Modern Methods in Heterogeneous Catalysis

Lectures at Fritz-Haber-Institut

28.11.2008

Diffusion in Porous Media

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Dimensions in Heterogeneous Catalysis

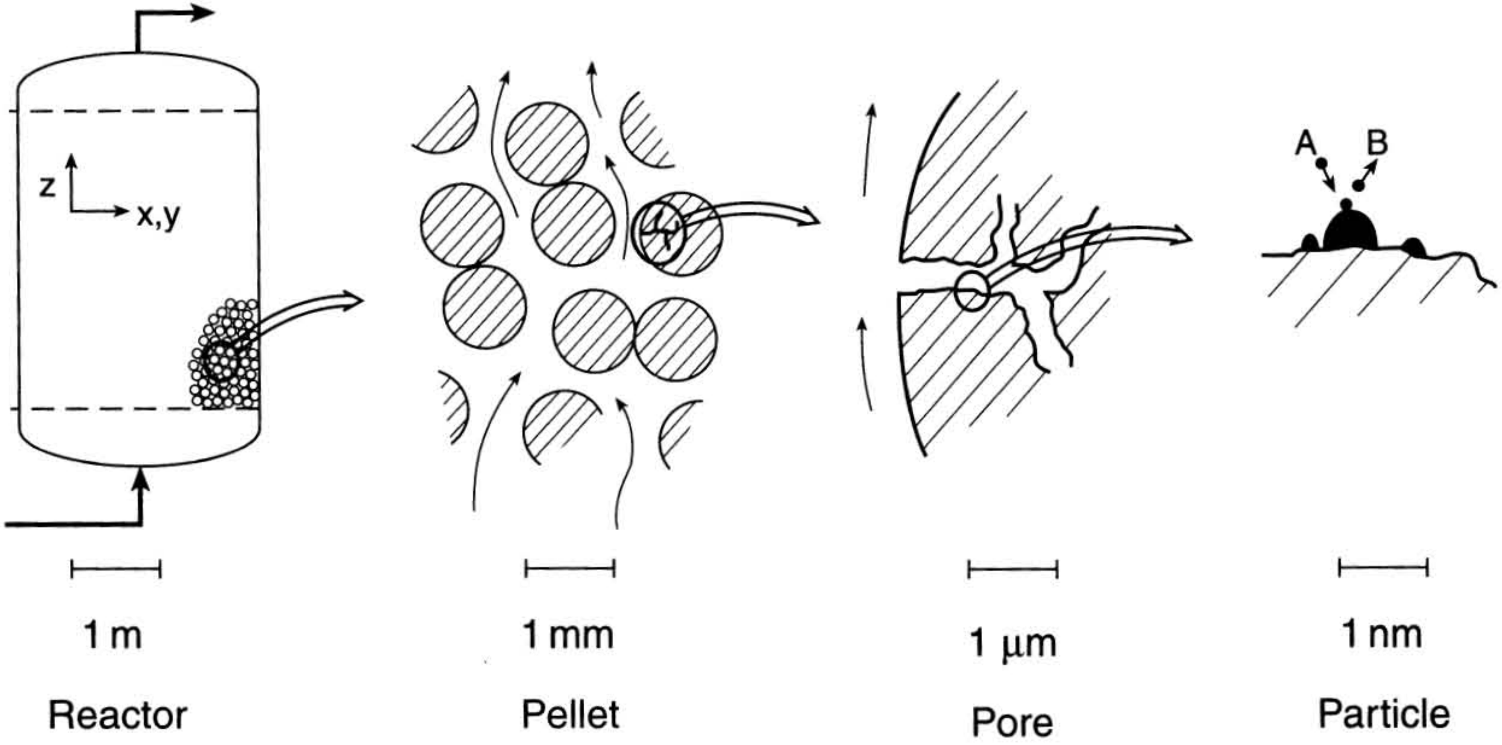

Figure 7–6 Different size scales in a packed bed catalytic reactor. We must consider the position z in the bed, the flow around catalyst pellets, diffusion within pores of pellets, and adsorption and reaction on reaction sites. These span distance scales from meters to Angstroms.

L.D. Schmidt, *The Engineering of Chemical Reactions*, Oxford University Press, Oxford–New York (1998) p. 277

Importance of transport for catalysis

- Material and energy balances are required for both the fluid, which occupies the interstitial region between catalyst particles, and the catalyst particles, in which the reactions occur

- Determination of rate limiting steps to ensure which step acts to influence the overall rate of reaction in the pellet

⬇

Interaction of chemical reaction and transport processes

MACROKINETICS

Outline

- Introduction
  - Porosity (definition, IUPAC)
  - Diffusion (laws, effective quantities, Knudsen diffusion, examples)
  - General transport equations for gases
- External mass transfer processes
  - Effectiveness factor, dimensionless quantities (Re, Sc)
- Internal mass transfer processes
  - Thiele modulus, case studies
- Influence of transport on
  - Activation energy, Reaction order, Selectivity
- Examples, experimental evaluation
- Summary

Recommended Literature

- R. Byron Bird et al.
  Transport Phenomena. J. Wiley 2007
- C.H. Bartholomev, R. J. Farrauto
  Fundamentals of industrial catalytic processes. AIChe 2006
- M. Baerns, H. Hofmann, A. Renken. Chemische Reaktionstechnik, LB der Technischen Chemie, Bd. 1,Wiley-VCH, 2002.
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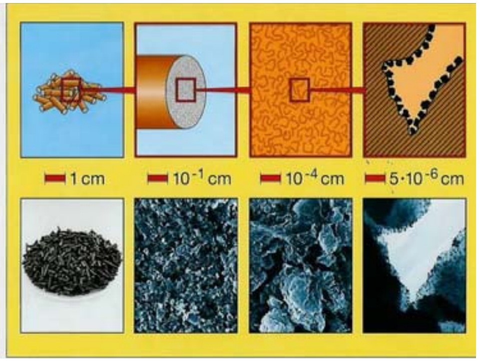
- Fixed-Bed Catalytic Reactors. Nob Hill Publ. 2004. (see web)
- IUPAC: Pure & Appl.Chem. <u>66</u> (1994) 1739.
- Lexikon Chemie, Brockhaus ABC. VEB F.A. Brockhaus Verlag, Leipzig1987.
- Technische Anorganische Chemie. Deutscher Verlag für Grundstoffindustrie GmbH, Leipzig1990.
- I.I. Ioffe, L.M. Pissmen. Heterogene Katalyse, Chemie und Technik, Akademie-Verlag Berlin, 1975.

Porosity – Background information

Porous materials in nature and industry

- Porous materials:
  sand stone, porous rock, filter paper, nano tubes…
- Main feature: cavities in a solid matrix
- Cavities can be partly or fully connected
- Accessible for gases

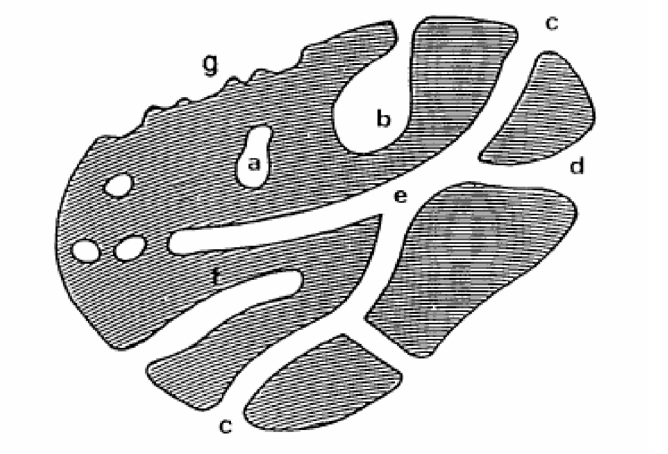
- Porosities are often desired and of importance in medicines, membranes, sorbents, ceramics, and catalysts



Pore types

- Pressing of support material leads to a network of micro-/meso-porous and macroporous areas: powder particles are micro-/mesoporous, pores between particles build up a macroporous network

- Types of pores
  - open pores: surface ~, column ~, hollow ~
  - isolated pores: inclusion ~
  - see IUPAC



IUPAC - Definitions

- Porous solid: a solid with pores, i.e. cavities, channels or interstices, which are deeper than they are wide

- Pore size: (generally pore width): the distance between two opposite walls of the pore
  - **Micropores** (< 2 nm),
  - **Mesopores** (2-50 nm)
  - **Macropores** (> 50 nm)

- Porosity ε: ratio of the total pore volume V_P to the apparent volume V of the particle or powder (excluding interparticle voids)

IUPAC - Quantitative description of porosity

- Value of the fraction depends on the method used to determine
  - the apparent volume V, which excludes interparticle voids (geometrical determination, fluid displacement)
  - the pore volume V_P (adsorption and capillary condensation…)

- Some methods have only access to „open pores“ (i.e. the methods using a fluid) whereas others may also have access to „closed pores“ (i.e. methods using radiation)

Pore properties - Structure

- Pore structure is a strong function of the preparation method, and catalysts can have pore volumes ranging from 0.1-1 cm^3/g pellet
- Pores can be the same size or there can be a bimodal distribution of two different sizes
- Pore sizes can be as small as molecular dimensions (nm) or as large as several millimeters

Types of porosity

- Difference between bed porosity and particle porosity
- Bed porosity (or void fraction) ε_B is defined as the volume of voids per volume of reactor
- The pellet void fraction or porosity is denoted by ε and $\varepsilon = \rho_P * V_g$ (ρ_P effective particle density, V_g pore volume)

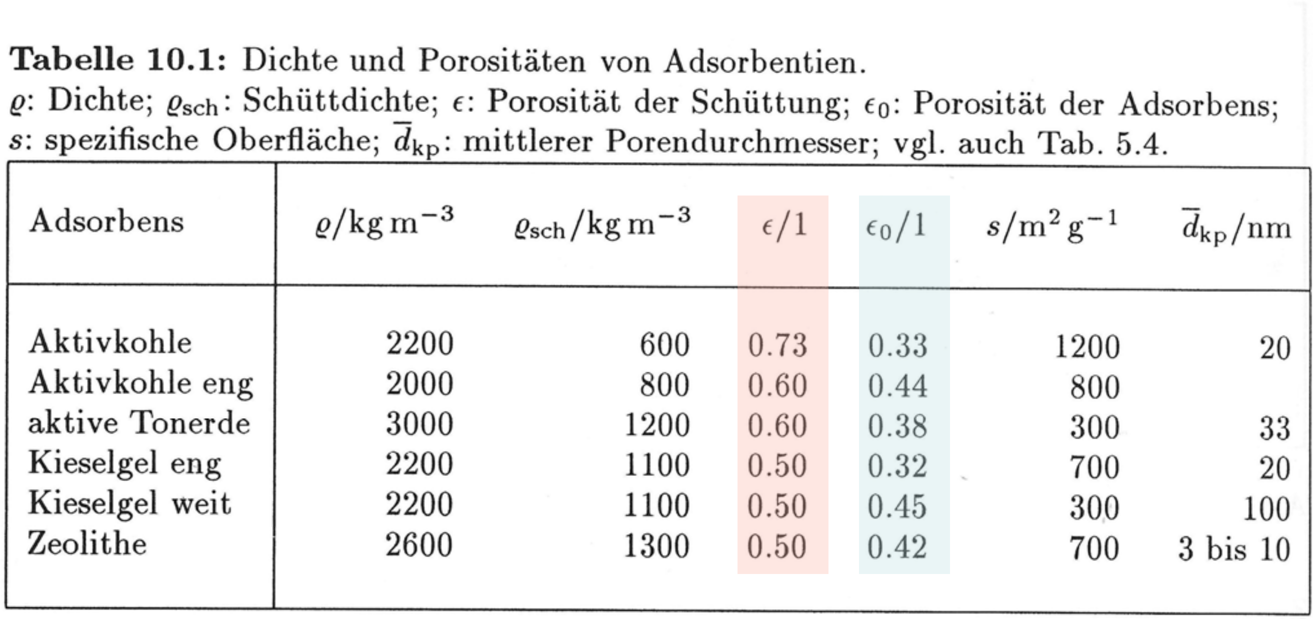


Tabelle 10.1: Dichte und Porositäten von Adsorbentien.
ϱ: Dichte; ϱ_{sch}: Schüttdichte; ϵ: Porosität der Schüttung; ϵ_0: Porosität der Adsorbens; s: spezifische Oberfläche; $\overline{d}_{\mathrm{kp}}$: mittlerer Porendurchmesser; vgl. auch Tab. 5.4.

Adsorbens	$\varrho/\mathrm{kg\,m^{-3}}$	$\varrho_{\mathrm{sch}}/\mathrm{kg\,m^{-3}}$	$\epsilon/1$	$\epsilon_0/1$	$s/\mathrm{m^2\,g^{-1}}$	$\overline{d}_{\mathrm{kp}}/\mathrm{nm}$
Aktivkohle	2200	600	0.73	0.33	1200	20
Aktivkohle eng	2000	800	0.60	0.44	800	
aktive Tonerde	3000	1200	0.60	0.38	300	33
Kieselgel eng	2200	1100	0.50	0.32	700	20
Kieselgel weit	2200	1100	0.50	0.45	300	100
Zeolithe	2600	1300	0.50	0.42	700	3 bis 10

Jakubith

Diffusion – Background

Diffusion – In general

- …is the transport of mass in gases, liquids and solids under the influence of a concentration gradient
- …proceeds spontaneously due to microscopic movement of mass
- … is an irreversible process which leads to an increase in entropy and is only reversible by supply of work

Diffusion – In special

- …mechanisms differ for gases/liquids and solids

- …for gases/liquids: statistical movement according to T

- …for solids: different mechanisms possible:
  - i) direct exchange of lattice places
  - ii) movement via interstitial lattice sites
  - iii) movement via lattice vacancies
  - iv) movement via lattice defects or on the grain surface
  - v) exchange of sites on the crystal surface

Examples - Diffusion in technical solids

- High temperature inorganic reactions

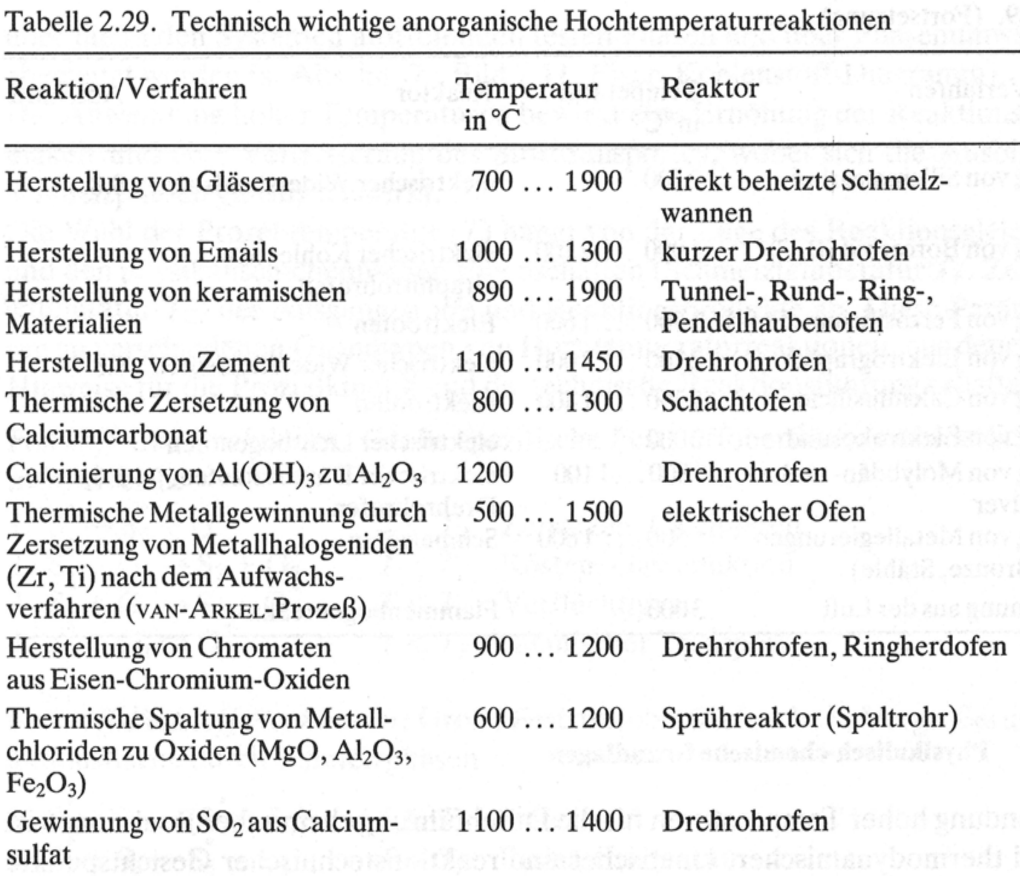


Tabelle 2.29. Technisch wichtige anorganische Hochtemperaturreaktionen

Reaktion/Verfahren	Temperatur in °C	Reaktor
Herstellung von Gläsern	700 ... 1900	direkt beheizte Schmelzwannen
Herstellung von Emails	1000 ... 1300	kurzer Drehrohrofen
Herstellung von keramischen Materialien	890 ... 1900	Tunnel-, Rund-, Ring-, Pendelhaubenofen
Herstellung von Zement	1100 ... 1450	Drehrohrofen
Thermische Zersetzung von Calciumcarbonat	800 ... 1300	Schachtofen
Calcinierung von $Al(OH)_3$ zu Al_2O_3	1200	Drehrohrofen
Thermische Metallgewinnung durch Zersetzung von Metallhalogeniden (Zr, Ti) nach dem Aufwachsverfahren (VAN-ARKEL-Prozeß)	500 ... 1500	elektrischer Ofen
Herstellung von Chromaten aus Eisen-Chromium-Oxiden	900 ... 1200	Drehrohrofen, Ringherdofen
Thermische Spaltung von Metallchloriden zu Oxiden (MgO, Al_2O_3, Fe_2O_3)	600 ... 1200	Sprühreaktor (Spaltrohr)
Gewinnung von SO_2 aus Calciumsulfat	1100 ... 1400	Drehrohrofen

Diffusion - quantitatively

- …generally increases with temperature and decreases with increasing density

- …the equilibration takes
  - minutes for gases
  - days/weeks for liquids
  - with measurable rate only close to the melting point

- …characteristic quantity: diffusion coefficient

- …can be described as molecular transport quantity or as effective quantity

Examples - Diffusion coefficients

	D [cm^2/s]	T [K]
H_2 in O_2	0.78	298
N_2 in O_2	0.19	298
H_2O vapour in air	0.23	298
CH_3OH in water	$1.2*10^{-5}$	298
Sugar in water	$0.5*10^{-5}$	298
Au in Cu	$2.1*10^{-11}$	1023
Fe in Al	$6.2*10^{-14}$	623
$^{36}Cl^-$ in AgCl	$3.2*10^{-16}$	623

Lexikon Chemie

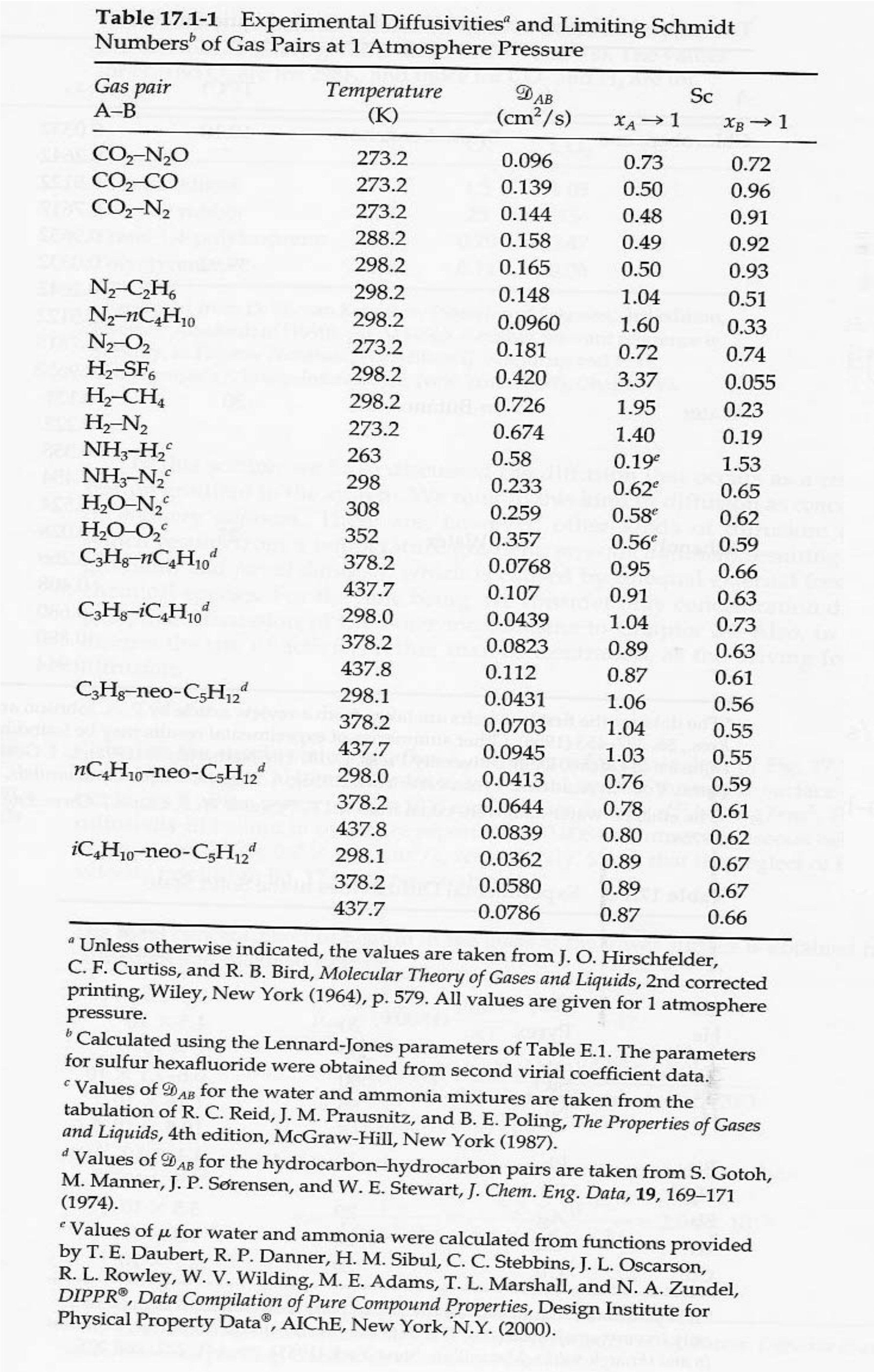


Table 17.1-1 Experimental Diffusivities[a] and Limiting Schmidt Numbers[b] of Gas Pairs at 1 Atmosphere Pressure

Gas pair A–B	*Temperature* (K)	$\mathscr{D}_{AB}$ (cm^2/s)	Sc $x_A \to 1$	Sc $x_B \to 1$
CO_2–N_2O	273.2	0.096	0.73	0.72
CO_2–CO	273.2	0.139	0.50	0.96
CO_2–N_2	273.2	0.144	0.48	0.91
	288.2	0.158	0.49	0.92
	298.2	0.165	0.50	0.93
N_2–C_2H_6	298.2	0.148	1.04	0.51
N_2–nC_4H_{10}	298.2	0.0960	1.60	0.33
N_2–O_2	273.2	0.181	0.72	0.74
H_2–SF_6	298.2	0.420	3.37	0.055
H_2–CH_4	298.2	0.726	1.95	0.23
H_2–N_2	273.2	0.674	1.40	0.19
NH_3–H_2[c]	263	0.58	0.19[e]	1.53
NH_3–N_2[c]	298	0.233	0.62[e]	0.65
H_2O–N_2[c]	308	0.259	0.58[e]	0.62
H_2O–O_2[c]	352	0.357	0.56[e]	0.59
C_3H_8–nC_4H_{10}[d]	378.2	0.0768	0.95	0.66
	437.7	0.107	0.91	0.63
C_3H_8–iC_4H_{10}[d]	298.0	0.0439	1.04	0.73
	378.2	0.0823	0.89	0.63
	437.8	0.112	0.87	0.61
C_3H_8–neo-C_5H_{12}[d]	298.1	0.0431	1.06	0.56
	378.2	0.0703	1.04	0.55
	437.7	0.0945	1.03	0.55
nC_4H_{10}–neo-C_5H_{12}[d]	298.0	0.0413	0.76	0.59
	378.2	0.0644	0.78	0.61
	437.8	0.0839	0.80	0.62
iC_4H_{10}–neo-C_5H_{12}[d]	298.1	0.0362	0.89	0.67
	378.2	0.0580	0.89	0.67
	437.7	0.0786	0.87	0.66

[a] Unless otherwise indicated, the values are taken from J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, 2nd corrected printing, Wiley, New York (1964), p. 579. All values are given for 1 atmosphere pressure.

[b] Calculated using the Lennard-Jones parameters of Table E.1. The parameters for sulfur hexafluoride were obtained from second virial coefficient data.

[c] Values of $\mathscr{D}_{AB}$ for the water and ammonia mixtures are taken from the tabulation of R. C. Reid, J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, 4th edition, McGraw-Hill, New York (1987).

[d] Values of $\mathscr{D}_{AB}$ for the hydrocarbon–hydrocarbon pairs are taken from S. Gotoh, M. Manner, J. P. Sørensen, and W. E. Stewart, *J. Chem. Eng. Data*, **19**, 169–171 (1974).

[e] Values of μ for water and ammonia were calculated from functions provided by T. E. Daubert, R. P. Danner, H. M. Sibul, C. C. Stebbins, J. L. Oscarson, R. L. Rowley, W. V. Wilding, M. E. Adams, T. L. Marshall, and N. A. Zundel, *DIPPR®, Data Compilation of Pure Compound Properties*, Design Institute for Physical Property Data®, AIChE, New York, N.Y. (2000).

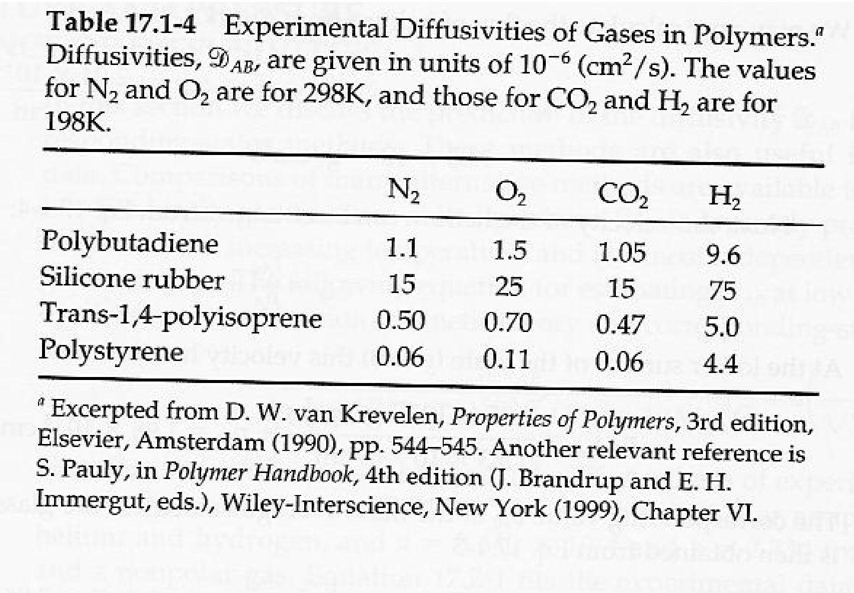


Table 17.1-4 Experimental Diffusivities of Gases in Polymers.[a] Diffusivities, $\mathscr{D}_{AB}$, are given in units of 10^{-6} (cm^2/s). The values for N_2 and O_2 are for 298K, and those for CO_2 and H_2 are for 198K.

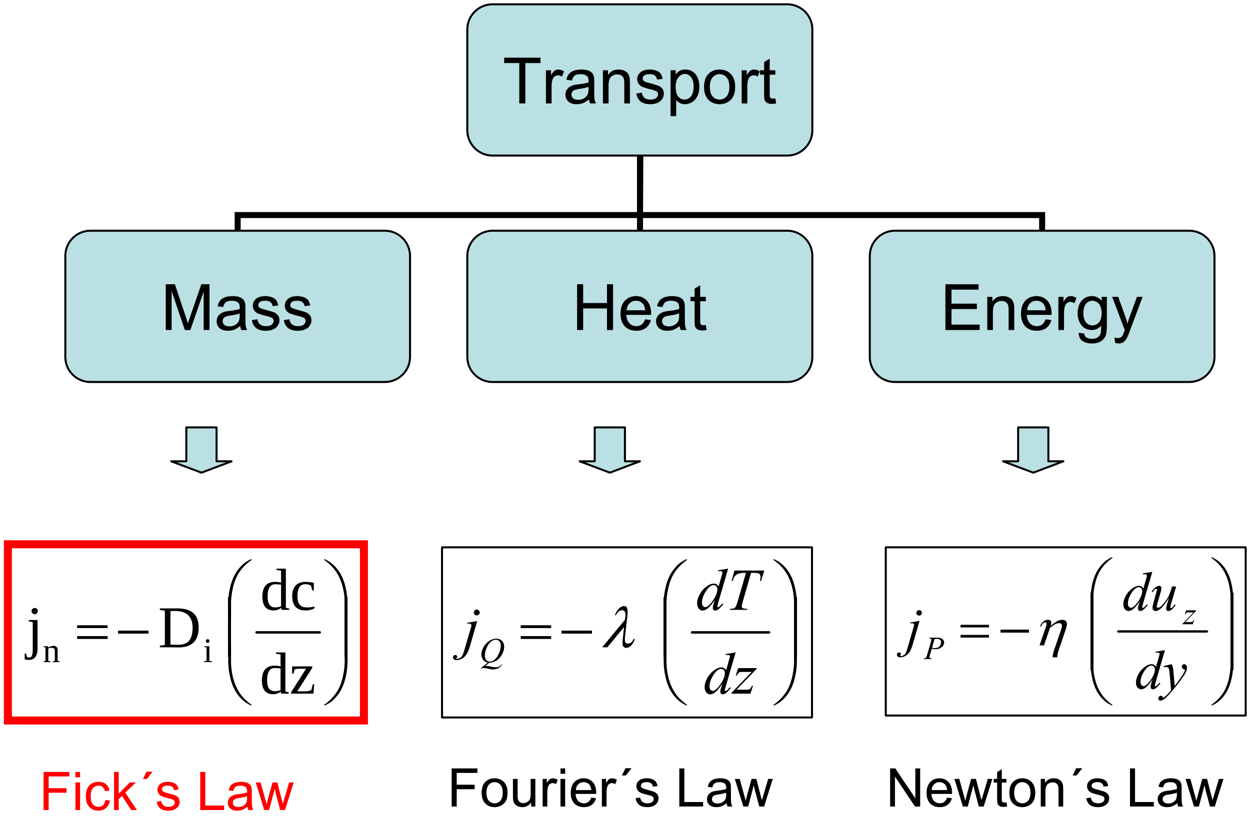
	N_2	O_2	CO_2	H_2
Polybutadiene	1.1	1.5	1.05	9.6
Silicone rubber	15	25	15	75
Trans-1,4-polyisoprene	0.50	0.70	0.47	5.0
Polystyrene	0.06	0.11	0.06	4.4

[a] Excerpted from D. W. van Krevelen, *Properties of Polymers*, 3rd edition, Elsevier, Amsterdam (1990), pp. 544–545. Another relevant reference is S. Pauly, in *Polymer Handbook*, 4th edition (J. Brandrup and E. H. Immergut, eds.), Wiley-Interscience, New York (1999), Chapter VI.

From „Transport Phenomena"

Transport by Diffusion

General view to transport equations for gases



Transport

Mass

Heat

Energy

$$\boxed{j_n = -D_i \left(\frac{dc}{dz}\right)}$$

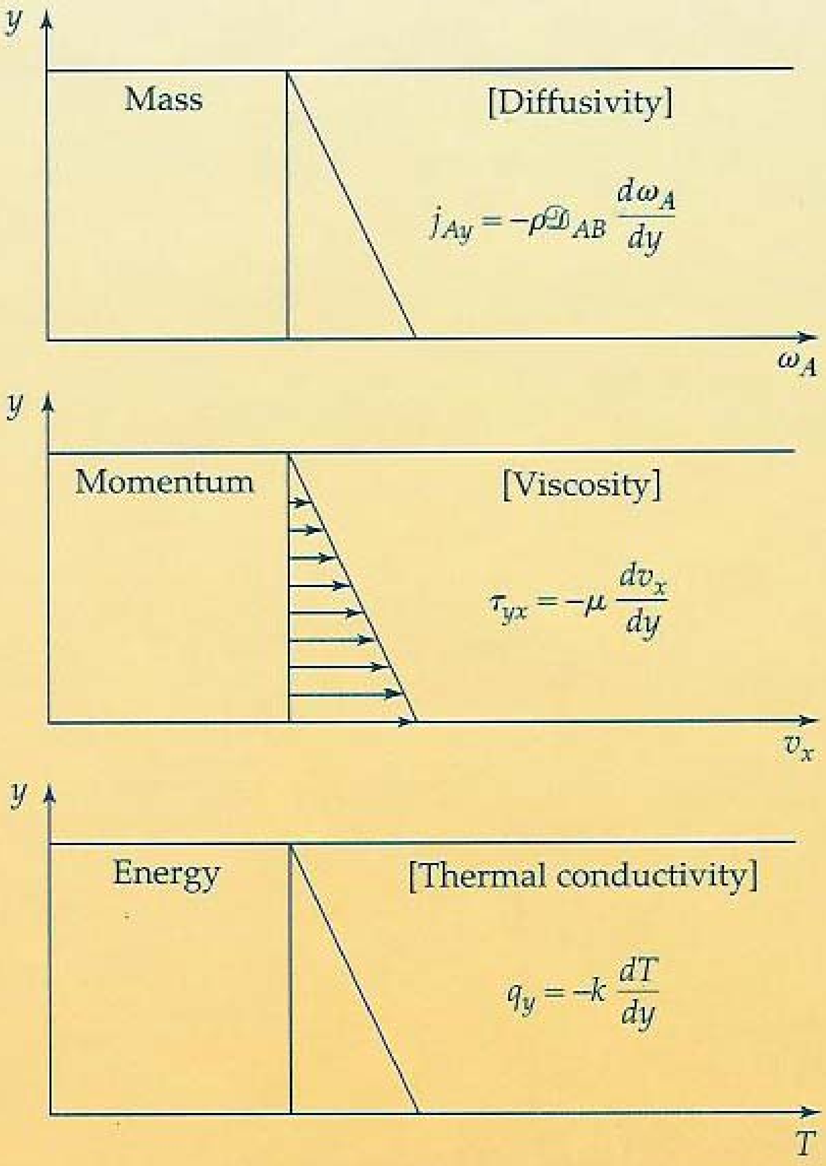
Fick´s Law

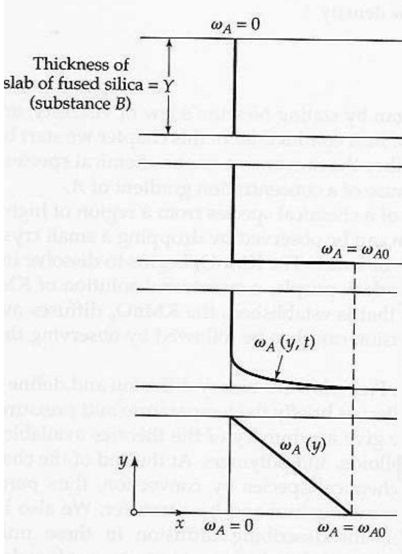
$$\boxed{j_Q = -\lambda \left(\frac{dT}{dz}\right)}$$

Fourier´s Law

$$\boxed{j_P = -\eta \left(\frac{du_z}{dy}\right)}$$

Newton´s Law


y
Mass
[Diffusivity]
$j_{Ay} = -\rho \mathscr{D}_{AB} \frac{d\omega_A}{dy}$
ω_A
y
Momentum
[Viscosity]
$\tau_{yx} = -\mu \frac{dv_x}{dy}$
v_x
y
Energy
[Thermal conductivity]
$q_y = -k \frac{dT}{dy}$
T



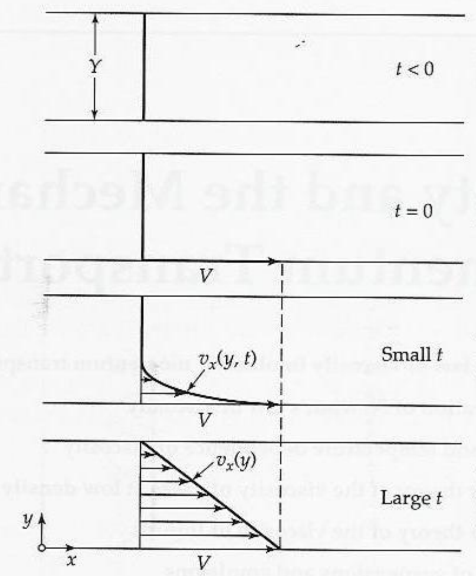


Fig. 1.1-1 The buildup to the steady, laminar velocity profile for a fluid contained between two plates. The flow is called "laminar" because the adjacent layers of fluid ("laminae") slide past one another in an orderly fashion.

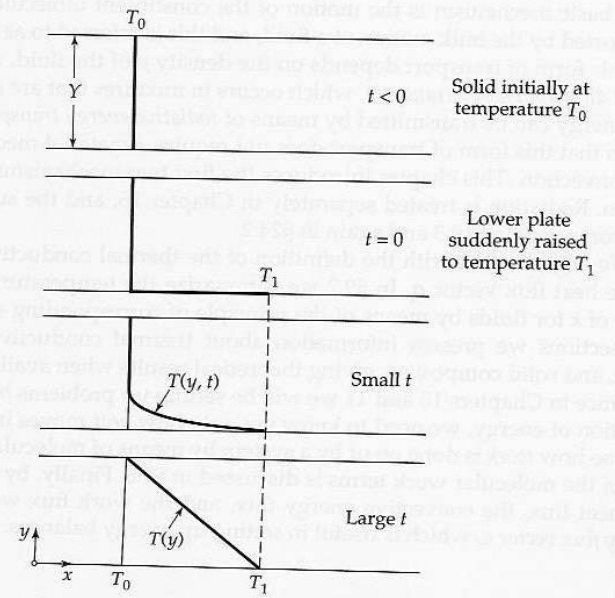


Fig. 9.1-1. Development of the steady-state temperature profile for a solid slab between two parallel plates. See Fig. 1.1-1 for the analogous situation for momentum transport.

Transport of mass - Diffusional laws (gases)

- Concentration gradient is stationary : Fick´s First Law

$$\boxed{j_n = -D_i \left(\frac{dc}{dz} \right)}$$

- Concentration gradient is not stationary : Ficks´s Second Law

$$\boxed{\left(\frac{\partial c_i}{\partial t} \right)_z = \frac{\partial}{\partial z} \left[D_i \frac{\partial c_i}{\partial z} \right]}$$

important for diffusion in porous catalysts !

Diffusion - Special diffusion phenomena

- Molecular diffusion

- Knudsen diffusion

- Surface diffusion
  - lateral diffusion
  - not of technical importance

- Configurational diffusion
  - pore diameter within molecular dimensions (0.3-1 nm) as for zeolites
  - diffusion coefficients are smaller by some orders of magnitude

Molecular diffusion coefficient

- Molecular diffusion coefficient for gases

$$D_M = \frac{1}{3} v \lambda \quad ; \text{v...average velocity; } \lambda\text{...mean free path length}$$

$$\boxed{D_M = \frac{2}{3}\left(\frac{kT}{\pi m}\right)^{\frac{1}{2}} \frac{kT}{\pi d^2 p}}$$

$$D_M \sim T^{\frac{3}{2}}, \sim \frac{1}{p}, \sim \frac{1}{m}, \sim \frac{1}{d^2}$$

- D_M during catalytic process nearly constant;
  reaction rate constant changes exponentially !

Molecular diffusion coefficient

- Kinetic gas theory delivers only inaccurate values for transport coefficients
- Binary diffusion coefficients D_{AB}^{gs} for mixtures of gases (up to p ≈ $2.5 \cdot 10^6$ Pa) (Hirschfelder/Curtiss/Bird)

$$\boxed{D_{AB}^{gs} = 0.001834 \frac{\sqrt{T^3 \dfrac{M_{r,A} + M_{r,B}}{2 M_{r,A} M_{r,B}}}}{p \sigma_{AB}^2 \Omega_D} \qquad , m^2 s^{-1}}$$

T	Temperature [K]
p	Pressure [bar]
$M_{r,A}, M_{r,B}$	Relative molecular masses of molecules A and B
σ_{AB}^2	Average collision factor of gases A and B
Ω_D	Collision integral with respect to force constants

Knudsen diffusion coefficient

- With decreasing pore diameter (or decreasing pressure), the pore diameter is smaller than the mean free path length $\lambda >> d_p$: D_{Kn} …Knudsen diffusion coefficient

$$D_{Kn} = \frac{1}{3} v\, d_p \quad ; v\text{...average velocity; } d_p\text{...pore diameter}$$

$$\boxed{D_{Kn} = \frac{1}{3} d_p \sqrt{\frac{8RT}{\pi M}}} \qquad D_{Kn} \sim T^{\frac{1}{2}}, \sim \frac{1}{M}, \sim d_p$$

- Depends not on pressure !

Diffusion in porous materials

- For d_p = const. and pressure decrease: transition from molecular diffusion to Knudsen diffusion

- Transition is not clearly defined; both equations apply

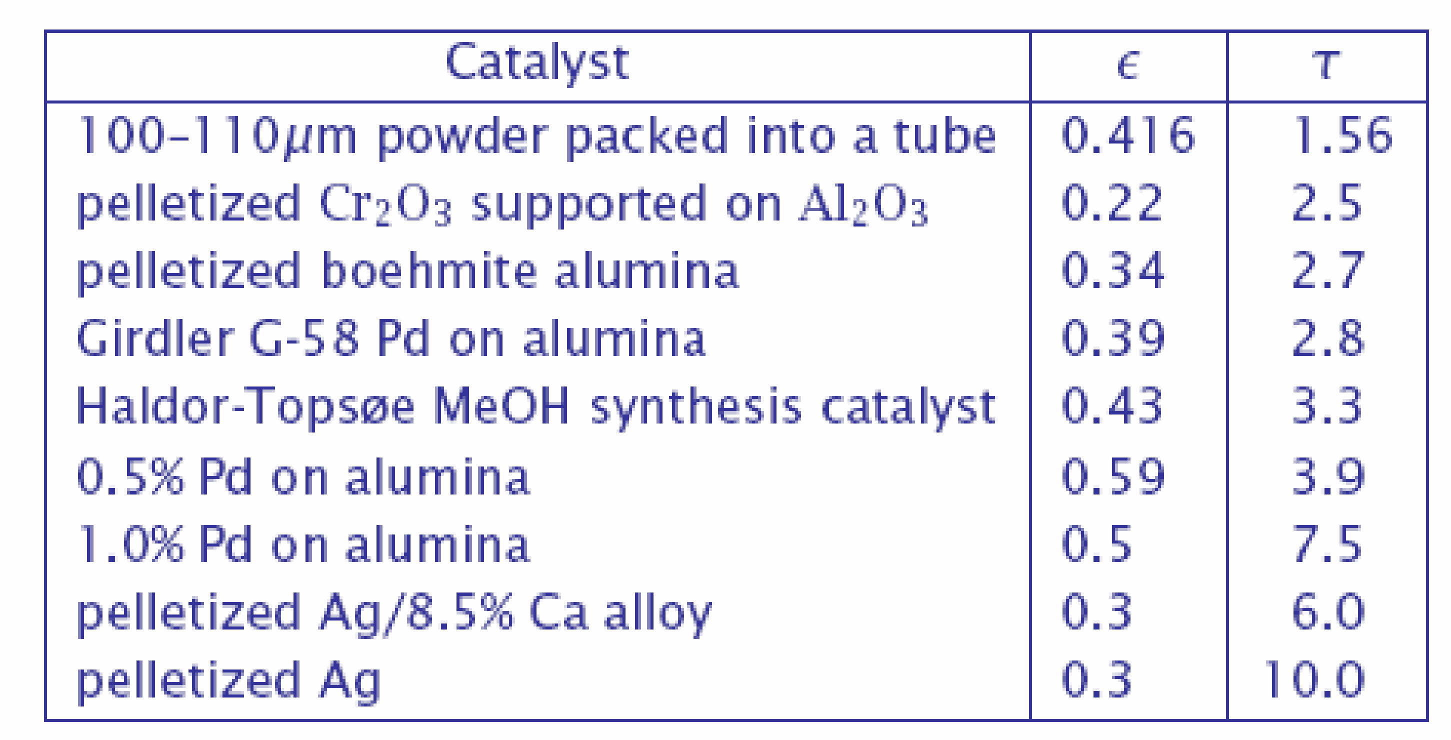
$$\boxed{\frac{1}{D^*} = \frac{1}{D_M} + \frac{1}{D_{Kn}}}$$

- Catalysts: irregular network of pores – effective D
- For very heterogeneous pore size distributions the term „effective D“ is not valid – complex models necessary

Effective diffusivities

- Use of porosity and tortuosity factor

$$\boxed{D_{\text{eff}} = \frac{\varepsilon}{\tau} D}$$



Catalyst	ϵ	τ
100–110μm powder packed into a tube	0.416	1.56
pelletized Cr_2O_3 supported on Al_2O_3	0.22	2.5
pelletized boehmite alumina	0.34	2.7
Girdler G-58 Pd on alumina	0.39	2.8
Haldor-Topsøe MeOH synthesis catalyst	0.43	3.3
0.5% Pd on alumina	0.59	3.9
1.0% Pd on alumina	0.5	7.5
pelletized Ag/8.5% Ca alloy	0.3	6.0
pelletized Ag	0.3	10.0

Diffusion - Current interest in science

- 10 000 paper/year dealing with diffusion phenomena
- Multitude of topics

- International Conferences:
  - 5th International Conference on Diffusion in Solids and Liquids

DSL2009-Rome, Italy/24-26 June, 2009

5th International Conference on Diffusion in Solids and Liquids – Mass Transfer, Heat Transfer and Microstructure and Properties

www.dsl2009-rome.com / contact@dsl2009-rome.com / DSL 2009 24-26 June, 2009 / Rome, Italy

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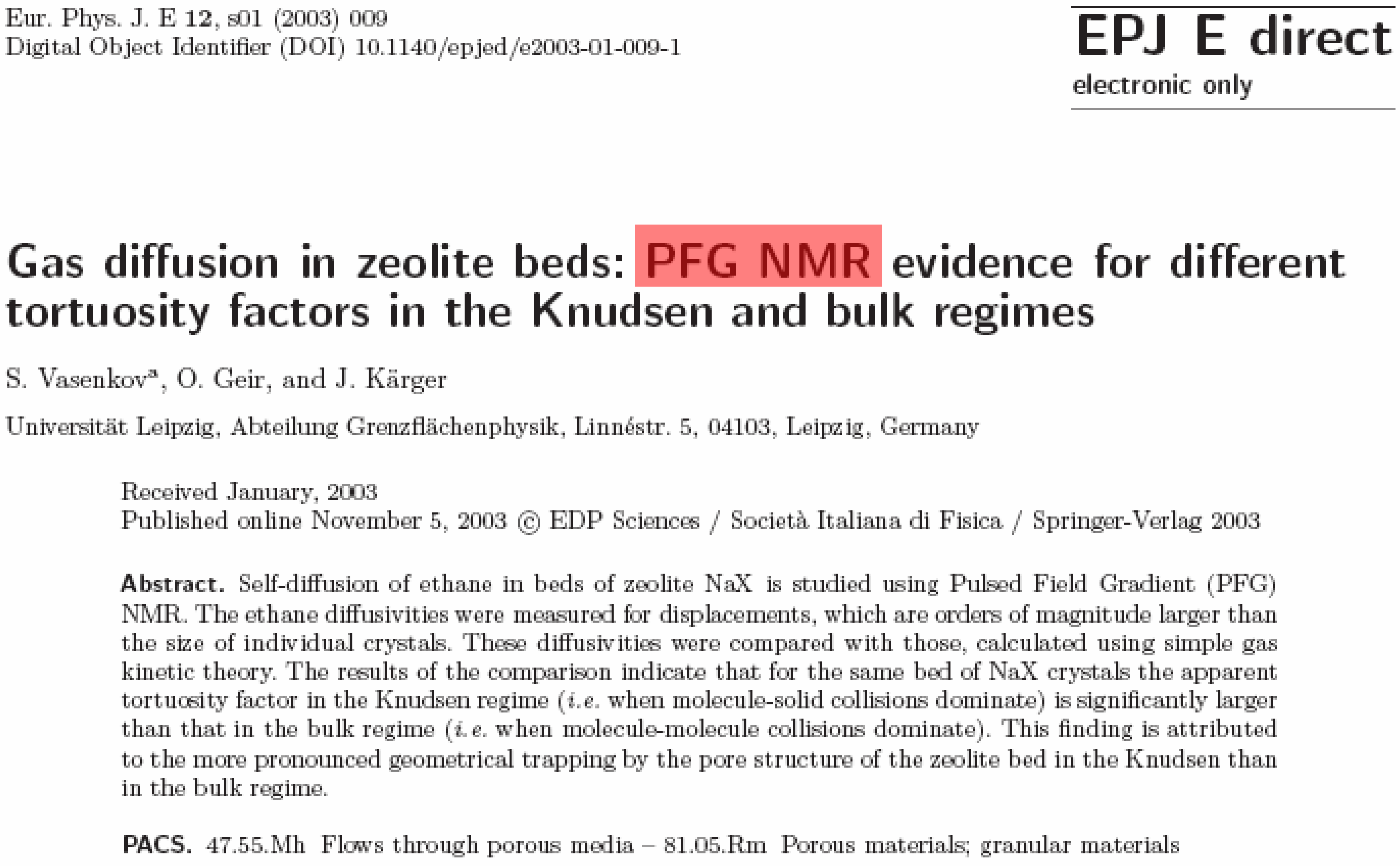
Literature examples



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Gas diffusion in zeolite beds: PFG NMR evidence for different tortuosity factors in the Knudsen and bulk regimes

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Received January, 2003

Abstract. Self-diffusion of ethane in beds of zeolite NaX is studied using Pulsed Field Gradient (PFG) NMR. The ethane diffusivities were measured for displacements, which are orders of magnitude larger than the size of individual crystals. These diffusivities were compared with those, calculated using simple gas kinetic theory. The results of the comparison indicate that for the same bed of NaX crystals the apparent tortuosity factor in the Knudsen regime (*i.e.* when molecule-solid collisions dominate) is significantly larger than that in the bulk regime (*i.e.* when molecule-molecule collisions dominate). This finding is attributed to the more pronounced geometrical trapping by the pore structure of the zeolite bed in the Knudsen than in the bulk regime.

PACS. 47.55.Mh Flows through porous media – 81.05.Rm Porous materials; granular materials

…continued

1 Introduction

The diffusion coefficient of gas molecules in random porous systems is usually presented as the diffusivity in a well-defined reference system divided by a tortuosity factor. Two extreme cases can be identified viz., the regimes of the Knudsen and of the bulk diffusion. In the first regime molecule-solid collisions dominate. In contrast, in the second regime molecule-molecule collisions occur much more frequently than molecule-solid collisions. The respective diffusivities in the Knudsen and bulk regimes (D_{iK} and D_{ib}) can be presented as

$$D_{\mathrm{iK}} = \frac{1}{\eta_{\mathrm{K}}} D_{0\mathrm{K}}, \quad D_{\mathrm{ib}} = \frac{1}{\eta_{\mathrm{b}}} D_{0\mathrm{b}}, \tag{1}$$

where η_{K}, $D_{0\mathrm{K}}$ and $\eta_{\mathrm{b}}, D_{0\mathrm{b}}$ are the tortuosity factors and the reference diffusivities in the Knudsen and in the bulk regimes, respectively. The reference diffusivity in the Knudsen regime is usually defined as that in straight parallel, non-overlapping cylindrical pores of infinite length with a diameter equal to the mean intercept length (d) in the considered real pore structure

$$D_{0\mathrm{K}} = \frac{1}{3}\bar{u}d, \tag{2}$$

where $\bar{u} = (8RT/\pi M)^{1/2}$ is a mean thermal speed, R is the gas constant, M is the molar mass and T is the absolute temperature. The reference diffusivity in the bulk regime is equal to that in the gas volume

$$D_{0\mathrm{b}} = \frac{1}{3}\bar{u}\lambda, \tag{3}$$

where λ is the molecular mean free path. Gas diffusivity in random porous systems in the general case of any particular gas concentration is given by the sum of the diffusion resistances associated with molecule-solid and molecule-molecule collisions [1]

$$\frac{1}{D_{\mathrm{inter}}} = \frac{1}{D_{\mathrm{iK}}} + \frac{1}{D_{\mathrm{ib}}}. \tag{4}$$

A traditional approach to the tortuosity factor in chemical engineering literature is based on the assumption that this factor reflects intrinsic geometrical properties of the porous structure and thus does not depend on the diffusion regime (Knudsen or bulk). However, the results of a number of recent MC simulations of gas diffusion in porous media have shown that the tortuosity factor in the Knudsen regime (η_{K}) can be several times larger than that in the bulk regime (η_{b}) for the same porous system [2,3,4]. This seems to indicate that molecular trajectories in the bulk regime are much less influenced by geometrical details of porous media than in the Knudsen regime. In the present paper we report the direct experimental evidence that η_{K} can indeed be much larger than η_{b} in beds of solid particles.

Pulsed Field Gradient (PFG) NMR can be applied to measure D_{inter} of gas molecules in various porous materials, including beds of non-adsorbing particles [5]. Due to technical reasons discussed below it is often easier using

---

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Colloids and Surfaces
A: Physicochemical and Engineering Aspects 206 (2002) 335–348

COLLOIDS AND SURFACES A

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Pore roughness effects on self- and transport diffusion in nanoporous materials

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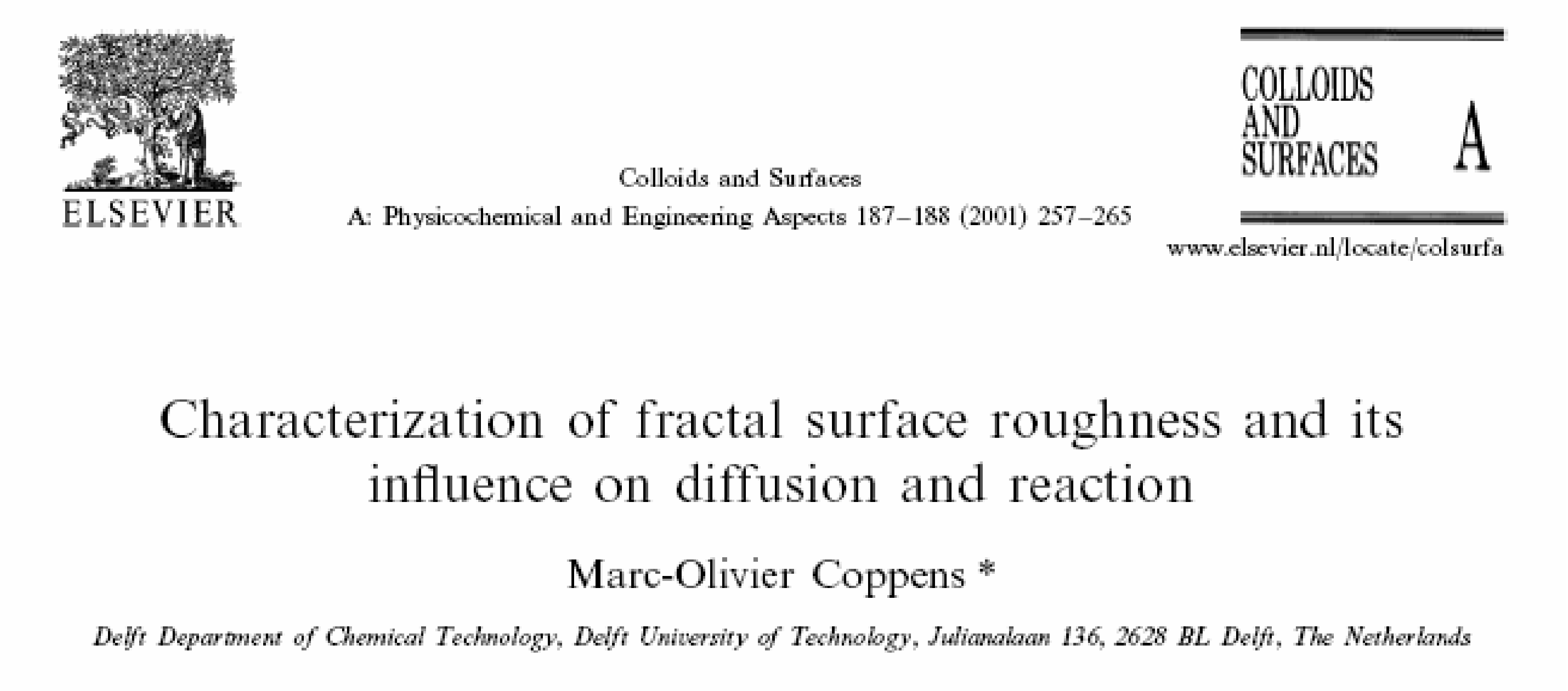

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Characterization of fractal surface roughness and its influence on diffusion and reaction

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PERGAMON

Chemical Engineering Science 56 (2001) 1869–1881

Chemical
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Reaction-transport simulations of non-oxidative methane conversion with continuous hydrogen removal — homogeneous–heterogeneous reaction pathways

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Diffusion of hydrocarbons in the reforming catalyst: molecular modelling

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Modeling Diffusion and Reaction of the n-Butane Isomerization on Sulfated Zirconias – A Transient TAP Study

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Transport problems in catalysis

Transport and catalysis

- One part of the catalytic cycle is the transport of reactants to the active surface

- Typical heterogeneous processes proceed at the surface of solids or porous particles, which are surrounded by gas or liquid

- If the chemical reaction proceeds very fast, the overall rate may be controlled by the transport of reactand from the fluid to the external surface of the catalyst particle or by diffusion inside the pores of the catalyst particle

1. Film mass transfer of the reactant A, i.e. bulk diffusion of A through the stagnant gas film or boundary layer surrounding the catalyst particle to the external catalyst surface.
2. Diffusion of species A (by either bulk or molecular (Knudsen) diffusion) through the porous network of the catalyst to the catalytic surface.
3. Adsorption of A onto the catalyst surface.
4. Reaction of A to B on catalytic sites on the catalyst surface.
5. Desorption of the product B molecules from the surface.
6. Diffusion of species B through the porous network to the pore mouth.
7. Film mass transfer of product B, i.e. bulk diffusion of B from the external catalyst surface through the stagnant gas film to the bulk gas stream.

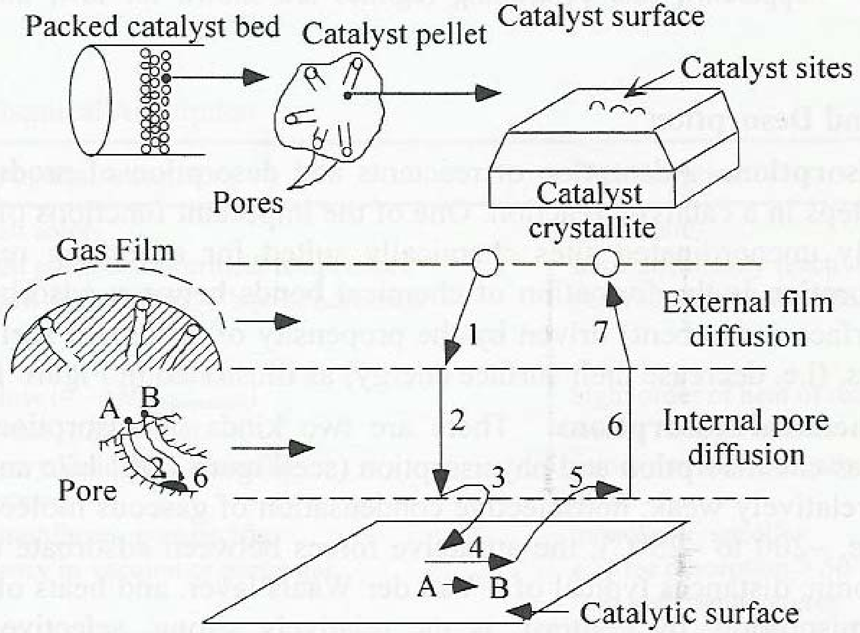


Figure 1.5 Steps in a heterogeneous catalytic reaction A → B in a porous, supported catalyst (adapted from Fogler, 1999; courtesy of Prentice Hall).

From „Fundamentals in industrial…

Transport regimes

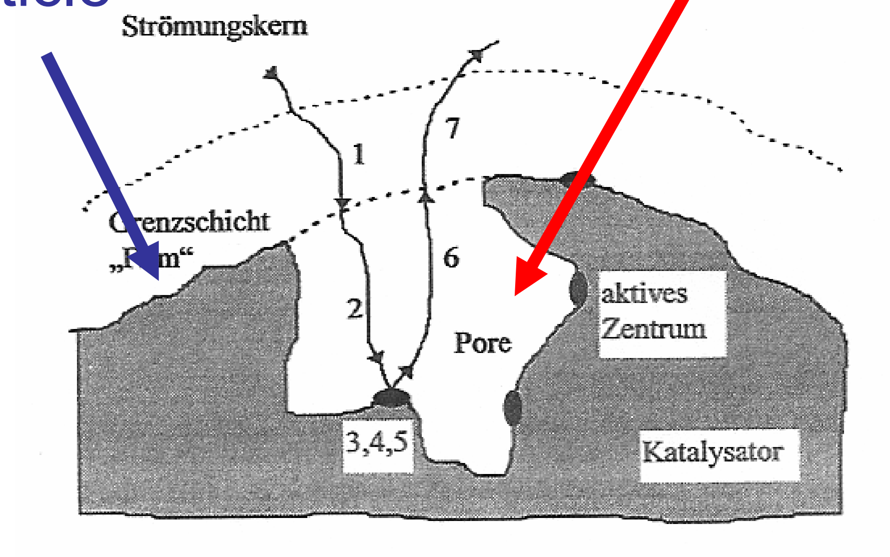
Transport

External

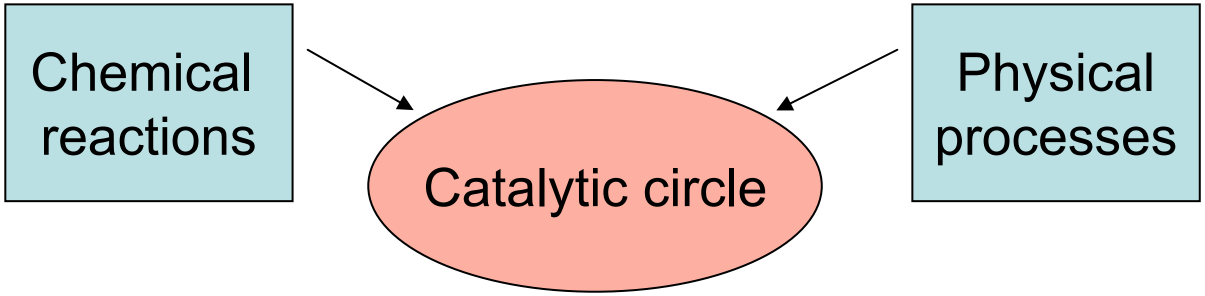
Internal

Diffusion to exterior surface of particle

Diffusion in pores



Rates in the catalytic cycle

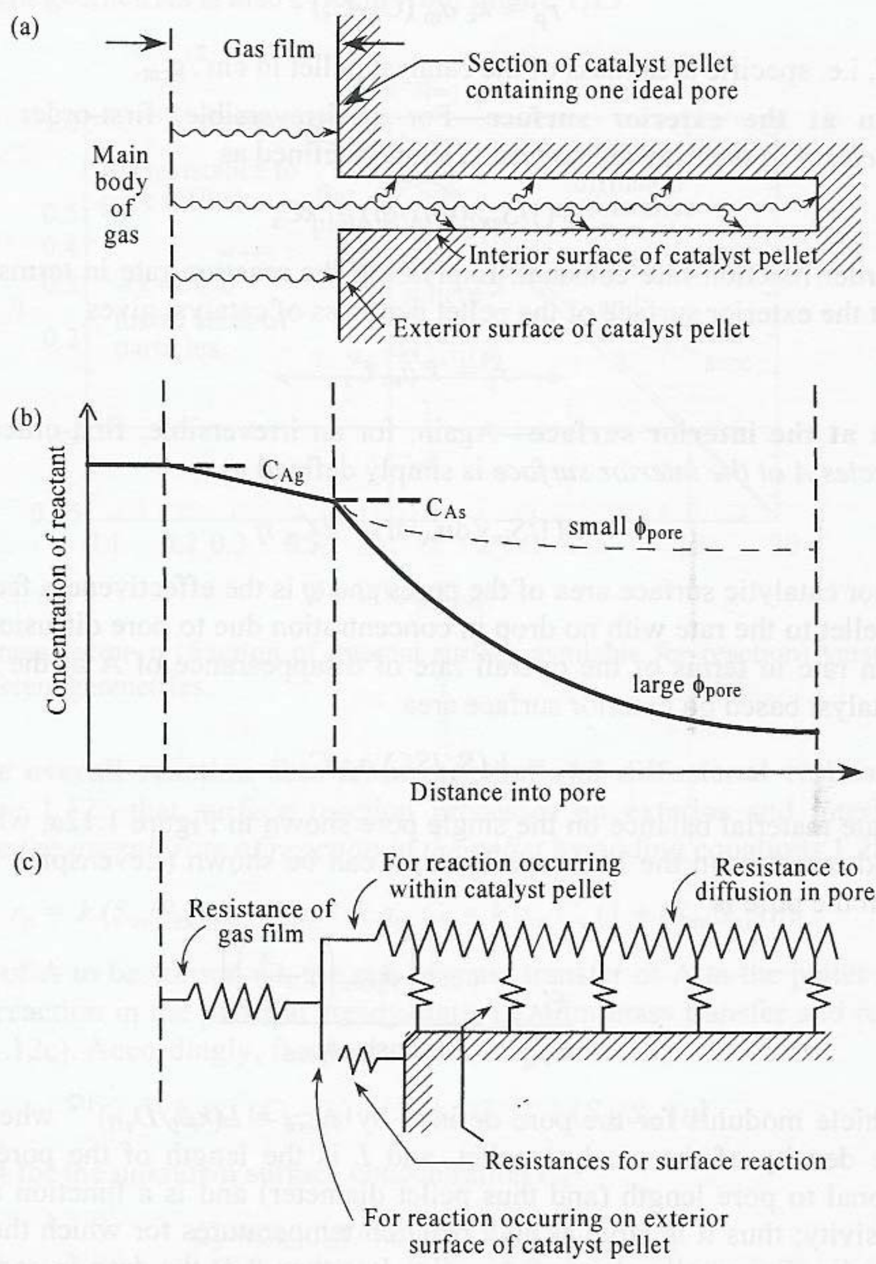


- $\text{rate}_{\text{diffusion}} >> \text{rate}_{\text{chemical reaction}}$: no influence on overall rate
    - substrate concentration in pores and on catalyst surface = gas concentration
- $\text{rate}_{\text{diffusion}} \approx \text{rate}_{\text{chemical reaction}}$: incomplete mass transfer, thus decrease in reaction rate

External or internal mass transfer control ?

To get insights in kinetics of chemical reactions the influence of diffusion on the reaction has to be known and to be eliminated

Criteria for diffusional influences ?



Simplified single-pore model for diffusion and catalytic reaction in a porous catalyst

From „Fundamentals in industrial…

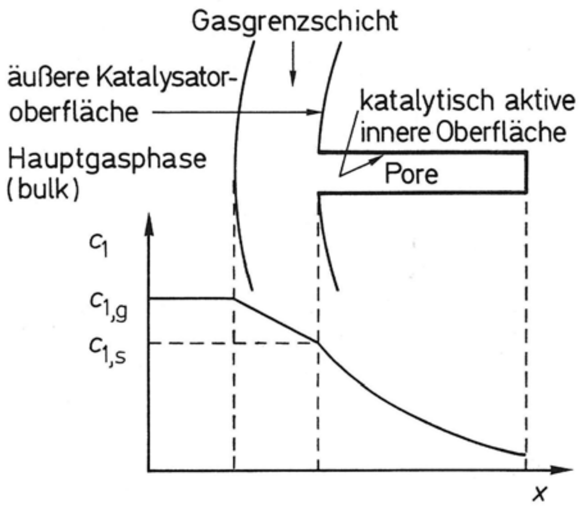
External mass transfer processes

External mass transfer - Model

- Influence of mass transfer: yes/no ?
  - coupling of flux equations for mass transfer (and heat transfer) with reaction rate equation

Model:

- System at stationary conditions
- Main quantities:
  - gas phase (bulk) concentration c_g
  - concentration at exterior surface c_s



(see Baerns)

External mass transfer – Rate equation

- Effective rates for transfer and reaction

$$r_{eff} = k_g\, a\,(c_{1,g} - c_{1,s})$$

k_g transfer coefficient

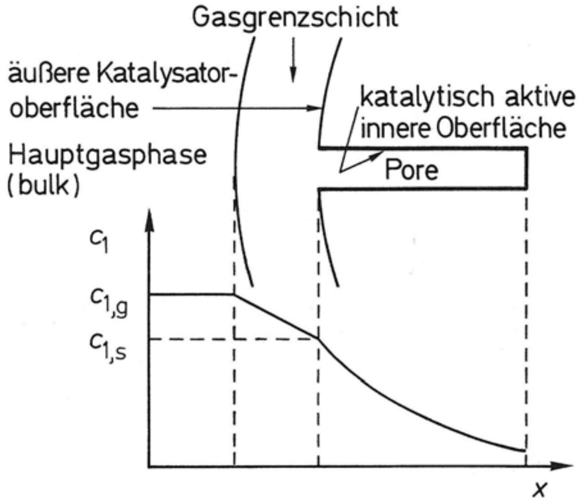
a specific surface area

$$r_{eff} = k\, c^{m}_{1,s} \qquad k = k_s\, a$$

$$\boxed{k_g\, a\,(c_{1,g} - c_{1,s}) = k\, c^{m}_{1,s}}$$

- Calculation of c_s possible

$$c_{1,s} = \frac{c_{1,g}}{1 + \frac{k}{k_g}\, a}$$



External mass transfer – Effective rate

- for m =1

$$r_{eff} = k\, c^{m}_{1,s} = \frac{k}{1+\frac{k}{k_g}a} c_{1,g}$$

$$\boxed{r_{eff} = k\, c_{1,g}}$$

- Case studies: $\frac{k}{k_g\, a} << 1$

mass transfer is fast compared to chemical reaction, no concentration gradient in film

External mass transfer – Da number

- Damköhler number II:

$$\mathrm{DaII} = \frac{k\, c^{m}_{1,g}}{k_g a\, c_{1,g}}$$

for any m

ratio of rate without mass transfer limitation ($c_{1,s}=c_{1,g}$) to rate with maximal mass transfer limitation ($c_{1,s} \rightarrow 0$)

- Definition of new quantity for the description of catalyst performance

External mass transfer – Effectiveness factor

- Definition of external effectiveness factor η_{ext} for a catalyst

$$\boxed{\eta_{ext} = \frac{r_{eff}}{r} = \frac{k_{eff}\ c_{1,g}}{k\ c_{1,g}} = \frac{1}{1 + DaII}}$$

ratio of reaction rate with diffusion limitation to reaction rate without diffusion limitation

(case for first order reaction)

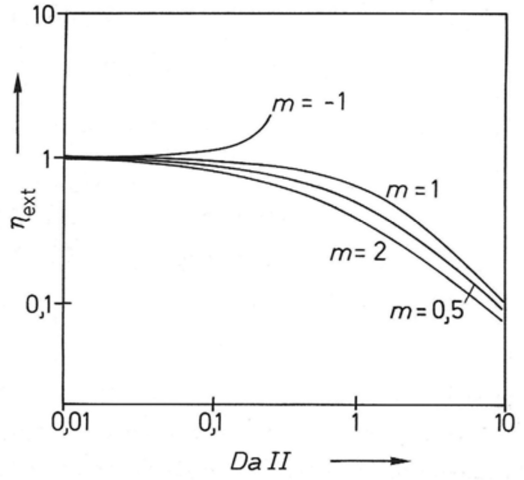
- η_{ext} for higher reaction order more complicated (see textbook)

External mass transfer – Effectiveness factor

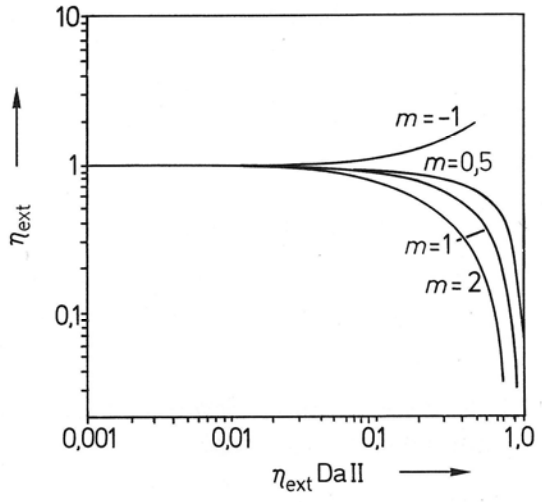
- External effectiveness factor η_{ext}

$$\boxed{\eta_{ext} = \frac{r_{eff}}{r}}$$

depending on m →



- Estimation of external transport influence possible by using experimental quantities



External mass transfer - Criteria

- Film around particle depends on flow conditions: laminar (or turbulent)

- Dimensionless Reynolds number Re

$$\boxed{Re = \frac{d_p\, v}{\mu}}$$

d_p…particle diameter
v …velocity of gas
μ …viscosity of gas

- Correlation between mass transfer coefficient k_g and reaction rate; for kinetic regime: transfer >> rate

External mass transfer - Criteria

- Check flow profile of reactor

$$\boxed{\frac{d_R}{d_p} > 30}$$

d_R …reactor diameter

d_p …particle diameter

- Fixed bed reactor → catalyst in powder form
- Re > 2 no back mixing effects
- Re, Sc (Schmidt) as dimensionless quantities
- Description of flux as function of Sc number

$$\boxed{j_D = f(\mathrm{Re}) = \frac{k_g\, p}{v_M} \mathrm{Sc}^{2/3} \qquad \mathrm{Sc} = \frac{\mu}{D_M}}$$

Experimental check

- Fixed bed reactor:

  for the condition of a constant residence time increase of linear velocity of the fluid around the particles until the resulting rate keeps constant

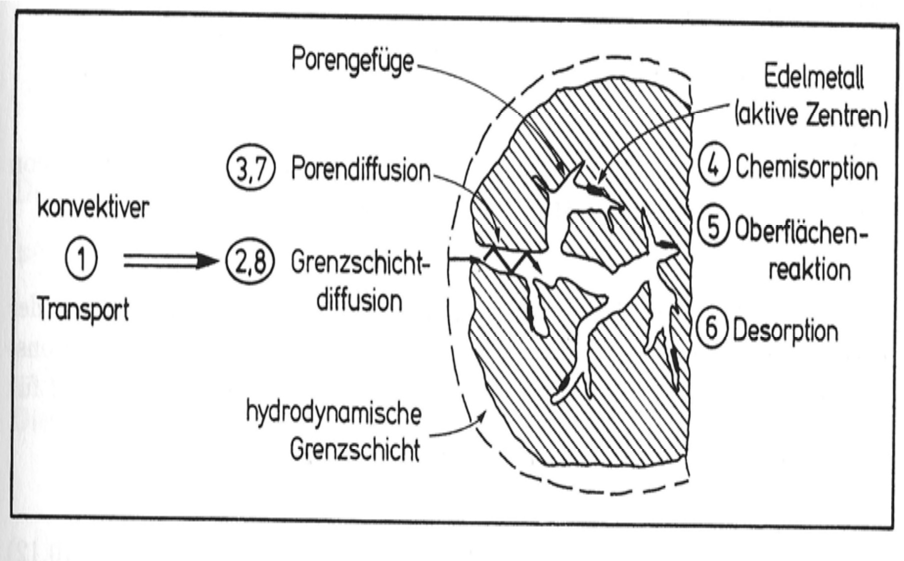
  ↷

  no influence of external transfer

  ! residence time decreases with increasing velocity of fluid, increase the bed height to compensate this

Internal mass transfer processes

Internal transport - Pore diffusion



- Transport of reactant through porous pore system to the active centres
- Diffusion is slow process thus the transport limits conversion
- Simple approximation of pore diffusion

Pore diffusion - Rates

1. Assumption:

- Catalyst pore with cross section S and length l
- Reaction in pore is 1st order : r = k*c

- Reaction rate R related to active surface S (V = S*l)
- Reaction rate r_V in pore volume

$$l * r_v = \frac{R}{S} = -l * k * c$$

see Jakubith

Pore diffusion – Diffusion coefficient

2. Assumption:

- Diffusion coefficient inside the pore differs from diffusion coefficient D^{gs}
- Correction by tortuosity factor and porosity
  → effective diffusion coefficient

$$\boxed{D^{gs}_{eff} \approx \frac{1}{10} D^{gs}}$$

first assumption, if no information available

Pore diffusion – Mass balance

- General mass balance for one-dimensional, steady-state case, reaction is 1st order

$$\boxed{D_{eff}\frac{d^2c}{dz^2} - k\,c = 0}$$

- Solution of differential equation with help of dimensionless variables Γ and ζ

$$\Gamma = \frac{c}{c_0}$$

$$\zeta = \frac{z}{l}$$

c_0 concentration in free gas space

l pore length

Pore diffusion – Thiele modulus

- Dimensionless mass balance

$$D_{eff}\frac{c_0}{l^2}\frac{d^2\frac{c}{c_0}}{d\left(\frac{z}{l}\right)^2}-c_0\,k\frac{c}{c_0}=0 \qquad \curvearrowright \qquad \boxed{\frac{d^2\Gamma}{d\zeta^2}-\frac{l^2\,k}{D_{eff}}\Gamma=0}$$

- Quotient $\varphi^2=\frac{l^2\,k}{D_{eff}}$ is a dimensionless term

- Thiele modulus $\boxed{\varphi=l\sqrt{\frac{k}{D_{eff}}}}$

Thiele Modulus φ

- The single dimensionless group appearing in the model is referred to as the Thiele number or Thiele modulus in recognition of Thiele´s pioneering contribution to this area:

  E.W. Thiele. Relation between catalytic activity and size of particle.
  Ind. Eng. Chem. 31(7) (1939) 916-920.

- In his original paper, Thiele used the term „modulus“ to emphasize that this then unnamed dimensionless group was positive. Later when Thiele´s name was assigned to this dimensionless group , the term modulus was retained.

Pore diffusion – Thiele modulus

- Thiele modulus $\varphi = l\sqrt{\frac{k}{D_{eff}}} = \frac{\text{reaction rate}}{\text{diffusion rate}}$

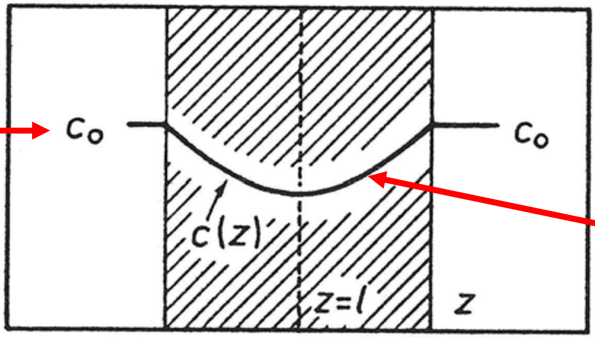
- New form of differential equation for mass balance

$$\boxed{\frac{d^2\Gamma}{d\zeta^2} = \varphi^2\,\Gamma}$$

- Solve with appropriate initial and boundary conditions

Pore diffusion – Solving of mass balance

- Boundary conditions



free
gas space

decrease of c
due to reaction

1. for $z = 0$, $c = c_0$ or for $\zeta = 0$, $\Gamma = 1$
2. for $z = l$, $dc/dz = 0$ or for $\zeta = 1$, $d\Gamma/d\zeta = 0$

- Solution of differential equation by exponential approximation

Pore diffusion – Case studies

- Concentration of reactant inside the pore

$$\boxed{\Gamma = \frac{\cosh \varphi (1-\zeta)}{\cosh \varphi} \quad \text{or} \quad \frac{c}{c_0} = \frac{\cosh \varphi (1-\frac{z}{l})}{\cosh \varphi}}$$

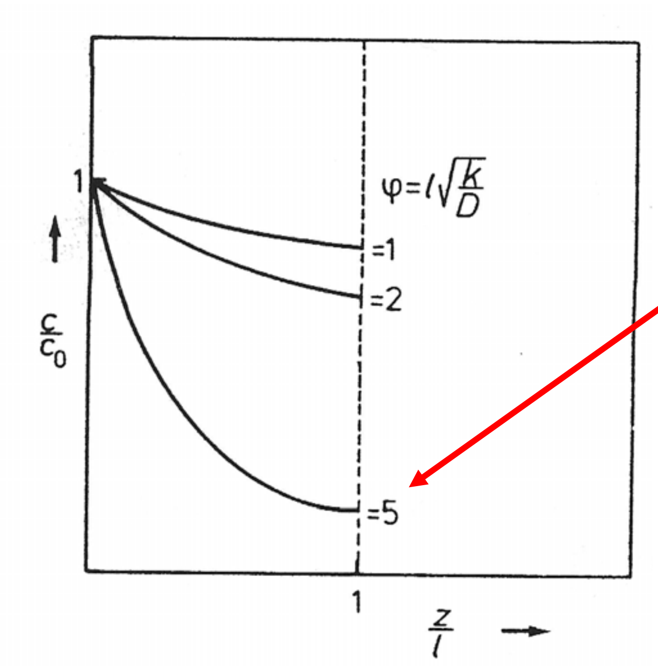
- with increasing temperature the Thiele modulus increases because of $\varphi = l\sqrt{\frac{k}{D_{eff}}}$ and $k = k_0 \exp\left[-\frac{E_A}{RT}\right]$

- Reactant converts already at z/l << 1

It is of technical importance to find the temperature where pore diffusion starts to influence the reaction **!**

Pore diffusion – Case studies

$$\Gamma = \frac{\cosh \varphi (1-\zeta)}{\cosh \varphi} \quad \text{or} \quad \frac{c}{c_0} = \frac{\cosh \varphi (1-\frac{z}{l})}{\cosh \varphi}$$



- with $\varphi \geq 3$ the reactant can not reach the interior of the pore
- no full utilization of the internal surface of the catalyst

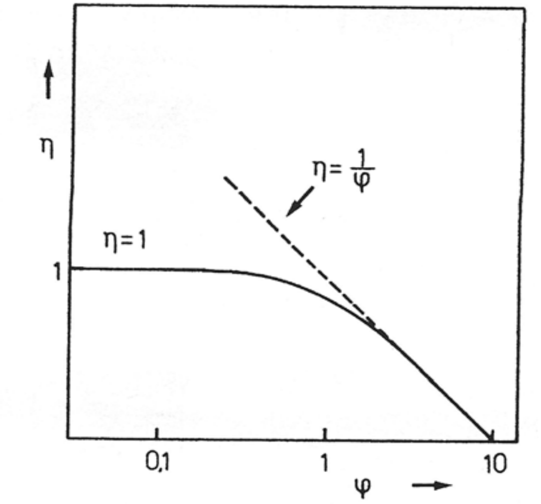
Pore diffusion - Criteria

- Thiele modulus $\varphi = l\sqrt{\frac{k}{D_{eff}}}$
- Criteria:
  - $\varphi << 1$
    - chemical reaction is rate-limiting
    - diffusion is fast, reactand can enter the pores of the catalyst and the concentration of the reactand is constant for the whole catalyst volume
  - $\varphi >> 1$
    - limitation of overall rate by diffusion of reactand in the pores
    - inside the pores the reactand converts fast
    - concentration of reactand decreases already close to the boundary layer

Internal transfer - Effectiveness factor η

- Reaction rate r_s $$r_s = l * r_v$$
- Effectiveness factor is defined as $$\boxed{\eta = \frac{r_s}{r_{s,\max}}} \quad \frac{\text{reaction rate}}{\text{max. reaction rate}}$$
- max. reaction rate is connected with c_0

$$\boxed{\eta = \frac{r_s}{r_{s,\max}} = \frac{k \int_0^l c(z)\,dz}{k\, l\, c_0}}$$



Effectiveness factor η - Case studies

- Effectiveness factor is a dimensionless pellet production rate that measures how effectively the catalyst is being used.

- For η near unity, the entire volume of the pellet is reacting at the same high rate because the reactant is able to diffuse quickly through the pellet.

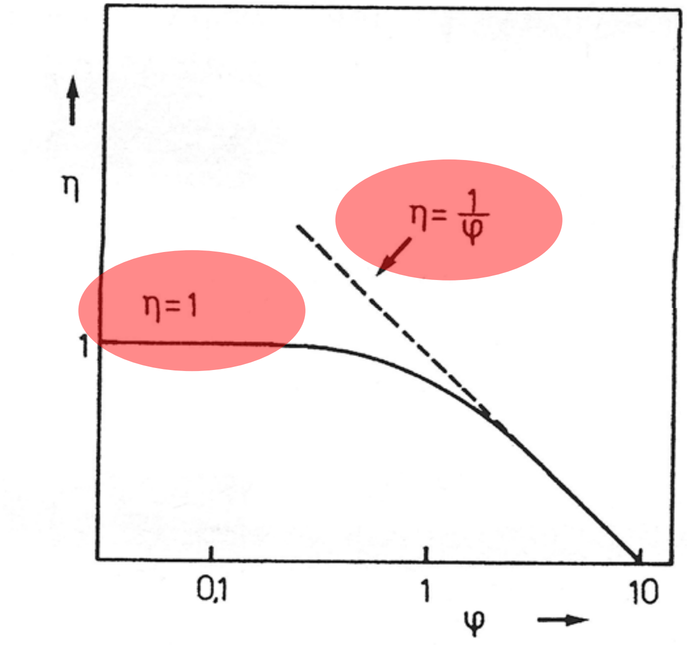
- For η near zero, the pellet reacts at low rate. The reactant is unable to penetrate significantly into the interior of the pellet and the reaction rate is small in a large portion of the pellet volume.

Effectiveness factor η - Case studies

- with solution function for Γ (see results for pore diffusion)

$$\eta = \int_0^l \frac{\cosh \varphi (1 - z/l)}{l \cosh \varphi} dz$$

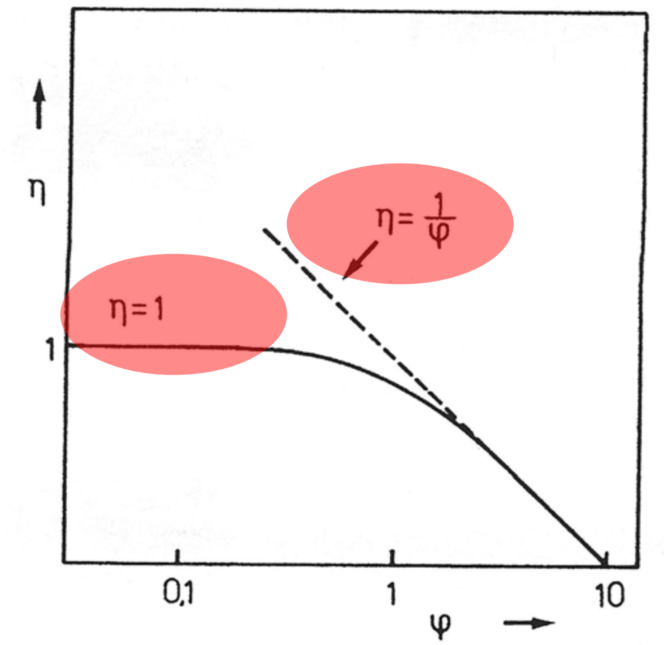
$$\boxed{\eta = \frac{\tanh \varphi}{\varphi}}$$



two characteristic regimes

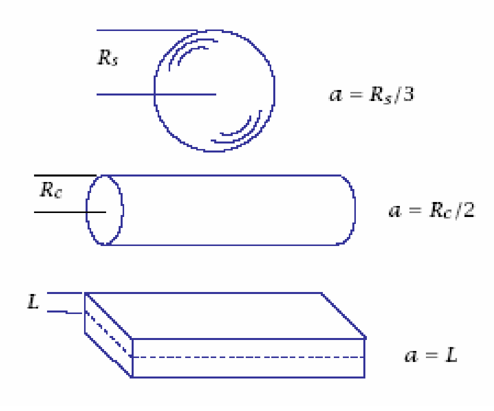
Effectiveness factor η - Case studies

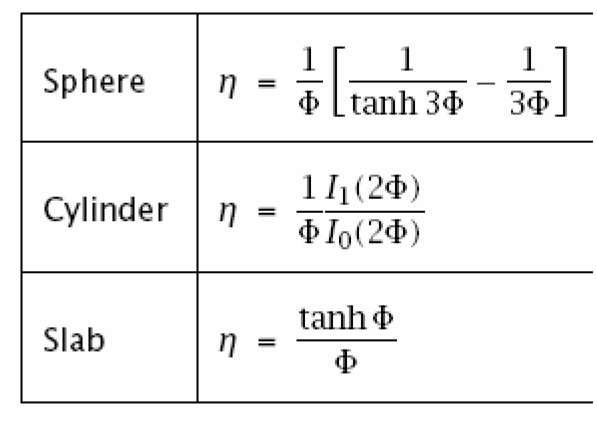
- for $\varphi \leq 0.3$, $\boxed{\eta \approx 1}$ regime of reaction control
- for $\varphi \geq 0.3$, $\boxed{\eta \approx \frac{1}{\varphi}}$ regime of pore diffusion control



Effectiveness factor - Geometry of pores

- Solution depends on characteristic length (volume-to surface ratio)
- Characteristic length differs for cylinder, sphere or slab; different analytical solutions

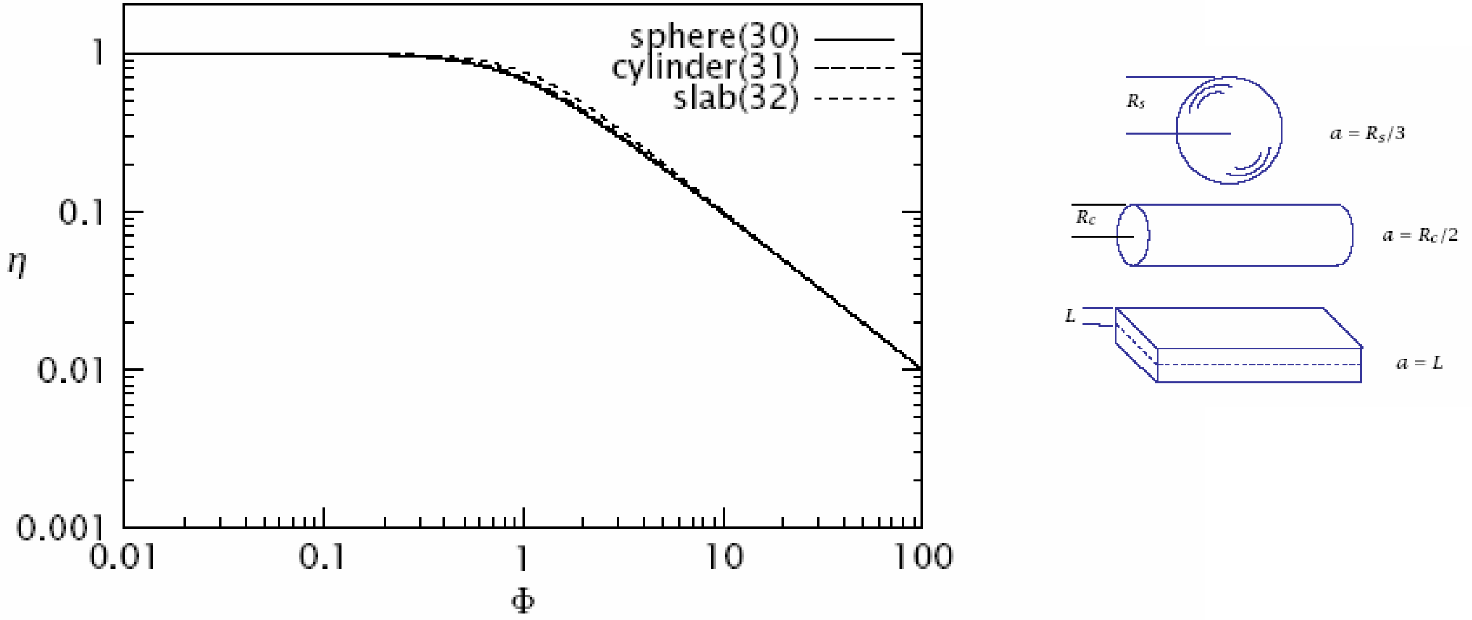




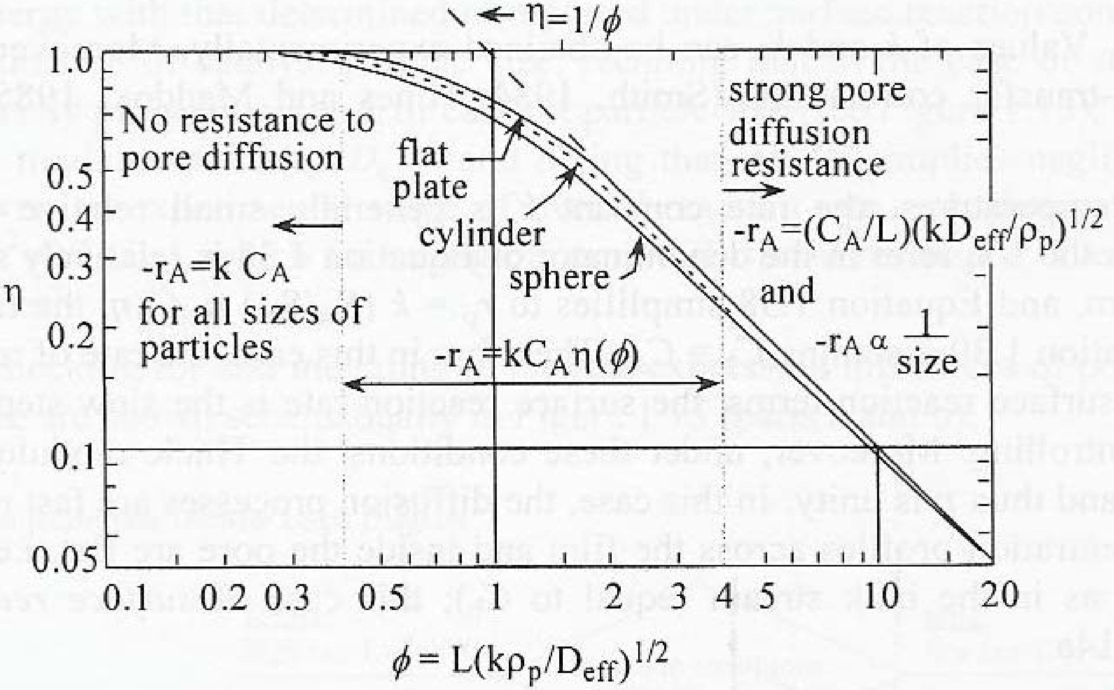
Sphere	$\eta = \frac{1}{\Phi}\left[\frac{1}{\tanh 3\Phi} - \frac{1}{3\Phi}\right]$
Cylinder	$\eta = \frac{1}{\Phi}\frac{I_1(2\Phi)}{I_0(2\Phi)}$
Slab	$\eta = \frac{\tanh\Phi}{\Phi}$

Effectiveness factor - Geometry of pores

The effectiveness factors versus Thiele modulus for the three geometries are



- functional forms (see table) are quite different, but solutions are quite similar
- identical asymptotes for small and large φ



Effectiveness factor η (fraction of internal surface available for reaction) versus Thiele modulus ϕ for
les of different geometries.

From „Fundamentals in industrial…

Examples (see Baerns)

***Beispiel* 6.2.** Beeinflussung des Reaktionsablaufs der Methanisierung von CO durch den Stoffübergang vom Gas an die äußere Katalysatoroberfläche (Grundlage: Lit. [60]).

Die effektive Geschwindigkeit der Reaktion

$$CO + 3H_2 \longrightarrow CH_4 + H_2O,$$

die unter Porendiffusionseinfluß an/in einem zylindrischen porösen Katalysatorpellet ($d = 6$ mm, $L = 5$ mm) abläuft, kann durch folgenden formalkinetischen Ansatz beschrieben werden.

$$r^e = \frac{a_1 p_{CO,s} p_{H_2,s} p^{-0,5}}{(1 + a_2 p_{CO,s} + a_3 p_{H_2,s})^2} \quad (\mathrm{mol \cdot h^{-1} \cdot g^{-1}})$$

bzw.

$$r_v^e = r^e \varrho_s \quad (\mathrm{mol \cdot h^{-1} \cdot cm^{-3}})$$

Hierin ist $a_i = a_i^\circ \exp(-A_i/T)$; der Index s weist darauf hin, daß es sich um die an der äußeren Katalysatoroberfläche herrschenden Partialdrücke handelt.

Für die Parameter gilt:

$$\begin{aligned}
a_1^\circ &= 4{,}8\ \mathrm{mol \cdot bar^{-1,5} \cdot g^{-1} \cdot h^{-1}}\\
A_1 &= 9{,}3 \cdot 10^2\ \mathrm{K}\\
a_2^\circ &= 2{,}4 \cdot 10^{-4}\ \mathrm{bar^{-1}}\\
A_2 &= -5{,}5 \cdot 10^3\ \mathrm{K}\\
a_3^\circ &= 3{,}2 \cdot 10^{-2}\ \mathrm{bar^{-1}}\\
A_3 &= -7{,}5 \cdot 10^2\ \mathrm{K}\\
\varrho_s &= 1{,}67\ \mathrm{g \cdot cm^{-3}}
\end{aligned}$$

Die Reaktionstemperatur soll 573 K, der Gesamtdruck $p = 25$ bar, das H_2/N_2-Verhältnis 3 : 1 und der CO-Partialdruck $p_{CO,g}$ im Gasraum 0,04 bar betragen.

Aufgabe a. Ermittlung der Größe des Stoffübergangskoeffizienten k_g für CO, der erforderlich ist, damit $p_{CO,s}$ mindestens 95% von $p_{CO,g}$ beträgt ($p_{CO,s} \geqq 0{,}95\, p_{CO,g}$).

Lösung

$$r_v^e = k_g a \frac{p_{CO,g} - p_{CO,s}}{RT}$$

$$r_v^e = 5{,}5\ \mathrm{mol \cdot m_{Kat}^{-3} \cdot s^{-1}}$$

mit

$$p_{CO,s} = 0{,}95\, p_{CO,g}$$

und

$$p_{H_2,s} = p_{H_2,g}$$

$$a = \frac{(2\pi d^2/4 + L\pi d)}{L\pi d^2/4}$$

$$k_g = 0{,}12\ \mathrm{m \cdot s^{-1}}$$

Aufgabe b. Die Reaktion verläuft unter den oben angegebenen Bedingungen im p_{CO}-Bereich zwischen 0 und 0.04 bar mit guter Näherung nach erster Ordnung für CO. Es ist zu überprüfen, ob für $k_g = 0{,}002$, $0{,}02$ und $0{,}2\,\mathrm{m/s}$ die Reaktion stoffübergangslimitiert ist; gleichzeitig sind die jeweiligen äußeren Katalysatorwirkungsgrade zu bestimmen.

Lösung

$$r_v^e = k\,p_{\mathrm{CO,s}}\,\varrho_s = 6{,}35\,\mathrm{mol}\cdot\mathrm{m}_{\mathrm{Kat}}^{-3}\cdot\mathrm{s}^{-1}$$

mit

$$k \approx \frac{a_1\,p_{\mathrm{H_2,g}}\,p^{-0,5}}{(1+a_3\,p_{\mathrm{H_2,g}})^2} = 0{,}342\,\mathrm{mol}\cdot\mathrm{g}^{-1}\cdot\mathrm{h}^{-1}\cdot\mathrm{bar}^{-1}$$

$$DaII = \frac{k\,p_{\mathrm{CO,g}}\,\varrho_s}{k_g\,a\,p_{\mathrm{CO,g}}/RT}$$

$$\eta_{\mathrm{ext}} = \frac{1}{1+DaII}$$

$k_g\,(\mathrm{m}\cdot\mathrm{s}^{-1})$	$DaII\,(-)$	$\eta_{\mathrm{ext}}\,(-)$
0,2	$3{,}55\cdot 10^{-2}$	0,966
0,02	$3{,}55\cdot 10^{-1}$	0,738
0,002	3,55	0,220

Aufgabe c. Für die unter b) genannten k_g-Werte sind die CO-Partialdrücke an der äußeren Katalysatoroberfläche zu ermitteln.

Lösung

$$r_v^e = k\,p_{\mathrm{CO,s}}\,\varrho_s = k_g\,a\,\frac{p_{\mathrm{CO,g}} - p_{\mathrm{CO,s}}}{RT}$$

(Vereinfachung: Bei der Berechnung von k wird angenommen, daß $a_2\,p_{\mathrm{CO,s}}$ durch $a_2\,p_{\mathrm{CO,g}}$ und $a_3\,p_{\mathrm{H_2,s}}$ durch $a_3\,p_{\mathrm{H_2,g}}$ angenähert werden kann).

$k_g\,(\mathrm{m}\cdot\mathrm{s}^{-1})$	$p_{\mathrm{CO,g}}$ (bar)	$p_{\mathrm{CO,s}}$ (bar)
0,2	0.04	0,0386
0,02	0.04	0,0295
0,002	0.04	0,0088

Beispiel 6.3. Beeinflussung des Reaktionsablaufs der Methanisierung von CO durch Porendiffusion im Katalysatorpellet.
(Grundlage: Lit. [60])

Die auf das Katalysatorpelletvolumen bezogene effektive Geschwindigkeit der Reaktion, die nicht durch äußere Transportvorgänge beeinflußt sein soll, kann über einen größeren Bereich der Partialdrücke ($p_{CO} \leqq 0{,}5$ bar; $1 \leqq p_{H_2} \leqq 25$ bar) durch folgenden formalkinetischen Ansatz beschrieben werden:

$$r_{\mathrm{eff}} = \frac{a_1 p_{\mathrm{CO,g}} p_{\mathrm{H_2,g}} p^{-0,5}}{(1 + a_2 p_{\mathrm{CO,g}} + a_3 p_{\mathrm{H_2,g}})^2} \cdot \varrho_{\mathrm{Kat}} \quad (\mathrm{mol} \cdot \mathrm{h}^{-1} \cdot \mathrm{cm}^{-3}_{\mathrm{Katalysator}})$$

hierin ist $a_i^0 = a_i \exp(-A_i/T)$; die an der äußeren Katalysatoroberfläche herrschenden Partialdrucke sind gleich denen der Gasphase.

Für die Parameter gilt:

$a_1^0/\mathrm{mol} \cdot \mathrm{bar}^{-1,5} \cdot \mathrm{g}^{-1} \cdot \mathrm{h}^{-1} = 4{,}8$

$A_1/\mathrm{K} = 9{,}3 \cdot 10^2$

$a_2^0/\mathrm{bar}^{-1} = 2{,}4 \cdot 10^{-4}$

$A_2/\mathrm{K} = -5{,}5 \cdot 10^3$

$a_3^0/\mathrm{bar}^{-1} = 3{,}2 \cdot 10^{-2}$

$A_3/\mathrm{K} = -7{,}5 \cdot 10^2$

$\varrho/\mathrm{g} \cdot \mathrm{cm}^{-3} = 1{,}67$

Aufgabe. Es ist für die nachstehenden Bedingungen jeweils durch Ermittlung des Porennutzungsgrades η quantitativ zu bestimmen, ob der Reaktionsablauf durch Porendiffusion beeinflußt wird.

Die Bestimmung von η soll für Reaktionstemperaturen von 523 K und 573 K, einen H_2-Partialdruck von 18,75 bar sowie verschiedene CO-Partialdrücke (0,05 – 0,1 – 0,2 – 0,5 bar) bei einem Gesamtdruck p von 25 bar erfolgen. Die Differenz zwischen p und der Summe der Partialdrücke an H_2 und CO soll in jedem Fall durch N_2, das sich als Inertgas im System befindet, ergänzt werden.

Unter den gewählten Reaktionsbedingungen beträgt der Porendiffusionskoeffizient $D^e = D_{CO} \cdot (\varepsilon/\tau) = 0{,}0045\ \text{cm}^2 \cdot \text{s}^{-1}$.

Lösungshinweis.

1. Für das zylindrische Pellet wird vereinfachend Kugelgestalt vorausgesetzt; der gleichwertige Kugelradius beträgt $r_K = 0{,}3$ cm.
2. Für die Verwendung des $\eta = f(\psi')$-Diagramms (s. Abb. 6.16) kann vereinfachend angenommen werden, daß die Reaktion nach erster Ordnung für CO verläuft. Das heißt, die Größe

   $$a_1 p_{H_2,g} p^{-0,5} (1 + a_2 p_{CO,g} + a_3 p_{H_2,g})^{-2}$$

   soll dafür in erster Näherung als konstant angesehen werden; dies trifft zu, wenn $(1 + a_3 p_{H_2,g}) > a_2 p_{CO,g}$.

Lösung. Der Weisz-Modul ψ' ergibt sich zu

$$\psi' = L_C^2 \frac{r_{eff}}{D_{CO}^e c_{CO,g}}$$

Die charakteristische Länge L_C ist gegeben durch

$$L_C = \frac{\text{Kugelvolumen}}{\text{äußere Kugeloberfläche}} = \frac{r_K}{3}$$

Folgende Ergebnisse werden für die verschiedenen gewählten Bedingungen erhalten:

T (°C)	p_{CO} (bar)	$r_{eff} \left(\frac{\text{mol}}{\text{h cm}^3}\right)$	$c_{CO,g} \left(\frac{\text{mol}}{\text{cm}^3}\right)$	ψ'	η
573	0,05	$2{,}54 \cdot 10^{-2}$	$1{,}05 \cdot 10^{-6}$	15	0,1
573	0,1	$4{,}60 \cdot 10^{-2}$	$2{,}10 \cdot 10^{-6}$	14	0,1
573	0,2	$7{,}60 \cdot 10^{-2}$	$4{,}20 \cdot 10^{-6}$	11	0,1
573	0,5	$11{,}75 \cdot 10^{-2}$	$10{,}50 \cdot 10^{-6}$	7	0,14
523	0,05	$1{,}60 \cdot 10^{-2}$	$1{,}15 \cdot 10^{-6}$	8,5	0,12
523	0,1	$2{,}59 \cdot 10^{-2}$	$2{,}30 \cdot 10^{-6}$	7	0,14
523	0,2	$3{,}58 \cdot 10^{-2}$	$4{,}60 \cdot 10^{-6}$	5	0,20
523	0,5	$3{,}95 \cdot 10^{-2}$	$11{,}50 \cdot 10^{-6}$	2	0,47

Aus der Aufstellung ergibt sich, daß der Reaktionsablauf sowohl bei 573 K als auch 523 K stark durch Porendiffusion bestimmt wird.

Influence of transport on the measurement of

- Activation energies
- Reaction orders
- Selectivities

Apparent versus Intrinsic Kinetics

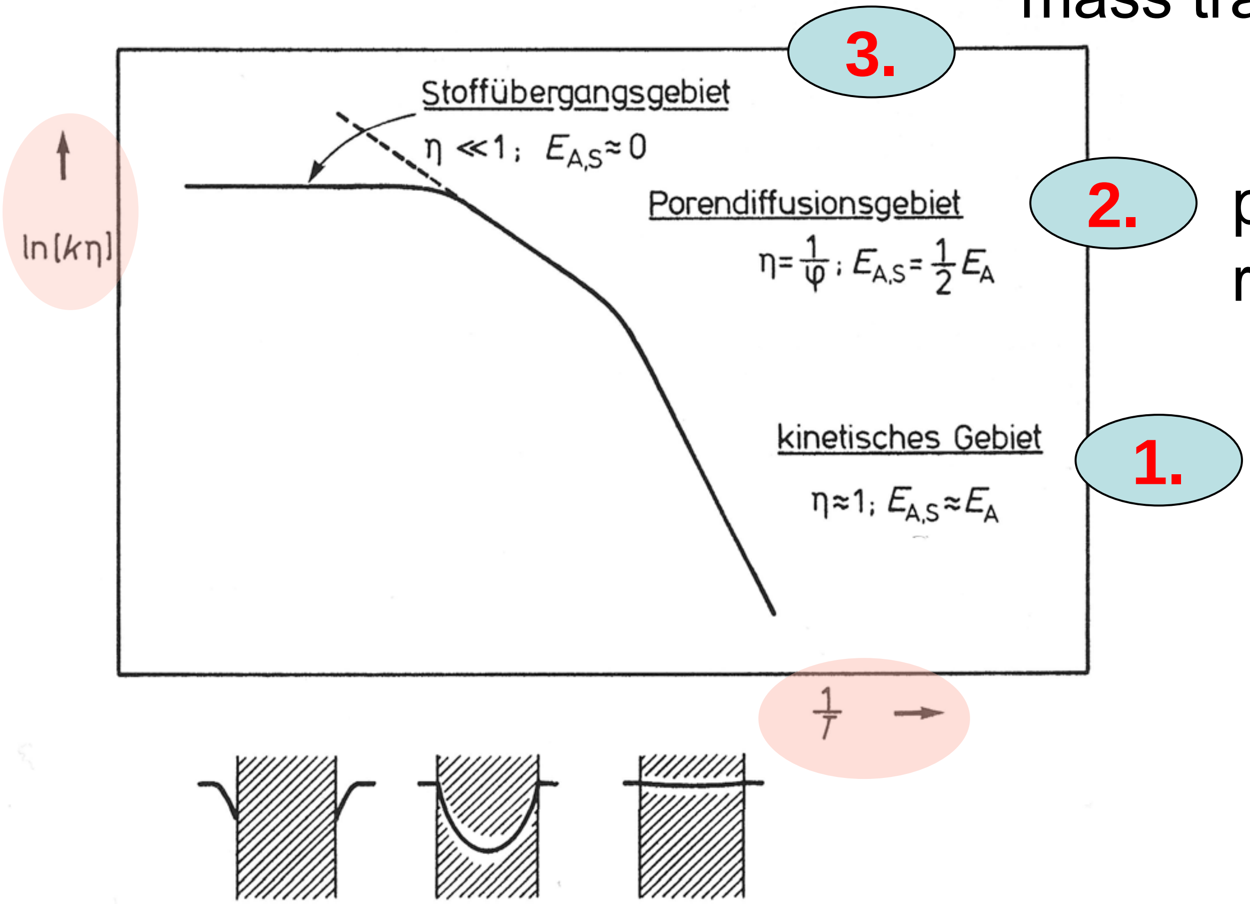
- Aim: determination of reaction order and rate constant for a catalytic reaction of interest
- Assumption: nth-order reaction A→B with $\boxed{r = k\,c_A^n}$
- The values of „k“ and „n“ are called the intrinsic rate constant and reaction order
- Typical experiment: change concentration c_A in the bulk fluid, measure the rate as function of c_A and find the values of the parameters „k“ and „n“ that best fit the measurements
- The intrinsic values have to be distinguished from what we may estimate from experimental data !

Apparent and Intrinsic Activation Energy

- Qualitative estimation of kinetic parameters under different rate-limiting steps
- Arrhenius plot: ln $(k^*\eta) = f(1/T)$
- ln $(k^*\eta)$ is the apparent rate constant related to the apparent activation energy $E_{A,s}$

$$\boxed{\ln[k\eta] = \ln k_0 - \frac{E_{A,s}}{RT}}$$

Arrhenius plot – Regimes of control

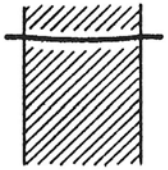


3. mass transfer regime

2. pore diffusion regime

1. kinetic regime

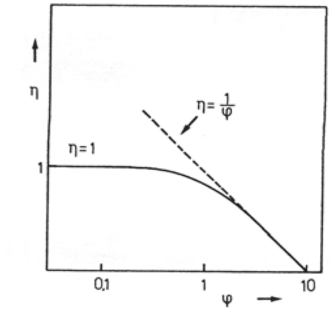
Arrhenius plot – Kinetic regime



- Thiele modulus φ is very small (φ <<)

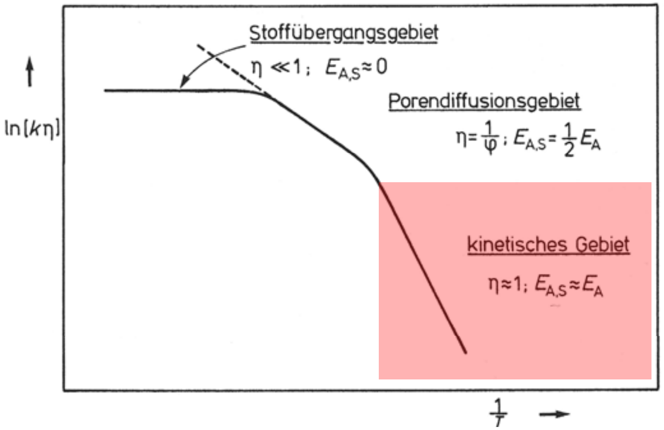
The internal surface of catalyst pore is totally utilized

- η ≈ 1; see fig. η = f(φ)



- k*η ≈ k

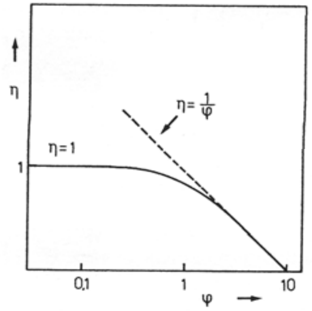
$$\boxed{E_{A,s} \approx E_A}$$



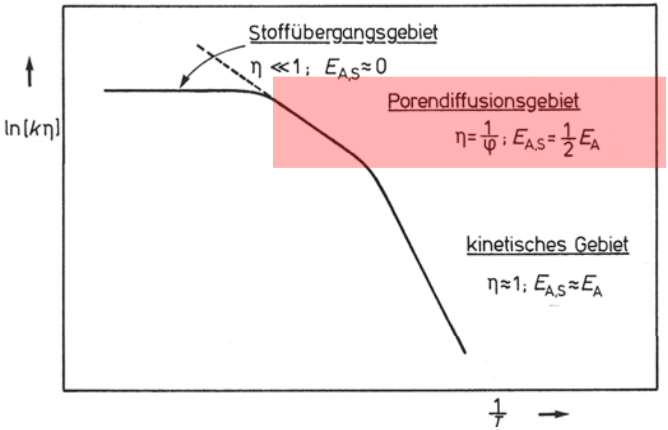
Arrhenius plot – Pore diffusion regime

- Case study:

- $\eta \approx 1/\varphi$; see fig. $\eta = f(\varphi)$



- ln (k*η) =ln k + ln η
- $\eta = 1/\varphi$ and $\varphi = l\sqrt{\frac{k}{D_{eff}}}$
- $$\ln[k*\eta] = \ln k - \ln\left[l\sqrt{\frac{k}{D_{eff}}}\right]$$



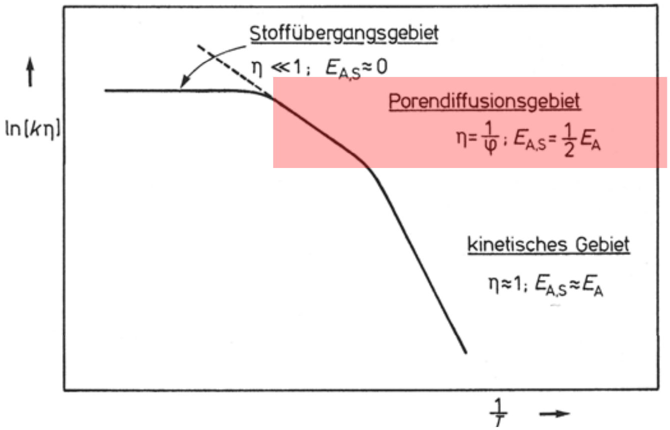
Arrhenius plot – Pore diffusion regime

$$\ln[k*\eta] = \ln k - \ln\left[l \sqrt{\frac{k}{D_{eff}}} \right]$$

$$\ln[k*\eta] = \frac{1}{2}\ln k - \ln l + \frac{1}{2}\ln D_{eff}$$

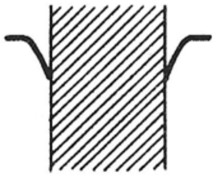
$$\ln[k*\eta] = \frac{1}{2}\ln k_0 - \frac{E_{A,s}}{2RT} - \ln l + \frac{1}{2}\ln D_{eff}$$

$$\boxed{E_{A,s} = \frac{E_A}{2}}$$



Arrhenius plot – Mass transfer regime

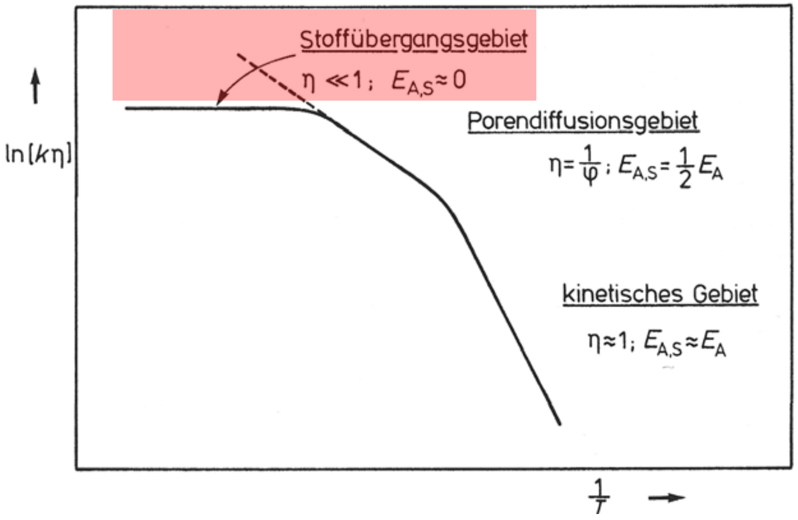
- For high temperatures $\varphi >> 1$ and $\eta << 1$



→

- Reaction is only determined by diffusion through the boundary film layer

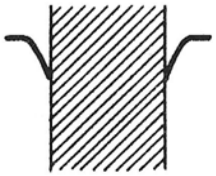
$$\boxed{E_{A,s} \approx 0}$$



Arrhenius plot – Mass transfer regime

- transfer contributes to rate
- for $k_g a << k$

$$\boxed{k_{eff} = \frac{1}{\frac{1}{k} + \frac{1}{k_g a}}}$$



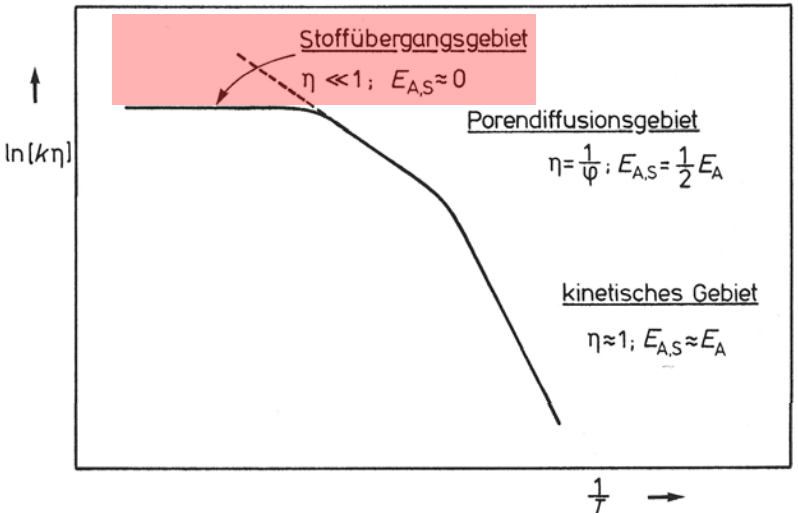
- $\boxed{k_{eff} = k_g a}$

- k_g is determined by D; D ~ $T^{3/2}$ thus k_g ~ $T^{3/2}$; formal

$$k_g \approx \exp\left(-\frac{E_{eff}}{2RT}\right)$$

- $E_{eff} = E_{Diff}$
- E_{Diff}~ 5 kJ/mol

$$\boxed{E_{A,s} \approx 0}$$



Interpretation of criteria for E_A

- The apparent activation energy $E_{A,s}$ of a heterogeneous catalytic reaction decreases with increasing temperature due to the increasing diffusive resistance to $E_{A,s} = E_A/2$
- Further increase in temperature leads to a shift of the place of reaction from the interior to the exterior of the catalyst
- At high temperatures only the transport through the boundary layer determines the rate of reaction

- Way out ? - use of smaller particles
- Disadvantages - pressure control in a fixed bed
  - dispersion increase in a fixed bed

Influence of transport on reaction order

- Catalytic reaction described by $\boxed{r = k\, c_A^n}$

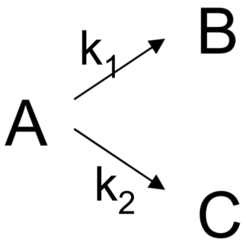
- Determination of „n“ may be misleading, if external or internal mass-transfer limitations exist due to $\eta = f(c)$

n_{app}:	0	1	2
n_{intr} :	0.5	1	1.5

- Check for rate-limiting processes

Influence of transport on selectivity

- Network of reactions (parallel, consecutive….)
- Selectivity of desired product is of interest
- See textbooks for case studies
- Simple example:



$$\boxed{r_1 = k_1 c_A^2}$$

$$\boxed{r_2 = k_2 c_A}$$

if c_A is limited, the first reaction is more influenced

Influence of transport on selectivity

- General approach:
  - set up of kinetic equations
  - determination of differential and integral selectivities according to kinetic equations
  - formulation of effective quantities
  - examine influence of η, Da number …

External and internal resistances – Biot n.

- Isothermal conditions
- If the mass-transfer rate from the bulk fluid to the exterior of the pellet is not high, then the boundary conditions have to be changed

- Biot number or dimensionless mass-transfer coefficient

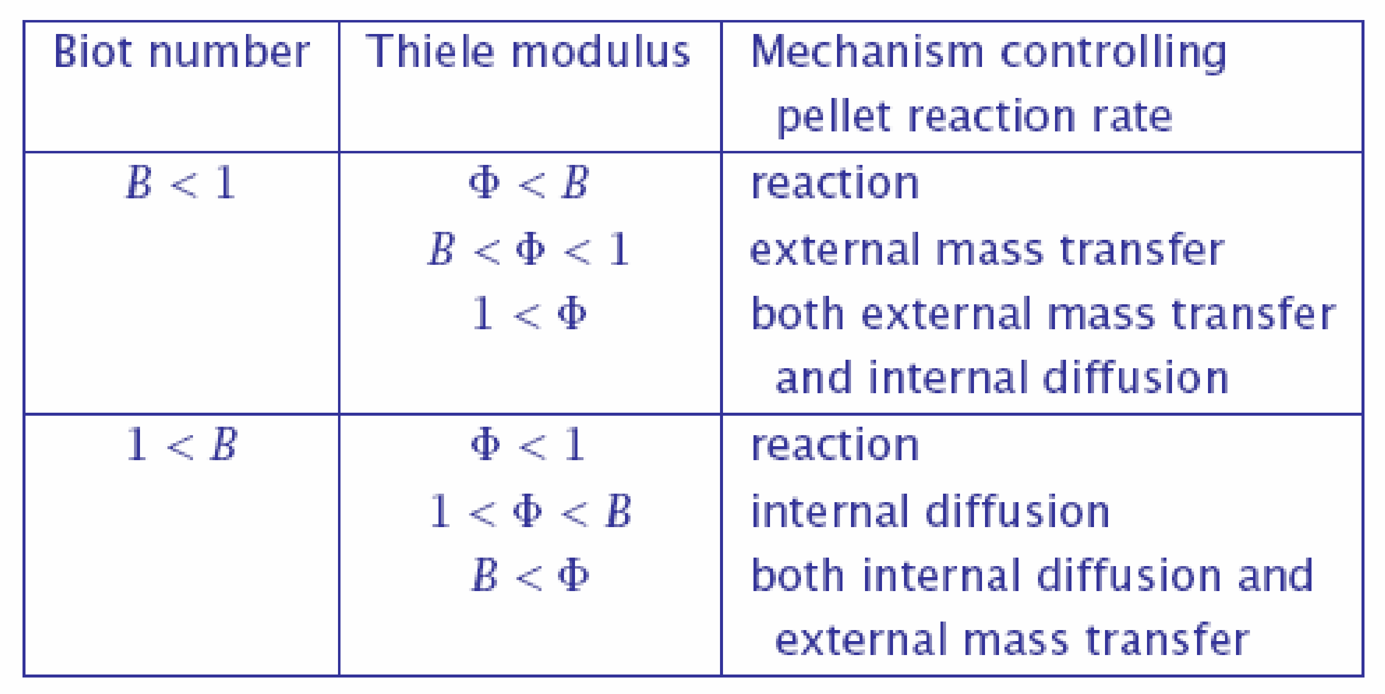
$$\boxed{Bi = \frac{k_g\, r_p}{D}}$$

- Relation between internal and external diffusion resistance
- Bi >> 1: transport limited by diffusion in the pores

External and internal resistances – Biot n.

- Biot number or dimensionless mass-transfer coefficient

$$\boxed{\mathrm{Bi} = \frac{k_g\, r_p}{D}}$$



Biot number	Thiele modulus	Mechanism controlling pellet reaction rate
$B < 1$	$\Phi < B$	reaction
	$B < \Phi < 1$	external mass transfer
	$1 < \Phi$	both external mass transfer and internal diffusion
$1 < B$	$\Phi < 1$	reaction
	$1 < \Phi < B$	internal diffusion
	$B < \Phi$	both internal diffusion and external mass transfer

External and internal resistances – Criteria

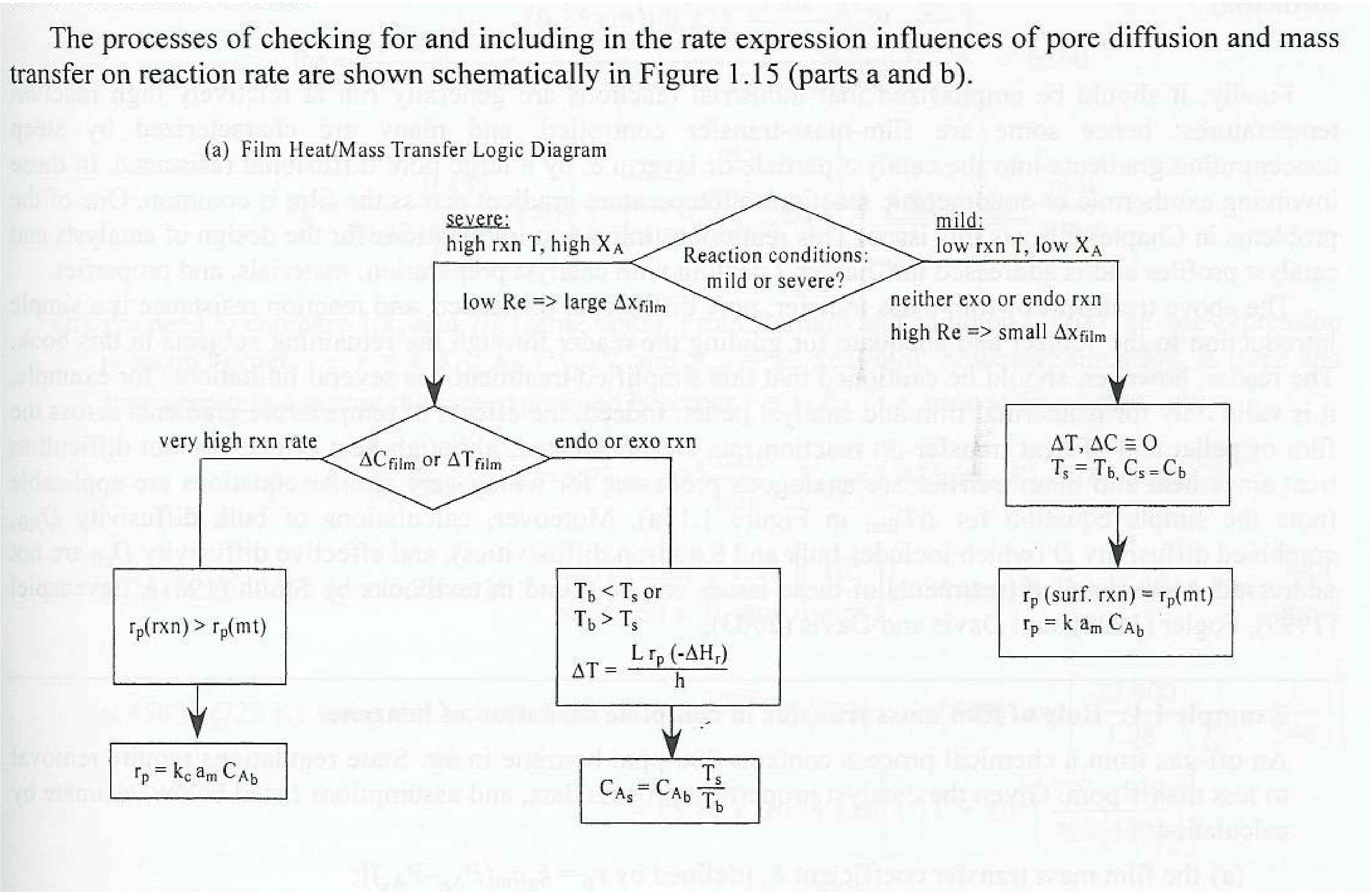
- Overall effectiveness factor η_{sum} is related to the transport resistances in the film and in the pore

$$\boxed{\eta_{sum} = \frac{1}{\frac{1}{\eta_k} + \frac{\varphi^2}{3Bi}}}$$

- Non-isothermal conditions: Weisz modulus, modified Thiele modulus, Sherwood number Sh, Nusselt number Nu !

Experimental check

- For a porous catalyst the limiting effect of pore diffusion would be decreasing if it is possible to reduce the length of the pores
- Practically: crush catalyst, grade into sizes; measurement of apparent rate depending on size fractions; with decreasing size the apparent rate increases until a constant value is reached
- Check the external transport; both limitations may occur simultaneously
- Elegant way of separation of pore diffusion and microkinetics: use of single pellet diffusion reactor



The processes of checking for and including in the rate expression influences of pore diffusion and mass transfer on reaction rate are shown schematically in Figure 1.15 (parts a and b).

(a) Film Heat/Mass Transfer Logic Diagram

From „Fundamentals in industrial…

(b) Pore Diffusion Logic Diagram (adapted from Fletcher, 2003)

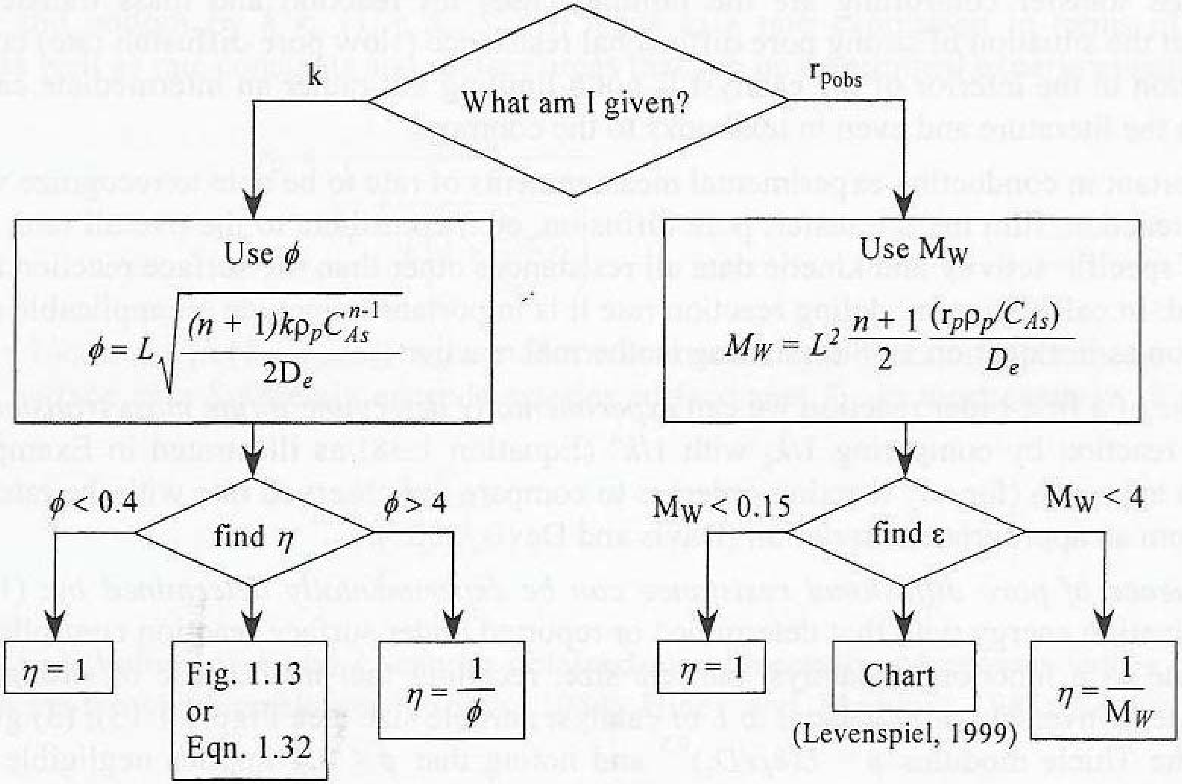


Figure 1.15 Influences of mass transfer on reaction rate (X_A = conversion of A, M_W = Wiesz modulus, Re = Reynolds number, mt = mass transfer, T_b = bulk gas temperature, T_s = surface temperature, h = heat transfer coefficient).

From „Fundamentals in industrial…

Example 1.2: Pore diffusional resistance for SCR solid monolith catalyst.

Selective catalytic reduction (SCR) of NO_x is an important, effective process for reducing NO_x emissions from electric power plants (see Ch. 11). Wong and Nobe (1984) have reported first-order reaction kinetics, i.e. $r_p = k\, C_{NO}$ for a 5% V_2O_5/TiO_2 catalyst. Nackos *et al.* (2004) have observed a first-order rate constant of 0.566 cm^3/g_{cat}-s at 226°C (499 K) and an activation energy of 109 kJ/mole for a commercially representative 1% V_2O_5/9% WO_3/TiO_2 catalyst.
Calculate the effectiveness factor and reaction rate at the inlet to a commercial SCR unit containing an extruded cellular monolith consisting of 1% V_2O_5/9% WO_3/TiO_2 with a channel wall thickness of 1.35 mm and open frontal area of 64% under typical commercial operating inlet conditions of 400 ppm NO, 350°C, and 1 atm. Assume catalyst in the square monolith walls can be treated as a flat plate. Additional data: $\rho_p = 1.48$; $D_e = 0.070$ cm^2/s. Also, assume film mass transfer resistance is negligible.

Equations for calculating effectiveness factor:

$$\eta = \frac{\tanh \phi}{\phi} \tag{1.32}$$

$$\phi = \left(\frac{V_{cat}}{S_{ex}}\right)\sqrt{\frac{k\rho_p}{D_e}} \tag{1.40}$$

$$\frac{V_{cat}}{S_{ex}} = \frac{L \times W \times T'}{2(L \times W)} = \frac{T'}{2}$$ (T' = thickness; factor of 2 accounts for each wall having 2 sides.)

(a) Calculation of ϕ and η:

$$k_{623} = k_{499} \exp\left\{\left[\frac{E_{act}}{R}\left(\frac{1}{623} - \frac{1}{499}\right)\right]\right\} = 106\ cm^3/g_{cat}\text{-s}$$

$$\phi = \left(\frac{T'}{2}\right)\sqrt{\left(k_{623}\frac{\rho_p}{D_e}\right)} = \underline{\underline{3.19}}$$

$$\eta = \frac{\tanh \phi}{\phi} = \underline{\underline{0.31}}$$

(b) Calculation of reaction rate:

$$r = k\, C_{NO}\, \eta$$

$$C_{NO} = \left(\frac{P\, y_{NO}}{82.1\, T}\right) = 7.82 \times 10^{-9}\ mol/cm^3$$

$$r = k\, C_{NO}\, \eta = \underline{\underline{2.58 \times 10^{-7}\ mol/g_{cat}\text{-s}}}$$

Summary

- ✓ Definition of porous systems
- ✓ Definition of diffusion and diffusion coefficients
- ✓ External transfer processes
  - ✓ Production rate via effectiveness factor
  - ✓ Case studies with use of Re, DaII
- ✓ Internal transfer processes
  - ✓ Mass balance for pore diffusion
  - ✓ Case studies depending on Thiele modulus

Summary

- ✓ Influence of transport on
  - ✓ Apparent activation energy
  - ✓ Reaction order
  - ✓ Selectivity
- ✓ Influence of both external and internal transfer
  - ✓ Biot number

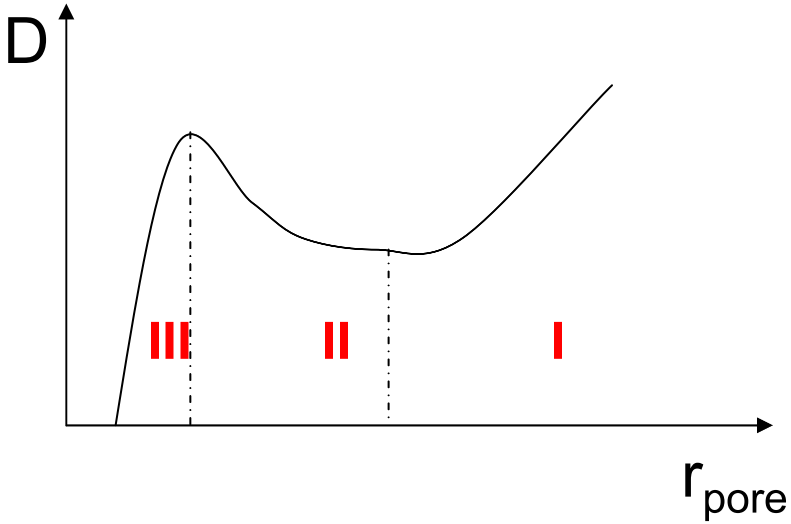
- ✓ Strategy to check for limiting processes:
  solve appropriate mass balance by use of dimensionless numbers

- ✓ The system is investigated from the outside to the inside

…Thanks for invitation and for attention!

Diffusion constant and pore radius

- Diffusion constants in pores for pore diameters which are comparable to substrate molecules



I Knudsen diffusion

II potentials of opposite pore walls overlap thus the resulting interaction of substrates and walls is effectively decreased and the diffusion coefficient increases

III pore diameter is in the range of the substrate diameter; strong dependence of D from the effective substrate diameter