Lecture Series at Fritz-Haber-Institute Berlin
„Modern Methods in Heterogeneous Catalysis“
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TAP
Temporal Analysis of Products

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

Dimensions in Heterogeneous Catalysis

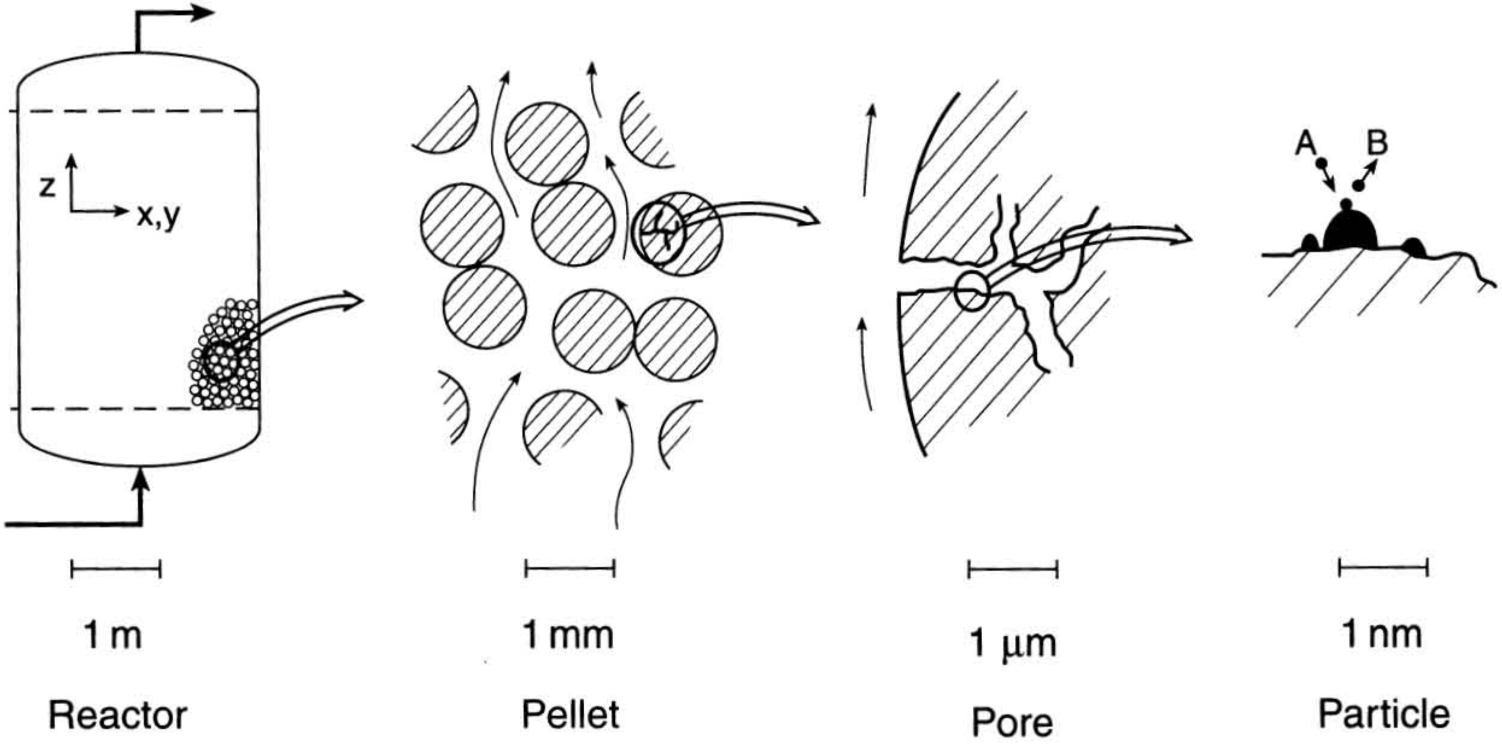


Figure 7–6 Different size scales in a packed bed catalytic reactor. We must consider the position *z* in the bed, the flow around catalyst pellets, diffusion within pores of pellets, and adsorption and reaction on reaction sites. These span distance scales from meters to Angstroms.

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

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.

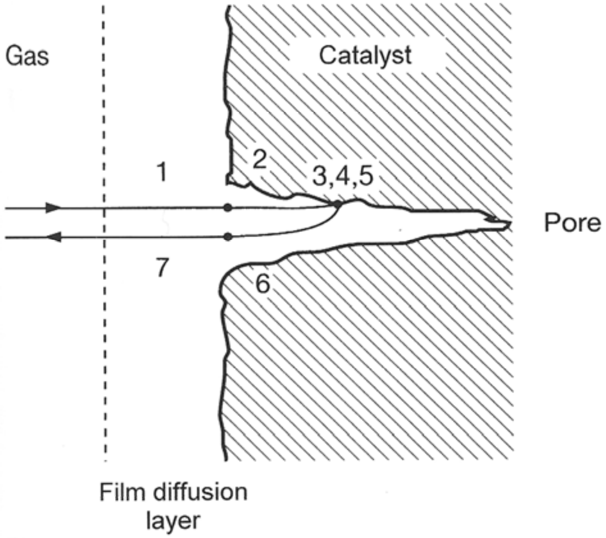
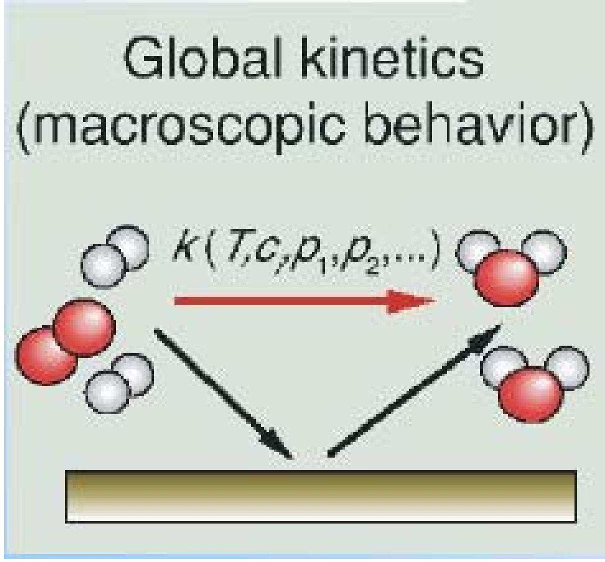
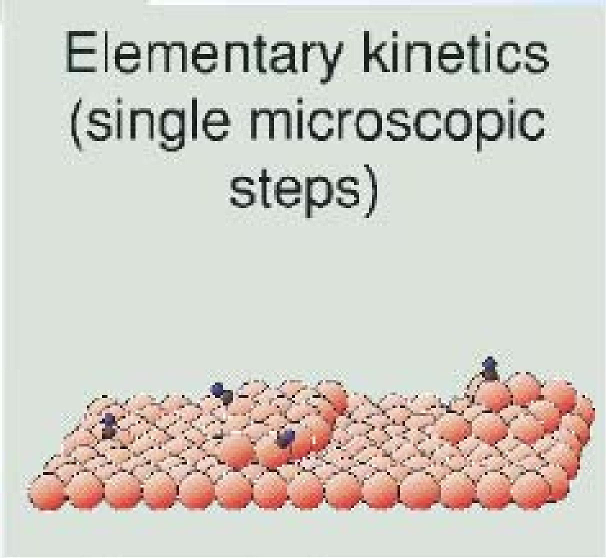


Fig. 4-1. Individual steps of a heterogeneously catalyzed gas-phase reaction

Kinetic measurements

Complexity of heterogeneously catalyzed reactions –
Macrokinetics and Microkinetics





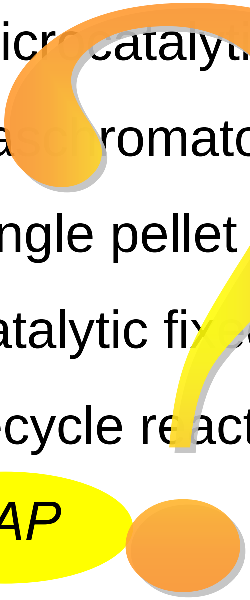
O. Deutschmann, XXXIV. Jahrestreffen Deutscher Katalytiker/ Fachtreffen Reaktionstechnik, Weimar 21.-23.3.2001

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 gas chromatographic reactor
- o single pellet diffusion reactor
- o catalytic fixed bed reactor
- o recycle reactor
- o *TAP*

Questions

- What distinguishes TAP from other lab reactors ?
- Which information do we need to understand TAP ?
- How can TAP applied in heterogeneous chemistry?

Outline

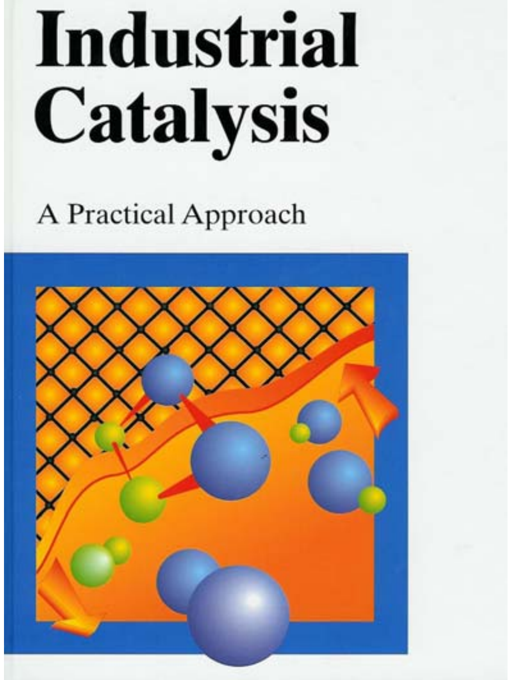
- Steady state and unsteady state experiments
- Diffusion and mathematics
- TAP-Method and modeling
- Applications

Recommended literature and books

- Gleaves JT et al. Appl. Cat. A 160 (1997) 55-88.
- Phanawadee P. PhD thesis Washington 1997.
- Chen S. PhD thesis Washington 1996.
- Yablonsky GS et al. J. Catal. 216 (2003) 120-134.
- Gleaves JT et al. Cat. Rev.-Sci. Eng. 30 (1988) 49-116.
- Dumesic JA et al (Ed) „The Microkinetics of Heterogeneous Catalysis“ ACS, Washington 1993.
- Stoltze P. Progress in Surface Science 65 (2000) 65-150.
- Kobayashi H et al.. Cat. Rev.-Sci. Eng. 10 (1974) 139-176.
- Engel T, Ert G. Adv. Catal. 28 (1979) 1-78.
- Ertl G. The dynamics of interactions between molecules and surfaces. Berichte Bunsengesellschaft für Physikalische Chemie 99 (1995) 1282.
- Creten G et al. J. Catal. 154 (1995) 151-152.
- Haber J. 1983. Concepts in catalysis by transition metal oxides. Bonelle JP et al. (Ed.) D. Reidel Publishing Company. Surface Properties and Catalysis by Nonmetals. 45, 1-45.
- Hinrichsen O. DECHEMA-Kurs „Angewandte Heterogene Katalyse“, Bochum 2001.
- Dewaele O, Froment GF. J. Catal. 184 (1999) 499-513.
- Christoffel EG „Laboratory Studies of Heterogeneous Catalytic Processes“ Stud.Surf.Sci.Catal. 42.
- Müller-Erlwein E. Chemische Reaktionstechnik, Teubner Stuttgart-Leipzig, 1998, 237.

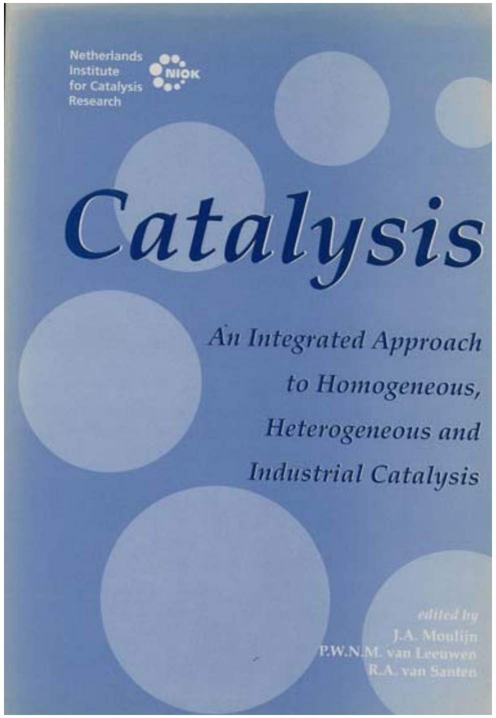
…continued

Jens Hagen



Industrial Catalysis

A Practical Approach



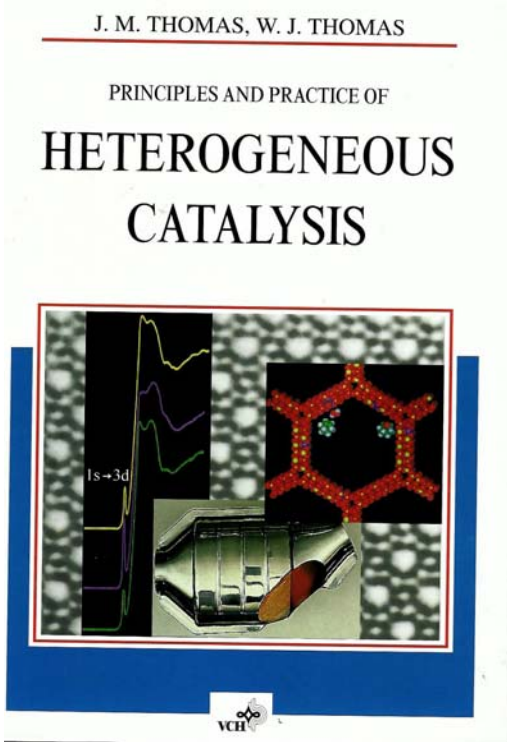
Netherlands Institute for Catalysis Research

NIOK

Catalysis

An Integrated Approach to Homogeneous, Heterogeneous and Industrial Catalysis

edited by
J.A. Moulijn
P.W.N.M. van Leeuwen
R.A. van Santen



J. M. THOMAS, W. J. THOMAS

PRINCIPLES AND PRACTICE OF

HETEROGENEOUS CATALYSIS

VCH

- Emig G., Klemm E.. Technische Chemie. Springer 2005.
- Baerns M., Behr A., Brehm A., Gmehling J., Hofmann H., Onken U., Renken A.. Technische Chemie, Viley VCH 2006.

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 is *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 techniques provide information on
  - Reaction intermediates (pulse response) (Gleaves 1988)
  - Reaction sequence in a multistep reaction (Kobayashi 1975)
  - Rate constants of elementary steps (Ertl 1979, Creten 1995)

Unsteady-state experiments

- Transient techniques provide information on
    - Investigation of *complex kinetic phenomena* (oscillating chemical reactions, hysteresis) that are *not observable under steady-state* conditions
    - Probe of 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

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

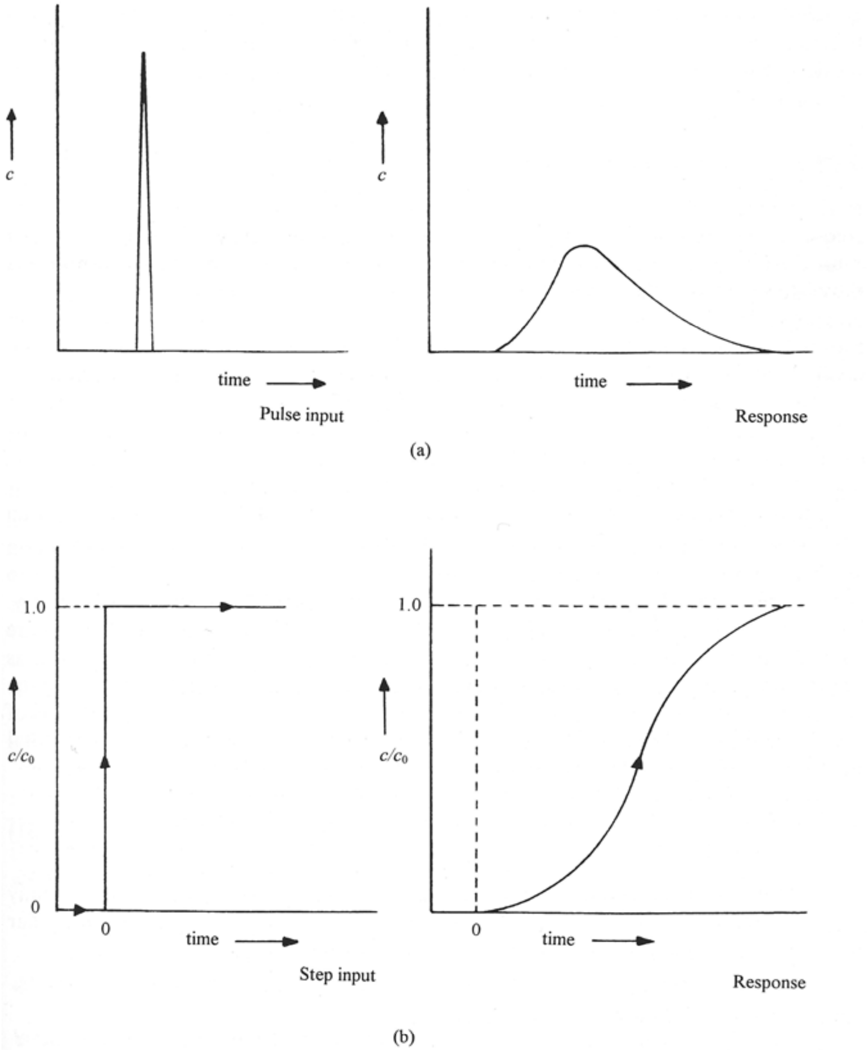


Figure 4.21 Response to a concentration change at the face of a porous pellet: (a) pulse input; (b) step input.

Diffusion and mathematics

Diffusion in porous solids

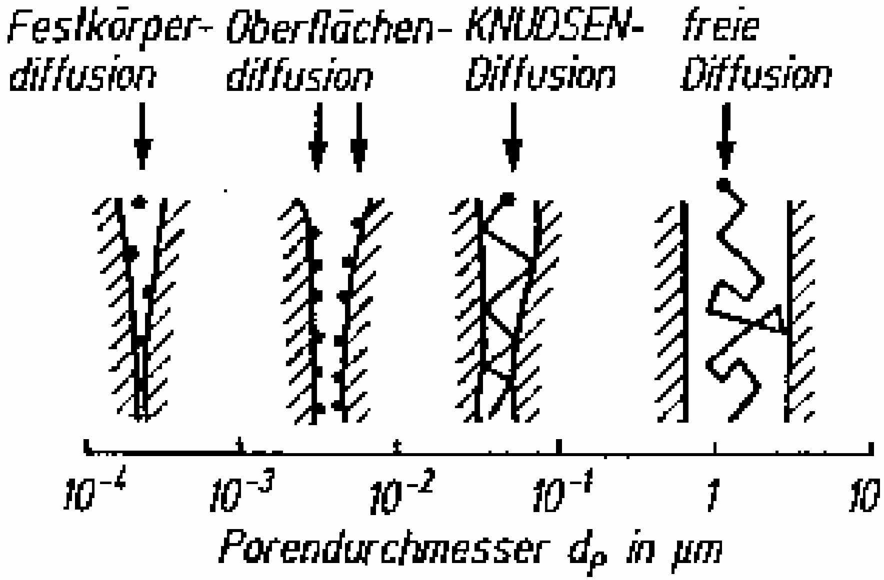
- ✓ *Characteristic value* to characterize the *influence of internal transport* phenomena of heterogeneous reactions on the surface between a fluid phase and a porous solid is Da^{II} (see textbooks)

- ✓ $Da^{II} = f\,(k, c_{external}, l_{characteristic}, D_{eff})$

- ✓ 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

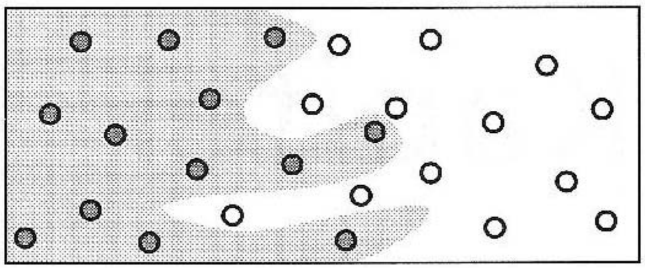


Abb. 24.1 Bei der Diffusion vermischen sich die Moleküle einer Substanz mit den Molekülen einer anderen Substanz.

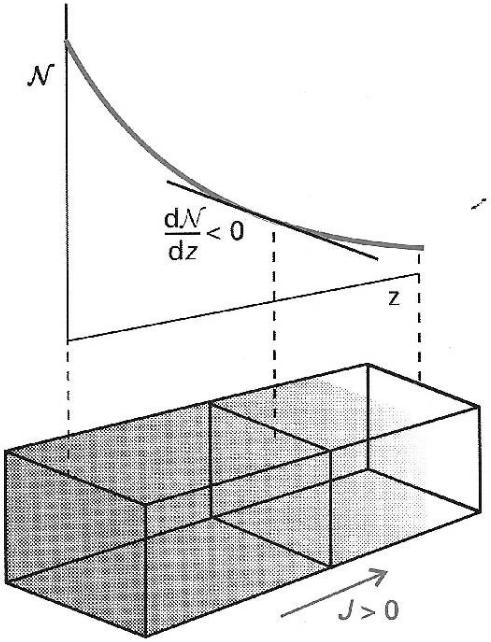


Abb. 24.7 Der Fluß von Teilchen gegen einen Konzentrationsgradienten. Das erste Ficksche Gesetz besagt, daß der Fluß der Materie (die Zahl der Teilchen pro Zeit- und

[redacted]

Atkins

Molecular diffusion

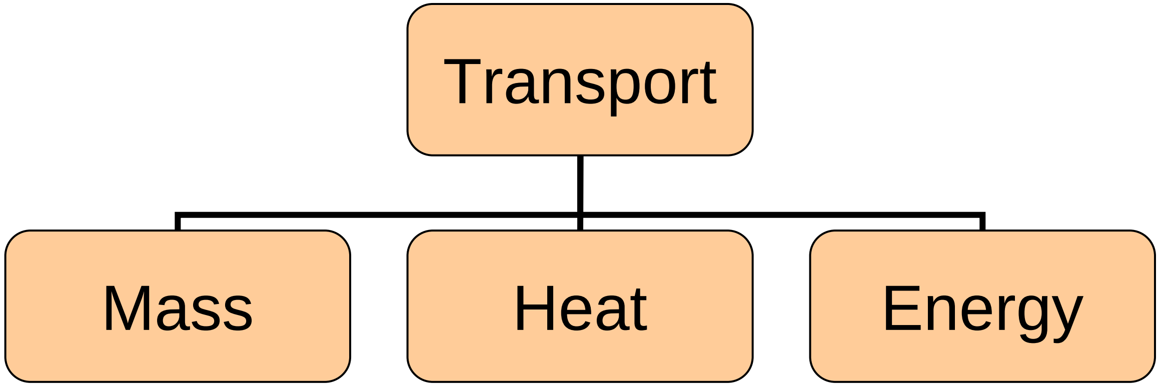
- mixture of two components A and B,
  concentration gradient (in one dimension y):
  under steady-state conditions the diffusional flow of one component is described by *1. Fick law*

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

- 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

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

Fick´s Law

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

Fourier´s Law

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

Newton´s Law
(viscosity)

General view to transport equations for gases

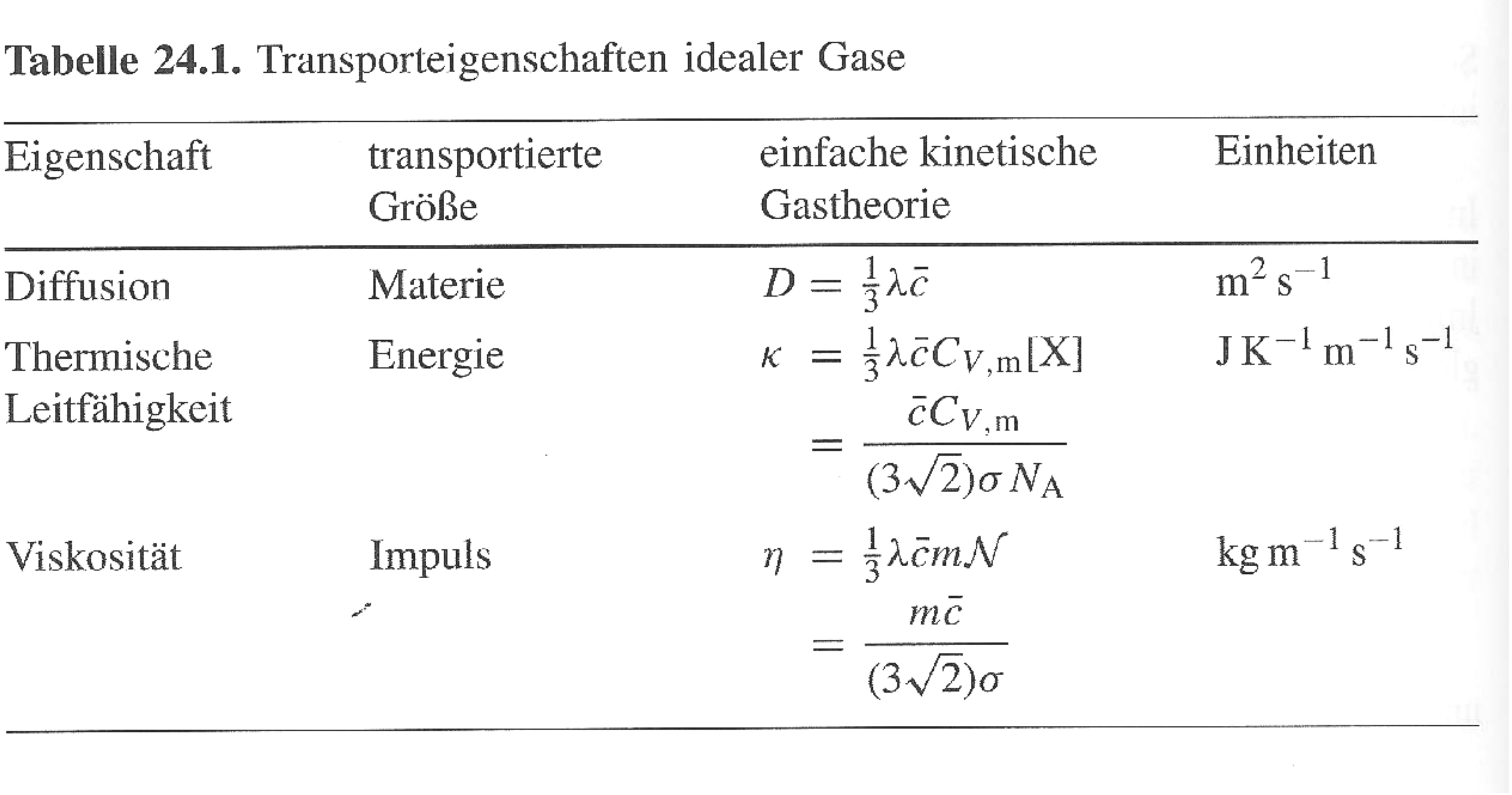


Tabelle 24.1. Transporteigenschaften idealer Gase

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

Molecular diffusion coefficient for gases

- Hirschfelder/Curtiss/Bird oder Chapman-Enskog relation for gases at low T, p (± 10% accuracy; extrapolation possible)

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

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*

$\Omega = f(k_B * T / \varepsilon_{AB})$

k_B…Boltzmann constant

ε_{AB}..force constant

(see tables in textbooks)

Molecular diffusion coefficient for gases

$$\Omega = f(k_B*T / \varepsilon_{AB})$$

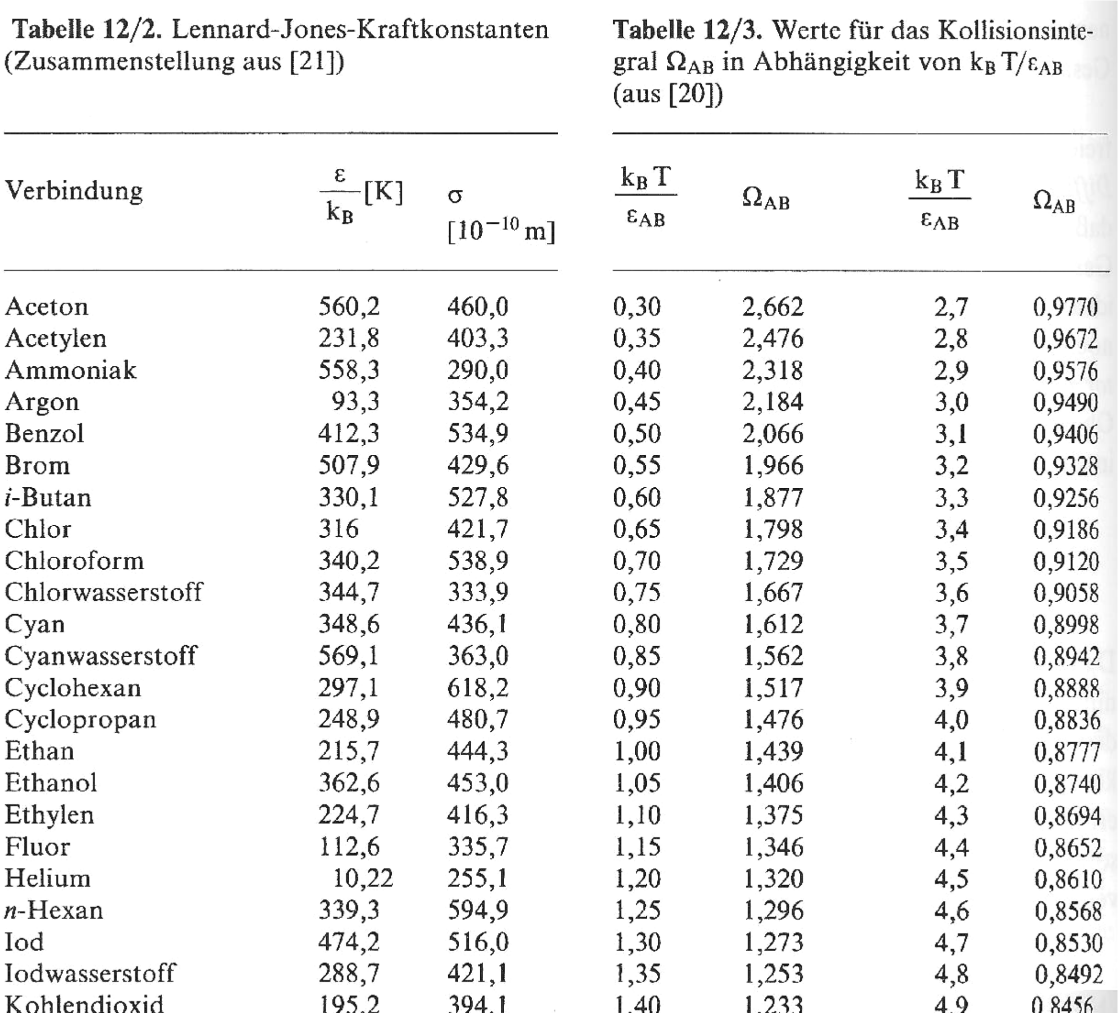


Tabelle 12/2. Lennard-Jones-Kraftkonstanten (Zusammenstellung aus [21])

Verbindung	$\frac{\varepsilon}{k_B}$ [K]	σ [10^{-10} m]
Aceton	560,2	460,0
Acetylen	231,8	403,3
Ammoniak	558,3	290,0
Argon	93,3	354,2
Benzol	412,3	534,9
Brom	507,9	429,6
i-Butan	330,1	527,8
Chlor	316	421,7
Chloroform	340,2	538,9
Chlorwasserstoff	344,7	333,9
Cyan	348,6	436,1
Cyanwasserstoff	569,1	363,0
Cyclohexan	297,1	618,2
Cyclopropan	248,9	480,7
Ethan	215,7	444,3
Ethanol	362,6	453,0
Ethylen	224,7	416,3
Fluor	112,6	335,7
Helium	10,22	255,1
n-Hexan	339,3	594,9
Iod	474,2	516,0
Iodwasserstoff	288,7	421,1
Kohlendioxid	195,2	394,1

Tabelle 12/3. Werte für das Kollisionsintegral Ω_{AB} in Abhängigkeit von $k_B T/\varepsilon_{AB}$ (aus [20])

$\frac{k_B T}{\varepsilon_{AB}}$	Ω_{AB}	$\frac{k_B T}{\varepsilon_{AB}}$	Ω_{AB}
0,30	2,662	2,7	0,9770
0,35	2,476	2,8	0,9672
0,40	2,318	2,9	0,9576
0,45	2,184	3,0	0,9490
0,50	2,066	3,1	0,9406
0,55	1,966	3,2	0,9328
0,60	1,877	3,3	0,9256
0,65	1,798	3,4	0,9186
0,70	1,729	3,5	0,9120
0,75	1,667	3,6	0,9058
0,80	1,612	3,7	0,8998
0,85	1,562	3,8	0,8942
0,90	1,517	3,9	0,8888
0,95	1,476	4,0	0,8836
1,00	1,439	4,1	0,8777
1,05	1,406	4,2	0,8740
1,10	1,375	4,3	0,8694
1,15	1,346	4,4	0,8652
1,20	1,320	4,5	0,8610
1,25	1,296	4,6	0,8568
1,30	1,273	4,7	0,8530
1,35	1,253	4,8	0,8492
1,40	1,233	4,9	0,8456

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

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

- 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

→ τ

- pores are connected by a network

Characterization of porous structures

- Porosity $\dfrac{\text{pore volume}}{\text{total volume, - mass}} \quad \left[\dfrac{m^3}{m^3}\right], \left[\dfrac{m^3}{kg}\right]$
- Pore radius, pore diameter
- Pore radius distribution, -density

$$H(r_p) = \int_{r_{p,\min}}^{r_p} h(r_p)\, dr_p \quad ; \quad h(r_p) = \frac{d\,H(r_p)}{dr_p}$$

- Specific surface area
- Tortuousity factor

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

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

Knudsen and molecular diffusion

- for porous solids experimental evaluation of diffusion coefficients

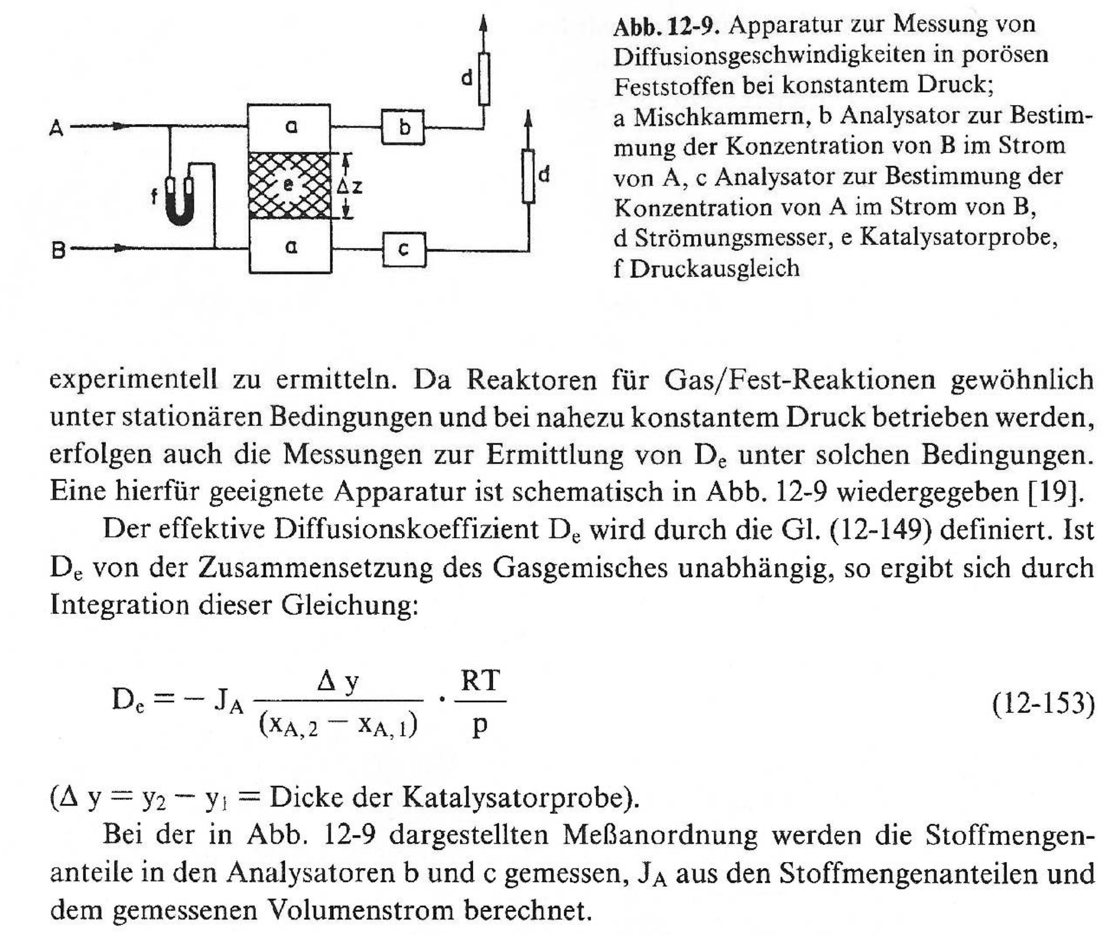


Abb. 12-9. Apparatur zur Messung von Diffusionsgeschwindigkeiten in porösen Feststoffen bei konstantem Druck; a Mischkammern, b Analysator zur Bestimmung der Konzentration von B im Strom von A, c Analysator zur Bestimmung der Konzentration von A im Strom von B, d Strömungsmesser, e Katalysatorprobe, f Druckausgleich

experimentell zu ermitteln. Da Reaktoren für Gas/Fest-Reaktionen gewöhnlich unter stationären Bedingungen und bei nahezu konstantem Druck betrieben werden, erfolgen auch die Messungen zur Ermittlung von D_e unter solchen Bedingungen. Eine hierfür geeignete Apparatur ist schematisch in Abb. 12-9 wiedergegeben [19].

Der effektive Diffusionskoeffizient D_e wird durch die Gl. (12-149) definiert. Ist D_e von der Zusammensetzung des Gasgemisches unabhängig, so ergibt sich durch Integration dieser Gleichung:

$$D_e = -J_A \frac{\Delta y}{(x_{A,2} - x_{A,1})} \cdot \frac{RT}{p} \qquad (12\text{-}153)$$

($\Delta y = y_2 - y_1$ = Dicke der Katalysatorprobe).

Bei der in Abb. 12-9 dargestellten Meßanordnung werden die Stoffmengenanteile in den Analysatoren b und c gemessen, J_A aus den Stoffmengenanteilen und dem gemessenen Volumenstrom berechnet.

Emig, Klemm

Background - Mathematics

- *Delta function* $f(x) = \delta(x-a)$
  - functional which acts on elements of a function
  - integral

$$\int_x^y \delta(t-a)\,dt = \begin{cases} 1 & x < a < y \\ 0 & a < x,\ y < a \end{cases} \qquad for\ x < y$$

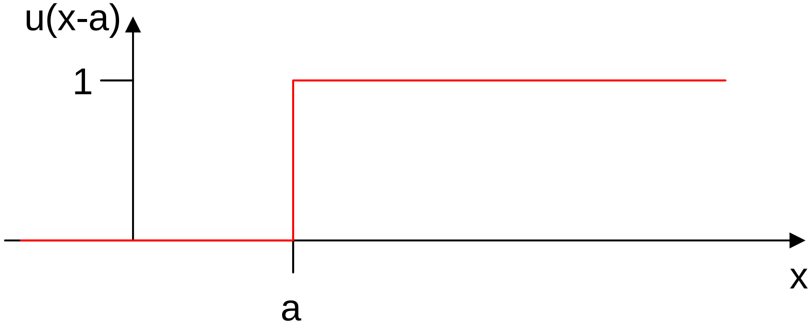
  - multiplication with a function f(x)

$$\int_{-\infty}^{+\infty} f(x)\ \delta(x-a)\,dx = f(a)$$

Background - Mathematics

- *Delta function*

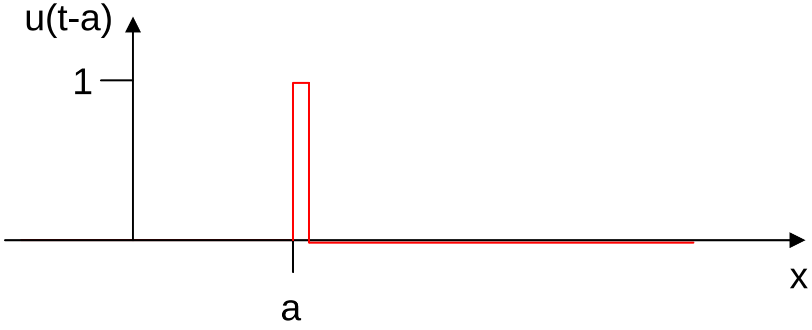
  - graphical representation as „Sprungfunktion“ (limes)



$$\delta(x-a) = \lim_{n\to\infty} \frac{1}{\pi(x-a)} \sin n(x-a)$$

$$\frac{du(x-a)}{dx} = \delta(x-a)$$

  - graphical representation as „Pulsfunktion“



$$\int \delta(t-a)\,dt = \begin{cases} 1 \\ 0 \end{cases}$$

Background - Mathematics

- *Laplace transformation*
  - aim: transformation of differential and integral expressions into algebraic expressions
  - definition

$$f(s) = \int_0^\infty e^{-st}\, F(t)\, dt$$

  - examples

$$f(s) = L[1] = \int_0^\infty e^{-st}\, dt = -\frac{1}{s} e^{-st}\Big|_0^\infty = \frac{1}{s}$$

$$f(s) = L\left[e^{\alpha t}\right] = \int_0^\infty e^{-st} e^{\alpha t}\, dt = \frac{1}{\alpha - s}$$

TAP – method and modeling

Transient experiments

- *Transients* are introduced into a system by *varying* one or more *state variables* (p, T, c, flow)

- Examples:

  - Molecular beam experiments
    pressure change

  - Temperature-programmed experiments
    temperature change

  - Step change experiments
    concentration change

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 information on the transport and kinetic parameters.

TAP – Features

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

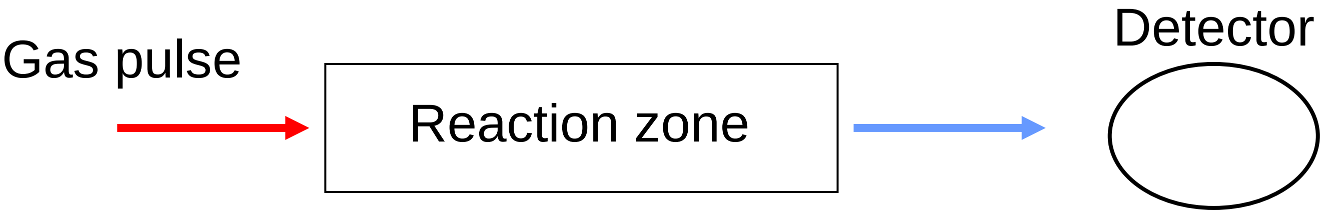
    or 10^{10} - 10^{9} moles
  - Example:

    - Sulfated zirconia: 100 m^2/g with 3 wt-% S,

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

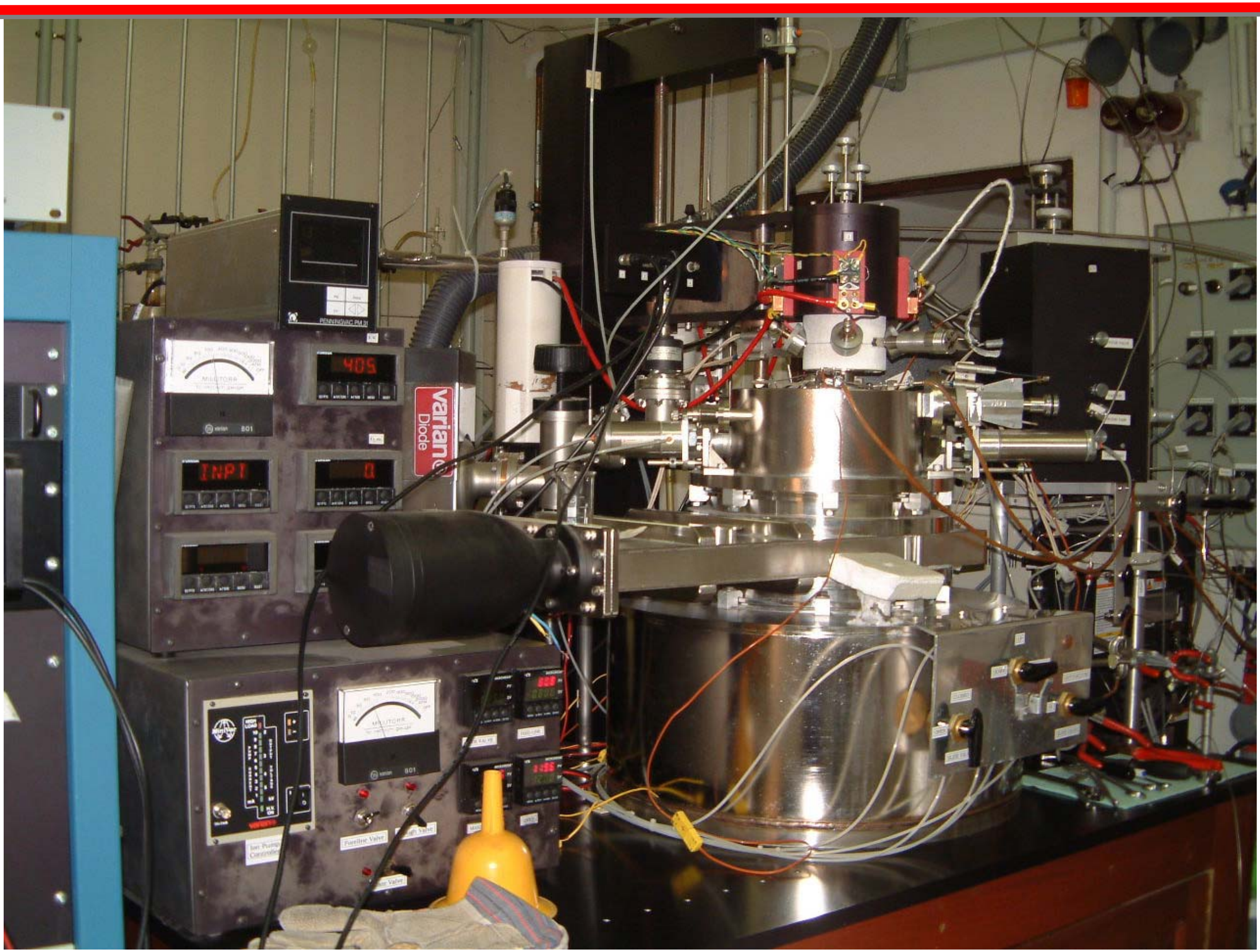
TAP – System hardware

Simplified schematic of a TAP pulse response experiment

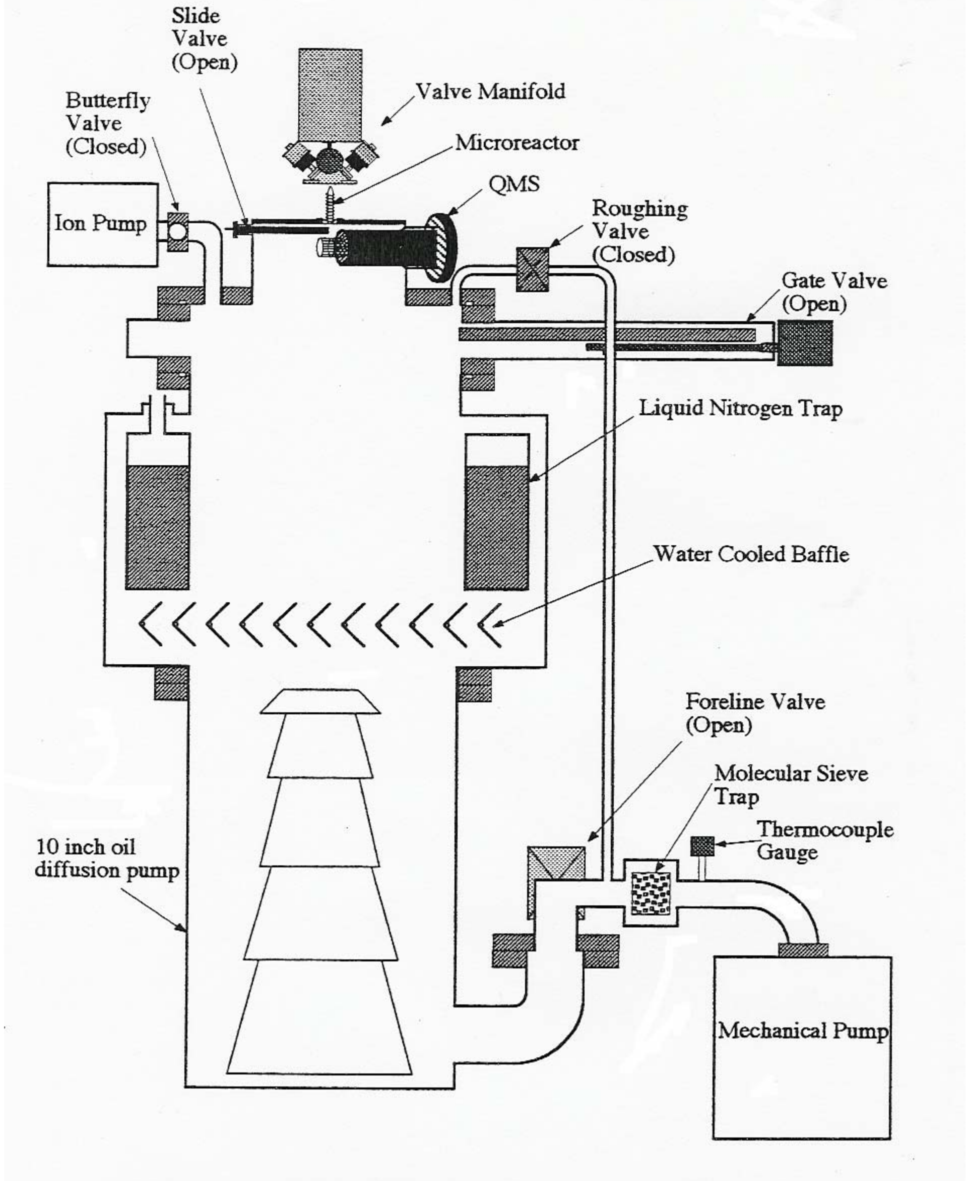


- Injection of a narrow gas pulse into an evacuated microreactor
- Gas pulses travel through the reactor
- Gas molecules (reactant and product) are monitored as a function of time and produce a transient response at the MS

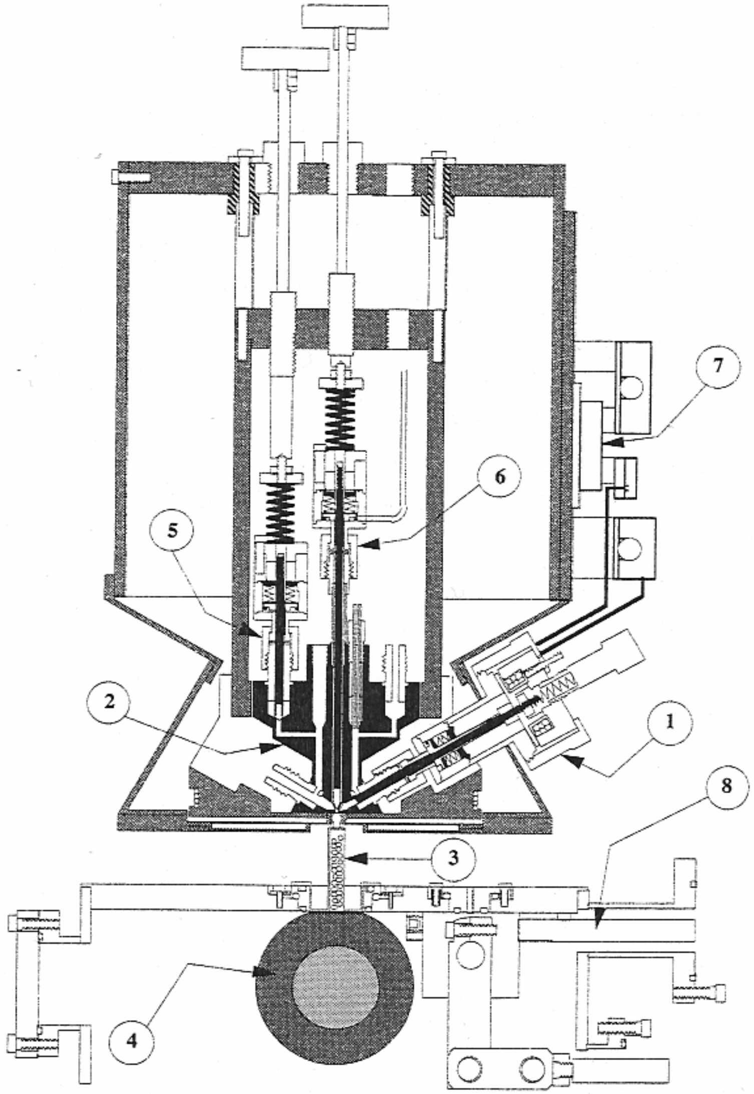
TAP – System hardware



TAP – System hardware

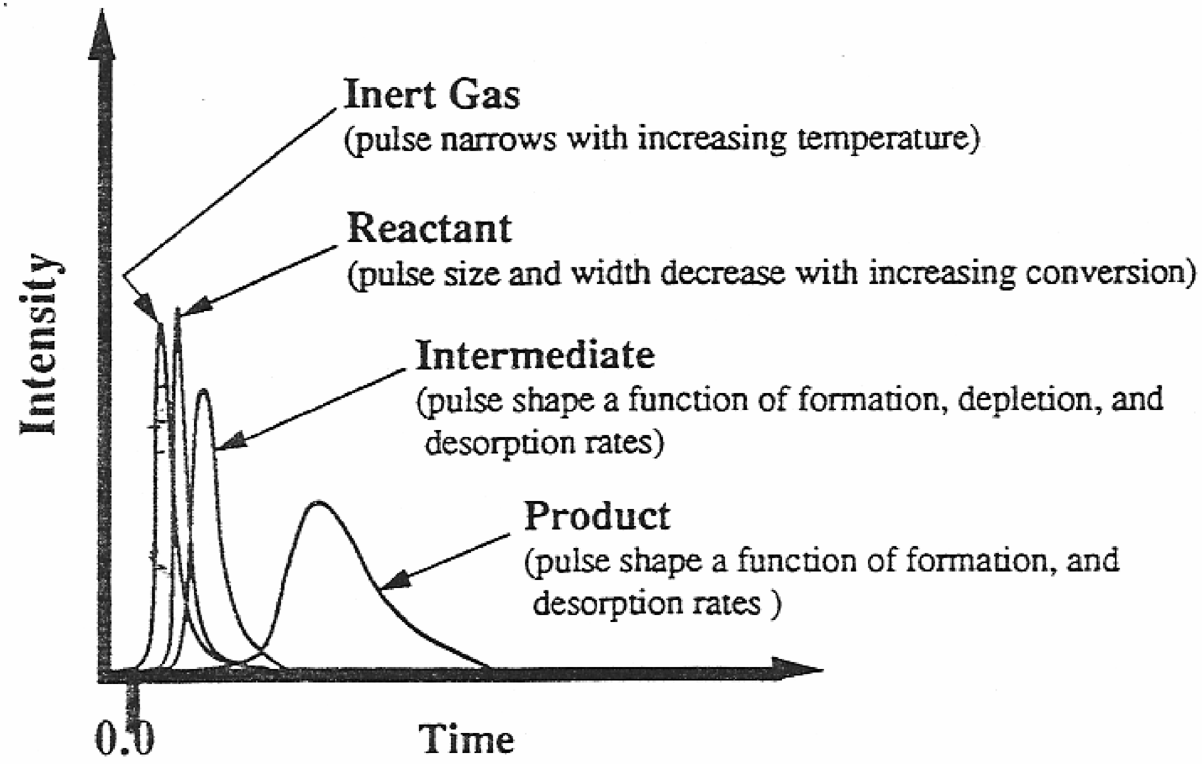


TAP – System hardware



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

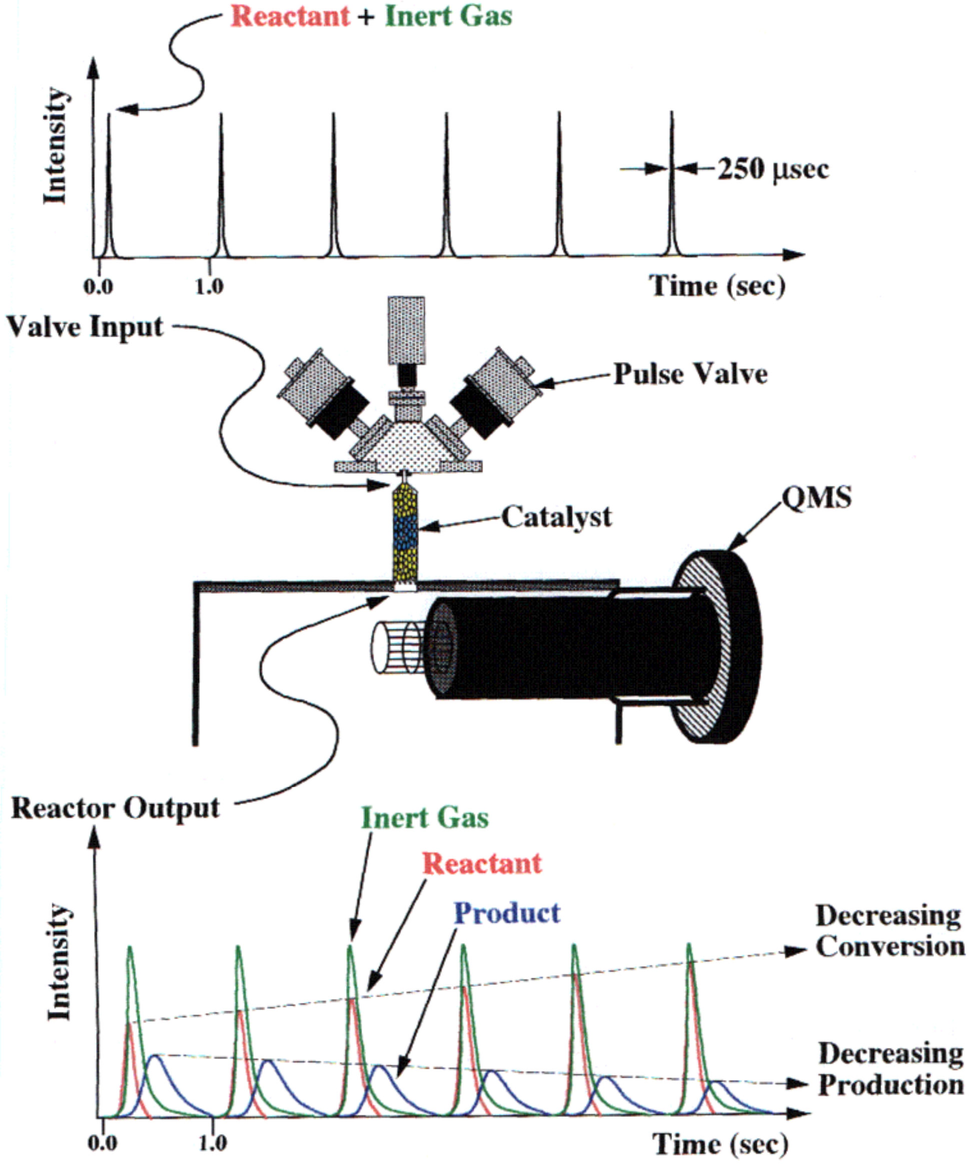
TAP – Response curves



Typical pulse response experimental outputs

TAP – Multipulse experiment

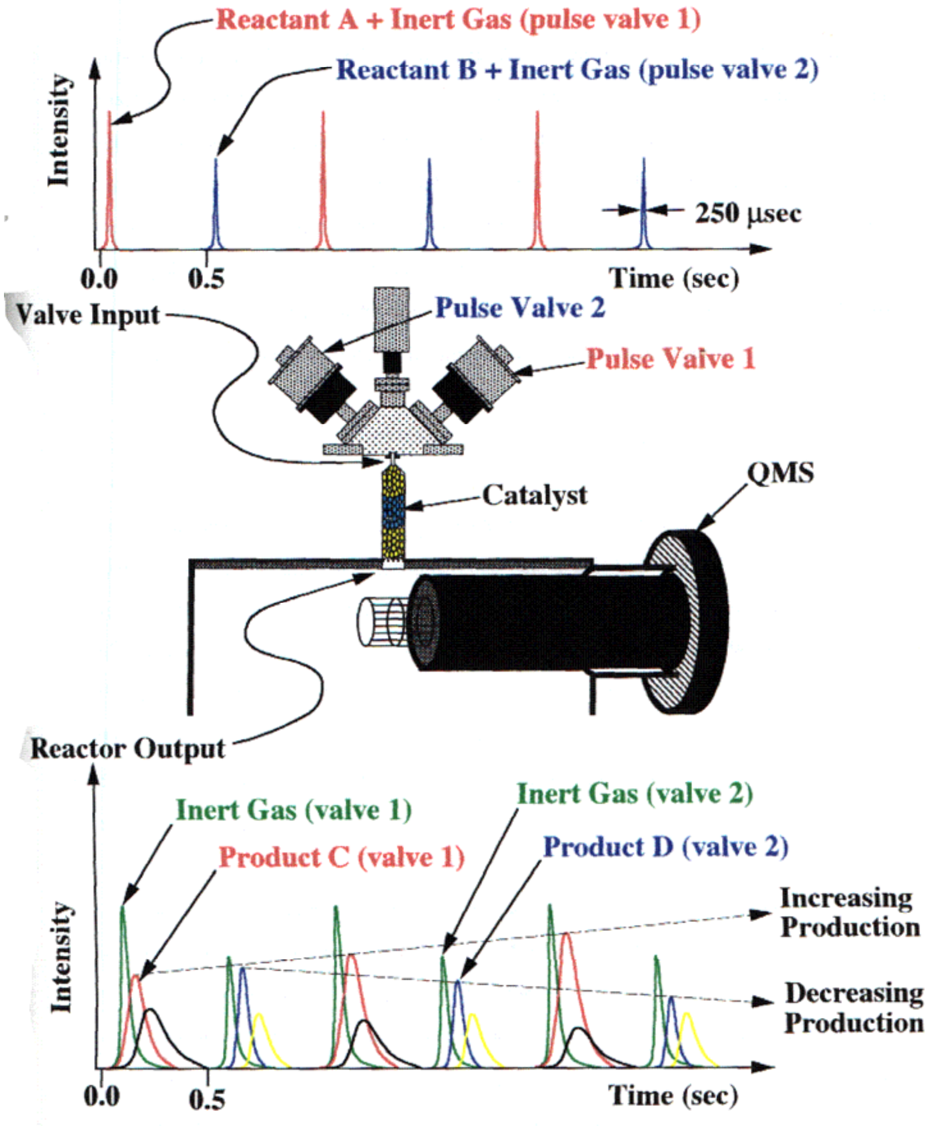
- Key features of **input**:
  - typical pulse intensity range from 10^{13} to 10^{17} molecules/pulse
  - pulse width 150-250 µs
  - pulse rates 1-50 s^{-1}
- Key features of **output**:
  - different products have different responses
  - individual product response can change with pulse number



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

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

TAP – General models

Currently there are three basic models in application based on partial-differential equations.

- *One-zone-model*
- *Three-zone-model*
- *Thin-zone-model*

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

The equation can be solved using different sets of initial and boundary conditions that correspond to different physical situations.

initial conditions: $0 \le z \le L$, $t = 0$, $C_A = \delta_z \dfrac{N_{pA}}{\varepsilon_b A}$

boundary conditions: $z = 0$, $\dfrac{\partial C_A}{\partial z} = 0$

$z = L$, $C_A = 0$

N_{pA} … number of moles of gas A in one pulse

A … cross-sectional area of the reactor (cm^2)

L … length of the reactor (cm)

TAP – Transport model

The gas flow at the reactor exit F_A (mol/s) is described by

$$\boxed{F_A = A\,D_{eA} \frac{\partial C_A}{\partial z}\Big|_{z=L}}$$

and the gas flux (mol/cm^2 s) by

$$\boxed{\mathrm{Flux}_{\mathrm{A}} = \frac{F_A}{A}}$$

To solve for the gas flow it is useful to express initial and boundary conditions in terms of dimensionless parameters.

TAP - Transport model

Use of dimensionless parameters

$\xi = \frac{z}{L}$ … dimensionless axial coordinate

$\overline{C}_A = \frac{C_A}{N_{PA} / \varepsilon_b A L}$ … dimensionless concentration

$\tau = \frac{t\, D_{eA}}{\varepsilon_b\, L^2}$ … dimensionless time

TAP – Transport model

Dimensionless form of mass balance

$$\boxed{\frac{\partial \overline{C}_A}{\partial \tau} = \frac{\partial^2 \overline{C}_A}{\partial \xi^2}}$$

initial conditions: $0 \le \xi \le 1$, $t = 0$, $\overline{C}_A = \delta_\xi$

boundary conditions: $\xi = 0$, $\frac{\partial \overline{C}_A}{\partial \xi} = 0$

$\xi = 1$, $\overline{C}_A = 0$

Solution:

- analytical a) method of separation of variables

b) Laplace transformation

- numerical for more complex problems

TAP – Transport model

Method of separation of variables:

solution for dimensionless concentration

$$\boxed{\overline{C}_A(\xi,\tau)=2\sum_{n=0}^{\infty}\cos\left((n+0.5)\pi\xi\right)\exp\left(-(n+0.5)^2\pi^2\tau\right)}$$

solution for dimensionless flow rate

$$\boxed{\overline{F}_A(\xi,\tau)=-\frac{\partial\overline{C}_A(\xi,\tau)}{\partial\xi}=\pi\sum_{n=0}^{\infty}(2n+1)\sin\left((n+0.5)\pi\xi\right)\exp\left(-(n+0.5)^2\pi^2\tau\right)}$$

dimensionless flow rate at the exit (ξ=1)

$$\boxed{\overline{F}_A=\pi\sum_{n=0}^{\infty}(-1)^n(2n+1)\exp\left(-(n+0.5)^2\pi^2\tau\right)}$$

TAP – Transport model

$$\overline{F}_A = \pi \sum_{n=0}^{\infty} (-1)^n (2n+1) \exp\left(-(n+0.5)^2 \pi^2 \tau\right)$$

Expression for the dimensionless exit flow rate
as a function of dimensionless time

Standard diffusion curve

For *any* TAP pulse response experiment that involves *only gas transport*, the plot of *the dimensionless exit flow rate* versus dimensionless time will give *the same curve* regardless the gas, reactor length, particle size, or reactor temperature.

TAP – Transport model

Due to initial condition the surface area under SDC is equal to unity – flow rate in dimensional form

$$\boxed{\frac{F_A}{N_{pA}} = \frac{D_{eA}\,\pi}{\varepsilon_b\,L^2}\sum_{n=0}^{\infty}(-1)^n(2n+1)\,\exp\left(-(n+0.5)^2\pi^2\,\frac{t\,D_{eA}}{\varepsilon_b\,L^2}\right)}$$

An important property of this dimensional dependence is that its *shape* is *independent on* the *pulse intensity* if the process occurs in the *Knudsen* regime.

TAP – Transport model

$$\boxed{\frac{F_A}{N_{pA}} = \frac{D_{eA}\,\pi}{\varepsilon_b\,L^2}\sum_{n=0}^{\infty}(-1)^n\,(2n+1)\,\exp\left(-(n+0.5)^2\,\pi^2\,\frac{t\,D_{eA}}{\varepsilon_b\,L^2}\right)}$$

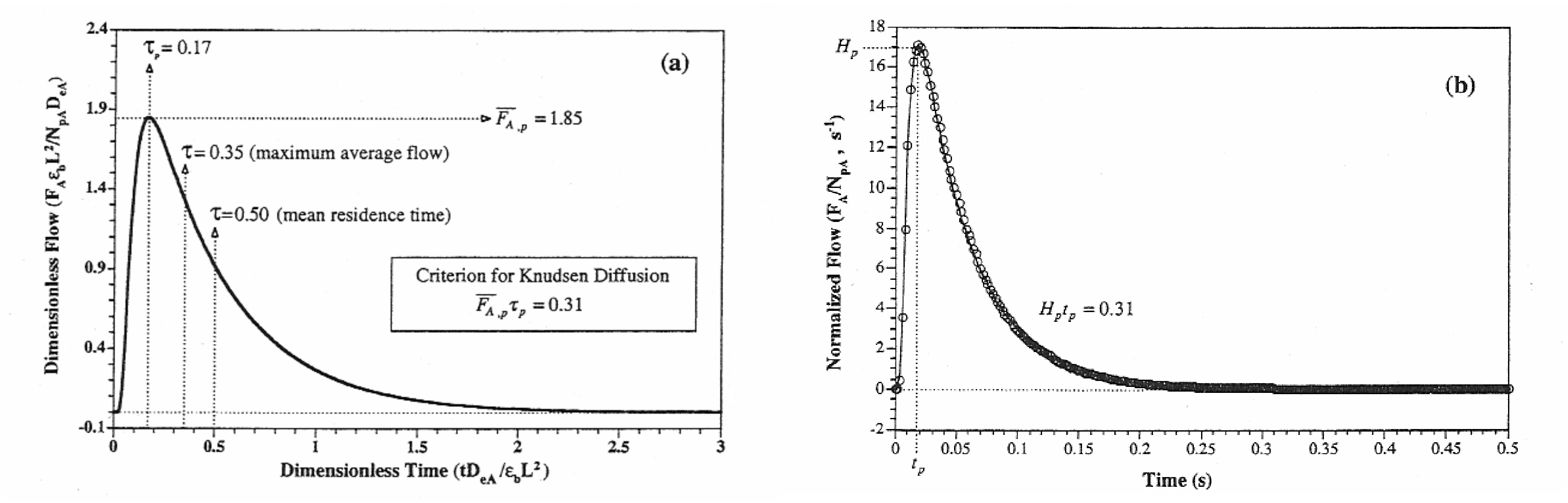
Characteristics of standard diffusion curve

$\tau_p = \frac{1}{6}$, $t_p = \frac{1}{6}\frac{\varepsilon_b\,L^2}{D_{eA}}$ … peak maximum

$\overline{F}_{A,p} = 1.85$, $H_p = 1.85\frac{D_{eA}}{\varepsilon_b\,L^2}$ … corresponding height

$\overline{F}_{A,p}\,\tau_p = H_p\,t_p \approx 0.31$ … *„fingerprint“* for Knudsen regime

TAP – Transport model



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

(2) Diffusion + irreversible adsorption

Flow rate F_A at reactor exit

$$\boxed{\frac{F_A}{N_{pA}} = \frac{D_{eA}\,\pi}{\varepsilon_b\,L^2}\exp(-k_a^{\prime} t)\sum_{n=0}^{\infty}(-1)^n(2n+1)\exp\left(-(n+0.5)^2\pi^2\frac{t\,D_{eA}}{\varepsilon_b\,L^2}\right)}$$

with

$$\boxed{k_a^{\prime} = \frac{a_s\,S_v\,(1-\varepsilon_b)\,k_a}{\varepsilon_b}}$$

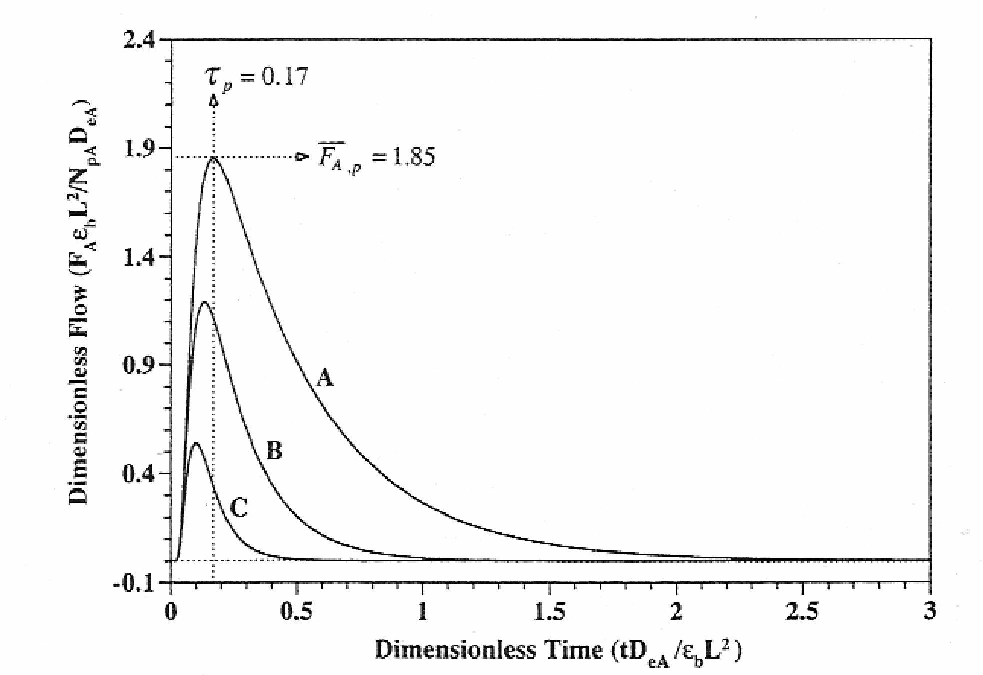
Exit flow curve for diffusion+irreversible adsorption

- is *smaller* than SDC by a *factor of exp(-k_a´t)*

- is always placed „inside“ the SDC (fingerprint)

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

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

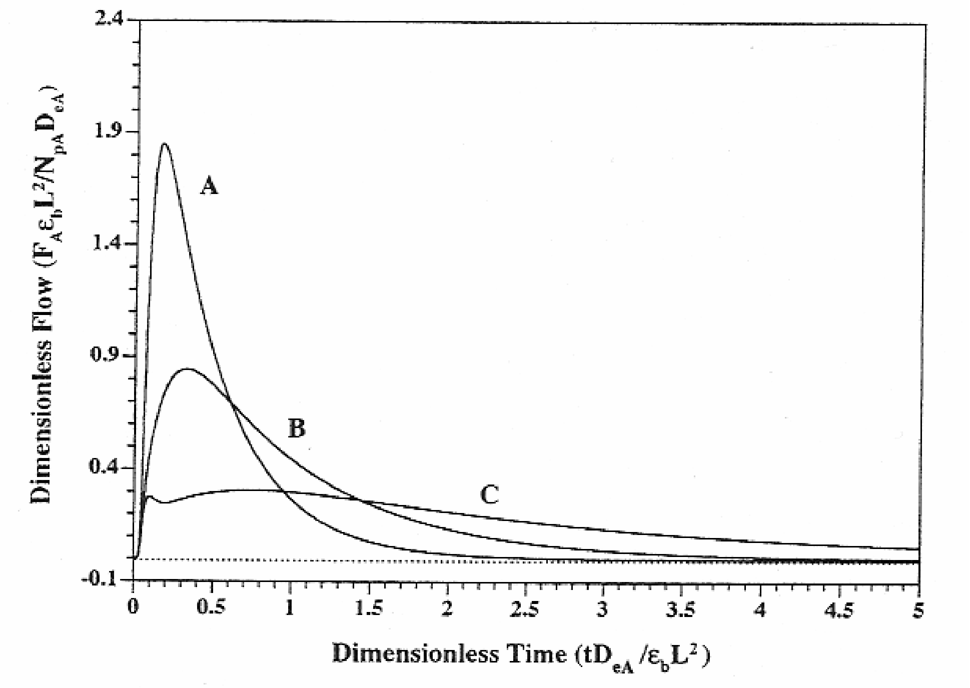
- for component A on the catalyst surface

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

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

TAP - Transport + adsorption model

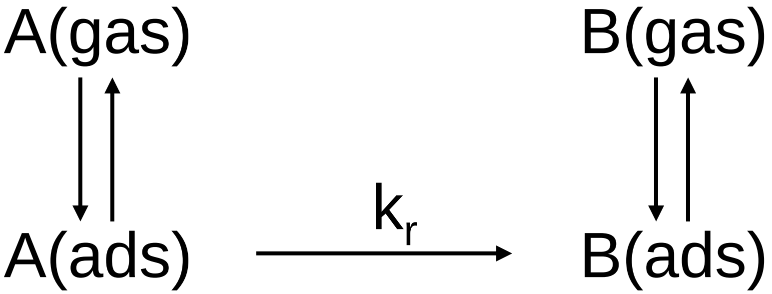
Exit flow curve for the diffusion+reversible adsorption case



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

TAP – Transport, adsorption, reaction

(3) Diffusion + reversible adsorption + irreversible reaction



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

$$\boxed{\frac{\partial \theta_A}{\partial t} = k_{aA}\, C_A - k_{dA}\, \theta_A - k_r\, \theta_A}$$

$$\boxed{\varepsilon_b \frac{\partial C_B}{\partial t} = D_{eB} \frac{\partial^2 C_B}{\partial z^2} - a_s\, S_v\, (1-\varepsilon_b)(k_{aB}\, C_B - k_{dB}\, \theta_B)}$$

$$\boxed{\frac{\partial \theta_B}{\partial t} = k_r\, \theta_A - k_{dB}\, C_B + k_{dB}\, \theta_B}$$

TAP – Transport, adsorption, reaction

(3) Diffusion + reversible adsorption + irreversible reaction

The *initial* and *boundary* conditions used in the transport-only case can be applied to the transport+reaction case as well.

Initial condition $t = 0 \quad , C_A = 0$

Inlet boundary condition $z = 0 \quad , -D_{eA,1}\frac{\partial C_{A,1}}{\partial z} = \delta(t)$

TAP – Transport, adsorption, reaction

(3) Diffusion + reversible adsorption + irreversible reaction

$$\boxed{-D_{eA,1}\frac{\partial C_{A,1}}{\partial z}=\delta(t)}$$

The inlet flux is respresented by a *delta function*. With this combination, *analytical solutions* in the Laplace-domain can be *easily derived* when the set of *differential equations* that describe the model is *linear*.

TAP – Characteristic values

Use of dimensionless parameters

$$\boxed{\bar{k}_a = k_a' \frac{\varepsilon_b L^2}{D_{eA}}}$$

dimensionless apparent adsorption rate constant

with $$k_a' = \frac{a_s S_v (1-\varepsilon_b) k_a}{\varepsilon_b}$$

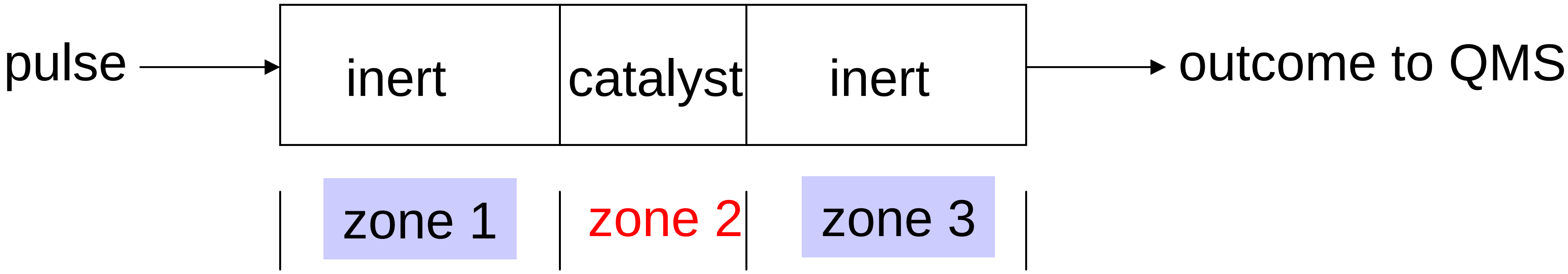
k_a' contains:

- the *kinetic characteristics* of the *active site* (k_a)
- the *structural characteristics* of the whole catalytic system $\frac{a_s S_v (1-\varepsilon_b)}{\varepsilon_b}$

TAP – Extended models

Three-zone-model

Additional boundary conditions between the different zones have to be applied



pulse

inert

catalyst

inert

outcome to QMS

zone 1

zone 2

zone 3

Evaluation of curve shapes and „fingerprints“ are basicly the same as for the one-zone-model

TAP – Theory

Moment-based quantitative description of TAP-experiments

- idea behind: observed TAP data consist of a set of exit flow rates versus time dependencies
- analytical solutions in integral form can be usually obtained
- analysis of some integral characteristics (moments) of the exit flow rate

- moments reflect important primary features of the observations

TAP – Theory - Moments

- moment M_n of the exit flow rate
  (i.e. not of concentration)

$$\boxed{M_n = \int_0^t t^n F(t)\, dt}$$

n…order of moment

- representation in dimensionless form

$$\boxed{\overline{m}_n = \int_0^\infty \tau^n\, \overline{F}_A\, d\tau \quad \text{with} \quad \tau = \frac{t}{(\varepsilon_b L^2/D_{eA})}}$$

TAP – Theory - Moments

Application to TAP experiments:

- for irreversible adsorption / reaction

$$\overline{m}_0 = 1 - X = \frac{1}{\cosh\sqrt{Da_I}} \quad \text{with} \quad Da_I = \frac{k_a' \, \varepsilon_b \, L^2}{D_{eA}}$$

Da_I … Damköhler number I

- mean dimensionless residence time

$$\tau_{res} = \frac{m_1}{m_0} = \frac{\sum_{n=0}^{\infty} \frac{A(n)}{[B(n) + Da_I]^2}}{\sum_{n=0}^{\infty} \frac{A(n)}{B(n) + Da_I}} \tau_{Dif}$$

$$A(n) = (-1)^n \, (2^n + 1)$$

$$B(n) = (n + 0.5)^2 \pi^2$$

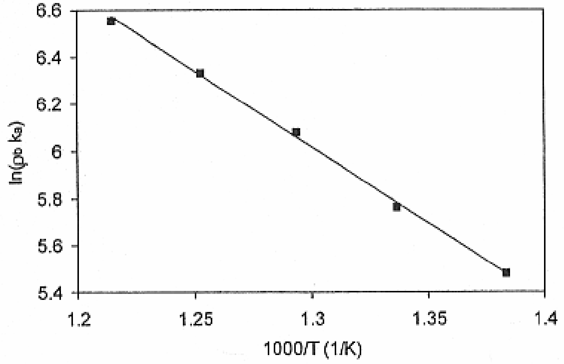
$$\tau_{Dif} = \frac{\varepsilon_b L^2}{D_{e,A}}$$

Applications

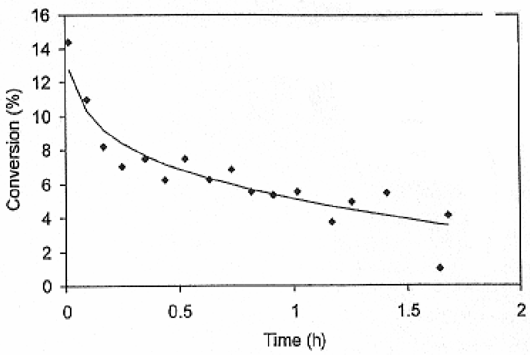
TAP - Examples

Mechanism and Kinetics of the Adsorption and Combustion of Methane on Ni/Al_2O_3 and NiO/Al_2O_3 (Dewaele et al. 1999)

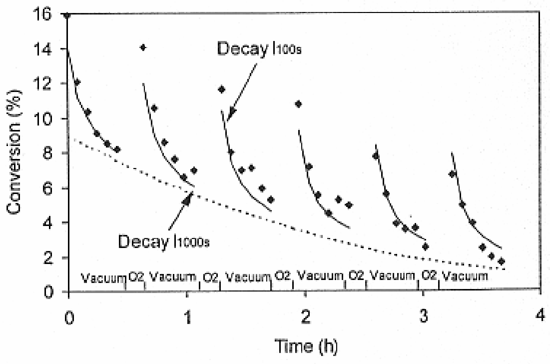
- Supported Ni catalysts for steam reforming of natural gas to synthesis gas
- Combination of TPR with single pulse experiments



Arrhenius plot of the methane adsorption rate coefficient $\rho_B k_a$ (s^{-1}) on the reduced Ni catalyst.



Evolution of the methane conversion at 823 K on 0.060 g of surface-oxidized catalyst in the absence of gas-phase oxygen as a function of time after surface oxidation. The methane pulse size: 2.04×10^{14} molecules. (◆) Experimental; (—) modeled according to Section 3.4.2.b.



Evolution of the methane conversion at 823 K on 0.060 g of surface-oxidized catalyst as a function of time after surface oxidation. Oxygen was fed (10^{-6} mol s^{-1}) for 10 min every 35 min. (◆) Experimental; (—) modeled according to Section 3.4.2.b.

TAP - Examples

Selective oxidation of n-butane to maleic anhydride (MA) over vanadium phosphorous oxide (VPO) (Gleaves et al. 1997)

- important heterogeneous selective oxidation
- complex reaction (electron transfer, fission of C-H-bonds, addition of oxygen, ring closure)
- literature: $(VO)_2P_2O_7$-lattice as active-selective phase, but it is not clear how the lattice supplies the oxygen
  - possible involvation of oxygen adspecies adsorbed on vanadium surface sites
  - possible involvation of bulk oxygen
  - possibly other crystal phases are active

TAP - Examples

Selective oxidation of n-butane to maleic anhydride (MA) over vanadium phosphorous oxide (VPO)

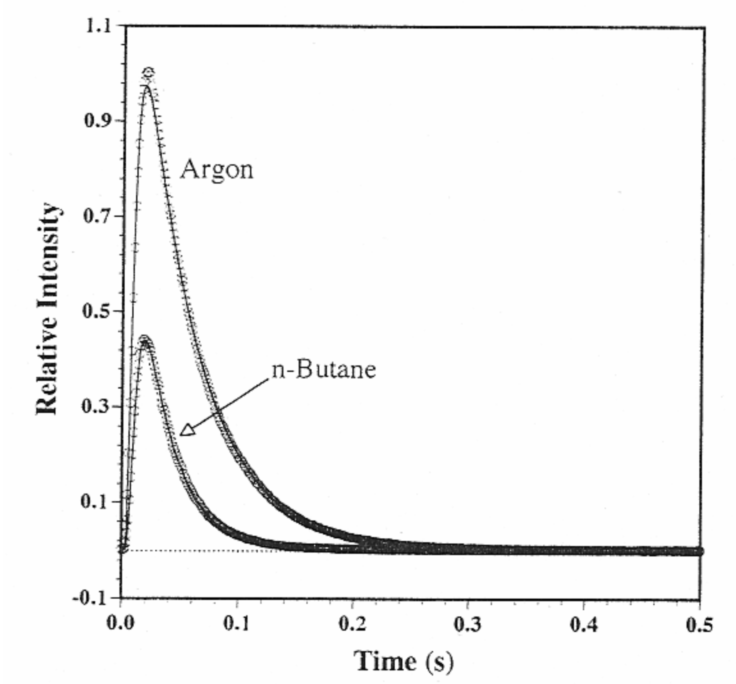
- Steady-state kinetic studies yielded different rate expressions and kinetic parameters – this may be related to differences in c. composition, c. structure, c. oxydation state, etc. → no unique information

- Aim of TAP investigations:
  Relate changes in kinetic dependencies to changes in the catalyst
- How to do ? Systematic alteration of the state of the catalyst and measuring kinetic dependencies

TAP - Examples

Selective oxidation of n-butane to maleic anhydride (MA) over vanadium phosphorous oxide (VPO)

Kinetics of n-butane conversion over VPO in the absence of gas phase oxygen



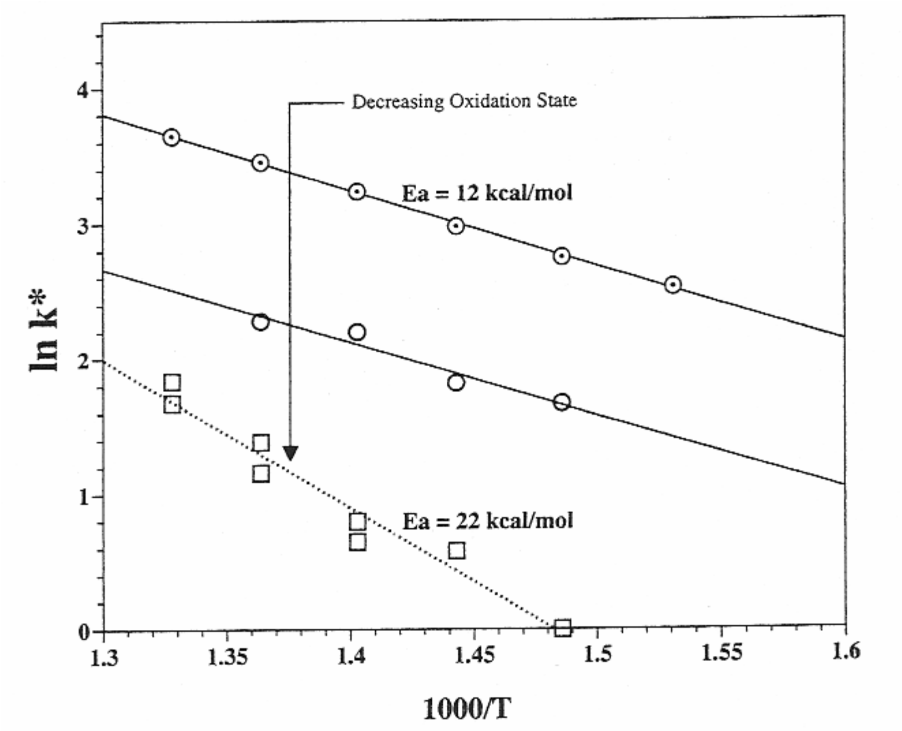
- n-butane curve lies completely within the generated diffusion curve ⟶ irreversible process

- initial step is irreversible (fissure of CC or CH bond)

TAP - Examples

Selective oxidation of n-butane to maleic anhydride (MA) over vanadium phosphorous oxide (VPO)

Kinetics of n-butane conversion on oxygen-treated VPO



Arrhenius plots for pulsed n-butane conversion over an oxygen-treated VPO catalyst sample as a function of oxidation state

- values of apparent activation energy is strongly dependent on the VPO oxidation state

- decreasing number of active centers

- TAP + Raman: V^{4+} V^{5+}

TAP – sulfated zirconia (SZ)

TAP investiagtions on sulfated zirconias

C. Breitkopf. *J. Mol. Catal. A: Chem. 226 (2005) 269.*

X. Li, K. Nagaoka, L. Simon, J.A. Lercher, S. Wrabetz, F.C. Jentoft, C. Breitkopf, S. Matysik, H. Papp.
J. Catal. 230 (2005) 214-225.

C. Breitkopf, S. Matysik, H. Papp. *Appl. Catal. A: Gen*. 301 (2006) 1.

C. Breitkopf, H. Papp. Proceedings of The 1st International Conference on Diffusion in Solids and Liquids DSL-2005, July 6-8, 2005, Aveiro, Portugal, 67. (oral presentation)

TAP – Investigation of poisoned samples

Comparison of active sample Kat1 with samples of Na-modified surfaces

3 % of active centres poisoned
40 % of active centres poisoned
all centres poisoned

Sulfation Step:

$5.7\text{x}10^{-3}$ mol $(NH_4)_2SO_4$	Kat1
$5\text{x}10^{-5}$ mol Na_2SO_4 + $5.7\text{x}10^{-3}$ mol $(NH_4)_2SO_4$	SZ-Na1
$5\text{x}10^{-4}$ mol Na_2SO_4 + $5.2\text{x}10^{-3}$ mol $(NH_4)_2SO_4$	SZ-Na2
$5\text{x}10^{-3}$ mol Na_2SO_4 + $0.7\text{x}10^{-3}$ mol $(NH_4)_2SO_4$	SZ-Na3

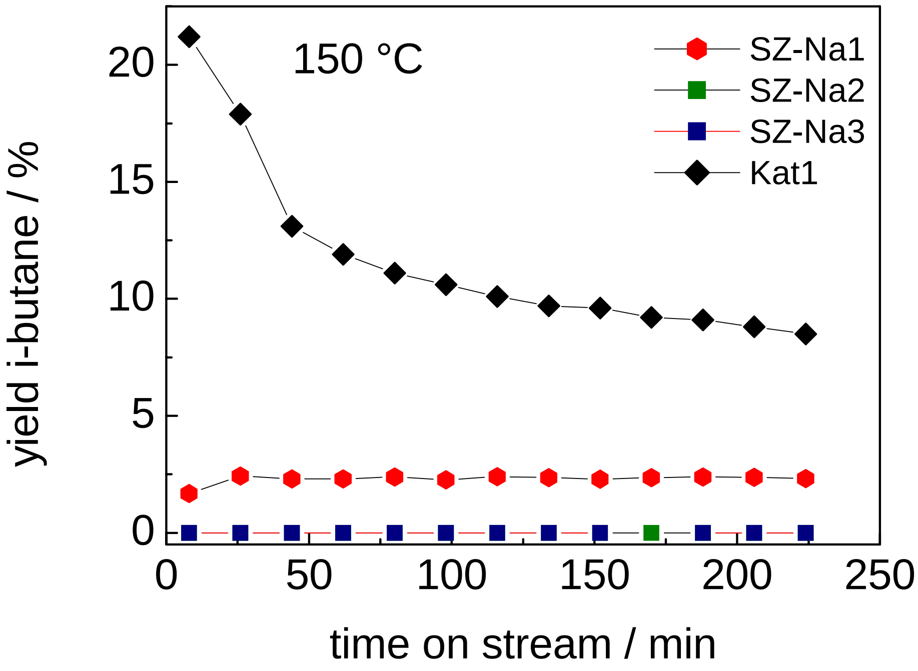
Calcination @ 873 K for 3 h

Characterization

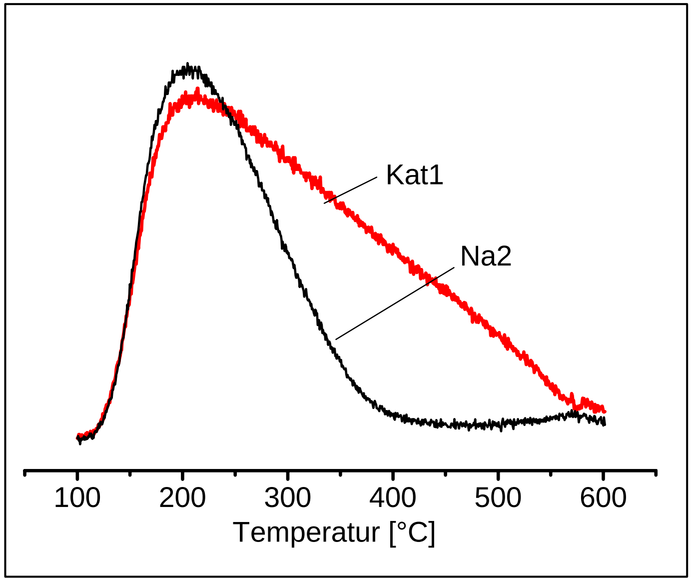
Sample	Kat1	SZ-Na1	SZ-Na2	SZ-Na3
BET [m^2/g]	103	76	45	10
Pore diameter [Å]	35	50	94	135
Pore volume [cm^3/g]	0.08	0.11	0.11	0.04
SO_4 content w.%	9.0	9.9	7.5	5.1
S atoms/m^2	$5.3*10^{18}$	$7.8*10^{18}$	$1.0*10^{19}$	$2.9*10^{19}$
Na^+ ions/m^2	-	$2.2*10^{17}$	$3.7*10^{18}$	$1.6*10^{20}$
S/Na^+	-	35.4	2.7	0.29

Catalysis and TPD

Activation: 2 h at 600°C in air, 30 ml/min
Reaction: 5 % n-butane (99.95 % purity) in N_2, 20 ml/min



TPD



Poisoning of 3 % of active Brønsted centres led to significant decrease in activity, loss of Brønsted centres led to inactive samples

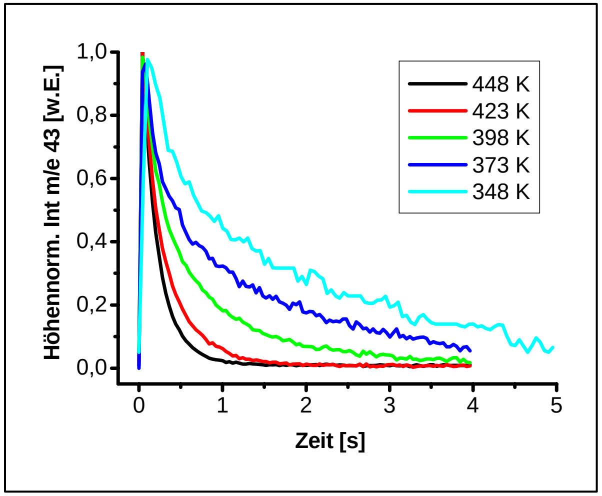
DRIFTS

Sample	L/B Ratio (by pyr ads.) at 323 K	Surface Content Na [%]	S=O mode [cm^{-1}] at 673 K
Kat1	0.9	-	1402
SZ-Na1	1.1	not detectable	1397
SZ-Na2	1.7	3.5	1389
SZ-Na3	13.0	8	-

L/B ratio determined according to Platon A, Thomas WJ. Ind. Engin. Chem. Res. 24 (2003) 5988.

TAP – n-butane single pulses

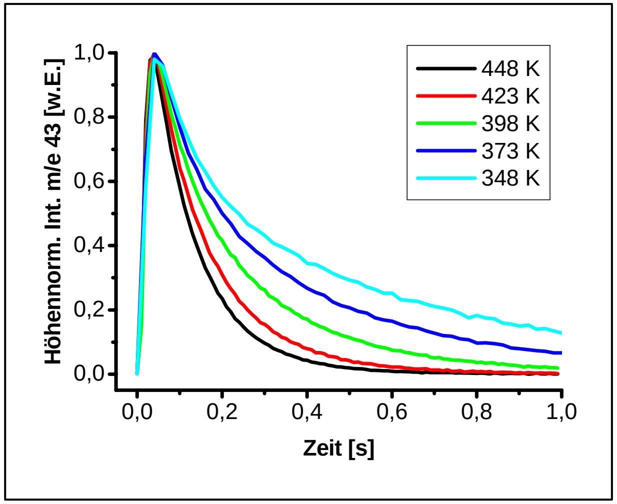
Kat1



τ (348 K) = 1.58 s
τ (423 K) = 0.49 s

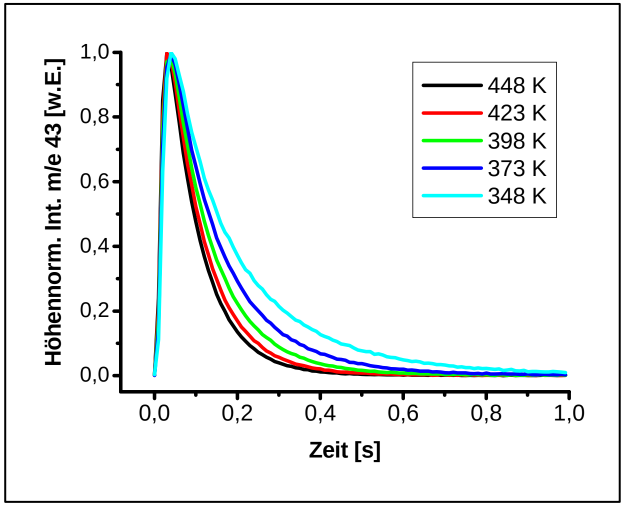
τ … residence time

SZ-Na1



τ (348 K) = 0.47 s
τ (423 K) = 0.16 s

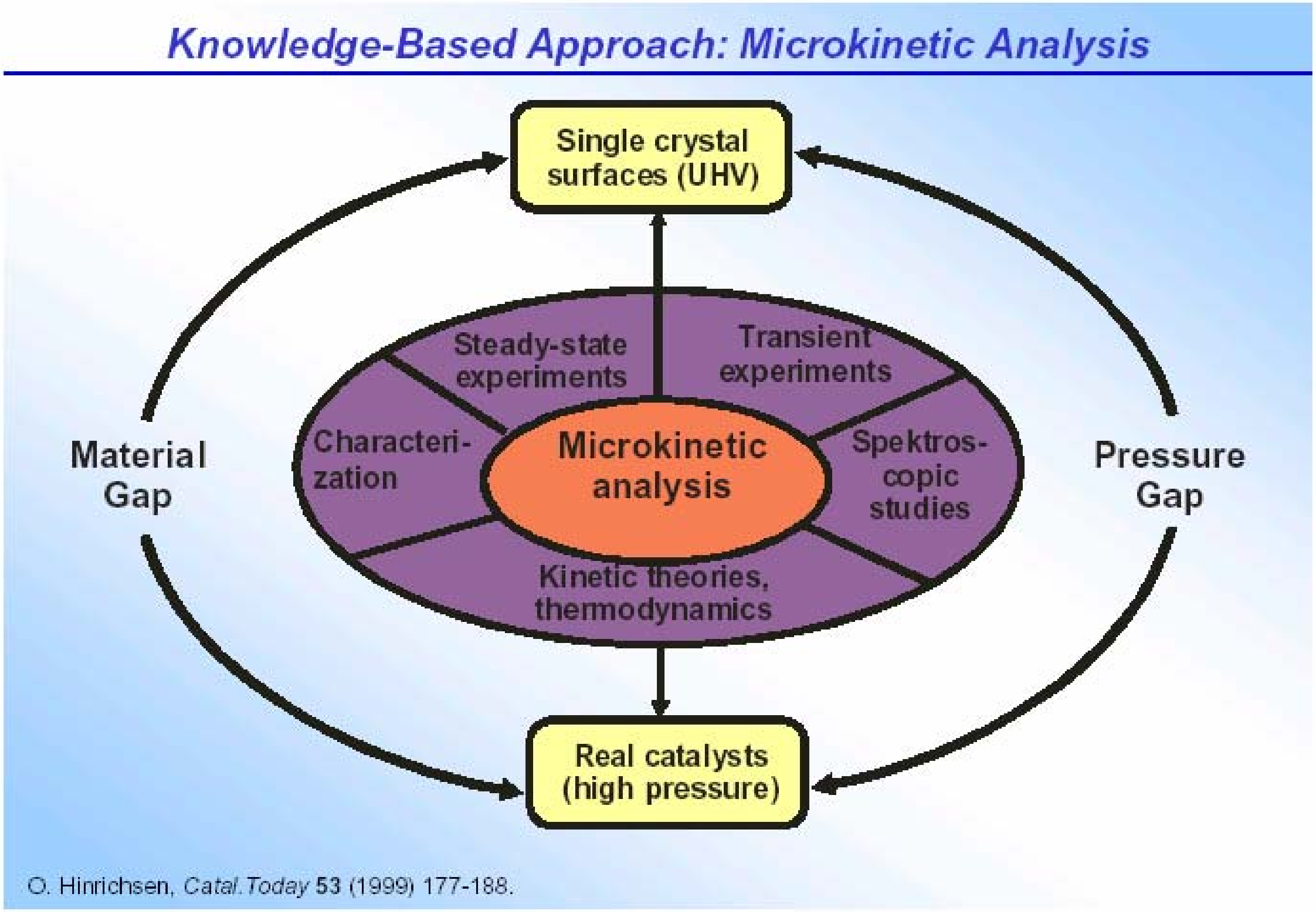
SZ-Na2



τ (348 K) = 0.20 s
τ (423 K) = 0.11 s

Interaction of n-butane single pulse with surface decreases with increasing amount of sodium

Kinetic modeling



Knowledge-Based Approach: Microkinetic Analysis

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

Thank you for your attention!