Madhvanand N. Kashid, Albert Renken,
and Lioubov Kiwi-Minsker

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and Lioubov Kiwi-Minsker

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The Authors

Dr. Madhvanand N. Kashid
Ecole Polytechnique Fédérale de Lausanne
EPFL-SB-ISIC-GGRC
1015 Lausanne
Switzerland

and

Syngenta Crop Protection Monthey SA
Route de l'Ile au Bois
1870 Monthey
Switzerland

Prof. Dr. Albert Renken
Ecole Polytechnique Fédérale de Lausanne
EPFL-SB ISIC-LGRC, Station 6
1015 Lausanne
Switzerland

Prof. Dr. Lioubov Kiwi-Minsker
Ecole Polytechnique Fédérale
EPFL-SB ISIC-LGRC, Sation 6
1015 Lausanne
Switzerland

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Contents

Preface

This book is written based on the potential use of microstructured devices in chemical equipment and the intensification of chemical processes. The term "microstructured devices" is coined based on their characteristic dimensions that are in the submillimeter range and on their different types such as mixers, reactors, heat exchangers, and separators. Owing to the small characteristic dimensions, diffusion times are short and the influence of transport phenomena on the rate of chemical reactions is efficiently reduced. Heat transfer is greatly enhanced compared to conventional systems, allowing a strict control of temperature and concentration gradients leading to an improved product yield and selectivity. In addition, safe reactor operation is possible under unconventional conditions such as high reaction temperatures and reactant concentrations. As a consequence, novel process windows can be opened, but not accessible with traditional systems. Therefore, microstructured devices are versatile tools for the development of sustainable chemical processes.

This book focuses on reaction engineering aspects, such as design and characterization, for homogeneous and multiphase reactions. On the basis of chemical reaction engineering fundamentals, it addresses the conditions under which these devices are beneficial, how they should be designed, and how such devices can be integrated or applied in a chemical process.

Designed as a pedagogical tool with target audience of university students and industrial professionals, it seeks to bring readers with no prior experience of these subjects to the point where they can comfortably enter into the current scientific and technical developments in the area. However, this book does not include the cross-disciplinary subjects such as fabrication techniques of these devices, integration of sensors and actuators, and their use for biological applications.

To facilitate comprehension, the topics are developed beginning with fundamentals in chemical reaction engineering with ample cross-referencing. The understanding of concepts is facilitated by clear descriptions of examples, supplied by exercises including solutions, and provided by figures and illustrations.

Finally, the authors want to highlight the complexity of microreaction engineering in particular. Therefore, this book must be viewed as a tool for stimulation of novel and meaningful solutions for the complex chemical reaction realities. It is also important to note that the growing interests and complementary developments of this subject require periodic updates.

Lausanne, Switzerland
May 2014

Madhvanand Kashid,
Albert Renken,
Lioubov Kiwi-Minsker

List of Symbols

Commonly Used Symbols

This is a list of commonly used symbols. Besides, there are some special symbols used for each chapter which are listed chapterwise.

Symbols	Significance	Unit
A	Exchange or surface area	m^2
a	Specific interfacial area or catalytic surface area per reactor volume	$m^2\ m^{-3}$
A_{cs}	Cross-section area	m^2
Bo	Bond number	—
Bo	Bodenstein number	—
Bi_m, Bi_{th}	Biot number (mass), Biot number (thermal)	—
C	Dimensionless concentration	—
Ca	Capillary (=) or Carberry (=) number	—
c_i	Concentration of molecule A_i	$mol\ m^{-3}$
c_p	Heat capacity of fluid or mixture	$J\ kg^{-1}\ K^{-1}$
DaI	First Damköhler number	—
$DaII$	Second Damköhler number	—
$DaII_{mx}$	Second Damköhler number for mixing	—
D_{ax}	Axial dispersion coefficient	$m^2\ s^{-1}$
De	Dean number	—
D_{eff}, D_m	Effective molecular diffusion coefficient, molecular diffusion coefficient	$m^2\ s^{-1}$
d_h	Hydraulic diameter	m
d_t	Diameter of channel (or tube)	m
E, E_a	Intrinsic activation energy, apparent activation energy of reaction j	$J\ mol^{-1}$
f	Ratio of residual concentration to initial	—
Fo	Fourier number	—
g	Gravitational acceleration	$m^2\ s^{-1}$
H	Height	m

(*continued overleaf*)

Symbols	Significance	Unit
h	Heat transfer coefficient	$\mathrm{W\,m^{-2}\,K^{-1}}$
Ha	Hatta number	—
J_i	Molar flux of species i	$\mathrm{mol\,m^{-2}\,s^{-1}}$
k, k_r, k_j	Reaction rate constant for homogeneous and quasi-homogenous, constant of heterogenous reaction, constant of reaction j	variable ($\mathrm{s^{-1}}$ $(\mathrm{mol\,m^{-3}})^{-(n-1)}$)
k_0	Pre-exponential or frequency factor	variable ($\mathrm{s^{-1}}$ $(\mathrm{mol\,m^{-3}})^{-(n-1)}$)
K_C	Reaction equilibrium constant	variable
K	thermodynamic equilibrium constant	—
k_G	Mass transfer coefficient in gas phase	$\mathrm{m\,s^{-1}}$
k_{GL}	Mass transfer coefficient in gas–liquid system	$\mathrm{m\,s^{-1}}$
k_L	Mass transfer coefficient in liquid phase	$\mathrm{m\,s^{-1}}$
k_La	Volumetric mass transfer coefficient	$\mathrm{s^{-1}}$
k_m	Mass transfer coefficient of heterogeneous reactions	$\mathrm{m\,s^{-1}}$
k_{ov}	Overall mass transfer coefficient	$\mathrm{m\,s^{-1}}$
L, $\mathrm{L_c}$, L_e, L_t	Length, characteristic length, length of entrance zone, length of tube or channel	m
$\dot{m}$	Mass flow rate	$\mathrm{kg\,s^{-1}}$
Nu	Nusselt number	—
n_i	Reaction order with respect to species A_i	—
n	Overall reaction order	—
n_i	No of moles of molecule A_i	mol
$\dot{n}_i$	Molar flow rate of molecule A_i	$\mathrm{mol\,s^{-1}}$
p	Pressure	Pa
P_i	Rate of production	$\mathrm{mol\,s^{-1}}$
Pr	Prandtl number	—
Pe	Péclet number	—
Q	Energy	J
$\dot{Q}$	Rate of heat flow	W
$\dot{q}$, $\dot{q}_r$, $\dot{q}_{\mathrm{ex}}$	Specific heat rate, of reaction, of heat exchange/transfer	$\mathrm{J\,m^{-3}\,s^{-1}}$
R	Ideal gas law constant	$\mathrm{J\,mol^{-1}\,K^{-1}}$
R	Radius	m
Re	Reynolds number	—
R_i	Overall reaction/transformation rate of molecule A_i	$\mathrm{mol\,m^{-3}\,s^{-1}}$
r_j, r_{eff}	Rate of reaction/transformation of reaction j, effective reaction rate	$\mathrm{mol\,m^{-3}\,s^{-1}}$
r_{ads}, r_{des}	Rates of adsorption, of desorption	—
$S_{k,i}$	Selectivity of product k with respect to reactant i	—
$s_{k,i}$	Instantaneous selectivity of product k with respect to reactant i	—
Se	Semenov number	—

Symbols	Significance	Unit
Sc	Schmidt number	—
Sh	Sherwood number	—
T, T_b, T_s	Temperature, bulk temperature, surface temperature	K
t, t_c, t_D, t_r, t_m, t_{mx}, t_{ax}, $t_{D,\text{ ax}}$, $t_{D,\text{ rad}}$	Time, characteristic cooling time, diffusion time, reaction time, mass transfer time, mixing time, axial dispersion time, axial molecular diffusion time, radial diffusion time	s
$\bar{t}$	Mean residence time	s
U	Overall heat transfer coefficient	W m^{-2} K^{-1}
U_i	Internal energy	J
U_v	Overall volumetric heat transfer coefficient	W m^{-3} K^{-1}
u, u_b, $u(r)$, u_G, u_L	Superficial velocity, velocity of gas bubble (slug), velocity at radial position r, superficial flow velocity of gas phase, superficial velocity of liquid phase	m s^{-1}
V, V_R	Volume, internal (reaction) volume	m^3
$\dot{V}$	Volumetric flow rate	m^3 s^{-1}
W	Width	m
$\dot{W}$, $\dot{W}_f$, $\dot{W}_s$	Rate of work done, by flow, by shaft	J s^{-1}
X	Conversion	—
$Y_{k,\,i}$	Yield of product k with respect to reactant i	—
Z	Dimensionless length	—
z	Length	m
Greek symbols		
α	Thermal diffusivity	m^2 s^{-1}
β	Prater number	—
$\delta(z)$	Dirac pulse	—
δ	Film thickness, catalytic layer or boundary layer	m
γ	Arrhenius number	—
$\dot{\gamma}$	Shear rate	s^{-1}
Δ	Symbol of difference	—
ΔG	Gibbs free energy	J mol^{-1}
ΔH_r, ΔH_a	Heat of reaction, heat of adsorption	J mol^{-1}
Δp	Pressure drop	Pa
ΔS	Entropy	J mol^{-1} K^{-1}
ΔT_{ad}	Adiabatic temperature rise	K
ε	Specific power dissipation	W kg^{-1}
ε_p, ε_{bed}	Porosity of catalyst pallet, of randomly packed bed	—
η	Efficiency factor	—
θ	Dimensionless time	—
λ, λ_{eff}, λ_f, λ_{wall}	Thermal conductivity, effective, of fluid, of wall	W m^{-1} K^{-1}

(continued overleaf)

Symbols	Significance	Unit
μ	Dynamic viscosity	Pa s
ν	Kinematic viscosity	$m^2\,s^{-1}$
$\nu_{i,j}$	Stoichiometric coefficient of species i in reaction j	—
ζ	Geometric factor	—
ρ	Density	$kg\,m^{-3}$
σ	Interfacial tension	$N\,m^{-1}$
τ, τ_{PFR}, τ_R	Residence time, of plug flow reactor, of reactor, residence time referred to reaction volume	s

Common Indices

Subscript	
0	Initial value
∞	Asymptotic or infinite value
app	Apparent or observed
av	Average
Ax	Axial
b	Bulk
c	Cooling
cap	Hemispherical cap
cat	Catalyst
eff	Effective
eq	Equilibrium
ex	External
film	Wall film
gen	General
I	Phase I
II	Phase II
in	Inlet
max	Maximum
min	Minimum
out	Outlet
op	Optimum
ov	Overall
P	Pallet
s	Surface
v	Volumetric
Superscript	
0	Values at standard conditions

Dimensionless Numbers

Dimensionless number	Significance	Definition
Adiabatic temperature rise	Property of reaction mixture, represent temperature rise in worst case and is independent of reactor type/reaction rate	$\Delta T_{\text{ad}} = \frac{(-\Delta H_r)cb}{\rho c_p}$
Arrhenius number	Relative importance of activation temperature (E/R) to system bulk temperature (T_b)	$\gamma = \frac{E}{RT_b}$
Biot number (mass)	Relates external mass or heat transfer rates at catalyst pallet surface to diffusion or conduction inside the pallet	$Bi_m = \frac{t_D}{t_m} = \frac{L_c^2}{D_e} k_m a_p$
Biot number (thermal)		$Bi_{\text{th}} = \frac{h \cdot L}{\lambda_e}$
Bodenstein number	Ratio of convective transport rate to (axial) diffusion transport rate	$Bo = \frac{u \cdot L}{D_{\text{ax}}}$
Carberry number	It gives effective reaction rate over mass transfer rate in catalytic reactions where no internal (pellet) mass and heat transfer resistances are considered	$Ca = \eta_{\text{ex}} DaII$
Capillary number	Used in fluid–fluid systems. It is ratio of viscous forces to *surface tension* acting across an interface, that is, interfacial tension	$Ca_i = \frac{u_b \cdot \mu_i}{\sigma}$
First Damköhler number	Used to set design criteria – ratio of residence time in the reactor to the characteristic reaction time	$DaI = \frac{\tau}{t_r}$
Second Damköhler number	Used to set design criteria – ratio of reaction rate to mass transfer rate	$DaII = \frac{t_m}{t_r}$
Second mixing Damköhler number	Used to set design criteria – ratio of reaction rate to mixing rate	$DaII_{\text{mx}} = \frac{t_{\text{mx}}}{t_r}$
Dean number	Used to characterize the flow in curved channels – it is product of *Re* and square root of channel diameter to curvature radius	$De = Re\left(\frac{d_h}{R''}\right)^{0.5}$
Efficiency (reactor) factor (fluid–fluid system)	Ratio of effective reaction rate and the maximal rate referred to the reactor volume corresponding to the maximum concentration in the reacting phase	$\eta = \frac{r_{\text{eff}}}{r_{\text{max}}}$
Effectiveness factor (porous catalyst)	Ratio of effective reaction rate and the rate of reaction at bulk concentration and temperature	$\eta_p = \frac{J_{\text{eff}}}{J_s} = \frac{D_e c_s / L \cdot \varphi \tanh(\varphi)}{k_r c_s L} = \frac{\tanh \varphi}{\varphi}$

(continued overleaf)

Dimensionless number	Significance	Definition
Effectiveness factor (mass transfer) or trade-off index	Used to access mass transfer performance with energy input	$\eta_m = \frac{DaI_m}{Eu} = \frac{k_m a_R \cdot L}{u_s} \cdot \frac{\rho \cdot u_s^2}{\Delta p}$
Euler number	It is ratio of pressure drop in a given reactor length to kinetic energy.	$Eu = \frac{\Delta p}{\rho \cdot u^2}$
Fourier number	It is ratio of residence time to diffusion time	$Fo = \frac{\tau}{t_D}$
Hatta number	Used for fluid–fluid systems and signifies whether the reaction takes place in the bulk or near the interface (of reaction phase). It is ratio of reaction rate to interfacial mass transfer rate	$Ha = \sqrt{\frac{t_m}{t_r}} = \delta_{II}\sqrt{\frac{k_r'}{D_{i,II}}} = \frac{\sqrt{k_r' D_{i,II}}}{k_{L,II}}$
Nusselt-number	Use to characterize relative importance of convective heat transfer over conductive heat transfer	$Nu = \frac{h \cdot d_h}{\lambda}$
Peclet number	Ratio of rate of convection to rate of diffusion/dispersion	$Pe_{\mathrm{ax}} = \frac{u \cdot d_t}{D_{\mathrm{ax}}}$ (tube) $Pe_{\mathrm{ax}} = \frac{u \cdot d_p}{\varepsilon_{bed} D_{\mathrm{ax}}}$ (packed bed)
Prandtl number	Used to characterize momentum and heat diffusion – ratio of momentum (viscous) diffusion to molecular diffusion	$Pr = \frac{\nu}{\alpha} = \frac{\nu}{\lambda/(\rho c_p)}$
Prater number	Ratio of maximum temperature difference catalyst center and surface temperature to the surface temperature	$\beta = \frac{\Delta T_{\max}}{T_s} = \frac{(-\Delta H_r)c_s}{T_s}\frac{D_e}{\lambda_e}$
Reynolds number	Most commonly used to characterize the fluid flow – gives relative importance of inertial forces over viscous forces	$Re = \frac{\rho u d_t}{\mu}$
Reynolds number (particle)		$Re_p = \frac{(u \ \ d_p)}{\nu}$
Reynolds number (foam)		$Re_{foam} = \frac{u \cdot d_s \cdot \rho}{\mu}$
Schmidt number	Used to characterize momentum and mass diffusion – ratio of momentum (viscous) diffusion to molecular diffusion	$Sc = \frac{\nu}{D_m}$
Sherwood number (particle)	Use to characterize relative importance of convective mass transfer over diffusional mass transfer	$Sh_p = \frac{d_p\, k_m}{D_m}$
Sherwood number		$Sh = \frac{k_m \cdot d_h}{D_m}$

Dimensionless number	Significance	Definition
Thiele modulus	Ratio of characteristic diffusion time in the catalyst and the characteristic reaction time	$\varphi^2 = \frac{t_D}{t_r} = \frac{L^2}{D_e}k$ $\varphi = L\sqrt{\frac{k_r}{D}}$; first order reaction; $\varphi_{\text{gen}} = \frac{V_p}{A_p}\sqrt{\frac{k_r c_s^{(n-1)}}{D_e}} \cdot \sqrt{\frac{n+1}{2}}$
Weisz modulus	Used to measure influence of transport process on reaction kinetics experimentally – ratio of effective reaction rate to (effective) diffusion rate	$\psi_s^2 = \frac{t_D}{t_{r,\text{eff}}} = \frac{R_{\text{sphere}}^2}{D_e}\frac{c_s}{r_{p,\text{eff}}} = \eta_p \varphi_s^2$ $\psi_{\text{gen}}^2 = \frac{t_D}{t_{r,\text{eff}}} = \left(\frac{V_p}{A_p}\right)^2 \frac{n+1}{2}\frac{r_{p,\text{eff}}}{D_e\, c_s} = \eta_p \varphi_{\text{gen}}^2$
Bond number	Relates body forces to surface tension forces	$BO = \frac{\rho g d_h^2}{\sigma}$
First Damköhler number (mass transfer)	Ratio of residence time in the reactor to the characteristic mass transfer time	$DaI_m = \frac{\tau_R}{t_m} = \frac{k_m a_R \cdot L}{u}$

Abbreviations

BSTR	Batchwise-operated stirred tank reactor
CSTR	Continuously-operated stirred tank reactor
CVD	Chemical vapor deposition
LIGA	Lithography, galvanization, and molding
MASI	most abundant surface intermediate
MSR	Microstructured reactors
PFR	Plug flow reactor
PRL	Power rate law
PVD	Physical vapor deposition
RTD	Residence time distribution
SMF	Sintered metal fiber
SLPC	Supported liquid phase catalyst
SCR, SAR, SHR	Serpentine channel reactor, split and recombine reactor, staggered herringbone reactor