Process Intensification and Green Chemistry

The effect of mixing on chemical reactions

EPFL
Master of Science in Chemical Engineering and Biotechnology
Dr. H. Randall

Rev. 1 04/2024

Content

- Introduction
  - Simultaneous mixing and chemical reaction, mixing classes, segregation
- Effect of complete segregation on reactor performance for simple reaction $A_1 \xrightarrow{k\ c_1^n} P$
  - Effect of n, effect of RTD
- Effect of segregation intensity on second order reactions $A_1 + A_2 \xrightarrow{k c_1 c_2} P$
  - Effect of segregation intensity on conversion in CSTR and PFR
  - Fully segregated CSTR with premixed feed
- Effect of segregation intensity on performance and selectivity of consecutive-competitive reactions
  - Effect of segregation intensity on selectivity and conversion
- Experimental mixing time characterization
  - Physical methods
  - Chemical methods (consecutive-competitive, parallel-competitive, examples, Villermaux-Dushman reaction)
  - IEM mixing model

Introduction

Simultaneous mixing and chemical reaction

1. Fast mixing - slow reactions

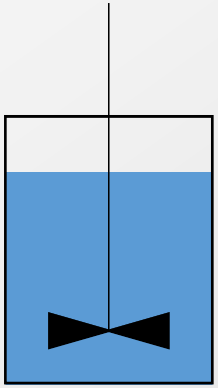
- If mixing time t_{mx} much smaller than reaction time t_r (i.e., reaction rate << mixing rate):
    - ➢Mixing and reaction can be considered to take place consecutively
    - ➢Concentration field is homogeneous throughout reactor
    - ➢No further effect of mixing on the transformation rate (performance)
    - ➢No further effect of mixing on the product distribution (selectivity)

Simultaneous mixing and chemical reaction

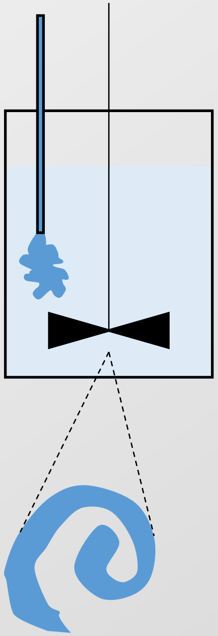
2. Slow mixing - fast reactions

- If mixing time t_{mx} comparable or longer than reaction time t_r (i.e., reaction rate ≥ mixing rate):
  - ➢Mixing and reaction take place simultaneously, not consecutively
  - ➢Reaction medium is inhomogeneous, each zone having different reaction rates
  - ➢Expected impact on the transformation rate (performance)
  - ➢Expected effect on the product distribution (selectivity) in case of complex reaction networks
- To avoid any effect of mixing on the process, t_{mx} should be at least 10 times lower than t_r

Mixing classes



- Macromixing
  - Distribution of one fluid through the other and equalization of average composition without decreasing local concentration variations
- Mesomixing
  - Reduction of size of regions with uniform composition
  - Increasing of contact between regions of different compositions
  - Ex: Feed rate >> local mixing rate → plume



- Micromixing
  - Mixing at molecular level
  - Controls chemical reaction as molecules must physically meet in order to react

- J. Baldyga, R. Pohorechi, Turbulent micromixing in chemical reactors - a review, The Chemical Engineering Journal 58 (1995) 183-195
- John R. Bourne, Mixing and the Selectivity of Chemical Reactions, Organic Process Research & Development 2003, *7,* 471-508
- E. L. Paul, V. A. Atiemo-Obeng and S. M. Kresta (Eds.), Handbook of Industrial Mixing: Science and Practice, 2004 Wiley & Sons

Macromixing

- “Distributive” mixing, occurs at the **macroscopic level** (scale of the vessel or reactor)
- It is another term for “blending” to a degree of homogeneity throughout a vessel
- Distribution of one fluid through the other and equalization of average composition without decreasing local concentration variations
- Achieved by **bulk motion** or convective transport until uniform distribution of fluid elements in the reactor volume
- Influences the RTD in a continuous reactor
- Example: mean circulation time in mechanically stirred reactor

$$\tau_c = \frac{V}{C_D N D_i^3} \quad \text{with} \quad 0.7 < C_D < 1$$

Optional

Mesomixing

Coarse-scale dispersive mixing via turbulent eddies

Two different mechanisms:

1. **Turbulent dispersion** of fresh fluid element introduced to the reactor, mixing with local surroundings

$$\tau_D = \frac{Q_f}{u\,D_{turb}} \; (r_{pipe} \ll L_D) \qquad \text{or} \qquad \tau_D = \frac{r_{pipe}^2}{u\,D_{turb}} \; (r_{pipe} \geq L_D)$$

$$D_{turb} = 0.12\,\varepsilon^{1/3}\,L_D^{4/3}$$

L_D: characteristic length for dispersion

2. **Inertial-convective breakup of large eddies (Eddy disintegration)** (> Kolmogorov scale)

Inertial-convective mesomixing timescale (Baldyga, 1997):

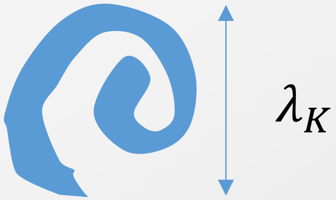
$$\tau_S = A\left(\frac{L_C^2}{\varepsilon}\right)^{1/3} \qquad 1 < A < 2 \text{ depending on turbulence level}$$

L_c: concentration macroscale

Micromixing (1)

General definition

- The final stage of mixing, occurring at much smaller length scales than macro- and mesomixing
- Occurs at the scale of smallest turbulent eddies and concentration striations



- Can be characterized e.g., by Kolmogorov and Batchelor scales

Micromixing (2)

Kolmogorov length scale

- Sizes of eddies range from largest integral scales of motion (e.g., close to impeller width, feed pipe diameter or tubular reactor diameter) down to the smallest scale of turbulence.
- Energy is transferred from large eddies to smaller ones (energy cascade) until the smallest scale of turbulence is reached (Kolmogorov scale):
    - At that scale, the local Reynolds number $Re = \frac{u \cdot \lambda_K}{\nu} = 1$
- Below that length scale, viscosity dominates, and turbulent energy is dissipated into heat.
- **Size of smallest eddy**: $\lambda_K = \left(\frac{\nu^3}{\varepsilon}\right)^{1/4}$
- Time to dissipate eddy of size λ_K: $\tau_K = \frac{u^2}{\varepsilon} = \left(\frac{\nu}{\varepsilon}\right)^{1/2}$
- **Time for mixing** by molecular diffusion within Kolmogorov scale:

$$\tau_K = \frac{\lambda_K{}^2}{D} = Sc \left(\frac{\boldsymbol{\nu}}{\boldsymbol{\varepsilon}}\right)^{\mathbf{1/2}}$$

Micromixing (3)

Optional

Batchelor length scale

- **Smallest length scale of concentration (or temperature) fluctuations**.
- Below that scale, molecular diffusion dominates.
- Size of the smallest element of fluid that can homogenize by molecular diffusion in one Kolmogorov time scale ($\tau_B = \tau_K$)
- Size of smallest eddy: $\lambda_B = (\tau_K D)^{1/2} = \left(\frac{\nu D^2}{\varepsilon}\right)^{1/4} = \frac{\lambda_K}{\sqrt{Sc}}$
    - For liquids ($Sc \gg 1$): $\lambda_B \ll \lambda_K$ ⇨ Smallest striation thickness given by the Batchelor scale
- Time to dissipate eddy of size λ_B: $\tau_B = \frac{{\lambda_B}^2}{D} = \left(\frac{\nu}{\varepsilon}\right)^{1/2}$

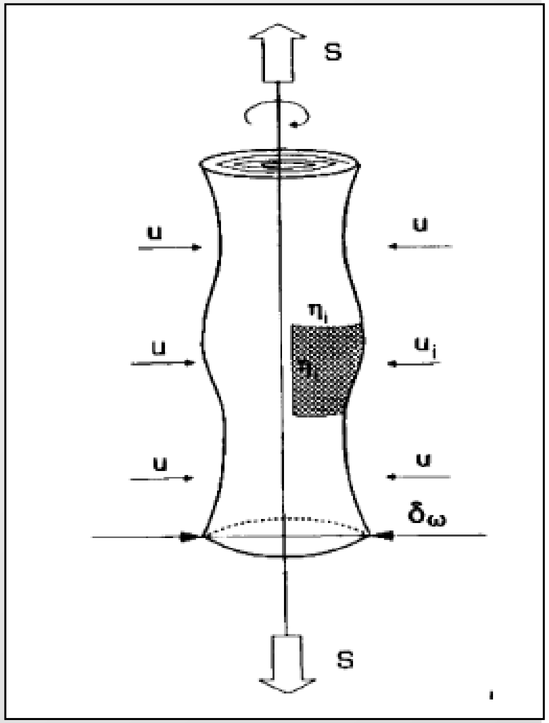
Micromixing (4)

More recent developments: engulfment

- Vortex tubes form in turbulent flow (high *Re*)
- Micromixing mechanism: small vortices (close to Kolmogorov scale λ_K) draw in (engulf) the surrounding fluid
- Characteristic time for micromixing by engulfment:

$$t_E = 17.2\sqrt{\frac{\nu}{\varepsilon}}$$

- Rapid micromixing occurs at high energy dissipation / low viscosity

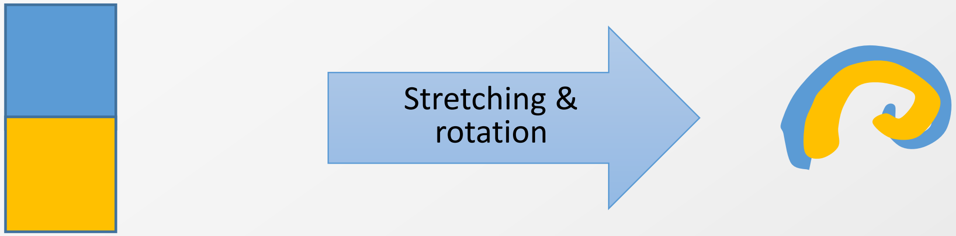


J. Baldyga, R. Pohorechi, The Chemical Engineering Journal 58 (1995) 183-195

Micromixing (5)

More recent developments: shear elongation & diffusion*

- The existence of a shear field leads to stretching and rotation of fluid lamellae



- Half-life of molecular diffusion within progressively thinning lamellae:

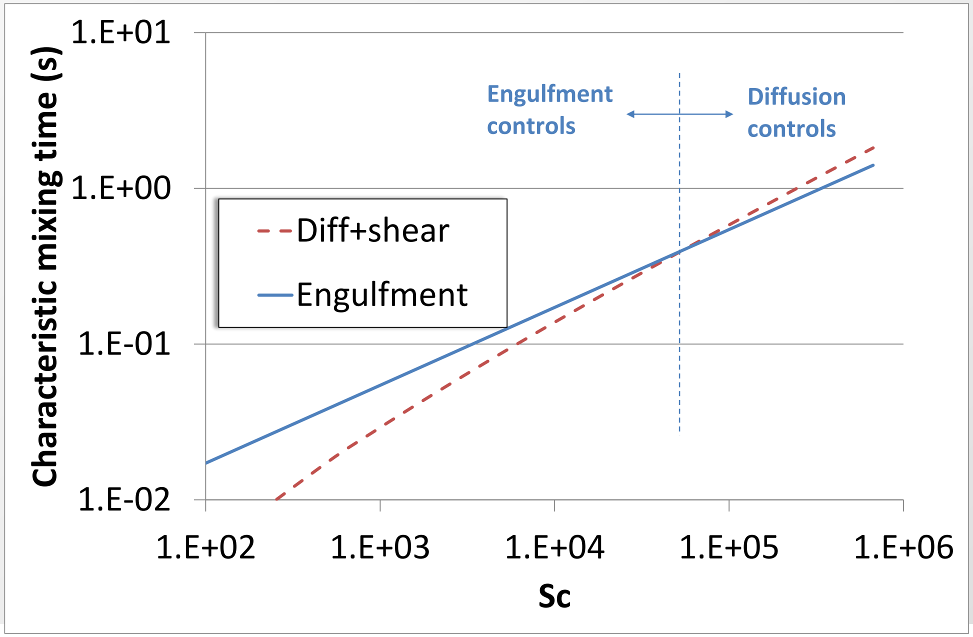
$$\tau_{Ds} \cong 2\sqrt{\frac{\nu}{\varepsilon}}\, arc\ sinh(0.05\, Sc)$$

*See chapter 7

Micromixing (6)

Time constant for engulfment vs stretching and diffusion

- $Sc = \left[\frac{Rate\ of\ motion\ spreading}{Rate\ of\ concentration\ smoothing\ by\ diffusion}\right]^2 = \left[\frac{(\nu t)^{1/2}}{(Dt)^{1/2}}\right]^2 = \frac{\nu}{D}$
- Liquids: Sc~1000
- At high *Sc* number (high viscosity), diffusion controls micromixing rate
- At low *Sc* number (low viscosity), engulfment controls micromixing rate

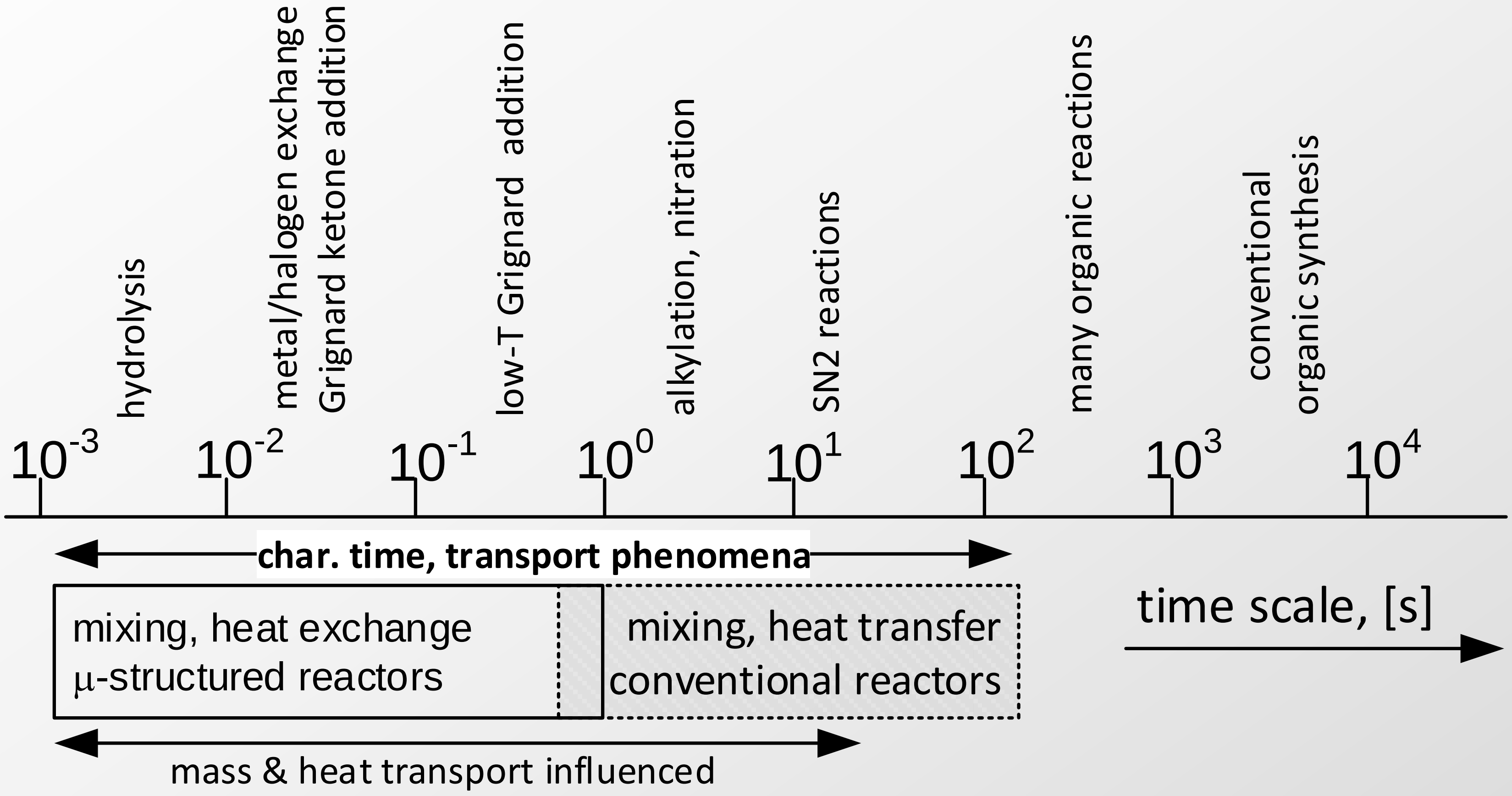


Optional

Ranking of mixing time constants

- Three different mixing scales exist, operating with a different mechanism and being characterized by a specific time constant
- The largest time constant is likely to determine the product distribution of fast multiple reactions
- Fast reactions in turbulent environment: meso- and micromixing times often smaller than macromixing time → reaction zone located close to feed point (does not spread to the entire vessel)
- The relevant (controlling) mixing mechanism can change with scale!
    - o Example for semibatch reactor:
        - Small tank size / low feed rate → likely micromixing control
        - Large tank size / higher feed rate → likely transition to mesomixing control

Examples of characteristic reaction times



hydrolysis

metal/halogen exchange

Grignard ketone addition

low-T Grignard addition

alkylation, nitration

SN2 reactions

many organic reactions

conventional organic synthesis

10^{-3} 10^{-2} 10^{-1} 10^{0} 10^{1} 10^{2} 10^{3} 10^{4}

char. time, transport phenomena

mixing, heat exchange
μ-structured reactors

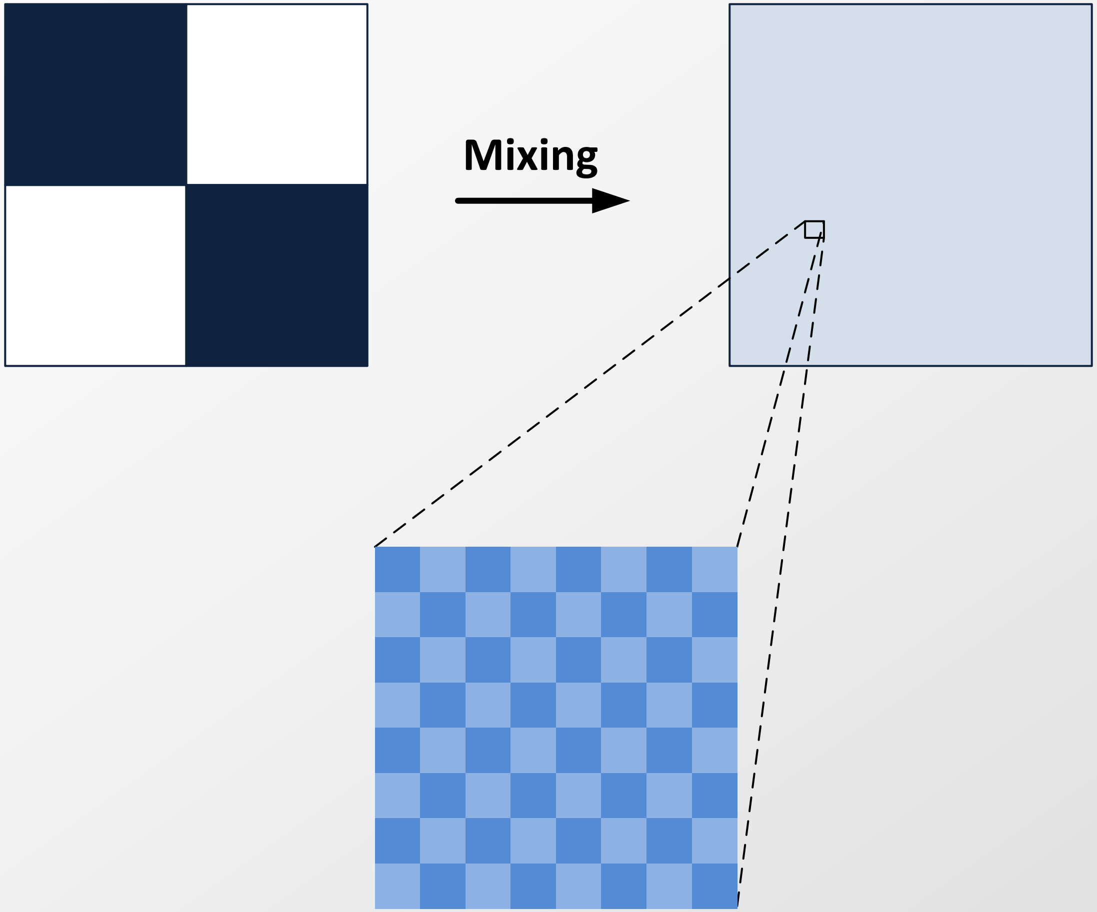
mixing, heat transfer
conventional reactors

time scale, [s]

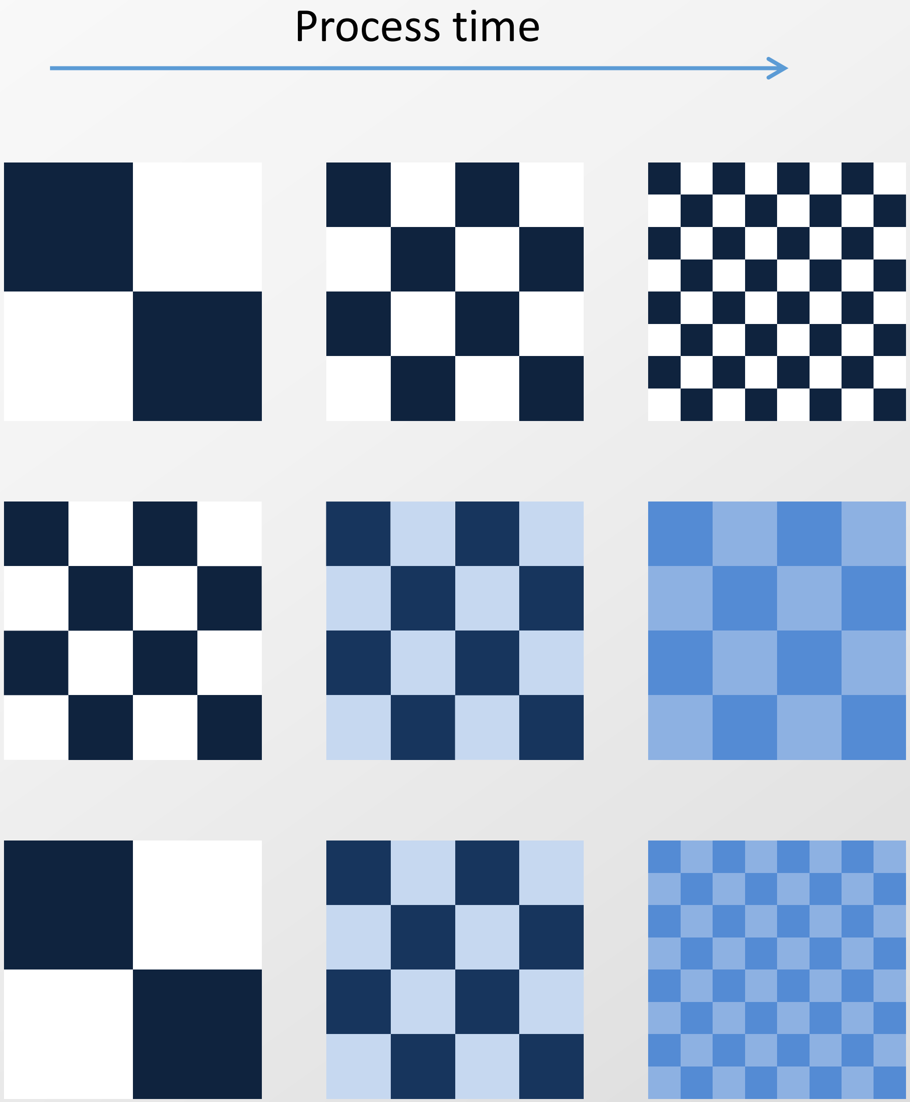
mass & heat transport influenced

Kashid, M., A. Renken, and L. Kiwi, *Microstructured devices for chemical processing. 2015: Wiley-VCH.*

Segregation



Segregation



Reduction in segregation scale:

Reduction in segregation intensity:

Reduction in segregation scale and intensity:

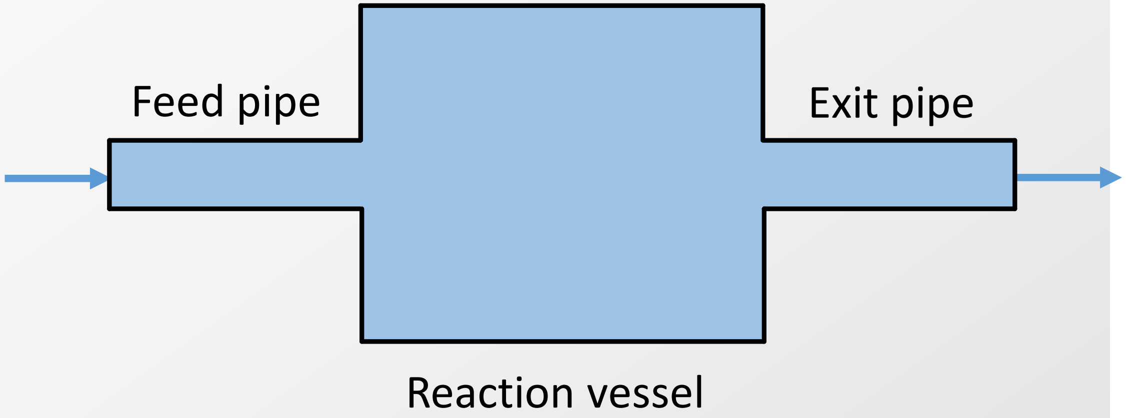
Segregation

- **Scale of segregation**
  - Measure of large-scale breakup process (bulk transport and eddy diffusion) without the action of diffusion
  - Size of the packets of B that can be distinguished from surrounding fluid A
- **Intensity of segregation**
  - Measure of difference in concentration between highest-concentration region and lowest concentration region
  - Decreases as a result of molecular diffusion
  - Does not require any turbulence but turbulence speeds up the mixing process by reducing the size of aggregates thus the diffusion time

Micro-mixed vs completely segregated fluids (2 extreme cases)

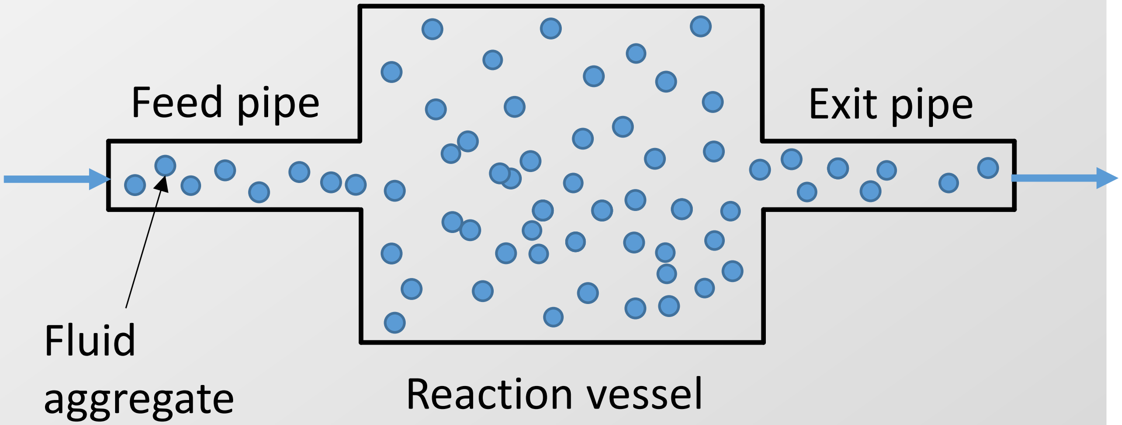
Micro-fluid (premixed feed)

- Micromixed feed
- Individual molecules lose their identity
- Uniform concentration



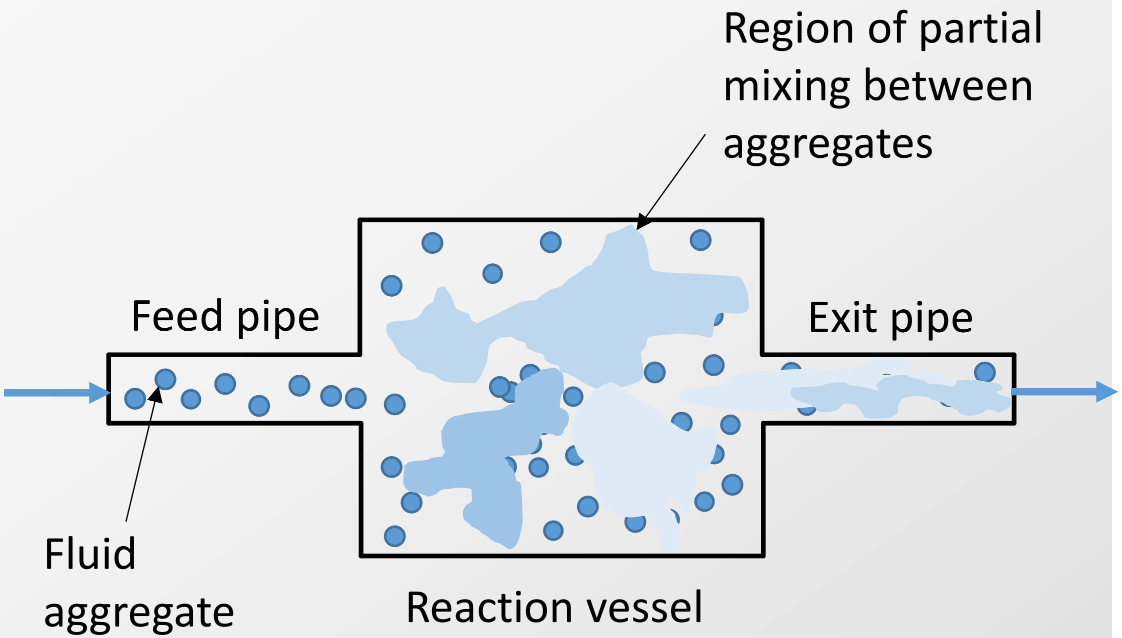
Fully segregated fluid (premixed feed)

- Fully segregated feed
- Fluid aggregates keep their identity (no exchange with other aggregates)
- Concentration differences between aggregates



Partially segregated fluid

- Fully segregated feed
- Fluid aggregates partially lose their identity (partial exchange with other aggregates)
- Concentration differences between regions exist



Segregation in reactors

Segregation in homogeneous systems is a function of the relative values of the following characteristic times

- Characteristic reaction time t_r
- Characteristic mixing time t_{mx}
- Characteristic processing time (ref. time) $\tau, \bar{t}$

Damköhler numbers:

$$DaI = \frac{\tau}{t_r}$$

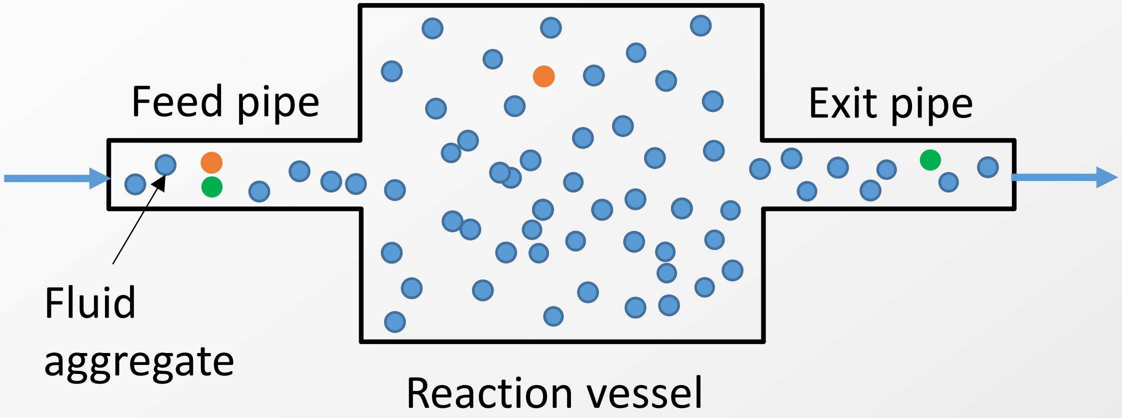
$$DaII_{mx} = \frac{t_{mx}}{t_r}$$

Quality of mixing as a function of the characteristic times

	$t_{mx} \ll t_r$	$t_{mx} \cong t_r$	$t_{mx} \gg t_r$
$t_{mx} \ll \tau$	Micromixed	Partial segregation	Complete segregation
$t_{mx} \cong \tau$	Partial segregation	Partial segregation	Complete segregation
$t_{mx} \gg \tau$	Complete segregation	Complete segregation	Complete segregation

Effect of complete segregation on reactor performance for simple reaction $A_1 \xrightarrow{k} P \quad r = k\, c_1^n$

Conversion in fully segregated fluid



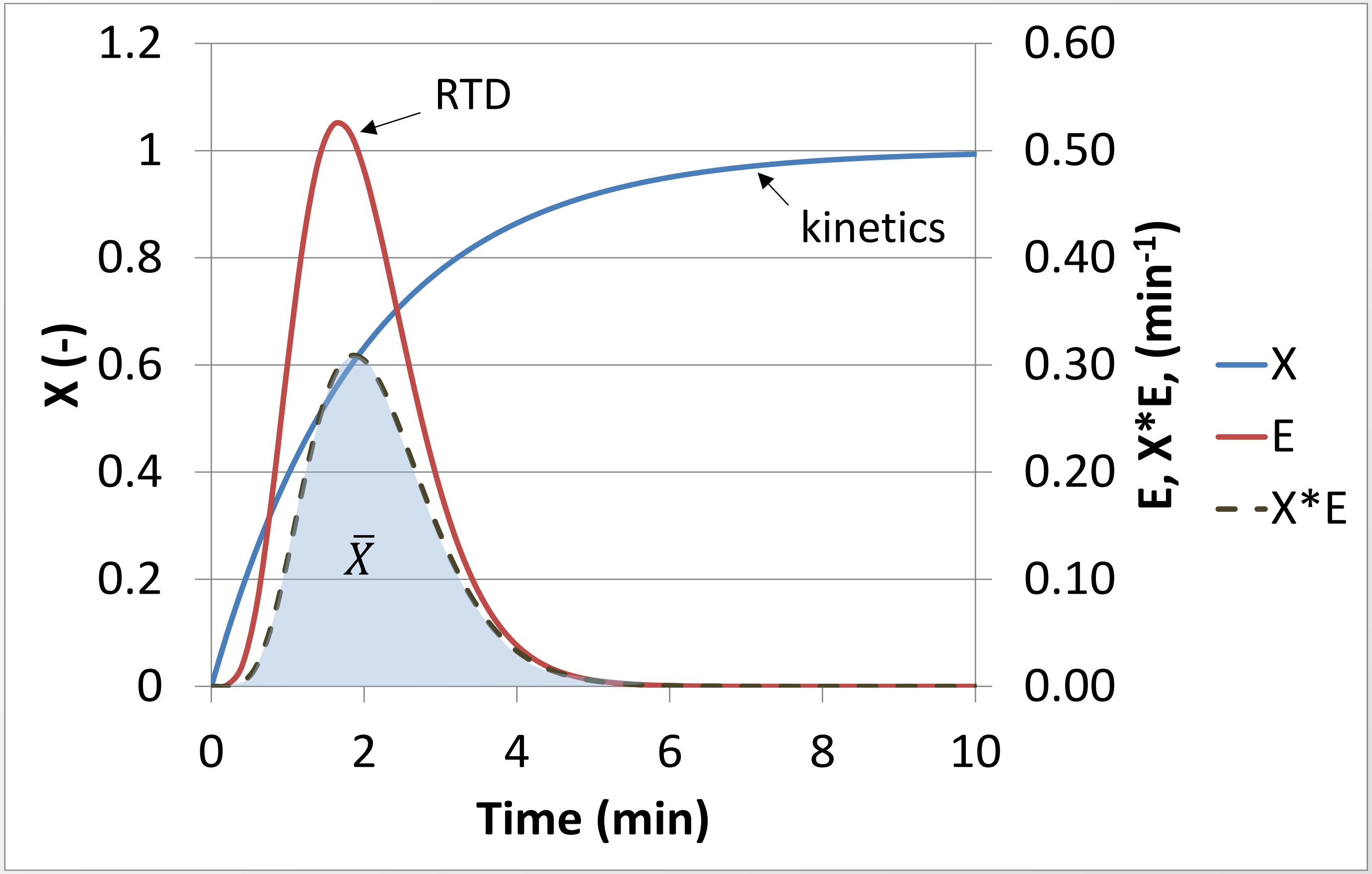
According to the RTD, each aggregate may spend different amounts of time in the reactor but keeps its identity:

Residence-time averaged exit concentration: $\bar{c}_1 = \int_0^\infty c_1(t)E(t)dt$

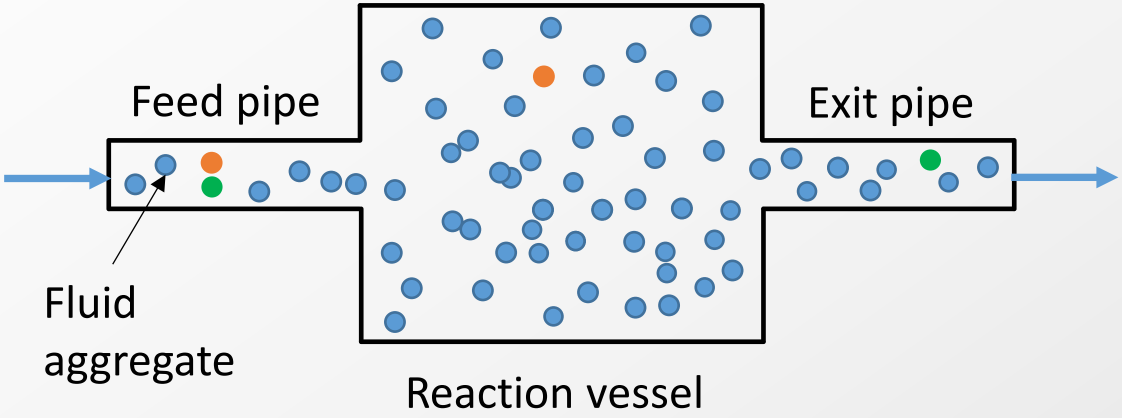
Residence-time averaged exit conversion: $\bar{X} = \int_0^\infty \underbrace{X(t)}_{\text{kinetics}}\underbrace{E(t)}_{\text{RTD}}dt$

Conversion in fully segregated fluid

$$\bar{X} = \int_0^\infty X(t)E(t)dt$$



Conversion in fully segregated fluid



- Example: conversion for first order reaction in ideal CSTR

$$E(t) = \frac{1}{\tau}\exp\left(-\frac{t}{\tau}\right) \quad \text{and} \quad c_1(t) = c_{1,0}\exp(-kt)$$

$$\bar{c}_1 = \int_0^\infty c_1(t)E(t)dt = \frac{c_{1,0}}{\tau}\int_0^\infty \exp\left[-\left(\frac{1}{\tau}+k\right)t\right]dt = \frac{c_{1,0}}{1+k\tau}$$

$$\bar{X} = \frac{c_{1,0}-\bar{c}_1}{c_{1,0}} = \frac{k\tau}{1+k\tau} = \frac{DaI}{1+DaI} = X(micromixed)$$

⇨ no effect of segregation on conversion for first order processes (see next slide)

Effect of segregation on first order processes

Microfluid

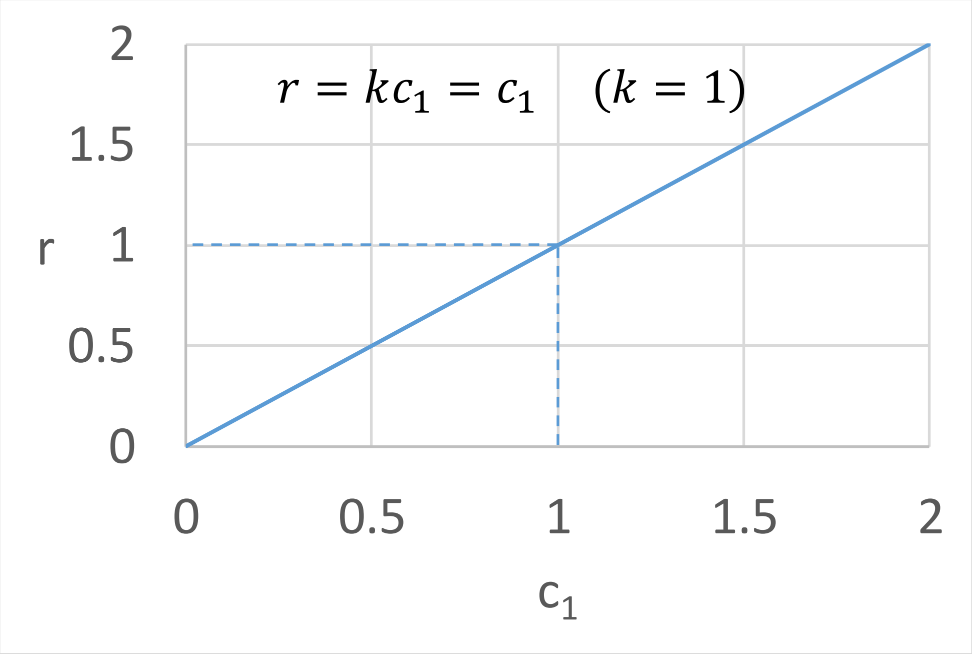
$c_1 = 1$
$r = 1$

Fully segregated fluid

$c_{1,1} = 0$
$r = 0$

$c_{1,2} = 2$
$r = 2$

$$\bar{r} = \frac{0+2}{2} = 1 = r(micro)$$



⇨ no effect of segregation on overall reaction rate for 1st order processes

Effect of segregation on second order processes

Microfluid

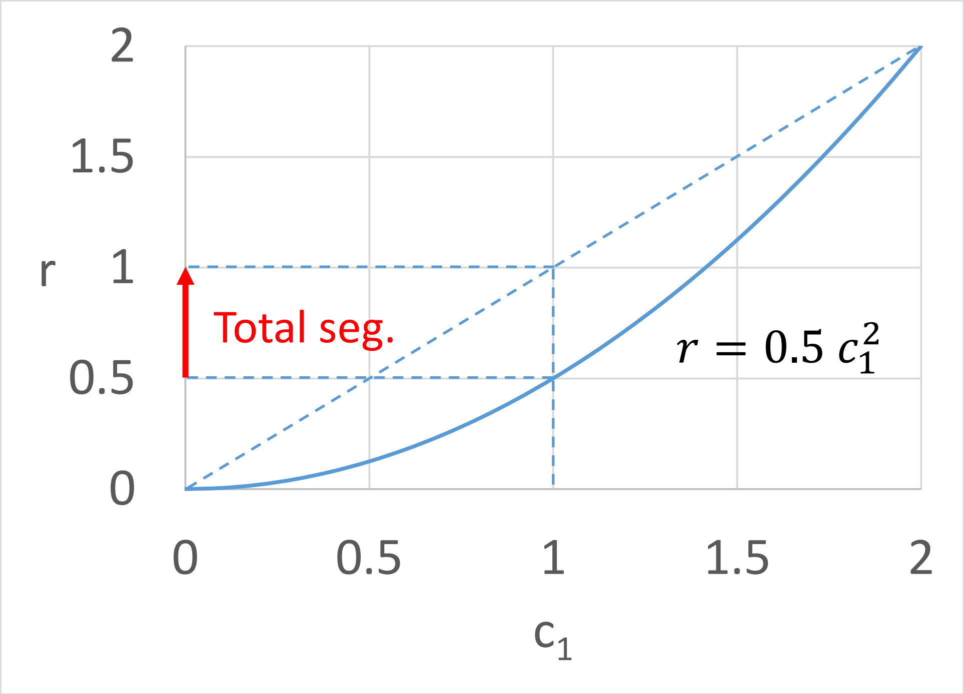
$c_1 = 1$
$r = 0.5$

Fully segregated fluid

$c_{1,1} = 0$
$r = 0$

$c_{1,2} = 2$
$r = 2$

$$\bar{r} = \frac{0+2}{2} = 1 > r(micro)$$



⇨ Positive effect of segregation on overall reaction rate for processes with n>1

Effect of segregation on half-order processes

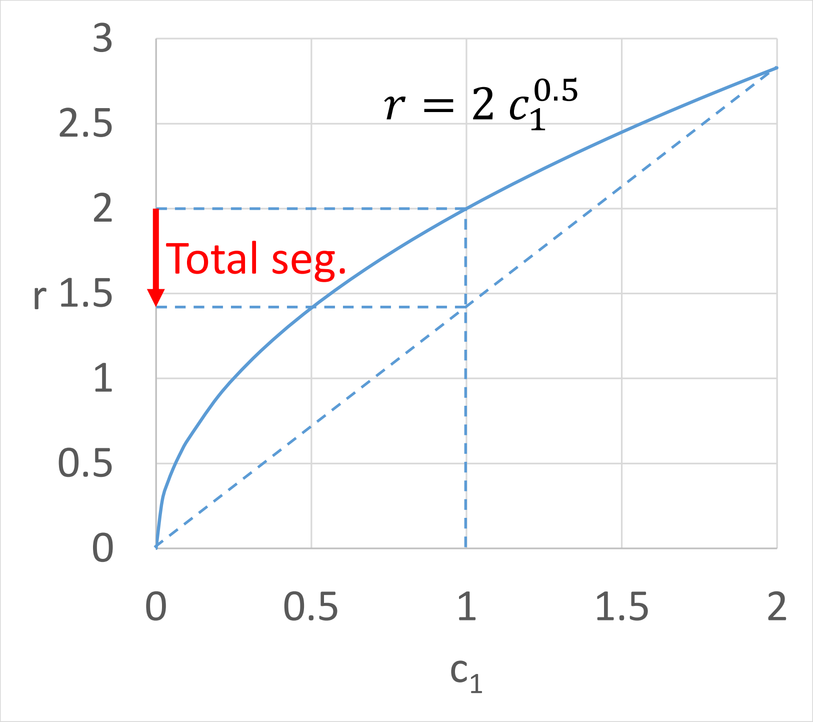
Microfluid

$$c_1 = 1$$
$$r = 2$$

Fully segregated fluid

$$c_{1,1} = 0 \qquad c_{1,2} = 2$$
$$r = 0 \qquad r = 2.8$$

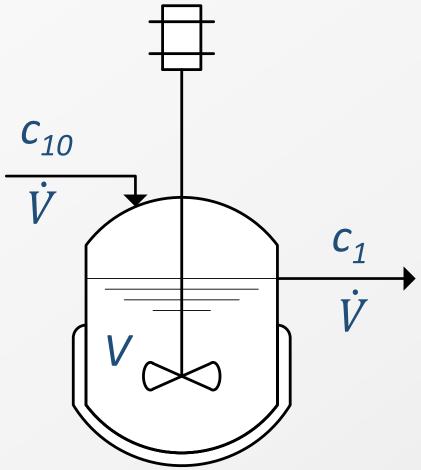
$$\bar{r} = \frac{0 + 2.8}{2} = 1.4 < r(micro)$$



⇨ Negative effect of segregation on overall reaction rate for processes with n<1

Effect of total segregation on conversion

Ideal CSTR, nth order reaction $A_1 \xrightarrow{k} P \quad r = k\, c_1^n$



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

$$DaI = \frac{\tau}{t_r} = k c_{10}^{n-1} \tau$$

$$X = 1 - \frac{c_1}{c_{10}}$$

Micromixed

$$\boxed{DaI = \frac{X}{(1-X)^n}}$$

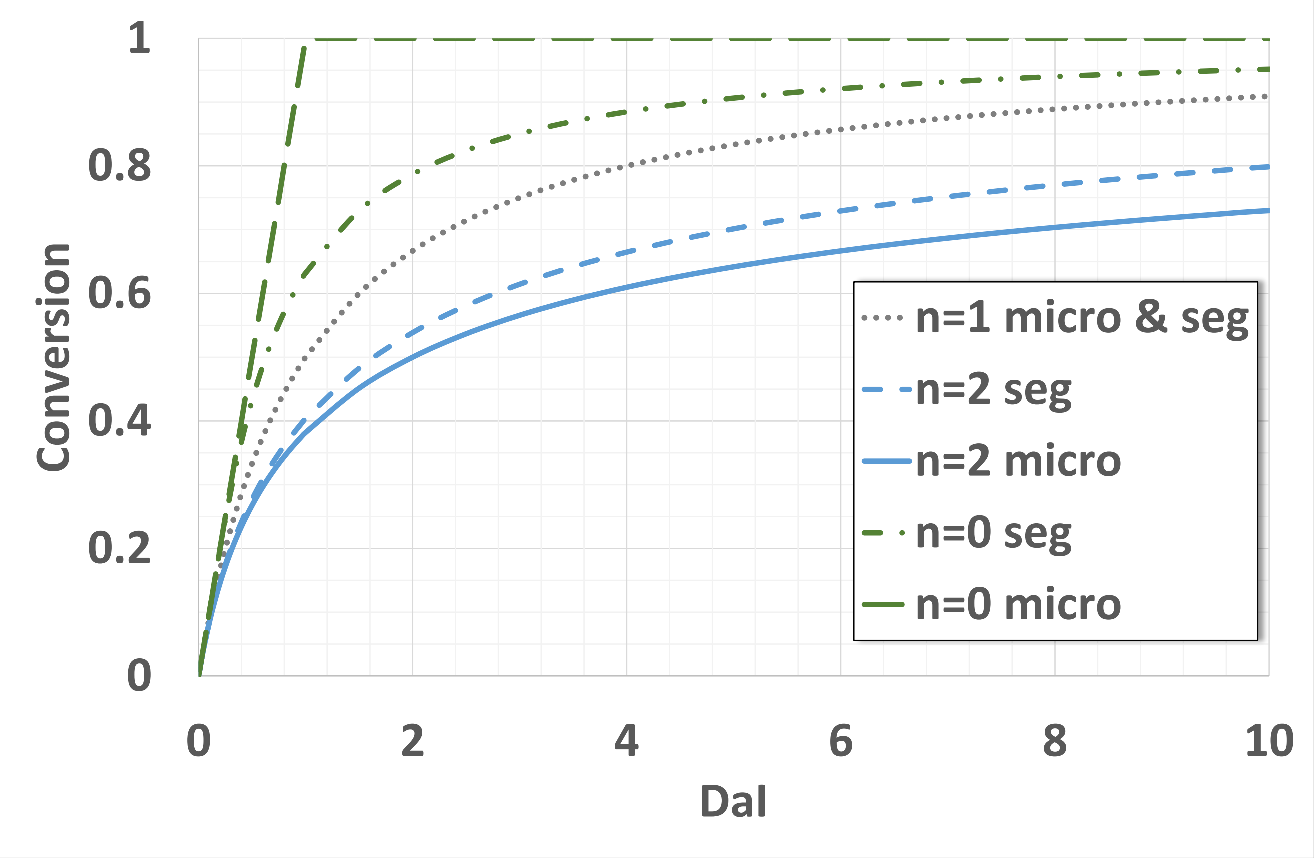
Macromixed (fully segregated)

$$\boxed{\bar{X} = \frac{1}{\tau} \int_0^\infty \left\{ 1 - \left[1 + (n-1) k c_{10}^{n-1} t \right]^{\frac{1}{1-n}} \right\} e^{-\frac{t}{\tau}} dt}$$

→ Numerical integration

Effect of total segregation on conversion

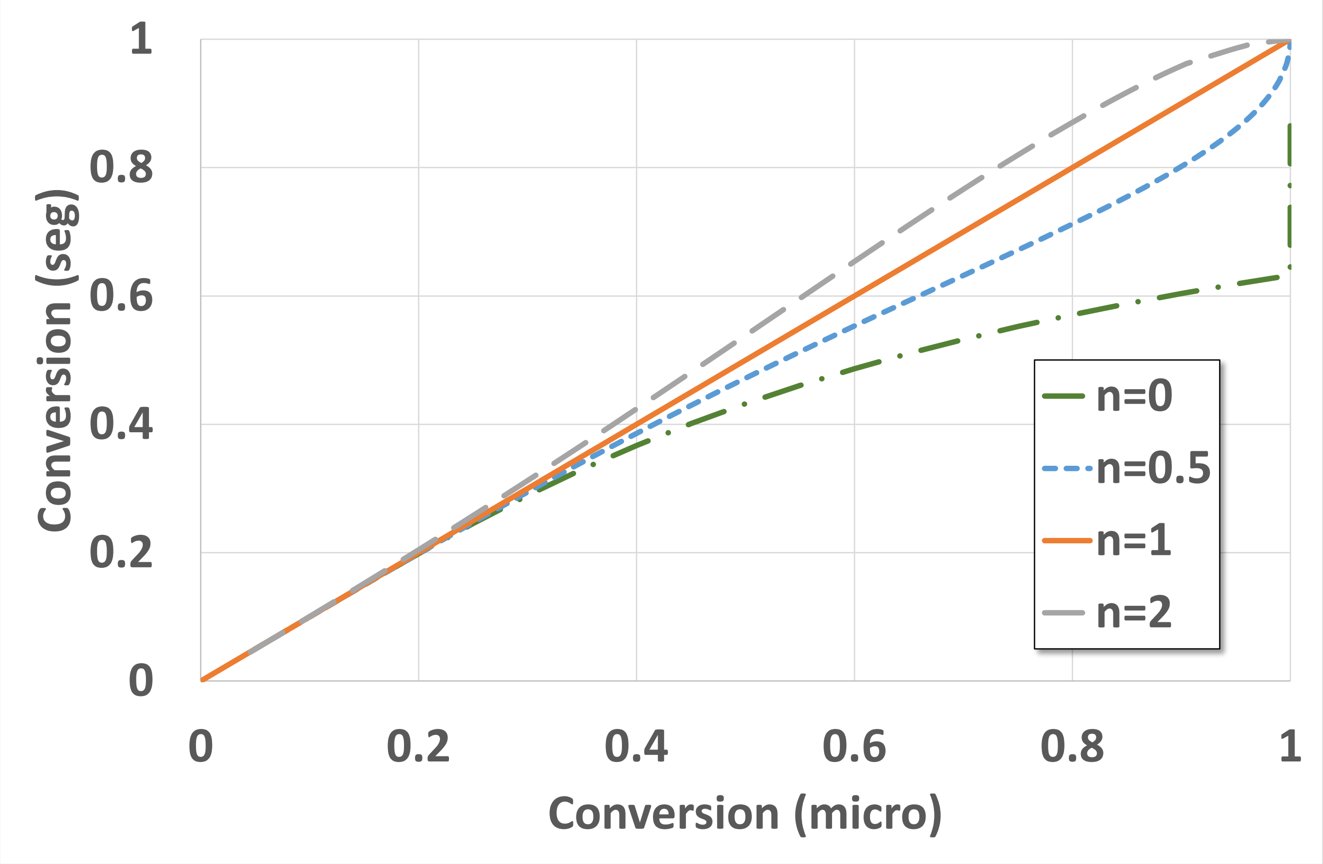
Ideal CSTR, n^th order reaction



n > 1 → positive effect of segregation on performance
n = 1 → no effect of segregation on performance
n < 1 → negative effect of segregation on performance

Effect of total segregation on conversion

Ideal CSTR, n^{th} order reaction



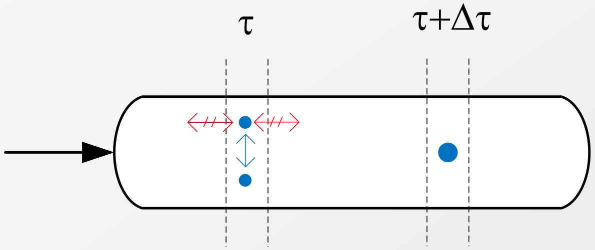
n > 1 → positive effect of segregation on performance
n = 1 → no effect of segregation on performance
n < 1 → negative effect of segregation on performance

Effect of segregation on conversion in PFR

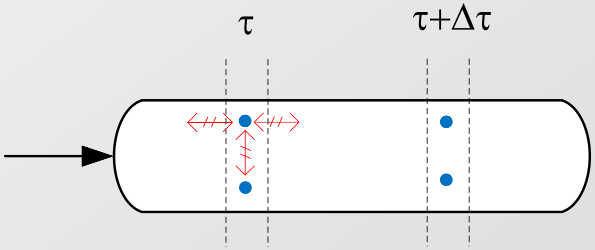
- In PFR, each aggregate or molecule spends same amount of time in reactor
- No mixing between molecules or aggregates of different ages

⇨ Each aggregate behaves as a batch reactor with equal processing time

⇨ No influence of segregation on performance



Plug flow, some degree of mixing (radial)



Plug flow, no mixing (full segregation)

⇨ Same result because radial mixing of aggregates with same concentration

PFR: micromixing vs complete segregation

n^{th} order reaction $\quad A_1 \xrightarrow{k} P \quad r = k\, c_1^n$

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

$$DaI = \frac{\tau}{t_r} = k c_{10}^{n-1} \tau$$

Micro and macromixing

$$\boxed{X = 1 - [1 + (n-1) DaI]^{\frac{1}{1-n}}}$$

Effect of segregation intensity on second order reactions

$$A_1 + A_2 \xrightarrow{k} P \quad r = kc_1c_2$$

Segregation characterization

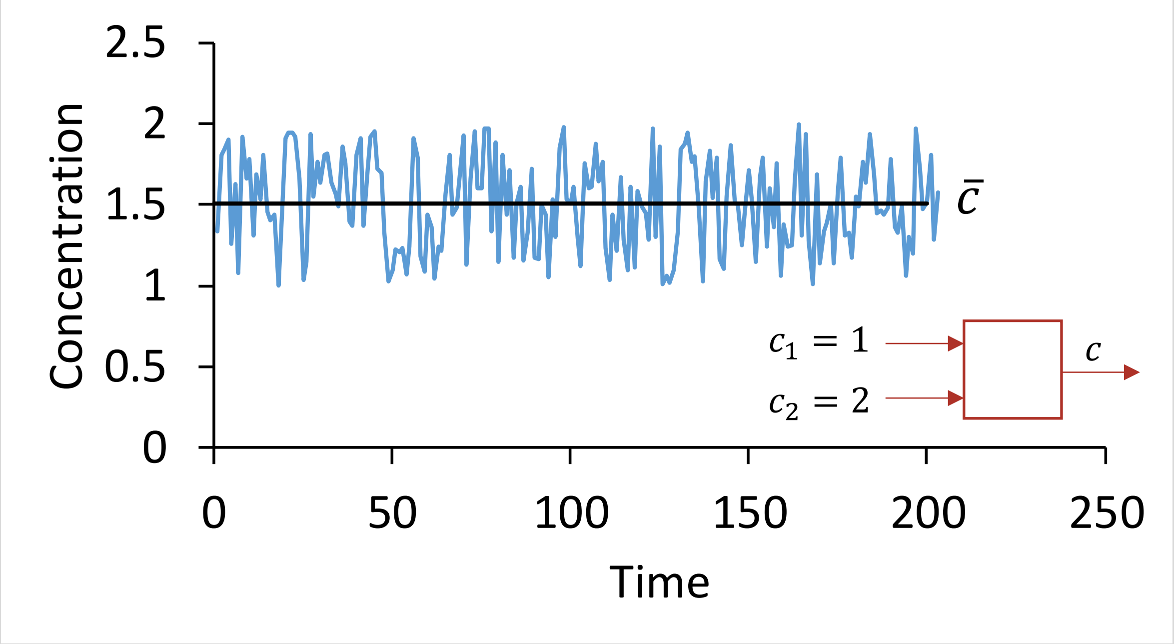
To describe *partial* segregation

- Intensity of segregation in turbulent flow: $I_s = \frac{\sigma^2}{\sigma_0^2}$

$$\boxed{\sigma^2} = \frac{1}{n}\sum(c - \bar{c})^2 \quad \text{and} \quad \sigma_0^2 = \frac{1}{n}\sum(c - \bar{c}_0)^2$$

Used to measure segregation ("unmixedness")

At time zero or in feed



Kinetics of segregation decay

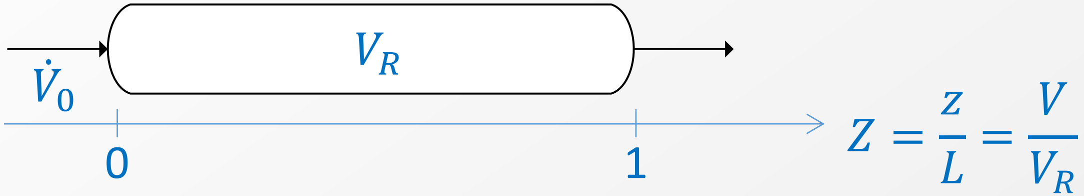
- Assumption: decay of concentration variance σ^2 is a first order process depending upon the intensity of mixing

$$r_d = -b_s\sigma_1^2 = -\frac{1}{t_{mx}}\sigma_1^2$$

b_s [s^{-1}] is a function of the mixing intensity

$$b_s \equiv \frac{1}{t_{mx}}$$

Segregation in PFR



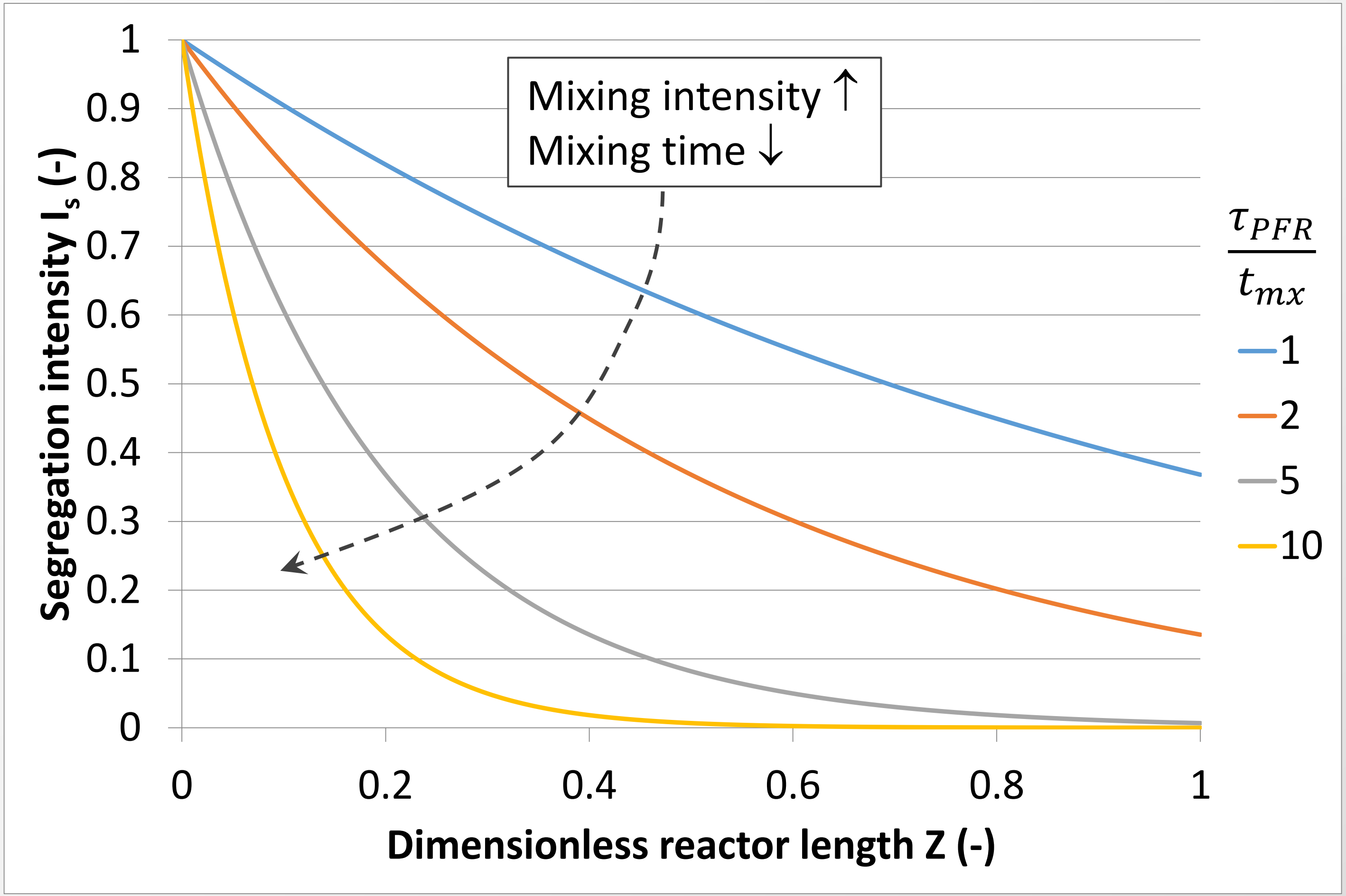
Concentration variance balance: $\frac{d\sigma_1^2}{d\tau} = r_d = -\frac{1}{t_{mx}}\sigma_1^2$

$$I_s = \frac{\sigma_1^2}{\sigma_{1,0}^2} = \exp(-\frac{\tau}{t_{mx}}) = \exp(-\frac{\tau_{PFR}}{t_{mx}}Z)$$

where $\tau = \frac{V}{\dot{V}_0}$

and $\tau_{PFR} = \frac{V_R}{\dot{V}_0}$ $\tau = Z\tau_{PFR}$ $V = ZV_R$

Segregation in a PFR

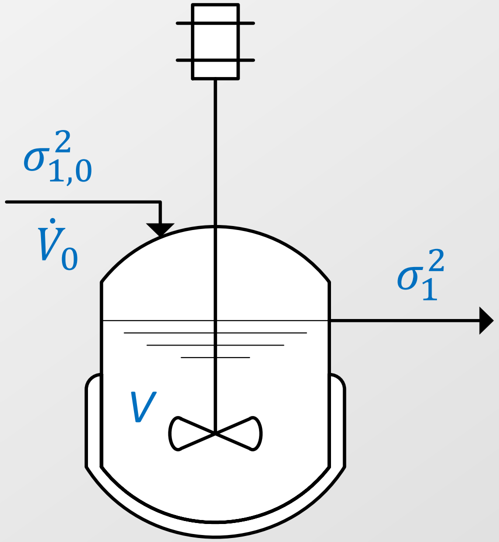


Segregation in an ideal CSTR

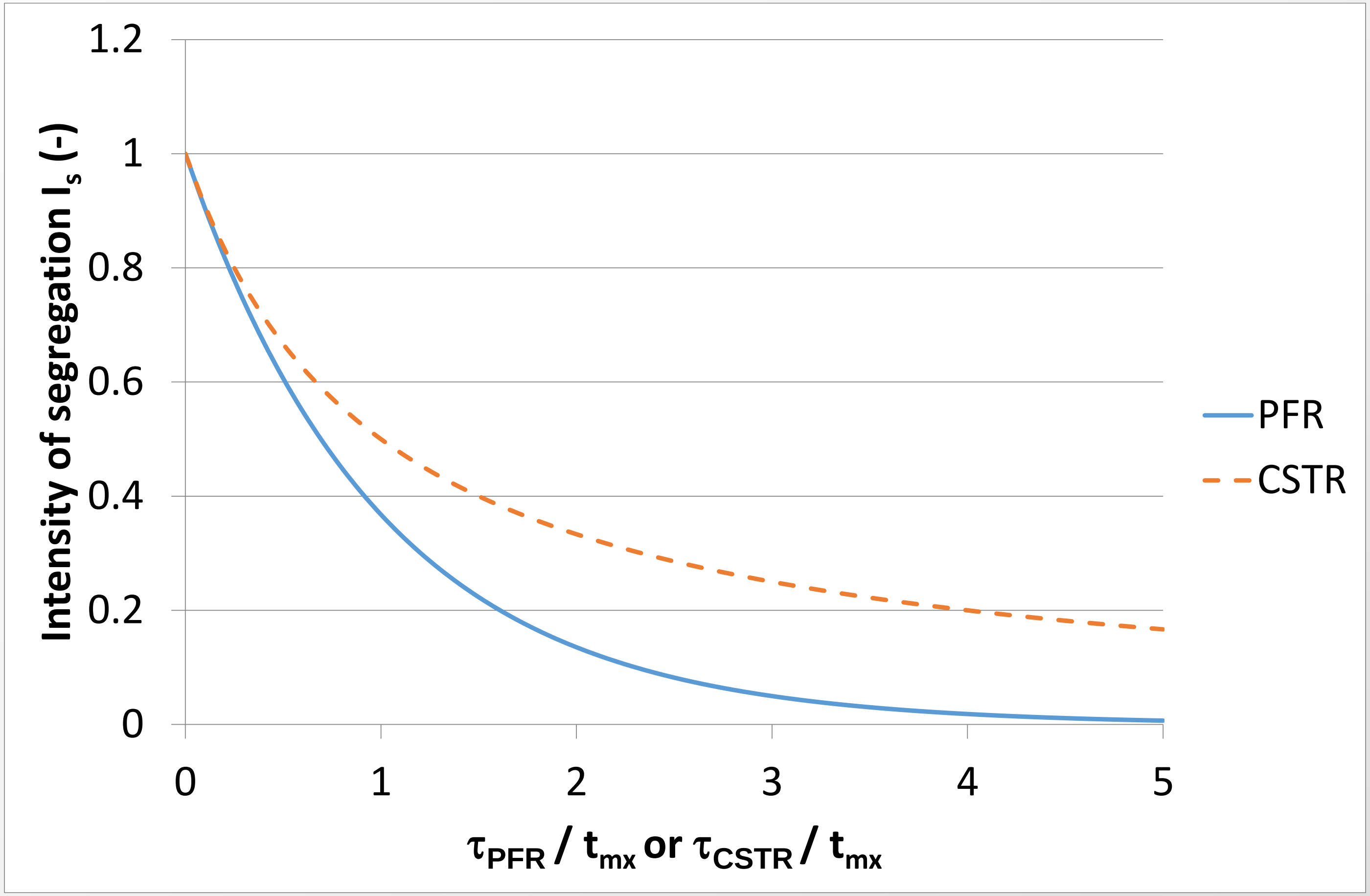
Segregation balance: $\dot{V}_0\left(\sigma_{1,0}^2 - \sigma_1^2\right) = -V r_d = V \frac{\sigma_1^2}{t_{mx}}$

$$I_s = \frac{\sigma_1^2}{\sigma_{1,0}^2} = \frac{1}{1 + \frac{\tau_{CSTR}}{t_{mx}}}$$

where $\tau_{CSTR} = \frac{V}{\dot{V}_0}$



Segregation in ideal CSTR vs PFR



→ Lower segregation in PFR vs ideal CSTR

Effect of segregation intensity on 2nd order bimolecular reactions $A_1 + A_2 \rightarrow P \quad r = kc_1c_2$

Segregation leads to an inhomogeneous reaction mixture

→Use of a *mean* reaction rate:

$$\bar{R}_1 = -\bar{r} = -k\overline{c_1c_2}$$

$$\overline{c_1c_2} = \bar{c}_1\bar{c}_2 + cov(c_1c_2)\,*$$

where $cov(c_1c_2) = \frac{1}{n}\sum(c_1 - \bar{c}_1)\,(c_2 - \bar{c}_2)$

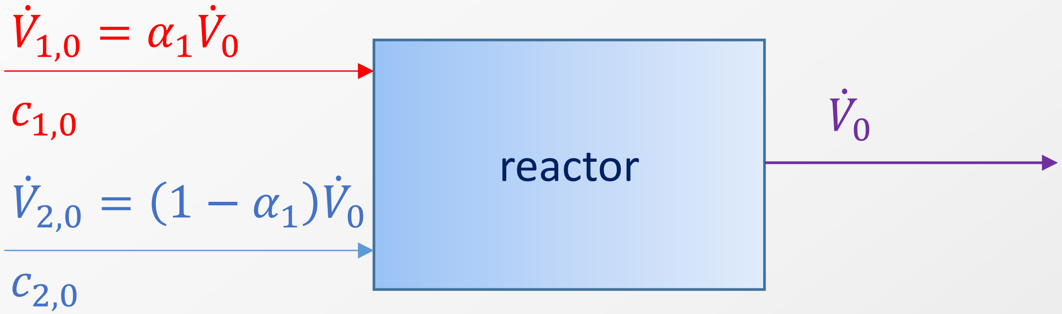
$$\boxed{\bar{R}_1 = -\mathrm{k}[\bar{c}_1\bar{c}_2 + cov(c_1c_2)]}$$

**Mean of product = product of means + covariance*

Effect of segregation intensity on 2nd order bimolecular reactions

Mixing of species A_1 and A_2

Complete segregation at reactor entrance



$$\alpha_1 = \frac{\dot{V}_{1,0}}{\dot{V}_{1,0} + \dot{V}_{2,0}} = \frac{\dot{V}_{1,0}}{\dot{V}_0}$$

$$\bar{c}_{1,0} = c_{1,0}\alpha_1$$

$$\bar{c}_{2,0} = (1 - \alpha_1)c_{2,0}$$

$$cov(c_1 c_2)_0 = \frac{1}{n}\sum\left(c_{1,0} - \bar{c}_{1,0}\right)\left(c_{2,0} - \bar{c}_{2,0}\right) = -\bar{c}_{1,0}\bar{c}_{2,0}$$

Effect of segregation intensity on 2nd order bimolecular reactions $A_1 + A_2 \rightarrow P \quad r = kc_1c_2$

Modified rate equation

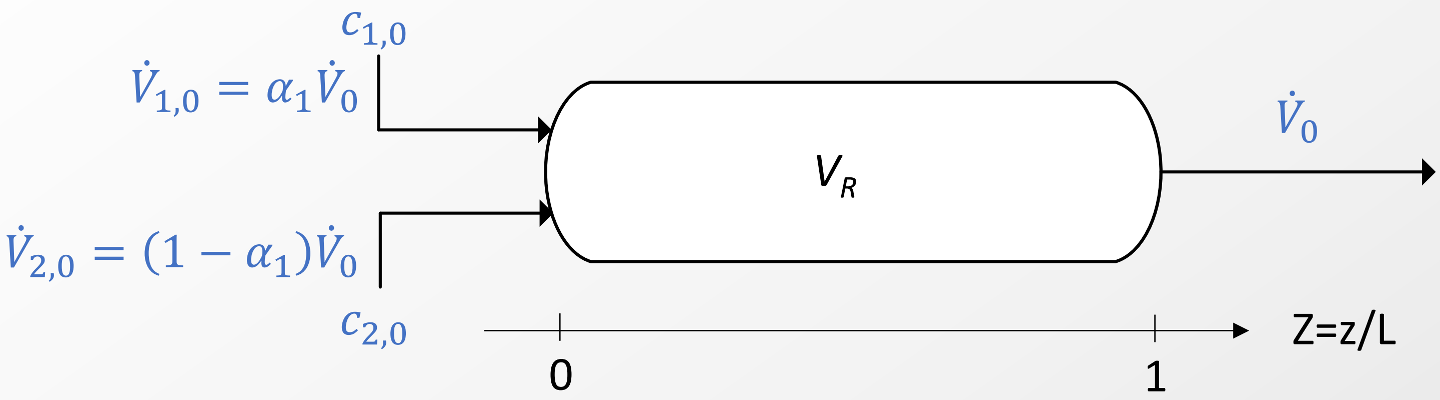
$$\bar{R}_1 = -\mathrm{k}(\bar{c}_1\bar{c}_2 + cov(c_1c_2))$$

$$I_s = \frac{cov(c_1c_2)}{cov(c_1c_2)_0}$$

$$cov(c_1c_2) = I_s \cdot cov(c_1c_2)_0 = -I_s \cdot \bar{c}_{1,0}\bar{c}_{2,0}$$

$$\boxed{\bar{R}_1 = -\mathrm{k}(\bar{c}_1\bar{c}_2 - I_s\bar{c}_{1,0}\bar{c}_{2,0}) = -\mathrm{k}\left(\bar{c}_1\bar{c}_2 - I_s c_{1,0}c_{2,0}\alpha_1(1-\alpha_1)\right)}$$

Effect of segregation intensity in PFR



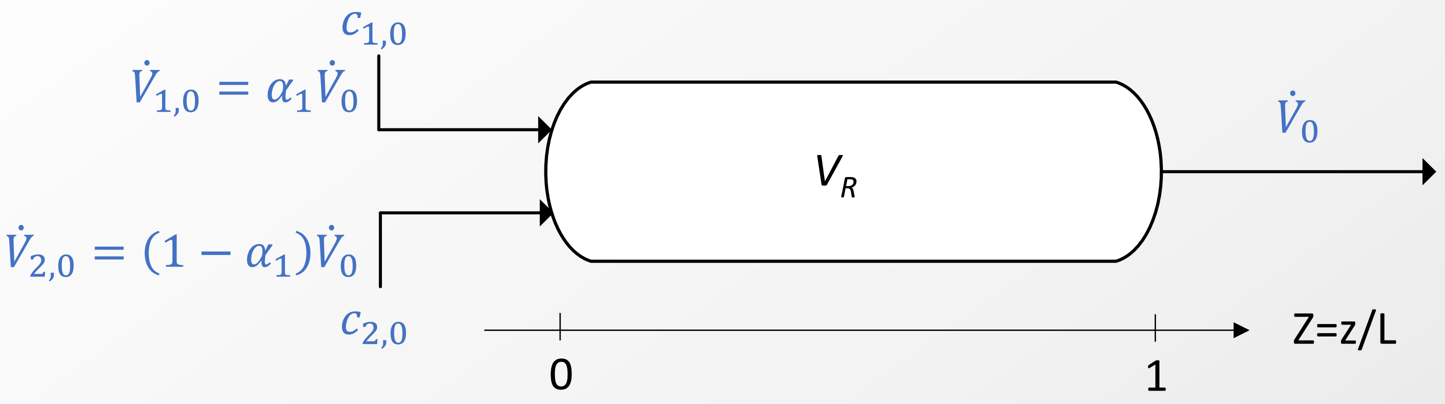
PFR: infinitesimal mass balance for component A_1:

$$\boxed{-\frac{d\bar{c}_1}{dZ} = \tau_{PFR}\bar{R}_1 = -\tau_{PFR}k\left(\bar{c}_1\bar{c}_2 - I_s\bar{c}_{1,0}\bar{c}_{2,0}\right)}$$

$$\left\{\begin{aligned} \bar{c}_2 &= \bar{c}_{2,0} - \bar{c}_{1,0} + \bar{c}_1 \\ f_1 &= \frac{\bar{c}_1}{\bar{c}_{1,0}} = (1 - X_1) \\ M &= \frac{\bar{c}_{2,0}}{\bar{c}_{1,0}} \\ DaI &= k\bar{c}_{1,0}\tau_{PFR} \end{aligned}\right.$$

$$\boxed{\frac{df_1}{dZ} = -DaI[f_1(f_1 + M - 1) - I_s M]}$$

Effect of segregation intensity in PFR



$$\boxed{\frac{df_1}{dZ} = -DaI\left[f_1(f_1+M-1) - I_s M\right]}$$

$$I_s = \exp\left(-\frac{\tau_{PFR}}{t_{mx}} Z\right) = \exp\left(-\frac{DaI}{DaII_{mx}} Z\right)$$

$$DaII_{mx} = \frac{t_{mx}}{t_r} = k\bar{c}_{1,0} t_{mx}$$

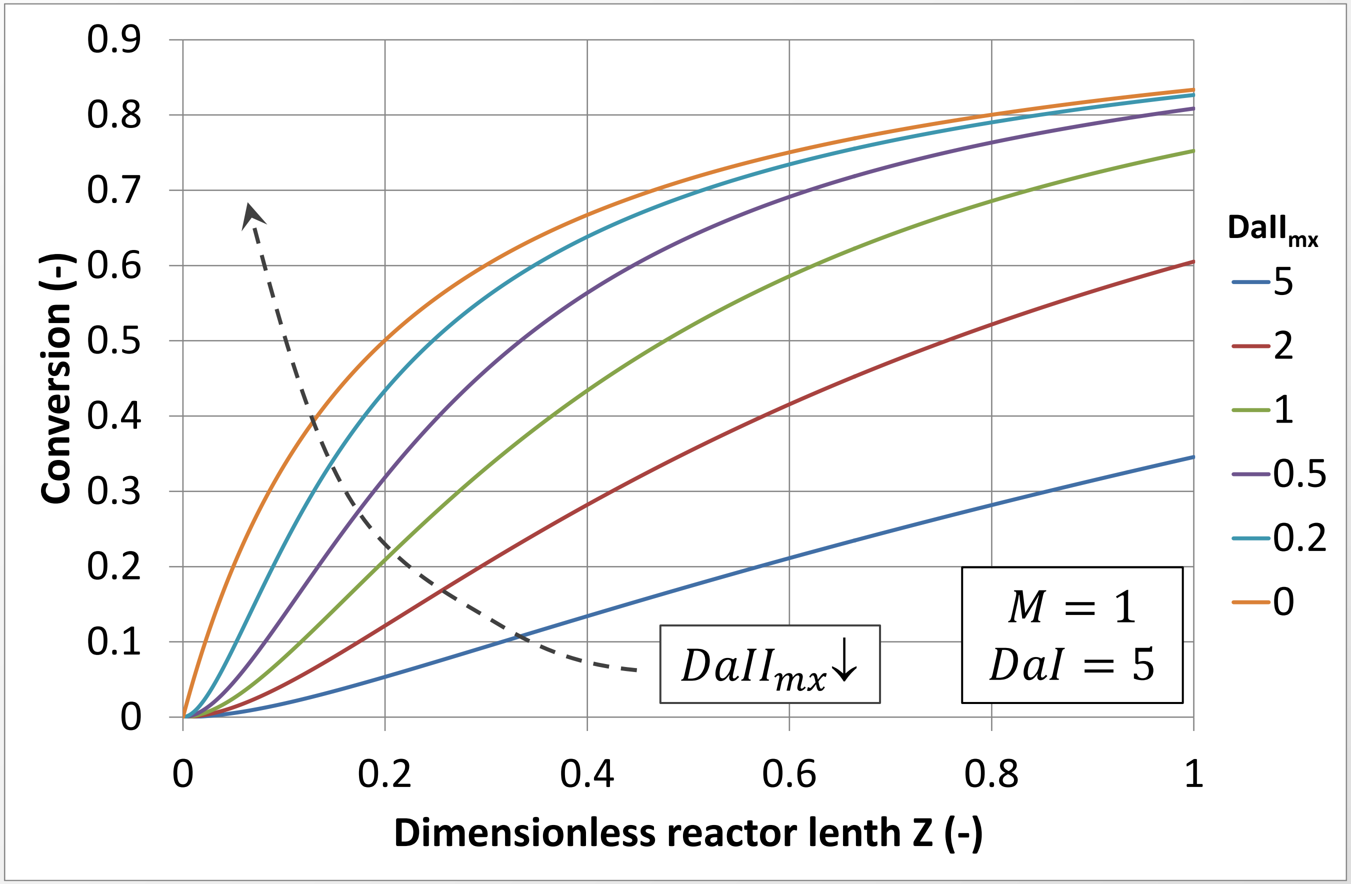
$$\boxed{\frac{df_1}{dZ} = -DaI\left[f_1(f_1+M-1) - \exp\left(-\frac{DaI}{DaII_{mx}} Z\right) M\right]}$$

→ Numerical integration

Effect of segregation intensity in PFR

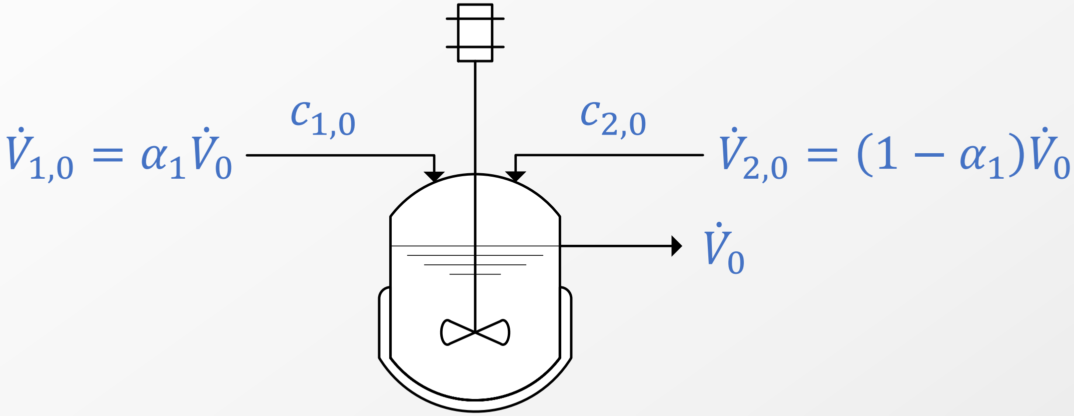
$$\boxed{\begin{array}{c} A_1 + A_2 \rightarrow P \\ r = kc_1c_2 \end{array}}$$

$$DaII_{mx} = \frac{t_{mx}}{t_r} = k\bar{c}_{1,0}t_{mx}$$



→ Higher conversion when mixing time ($DaII_{mx}$) decreases

Effect of segregation intensity in ideal CSTR



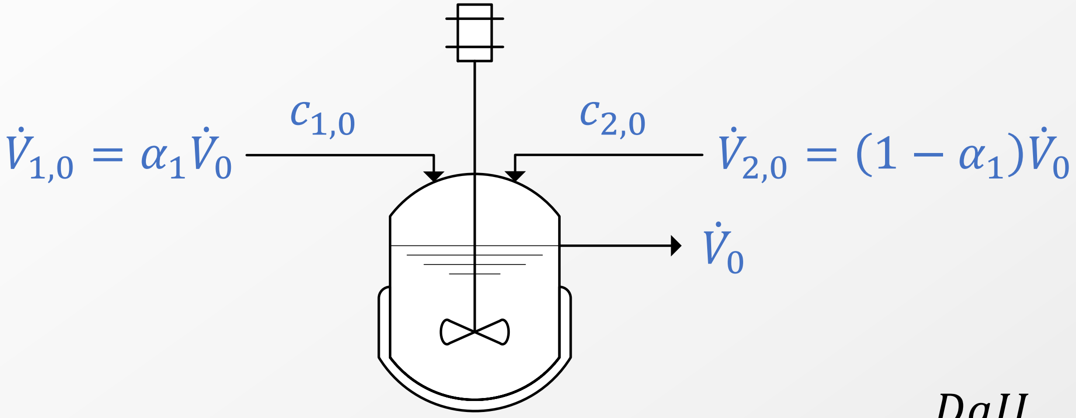
CSTR: mass balance for component A_1 :

$$\boxed{\bar{c}_1 = \bar{c}_{1,0} + \tau_{CSTR}\,\bar{R}_1 = \bar{c}_{1,0} - k\,\tau_{CSTR}\left(\bar{c}_1\bar{c}_2 - I_s\bar{c}_{1,0}\bar{c}_{2,0}\right)}$$

$$\left\{\begin{aligned} \bar{c}_2 &= \bar{c}_{2,0} - \bar{c}_{1,0} + \bar{c}_1 \\ M &= \frac{\bar{c}_{2,0}}{\bar{c}_{1,0}} \\ DaI &= k\bar{c}_{1,0}\tau_{CSTR} \\ X_1 &= 1 - \frac{\bar{c}_1}{\bar{c}_{1,0}} \end{aligned}\right.$$

$$\boxed{X_1 = \frac{\left(1 + M + \frac{1}{DaI}\right) - \sqrt{\left(1 + M + \frac{1}{DaI}\right)^2 - 4M(1 - I_s)}}{2}}$$

Effect of segregation intensity in ideal CSTR



$$DaII_{mx} = \frac{t_{mx}}{t_r} = k\bar{c}_{1,0}t_{mx}$$

$$X_1 = \frac{\left(1 + M + \frac{1}{DaI}\right) - \sqrt{\left(1 + M + \frac{1}{DaI}\right)^2 - 4M(1 - I_s)}}{2}$$

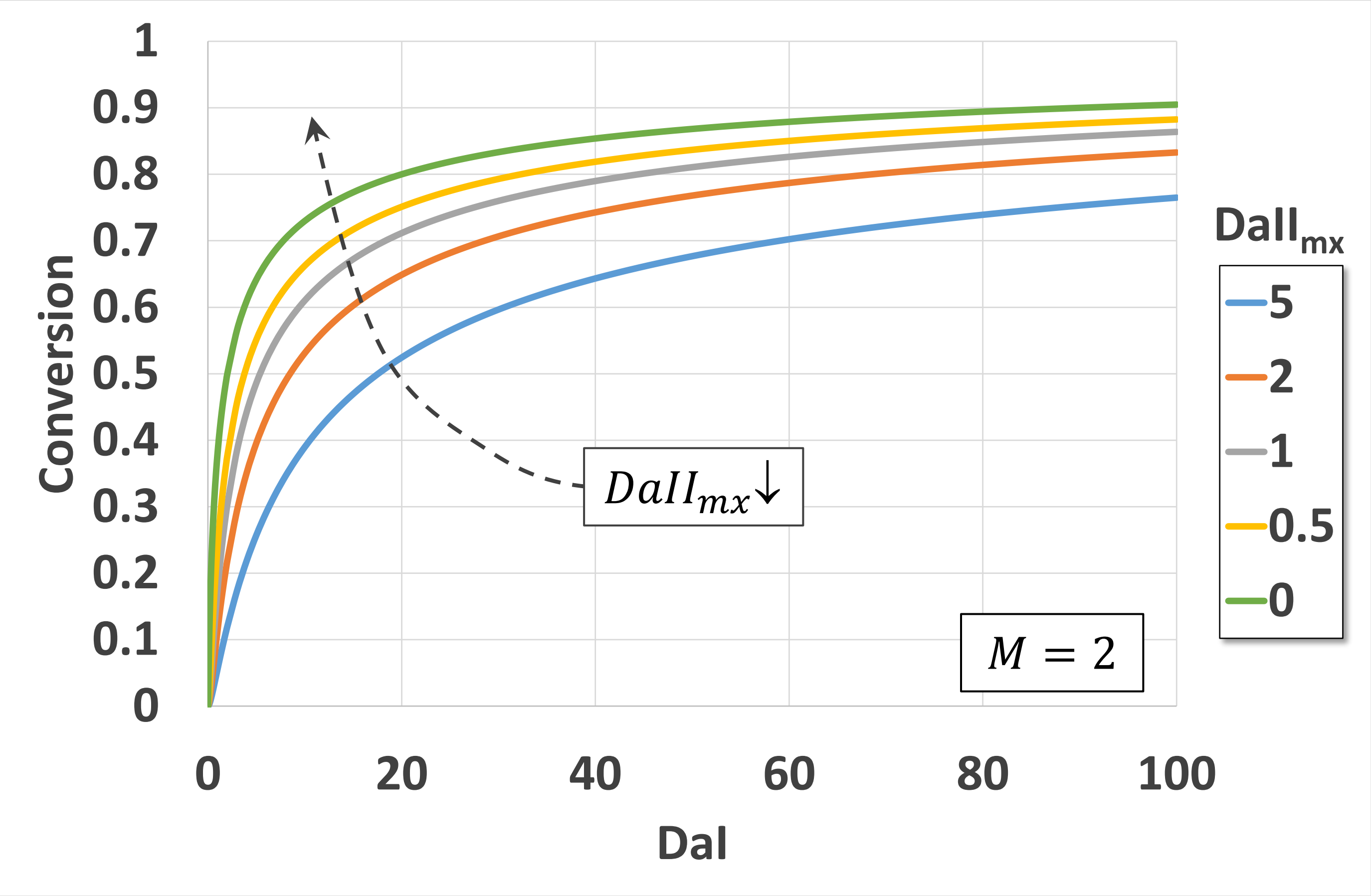
$$I_s = \frac{1}{1 + \frac{\tau_{CSTR}}{t_{mx}}} = \frac{1}{1 + \frac{DaI}{DaII_{mx}}}$$

$$X_1 = \frac{\left(1 + M + \frac{1}{DaI}\right) - \sqrt{\left(1 + M + \frac{1}{DaI}\right)^2 - 4M\left(\frac{\frac{DaI}{DaII_{mx}}}{1 + \frac{DaI}{DaII_{mx}}}\right)}}{2}$$

Effect of segregation intensity in ideal CSTR

$$\boxed{\begin{gathered}A_1 + A_2 \rightarrow P \\ r = kc_1c_2\end{gathered}}$$

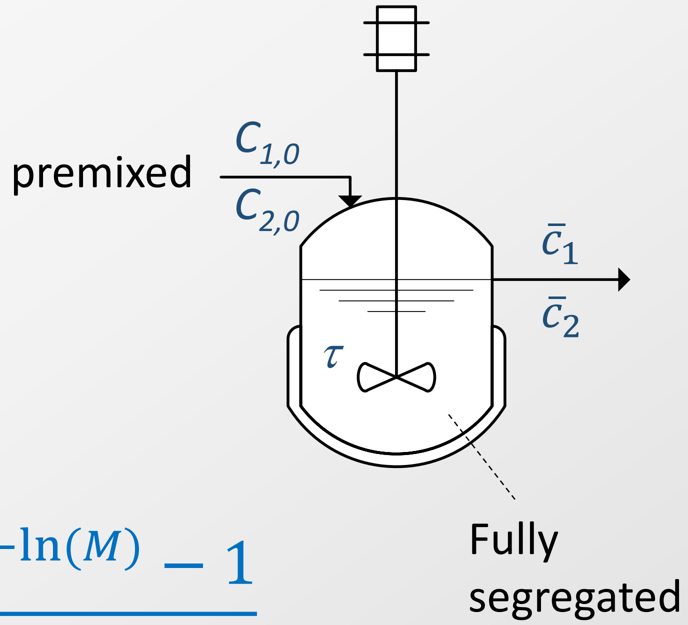
$$DaII_{mx} = \frac{t_{mx}}{t_r} = k\bar{c}_{1,0}t_{mx}$$



→ Higher conversion when mixing time ($DaII_{mx}$) decreases

Conversion in fully segregated CSTR with premixed feed

$$\boxed{\begin{gathered} A_1 + A_2 \rightarrow P \\ r = k c_1 c_2 \end{gathered}}$$



Mean conversion: $$\bar{X}_1 = \int_0^{\infty} X_1(t) E(t) dt$$

Kinetics: $$X_1(t) = \frac{M e^{k c_{1,0} t (1-M) - \ln(M)} - 1}{e^{k c_{1,0} t (1-M) - \ln(M)} - 1}$$

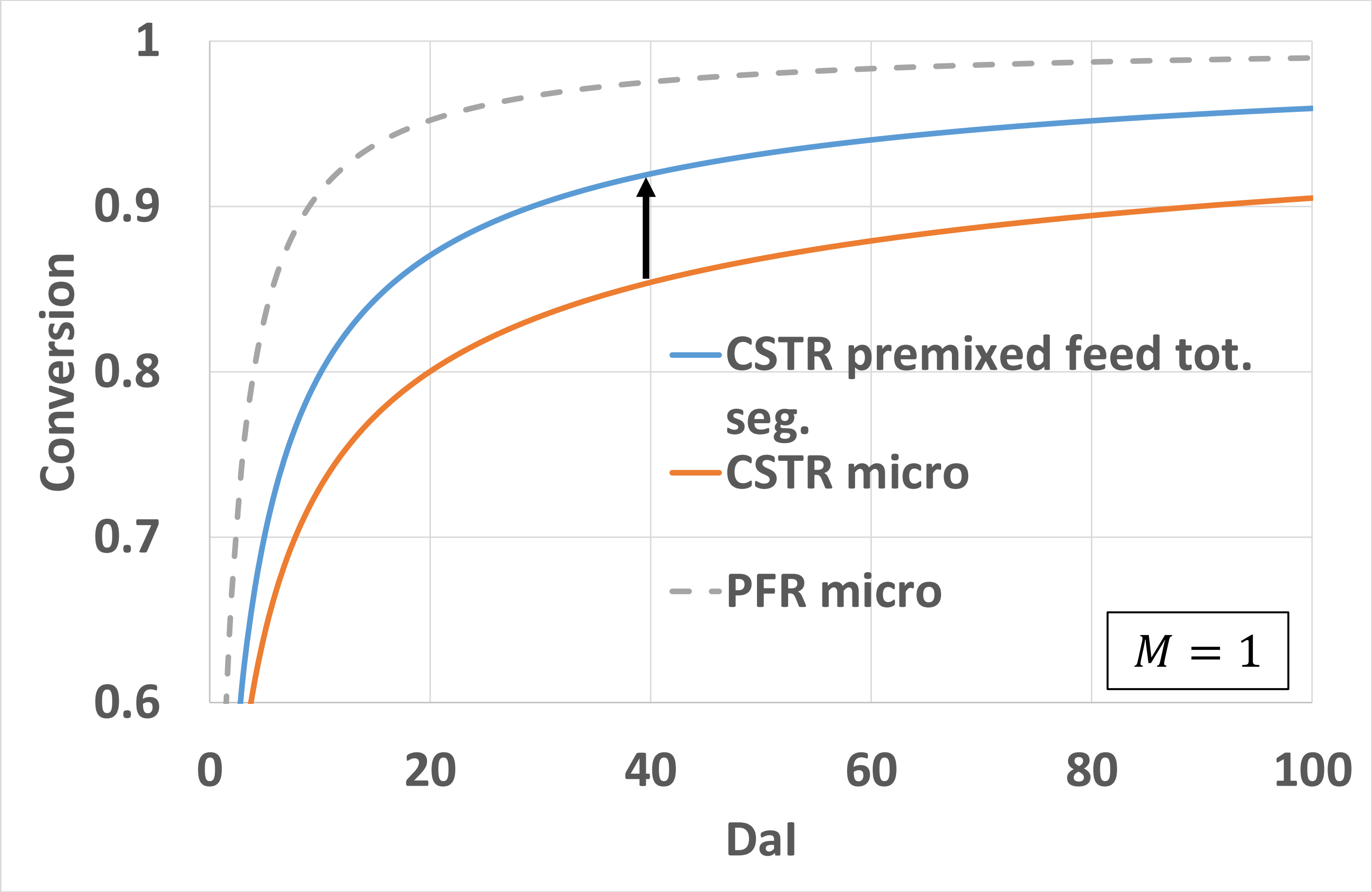
RTD: $$E(t) = \frac{1}{\tau} e^{-t/\tau}$$

Mean conversion: $$\boxed{\bar{X}_1(t) = \frac{1}{\tau} \int_0^{\infty} \frac{M e^{k c_{1,0} t (1-M) - ln(M)} - 1}{e^{k c_{1,0} t (1-M) - ln(M)} - 1} e^{-t/\tau} dt}$$

→ Numerical integration

Fully segregated CSTR with premixed feed *vs* micromixed PFR and CSTR

$$\boxed{\begin{gathered} A_1 + A_2 \rightarrow P \\ r = kc_1c_2 \end{gathered}}$$



→ Higher conversion in fully segregated CSTR with pre-mixed feed vs micromixed CSTR

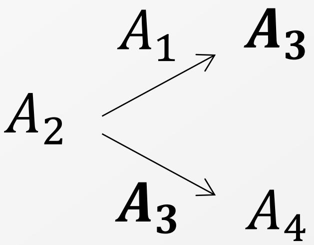
Effect of segregation intensity on performance and selectivity of consecutive-competitive reactions

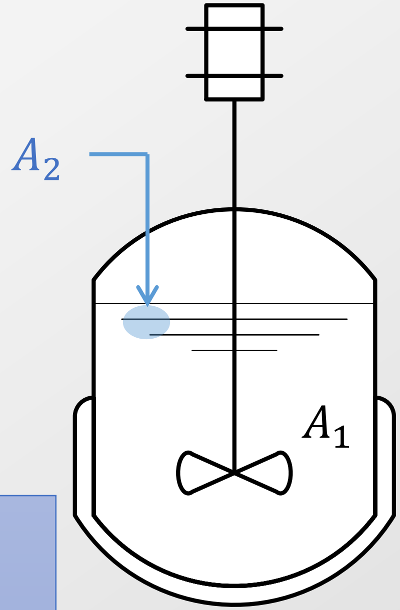
$$A_1 + A_2 \xrightarrow{k_1} A_3$$

$$A_3 + A_2 \xrightarrow{k_2} A_4$$

Effect of segregation on product distribution (qualitative)

$$A_1 \overset{A_2}{\rightarrow} \boldsymbol{A_3} \overset{A_2}{\rightarrow} A_4 \qquad \equiv$$





Slow mixing of A_1 and A_2:

→ Formation of zones with excess A_2

→ A_1 in these A_2-rich zones is quickly converted to A_3

→ A_2 is still present in the zones and, for lack of A_1 (which cannot be transported to the zone fast enough because of the slow mixing process), reacts with A_3 to form A_4)

Effect of segregation intensity

Modified rate equations $A_1 \overset{A_2}{\rightarrow} \boldsymbol{A_3} \overset{A_2}{\rightarrow} A_4$

$$A_1 + A_2 \overset{k_1}{\rightarrow} \boldsymbol{A_3} \qquad r_1 = k_1\overline{c_1 c_2} = k_1[\bar{c}_1\bar{c}_2 + cov(c_1c_2)]$$

$$\boldsymbol{A_3} + A_2 \overset{k_2}{\rightarrow} A_4 \qquad r_2 = k_2\overline{c_3 c_2} \cong k_2\bar{c}_3\bar{c}_2 \qquad (cov(c_3c_2) \cong 0\,)^*$$

$$\left\{\begin{aligned}
\bar{R}_1 &= -r_1 = -k_1[\bar{c}_1\bar{c}_2 + cov(c_1c_2)] \\
\bar{R}_2 &= -r_1 - r_2 = -k_1[\bar{c}_1\bar{c}_2 + cov(c_1c_2)] - k_2\bar{c}_3\bar{c}_2 \\
\bar{R}_3 &= r_1 - r_2 = k_1[\bar{c}_1\bar{c}_2 + cov(c_1c_2)] - k_2\bar{c}_3\bar{c}_2
\end{aligned}\right.$$

where: $cov(c_1c_2) = I_s \cdot cov(c_1c_2)_0 = -I_s \cdot \bar{c}_{1,0}\bar{c}_{2,0}$

Conc. of A_4 obtained from the mass balance: $\bar{c}_4 = \bar{c}_{2,0} - \bar{c}_2 - \bar{c}_3$

**Bourne, J.R. and Toor, H.L. (1977), AIChE J., 23 (4), 602–604*

Effect of segregation intensity

Application to PFR $A_1 \overset{A_2}{\rightarrow} \boldsymbol{A_3} \overset{A_2}{\rightarrow} A_4$

PFR: infinitesimal mass balance for component i ⇨ $\boxed{-\frac{d\bar{c}_i}{dZ} = \tau_{PFR}\,\bar{R}_i}$

Numerical integration

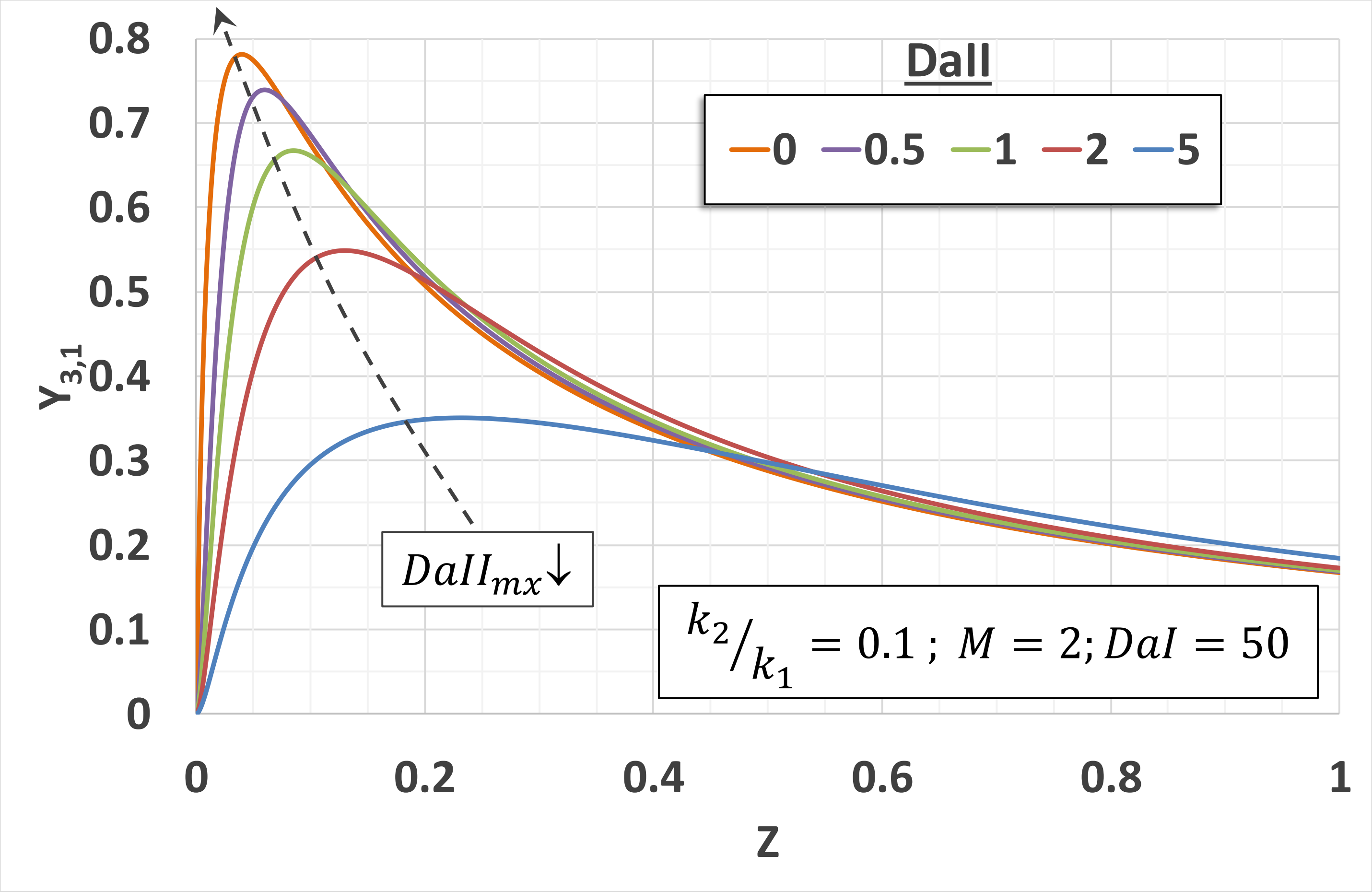
$$\left\{\begin{aligned}
-\frac{d\bar{c}_1}{\tau_{PFR}dZ} &= -k_1\left[\bar{c}_1\bar{c}_2 - I_s\cdot\bar{c}_{1,0}\bar{c}_{2,0}\right] = -k_1\left[\bar{c}_1\bar{c}_2 - \exp\left(-\frac{DaI}{DaII_{mx}}Z\right)\bar{c}_{1,0}\bar{c}_{2,0}\right]\\
-\frac{d\bar{c}_2}{\tau_{PFR}dZ} &= -k_1\left[\bar{c}_1\bar{c}_2 - \exp\left(-\frac{DaI}{DaII_{mx}}Z\right)\bar{c}_{1,0}\bar{c}_{2,0}\right] - k_2\bar{c}_3\bar{c}_2\\
-\frac{d\bar{c}_3}{\tau_{PFR}dZ} &= k_1\left[\bar{c}_1\bar{c}_2 - \exp\left(-\frac{DaI}{DaII_{mx}}Z\right)\bar{c}_{1,0}\bar{c}_{2,0}\right] - k_2\bar{c}_3\bar{c}_2
\end{aligned}\right.$$

$$\bar{c}_4 = \bar{c}_{2,0} - \bar{c}_2 - \bar{c}_3$$

$$DaI = k_1\bar{c}_{1,0}\tau_{PFR}$$

$$DaII_{mx} = k_1\bar{c}_{1,0}t_{mx}$$

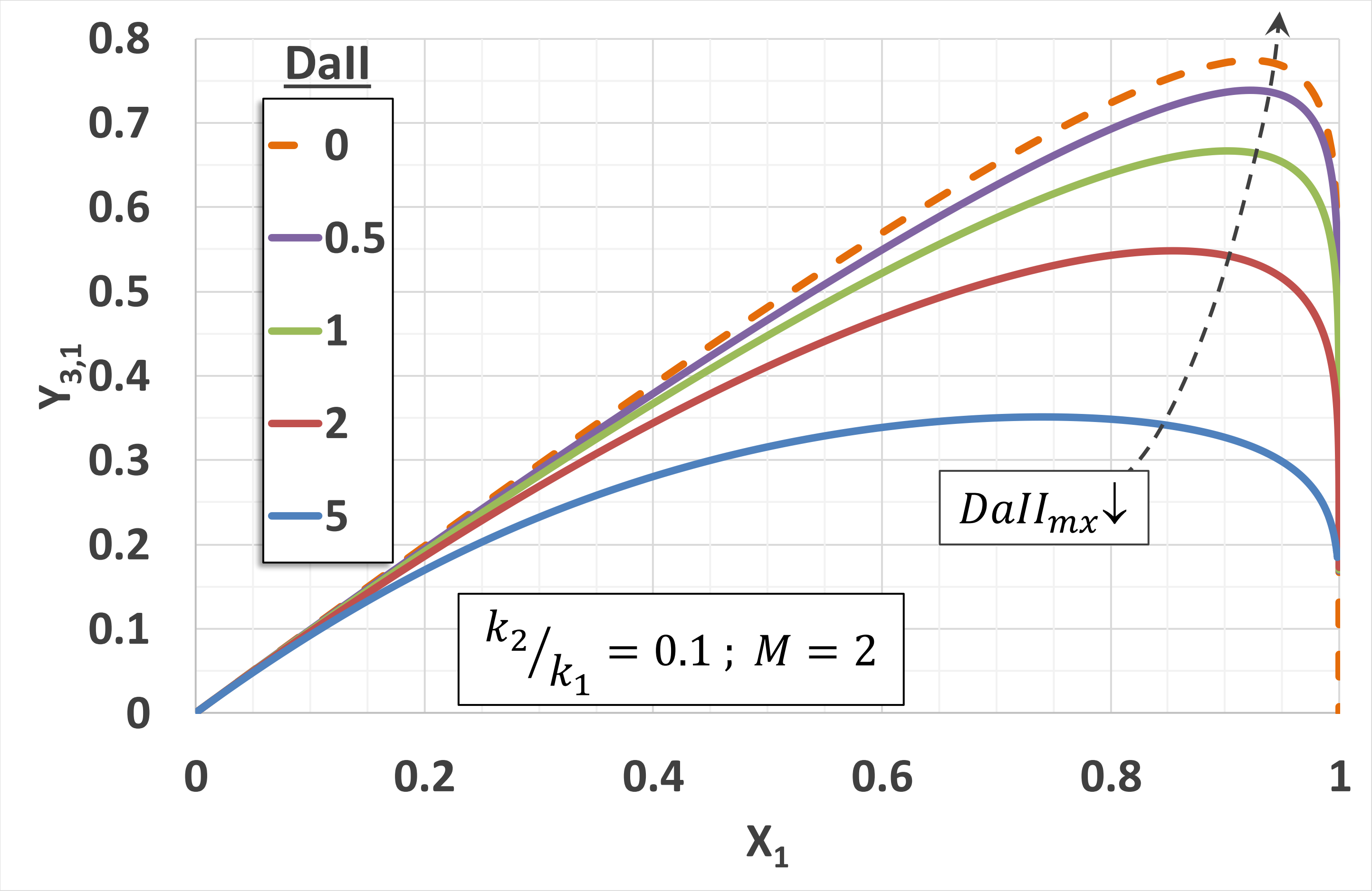
Effect of segregation intensity on intermediate product yield (PFR) $A_1 \overset{A_2}{\rightarrow} \boldsymbol{A_3} \overset{A_2}{\rightarrow} A_4$



→ Higher yield when mixing time ($DaII_{mx}$) decreases

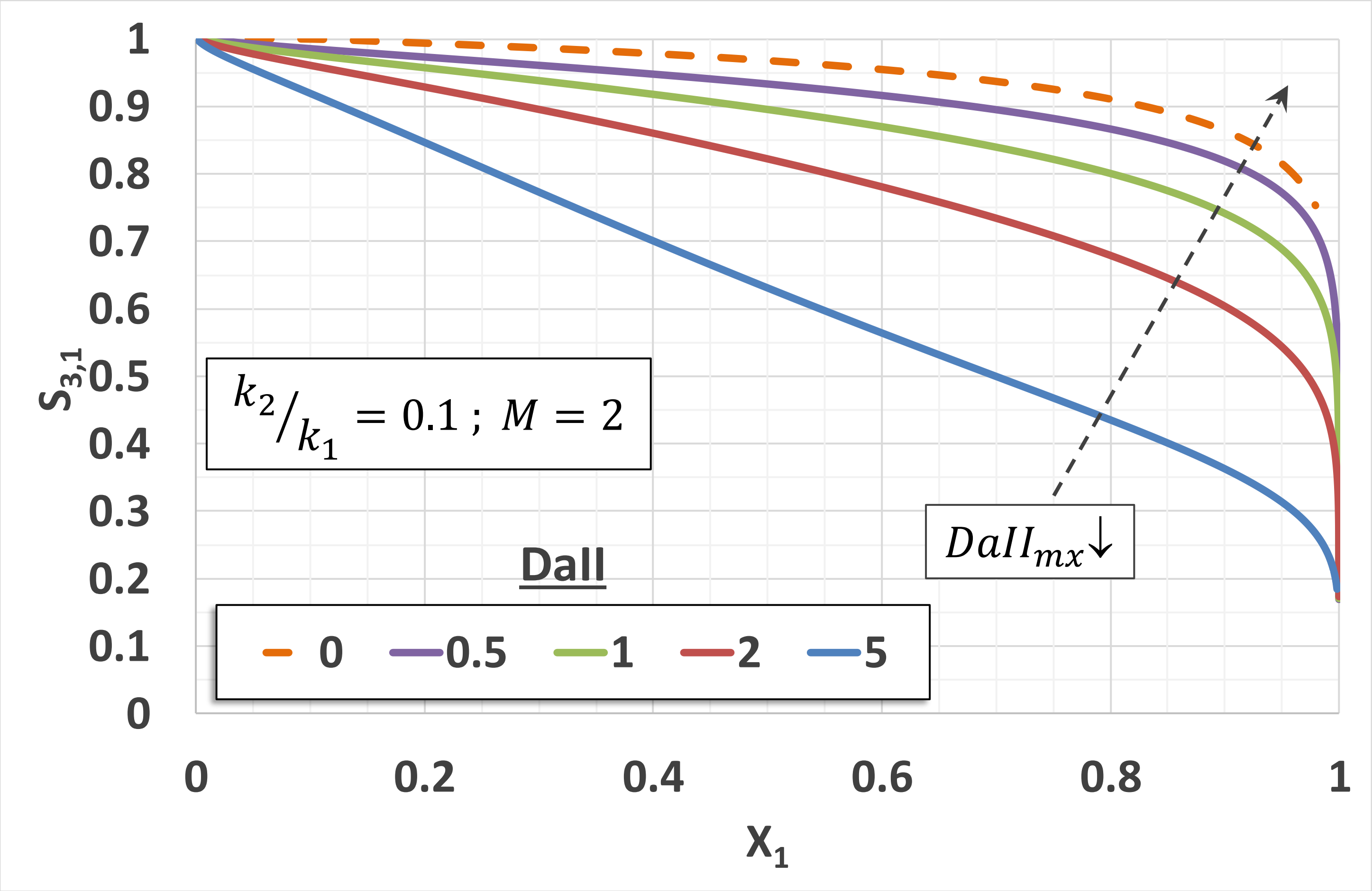
Effect of segregation intensity on intermediate product yield (PFR)

$A_1 \overset{A_2}{\rightarrow} \boldsymbol{A_3} \overset{A_2}{\rightarrow} A_4$



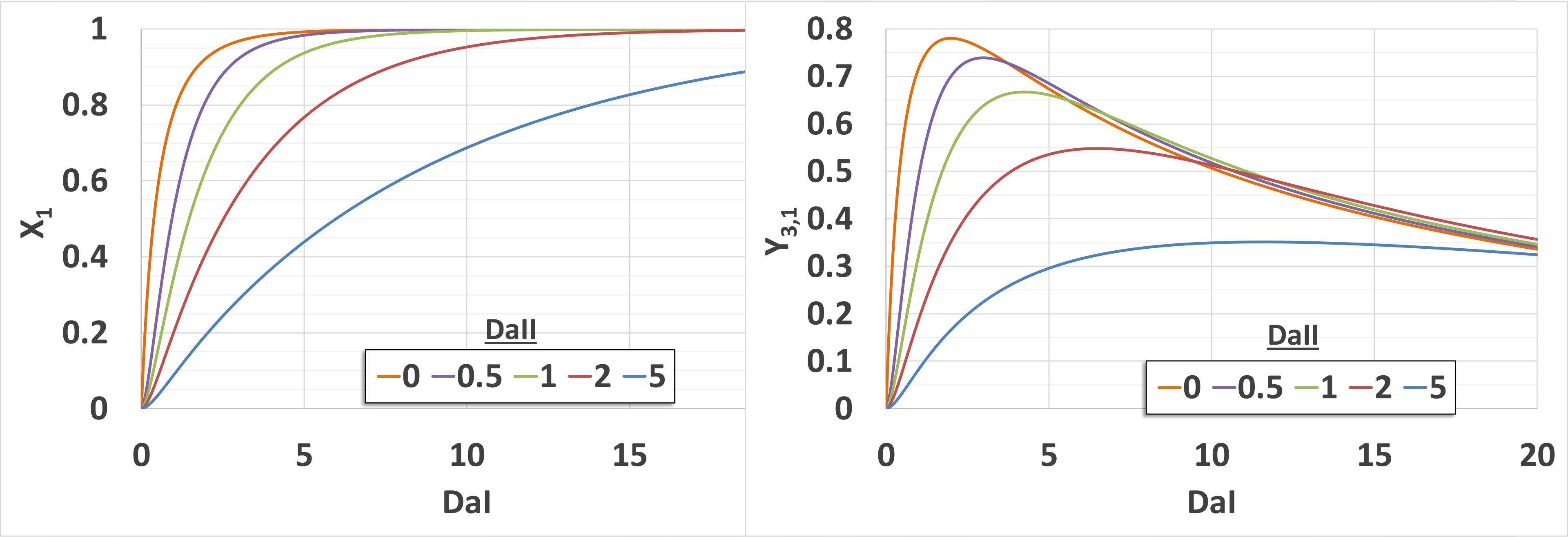
→ Higher yield when mixing time ($DaII_{mx}$) decreases

Effect of segregation intensity on intermediate product selectivity (PFR) $A_1 \xrightarrow{A_2} \boldsymbol{A_3} \xrightarrow{A_2} A_4$



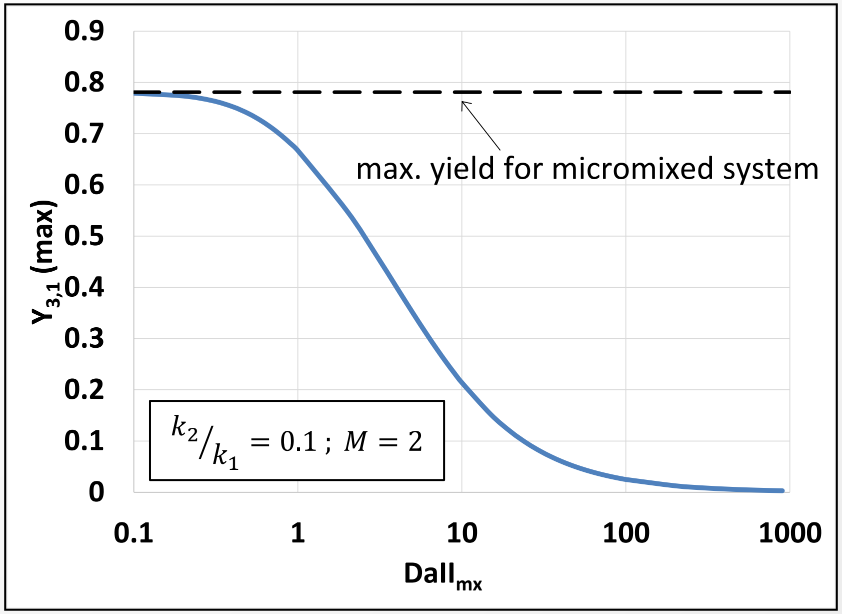
→ Higher selectivity when mixing time ($DaII_{mx}$) decreases

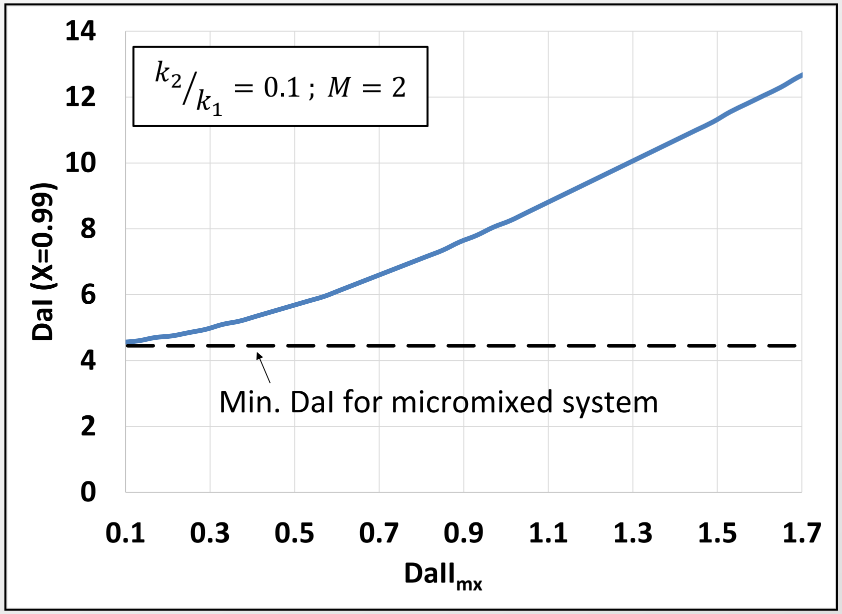
Effect of segregation intensity on conversion and intermediate product yield (PFR) $A_1 \xrightarrow{A_2} \boldsymbol{A_3} \xrightarrow{A_2} A_4$



→ Higher conversion and higher yield when mixing time ($DaII_{mx}$) decreases

Effect of segregation intensity on performance and selectivity (PFR) $A_1 \xrightarrow{A_2} \boldsymbol{A_3} \xrightarrow{A_2} A_4$



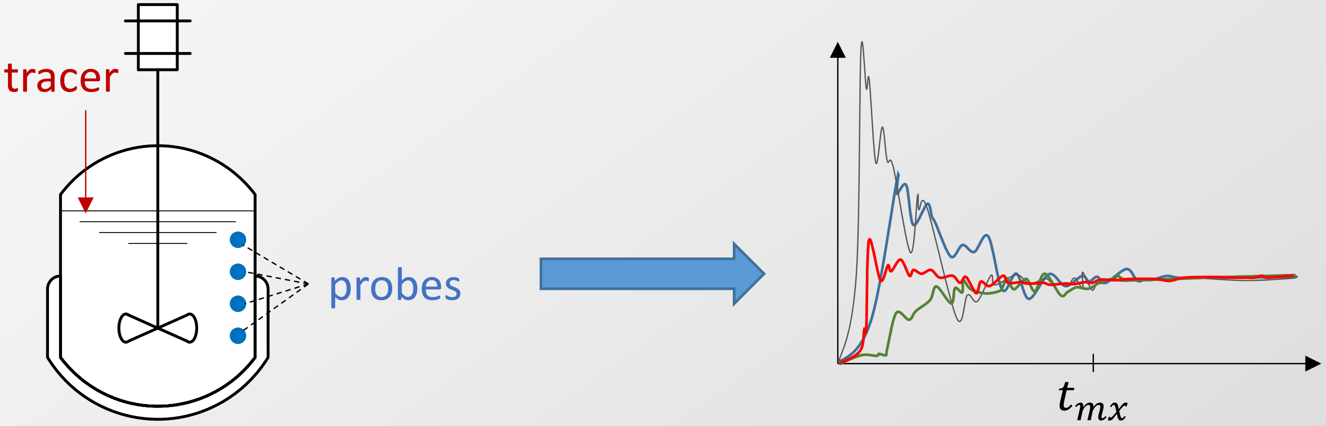


→ Higher maximum yield when mixing time ($DaII_{mx}$) decreases
→ Lower DaI required to reach 99% conversion when mixing time ($DaII_{mx}$) decreases
→ Negligible effect of segregation when $\boldsymbol{t_{mx} \leq 0.1 t_r}$ (i.e., $DaII_{mx} \leq 0.1$)

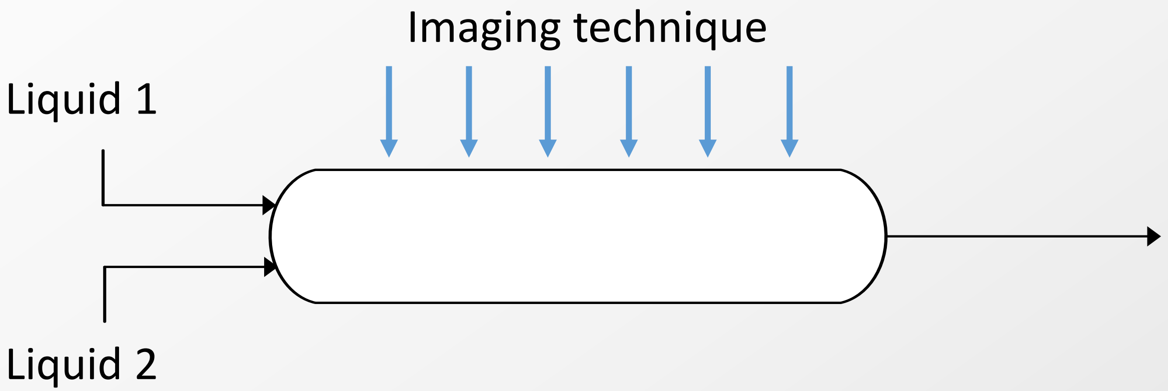
Experimental mixing characterization

Physical methods – batch reactor

- Inject inert tracer into reactor
- Monitor tracer concentration or physical property (electrical conductivity, pH, color, temperature, etc.) vs time in key reactor locations
- Mixing time = time to reach ‘uniformity’ in the reactor
  - many definitions of degree of uniformity exist (t_{m95}, t_{m99}, etc.)
  - t_{mx} is a function of the definition



Physical methods – continuous system : dilution method



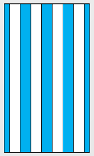
- Dilution method: liquid 1 is transparent, liquid 2 contains a dye
- Requires transparent device (or viewing window) and imaging technique (video camera or high-speed camera) to visualize spreading of dye along flow axis
- Visualization of color spreading along the mixer ⇨ mixing is judged complete when the concentration of the dye is uniform across the channel cross section
- More precise method: measurement of conc. variance decay (segregation) along reactor to estimate mixing time. Requires measurement of the local concentration in a controlled volume and express its fluctuation with respect to the mean.

Physical methods – alternative methods

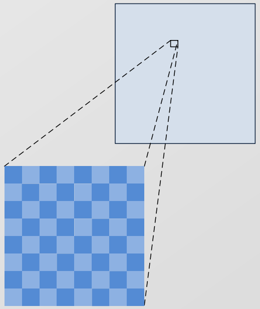
- Induced color change (pH change for example)
  - Allows to visualize interfaces (reactions occurring at the interface)
- Change in electrical conductivity

Physical methods – drawbacks

- Need for transparent mockup (glass or polymeric)
- Visualization of the mixing process is perpendicular to the flow
  - Images provide information averaged over the depth of the microchannel
  - Difference between a perfectly mixed system and a multi-layered system cannot be distinguished (optical artifact)



- Degree of mixing depends on spatial resolution of the probe used to measure local concentration
  - Use of fluorescent dye (fluorescein or rhodamin) with confocal scanning microscopy allows distinguishing between perfect mixing and multi-lamellae by providing 3D imaging of the flow
- Physical methods inadequate if sampling volume is larger than smallest segregation scales



⇨Chemical methods offer a solution to this major drawback

Chemical methods

- Use of fast, competitive chemical reactions that are strongly influenced by mixing
- **Offline** measurement of the product distribution to characterize the mixing efficiency
- When t_r and t_{mx} are of the same order of magnitude, consumption rate is lower than intrinsic reaction rate
- Reagent concentrations need to be adjusted to tune reaction rates
- Models for the coupling of mixing and reaction are used to estimate t_{mx} (e.g., Interaction by Exchange with the Mean or Engulfment models)

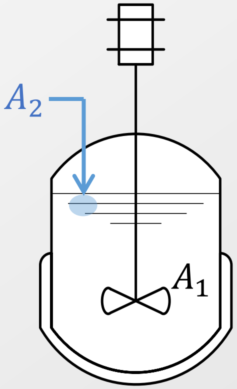
Chemical methods

Consecutive competitive reactions

$$A_1 + A_2 \xrightarrow{inst.} A_3$$

$$A_3 + A_2 \xrightarrow{fast} A_5$$

$$A_1 \overset{A_2}{\rightarrow} A_3 \overset{A_2}{\rightarrow} A_5$$



- Reaction 1 is instantaneous (e.g., acid-base) $t_{r1} \ll t_{r2}$
- Reaction 2 is ‘tuned’ so that $t_{r2} \cong t_{mx}$
- Stoichiometric defect of A_2 relatively to A_1
- Fast mixing ($t_{mx} \ll t_{r2}$) ⇨ only A_3 formed
- Slow mixing (t_{mx} close to t_{r2}) ⇨ A_5 is also formed
- Conc. of A_5 increases if mixing slows down

Chemical methods

Consecutive competitive reactions

Definition of segregation index (X_S)*

$$A_1 + A_2 \xrightarrow{inst.} A_3$$

$$A_3 + A_2 \xrightarrow{fast} A_5$$

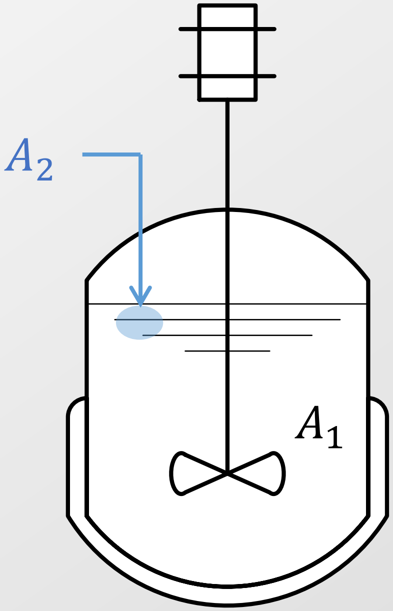
$$A_1 \overset{A_2}{\rightarrow} A_3 \overset{A_2}{\rightarrow} A_5$$

$$X_S = \frac{Reagent\ consumption\ to\ A_5}{Total\ reagent\ consumption} = \frac{2c_5}{2c_5 + c_3}$$

$0 < X_S < 1$

$X_S = 0$: micromixed system

$X_S = 1$: fully segregated system



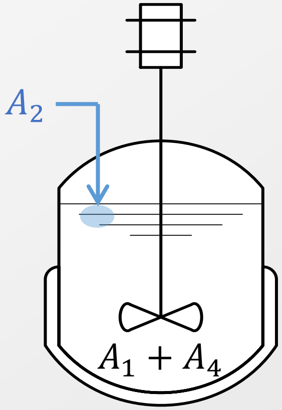
- Overall, $\bar{c}_2 < \bar{c}_1$
- Locally, if slow mixing ⇨ $c_2 > c_1$ ⇨ formation of A_5

*Bourne, Kozicki, Rys, 1981

Chemical methods

Parallel competitive reactions

$$\boxed{\begin{array}{ll} A_1 + A_2 \xrightarrow{inst.} A_3 & A_1 \xrightarrow{A_2} A_3 \\ A_4 + A_2 \xrightarrow{fast} A_5 & A_4 \xrightarrow{A_2} A_5 \end{array}}$$



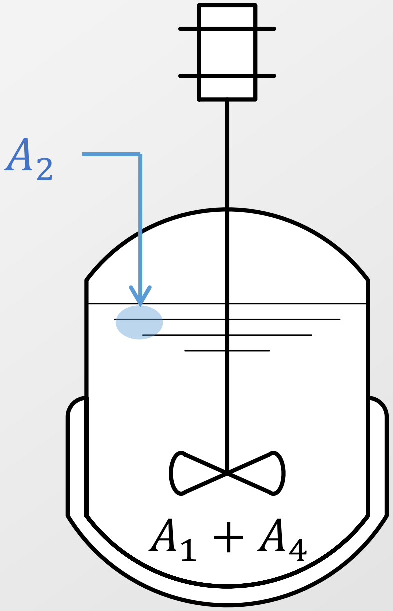
- Reaction 1 is instantaneous (e.g., acid-base) $t_{r1} \ll t_{r2}$
- Reaction 2 is tuned so that $t_{r2} \cong t_{mx}$
- Stoichiometric defect of A_2 relatively to A_1+ A_4
- Fast mixing ($t_{mx} \ll t_{r2}$) ⇨ only A_3 formed
- Slow mixing (t_{mx} close to t_{r2}) ⇨ A_5 is also formed
- Conc. of A_5 increases if mixing slows down
- t_{r2} can be independently tuned by adjusting c_4 (an advantage over the consecutive competitive method)

Chemical methods

Parallel competitive reactions

$$A_1 + A_2 \xrightarrow{inst.} A_3 \qquad A_1 \xrightarrow{A_2} A_3$$

$$A_4 + A_2 \xrightarrow{fast} A_5 \qquad A_4 \xrightarrow{A_2} A_5$$



$$X_S = \frac{A_5\ yield\ (exp.)}{A_5\ yield\ (complete\ seg.)} = \frac{Y}{Y_{CS}} = \frac{c_5}{c_{2,0}} \frac{c_{1,0} + c_{4,0}}{c_{4,0}}$$

Micromixed conditions:

$$\frac{c_5}{c_3} = \frac{R_5}{R_3} = \frac{k_2 c_4 c_2}{k_1 c_1 c_2} = \frac{k_2 c_4}{k_1 c_1}$$

Fully segregated conditions:

$$\frac{c_5}{c_3} = \frac{R_5}{R_3} = \frac{k_{mx} c_4}{k_{mx} c_1} = \frac{c_4}{c_1}$$

- Overall, $\bar{c}_2 < \bar{c}_1 + \bar{c}_4$
- Locally, if slow mixing ⇨ $c_2 > c_1 + c_4$ ⇨ formation of A_5

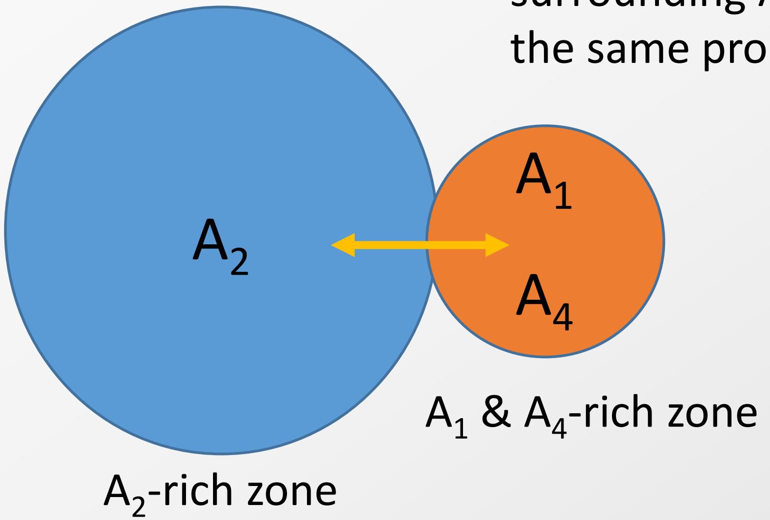
Parallel competitive reactions

Full segregation

$$A_1 + A_2 \xrightarrow{inst.} A_3 \qquad A_1 \overset{A_2}{\rightarrow} A_3$$

$$A_4 + A_2 \xrightarrow{fast} A_5 \qquad A_4 \overset{A_2}{\rightarrow} A_5$$

Full segregation ⇨ local excess of A_2 ⇨ full conversion of surrounding A_1 & A_4 fluid aggregates ⇨ A_1 & A_4 consumed in the same proportion as in the feeds (i.e., no selectivity)



$$Y_{CS} = \frac{c_{4,0}}{c_{1,0} + c_{4,0}}$$

← A_2 converted to A_5

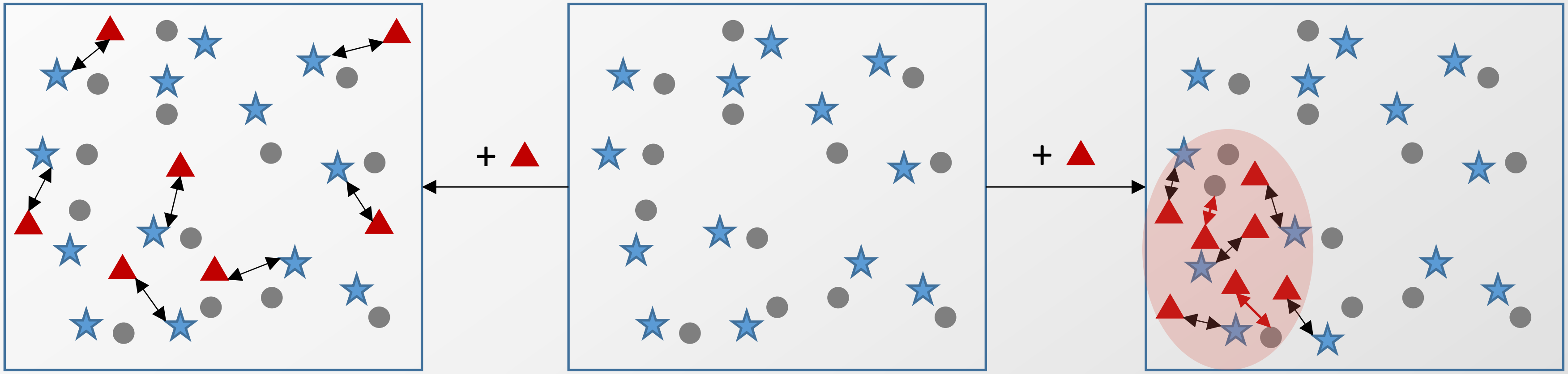
← Total A_2 consumed

Parallel competitive reactions

Effect of mixing on by-product formation

★ + ▲ $\xrightarrow{\text{fast}}$ Main product

● + ▲ $\xrightarrow{\text{slow}}$ By-product



Fast mixing

Reagent ▲ well distributed into reaction mixture before reaction takes place ⇨ only main product formed

Slow mixing

Reaction takes place locally, before reagent ▲ can be distributed into reaction mixture ⇨ some by-product formed

Neutralization and ester hydrolysis

$NaOH + HCl \overset{k_1}{\rightarrow} NaCl + H_2O$ (neutralization, ‘instantaneous’)

$NaOH + CH_2ClCOOC_2H_5 \overset{k_2}{\rightarrow} CH_2ClCOONa + C_2H_5OH$ (hydrolysis, fast)

- Parallel competitive reaction network
- Add NaOH solution to solution of HCl and ethyl monochloroacetate
- Well known kinetics
- Simple analysis (GC) of residual ester or ethanol formed to characterize degree of micromixing

M. Jasińska, Chemical and Process Engineering 2015, 36 (2), 171-208

Neutralization and acetal hydrolysis

$$NaOH + HCl \overset{k_1}{\rightarrow} NaCl + H_2O$$ (neutralization, ‘instantaneous’)

$$H_2O + CH_3C(OCH_3)_2CH_3 \underset{H^+}{\overset{k_2}{\rightarrow}} (CH_3)_2CO + 2CH_3\text{OH}$$ (hydrolysis, fast)

- Parallel competitive reaction network
- Add HCl solution to solution of NaOH and dimethoxypropane
- Reaction 1 irreversible, very fast with respect to mixing, moderately exothermic (-55.8 kJ/mol)
- Reaction 2 irreversible in diluted aq. solutions and acid-catalyzed.
- Ideally (micromixed system), no acetal hydrolysis ⇨ no methanol formed
- Analysis of methanol formed to characterize degree of micromixing (or segregation)

M. Jasińska, Chemical and Process Engineering 2015, 36 (2), 171-208

Villermaux-Dushman reaction

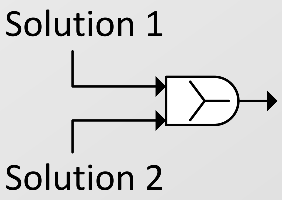
(iodide-iodate reaction)

$H_2BO_3^- + H^+ \xrightarrow{k_1} H_3BO_3$ (neutralization, ‘instantaneous’)

$5I^- + IO_3^- + 6H^+ \Leftrightarrow 3I_2 + 3H_2O$ (redox, fast)

$I_2 + I^- \overset{K_B}{\Leftrightarrow} \boldsymbol{I_3^-}$ (equilibrium, ‘instantaneous’)

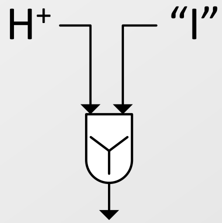
- Parallel competitive reaction network
- Solution 1: Sulfuric acid solution (stoichiometric defect of H^+)
- Solution 2: Iodide I^- and iodate IO_3^- in $H_2BO_3^-/H_3BO_3$ buffer
- Ideally, H^+ reacts only with $H_2BO_3^-$ ⇨ no I_2 formed if micromixing
- Concentration of iodine I_2 is a measure of degree of segregation
- I_2 reacts rapidly with I^- (eq. reaction, K_B well known) to yield triiodide anions I_3^-
- I_3^- easily analyzed by UV/vis spectrophotometry (353 nm)



Villermaux-Dushman reaction

(iodide-iodate reaction)

$$\boxed{\begin{array}{ll} H_2BO_3^- + H^+ \overset{k_1}{\rightarrow} H_3BO_3 & \text{(neutralization, ‘instantaneous’)} \\ 5I^- + IO_3^- + 6H^+ \Leftrightarrow 3I_2 + 3H_2O & \text{(redox, fast)} \\ I_2 + I^- \overset{K_B}{\Leftrightarrow} I_3^- & \text{(equilibrium, ‘instantaneous’)} \end{array}}$$



- Mixing quality determined by segregation index X_S

For equal volumetric flowrates of the two solutions

$$\boxed{X_S = \frac{Y}{Y_{CS}}}$$

$$Y = \frac{2\left(\dot{n}_{I_2} + \dot{n}_{I_3^-}\right)}{\dot{n}_{H^+,0}} = \frac{4\left(c_{I_2} + c_{I_3^-}\right)}{c_{H^+,0}} \qquad \left(\frac{H^+ consumed\ by\ reaction\ 2}{Total\ H^+}\ \text{experimental}\right)$$

$$Y_{CS} = \frac{6c_{IO_3^-,0}}{6c_{IO_3^-,0} + c_{H_2BO_3^-,0}} \qquad \left(\frac{H^+ consumed\ by\ reaction\ 2}{Total\ H^+}\ \text{complete segregation}\right)$$

Villermaux-Dushman reaction

(iodide-iodate reaction)

$$H_2BO_3^- + H^+ \overset{k_1}{\rightarrow} H_3BO_3$$ (neutralization, ‘instantaneous’)

$$5I^- + IO_3^- + 6H^+ \Leftrightarrow 3I_2 + 3H_2O$$ (redox, fast)

$$I_2 + I^- \overset{K_B}{\Leftrightarrow} I_3^-$$ (equilibrium, ‘instantaneous’)

- Mixing quality can also be characterized by micromixedness ratio $\boldsymbol{\alpha}$

$$X_S = \frac{V_{CS}}{V_{CS}+V_{PM}} \quad \rightarrow \quad \boxed{\alpha \equiv \frac{V_{PM}}{V_{CS}} = \frac{1-X_S}{X_S}}$$

V_{PM}: Perfectly mixed volume

V_{CS}: Completely segregated volume

Villermaux-Dushman reaction

Determination of c_{I_2} and $c_{I_3^-}$

$$\boxed{c_{I_3^-} = \frac{A}{\varepsilon_{353}\, l}}$$

ε_{353} = 2606 $[m^2 mol^{-1}]$ (Beer-Lambert)

$$I_2 + I^- \overset{K_B}{\Leftrightarrow} I_3^- \qquad K_B = \frac{c_{I_3^-}}{c_{I_2}\, c_{I^-}} \quad [l\, mol^{-1}]$$

$$\log_{10} K_B = \frac{555}{T} + 7.355 - 2.575 \log_{10} T$$ (T in K)

(Equilibrium data)

$$c_{I^-} = c_{I^-,0} - \frac{5}{3}\left(c_{I_2} + c_{I_3^-}\right) - c_{I_3^-}$$ (Iodine balance)

$$\boxed{\Rightarrow -\frac{5}{3} c_{I_2}^2 + \left(c_{I^-,0} - \frac{8}{3} c_{I_3^-}\right) c_{I_2} - \frac{c_{I_3^-}}{K_B} = 0}$$

Villermaux-Dushman reaction

Experimental considerations

- Adjustment of reagent concentrations to t_{mx} is necessary, as **X_S is a function of t_{r1} and t_{r2}**.
    - At constant concentrations (i.e., constant t_{r1} and t_{r2}), changes in X_S correctly account for variations in t_{mx}
    - X_S measured in reactors using different concentrations cannot be compared!
- Adjustment of the acid concentration to the validity range of the Beer-Lambert law for I_3^-
- The final pH should be close to 7. At lower final pH, iodine (I_2) might be formed despite perfect mixing conditions. At high pH, iodine is unstable and dissociates.

Commenge & Falk, Chem. Eng. Proc. 50 (2011) 979-990

Villermaux-Dushman reaction

Choice of concentrations

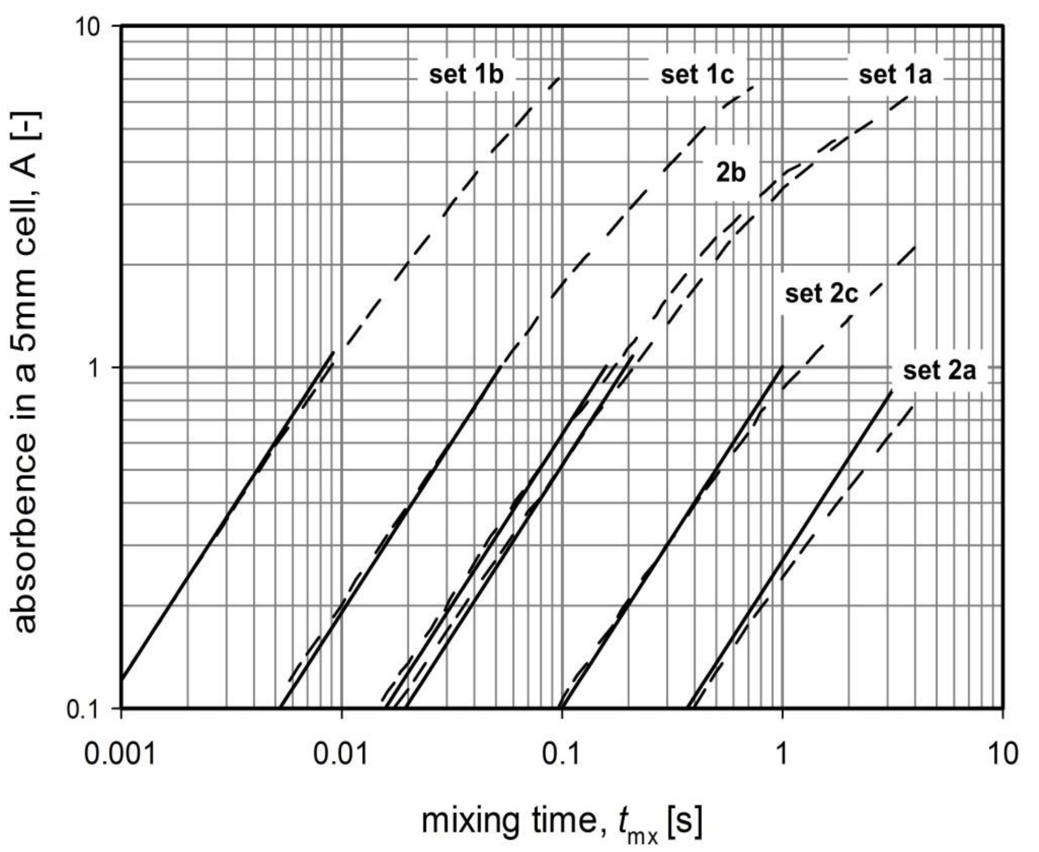
	C (mol/l)	set 1a	set 1b	set 1c	set 2a	set 2b	set 2c
Solution 1	$[H^+]$	0.03	0.06	0.04	0.015	0.03	0.02
Solution 2	[KI]	0.032	0.032	0.032	0.016	0.016	0.016
	$[KIO_3]$	0.006	0.006	0.006	0.003	0.003	0.003
	[NaOH]	0.09	0.09	0.09	0.045	0.045	0.045
	$[H_3BO_3]$	0.09	0.09	0.09	0.045	0.045	0.045

Commenge & Falk, Chem. Eng. Proc. 50
(2011) 979-990

Villermaux-Dushman reaction

Choice of concentrations

Predicted absorbance as a function of t_{mx}



Dashed lines: IEM model

Solid lines: simplified correlation (next slide)

Based on initial estimation of mixing time (see below), choose concentration set which will provide absorbance <u>close to unity</u> with experimental cell length (validity of Lambert-Beer law)

$$\varepsilon = \frac{Q\Delta p}{\rho V}$$

$$\varepsilon = \frac{8\nu u_m^2}{R^2}$$ (circular geometry)

$$\boxed{t_{mx} \cong 0.15\varepsilon^{-0.45}}$$

Commenge & Falk, Chem. Eng. Proc. 50 (2011) 979-990

Villermaux-Dushman reaction

Calculation of mixing time

Once that *A* has been experimentally determined, calculate t_{mx}:

$$\boxed{t_{mx}[s] = 0.33\,A'\,c_{H^+,0}^{-4.55}\;c_{I^-,0}^{-1.5}\;c_{IO_3^-,0}^{5.8}\;c_{NaOH,0}^{-2}\;c_{H_3BO_3,0}^{-2}}$$

Unit of concentrations $\boldsymbol{c_i : mol \cdot l^{-1}}$

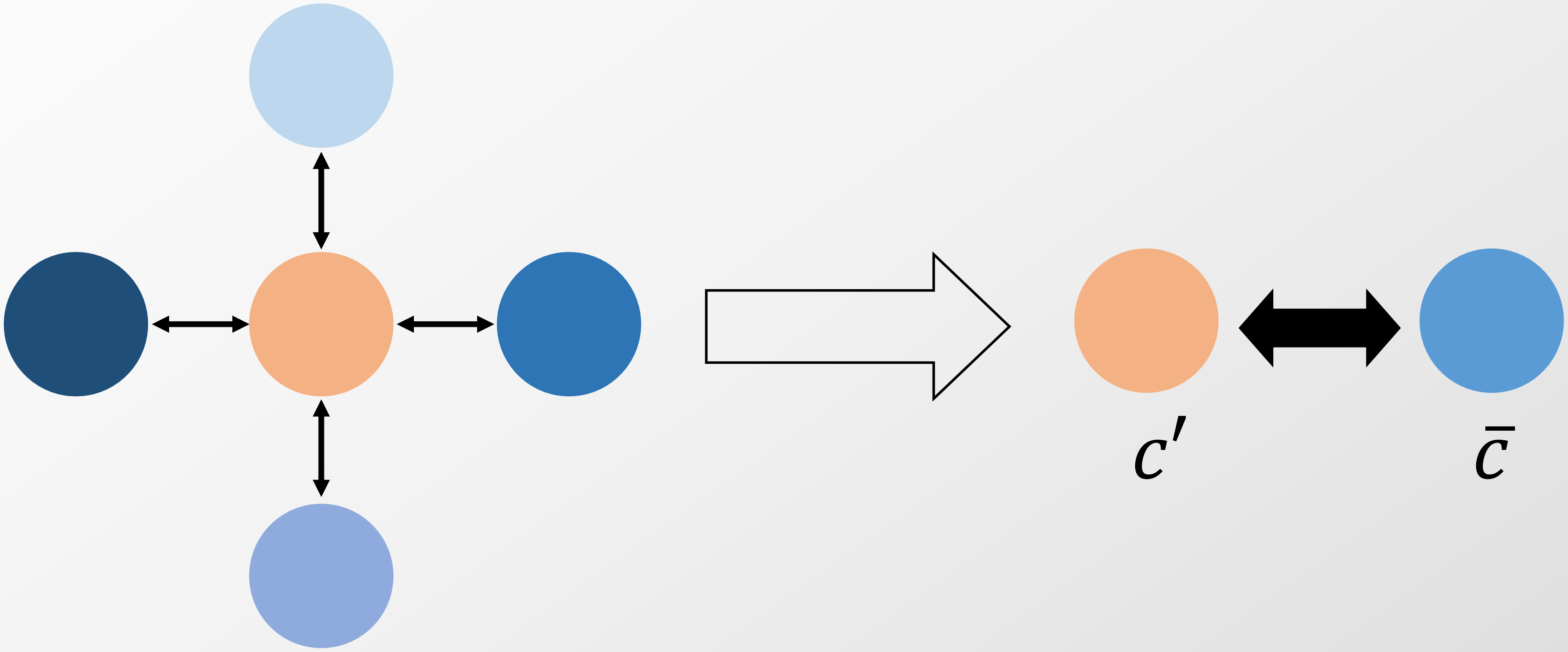
Where :

- *A* is the absorbance in the experimental cell of length *x* (mm)
- *A'* is the absorbance for a 1 mm optical path length
- $A' = A/x$

Commenge & Falk, Chem. Eng. Proc. 50 (2011) 979-990

IEM mixing model

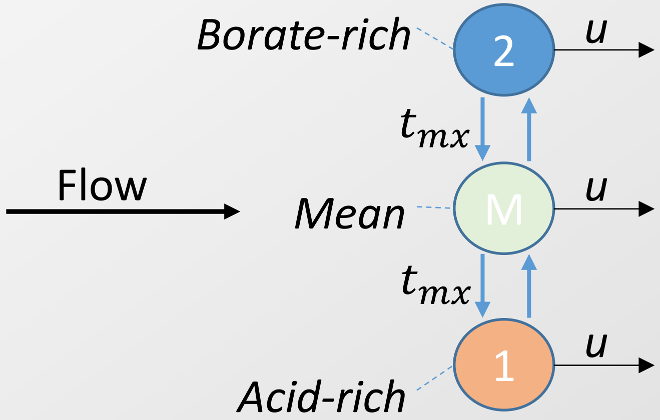
Interaction by Exchange with the Mean



Harada, 1963; Villermaux & Devillon, 1972, Costa & Trevisoi, 1972

IEM mixing model

- Interaction of mixing and reaction needs to be considered to calculate segregation index as a function of mixing time
- IEM (Interaction by Exchange with the Mean) mixing model offers a simple solution
- IEM assumptions
  - Acid-rich zone and borate-rich zones exchange mass with a characteristic time constant equivalent to the mixing time
  - Plug-flow behavior in micromixer ⇨ each acid-rich aggregate is in constant interaction with a borate-rich aggregate of the same age

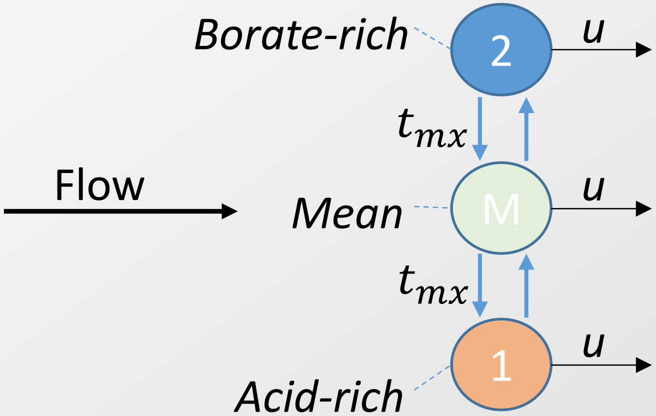


IEM mixing model

- Acid stream (subscript 1): volume fraction α
- Iodide-iodate-borate stream (subscript 2): volume fraction $(1-\alpha)$

$$\frac{dc_{i,1}}{d\tau} = \frac{\overline{c_i} - c_{i,1}}{t_{mx}} + R_{i,1} \qquad \frac{dc_{i,2}}{d\tau} = \frac{\overline{c_i} - c_{i,2}}{t_{mx}} + R_{i,2}$$

$$\overline{c_i} = \alpha c_{i,1} + (1-\alpha) c_{i,2}$$



IEM mixing model

- Kinetics of the redox reaction

$$5I^- + IO_3^- + 6H^+ \overset{r_2}{\rightarrow} 3I_2 + 3H_2O$$

$r_2 = k_2 c_{I^-}^2 \, c_{IO_3^-} \, c_{H^+}^2$ k_2 is a function of the ionic strength

$I = \frac{1}{2}\sum_{i=1}^{n} c_i z_i^2$ (ionic strength)

$$I < 0.16 \text{ mol } l^{-1} \rightarrow \log k_2 = 9.28 - 3.66\sqrt{I}$$

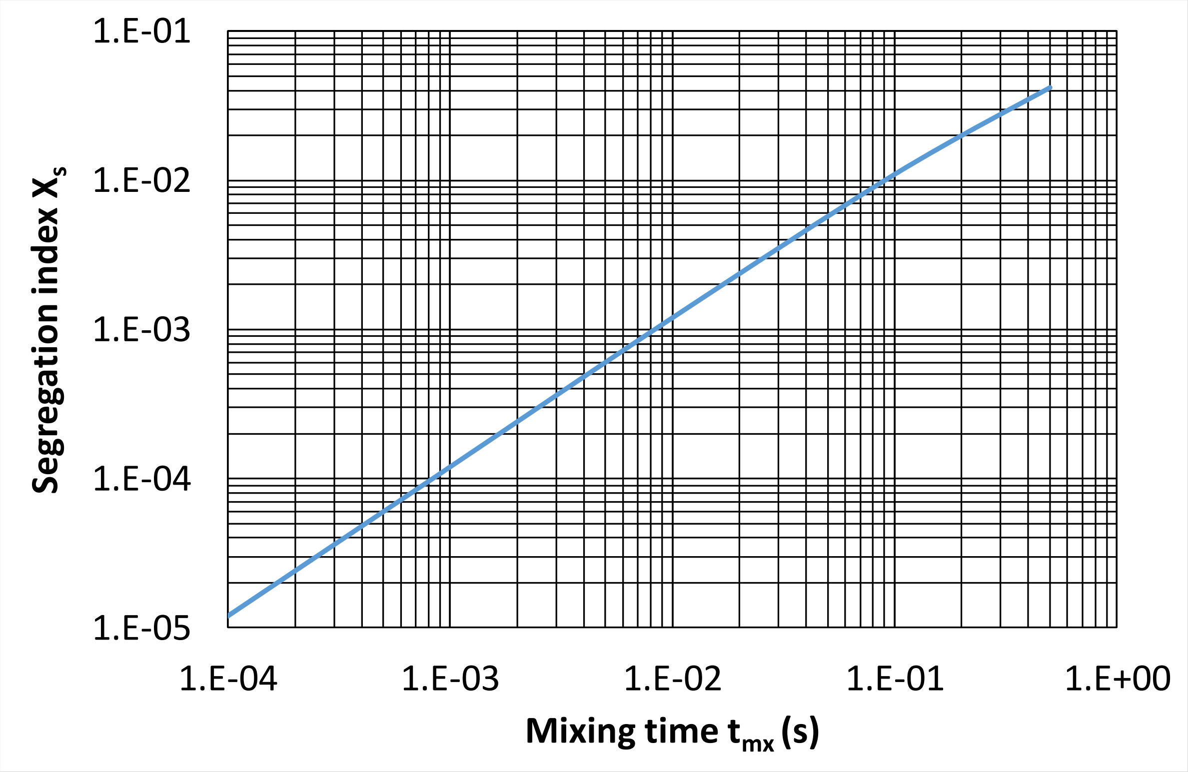
$$I > 0.16 \text{ mol } l^{-1} \rightarrow \log k_2 = 8.38 - 1.51\sqrt{I} + 0.23I$$

IEM mixing model

- Solve system of differential equations for all components *i* in both streams 1 and 2 using a given initial concentration set and a given value of t_{mx}
- Compute final I_2 and I_3^- concentrations at total conversion of H^+
- Calculate segregation index $X_S = f(I_2, I_3^-)$
- This provides one couple $(X_S; t_{mx})$
- Change the value of t_{mx} and repeat the procedure to obtain graph $X_S = \mathrm{f}(t_{mx})$
- Optical density *A* can be calculated from I_3^- concentration (Lambert-Beer) for every t_{mx} to get graph $A = \mathrm{f}(t_{mx})$

IEM mixing model

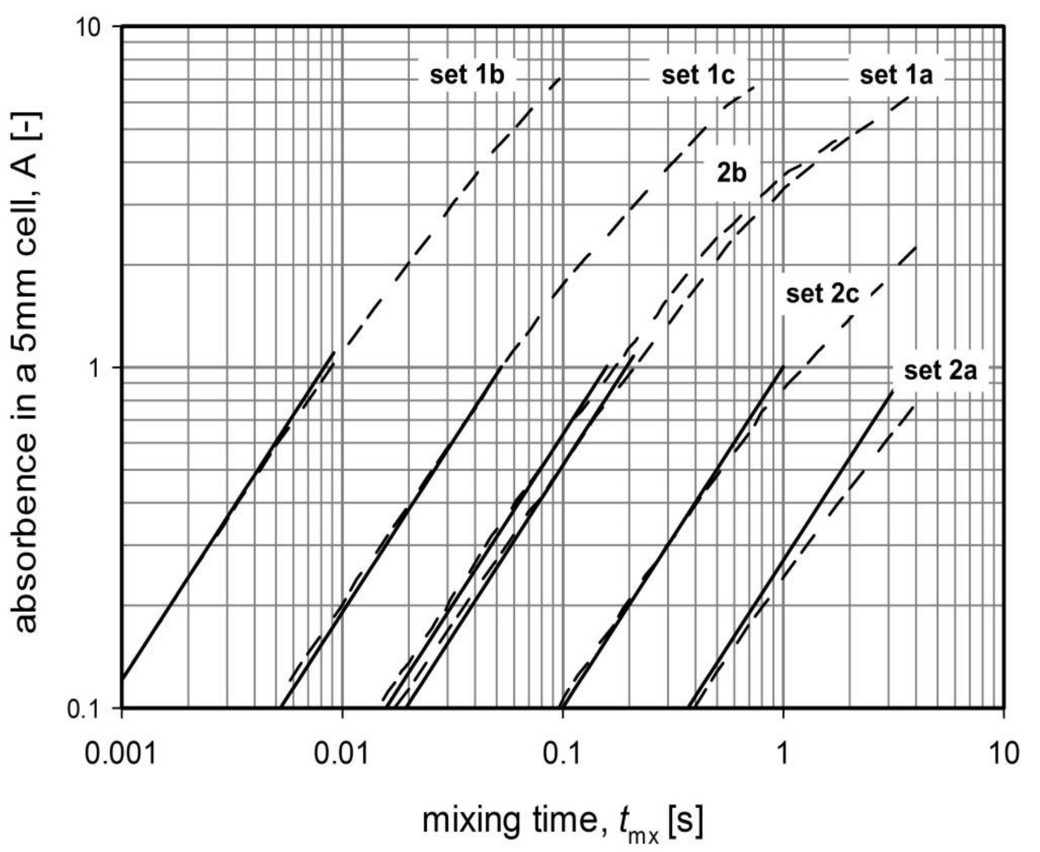
- Predicted segregation index as a function of mixing time for a given set of initial concentrations



$$c(KI) = 0.0319\frac{mol}{l}; c(KIO_3) = 0.00635\frac{mol}{l}; c(NaOH) = c(H_3BO_3) = 0.0898\frac{mol}{l}; c(H_2SO_4) = 0.015\frac{mol}{l}$$

IEM mixing model

- Predicted absorbance (5 mm optical path) as a function of mixing time for various sets of initial concentrations (dashed lines)



Solid lines: simplified correlation

Example of experimental setup for mixing characterization