Apparent order of process with respect to reactant A
$n''_{B,app}$	Apparent order of process with respect to reactant B
$n_{o,app}$	Overall apparent order of process
r	Micropore radius
r^+	Macropore radius
R_g	Gas constant
T	Absolute temperature

Greek Letters

γ	Relative diffusivity
η', η''	Effectiveness factor for second order reactions
\mathbf{n}	Effectiveness factor for first order reactions
λ	Mean free path of gaseous molecule
ν	Stoichiometric coefficient
θ	Macro-micro-pore model geometric modulus, $[(D_A/D_A^+)(l^2/r^+l)]^{1/2}$
ξ	$\Omega''/m^{3/2}$
ρ	Micropore coordinate/micropore length
ρ^+	Macropore coordinate/macropore length
ϕ', ϕ''	Rate of disappearing of reactant A per unit catalyst surface
Ω', Ω''	Generalized Thiele modulus for second order reactions
$\mathbf{\Omega}$	Generalized Thiele modulus for first order reactions

BASIC EQUATIONS

I. $\nu A \rightarrow \text{Products}$

Effectiveness factor. The governing equation in reduced dimensions for the micropore of length l is:

$$\frac{d^2a}{d\rho^2} = m^2a^2, \quad (1)$$

with boundary conditions

$$\rho = 0 \quad a = a^+, \quad \rho = 1 \quad da/d\rho = 0.$$

In the macropore of length l^+ the material balance equation becomes:

$$\frac{d^2a^+}{d\rho^{+2}} = 2\theta^2 \left(-\frac{da^+}{d\rho^+} \right)_{\rho=0}, \quad (2)$$

with boundary conditions

$$\rho^+ = 0 \quad a^+ = 1, \quad \rho^+ = 1 \quad da^+/d\rho^+ = 0.$$

In Eqs. (1) and (2) $m \equiv (2K[A]_0/rD_A)^{1/2} l$ is the micropore diffusion-reaction modulus and $\theta \equiv [(D_A/D_A^+)(l^2/r^+l)]^{1/2}$ is the geo-

metric modulus of the macro-micro-pore structure. The micropore diffusivity/macro-pore diffusivity ratio may be related to the micropore and macropore radius by the Wheeler's equation (17).

$$D = D_o(1 - e^{-2(\text{pore radius})/\lambda})$$

where D_o is the ordinary diffusivity for bulk gas.

In strong pore diffusion regimes, i.e., the reactant concentration drops to a very small value, approximately zero, at the pore-ends, by applying the asymptotic method (5) to the Eqs. (1) and (2), we obtain:

$$-\left(\frac{da^+}{d\rho^+}\right)_{\rho^+=0} = \left(\frac{128}{75}\right)^{1/4} m^{1/2}\theta, \quad (3)$$

and the effectiveness factor, which is defined as

$$\eta = \frac{\left[\tanh\left(\frac{\Omega^2}{2\theta^2}\right)^{1/3} \right]^{1/2} \tanh\left\{ (2\Omega\theta^2)^{1/3} \left[\tanh\left(\frac{\Omega^2}{2\theta^2}\right)^{1/3} \right]^{1/2} \right\}}{\Omega}, \quad (8)$$

$$\eta' \equiv \frac{-(da^+/d\rho^+)_{\rho^+=0}}{2m^2\theta^2}, \quad (4)$$

results

$$\eta' = \Omega'^{-1}, \quad (5)$$

where

$$\Omega' \equiv \left(\frac{75}{8}\right)^{1/4} m^{3/2}\theta. \quad (6)$$

From Eq. (5) Ω' can be assumed as the generalized Thiele modulus for the macro-micro-pore model.

In terms of Ω' the effectiveness factor becomes:

$$\eta' = \left(\frac{75}{32}\right)^{1/3} \frac{-(da^+/d\rho^+)_{\rho^+=0}}{\Omega'^{1/2}\theta^{2/3}}. \quad (7)$$

The system of differential equations (1) and (2) has been solved by the IBM 7090 digital computer and values of the effectiveness factor have been reported in Table 1 against the generalized Thiele modulus for different values of θ . The effectiveness factor for the second order reaction is compared with the effectiveness factor for the first order reaction. In the last case the analytic solution is quite elementary, given by:

$$\Omega \equiv 2^{1/2}m^{3/2}\theta, \text{ with } m \equiv \left(\frac{2K}{rD_A}\right)^{1/2} l. \quad (9)$$

The chemical and strong pore diffusion regimes in the single-pore model are separated by an intermediate regime which drops in the range 0.5–5 of the generalized Thiele modulus (5). In this region the

TABLE I
EFFECTIVENESS FACTOR VS. GENERALIZED THIELE MODULUS FOR THE REACTION $\nu A \rightarrow X$

Generalized Thiele modulus	Effectiveness factor							
	First order reaction				Second order reaction			
	$\theta = 50$	$\theta = 100$	$\theta = 500$	$\theta = 1000$	$\theta = 50$	$\theta = 100$	$\theta = 500$	$\theta = 1000$
0.05	0.906	0.861	0.692	0.597	0.873	0.821	0.650	0.596
0.1	0.799	0.721	0.499	0.407	0.746	0.688	0.464	0.394
0.2	0.628	0.530	0.327	0.260	0.574	0.484	0.306	0.250
0.3	0.513	0.420	0.250	0.199	0.469	0.387	0.235	0.190
0.5	0.379	0.304	0.178	0.141	0.399	0.280	0.168	0.135
1	0.241	0.192	0.112	0.089	0.219	0.182	0.106	0.085
1.5	0.184	0.146	0.086	0.068	0.172	0.139	0.081	0.065
2	0.152	0.121	0.071	0.056	0.146	0.116	0.067	0.054
3	0.116	0.092	0.054	0.043	0.112	0.090	0.052	0.042
5	0.082	0.065	0.038	0.031	0.081	0.063	0.037	0.030

functions effectiveness factor vs. generalized Thiele modulus for first and second order reactions show the greatest difference being approximately 5%. From Table 1 it results that also in the macro-micro-pore model the functions effectiveness factor vs. generalized Thiele modulus for first and second order reactions follow one another quite closely and the greatest difference is about 10% for $\theta > 50$ in the intermediate range of the generalized Thiele modulus.

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

$$E'_{\text{app}} \equiv - \frac{\partial \ln \phi'}{\partial (1/R_g T)}, \quad (10)$$

and

$$n'_{\text{A,app}} = \frac{\partial \ln \phi'}{\partial \ln [A]_0}, \quad (11)$$

where ϕ' is the rate of disappearing of reactant A per unit catalyst surface, given by

$$\phi' = K\eta'[A]_0^2. \quad (12)$$

From Eqs. (10), (11), and (12) we obtain:

$$\frac{E'_{\text{app}}}{E_r} = 1 + \frac{3}{4} \left(1 - \frac{E_d}{E_r} \right) \frac{\partial \ln \eta'}{\partial \ln \Omega'}, \quad (13)$$

and

$$n'_{\text{A,app}} = 2 + \frac{3}{4} \frac{\partial \ln \eta'}{\partial \ln \Omega'}, \quad (14)$$

where E_r is the reaction activation energy from the Arrhenius' law and E_d is the diffusion activation energy (the dependence of D_A/D_A^+ on temperature is assumed negligible).

By substituting $\frac{3}{4} (\partial \ln \eta' / \partial \ln \Omega')$ from Eq. (13) into Eq. (14) for $E_d/E_r \neq 1$ (practically $E_d \ll E_r$), the equation common to isothermal second order processes (15, 18) is derived:

$$n'_{\text{A,app}} = 2 + \left(\frac{E'_{\text{app}}}{E_r} - 1 \right) / \left(1 - \frac{E_d}{E_r} \right). \quad (15)$$

From Eq. (5) the strong pore diffusion regimes are characterized by the simple relations:

$$\frac{E'_{\text{app}}}{E_r} = \frac{1}{4} + \frac{3}{4} \frac{E_d}{E_r}, \quad (16)$$

and

$$n'_{\text{A,app}} = \frac{5}{4}.$$

In diffusion limited regimes, the macro-micro-pore model gives, for $E_d/E_r \simeq 0$, lower values of both apparent activation energy and order of process if compared with the single-pore model. In the last case we have:

$$\frac{\text{(Apparent activation energy of process)}}{E_r} = \frac{1}{2} + \frac{1}{2} \frac{E_d}{E_r}, \quad (17)$$

and

$$\text{Apparent order of process} = \frac{3}{2}. \quad (18)$$

II. $A + B \rightarrow \text{Products}$

Effectiveness factor. As the molar flux of reactant A at the steady state must be equal to the molar flux of the reactant B from the stoichiometry of reaction, the following equations relate the concentration of B to that of A in micropore and macropore:

$$b = \gamma a + b_0 - \gamma, \quad (19)$$

$$b^+ = \gamma a^+ + b_0 - \gamma, \quad (20)$$

where $b_0 \equiv [B]_0/[A]_0$ and $\gamma \equiv D_A/D_B = D_A^+/D_B^+$ is the ratio of diffusivity of reactants, assumed constant in both micropore and macropore. If $b_0 = \gamma$, the reaction rate equation is quite equivalent to that above discussed and in strong pore diffusion regimes the concentration of both reactants drops to zero at the pore-ends. Because the reactant A has been taken as a reference in the Eqs. (19) and (20), the general case of a second order process involving two reactants must be treated with the assumption of $b_0 > \gamma$. That gives $b, b^+ > 0$ at $a, a^+ = 0$ and the controlling regime may be based upon the limiting reactant A.

The material balance equations in the micropore and in the macropore are, respectively:

$$\frac{d^2 a}{d\rho^2} = m^2 a (\gamma a + b_0 - \gamma), \quad (21)$$

$$\frac{d^2 a^+}{d\rho^{+2}} = 2\theta^2 \left(-\frac{da}{d\rho} \right)_{\rho=0}, \quad (22)$$

with boundary conditions

$$\begin{aligned} \rho = 0 \quad a = a^+, \quad \rho = 1 \quad da/d\rho = 0, \\ \rho^+ = 0 \quad a^+ = 1, \quad \rho^+ = 1 \quad da^+/d\rho^+ = 0. \end{aligned}$$

By applying the asymptotic method (5) to the Eqs. (21) and (22), when the concentration of A drops to zero at the pore-ends, we obtain as generalized Thiele modulus:

$$\Omega'' \equiv \frac{\gamma^{1/2} m^{3/2} \theta b_0}{\left[\left(b_0 - \frac{\gamma}{3} \right)^{3/2} - \frac{3}{5\gamma} \left(b_0 - \frac{\gamma}{3} \right)^{5/2} + \frac{3(b_0 - \gamma)^{5/2}}{5\gamma} \right]^{1/2}}, \quad (23)$$

and the effectiveness factor $\eta'' \equiv - (da^+/d\rho^+)_{\rho^+=0} / 2 m^2 \theta^2 b_0$, in terms of Ω'' becomes:

$$\eta'' = \frac{\gamma^{2/3} b_0^{1/3} (-da^+/d\rho^+)_{\rho^+=0}}{2 \left[\left(b_0 - \frac{\gamma}{3} \right)^{3/2} - \frac{3}{5\gamma} \left(b_0 - \frac{\gamma}{3} \right)^{5/2} + \frac{3(b_0 - \gamma)^{5/2}}{5\gamma} \right]^{2/3} \theta^{2/3} \Omega''^{4/3}} \quad (24)$$

Values of the effectiveness factor, calculated by the computer, are presented in Table 2. Also in this type of reaction, the functions effectiveness factor vs. generalized Thiele modulus follow very closely the functions, above given, concerning the first order reaction and the greatest difference for the examined values of b_0 and θ ($\gamma = 1$) is about 6% in the intermediate region between chemical and strong pore diffusion regimes.

Apparent kinetics. The apparent activation energy of process, $E''_{app} \equiv -[\partial \ln \phi'' / \partial (1/R_g T)]$ where $\phi'' = K \eta'' [A]_0 [B]_0$ is given by:

$$\frac{E''_{app}}{E_r} = 1 + \frac{3}{4} \left(1 - \frac{E_d}{E_r} \right) \left(\frac{\partial \ln \eta''}{\partial \ln \Omega''} \right)_{b_0} \quad (25)$$

if equal diffusion activation energies of reactants are assumed ($E_d = E_{d,A} = E_{d,B}$). The apparent order of process with respect to A, $n''_{A,app} \equiv \partial \ln \phi'' / \partial \ln [A]_0$, results:

$$\begin{aligned} n''_{A,app} &= 1 + \left(\frac{\partial \ln \eta''}{\partial \ln [A]_0} \right)_{[B]_0} \\ &= 1 + \left(\frac{\partial \ln \eta''}{\partial \ln \Omega''} \right)_{b_0} \frac{\partial \Omega''}{\partial \ln [A]_0} \\ &\quad + \left(\frac{\partial \ln \eta''}{\partial b_0} \right)_{\Omega''} \frac{\partial b_0}{\partial \ln [A]_0}. \end{aligned} \quad (26)$$

Because is:

$$\frac{\partial \Omega''}{\partial \ln [A]_0} = \frac{3}{4} \Omega'' - \frac{d\xi}{d \ln b_0} \text{ with } \xi \equiv \frac{\Omega''}{m^{3/2}}, \quad (27)$$

$$\frac{\partial b_0}{\partial \ln [A]_0} = -b_0,$$

we obtain:

$$n''_{A,app} = 1 + \left(\frac{3}{4} \Omega'' - \frac{d\xi}{d \ln b_0} \right) \left(\frac{\partial \ln \eta''}{\partial \Omega''} \right)_{b_0}$$

$$- \left(\frac{\partial \ln \eta''}{\partial \ln b_0} \right)_{\Omega''}. \quad (28)$$

The apparent order of process with respect to B, $n''_{B,app} \equiv \partial \ln \phi'' / \partial \ln [B]_0$, results:

$$\begin{aligned} n''_{B,app} &= 1 + \frac{d\xi}{d \ln b_0} \left(\frac{\partial \ln \eta''}{\partial \Omega''} \right)_{b_0} \\ &\quad + \left(\frac{\partial \ln \eta''}{\partial \ln b_0} \right)_{\Omega''}. \end{aligned} \quad (29)$$

From Eqs. (28) and (29), the overall apparent order of process $n_{o,app} \equiv n''_{A,app} + n''_{B,app}$, is given by:

$$n_{o,app} = 2 + \frac{3}{4} \left(\frac{\partial \ln \eta''}{\partial \ln \Omega''} \right)_{b_0}. \quad (30)$$

By substituting $3/4 (\partial \ln \eta'' / \partial \ln \Omega'')_{b_0}$ into Eq. (25), the general relation between $n_{o,app}$, (E''_{app}/E_r) , (E_d/E_r) is obtained:

$$n_{o,app} = 2 + \left(\frac{E''_{app}}{E_r} - 1 \right) / \left(1 - \frac{E_d}{E_r} \right). \quad (31)$$

It is worthy to be remarked that the Eqs. (25), (30), and (31), concerning the apparent activation energy and overall order of process, are quite alike the corresponding Eqs. (13), (14), and (15). A similar behavior may be derived also for the single-pore model.

In strong pore diffusion regimes, when $(\partial \ln \eta'' / \partial \Omega'') = -(1/\Omega'')$ and $(\partial \ln \eta'' /$

TABLE 2
EFFECTIVENESS FACTOR VS. GENERALIZED THIELE MODULUS FOR THE REACTION $A + B \rightarrow$ PRODUCTS
WITH $\gamma = 1$

Generalized Thiele modulus	Effectiveness factor					
	$b_0 = 2$			$b_0 = 5$		
	$\theta = 50$	$\theta = 100$	$\theta = 500$	$\theta = 50$	$\theta = 100$	$\theta = 500$
0.05	0.883	0.834	0.667	0.896	0.847	0.687
0.1	0.763	0.684	0.478	0.782	0.703	0.493
0.2	0.591	0.501	0.315	0.612	0.517	0.323
0.3	0.485	0.399	0.242	0.501	0.412	0.247
0.5	0.362	0.292	0.173	0.372	0.300	0.176
1	0.233	0.186	0.109	0.238	0.189	0.111
1.5	0.178	0.142	0.084	0.182	0.145	0.085
2	0.147	0.119	0.069	0.151	0.119	0.070
3	0.113	0.091	0.053	0.115	0.091	0.053
5	0.080	0.064	0.038	0.082	0.065	0.038

$\partial \ln b_0)_{\theta} = 0$, the apparent reaction order with respect to A results:

$$n''_{A,app} = \frac{5}{4} \frac{3b_0 \left[\left(b_0 - \frac{\gamma}{3} \right)^{1/2} - \frac{1}{\gamma} \left(b_0 - \frac{\gamma}{3} \right)^{3/2} + \frac{(b_0 - \gamma)^{3/2}}{\gamma} \right]}{4 \left[\left(b_0 - \frac{\gamma}{3} \right)^{3/2} - \frac{3}{5\gamma} \left(b_0 - \frac{\gamma}{3} \right)^{5/2} + \frac{3(b_0 - \gamma)^{5/2}}{5\gamma} \right]} \quad (32)$$

Because the overall apparent order of process is from Eq. (30):

$$n_{o,app} = \frac{5}{4}, \quad (33)$$

the apparent order of process with respect to B may be obtained from Eqs. (32) and (33) by:

$$n''_{B,app} = \frac{5}{4} - n''_{A,app}. \quad (34)$$

Eqs. (32) and (33) may be compared with the corresponding Equations in the single-pore model which are:

$$\text{Apparent order of process with respect to A} = \frac{3}{2} - \frac{b_0}{2[b_0 - (\gamma/3)]}, \quad (35)$$

and

$$\text{Overall apparent order of process} = \frac{3}{2}. \quad (36)$$

SUMMARY

Isothermal second order reactions of the type $\nu A \rightarrow$ products and $A + B \rightarrow$ products have been investigated in the macro-micro-

pore catalyst model. The system of differential equations deduced as material bal-

ances in micropore and macropore has been solved by a digital computer and values of effectiveness factor have been reported against a generalized Thiele modulus, the use of which tends to approximately bring together the curves effectiveness factor vs. Thiele modulus for first and second order reactions. Equations concerning the falsification of activation energy and order of process under diffusion effect conditions have been presented.

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