Tutorial lecture on

Interplay between reactivity and transport phenomena in heterogeneous catalysis

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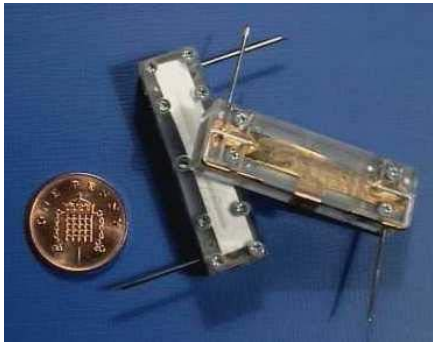
Chemical reactor

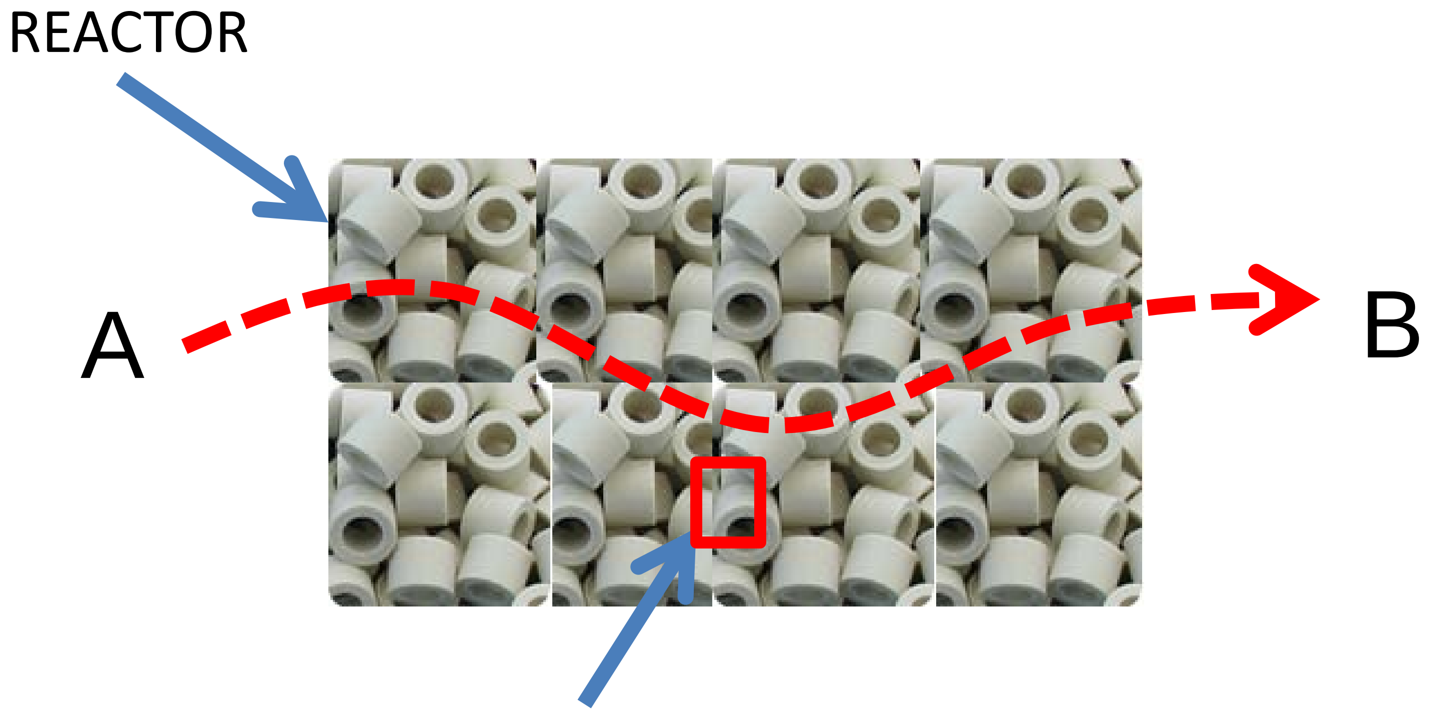
The **reactor** is the device within which the physicochemical transformations are caused.

It can assume **various shapes and modes of operations** and be operated in a number of possible environments of pressure and temperature.



(images from internet)

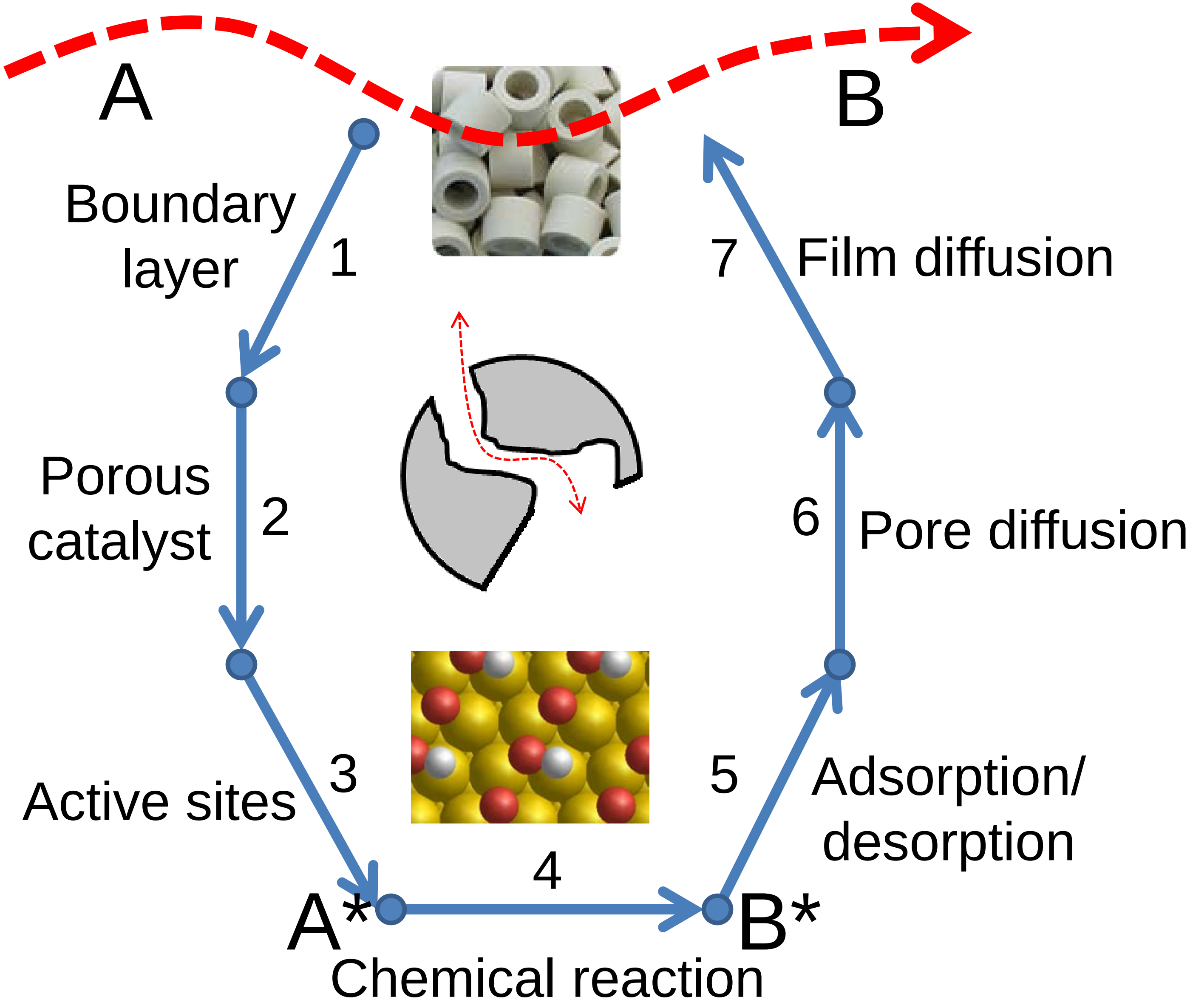
Heterogeneous catalytic reactor



CATALYST SUPPORT: ACTIVE SITES ARE DEPOSITED WITHIN THESE POROUS SOLIDS

Heterogeneous catalytic reactions by their nature involve a separate phase of catalyst embedded in a phase of reacting species.

The way to the active sites



A

B

Boundary layer

1

7

Film diffusion

Porous catalyst

2

6

Pore diffusion

Active sites

3

5

Adsorption/ desorption

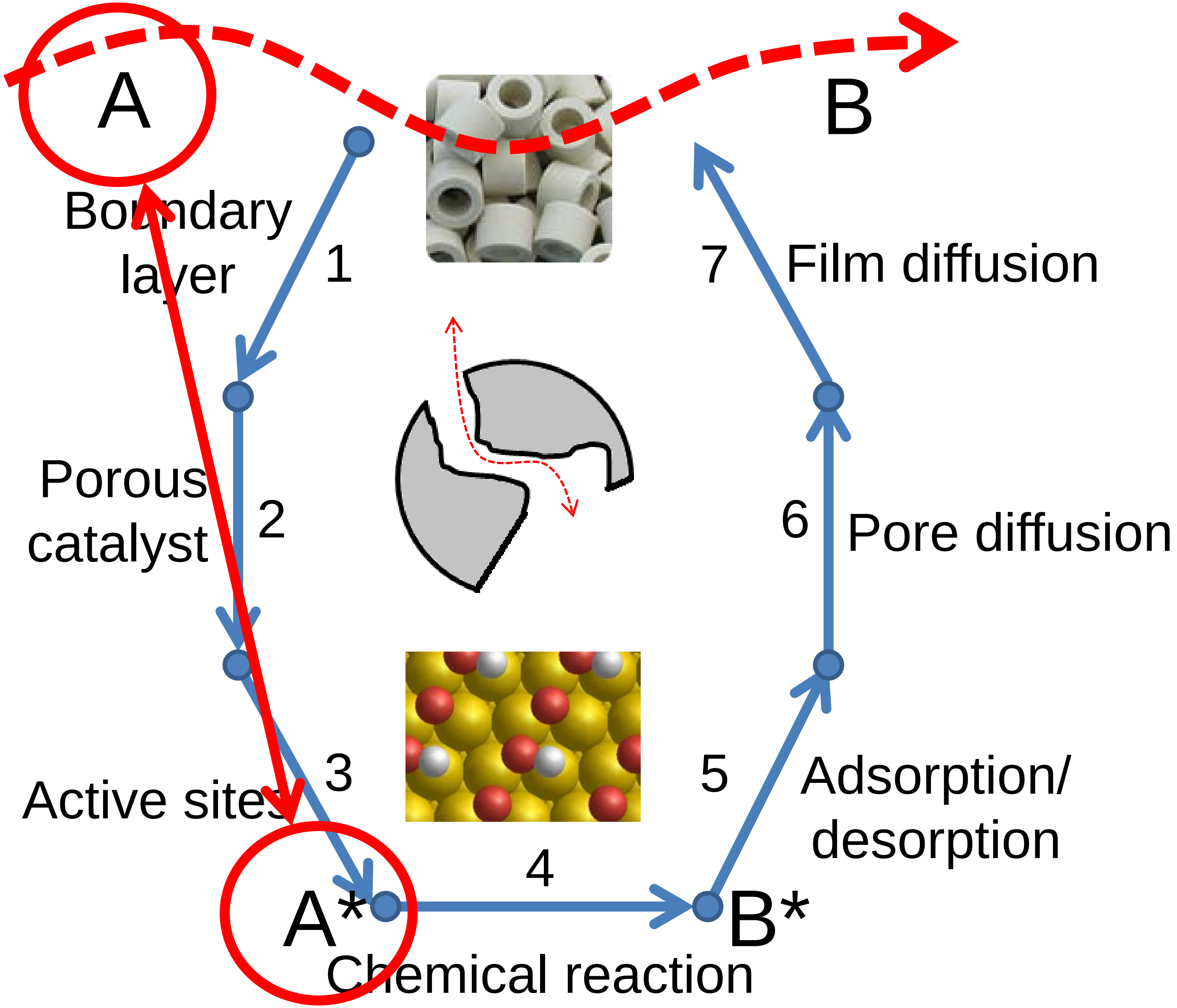
4

A*

B*

Chemical reaction

The way to the active sites



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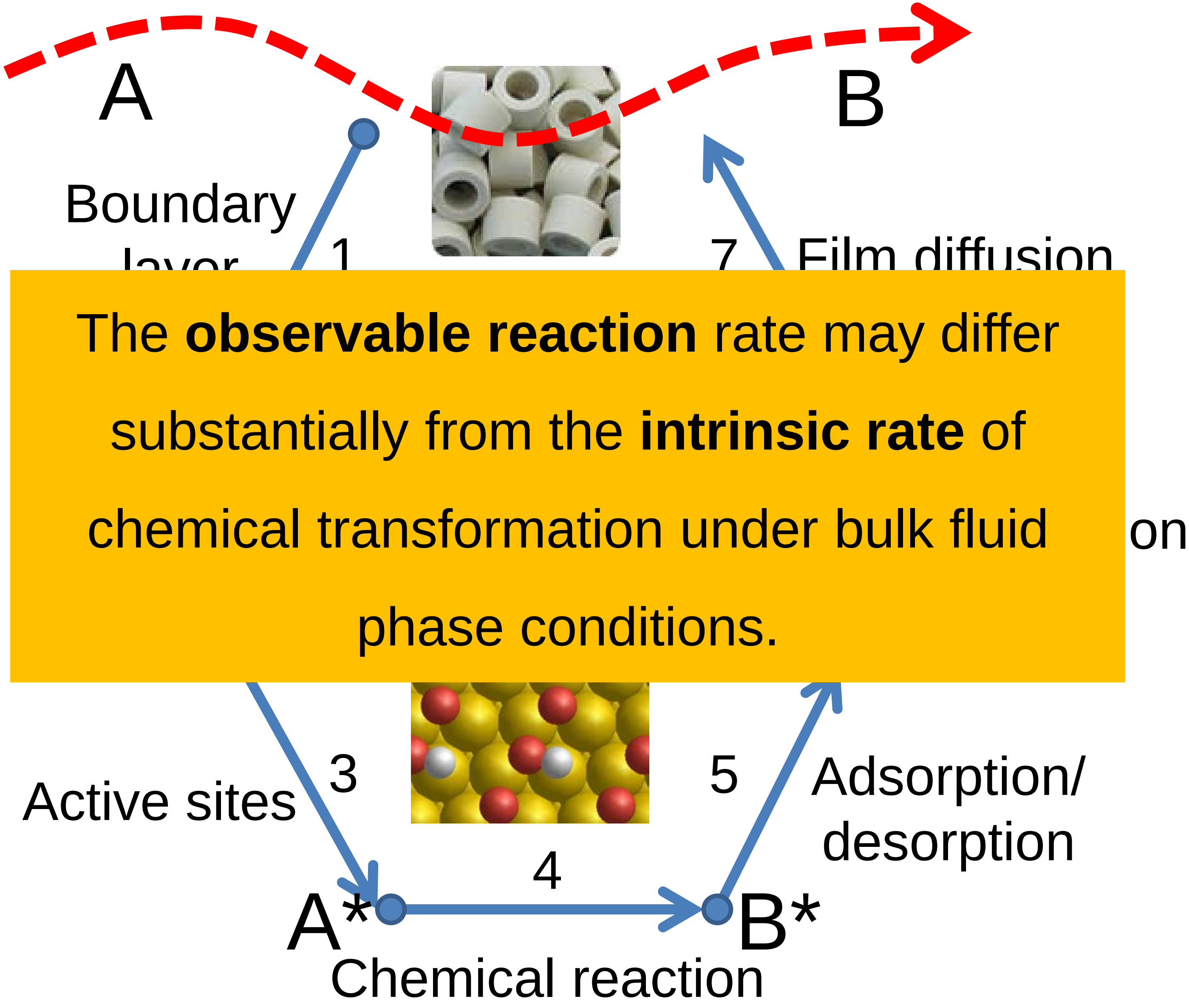


A

B

Boundary layer

1

7

Film diffusion

on

Active sites

3

5

Adsorption/ desorption

4

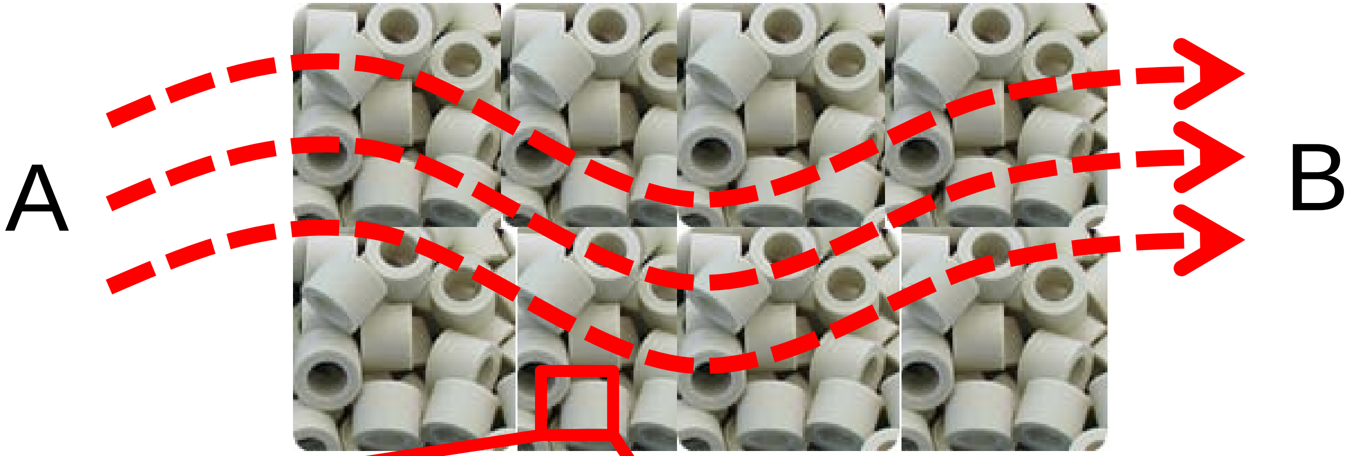
A*

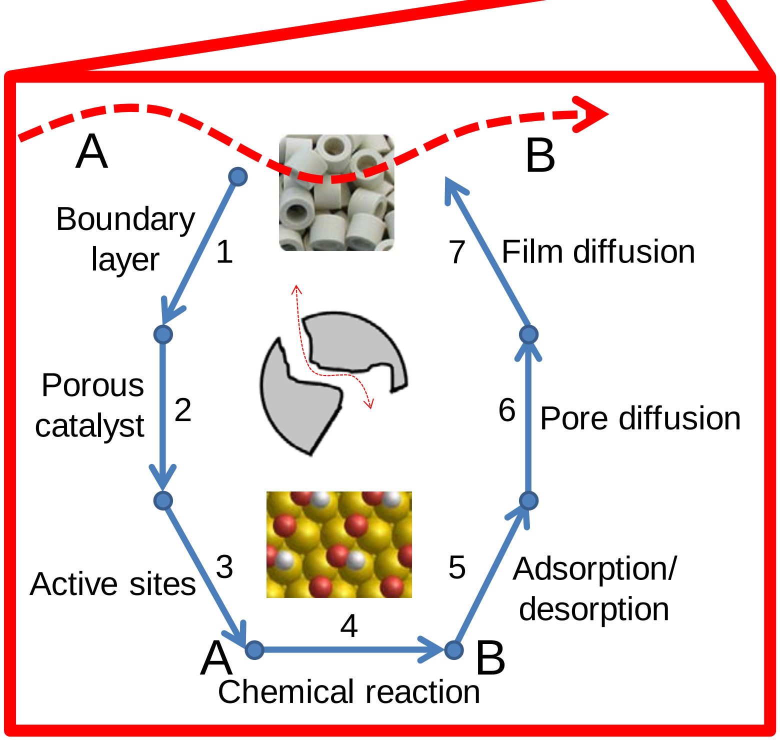
B*

Chemical reaction

The **observable reaction** rate may differ substantially from the **intrinsic rate** of chemical transformation under bulk fluid phase conditions.

Catalysts at work





How do **transport phenomena** and **distribution of residence times** in the reactor affect the **observed** reaction rate?

Outline

1) Effect of the distribution of the contact times in the reactor on the observed reaction rate

2) Inter-phase and intra-phase transport phenomena and their impact on the observed reaction rate

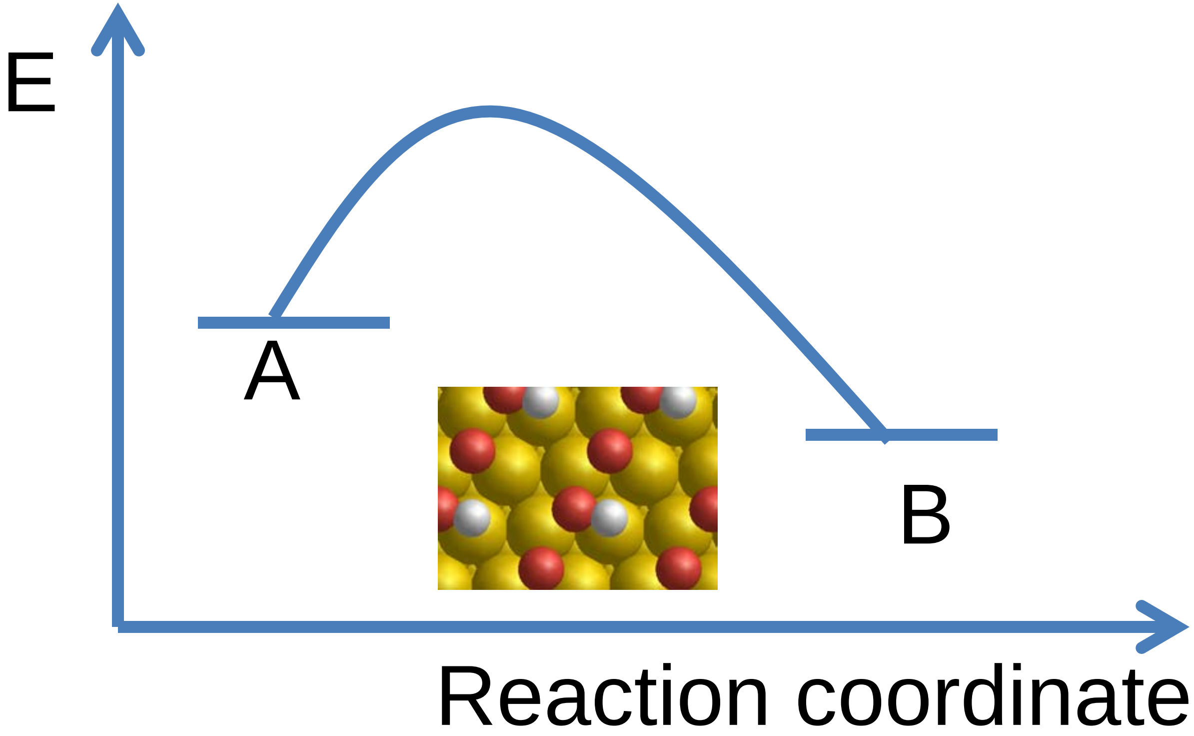
3) Show-case: effect of transport phenomena on catalyst reactivity

4) Take-home messages

Reactivity (for this talk)

$$\mathrm{A} \rightarrow \mathrm{B}$$

$$r = kc_A \ [\mathrm{mol/m^3} / s] \qquad k = k_0 \exp\left(-\frac{E}{RT}\right)$$



Outline

1) **Effect of the distribution of the contact times in the reactor on the observed reaction rate**

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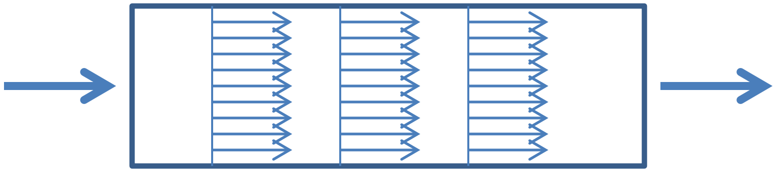
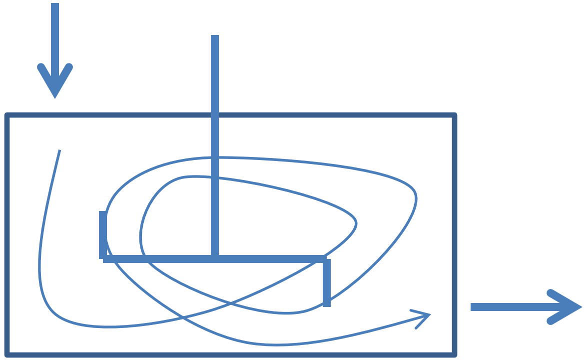
4) Take-home messages

How long molecules stay in the reactor?

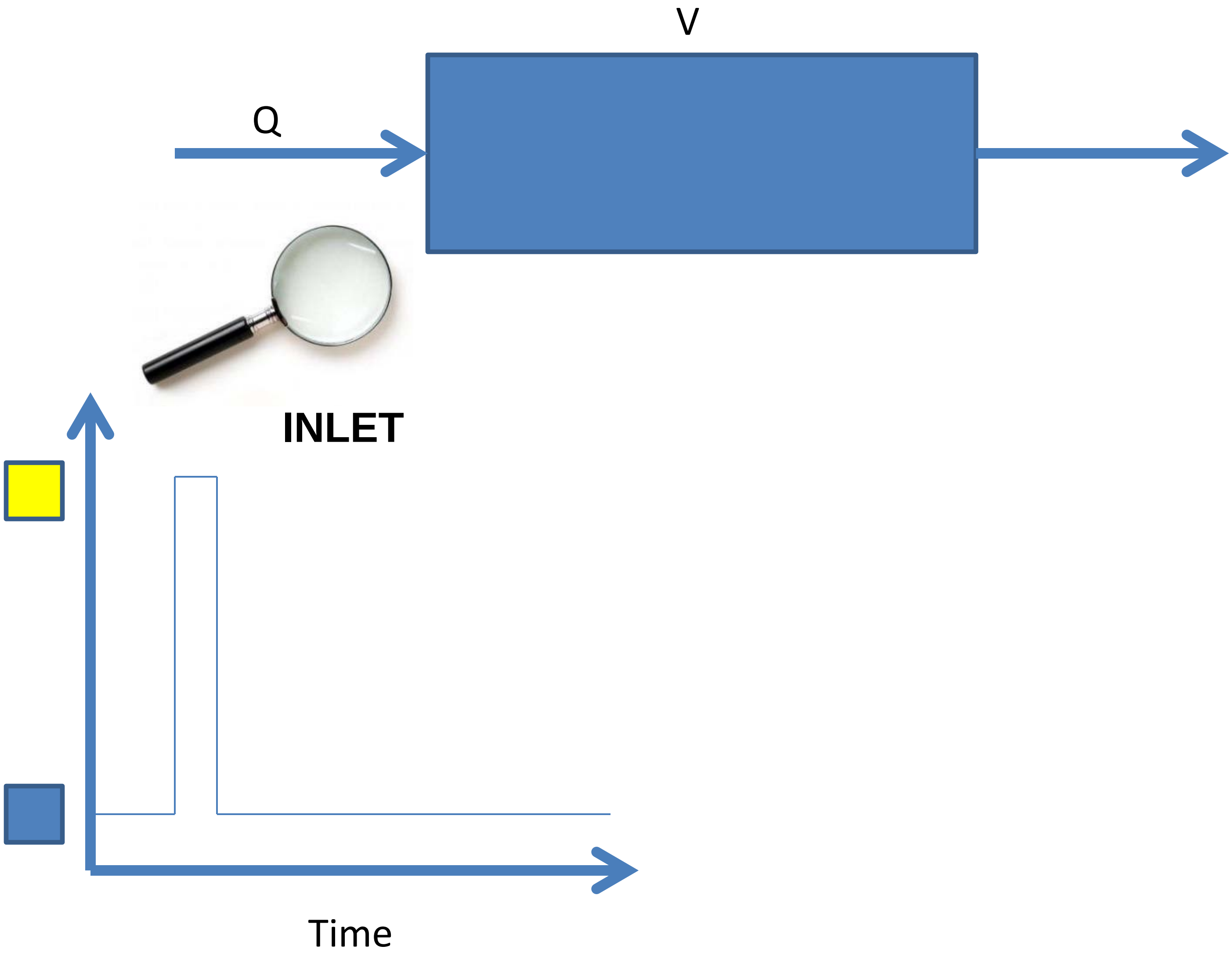
PLUG-FLOW-REACTOR:
all molecules have same residence time and concetrations vary only along the length of the tubular reactor.



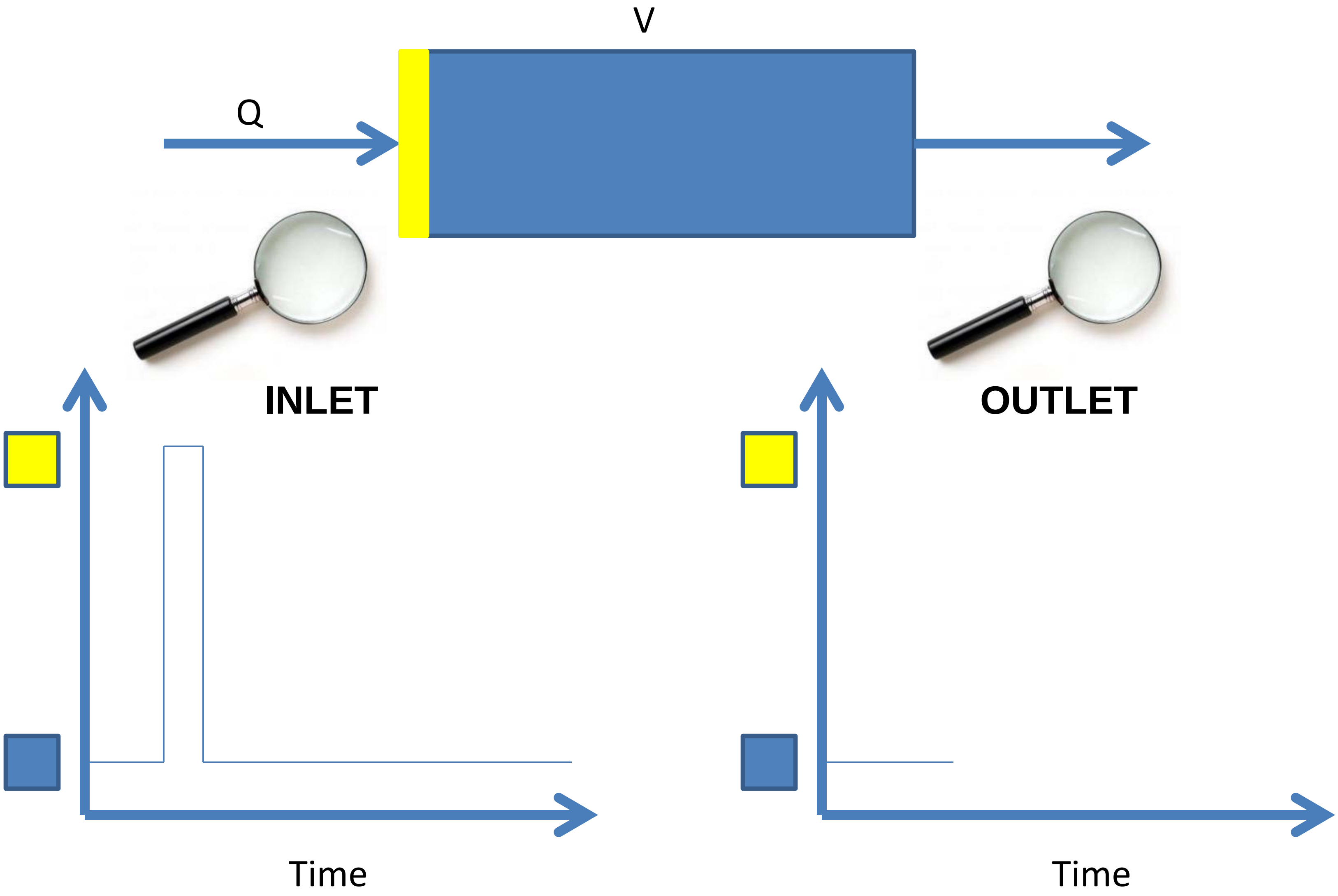
CONTINUOUS-FLOW STIRRED TANK REACTOR:
due to vigorous agitation, the reactor contents are well mixed, so that effluent composition equals that in the tank



Residence time distribution in PFR



Residence time distribution in PFR



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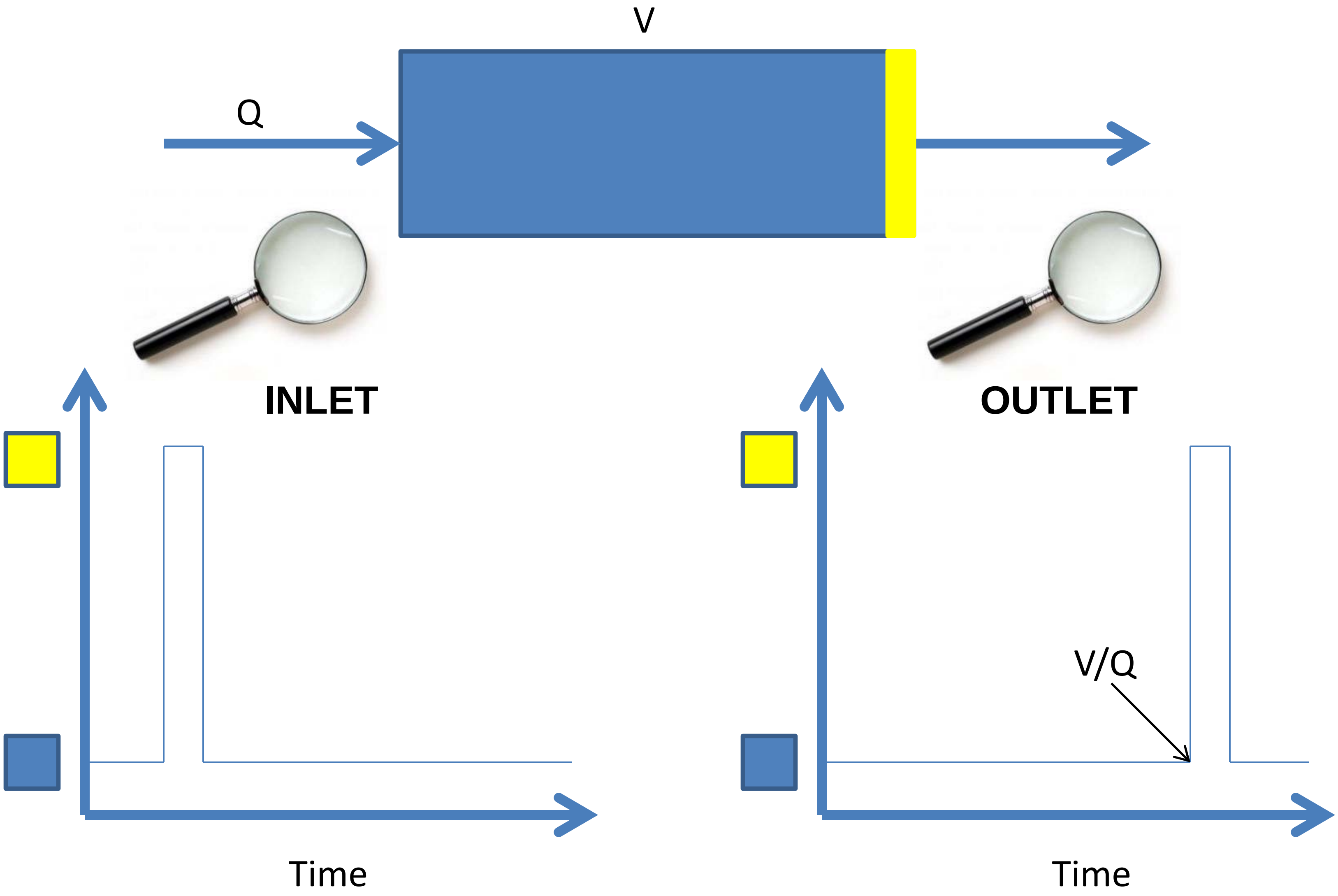
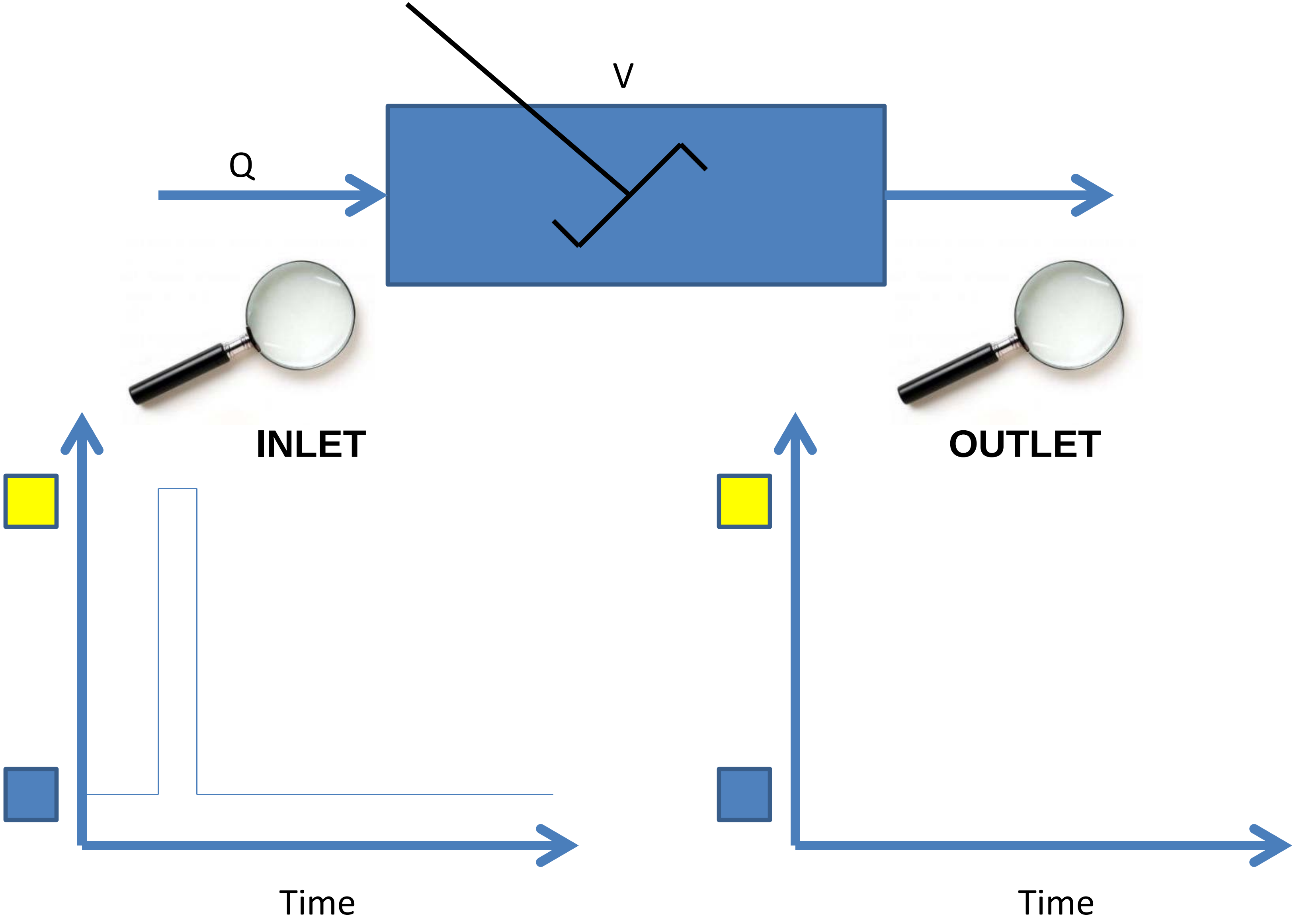
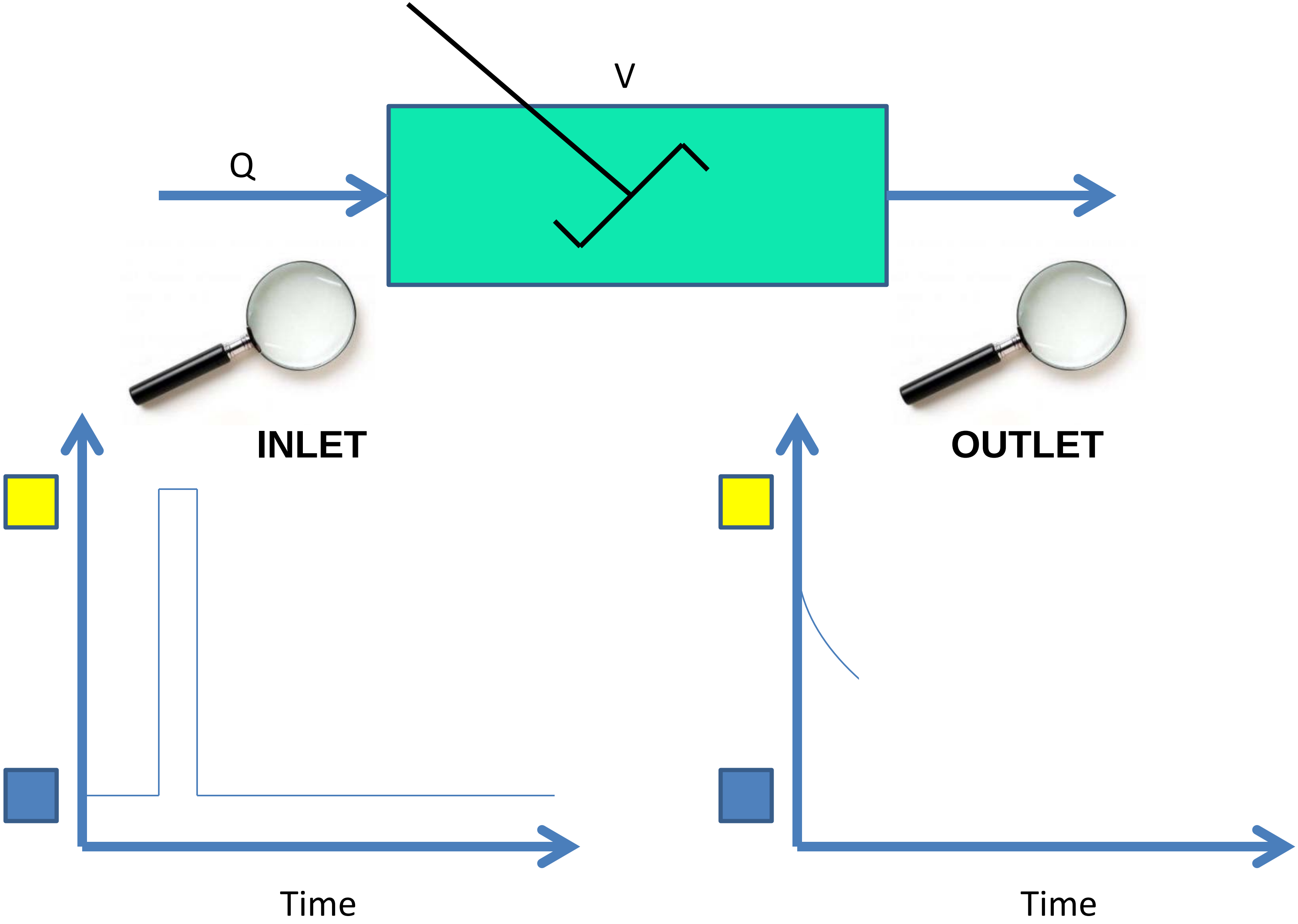


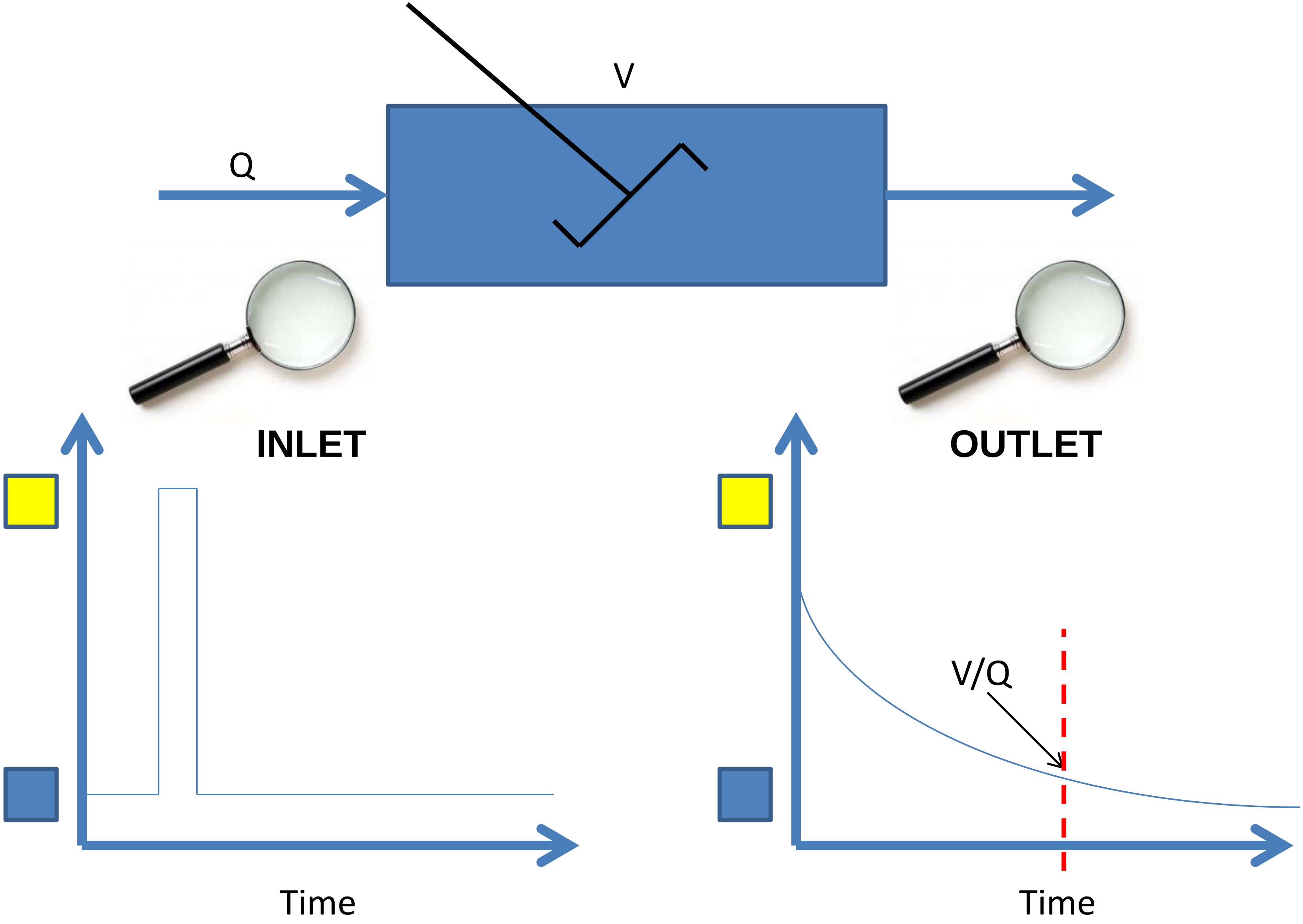
Residence time distribution in CSTR



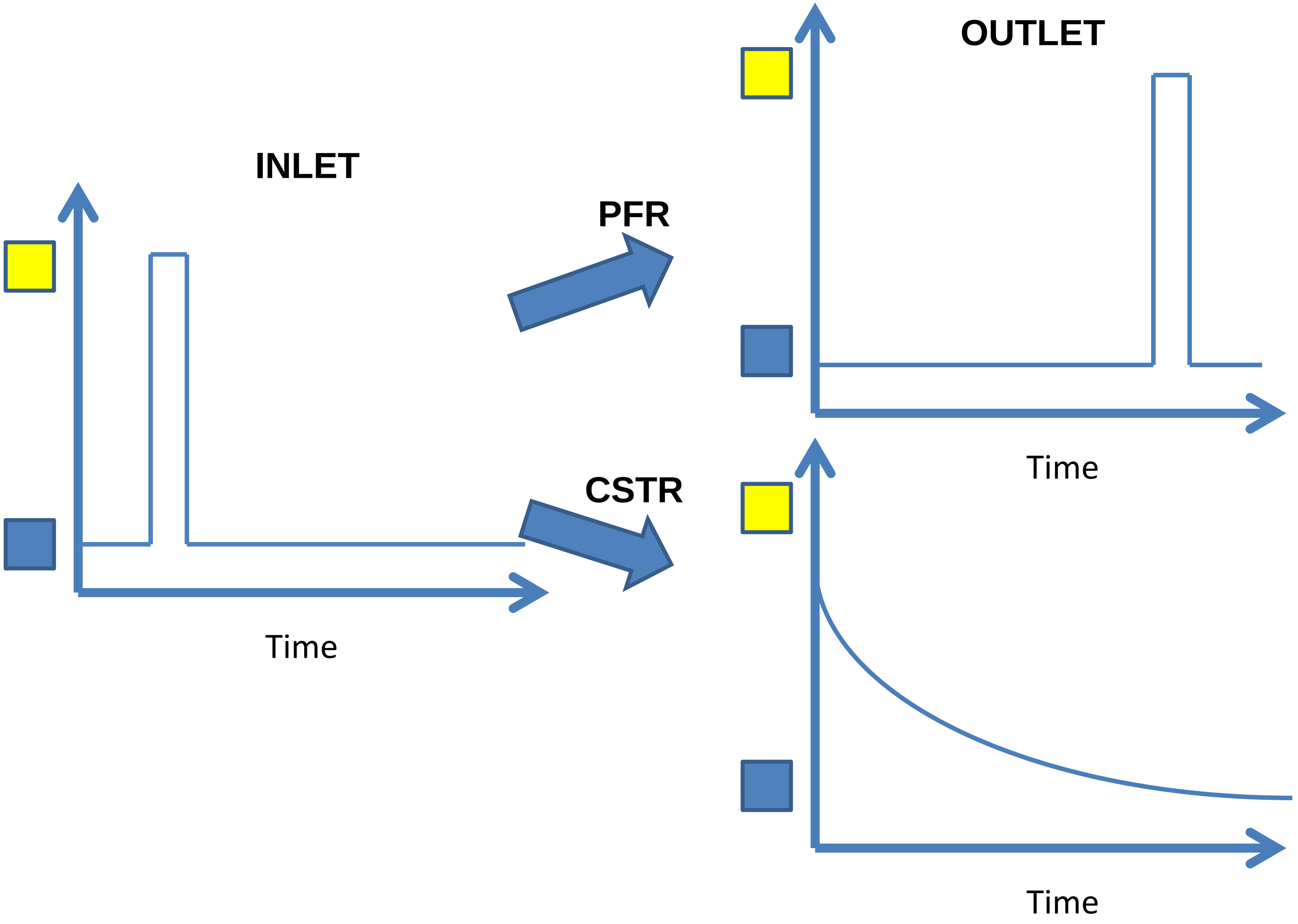
Residence time distribution in CSTR



Residence time distribution in CSTR



PFR Vs.CSTR reactor



OUTLET

INLET

PFR

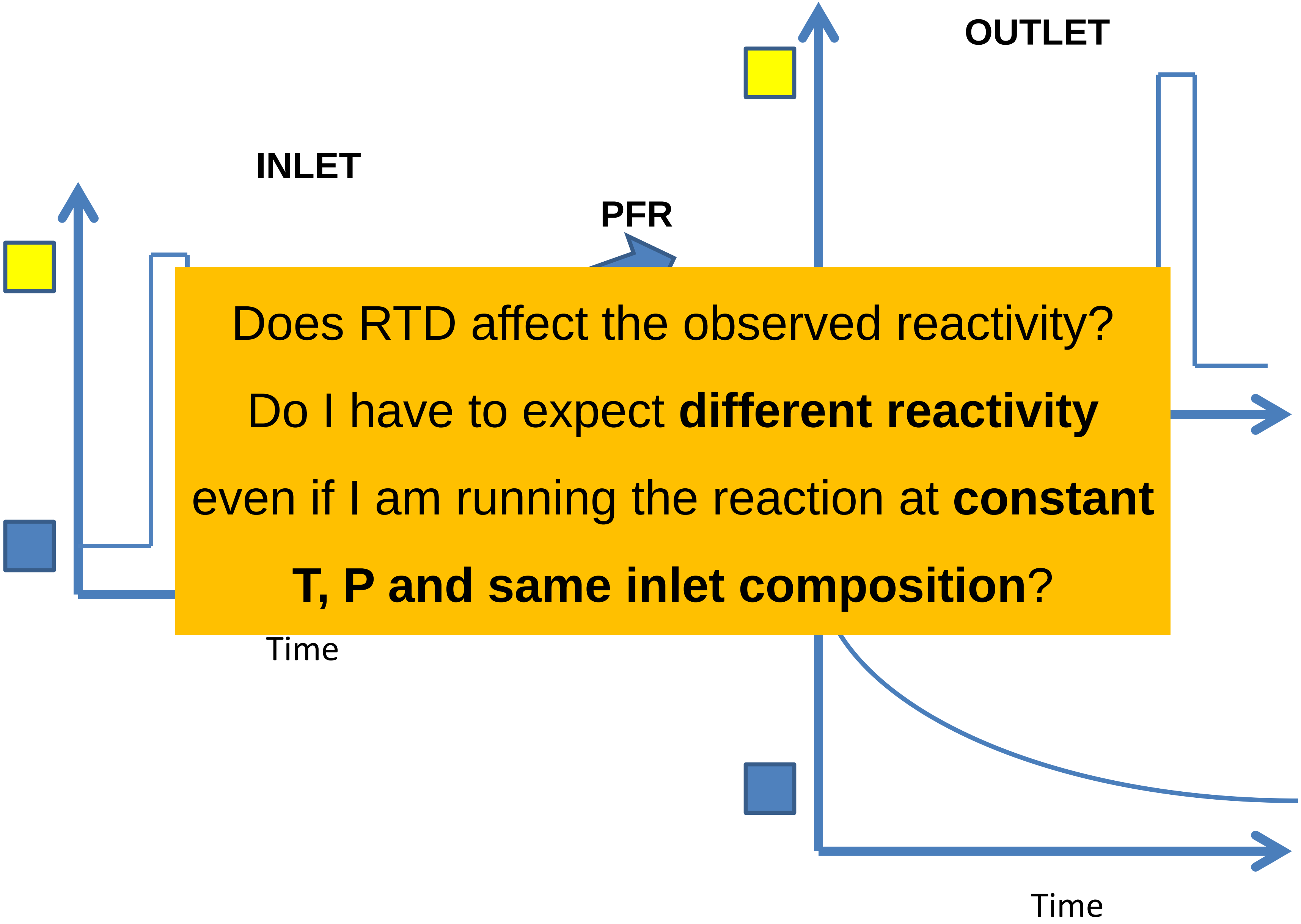
Time

CSTR

Time

Time

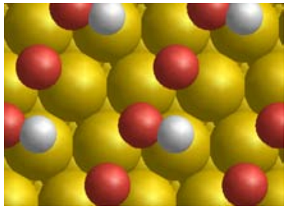
PFR Vs.CSTR reactor



Does RTD affect the observed reactivity?

Do I have to expect **different reactivity** even if I am running the reaction at **constant T, P and same inlet composition**?

Effect of RTD on observed reaction rate



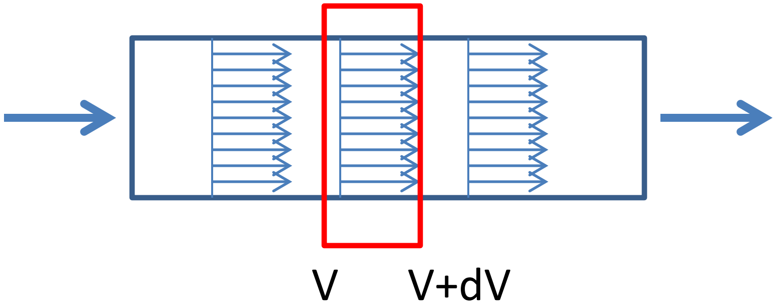
$$A \rightarrow B \qquad r = kc_A \ [\mathrm{mol/m^3}/s]$$

Q = 10 m^3/s V = 5 m^3

$c_{A,0}$=1 kmol/m^3 **k = 5 s^{-1} @ T = 500K – P = 1 atm**

We want to run the reaction isothermally and pressure drops are negligible

PLUG FLOW REACTOR



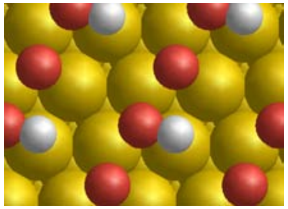
Every "small" element travels along the reactor without mixing with the rest

$$\tau = \frac{V}{Q}$$

IN-OUT+PROD = ACC

$$Qc_A\big|_V - Qc_A\big|_{V+dV} - kc_A dV = 0$$

Effect of RTD on observed reaction rate



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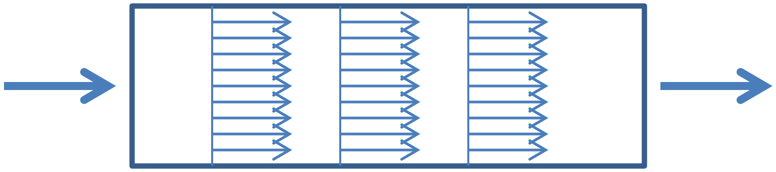


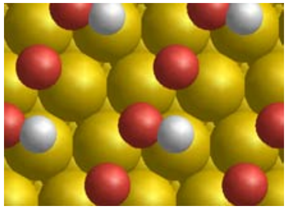
Every "small" element travels along the reactor without mixing with the rest

$$\tau = \frac{V}{Q}$$

Mass balance equation:

$$\frac{dc_A}{d\tau} = -kc_A \dashrightarrow c_A = c_{A,0}\exp(-k\tau) \dashrightarrow \chi = \frac{c_{A,0} - c_A}{c_{A,0}} = 91\%$$

Effect of RTD on observed reaction rate



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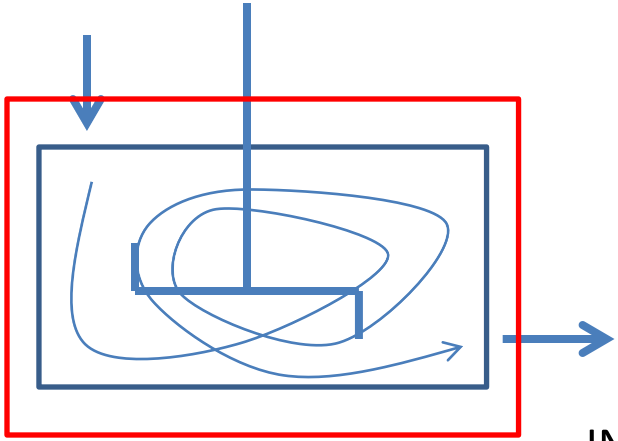
CONTINUOUS STIRRED TANK REACTOR (CSTR)



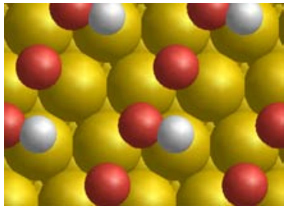
Mixing is so fast that concentration of every species is uniform and homogeneous in the reactor

$$\bar{\tau} = \frac{V}{Q}$$

IN-OUT+PROD = ACC

$$Qc_{A,0} - Qc_A - kc_A V = 0$$

Effect of RTD on observed reaction rate



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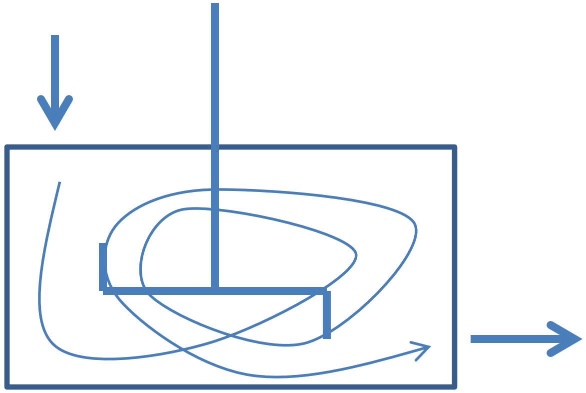


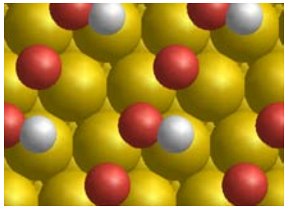
Mixing is so fast that concentration of every species is uniform and homogeneous in the reactor

$$\bar{\tau} = \frac{V}{Q}$$

Mass balance equation:

$$c_{A,0} - c_A - \tau k c_A = 0 \dashrightarrow c_A = \frac{c_{A,0}}{1 + k\tau} \dashrightarrow \chi = \frac{c_{A,0} - c_A}{c_{A,0}} = 71\%$$

Effect of RTD on observed reaction rate



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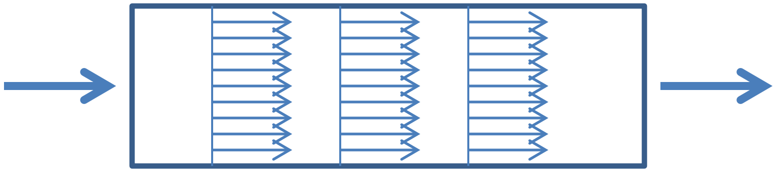
$c_{A,0} = 1\ \text{kmol/m}^3$ **$k = 5\ \text{s}^{-1}$ @ $T = 500\text{K}$ – $P = 1$ atm**

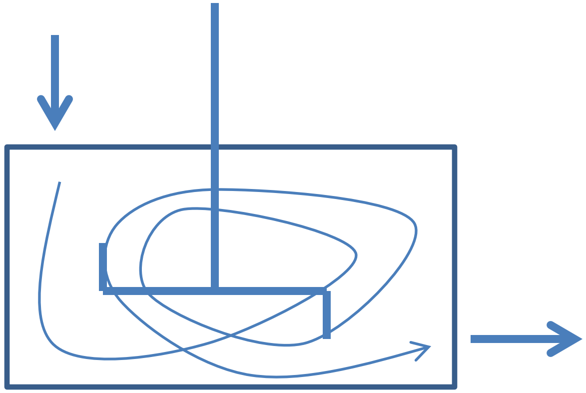
We want to run the reaction isothermally and pressure drops are negligible

PFR



$$\chi = \frac{c_{A,0} - c_A}{c_{A,0}} = 91\%$$

CSTR



$$\chi = \frac{c_{A,0} - c_A}{c_{A,0}} = 71\%$$

Outline

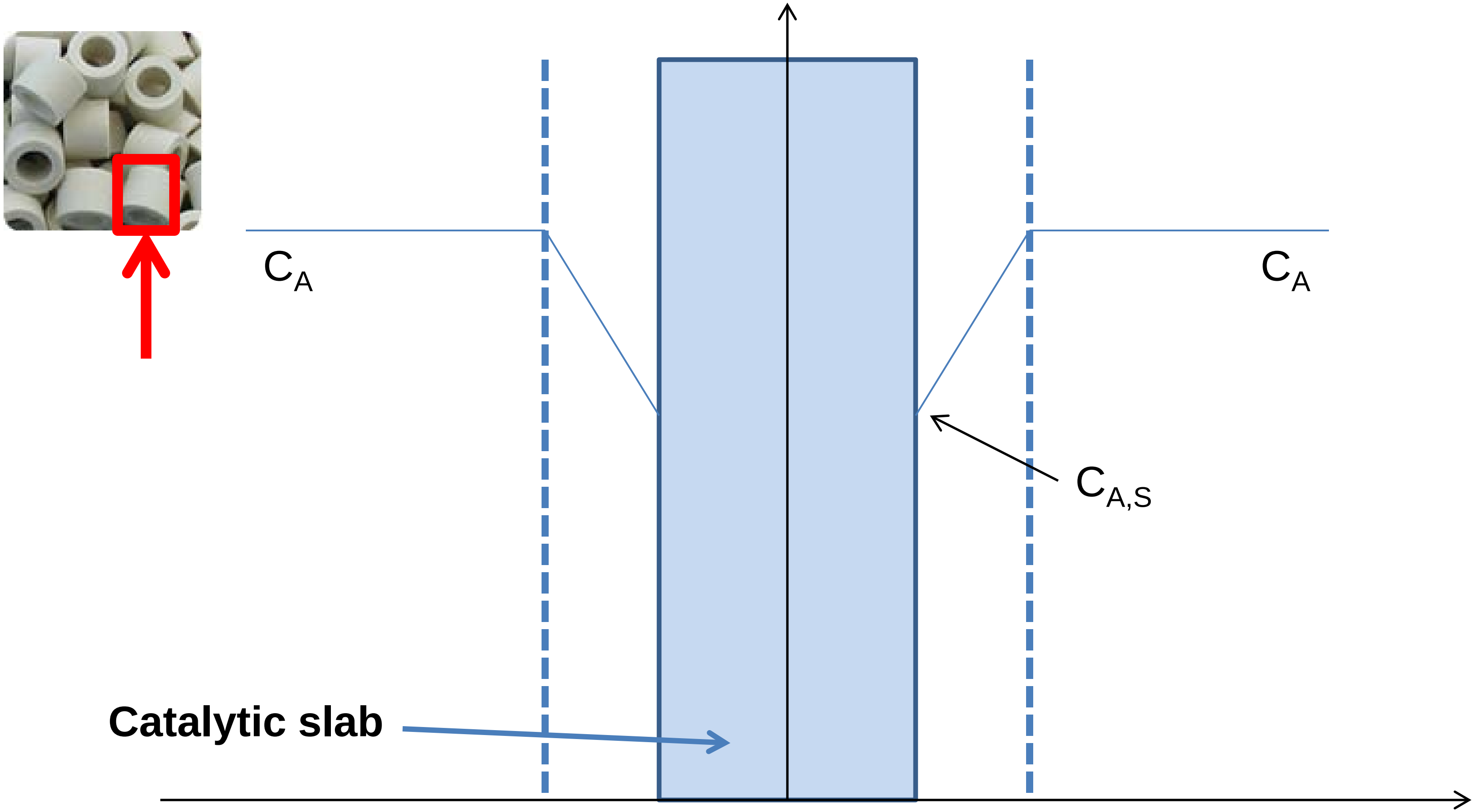
1) Effect of the distribution of the contact times in the reactor on the observed reaction rate

2) **Inter-phase and intra-phase transport phenomena and their impact on the observed reaction rate**

3) Show-case: effect of transport phenomena on catalyst reactivity

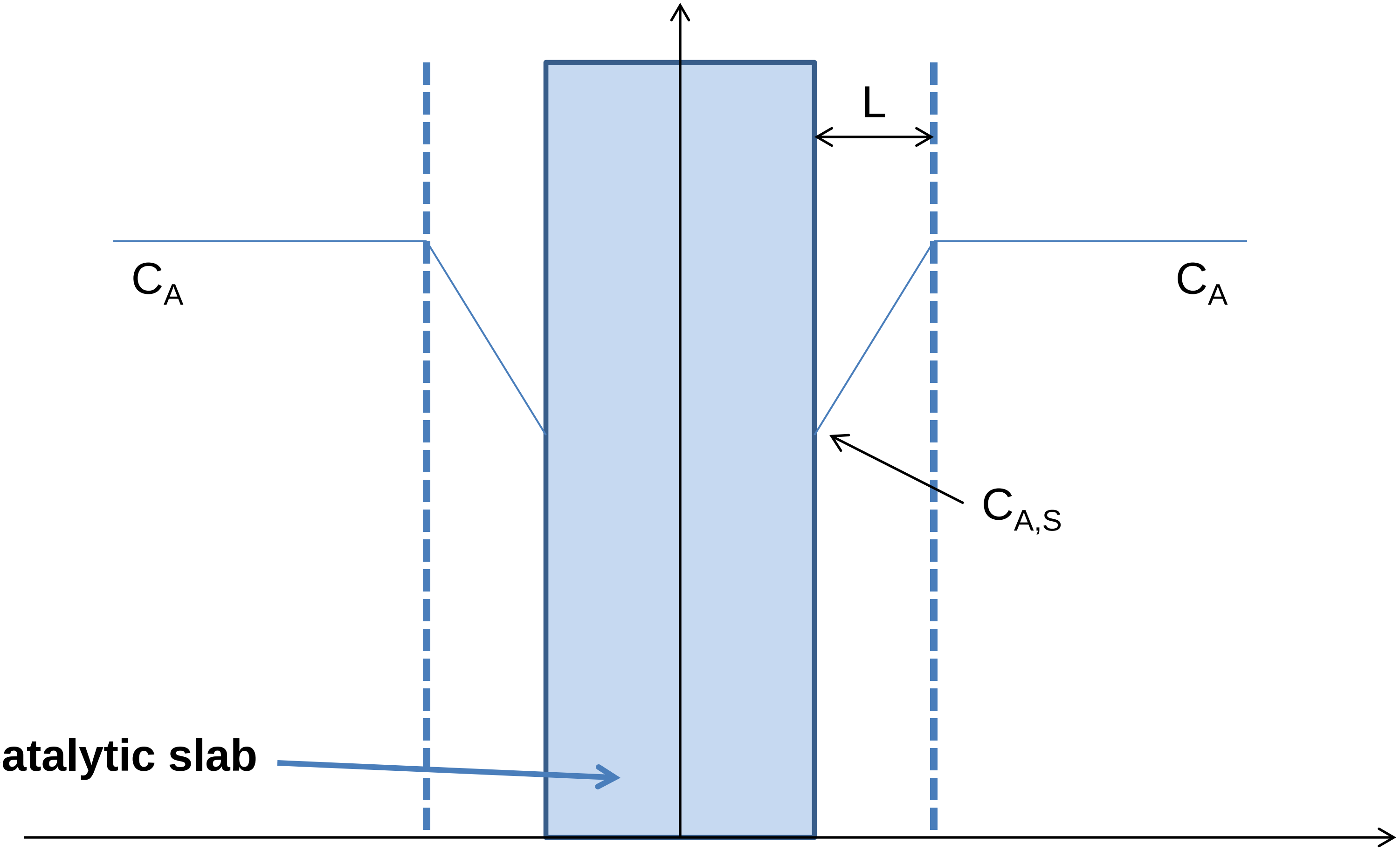
4) Take-home messages

Inter- and Intra-phase transport phenomena



$$\mathrm{A} \longrightarrow \mathrm{B} \qquad r = kc_A \ [\mathrm{mol/m^3} / s]$$

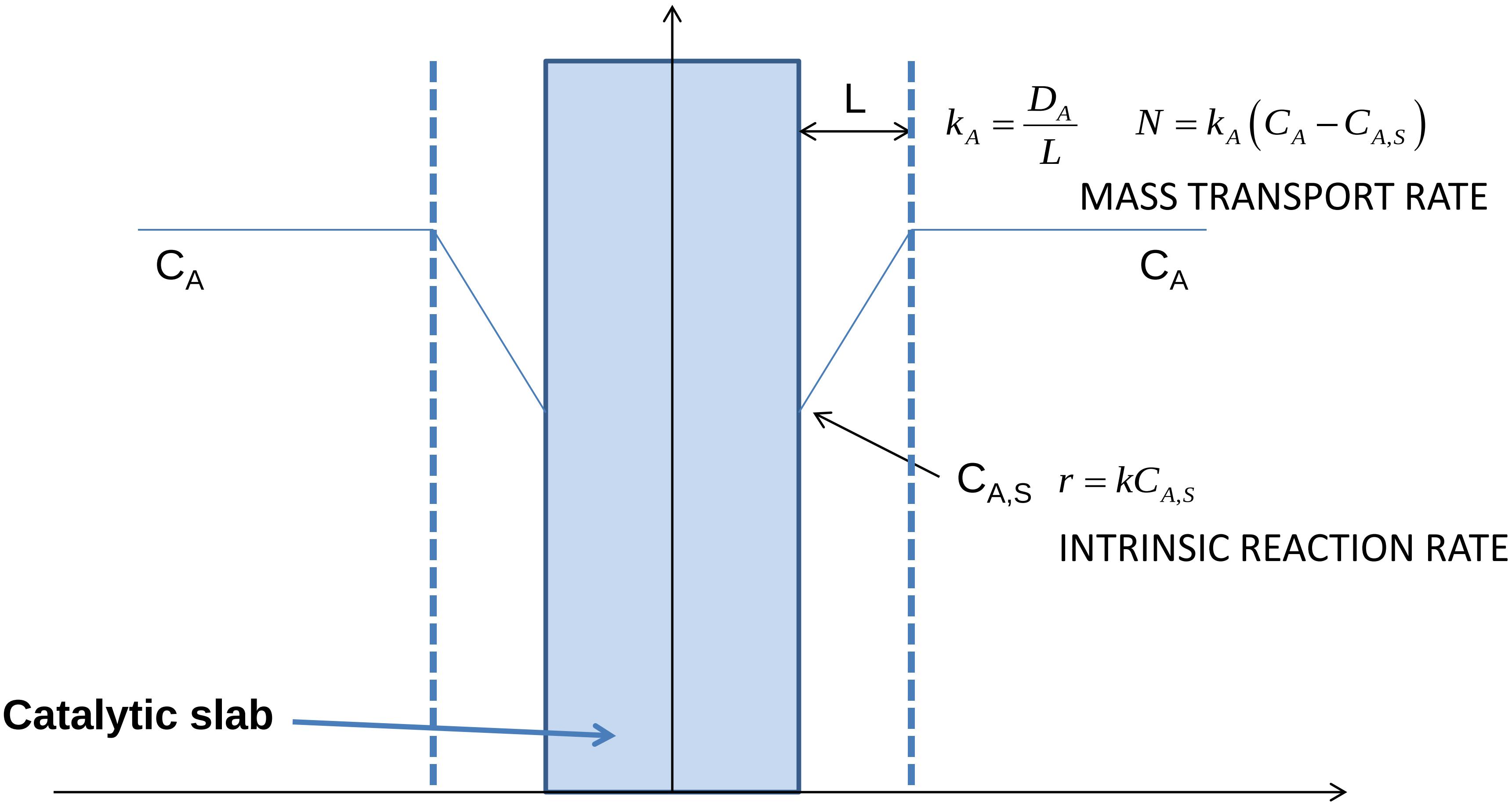
Interphase transport phenomena



Catalytic slab

$$A \rightarrow B \qquad r = kc_A \ [\text{mol/m}^3 / s]$$

Interphase transport phenomena



$$k_A = \frac{D_A}{L} \qquad N = k_A\left(C_A - C_{A,S}\right)$$

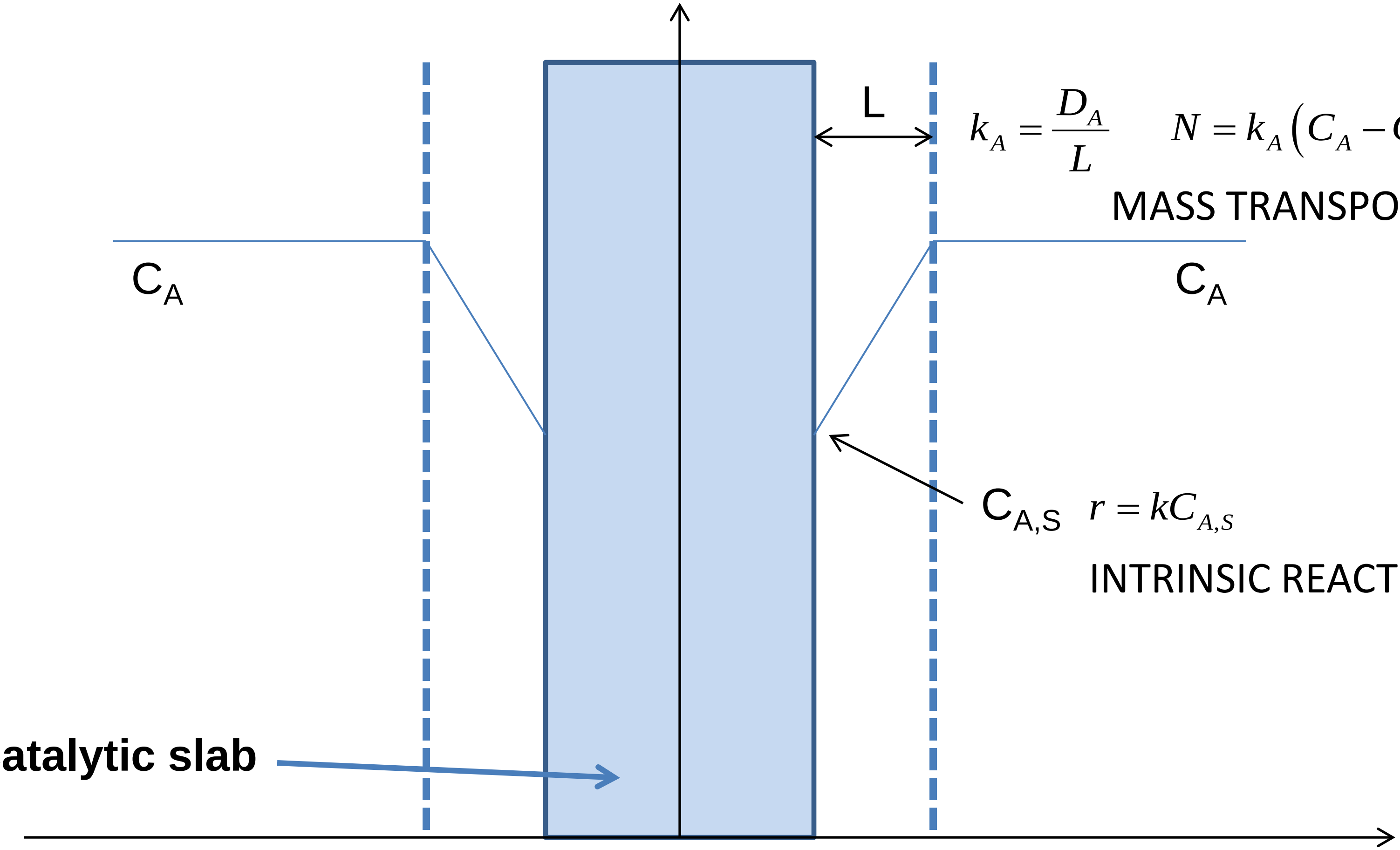
MASS TRANSPORT RATE

$$r = kC_{A,S}$$

INTRINSIC REACTION RATE

$$\text{A} \rightarrow \text{B} \qquad r = kc_A \ [\text{mol/m}^3 / s]$$

Interphase transport phenomena



$k_A = \dfrac{D_A}{L}$ $\quad N = k_A\left(C_A - C_{A,S}\right)$

MASS TRANSPORT RATE

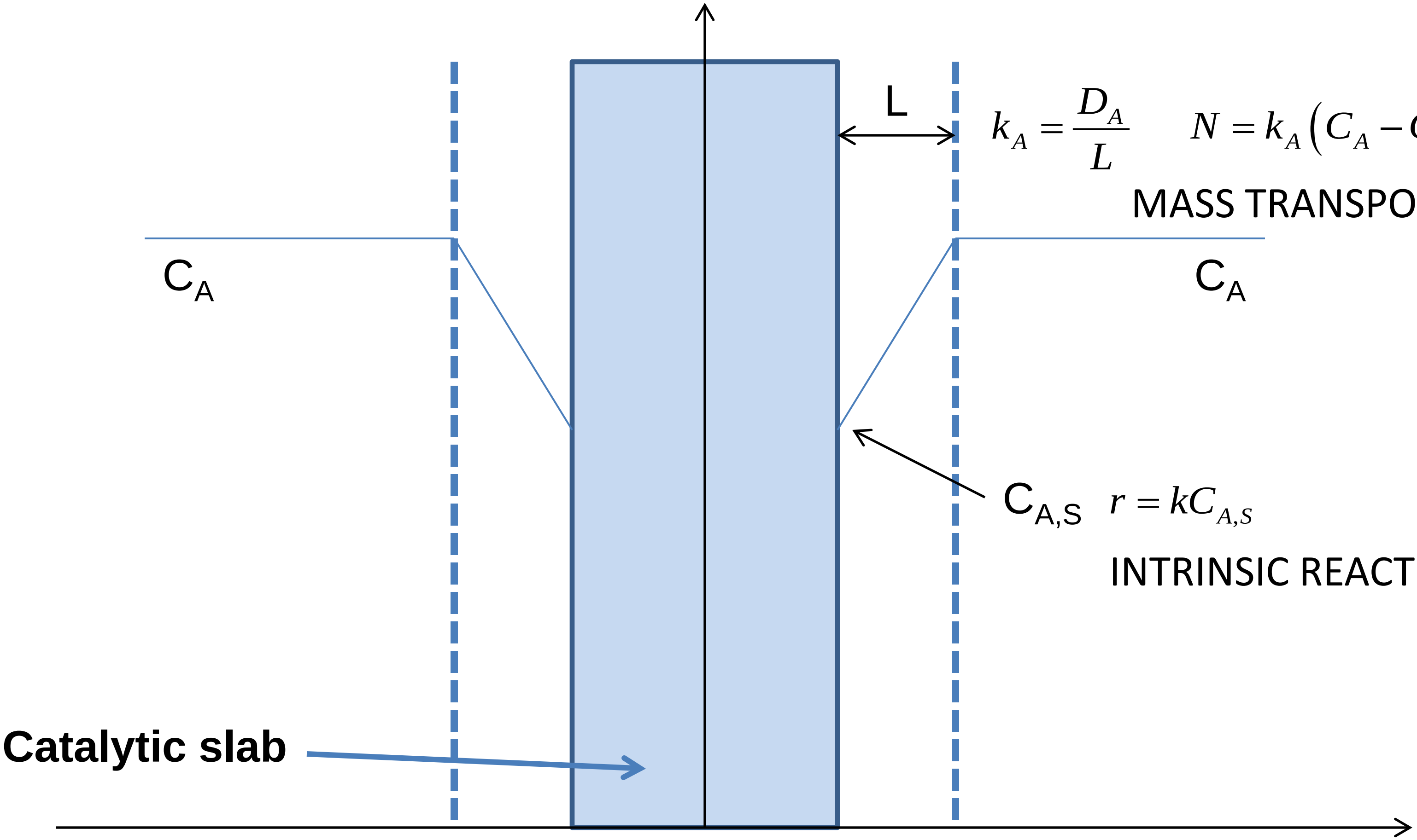
$C_{A,S}$ $\quad r = kC_{A,S}$

INTRINSIC REACTION RATE

Catalytic slab

$$kC_{A,S}V = k_A\left(C_A - C_{A,S}\right)S$$

Interphase transport phenomena



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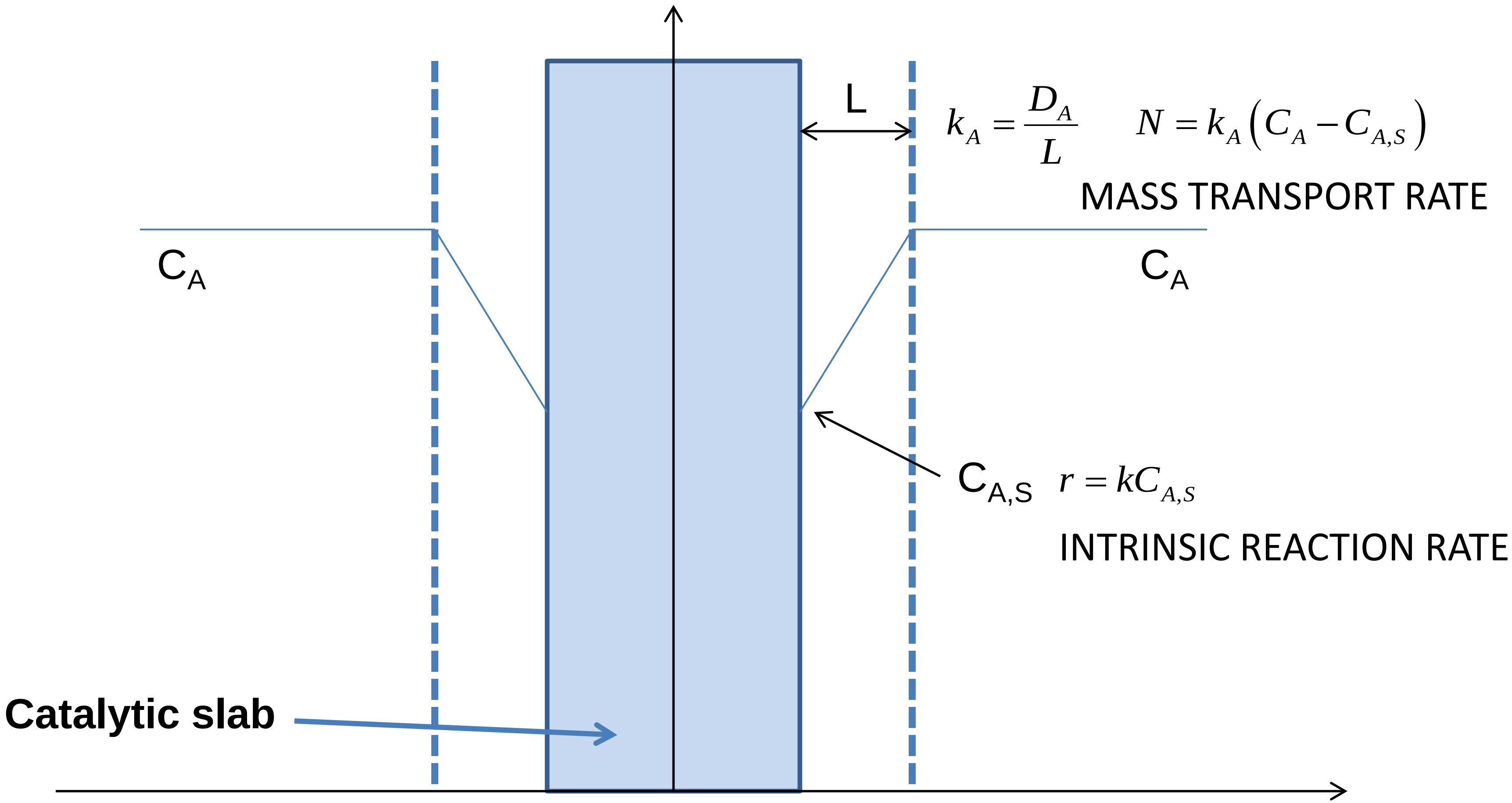
MASS TRANSPORT RATE

$$r = kC_{A,S}$$

INTRINSIC REACTION RATE

$$kC_{A,S} = k_A\left(C_A - C_{A,S}\right)\frac{S}{V} = k_A^*\left(C_A - C_{A,S}\right)$$

Interphase transport phenomena



$$k_A = \frac{D_A}{L} \qquad N = k_A\left(C_A - C_{A,S}\right)$$

MASS TRANSPORT RATE

$$r = kC_{A,S}$$

INTRINSIC REACTION RATE

$$C_{A,S} = \frac{C_A}{1 + \dfrac{k}{k_A^*}} = \frac{C_A}{1 + Da}$$

Interphase transport phenomena

$$C_{A,S} = \frac{C_A}{1+\frac{k}{k_A^*}} = \frac{C_A}{1+Da}$$

$$r_{obs} = kC_{A,S} = k\frac{C_A}{1+\frac{k}{k_A^*}} = \left(\frac{1}{k}+\frac{1}{k_A^*}\right)^{-1} C_A = k_{obs}C_A$$

Da << 1

$$r_{obs} = kC_A$$

CHEMICAL REGIME

Da>>1

$$r_{obs} = k_A^* C_A$$

MASS TRANSFER REGIME

Effect on observable reaction rate

Da<<1

$$r_{obs} = kC_A$$

CHEMICAL REGIME

$$k_{obs} = k = k_0 \exp\left(\frac{-E}{RT}\right)$$

Da >> 1

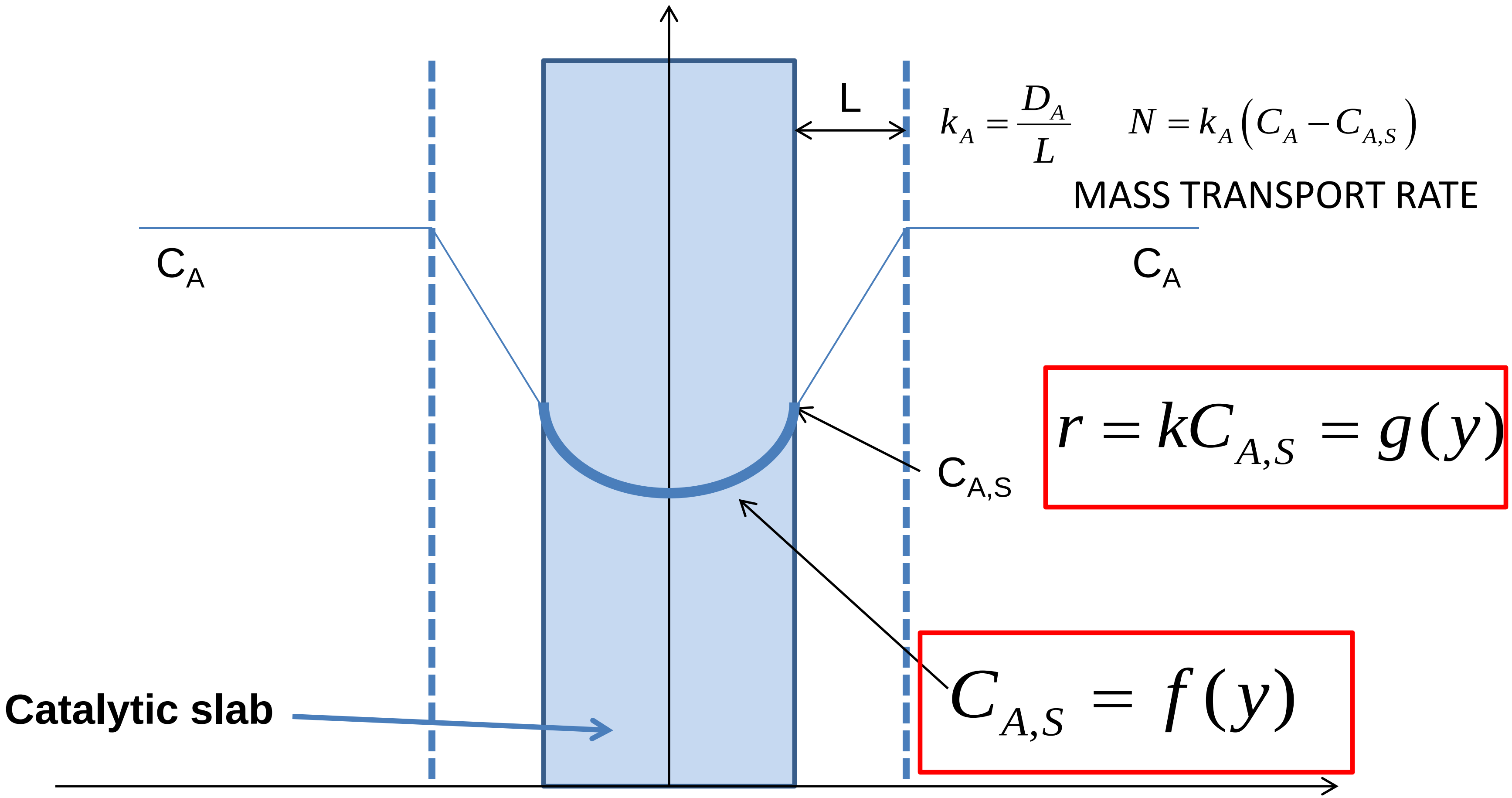
$$r_{obs} = k_A^* C_A$$

MASS TRANSFER REGIME

$$k_{obs} = k_A^* = k_0 \exp\left(\frac{-E \rightarrow 0}{RT}\right)$$

Transport coefficient has very weak dependence on temperature

Intraphase transport phenomena



$$k_A = \frac{D_A}{L} \qquad N = k_A\left(C_A - C_{A,S}\right)$$

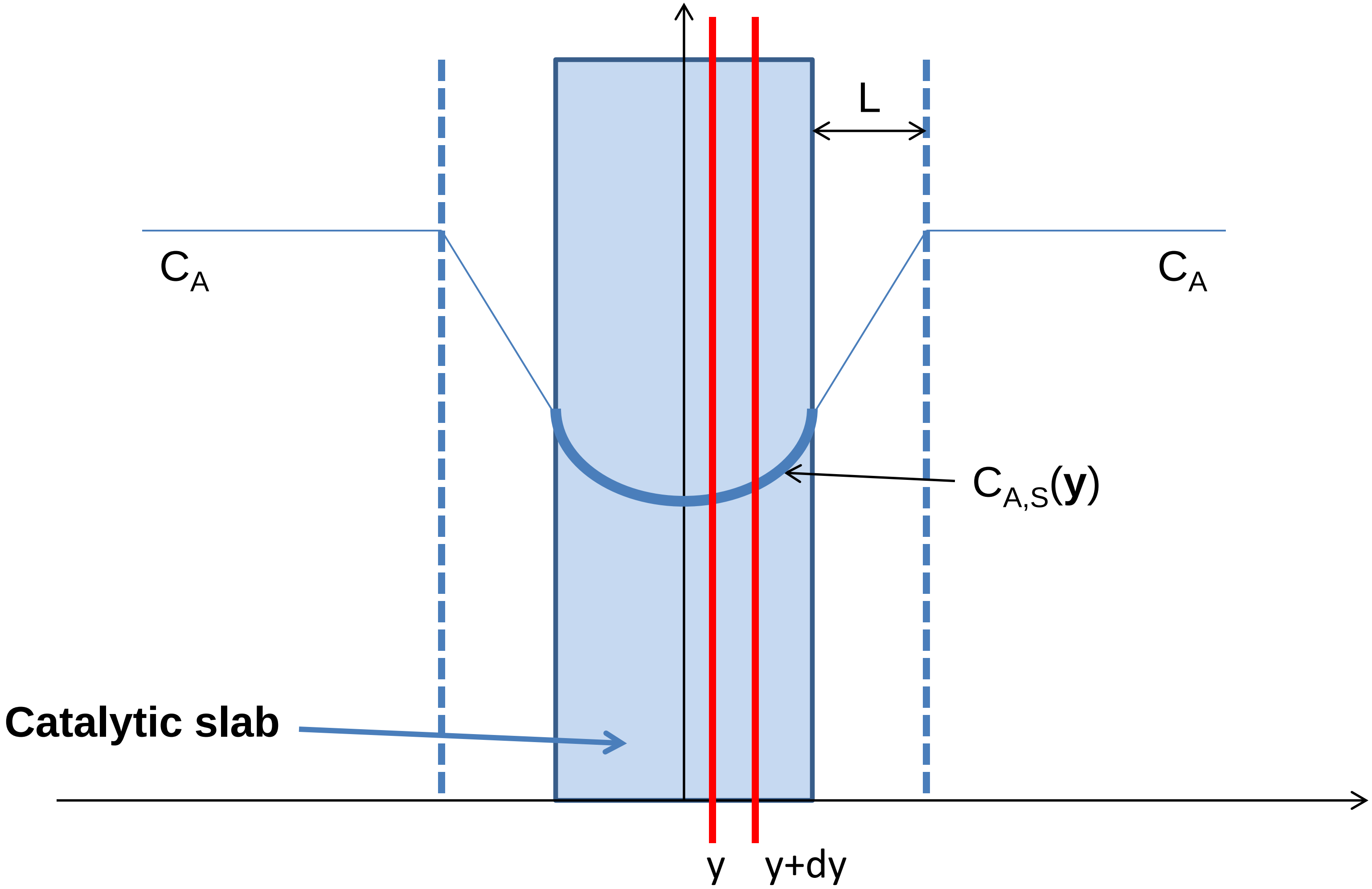
MASS TRANSPORT RATE

$$\boxed{r = kC_{A,S} = g(y)}$$

$$\boxed{C_{A,S} = f(y)}$$

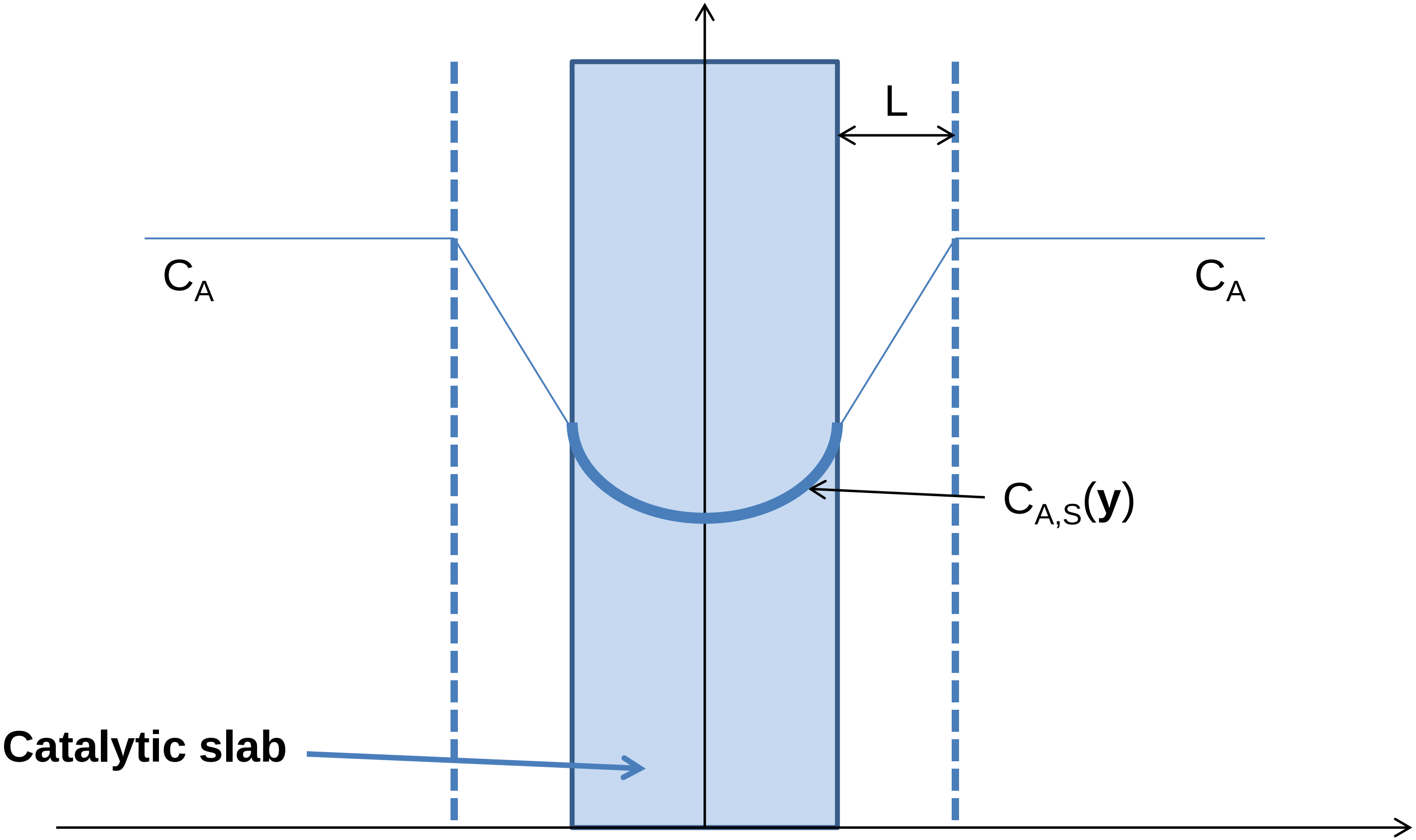
WE CONSIDER NOW THE POSSIBILITY THAT TRANSPORT WITHIN THE SLAB CAN BECOME LIMITING

Intraphase transport phenomena



$$-D_A^{eff}\,S\,\frac{dC_A(y)}{dy}\bigg|_y-\left(-D_A^{eff}\,S\,\frac{dC_A(y)}{dy}\bigg|_{y+dy}\right)-kC_A(y)Sdy=0$$

Intraphase transport phenomena



$$D_A^{eff}\frac{d^2C_A(y)}{dy^2}=kC_A(y)\qquad \begin{cases}\left.\dfrac{dC_A}{dy}\right|_0=0\\[2ex] C_A(y=L)=C_{A,S}\end{cases}$$

Intraphase transport phenomena

$$D_A^{eff}\frac{d^2C_A(y)}{dy^2}=kC_A(y)\qquad\begin{cases}\left.\dfrac{dC_A}{dy}\right|_0=0\\ C_A(y=L)=C_{A,S}\end{cases}$$

$$\boxed{C_A(y)=\frac{\cosh\left(\phi\dfrac{y}{L}\right)}{\cosh(\phi)}C_{A,S}}$$

where: $$\phi=L\sqrt{\frac{k}{D_A^{eff}}}\approx\frac{reaction\ rate}{diffusion\ rate}$$

THIELE MODULUS

Intraphase concentration gradients

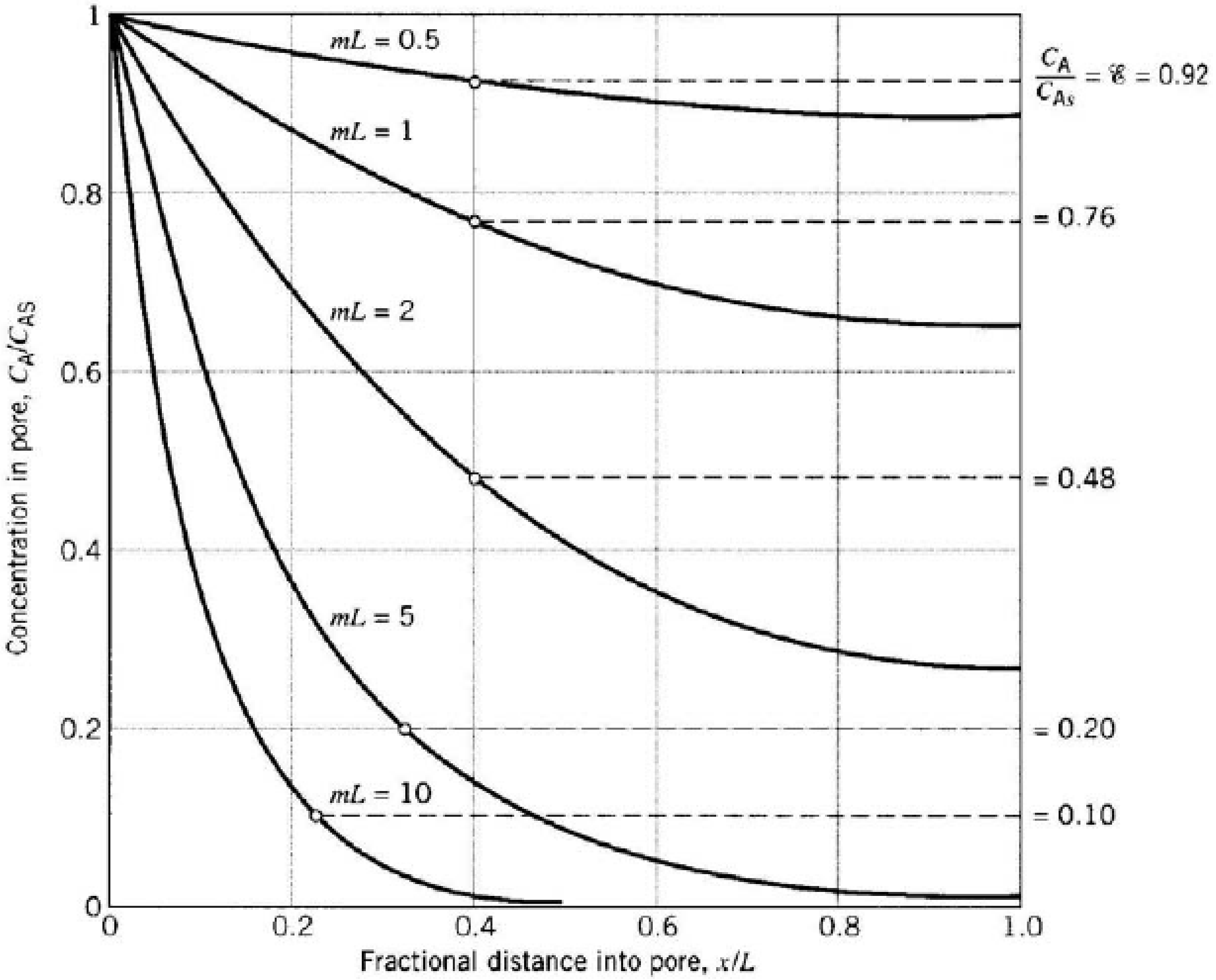


Figure 18.4 Distribution and average value of reactant concentration within a catalyst pore as a function of the parameter $mL = L\sqrt{k/\mathscr{D}}$

So what?

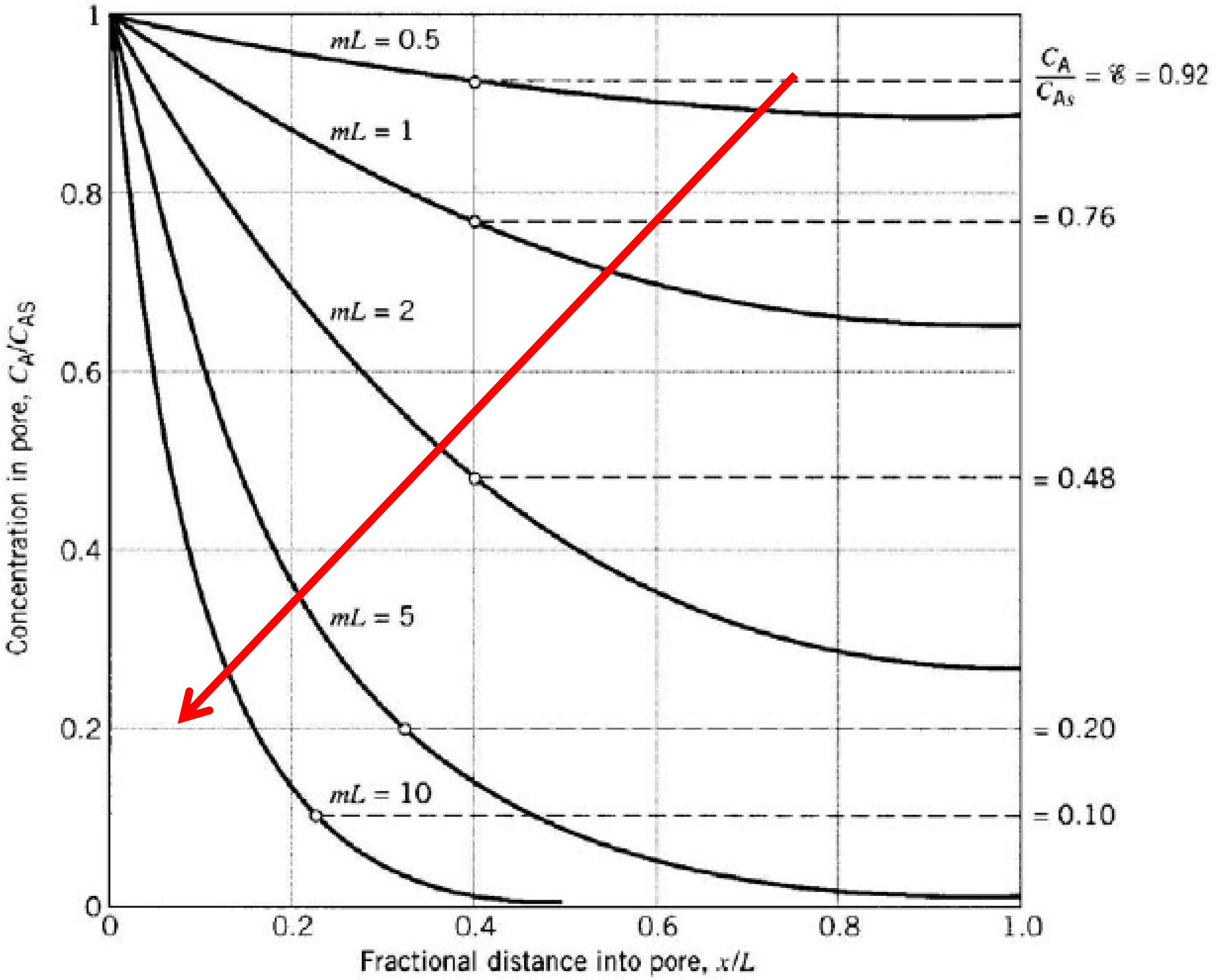
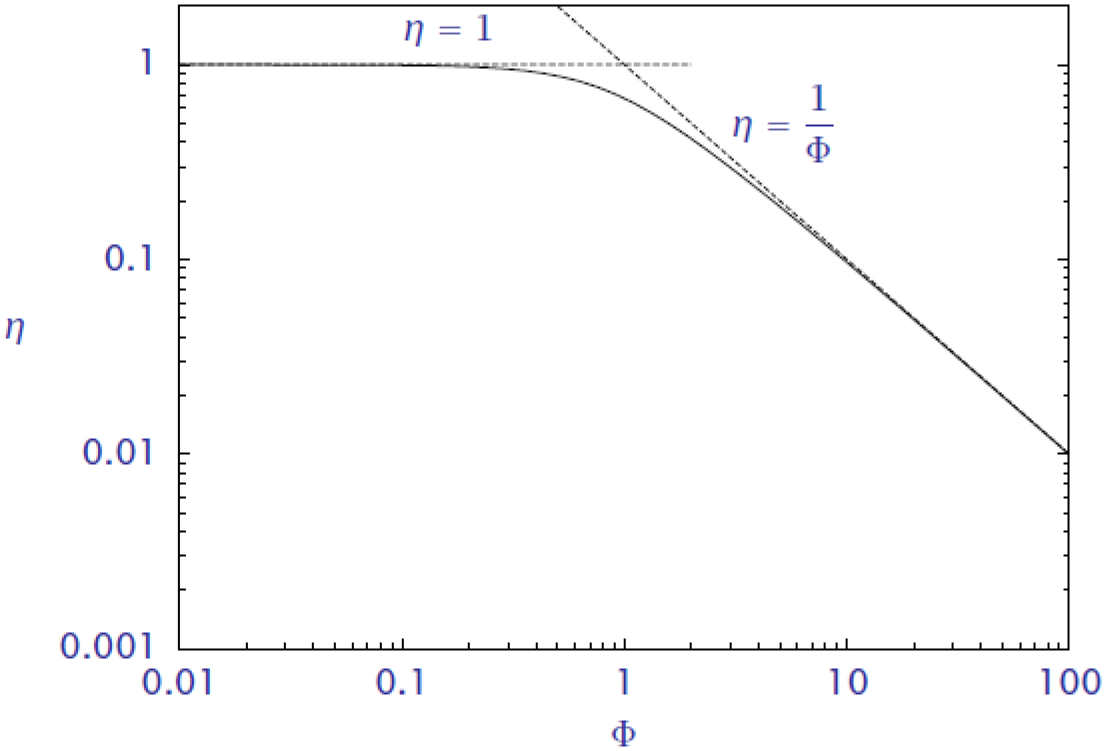


Figure 18.4 Distribution and average value of reactant concentration within a catalyst pore as a function of the parameter $mL = L\sqrt{k/\mathscr{D}}$

At what extent am I using the catalyst?

$$\eta = \frac{R_{obs}}{R_S} = \frac{\int_V kC_A(V)dV}{kC_{A,S}V} = \frac{\tanh(\phi)}{\phi}$$



Effect on observable reaction rate

$$\eta = \frac{R_{obs}}{R_S} = \frac{\int_V kC_A(V)dV}{kC_{A,S}V} = \frac{\tanh(\phi)}{\phi}$$

For high values of Thiele modulus (internal mass transfer limitations):

$$\eta \to \frac{1}{\phi}$$

$$R_{obs} = \eta R_S = \frac{1}{\phi} R_S = \frac{1}{\phi} kC_{A,S} = \left(\frac{1}{L} \sqrt{\frac{D_A^{eff}}{k}} \right) kC_{A,S} = k_{obs} C_{A,S}$$

$$k_{obs} = \left(\frac{1}{L} \sqrt{\frac{D_A^{eff}}{k}} \right) k = \frac{1}{L} \sqrt{D_A^{eff} k}$$

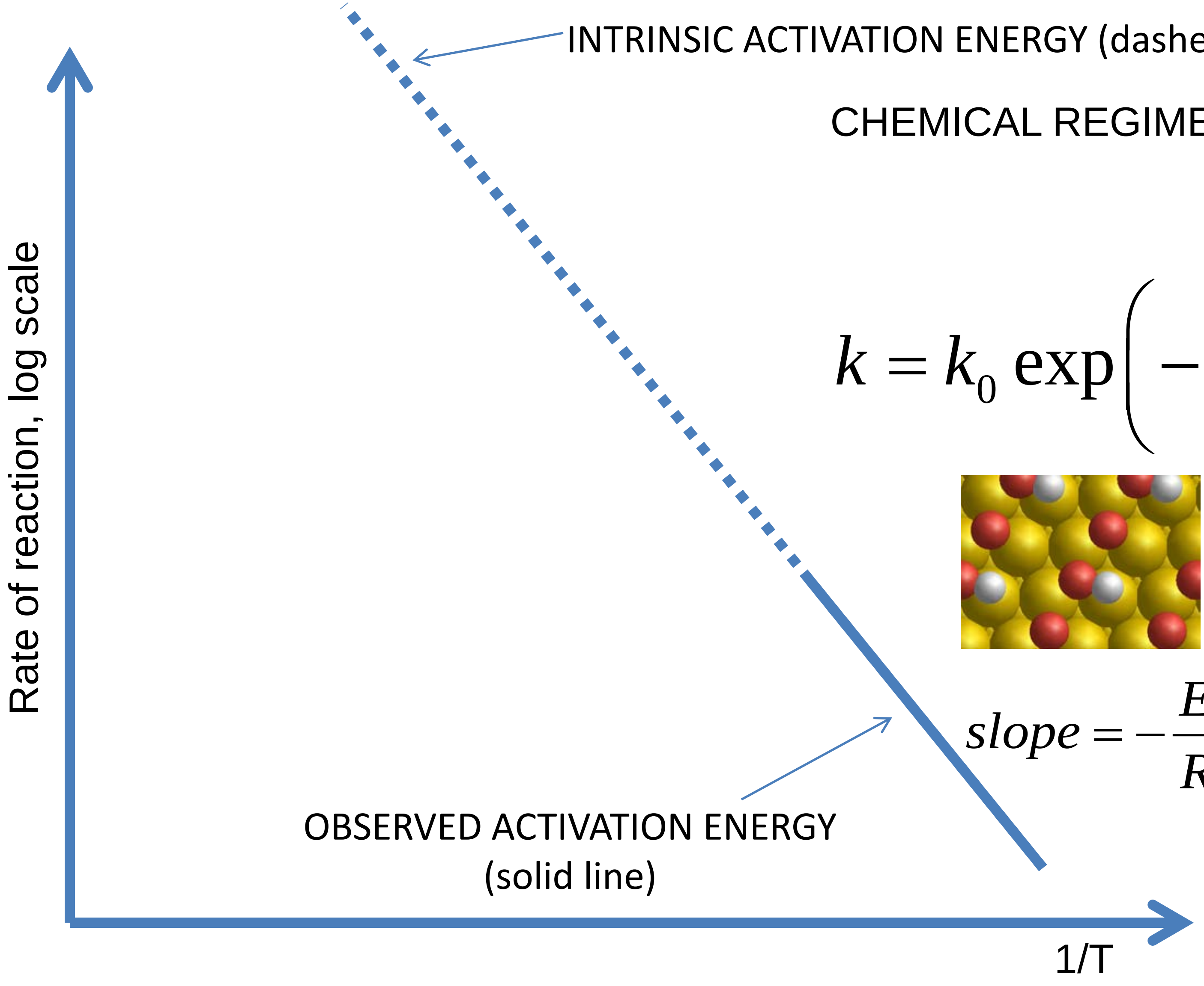
Effect on observable reaction rate

$$\begin{cases} k_{obs} = \left(\frac{1}{L}\sqrt{\frac{D_A^{eff}}{k}}\right)k = \frac{1}{L}\sqrt{D_A^{eff}k} = k_{obs}\exp\left(-\frac{E_{obs}}{RT}\right) \\ k = k_0\exp\left(-\frac{E}{RT}\right) \end{cases}$$

$$\downarrow$$

$$\boxed{E_{obs} = \frac{E}{2}}$$

Interplay between kinetic and transport



INTRINSIC ACTIVATION ENERGY (dashed line)

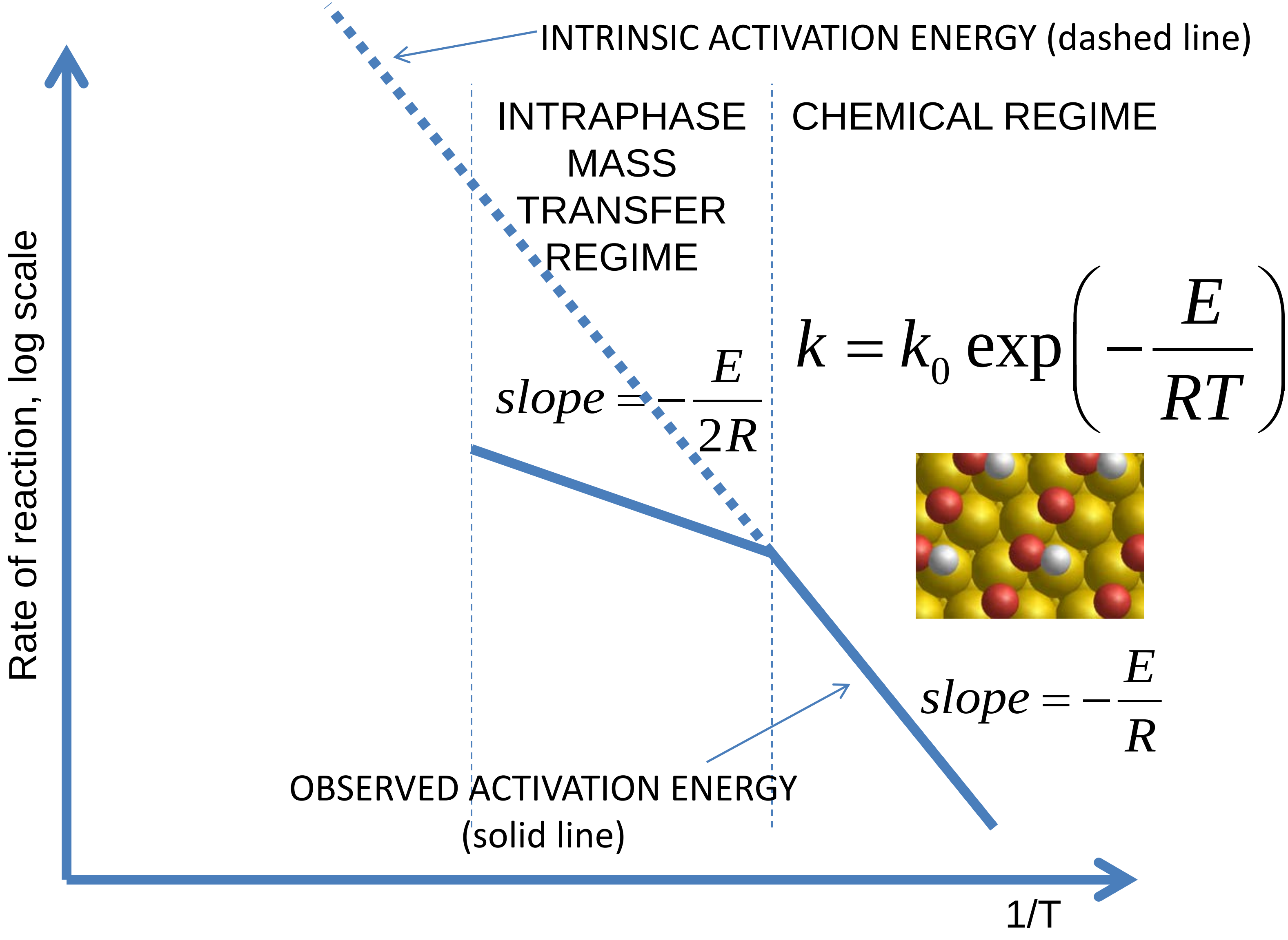
CHEMICAL REGIME

$$k = k_0 \exp\left(-\frac{E}{RT}\right)$$

$$slope = -\frac{E}{R}$$

OBSERVED ACTIVATION ENERGY
(solid line)

Interplay between kinetic and transport



INTRINSIC ACTIVATION ENERGY (dashed line)

INTRAPHASE MASS TRANSFER REGIME

CHEMICAL REGIME

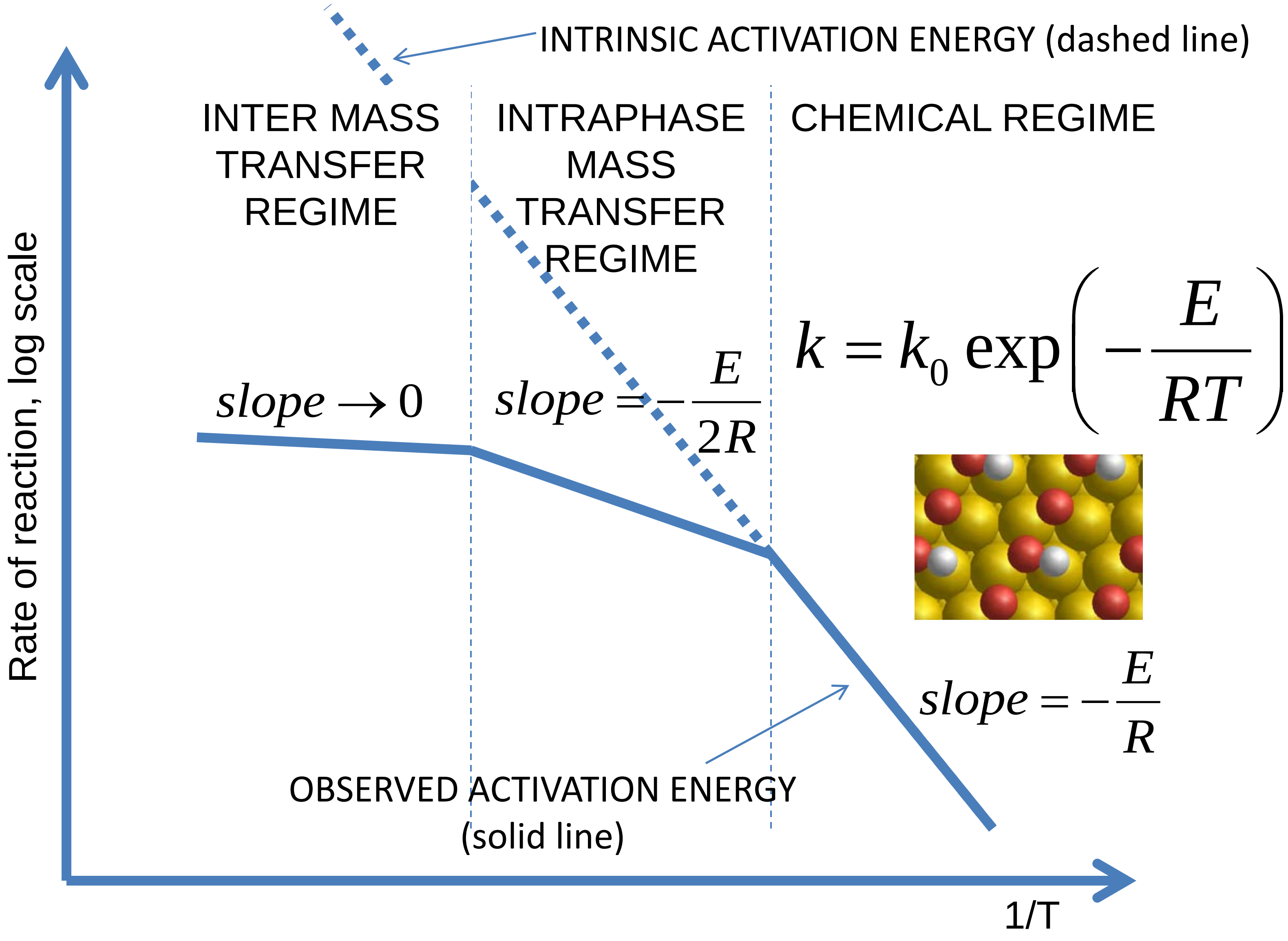
$$k = k_0 \exp\left(-\frac{E}{RT}\right)$$

$$slope = -\frac{E}{2R}$$

$$slope = -\frac{E}{R}$$

OBSERVED ACTIVATION ENERGY (solid line)

Interplay between kinetic and transport



INTRINSIC ACTIVATION ENERGY (dashed line)

INTER MASS TRANSFER REGIME

INTRAPHASE MASS TRANSFER REGIME

CHEMICAL REGIME

$$k = k_0 \exp\left(-\frac{E}{RT}\right)$$

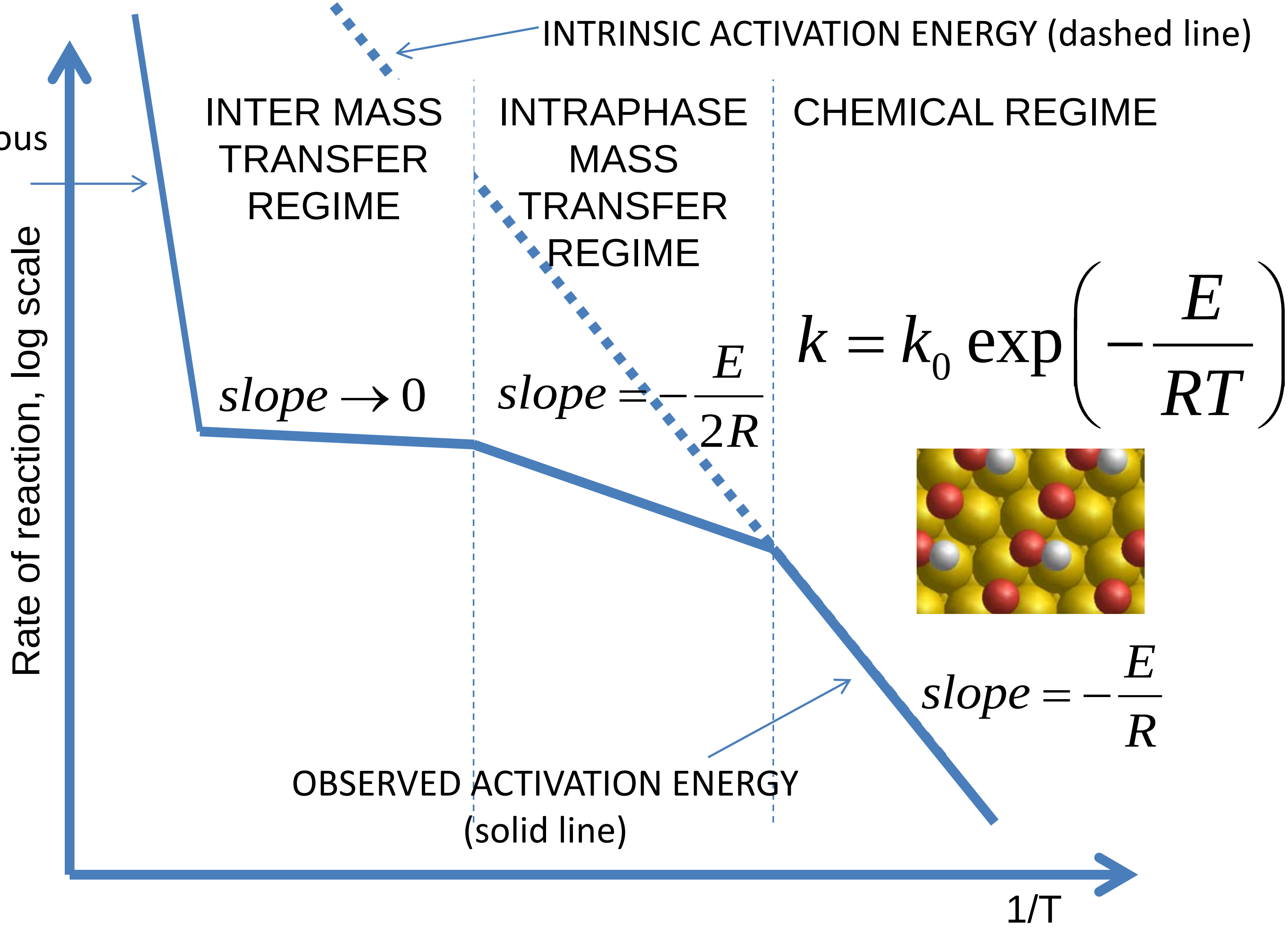
$$slope \rightarrow 0$$

$$slope = -\frac{E}{2R}$$

$$slope = -\frac{E}{R}$$

OBSERVED ACTIVATION ENERGY (solid line)

Interplay between kinetic and transport



INTRINSIC ACTIVATION ENERGY (dashed line)

Homogeneous reaction

INTER MASS TRANSFER REGIME

INTRAPHASE MASS TRANSFER REGIME

CHEMICAL REGIME

$$k = k_0 \exp\left(-\frac{E}{RT}\right)$$

$slope \rightarrow 0$

$slope = -\frac{E}{2R}$

$slope = -\frac{E}{R}$

OBSERVED ACTIVATION ENERGY (solid line)

Rate of reaction, log scale

1/T

Outline

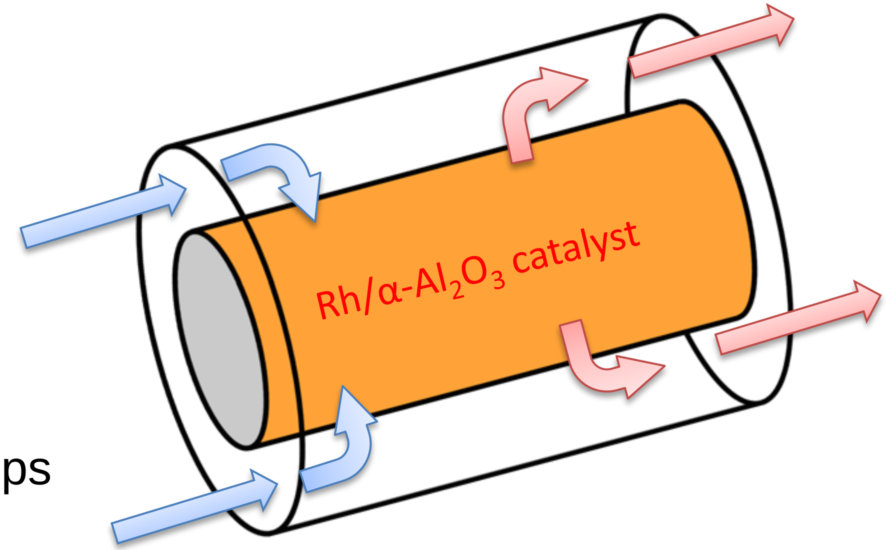
1) Effect of the distribution of the contact times in the reactor on the observed reaction rate

2) Inter-phase and intra-phase transport phenomena and their impact on the observed reaction rate

3) **Show-case: effect of transport phenomena on catalyst reactivity**

4) Take-home messages

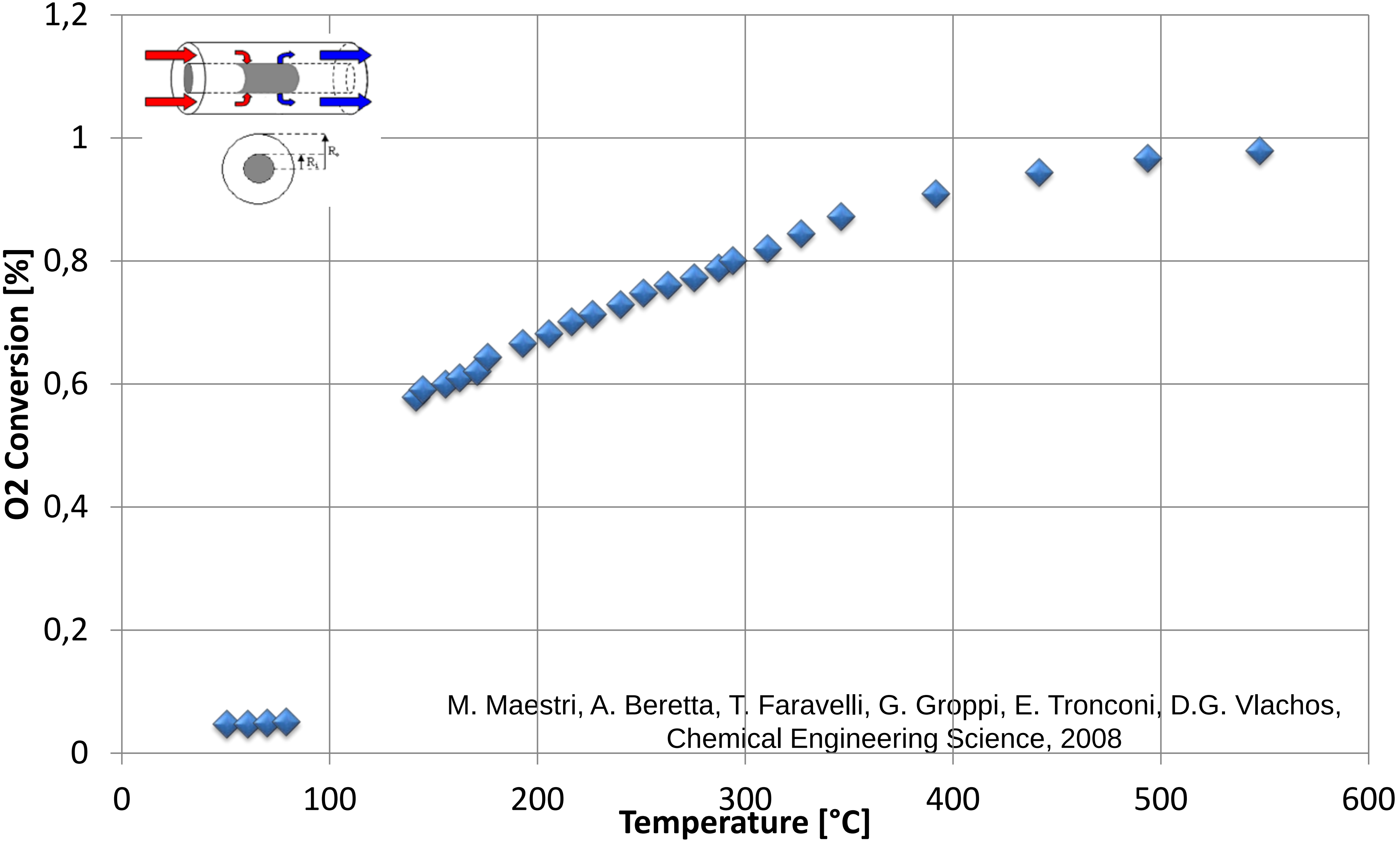
Annular Reactor



- ✓ Laminar flow $\Rightarrow$ negligible pressure drops
- ✓ High GHSV $\Rightarrow$ $10^6 - 10^7$ Nl/Kg_{cat}/h
- ✓ $\Rightarrow$ distance from chemical equilibrium
- ✓ Small annular gap (0.5 mm) and thin catalyst layers
- ✓ Regular geometry (easy modeling)
- ✓ Thermal equilibrium across the section of the ceramic tube
- ✓ Isothermal conditions are easily reached (efficient heat dissipation by radiation, dilution)

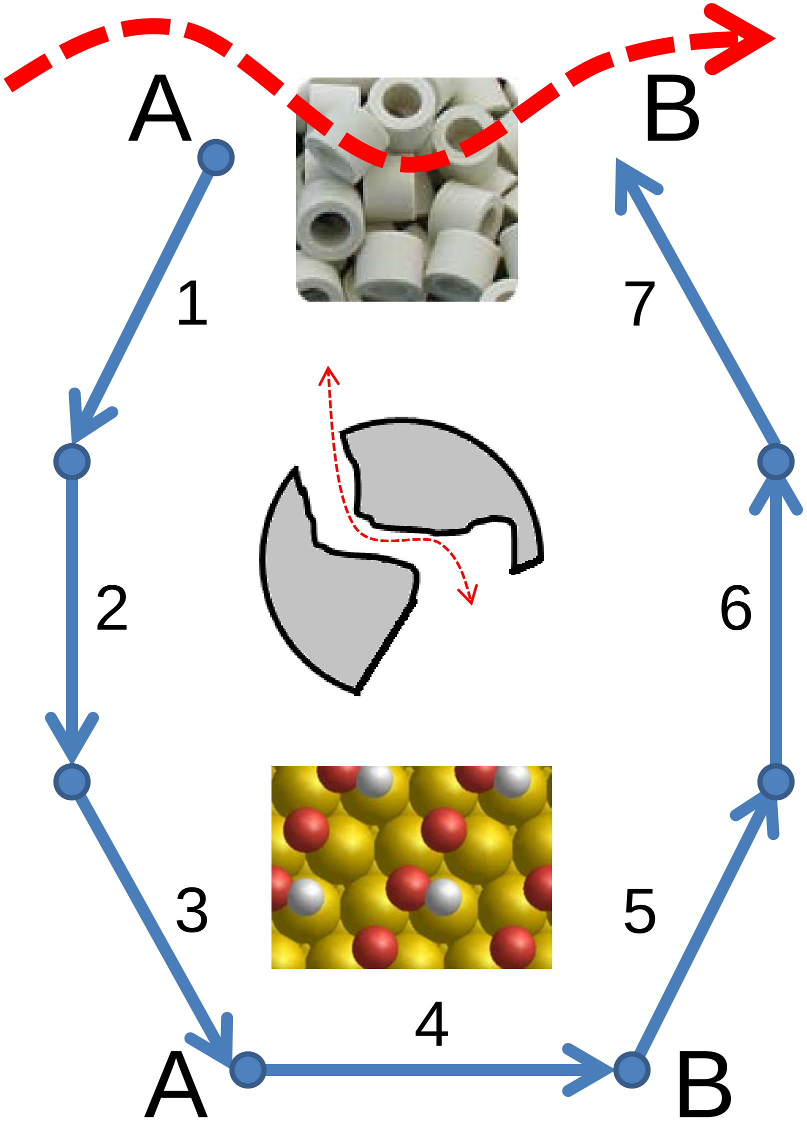
Annular reactor - experiments

Combustion of a fuel-rich H_2 over Rh catalyst in an annular reactor (*)



M. Maestri, A. Beretta, T. Faravelli, G. Groppi, E. Tronconi, D.G. Vlachos, Chemical Engineering Science, 2008

Governing equations



$$\begin{cases}\dfrac{\partial(\rho\omega_i)}{\partial t} + \nabla(\rho\boldsymbol{U}\omega_i) = \nabla(\rho D_i \nabla\omega_i) + \sum_j R_j \nu_{ij} MW_i \\ c_p \dfrac{\partial(\rho T)}{\partial t} + c_p \nabla(\rho\boldsymbol{U}T) = \nabla(\mathrm{k}\nabla \mathrm{T}) + \sum_j R_j \Delta H_j \\ \dfrac{\partial(\rho\boldsymbol{U})}{\partial t} + \nabla(\rho\boldsymbol{U}\boldsymbol{U}) = -\nabla p + \nabla(\mu\nabla\boldsymbol{U}) + \rho\boldsymbol{g} \\ \dfrac{\partial\rho}{\partial t} + \nabla(\rho\boldsymbol{U}) = 0\end{cases}$$

Fluid Phase

$$\begin{cases}\dfrac{\partial(\rho^{mix}\omega_i)}{\partial t} = \nabla\left(\rho^{mix} D_{eff,i} \nabla\omega_i\right) + \left(\sum_j R_{het,j} \nu_{ij} MW_i\right) \cdot a_{cat} \\ c_{p,sol} \dfrac{\partial(\rho_{sol} T)}{\partial t} = \nabla\left(\mathrm{k}_{eff} \nabla \mathrm{T}\right) + \sum_j R_{het,j} \Delta H_j \cdot a_{cat} \\ \Gamma_{site} \dfrac{\partial\vartheta_i}{\partial t} = R_{i,surf}\end{cases}$$

Solid Phase

CatalyticFOAM
multiRegion

Governing equations

Non-catalytic walls

$$\nabla \omega_k \big|_{inert} = 0$$

$$T \big|_{inert} = f\left(t, T\right)$$

$$\nabla T \big|_{inert} = g\left(t, T\right)$$

Catalytic walls

$$\rho \Gamma_{k,mix} \left(\nabla \omega_k\right) \big|_{catalytic} = -\alpha_{cat} \dot{\Omega}_k^{het} \qquad k = 1,\ldots,NG$$

$$\lambda \left(\nabla T\right) \big|_{catalytic} = -\alpha_{cat} \sum_{j=1}^{NR} \Delta H_j^{het} \dot{r}_j^{het}$$

$$\sigma_{cat} \frac{\partial \theta_i}{\partial t} = \dot{\Omega}_i^{het} \qquad i = 1,\ldots,NS$$

Adsorbed (surface) species

Detailed microkinetic models

1. H2+2Rh(s)=>2H(s)
2. 2H(s)=>H2+2Rh(s)
3. O2+2Rh(s)=>2O(s)
4. 2O(s)=>O2+2Rh(s)
5. OH(s)+Rh(s)=>H(s)+O(s)
6. H(s)+O(s)=>OH(s)+Rh(s)
7. H2O(s)+Rh(s)=>H(s)+OH(s)
8. H(s)+OH(s)=>H2O(s)+Rh(s)
9. H2O(s)+O(s)=>2OH(s)
10. 2OH(s)=>H2O(s)+O(s)
11. OH+Rh(s)=>OH(s)
12. OH(s)=>OH+Rh(s)
13. H2O+Rh(s)=>H2O(s)
14. H2O(s)=>H2O+Rh(s)
15. H+Rh(s)=>H(s)
16. H(s)=>H+Rh(s)
17. O+Rh(s)=>O(s)
18. O(s)=>O+Rh(s)

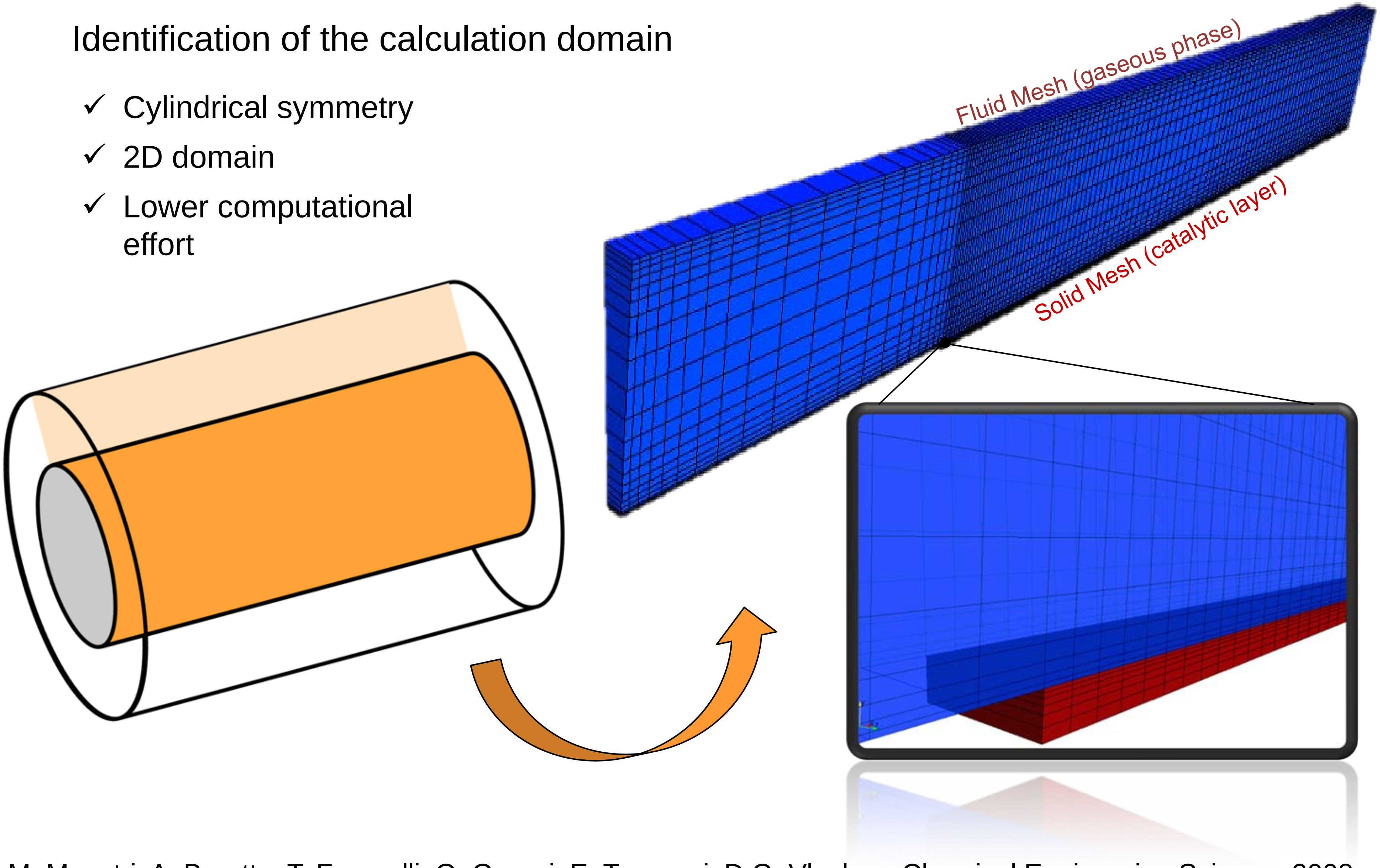
$$r_j = A_j \cdot T^{\beta_j} \cdot \exp\left(-\frac{E_{att,j}(\theta_i)}{RT}\right) \prod_{i=1}^{NC} (c_i)^{\nu_{ij}}$$

M. Maestri, Microkinetic analysis of complex chemical processes at surface, in "New strategy for chemical synthesis and catalysis", Wiley-VCH (2012)

Fluid and solid regions

Identification of the calculation domain

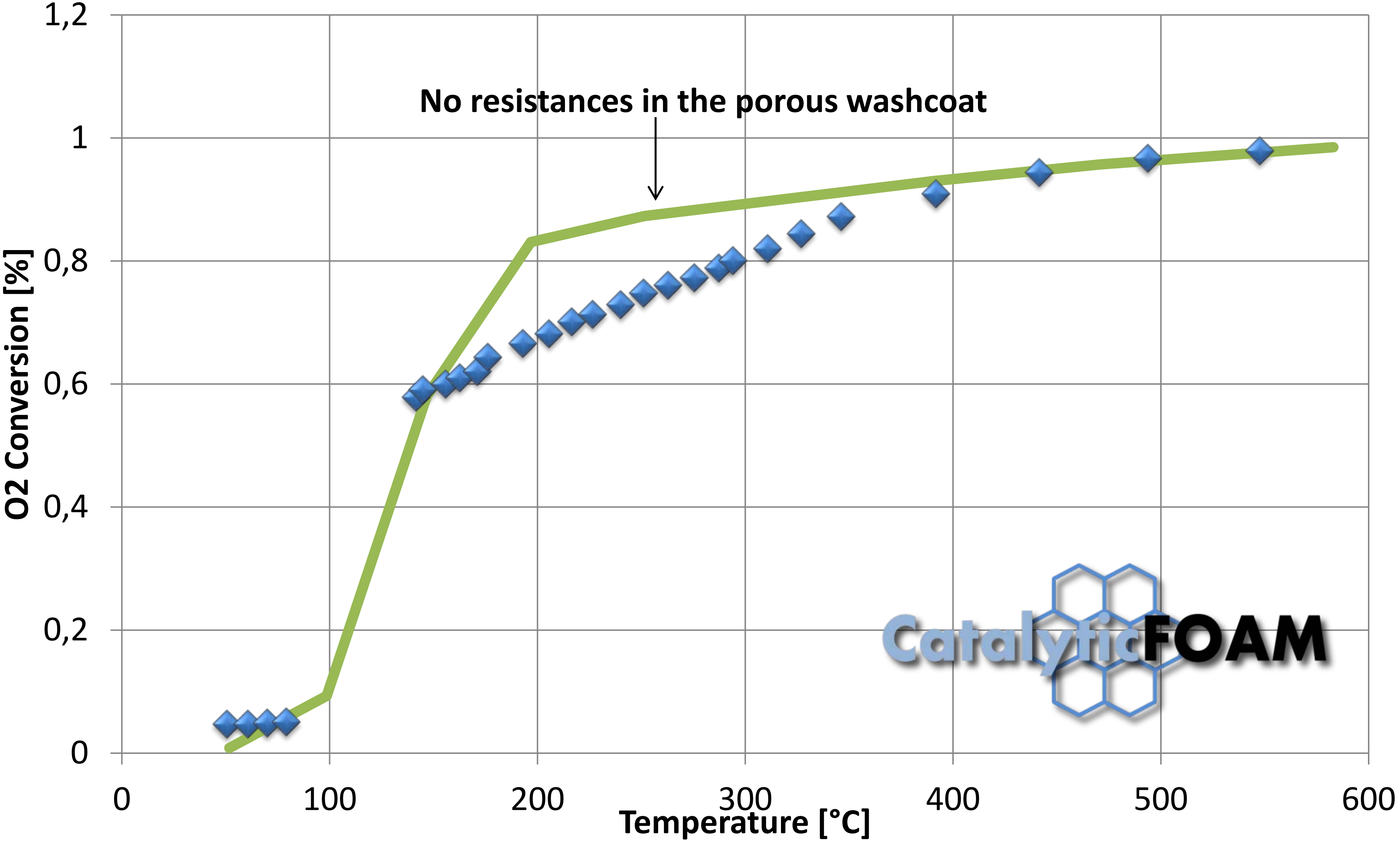
- ✓ Cylindrical symmetry
- ✓ 2D domain
- ✓ Lower computational effort



M. Maestri, A. Beretta, T. Faravelli, G. Groppi, E. Tronconi, D.G. Vlachos, Chemical Engineering Science, 2008

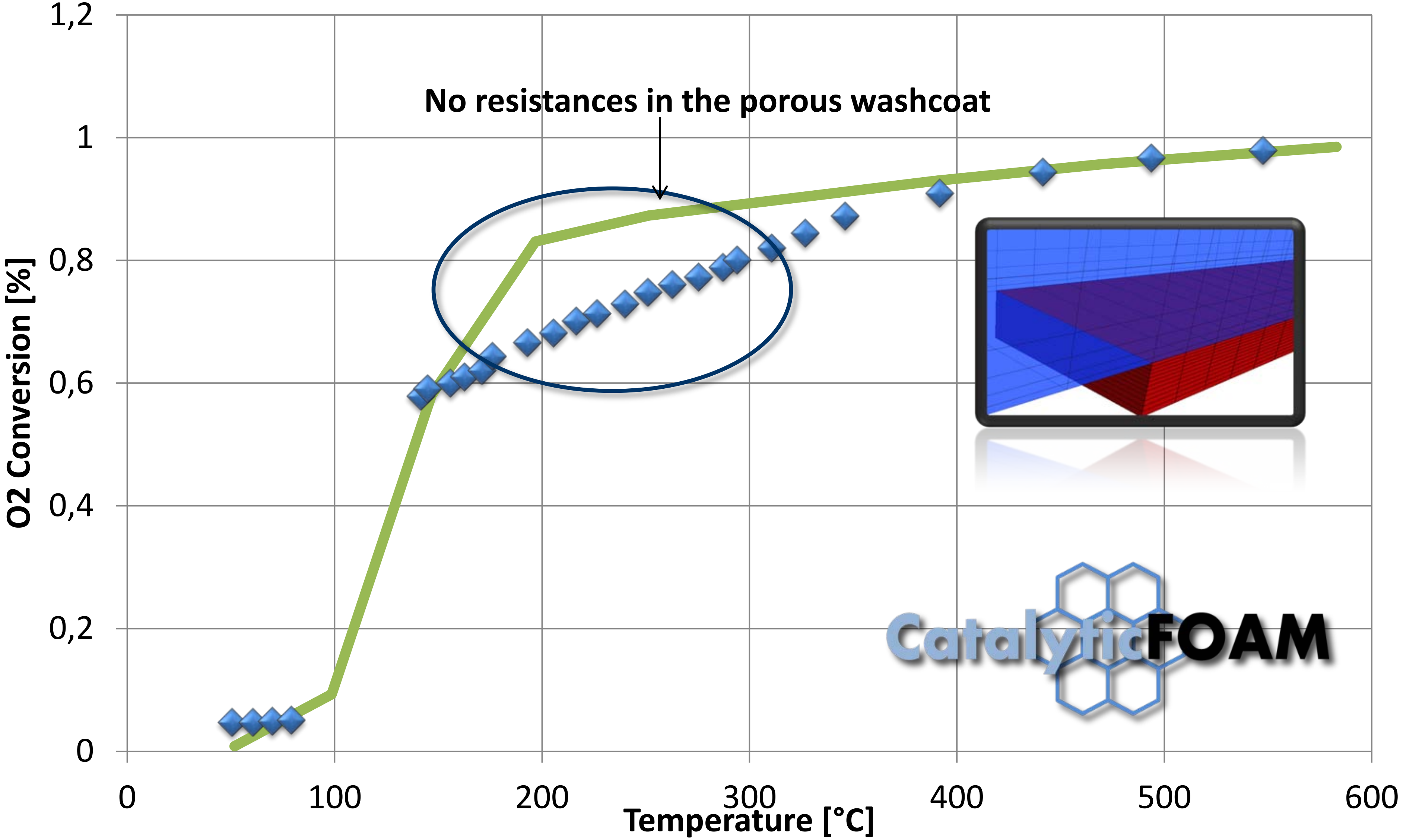
Annular reactor

Combustion of a fuel-rich H_2 over Rh catalyst in an annular reactor $^{(*)}$



Annular reactor

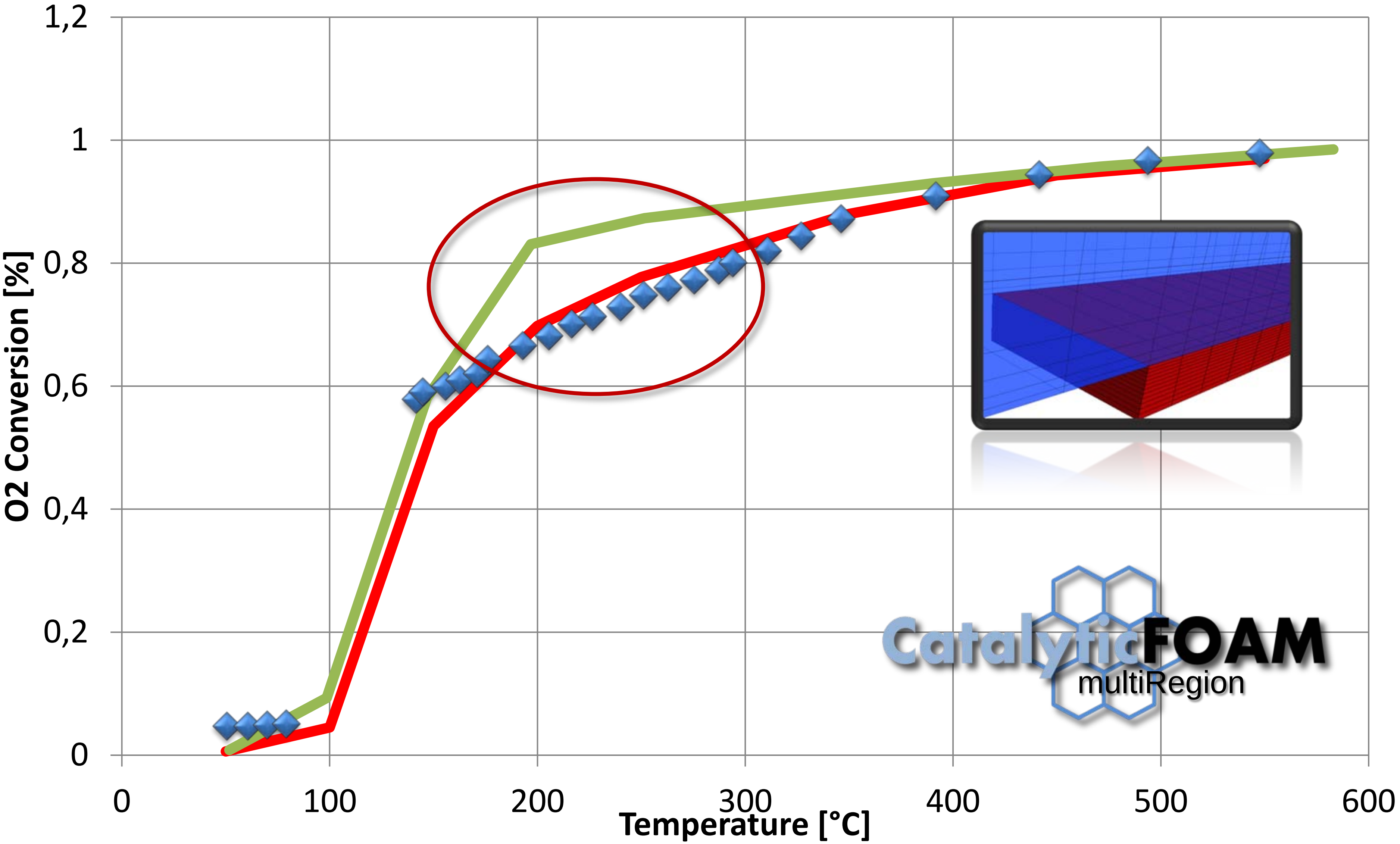
Combustion of a fuel-rich H_2 over Rh catalyst in an annular reactor (*)



No resistances in the porous washcoat

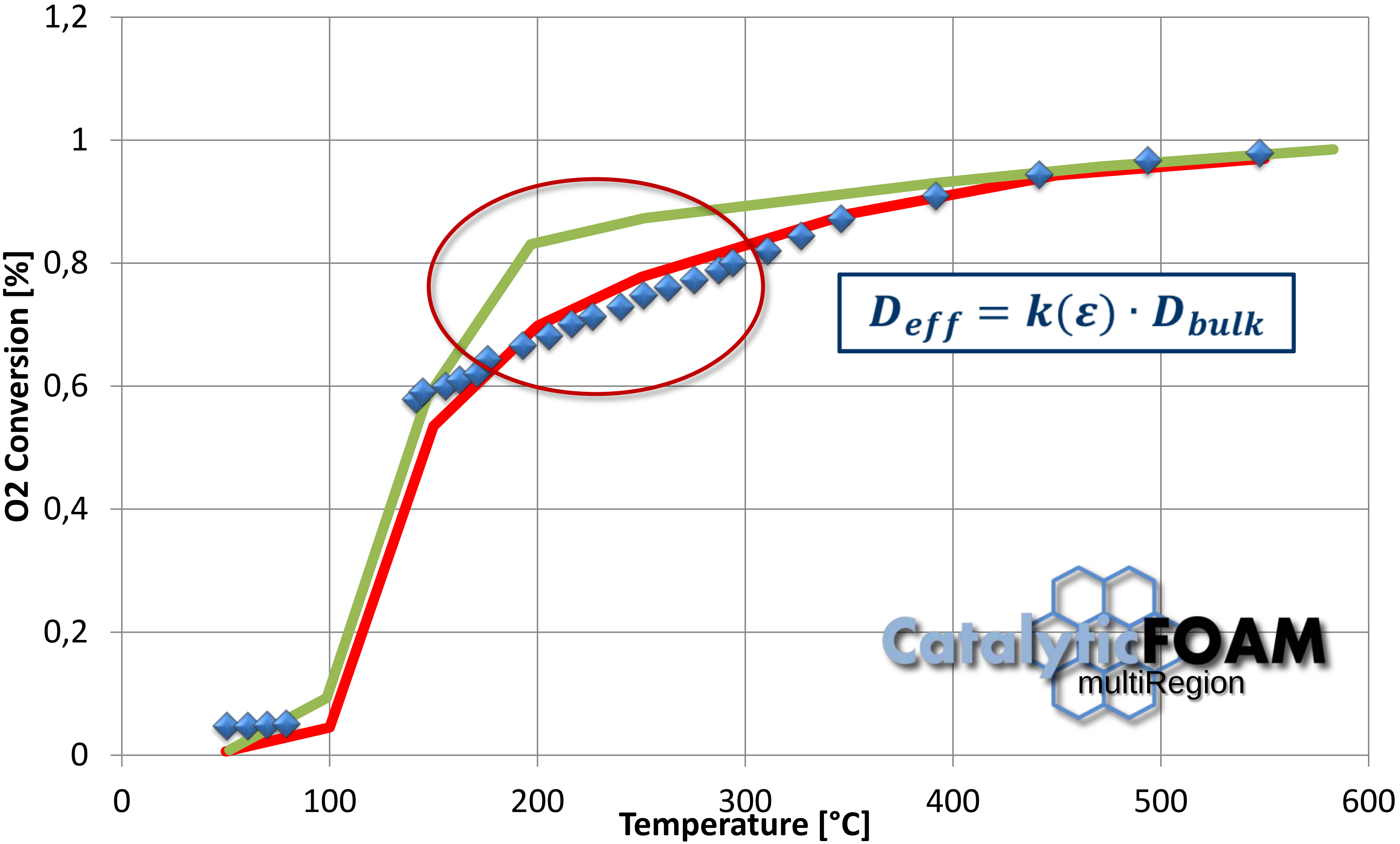
Model results

Combustion of a fuel-rich H_2 over Rh catalyst in an annular reactor



Model results

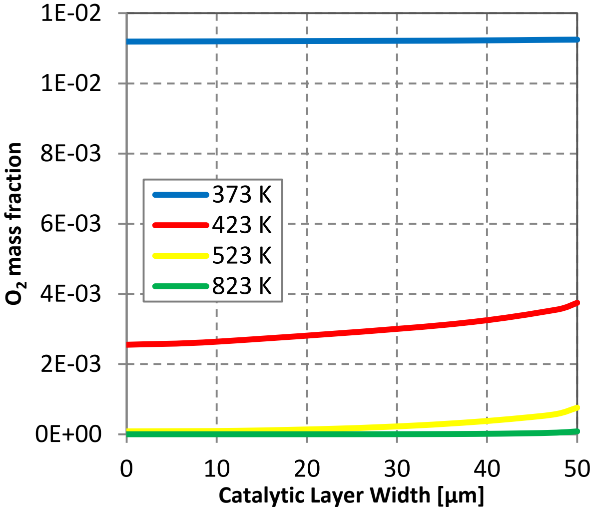
Combustion of a fuel-rich H_2 over Rh catalyst in an annular reactor

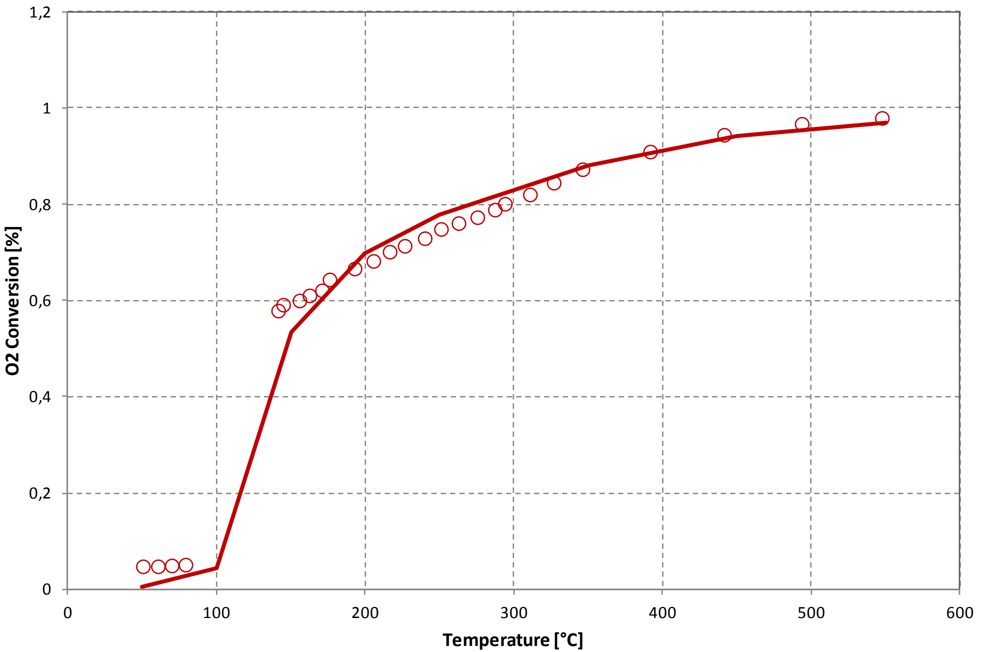


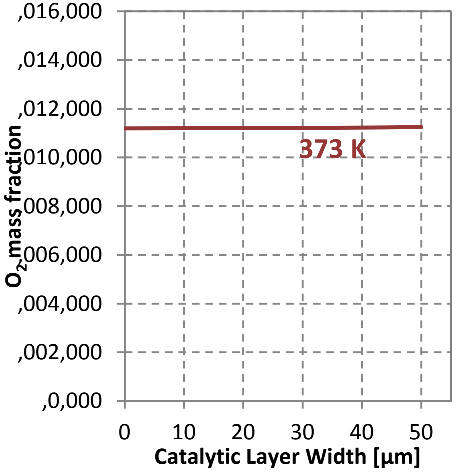
$$D_{eff} = k(\varepsilon) \cdot D_{bulk}$$

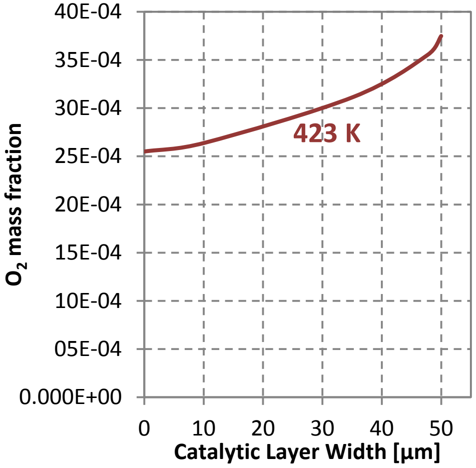
Intraphase gradients

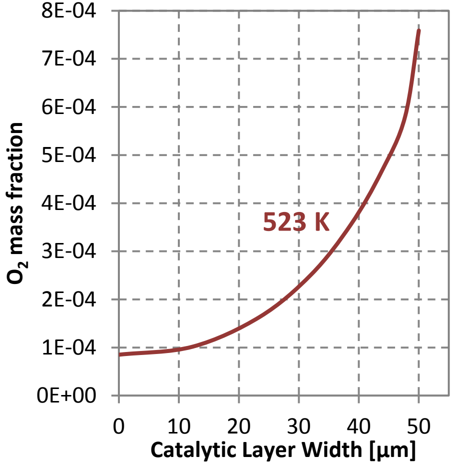
Different controlling regimes at different T

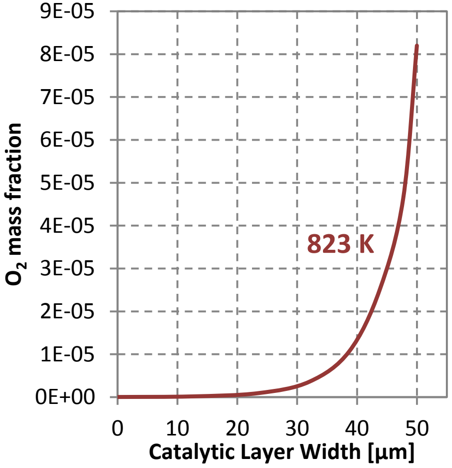




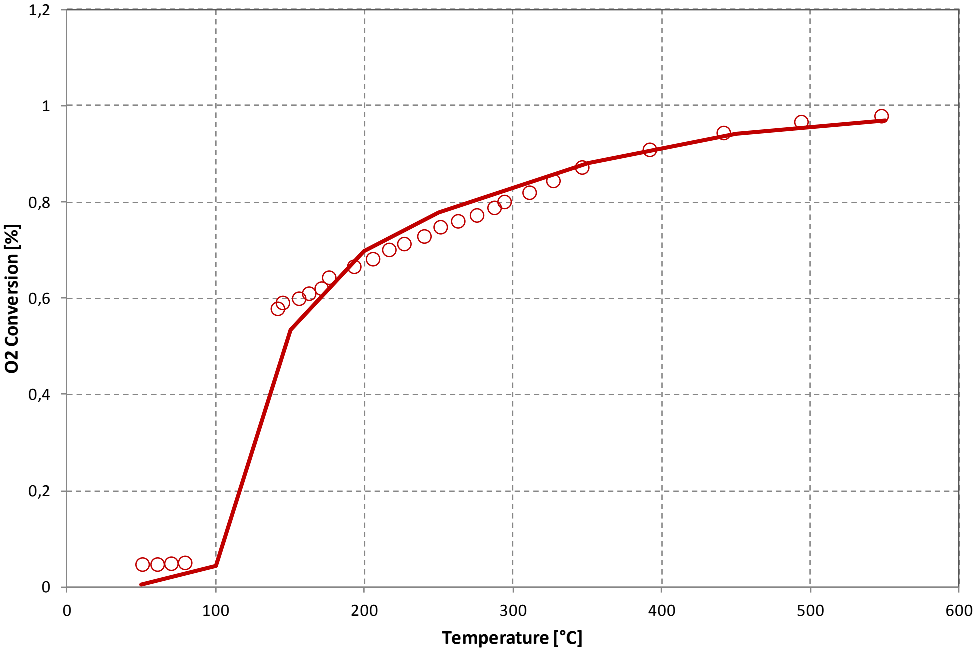


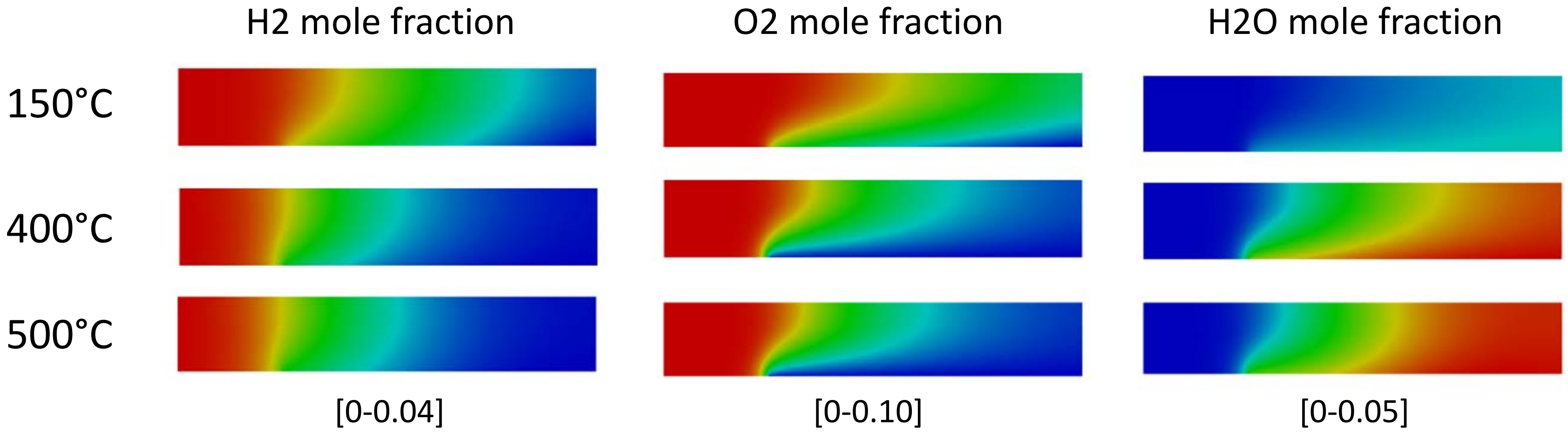






Interphase gradients





Outline

1) Effect of the distribution of the contact times in the reactor on the observed reaction rate

2) Inter-phase and intra-phase transport phenomena and their impact on the observed reaction rate

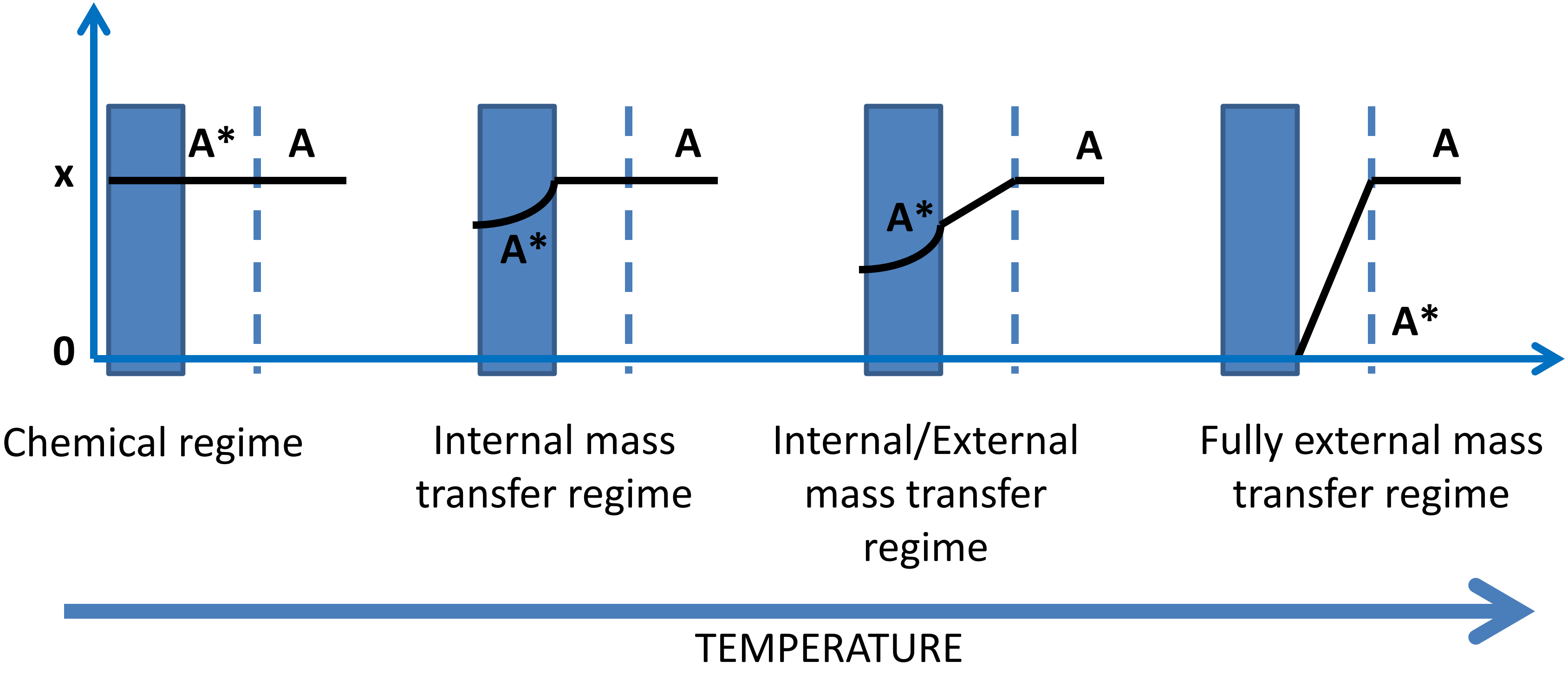
3) Show-case: effect of transport phenomena on catalyst reactivity

4) **Take-home messages**

Take-home messages

1) Physical transport may have a strong influence on the rate of the overall process and may introduce additional dependences on the operating conditions

2) The observable reaction rate may differ substantially from the intrinsic rate of the chemical transformation under bulk fluid phase composition



Take-home messages

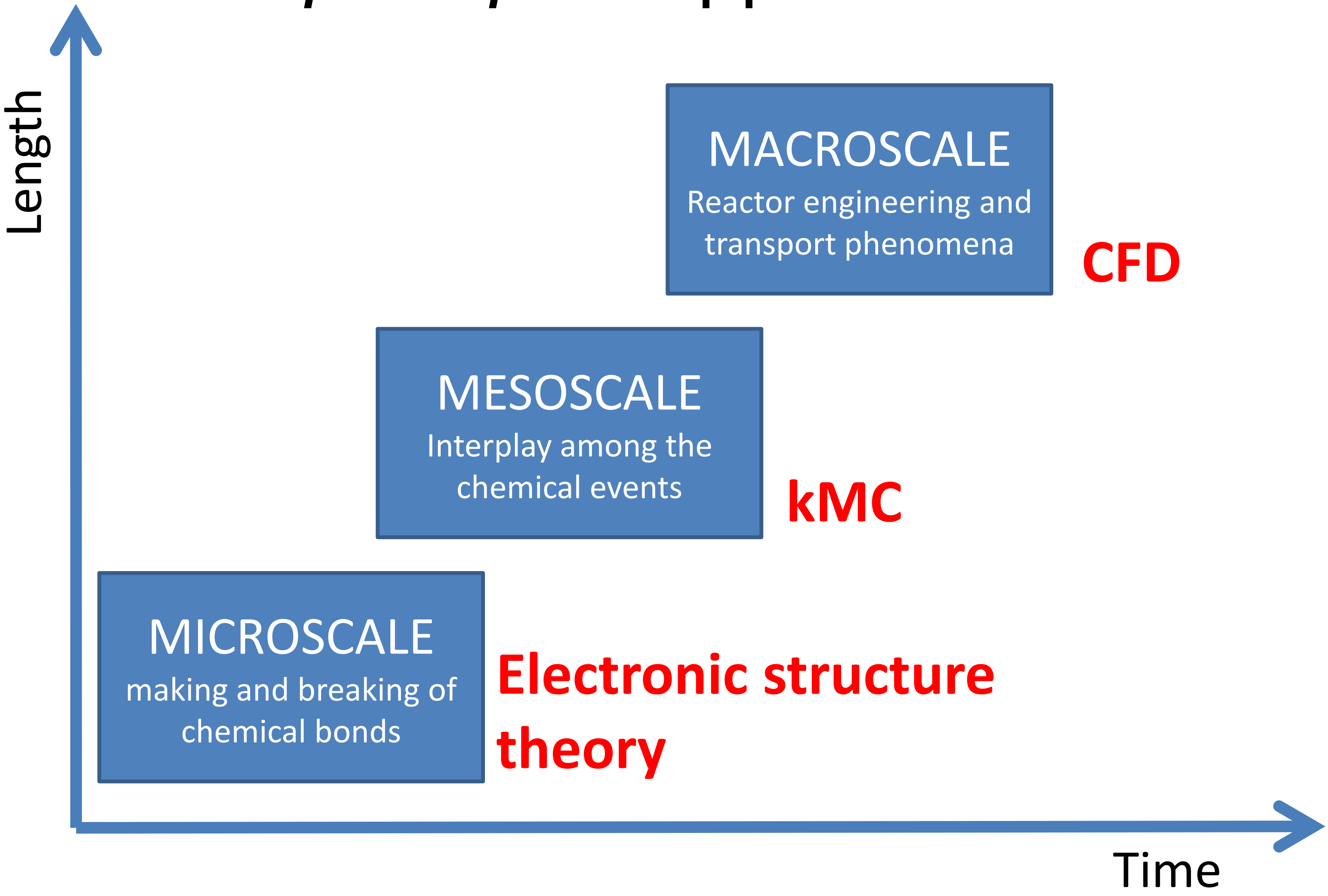
1) Physical transport may have a strong influence on the rate of the overall process and may introduce additional dependences on the operating conditions

2) The observable reaction rate may differ substantially from the intrinsic rate of the chemical transformation under bulk fluid phase composition

3) You need to be aware of such interplay and related effects in order to:
    1) understand what you are measuring
    2) understand what you are comparing
    3) scale-up properly and successfully your reaction
    4) force your catalyst to the desired observed functionality (selectivity €€€!! – safe operation)

4) Reactivity measurement is intrinsically a multiscale phenomenon: make sure you minimize the effect of transport (dilution, temperature, geometry)

A *first-principles* approach to CRE



Length

MACROSCALE
Reactor engineering and transport phenomena

CFD

MESOSCALE
Interplay among the chemical events

kMC

MICROSCALE
making and breaking of chemical bonds

Electronic structure theory

Time

Laboratory
of Catalysis and
Catalytic Processes
LCCP

Politecnico di Milano

Raffaello, The school of Athens, 1509, Apostolic Palace, Roma

Thank you for your attention!

www.catalyticfoam.polimi.it

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