An introduction to kinetics in heterogeneous catalysis -

How to measure properly activity and selectivity, what are underlying fundamentals, how looks like the mathematical description

A.C. van Veen
(andre.vanveen@rub.de)
Ruhr Universität Bochum
Room NC 5/69
Universitätsstraße 150
D-44780 Bochum

References

- O. Levenspiel, “Chemical reaction engineering”, 3rd edition, Wiley (1999), ISBN 0-471-25424-X.
- M. Baerns, H. Hofmann, A. Renken, “Chemische Reaktionstechnik”, 2nd edition, Thieme (1992), ISBN 3-13-687502-8.

Table of contents

- Introduction.
- Reactor types and characteristics.
- From conversion and selectivity to mechanistic information.
- Rate expression and constants, kinetic formalisms.
- Operating conditions and experimental setup.
- Towards kinetic modeling of experiments

Introduction

Objectives of the lecture:
- Macro / microscopic meaning of activity and selectivity.
- The 1-dimensional pseudo homogeneous model without dispersion
- Good experimental design to achieve intrinsic information

Beyond the scope of the lecture are:
1. More complex reactor models (radial dimension)
2. Calculations accounting for transfer limitations
3. Details on parameter estimation in heterogeneous catalysis
4. Statistical treatment of results:
    - ♦ Error propagation.
    - ♦ Confidence intervals.
    - ♦ Model discrimination.

Reactors: Different scale – different objectives

Industry:

Produce a chemical so that **costs of the process** are minimal:

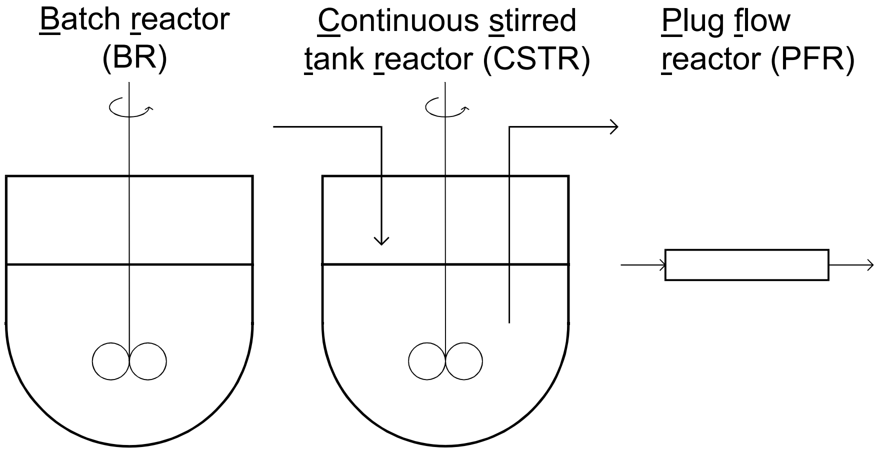
- Obtain high conversions: Recycle streams are costly and require a purge!
- Restrict the product spectrum: The reactor is only a part of a process.
- Use one optimum reactant composition: Process integration and capacity limits of downstream units require steady operation.

Laboratory:

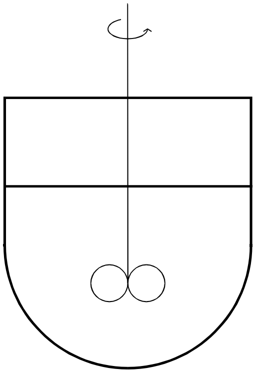
Obtain as much **information on a reaction network** as possible:

- Operate with partial conversion: Nothing says less than a “full reactant conversion” case!
- Have the possible product spectrum represented: Intermediates formation bares valuable information on the mechanism.
- Vary the reactant composition and add products: Stoichiometric decoupling is compulsory for uncorrelated parameter estimation
- Use a simple describable reactor: Isothermal conditions, plug flow or CSTR but no mixed situations.

Reactor types



Batch reactor

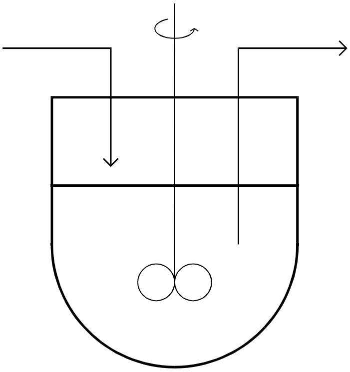


- Closed system
- Performance data as a function of time
- Reaction over the reactor at the same concentration level
- Might also originate from a tubular reactor with closed (fast) recycle loop

⇒Data analysis over time, i.e. c(p) vs. t, high conversions straight forward, but mind adsorption and inert purge

---

Continuous stirred tank reactor



- Open system
- Performance data as a function of flow rate
- Reaction over the reactor (catalyst) at the same concentration (partial pressure)
- Might also originate from a tubular reactor with injection, (fast) recycle loop and purge

⇒Data analysis over residence time, i.e. c (p) vs. τ, differential conversions straight forward, but mind adsorption and inert purge

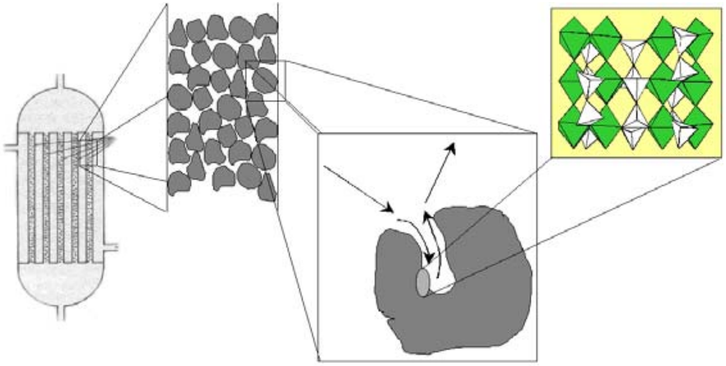
Plug flow reactor

- Open system
- Performance data as a function of flow rate
- Reaction over the reactor at varying concentration level
- Fluid segments cross the reactor individually
- Reaction time scales to the positions in the reactor

⇒Data analysis over residence time, i.e. c (p) vs. τ, mind high conversions without integration over the reactor

---

Areas of balancing



	Reactor	Catalyst bed	Catalyst particle	Active site
What?				
Who?	Engineers?	Inorganic chemistry?	Industrial chemistry?	Physical /Theoretical chemistry?

Macroscopic definitions

Conversion, selectivity and yield are dimensionless numbers ranging from 0 to 1 or 0 to 100%

Conversion $$X_e = \frac{\dot{n}_{e,0} - \dot{n}_e}{\dot{n}_{e,0}} \qquad \frac{\text{converted educt}}{\text{supplied educt}}$$

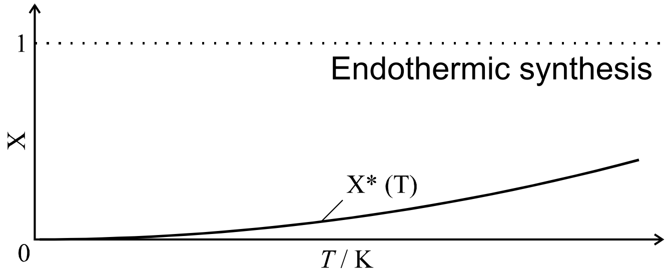
Selectivity $$S_p = \frac{\dot{n}_p}{\dot{n}_{e,0} - \dot{n}_e} \cdot \frac{-\nu_e}{\nu_p} \qquad \frac{\text{formed product}}{\text{converted educt}}$$

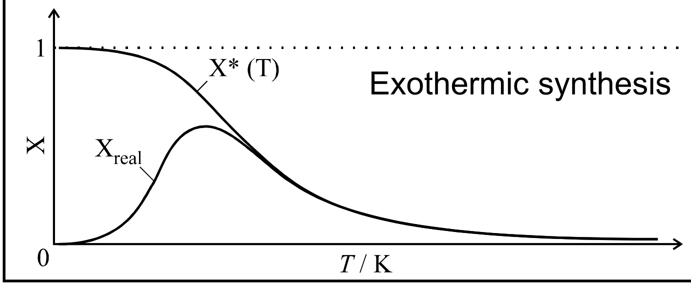
Yield $$Y_p = \frac{\dot{n}_p}{\dot{n}_{e,0}} \cdot \frac{-\nu_e}{\nu_p} \qquad \frac{\text{formed product}}{\text{supplied educt}}$$

As selectivity and yield definitions contain stoichiometric coefficients, these numbers are in general only meaningful if the respective stoichiometric equations are given

---

Mind the thermodynamics





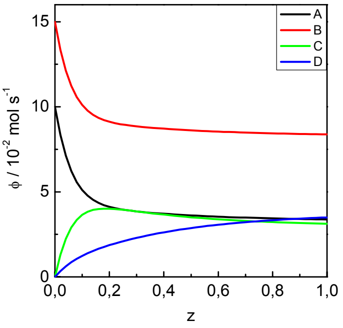
Endothermic synthesis: Equilibrium conversion increases with T

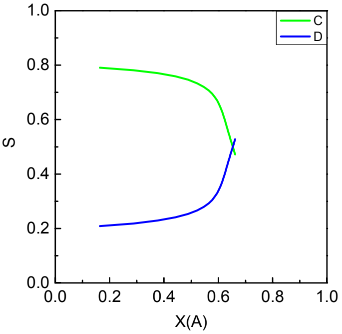
Exothermic synthesis: Equilibrium conversion decreases with T. Real conversion increases for kinetic reason and might be capped.

Is the knowledge of X, S, Y sufficient?

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C$$

$$A + B \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} D$$





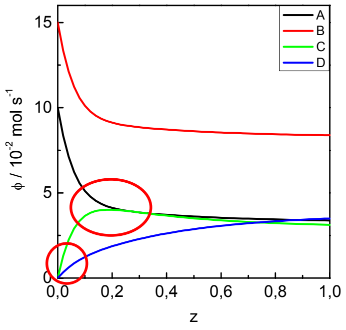
- Never compare selectivity at different conversion levels
- Judge a catalyst on yield basis is better, but the specific activity information in easily lost

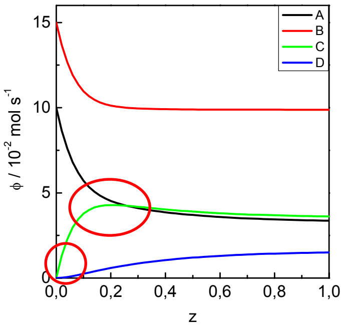
---

Product formation: parallel or sequential

$$D \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C$$

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} D$$





- Identifying a maximum does not “reveal” a sequential mechanism
- The profiles might mislead in case of equilibrium reactions

S versus X plot – parallel product formation

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C$$

$r_1 = \rho\, k_1\, p_A\, p_B$

$r_{-1} = \rho\, k_{-1}\, p_C$

$$A + B \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} D$$

$r_2 = \rho\, k_2\, p_A\, p_B$

$r_{-2} = \rho\, k_{-2}\, p_D$

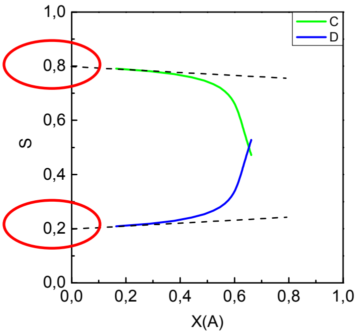
$\rho = 10\ \mathrm{mol\ m^{-3}}$

$k_1 = \boxed{4\ 10^{-9}}\ \mathrm{Pa^{-2}\ s^{-1}}$

$k_{-1} = 2\ 10^{-4}\ \mathrm{Pa^{-1}\ s^{-1}}$

$k_2 = \boxed{1\ 10^{-9}}\ \mathrm{Pa^{-2}\ s^{-1}}$

$k_{-2} = 4\ 10^{-5}\ \mathrm{Pa^{-1}\ s^{-1}}$



- Extrapolation of selectivity at zero conversion: finite values for parallel reactions
- Selectivity ratio equals ratio of initial formation **rates** (not constants!)

S versus X plot – sequential product formation

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C$$

$r_1 = \rho\, k_1\, p_A\, p_B$

$r_{-1} = \rho\, k_{-1}\, p_C$

$$A + C \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} D$$

$r_2 = \rho\, k_2\, p_A\, p_C$

$r_{-2} = \rho\, k_{-2}\, p_D$

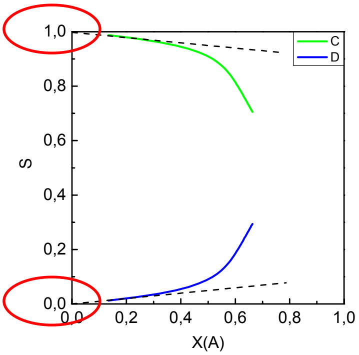
$\rho = 10\ \mathrm{mol\ m^{-3}}$

$k_1 = 4\ 10^{-9}\ \mathrm{Pa^{-2}\ s^{-1}}$

$k_{-1} = 2\ 10^{-4}\ \mathrm{Pa^{-1}\ s^{-1}}$

$k_2 = 1\ 10^{-9}\ \mathrm{Pa^{-2}\ s^{-1}}$

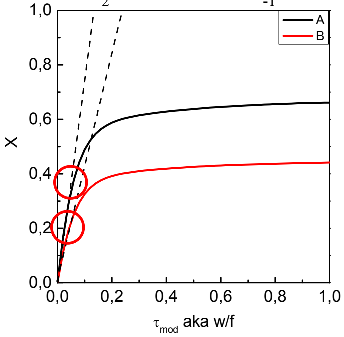
$k_{-2} = 4\ 10^{-5}\ \mathrm{Pa^{-1}\ s^{-1}}$



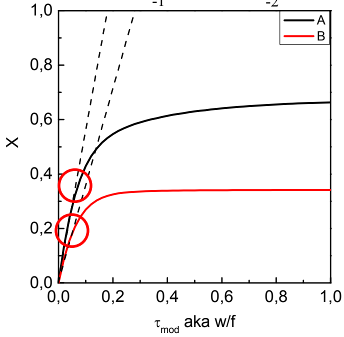
- Extrapolation of selectivity at zero conversion: Zero selectivity for secondary products

What is the proper range to make extrapolations

$$D \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C$$



$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} D$$



- Conversion increases under differential conditions linear with w/f
- The origin must be precisely passed

What is catalytic activity?
What is catalytic selectivity?

Catalytic activity relates to the density of sites ρ and their individual activity related to k in the surface reaction step. However, adsorption and desorption interplay as well!

Catalytic selectivity (at molecular level) relates to ratio of **reaction rates** in selective and unselective reaction paths. However, adsorption and desorption interplay as well!

How to describe the reaction?

General term for the reaction rate

$$r = \frac{1}{V}\frac{1}{\nu_i}\frac{dn_i}{dt} \quad [\text{mol s}^{-1}\text{ m}^{-3}]$$

Terms for the reaction rate in homogeneous catalysis

$r = k(T)\, c_A$ 1st order: k [s^{-1}]

$r = k(T)\, c_A^2$ or $r = k(T)\, c_A\, c_B$ 2nd order: k [$m^3\ mol^{-1}\ s^{-1}$]

$$k(T) = k_0 \exp(-E_A / R\,T)$$

Concentrations are here only convenient as the reaction volume hardly changes

---

How to describe the reaction rate(s)?

Terms for the reaction rate in heterogeneous catalysis:

$r = k(T)\, p_1^{m_1}\, p_2^{m_2}$ Formal kinetics: power law

“Well, one does not know much of the mechanism and fits parameters”

$$r = \frac{k(T)\, p_1^{m_1}\, p_2^{m_2}}{(1 + K_1(T)\, p_1 + K_2(T)\, p_2)^{m_3}}$$ Formal kinetics: hyperbolic form

“One knows the mechanism a bit and makes simplifications”

Micro kinetics: Set of many parallel equations for adsorption and desorption, reaction

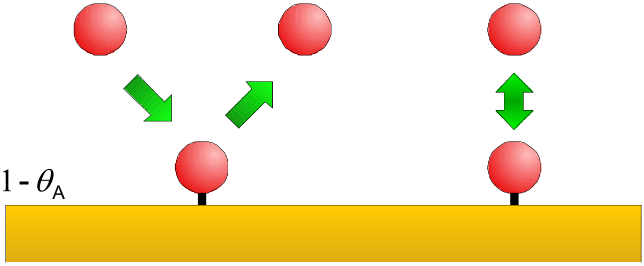
$$r = \frac{1}{\nu_i\, \Delta V}\frac{dn_{reac,i}}{dt} = \frac{1}{\nu_i\, \Delta V}\dot{n}_{reac,i} = \rho\, k_0 \exp(-E_a / R\,T)\, f(p_x, \Theta_x)$$

Rate expressions of sorption processes

(atom adsorption and successive desorption)

$$r_{\text{ads,A}} = \rho\, k_{\text{ads,A}}\, p_{\text{A}}\, \theta_{*} \qquad r_{\text{des,A}} = \rho\, k_{\text{des,A}}\, \theta_{\text{A}}$$

$$\text{A} + * \underset{k_{\text{des,A}}}{\overset{k_{\text{ads,A}}}{\rightleftharpoons}} \text{A--}*$$



$$\theta_{*} = 1 - \theta_{\text{A}}$$

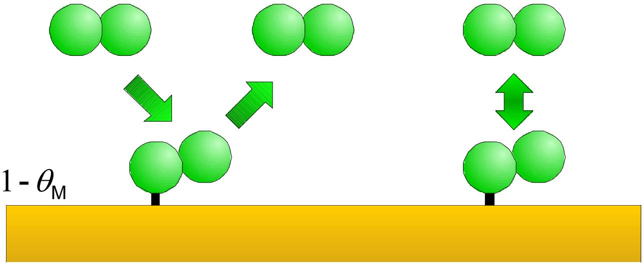
In fast equilibrium: $\theta_{\text{A}} = \dfrac{k_{\text{ads,A}}\, p_{\text{A}}}{k_{\text{des,A}} + k_{\text{ads,A}}\, p_{\text{A}}} = \dfrac{K_{\text{A}}\, p_{\text{A}}}{1 + K_{\text{A}}\, p_{\text{A}}}$ with $K_{\text{A}} = \dfrac{k_{\text{ads,A}}}{k_{\text{des,A}}}$

Rate expressions of sorption processes

(molecular adsorption and successive desorption)

$$r_{\text{ads,M}} = \rho\, k_{\text{ads,M}}\, p_{\text{M}}\, \theta_{*} \qquad r_{\text{des,M}} = \rho\, k_{\text{des,M}}\, \theta_{\text{M}}$$

$$\text{M} + * \underset{k_{\text{des,M}}}{\overset{k_{\text{ads,M}}}{\rightleftharpoons}} \text{M--}*$$



$$\theta_{*} = 1 - \theta_{\text{M}}$$

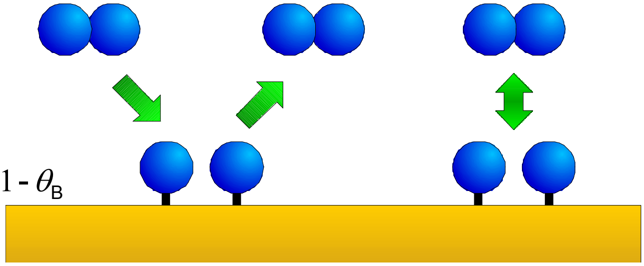
In fast equilibrium: $\theta_{\text{M}} = \dfrac{k_{\text{ads,M}}\, p_{\text{M}}}{k_{\text{des,M}} + k_{\text{ads,M}}\, p_{\text{M}}} = \dfrac{K_{\text{M}}\, p_{\text{M}}}{1 + K_{\text{M}}\, p_{\text{M}}}$ with $K_{\text{M}} = \dfrac{k_{\text{ads,M}}}{k_{\text{des,M}}}$

Rate expressions of sorption processes

(dissociated adsorption and successive desorption)

$$r_{\mathrm{ads,B}} = \rho\, k_{\mathrm{ads,B}}\, p_{\mathrm{B}}\, \theta_*^2 \qquad r_{\mathrm{des,B}} = \rho\, k_{\mathrm{des,B}}\, \theta_{\mathrm{B}}^2$$

$$\mathrm{B}_2 + 2\,* \underset{k_{\mathrm{des,B}}}{\overset{k_{\mathrm{ads,B}}}{\rightleftharpoons}} 2\,\mathrm{B}\text{--}*$$



$$\theta_* = 1 - \theta_{\mathrm{B}}$$

In fast equilibrium: $\theta_{\mathrm{B}} = \dfrac{\sqrt{k_{\mathrm{ads,B}}\ p_{\mathrm{B}}}}{\sqrt{k_{\mathrm{des,B}}} + \sqrt{k_{\mathrm{ads,B}}\ p_{\mathrm{B}}}} = \dfrac{\sqrt{K_{\mathrm{B}}\ p_{\mathrm{B}}}}{1 + \sqrt{K_{\mathrm{B}}\ p_{\mathrm{B}}}}$ with $K_{\mathrm{B}} = \dfrac{k_{\mathrm{ads,B}}}{k_{\mathrm{des,B}}}$

Towards reaction – Co-adsorption

As soon as one thinks of reaction there shall be co-adsorption of reactants. Thus, two points are important to underline:

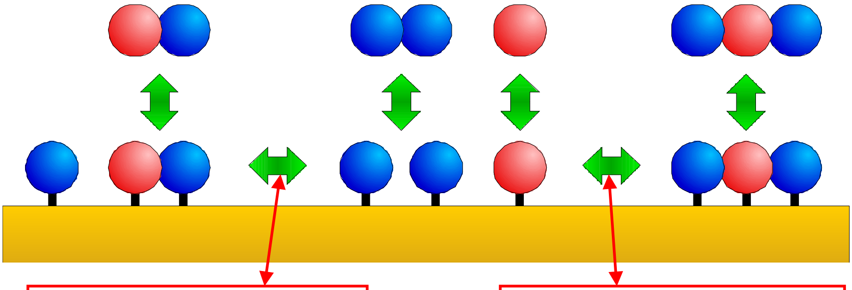
$\theta_* = 1 - \theta_{\mathrm{B}}$ might not hold anymore, but $\theta_* = 1 - \theta_{\mathrm{A}} - \theta_{\mathrm{B}}$

On the other hand, adsorption could also proceed on multiple sites

- Knowing the adsorption of reactants is not trivial information
- There might be cooperation of different sites

The micro-kinetic reaction on the surface

(parallel product formation)



Primary product 1

Educts

Primary product 2

$$r_1 = r_{\mathrm{e}\rightarrow \mathrm{P1,ads}} = \rho\, k_1\, \theta_\mathrm{A}\, \theta_\mathrm{B}$$

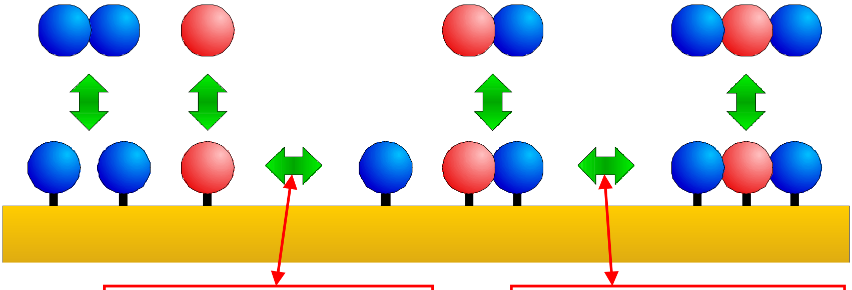
$$r_{-1} = r_{\mathrm{P1,ads}\rightarrow \mathrm{e}} = \rho\, k_{-1}\, \theta_\mathrm{P1}$$

$$r_2 = r_{\mathrm{e}\rightarrow \mathrm{P2,ads}} = \rho\, k_2\, \theta_\mathrm{A}\, \theta_\mathrm{B}^2$$

$$r_{-2} = r_{\mathrm{P2,ads}\rightarrow \mathrm{e}} = \rho\, k_{-2}\, \theta_\mathrm{P2}$$

The micro-kinetic reaction on the surface

(sequential product formation)



Educts

Primary product

Secondary product

$$r_1 = r_{\rightarrow \mathrm{P1,ads}} = \rho\, k_1\, \theta_\mathrm{A}\, \theta_\mathrm{B}$$

$$r_{-1} = r_{\mathrm{P1,ads}\rightarrow} = \rho\, k_{-1}\, \theta_\mathrm{P1}$$

$$r_2 = r_{\rightarrow \mathrm{P2,ads}} = \rho\, k_2\, \theta_\mathrm{B}\, \theta_\mathrm{P1}$$

$$r_{-2} = r_{\mathrm{P2,ads}\rightarrow} = \rho\, k_{-2}\, \theta_\mathrm{P2}$$

Models assuming rate limiting steps (1)

Case 1: **Eley-Rideal-mechanism**
Component A_1 is chemisorbed, component A_2 is in gas-phase. The reaction proceeds **slow** between chemisorbed A_1 and A_2 from the gas-phase.

$$A_1 + * \quad \underset{k_{des,1}}{\overset{k_{ads,1}}{\rightleftharpoons}} \quad A_1\text{--}* \qquad \theta_1 = \frac{K_1 \cdot p_1}{1 + K_1 \cdot p_1}$$

$$A_1\text{--}* \;+\; A_{2\,(g)} \quad \longrightarrow \quad \text{products} \qquad r = k \cdot \theta_1 \cdot p_2$$

$$r = k \cdot \frac{K_1 \cdot p_1 \cdot p_2}{1 + K_1 \cdot p_1}$$

$K_1 \cdot p_1$ large (>> 1): $r \approx k \cdot p_2$ Order of A_1 is 0

$K_1 \cdot p_1$ small (<< 1): $r \approx k \cdot K_1 \cdot p_1 \cdot p_2$ Order of A_1 is 1

Models assuming rate limiting steps (2)

Case 2: **Langmuir-Hinshelwood-mechanism**
Component A_1 is chemisorbed, component A_2 is chemisorbed. The reaction proceeds **slow** between chemisorbed A_1 and A_2 at the surface.

$$A_1 + * \quad \underset{k_{des,1}}{\overset{k_{ads,1}}{\rightleftharpoons}} \quad A_1\text{--}* \qquad \theta_1 = \frac{K_1 \cdot p_1}{1 + K_1 \cdot p_1 + K_2 \cdot p_2}$$

$$A_2 + * \quad \underset{k_{des,2}}{\overset{k_{ads,2}}{\rightleftharpoons}} \quad A_2\text{--}* \qquad \theta_2 = \frac{K_2 \cdot p_2}{1 + K_1 \cdot p_1 + K_2 \cdot p_2}$$

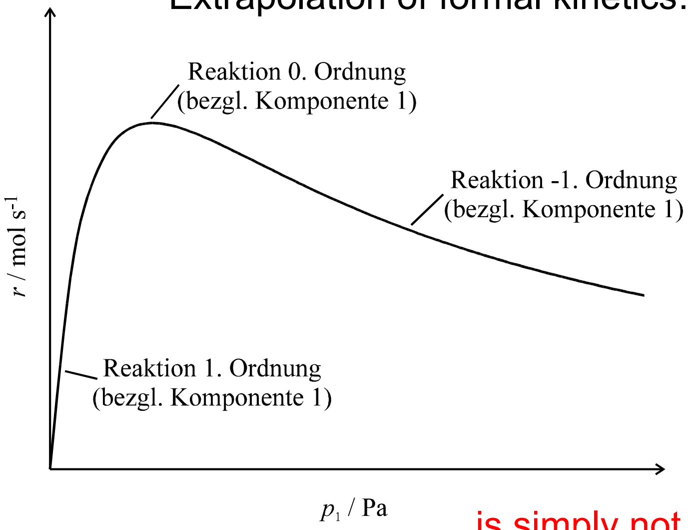
$$A_1\text{--}* \;+\; A_2\text{--}* \quad \longrightarrow \quad \text{products} \qquad r = k \cdot \theta_1 \cdot \theta_2$$

$$r = k \cdot \frac{K_1 \cdot p_1 \cdot K_2 \cdot p_2}{\left(1 + K_1 \cdot p_1 + K_2 \cdot p_2\right)^2}$$

$K_1 \cdot p_1$ large (>> 1): $r \approx k \cdot \dfrac{K_2 \cdot p_2}{K_1 \cdot p_1}$ Order of A_1 is –1

$K_1 \cdot p_1$ small (<< 1): $r \approx k \cdot \dfrac{K_1 \cdot K_2 \cdot p_2}{\left(1 + K_2 \cdot p_2\right)^2} \cdot p_1 = k^* \cdot p_1$ Order of A_1 is 1

Extrapolation of formal kinetics…



…is simply not possible

Are models assuming a rate limiting step sufficient?

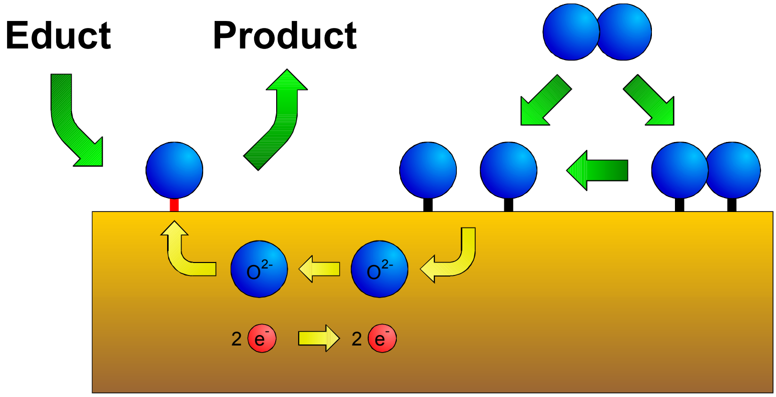
According to what one assumes as rate limiting step, one can derive a suitable kinetic expression!
(refer to Hougen-Watson terms)

- The rate limiting step might change with temperature
- There might be coupling between steps

One should move to micro kinetics accounting for all steps

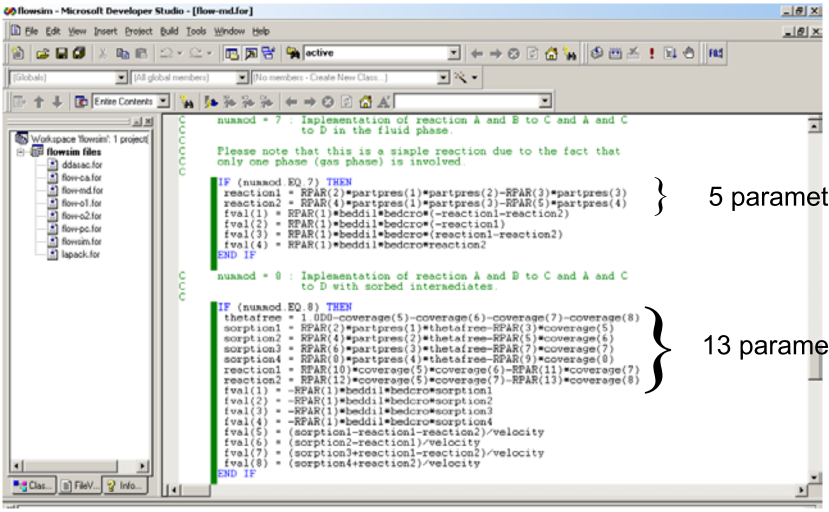
Mars-van Krevelen mechanism

(Two rate limiting steps!)



Best to do only micro kinetics?

In principle: yes! (but how to determine all those parameters?)



```
C      nummod = 7 : Implementation of reaction A and B to C and A and C
C                   to D in the fluid phase.
C
C      Please note that this is a simple reaction due to the fact that
C      only one phase (gas phase) is involved.
C
       IF (nummod.EQ.7) THEN
        reaction1 = RPAR(2)*partpres(1)*partpres(2)-RPAR(3)*partpres(3)
        reaction2 = RPAR(4)*partpres(1)*partpres(3)-RPAR(5)*partpres(4)
        fval(1) = RPAR(1)*beddil*bedcro*(-reaction1-reaction2)
        fval(2) = RPAR(1)*beddil*bedcro*(-reaction1)
        fval(3) = RPAR(1)*beddil*bedcro*(reaction1-reaction2)
        fval(4) = RPAR(1)*beddil*bedcro*reaction2
       END IF

C      nummod = 8 : Implementation of reaction A and B to C and A and C
C                   to D with sorbed intermediates.
C
       IF (nummod.EQ.8) THEN
        thetafree = 1.0D0-coverage(5)-coverage(6)-coverage(7)-coverage(8)
        sorption1 = RPAR(2)*partpres(1)*thetafree-RPAR(3)*coverage(5)
        sorption2 = RPAR(4)*partpres(2)*thetafree-RPAR(5)*coverage(6)
        sorption3 = RPAR(6)*partpres(3)*thetafree-RPAR(7)*coverage(7)
        sorption4 = RPAR(8)*partpres(4)*thetafree-RPAR(9)*coverage(8)
        reaction1 = RPAR(10)*coverage(5)*coverage(6)-RPAR(11)*coverage(7)
        reaction2 = RPAR(12)*coverage(5)*coverage(7)-RPAR(13)*coverage(8)
        fval(1) = -RPAR(1)*beddil*bedcro*sorption1
        fval(2) = -RPAR(1)*beddil*bedcro*sorption2
        fval(3) = -RPAR(1)*beddil*bedcro*sorption3
        fval(4) = -RPAR(1)*beddil*bedcro*sorption4
        fval(5) = (sorption1-reaction1-reaction2)/velocity
        fval(6) = (sorption2-reaction1)/velocity
        fval(7) = (sorption3+reaction1-reaction2)/velocity
        fval(8) = (sorption4+reaction2)/velocity
       END IF
```

} 5 parameters

} 13 parameters

Towards transient experiments

Why are transient kinetic experiments very useful?

- Separation of elementary steps
  (information on individual rate constants or the site density)
- High information density
- Rapid data acquisition

Why are transient kinetic experiments not the only used ones?

1. Data interpretation is usually more complicated
   (A suitable/uncomplicated mathematical description is required)
2. The experimental effort is usually much higher
   - ♦ The influence of the apparatus on the signal (dead volumes, adsorption) must be minimized.
   - ♦ Heating ramps have to be perfectly linear.
   - ♦ A very sensitive on-line analysis is required.

Thermal desorption analysis - Principle

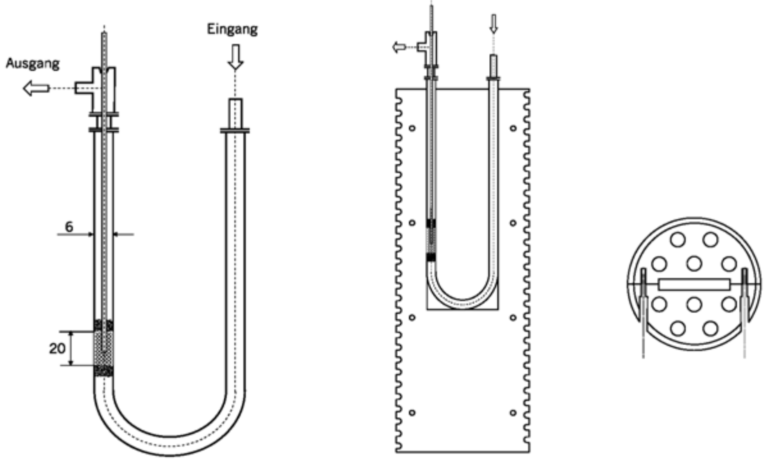
Thermal desorption analysis uses **desorption rate / uniform surface temperature** data from **linear ramped** sample heating starting from a **know initial coverage.** Available information includes:

- Type of adsorption (molecular / atomic = dissociated)
- Desorption kinetics (frequency factor and activation energy)
- Interaction of adsorbed species

Prerequisites:

1. The apparatus does not influence the signal shape
   (Immediate flushing of desorbed species)
2. Heating rate variation is possible over a wide range
   (typically a variation of almost 2 orders of magnitude desired)
3. The adsorption must be controlled to establish coverage data

TPD reactor



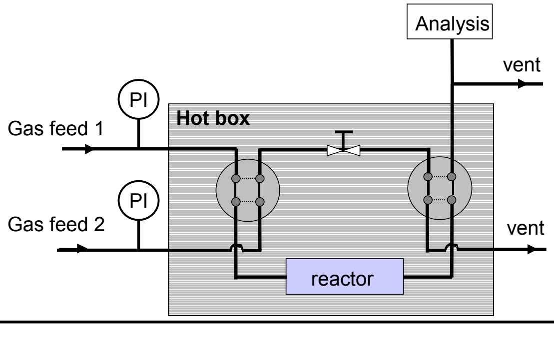
- Isothermal fixed bed located in a “pocket oven” (ramps 0.5 – 25 K min^{-1})
- Detection of the desorbed quantity diluted in the inert carrier

---

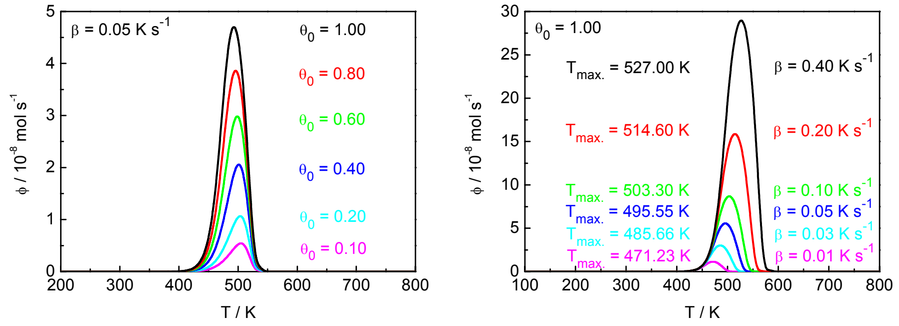
A catalytic test bench

A catalytic test bench for continuous reactors has typically 3 sections:

- Gas feed section: Provide a constant flow where reactant ratios may be varied as well as the overall feed rate. Systems often include a second line for pretreatment or purging of catalysis in bypass.
- Reactor / bypass section: Often housed in a hot box to avoid condensation of reactants / products.
- Analysis section: Typically online detection for quantitative analysis, usually exploitation along with an inert tracer in small concentration.

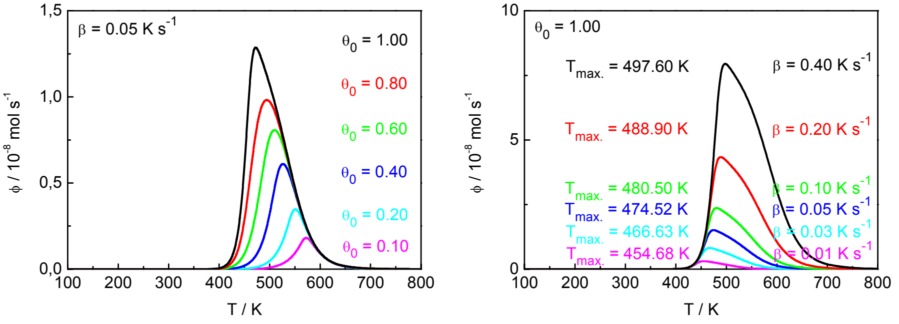


TPD experiment - molecular adsorption



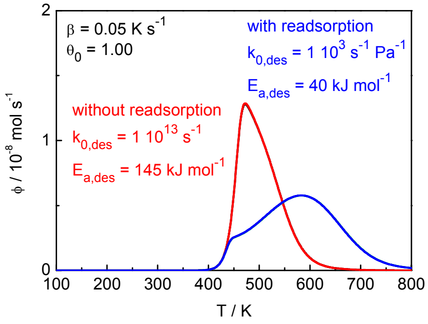
- Declining branches overlap for initial coverage variation
- Rising branches overlap for heating ramp variation
- Rapid decline of the signal after reaching the maximum

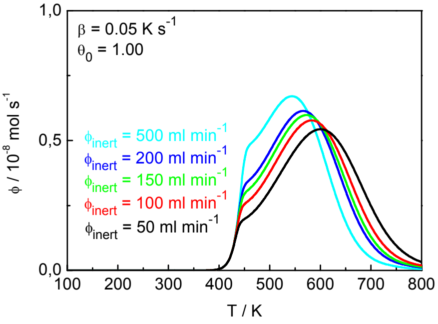
TPD experiment - dissociated adsorption



- Declining branches overlap for initial coverage variation
- Rising branches overlap for heating ramp variation
- Slow decline of the signal after reaching the maximum

TPD experiment - readsorption

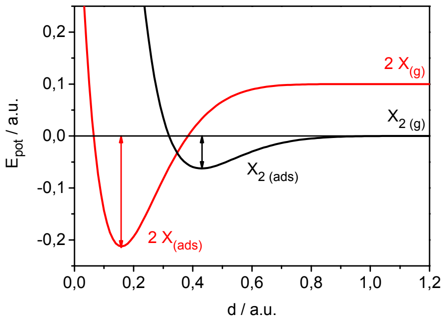




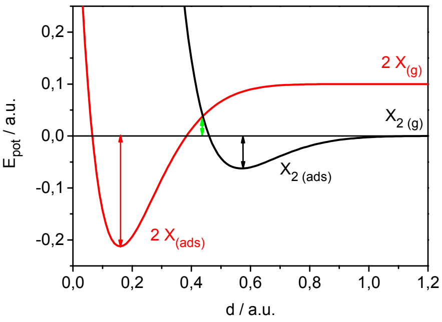
- Readsorption broadens TPD responses
- The impact of readsorption varies with the inert flow

Energetics of ad- and desorption

- Non activated adsorption

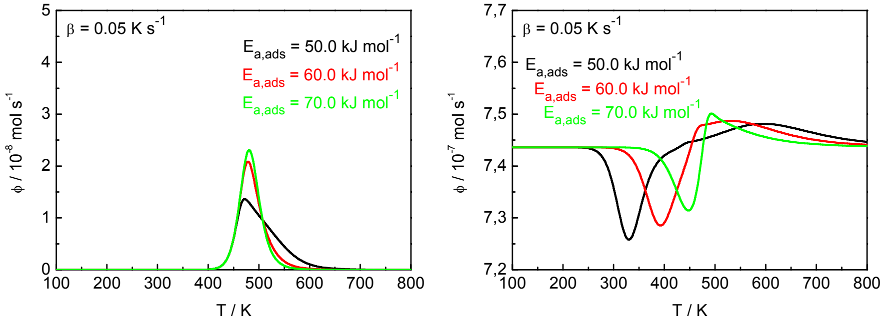


- Activated adsorption



- Lennard-Jones potentials cross
- The activation energy of adsorption increases also that of the desorption

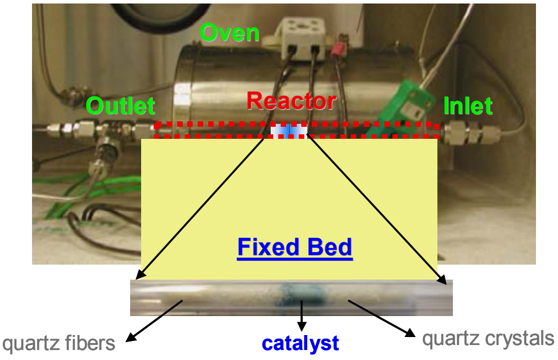
TPA experiment – Study an activated adsorption



- TPD responses for 60 and 70 kJ mol^{-1} similar
- TPA traces are clearly distinguishable
- Complementary TPA study required to complete the information pool

---

Catalytic fixed bed reactor – basics (1)



- Catalyst sandwiched between inert beds
- (Movable) thermocouple in the bed centre
- Fixation by quartz wool plugs

Catalytic fixed bed reactor – basics (2)

Reactant flow rates should be high enough

- Upper flow limit: Pressure drop over the catalyst bed
- Upper flow limit: Sufficient conversion for reasonable analysis
- Lower flow limit: Strong dispersion
- Lower flow limit: Use of a too shallow catalyst bed
  The minimum bed length should be equal to the inner tube diameter
- Lower flow limit: “External” mass transfer limitation:
  The stagnant film thickness increases with decreasing flow and the concentration at the catalyst particle differs from the fluid bulk.
  ⇒ Reaction at lower concentration level, thus underestimation of the specific activity.

Catalytic fixed bed reactor – basics (3)

Catalyst particles should have a well defined size (sieve fraction)

- Defined sieve fraction: Achieve homogeneous radial gas distribution
- Lower size limit: Increasing pressure drop with decreasing size
- Upper size limit: Channeling or bypassing
  The maximum particle size should be **1/10th** of the inner tube diameter
- Upper size limit: “Internal” mass transfer limitation:
  Pores in particles are too long and compounds react before reaching the end of the pore.
  ⇒ Only part of the active sites (towards the pore mouth) react, thus underestimation of the specific activity.

Catalytic fixed bed reactor – test for limitations

External mass transfer limitation:

Lab-Test: Probing the specific catalyst activity at different flow rate, i.e. identical conversion at identical w/f (at comparable pressure drop) (Dilution in bigger inert particles)

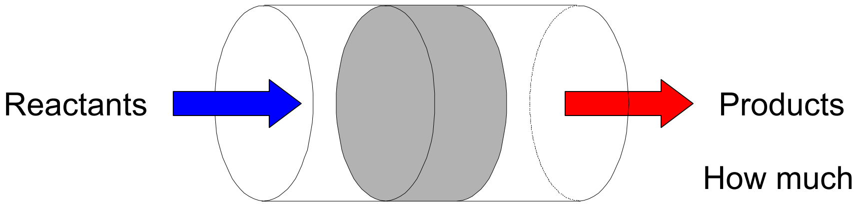
Numerical criterion: Estimation of the external degree of catalyst usage from the **Damköhler number II (DaII)**, ideally < 0.1

Internal mass transfer limitation:

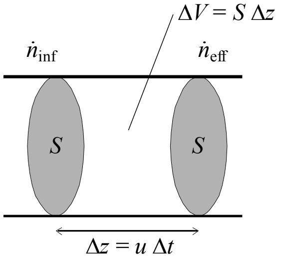
Lab-Test: Probing if the specific catalyst activity is the same as for smaller particles (at comparable pressure drop) (Dilution in bigger inert particles

Numerical criterion: Estimation of the degree of pore usage from the **(modified) Thiele (Φ) or Weisz (Ψ') modulus**, ideally < 0.3

Mathematical description of the PFR



How much?
What?



Deriving the spatial derivative form

$$\Delta n_{\text{acc},\text{i}} = \Delta n_{\text{inf},\text{i}} + \Delta n_{\text{reac},\text{i}} - \Delta n_{\text{eff},\text{i}}$$

$$\dot{n}_{\text{eff,i}} = \dot{n}_{\text{inf,i}} + \left.\frac{d\dot{n}_{\text{i}}}{dz}\right|_{0} u \; \Delta t$$

$$r_{\text{j}} = \frac{1}{\nu_{\text{j,i}} \; \Delta V} \frac{dn_{\text{reac,j,i}}}{dt} = \frac{1}{\nu_{\text{j,i}} \; \Delta V} \dot{n}_{\text{j,i}} = \rho \, k_{0,\text{j}} \, \exp\left(- E_{\text{a,j}} / \mathrm{R} \, T \right) f_{\text{j}}\left(p_{\text{x}}, \Theta_{\text{x}} \right)$$

$$\frac{d\dot{n}_{\text{acc,i}}}{dt} = - \frac{d\dot{n}_{\text{i}}}{dz} u + S \, u \, \rho \sum_{\text{j}} \nu_{\text{j,i}} \, k_{0,\text{j}} \, \exp\left(- E_{\text{a,j}} / \mathrm{R} \, T \right) f\left(p_{\text{x}}, \Theta_{\text{x}} \right)$$

Thanks for your attention