Institut für Energietechnik

Lecture Series at Fritz-Haber-Institute Berlin
„Modern Methods in Heterogeneous Catalysis“
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Transient methods for the determination of transport and adsorption phenomena

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Transient methods are a powerful tool for gaining insights into the mechanisms of complex catalytic reactions.

Transient view to processes needed

Transient behaviour of chemical processes is subject of interest

- *Optimization of plant processes*

  Plants are sometimes operated under *non-stationary conditions* (e.g. start-up, shut-down, switch between stationary states).

  Overall *economics* may be improved by proper control of these non-stationary processes.

  Product losses or switching times should be minimized.

- *Safety analysis*

  Modern *safety analysis* requires full control of all processes including the behaviour during *technical faults*.

  A *reliable procedure* to eliminate an insafe processe is necessary.

Chemical Engineering Journal 82 (2001) 329–346

Transient view to processes needed

Experiments under dynamic conditions can give important additional insights into the reaction mechanism.

- *Deduction* of *overall reaction kinetics* from mechanism and kinetic expressions of elementary steps is possible, inverse problem not
- *Impossible* (at present state) to *determine reaction mechanism* and intermediate species on the catalyst surface *from* the *gas composition in* the *reactor*

Problems may be solved by

Determination of intermediates to reveal as much as possible of data to support mechanistic discussion

- TAP, FR
- In situ spectroscopy

Approximation of real mechanism by idealized model mechanisms
(! Limits)

- Inhomogeneous modeling of surface sites necessary
- Microkinetic modeling

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 desroption NMR
  - Zero bed-depth chromatography
  - Single-crystal membrane
  - **Frequency response**
  - **TAP**

What we will speak about today?

- ☐ *Introduction to macro- and microkinetics*
- ☐ *Steady-state and unsteady-state experiments*
- ☐ *General aspects of pulse methods (adsorption and diffusion)*
- ☐ *Frequency Response approach*
- ☐ *Temporal Analysis of Products*

Macrokinetics and Microkinetics

Complexity of Macro- and Microworld

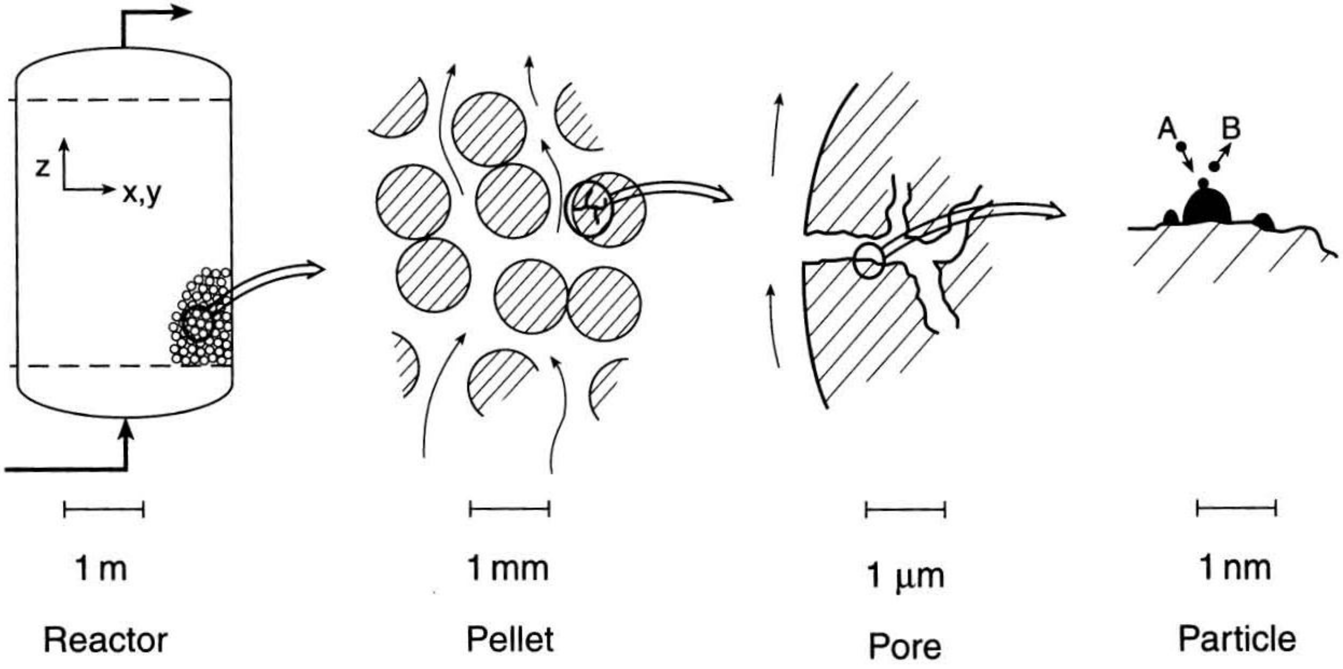
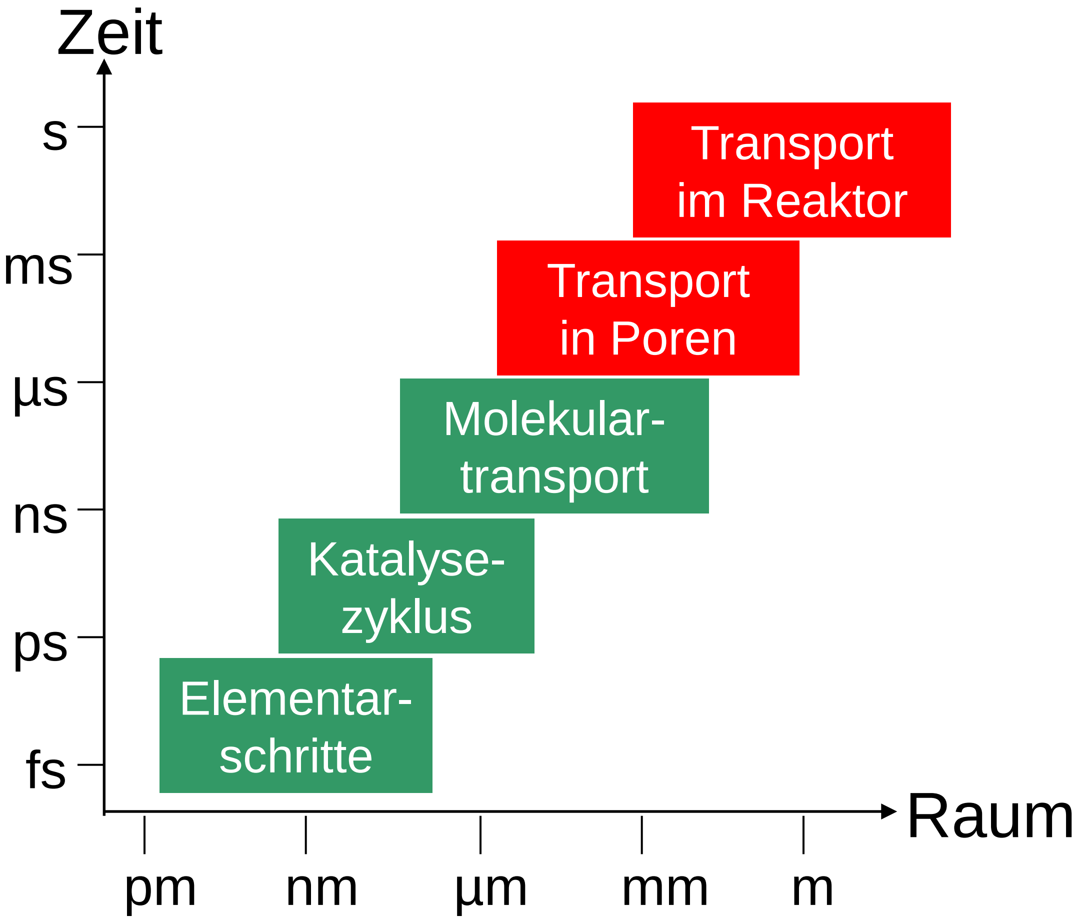


Figure 7–6 Different size scales in a packed bed catalytic reactor. We must consider the position *z* in the bed, the flow around catalyst pellets, diffusion within pores of pellets, and adsorption and reaction on reaction sites. These span distance scales from meters to Angstroms.

Complexity of Macro- and Microworld



Transport im Reaktor

Transport in Poren

Molekular-transport

Katalyse-zyklus

Elementar-schritte

multidimensional space-time problem

simultaneous knowledge of ***ADSORPTION and DIFFUSION*** -
is necessary to describe complex processes

Macrokinetics and Microkinetics

1) Diffusion of the starting materials through the boundary layer to the catalyst surface.
2) Diffusion of the starting materials into the pores (pore diffusion).
3) Adsorption of the reactants on the inner surface of the pores.
4) Chemical reaction on the catalyst surface.
5) Desorption of the products from the catalyst surface.
6) Diffusion of the products out of the pores.
7) Diffusion of the products away from the catalyst through the boundary layer and into the gas phase.

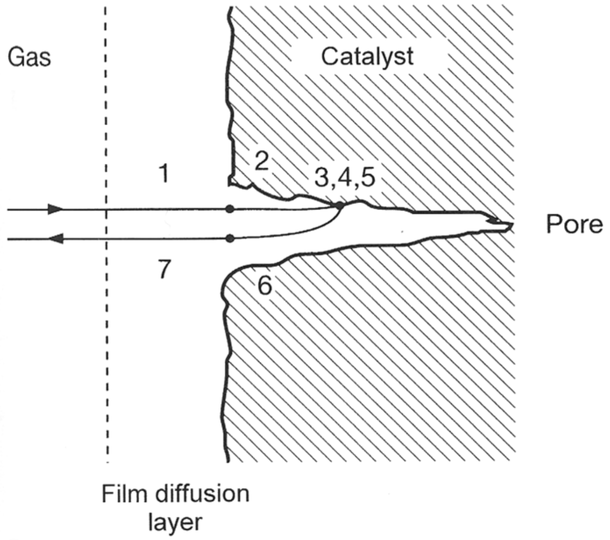
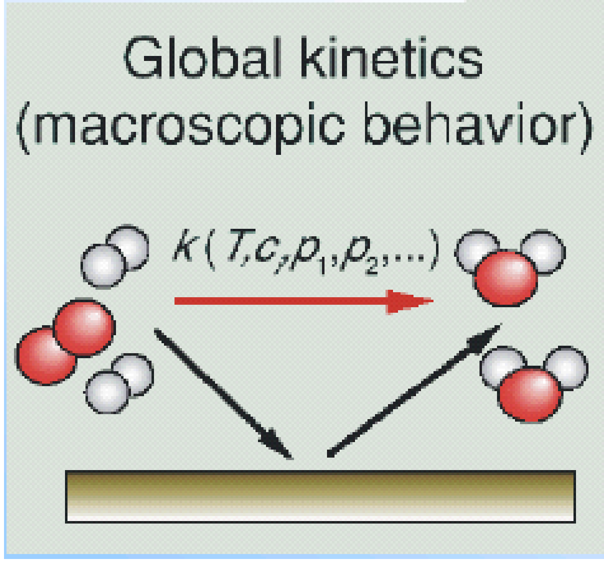
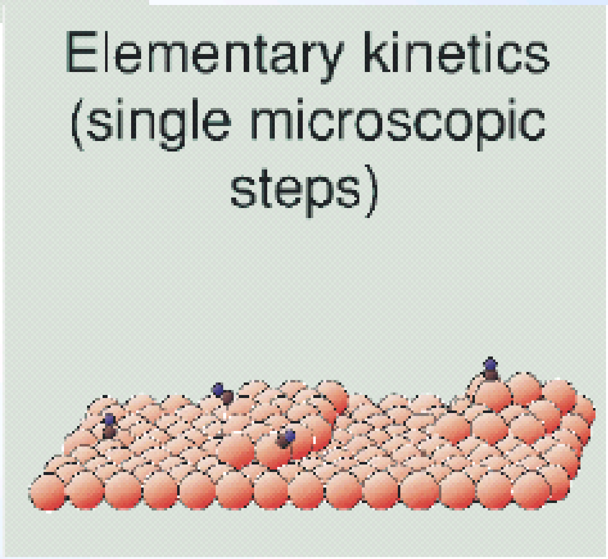


Fig. 4-1. Individual steps of a heterogeneously catalyzed gas-phase reaction

Kinetic measurements

Complexity of heterogeneously catalyzed reactions –
Macrokinetics and Microkinetics





O. Deutschmann, XXXIV. Jahrestreffen Deutscher Katalytiker/ Fachtreffen Reaktionstechnik, Weimar 21.-23.3.2001

Kinetic measurements in practise

Tasks of lab investigations

- o catalyst preparation
- o catalyst screening
  - o activity
  - o selectivity
  - o stability
- o scale-up
- o process optimization

Laboratory reactors

- o microcatalytic pulse reactor
- o gaschromatographic reactor
- o single pellet diffusion reactor
- o catalytic fixed bed reactor
- o recycle reactor
- o *TAP*

Method

- ○ Frequency Response

Steady-state and unsteady-state experiments

Kinetic investigations

Evaluation of the reaction mechanism

Constructing of a mathematical model

Parameter estimation

How to do…?

- Steady-state or unsteady-state experiment ?
- Quantitative evaluation of kinetic data ?

Steady-state experiments

- Most common reaction technique used in heterogeneous catalysis

- Achieved by operation such that *temperature*, *pressure*, *concentration*, and *flow rate* at any point in the reactor are *time invariant*

- Access to activity, selectivity, reaction order, activation energy

Steady-state experiments

- Advantages:
  - Easy to build and operate
  - Results can be described with mathematical models based on algebraic equations
  - Most industrial processes are operated under steady-state conditions

- Disadvantages:
  - Provide global kinetic parameters, limited information on individual reaction steps
  - Interpretations often based on „simple“ assumptions

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

Unsteady-state experiments

- Transient techniques provide information on
  - *Reaction intermediates* (pulse response) (Gleaves 1988)
  - Reaction *sequences* in a multistep reaction (Kobayashi 1975)
  - *Rate* constants of *elementary steps* (Ertl 1979, Creten 1995)
  - *Complex kinetic phenomena* (oscillating chemical reactions, hysteresis) that are *not observable under steady-state* conditions
  - Catalyst *surfaces* that are not easily observed under steady-state conditions (oxidation catalysis) (Haber 1983)

Unsteady-state experiments

- Disadvantages
  - Not easy to build up, expensive
  - Main problem: *theory is very complex*

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

General aspects of pulse methods (adsorption and diffusion)

Pulse methods

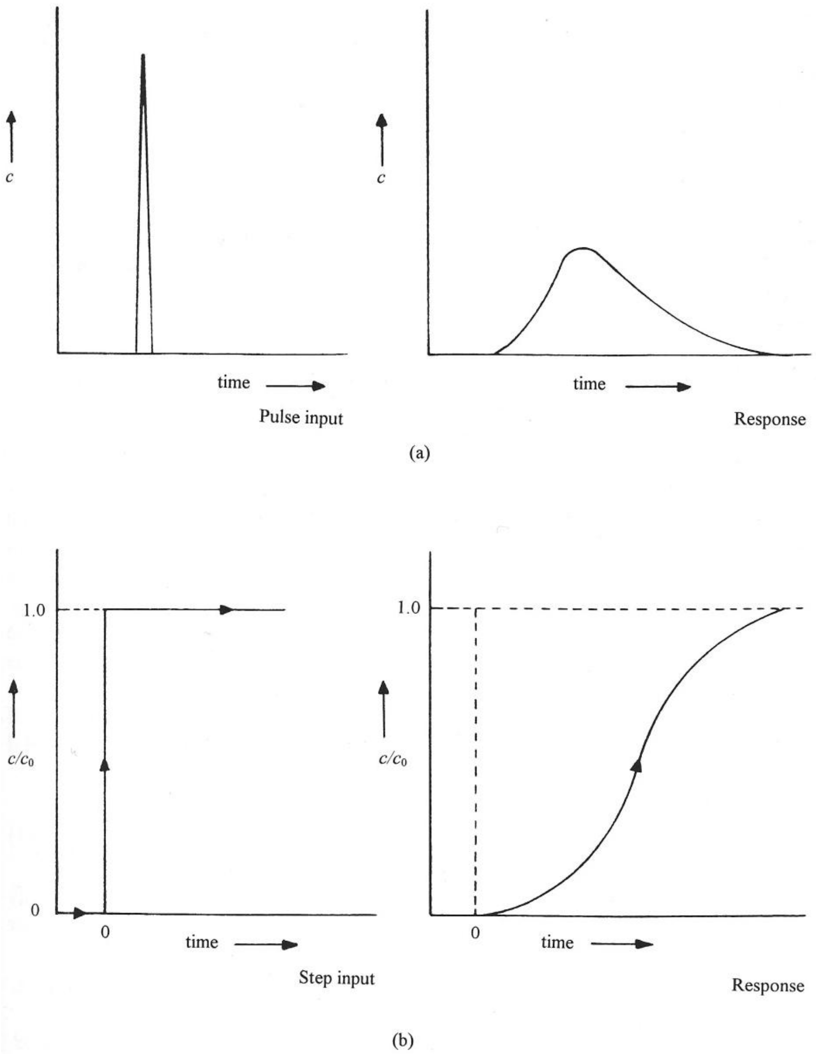


Figure 4.21 Response to a concentration change at the face of a porous pellet: (a) pulse input; (b) step input.

Pulse methods

- response to *pertubations* → describe mathematically the transient behaviour

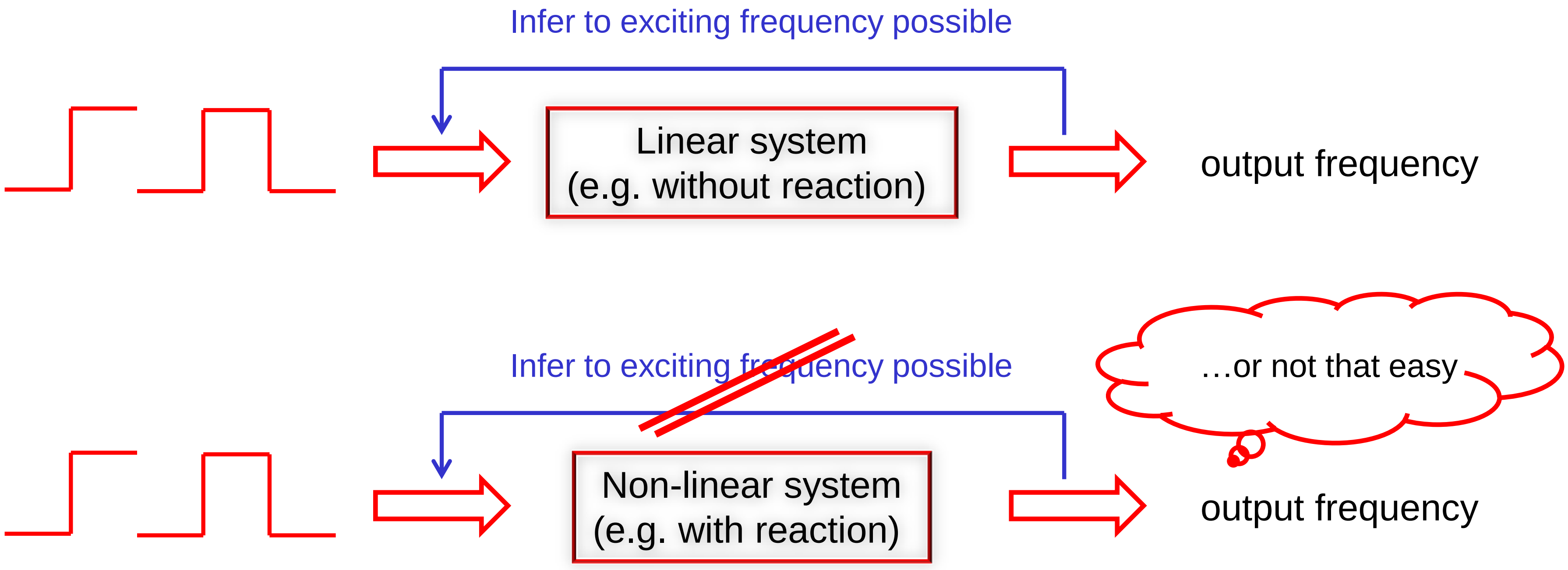
- evaluation of rate parameters from response measurements such as mass transfer coefficients, diffusivities, and chemical kinetic constants

- use of: - fixed-bed (column) chromatography
  - isotope technique
  - slurry adsorber
  - single-pellet

Signals

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

! Variation in composition exites 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

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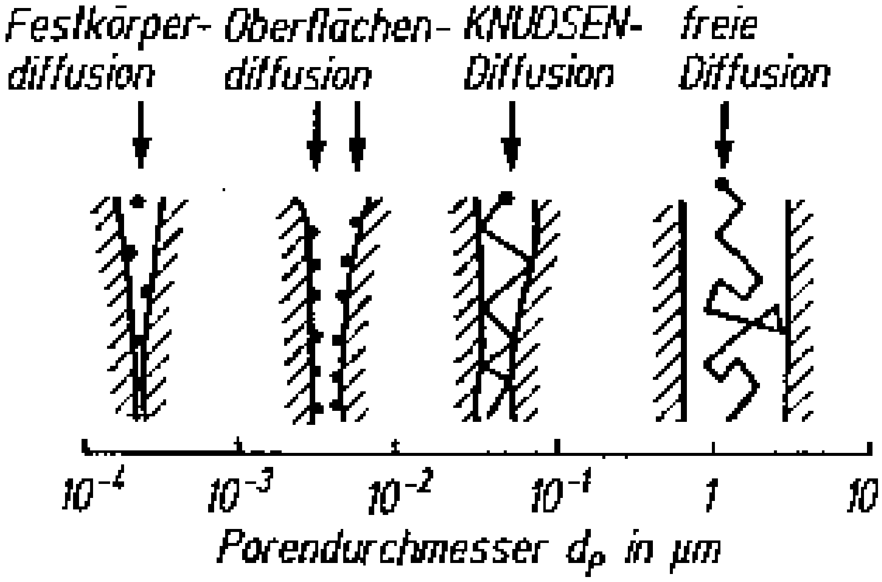
Diffusion in porous solids

- ✓ *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*

Diffusion mechanisms

Transport mechanisms in porous solids



Pore diffusion depending on pore diameter

Molecular diffusion

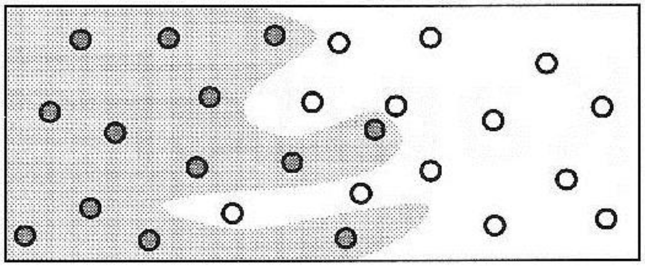


Abb. 24.1 Bei der Diffusion vermischen sich die Moleküle einer Substanz mit den Molekülen einer anderen Substanz.

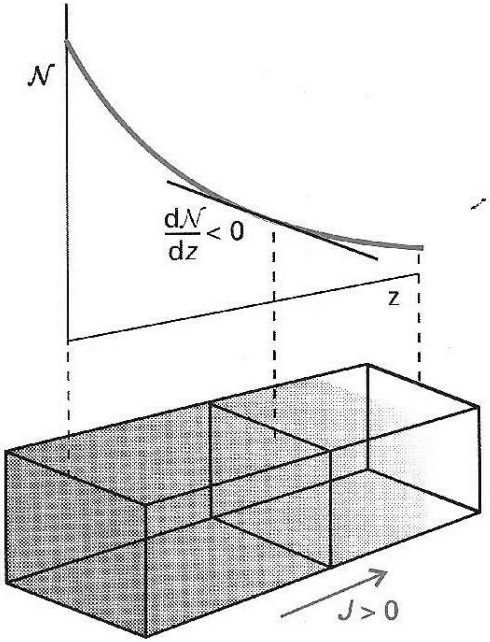


Abb. 24.7 Der Fluß von Teilchen gegen einen Konzentrationsgradienten. Das erste Ficksche Gesetz besagt, daß der Fluß der Materie (die Zahl der Teilchen pro Zeit- und Flächeneinheit) proportional zu dem Dichtegradienten am betreffenden Punkt ist.

Atkins

Molecular diffusion

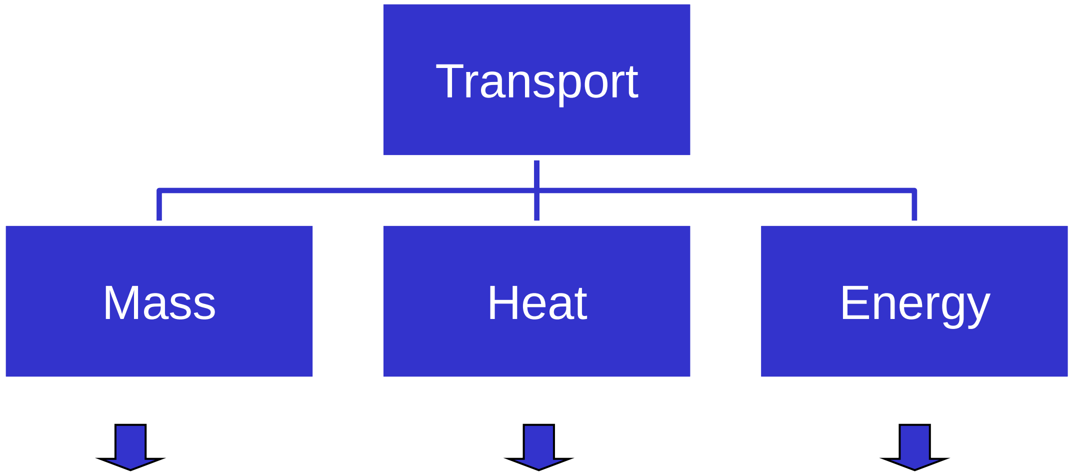
- mixture of two components A and B,
  concentration gradient (in one dimension y):
  under steady-state conditions the diffusional flow of one component is described by *1. Fick law*

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

- 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)

General view to transport equations for gases



Flux of
mass density

Flux of
heat density

Flux of
momentum

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

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
(viscosity)

General view to transport equations for gases

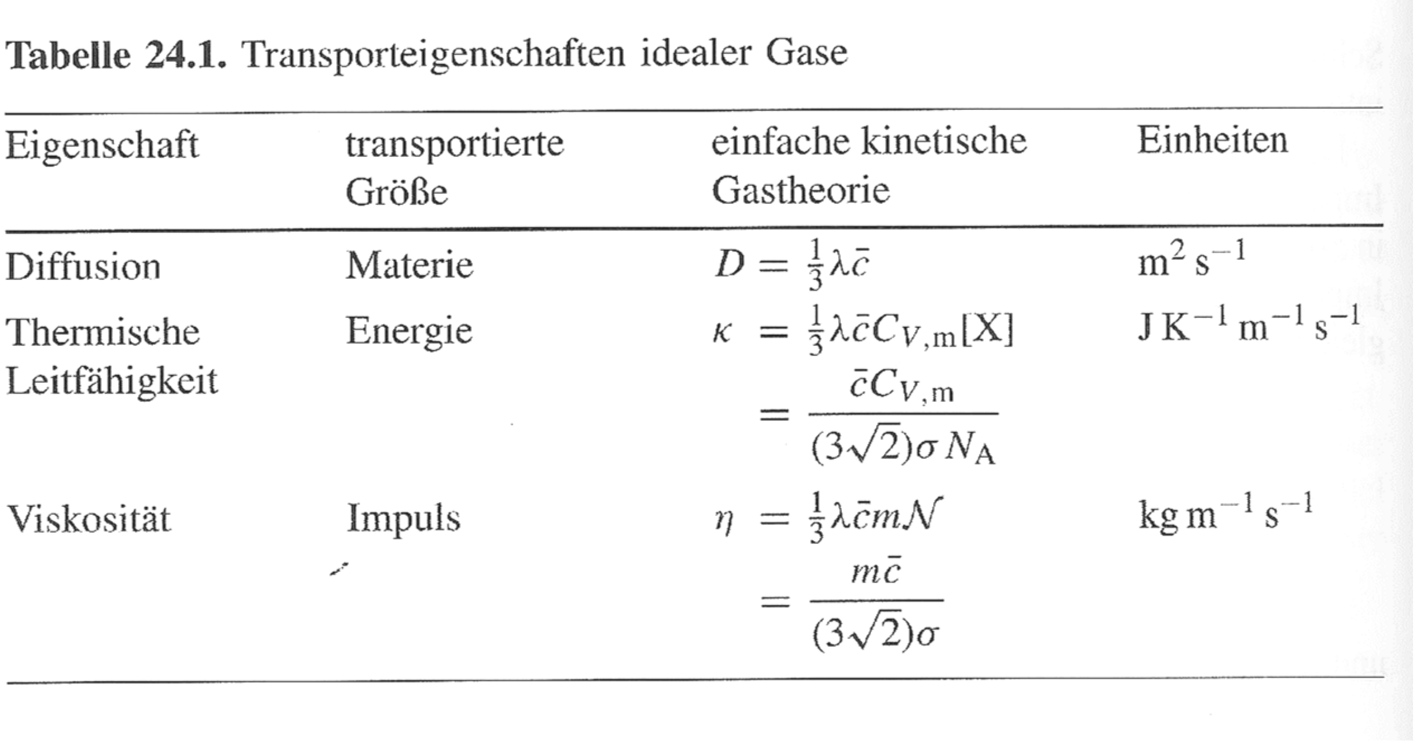


Tabelle 24.1. Transporteigenschaften idealer Gase

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

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)

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

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

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

- 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

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

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

Frequency Response Method

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)

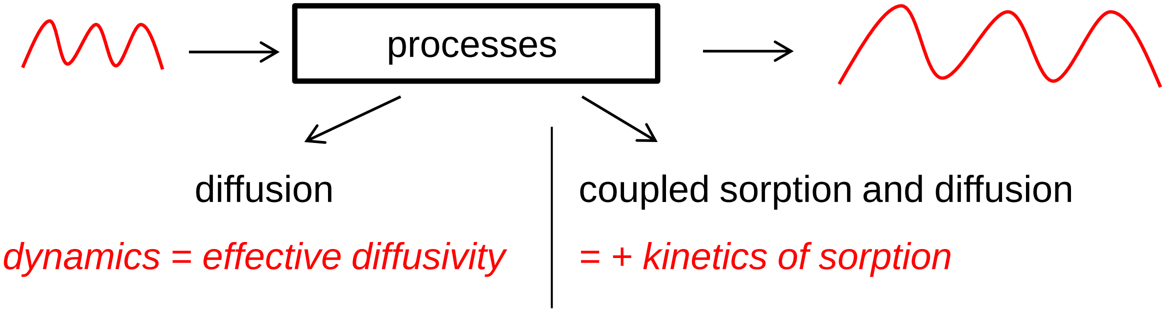
Frequency response

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

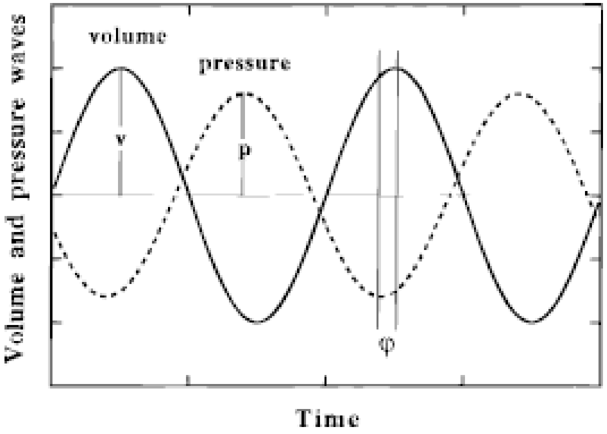


Figure 1. Input volume perturbation and output pressure response in frequency response experiments.

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 : $\varphi = \tan^{-1}$ […..]

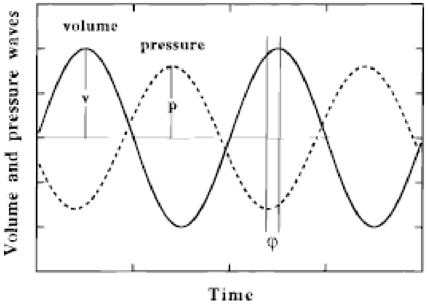


Figure 1. Input volume perturbation and output pressure response in frequency response experiments.

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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)

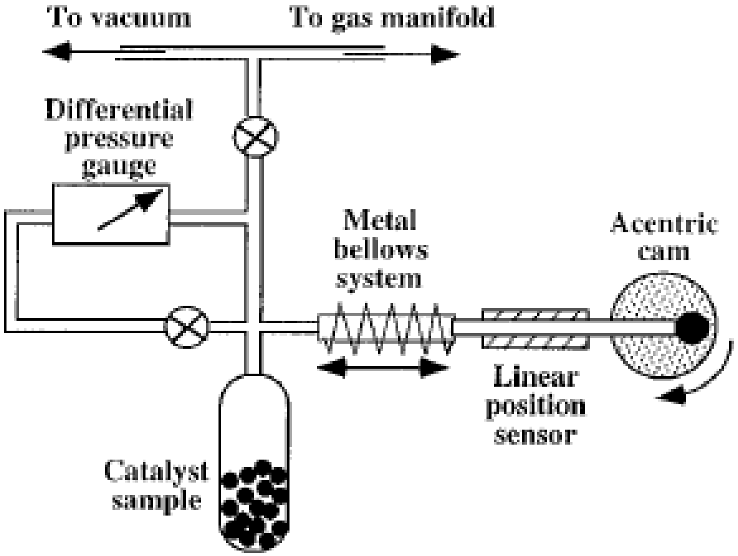

Figure 2. Schematic diagram of frequency response apparatus.

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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)

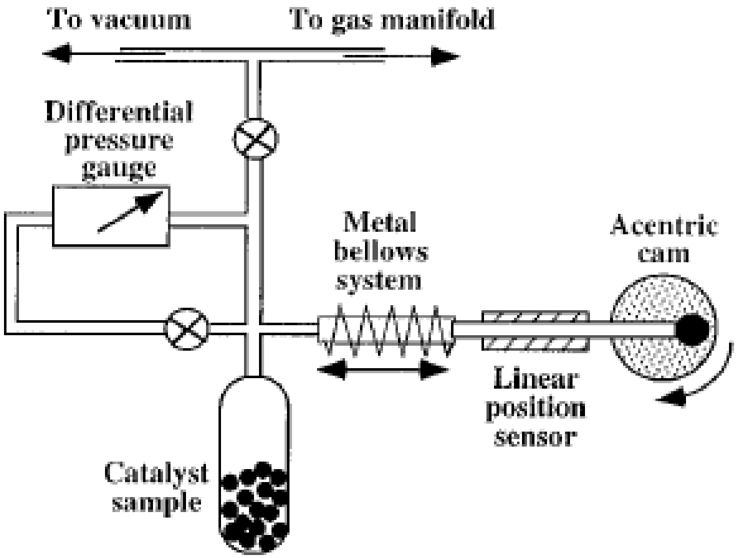

Figure 2. Schematic diagram of frequency response apparatus.

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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

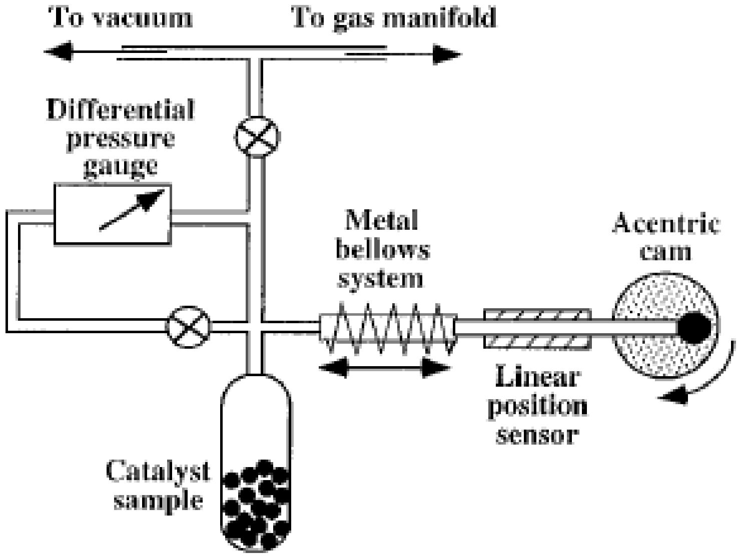

Figure 2. Schematic diagram of frequency response apparatus.

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Frequency response

Theoretical contributions

Adsorption

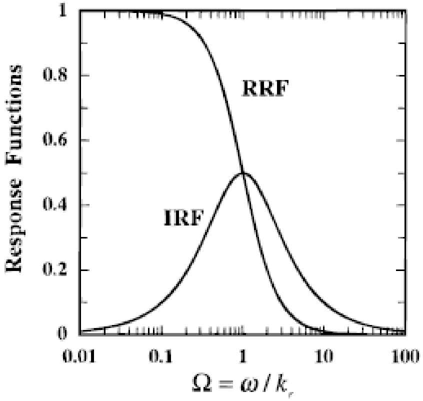
Diffusion

Adsorption and diffusion

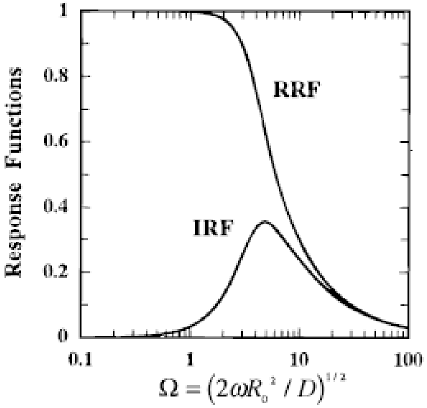
- all responses can be divided into an *real* and an *imaginary* part

- real response function = RRF, imaginary response function = IRF

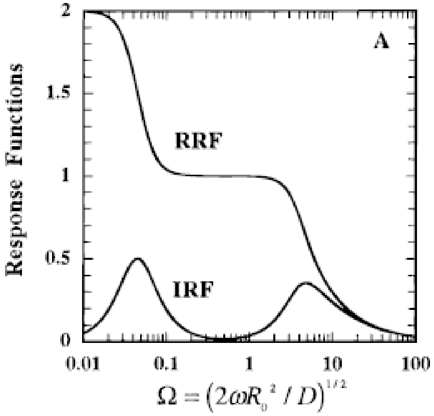
$$\mathrm{RRF} = \mathrm{Re}\left[\frac{1}{H(\mathrm{i}\omega)} - 1\right] \qquad \mathrm{IRF} = -\mathrm{Im}\left[\frac{1}{H(\mathrm{i}\omega)} - 1\right]$$



RRF and IRF components for adsorption processes



RRF and IRF components for diffusion processes



RRF and IRF components for coupled diffusion and adsorption processes

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Frequency response

Theoretical contributions

Adsorption

Diffusion

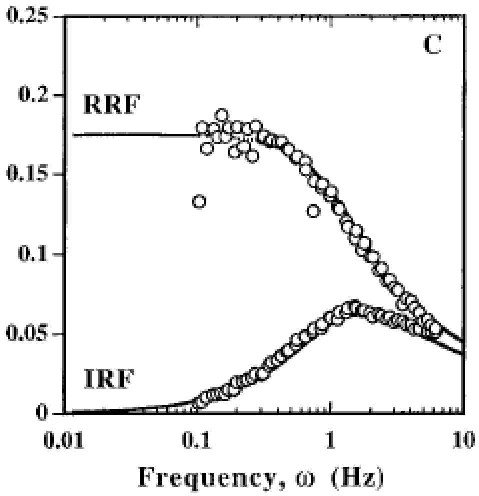
Adsorption and diffusion

- all responses can be divided into a *real* and an *imaginary* part

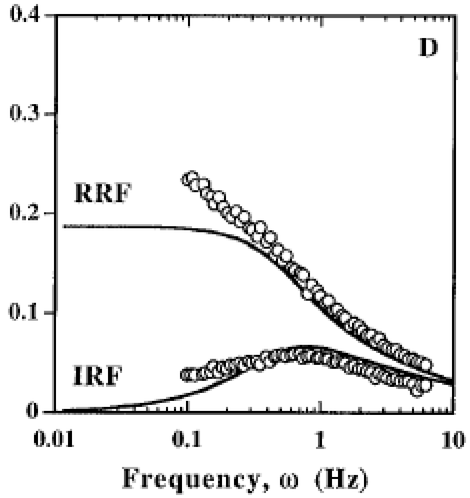
- real response function = RRF, imaginary response function = IRF

Application to

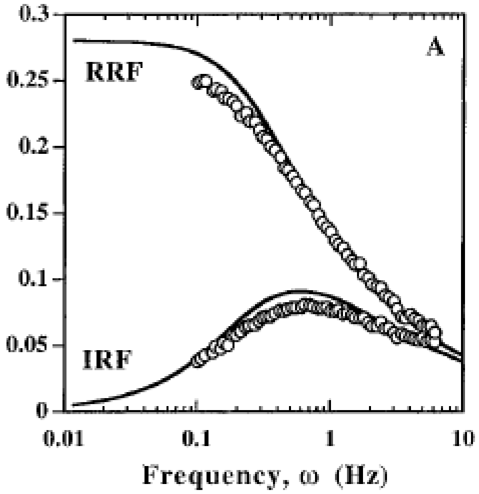
N_2,



Xe,



iso-butane



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Frequency response

Advantages

- FR allows to apply an *additional degree of freedom* in choosing frequencies to *decouple multiple dynamic processes*
- FR delivers a *high accuracy* in realizing a *smooth forcing function*
- FR is able to *conduct* experiments *at mean operating conditions*
- FR anaylsis is relatively *easy*
- FR enables to *discriminate* between *different rate-limiting steps*
- 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

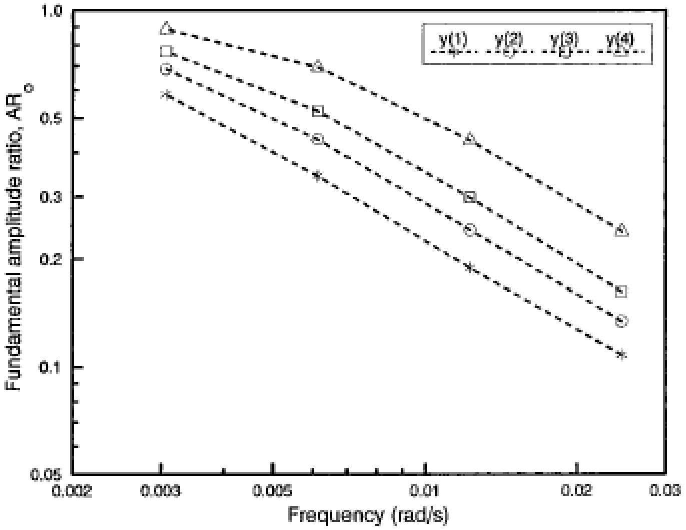


Figure 2. Bode plot for fundamental amplitude ratios.

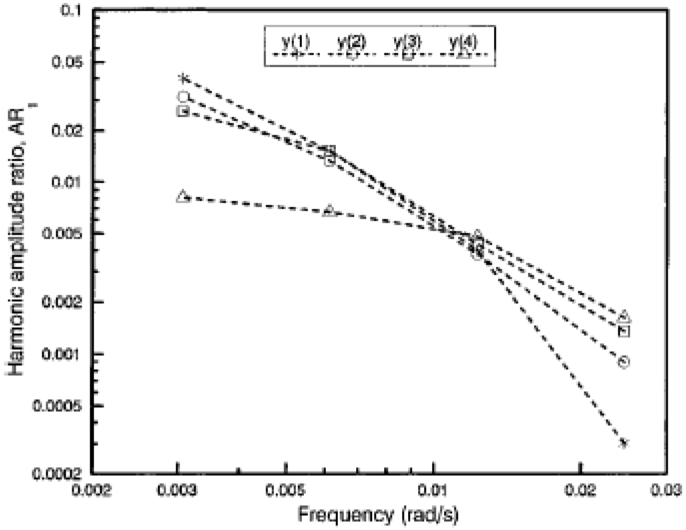


Figure 3. Bode plot for first harmonic amplitude ratios.

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

Frequency response

Full- and single-step frequency response

- Full FR can separate two simultaneous diffusion processes
- Single-step FR can follow very rapid uptake rates in millisecond timescale

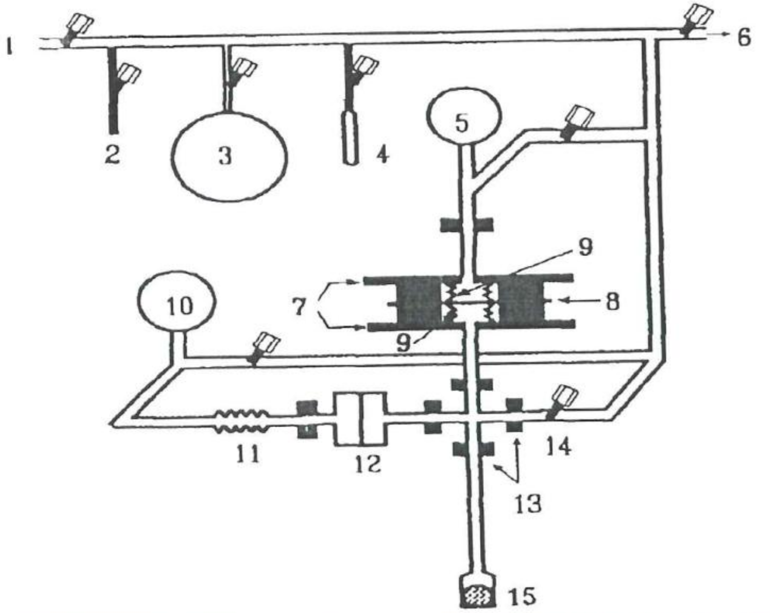


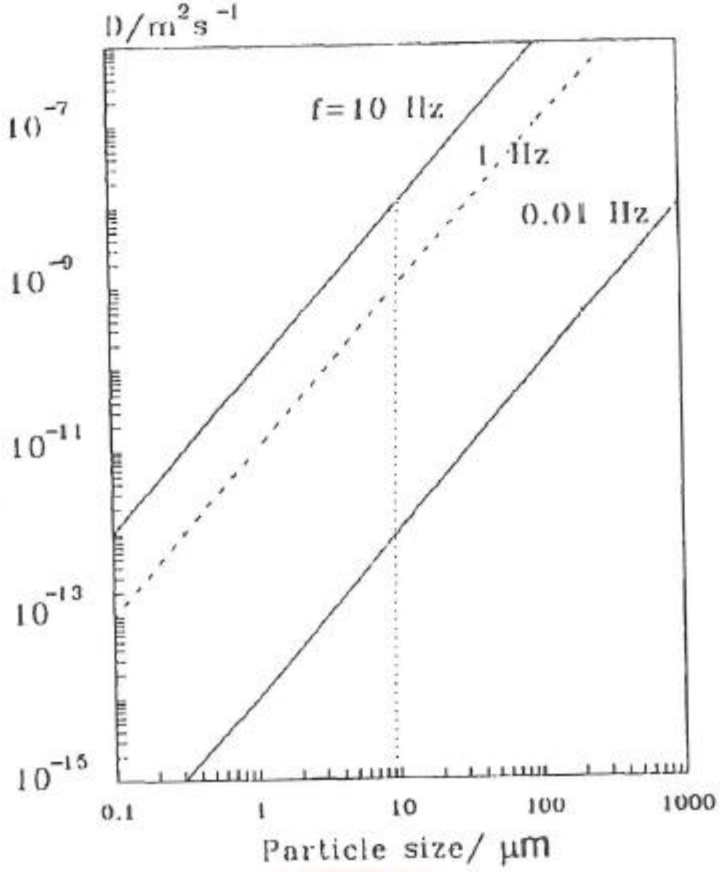
Figure 1 Frequency response apparatus: 1, vent; 2, gas sorbate inlet; 3, gas sorbate; 4, liquid sorbate; 5 and 10, reference pressure sides; 6, oil diffusion and rotary pumps; 7, electromagnets; 8, moving disc; 9, bellows; 11, flexible glass–metal; 12, differential Baratron; 13, vacuum connectors; 14, vacuum gas tap; 15, zeolite in glass-wool

Gas Separation & Purification 1983 Vol 7 No 2 83

Principal features of FR

- a dose of sorbate is brought into sorption equilibrium with the sorbent
- a square –wave modulation of ± 1% is then applied to the gas pahse equilibrium volume
- the bellow contracts and expands according to the frequency range (0.01-10 Hz)

Frequency response



Relationship between diffusion coefficient D, frequency f, and crystal size r

- the range of diffusivities that can be covered depends on the size of the adsorbent crystals

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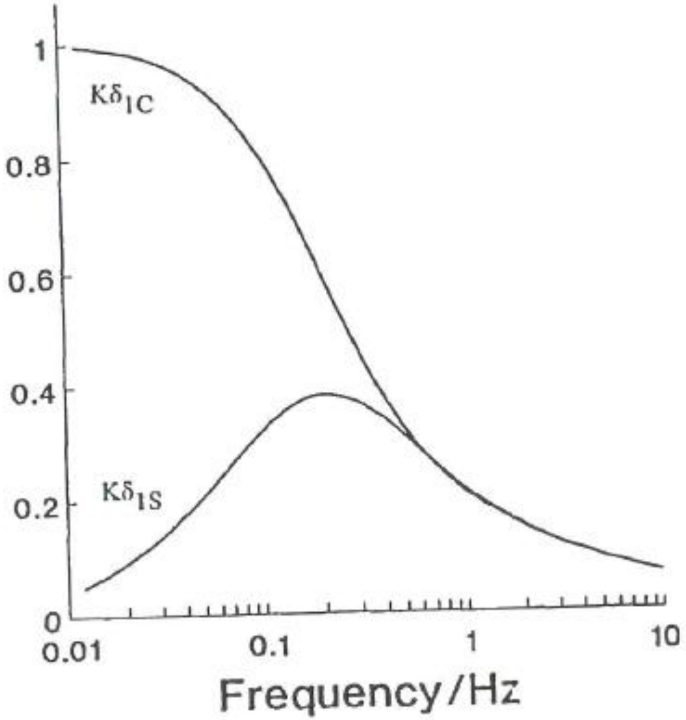
Frequency response



Ideal shape of the phase-lag and amplitude versus frequency

- These ideal shaped curves lead to characteristic functions as can be seen in the figure
- Each deviation from ideal behaviour leads to a change in curve shape and gives a „fingerprint“ corresponding to the underlying processes

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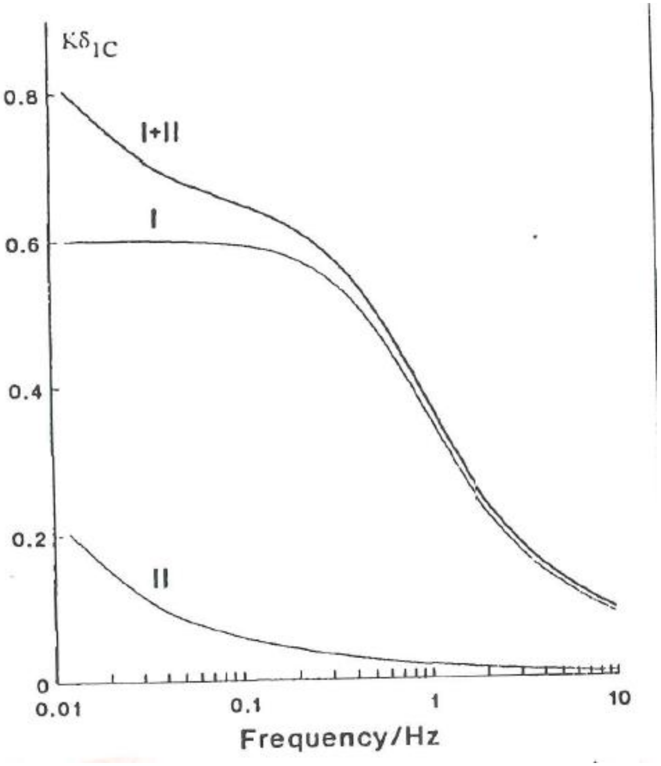
Frequency response



Real shape of the phase-lag and amplitude versus frequency

- characteristic function versus frequency for two diffusion processes (I+II)
- adsorption K_I= 0.6 and K_{II}= 0.3
- diffusion $D_I = 10^{-9}\ m^2s^{-1}$, $D_{II} = 10^{-11}\ m^2s^{-1}$

→ diffusion differs for a factor of 100 and adsorption process is twice as large for the faster process

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Frequency response

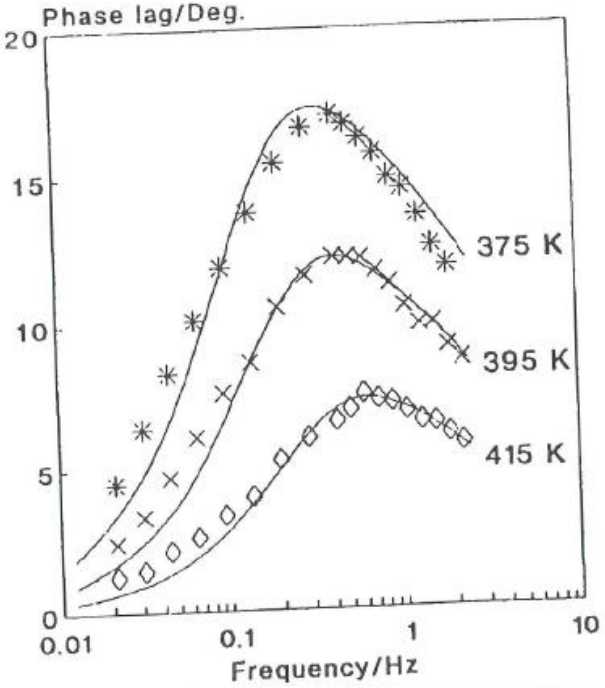


Figure 10 Phase lag versus frequency curves for benzene diffusing in 60 mg of silicalite-1 at 0.862 Torr. Solid lines are theoretically calculated by using Equations (1) and (2)

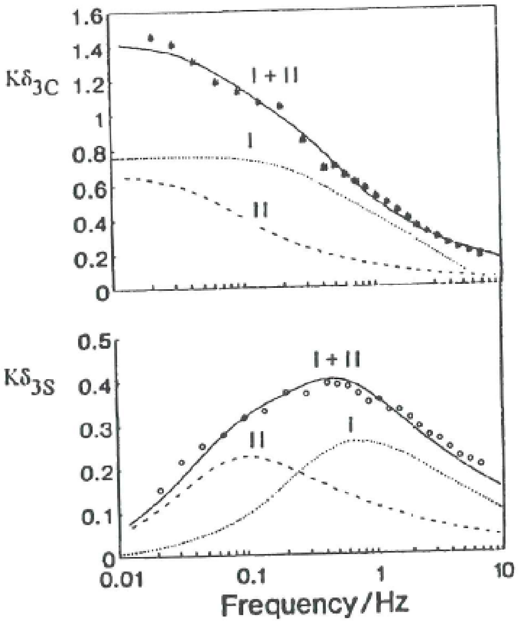


Figure 11 Characteristic functions versus frequency curves for *p*-xylene diffusing in 50 mg of silicalite-1 at 0.431 Torr and 395 K fitted theoretically by lines (I + II) calculated by using Equations (7) and (8) with two diffusion coefficients, $D_I = 1.8 \times 10^{-11}$ and $D_{II} = 2.6 \times 10^{-12}$ m^2 s^{-1}

Table 1 Isosteric heats of adsorption, activation energies of diffusion and diffusivities of aromatics in silicalite-1 at low coverage and temperatures from 390 to 400 K

Sorbate	Q_{st} (kJ mol^{-1})	E_a (kJ mol^{-1})	D_0 (m^2 s^{-1})	Method
Benzene	63	24 ± 2	2×10^{-13}	FR
		25	1×10^{-13}	SSFR
Ethylbenzene	87.5	24 ± 2	2×10^{-13}	FR
p-Xylene	80	19 ± 2	2×10^{-11} straight channel	FR
		39 ± 4	2×10^{-12} sinusoidal channel	FR

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: efefct 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

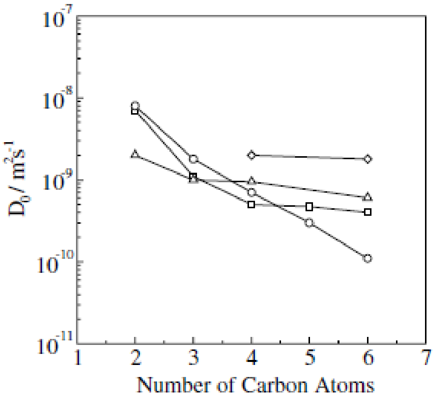
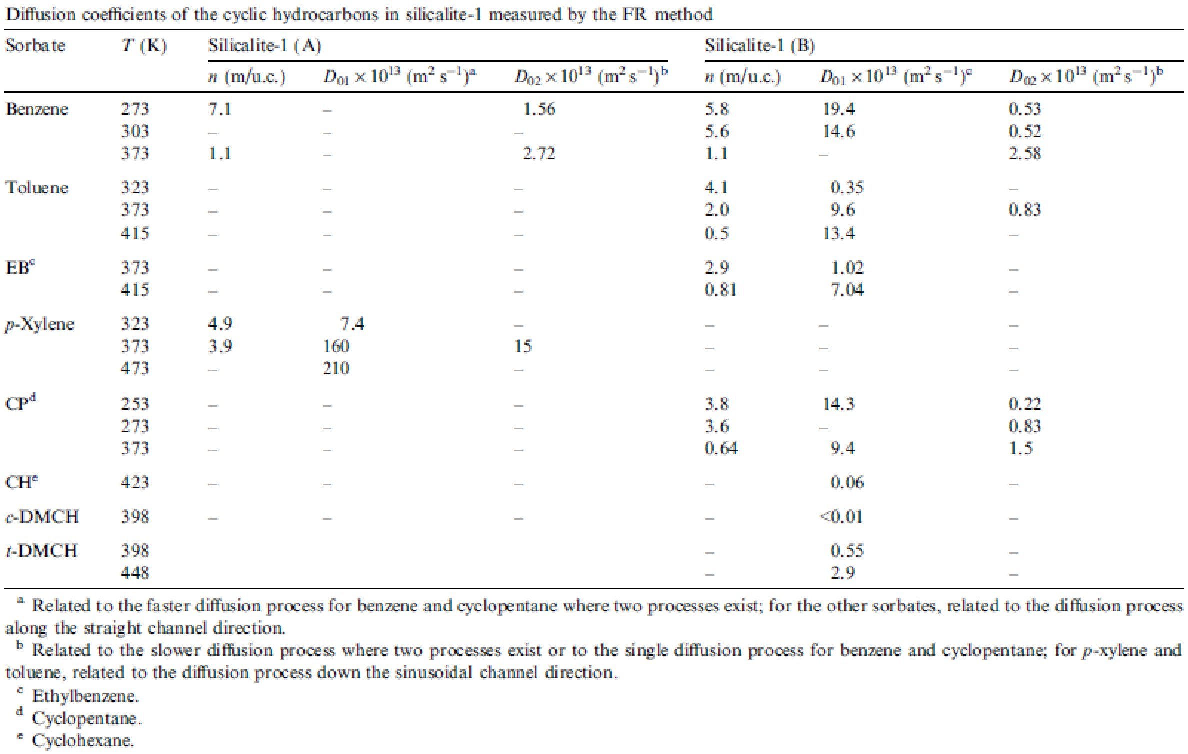


Fig. 9. Chain-length dependence of the self-diffusion coefficients of the *n*-alkanes in silicalite-1 at 303 K derived from the FR technique (—□—) compared with the results measured by PFG NMR [46] at 298 K (—○—), QENS [47] (—△—) and molecular dynamic calculations [45] (—◇—).



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.)	$D_{01} \times 10^{13}$ ($m^2 s^{-1}$)[a]	$D_{02} \times 10^{13}$ ($m^2 s^{-1}$)[b]	n (m/u.c.)	$D_{01} \times 10^{13}$ ($m^2 s^{-1}$)[c]	$D_{02} \times 10^{13}$ ($m^2 s^{-1}$)[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

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.

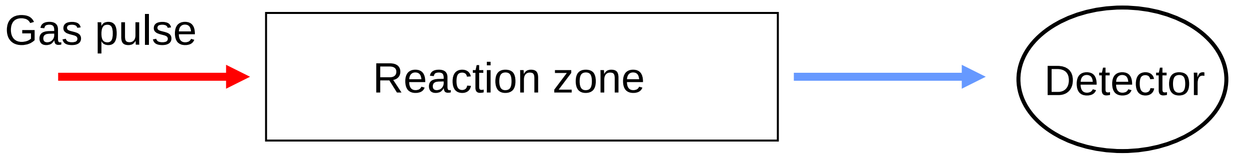
TAP – Features

- *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 → $5 \cdot 10^{18}$ S/m^2
    - 1 pulse of *n*-butane: $1 \cdot 10^{14}$ molecules
    - per pulse 1/50000 of surface addressed

TAP – System hardware

Simplified schematic of a TAP pulse response experiment



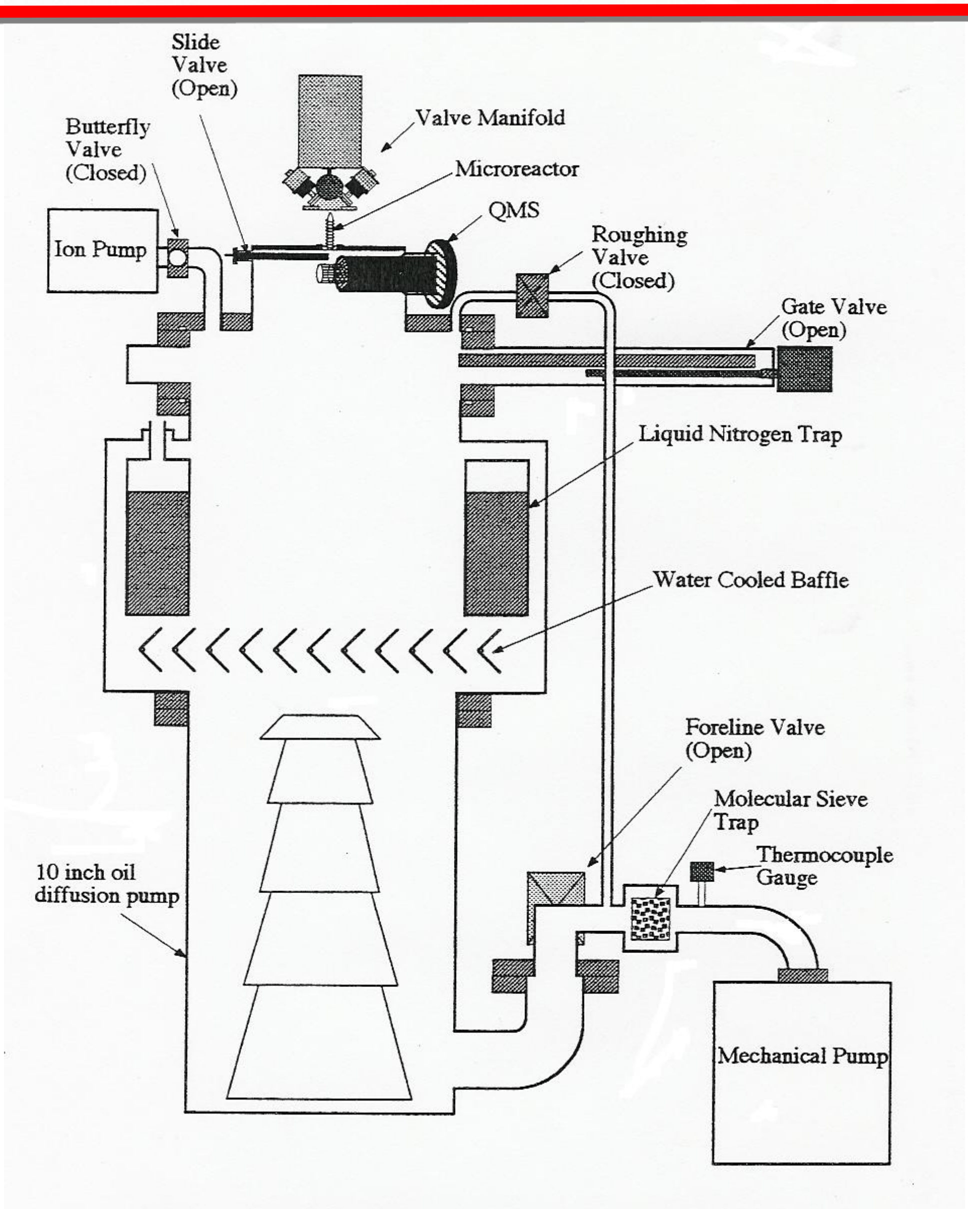
Gas pulse

Reaction zone

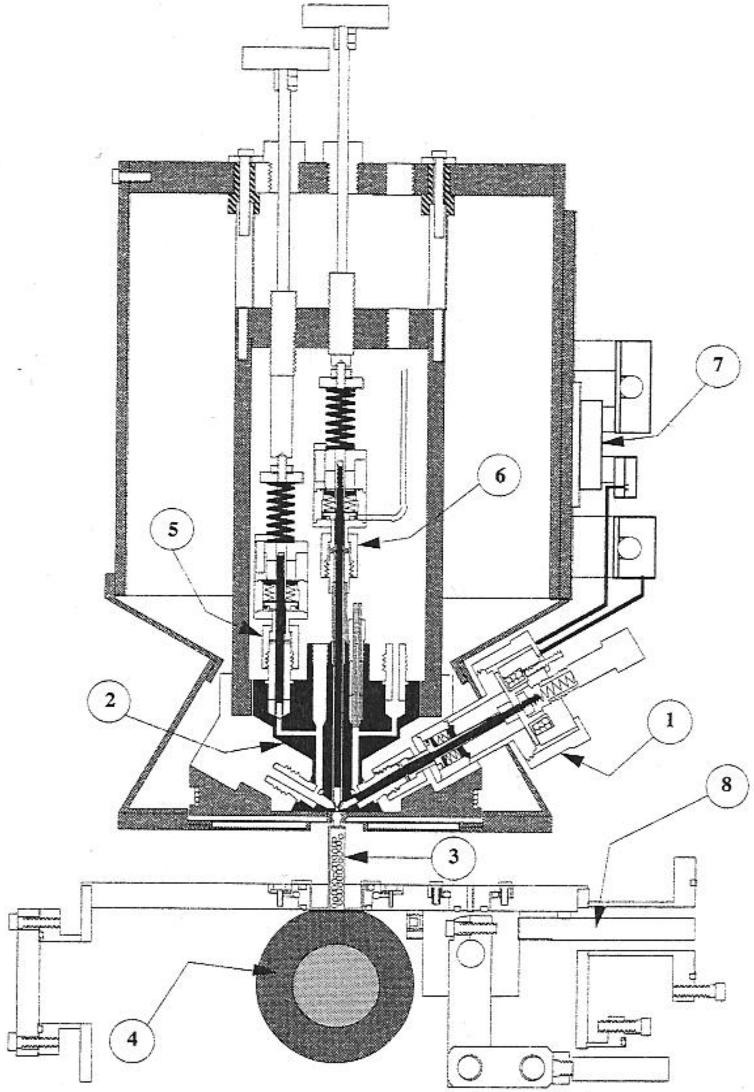
Detector

- 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



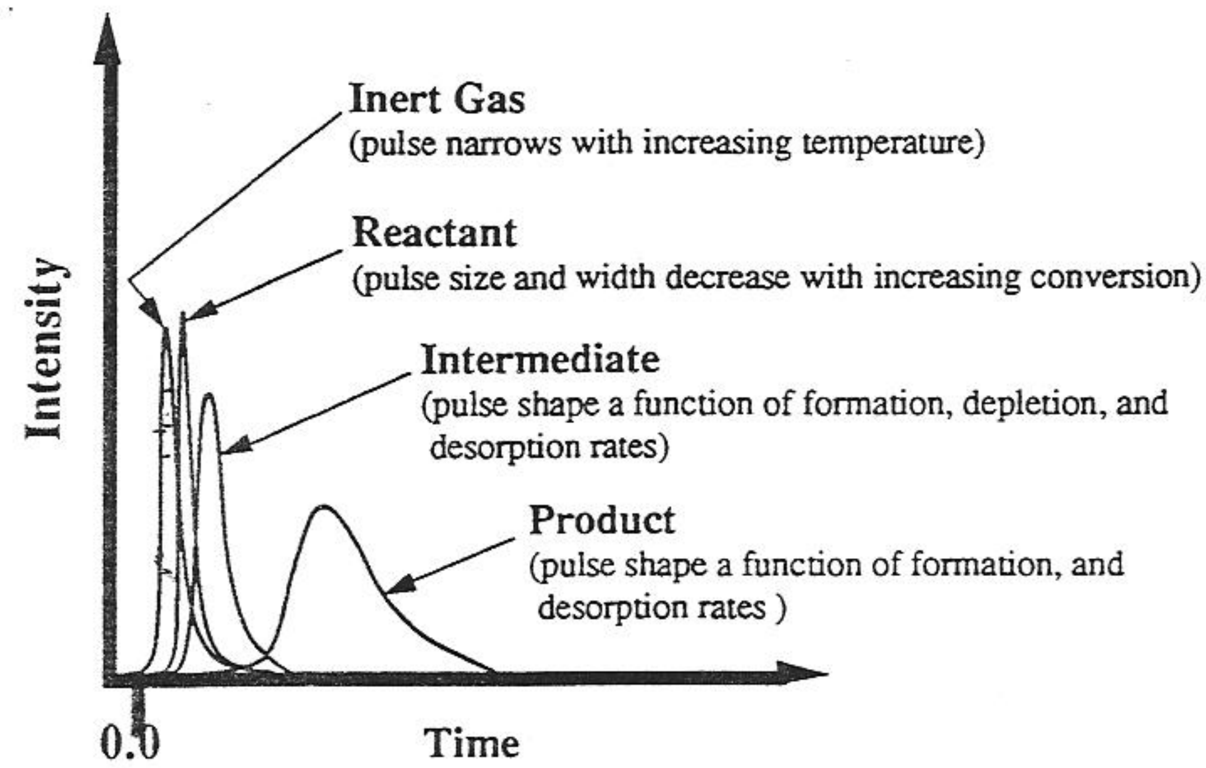
TAP – System hardware



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

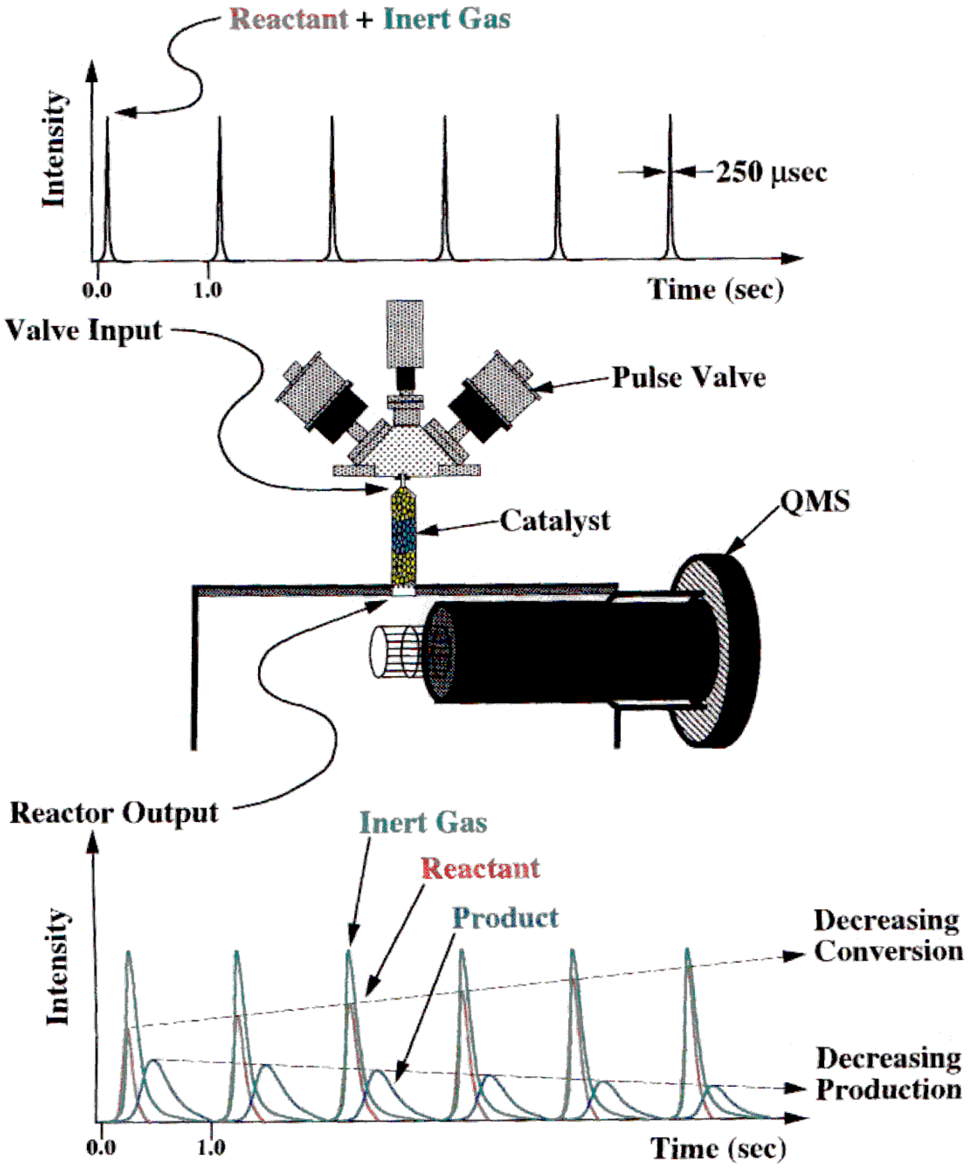
Characteristic pulse response experimental outputs



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}

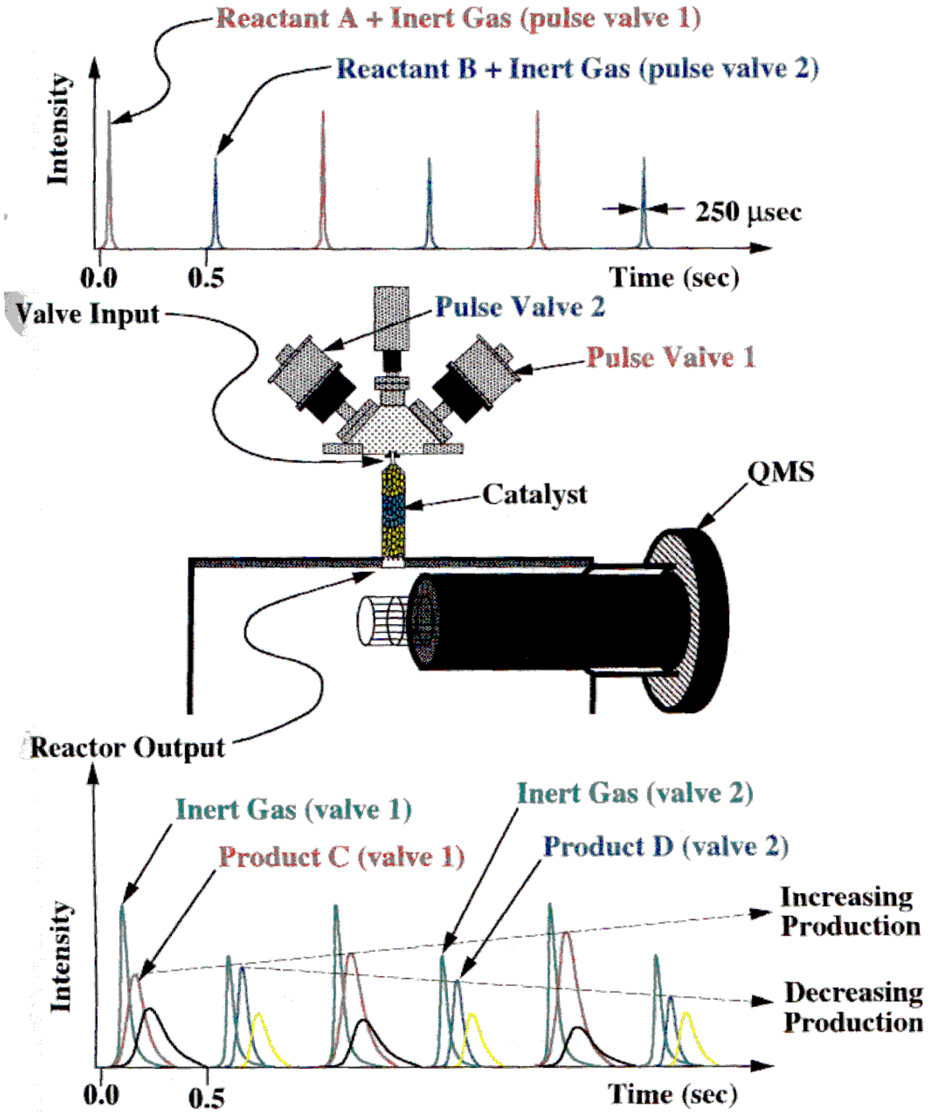
- Key features of **output**:
  - different products have different responses
  - individual product response can change with pulse number



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)

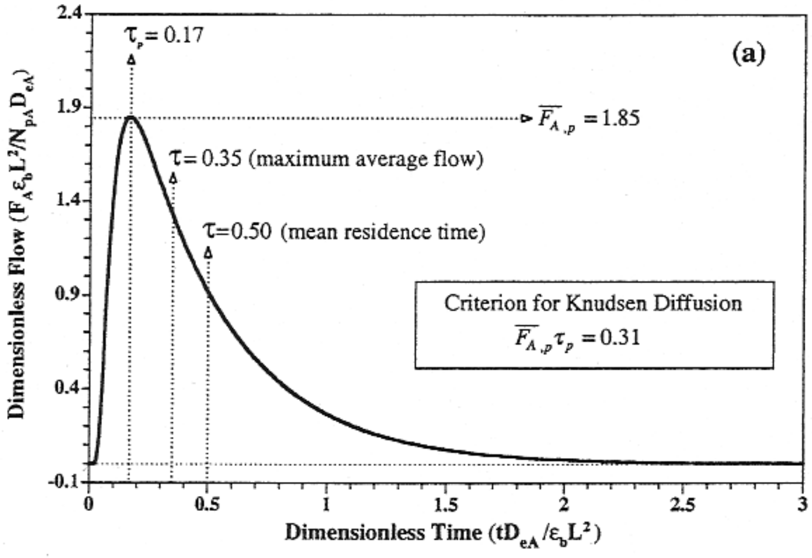
t … time (s)

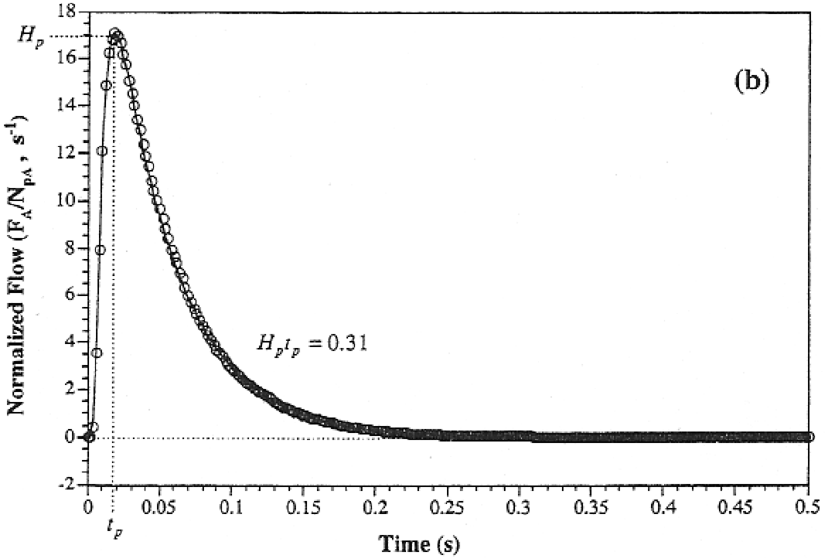
z … axial coordinate (cm)

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)

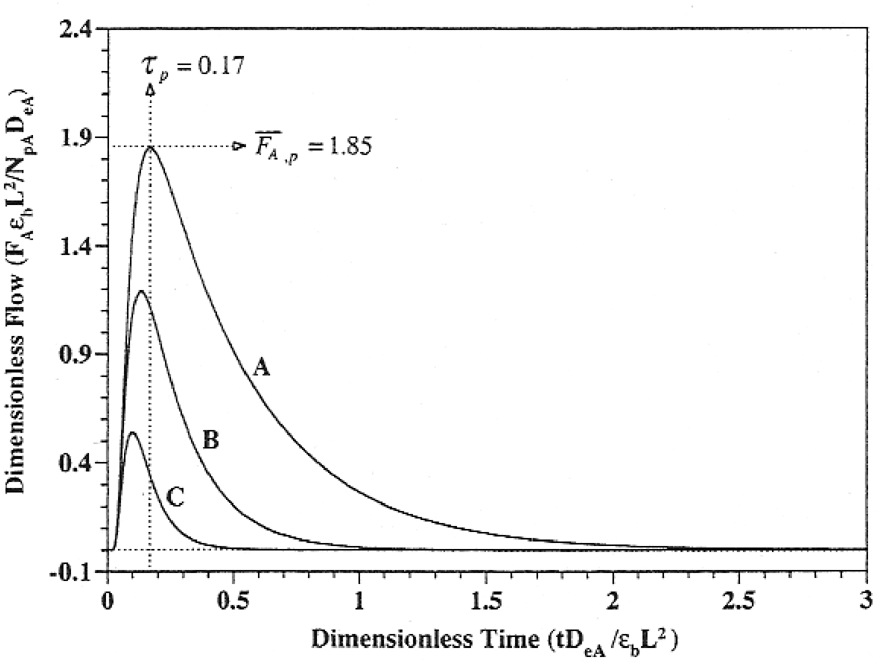
$$\boxed{\varepsilon_b \frac{\partial C_A}{\partial t} = D_{eA} \frac{\partial^2 C_A}{\partial z^2} - a_s S_v (1-\varepsilon_b) k_a C_A}$$

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

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

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

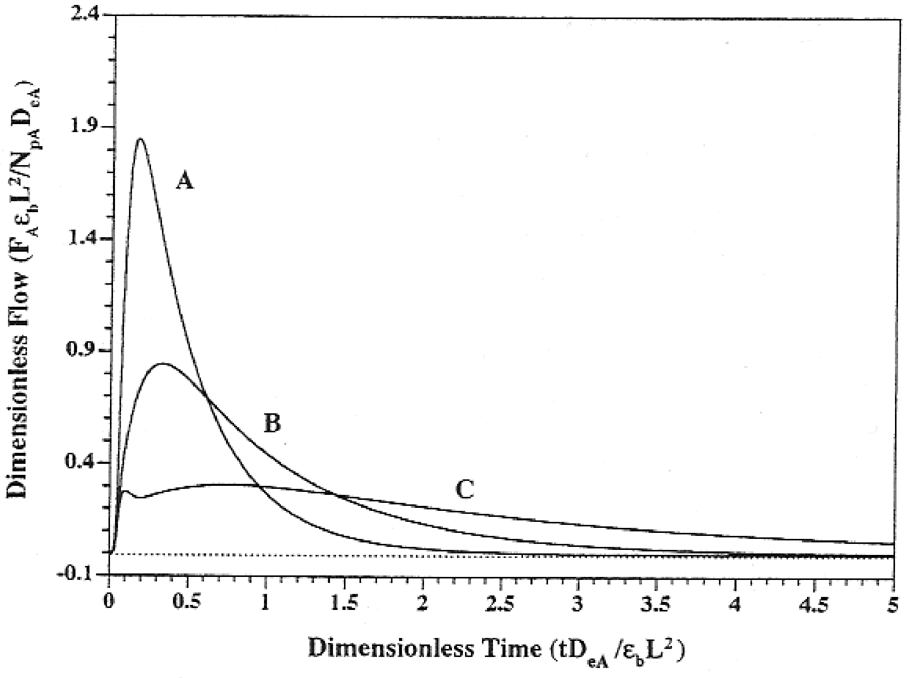
- for component A on the catalyst surface

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

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 of TAP

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.* <u>*226*</u> *(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.*

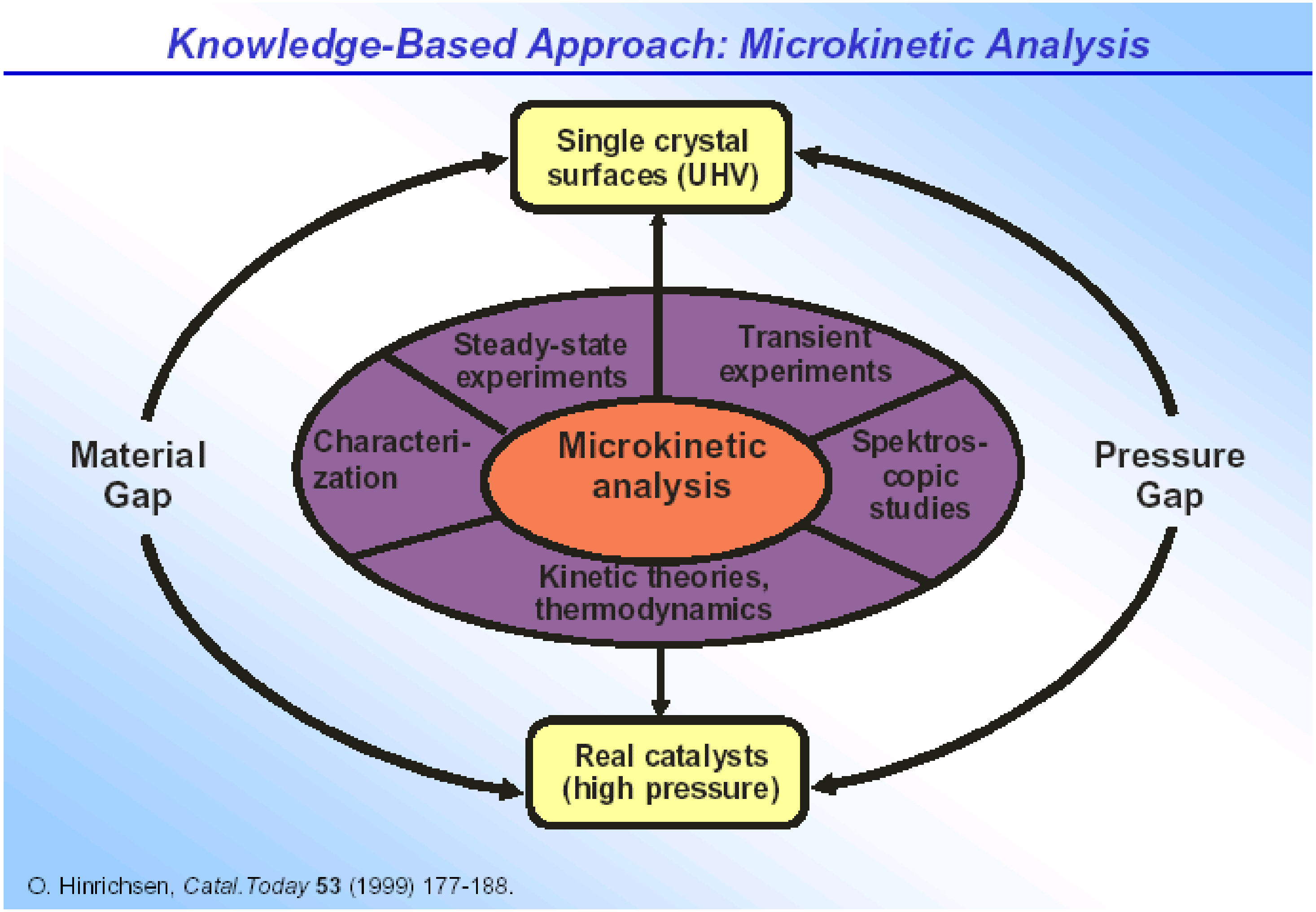
An Integrated Catalytic and Transient Study of Sulfated Zirconias:
Investigation of the Reaction Mechanism and the Role of Acidic Sites in n-Butane Isomerization
C. Breitkopf. *ChemCatChem 1(2) 2009.*

Diffusion and reaction in hierarchical structured metal oxides - a transient TAP study
Galinsky, M.; Lutecki, M.; Breitkopf, C.:
Diffusion and Defect Data--Solid State Data, Pt. A: Defect and Diffusion Forum (2010), 297-301

Synthesis and characterization of nanostructured sulfated zirconias
Lutecki, M.; Solcova, O.; Werner, St.; Breitkopf, C.:
Journal of Sol-Gel Science and Technology (2010), 53(1), 13-20

Sorption of Alkanes on Sulfated Zirconias - Modeling of TAP Response Curves
Matthias Galinsky, Michal Lutecki; Jürgen Böhm; Helmut Papp; Cornelia Breitkopf
accepted for publication in Chem. Eng. Sci.

Kinetic modeling



Knowledge-Based Approach: Microkinetic Analysis

O. Hinrichsen, *Catal. Today* **53** (1999) 177-188.

Thank you for your attention!

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- Müller-Erlwein E. Chemische Reaktionstechnik, Teubner Stuttgart-Leipzig, 1998, 237.

Recommended literature and books

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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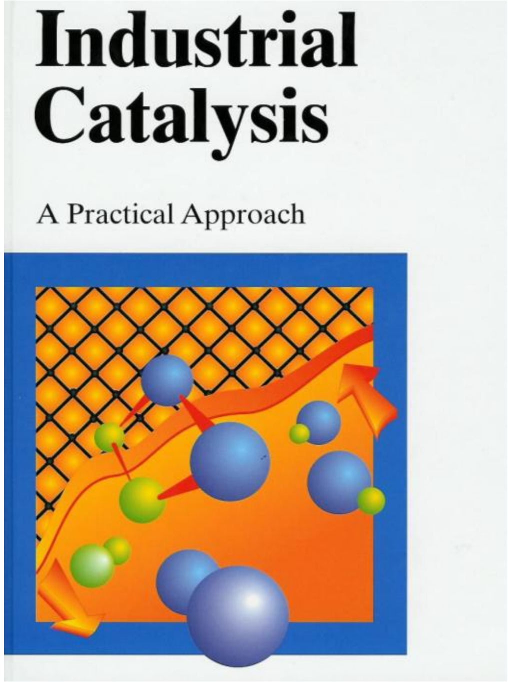
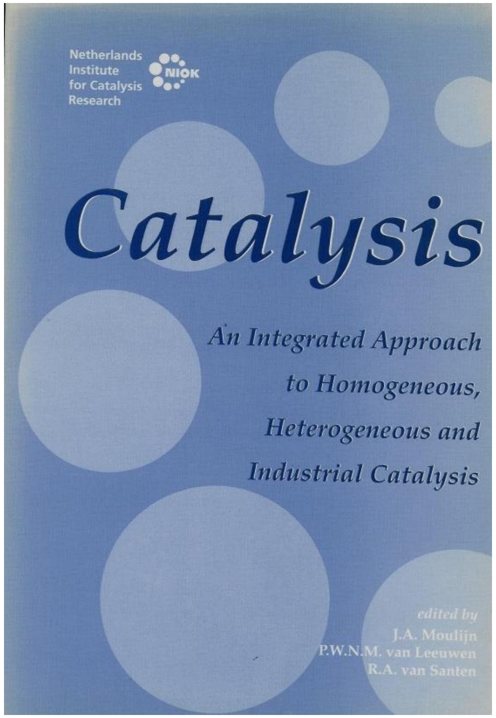
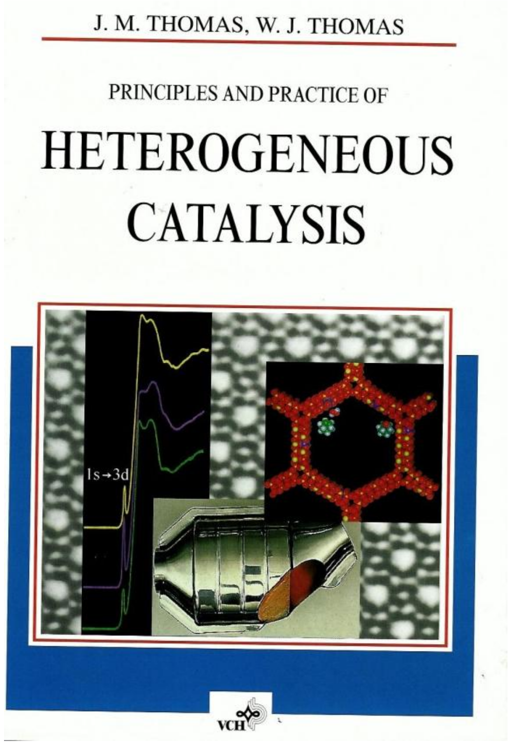
…continued

Jens Hagen







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