

Modern Methods in Heterogeneous Catalysis

Lectures at Fritz-Haber-Institut

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Diffusion in Porous Media

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Dimensions in Heterogeneous Catalysis

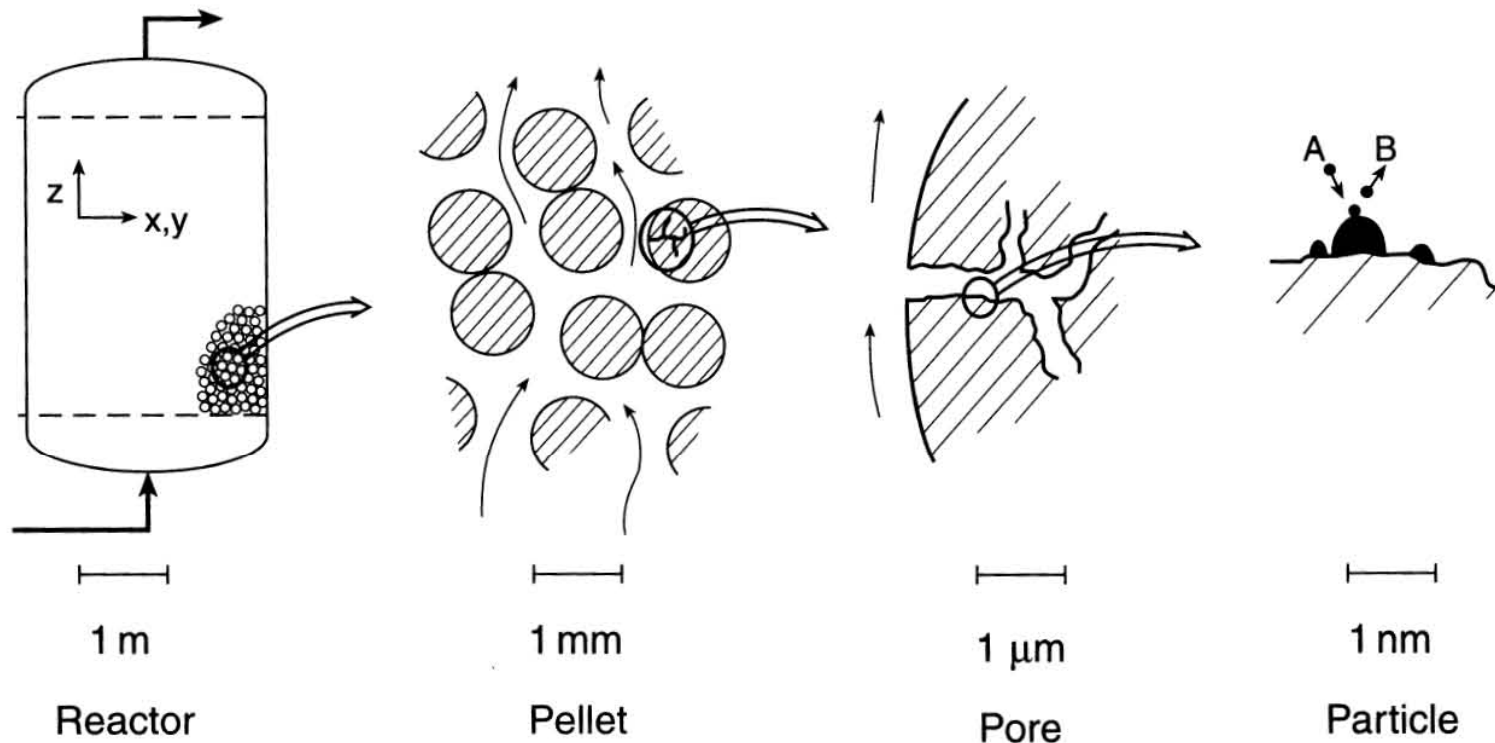


Figure 7-6 Different size scales in a packed bed catalytic reactor. We must consider the position z in the bed, the flow around catalyst pellets, diffusion within pores of pellets, and adsorption and reaction on reaction sites. These span distance scales from meters to Angstroms.

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 for estimation of \sim
- Influence of transport on
 - Activation energy
 - Reaction order
 - Selectivity
- Summary

Recommended Literature

- M. Baerns, H. Hofmann, A. Renken. Chemische Reaktionstechnik, LB der Technischen Chemie, Bd. 1, Wiley-VCH, 2002.
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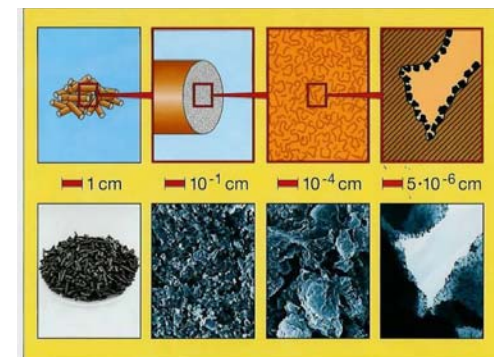
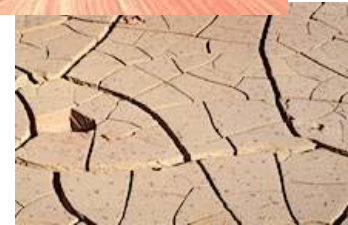
- I.I. Ioffe, L.M. Pissmen. Heterogene Katalyse, Chemie und Technik, Akademie-Verlag Berlin, 1975.
- Heterogene Katalyse, Eine Einführung in die Theorie. Lehrmaterial der AG „Heterogene Katalyse“, Sektion Verfahrenscheme der TH Chemie „Carl Schorlemmer“, Leuna-Merseburg, Merseburg 1972.

Porosity – Background information

Porous materials in nature and industry

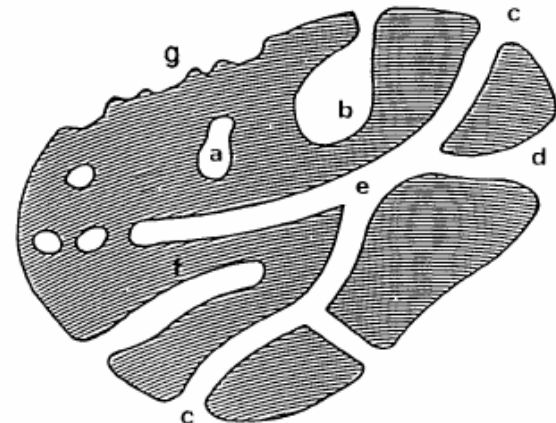
- Porous materials:
sand stone, porous rock, filter paper, nano tubes...
- Main feature: **cavities** in a solid matrix
- Cavities can be partly or fully connected
- Accessible for gases

- 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 cm³/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 $\epsilon = \rho_P \cdot V_g$ (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; \bar{d}_{kp} : mittlerer Porendurchmesser; vgl. auch Tab. 5.4.

Adsorbens	$\rho/\text{kg m}^{-3}$	$\rho_{sch}/\text{kg m}^{-3}$	$\epsilon/1$	$\epsilon_0/1$	$s/\text{m}^2 \text{g}^{-1}$	\bar{d}_{kp}/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

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 $\text{Al}(\text{OH})_3$ zu Al_2O_3	1200	Drehrohrofen
Thermische Metallgewinnung durch Zersetzung von Metallhalogeniden (Zr, Ti) nach dem Aufwachsverfahren (VAN-ARKELE-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

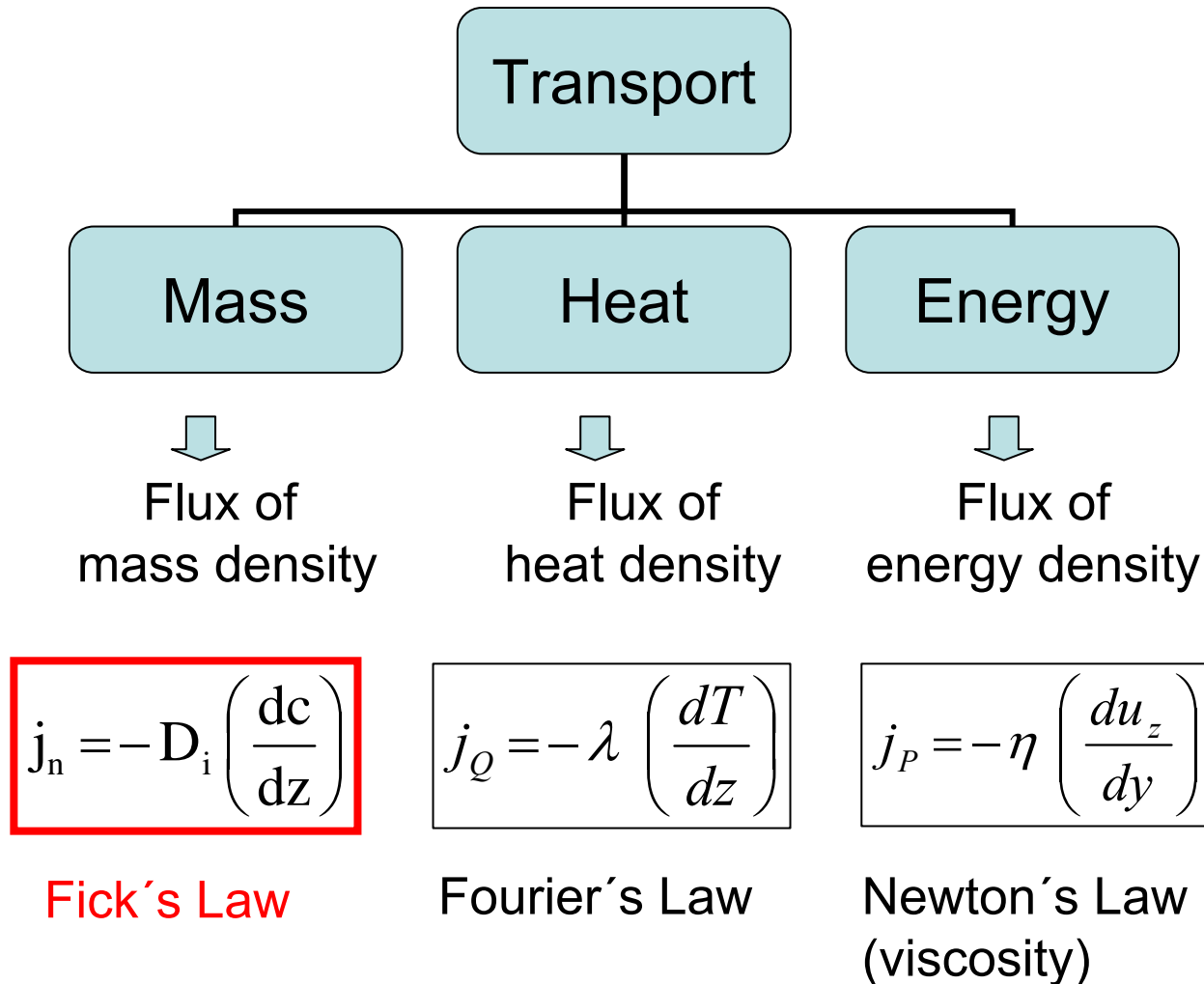
- ...generally increases with **temperature** and decreases with increasing **density**
- ...the equilibration takes
 - minutes for gases
 - days/weeks for liquids
 - with measurable rate only close to the melting point
- ...characteristic quantity: **diffusion coefficient**
- ...can be described as **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 ₂ O vapour in air	0.23	298
CH ₃ OH 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

Transport by Diffusion

General view to transport equations for gases



Transport of mass - Diffusional laws (gases)

- Concentration gradient is stationary : **Fick's First Law**

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

- Concentration gradient is not stationary : **Ficks's Second Law**

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

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

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

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

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

- 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 $p \approx 2.5 \cdot 10^6$ Pa) (Hirschfelder/Curtiss/Bird)

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

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 $\lambda \gg d_p$: D_{Kn} ... Knudsen diffusion coefficient

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

$$D_{Kn} = \frac{1}{3} d_p \sqrt{\frac{8RT}{\pi M}}$$

$$D_{Kn} \sim T^{\frac{1}{2}}, \sim \frac{1}{M}, \sim d_p$$

- Depends not on pressure !

Diffusion in porous materials

- For $d_p = \text{const.}$ and pressure decrease: transition from molecular diffusion to Knudsen diffusion
- Transition is not clearly defined; both equations apply

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

- 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

$$D_{\text{eff}} = \frac{\epsilon}{\tau} D$$

Catalyst	ϵ	τ
100–110 μm 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:
 - First International Conference on Diffusion in Solids and Liquids
6-8 of July, 2005, Aveiro, Portugal
 - Diffusion Fundamentals, Basic Principles of Theory, Experiment and Application,
September 21st-24th, Leipzig, Germany

Literature examples

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

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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

$$D_{iK} = \frac{1}{\eta_K} D_{0K}, \quad D_{ib} = \frac{1}{\eta_b} D_{0b}, \quad (1)$$

where η_K , D_{0K} and η_b , D_{0b} 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

$$D_{0K} = \frac{1}{3} \bar{u} d, \quad (2)$$

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

$$D_{0b} = \frac{1}{3} \bar{u} \lambda, \quad (3)$$

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]

$$\frac{1}{D_{inter}} = \frac{1}{D_{iK}} + \frac{1}{D_{ib}}. \quad (4)$$

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

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Colloids and Surfaces

A: Physicochemical and Engineering Aspects 187–188 (2001) 257–265

COLLOIDS
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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
Engineering Science

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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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Proceedings of The 1st International Conference on Diffusion in Solids and Liquids
DSL-2005, July 6-8, 2005, University of Aveiro, Aveiro, Portugal

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

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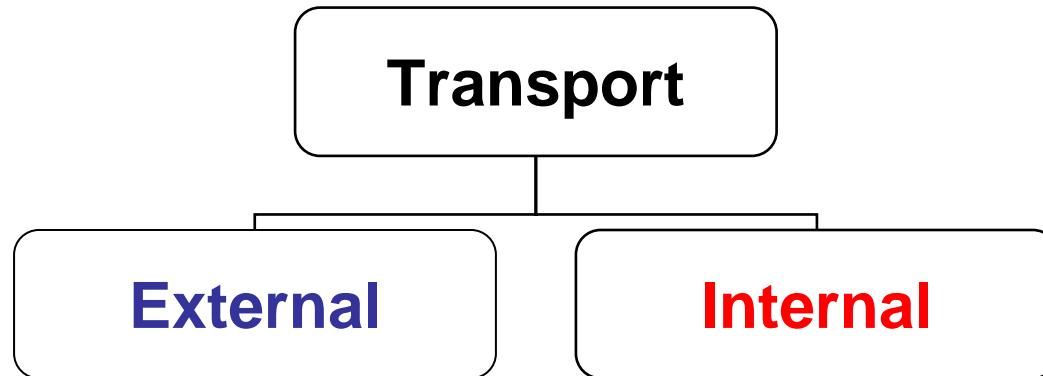
*Corresponding author. Fax: +49 341 973 634 3; Email: cbreit@chemie.uni-leipzig.de

Transport problems in catalysis

Transport and catalysis

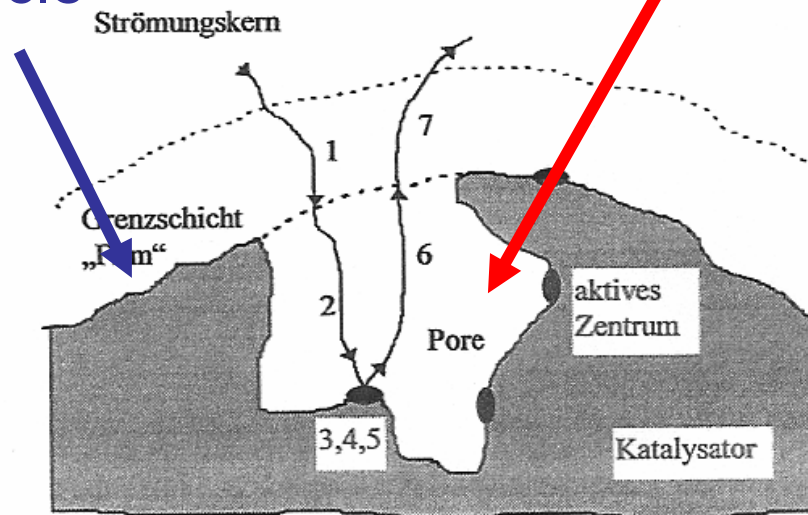
- One part of the catalytic cycle is the **transport** of reactants **to the active surface**
- Typical heterogeneous processes proceed at the surface of solids or porous particles, which are surrounded by gas or liquid
- If the chemical reaction proceeds very fast, the **overall rate** may be **controlled** 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

Transport regimes

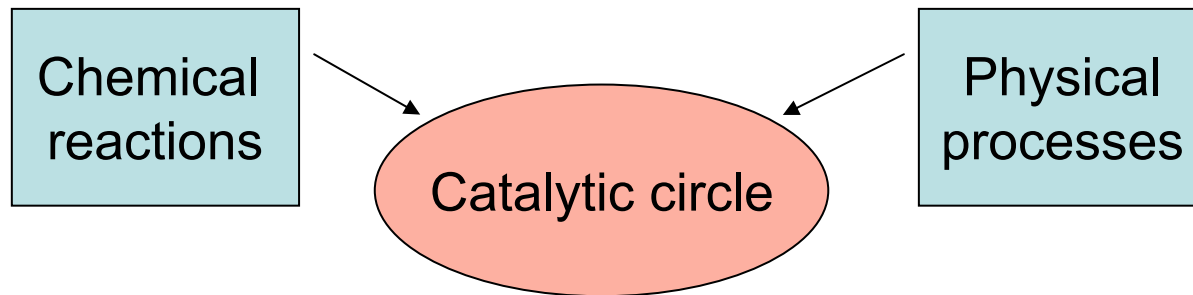


Diffusion to exterior surface of particle

Diffusion in pores



Rates in the catalytic cycle



- $\text{rate}_{\text{diffusion}} \gg \text{rate}_{\text{chemical reaction}}$: 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 ?

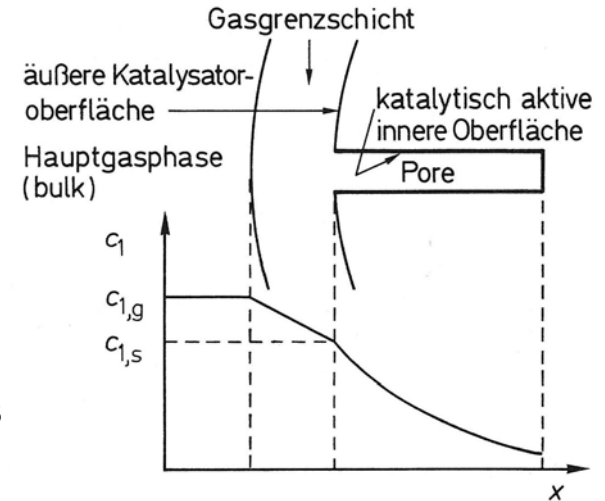
External mass transfer processes

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

$$r_{\text{eff}} = k_g a (c_{1,g} - c_{1,s}) \quad k_g \text{ transfer coefficient}$$
$$a \text{ specific surface area}$$

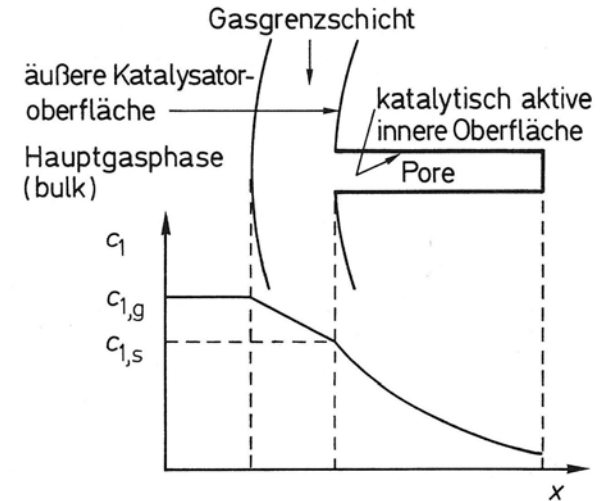
$$r_{\text{eff}} = k c_{1,s}^m \quad k = k_s a$$



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

- Calculation of c_s possible

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



External mass transfer – Effective rate

- for $m = 1$

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

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

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

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

External mass transfer – Da number

- Damköhler number II:

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

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

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

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)

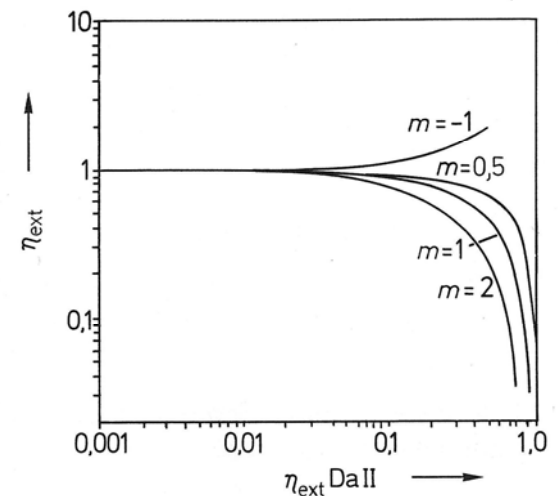
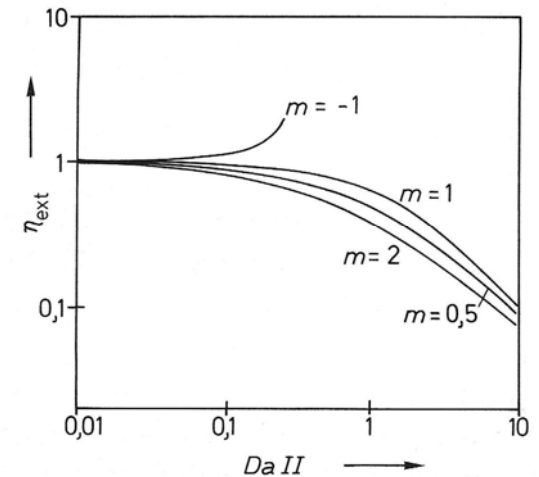
External mass transfer – Effectiveness factor

- External effectiveness factor η_{ext}

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

depending on $m \rightarrow$

- 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**

$$\text{Re} = \frac{d_p v}{\mu}$$

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

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

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

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

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

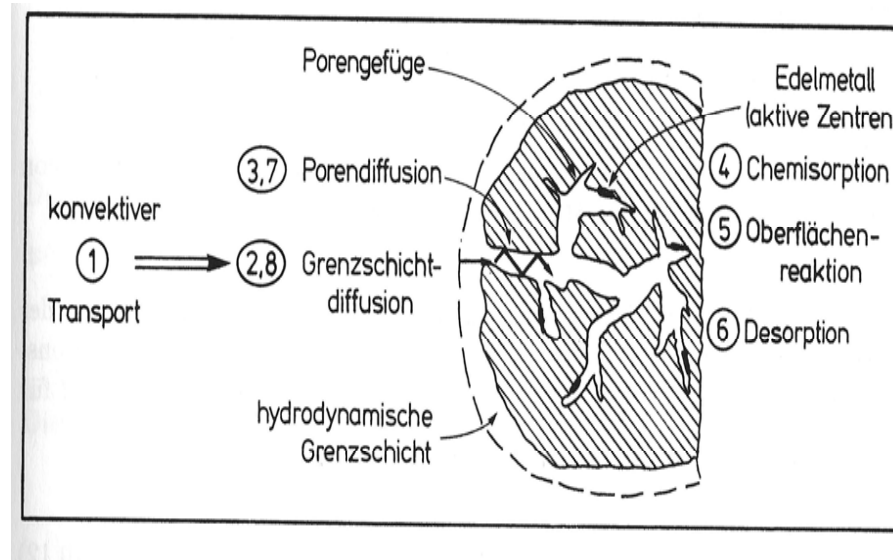


no influence of external transfer

! 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 : $r = k \cdot c$
- Reaction rate R related to active surface S ($V = S \cdot l$)
- Reaction rate r_v in pore volume

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

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

$$D_{\text{eff}}^{\text{gs}} \approx \frac{1}{10} D^{\text{gs}}$$

first assumption, if no information available

Pore diffusion – Mass balance

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

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

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


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

c_0 concentration in free gas space
 l pore length

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

Pore diffusion – Thiele modulus

- Dimensionless mass balance

$$D_{\text{eff}} \frac{c_0}{l^2} \frac{d^2 \frac{c}{c_0}}{d\left(\frac{z}{l}\right)^2} - c_0 k \frac{c}{c_0} = 0$$


$$\frac{d^2 \Gamma}{d\zeta^2} - \frac{l^2 k}{D_{\text{eff}}} \Gamma = 0$$

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

- Thiele modulus

$$\varphi = l \sqrt{\frac{k}{D_{\text{eff}}}}$$

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 $\phi = 1 \sqrt{\frac{k}{D_{\text{eff}}}} = \frac{\text{reaction rate}}{\text{diffusion rate}}$

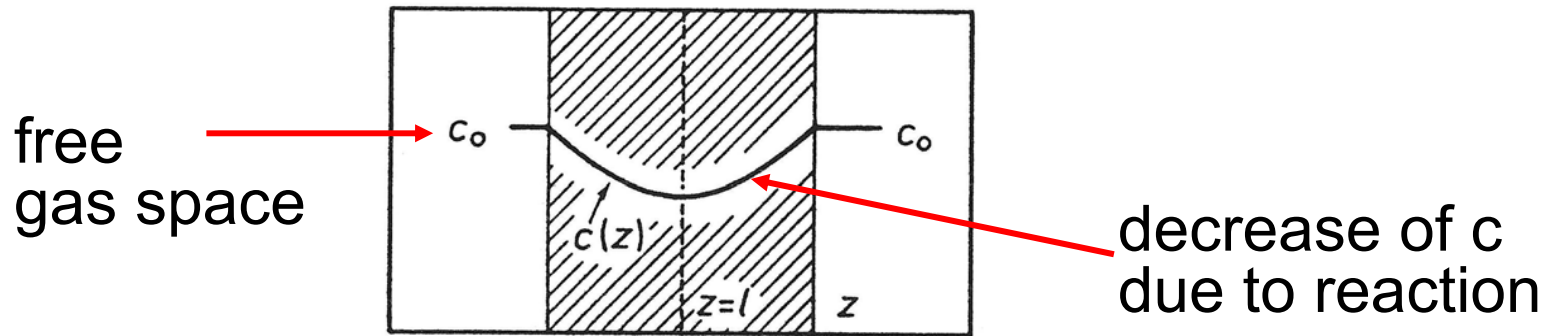
- New form of differential equation for mass balance

$$\frac{d^2\Gamma}{d\zeta^2} = \phi^2 \Gamma$$

- Solve with appropriate initial and boundary conditions

Pore diffusion – Solving of mass balance

- Boundary conditions



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

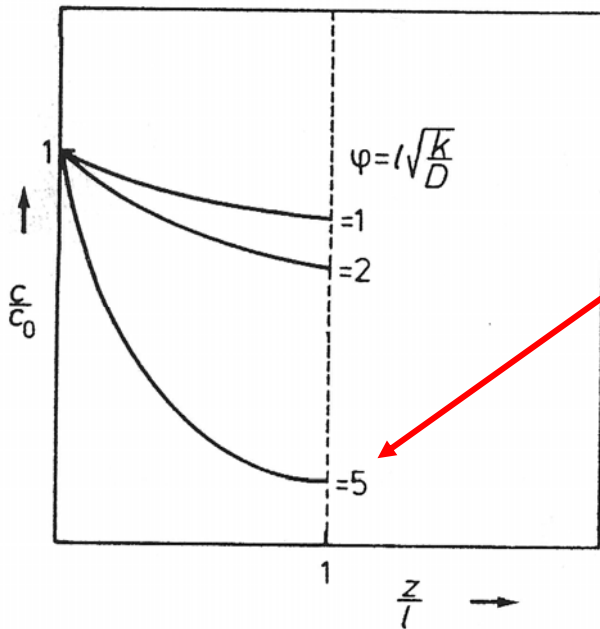
$$\Gamma = \frac{\cosh \varphi (1 - \zeta)}{\cosh \varphi} \quad \text{or} \quad \frac{c}{c_0} = \frac{\cosh \varphi (1 - \frac{z}{l})}{\cosh \varphi}$$

- with increasing temperature the Thiele modulus increases because of $\varphi = l \sqrt{\frac{k}{D_{\text{eff}}}}$ and $k = k_0 \exp\left[-\frac{E_A}{RT}\right]$
- Reactant converts already at $z/l \ll 1$

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 $\varphi = l \sqrt{\frac{k}{D_{\text{eff}}}}$
- Criteria:
 - $\varphi \ll 1$
 - 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
 - $\varphi \gg 1$
 - 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 $r_s = l * r_v$

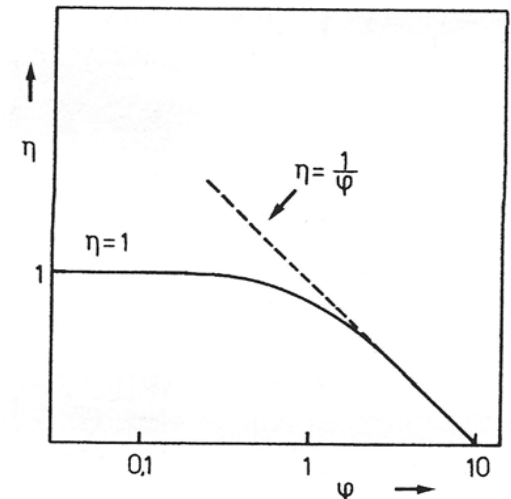
- Effectiveness factor is defined as

$$\eta = \frac{r_s}{r_{s, \max}} \quad \frac{\text{reaction rate}}{\text{max. reaction rate}}$$

- max. reaction rate is connected with c_0



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



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.

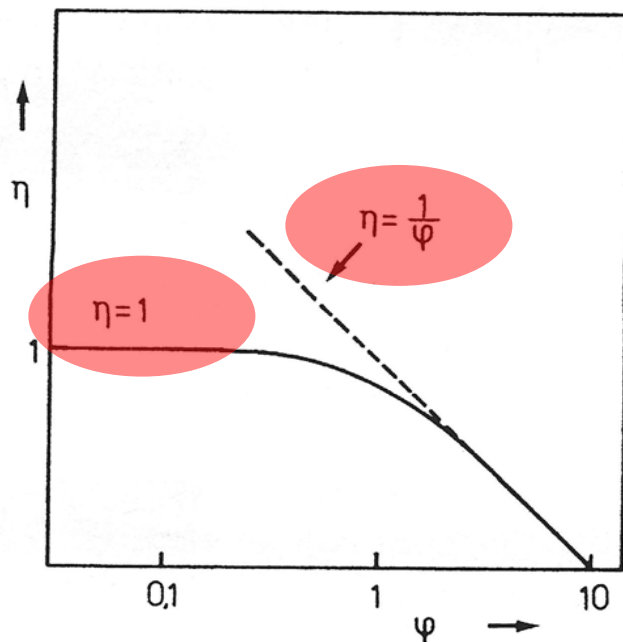
Effectiveness factor η - Case studies

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

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



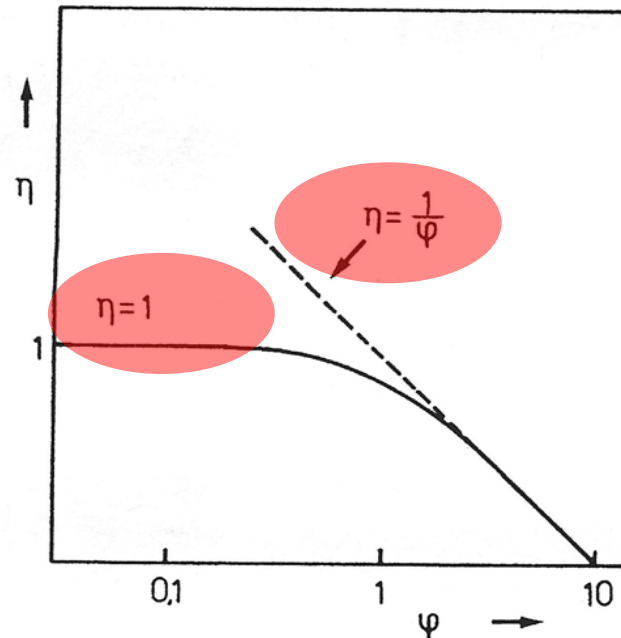
$$\eta = \frac{\tanh \varphi}{\varphi}$$



two characteristic regimes

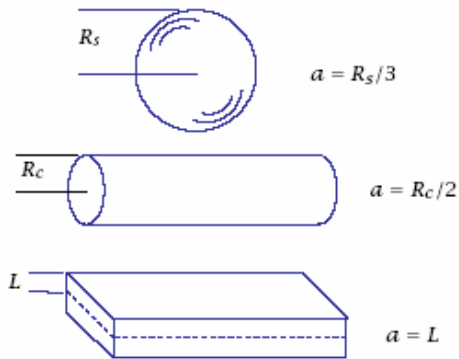
Effectiveness factor η - Case studies

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



Effectiveness factor - Geometry of pores

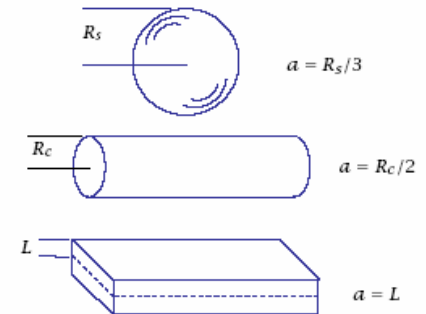
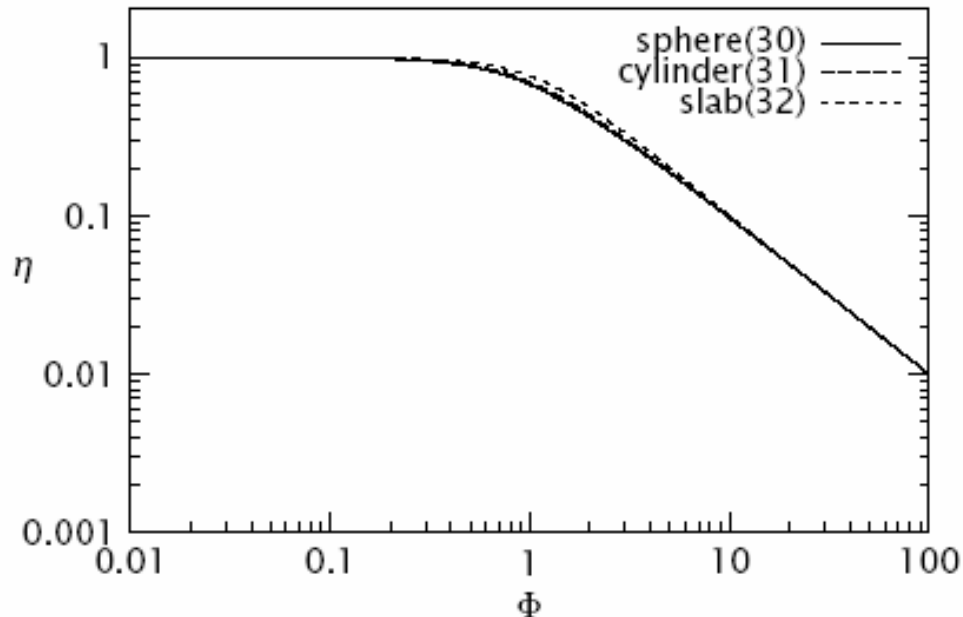
- Solution depends on characteristic length (volume-to surface ratio)
- Characteristic length differs for cylinder, sphere or slab; different analytical solutions



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

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



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

$$r^e = \frac{a_1 p_{\text{CO},s} p_{\text{H}_2,s} p^{-0,5}}{(1 + a_2 p_{\text{CO},s} + a_3 p_{\text{H}_2,s})^2} \quad (\text{mol} \cdot \text{h}^{-1} \cdot \text{g}^{-1})$$

bzw.

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

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:

$$a_1^\circ = 4,8 \text{ mol} \cdot \text{bar}^{-1,5} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$$

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

$$a_2^\circ = 2,4 \cdot 10^{-4} \text{ bar}^{-1}$$

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

$$a_3^\circ = 3,2 \cdot 10^{-2} \text{ bar}^{-1}$$

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

$$\varrho_s = 1,67 \text{ g} \cdot \text{cm}^{-3}$$

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

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

Lösung

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

$$r_v^e = 5,5 \text{ mol} \cdot \text{m}_{\text{Kat}}^{-3} \cdot \text{s}^{-1}$$

mit

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

und

$$p_{\text{H}_2,s} = p_{\text{H}_2,g}$$

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

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

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 $0,2$ m/s die Reaktion stoffübergangslimitiert ist; gleichzeitig sind die jeweiligen äußeren Katalysatorwirkungsgrade zu bestimmen.

Lösung

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

mit

$$k \approx \frac{a_1 p_{\text{H}_2,g} p^{-0,5}}{(1 + a_3 p_{\text{H}_2,g})^2} = 0,342 \text{ mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$$

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

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

$k_g (\text{m} \cdot \text{s}^{-1})$	$DaII (-)$	$\eta_{\text{ext}} (-)$
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

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

(Vereinfachung: Bei der Berechnung von k wird angenommen, daß $a_2 p_{\text{CO},s}$ durch $a_2 p_{\text{CO},g}$ und $a_3 p_{\text{H}_2,s}$ durch $a_3 p_{\text{H}_2,g}$ angenähert werden kann).

$k_g (\text{m} \cdot \text{s}^{-1})$	$p_{\text{CO},g} (\text{bar})$	$p_{\text{CO},s} (\text{bar})$
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 ($p_{\text{CO}} \leq 0,5 \text{ bar}$; $1 \leq p_{\text{H}_2} \leq 25 \text{ bar}$) durch folgenden formalkinetischen Ansatz beschrieben werden:

$$r_{\text{eff}} = \frac{a_1 p_{\text{CO,g}} p_{\text{H}_2,g} p^{-0,5}}{(1 + a_2 p_{\text{CO,g}} + a_3 p_{\text{H}_2,g})^2} \cdot \varrho_{\text{Kat}} \quad (\text{mol} \cdot \text{h}^{-1} \cdot \text{cm}_{\text{Katalysator}}^{-3})$$

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

Für die Parameter gilt:

$a_1^0 / \text{mol} \cdot \text{bar}^{-1,5} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$	$= 4,8$
A_1 / K	$= 9,3 \cdot 10^2$
a_2^0 / bar^{-1}	$= 2,4 \cdot 10^{-4}$
A_2 / K	$= -5,5 \cdot 10^3$
a_3^0 / bar^{-1}	$= 3,2 \cdot 10^{-2}$
A_3 / K	$= -7,5 \cdot 10^2$
$\varrho / \text{g} \cdot \text{cm}^{-3}$	$= 1,67$

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 $r_K = 0,3 \text{ cm}$.
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

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

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

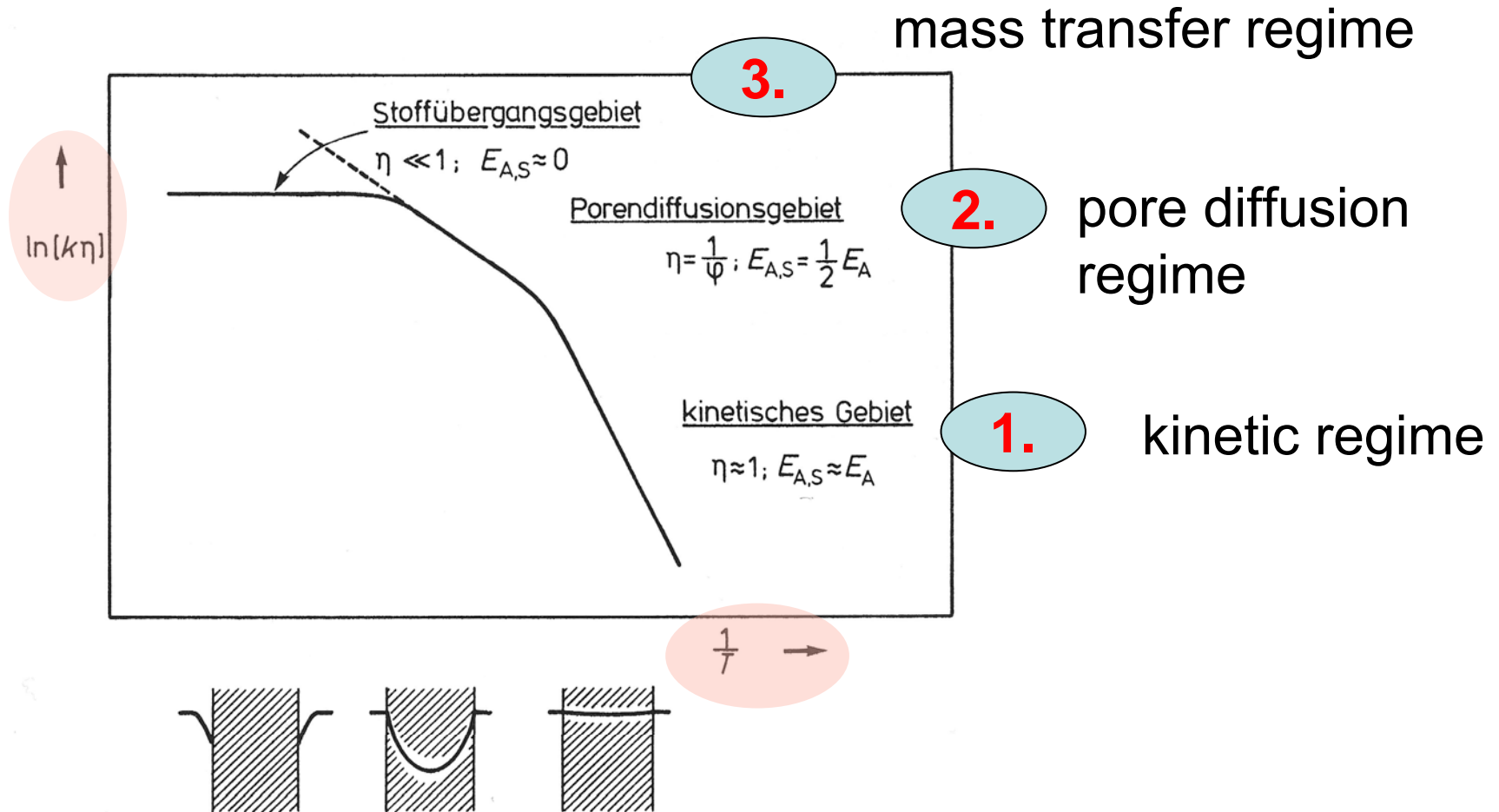
- Aim: determination of reaction order and rate constant for a catalytic reaction of interest
- Assumption: nth-order reaction $A \rightarrow B$ with $r = k c_A^n$
- The values of „k“ and „n“ are called the intrinsic rate constant and reaction order
- Typical experiment: change concentration c_A in the 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 $E_{A,s}$

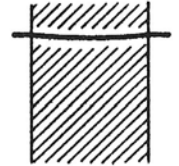
$$\ln [k\eta] = \ln k_0 - \frac{E_{A,s}}{RT}$$

Arrhenius plot – Regimes of control



Arrhenius plot – Kinetic regime

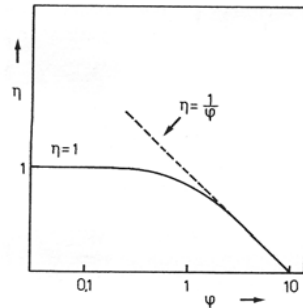
- Thiele modulus φ is very small ($\varphi \ll 1$)



The internal surface of catalyst pore is totally utilized



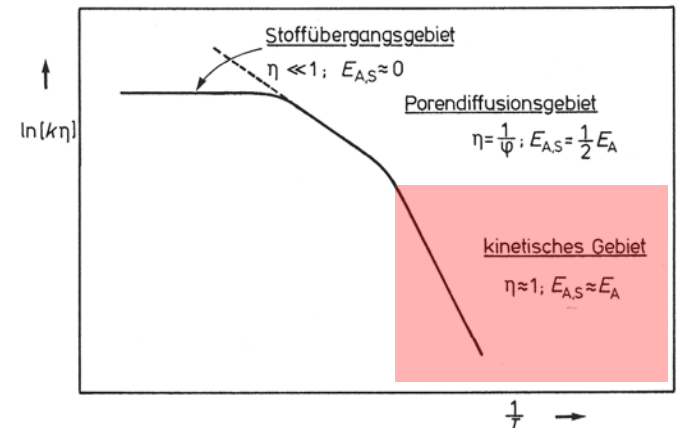
- $\eta \approx 1$; see fig. $\eta = f(\varphi)$



- $k^*\eta \approx k$



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

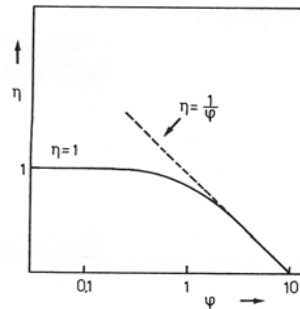


Arrhenius plot – Pore diffusion regime

- Case study: 



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



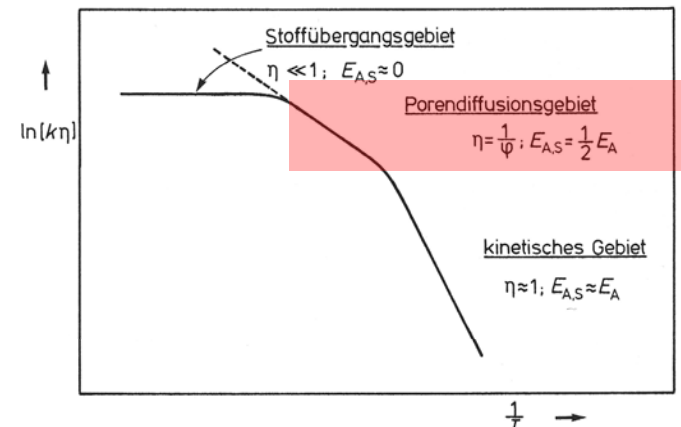
- $\ln(k^*\eta) = \ln k + \ln \eta$



- $\eta = 1/\phi$ and $\phi = 1 \sqrt{\frac{k}{D_{\text{eff}}}}$



- $\ln[k^*\eta] = \ln k - \ln \left[1 \sqrt{\frac{k}{D_{\text{eff}}}} \right]$



Arrhenius plot – Pore diffusion regime

$$\ln[k * \eta] = \ln k - \ln \left[1 \sqrt{\frac{k}{D_{\text{eff}}}} \right]$$



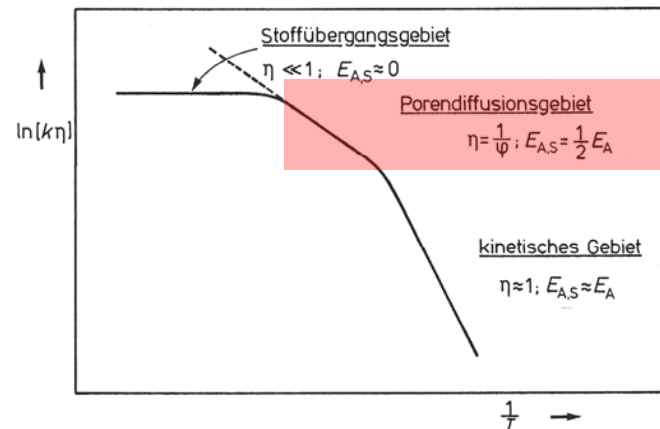
$$\ln[k * \eta] = \frac{1}{2} \ln k - \ln 1 + \frac{1}{2} \ln D_{\text{eff}}$$



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

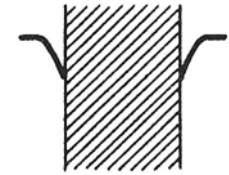


$$E_{A,s} = \frac{E_A}{2}$$



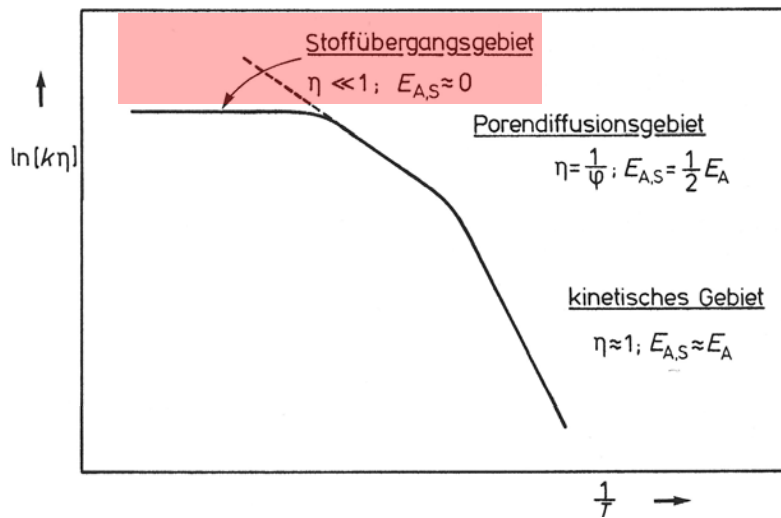
Arrhenius plot – Mass transfer regime

- For high temperatures $\phi \gg 1$ and $\eta \ll 1$



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

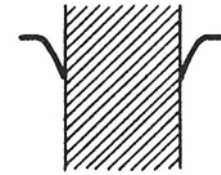
$$E_{A,s} \approx 0$$



Arrhenius plot – Mass transfer regime

- transfer contributes to rate
- for $k_g a \ll k$

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



↷

$$k_{\text{eff}} = k_g a$$

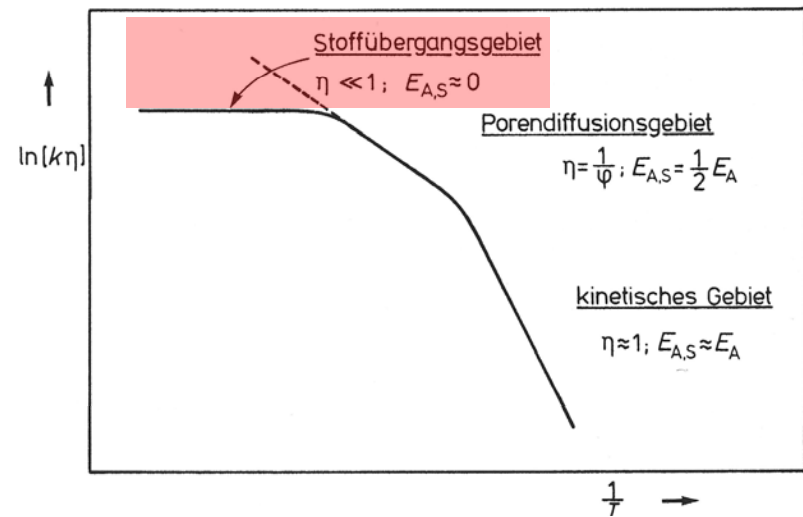
- k_g is determined by D ; $D \sim T^{3/2}$ thus $k_g \sim T^{3/2}$; formal

↷

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

- $E_{\text{eff}} = E_{\text{Diff}}$
- $E_{\text{Diff}} \sim 5 \text{ kJ/mol}$

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



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

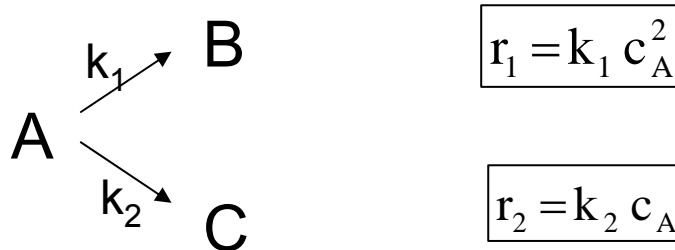
- Catalytic reaction described by $r = k c_A^n$
- Determination of „n“ may be misleading, if external or internal mass-transfer limitations exist due to $\eta = f(c)$

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:



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

$$\text{Bi} = \frac{k_g r_p}{D}$$

- **Relation between internal and external diffusion resistance**
- $\text{Bi} \gg 1$: transport limited by diffusion in the pores

External and internal resistances – Biot n.

- Biot number or dimensionless mass-transfer coefficient

$$\text{Bi} = \frac{k_g r_p}{D}$$

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

$$\eta_{\text{sum}} = \frac{1}{\frac{1}{\eta_k} + \frac{\phi^2}{3\text{Bi}}}$$

- 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

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 , Da_{II}
- ✓ Internal transfer processes
 - ✓ Mass balance for pore diffusion
 - ✓ Case studies depending on Thiele modulus

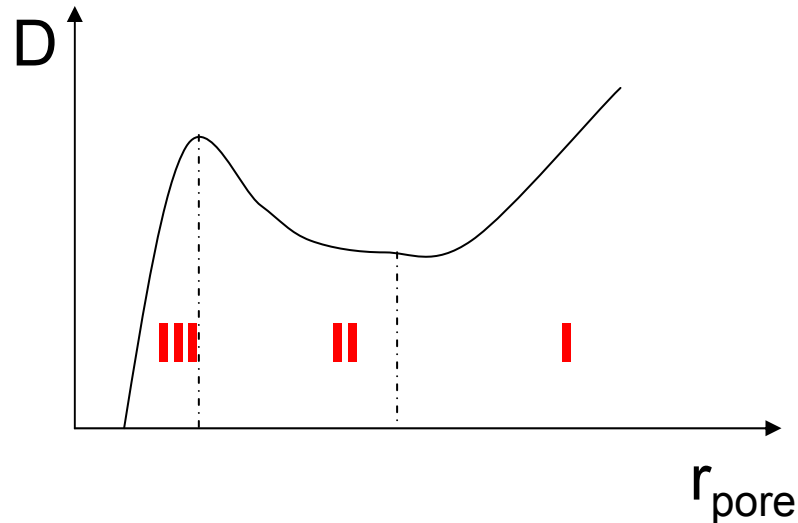
Summary

- ✓ 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