Mass Transfer in Heterogeneous Catalysis

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For more details see:
Roland Dittmeyer and Gerhard Emig
Molecular Level: e.g. Langmuir-Hinshelwood Kinetics

\[ \theta_A = \frac{K_A p_A}{1 + K_A p_A} \]

Adsorption

Reaction = sequential steps

Desorption

\[ r = k \theta_A \theta_B = \frac{k K_A p_A K_B p_B}{(1 + K_A p_A + K_B p_B)^2} \]

p_A = partial pressure near surface
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Fig. 1 Basic types of catalytic fixed-bed reactors. (a) Adiabatic fixed-bed reactor; (b) multitubular fixed-bed reactor.
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Fig. 3: Common shapes of monolith catalysts. (a) Square-channel monolith; (b) parallel-plate monolith; (c) corrugated-plate packing.
Pressure drop in a fixed bed

\[ \bar{u} = \frac{1}{32} \frac{d^2}{\eta} \frac{\Delta p}{L} \]

\[ \bar{u} = F(\varepsilon) \frac{d_k^2}{\eta} \frac{\Delta p}{L} = \frac{u_0}{\varepsilon} \quad F(\varepsilon) = \frac{1}{150} \left( \frac{\varepsilon}{1 - \varepsilon} \right)^2 \]

\[ u_0 = \frac{\varepsilon^3}{150 (1 - \varepsilon)^2} \frac{d_k^2 \Delta p}{\eta L} \]

\[ \Delta p = \frac{L}{d_k} \lambda(Re) \frac{1}{2} \rho u_0^2 \]

\[ \lambda(Re) = \frac{(1 - \varepsilon)^2}{\varepsilon^3} \frac{300}{Re} \quad \text{laminar} \]

\[ \lambda(Re) = \frac{(1 - \varepsilon)}{\varepsilon^3} \left[ \frac{300(1 - \varepsilon)}{Re} + 3.5 \right] \quad \text{laminar und turbulent, Ergun-Gl.} \]
Sequential steps:
Pressure driven flow, Film diffusion, Pore diffusion

Fig. 1 Individual steps of a simple, heterogeneous catalytic fluid–solid reaction $A_1 \rightarrow A_2$ carried out on a porous catalyst.
Steps of Heterogeneous Reaction

1. Diffusion of reactant to catalyst
2. Transport of reactant within catalyst pores
3. Adsorption of reactant on catalyst surface
4. Reaction
5. Desorption of products from catalyst surface
6. Transport of products out of catalyst pores
7. Diffusion of products away from catalyst

Transport and reaction occur simultaneously
(at a catalyst under steady state conditions)
Impact of mass transfer limitation

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Feed

k > D

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Mass Transport and Heterogeneous Catalysis

Principles

Influence of mass transport on the temperature dependence of het. catalysis

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Fig. 3 Transition from the kinetic regime to the diffusion-controlled regime of a heterogeneous catalytic fluid–solid reaction carried out on a porous catalyst.
Fig. 2 Stationary concentration (reactant) and temperature profiles inside and around a porous catalyst pellet during an exothermic, heterogeneous catalytic fluid-solid reaction: (a) without transport influence; (b) limited only by intraparticle diffusion; (c) limited by interphase and intraparticle diffusion; (d) limited only by interphase diffusion (dense pellet).
Time Scales in a Reactor

residence time  \( \tau = \frac{V_R}{V_F} \)

Mixing time  \( \Theta \)

Time constant of reaction  =  \( \frac{C_{M,0}}{R_0} \)

Time constant of diffusion  =  \( \frac{R^2}{D_e} \)
Description of pore diffusion

\[ \vec{j} = -D \nabla c \]

1. Fick's Law

\[ D_g = \frac{1}{2} \Lambda w \]

\[ \Lambda = \frac{k_B T}{\sqrt{2\pi\sigma^2 p}} \quad \text{Average free path length} \]

\[ w = \sqrt{\frac{8k_B T}{\pi m}} \quad \text{Average molecular velocity} \]

\[ D_g \sim T^{1.5} \quad \text{und} \quad D_g \sim 1/p \]
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a) Diffusion in pores $d_p \gg \lambda$

$$D_{\text{eff}} = D_g \frac{\varepsilon}{\tau}$$

b) Knudsen – Diffusion $d_p = \lambda$

$$D_{\text{eff}} = D_K \frac{\varepsilon}{\tau} = \frac{1}{2} \frac{d_p}{2} \frac{\varepsilon}{\tau}$$

$$D_K \sim T^{0.5}$$

c) Intermediate range

$$D_{\text{eff}} = \frac{1}{1} \frac{\varepsilon}{\tau} + \frac{1}{1} \frac{\varepsilon}{\tau}$$

$$\frac{1}{D_g} + \frac{1}{D_K}$$

$$\rightarrow \frac{\varepsilon}{\tau}$$

$$j_x = -D_{\text{eff}} \text{grad} C_x$$
Simultaneous reaction and pore diffusion in a spherical particle

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**Mass balance**

\[
\int \frac{dc_i}{dt} dV = -\oint (\vec{j} \cdot d\vec{a}) + \int \nu_i r \, dV
\]

\[
\oint (\vec{j} \cdot d\vec{a}) = \int \text{div} \vec{j} \, dV
\]

\[
\frac{dc_i}{dt} = -\text{div} \vec{j}_i + \nu_i r
\]

**One dimensional**

\[
\text{div} \vec{j} = \frac{d}{dz} j_z
\]

**Spherical geometry**

\[
\text{div} \vec{j} = \frac{1}{R^2} \frac{d}{dR} (R^2 j_R)
\]
Mass balance of spherical particle in steady state

\[ 0 = -\frac{1}{R^2} \frac{d}{dR} \left( R^2 j_R \right) + v_i r \]

Solution of mass balance and description of average reaction rate

\[ D_{\text{eff}} \left( \frac{d^2 c}{dR^2} + \frac{2}{R} \frac{dc}{dR} \right) = k \ c^n \]

with \( r = kc^n \) and \( v = -1 \)

\[ c(R = R_0) = c_0 \]

\[ \frac{dc}{dR} \bigg|_{R=0} = 0 \]

\[ \Phi_0 = R_0 \sqrt{\frac{kc_{n-1}}{D_{\text{eff}}}} \]

renormalized parameter

\( = \) Thiele-Modulus

\[ c(R) = c_0 \frac{R_0}{R} \frac{\sinh \left( \frac{R}{R_0} \Phi_0 \right)}{\sinh \Phi_0} \]

radial concentration profile within spherical pellet
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Fig. 4  Normalized concentration profiles of reactant $A_1$ versus the dimensionless pellet radius, calculated from Eq. (49) for different values of the Thiele modulus $\phi$ (isothermal, first-order irreversible reaction in a sphere).

$k > D$

$k < D$
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\[ rV_s = A_s D_{\text{eff}} \left. \frac{dc}{dR} \right|_{R=R_0} \]  \quad r = r_{\text{het}}

\[ r_{\text{het}} = \frac{3}{R_0} D_{\text{eff}} \frac{c_0}{R_0} \left( \frac{\Phi_0}{\tanh \Phi_0} - 1 \right) \]

\[ r_{\text{hom}} = k c_0 \quad \text{Reaction without mass transport limitation} \]

\[ \eta = \frac{r_{\text{het}}}{r_{\text{hom}}} = \frac{3}{\Phi_0} \left( \frac{1}{\tanh \Phi_0} - \frac{1}{\Phi_0} \right) \quad \text{Effectiveness factor} \]
Fig. 5 Effectiveness factor $\eta$ as a function of the Thiele modulus $\phi$ for different pellet shapes. Influence of intraparticle diffusion on the effective reaction rate (isothermal, first-order irreversible reaction).

Fig. 7 Effectiveness factor $\eta$ as a function of the generalized Thiele modulus $\phi_{pn}$ for different reaction orders. Influence of intraparticle diffusion on the effective reaction rate (isothermal, first-order irreversible reaction in a flat plate).
Influence of temperature

\[ \eta \approx \frac{3}{\Phi_0} \]

\[ r_{\text{het}} = \frac{3}{\Phi_0} k c_0 = \frac{3}{R_0} \sqrt{\frac{D_{\text{eff}}}{k}} \quad k c_0 = k_{\text{eff}} c_0 \]

\[ k_{\text{eff}} \cong \sqrt{D_{\text{eff}} k} \]

\[ E_{\text{eff}} = \frac{1}{2} (E + E_D) \]

Influence of pore diffusion on effective rate constant
Film diffusion und Reaction

\[
\dot{n}_{\text{Diff}} = S_a D \frac{c_0 - c_W}{\delta}
\]

\[
\dot{n}_{\text{Diff}} = S_a \beta (c_0 - c_W), \quad \text{mit} \quad \beta = \frac{D}{\delta}
\]

\[
r = \frac{1}{v_i} \frac{1}{V} \frac{dn_i}{dt} \left[ \frac{mol}{s^*m^3} \right]
\]

\[
r_S = \frac{1}{v_i} \frac{1}{S_a} \frac{dn_i}{dt} \left[ \frac{mol}{s^*m^2} \right]
\]

\[
r = r_S a, \quad k = k_S a \quad \text{mit:} \quad a = \frac{S_a}{V}
\]

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How to get to the active site?

Discussion of a first order reaction with $r_s = k_s c_w$

$\beta (c_0 - c_w) = k_s c_w$

$c_w = \frac{c_0 \beta}{\beta + k_s}$

Border cases:

$k_s << \beta \quad c_w = c_0 \quad$ (no layer formation)

$k_s >> \beta \quad c_w \approx 0$
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$$r_S = k_S c_W = \frac{\beta k_S}{\beta + k_S} c_0 = k_{S,\text{eff}} c_0$$

$$\frac{1}{k_{S,\text{eff}}} = \frac{1}{k_S} + \frac{1}{\beta}$$

Calculation of eff. volume related rate constant

$$k_{\text{eff}} = a k_{S,\text{eff}} = \frac{a}{\frac{1}{k_S} + \frac{1}{\beta}} = \frac{1}{\frac{1}{k} + \frac{1}{a\beta}}$$

$$a = \frac{\text{Particle surface}}{\text{Particle volume}} = \frac{\pi d^2}{\frac{\pi}{6} d^3} = \frac{6}{d_{\text{sphere}}}$$

$$\frac{1}{k_{\text{eff}}} = \frac{1}{a\beta} + \frac{1}{\eta k}$$
Temperature dependence:

\[ \ln k_{\text{eff}} \]

\[ E_{\text{eff}} \approx 0 \]

\[ \eta \ll 1, \ E_{\text{eff}} \approx \frac{1}{2} E \]

\[ \eta = 1, \ E_{\text{eff}} = E \]

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Criteria to exclude mass transfer limitations

\[ \phi_{pn} = \frac{V_p}{S_p} \sqrt{\frac{n + 1}{2} \frac{k c_b^{n-1}}{D_e}} = \phi_p \sqrt{\frac{n + 1}{2}} \]

Generalized Thiele-Modulus

Criterion with measurable data only: Weisz-Modul

\[ \psi = \frac{R^2 r_e}{D_e c_b} < 1 \quad \psi_{pn} = \left( \frac{V_p}{S_p} \right)^2 \frac{n + 1}{2} \frac{r_e}{D_e c_b} \]

\[ \psi = \eta \phi^2; \quad \psi_{pn} = \eta \phi_{pn}^2 \]

How to get to the active site?
Experimental check

for pore diffusion

Reduce particle size
→ decrease $\phi$
→ increase $\eta$ $\rightarrow$ 1

at constant $\tau$, $T$, $c_i$

for film diffusion

Decrease reactor diameter
$\tau = V_R / V_f$
→ increase $u = V_f / q$
→ increase $\beta = D / \delta$

at constant $\tau$, $T$, $c_i$
Tab. 3 Experimental diagnostic criteria for the absence of interphase and combined intraparticle and interphase transport effects in simple, irreversible reactions (power law kinetics only)

<table>
<thead>
<tr>
<th>Application</th>
<th>No.</th>
<th>Criterion</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interphase mass transfer ((T = \text{constant}))</td>
<td>1</td>
<td>(\frac{n k_e}{k_f a} &lt; 0.1; \quad n = 1)</td>
<td>[36]</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>(\frac{R r_e}{k_f c_b} &lt; \frac{0.15}{</td>
<td>n</td>
</tr>
<tr>
<td>Interphase heat transfer ((c = \text{constant}))</td>
<td>3</td>
<td>(</td>
<td>\chi</td>
</tr>
<tr>
<td>Intra-/interphase heat and mass transfer (\text{combined effect})</td>
<td>4</td>
<td>(\frac{R^2 r_e}{D_e c_b} &lt; \frac{1 + 0.33 y \chi}{</td>
<td>n - y \beta</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>(</td>
<td>y \beta + 0.3 n y \chi</td>
</tr>
</tbody>
</table>

\(\chi\) as defined by criterion No. 3

<5\% deviation of \(\eta\) from \(\eta_{\text{iso}}\)
## Tab. 2 Experimental diagnostic criteria for the absence of intraparticle transport effects in simple, irreversible reactions (power law kinetics only)

<table>
<thead>
<tr>
<th>Application</th>
<th>No.</th>
<th>Criterion</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore diffusion ($T = constant$)</td>
<td>1</td>
<td>$\frac{r^2 re}{D_c c_s} &lt; 1$; $n = 1$</td>
<td>[11]</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>$\frac{r^2 re}{D_c c_s}$</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>$&lt; 0.6$; $n = 0$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$&lt; 0.3$; $n = 1$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>$\frac{r^2 re}{D_c c_s} &lt; \frac{1}{</td>
<td>n</td>
</tr>
<tr>
<td>Heat conduction ($c = constant$)</td>
<td>4</td>
<td>$\frac{R^2</td>
<td>\Delta H_R</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$&lt; 5%$ deviation of $\eta$ from $\eta_{iso}$</td>
<td></td>
</tr>
<tr>
<td>Pore diffusion and heat conduction</td>
<td>5</td>
<td>$\frac{r^2 re}{D_c c_s} &lt; \frac{1}{</td>
<td>n - \gamma \beta</td>
</tr>
<tr>
<td>(combined effect)</td>
<td>6</td>
<td>$\frac{r^2 re}{D_c c_s} &lt; 13$; $n \approx \gamma \beta$</td>
<td>[55]</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>$</td>
<td>\gamma \beta</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$&lt; 5%$ deviation of $\eta$ from $\eta_{iso}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>$\frac{r^2 re}{D_c c_s} e^{\left(\frac{\gamma \beta}{1 + \beta}\right)} &lt; 1$</td>
<td>[38]</td>
</tr>
</tbody>
</table>