Process Intensification and Green Chemistry

Miniaturization

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Master of Science in Chemical Engineering and Biotechnology
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Content

- Characteristic process times
- Process efficiency
- Number of operation units (NOU)
- Coupling of characteristic times
- Effect of scale on process parameters

Characteristic times approach

In chemical reactors, a variety of phenomena may contribute to the overall reactor performance:

- Homogeneous and/or heterogeneous reactions
- Heat and/or mass transfer in fluid phases
- Fluid/fluid or fluid/wall mass transfer
- Physical effects (gravity, surface tension, electrical forces,…)

⇨A simple approach to understand their relative impacts consists in **comparing their characteristic times**

Commenge and Falk (2009). Aubin, Commenge, Falk, Prat (2015)

The reference time

The reference time is a function of the type of reactor:

- Batch reactor: residence time
- Semi-batch reactor: feed time
- Continuous reactors: space time $\tau = \frac{V}{Q}$
- Heterogeneous reactor: modified space time $\tau_{mod} = \frac{m_{cat}}{Q}$

The fundamental characteristic times

The characteristic time (t_{op}) for a chemical/physical phenomenon is linked to the time required for the system to evolve from a non-equilibrium to an equilibrium state

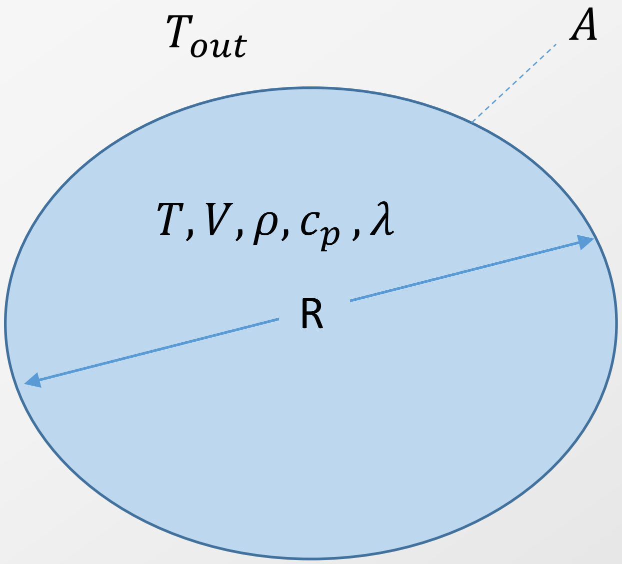
- In practice, for a property x:

$$t_{op} = \frac{x}{Rate\ of\ transformation\ of\ x}$$

- Example:
  - First-order homogeneous reaction
  - Property x: molar concentration *c*
  - Rate of transformation of *c*: $r = kc$

$$\Rightarrow \boldsymbol{t_{op}} = \frac{Initial\ conc.\left[\frac{mol}{m^3}\right]}{Initial\ rate\left[\frac{mol}{m^3 \cdot s}\right]} = \frac{c_0}{k \cdot c_0} = \frac{\mathbf{1}}{\boldsymbol{k}}[s]$$

Heat conduction



Heat content

$$Q_0 = \rho c_p (T - T_{out}) \quad \left[\frac{J}{m^3}\right]$$

Heat transfer rate

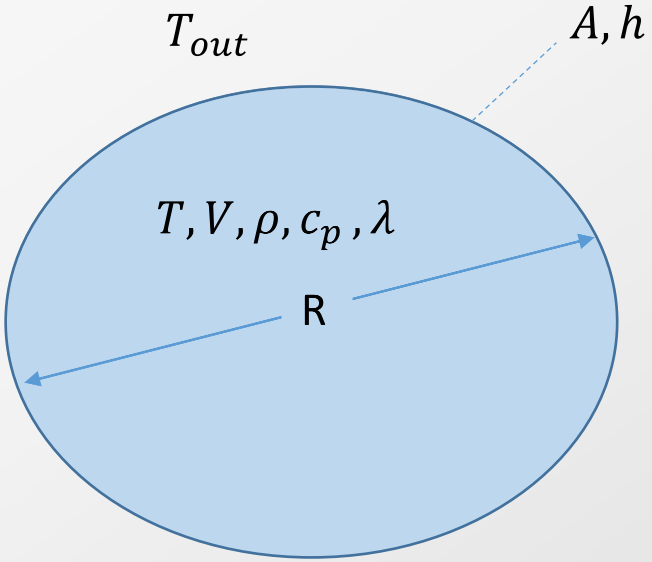
$$\frac{A}{V} \propto \frac{1}{R}$$

$$\dot{Q}_0 = \lambda \frac{A}{V} \frac{(T - T_{out})}{R} \propto \lambda \frac{(T - T_{out})}{R^2} \quad \left[\frac{W}{m^3}\right]$$

Characteristic time

$$\boldsymbol{t_{cond}} = \frac{Q_0}{\dot{Q}_0} = \frac{\rho c_p (T - T_{out})}{\lambda \frac{(T - T_{out})}{R^2}} = \boldsymbol{\frac{\rho c_p}{\lambda} R^2} \quad [s]$$

Heat convection



Heat content

$$Q_0 = \rho c_p (T - T_{out}) \quad \left[\frac{J}{m^3}\right]$$

Heat transfer rate

$$Nu = \frac{hR}{\lambda} \rightarrow h = \frac{Nu\lambda}{R}$$

$$\frac{A}{V} \propto \frac{1}{R}$$

$$\downarrow$$

$$\dot{Q}_0 = h\frac{A}{V}(T - T_{out}) \propto h\frac{(T - T_{out})}{R} = \frac{Nu\lambda(T - T_{out})}{R^2} \quad \left[\frac{W}{m^3}\right]$$

Characteristic time

$$\boldsymbol{t_{heat}} = \frac{Q_0}{\dot{Q}_0} = \frac{\rho c_p (T - T_{out})}{\frac{Nu\lambda(T - T_{out})}{R^2}} = \boldsymbol{\frac{\rho c_p}{Nu\lambda} R^2} \quad [s]$$

Fundamental characteristic times

Phenomenon	Characteristic time	Example of R
nth-order homogeneous reaction	$t_{hom} = \frac{1}{kc_0^{n-1}}$	
Gravity	$t_{grav} = \sqrt{\frac{2R}{g}}$	Height, channel radius
Viscosity	$t_{visc} = \frac{\rho R^2}{\mu}$	Droplet radius, channel radius
Surface tension	$t_{surf} = \sqrt{\frac{\rho R^3}{2\sigma\cos(\theta)}}$	Droplet radius, channel radius
1st order heterogeneous reaction	$t_{het,1} = \frac{R}{2k_s}$	Reciprocal surface-to-volume ratio
nth order heterogeneous reaction	$t_{het,1} = \frac{R}{2k_s c_0^{n-1}}$	Reciprocal surface-to-volume ratio

Fundamental characteristic times

Phenomenon	Characteristic time	Example of R
Diffusive mass transfer	$t_{diff} = \frac{R^2}{D}$	Diffusion path length
Convective mass transfer (constant Sh)	$t_{mass} = \frac{R^2}{ShD}$	Channel radius
Heat conduction	$t_{cond} = \frac{\rho c_p R^2}{\lambda}$	Length of heat conduction, wall thickness
Convective heat transfer (constant Nu)	$t_{heat} = \frac{\rho c_p}{\lambda} \frac{R^2}{Nu}$	Channel radius

Comments on characteristic times, taking diffusive mass transfer as an example

- Definitions of t_{diff} depend on what is actually meant by diffusion *time*
  - ➢ Time to achieve complete mixing? Would be infinite!
  - ➢ Time to achieve 90% mixing?
  - ➢ Etc.
- A simple solution is to use $t_{diff} = R^2/D$, where R is the diffusion path length. After that time, full mixing is obviously not achieved, but it provides an “order of magnitude” value which is useful to either:
  - ➢ Compare the diffusion time to the characteristic times of other processes (reaction, heat transfer, etc.);
  - ➢ Assess the effect of system size (characterized by R) on the characteristic time of the process of concern (diffusion in this case). There is no need for a complex shape factor for these purposes.

⇨ Don’t focus too much on the absolute value of the characteristic times that you get from the equations. Instead, use them to assess the changes in the characteristic times when varying the system size, or on the relative values between the characteristic times of two different processes.

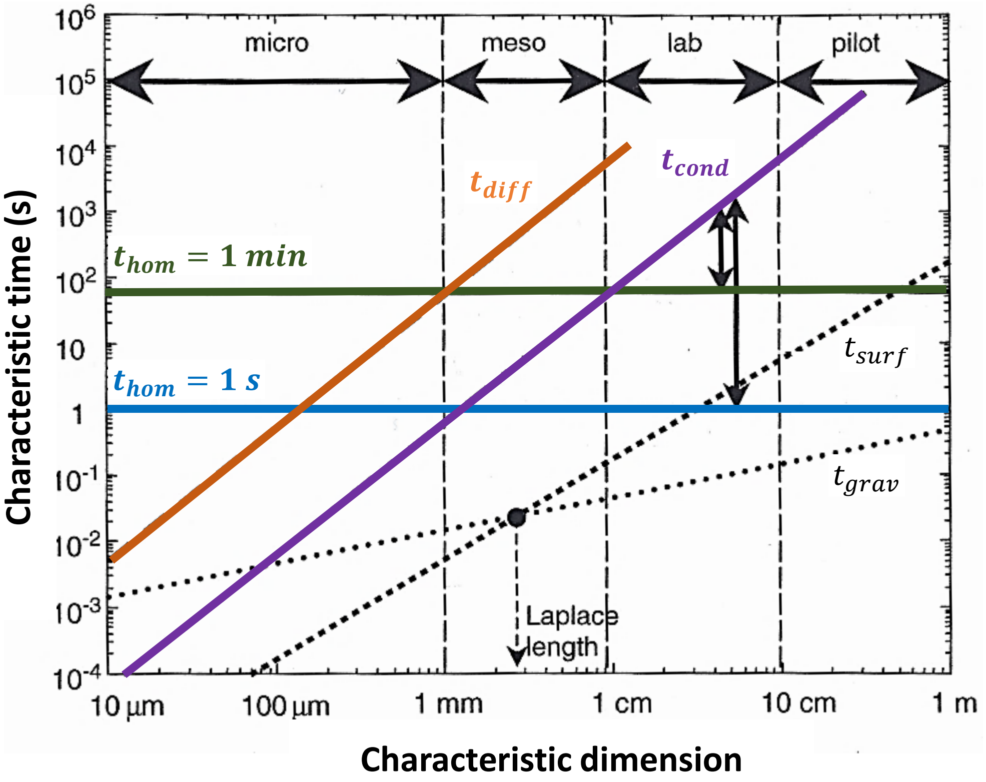
Opportunities of miniaturization

The different size-dependence of the various physical and chemical phenomena lead to the following opportunities:

- Selective intensification of heat transfer vs reaction
  - More homogeneous (or isothermal) temperature for kinetic studies or controlling fast exothermic reactions while preventing runaway.
- Selective intensification of mass transfer vs reaction
  - Increase in conversion and selectivity of competing mass-transfer limited heterogeneous reactions
  - Increase in selectivity of mass-transfer limited heterogeneous vs homogeneous reactions
- Selective intensification of heterogeneous reaction vs homogeneous reaction (“grid effect”)
  - E.g., control radical chain reactions leading to explosions in order to operate microreactors in the explosion regime

Scales of homogeneous chemistry

Characteristic times as a function of dimension



Air/water systems → Laplace length~3 mm

Below the Laplace length, surface tension effects greater than gravity effects

Process efficiency

The process efficiency η is the fraction of the maximum amount of a property *x*, which has been transferred or converted:

- In practice, for a property *x*:

$$\eta = \frac{x\ transferred\ or\ converted}{Maximum\ transferrable\ or\ convertible\ x}$$

- Example
  - Chemical reaction: $\eta = \frac{c_0 - c}{c_0} = conversion$

Process efficiency

Example 1: first order homogeneous reaction in a plug-flow reactor

- Variation of property *c* proportional to itself (first-order process): $r = kc$
- PFR at steady-state: $\frac{dc}{d\tau} = -kc \rightarrow c = c_0 \exp(-k\tau)$

$$⇨ \; \eta = \frac{c_{in} - c_{out}}{c_{in} - 0} = 1 - \exp\left(-\frac{\tau}{t_{op}}\right) = \boldsymbol{1 - exp(-Da)}$$

where :

$$t_{op} = t_{hom,1} = \frac{1}{k}$$

$$Da = \frac{\text{ref. time}}{\text{charact. time}} = \frac{\tau}{t_{op}} = k\tau \quad \text{(Damköhler number)}$$

Process efficiency

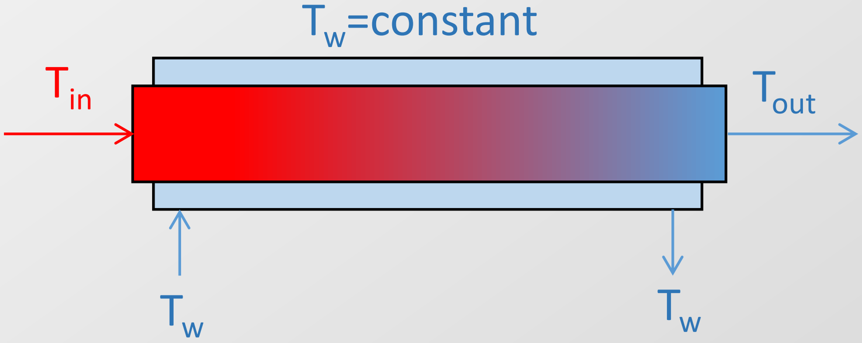
Example 2: heat transfer in a plug-flow heat exchanger

- Variation of property *T* proportional to itself (first-order process): $\frac{dT}{d\tau} = -\frac{UA}{\rho V c_p}(T - T_w)$

$$\Rightarrow \boldsymbol{\eta} = \frac{T_{in} - T_{out}}{T_{in} - T_w} = 1 - \exp\left(-\frac{\tau}{t_{op}}\right) = \mathbf{1} - \boldsymbol{exp}(-\boldsymbol{NTU})$$

Where:

$$t_{op} = t_{heat} = \frac{\rho V c_p}{UA}$$



$$NTU = \frac{\tau UA}{\rho V c_p} = \frac{\tau}{t_{op}}$$

(Nb. of transfer units)

Process efficiency

Example 3: first order homogeneous reaction in CSTR

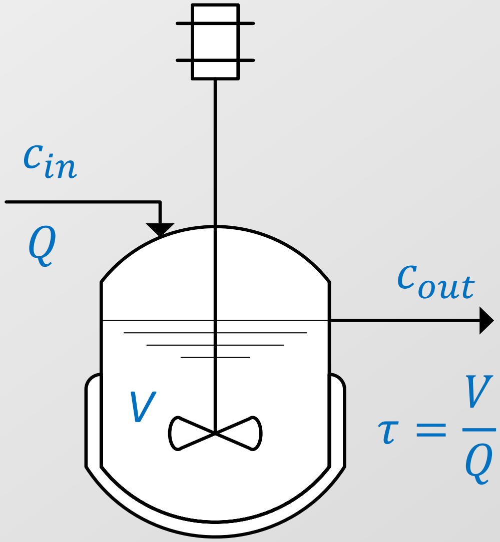
- Variation of property *c* is proportional to itself (first-order process): $r = kc$
- CSTR at steady-state: $\frac{c_{in} - c_{out}}{\tau} = r = kc_{out}$

$$\Rightarrow \eta = \frac{c_{in} - c_{out}}{c_{in} - 0} = \frac{\frac{\tau}{t_{op}}}{1 + \frac{\tau}{t_{op}}} = \frac{Da}{1 + Da}$$

where :

$$t_{op} = t_{hom,1} = \frac{1}{k}$$

$$Da = k\tau$$

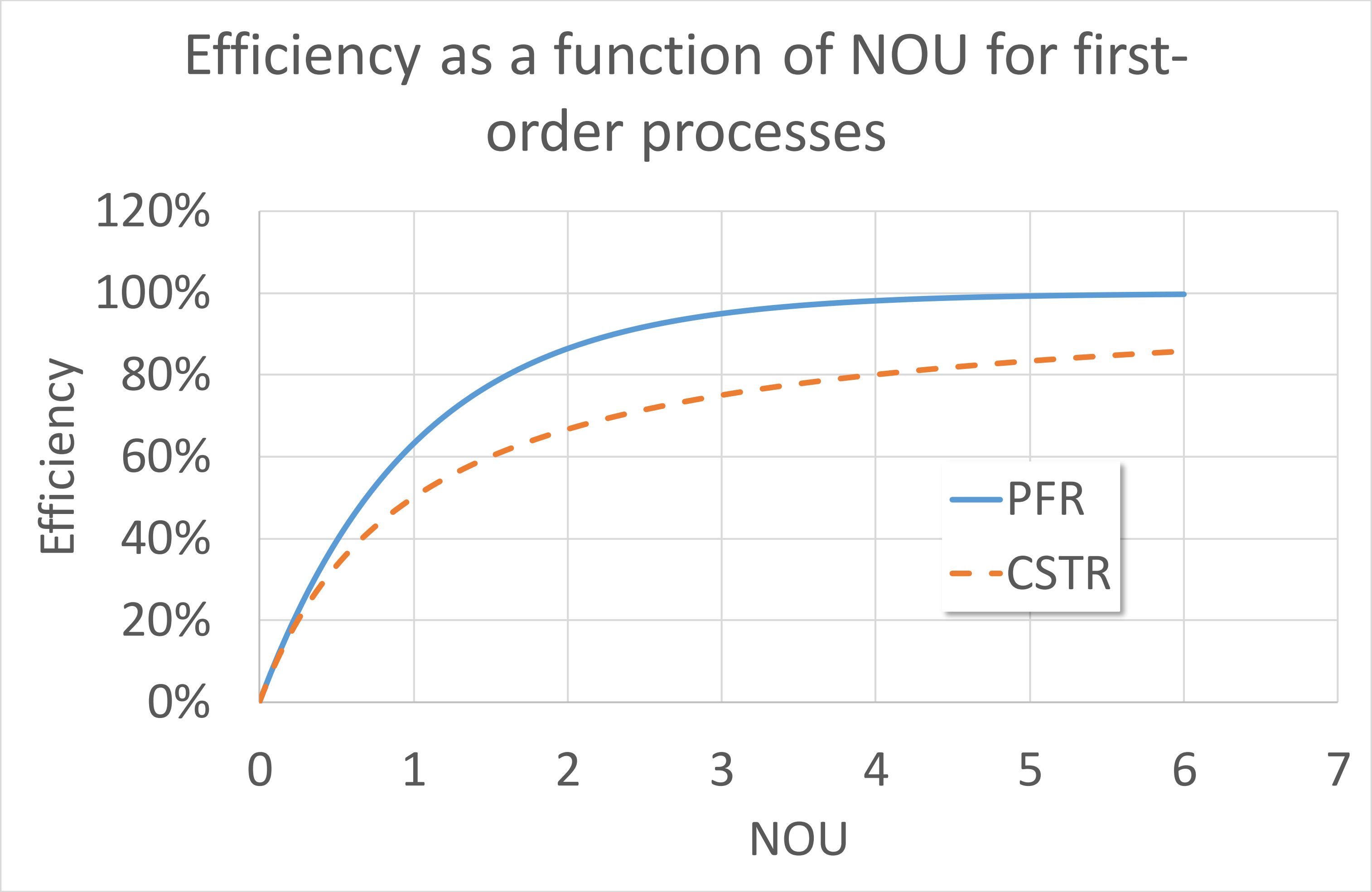


Number of operation units (NOU)

- A generalization of NTU (heat/mass transfer) and Damköhler number (reaction) concepts:

$$NOU = \frac{reference\ time}{characteristic\ time\ of\ global\ operation} = \frac{\tau}{t_{op}}$$

Effect of NOU on η

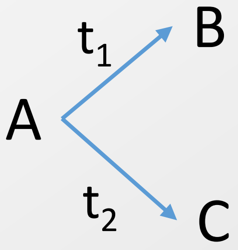


Coupling of characteristic times

- Parallel coupling

$$\frac{1}{t_{glob}} = \frac{1}{t_1} + \frac{1}{t_2}$$

Example: parallel reactions



Fastest phenomenon dominates

- Consecutive coupling

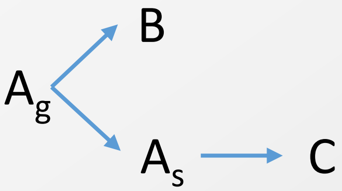
$$t_{glob} = t_1 + t_2$$

Example: consecutive reactions

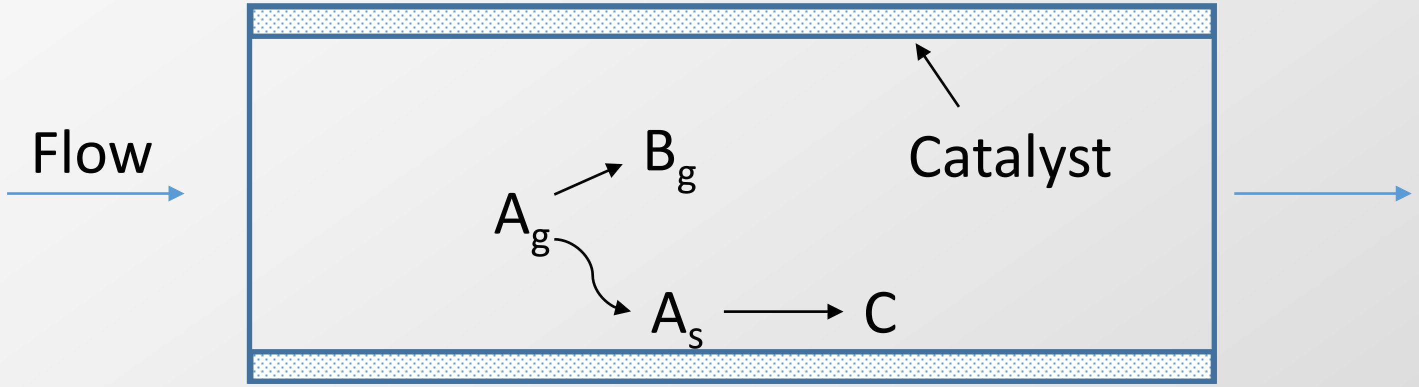
$$A \xrightarrow{t_1} B \xrightarrow{t_2} C$$

Slowest phenomenon dominates

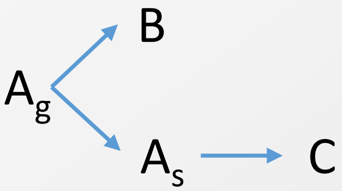
Example 1 of coupling



- Parallel-consecutive coupling:
  - 1^{st} order hom. reaction A → B $\quad t_{hom} = \frac{1}{k_{hom}}$
  - Mass transfer A → catalyst surface $\quad t_{mass} = \frac{R^2}{ShD_m}$
  - 1^{st} order het. reaction A → C $\quad t_{het} = \frac{R}{2k_s}$



Example 1 of coupling



$$\frac{1}{t_{op}} = \frac{1}{t_{hom}} + \frac{1}{t_{mass} + t_{het}}$$

$$\Rightarrow t_{op} = \frac{1}{k_{hom} + \frac{1}{\frac{R^2}{ShD_m} + \frac{R}{2k_s}}}$$

- Conversion *X* for first-order process in PFR:

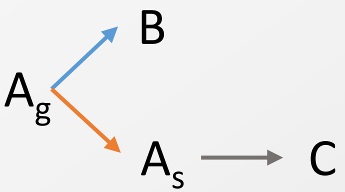
Process efficiency

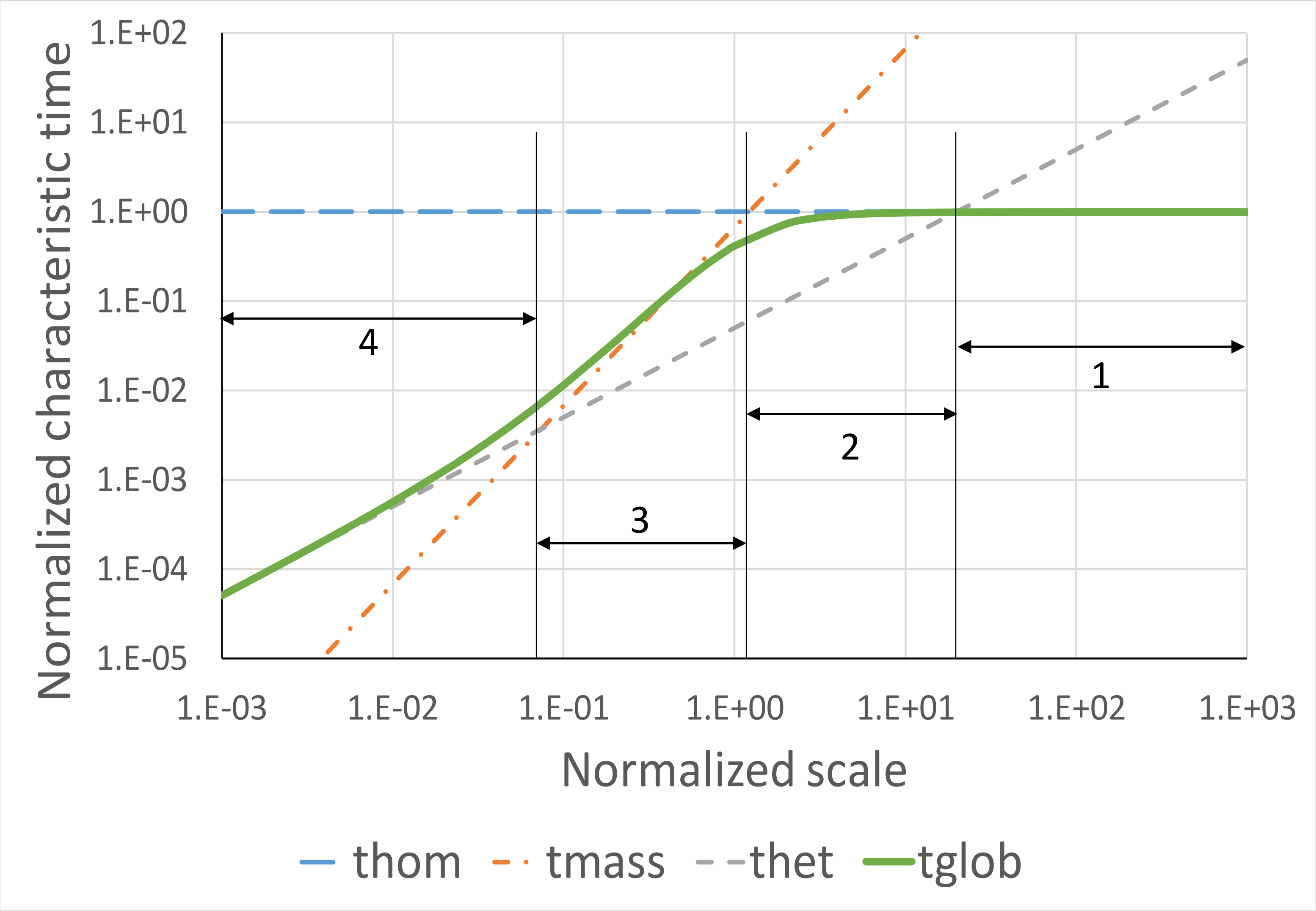
No of operation units

$$\eta = X = 1 - \exp(-NOU) = 1 - \exp\left(-\frac{\tau}{t_{op}}\right)$$

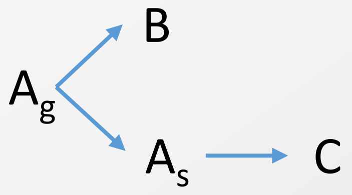
Example 1 of coupling

Effect of scale on process time





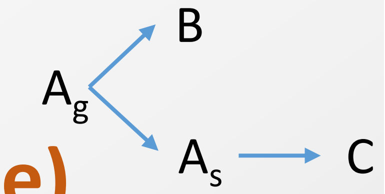
Example 1 of coupling

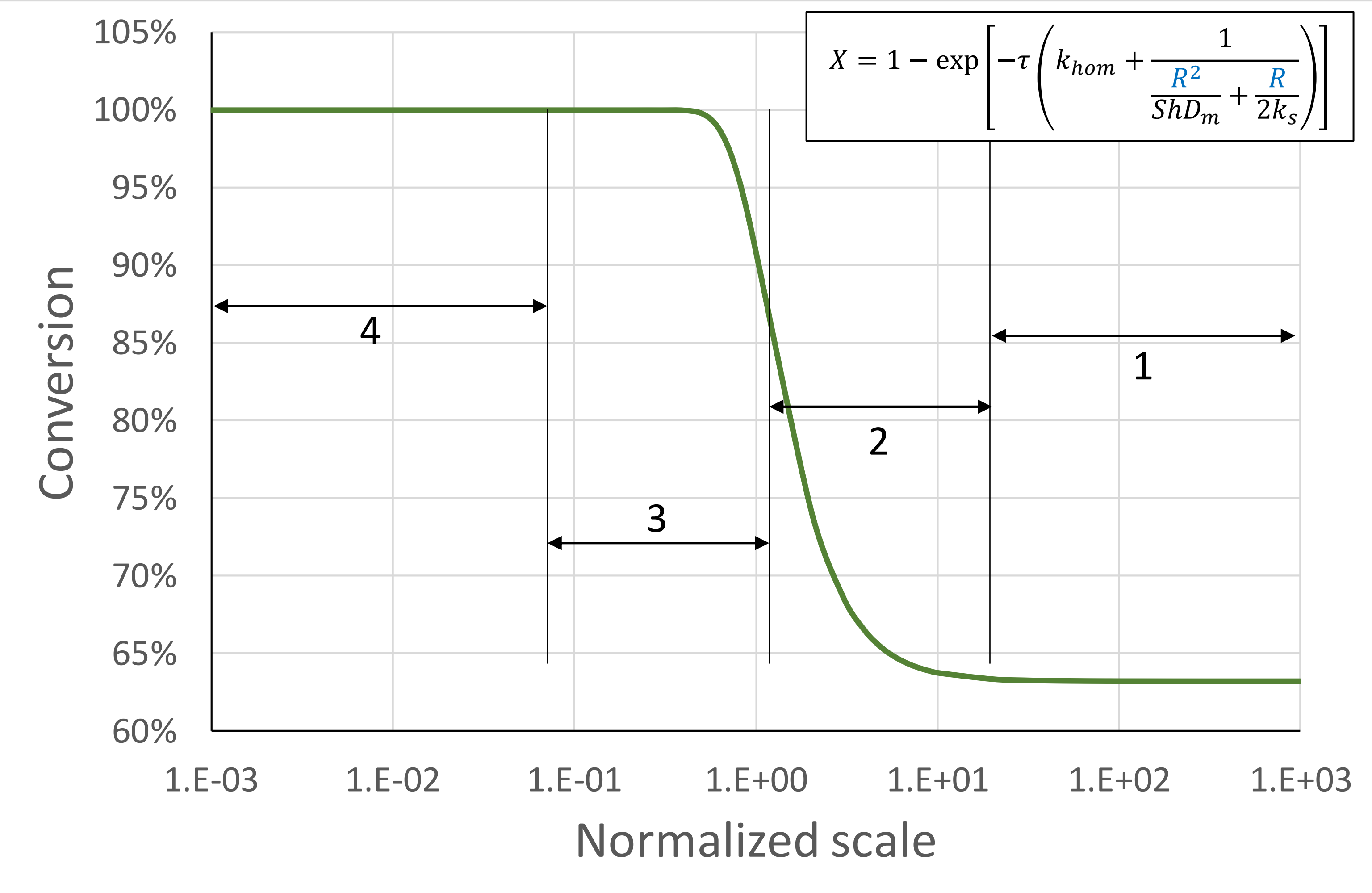


- Domain 1: $t_{hom} < t_{het} < t_{mass}$
    - ○ Homogeneous reaction is the fastest (t_{hom} the smallest)
    - ⇨ Homogeneous reaction totally governs the overall process
- Domain 2: $t_{het} < t_{hom} < t_{mass}$
    - ○ Heterogeneous reaction is the fastest (t_{het} the smallest) but t_{mass} is larger than t_{hom} (i.e., slow mass transfer)
    - ⇨Homogeneous reaction mostly governs the overall process
- Domain 3: $t_{het} < t_{mass} < t_{hom}$
    - ○ Mass transfer faster than homogeneous reaction but t_{mass} is larger than t_{het} (slow mass transfer)
    - ⇨Mass transfer governs the overall process
- Domain 4: $t_{mass} < t_{het} < t_{hom}$
    - ○ Mass transfer faster than heterogeneous reaction
    - ⇨Heterogeneous reaction governs the process

Example 1 of coupling

Effect of scale on process efficiency (plug-flow reactor, constant space-time)

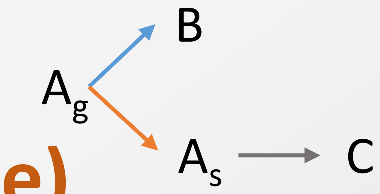


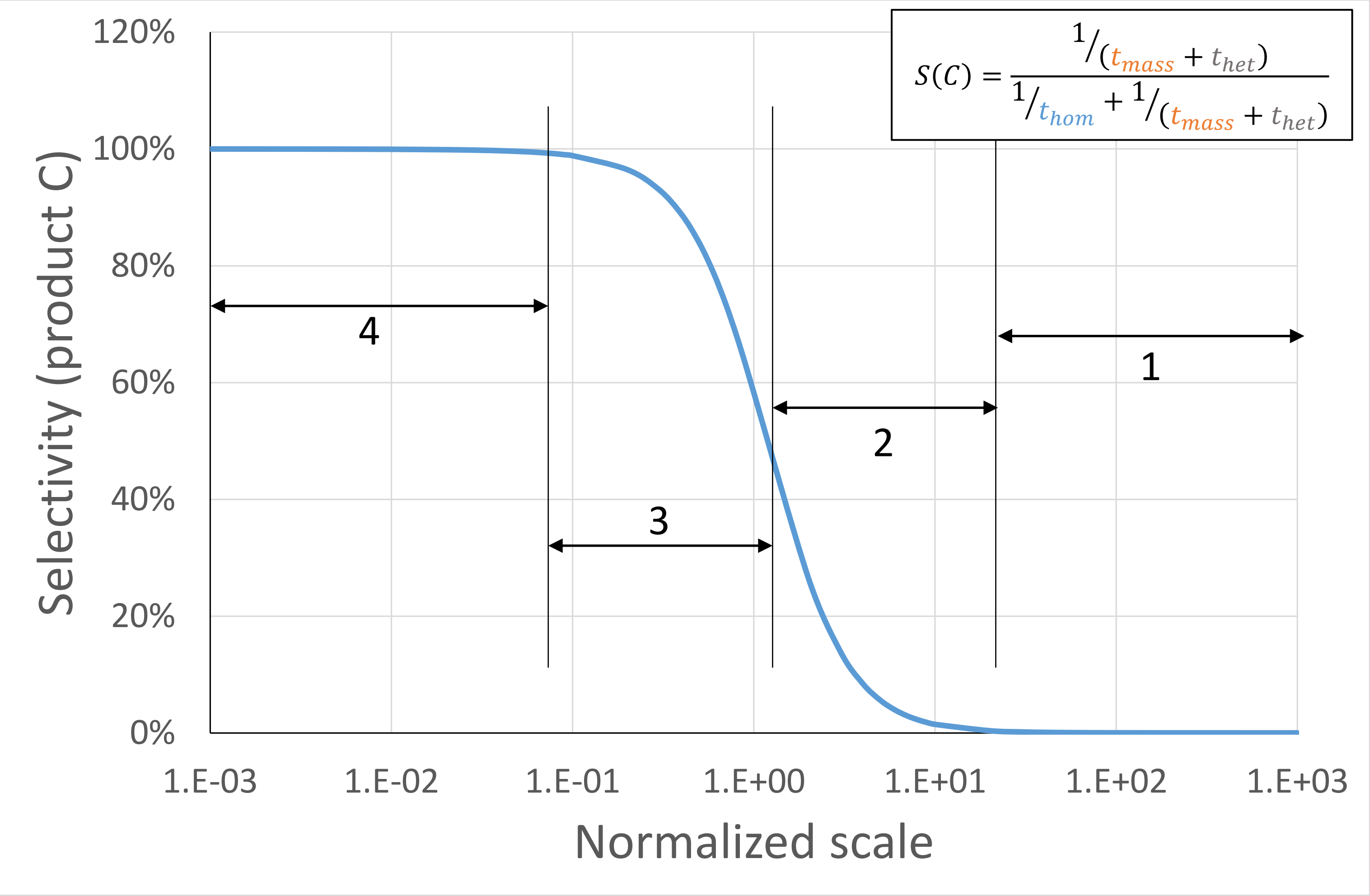


$$X = 1 - \exp\left[-\tau\left(k_{hom} + \frac{1}{\frac{R^2}{ShD_m} + \frac{R}{2k_s}}\right)\right]$$

Example 1 of coupling

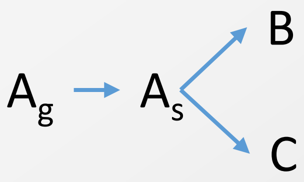
Effect of scale on selectivity (plug-flow reactor, constant space-time)





$$S(C) = \frac{{}^{1}/_{(t_{mass} + t_{het})}}{{}^{1}/_{t_{hom}} + {}^{1}/_{(t_{mass} + t_{het})}}$$

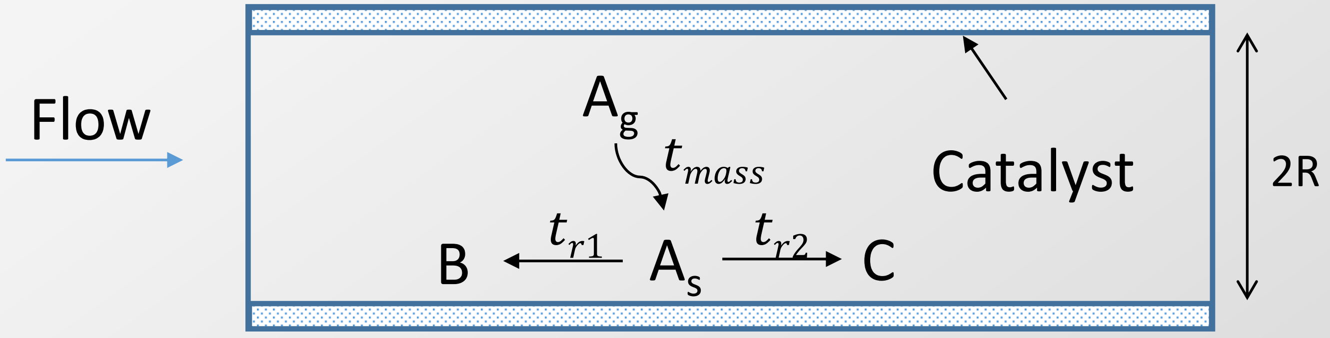
Example 2 of coupling



- Consecutive-parallel coupling:

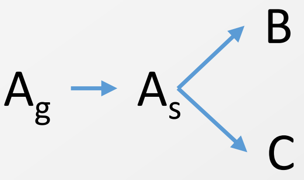
$$\underbrace{a_s = \frac{2}{R}; k_g = \frac{ShD_m}{2R}}$$

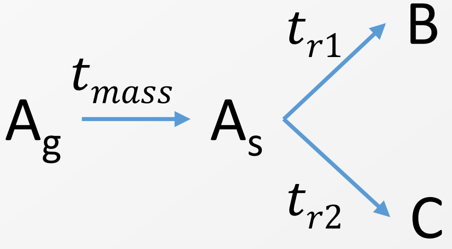
  - Mass transfer A → cat. surface $$t_{mass} = \frac{1}{a_s k_g} = \frac{R^2}{2ShD_m}$$
  - Het. reaction A → B (order m_1) $$t_{r1} = \frac{1}{a_s k_{1s} \left(c_{A,0}^{s}\right)^{(m_1 - 1)}}$$
  - Het. reaction A → C (order m_2) $$t_{r2} = \frac{1}{a_s k_{2s} \left(c_{A,0}^{s}\right)^{(m_2 - 1)}}$$



Example 2 of coupling

Effect of scale on relative selectivity





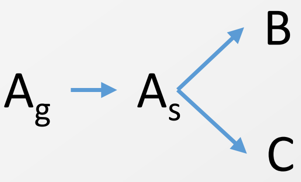
$$S_{B/C} = \frac{k_1 (c_A^s)^{m_1}}{k_2 (c_A^s)^{m_2}} = \frac{k_1}{k_2}(c_A^s)^{m_1-m_2}$$

$$\underbrace{\frac{(c_A - c_A^s)}{t_{mass}} = \frac{c_A^s}{t_{r1}} + \frac{c_A^s}{t_{r2}}}_{\text{Steady-state at catalyst surface}} \rightarrow \; c_A^s = \left[\frac{t_{r1}t_{r2}}{t_{r1}t_{r2} + t_{mass}(t_{r1} + t_{r2})}\right] c_A$$

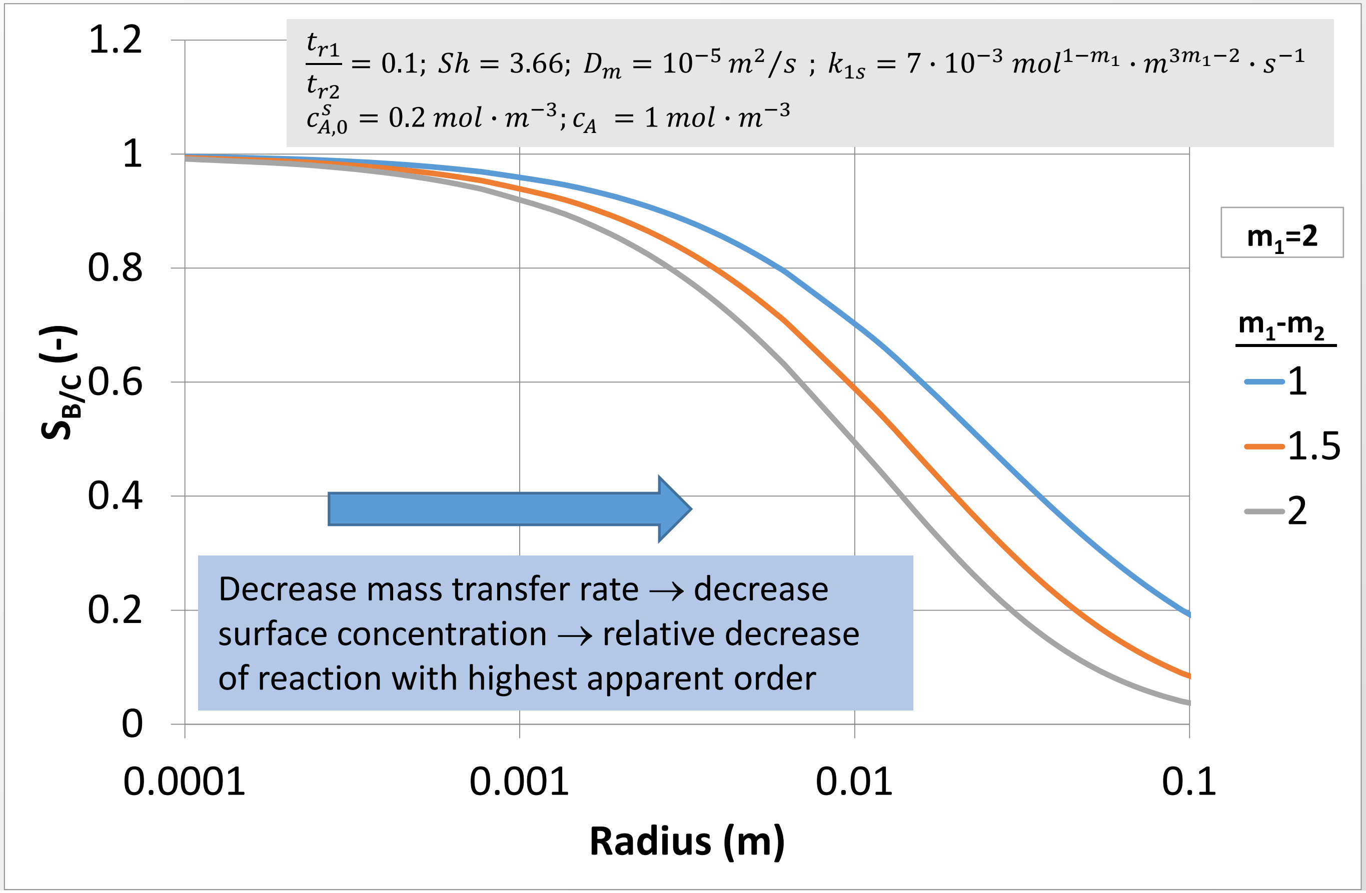
$$\rightarrow S_{B/C} = \left[\frac{k_1}{k_2}(c_A)^{m_1-m_2}\right] \underbrace{\left[1 + \frac{t_{mass}}{t_{r1}} + \frac{t_{mass}}{t_{r2}}\right]^{(m_2-m_1)}}_{F_{mass}\text{ (includes mass transfer effects)}}$$

Example 2 of coupling

Effect of scale on relative selectivity (PFR)



$$t_{mass} = \frac{R^2}{2\,ShD_m};\; t_{r1} = \frac{R}{2k_{1s}\left(c_{A,0}^{s}\right)^{(m_1-1)}}$$

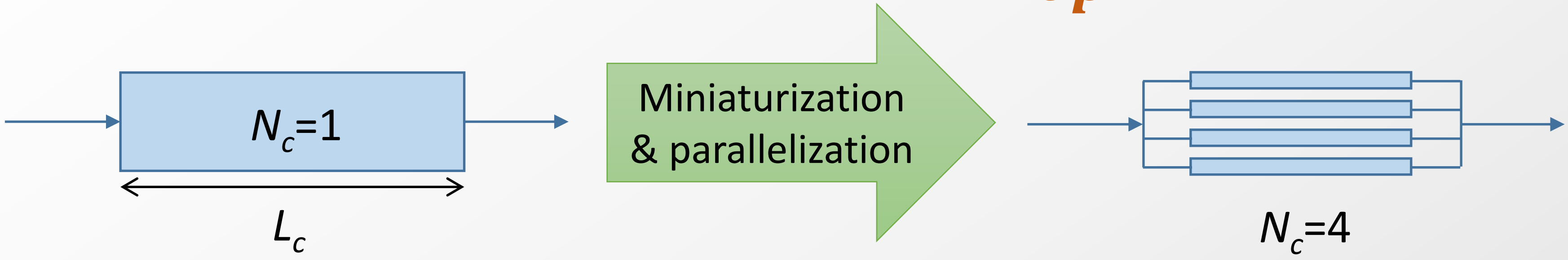


$\frac{t_{r1}}{t_{r2}} = 0.1;\ Sh = 3.66;\ D_m = 10^{-5}\,m^2/s\ ;\ k_{1s} = 7\cdot 10^{-3}\,mol^{1-m_1}\cdot m^{3m_1-2}\cdot s^{-1}$
$c_{A,0}^{s} = 0.2\,mol\cdot m^{-3};\ c_A = 1\,mol\cdot m^{-3}$

Decrease mass transfer rate → decrease surface concentration → relative decrease of reaction with highest apparent order

Effect of scale on process parameters

Constant *Q* and *NOU*. $t_{op} \propto R^m$



- $NOU = \frac{\tau}{t_{op}} = \frac{V}{Q t_{op}} \propto \frac{N_c L_c R^2}{Q R^m} \propto N_c L_c R^{2-m} = constant$

$\Rightarrow N_c L_c \propto R^{m-2}$

$$L_c \propto \frac{R^{m-2}}{N_c}$$

- $V \propto N_c L_c R^2 \propto R^m$
- $S \propto N_c R^2$
- $\Delta p(lam) \propto u_b \frac{L_c}{R^2} \propto \frac{Q}{N_c R^2} \frac{L_c}{R^2} \propto \frac{L_c}{N_c R^4} \propto \frac{R^{m-6}}{N_c^2}$

Effect of scale on process parameters

Constant *Q* and *NOU*. $t_{op} \propto R^m$

<u>Table for m=0</u> (Ex: nth order hom. reaction)

The table describes the effect of a change in R *on various variables when keeping one of them constant (indicated in bold)*

Operation time t_{op}	Ref. time τ	Volume V	Channel no. N_c	Channel length L_c	Cross section S	Pressure drop Δp
Constant	Constant	Constant	**Constant**	$\propto R^{-2}$	$\propto R^2$	$\propto R^{-6}$
Constant	Constant	Constant	$\propto R^{-2}$	**Constant**	Constant	$\propto R^{-2}$
Constant	Constant	Constant	$\propto R^{-3}$	$\propto R$	$\propto R^{-1}$	**Constant**

Ex: $\boldsymbol{R} \rightarrow \frac{\boldsymbol{R}}{\boldsymbol{2}}$ at **constant** $\boldsymbol{L_c} \Rightarrow N_c \longrightarrow N_c \times 2^2 = \boldsymbol{N_c} \times \boldsymbol{4}$ and $\Delta p \rightarrow \Delta p \times 2^2 = \Delta \boldsymbol{p} \times \boldsymbol{4}$

Effect of scale on process parameters

Constant Q and NOU. $t_{op} \propto R^m$

Table for m=1 (Ex: 1st order het. reaction)

Operation time t_{op}	Ref. time τ	Volume V	Channel no. N_c	Channel length L_c	Cross section S	Pressure drop Δp
$\propto R$	$\propto R$	$\propto R$	**Constant**	$\propto R^{-1}$	$\propto R^2$	$\propto R^{-5}$
$\propto R$	$\propto R$	$\propto R$	$\propto R^{-1}$	**Constant**	$\propto R$	$\propto R^{-3}$
$\propto R$	$\propto R$	$\propto R$	$\propto R^{-2}$	$\propto R$	**Constant**	$\propto R^{-1}$
$\propto R$	$\propto R$	$\propto R$	$\propto R^{-2.5}$	$\propto R^{1.5}$	$\propto R^{-0.5}$	**Constant**

Ex: $\boldsymbol{R} \rightarrow \frac{\boldsymbol{R}}{\boldsymbol{3}}$ at **constant** $\boldsymbol{\Delta p} \Rightarrow N_c \longrightarrow N_c \times 3^{2.5} = \boldsymbol{N_c} \times \mathbf{15.6}$ and $L_c \rightarrow \frac{L_c}{3^{1.5}} = \frac{\boldsymbol{L_c}}{\mathbf{5.2}}$

Effect of scale on process parameters

Constant *Q* and *NOU*. $t_{op} \propto R^m$

Table for m=2 (Ex: Diffusive mass transfer)

Operation time t_{op}	Ref. time τ	Volume V	Channel no. N_c	Channel length L_c	Cross section S	Pressure drop Δp
$\propto R^2$	$\propto R^2$	$\propto R^2$	**Constant**	**Constant**	$\propto R^2$	$\propto R^{-4}$
$\propto R^2$	$\propto R^2$	$\propto R^2$	$\propto R^{-2}$	$\propto R^2$	**Constant**	**Constant**

Ex: $\boldsymbol{R} \rightarrow \frac{\boldsymbol{R}}{\mathbf{4}}$ at **constant** L_c

$\Rightarrow \Delta p \longrightarrow \Delta p \times 4^4 = \Delta \boldsymbol{p} \times \mathbf{256}$ and $\tau \rightarrow \frac{\boldsymbol{\tau}}{\mathbf{4^2}} = \frac{\boldsymbol{\tau}}{\mathbf{16}}$