IET Institut für Energietechnik

Lecture Series at Fritz-Haber-Institute Berlin
„Modern Methods in Heterogeneous Catalysis“
09.12.2011

Diffusion in porous media – measurement and modeling

Cornelia Breitkopf

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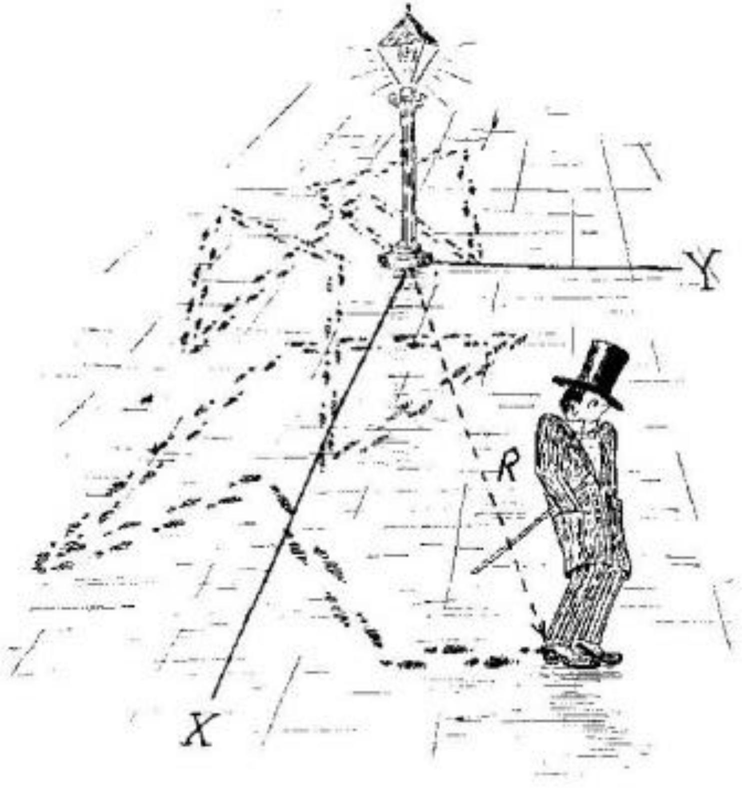
Diffusion – what is that?

Diffusion – what is that?

Dresden, Frauenkirche 2010



From G. Gamow „One, Two, Three…Infinity“
The Viking Press, New York, 1955.

Diffusion – application to societies

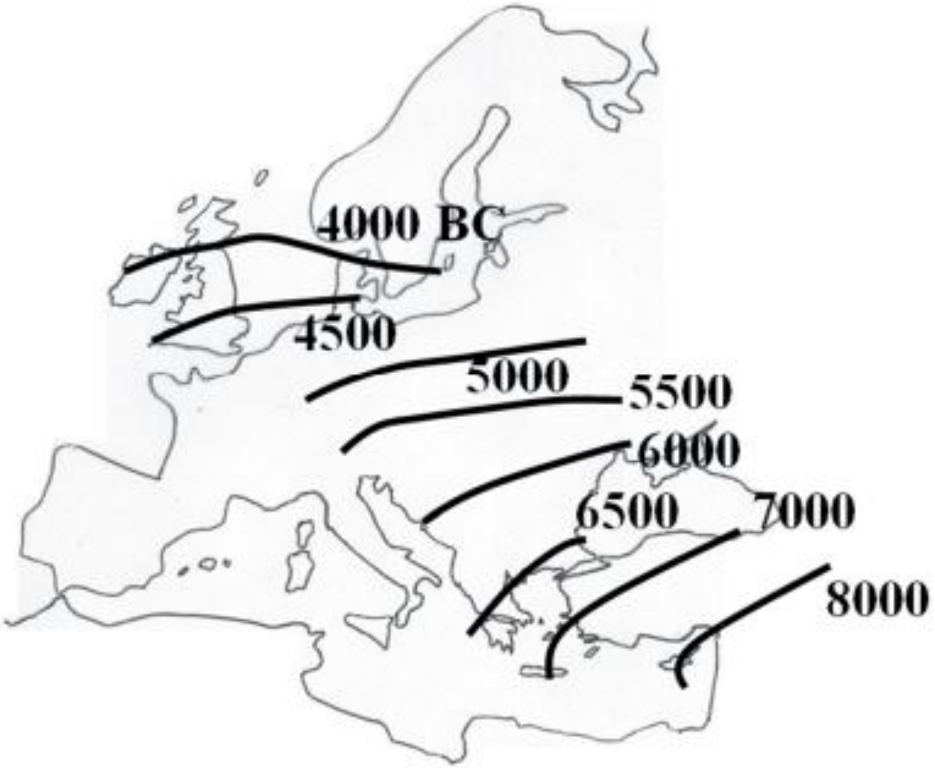
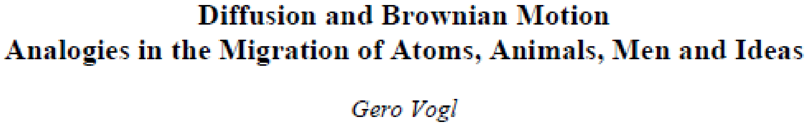


Fig. 5: Advance of agriculture from the Near East and Anatolia over a distance of 4.000 km via Greece and the Balkans to Central and finally Western and Northern Europe [after 18], dates BC according to present state of knowledge, courtesy of E. Lenneis.

in:



Diffusion and Brownian Motion
Analogies in the Migration of Atoms, Animals, Men and Ideas

Gero Vogl

Diffusion – application to societies

diffusion-fundamentals

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Diffusion and Brownian Motion
Analogies in the Migration of Atoms, Animals, Men and Ideas

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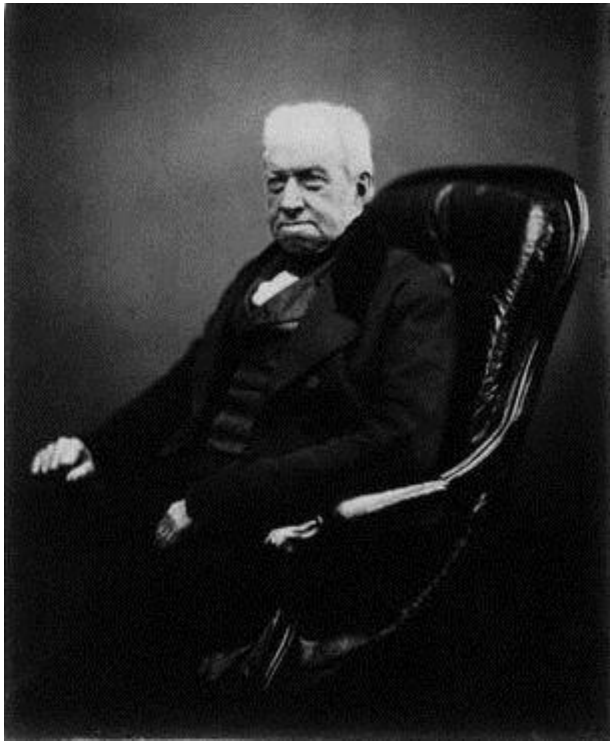
Abstract

The macroscopic laws of diffusion were laid down for the case of liquids by Adolf Fick 150 years ago who realised the analogy of diffusion and heat conduction. 100 years ago Einstein and Smoluchowski put up the equation named after these scientists teaching us how to trace down the motion of a single diffusing particle and thus to understand long time unexplained Brownian motion as a fluctuation phenomenon. In the last fifty years these laws and their combination were boldly but successfully applied to the diffusion, migration, dispersion of single atoms, men, animals and ideas.

We start by showing how the Einstein-Smoluchowski equation makes possible to induce diffusivity from microscopic information on details of the diffusion jump in solids. We then report on Brownian motion and diffusion of our fore-fathers in the Neolithicum following Cavalli-Sforza's ideas and show how this diffusion must have been a mixture of demic diffusion, i.e. the diffusion of people, and the diffusion of technological ideas. Next we risk a glimpse to the immigration of early Americans. We point out the discrepancy a physicist faces in the conclusions of the Archaeologists. We finally discuss the ultra-fast dispersion of the horse-chestnut leaf miner throughout Europe following recent work of ecologists.

Diffusion – first experiment

Robert Brown



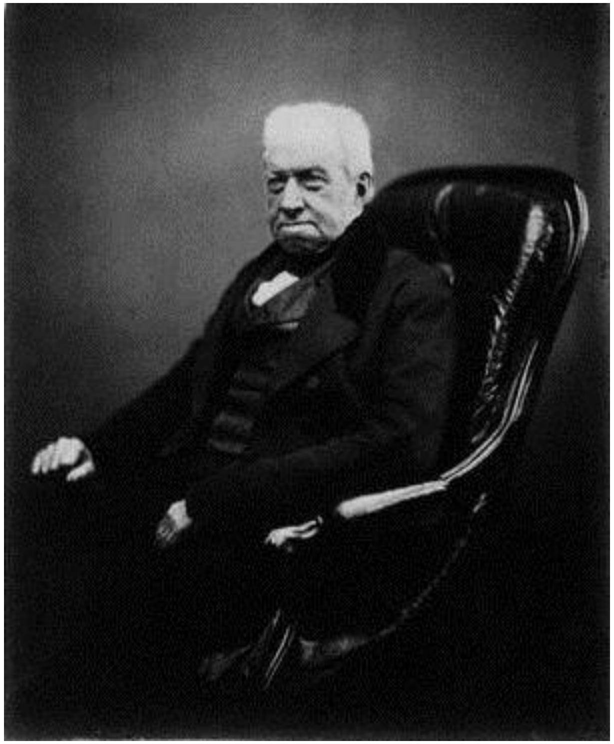
Robert Brown, (1773-1958)

“Scottish botanist best known for his description of the natural continuous **motion** of minute particles in solution, which came to be called **Brownian movement**.”

http://www.britannica.com/EBchecked/topic/81618/Robert-Brown

Diffusion – first experiment

Robert Brown

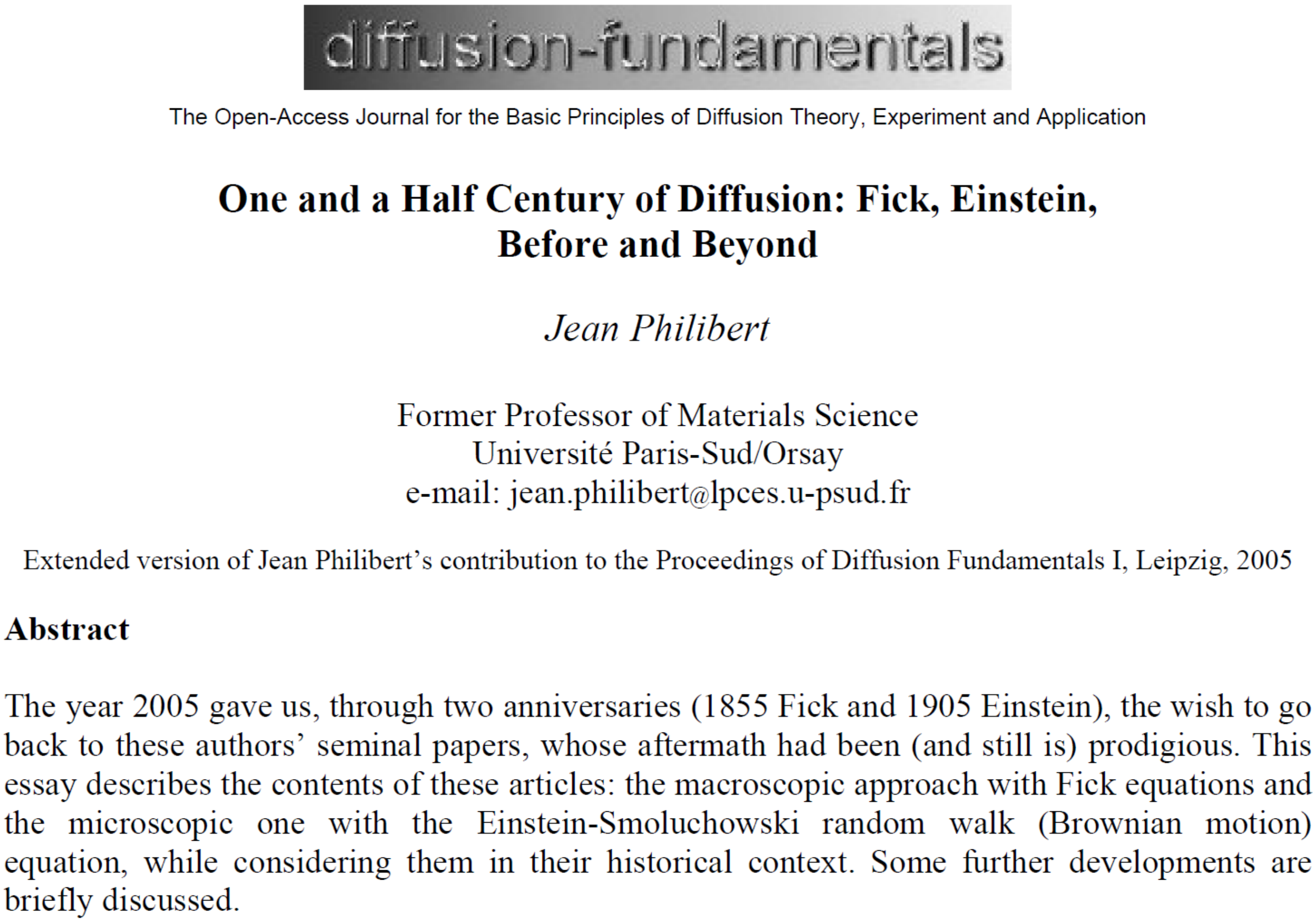


"In 1827, while examining grains of pollen of the plant *Clarkia pulchella* suspended in water under a microscope, Brown observed minute particles, now known to be amyloplasts (starch organelles) and spherosomes (lipid organelles), ejected from the pollen grains, executing a continuous jittery motion. He then observed the same motion in particles of inorganic matter, enabling him to rule out the hypothesis that the effect was life-related….."

http://en.wikipedia.org/wiki/Robert_Brown_(botanist)

Diffusion – short history

http://www.uni-leipzig.de/diffusion/pdf/volume4/diff_fund_4(2006)6.pdf



diffusion-fundamentals

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

One and a Half Century of Diffusion: Fick, Einstein, Before and Beyond

Jean Philibert

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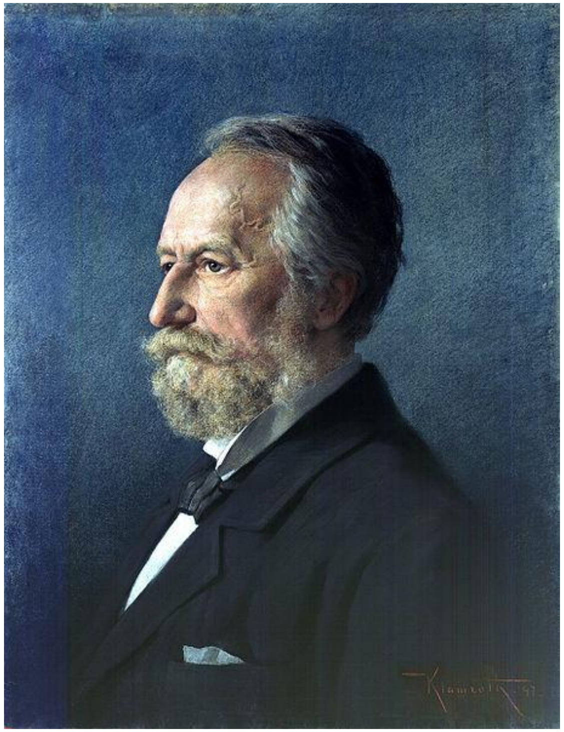
Extended version of Jean Philibert's contribution to the Proceedings of Diffusion Fundamentals I, Leipzig, 2005

Abstract

The year 2005 gave us, through two anniversaries (1855 Fick and 1905 Einstein), the wish to go back to these authors' seminal papers, whose aftermath had been (and still is) prodigious. This essay describes the contents of these articles: the macroscopic approach with Fick equations and the microscopic one with the Einstein-Smoluchowski random walk (Brownian motion) equation, while considering them in their historical context. Some further developments are briefly discussed.

Diffusion – short history

A. E. Fick



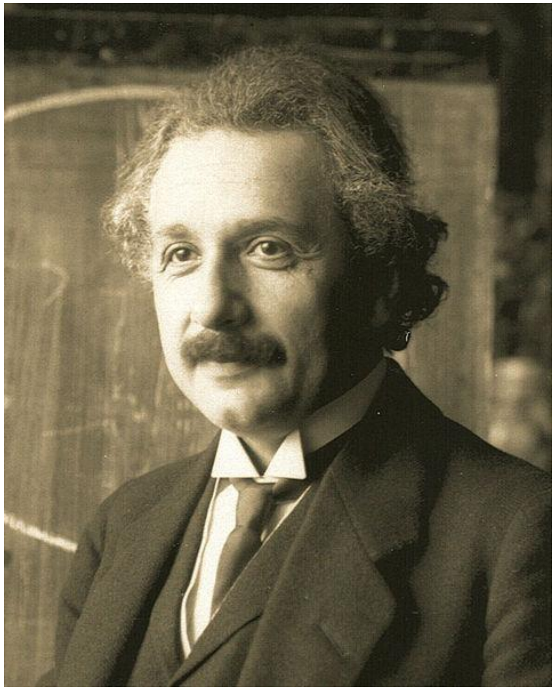
“**Adolf Eugen Fick** (1829-1901) was a German physiologist. He started to study mathematics and physics, but then realized he was more interested in medicine. He earned his doctorate in medicine at Marburg in 1851.”

“In 1855 he introduced Fick's law of diffusion, which governs the diffusion of a gas across a fluid membrane.”

http://en.wikipedia.org/wiki/Adolf_Fick

Diffusion – short history

Albert Einstein (1879-1955)



Marian von Smoluchowski (1872-1917 was a phyiscist.

http://de.wikipedia.org/wiki/Albert_Einstein

http://de.wikipedia.org/wiki/Marian_Smoluchowski

Diffusion – short history

A. Einstein, M.Smoluchowski

In physics (namely, in kinetic theory) the **Einstein relation** (also known as **Einstein– relation**) is a previously unexpected connection revealed independently by Albert Einstein in 1905 and by Marian Smoluchowski (1906) in their papers on Brownian motion.
Two important special cases of the relation are:

$$D = \frac{\mu_q\, k_B T}{q}$$

(diffusion of charged particles)

$$D = \frac{k_B T}{6\pi\,\eta\, r}$$

("**Einstein–Stokes equation**", for diffusion of spherical particles through liquid with low Reynolds number)

$$D = \mu\, k_B T$$

$$D = \mu\, k_B T$$

The more general form of the equation is:

where the "mobility" μ is the ratio of the particle's terminal drift velocity to an applied force, $\mu = v_d / F$.
This equation is an early example of a fluctuation-dissipation relation. It is frequently used in the electrodiffusion phenomena.

http://en.wikipedia.org/wiki/Einstein_relation_(kinetic_theory)

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

What ?

- *Introduction to porosity, diffusion*
- *Overview to methods for diffusion in porous (and other) systems*
- *General aspects of pulse methods*
- *Frequency Response approach*
- *Temporal Analysis of Products*
- *Literature recommendations*

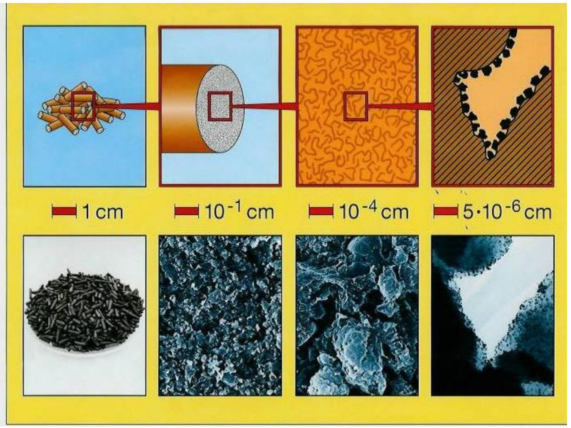
Porosity

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 probe molecules

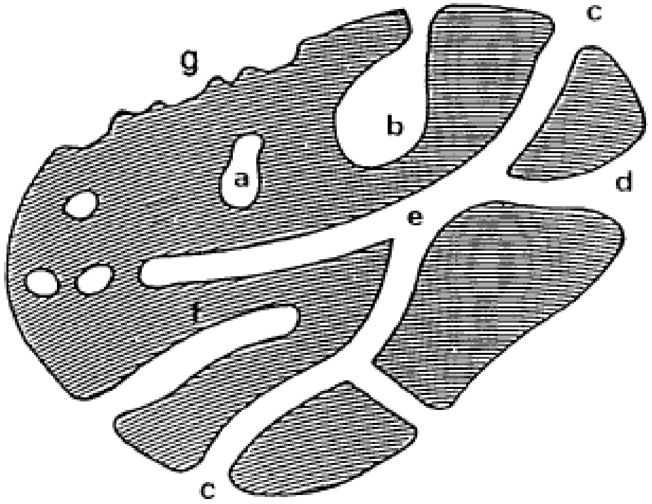
- porosities are often desired and of importance in medicine, membranes, sorbents, ceramics, and *catalysts*



Pore types

- pressing of support material leads to a network of micro-/meso- 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)

Types of porosity

- bed porosity and particle porosity have to be differentiated **!**
- *bed porosity* (or void fraction) ε_B is defined as the volume of voids per volume of reactor
- *porosity* (or pellet void fraction) is defined as $\varepsilon = \rho_P * V_g$
  (ρ_P effective particle density, V_g pore volume)

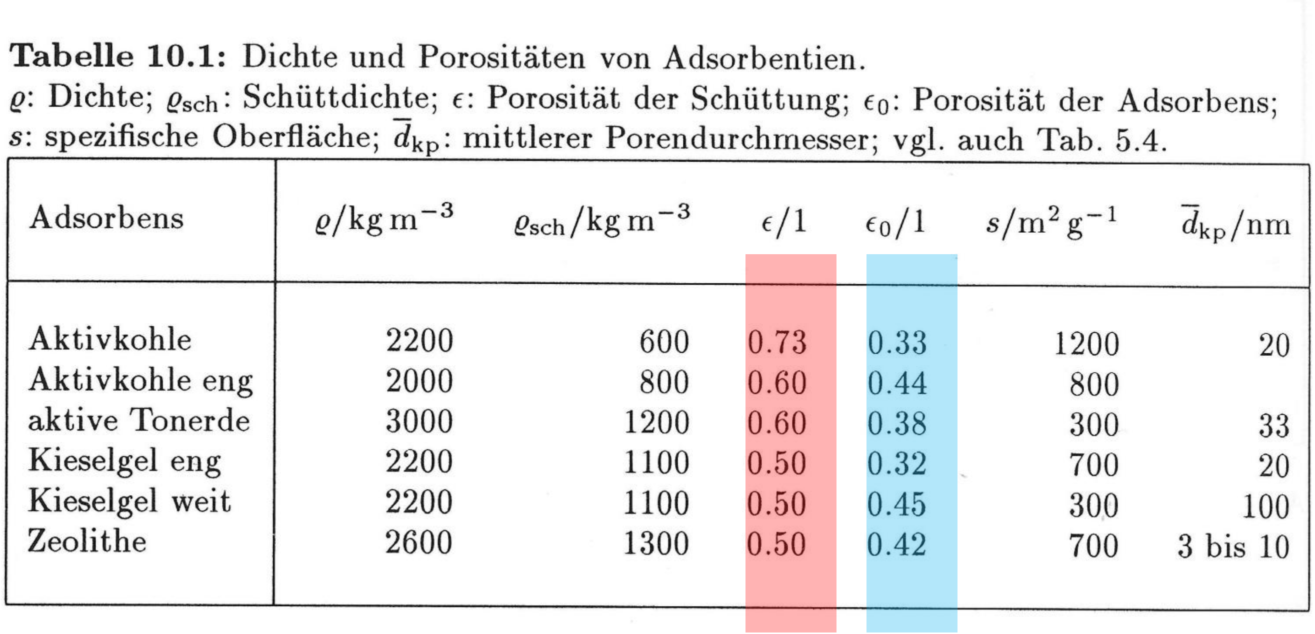


Tabelle 10.1: Dichte und Porositäten von Adsorbentien.
ϱ: Dichte; ϱ_{sch}: Schüttdichte; ϵ: Porosität der Schüttung; ϵ_0: Porosität der Adsorbens; s: spezifische Oberfläche; $\overline{d}_{\mathrm{kp}}$: mittlerer Porendurchmesser; vgl. auch Tab. 5.4.

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 (see textbooks of thermodynamics)

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
- …generally *decreases* with increasing density
- …the equilibration takes
  - minutes for gases
  - days/weeks for liquids
  - with measurable rate only close to the melting point for solids
- …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

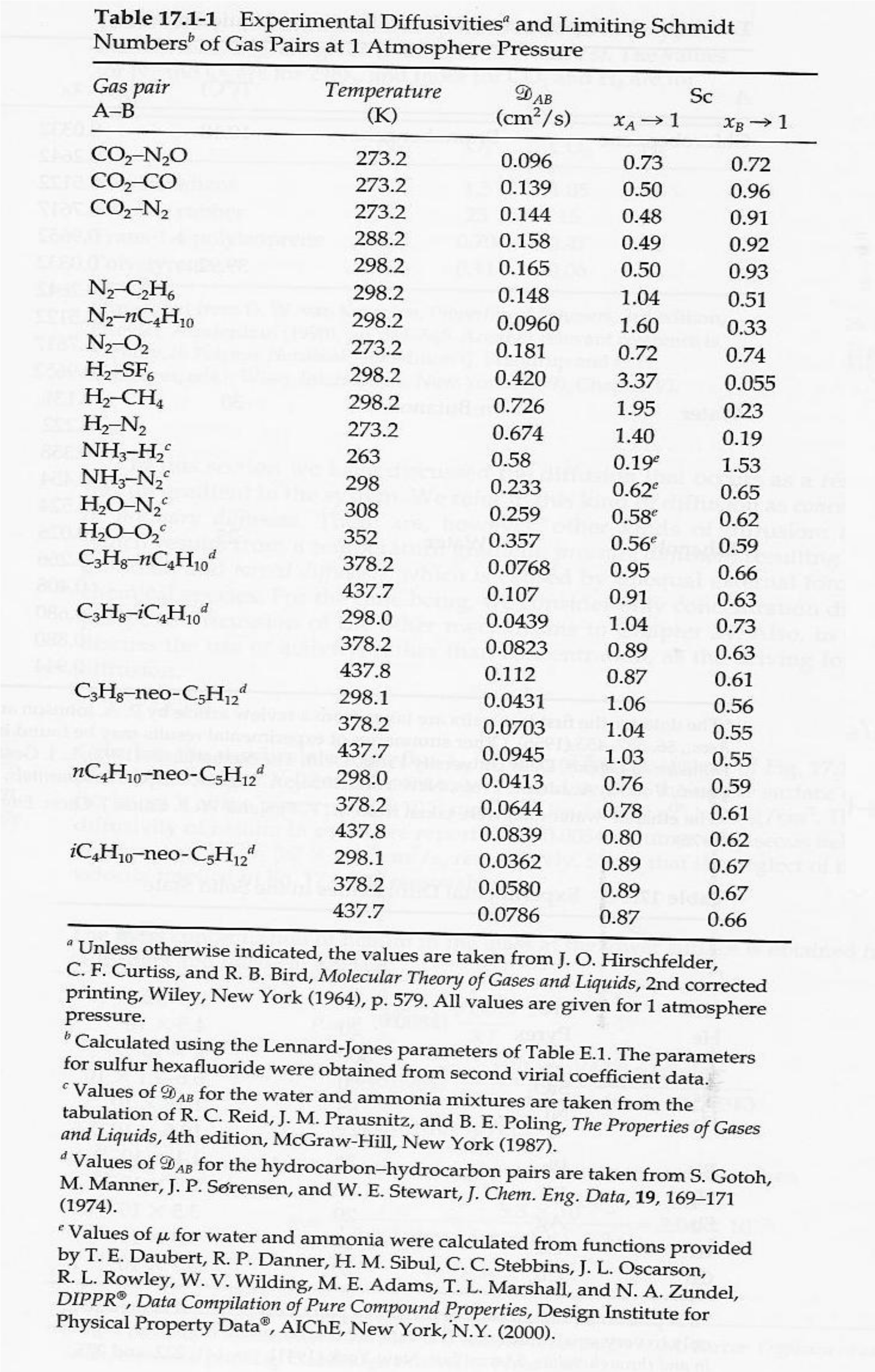


Table 17.1-1 Experimental Diffusivities[a] and Limiting Schmidt Numbers[b] of Gas Pairs at 1 Atmosphere Pressure

Gas pair A–B	*Temperature* (K)	$\mathscr{D}_{AB}$ (cm²/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–$n$$C_4H_{10}$	298.2	0.0960	1.60	0.33
N_2–O_2	273.2	0.181	0.72	0.74
H_2–SF_6	298.2	0.420	3.37	0.055
H_2–CH_4	298.2	0.726	1.95	0.23
H_2–N_2	273.2	0.674	1.40	0.19
NH_3–H_2[c]	263	0.58	0.19[e]	1.53
NH_3–N_2[c]	298	0.233	0.62[e]	0.65
H_2O–N_2[c]	308	0.259	0.58[e]	0.62
H_2O–O_2[c]	352	0.357	0.56[e]	0.59
C_3H_8–$n$$C_4H_{10}$[d]	378.2	0.0768	0.95	0.66
	437.7	0.107	0.91	0.63
C_3H_8–$i$$C_4H_{10}$[d]	298.0	0.0439	1.04	0.73
	378.2	0.0823	0.89	0.63
	437.8	0.112	0.87	0.61
C_3H_8–neo-C_5H_{12}[d]	298.1	0.0431	1.06	0.56
	378.2	0.0703	1.04	0.55
	437.7	0.0945	1.03	0.55
$n$$C_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
$i$$C_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).

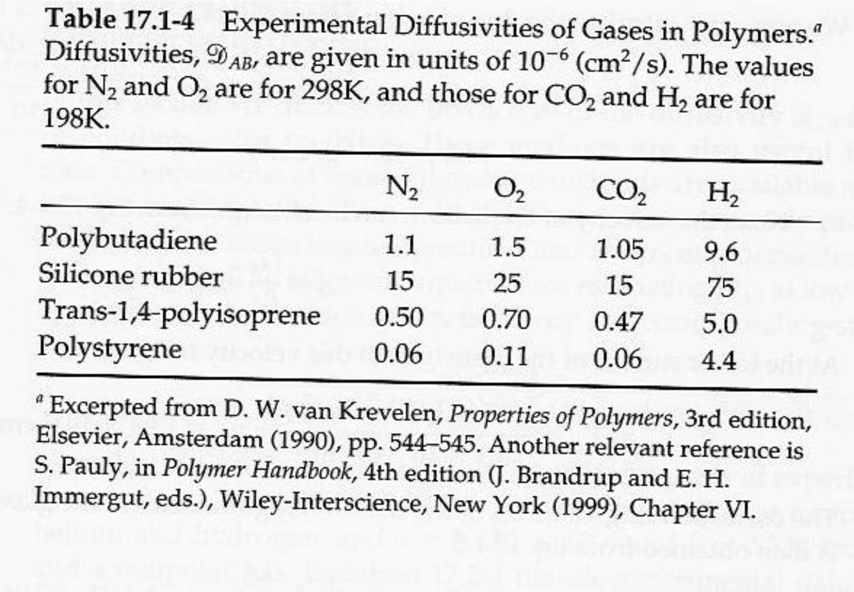


Table 17.1-4 Experimental Diffusivities of Gases in Polymers.[a] Diffusivities, $\mathscr{D}_{AB}$, are given in units of 10^{-6} (cm²/s). The values for N_2 and O_2 are for 298K, and those for CO_2 and H_2 are for 198K.

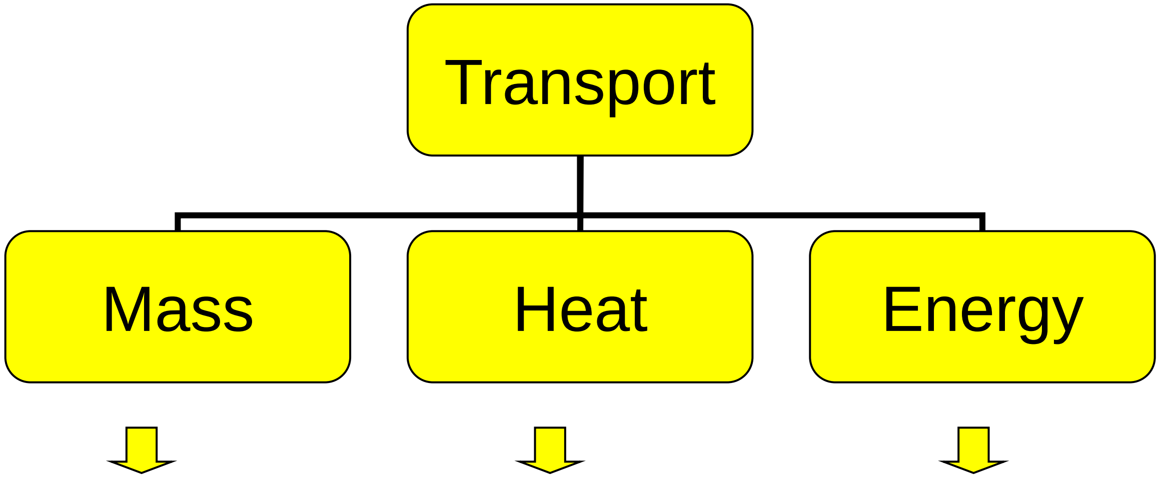
	N_2	O_2	CO_2	H_2
Polybutadiene	1.1	1.5	1.05	9.6
Silicone rubber	15	25	15	75
Trans-1,4-polyisoprene	0.50	0.70	0.47	5.0
Polystyrene	0.06	0.11	0.06	4.4

[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

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

Fick´s Law

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

Fourier´s Law

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

Newton´s Law

General view to transport equations for gases

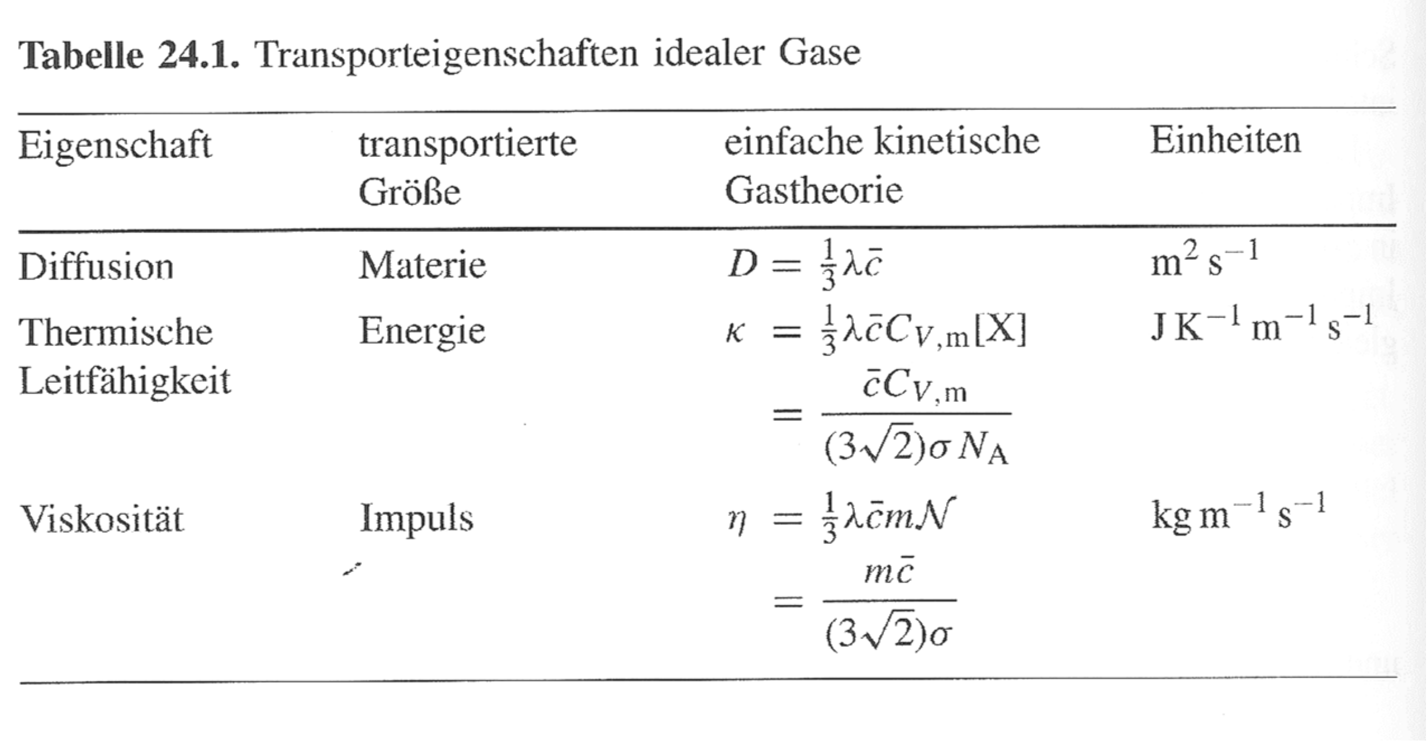
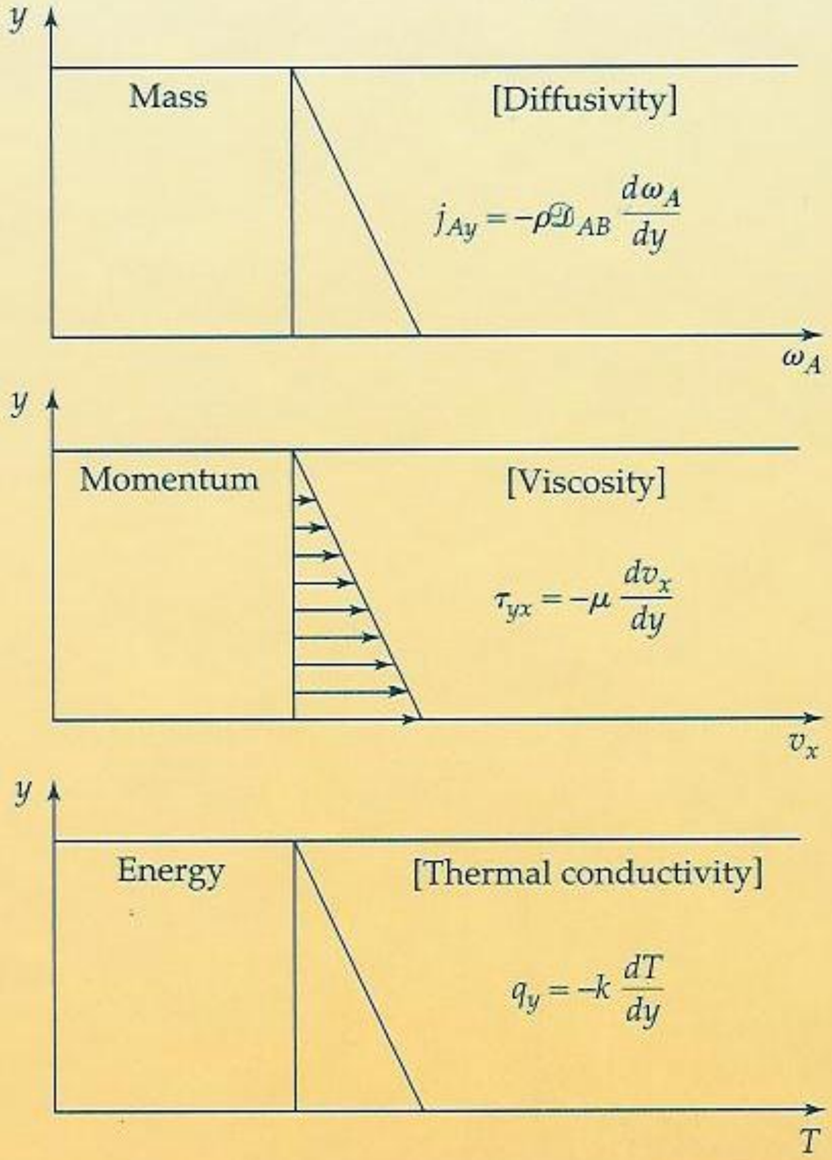


Tabelle 24.1. Transporteigenschaften idealer Gase

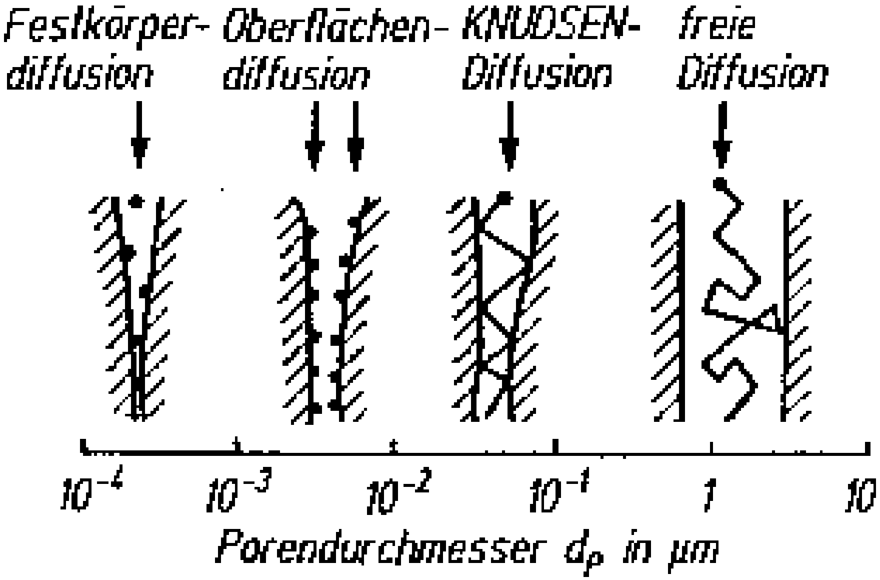
Eigenschaft	transportierte Größe	einfache kinetische Gastheorie	Einheiten
Diffusion	Materie	$D = \frac{1}{3}\lambda\bar{c}$	$\mathrm{m^2\,s^{-1}}$
Thermische Leitfähigkeit	Energie	$\kappa = \frac{1}{3}\lambda\bar{c}C_{V,\mathrm{m}}[\mathrm{X}] = \frac{\bar{c}C_{V,\mathrm{m}}}{(3\sqrt{2})\sigma N_\mathrm{A}}$	$\mathrm{J\,K^{-1}\,m^{-1}\,s^{-1}}$
Viskosität	Impuls	$\eta = \frac{1}{3}\lambda\bar{c}m\mathcal{N} = \frac{m\bar{c}}{(3\sqrt{2})\sigma}$	$\mathrm{kg\,m^{-1}\,s^{-1}}$

Atkins


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

Diffusion mechanisms

Transport mechanisms in porous solids



Pore diffusion depending on pore diameter

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

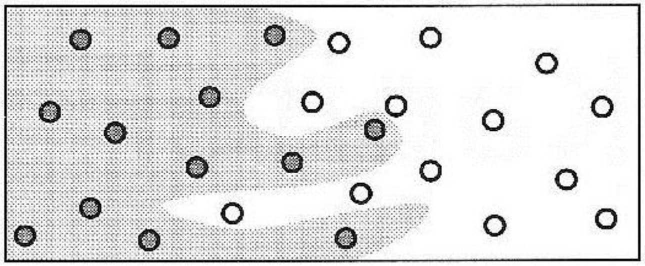


Abb. 24.1 Bei der Diffusion vermischen sich die Moleküle einer Substanz mit den Molekülen einer anderen Substanz.

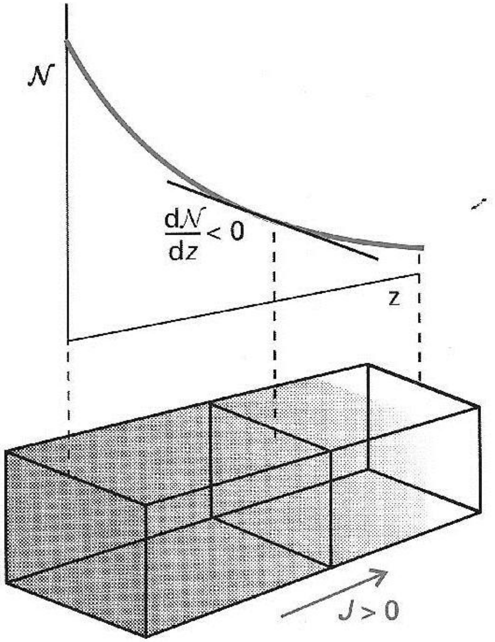


Abb. 24.7 Der Fluß von Teilchen gegen einen Konzentrationsgradienten. Das erste Ficksche Gesetz besagt, daß der Fluß der Materie (die Zahl der Teilchen pro Zeit- und Flächeneinheit) proportional zu dem Dichtegradienten am betreffenden Punkt ist.

Atkins

Molecular diffusion

- mixture of two components A and B, concentration gradient (in one dimension y): under steady-state conditions the diffusional flow of one component is described by *1. Fick law*

$$\boxed{J_A = -D_{AB}\left(\frac{dc_A}{dy}\right)}$$

- D_{AB} ...*binary molecular diffusion coefficient* of component A diffusing through B

- D_{AB} = f(molecular properties of A and B, T, c or p)

Ficks´s Second Law

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

Molecular diffusion coefficient

- Molecular diffusion coefficient for gases

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

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

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

- 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)

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

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

- under *low pressure conditions* *and/or* for *small pores*:
  collision of gas with pore wall > collision of gas with gas

- *mean free path length* of molecule > pore diameter

$$\boxed{\Lambda = \frac{1}{\sqrt{2}\,\pi\sigma^2}\frac{V}{N_A}}$$

Λ …mean free path length
σ^2…molecular cross-section
V… gas molar volume at p

- N_A/V at 298 K : $c_{ges} \approx 3.10^{19}$ *p (molecules/cm^3)
  (dimension of p 10^5 Pa)

- mean free path length with typical σ (9-20*10^{-16} cm^2)

$$\boxed{\Lambda \cong \frac{10^2}{p} \qquad (nm)}$$

Knudsen diffusion

$$\boxed{\Lambda \cong \frac{10^2}{p} \qquad (nm)}$$

- *Conditions* for Knudsen diffusion

d_{pore} [nm]	<1000	<100	<10	<2
p [bar]	0.1	1	10	50

Knudsen diffusion

- Knudsen flow through one zylindrical pore

$$\boxed{D_{K,i} = \frac{d_p}{3}\sqrt{\frac{8RT}{\pi M}} \qquad \approx 10^{-6}\,\frac{m^2}{s}\,(at\,293\,K, 0.01\,MPa)}$$

- for porous solids, the relative pore volume ε_b and the tortuousity factor τ_K have to be considered

$$\boxed{D^{eff}{}_{K,i} = \frac{\varepsilon_P}{\tau_K}\frac{d_p}{3}\sqrt{\frac{8RT}{\pi M}}}$$

effective diffusion coefficient

- *estimation of* τ is a complex procedure (see literature)

Effective diffusion coefficients

- diffusional flow in the pores may be described by an *effective diffusion coefficient*

- relation to surface: surface of pore mouths is representing only a part of the outer surface of a particle

⤵ ε

- pores are not ideally cylindrical

- pores are connected by a network ⤵ τ

Diffusion in porous solids

- ✓ *Characteristic value* to characterize the *influence of internal transport* phenomena of heterogeneous reactions on the surface between a fluid phase and a porous solid is Da^{II} (see textbooks)
- ✓ $Da^{II} = f\ (k, c_{external}, l_{characteristic}, D_{eff})$
- ✓ if fluid is gaseous: *diffusion* in pores *depends on* dimensions of *pore system*

Transition region of diffusion

- for heterogeneous reactions in a porous solid, the conditions of pressure or pore diameter may be such that the system is between Knudsen and molecular diffusion

- *mean free path length ≈ pore diameter*

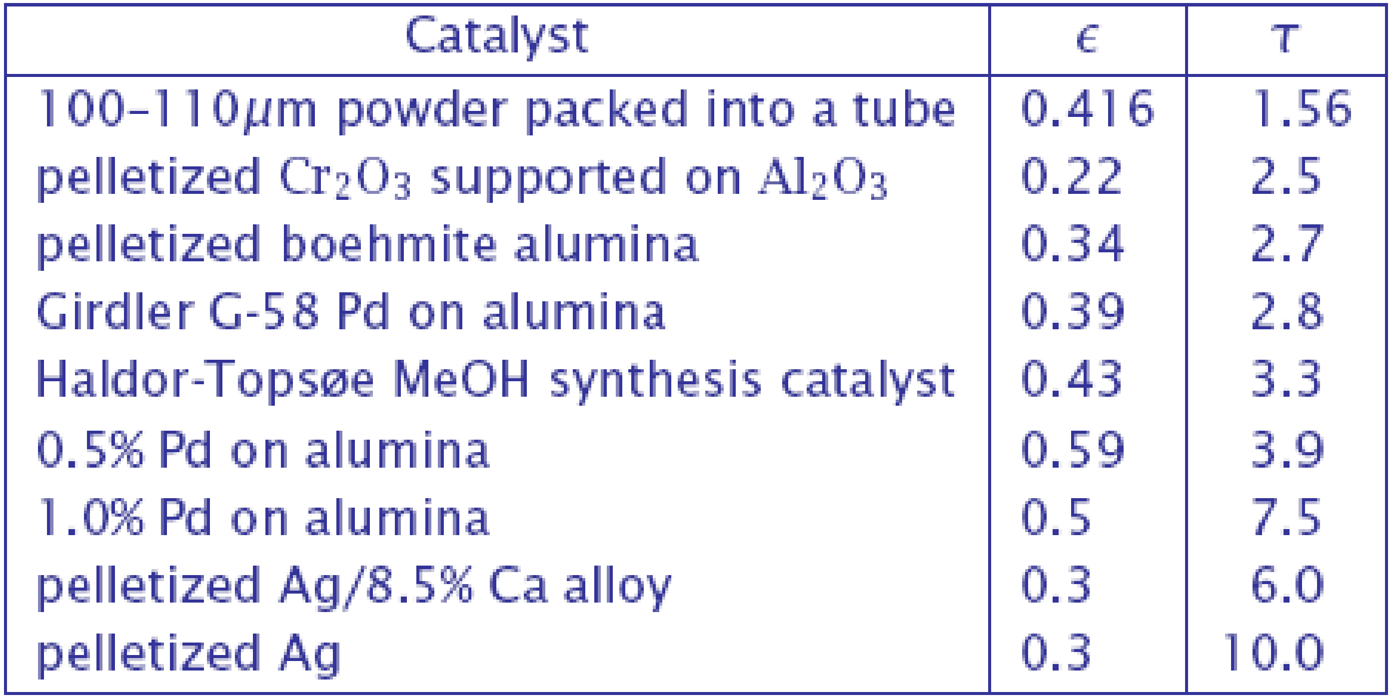
- both equations for D_M and D_{Kn} apply

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

Effective diffusivities

- Use of porosity and tortuosity factor

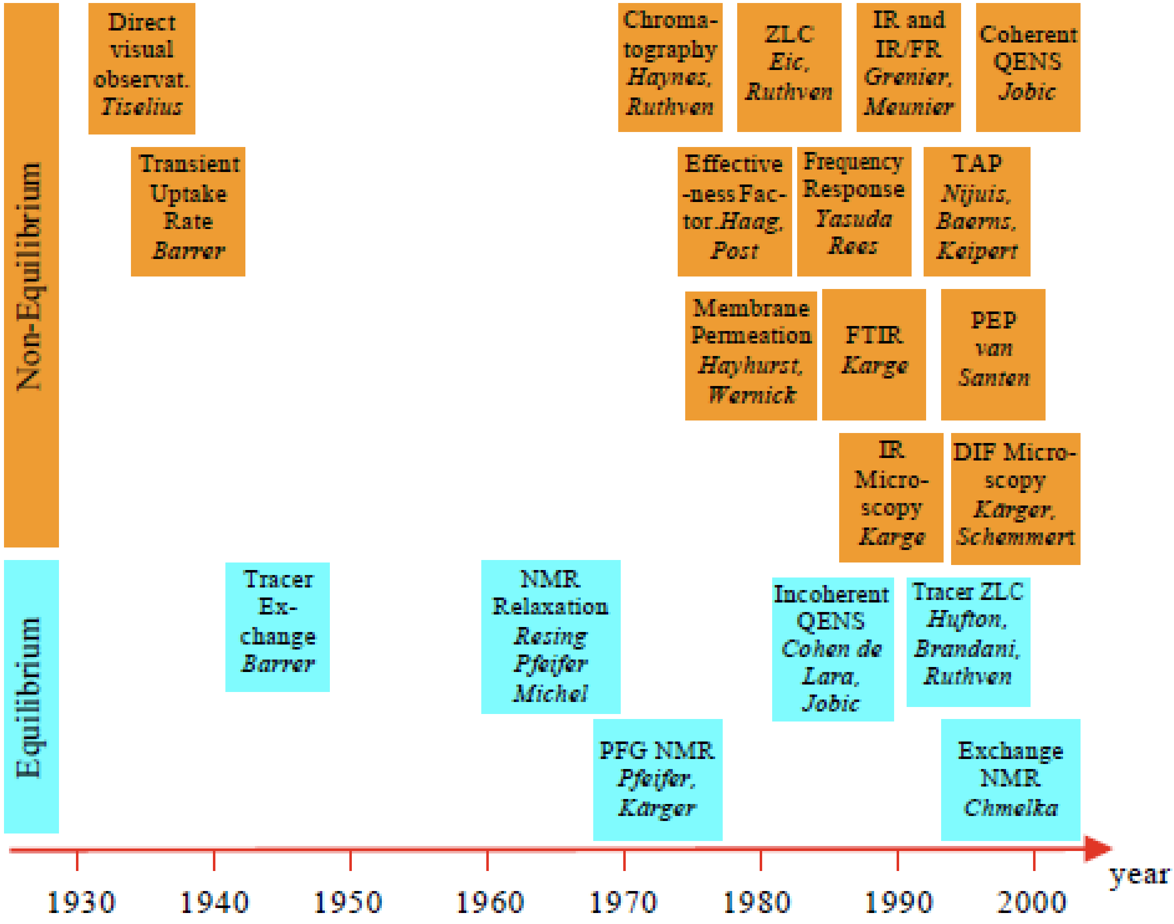
$$\boxed{D_{eff} = \frac{\varepsilon}{\tau} D}$$



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

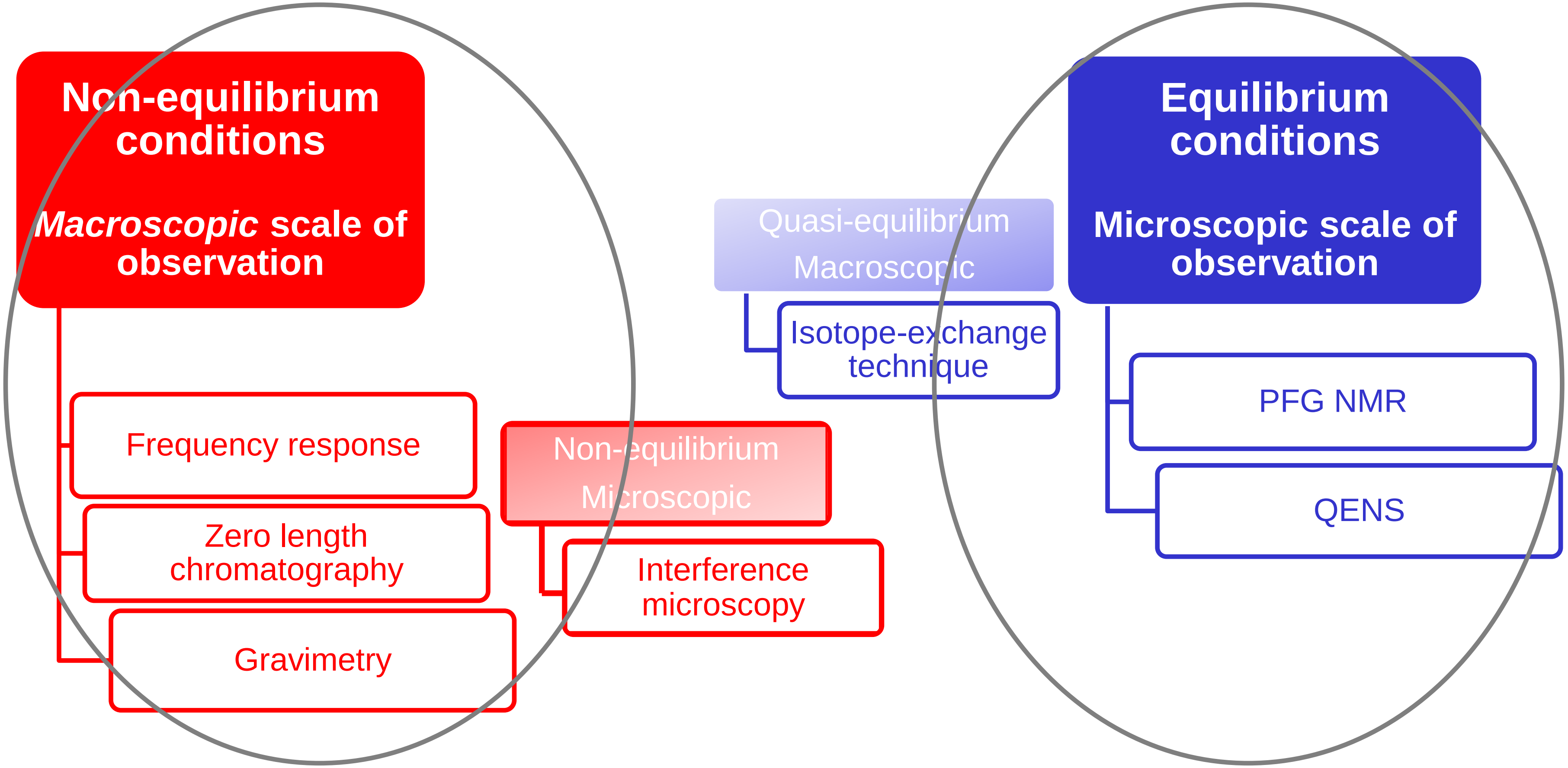
Diffusion – Measuring techniques

Diffuison – measuring techniques



J. Kärger, University Leipzig
Vasenkov & Kärger. *Magn. Res. Imag*. 23 (2005) 139.

Diffusion – overview according to exper. conditions



Non-equilibrium conditions

***Macroscopic* scale of observation**

- Frequency response
- Zero length chromatography
- Gravimetry

Non-equilibrium
Microscopic

- Interference microscopy

Quasi-equilibrium
Macroscopic

- Isotope-exchange technique

Equilibrium conditions

Microscopic scale of observation

- PFG NMR
- QENS

PFG NMR

PFG NMR *Pulsed **f**ield **g**radient **NMR***

(PGSE ***P**ulsed **g**radient **s**pin **e**cho technique)

- ***PFG NMR …**measures* directly the ***probability distribution of molecular displacements*** of the probe molecules within the sample, averaged over each individual starting point
- ***PFG NMR …***is *sensitive* to the ***mean molecular displacements*** within the sample in the direction of the field gradients applied, measured in the time interval between the field gradient pulses
- ***PFG NMR …***is a ***non-invasive*** *technique*
- ***PFG NMR …time variation*** allows a distinction between individual and ***different ranges of molecular transport*** in complex systems

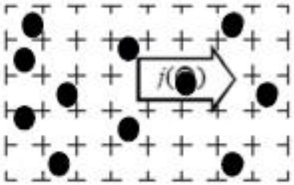
PFG NMR

- ***PFG NMR…***enables to measure diffusion in ***materials*** from *100 nm….100 µm* → intracrystalline and long-range diffusion

- ***PFG NMR…***has a ***lower limit*** for measurement of ***$D \sim 10^{-14}$ m^2/s***

PFG NMR and terms of diffusion

- Transport Diffusion

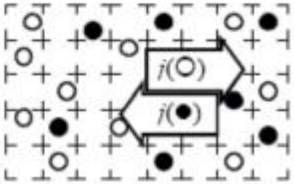


$$j_x = -D_T \frac{\partial c}{\partial x}$$

(Fick's 1st law)

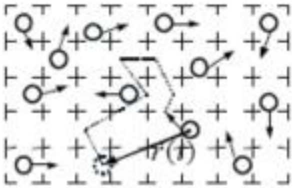

Leipzig, Einstein, Diffusion

- Self-diffusion by Tracer Exchange



$$j_x^* = -D \frac{\partial c^*}{\partial x}$$

- Self-diffusion by following the individual molecules (QENS, PFG NMR)



$$< x^2(t) > = 2Dt$$

Einstein Equation

QUENS

QUENS ***Quasi-elastic neutron scattering***

- ***QUENS…***is a sensitive probe for studying the ***structure*** and ***dynamics of materials on the atomic and molecular level***

- ***QUENS…***is working in the ***submicroscopic scale***

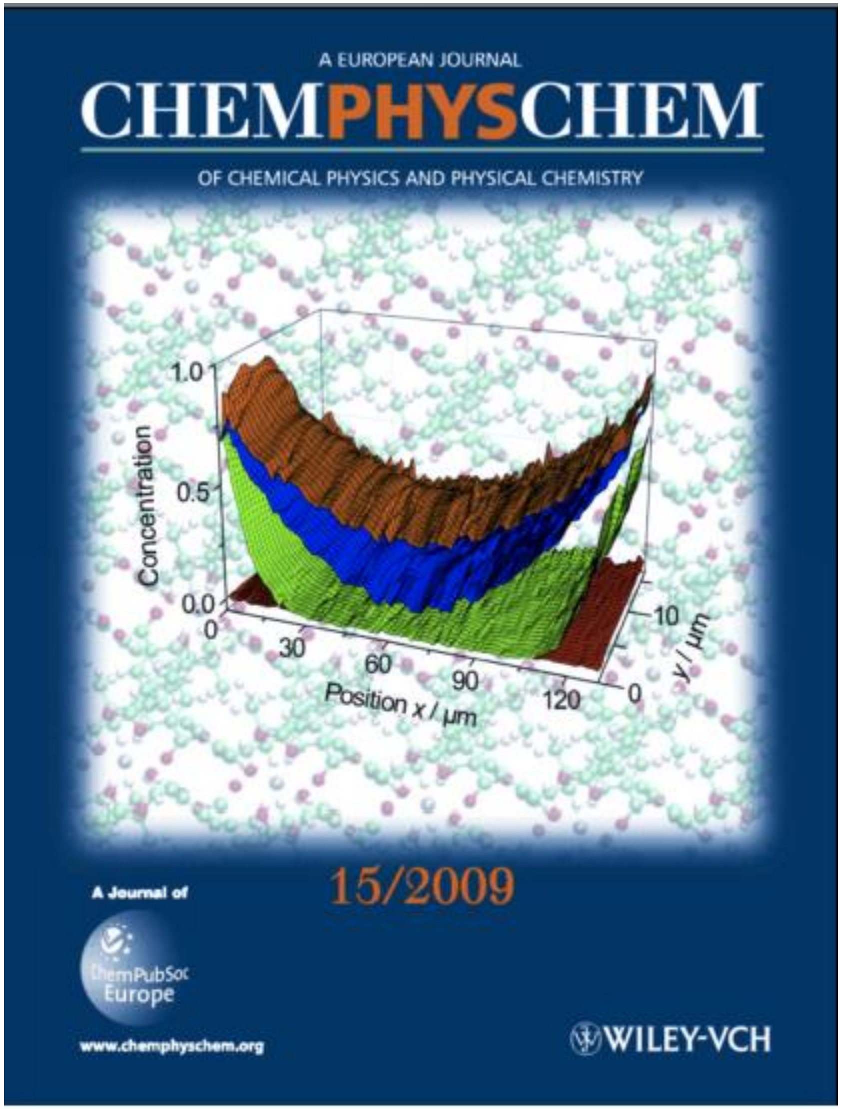
- ***QUENS…***studies the ***dynamics*** of the ***framework and*** of ***the adsorbed molecules***

- ***QUENS…***allows to follow the ***location*** of ***cations, water, adsorbed moelcules*** thus visualizing the ***elementary processes of diffusion***

- ***QUENS…***has a ***lower limit*** for measurement of ***$D \sim 10^{-14}$ m^2/s***

- ***QUENS…***is applying mainly ***hydrogenated probe molecules*** (large neutron cross section of H_2)

IR imaging



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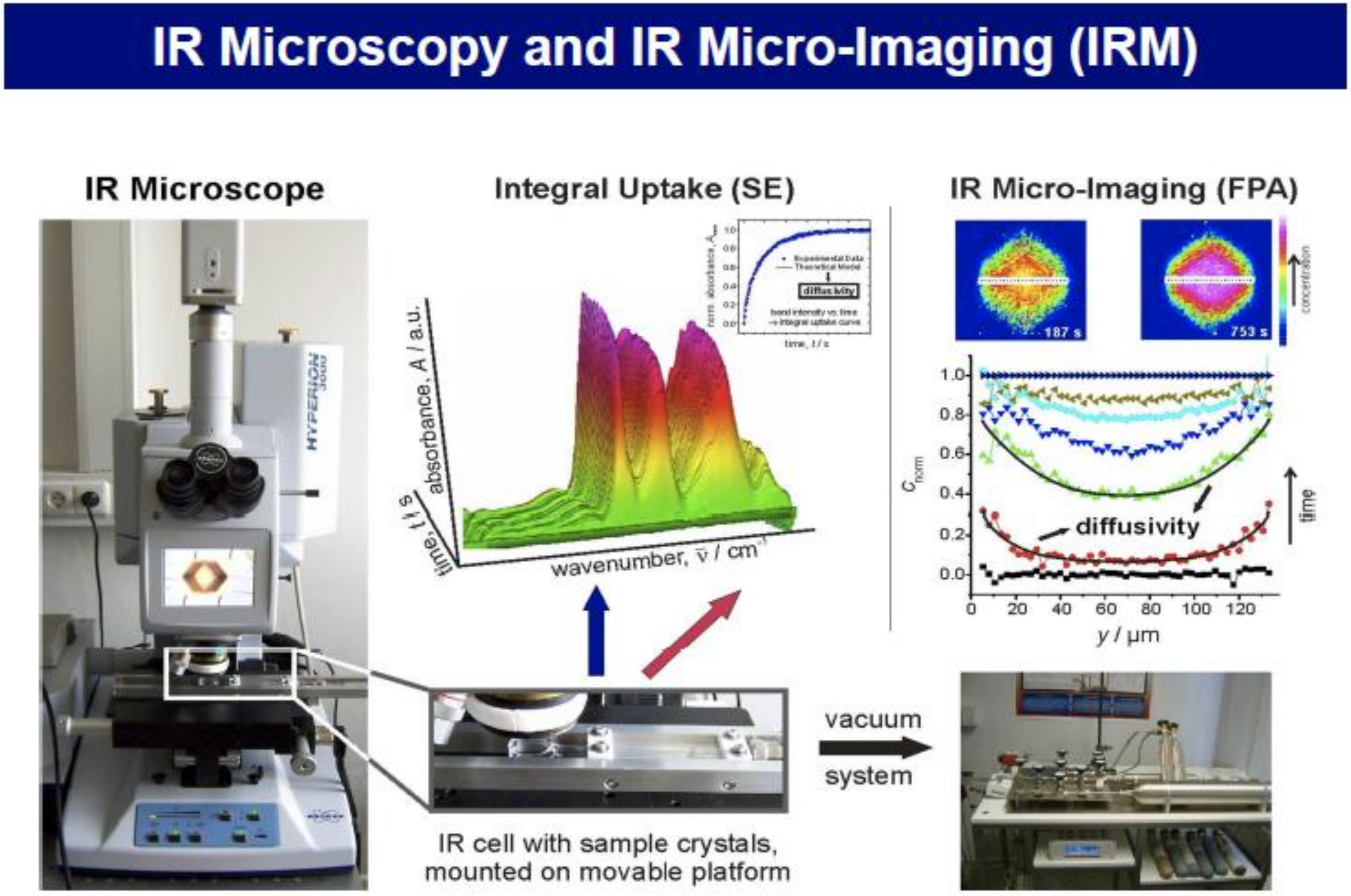
IR microscopy and IR imaging (IRM)



Diffusion – measurement in solids

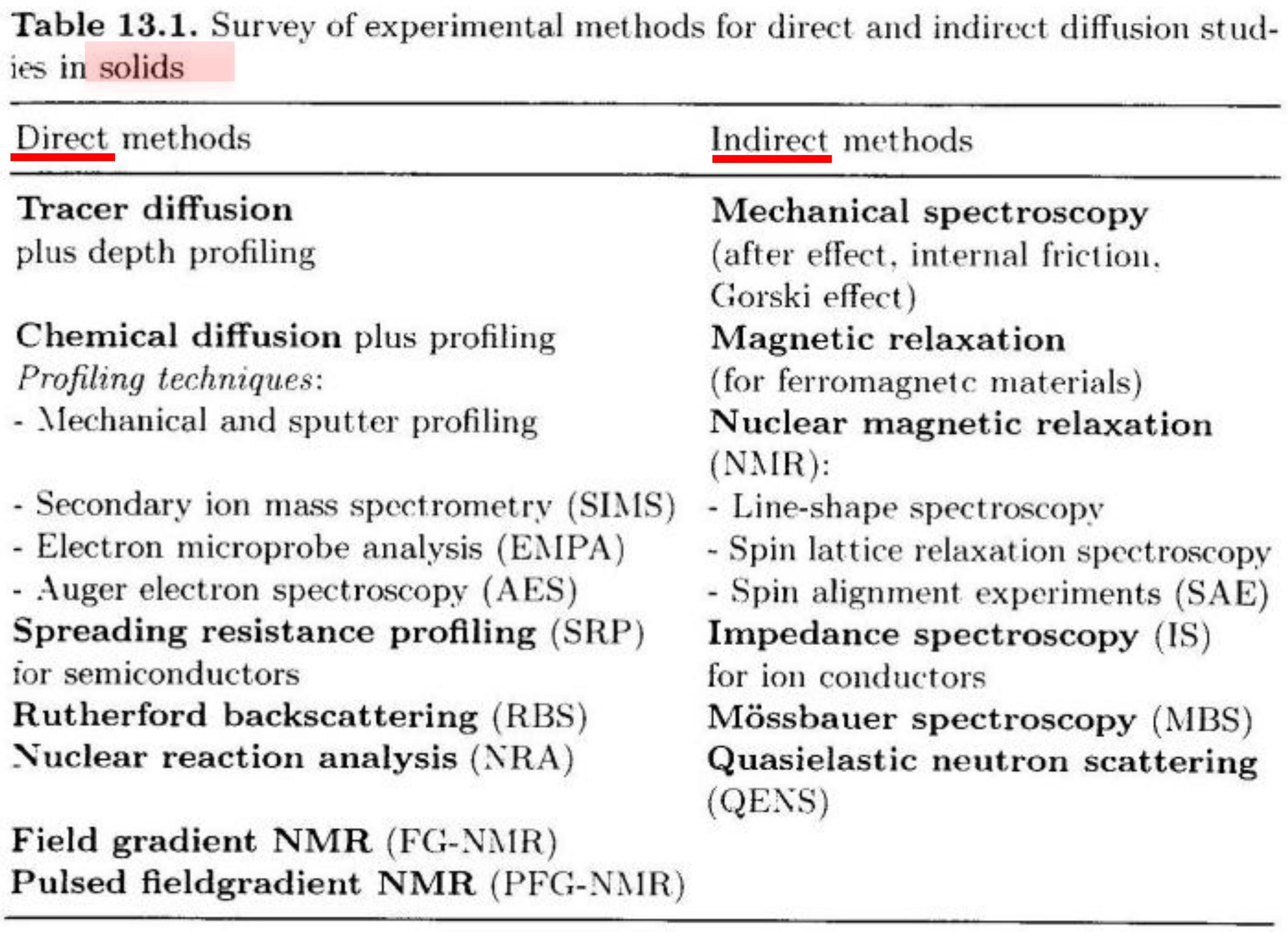


Table 13.1. Survey of experimental methods for direct and indirect diffusion studies in solids

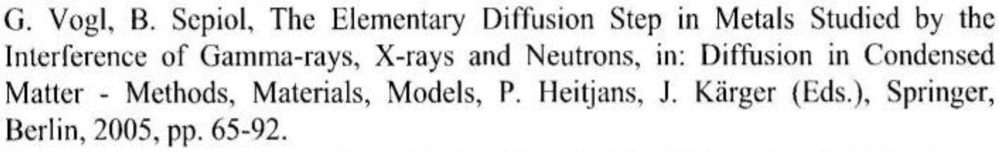
Direct methods	Indirect methods
Tracer diffusion plus depth profiling	**Mechanical spectroscopy** (after effect, internal friction, Gorski effect)
Chemical diffusion plus profiling *Profiling techniques*: - Mechanical and sputter profiling - Secondary ion mass spectrometry (SIMS) - Electron microprobe analysis (EMPA) - Auger electron spectroscopy (AES)	**Magnetic relaxation** (for ferromagnetc materials) **Nuclear magnetic relaxation** (NMR): - Line-shape spectroscopy - Spin lattice relaxation spectroscopy - Spin alignment experiments (SAE)
Spreading resistance profiling (SRP) for semiconductors	**Impedance spectroscopy** (IS) for ion conductors
Rutherford backscattering (RBS)	**Mössbauer spectroscopy** (MBS)
Nuclear reaction analysis (NRA)	**Quasielastic neutron scattering** (QENS)
Field gradient NMR (FG-NMR) **Pulsed fieldgradient NMR** (PFG-NMR)	

From: H. Mehrer, Diffusion in Solids. Springer 2007. S. 209

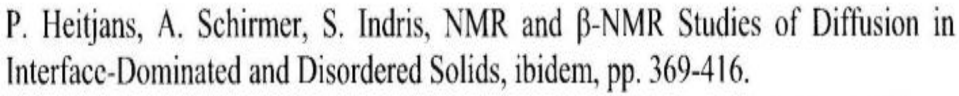
Diffusion – solid diffusion

…further reading

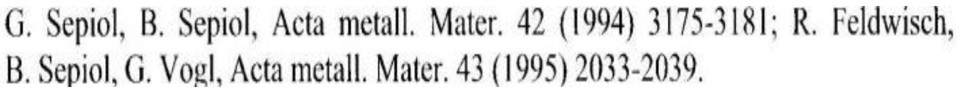
Neutron scattering
X-ray scattering
γ-absorption


G. Vogl, B. Sepiol, The Elementary Diffusion Step in Metals Studied by the Interference of Gamma-rays, X-rays and Neutrons, in: Diffusion in Condensed Matter - Methods, Materials, Models, P. Heitjans, J. Kärger (Eds.), Springer, Berlin, 2005, pp. 65-92.

NMR


P. Heitjans, A. Schirmer, S. Indris, NMR and β-NMR Studies of Diffusion in Interface-Dominated and Disordered Solids, ibidem, pp. 369-416.

Mössbauer spectroscopy


G. Sepiol, B. Sepiol, Acta metall. Mater. 42 (1994) 3175-3181; R. Feldwisch, B. Sepiol, G. Vogl, Acta metall. Mater. 43 (1995) 2033-2039.

General aspects of pulse methods (adsorption and diffusion)

Pulse methods

- response to *pertubations* → describe mathematically the transient behaviour
- evaluation of rate parameters from response measurements such as mass transfer coefficients, diffusivities, and chemical kinetic constants
- use of:
  - fixed-bed (column) chromatography
  - isotope technique
  - slurry adsorber
  - single-pellet

Pulse methods

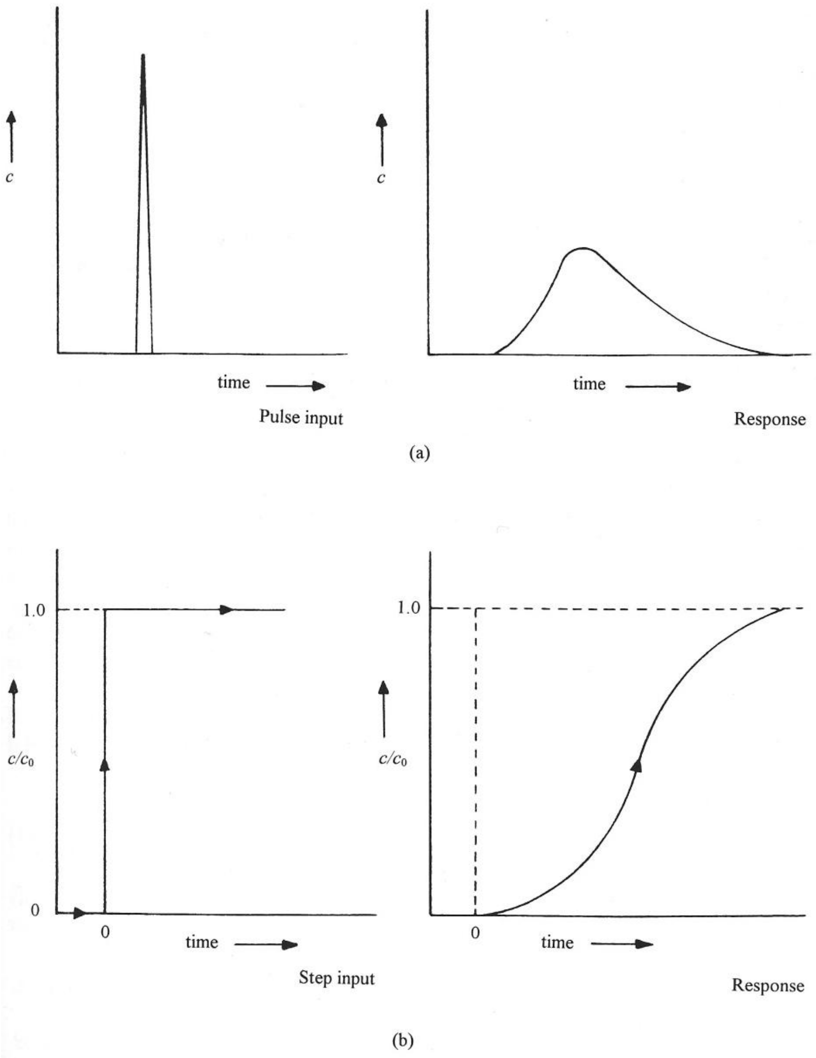
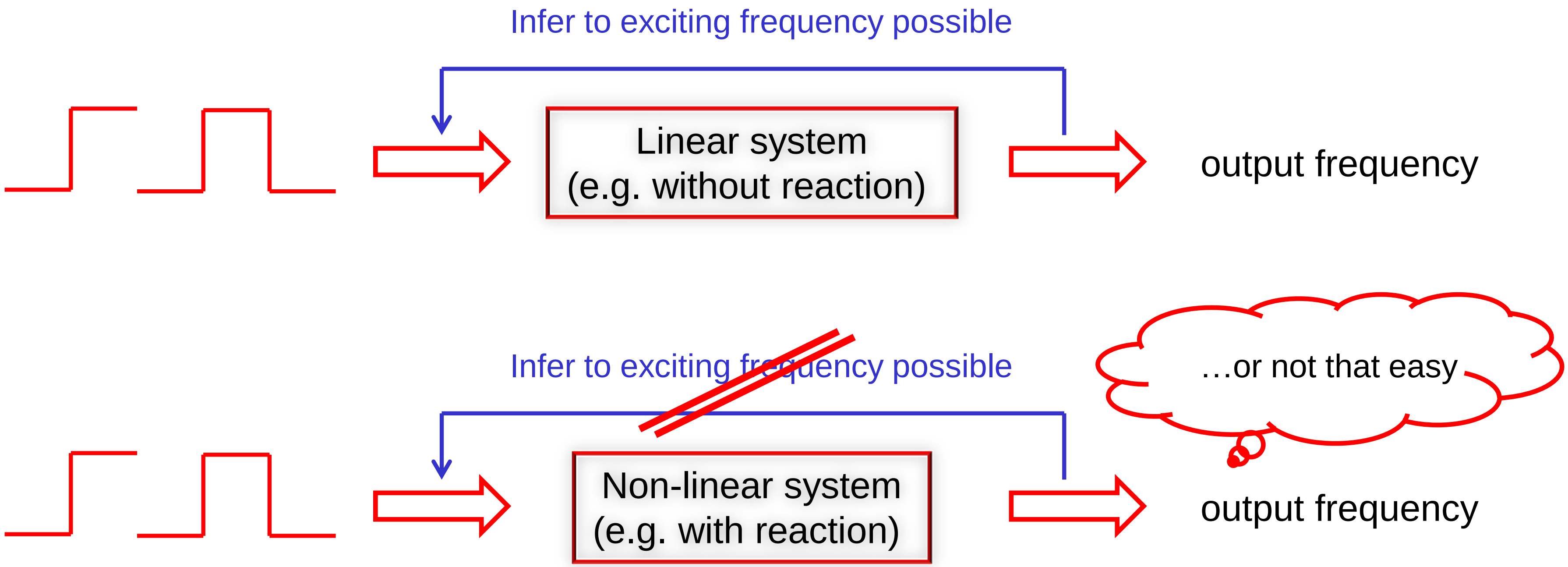


Figure 4.21 Response to a concentration change at the face of a porous pellet: (a) pulse input; (b) step input.

Signals

Interpretation of signals depends on *linearity* or *non-linearity* of the investigated system

! Variation in composition excites all frequencies of the system



Infer to exciting frequency possible

Linear system
(e.g. without reaction)

output frequency

Infer to exciting ~~frequency~~ possible

…or not that easy

Non-linear system
(e.g. with reaction)

output frequency

…chemical reactors without any reaction may be regarded as linear

Chemical Engineering Journal 82 (2001) 329–346

Frequency Response Method

Application background – sorption, diffusion

- Zeolites and microporous solids as *adsorbents* in *gas separation* processes
  - separation factors depend on differences in standard free energies of adsorption of the components
  - when sizes between adsorbates and channels are similar – diffusion also influences separation

- Commercial separation units contain pellets - + inert binder

→ *intercrystalline* and *intracrystalline diffusion* may be important

in combination with *adsorption*

Application background – sorption, diffusion

Methods for determination of inter- and intracrystalline diffusion

- Measure of uptake rates of an adsorbate molecule from the gas phase into the zeolite pellet

  ! often spurious diffusion coefficients because of complex interplay with heats of adsorption and bed-depth mass transport effects

- Several methods try to eliminate these problems:
  - Pulsed field gradient NMR
  - Tracer desorption NMR
  - Zero bed-depth chromatography
  - Single-crystal membrane
  - **Frequency response**
  - **TAP**

Frequency response

Provide opportunities to

- o determine *rate processes* within porous systems by measuring the pressure response of a closed system to a small fluctuation in its volume
- o obtain *kinetic parameters* for chemical reactions and adsorption-desorption steps on surfaces
- o measure *effective diffusivities* within microporous solids

Frequency response

Provide opportunities to

o study *coupled adsorption* and *diffusion* processes with different *characteristic time scales*

! These rate processes *cannot* be adequately *resolved by pulse*

or *step transient methods*, by *TPD* or by *elution chromatography.*

o determine *coupling* of adsorption and transport particularly for *high surface area materials*

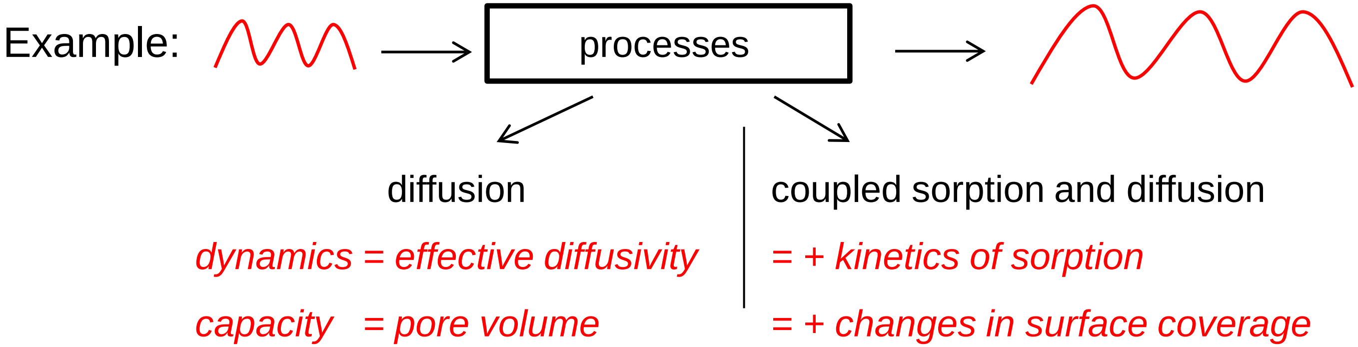
(number of exchanging molecules inside > number of exchanging molecules outside)

Frequency response

Principle

o FR exploits the *change* in *amplitude* and *phase* produced by a dynamic system that is pertubed periodically around its equilibrium point

o amplitude change (*attenuation*) and phase shift (*lag*) are *directly related* to the *dynamics and capacities* of the processes (sorption and diffusion) governing the return to the equilibrium



Example:

processes

diffusion

dynamics = effective diffusivity

capacity = pore volume

coupled sorption and diffusion

= + kinetics of sorption

= + changes in surface coverage

Frequency response

Graphical description of the frequency modulation approach

- at each *frequency* ω, the *system volume* is pertubed *sinusoidally* with *amplitude* v (solid line)
- *the system pressure* responds in a sinusoidal manner with a *fluctuation amplitude p* (dotted line)
- The fluctuation amplitude *p* is lower than ν and is *delayed* by an *angle* φ

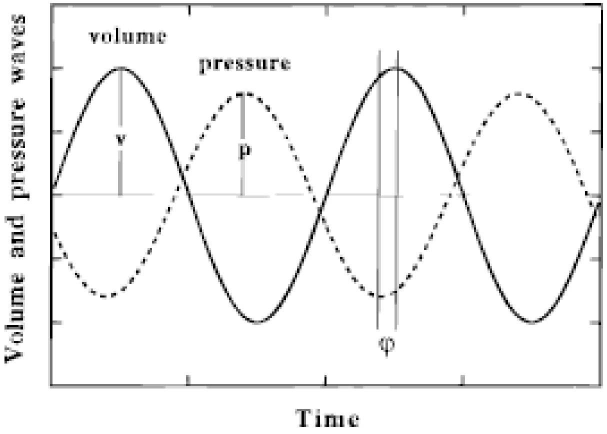


Figure 1. Input volume perturbation and output pressure response in frequency response experiments.

J. Phys. Chem. B **1997**, *101*, 614–622

Frequency response

Extraction of rate parameters

- capacities and dynamics of underlying processes are obtained by *fitting* of the *experimental transfer function* H(ν, *p*, φ*) to the* *theoretical transfer function* H(i ω)
- measured quantities ν, *p*, φ
- transfer function: analytical expression in frequency domain which contains parameters
- magnitude of function measures the ratio of the pressure response to the volume pertubation: $|H| = p/\nu$
- quantifies phase lag : $\varphi = \tan^{-1}$ […..]

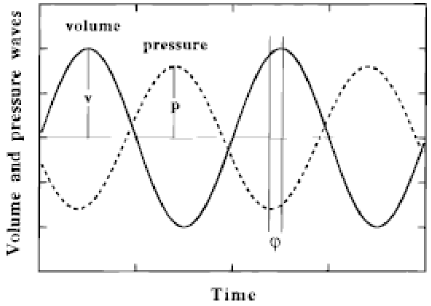


Figure 1. Input volume perturbation and output pressure response in frequency response experiments.

J. Phys. Chem. B **1997**, *101*, 614–622

Frequency response

Experimental apparatus

- Pertubation frequencies between 0.05 – 10 Hz
- System volume V = 141,91 cm^3 can be modulated by 1,38 % (ΔV = 1,96 cm^3)
- Modulation by metal bellow
- System volume at T = 223-400 K (pretreatment e.g. heating before experiment via resistive heating device)

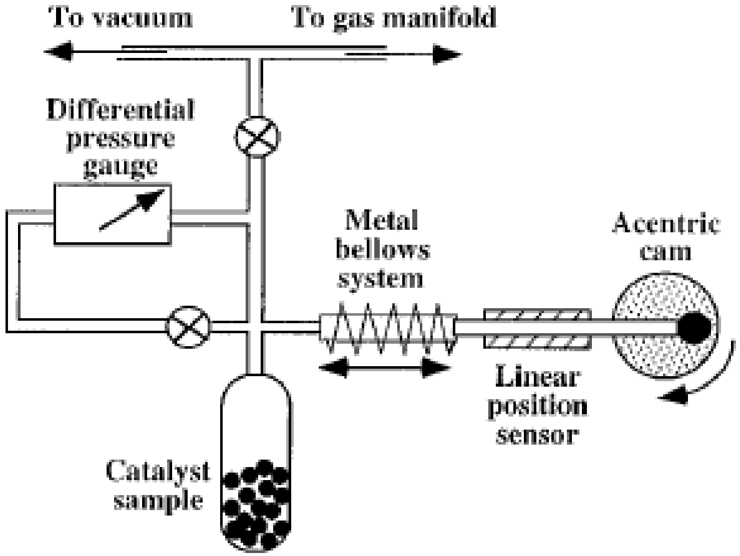


Figure 2. Schematic diagram of frequency response apparatus.

J. Phys. Chem. B **1997**, *101*, 614−622

Frequency response

Experimental apparatus

- geometry of system volume minimizes hydrodynamic delays that are not related to dynamics of intraparticle processes
- volume = sample cell, steel bellow and pressure gauge (MKS model 223 BD, 0-130 Pa)
- steel bellow driven by a rotary motor with an acentric cam
- dynamic system pressures of 10^{-9} Pa by pump system (turbo+mechanical)

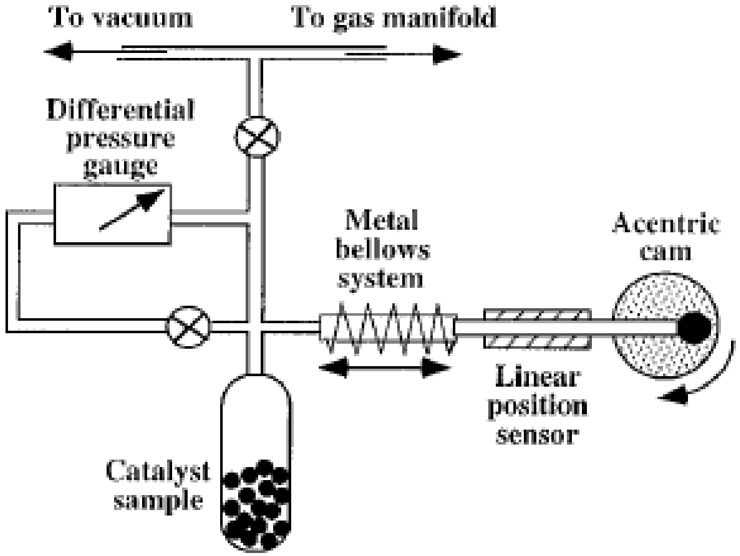


Figure 2. Schematic diagram of frequency response apparatus.

J. Phys. Chem. B **1997**, *101*, 614−622

Frequency response

Experimental apparatus

- position of bellow is determined by linear variable differential transformer
- Data aquisition: input voltage of motor, phase lags, amplitude attenuations
- Typical sample amount: mesoporous silica spheres (Shell S980B, 204 m^2/g) ≈ 16 g

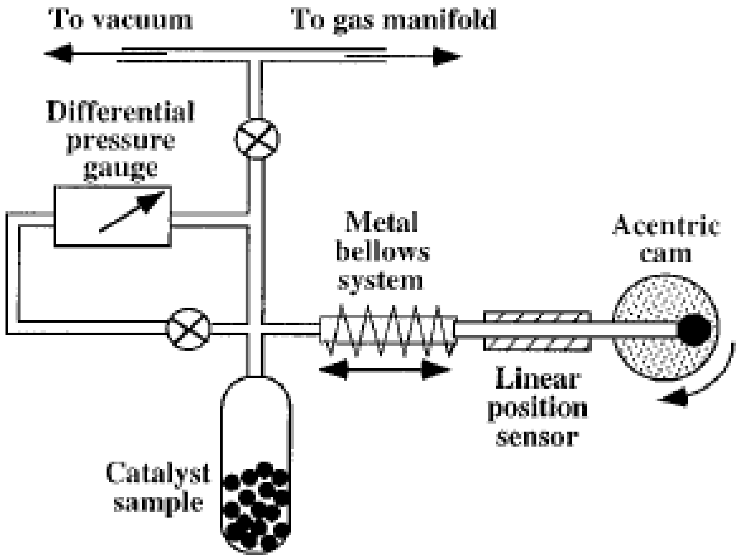


Figure 2. Schematic diagram of frequency response apparatus.

J. Phys. Chem. B **1997**, *101*, 614−622

Frequency response

Theoretical contributions

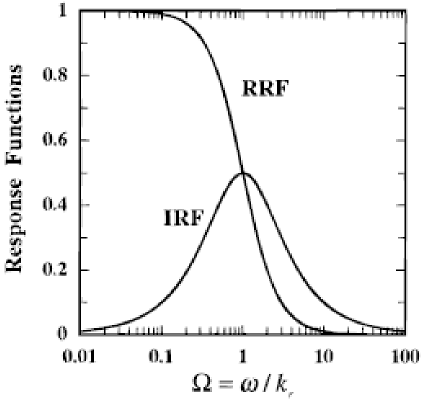
Adsorption

Diffusion

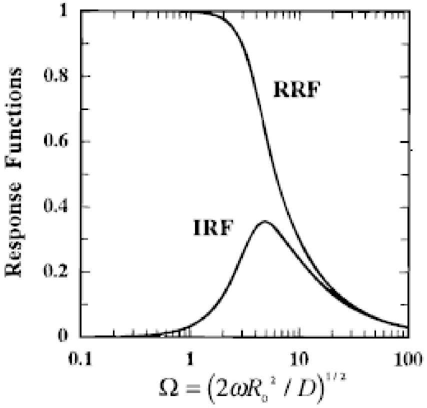
Adsorption and diffusion

- all responses can be divided into an *real* and an *imaginary* part
- real response function = RRF, imaginary response function = IRF

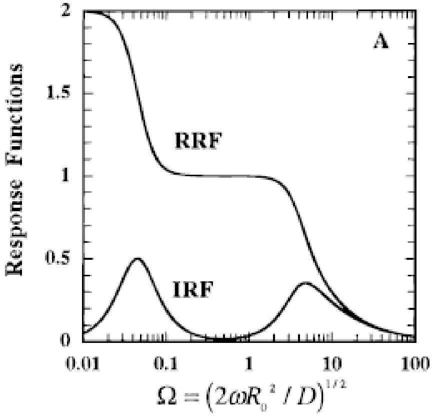
$$\mathrm{RRF} = \mathrm{Re}\left[\frac{1}{H(\mathrm{i}\omega)} - 1\right] \qquad \mathrm{IRF} = -\mathrm{Im}\left[\frac{1}{H(\mathrm{i}\omega)} - 1\right]$$



RRF and IRF components for adsorption processes



RRF and IRF components for diffusion processes



RRF and IRF components for coupled diffusion and adsorption processes

J. Phys. Chem. B **1997**, *101*, 614–622

Frequency response

Theoretical contributions

Adsorption

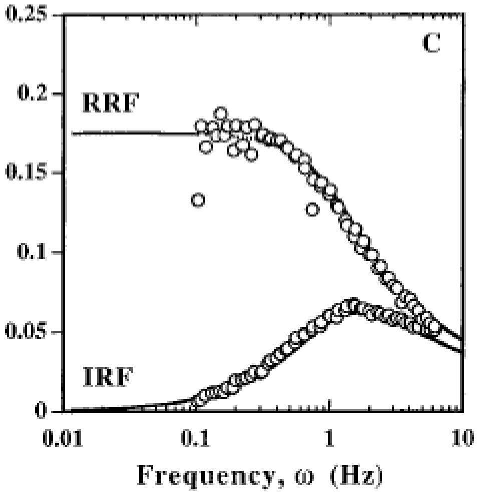
Diffusion

Adsorption and diffusion

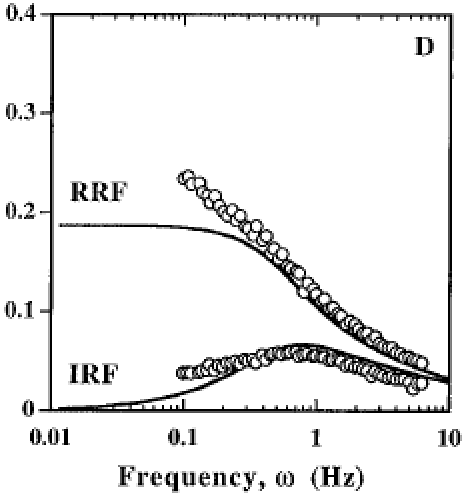
- all responses can be divided into a *real* and an *imaginary* part
- real response function = RRF, imaginary response function = IRF

Application to

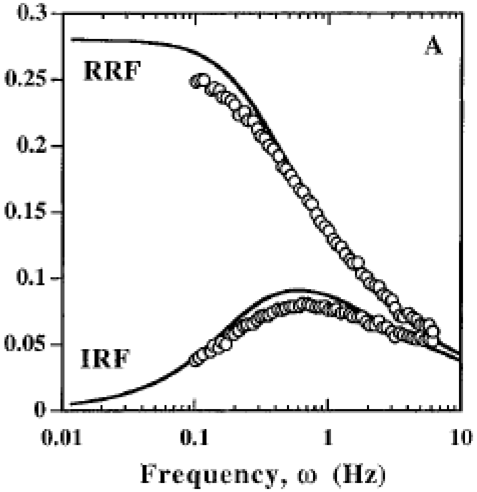
N_2,



Xe,



iso-butane



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Frequency response

Advantages

o FR allows to apply an *additional degree of freedom* in choosing frequencies to *decouple multiple dynamic processes*

o FR delivers a *high accuracy* in realizing a *smooth forcing function*

o FR is able to *conduct* experiments *at mean operating conditions*

o FR anaylsis is relatively *easy*

o FR enables to *discriminate* between *different rate-limiting steps*

o FR *weights* all parts of *response uniformly* (no error build up in data analysis)

Frequency response

Evaluation

o *Bode plot* is a graph of the transfer function of a linear, time-invariant system versus frequency, plotted with a *log-frequency axis*, to show the system's frequency response

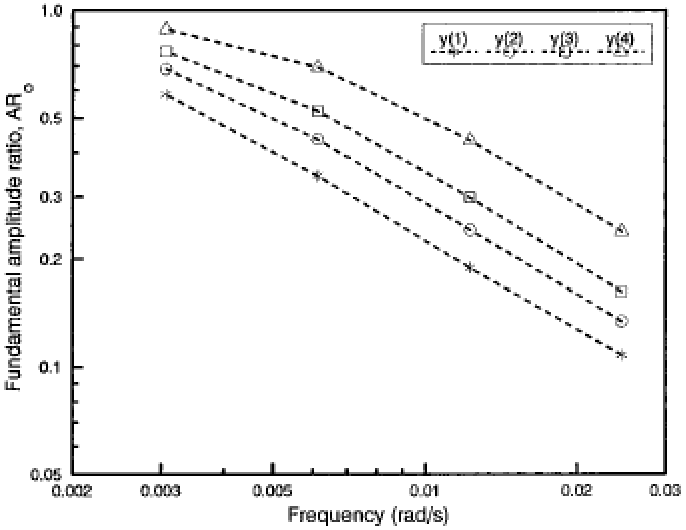


Figure 2. Bode plot for fundamental amplitude ratios.

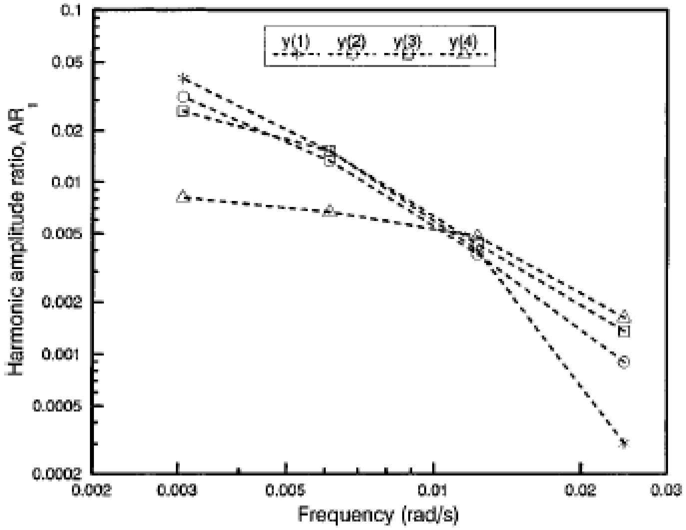


Figure 3. Bode plot for first harmonic amplitude ratios.

Ind. Eng. Chem. Res., Vol. 35, No. 4, 1996 **1477**

Anomalities in adsorption of hydrocarbons in zeolites

Anomalous adsorption properties can be attributed to *entropic* or *enthalpic* effects or combination of both effects

- ➢ to energetically heterogeneous adsorption sites
- ➢ to strong sorbate-sorbate interactions

How and when to realize such effects

→ like heterogeneity of sites?

- ➢ complex profiles of isosteric heat of adsorption in calorimetry
- ➢ computer simulations of adsorption complexes

→ sorbate-sorbate interactions

- ➢ more to consider for aromatics than for alkanes in zeolites
- ➢ will lead to redistribution and /or reorientation of sorbed molecules

Anomalities in diffusion of hydrocarbons in zeolites

Anomalous diffusion properties can be also attributed to *entropic* or *enthalpic* effects or combination of both effects and depend (next to T, p) on

- ➢ characteristics of sorbate
- ➢ structure of zeolite channel

How and when to realize such effects

→ characteristic of sorbate (channel)

- ➢ bimodal FR spectra for C_1-C_6 which results from dissipation of heat of adsorption between sorbent and surrounding
- ➢ at low loadings: pure single diffusion
- ➢ at high loadings: effect of heat of adsorption on diffusion
- ➢ chain-length dependence of intracrystalline diffusion coefficients
- ➢ Saturated cyclic hc diffuse more slowly than their aromatic equivalents

Anomalities in adsorption and diffusion of hydrocarbons in zeolites

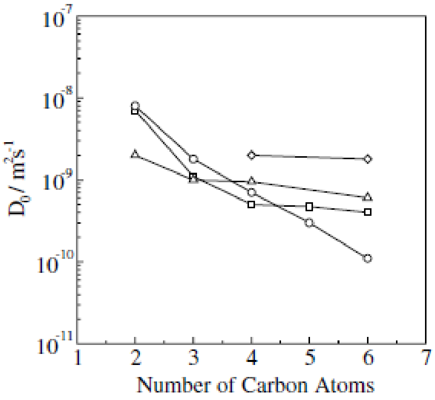
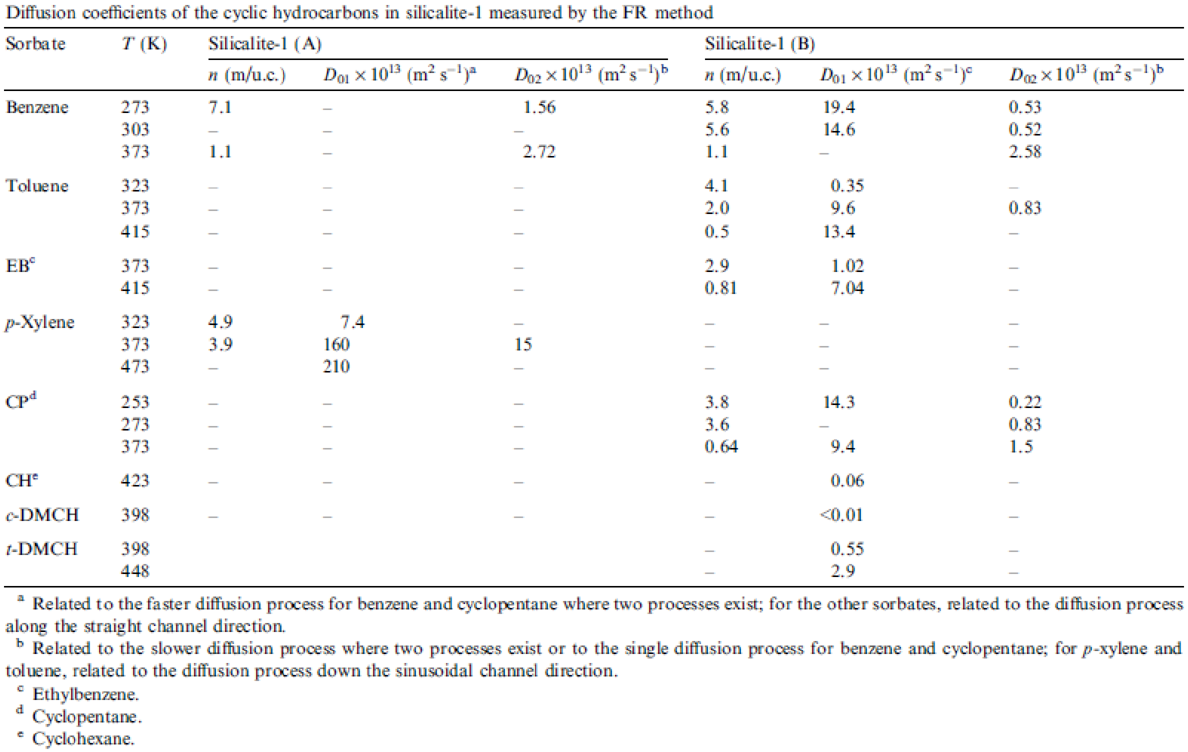


Fig. 9. Chain-length dependence of the self-diffusion coefficients of the *n*-alkanes in silicalite-1 at 303 K derived from the FR technique (—□—) compared with the results measured by PFG NMR [46] at 298 K (—○—), QENS [47] (—△—) and molecular dynamic calculations [45] (—◇—).



Diffusion coefficients of the cyclic hydrocarbons in silicalite-1 measured by the FR method

Sorbate	T (K)	Silicalite-1 (A)			Silicalite-1 (B)		
		n (m/u.c.)	$D_{01}\times10^{13}$ (m^2 s^{-1})[a]	$D_{02}\times10^{13}$ (m^2 s^{-1})[b]	n (m/u.c.)	$D_{01}\times10^{13}$ (m^2 s^{-1})[c]	$D_{02}\times10^{13}$ (m^2 s^{-1})[b]
Benzene	273	7.1	–	1.56	5.8	19.4	0.53
	303	–	–	–	5.6	14.6	0.52
	373	1.1	–	2.72	1.1	–	2.58
Toluene	323	–	–	–	4.1	0.35	–
	373	–	–	–	2.0	9.6	0.83
	415	–	–	–	0.5	13.4	–
EB[c]	373	–	–	–	2.9	1.02	–
	415	–	–	–	0.81	7.04	–
p-Xylene	323	4.9	7.4	–	–	–	–
	373	3.9	160	15	–	–	–
	473	–	210	–	–	–	–
CP[d]	253	–	–	–	3.8	14.3	0.22
	273	–	–	–	3.6	–	0.83
	373	–	–	–	0.64	9.4	1.5
CH[e]	423	–	–	–	–	0.06	–
c-DMCH	398	–	–	–	–	<0.01	–
t-DMCH	398				–	0.55	–
	448				–	2.9	–

[a] Related to the faster diffusion process for benzene and cyclopentane where two processes exist; for the other sorbates, related to the diffusion process along the straight channel direction.

[b] Related to the slower diffusion process where two processes exist or to the single diffusion process for benzene and cyclopentane; for *p*-xylene and toluene, related to the diffusion process down the sinusoidal channel direction.

[c] Ethylbenzene.

[d] Cyclopentane.

[e] Cyclohexane.

L. Song et al. / Microporous and Mesoporous Materials 104 (2007) 115–128

TAP – method and modeling

Unsteady-state experiments

- *Transient conditions* can be achieved by introducing different *input signals* into the reactor

  → variety of methods

  - variation of residence time τ
  - variation of temperature T
  - variation of feed composition c, p
  - combination of variation of τ, T, c or p

- *Changes in composition* show clearest deviation from steady-state – therefore used quite often

- Signals may be introduced as step or square wave

Steady-state and transient methods

Steady-state methods

- measure overall performance
- give integrated picture of reaction system
- have minimum reactor residence time of 1 s

Transient methods

- give information on individual steps
- operate in millisecond time regime; resolution increase

TAP – A transient technique

- The *key feature* which distinguishes it from other pulse experiments is that *no carrier gas* is used and, gas transport is the result of a pressure gradient.

- At low pulse intensities the total gas pressure is very small, and gas transport occurs via *Knudsen diffusion* only.

- Pulse residence time under vacuum conditions is much shorter than in conventional pulse experiments. Thus a *high time resolution* is achievable.

TAP – Features

- *Extraction of kinetic parameters* differs compared to steady-state and surface science experiments
  - Steady-state: kinetic information is extracted from the transport-kinetics data by experimentally eliminating effects of transport
  - Surface science: gas phase is eliminated
  - In *TAP* pulse experiments *gas transport is not eliminated*. The pulse response data provides in-formation on the transport and kinetic parameters.

TAP – Features

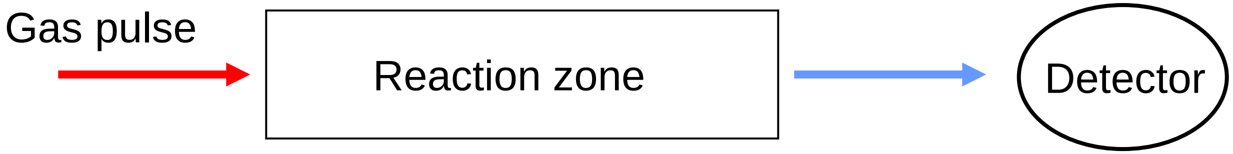
- *TAP pulse* experiments are *state-defining*
  - *Typical pulse* contains ≈ *10^{13} – 10^{14} molecules*

    or 10^{10} - 10^{9} moles
  - Example:

    - Sulfated zirconia: 100 m^2/g with 3 wt.% sulfur → $5*10^{18}$ S/m^2
    - 1 pulse of *n*-butane: $1*10^{14}$ molecules
    - per pulse 1/50000 of surface addressed

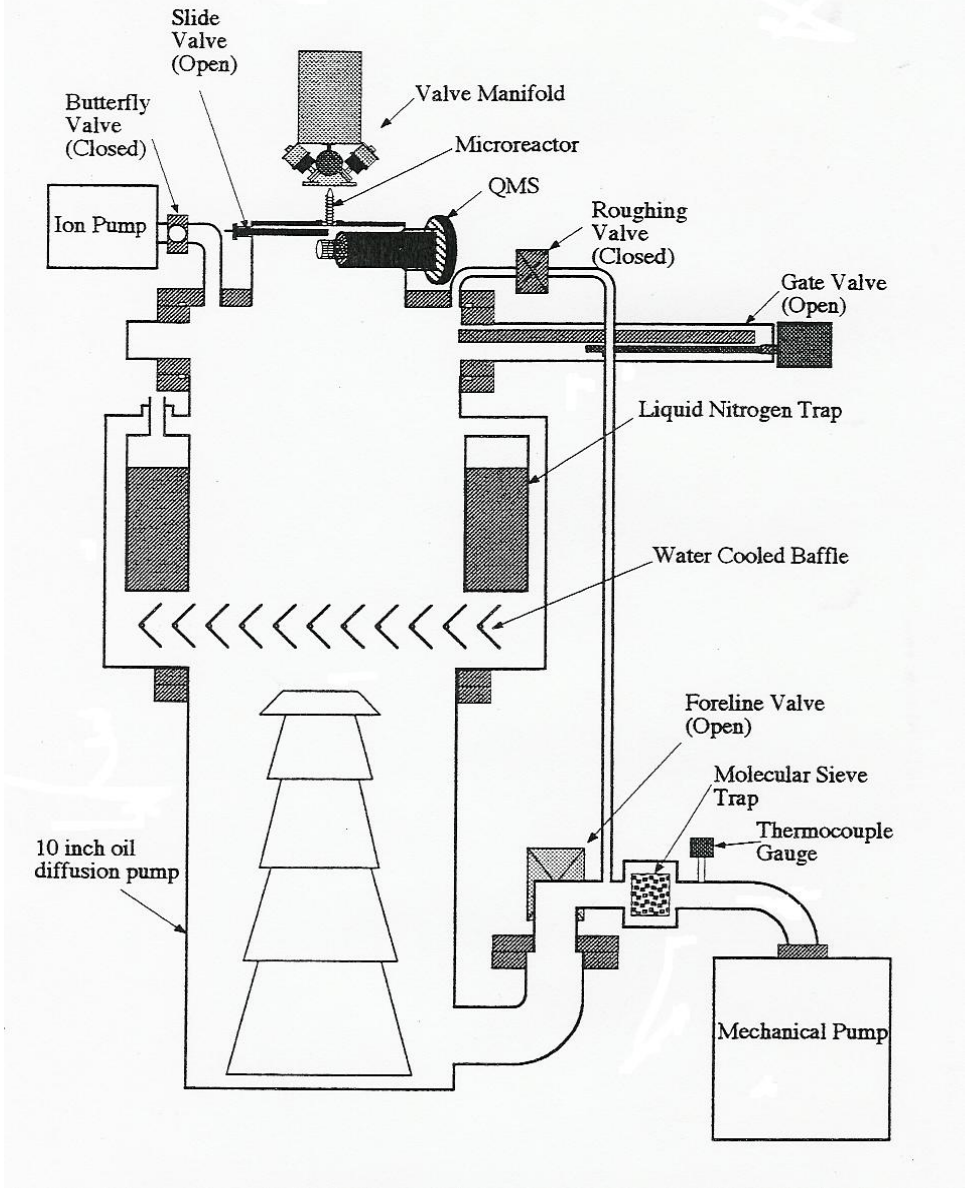
TAP – System hardware

Simplified schematic of a TAP pulse response experiment

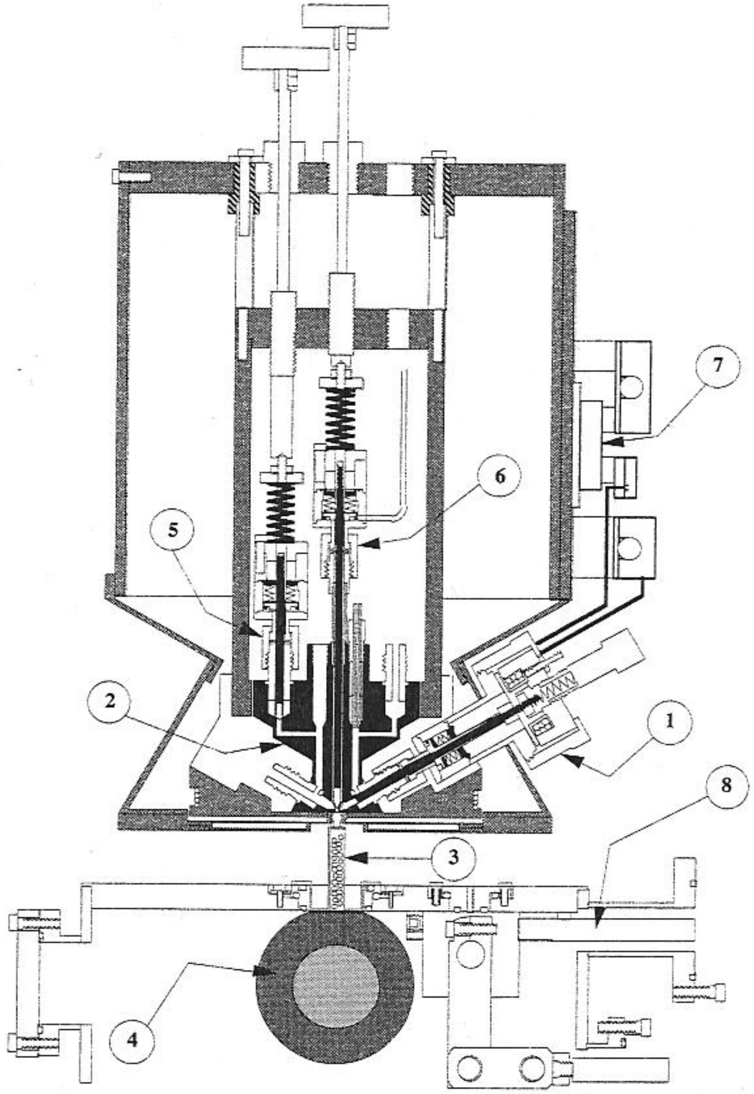


- Injection of a narrow gas pulse into an evacuated microreactor
- Gas pulses travel through the reactor
- Gas molecules (reactant and product) are monitored as a function of time and produce a transient response at the MS

TAP – System hardware



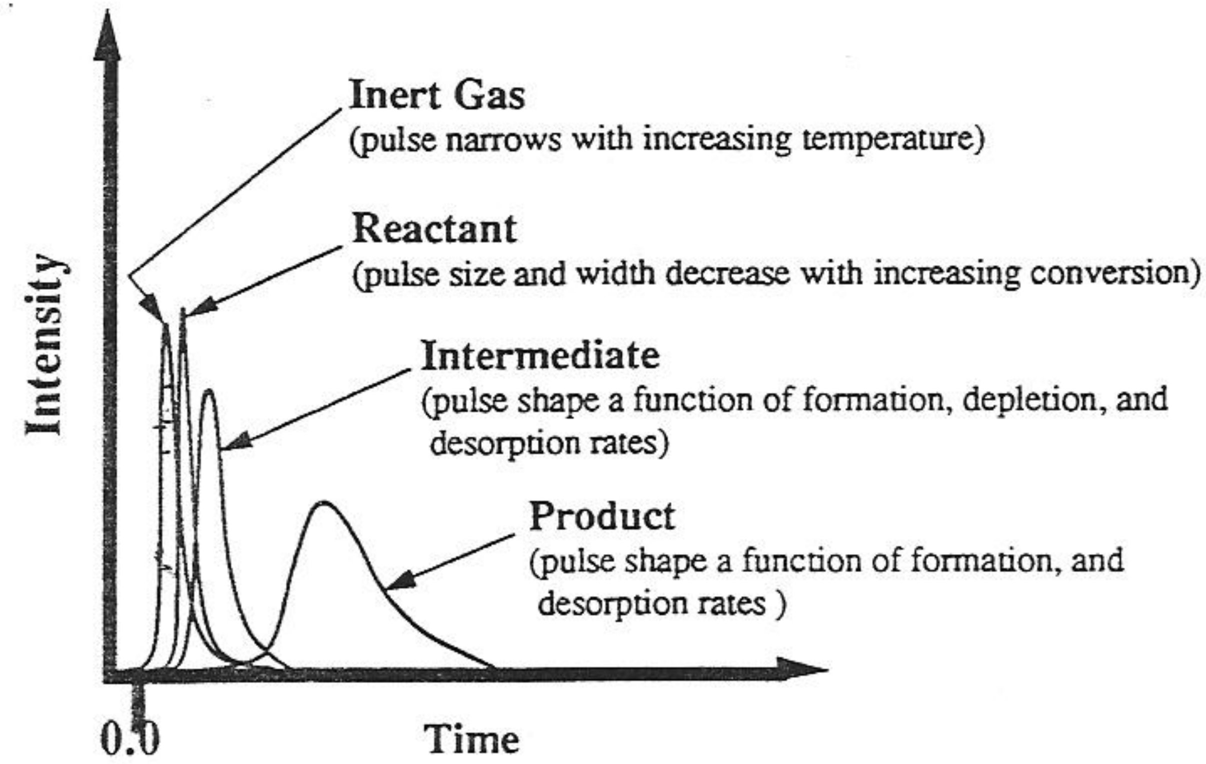
TAP – System hardware



1) High speed pulse valve
2) Pulse valve manifold
3) Microreactor
4) Mass spectrometer
5) Vacuum valve
6) Manual flow valve
7) Mosfet switch

TAP – Response curves

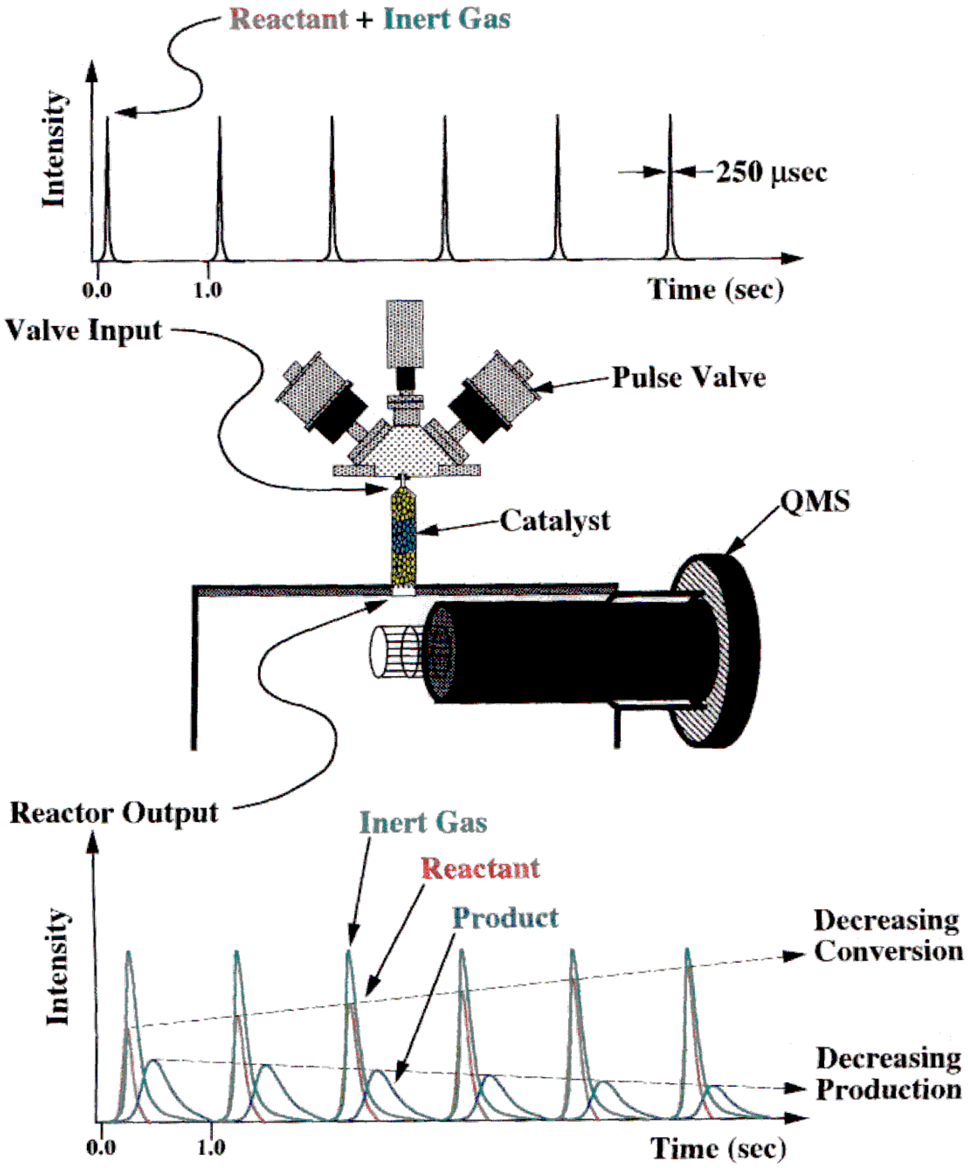
Characteristic pulse response experimental outputs



TAP – Multipulse experiment

- Key features of **input**:
  - typical pulse intensity range from 10^{13} to 10^{17} molecules/pulse
  - pulse width 150-250 µs
  - pulse rates 1-50 s^{-1}

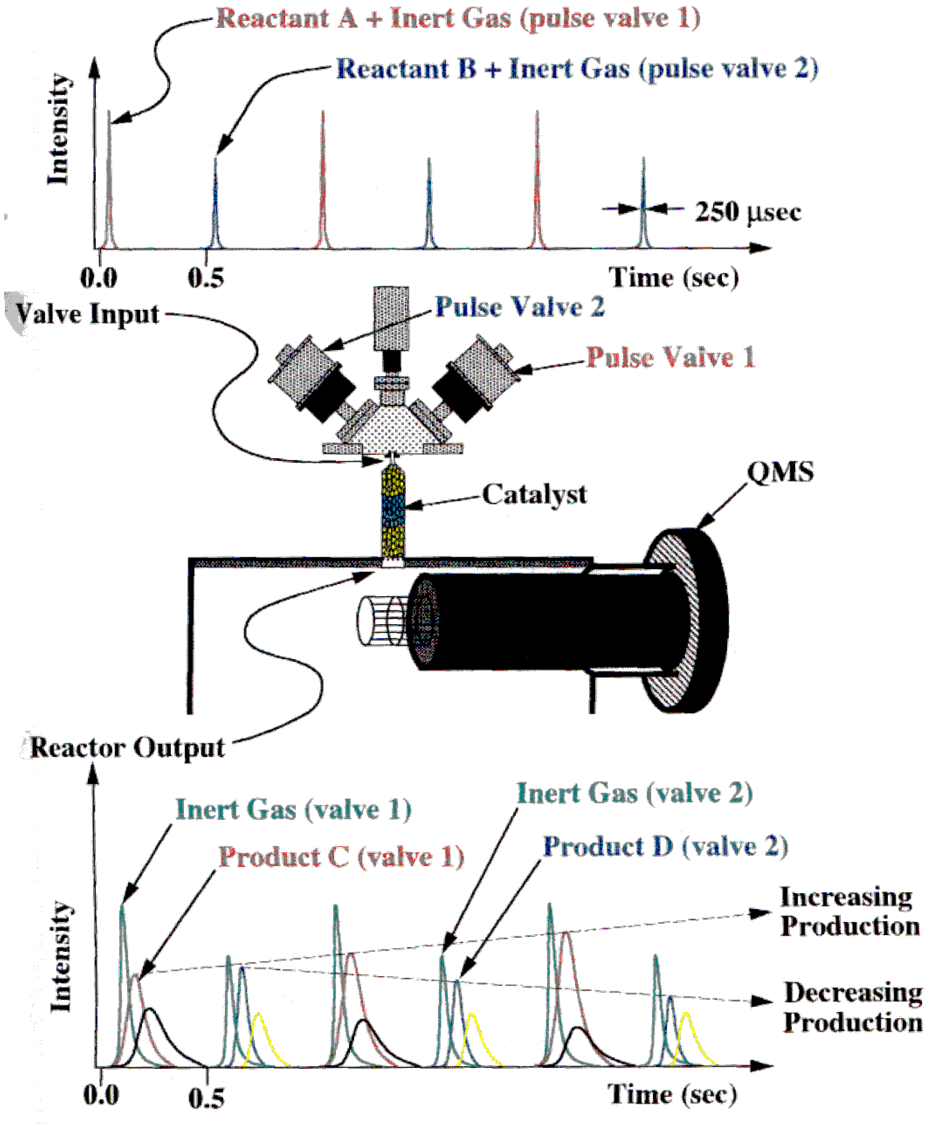
- Key features of **output**:
  - different products have different responses
  - individual product response can change with pulse number



TAP – Pump probe experiment

- Key features of **input**:
  - different reaction mixtures are introduced sequentially from separate pulse valves

- Key features of **output**:
  - output transient response spectrum coincides with both valve inputs



TAP – Transient response data

In contrast to traditional kinetic methods, that measure concentrations, the *observable quantity* in TAP pulse response experiments is the *time dependent gas flow* escaping from the outlet of the microreactor.

The outlet flow is measured with a *MS* (QMS) that detects individual components of the flow with great sensitivity.

The *composition* of the flow provides information on the types of *chemical transformation* in the microreactor.

The *time dependence* of the flow contains information on *gas transport* and *kinetics*.

TAP – Theory

Goal

- Interpretation of pulse response data
  - determine typical processes
  - find parameters for these processes
  - develop a model

- Analysis of experiments that provide parameters of diffusion, irreversible adsorption or reaction and reversible reaction

TAP – General models

The mathematical framework for the one-zone-model was first published in 1988 (Gleaves).

Basic *assumptions* of one-zone-model:

- catalyst and inert particle *bed is uniform*
- *no radial gradient* of *concentration* in the bed
- *no temperature gradient* (axial or radial)
- *diffusivity* of each gas is *constant*

TAP – Gas transport model

The gas transport is the result of Knudsen diffusion.

An important *characteristic* of this tranport process is that the *diffusivities* of the individual components of a gas mixture are *independent* of the *presssure* or the *composition* of the mixture.

$$\boxed{D_{e1}\frac{\sqrt{M_1}}{\sqrt{T_1}} = D_{e2}\frac{\sqrt{M_2}}{\sqrt{T_2}}}$$

$D_{e,i}$ …effective Knudsen diffusivity
M_i …molecular weight
T_i …temperature
1,2 …gas 1, gas 2

TAP – Transport model

(1) Diffusion only case –

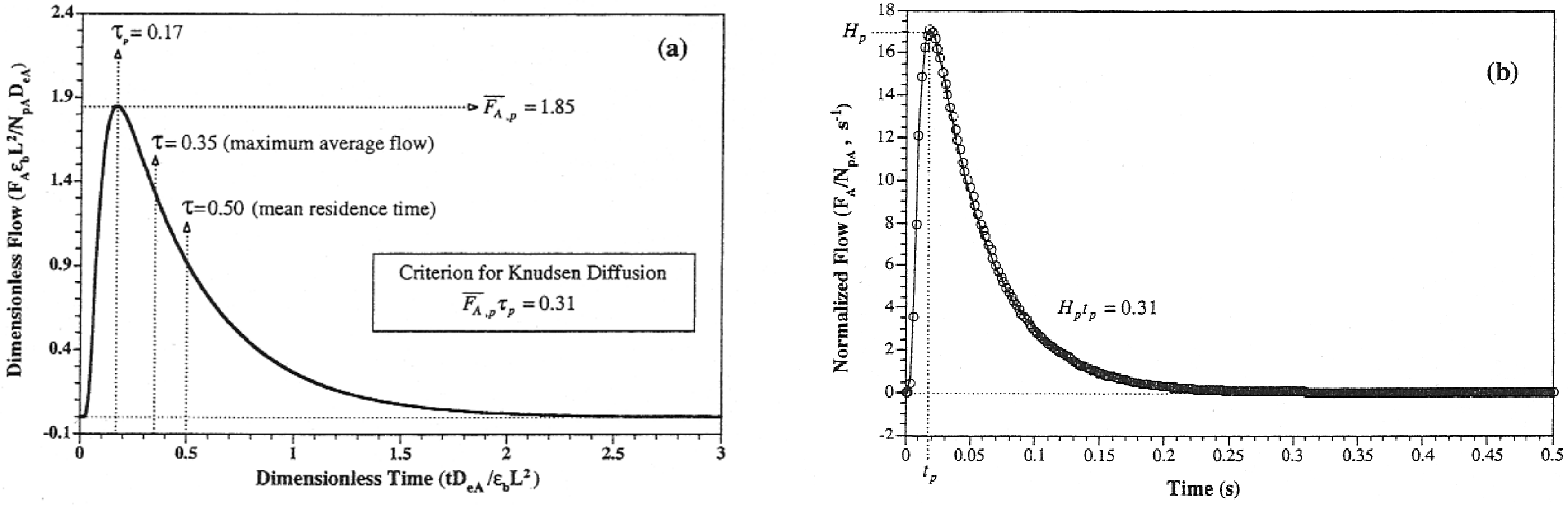
Mass balance for a non-reacting gas A transported by Knudsen diffusion

$$\boxed{\varepsilon_b \frac{\partial C_A}{\partial t} = D_{eA} \frac{\partial^2 C_A}{\partial z^2}}$$

C_A … concentration of gas A (mol/cm^3)
D_{eA} … effective Knudsen diffusivity of gas A (cm^2/s)
t … time (s)
z … axial coordinate (cm)
ε_b … fractional voidage of the packed bed in the reactor

TAP – Transport model

Characteristic fingerprints for response curves



a) Standard diffusion curve showing key time characteristics and the criterion for Knudsen diffusion

b) Comparison of standard curve with experimental inert gas curve over inert packed bed

TAP – Transport + adsorption model

(2) Diffusion + irreversible adsorption

(adsorption is first order in gas concentration)

$$\boxed{\varepsilon_b \frac{\partial C_A}{\partial t} = D_{eA} \frac{\partial^2 C_A}{\partial z^2} - a_s\, S_v\, (1-\varepsilon_b)\, k_a\, C_A} \qquad \boxed{\frac{\partial \theta_A}{\partial t} = k_a\, C_A}$$

a_s … surface concentration of active sites (mol/cm^2 of catalyst)

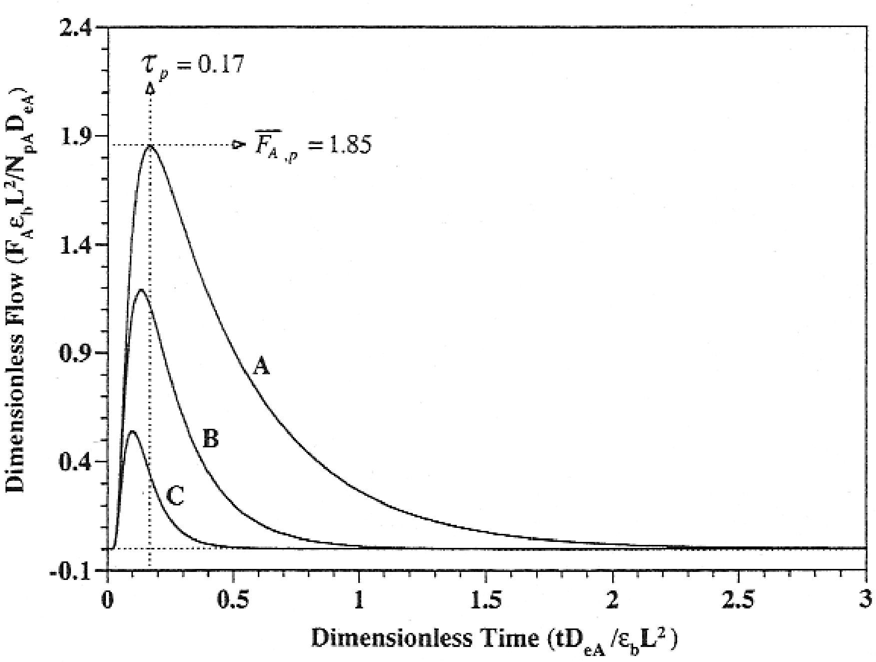
k_a … adsorption rate constant (cm^3 of gas/mol s)

S_v … surface area of catalyst per volume of catalyst (cm^{-1})

θ_A … fractional surface coverage of A

TAP - Transport + adsorption model

Exit flow curve for the diffusion+irreversible adsorption case



Comparison of irreversible adsorption curves
with standard diffusion curve
(A) k_a=0 (SDC), (B) k_a=3 (C) k_a=10

TAP – Transport and adsorption model

(3) Diffusion + reversible adsorption

Mass balances

- for component A in gas phase

$$\boxed{\varepsilon_b \frac{\partial C_A}{\partial t} = D_{eA} \frac{\partial^2 C_A}{\partial z^2} - a_s S_v (1-\varepsilon_b)(k_a C_A - k_d \theta_A)}$$

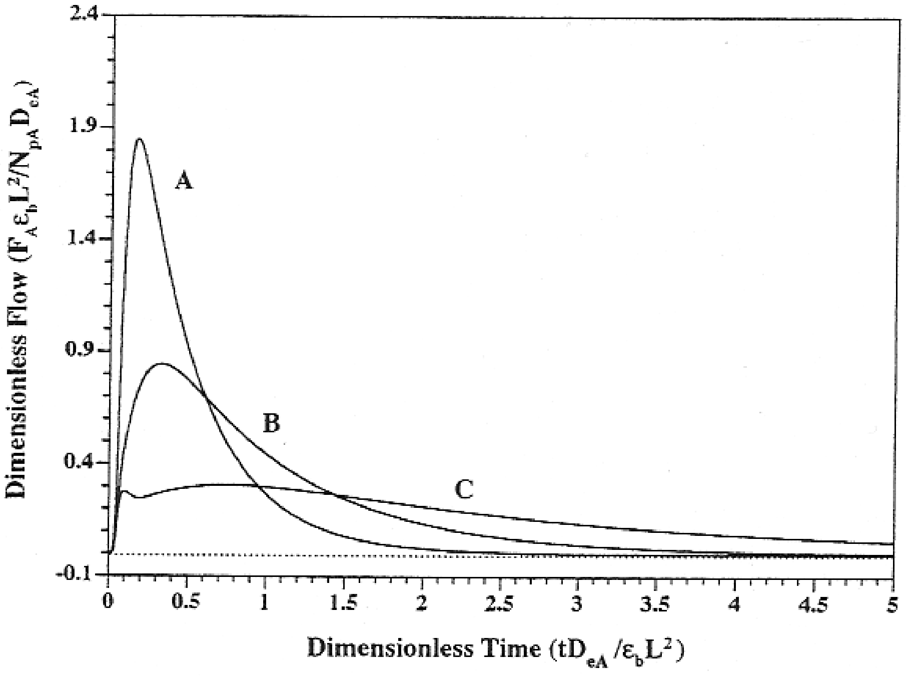
- for component A on the catalyst surface

$$\boxed{\frac{\partial \theta_A}{\partial t} = k_a C_A - k_d \theta_A}$$

k_d …desorption rate constant (s^{-1})

TAP - Transport + adsorption model

Exit flow curve for the diffusion+reversible adsorption case



Comparison of reversible adsorption curves with standard diffusion curve
(A) k_a=0 (SDC), (B) k_a=20, k_d=20, (C) k_a=20, k_d=5

Applications

Sulfated zirconias - catalysts and porous model systems

A transient TAP study of the adsorption of C4-hydrocarbons on sulfated zirconias
C. Breitkopf. *J. Mol. Catal. A: Chem.* *226* *(2005) 269.*

Improvement of the catalytic isomerization performance for sulfated zirconias by use of templating techniques
M. Lutecki, C. Breitkopf, *Appl. Catal. A: General (2009), 352(1-2), 171-178.*

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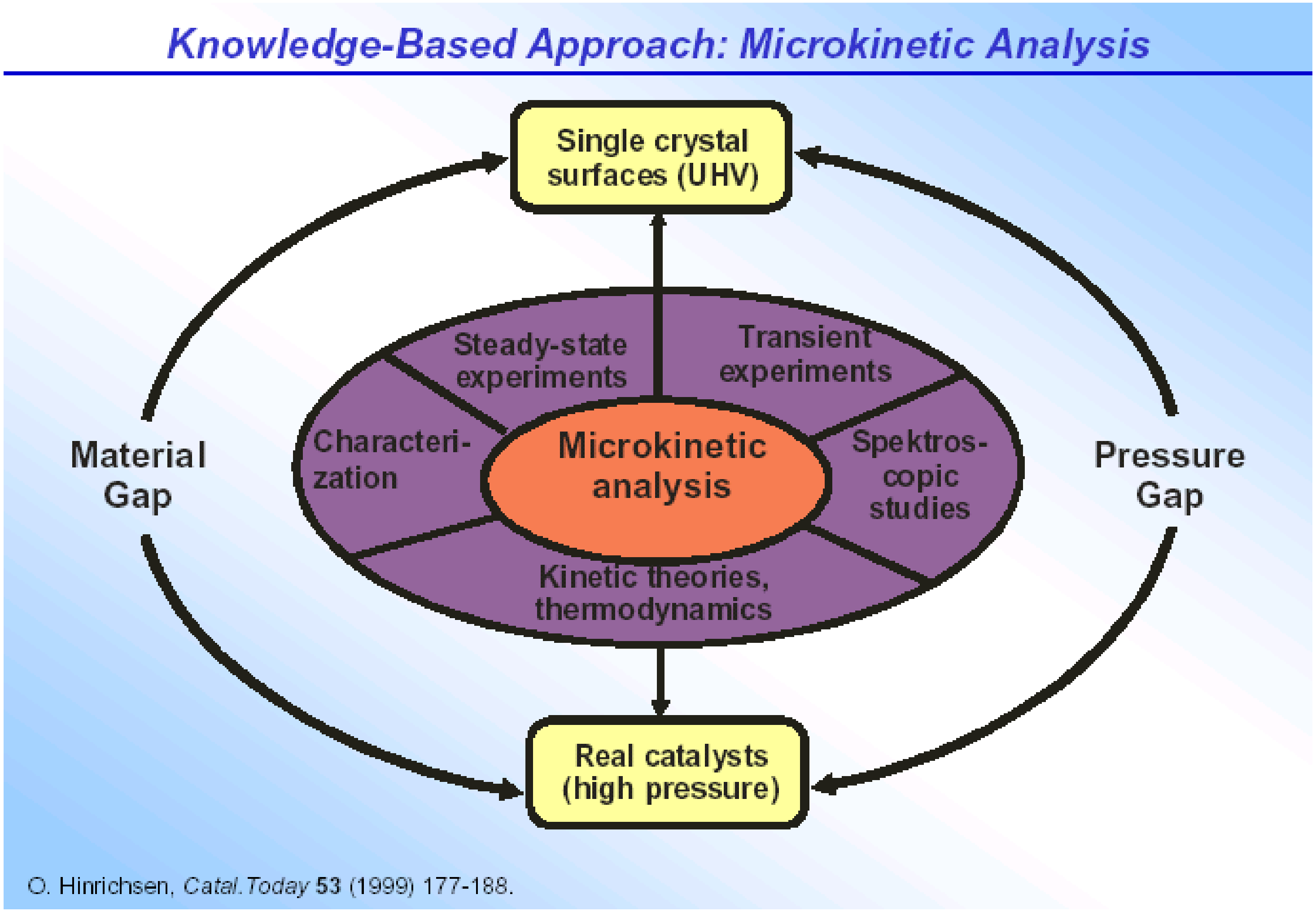
Matthias Galinsky, Michal Lutecki; Jürgen Böhm; Helmut Papp; Cornelia Breitkopf
accepted for publication in Chem. Eng. Sci.

Kinetic modeling



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Thank you for your attention!

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Frequency Response

Chemical Engineering Journal 82 (2001) 329–346	Modeling of microkinetics in heterogeneous catalysis by means of frequency response techniques
Microporous and Mesoporous Materials 104 (2007) 115–128	Adsorption and diffusion properties of hydrocarbons in zeolites
IEEE TRANSACTIONS ON INSTRUMENTATION AND MEASUREMENT, VOL. 60, NO. 1, JANUARY 2011	Improved Variance Estimates of FRF Measurements in the Presence of Nonlinear Distortions Via Overlap
J. Phys. Chem. B **2005,** *109,* 2421−2431	**Frequency Response Study of the Dynamics of the Platinum Catalyzed Interconversion of Methylcyclohexane, Toluene, and Hydrogen near Equilibrium**[†]
Applied Surface Science 253 (2007) 8802–8809	A frequency response study of thiophene adsorption in zeolite catalysts
Ind. Eng. Chem. Res. **1996,** *35,* 1475−1479	**Nonlinear Sorption Isotherm of Zeolites by Frequency Response Analysis**
J. Phys. Chem. C **2009,** *113,* 20435–20444	**Comparison of the Transport of Aromatic Compounds in Small and Large MFI Particles**
J. Phys. Chem. B **2005,** *109,* 2421−2431	**Frequency Response Study of the Dynamics of the Platinum Catalyzed Interconversion of Methylcyclohexane, Toluene, and Hydrogen near Equilibrium**[†]
The Journal of Physical Chemistry, Vol. 80, No. 17, 1976	**Frequency Response Method for Study of the Kinetic Behavior of a Gas–Surface System. 1. Theoretical Treatment**

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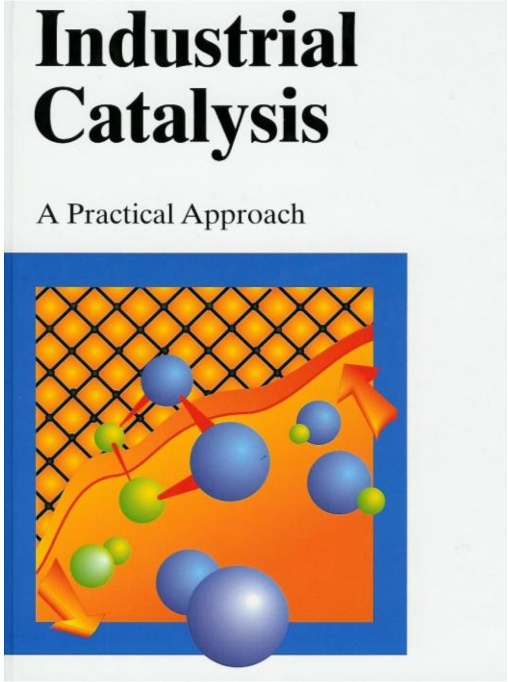
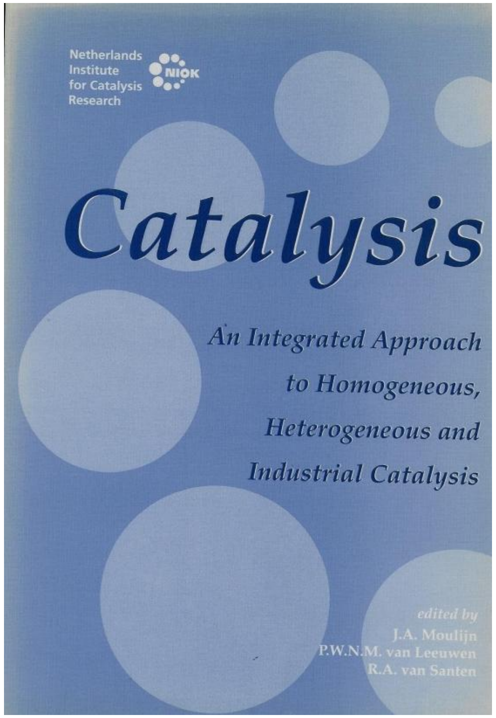
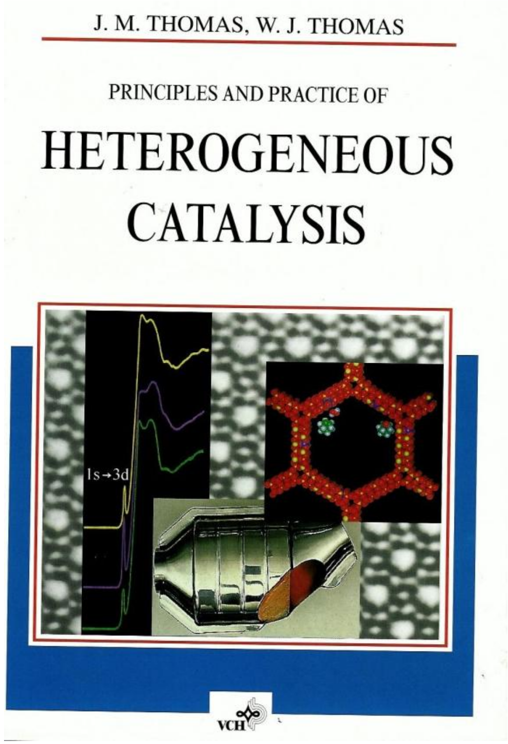
…continued

Jens Hagen







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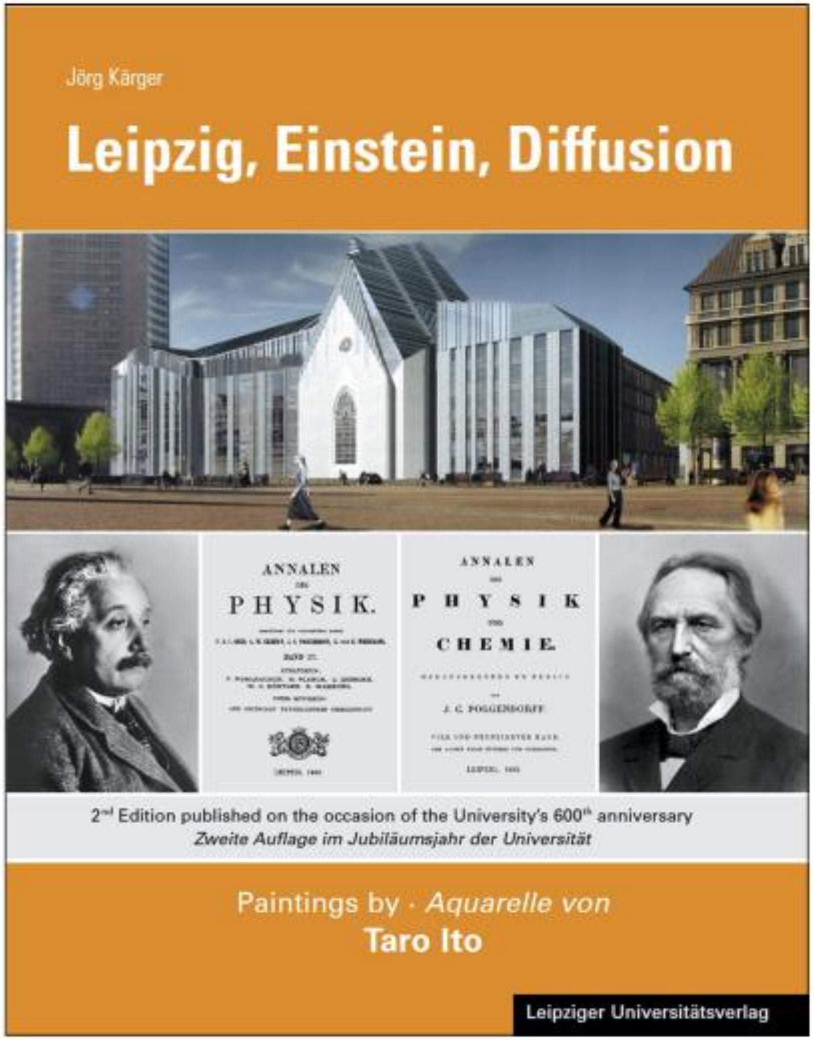

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Leipzig, Einstein, Diffusion

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