TAP
Temporal Analysis of Products

SSITKA
Steady State Isotopic Transient Kinetic Analysis

Modern Methods in Heterogeneous Catalysis

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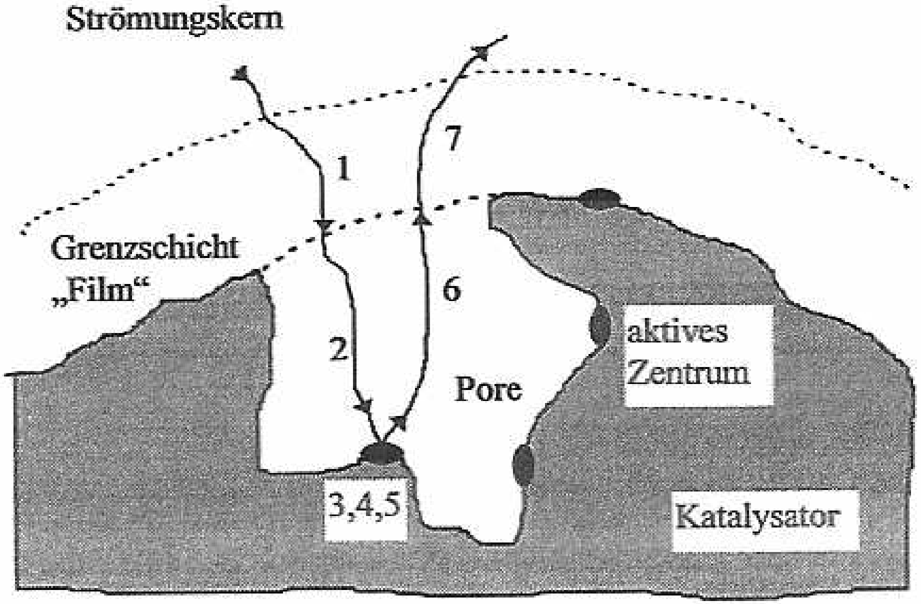
Transient methods are a powerful tool for gaining insights into the mechanisms of complex catalytic reactions.

Outline

- Microkinetic modeling
- Laboratory reactors
- Background
    - Diffusion, mathematics
- TAP
    - System hardware, theory, examples
- SSITKA
    - Theory, examples

Macrokinetics and Microkinetics

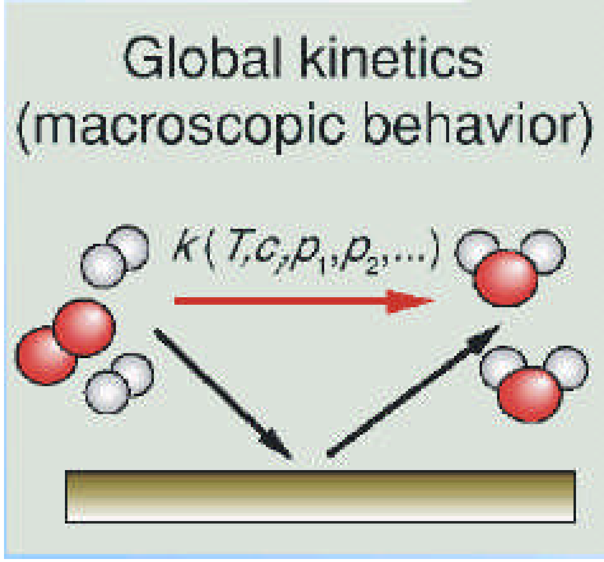
1. *Filmdiffusion der Edukte.* Die Edukte werden aus dem Strömungskern durch den Film an die äußere Oberfläche des Katalysatorteilchens transportiert;
2. *Porendiffusion der Edukte.* Da Strömung fehlt, wird Stofftransport von der Oberfläche in die Poren bzw. innerhalb der Poren durch Diffusion bewirkt,
3. *Adsorption der Edukte* am aktiven Zentrum aus der Gasphase
4. *Oberflächenreaktion* am aktiven Zentrum
5. *Desorption der Produkte* vom aktiven Zentrum in die Gasphase
6. *Porendiffusion der Produkte*;
7. *Filmdiffusion der Produkte.*

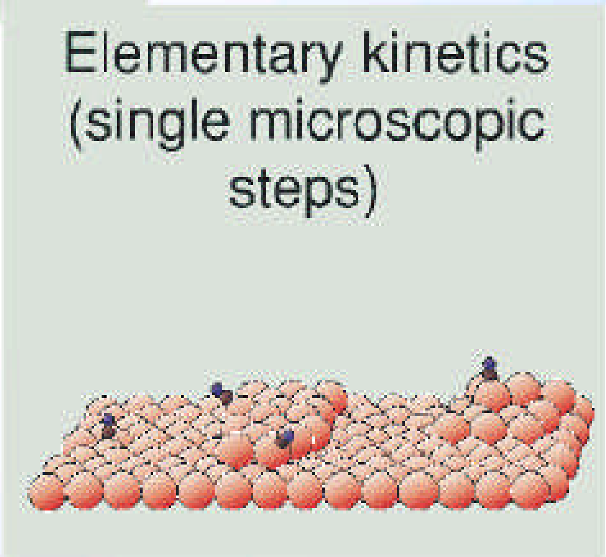


Schematische Darstellung der Teilschritte der heterogenen Katalyse

Kinetic measurements

Complexity of heterogeneously catalyzed reactions – Macrokinetics and Microkinetics





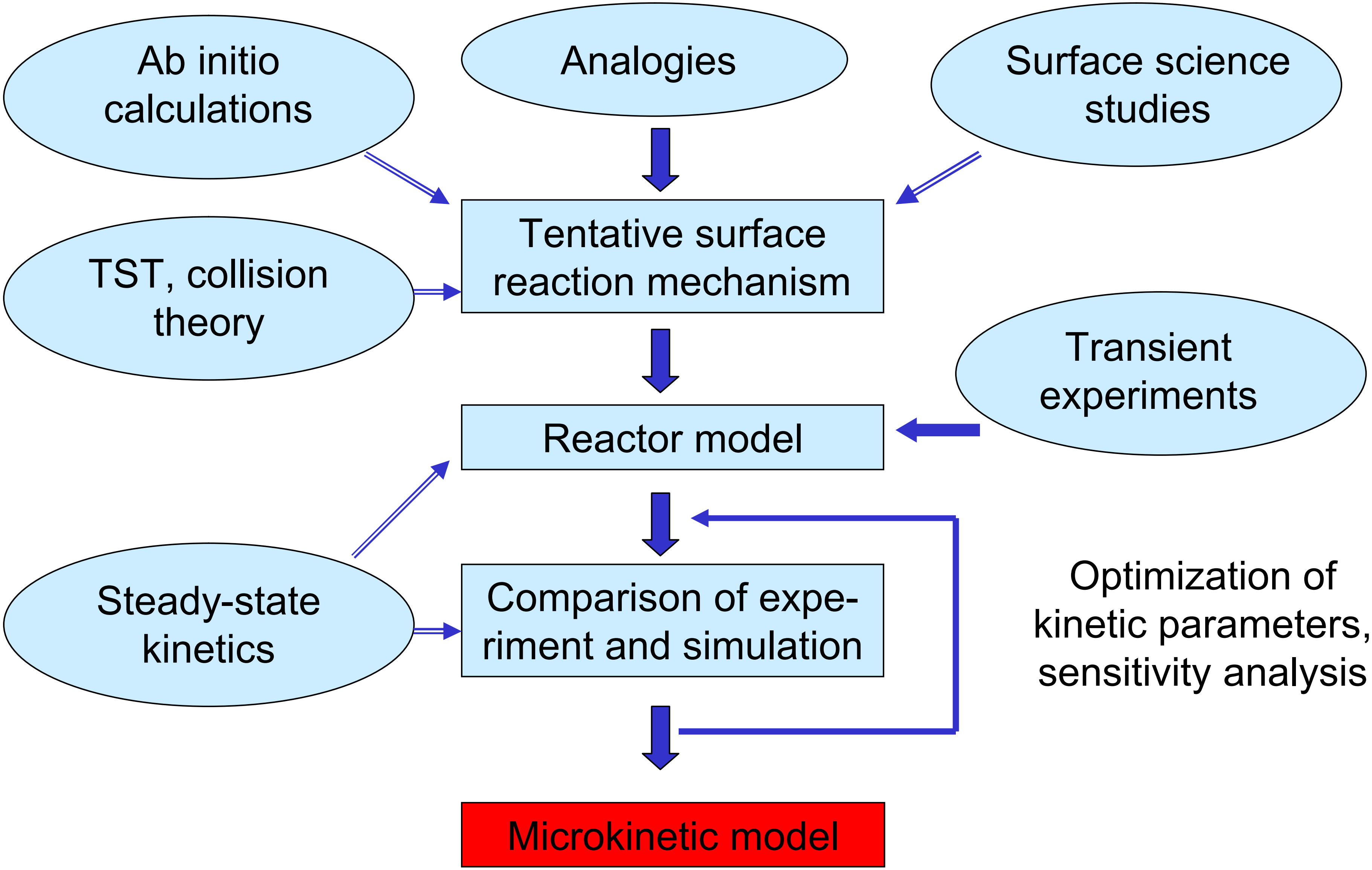
Microkinetic modeling

J.A.Dumesic

„Microkinetic analysis is an examination of catalytic reactions in terms of *elementary chemical reactions* that occur on the catalyst *surface* and their *relation* with each other and with the surface during a catalytic circle.“

Review article: P. Stoltze

Microkinetic model development



Ab initio calculations

Analogies

Surface science studies

TST, collision theory

Tentative surface reaction mechanism

Transient experiments

Reactor model

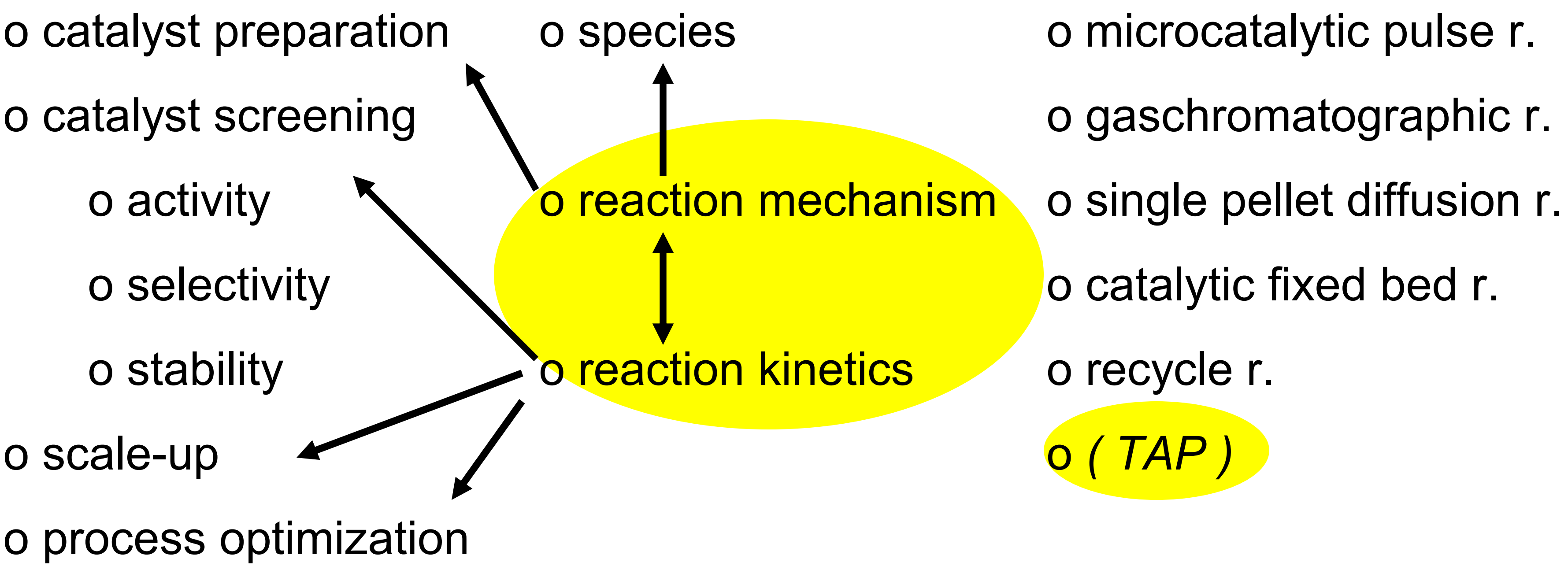
Steady-state kinetics

Comparison of experiment and simulation

Optimization of kinetic parameters, sensitivity analysis

Microkinetic model

Kinetic measurements



Tasks of laboratory investigations of heterogeneous catalytic processes

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

Complex reaction

- o species
- o reaction mechanism
- o reaction kinetics

Laboratory reactors

- o microcatalytic pulse r.
- o gaschromatographic r.
- o single pellet diffusion r.
- o catalytic fixed bed r.
- o recycle r.
- o *(TAP)*

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

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

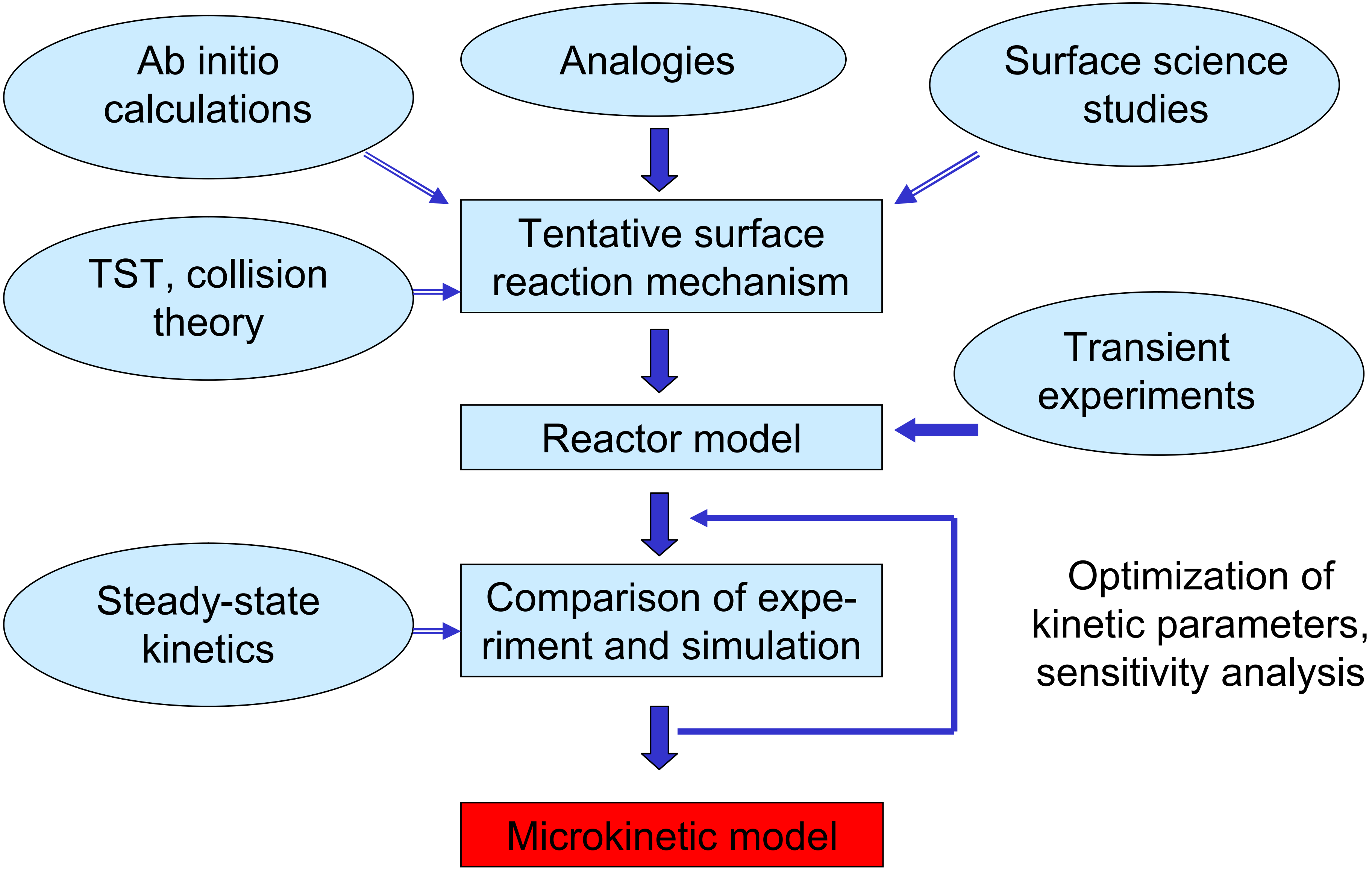
  - Temperature-programmed experiments
    temperature change

  - 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.

Microkinetic model development



Ab initio calculations

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Reactor model

Steady-state kinetics

Comparison of experiment and simulation

Optimization of kinetic parameters, sensitivity analysis

Microkinetic model

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.

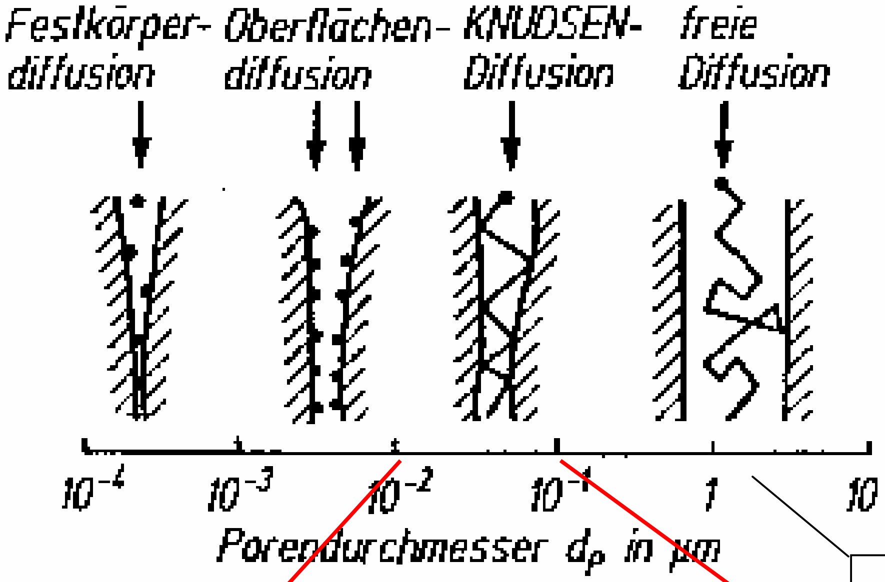
TAP – Features

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

    or 10^{10} moles
  - Example:
    - sample surface of 10 m^2/g
    - a single pulse would be equivalent to 1/10000 of the total surface per gram of sample
    - conventional pulsed reactor experiments address approximately 20 % of the surface per pulse

Background - Diffusion

Transport mechanisms in porous solids



Pore diffusion depending on pore diameter

$$D_{free} = \frac{1}{3} \Lambda w$$

$$\boxed{D_{Knudsen} = \frac{1}{3} d_p \, w = \frac{1}{3} \, d_p \sqrt{\frac{8RT}{\mathrm{p} \, M}}}$$

Λ …mean free path length

w …mean velocity of molecule

Background - Diffusion

Characterization of porous structures

- Porosity $$\frac{\text{pore volume}}{\text{total volume, - mass}} \qquad \left[\frac{m^3}{m^3}\right], \left[\frac{m^3}{kg}\right]$$
- 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

Background - Diffusion

Knudsen diffusion

- 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 ($9\text{-}20 \cdot 10^{-16}$ cm^2)

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

Background - Diffusion

Knudsen diffusion

- Knudsen flow through one zylindrical pore

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

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

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

Background - Mathematics

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

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

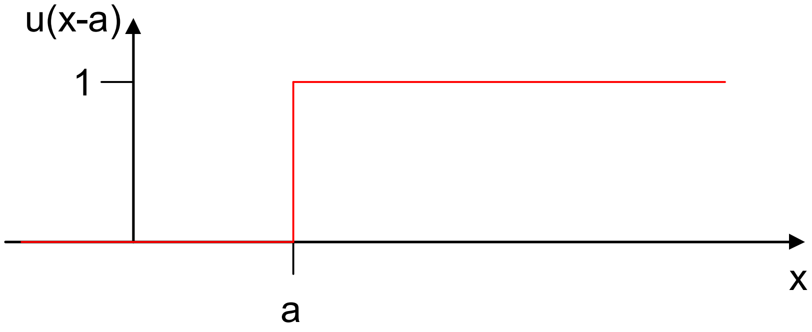
  - multiplication with a function f(x)

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

Background - Mathematics

- *Delta function*

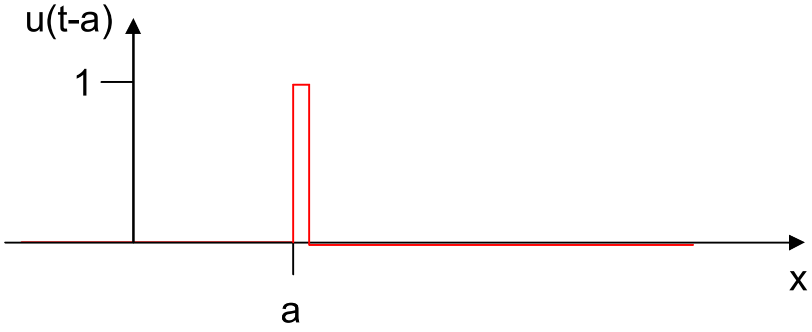
  - graphical representation as „Sprungfunktion“ (limes)



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

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

  - 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

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

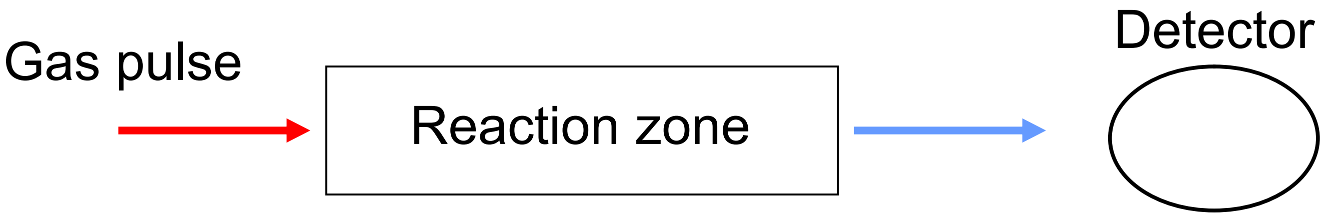
  - examples

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

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

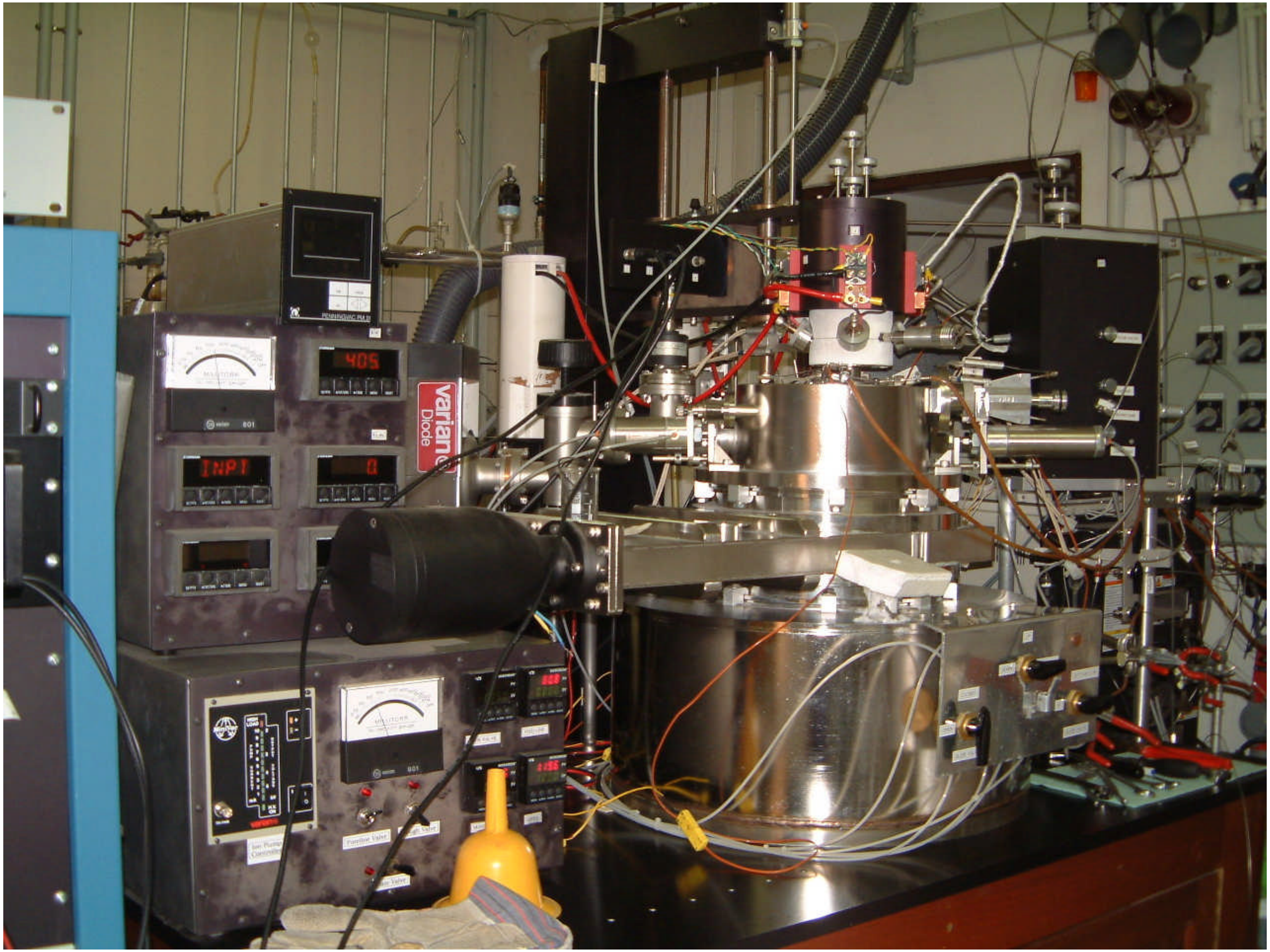
TAP – System hardware

Simplified schematic of a TAP pulse response experiment

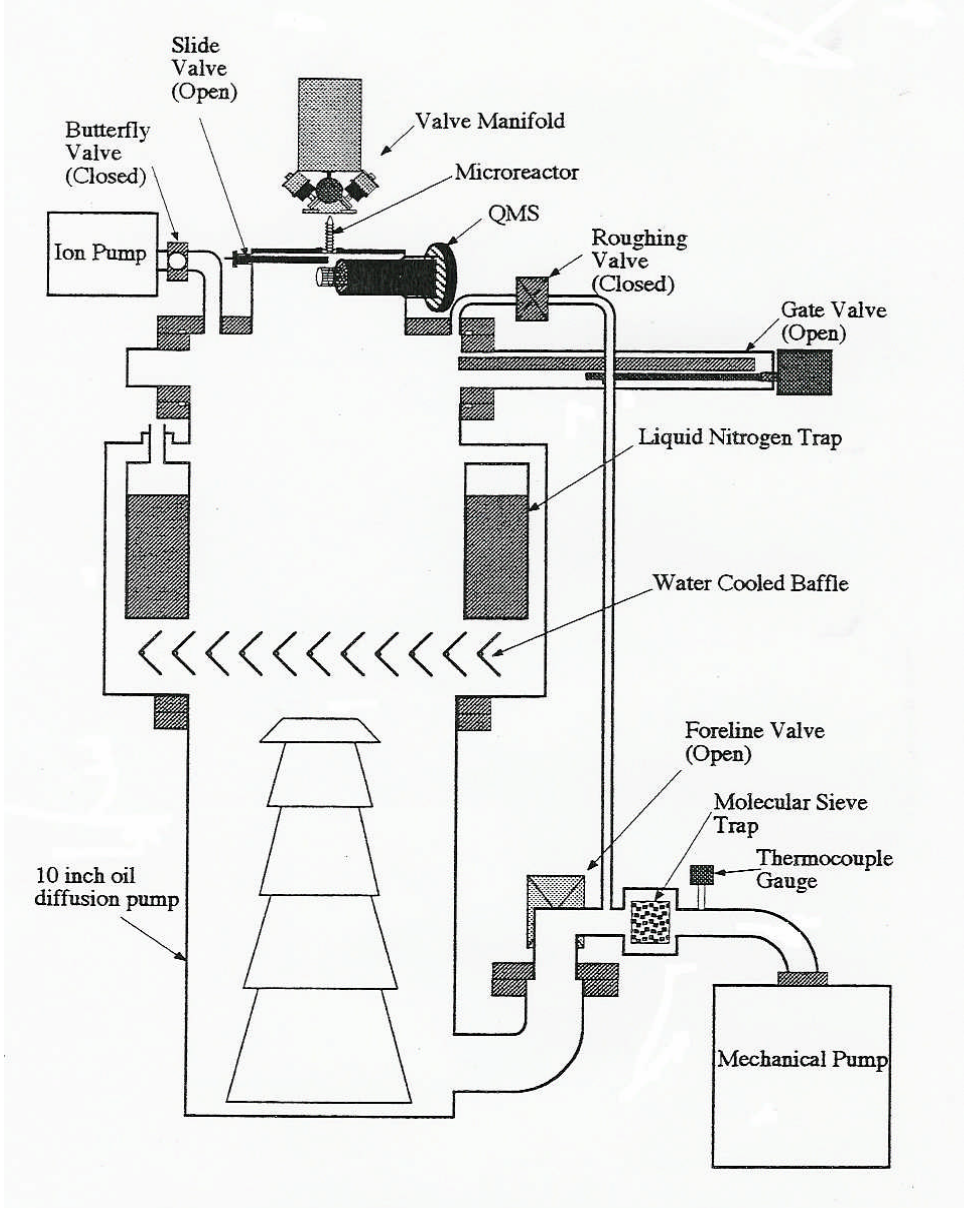


- Injection of a narrow gas pulse into an evacuated microreactor
- Gas pulses travel through the reactor
- Gas molecules (reactant and product) are monitored as a function of time and produce a transient response at the MS

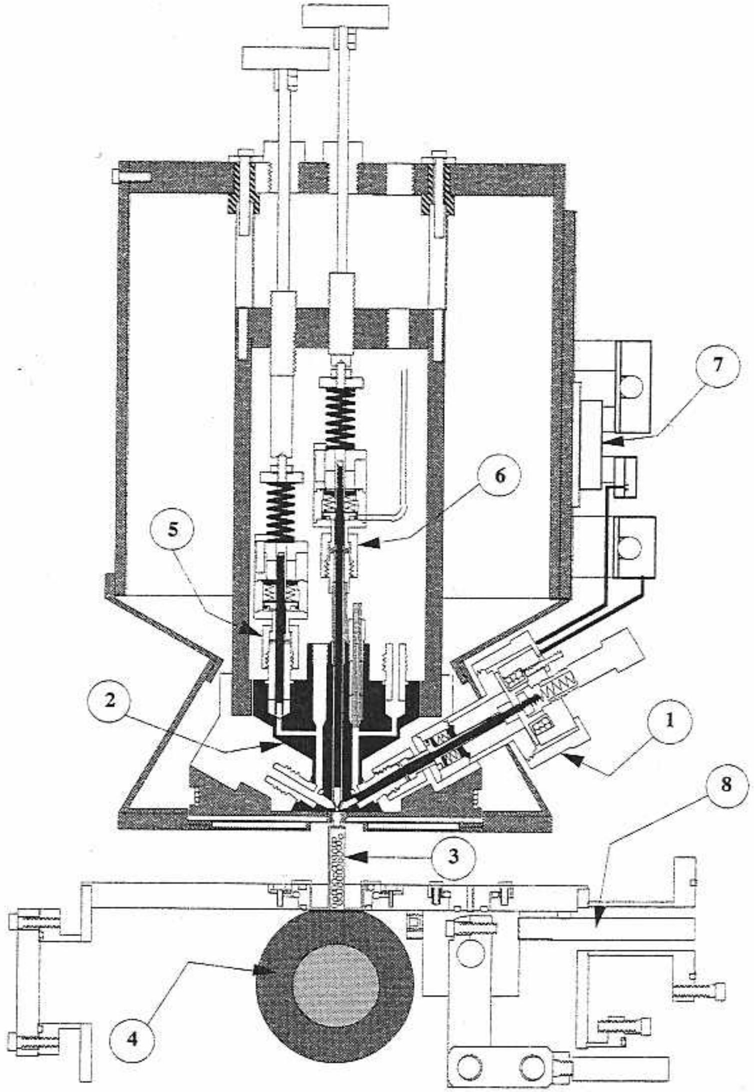
TAP – System hardware



TAP – System hardware

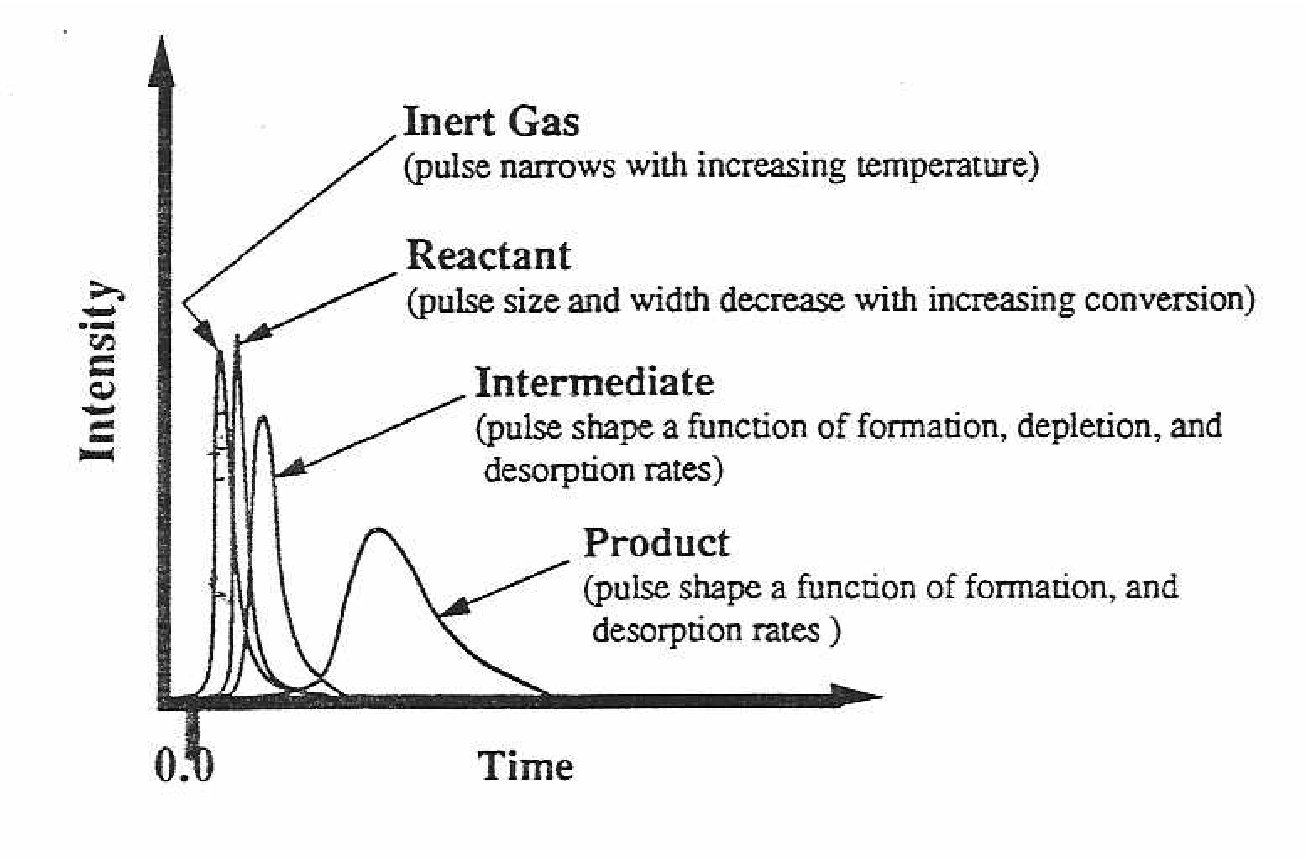


TAP – System hardware



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

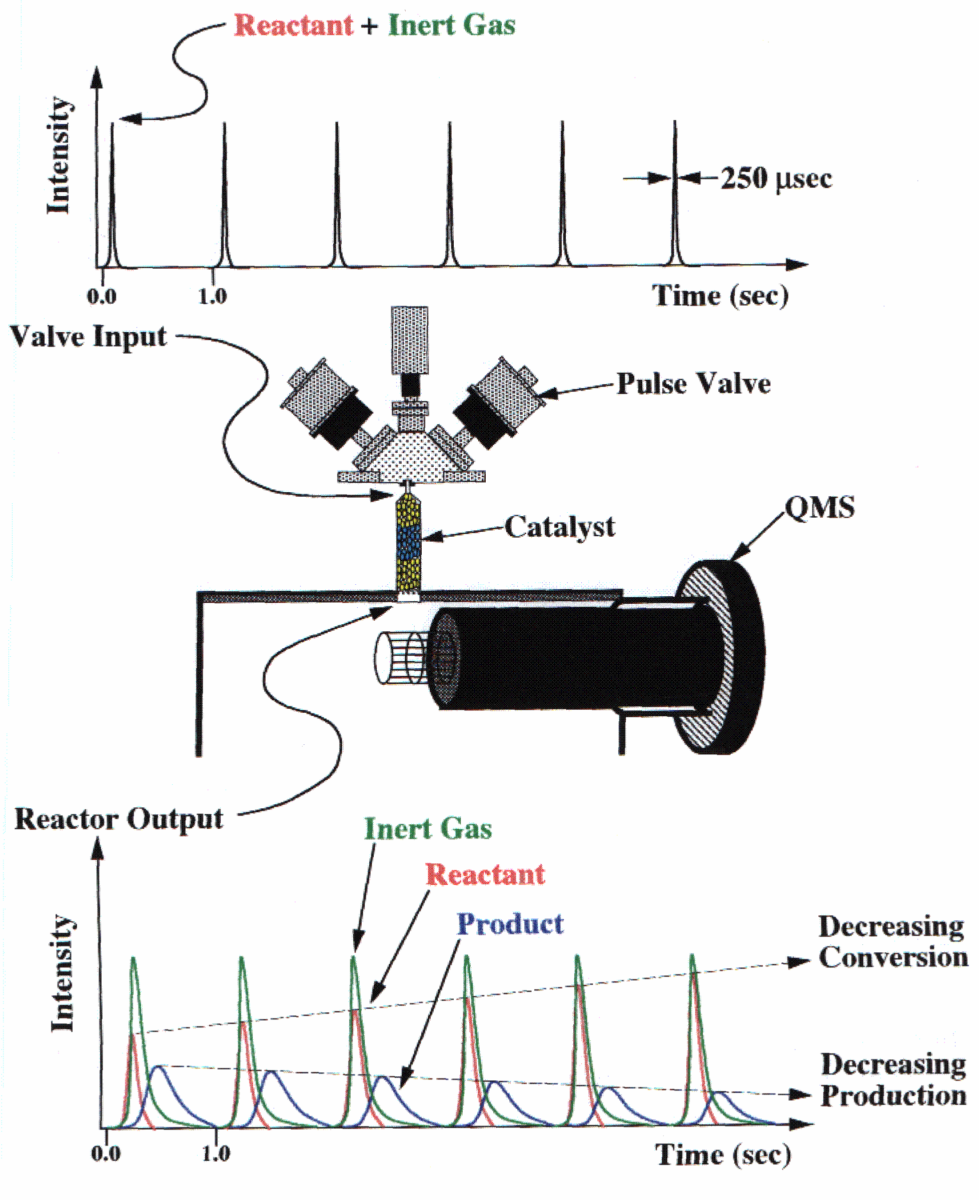


Typical pulse response experimental outputs

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}

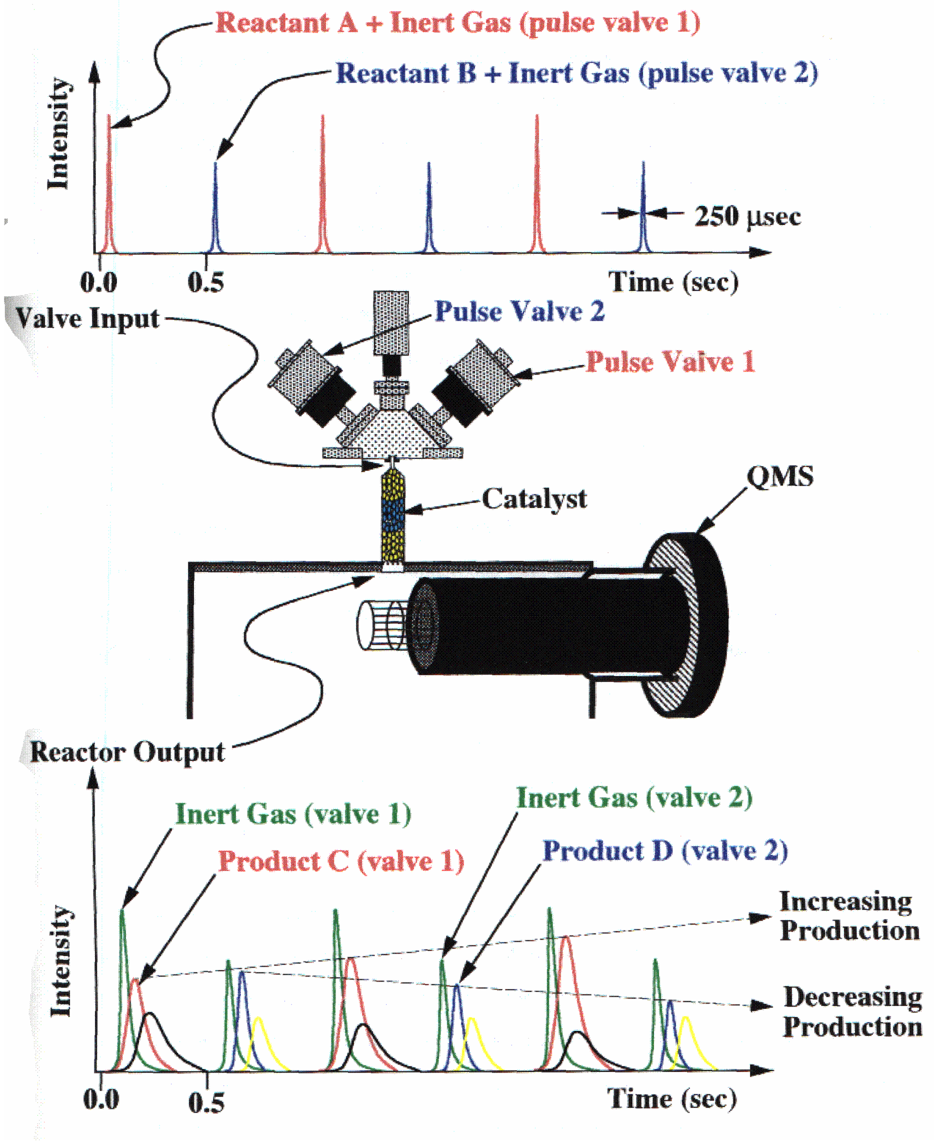
- Key features of **output**:
  - different products have different responses
  - individual product response can change with pulse number



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

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

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

$\mathrm{t} = \frac{t\, D_{eA}}{\mathrm{e}_b\, L^2}$ … dimensionless time

TAP – Transport model

Dimensionless form of mass balance

$$\boxed{\frac{\partial \overline{C}_A}{\partial t} = \frac{\partial^2 \overline{C}_A}{\partial x^2}}$$

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

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

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

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

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

solution for dimensionless flow rate

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

dimensionless flow rate at the exit (x=1)

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

TAP – Transport model

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

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

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

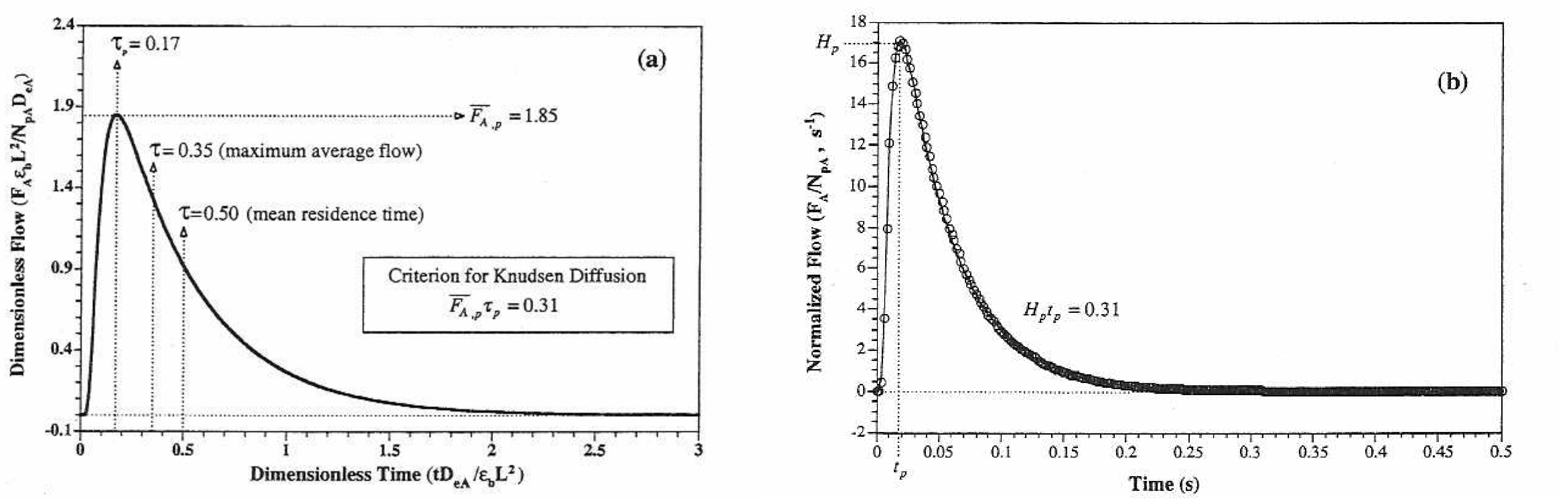
Characteristics of standard diffusion curve

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

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

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

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

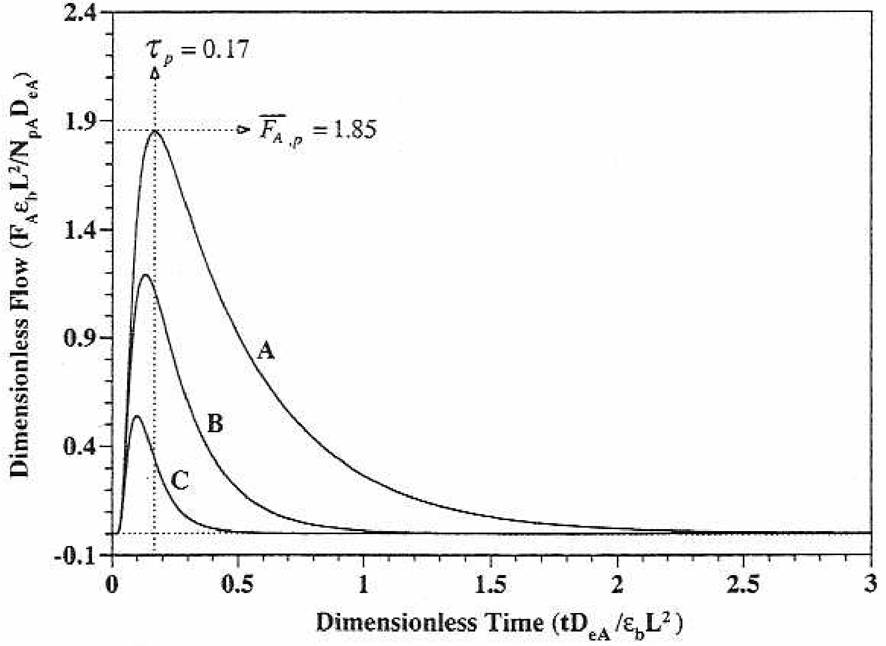
with $\boxed{k_a^{\prime} = \frac{a_s S_v (1-\varepsilon_b) k_a}{\varepsilon_b}}$

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

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

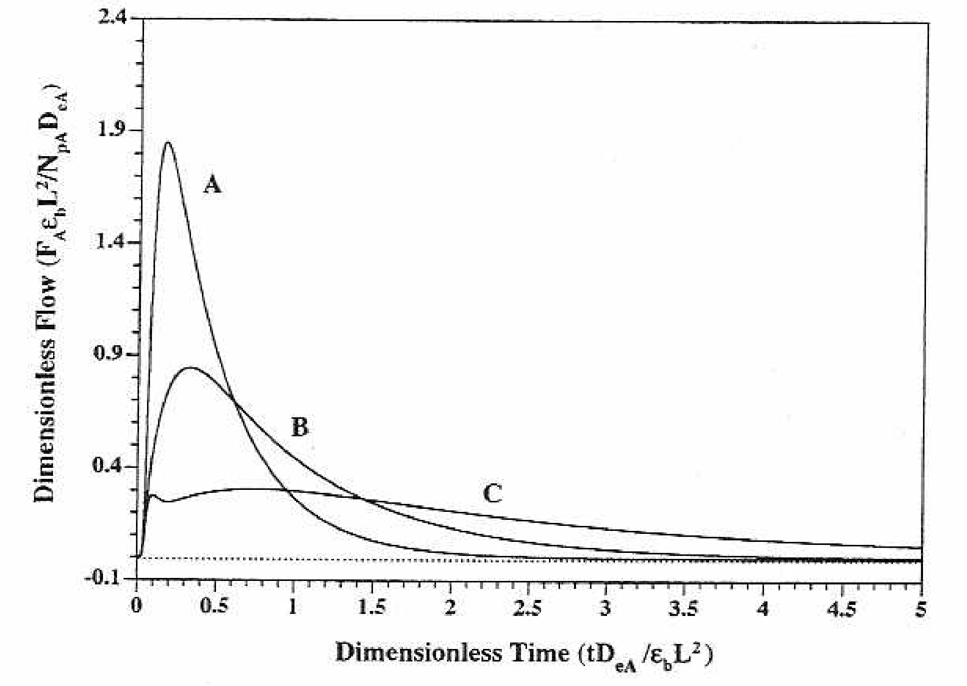
- for component A on the catalyst surface

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

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

TAP - Transport + adsorption model

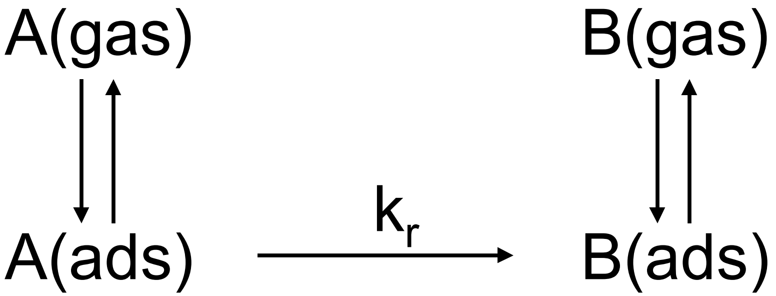
Exit flow curve for the diffusion+reversible adsorption case



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 $$z = 0 \quad , -D_{eA,1}\frac{\partial C_{A,1}}{\partial z} = \mathrm{d}\,(t)$$

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

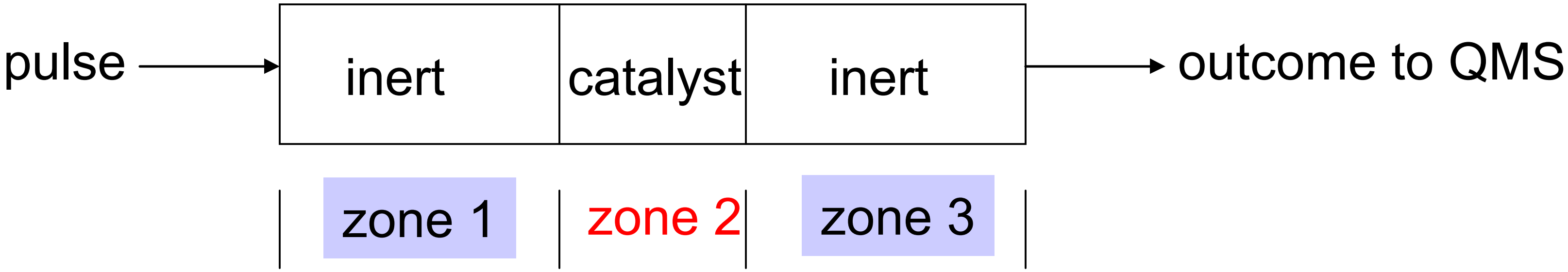
k_a' contains:

- 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

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

TAP – Theory - Moments

Application to TAP experiments:

- for irreversible adsorption / reaction

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

Da_I … Damköhler number I

- mean dimensionless residence time

$$\mathrm{t}_{res} = \frac{m_1}{m_0} = \frac{\sum_{n=0}^{\infty} \frac{A(n)}{\left[B(n)+Da_I\right]}}{\sum_{n=0}^{\infty} \frac{A(n)}{B(n)+Da_I}}\,\mathrm{t}_{Dif}$$

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

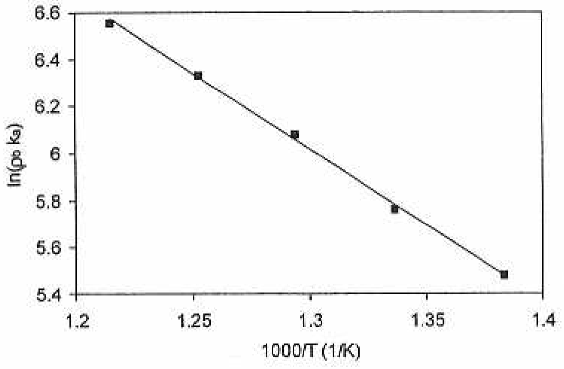
$$B(n) = (n + 0.5)^2\,\mathrm{p}^2$$

$$\mathrm{t}_{Dif} = \frac{\mathrm{e}_b L^2}{D_{e,A}}$$

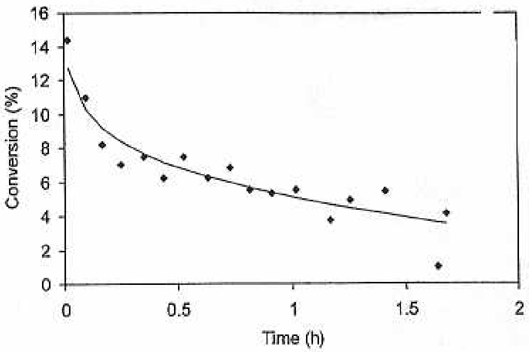
TAP - Examples

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

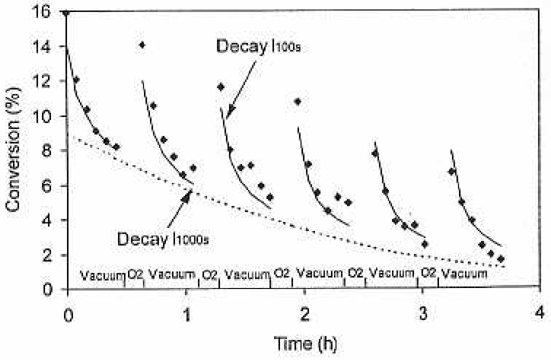
- Supported Ni catalysts for steam reforming of natural gas to synthesis gas
- Combination of TPR with single pulse experiments



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)

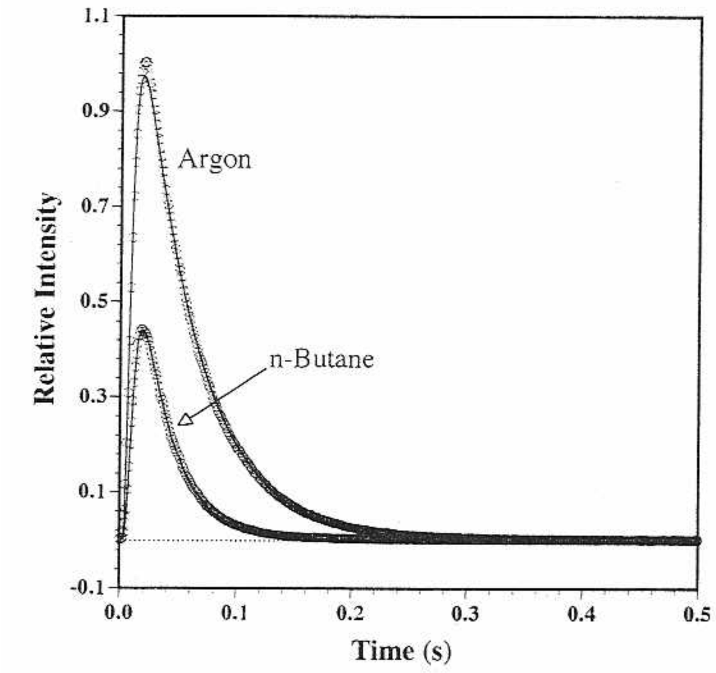
- Steady-state kinetic studies yielded different rate expressions and kinetic parameters – this may be related to differences in c. composition, c. structure, c. oxydation state, etc. ⟶ no unique information

- 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



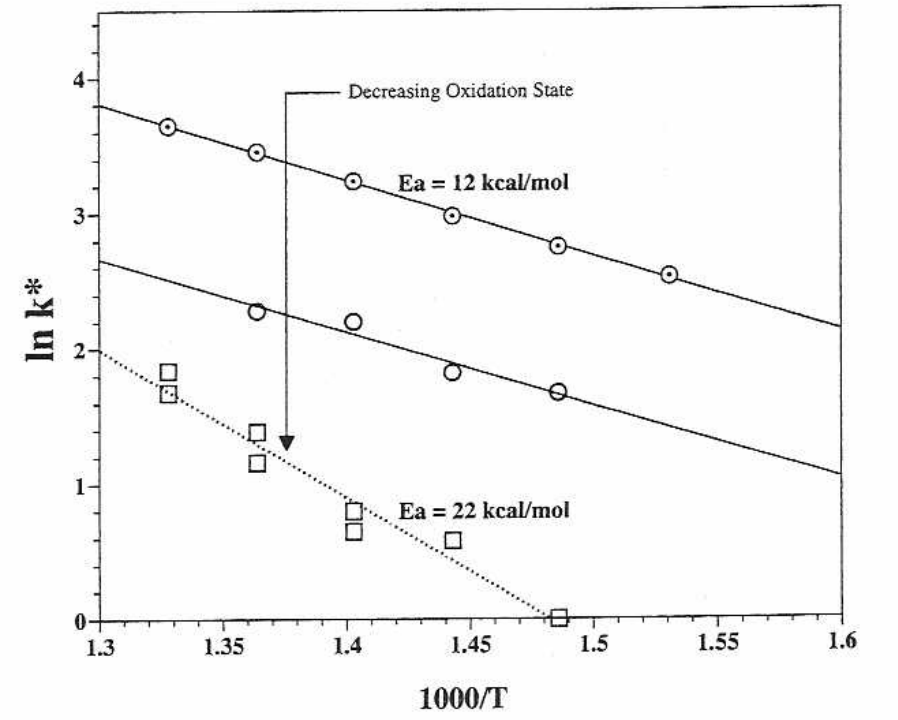
- n-butane curve lies completely within the generated diffusion curve ⟶ irreversible process

- 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

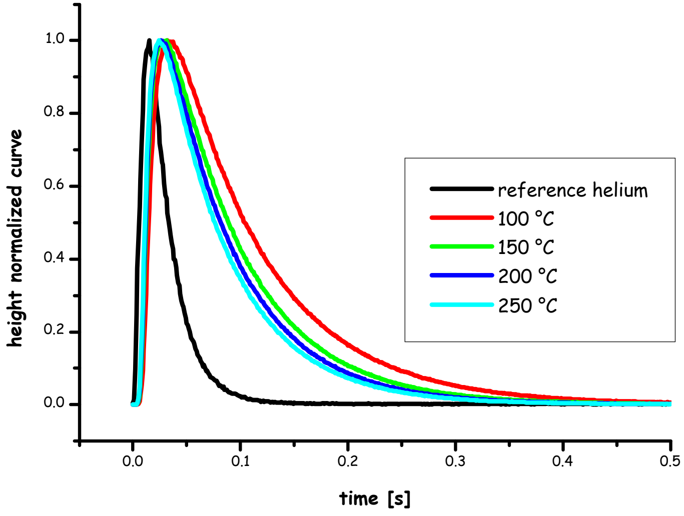
- values of apparent activation energy is strongly dependent on the VPO oxidation state
- decreasing number of active centers
- TAP + Raman: V^{4+} V^{5+}

TAP - Examples

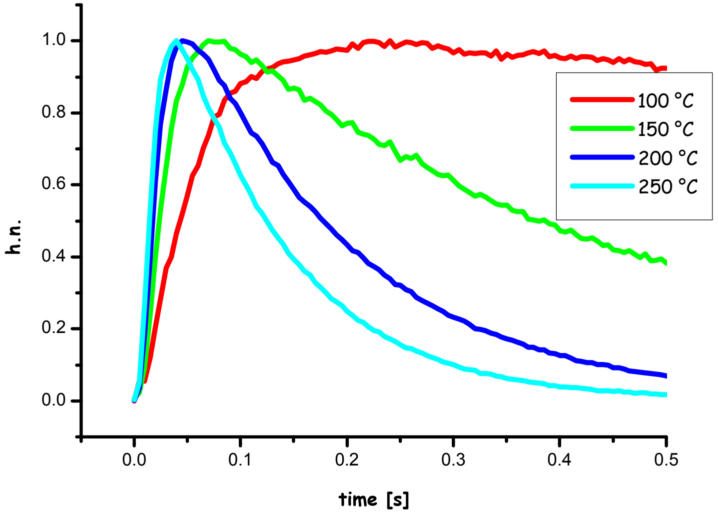
N-Butane Isomerization on Sulfated Zirconia Catalysts (SPP-1091, Acid-Base Catalyzed Alkane Activation)

Pulses of n-butane

over inert material



over SZ



τ [s] at 100 °C:

0.107

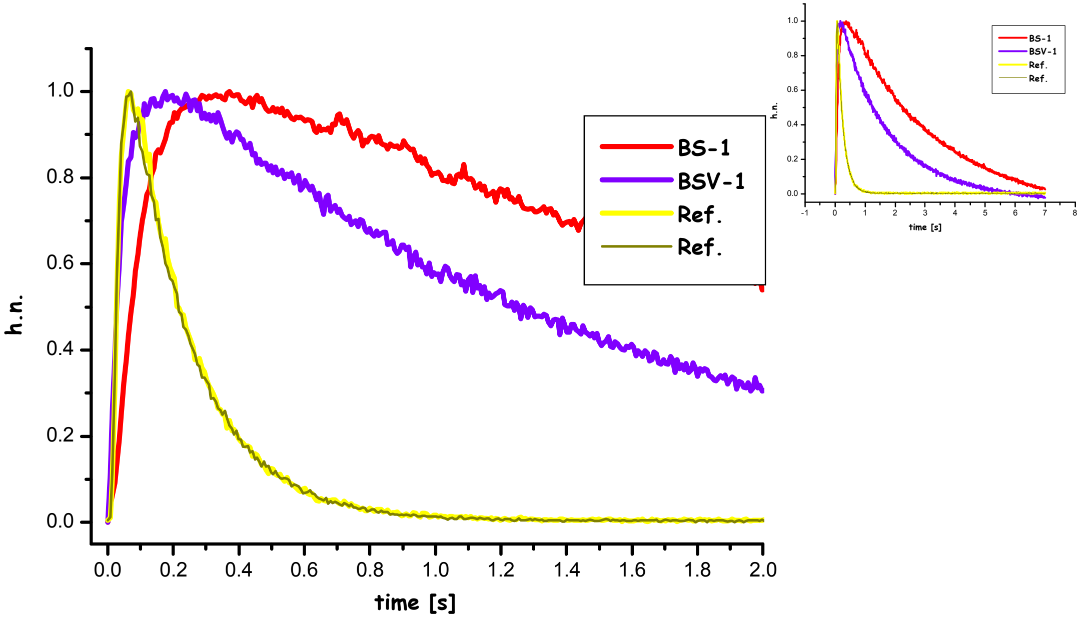
0.500

TAP - Examples

N-Butane Isomerization over Sulfated Zirconia Catalysts (SPP-1091, Acid-Base Catalyzed Alkane Activation)

Influence of sulfation - pulses of n-butane

SZ, calcined unsulfated precursor, inert

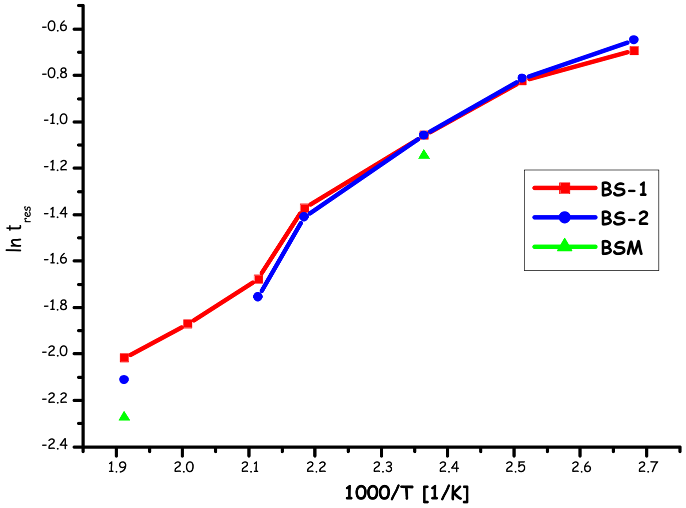


TAP - Examples

N-Butane Isomerization over Sulfated Zirconia Catalysts (SPP-1091, Acid-Base Catalyzed Alkane Activation)

Activation plots for active SZ, inactive SZ, industrial reference

at begin of reaction

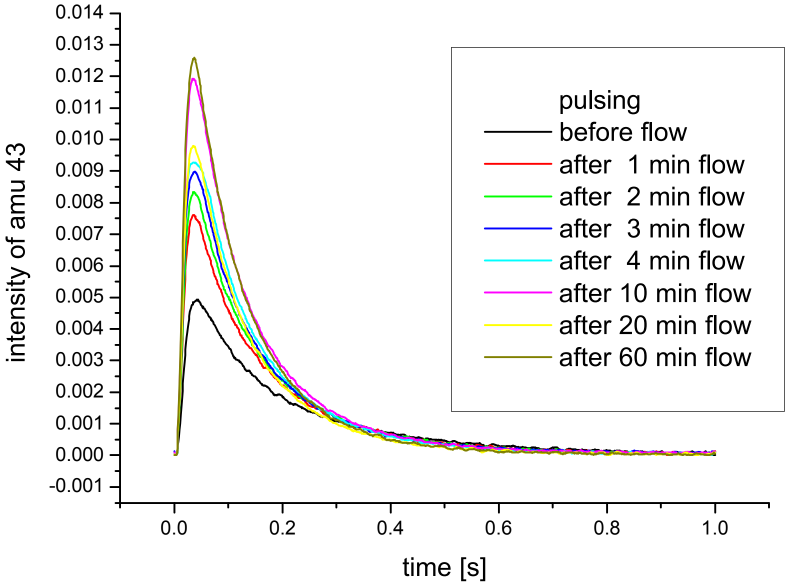


E_{Akt} (BS-1) » E_{Akt} (BS-2) at beginning

TAP - Examples

N-Butane Isomerization over Sulfated Zirconia Catalysts (SPP-1091, Acid-Base Catalyzed Alkane Activation)

Variation of activation state through switch between vacuum and atmospheric flow conditions at 150 °C



SSITKA

Steady State Isotopic Transient Kinetic Analysis

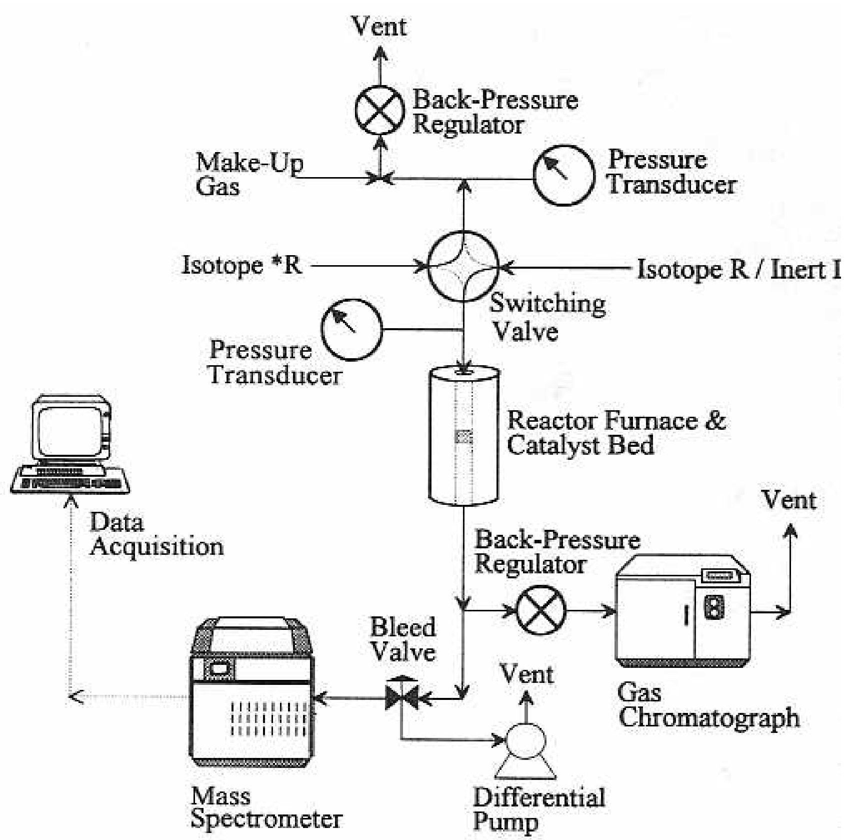
SSITKA - Theory

- Initially developed by Happel 1978, Bennett 1982 and Biloen 1983
- Determination of kinetics and catalyst surface reaction intermediates *in situ*
- The technique is based upon the *detection of isotopic labels* in the reactor effluent species versus time following a switch (step change) in the isotopic labeling of one of the reactant species in the reactor feed.
- Isothermic and isobaric conditions !
- Reactant and product concentrations remain undisturbed during step change !

Steady-state reaction conditions are maintained under isotopic-transient operation

SSITKA - Theory

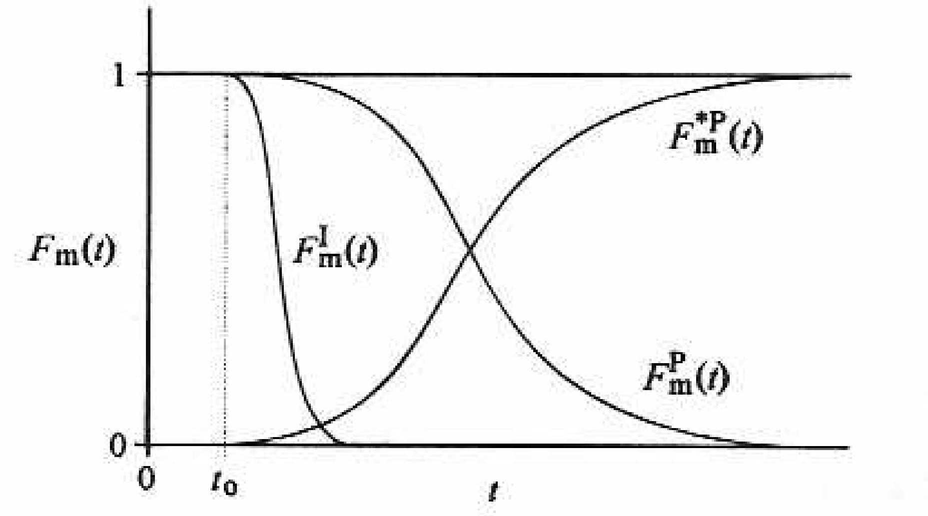
Review article*: Shannon, Goodwin 1995*



Typical reaction system for SSITKA experimentation

SSITKA - Theory

- The step-input response is a statistical distribution representing the probability that an isotopic label remains adsorbed on the catalyst surface or appears in the effluent stream with time.



Typical normalized isotopic-transient responses

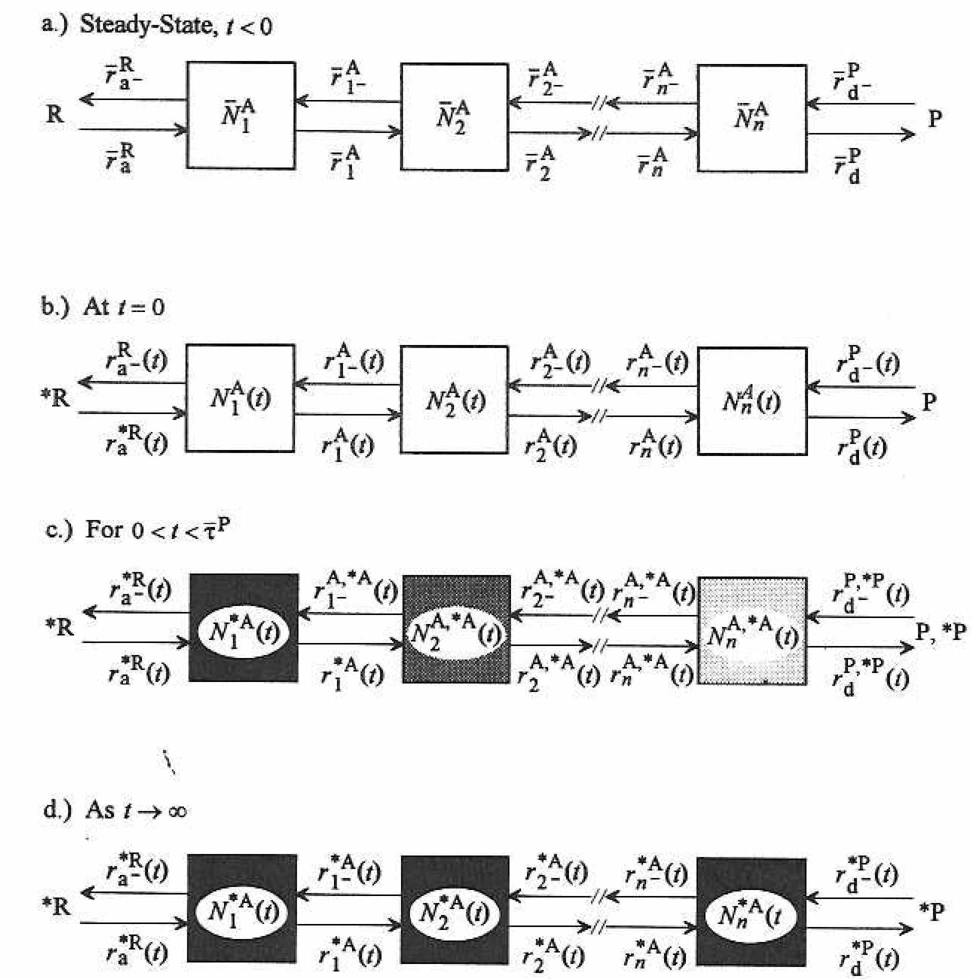
SSITKA - Theory

- Characteristic values
  - Step-input response of the product for the new isotopic label $F_m^{*P}(t)$
  - Step-decay response of the old isotopic label (prior to switch) $F_m^{P}(t)$
  - Relationship $F_m^{P}(t) = 1 - F_m^{*P}(t)$
  - Inert-tracer transient response for determination of gas-phase holdup $F_m^{I}(t)$

SSITKA - Theory

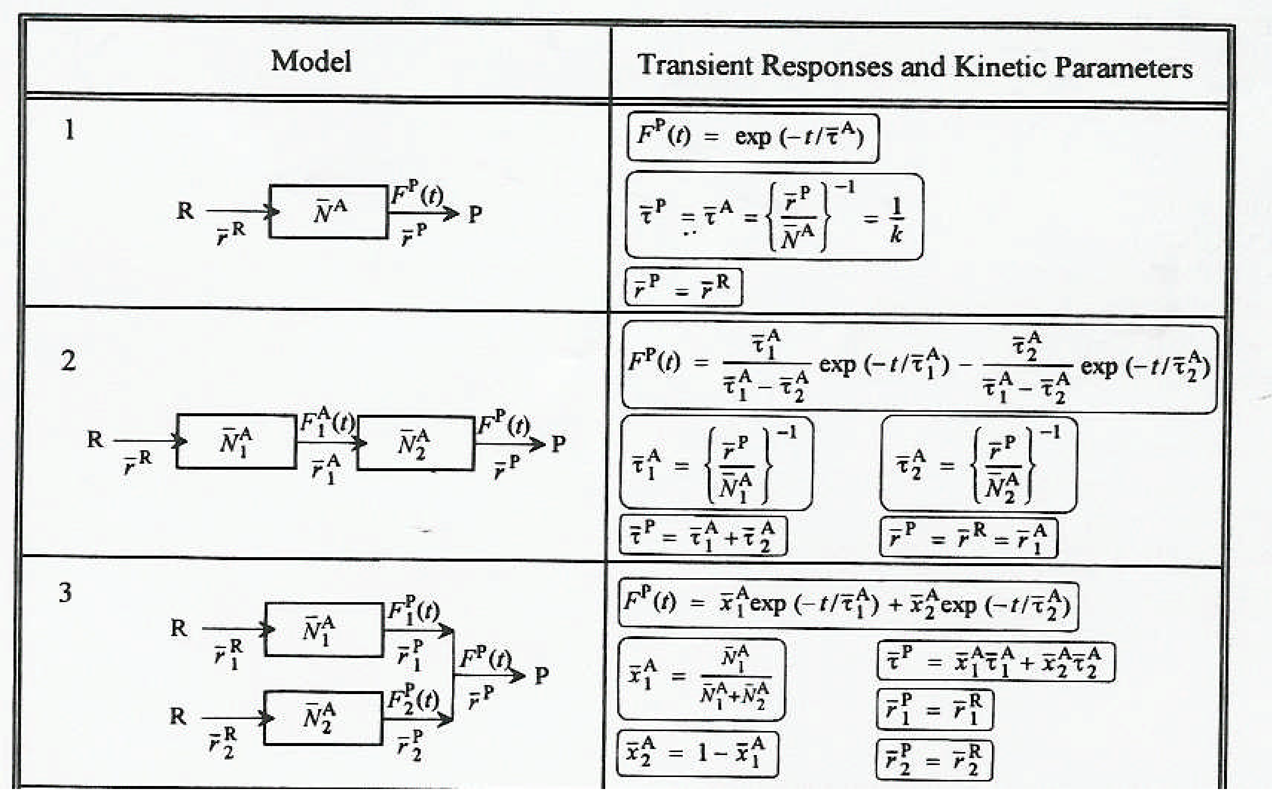
- In SSITKA, it is common to consider the *catalyst surface* to be composed of a *system of interconnected pools*, also termed *compartments*, where each pool represents a homogeneous or well-mixed subsystem within the reaction pathway.
- A *seperate pool* is assumed to exist *for each unique adsorbed reaction-intermediate* species or type of catalytically active site.
- It is assumed that there is essentially no mixing or holdup time associated with each pool or within the reaction pathway *except* for the residence time of a reaction-intermediate species adsorbed on the catalyst surface.

SSITKA - Theory



Catalyst-surface model showing the isotopic distribution between n pools in series following an isotopic switch, R →*R, at the reaction volume inlet

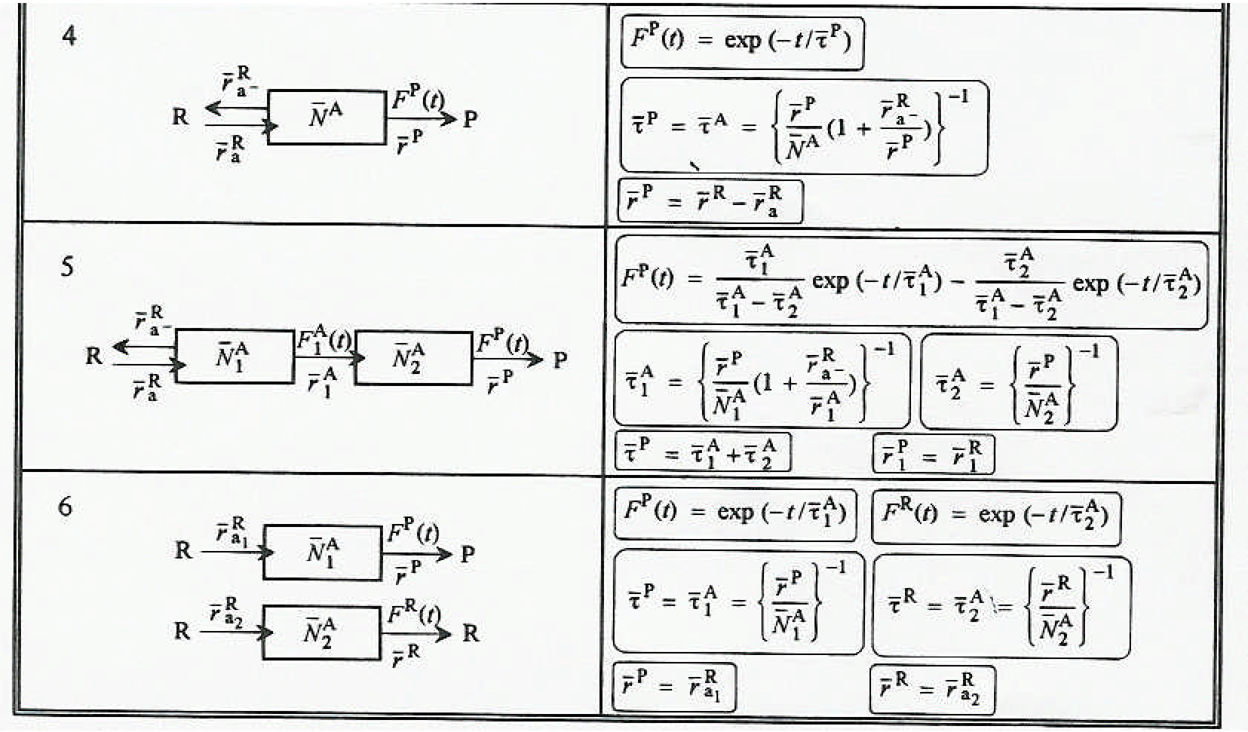
SSITKA - Theory



Model	Transient Responses and Kinetic Parameters
1 $\mathrm{R} \xrightarrow[\bar{r}^{\mathrm{R}}]{} \boxed{\bar{N}^{\mathrm{A}}} \xrightarrow[\bar{r}^{\mathrm{P}}]{F^{\mathrm{P}}(t)} \mathrm{P}$	$\boxed{F^{\mathrm{P}}(t) = \exp(-t/\bar{\tau}^{\mathrm{A}})}$ $\boxed{\bar{\tau}^{\mathrm{P}} = \bar{\tau}^{\mathrm{A}} = \left\{\frac{\bar{r}^{\mathrm{P}}}{\bar{N}^{\mathrm{A}}}\right\}^{-1} = \frac{1}{k}}$ $\boxed{\bar{r}^{\mathrm{P}} = \bar{r}^{\mathrm{R}}}$
2 $\mathrm{R} \xrightarrow[\bar{r}^{\mathrm{R}}]{} \boxed{\bar{N}_1^{\mathrm{A}}} \xrightarrow[\bar{r}_1^{\mathrm{A}}]{F_1^{\mathrm{A}}(t)} \boxed{\bar{N}_2^{\mathrm{A}}} \xrightarrow[\bar{r}^{\mathrm{P}}]{F^{\mathrm{P}}(t)} \mathrm{P}$	$\boxed{F^{\mathrm{P}}(t) = \frac{\bar{\tau}_1^{\mathrm{A}}}{\bar{\tau}_1^{\mathrm{A}} - \bar{\tau}_2^{\mathrm{A}}} \exp(-t/\bar{\tau}_1^{\mathrm{A}}) - \frac{\bar{\tau}_2^{\mathrm{A}}}{\bar{\tau}_1^{\mathrm{A}} - \bar{\tau}_2^{\mathrm{A}}} \exp(-t/\bar{\tau}_2^{\mathrm{A}})}$ $\boxed{\bar{\tau}_1^{\mathrm{A}} = \left\{\frac{\bar{r}^{\mathrm{P}}}{\bar{N}_1^{\mathrm{A}}}\right\}^{-1}}$ $\boxed{\bar{\tau}_2^{\mathrm{A}} = \left\{\frac{\bar{r}^{\mathrm{P}}}{\bar{N}_2^{\mathrm{A}}}\right\}^{-1}}$ $\boxed{\bar{\tau}^{\mathrm{P}} = \bar{\tau}_1^{\mathrm{A}} + \bar{\tau}_2^{\mathrm{A}}}$ $\boxed{\bar{r}^{\mathrm{P}} = \bar{r}^{\mathrm{R}} = \bar{r}_1^{\mathrm{A}}}$
3 $\mathrm{R} \xrightarrow[\bar{r}_1^{\mathrm{R}}]{} \boxed{\bar{N}_1^{\mathrm{A}}} \xrightarrow[\bar{r}_1^{\mathrm{P}}]{F_1^{\mathrm{P}}(t)}$ $\mathrm{R} \xrightarrow[\bar{r}_2^{\mathrm{R}}]{} \boxed{\bar{N}_2^{\mathrm{A}}} \xrightarrow[\bar{r}_2^{\mathrm{P}}]{F_2^{\mathrm{P}}(t)}$ $\xrightarrow[\bar{r}^{\mathrm{P}}]{F^{\mathrm{P}}(t)} \mathrm{P}$	$\boxed{F^{\mathrm{P}}(t) = \bar{x}_1^{\mathrm{A}} \exp(-t/\bar{\tau}_1^{\mathrm{A}}) + \bar{x}_2^{\mathrm{A}} \exp(-t/\bar{\tau}_2^{\mathrm{A}})}$ $\boxed{\bar{x}_1^{\mathrm{A}} = \frac{\bar{N}_1^{\mathrm{A}}}{\bar{N}_1^{\mathrm{A}} + \bar{N}_2^{\mathrm{A}}}}$ $\boxed{\bar{\tau}^{\mathrm{P}} = \bar{x}_1^{\mathrm{A}}\bar{\tau}_1^{\mathrm{A}} + \bar{x}_2^{\mathrm{A}}\bar{\tau}_2^{\mathrm{A}}}$ $\boxed{\bar{r}_1^{\mathrm{P}} = \bar{r}_1^{\mathrm{R}}}$ $\boxed{\bar{x}_2^{\mathrm{A}} = 1 - \bar{x}_1^{\mathrm{A}}}$ $\boxed{\bar{r}_2^{\mathrm{P}} = \bar{r}_2^{\mathrm{R}}}$

Catalyst-surface mechanistic models, transient responses, and kinetic parameters

SSITKA - Theory



4	$\boxed{F^P(t) = \exp(-t/\bar{\tau}^P)}$ $\boxed{\bar{\tau}^P = \bar{\tau}^A = \left\{\frac{\bar{r}^P}{\bar{N}^A}\left(1 + \frac{\bar{r}^R_{a-}}{\bar{r}^P}\right)\right\}^{-1}}$ $\boxed{\bar{r}^P = \bar{r}^R - \bar{r}^R_a}$
5	$\boxed{F^P(t) = \frac{\bar{\tau}^A_1}{\bar{\tau}^A_1 - \bar{\tau}^A_2}\exp(-t/\bar{\tau}^A_1) - \frac{\bar{\tau}^A_2}{\bar{\tau}^A_1 - \bar{\tau}^A_2}\exp(-t/\bar{\tau}^A_2)}$ $\boxed{\bar{\tau}^A_1 = \left\{\frac{\bar{r}^P}{\bar{N}^A_1}\left(1 + \frac{\bar{r}^R_{a-}}{\bar{r}^A_1}\right)\right\}^{-1}}$ $\boxed{\bar{\tau}^A_2 = \left\{\frac{\bar{r}^P}{\bar{N}^A_2}\right\}^{-1}}$ $\boxed{\bar{\tau}^P = \bar{\tau}^A_1 + \bar{\tau}^A_2}$ $\boxed{\bar{r}^P_1 = \bar{r}^R_1}$
6	$\boxed{F^P(t) = \exp(-t/\bar{\tau}^A_1)}$ $\boxed{F^R(t) = \exp(-t/\bar{\tau}^A_2)}$ $\boxed{\bar{\tau}^P = \bar{\tau}^A_1 = \left\{\frac{\bar{r}^P}{\bar{N}^A_1}\right\}^{-1}}$ $\boxed{\bar{\tau}^R = \bar{\tau}^A_2 = \left\{\frac{\bar{r}^R}{\bar{N}^A_2}\right\}^{-1}}$ $\boxed{\bar{r}^P = \bar{r}^R_{a_1}}$ $\boxed{\bar{r}^R = \bar{r}^R_{a_2}}$

Catalyst-surface mechanistic models, transient responses, and kinetic parameters

Table 1. Reactions Studied by Steady-State Isotopic-Transient Methods

reaction	catalyst	ref(s)
methanation and Fischer–Tropsch synthesis	Fe	30, 31[a]
	Fe/Al_2O_3	32
	Co	3, 11, 29, 33[b]
	Co/Al_2O_3	34,[c] 35,[d] 36[d]
	Co/SiO_2	31, 37, 38, 39[e]
	Ni	12,[f] 40,[f] 41,[f] 42
	Ni/Al_2O_3	22, 23
	Ni/SiO_2	3, 11, 40,[g] 43,[g] 44,[g] 45,[g] 46,[g] 47
	Ru/Al_2O_3	3, 11, 29, 37, 48, 49
	Ru/SiO_2	16, 17, 50, 51, 52, 53,[h] 97
	Ru/TiO_2	16, 54, 55
	Rh/MgO	56
	Rh/Al_2O_3	57, 58, 59
	Rh/SiO_2	33,[b] 60,[b] 61,[i] 62[b]
	Pt/TiO_2	47
ammonia synthesis	Fe	15,[j] 27[j]
	Ru/SiO_2	63[j]
ammonia oxidation and NO selective catalytic reduction	V_2O_5	64, 65
ethane hydrogenolysis	Co/SiO_2	66
	Ru/SiO_2	19
methanol synthesis	Pd/SiO_2	67, 68[k]
benzene hydrogenation	Ni	28, 70[l]
	Ni/SiO_2	28, 70[l]
methane coupling	MgO	71,[k] 72, 73
	Li/MgO	72, 73, 74, 75
	TiO_2	76[k]
	NiO	73
	Sr/La_2O_3	77
	SnO_2	73
	Sn/MgO	73
	La_2O_3	69, 71,[k] 77
	Sm_2O_3	73, 75, 78, 79
methane partial oxidation	V_2O_5/Al_2O_3	80[m]
	V_2O_5/SiO_2	80,[m] 81, 82
	MoO_3	83[n]
	MoO_3/SiO_2	84[n]
	Pr_6O_{11}	85[b]
	Sm_2O_3	85,[b] 86,[b] 87,[b] 88[b]
	Li/Sm_2O_3	85[b]
NO–CO reaction	Rh/La_2O_3	89
	$Pt/Rh/NiO/CeO_2/Al_2O_3$	89[o]
CO oxidation	Rh/La_2O_3	89
	$Pt/Rh/NiO/CeO_2/Al_2O_3$	89[o]
propylene partial oxidation	Sb/Sn/V Oxide	90
propane dehydrogenation	Pt/Al_2O_3	91
	$Pt/Sn/Al_2O_3$	91
isobutene hydrogenation and isobutane dehydrogenation	Cr_2O_3	92,[p] 93[p]
vinyl acetate synthesis	$Pd/Cd/K/SiO_2$	94
	$Pd/Au/K/SiO_2$	94
ethylene hydroformylation	Rh/SiO_2	95,[b] 96[b]

[a] Promoted ($SiO_2/Cu/K$) Fe. [b] Pulse technique. [c] Pt or Re promoted. [d] La promoted. [e] Zr promoted. [f] Raney nick [g] Commercial–kieselguhr support. [h] K doped. [i] V promoted. [j] Commercial–promoted ($Al_2O_3/K_2O/CaO$) Fe catalyst. [k] Li promote [l] Also Ni and Ni–K/SiO_2. [m] Also bulk and supports. [n] Various molybdena species. [o] Commercial–automotive catalyst. [p] Chrom gel.

SSITKA – Kinetic parameters

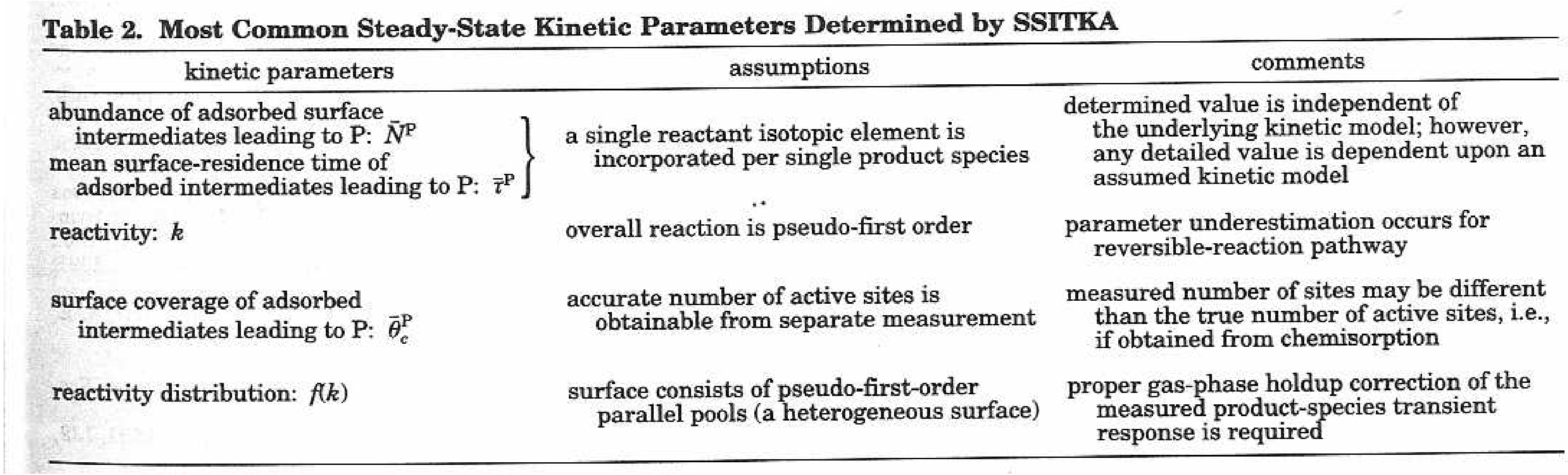


Table 2. Most Common Steady-State Kinetic Parameters Determined by SSITKA

kinetic parameters	assumptions	comments
abundance of adsorbed surface intermediates leading to P: $\bar{N}^{\mathrm{P}}$ mean surface-residence time of adsorbed intermediates leading to P: $\bar{\tau}^{\mathrm{P}}$	a single reactant isotopic element is incorporated per single product species	determined value is independent of the underlying kinetic model; however, any detailed value is dependent upon an assumed kinetic model
reactivity: k	overall reaction is pseudo-first order	parameter underestimation occurs for reversible-reaction pathway
surface coverage of adsorbed intermediates leading to P: $\bar{\theta}_{c}^{\mathrm{P}}$	accurate number of active sites is obtainable from separate measurement	measured number of sites may be different than the true number of active sites, i.e., if obtained from chemisorption
reactivity distribution: $f(k)$	surface consists of pseudo-first-order parallel pools (a heterogeneous surface)	proper gas-phase holdup correction of the measured product-species transient response is required

SSITKA - Examples

Selective NO reduction over Co-ZSM-5
(Sadovskaya et al. 2001)

- SCR of NO with CH_4 in the presence of excess oxygen
- Controversial discussion of formation mechanism of surface NO_x species
- IR investigation in presence of O_2 showed bands for nitrite and nitrate complexes and for $NO_x^{\delta+}$

- Focus on formation of adsorbed NO_x species in absence and presence of oxygen, but in absence of methane by using doubly labeled nitric oxide

SSITKA - Examples

Selective NO reduction over Co-ZSM-5

(Sadovskaya et al. 2001)

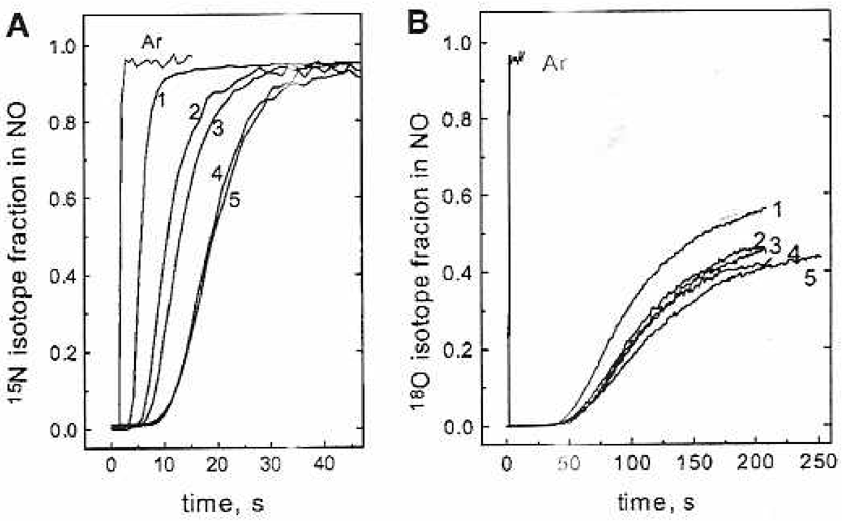
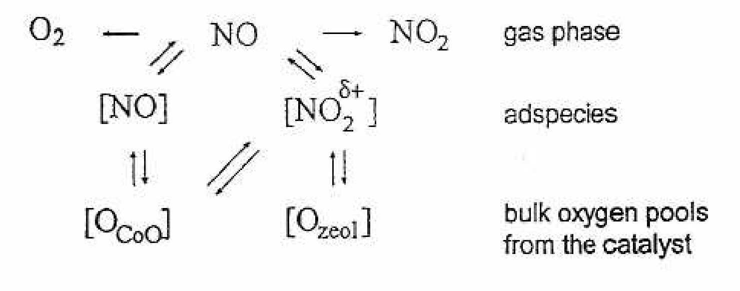


FIG. 1. Time dependencies of (A) ^{15}N and (B) ^{18}O isotopic fractions in NO compared to Ar response observed after ^{14}N^{16}O to ^{15}N^{18}O replacement in (1) NO + He flow and in NO + O_2 + He flows at (2) 0.15%, (3) 0.3%, (4) 1.5%, and (5) 3% oxygen content.

SSITKA - Examples

Selective NO reduction over Co-ZSM-5

(Sadovskaya et al. 2001)



$$\frac{\partial \alpha_{NO}^{18}}{\partial t} + \frac{U}{V}\frac{\partial \alpha_{NO}^{18}}{\partial \xi} = \frac{G}{V C_{NO} N}\left(\sum_{i=1}^{2} W_i\left(\alpha_i^{18} - \alpha_{NO}^{18}\right) - (R_1 + R_2)\alpha_{NO}^{18}\right)$$

$$\frac{\partial \alpha_i^{15}}{\partial t} = \frac{W_i}{\theta_i}\left(\alpha_{NO}^{18} - \alpha_i^{18}\right) + \sum_{j=1}^{m} \beta_j\left(\alpha_j^{18} - \alpha_i^{18}\right)$$

$$\frac{\partial \alpha_j^{18}}{\partial t} = \sum_{i=1}^{2} m_i \beta_i\left(\alpha_i^{18} - \alpha_j^{18}\right) + \sum_{k=1}^{m} m_k \beta_k\left(\alpha_k^{18} - \alpha_j^{18}\right)$$

$$\frac{\partial \alpha_{O_2}^{18}}{\partial t} + \frac{U}{V}\frac{\partial \alpha_{O_2}^{18}}{\partial \xi} = \frac{G}{V C_{O_2} N} R_i \alpha_{NO}^{18}$$

$$\frac{\partial \alpha_{NO_2}^{18}}{\partial t} + \frac{U}{V}\frac{\partial \alpha_{NO_2}^{18}}{\partial \xi} = \frac{G}{V C_{NO_2} N} R_2 \alpha_{NO}^{18},$$

SSITKA - Examples

Selective NO reduction over Co-ZSM-5

(Sadovskaya et al. 2001)

- Cobalt mononitrosyls, $NO_x^{\delta+}$ species, nitrite complexes have average lifetimes of 0.1, 1, and 100 s
- Observation in agreement with DRIFT
- Concentration of mononitrosyls was found proportional to NO content in feed gas; no saturation
- $NO_x^{\delta+}$ species approached maximum coverage within the same concentration range; only part of cobalt active species participate in $NO_x^{\delta+}$ species formation

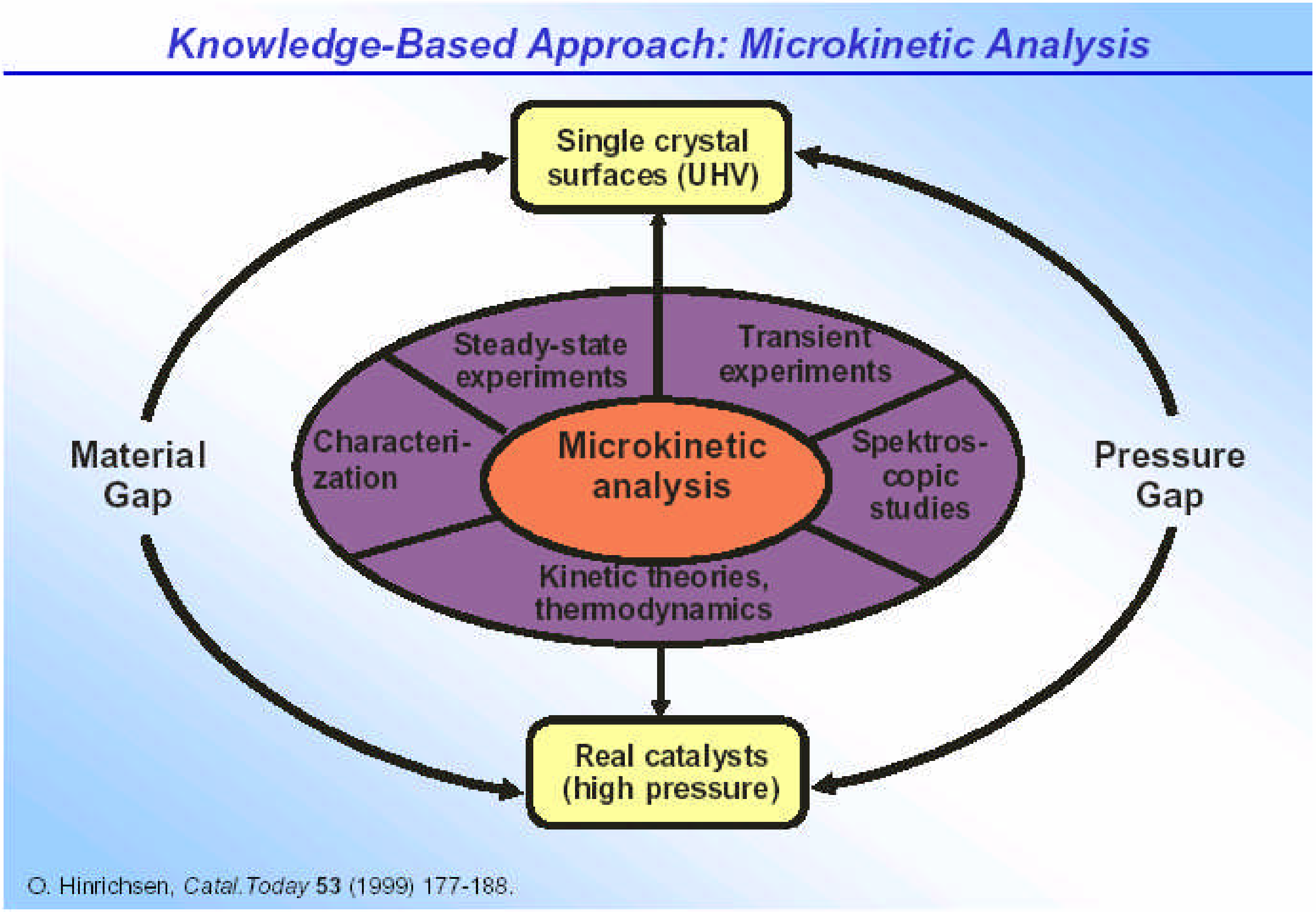
SSITKA - Examples

Selective NO reduction over Co-ZSM-5

(Sadovskaya et al. 2001)

- Rate of gaseous NO_2 formation comparable with nitrite formation and substantially lower than that of $NO_x^{\delta+}$ formation
- Conclusion: $NO_x^{\delta+}$ can not originate from NO_2 formation but formed in two sequential steps (i) molecular oxygen adsorption and (ii) NO reaction with oxidized surface sites
- Rate of oxygen exchange within $NO_x^{\delta+}$ lower than their formation indicating that the two oxygens are nonequivalent

Kinetic modeling



Knowledge-Based Approach: Microkinetic Analysis

Single crystal surfaces (UHV)

Material Gap

Steady-state experiments

Transient experiments

Characterization

Microkinetic analysis

Spektroscopic studies

Kinetic theories, thermodynamics

Pressure Gap

Real catalysts (high pressure)

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

Way down South in the land of cotton
Where good mints juleps are not forgotten
An old farmer sits on his plantation
Thinking up problems to astound the nation
***Lindemann and Hinshelwood* can stand it no more**
While *Smith* and *Carberry* have run for the door
Now there is one as he told it to me
And I give it to you, completely for free
We know *kinetics* is a staid sort of sport
If *reaction order* is all there´s to report
So we´ve studied about *reactor design*
In detail and elegance quite so fine
Mixing models have been disussed
Where *proper equations* are a must
Age distributions become important here
An intricate analysis, it is clear
Now this is the question to give you fits
An excellent chance to test your wits
Of these distributions there are many it´s sure
Derived from a *theory* assuredly most pure

Residence time, internal, and exit age
All we owe to Danckwerts, that clever sage
What are they, please, a clear explanation
Combining words with an _appropriate equation_
Relationships between them are almost horrendous
A discussion of this would be simply tremendous
When you´ve written all this consider you´re done
Now wasn´t that all just good clean fun
If you did what was aked, and that I hope
Then with _chemical reactors_ you´re able to cope
One final thing I must now say
Of the light of knowledge a final ray
Reaction kinetics is in a mess
In spite of _Eyring_ and _Arrhenius_
Alas, was it ever thus so

The more we learn, the less we know !

John B. Butt

SSITKA

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