

# **Fundamentals of Chemical Reaction Engineering**



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## FUNDAMENTALS OF CHEMICAL REACTION ENGINEERING

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**To Mary, Kathleen, and our parents Ruth and Ted.**





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This book is an introduction to the quantitative treatment of chemical reaction engineering. The level of the presentation is what we consider appropriate for a one-semester course. The text provides a *balanced* approach to the understanding of: (1) *both* homogeneous and heterogeneous reacting systems and (2) *both* chemical reaction engineering and chemical reactor engineering. We have emulated the teachings of Prof. Michel Boudart in numerous sections of this text. For example, much of Chapters 1 and 4 are modeled after his superb text that is now out of print (*Kinetics of Chemical Processes*), but they have been expanded and updated. Each chapter contains numerous worked problems and vignettes. We use the vignettes to provide the reader with discussions on real, commercial processes and/or uses of the molecules and/or analyses described in the text. Thus, the vignettes relate the material presented to what happens in the world around us so that the reader gains appreciation for how chemical reaction engineering and its principles affect everyday life. Many problems in this text require numerical solution. The reader should seek appropriate software for proper solution of these problems. Since this software is abundant and continually improving, the reader should be able to easily find the necessary software. This exercise is useful for students since they will need to do this upon leaving their academic institutions. Completion of the entire text will give the reader a good introduction to the fundamentals of chemical reaction engineering and provide a basis for extensions into other nontraditional uses of these analyses, for example, behavior of biological systems, processing of electronic materials, and prediction of global atmospheric phenomena. We believe that the emphasis on chemical *reaction* engineering as opposed to chemical *reactor* engineering is the appropriate context for training future chemical engineers who will confront issues in diverse sectors of employment.

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We dedicate this book to our wives and to our parents for their constant support.

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Charlottesville, VA

# Nomenclature

$a_i$	activity of species $i$
$a_v$	external catalyst particle surface area per unit reactor volume
$A_i$	representation of species $i$
$A_C$	cross sectional area of tubular reactor
$A_C^p$	cross sectional area of a pore
$A_H$	heat transfer area
$\bar{A}$	pre-exponential factor
$Bo_a$	dimensionless group analogous to the axial Peclet number for the energy balance
$C_i$ or $[A_i]$	concentration of species $i$
$C_{iB}$	concentration of species $i$ in the bulk fluid
$C_{iS}$	concentration of species $i$ at the solid surface
$C_p$	heat capacity per mole
$\bar{C}_p$	heat capacity per unit mass
$d_e$	effective diameter
$d_p$	particle diameter
$d_t$	diameter of tube
$D_a$	axial dispersion coefficient
$D^e$	effective diffusivity
$D_{ij}$	molecular diffusion coefficient
$D_{Ki}$	Knudsen diffusivity of species $i$
$D_r$	radial dispersion coefficient
$D_{TA}$	transition diffusivity from the Bosanquet equation
$Da$	Damkohler number
$\bar{D}a$	dimensionless group
$E$	activation energy
$E_D$	activation energy for diffusion
$E(t)$	$E(t)$ -curve; residence time distribution
$\bar{E}$	total energy in closed system
$f_f$	friction factor in Ergun equation and modified Ergun equation
$f_i$	fractional conversion based on species $i$
$f_i^{\text{eq}}$	fractional conversion at equilibrium

$\bar{f}_i$	fugacity of species $i$
$\bar{f}_i^0$	fugacity at standard state of pure species $i$
$ff$	frictional force
$F_i$	molar flow rate of species $i$
$g$	gravitational acceleration
$(g/g_c)\bar{z}$	gravitational potential energy per unit mass
$g_c$	gravitational constant
$gm$	mass of catalyst
$\Delta G$	change in Gibbs function (“free energy”)
$h$	Planck’s constant
$h_i$	enthalpy per mass of stream $i$
$h_t$	heat transfer coefficient
$H$	enthalpy
$\Delta H$	change in enthalpy
$\Delta H_r$	enthalpy of the reaction (often called heat of reaction)
$H_w$	dimensionless group
$\bar{H}_w$	dimensionless group
$\bar{I}$	ionic strength
$J$	Colburn $J$ factor
$\bar{J}_i$	flux of species $i$ with respect to a coordinate system
$k$	rate constant
$\bar{k}$	Boltzmann’s constant
$\bar{k}_c$	mass transfer coefficient
$K_a$	equilibrium constant expressed in terms of activities
$K_C$	portion of equilibrium constant involving concentration
$K_P$	portion of equilibrium constant involving total pressure
$K_X$	portion of equilibrium constant involving mole fractions
$K_\phi$	portion of equilibrium constant involving activity coefficients
$L$	length of tubular reactor
$L_c$	length of microcavity in Vignette 6.4.2
$L_p$	generalized length parameter
$\bar{L}$	length in a catalyst particle
$\bar{m}_i$	mass of stream $i$
$\dot{m}_i$	mass flow rate of stream $i$
$M_i$	molecular weight of species $i$
$\bar{M}$	ratio of concentrations or moles of two species
$\overline{MS}$	total mass of system
$n_i$	number of moles of species $i$

$N_i$	flux of species $i$
$NCOMP$	number of components
$NRXN$	number of independent reactions
$P$	pressure
$Pe_a$	axial Peclet number
$Pe_r$	radial Peclet number
$PP$	probability
$q$	heat flux
$Q$	heat transferred
$\dot{Q}$	rate of heat transfer
$r$	reaction rate
$r_t$	turnover frequency or rate of turnover
$\bar{r}$	radial coordinate
$\bar{r}_t$	radius of tubular reactor
$R$	recycle ratio
$R_g$	universal gas constant
$R_p$	radius of pellet
$R_{pore}$	radius of pore
$\bar{R}$	dimensionless radial coordinate in tubular reactor
$\bar{R}_{cc}$	correlation coefficient
$Re$	Reynolds number
$s_i$	instantaneous selectivity to species $i$
$\Delta S$	change in entropy
$S_c$	sticking coefficient
$S_i$	overall selectivity to species $i$
$S_p$	surface area of catalyst particle
$\bar{S}$	number of active sites on catalyst
$SA$	surface area
$Sc$	Schmidt number
$SE$	standard error on parameters
$Sh$	Sherwood number
$t$	time
$\langle t \rangle$	mean residence time
$\bar{t}^*$	student t-test value
$T$	temperature
$T_B$	temperature of bulk fluid
$T_S$	temperature of solid surface
$TB$	third body in a collision process
$u$	linear fluid velocity (superficial velocity)

$\bar{u}(\bar{r})$	laminar flow velocity profile
$U$	overall heat transfer coefficient
$\bar{U}_i$	internal energy
$v$	volumetric flow rate
$V$	volume
$V_i$	mean velocity of gas-phase species $i$
$V_p$	volume of catalyst particle
$V_R$	volume of reactor
$V_{\text{total}}$	average velocity of all gas-phase species
$W_c$	width of microcavity in Vignette 6.4.2
$x$	length variable
$x_p$	half the thickness of a slab catalyst particle
$X_i$	mole fraction of species $i$
$\bar{X}^2$	defined by Equation (B.1.5)
$y$	dimensionless concentration
$Y_i$	yield of species $i$
$z$	axial coordinate
$\bar{z}$	height above a reference point
$Z$	dimensionless axial coordinate
$\bar{Z}_i$	charge of species $i$
$\alpha_i$	when used as a superscript is the order of reaction with respect to species $i$
$\bar{\alpha}_i$	coefficients; from linear regression analysis, from integration, etc.
$\alpha\alpha_1$	parameter groupings in Section 9.6
$\alpha\alpha_2$	parameter groupings in Section 9.6
$\beta$	Prater number
$\beta_T$	dimensionless group
$\beta\beta_i$	dimensionless groups
$\gamma$	Arrhenius number
$\bar{\gamma}_i$	activity coefficient of species $i$
$\Gamma$	dimensionless temperature in catalyst particle
$\bar{\Gamma}$	dimensionless temperature
$\delta(t)$	Dirac delta function
$\bar{\delta}$	thickness of boundary layer
$\varepsilon_i$	molar expansion factor based on species $i$
$\bar{\varepsilon}$	deviation of concentration from steady-state value
$\bar{\varepsilon}_B$	porosity of bed
$\bar{\varepsilon}_p$	porosity of catalyst pellet

$\eta$	intraphase effectiveness factor
$\eta_o$	overall effectiveness factor
$\bar{\eta}$	interphase effectiveness factor
$\theta$	dimensionless time
$\theta_i$	fractional surface coverage of species $i$
$\bar{\theta}$	dimensionless temperature
$\lambda$	universal frequency factor
$\lambda^e$	effective thermal conductivity in catalyst particle
$\lambda_\lambda$	parameter groupings in Section 9.6
$\bar{\lambda}_r$	effective thermal conductivity in the radial direction
$\mu_i$	chemical potential of species $i$
$\bar{\mu}$	viscosity
$\xi$	number of moles of species reacted
$\rho$	density (either mass or mole basis)
$\rho_B$	bed density
$\rho_p$	density of catalyst pellet
$\sigma_i$	standard deviation
$\bar{\sigma}_i$	stoichiometric number of elementary step $i$
$\tau$	space time
$\bar{\tau}$	tortuosity
$\nu_i$	stoichiometric coefficient of species $i$
$\phi$	Thiele modulus
$\phi_0$	Thiele modulus based on generalized length parameter
$\bar{\phi}_i$	fugacity coefficient of species $i$
$\Phi$	extent of reaction
$\chi$	dimensionless length variable in catalyst particle
$\psi$	dimensionless concentration in catalyst particle for irreversible reaction
$\bar{\psi}$	dimensionless concentration in catalyst particle for reversible reaction
$\Psi$	dimensionless concentration
$\omega$	dimensionless distance in catalyst particle

Notation used for stoichiometric reactions and elementary steps

	Stoichiometric reaction	Elementary step
Irreversible (one-way)	$\Rightarrow$	$\rightarrow$
Reversible (two-way)	$\rightleftharpoons$	$\rightleftharpoons$
Equilibrated	$\rightleftharpoons$	$\rightleftharpoons$
Rate-determining		$\nrightarrow$ or $\nleftarrow$