

Mass Transfer in Heterogeneous Catalysis

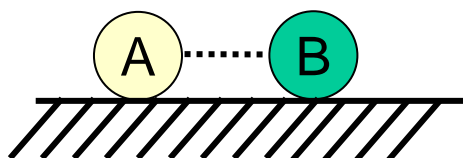
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For more details see:

Roland Dittmeyer and Gerhard Emig

Simultaneous Heat and Mass Transfer and Chemical Reaction,
chapter 6.3 in Handbook of Heterogeneous Catalysis Eds. G. Ertl, et.al
Wiley-VCH, Weinheim, 2007

Molecular Level: e.g. Langmuir-Hinshelwood Kinetics



Adsorption

Reaction = sequential steps

Desorption

$$\theta_A = \frac{K_A p_A}{1 + K_A p_A}$$

p_A = partial pressure near surface

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



How to get to the active site ?

Block Course "Reactivity and Catalysis"

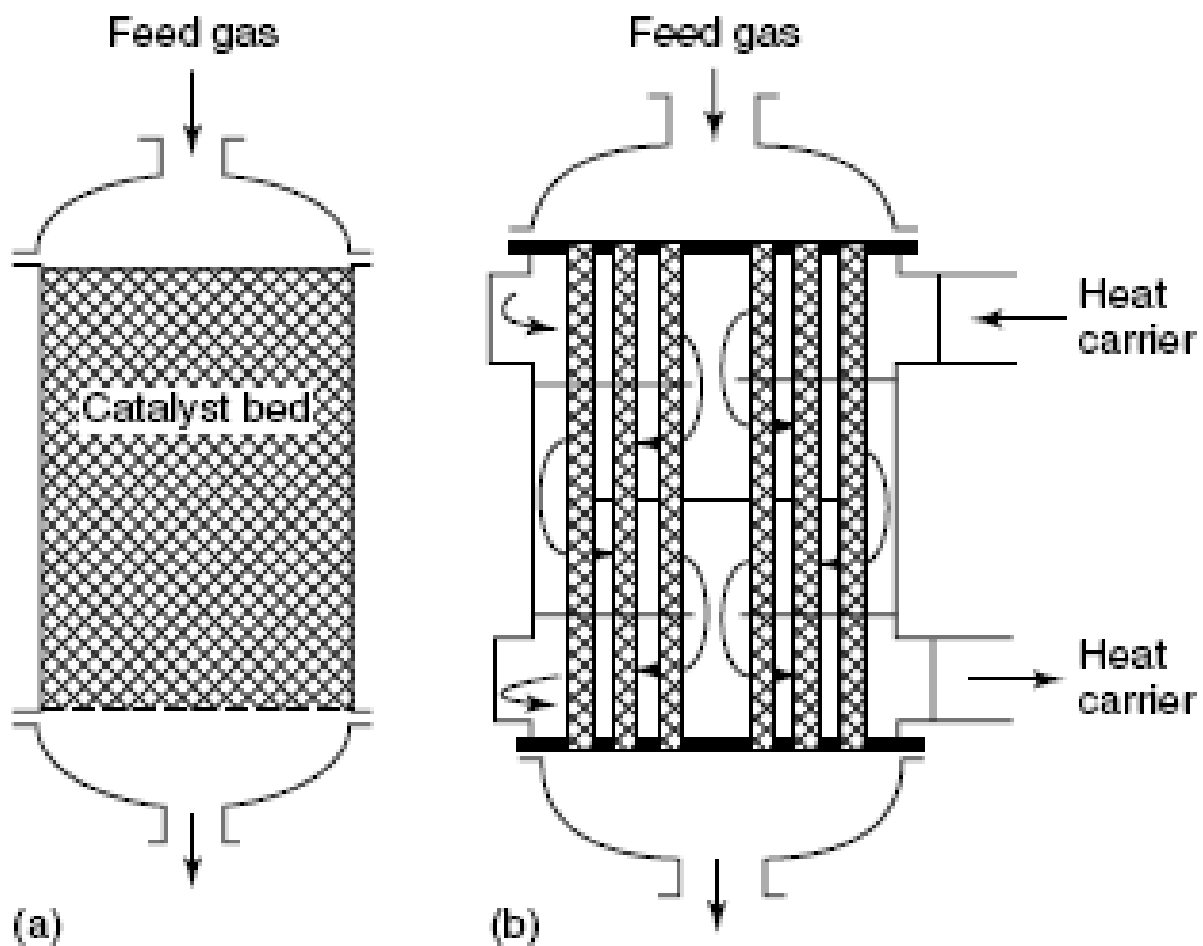
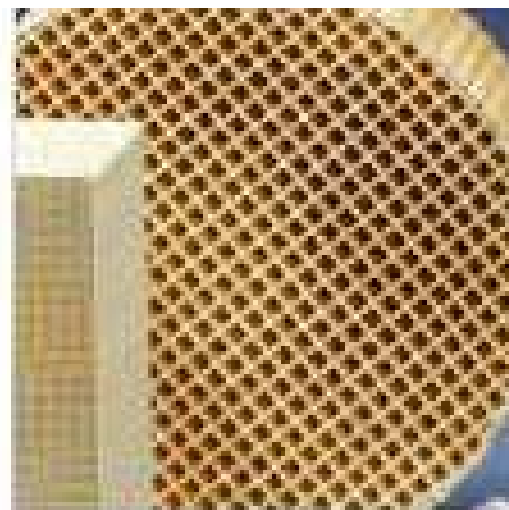


Fig. 1 Basic types of catalytic fixed-bed reactors. (a) Adiabatic fixed-bed reactor; (b) multitubular fixed-bed reactor.



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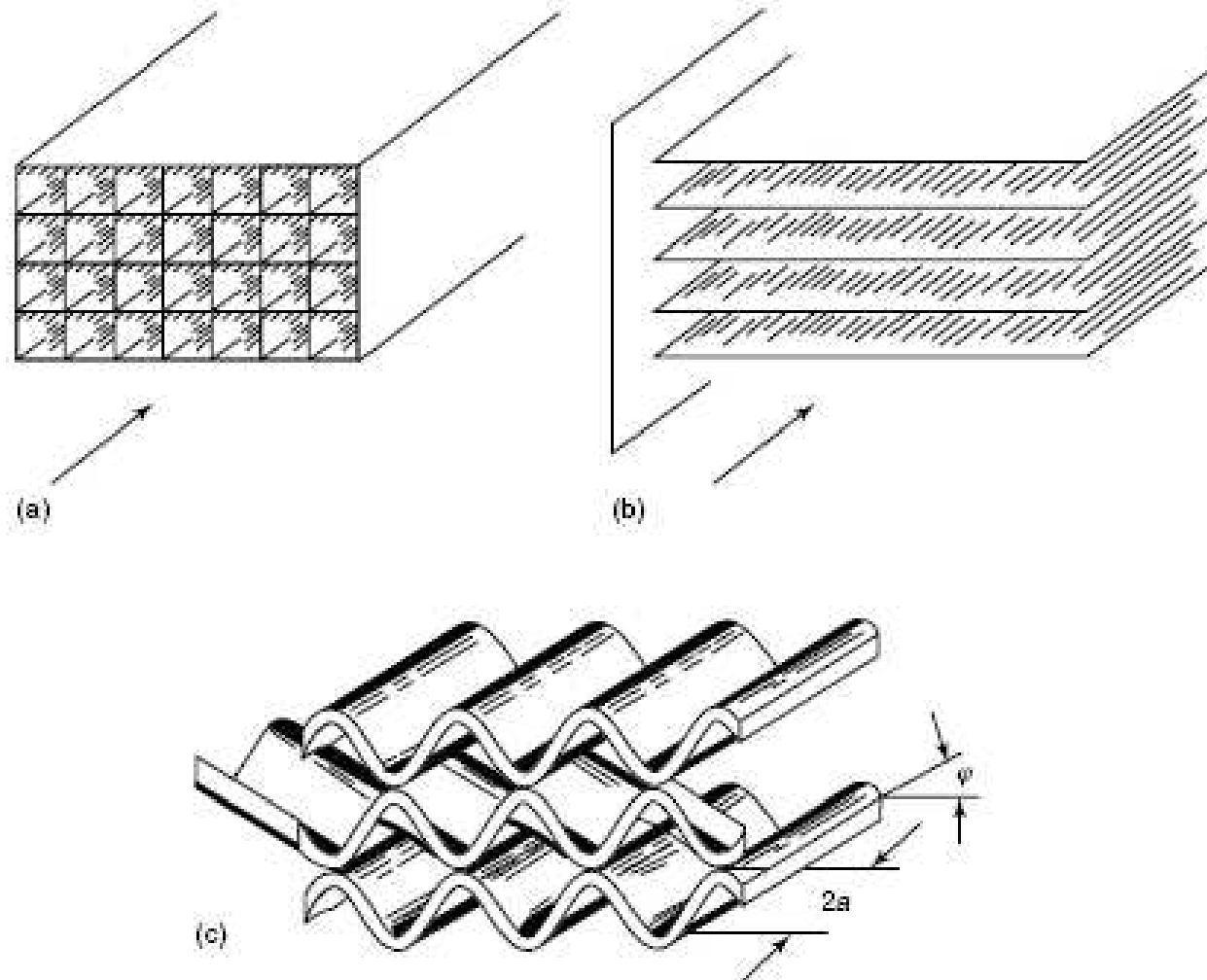
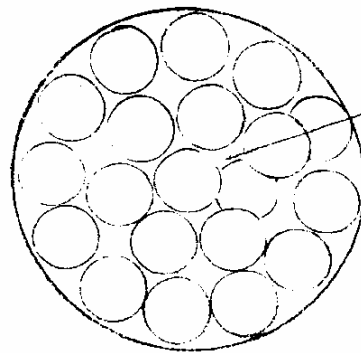


Fig. 3 Common shapes of monolith catalysts. (a) Square-channel monolith; (b) parallel-plate monolith; (c) corrugated-plate packing.

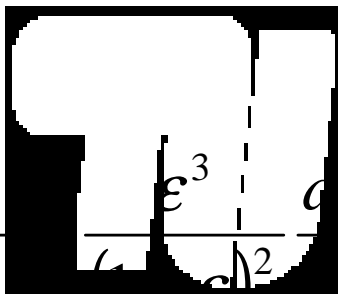
Pressure drop in a fixed bed



Kanal

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

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



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

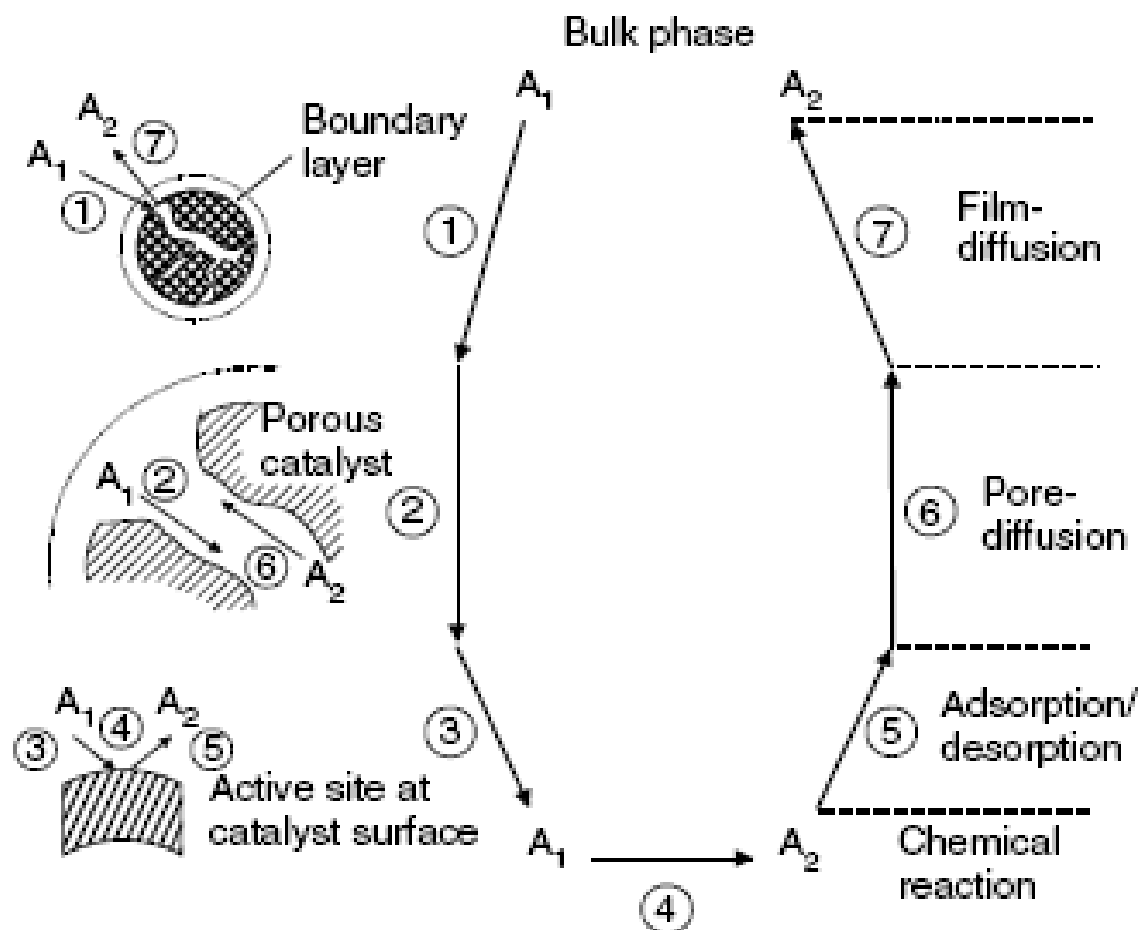
$$\Delta p = \frac{L}{d_k} \lambda(Re) \frac{1}{2} \rho u_0^2$$

$$\lambda(Re) = \frac{(1-\varepsilon)^2}{\varepsilon^3} \frac{300}{Re}$$

laminar

$$\lambda(Re) = \frac{(1-\varepsilon)}{\varepsilon^3} \left[\frac{300(1-\varepsilon)}{Re} + 3,5 \right]$$

laminar und turbulent, Ergun-Gl.



Sequential steps:

Pressure driven flow,
Film diffusion,
Pore diffusion

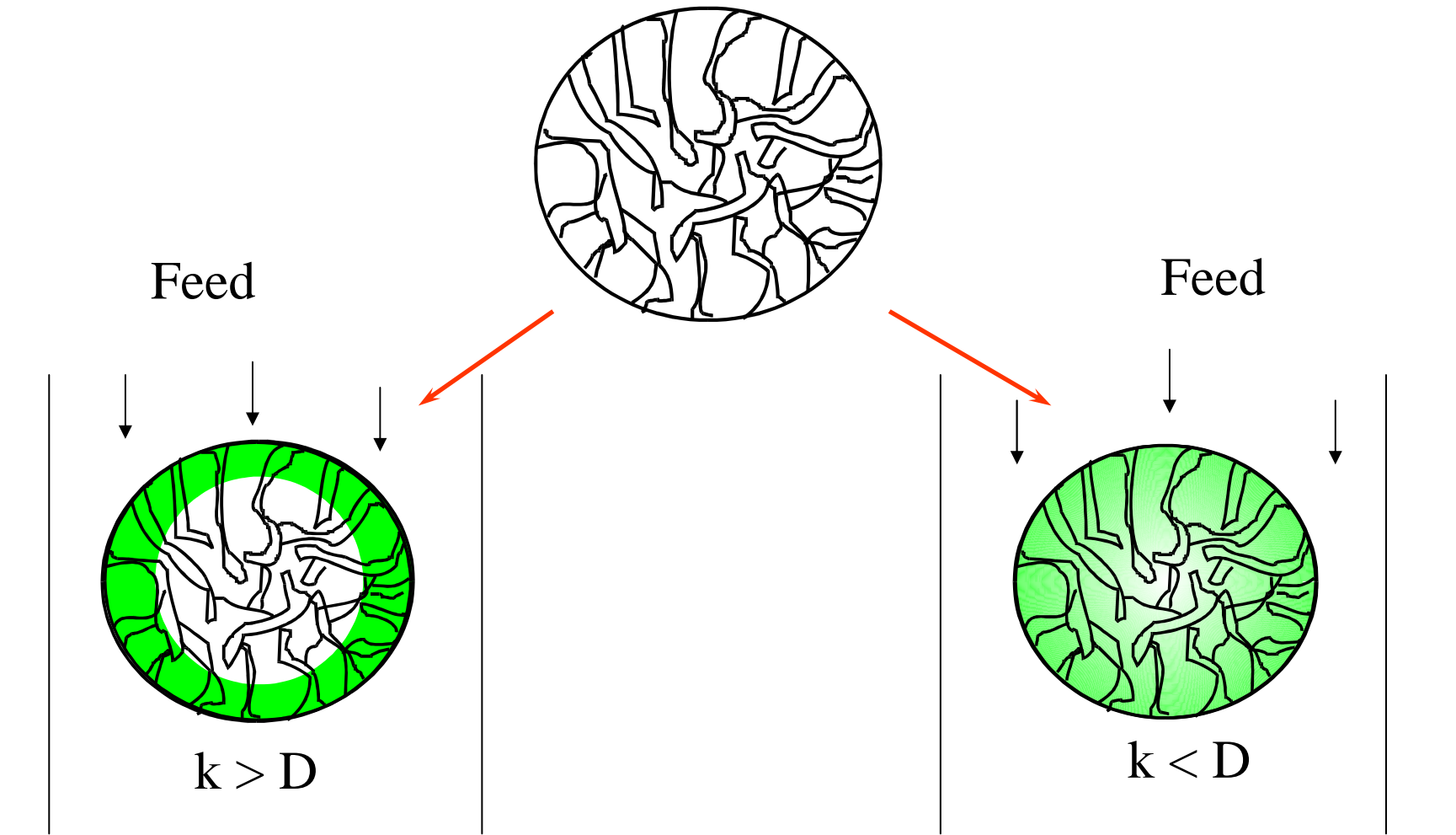
Fig.1 Individual steps of a simple, heterogeneous catalytic fluid–solid reaction $A_1 \rightarrow A_2$ carried out on a porous catalyst.

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

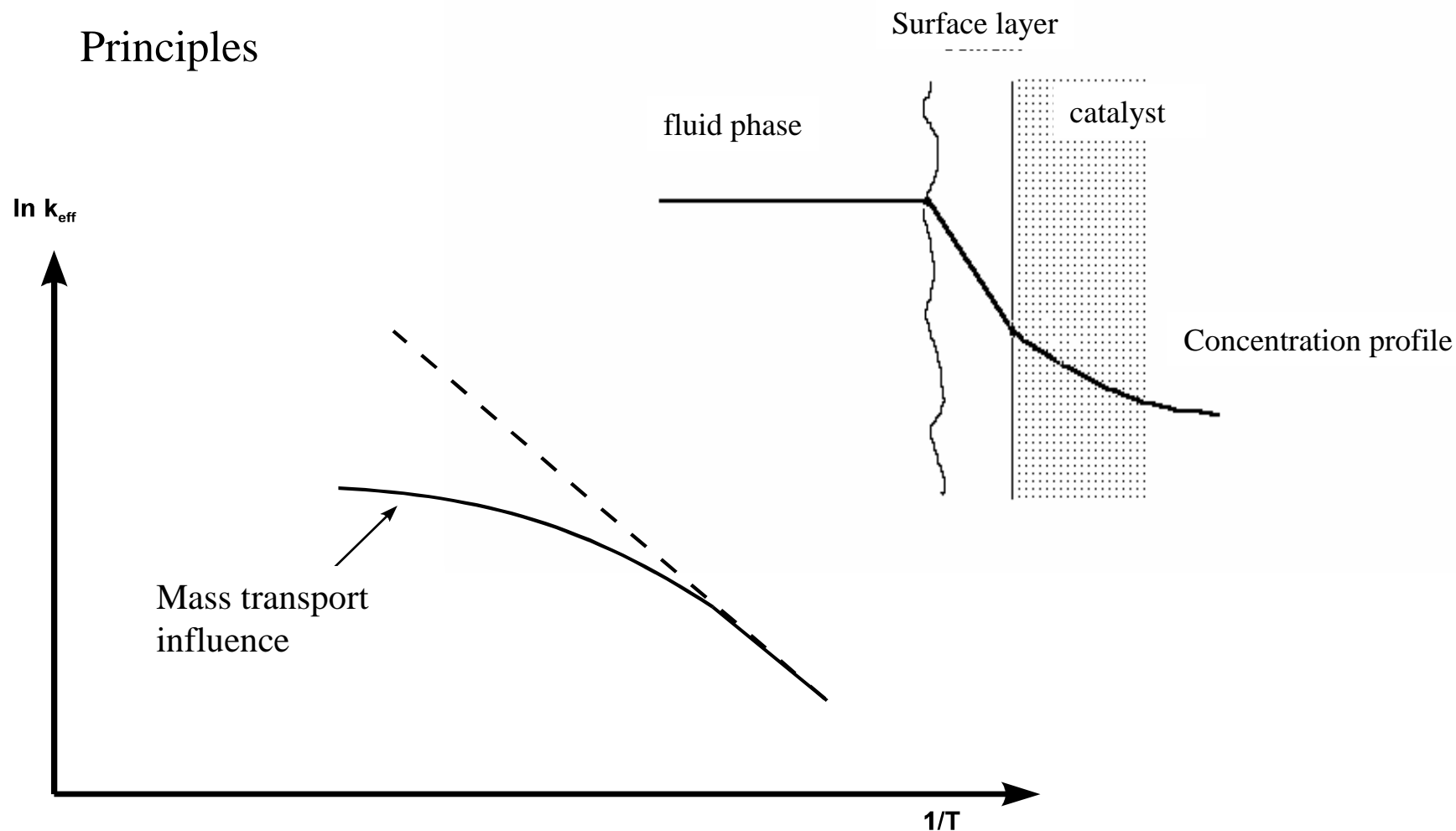


How to get to the active site ?

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Mass Transport and Heterogeneous Catalysis

Principles



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

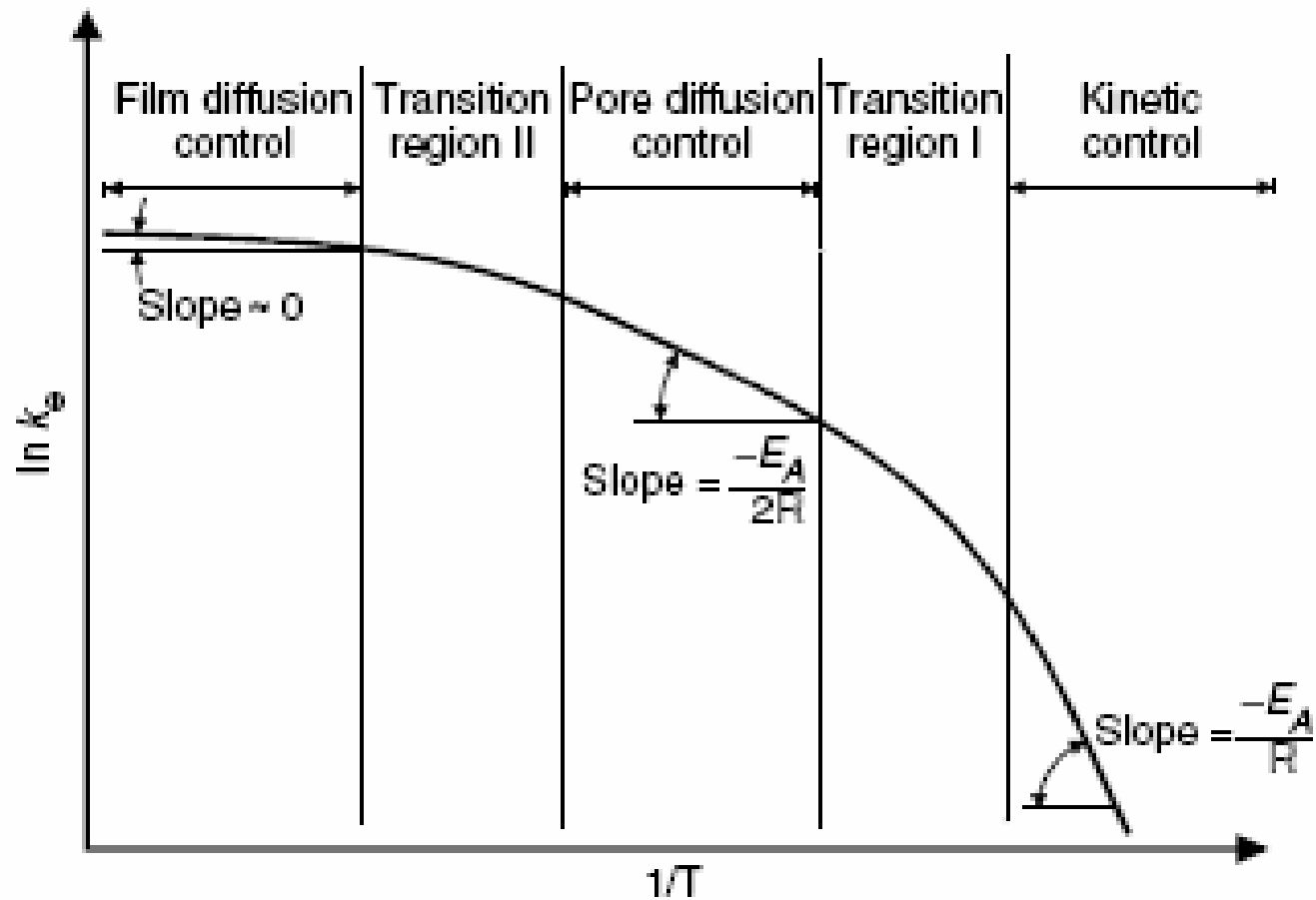


Fig. 3 Transition from the kinetic regime to the diffusion-controlled regime of a heterogeneous catalytic fluid–solid reaction carried out on a porous catalyst.

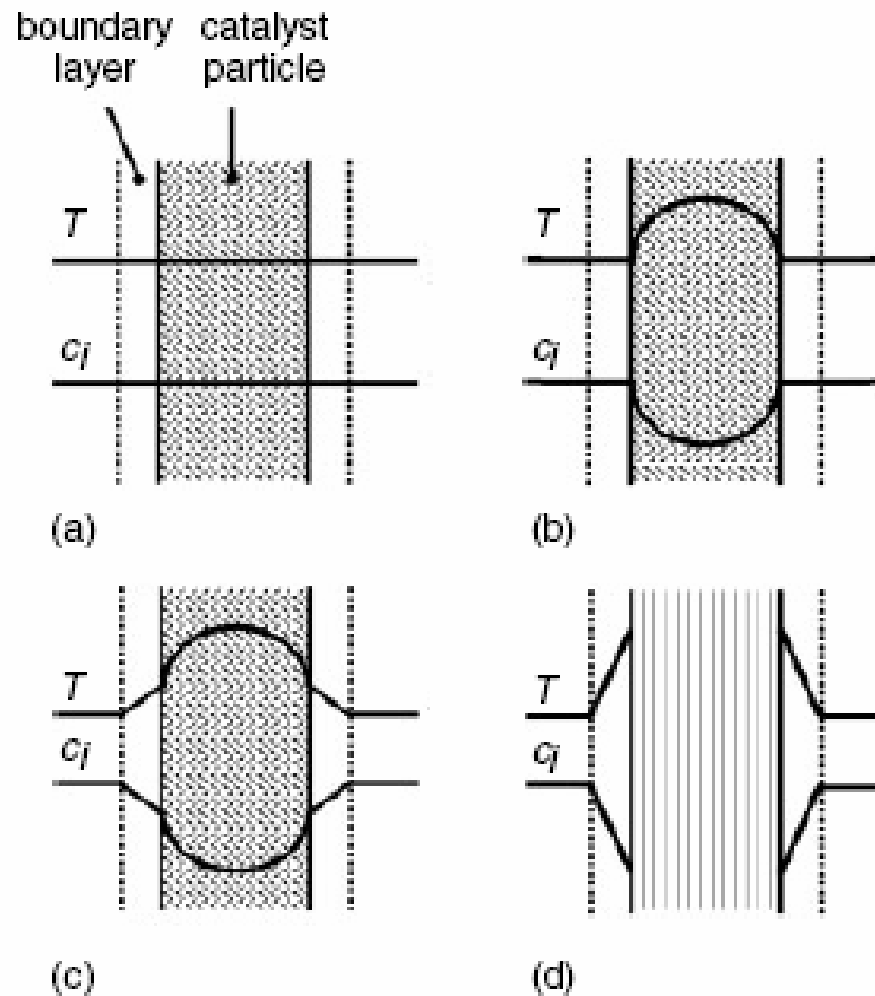


Fig. 2 Stationary concentration (reactant) and temperature profiles inside and around a porous catalyst pellet during an exothermic, heterogeneous catalytic fluid–solid reaction: (a) without transport influence; (b) limited only by intraparticle diffusion; (c) limited by interphase and intraparticle diffusion; (d) limited only by interphase diffusion (dense pellet).

Time Scales in a Reactor

residence time $\tau = V_R/V_F$

Mixing time Θ

Time constant of reaction = $C_{M,0}/R_0$

Time constant of diffusion = R^2/D_e

Description of pore diffusion

$$\vec{j} = -D \text{grad} c$$

1. Fick's Law

$$D_g = \frac{1}{2} \Lambda w$$

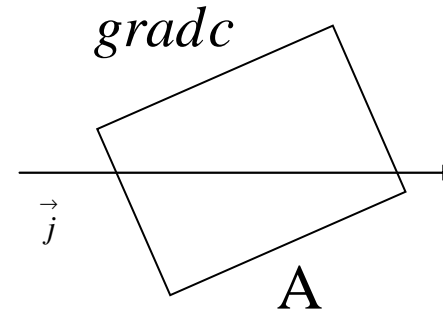
$$\Lambda = \frac{k_B T}{\sqrt{2} \pi \sigma^2 p}$$

Average free path length

$$w = \sqrt{\frac{8k_B T}{\pi m}}$$

Average molecular velocity

$$D_g \sim T^{1,5} \quad \text{und} \quad D_g \sim 1/p$$



a) Diffusion in pores $d_p \gg \lambda$

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

b) Knudsen – Diffusion $d_p = \lambda$

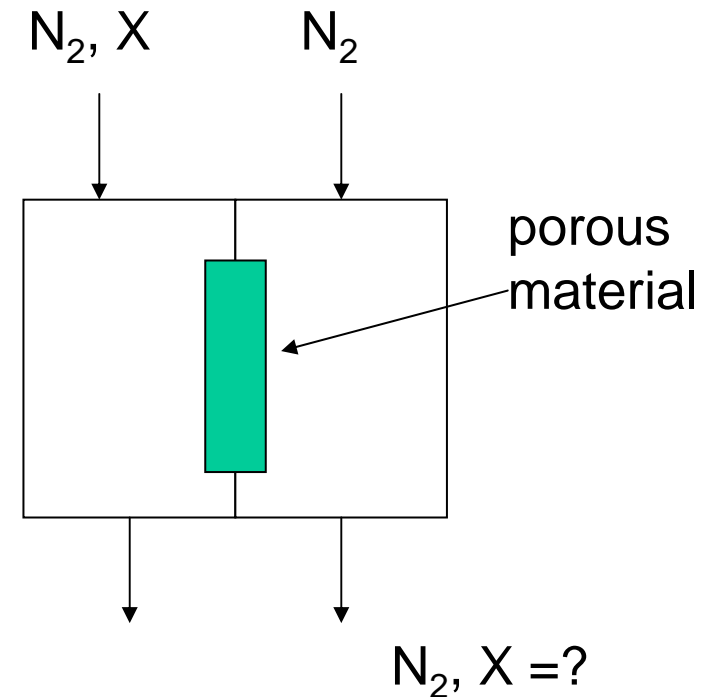
$$D_{\text{eff}} = D_K \frac{\varepsilon}{\tau} = \frac{1}{2} \frac{d_p}{2} w \frac{\varepsilon}{\tau}$$

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

c) Intermediate range

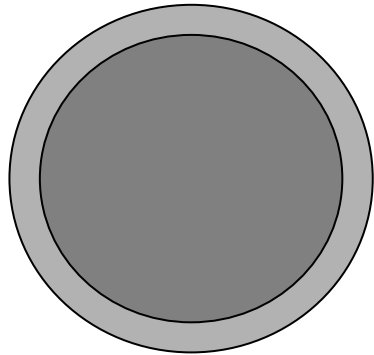
$$D_{\text{eff}} = \frac{1}{\frac{1}{D_g} + \frac{1}{D_K}} \frac{\varepsilon}{\tau}$$

Wicke-Kallenbach-Experiment



$$\vec{j}_x = -D_e \text{grad} c_x$$

Simultaneous reaction and pore diffusion in a spherical particle



dV

temporal change of materials within volume element = changes of material amount by transport + changes caused by reactions

Mass balance

$$\int_V \frac{dc_i}{dt} dV = -\oint (\vec{j}_i d\vec{o}) + \int_V v_i r dV$$

$$\oint (\vec{j} d\vec{o}) = \int_V \text{div } \vec{j} dV$$

$$\frac{dc_i}{dt} = -\text{div } \vec{j}_i + v_i r$$

one dimensional

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

Spherical geometry

$$\text{div } \vec{j} = \frac{1}{R^2} \frac{d}{dR} (R^2 j_R)$$

$$0 = -\frac{1}{R^2} \frac{d}{dR} (R^2 j_{iR}) + v_i r \quad \text{Mass balance of spherical particle in steady state}$$

Solution of mass balance and description of average reaction rate

$$D_{\text{eff}} \left(\frac{d^2 c}{dR^2} + \frac{2}{R} \frac{dc}{dR} \right) = k c^n \quad \text{with } r = k c^n \text{ and } v = -1$$

$$c(R = R_0) = c_0$$

$$\left. \frac{dc}{dR} \right|_{R=0} = 0$$

$$\Phi_0 = R_0 \sqrt{\frac{k c_0^{n-1}}{D_{\text{eff}}}}$$

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

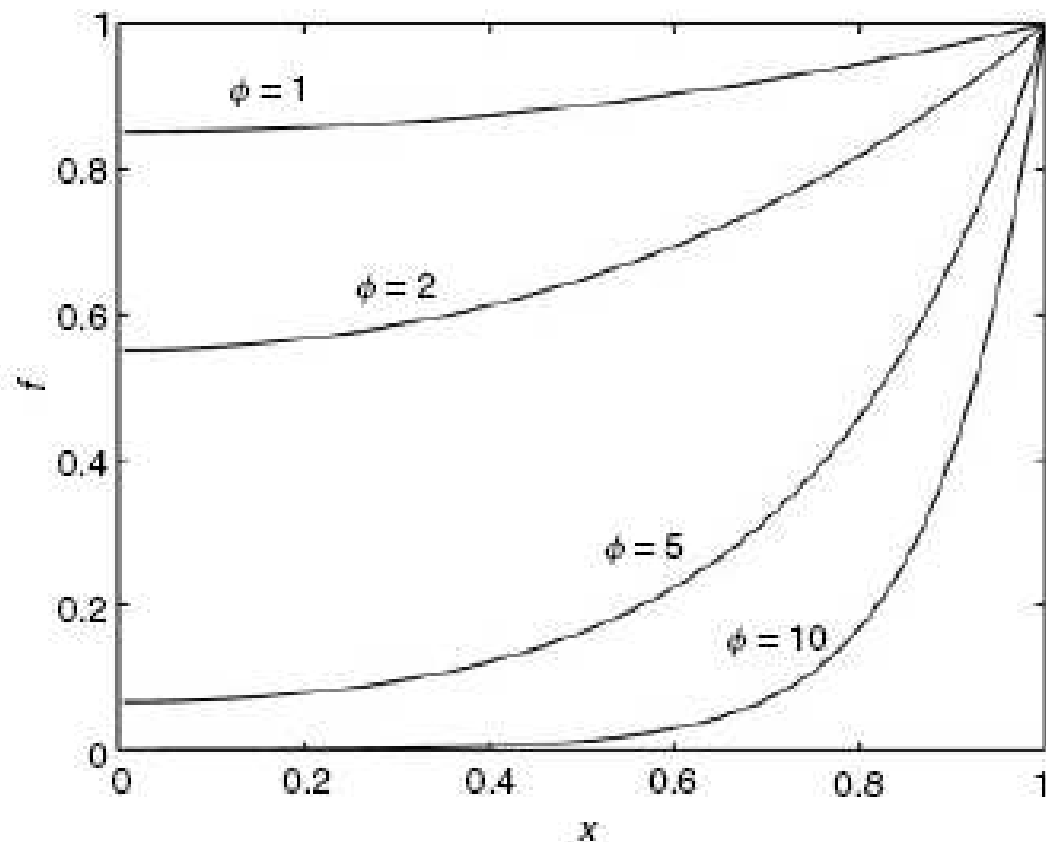
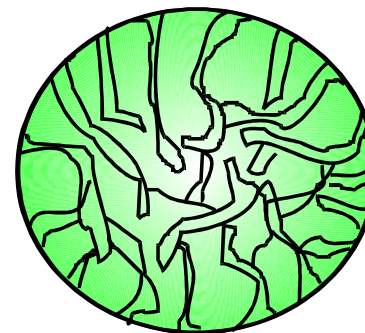
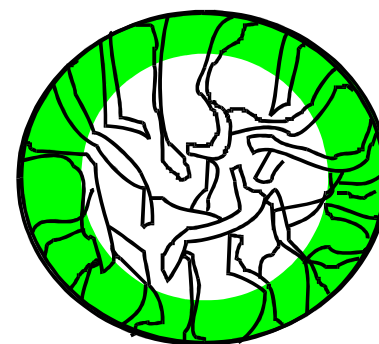


Fig. 4 Normalized concentration profiles of reactant A_1 versus the dimensionless pellet radius, calculated from Eq. (49) for different values of the Thiele modulus ϕ (isothermal, first-order irreversible reaction in a sphere).



$k < D$



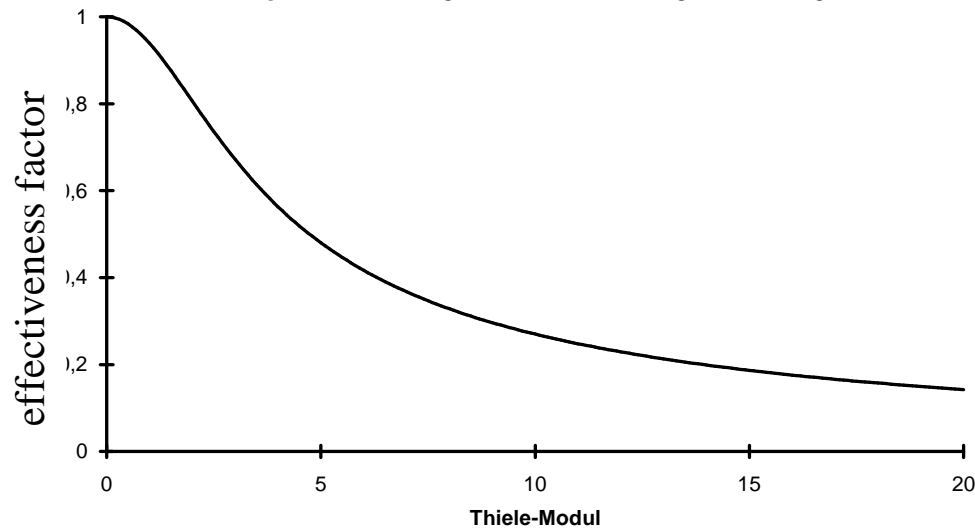
$k > D$

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

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

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

$$\eta = \frac{r_{\text{het}}}{r_{\text{hom}}} = \frac{3}{\Phi_0} \left(\frac{1}{\tanh \Phi_0} - \frac{1}{\Phi_0} \right) \quad \text{Effectiveness factor}$$



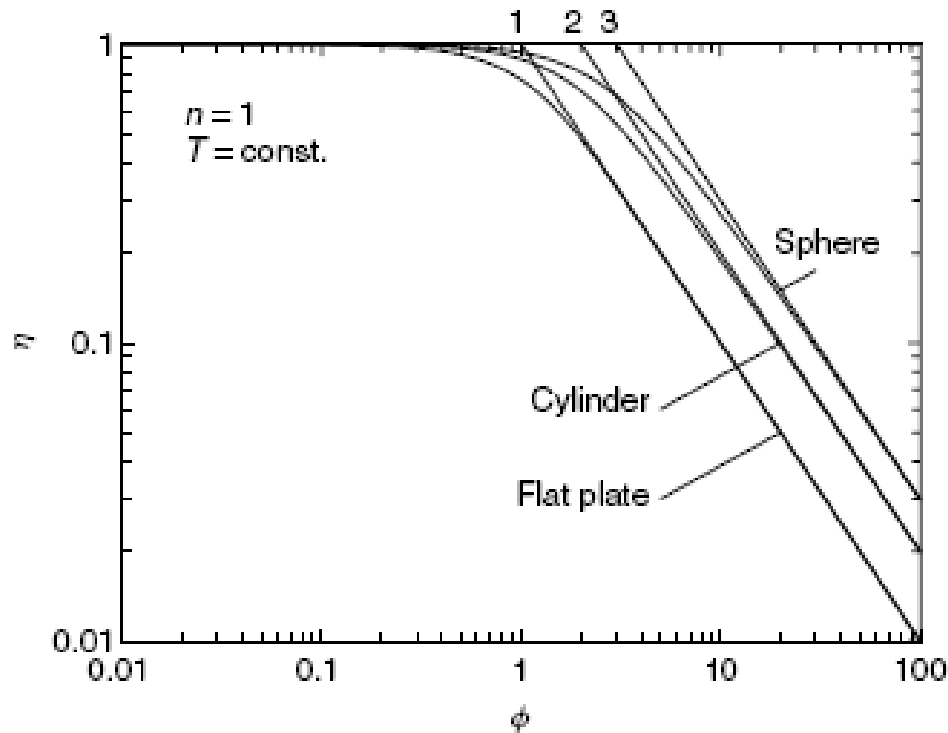


Fig. 5 Effectiveness factor η as a function of the Thiele modulus ϕ for different pellet shapes. Influence of intraparticle diffusion on the effective reaction rate (isothermal, first-order irreversible reaction).

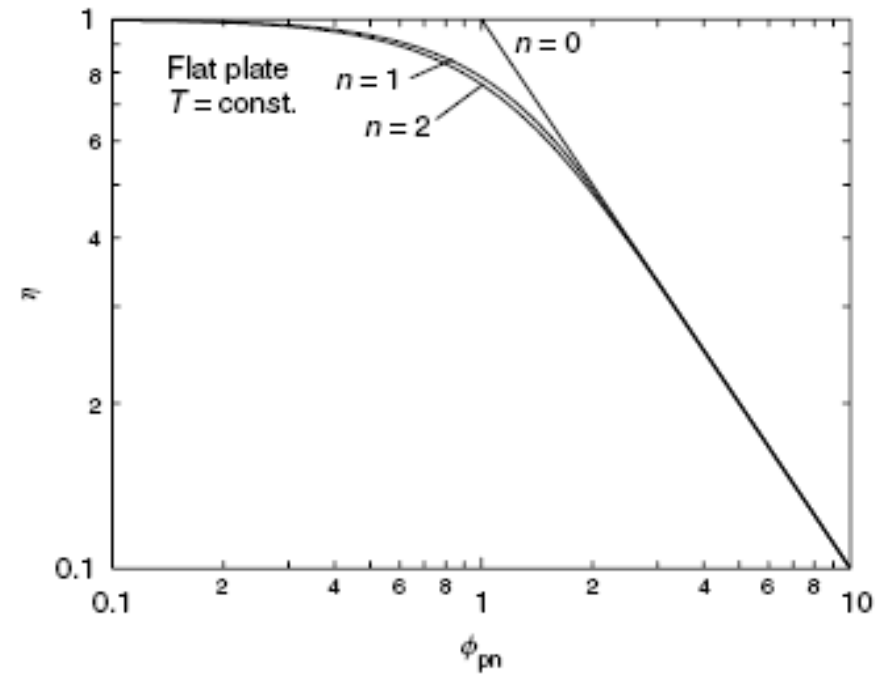


Fig. 7 Effectiveness factor η as a function of the generalized Thiele modulus ϕ_{pn} for different reaction orders. Influence of intraparticle diffusion on the effective reaction rate (isothermal, first-order irreversible reaction in a flat plate).

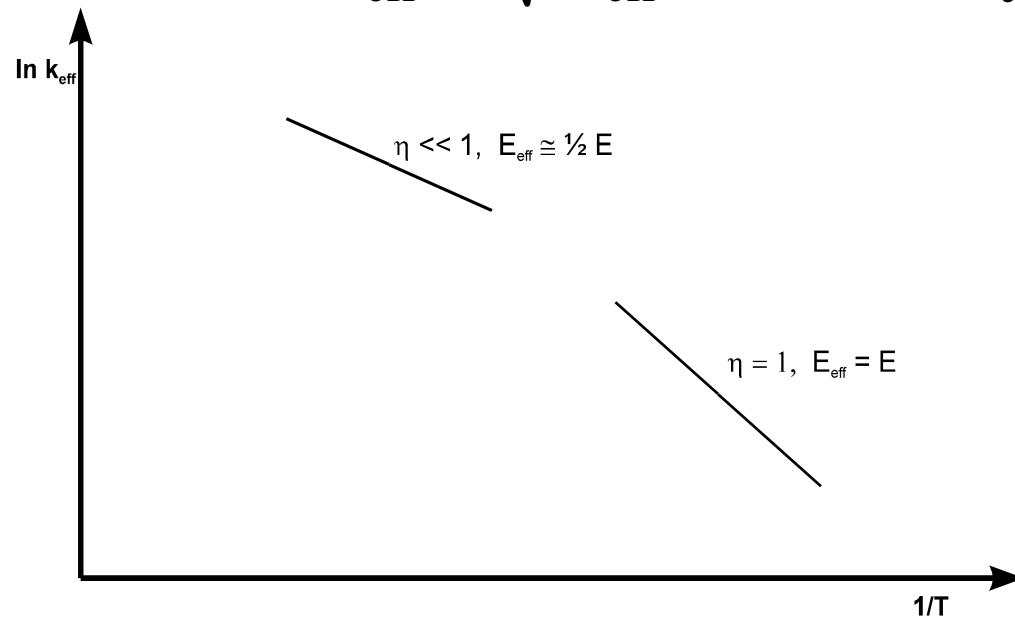
Influence of temperature

$$\eta \approx \frac{3}{\Phi_0}$$

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

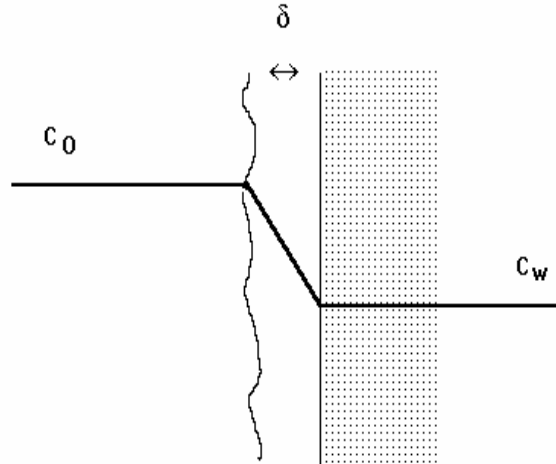
$$k_{\text{eff}} \cong \sqrt{D_{\text{eff}} k}$$

$$E_{\text{eff}} = \frac{1}{2}(E + \cancel{E_D})$$



Influence of pore diffusion on effective rate constant

Film diffusion und Reaction



$$\dot{n}_{\text{Diff}} = S_a D \frac{c_0 - c_w}{\delta}$$

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

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

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

$$r = r_s a, \quad k = k_s a \quad \text{mit: } a = \frac{S_a}{V}$$

$$\dot{n} = S_a \beta (c_0 - c_w) = S_a r_s (c_w)$$

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

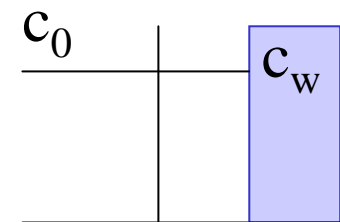
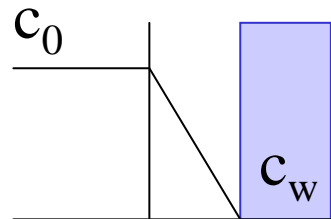
$$\beta (c_0 - c_w) = k_s c_w$$

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

Border cases:

$$k_s \ll \beta \quad c_w = c_0 \quad (\text{no layer formation})$$

$$k_s \gg \beta \quad c_w \approx 0$$



$$r_S = k_S c_W = \frac{\beta k_S}{\beta + k_S} c_0 = k_{S,eff} c_0$$

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

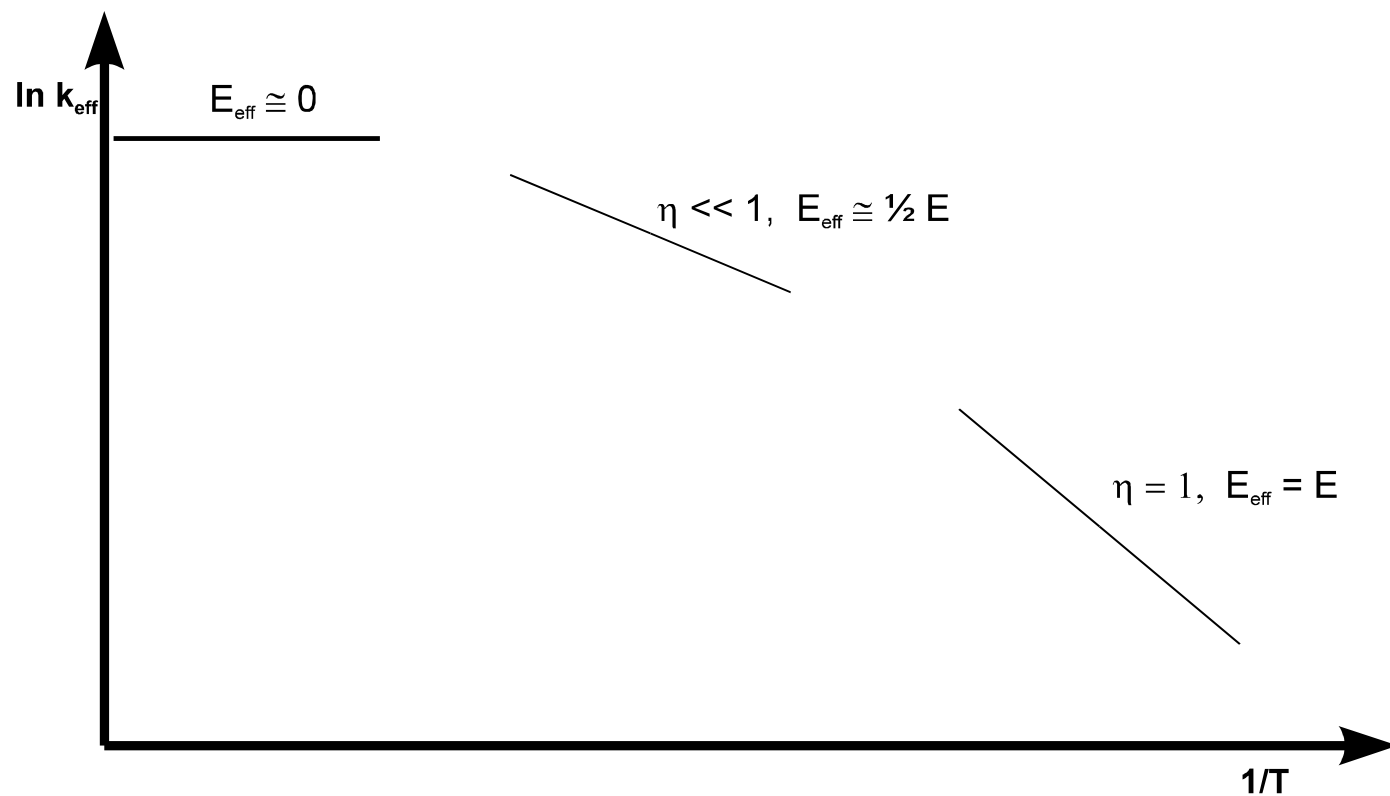
Calculation of eff. volume related rate constant

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

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

$$\frac{1}{k_{eff}} = \frac{1}{a\beta} + \frac{1}{\eta k}$$

Temperature dependance:



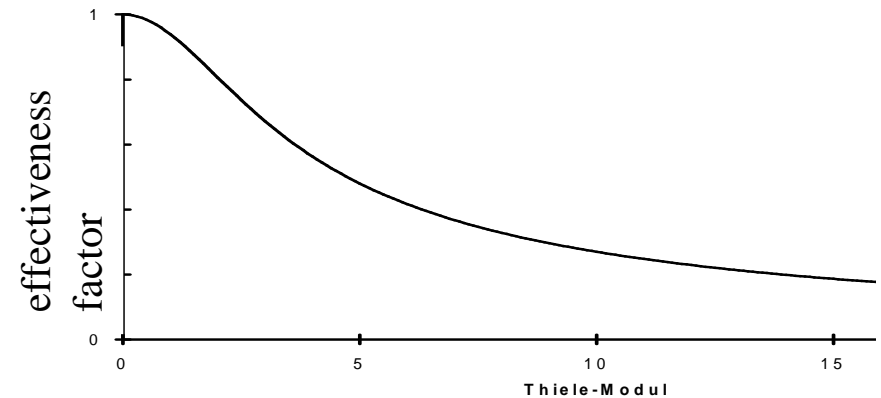
Criteria to exclude mass transfer limitations

$$\phi_{Pn} = \frac{V_P}{S_P} \sqrt{\frac{\frac{n+1}{2} k c_b^{n-1}}{D_e}} = \phi_P \sqrt{\frac{n+1}{2}} \quad \text{Generalized Thiele-Modulus}$$

Criterion with measurable data only: Weisz-Modul

$$\psi = \frac{R^2 r_e}{D_e c_b} < 1 \quad \psi_{Pn} = \left(\frac{V_P}{S_P} \right)^2 \frac{n+1}{2} \frac{r_e}{D_e c_b}$$

$$\psi = \eta \phi^2; \quad \psi_{Pn} = \eta \phi_{Pn}^2$$



Experimental check

for pore diffusion

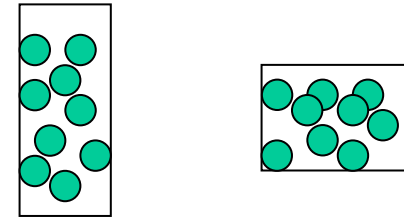


Reduce particle size

- decrease ϕ
- increase η to 1

at constant τ , 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 τ , 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)

Application	No.	Criterion	Ref.
Interphase mass transfer ($T = \text{constant}$)	1	$\frac{\eta k_e}{k_f a} < 0.1; \quad n = 1$	[36]
	2	$\frac{Rr_e}{k_f c_b} < \frac{0.15}{ n }; \quad n \neq 0$	[55]
Interphase heat transfer ($c = \text{constant}$)	3	$ \chi = \frac{R \Delta H_R r_e}{h_f T_b} < \frac{0.15RT_b}{E_A}$ $< 5\%$ deviation of η from η_{iso}	[61]
Intra-/interphase heat and mass transfer (combined effect)	4	$\frac{R^2 r_e}{D_e c_b} < \frac{1 + 0.33\gamma\chi}{ n - \gamma\beta (1 + 0.33n\omega)}$ $\omega = \frac{Rr_e}{k_f c_b}$ χ as defined by criterion No. 3	[55]
	5	$ \gamma\beta + 0.3n\gamma\chi < 0.05n$ χ as defined by criterion No. 3 $< 5\%$ deviation of η from η_{iso}	[55]

Tab. 2 Experimental diagnostic criteria for the absence of intraparticle transport effects in simple, irreversible reactions (power law kinetics only)

<i>Application</i>	<i>No.</i>	<i>Criterion</i>	<i>Ref.</i>
Pore diffusion ($T = \text{constant}$)	1	$\frac{R^2 r_e}{D_e c_s} < 1; \quad n = 1$	[11]
	2	$\frac{R^2 r_e}{D_e c_s} \begin{cases} < 6; & n = 0 \\ < 0.6; & n = 1 \\ < 0.3; & n = 2 \end{cases}$	[57]
	3	$\frac{R^2 r_e}{D_e c_s} < \frac{1}{ n }; \quad n > 0$	[58]
Heat conduction ($c = \text{constant}$)	4	$\frac{R^2 \Delta H_R r_e}{\lambda_e T_s} < \frac{RT_s}{E_A}$ <5% deviation of η from η_{iso}	[59]
	5	$\frac{R^2 r_e}{D_e c_s} < \frac{1}{ n - \gamma\beta }; \quad n \neq \gamma\beta$	[60]
Pore diffusion and heat conduction (combined effect)	6	$\frac{R^2 r_e}{D_e c_s} < 13; \quad n \approx \gamma\beta$	[55]
	7	$ \gamma\beta < 0.05n$ <5% deviation of η from η_{iso}	[55]
	8	$\frac{R^2 r_e}{D_e c_s} e^{\left(\frac{\gamma\beta}{1+\beta}\right)} < 1$	[38]