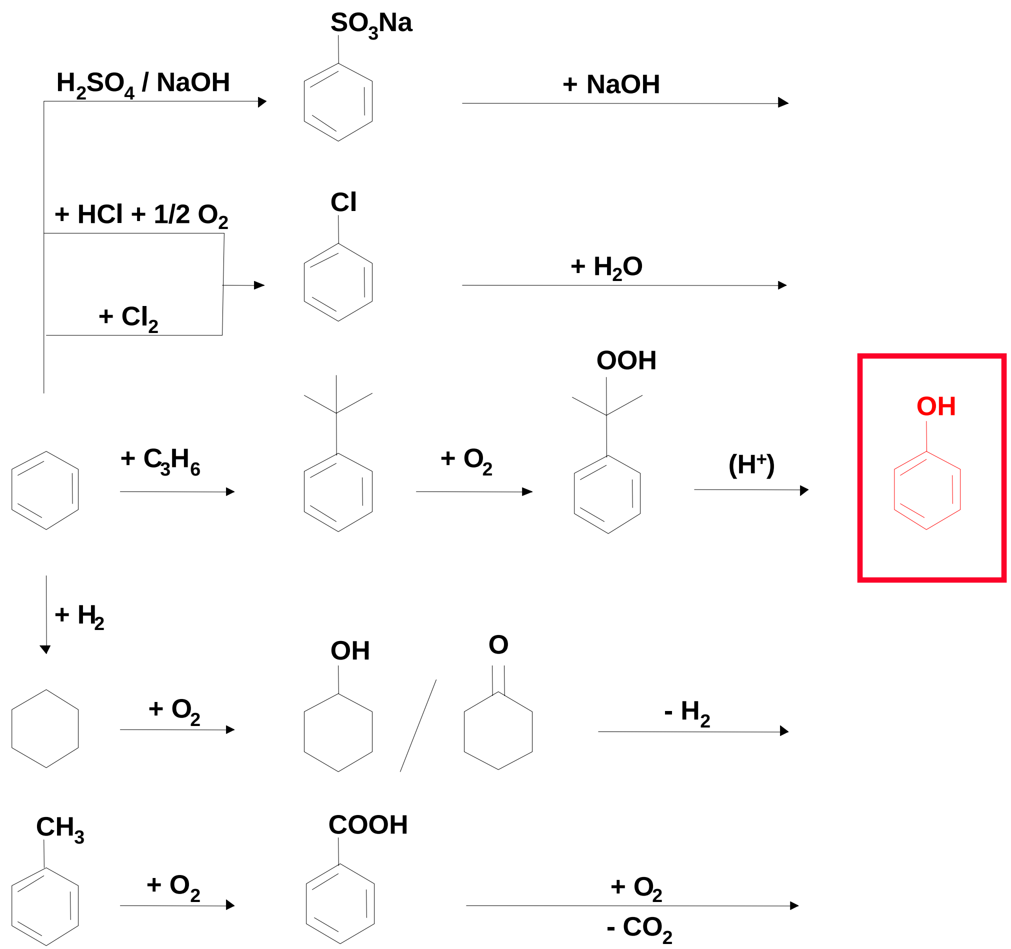
Chemical Reaction Engineering Basics Required to Understand Membrane Reactors

Andreas Seidel-Morgenstern

- **Classical reactor concepts**
- **Reaction rates and reactor models**
- **Mass transfer through membranes**
- **Product removal with membranes**
- **Reactant dosing with membranes**

Abundance of chemistry - possible pathways to produce phenol



via benzenesulfonate

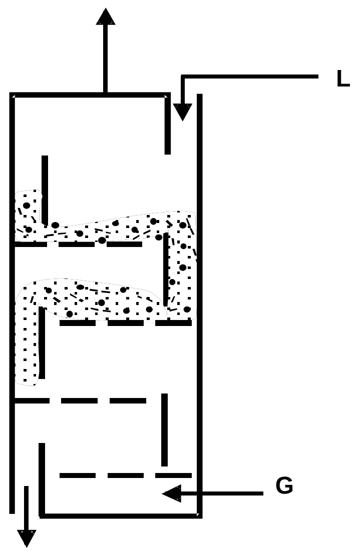
via chlorobenzene

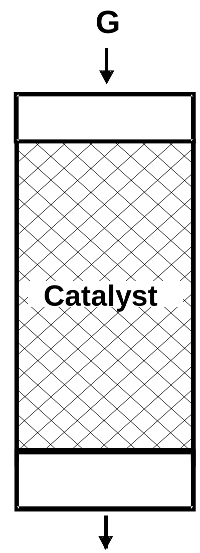
via cumene

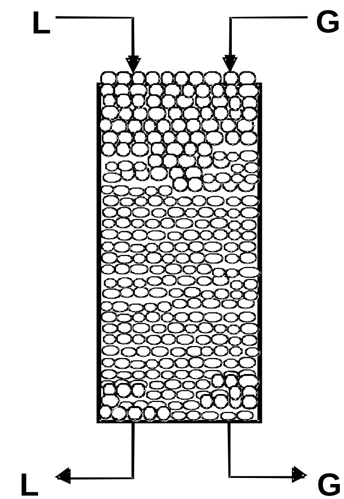
via cyclohexanole/-one

via toluene

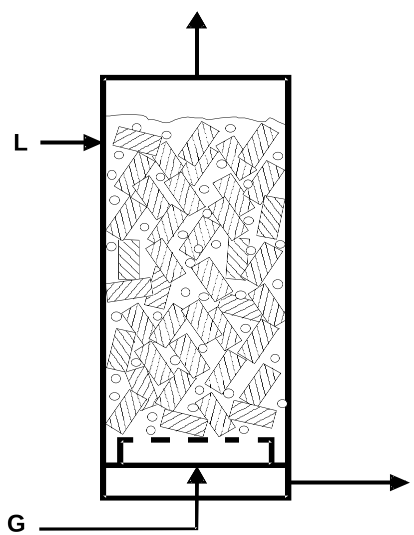
View in the spectrum of reactors

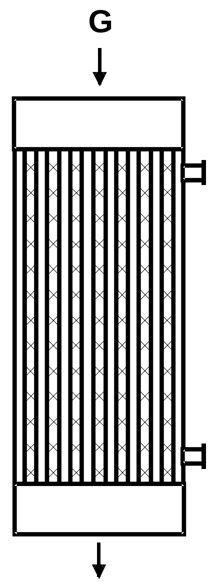


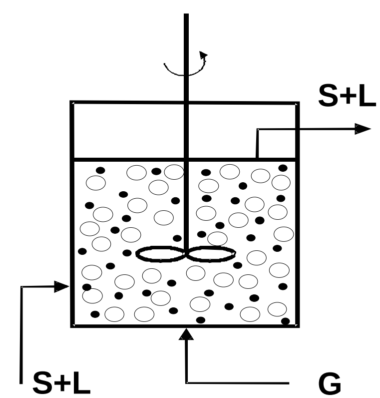




Gas / Liquid **Gas / Solid** **Gas / Liquid / Solid**







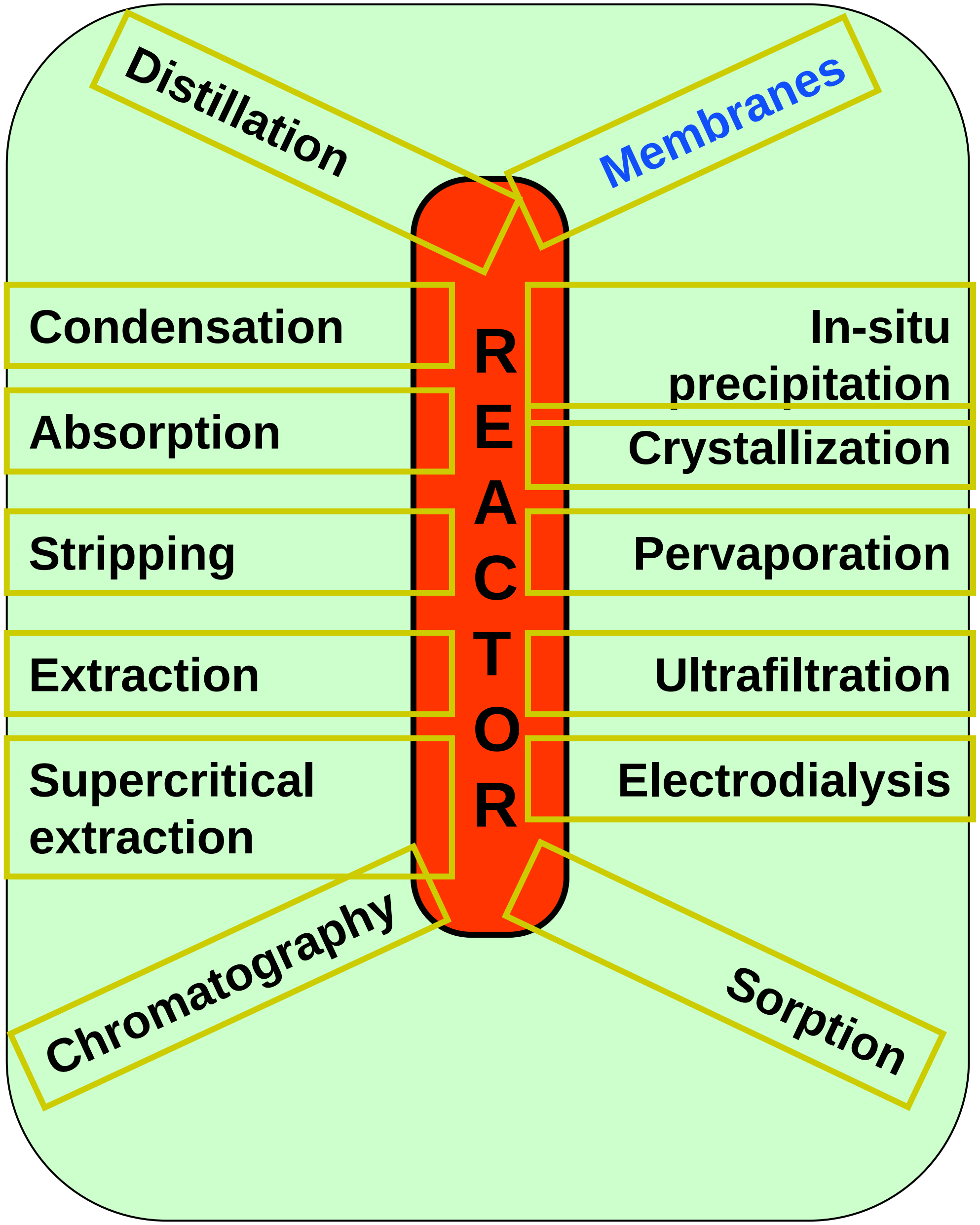
Classical problems

- reactions to slow
- reversibility
- selectivity restricted, yields low
- preheating for exothermic reactions required
- severe thermal effects

Attempts to solve these problems

- search for “alternative chemistry”
- development of selective catalysts
- optimization of operating parameters
- search for new reactor concepts
    - autothermal reactors
    - ...
    - coupling of reaction and separation

Possibilities of coupling reaction and separation



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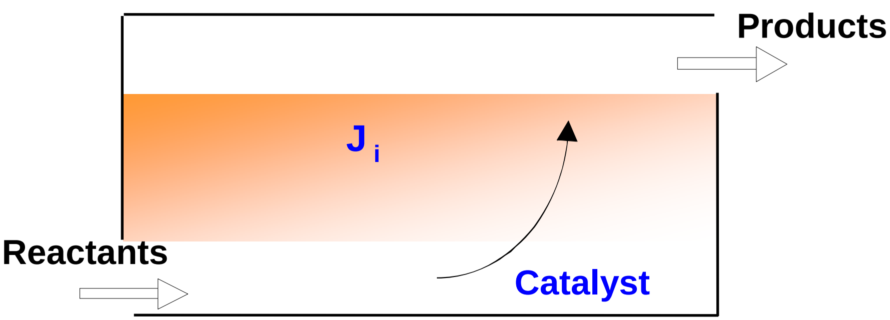
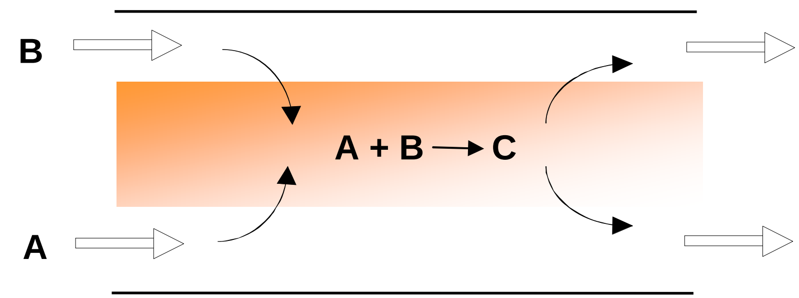
Concepts for membrane reactors

Retaining catalysts



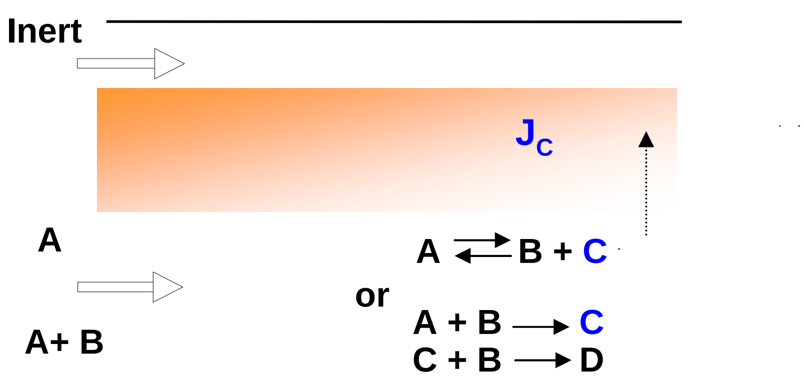
- homogeneous and enzyme catalysis

Membranes as active „contactor“



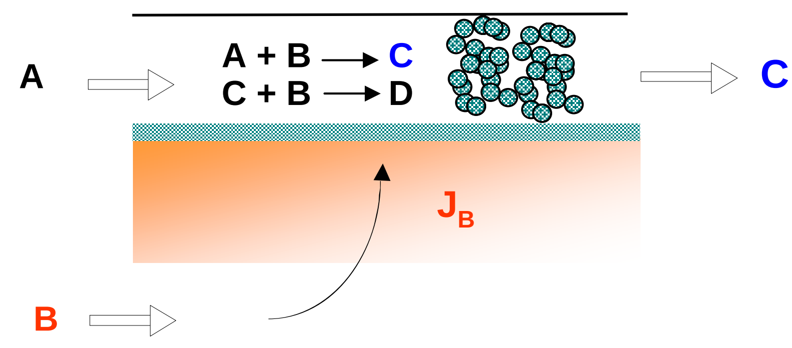
- *c*onversion front in membrane
- total conversion of toxic components

Selective product removal („Extractor“)



- conversion enhancement for reversible reactions
- selectivity improvements

Controlled reactant dosing („Distributor“)



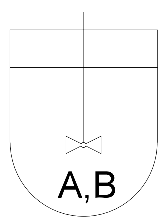
- dosing of critical components
- selectivity improvements

Classification criteria

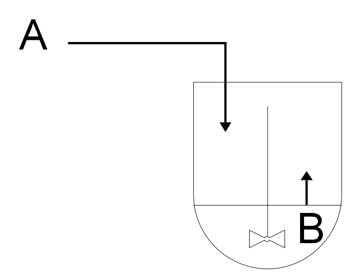
A) Phases involved (G/L, G/S, G/L/S, …)
B) Isothermal, adiabatic, polytropic
C) One reaction vs. reaction network
D) Single path operation vs. recycling concepts
E) Degree of mixing (perfect, intermediate, no mixing)
F) Mode of operation (discontinuous vs. continuous)
G) . . .

Discontinuous operation

BR (Batch Reactor, perfect mixing)



SBR (Semi Batch Reactor)



Continuous operation

CSTR (perfect mixing), PFTR (no mixing)

Reaction rates

➡ key information required for quantitative analysis, couple mass and energy balances

Definition:	$r = \frac{1}{Scale} \frac{1}{\nu_i} \frac{dn_i}{dt}$	$i = 1, N$

uses stoichiometric balance:
(thus *r* does not depend on component)

$$\frac{dn_i}{\nu_i} = \frac{dn_j}{\nu_j}$$

Scale: often V_R (if $V_R = const.$: $r = \frac{1}{\nu_i} \frac{dc_i}{dt}$)

How can the rate be influenced?

$$r = r(T, c_1, c_2, ..., c_N, catalyst)$$

$r = f(T) \cdot g(c_1, c_2, ..., c_N)$	$f(T) = ?$	$g(\bar{c}) = ?$

Concentration and temperature dependencies of reaction rates

Collision theory (kinetic theory of gases and statistical mechanics)

$$N_{coll} = \left[8\pi RT\left(\frac{1}{M_A}+\frac{1}{M_B}\right)\right]^{1/2}\delta_{AB}^2 c_A c_B$$

N_{coll} - (big) number of collisions between molecules
δ_{AB} - mean molecule diameter

$$N_{coll}^{eff} = N_{coll}\, e^{-\frac{E}{RT}}$$

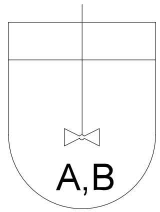
N_{coll}^{eff} - (smaller) number of effective collisions
E - activation energy

$$f(T) = k_\infty^* T^{1/2} e^{-\frac{E}{RT}} \qquad g(c_A, c_B) = c_A c_B$$

Formal generalisation and application:

$$f(T) = k_\infty \exp\left(-\frac{E}{RT}\right) \qquad g(\bar{c}) = \prod_{i=1}^{Reactants} c_i^{|\nu_i|}$$

Reaction orders and concentration time curves in a BR



$$\frac{dn_i}{dt} = V_R \nu_i r \qquad i = 1, N$$

if $V_R = const.$: $$\frac{dc_i}{dt} = \nu_i r \qquad i = 1, N$$

Example: A → B

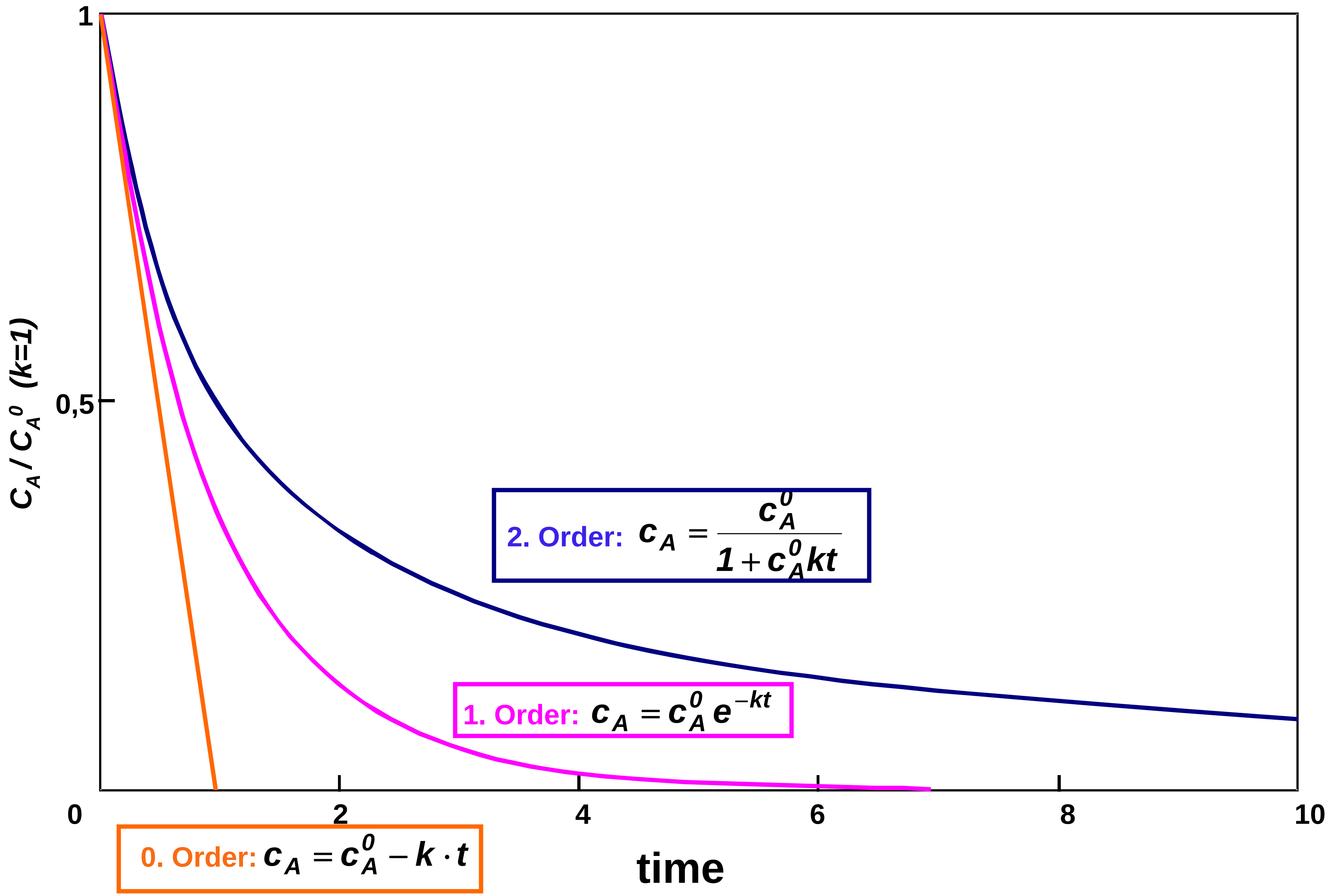
$\nu_A = -1$ $\quad r = kc_A^n \quad$ n : order of reaction

First order: $$\frac{dc_A}{dt} = -k \cdot c_A \qquad c_A = c_A^0 e^{-kt}$$

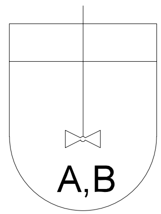
Second order: $$\frac{dc_A}{dt} = -k \cdot c_A^2 \qquad c_A = \frac{c_A^0}{1 + c_A^0 kt}$$

Zero order: $$\frac{dc_A}{dt} = -k \qquad c_A = c_A^0 - k \cdot t$$

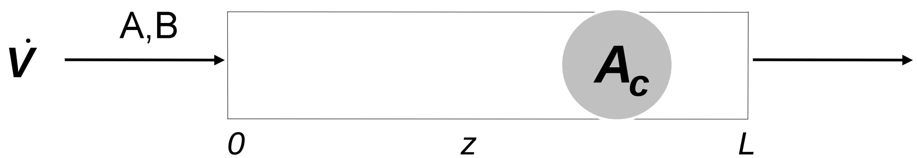
Reaction orders and concentration time curves in a BR



Mass balances BR and PFTR



BR: perfectly mixed



PFTR: plug flow, steady state

$$\frac{dc_i}{dt} = \sum_{j=1}^{M} \nu_{ij} r_j$$

$$\frac{dc_i}{dz} = \frac{A_c}{\dot{V}} \sum_{j=1}^{M} \nu_{ij} r_j$$

similar ODE systems (initial value problems)

Dimensionless mass balances

$$\tau \frac{\partial X}{\partial t} = \frac{\tau}{c_A^0} div\ \vec{j}_A + Da \cdot \Phi(X)$$

with

$$X = \left(c_A^0 - c_A\right) / c_A^0 \qquad r = r_0(T)\Phi(X)$$

(conversion)

$$Da = \frac{(-\nu_A) r_0 \tau}{c_A^0}$$

(Damköhler number)

$$\left(\tau = t \quad or \quad \tau = \frac{LA_c}{\dot{V}}\right)$$

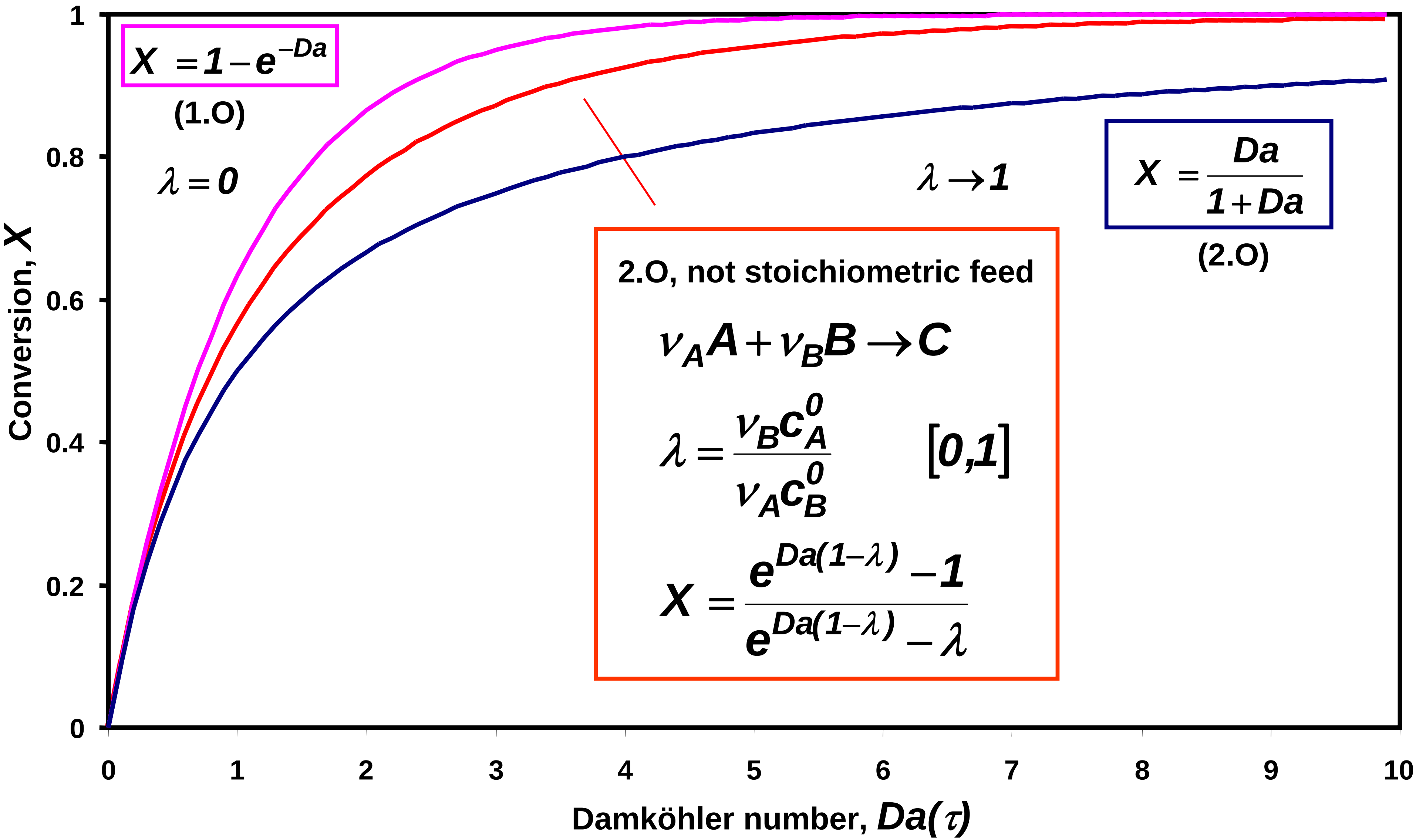
BR and PFTR:

$$Da(\tau) = \int_0^{X(\tau)} \frac{dX}{\Phi(X)}$$

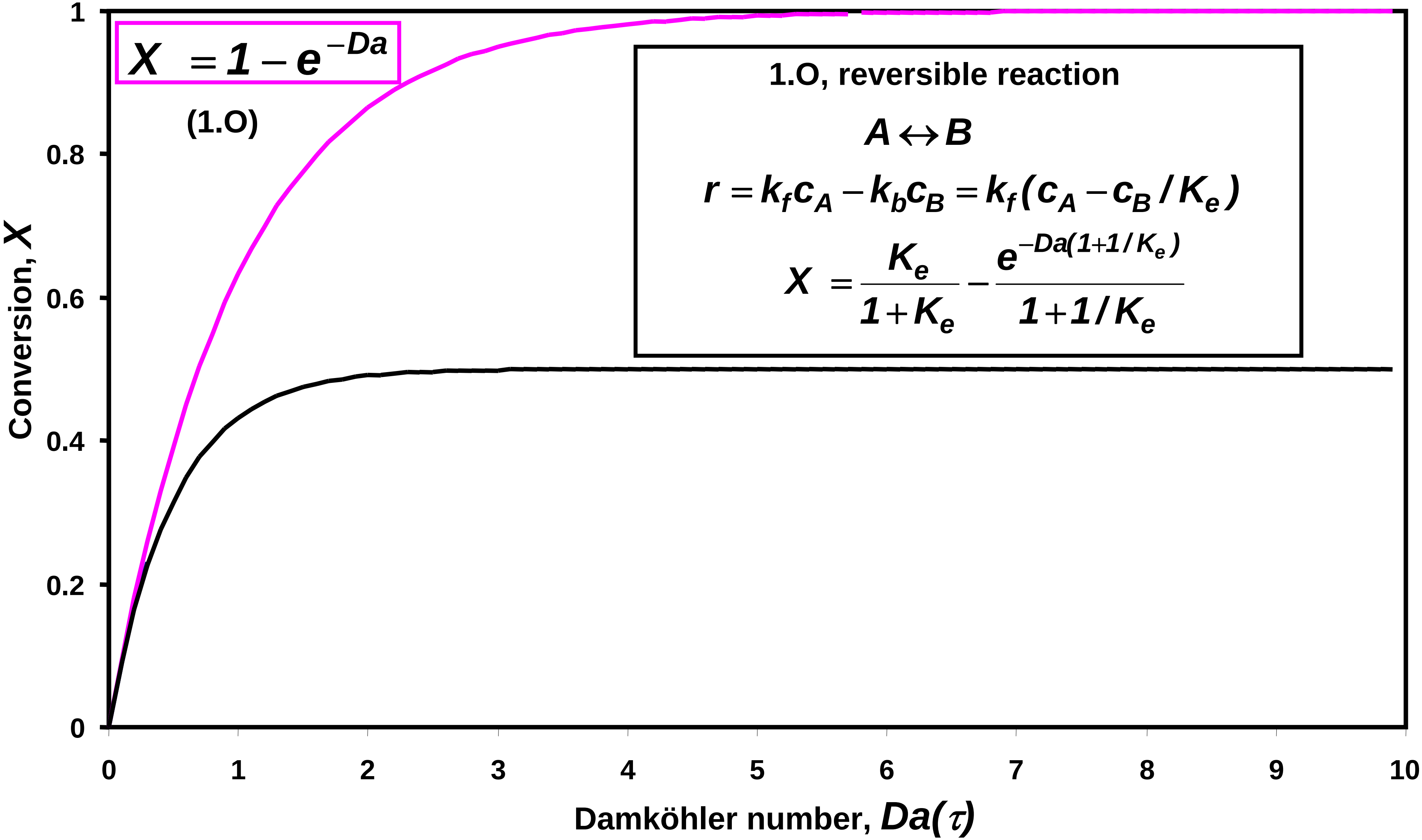
Example: (1. Order) $\quad r = kc_A, \quad r_0 = kc_A^0, \quad \Phi(X) = 1 - X$

$$X(\tau) = 1 - e^{-Da(\tau)}$$

Conversion vs. Damköhler number (BR and PFTR)



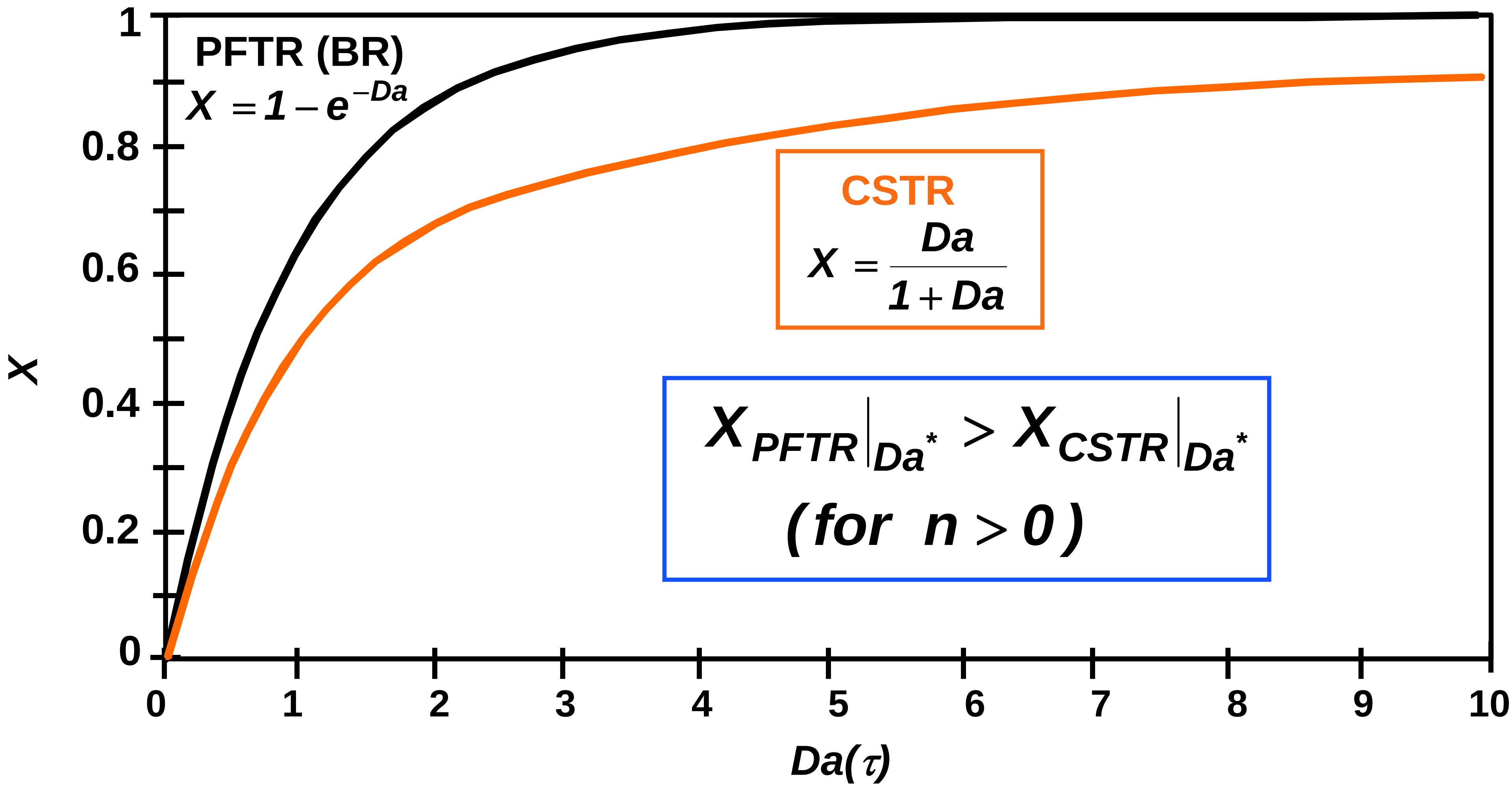
Reversibility



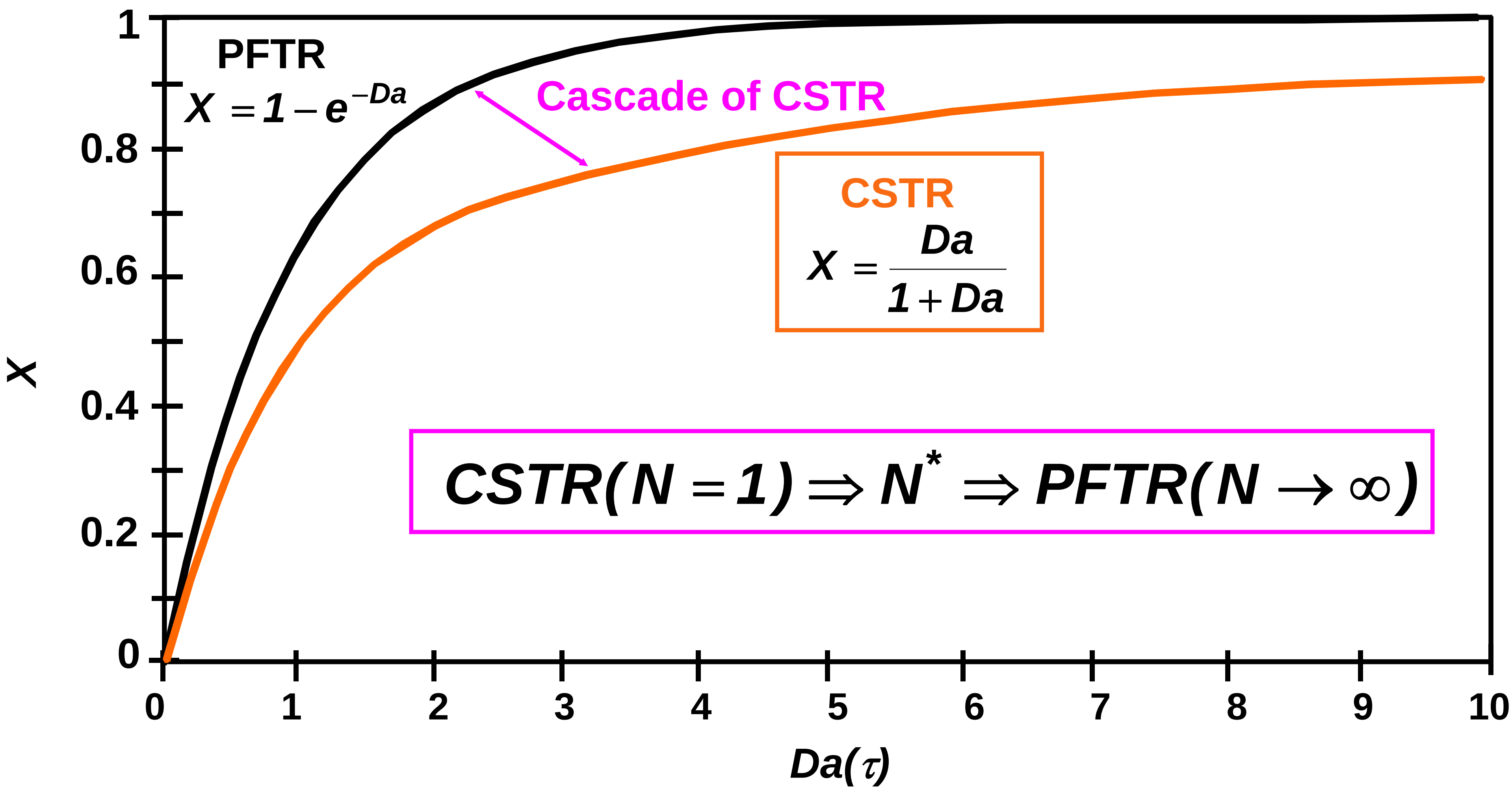
PFTR vs. CSTR (1. Order, $\Phi(X)=1-X$)

PFTR (BR): $Da = \int_0^X \frac{dX}{\Phi(X)}$

CSTR: $Da = \frac{X}{\Phi(X)}$



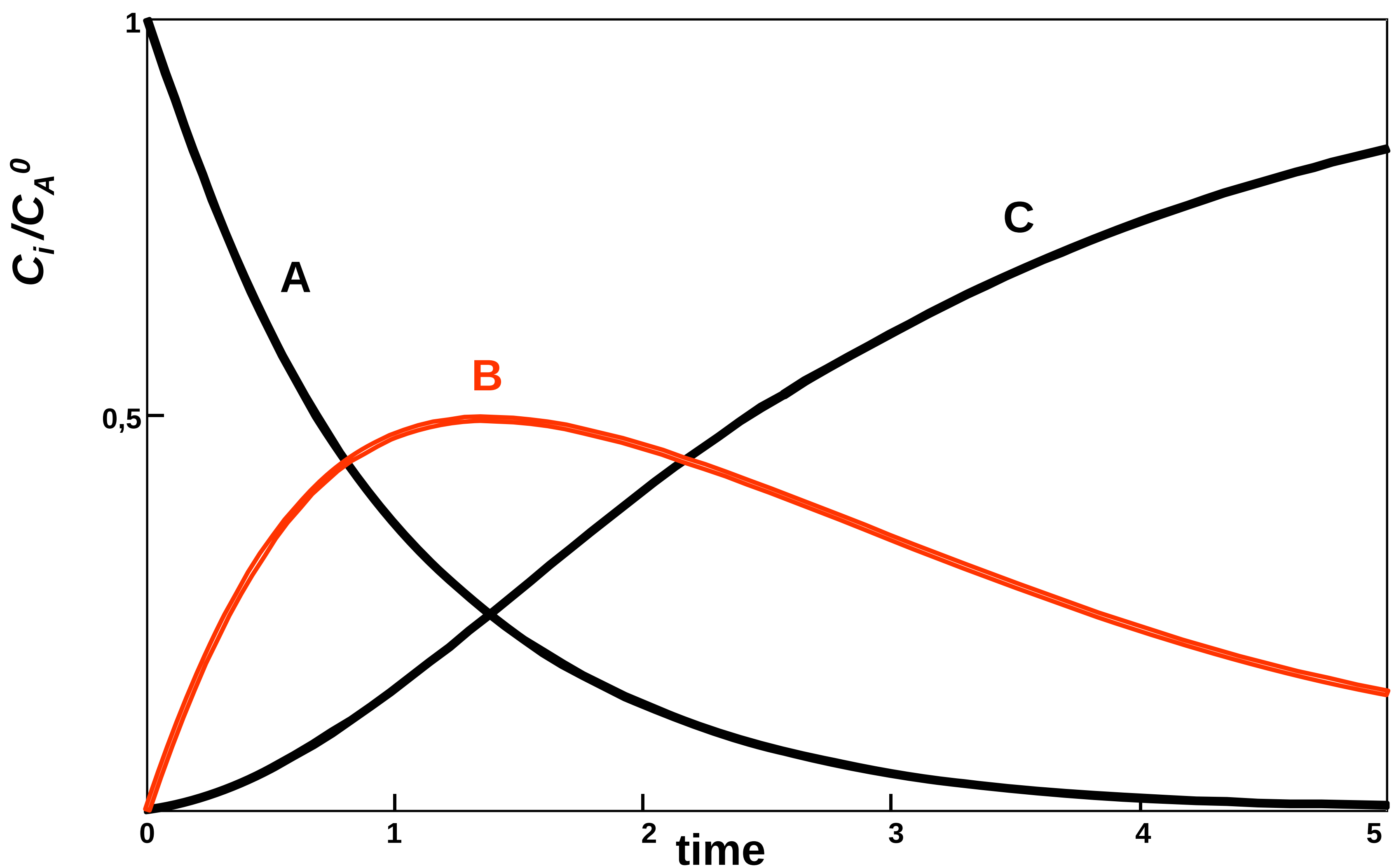
CSTR – Cascade of CSTR - PFTR



Consecutive reactions in a BR (PFTR)

$$\frac{dc_i}{dt} = \sum_{j=1}^{M} \nu_{ij} r_j$$

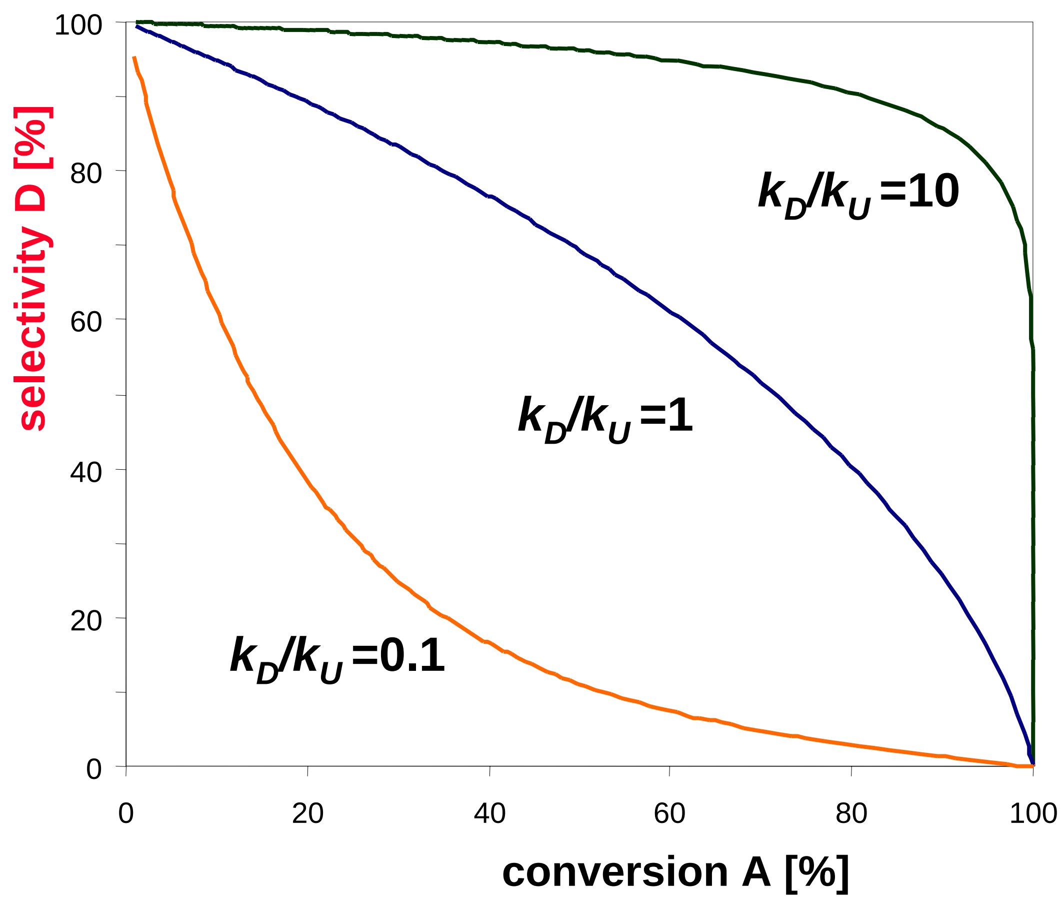
$$A \xrightarrow{r_1 = k_1 c_A} B \xrightarrow{r_2 = k_2 c_B} C$$



Selectivity vs. Conversion (PFTR)

$$A \xrightarrow[r_D]{+B} D \text{ (desired)} \qquad r_D = k_D c_A c_B$$

$$D \xrightarrow[r_U]{+B} U \qquad r_U = k_U c_D c_B$$



Heterogeneous catalysis
(adsorption and Langmuir-Hinshelwood kinetics)

instead of: $A + B \rightarrow C$ $\quad r = k p_A p_B$

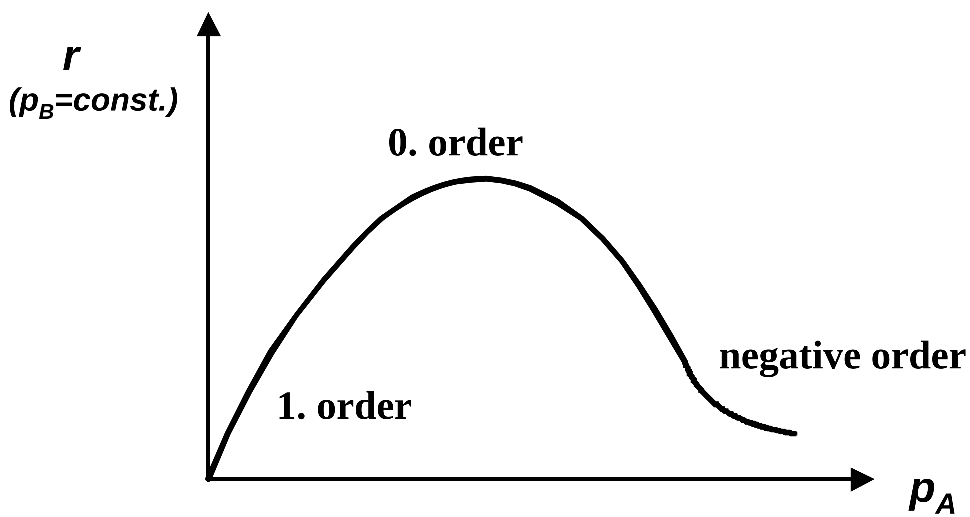
now: $A_{ads} + B_{ads} \rightarrow C$ $\quad r = k \Theta_A \Theta_B$

Problem: Θ_i **not directly accessible**

Assumption: established adsorption equilibrium

$$r = k\Theta_A\Theta_B = k\frac{K_A p_A K_B p_B}{(1 + K_A p_A + K_B p_B)^2}$$

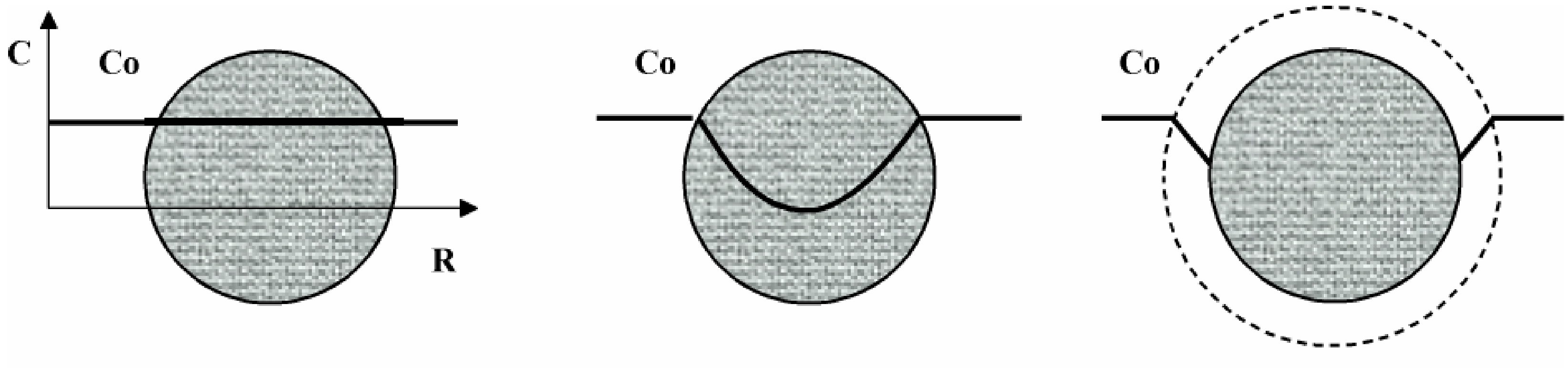
with $\quad \Theta_i = \dfrac{K_i p_i}{(1 + K_A p_A + K_B p_B)}$



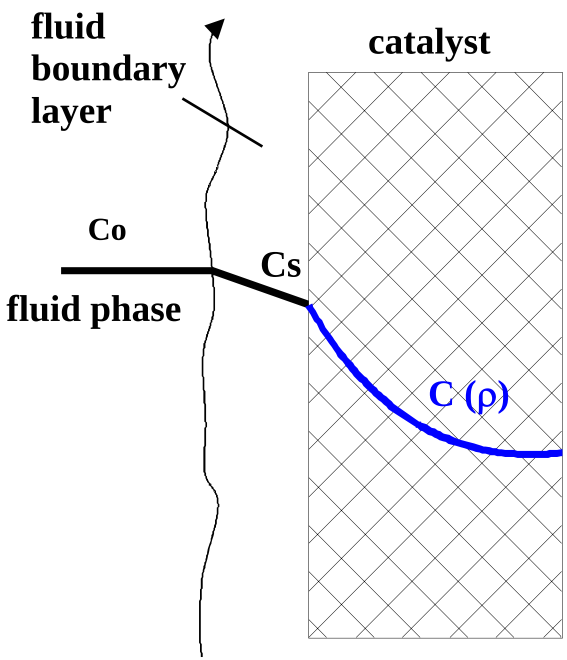
$$r \approx \frac{1}{Scale}$$

often: $Scale = m_{Cat}$

Heterogeneous catalysis
(mass transfer limitations)



kinetically controlled | **pore diffusion** | film diffusion



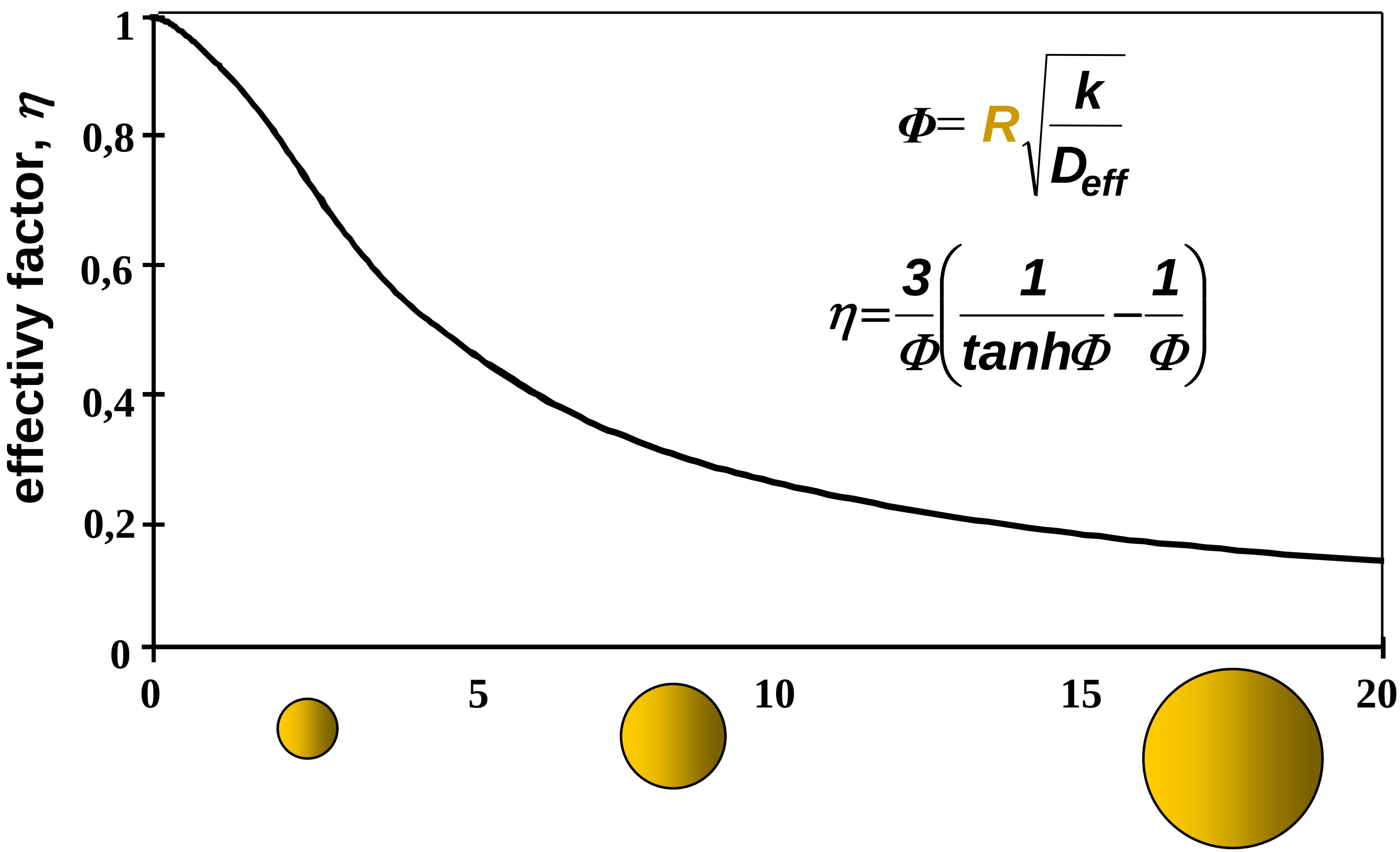
$$D_{eff}\left(\frac{d^2c}{d\rho^2}+\frac{2}{R}\frac{dc}{d\rho}\right)=k\,c$$

BC: $c(\rho=R)=c_0\,,\quad \left.\frac{dc}{d\rho}\right|_{\rho=0}$

$$c(\rho)=c_0\,\frac{R}{\rho}\,\frac{\sinh(\Phi\frac{\rho}{R})}{\sinh(\Phi)} \quad \text{with} \quad \Phi=R\sqrt{\frac{k}{D_{eff}}}$$

Thiele modulus

Pore diffusion and effectivity factor η



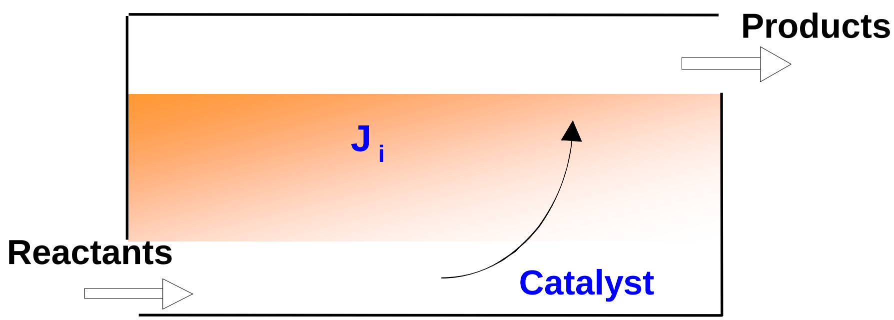
Thiele modulus Φ (~reaction rate / diffusion rate)

$$r_{eff} = \eta \cdot r$$

(instead of solving diffusion equation)

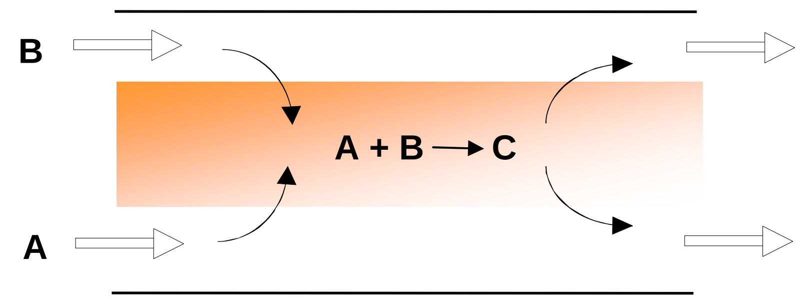
Concepts for membrane reactors

Retaining catalysts



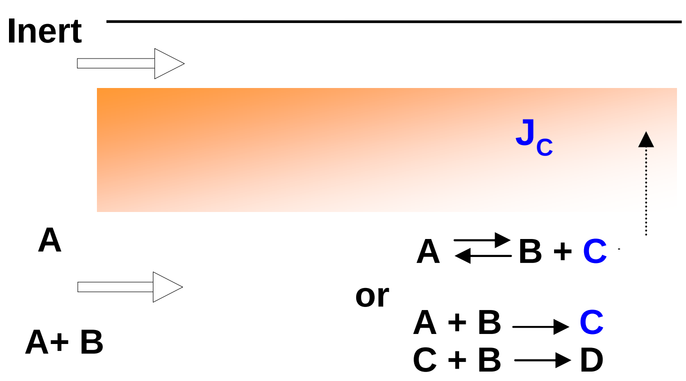
- homogeneous and enzyme catalysis

Membranes as active „contactor“



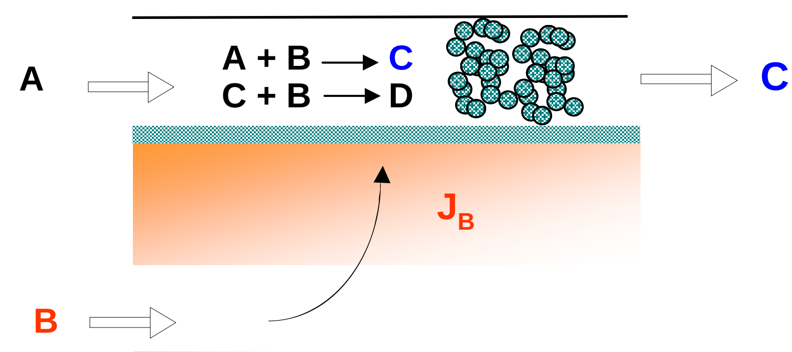
- *conversion front in membrane*
- total conversion of toxic components

Selective product removal („Extractor“)



- conversion enhancement for reversible reactions
- selectivity improvements

Controlled reactant dosing („Distributor“)



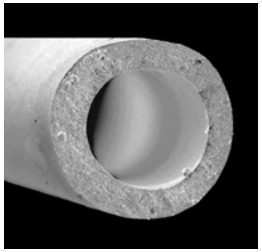
- dosing of critical components
- selectivity improvements

Temperature resistent inorganic membranes

Dense membranes:

- **metals (**Pd, Pd-Ru, Pd-Ag)
- **solid ion conducting electrolytes**
  (ZrO_2 -Y_2O_3 , ThO_2 - Y_2O_3 , Perovskites ABO_3)

→ **selective, limited permeability**



IGB-Stuttgart
Perovskite hollow fibre
(ø 1 mm)

Porouse membranes:
(symmetric / asymmetric)

- **metals** (sintered metall powder)
- **porous glasses** (acidic leaching)
- **ceramic membranes** (Al_2O_3, TiO_2) (sol-gel processes)
- **zeolites** (crystallisation)

→ **less selective, more permeabel**

Ceramic module
HITK, Hermsdorf

Transport mechanisms in membranes

(previous workshop)

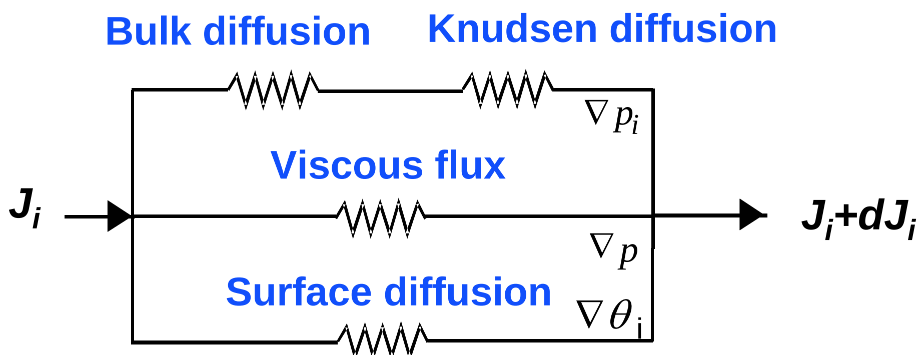
- convection
- molecular diffusion
- Knudsen diffusion
- surface diffusion
- configurational diffusion
- solution and diffusion
- ion and electron conduction
- . . .

essential parameters:

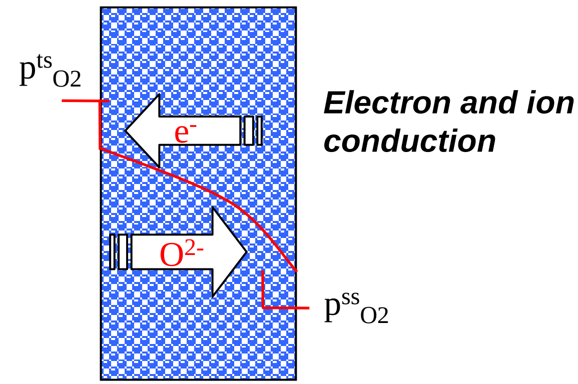
- properties of membrane
- properties of fluid
- operating conditions (driving forces)

Mass transfer mechanisms and models

Porous membrane



Dense membrane



Stefan-Maxwell theory (Dusty Gas Model, DGM)

$$\sum_{\substack{j=1\\ j\neq i}}^{N} \frac{x_j J_i^P - x_i J_j^P}{\frac{\varepsilon}{\tau} D_{ij}^{o}} + \frac{J_i^P}{D_{K,i}^{eff}} = -\frac{p}{RT}\nabla x_i - \frac{x_i}{RT}\left(1+\frac{B_o}{\eta\, D_{K,i}^{eff}}\, p\right)\nabla p$$

(Wesselingh and Krishna, Mass transfer in multicomponent mixtures, Delft University Press, 2000)

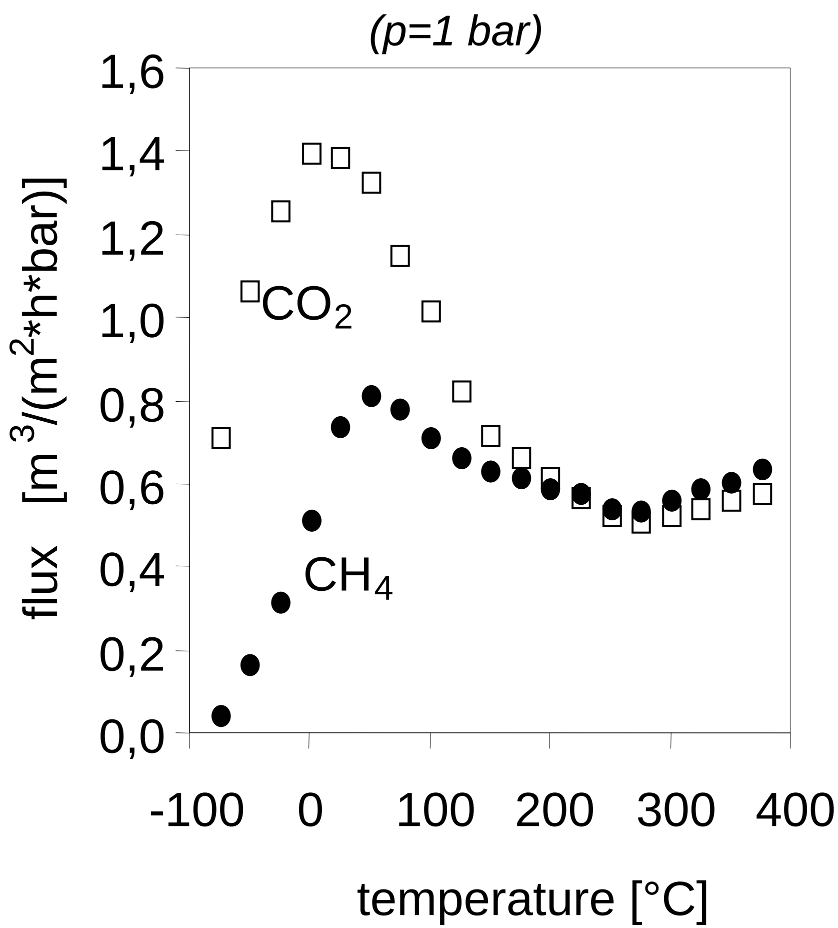
Wagner theory

$$J_{O_2} = -\frac{RT}{4^2 F^2 L_M}\int_{\ln p_{O_2}^{ss}}^{\ln p_{O_2}^{ts}} \frac{\sigma_{el}\cdot\sigma_{ion}}{\sigma_{el}+\sigma_{ion}}\, d\ln p_{O_2}$$

(Bouwmeester, Catalysis Today, 82, 2003, 141)

Illustration of complex influence of temperature on fluxes

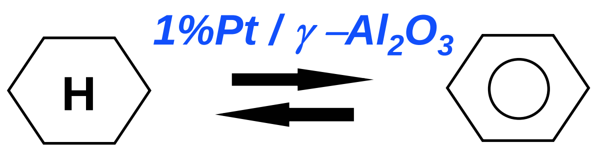
Silicalite layer (~10 μm) on a stainless steel support



van den Broeke, Bakker, Kapteijn, Moulijn
AIChE Journal 45 (1999) 976-985

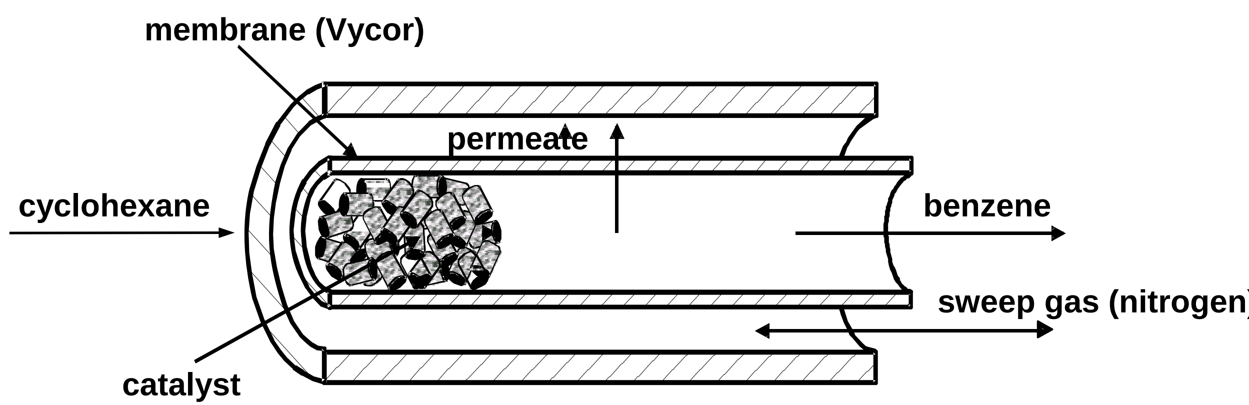
Example 1: Product removal in a membrane reactor („Extractor“)

Model reaction



$+ \ 3\ H_2 \qquad \Delta H_R = 205$ kJ/mol

- ⋆ **at low temperatures possible, high selectivities**
- ⋆ **quantification of the reaction rates in a <u>Berty reactor</u>**



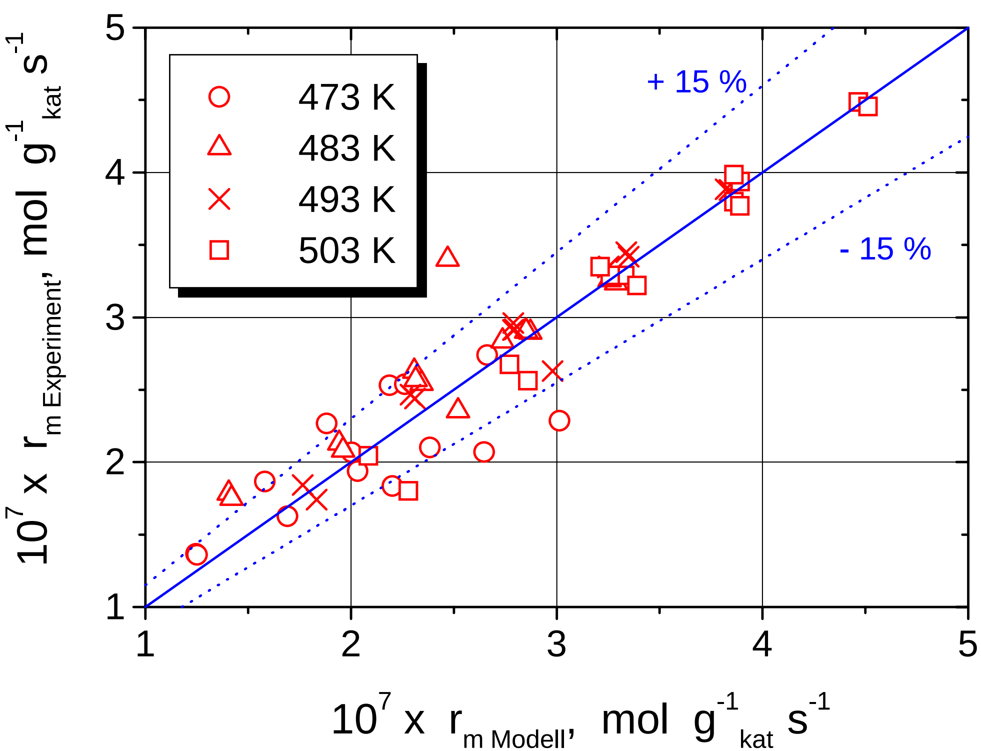
Membrane: Vycor glass (d_p appr. 4 nm)

- ⋆ **quantification of mass transfer of reactants with <u>transient diffusion experiments</u>**

Determination of reaction rates in a Berty-reactor

Experimental conditions

$$T = 473 \ldots 503 \text{ K}$$
$$p = 10^5 \text{ Pa}$$
$$x_{cyc} = 2 \ldots 6 \text{ Vol-\%}$$
$$\text{space velocity: } 400 \ldots 1000 \left[\text{h}^{-1}\right]$$



„Best" reaction rate equation

$$r = k \frac{P_{cyc} - P_{ben} P_{hyd}^3 / K_p}{1 + k_{ads} P_{ben}}$$

benzene adsorbed on catalyst

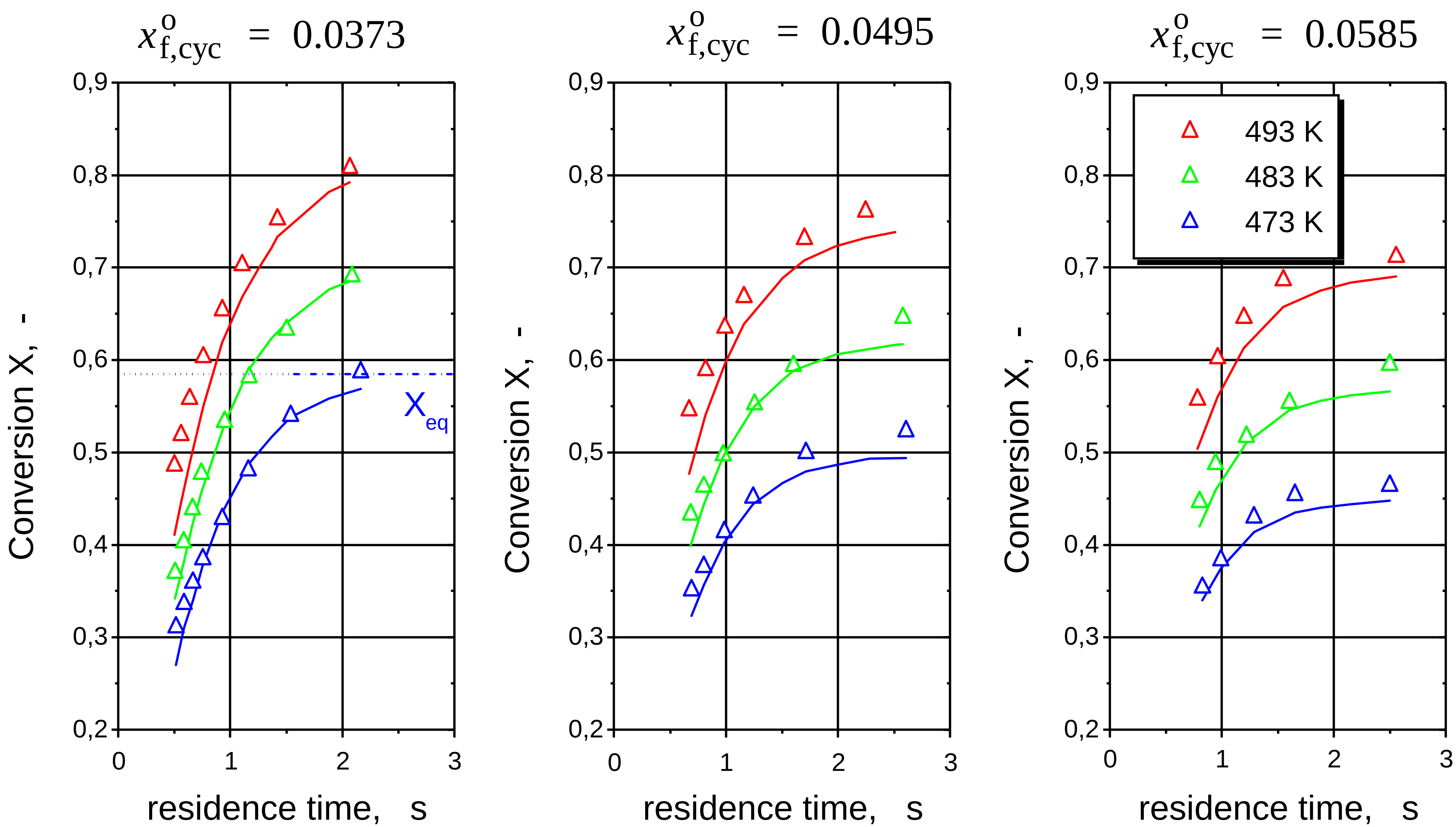
Results (reaction kinetics)

$$k = 7 \cdot 10^{-7} \cdot \exp(-44600 / RT) \left[\frac{\text{mol}}{\text{g s Pa}}\right]$$

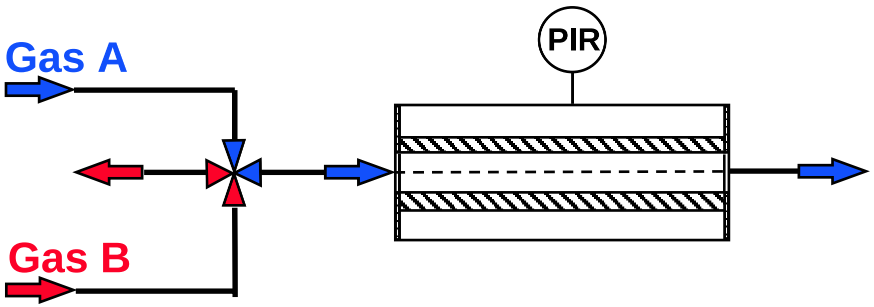
$$k_{ads} = 1{,}5 \cdot 10^{-8} \cdot \exp(39930 / RT) \left[\frac{1}{\text{Pa}}\right]$$

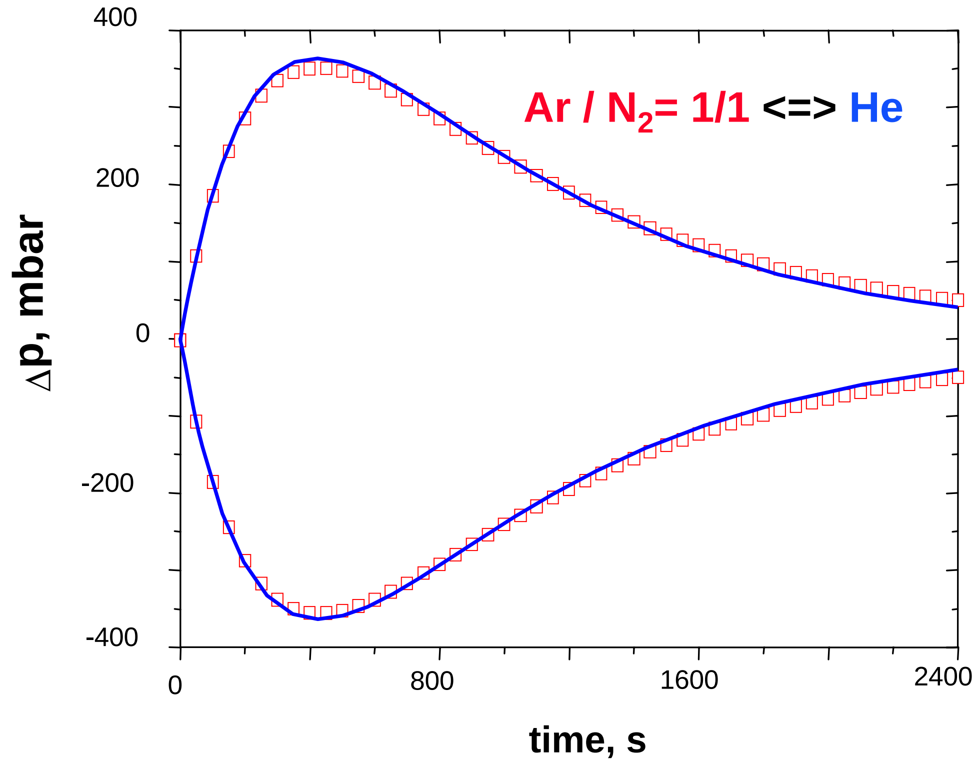
Conventional fixed-bed reactor (FBR)

Reactor model: $$0 = -\frac{p_f}{RT}\frac{1}{q_f}\frac{\partial\left(\dot{V}_f\ x_{f,i}\right)}{\partial z} + D_{ax}\frac{p_f}{RT}\frac{\partial^2 x_{f,i}}{\partial z^2} + R_i$$



Transient diffusion experiment





Results (transport through membrane)

Dusty Gas Model parameters of Vycor:

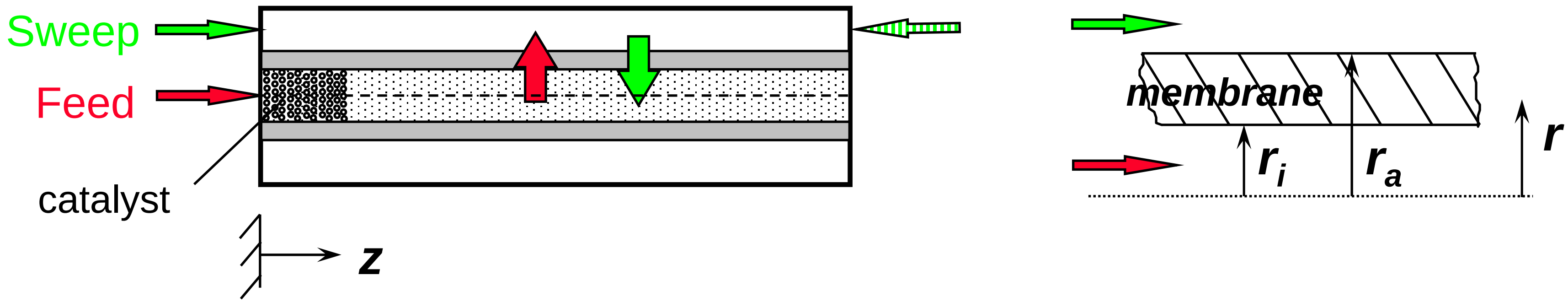
$\varepsilon / \tau = 0.03$

$K_o = 6.6\ 10^{-11}$ m ($\rightarrow D_{K,i}$)

$B_o = 11.3\ 10^{-20}$ m^2

rates of H_2 transport compatible to rates of reaction

Mass balances (tubular membrane reactor)



Mass balance of the feed volume

$$0 = -\frac{p_f}{RT}\frac{1}{q_f}\frac{\partial\left(\dot{V}_f\, x_{f,i}\right)}{\partial z} + D_{ax}\frac{p_f}{RT}\frac{\partial^2 x_{f,i}}{\partial z^2} - \frac{2\pi\, r_i}{q_f}\, J_i\Big|_{r=r_i} + R_i$$

Mass balance of the membrane

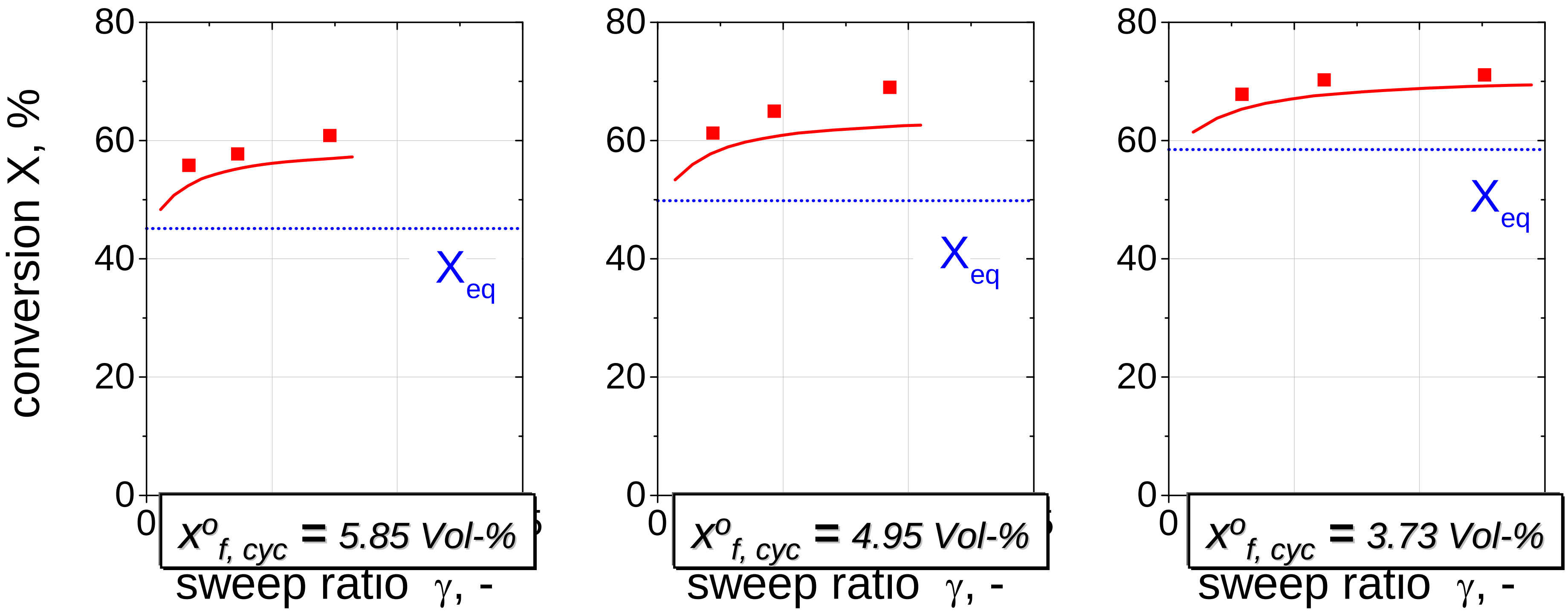
$$0 = \frac{1}{r}\frac{\partial}{\partial r}\left(r\, J_i\right)$$

Mass balance of the sweep volume

$$0 = \pm\frac{p_s}{RT}\frac{1}{q_s}\frac{\partial\left(\dot{V}_s\, x_{s,i}\right)}{\partial z} + D_{ax}\frac{p_s}{RT}\frac{\partial^2 x_{s,i}}{\partial z^2} + \frac{2\pi\, r_a}{q_s}\, J_i\Big|_{r=r_a}$$

Membrane reactor (MR)

pressure conditions	$p_f = p_s$	= 1 bar
temperature	T	= 473 K
mole fraction (feed side)	$x^0_{f,cyc}$	= 3.73 ... 5.85 Vol-%
mole fraction (sweep side)	$x^0_{s,cyc}$	= 0.0 Vol-%
flow rate (feed side)	V^o_f	= 25 ml/min
sweep ratio	γ	$= V^o_s / (x^0_{f,cyc} V^o_f)$

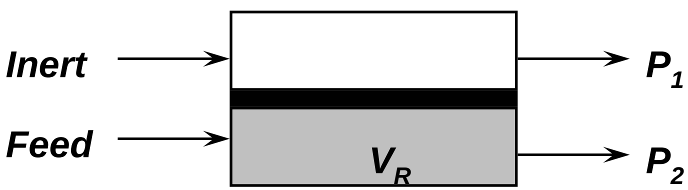


(Tuchlenski, Ph.D., Magdeburg)

Evaluation of an „Extractor“ membrane reactor

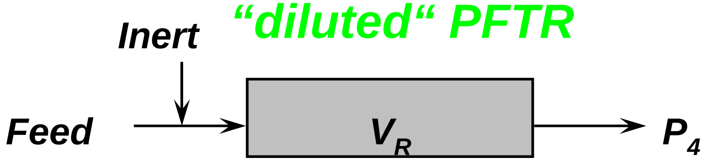
(equilibrium limited reaction A $\rightleftarrows$ B + C)

membrane reactor



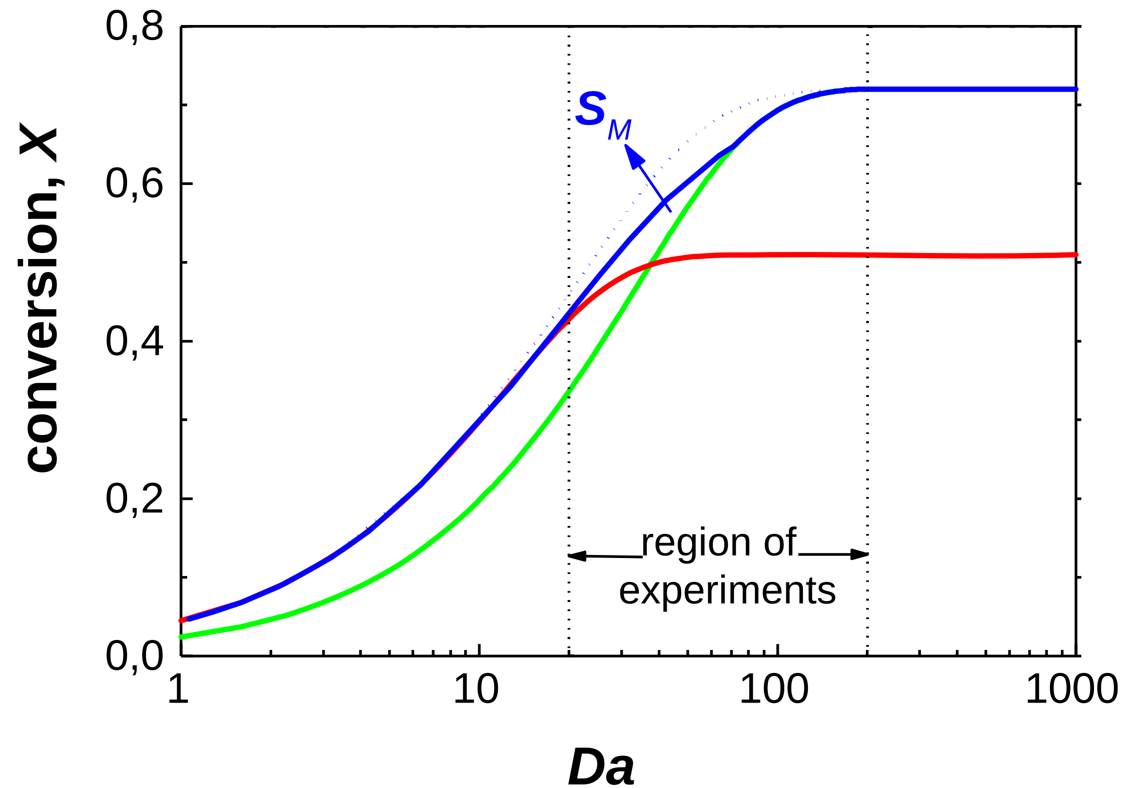
undiluted PFTR

“diluted“ PFTR



(constant feed flow and V_R)

$$Da = \frac{\text{reaction rate}}{\text{convection rate}} \qquad \Phi = \frac{\text{reaction rate}}{\text{diffusion rate } (S_M \ldots)}$$



sweep gas must be included in reactor analysis

(Reo, Bernstein, Lund, AIChE J., 1997, 495 and Chem. Eng. Sci., 1997, 3075)

Example 2: Membrane as a "Distributor"

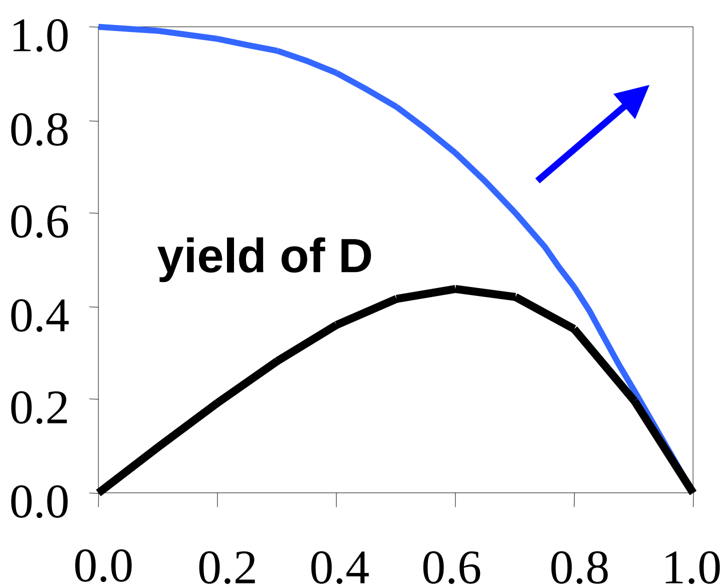
(impact of reaction orders on selectivity)

$$A \xrightarrow[r_D]{+B} D \quad \text{(desired)} \qquad r_D = k_D \cdot p_A^{\alpha} \cdot p_B^{\beta_1}$$

$$D \xrightarrow[r_U]{+B} U \qquad r_U = k_U \cdot p_D^{\delta} \cdot p_B^{\beta_2}$$

$$S_D = \frac{r_D - r_U}{r_D} = 1 - \frac{k_U}{k_D} \cdot \frac{p_D^{\delta}}{p_A^{\alpha}} \cdot p_B^{\beta_2 - \beta_1}$$

Selectivity with respect to D

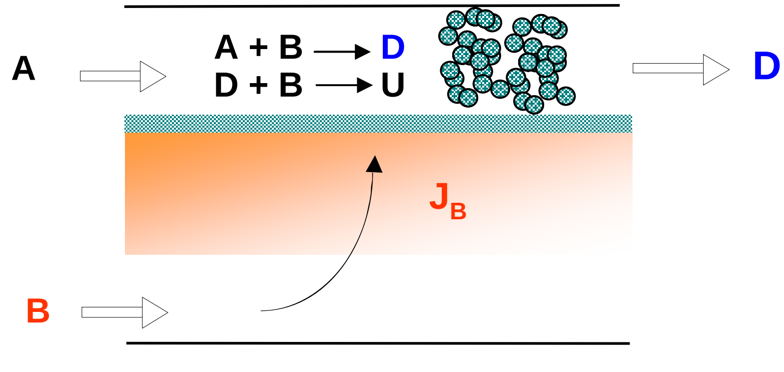


p_D small
(product removal)

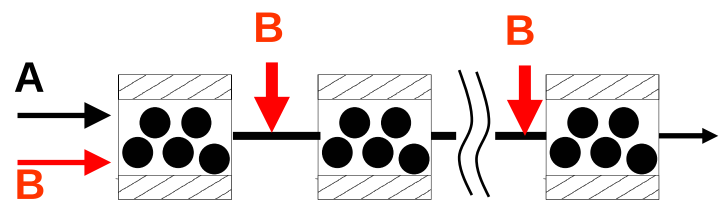
$\beta_2 > \beta_1$:
p_B small (dilution)

→ **<u>dosing of B ("Distributor")</u>**

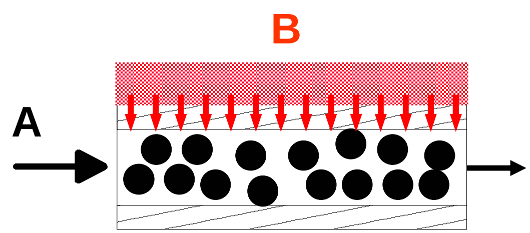
Controlled dosing of reactants („Distributor“)



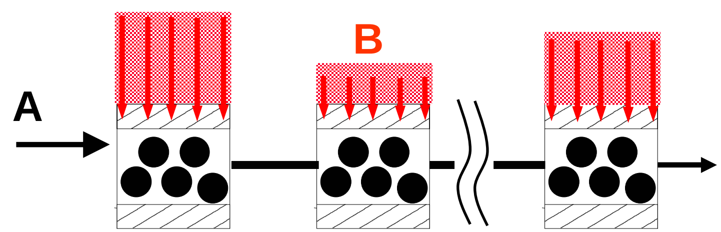
discrete
(series of FBR)



continuously
(single MR)

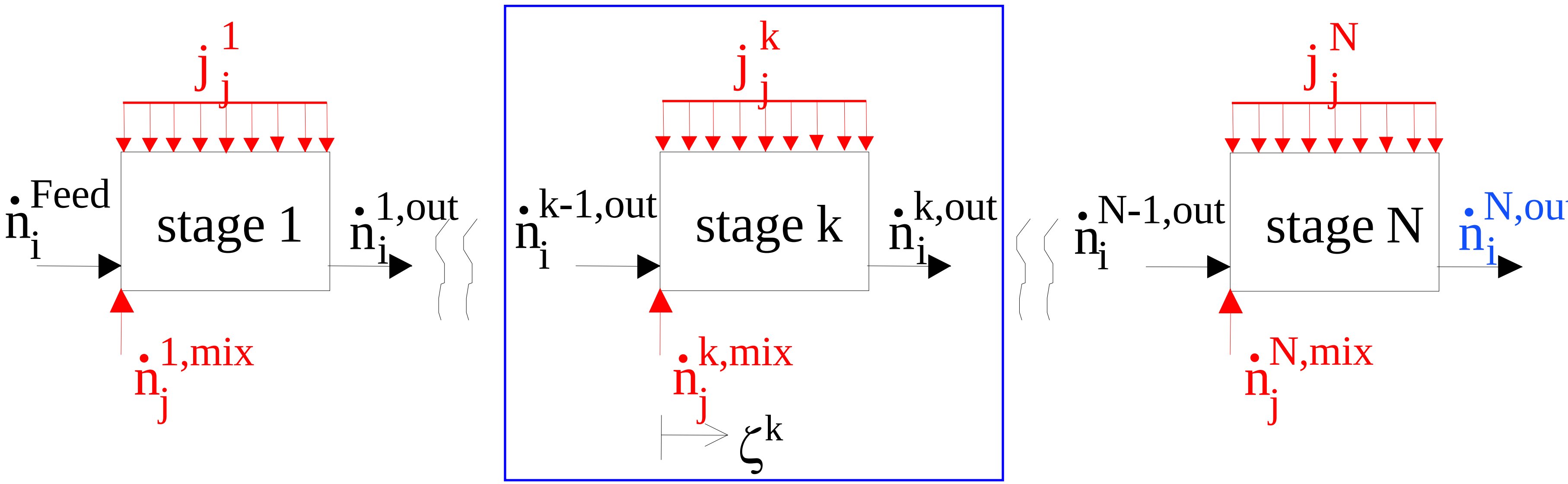


stagewise continuously
(series of MR)



potential e. g. for hydrogenations, oxidations and oxidative dehydrogenations

Simplified reactor model: isothermal PFTR stages, steady state

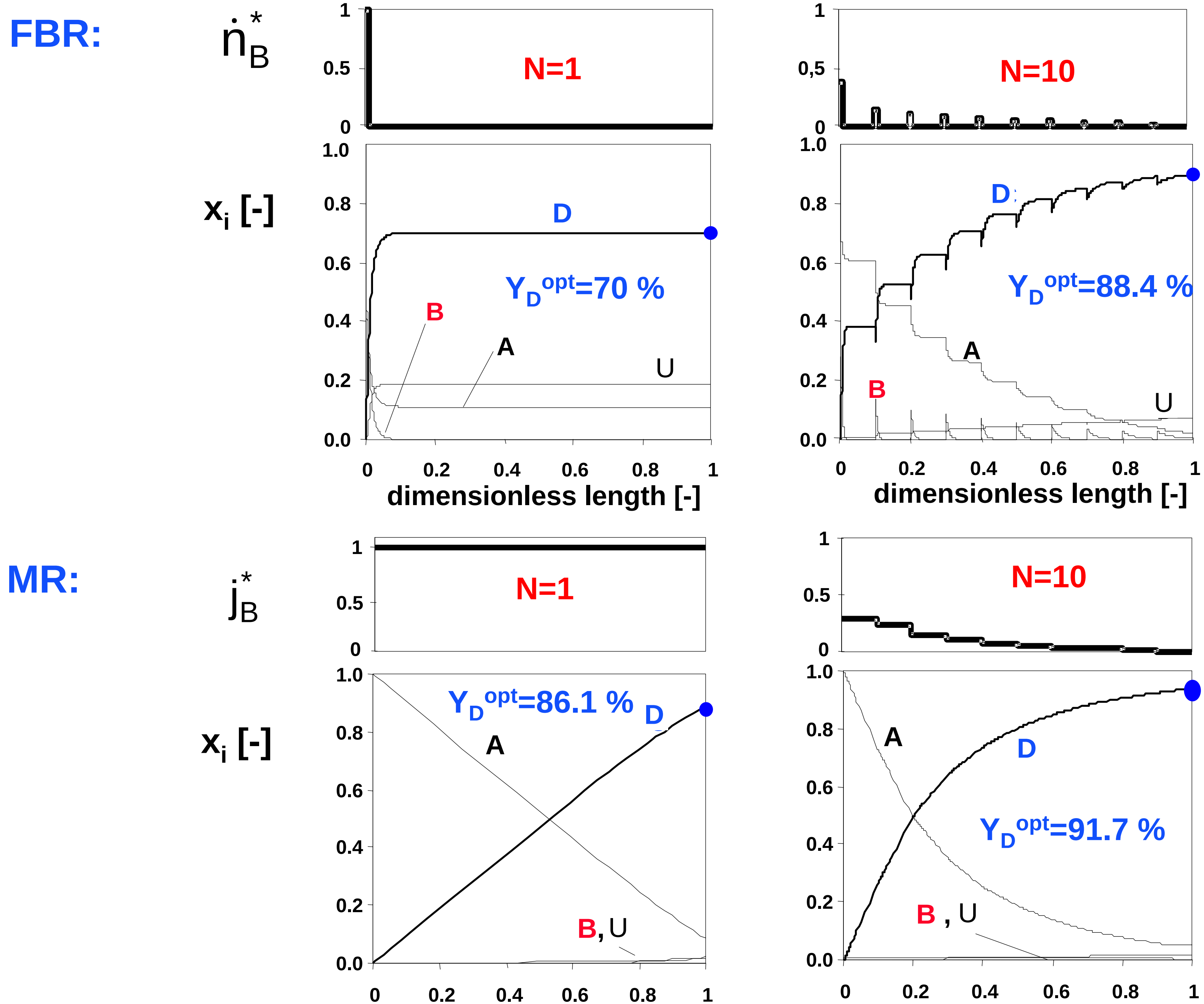


$$\frac{d\dot{n}_i^k}{d\xi^k} = P^k \cdot \underline{\dot{j}_i^k} + A^k \cdot \sum_{j=1}^{M} \nu_{ij} \cdot r_j \qquad k=1,N$$

Optimization:
- → **analytical solutions for special cases**
- → **Pontryagin‘s maximum principle**
- → **numerical optimization (SQP)**

(Thomas, Pushpavanam, Seidel-Morgenstern, Ind. Eng. Chem. Res., 2004, 969 ; Tota et al., Trans IChemE, 82, 2004, 236)

Segmented reactors: Optimization with SQP (β_2/β_1=2)



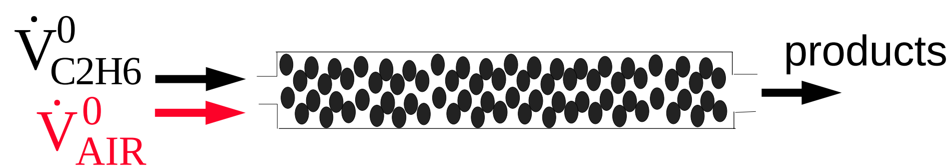
Oxidative dehydrogenation of ethane to ethylene

Catalyst: γ–Al_2O_3/VO_X (d_p=1.8 mm, 1.4 % V)

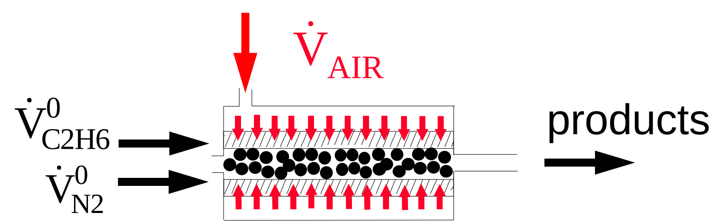
Membrane: Ceramic composite membrane (HITK, Hermsdorf)

Conditions: T = 400 - 650 °C, p= 1 bar, $GHSV_{ov}$ = 6000 - 38000 h^{-1}
c_{ethane}= 0-1 vol%, c_{O2}= 0-20.3 vol%

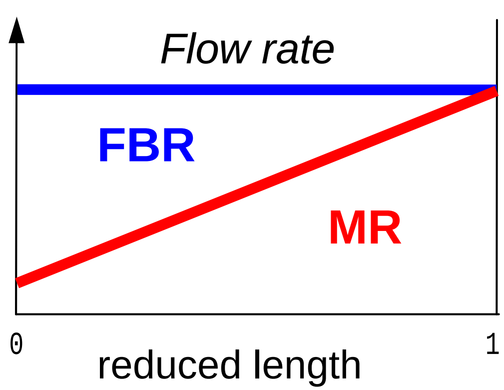
Fixed-bed reactor (FBR)

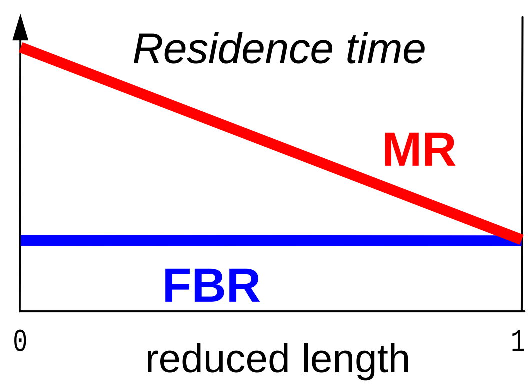


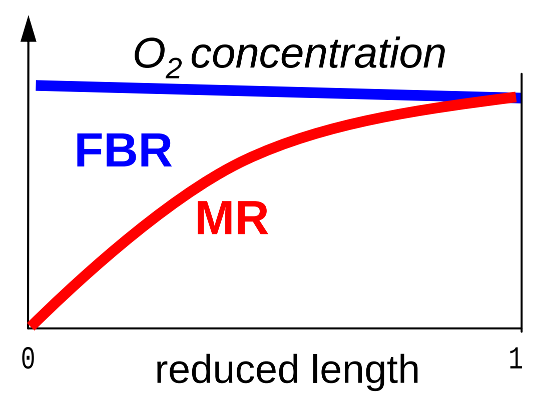
Membrane reactor (MR)



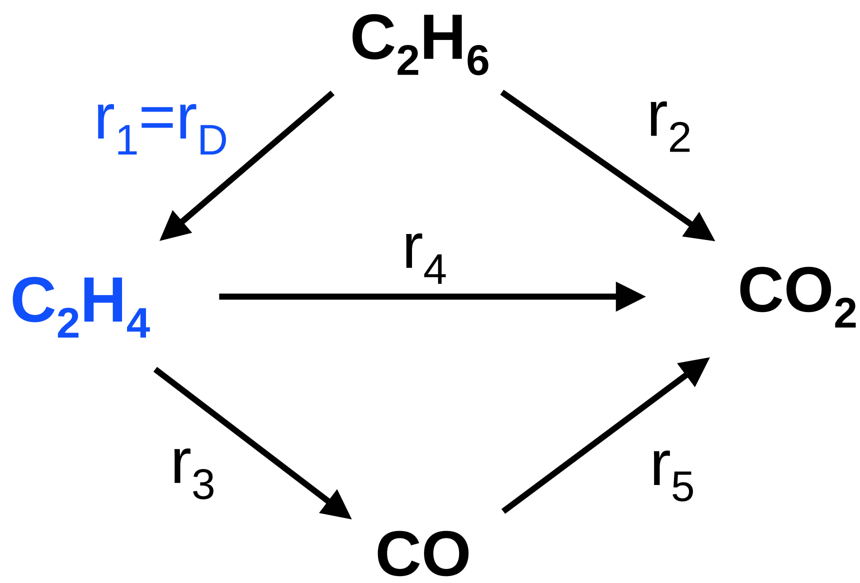
(„dead end“ configuration)







Reaction scheme and kinetic parameters



Analysis of 70 FBR runs

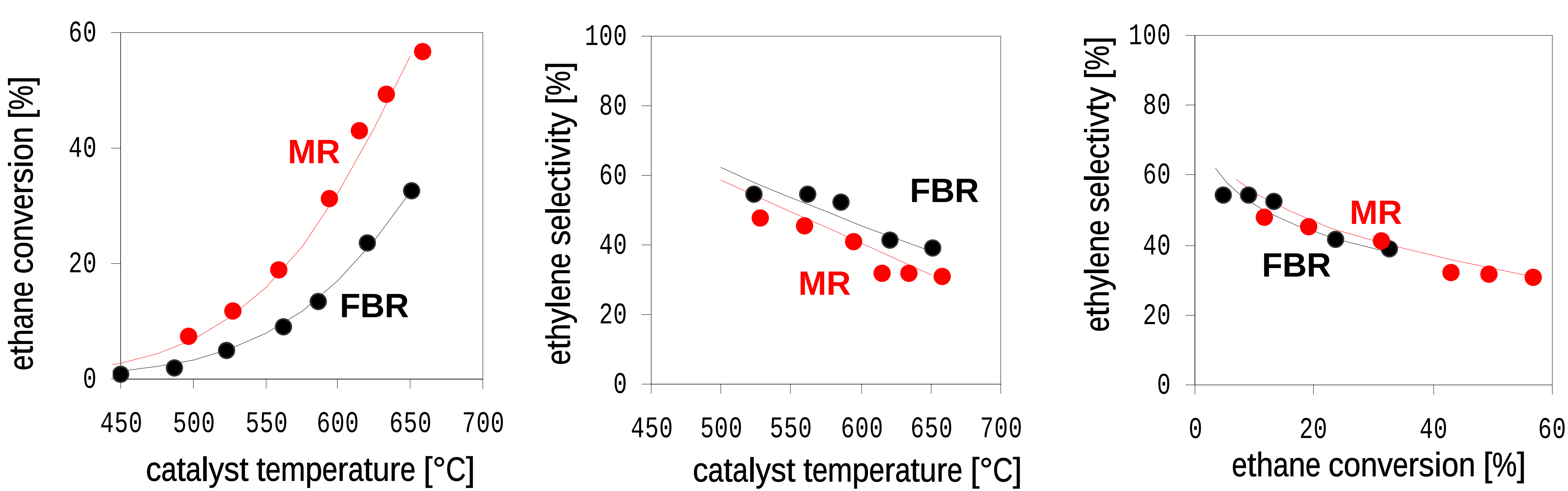
	α [–]	β [–]	
r_1	0.88	**0.02**	!
r_2	0.75	0.24	
r_3	0.84	0.11	
r_4	0.87	0.2	
r_5	1.12	0.13	

$$r_j = k_j(T) \cdot p_C^{\alpha_j} \cdot p_{O_2}^{\beta_j}$$

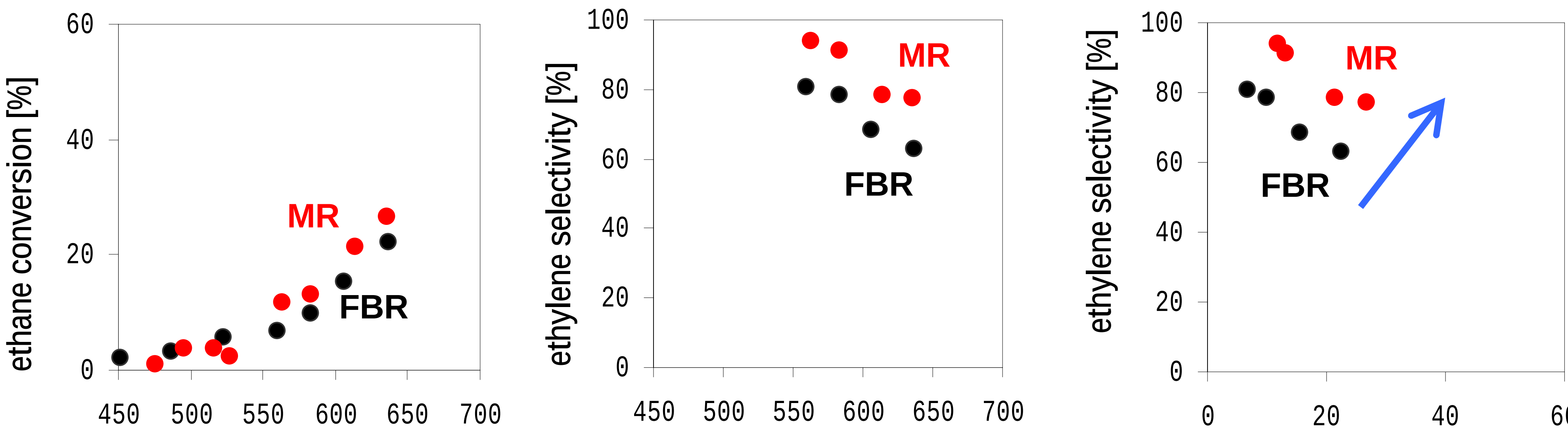
(Klose et al., Appl. Catal. A., 260, 2004, 101)

Comparison between FBR and MR

oxygen excess (x_{O2}^0 = **19-20 vol%**, x_{C2H6}^0 = 0.7 vol%, GHSV 38000 h^{-1}) → τ **relevant**

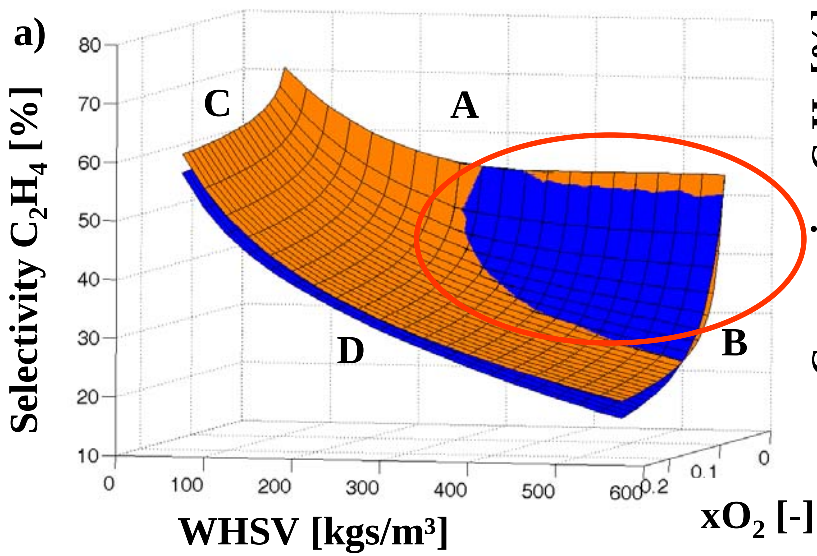


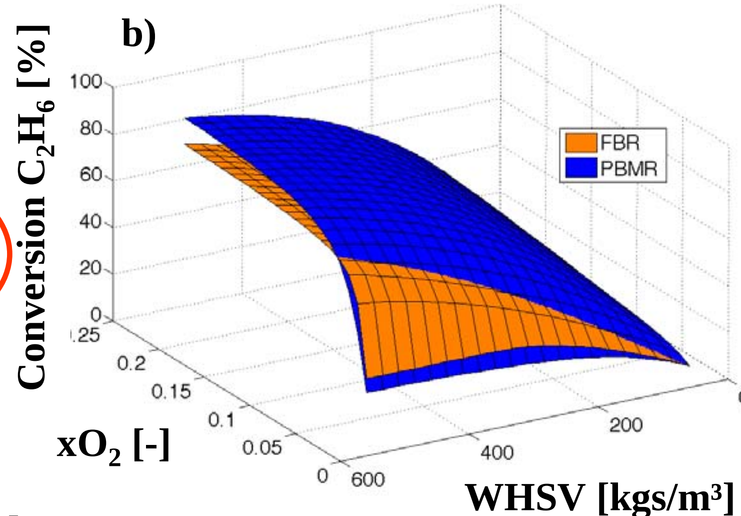
oxygen shortage (x_{O2}^0 = **0.4 vol%**, x_{C2H6}^0 = 0.7 vol%, GHSV 38000 h^{-1}) → x_i **relevant**

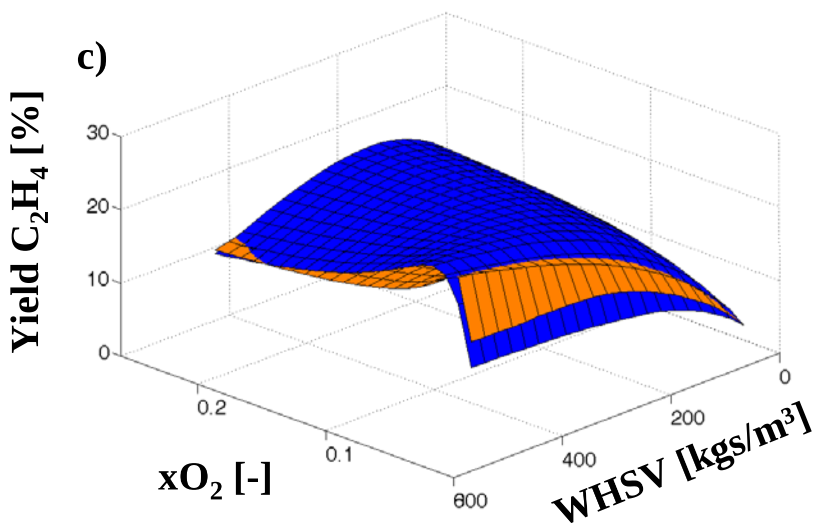


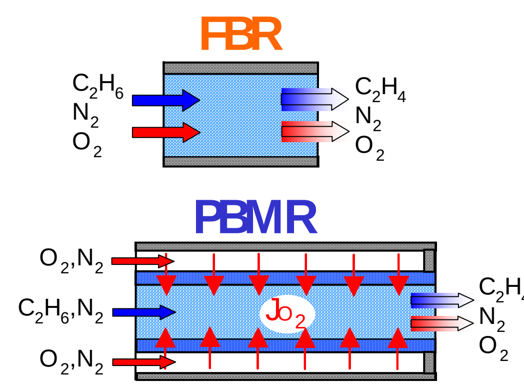
Comparison between FBR and MR – Simulation study

oxygen excess (x_{C2H6}^{in} = 1.5%, x_{O2}^{in} = 0.5-21 %, WHSV = 50-550kgs/m³, T = 600 °C, F_{TS}/F_{SS} = 1/8)

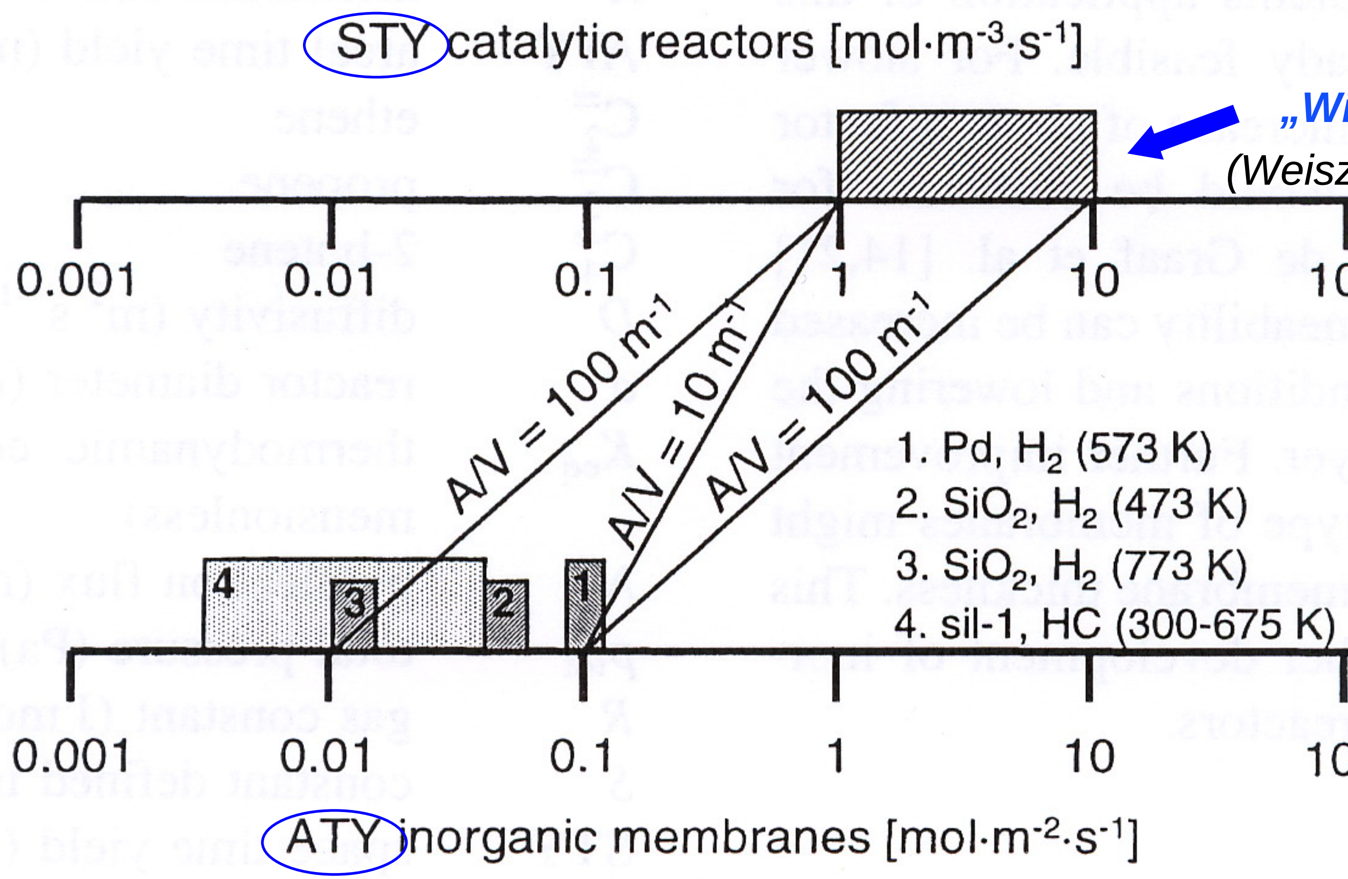








Compatibility between reaction and transport



„Window of reality"

(Weisz, CHEMTECH, July 1992, 424)

A/V=4/d

d: 0.04 - 0.4 m

(„realistic" region)

(van de Graaf, Zwiep, Kapteijn, Moulijn, Appl. Catal. A, 178, 1999, 225)

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