CHEMICAL REACTION ENGINEERING

Beyond the Fundamentals

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CHEMICAL REACTION ENGINEERING

Beyond the Fundamentals

Dedicated to my former students and colleagues at Iowa State University (USA) and National Chemical Laboratory (India), from whom I learned so much.

L.K. Doraiswamy

Dedicated to L.K. Doraiswamy (1927–2012) and his continuing legacy in Chemical Reaction Engineering.

D. Uner

Preface

> When one sees Eternity in things that pass away and infinity in finite things, then one has pure knowledge.
>
> But if one merely sees the diversity of the things, with their divisions and limitations, then one has impure knowledge.
>
> And if one selfishly sees a thing as if it were everything, independent of the ONE and the many, then one is in the darkness of ignorance.
>
> **Bhagavad Gita XVIII, 20–22**

Academically oriented books can broadly be placed under three categories: undergraduate texts, advanced books in broad areas/disciplines, and monographs in specific areas. Chemical engineering is no exception. In this important area, more specifically its most expansive component, chemical reaction engineering (CRE), what is missing is a "textbook" for graduate-level teaching to twenty-first-century graduate students. The question arises: Should there be a text at all for any graduate course? One can argue both for and against following a single textbook for a graduate course. So we would like, at the outset, to state our purpose in writing this book. Our objective is to create a book that spans the extremes of an undergraduate text and a highly advanced book that does not even remotely revisit the undergraduate material. Stated differently, it may be regarded as a ramp connecting the two levels, increasingly encompassing the higher level but stopping appropriately short. It should prepare graduate students for the needs of twenty-first-century chemical engineering research and technology.

To accomplish this objective, several factors had to be seriously considered: language and format; striking a balance between crossing the t's and dotting the i's, on the one hand, and letting the student do most of it, on the other hand; giving problems as home assignments with precise solutions along with a solution manual (assumed to be miraculously out of the students' reach); and including some recent additions to the well-traversed repertoire of CRE as well as a few nontraditional areas as fresh infusions into this highly absorptive area. We shall see how a

consideration of these factors resulted in the structure and the format in which this book has finally emerged.

Undergraduate texts are for the complete beginner. They must drive home the basic principles unambiguously with no room for interpretation or mistaken understanding. Every detail must be explained and computational methods clearly illustrated. Only the most important books and publications need to be referred, with emphasis on language and illustration that would ensure utter clarity of the foundational building blocks of the area. Problems worked out in the text or assigned as homework should mostly, if not always, have only a single solution. We make a point of this because, as one moves up the complexity scale, alternative solutions depending on different physical pictures and use of different correlations increasingly come into play. Books to address this situation belong to a different category and must conform to the level and needs of students cutting their first teeth at the graduate level.

Undergraduate texts in CRE are strong in homogeneous reactions and gas–solid reactions where the solid is a catalyst, with rapidly decreasing attention to gas–liquid, gas–liquid–solid (slurry), and gas–solid reactions where the solid is a reactant. Varying degrees of attention are given to the question of nonideality and its role in reactor performance. Experimental methods for collecting basic kinetic data and simple statistical methods for analyzing them also form part of the undergraduate curriculum. Rigorous methods of treating complex reactions are avoided. Also, due to the limitations in context, very little attention is given to emerging methods and newer concepts.

So, as students get their first taste of a graduate course in CRE, they are normally well grounded in the elements of it, *thanks to the excellent books that are available.* A survey of the literature shows that there are many good books on certain advanced aspects of CRE as well, which have been catering to the needs of a graduate program in CRE. We would like to mention, in particular, the 1985 book *Chemical Reactor Analysis* by Gilbert Froment and Kenneth Bischoff and its 3rd edition in 2010, *Chemical Reactor Analysis and Design* with Juray De Wilde as the third author. This new edition addresses computational fluid dynamics (CFD) and a few other related tools of CRE. *Chemical Reactor Analysis and Design Fundamentals* by J.B. Rawlings and J.G. Ekerdt entered the field with well-presented emphasis on the use of computers in the design and analysis of chemical reactors but still essentially at the undergraduate level. During the many years that we have taught CRE at both the undergraduate and graduate levels in the United States, India, and Turkey, we noticed that no book particularly suited as a first year graduate text in CRE is available. The requirements of such a book, which may loosely be regarded as intermediate between an undergraduate text and an advanced book that takes all undergraduate material for granted, may be stated as follows:

- There should be a distinct connectivity with what the students learned as undergraduate juniors/seniors.
- The format of the book should be different from that of a typical undergraduate text, in that spoonfeeding must be minimized, and full solutions to a problem should not always be given—leaving it open in some cases for alternative solutions to be suggested by the students.
- Attenuated explanations should be adequate in many, if not all, cases, leaving it to the students to supply the rest.
- Derivations for important equations should be fully given; for other associated equations, only the final solutions need be presented, with all the equations for a given class of situations, such as for gas–liquid reactions under different conditions, consolidated in tabular form. Students should be encouraged to derive those equations (as home assignments).
- Chapter-end exercises should span the whole range of Bloom's taxonomy of educational objectives: knowledge, understanding, application, analysis, synthesis, evaluation, and even valuation. These problems will give the student a feeling for the stage of his/her learning. As desirable in a graduate level text, we emphasize the higher-level skills associated with analysis, synthesis, and evaluation in a limited number of open-ended chapter-end "Explore yourself" problems. We decided to provide up-to-date problems and self-paced learning modules at the website of the book at www.metu.edu.tr/~uner in a continuously updated fashion.
- Students are seldom exposed to analyses/equations for cases not described in the book. This situation should be specifically addressed by including representative equations as exercises in derivation under on-line learning modules.

The format of the book has been designed to accommodate all these features. The material is divided into three parts, comprising a total of 17 chapters.

Part I: Fundamentals Revisited is devoted to a recapitulation of the salient features of the undergraduate course in CRE. The material is recast, wherever needed, in a format that would easily dovetail into the more advanced chapters to follow. Still, we introduce the concepts of mixing, unsteady-state operations, multiple steady states, and complex reactions in this part as they are fundamental to the design of reactors in a world driven by emphasis on high selectivity, raw material economy, and green engineering.

Part II: Building on Fundamentals is dedicated, if we may, to skill building, especially in the area of catalysis and catalytic reactions. This part covers chemical thermodynamics with special emphasis on the thermodynamics of adsorption and complex reactions; a brief section on the fundamentals of chemical kinetics, with special emphasis on microkinetic

analysis, as we believe that good literacy in CRE requires a clear understanding of mechanisms postulated and tested by microkinetic analysis; and heat and mass transfer effects in catalysis from a classical point of view. Finally, we devote a full chapter to giving graduate students the tools of the trade for making accurate kinetic measurements and analyzing the data obtained.

Part III: Beyond the Fundamentals is concerned, as the name implies, with material not commonly covered in present-day textbooks. This part begins with the treatment of solid catalyzed fluid-phase reactions and proceeds to reactions involving at least one liquid phase as separate chapters. It is addressed to the advanced learner trying to find out aspects of reactors involving more than one phase and intending to go in the direction of innovation in terms of process intensification and sustainable engineering. The fundamental background available in the literature is succinctly summarized to equip the advanced learner with the concepts and the wherewithal to deal with a variety of situations, including such little explored territories as the cell as a chemical reactor.

While writing the book, we deliberated at length on whether to focus on a single computational tool, or opt for more. The final decision was to keep the learner, and also the instructor, free to choose any computational tool of their preference and not to limit them to one of our choice. This might tend to somewhat limit the span of some of our examples, but we have remained loyal to the central philosophy of the book: to point out the vast territory and prod the learner to learn more—and explore.

We attempt in this book a unique approach toward examples. Instead of giving many brief examples embedded in texts within chapters, we give elaborate accounts of technologies and designs as INTERLUDES between chapters. Some of the interludes are laden with plenty of questions for the learner to answer—and learn. Some interludes are fully solved design problems. This, we believe, will give the reader and the instructor great flexibility between covering the background on a subject and covering an example in sufficient detail.

As with any other book, this too comes, no doubt, with its own share of merits and demerits; we worked hard to have more of the former and less of the latter, but still the final judgment must rest with the user. We would be glad to have any errors brought to our attention. And finally, the broad objective of this book has been to provide the student, particularly the advanced learner, with a new perspective of *Chemical Reaction Engineering: Beyond the Fundamentals*—coupled with the incentive and the wherewithal to transition from solving close-ended problems to exploring open-ended ones. The extent to which this has happened would be a fitting measure of our success.

Acknowledgments

This book has its origin in Doraiswamy's 2001 *Organic Synthesis Engineering* published by Oxford University Press (OUP). When it was decided to completely revise and shorten the book with the objective of providing a textbook for a first graduate course in CRE, and OUP showed no interest in this effort, we asked them for permission to use it as the basis for writing the proposed book for publication by Taylor & Francis. We are thankful to OUP, in particular to senior editor Jeremy Lewis, with whom Doraiswamy was dealing with in this matter, for permission to do so. Numerous examples were covered from Doraiswamy's earlier publications, especially from Doraiswamy and Sharma's "Heterogeneous Reactions: Analysis, Examples and Reactor Design," and the massive chapter by Joshi and Doraiswamy on "Chemical Reaction Engineering" in *Albright's Encyclopaedia of Chemical Engineering*. The incredible support from the team at Taylor & Francis, in particular by our editor Barbara Glunn, is deeply appreciated.

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Notations

$[A]$	Concentration (moles per volume) of species A
A	Reactant
a	Area per unit volume, 1/m
A_h	Heat transfer surface, m^2
A_m	Area of membrane, m^2
A_p	Area of particle, m^2
Ar	Archimedes number
Bd	Bond number
Bi	Biot number
C_p	Heat capacity
C_{pA}	Heat capacity of reactant, kcal/mol K
Da	Damköhler number
D_{AB}	Diffusion coefficient of a binary system
d_e	Equivalent reactor diameter
D_j	Diffusivity of species j, m^2/s or mol/m atm s
d_M	Molecular diameter, m
Dn	Dean number
d_t	Tube diameter
E	Total energy
F_i	Molar flow rate of i, mol/s
F_j	Flow rate of species j, mol/s
Fo	Fourier number
Fr	Froude number
F_j^T, F_j^S	Flow rates of species j in inner tube and outer shell, respectively, mol/s

Ga	Galileo number
G_j^T, G_j^S	Flow rates per unit area of species j in inner tube and outer shell, respectively, mol/m^2 s
H	Enthalpy
H	Product (hydrogen)
ΔH	Change in molar enthalpy
I	Inert (sweep) gas, usually argon
K	Reaction equilibrium constant
k	General symbol for rate constant (m^3/mol)$^{n-1}$(1/s)
k_B	Boltzmann constant
KE	Kinetic energy
Kn	Knudsen number
k^o	Arrhenius frequency factor, same units as the rate constant
k_{per}	Percolation rate constant, appropriate units (usually 1/s)
L	Reactor length, m
m	Mass; order of reaction
M_H	Hatta modulus
M_j	Molecular weight of species j
n	Order of reaction
N_i	Number of moles of species i
N_0	Avogadro number
P	Total pressure
PE	Potential energy
Pe	Peclet number
P^S, P^T	Pressures on the shell and tube sides
p_j^S, p_j^T	Shell and tube side partial pressures of species j
q	Heat transferred
Q_A	Volumetric flow rate of A
Q_j	Volumetric flow rate of species j, m^3/s
R	Reactant; radius
R_1	Inner radius of membrane tube, m
R_2	Outer radius of membrane tube, m

R_3	Inner radius of shell, m
Re	Reynolds number
R_g	Gas constant, kcal/mol k
r_i	Rate of reaction of species i
r_j	Rate of reaction of species j, mol/m^{3}s
S	Product
Sc	Schmidt number
Sh	Sherwood number
S_R	Selectivity of R (moles of R formed/moles of A converted)
T	Temperature, °C or K
t	Time
$\bar{t}$	Residence time (volume/volume per unit time) (V/Q_0), s
t_m	Thickness of membrane wall, m
T_w	Wall temperature, K
U	Internal energy; overall heat transfer coefficient, kcal/m^2 K s
u	Velocity, m/s
V	Reactor volume, m^3
ν_i	Stoichiometric coefficient of species i
W	Work
X_A	Conversion of species A
X_e^S, X_e^T	Equilibrium conversion on the shell and tube sides
y_A	Mole fraction of species A
Y_R	Yield of R (moles of R formed/moles of A fed)

Greek

α	Ratio of sweep gas to feed gas flow rates at inlet (Chapter 13)
α	Coefficient of thermal expansion
β	Ratio of ethane to oxygen
γ_{bu}	Efficiency of bulk liquid utilization
δ	Molar change parameter; constrictivity
ε	Effectiveness factor

ε_A	Volume change parameter of species A
η	Enhancement factor
θ	Surface coverage of adsorbed species
λ	Thermal conductivity
λ	Mean free path, m (Chapter 13)
ℓ	Length parameter, m
μ	Viscosity
$\Delta\nu$	Volumetric difference between products and reactants
ν_i	Stoichiometric coefficient of species i
ν_j	Stoichiometric coefficient of species j
ξ	Extent of reaction
ρ	Density
$\sigma_{A,B}$	Mean molecular diameter of A and B
τ	Tortuosity
ϕ	Thiele modulus
ϕ_p	Porosity
ψ_i	Feed stoichiometry, $[i]/[A]_0$, $i \neq A$
$\prod_j$	Specific rate of permeation of species j, mol/m^{2}s
Ω	Activity
Γ	Heat transfer rate, $UA_m/C_{pA}F_{A0}$

Subscripts/superscripts

Subscripts

0	Initial/input, initial/entrance conditions (Chapter 13)
1	Output/exit
i	For/belonging to species i
rxn	Reaction
s	Shaft
SS	Steady state
t	Total
w	Wall

+	Generation
–	Removal

Superscripts

S	Shell side
T	Tube side

Overview

Chemical reactions all around us

Chemical reaction engineering (CRE) embraces a wide variety of chemical reactions involving all the three states of matter: gas, liquid, and solid. Till recently, it was confined to reactor sizes encountered in typical inorganic and organic conversions, such as those in the fertilizer, petrochemical, and organic chemicals industries. In Table O.1, we summarize the classes of reactions with respect to the states of aggregation of the contacting phases and an example. They are considered in varying degrees of detail, appropriate to their importance and the state of development, in the subsequent chapters of the book.

Enzymes are increasingly being used as catalysts due to their extraordinarily high selectivities and amenability to low-temperature operation. They are used both in the liquid phase and anchored to solid substrates. Some flowers and seeds act as nanoscale natural reactors, and emulating them in the laboratory is one of the challenges faced by CRE today. Another emerging class of reactors known as microfluidic reactors and the whole concept of miniaturization will almost certainly come to the fore as future generation realities of the chemical industry.

Table O.1 Chemical Reactions Classified According to the Contacting Phases and an Example from Industry

Solid catalyzed vapor-phase reactions	Ammonia synthesis Xylene isomerization
Gas–liquid reactions	Absorption of gases to produce acids such as nitric acid or sulfuric acid
Gas–solid reactions	Smelting of ores
Solid–liquid reactions	Hydration of lime
Liquid–liquid reactions	Hydrolysis of oil, production of biodiesel
Solid–liquid–gas (slurry) reactions	Hydrogenation of glucose to sorbitol
Solid–solid reactions	Catalytic oxidation of diesel soot
Solid catalyzed gas–solid reactions	Preparation of methylchlorosilanes