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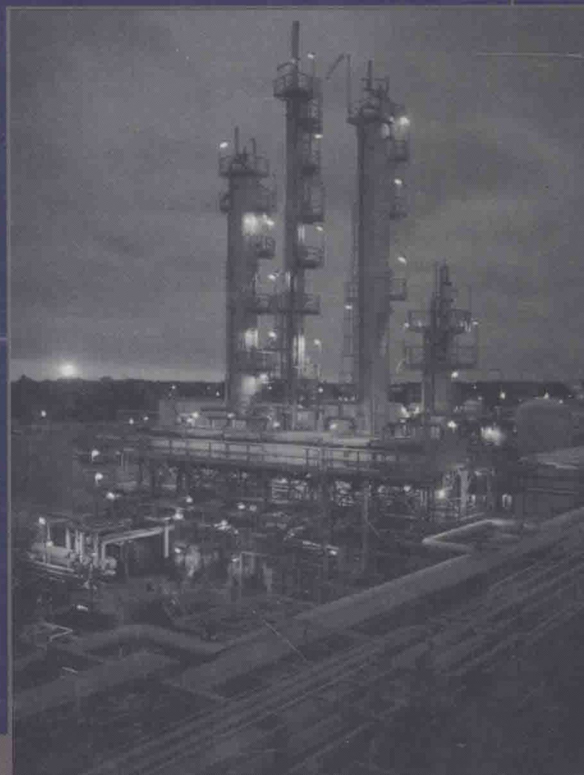
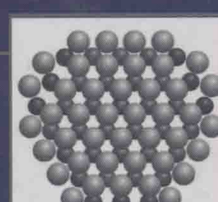


FUNDAMENTALS OF INDUSTRIAL CATALYTIC PROCESSES

SECOND EDITION



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Second Edition

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WILEY-INTERSCIENCE
A JOHN WILEY & SONS, INC., PUBLICATION

AIChE

Published by John Wiley & Sons, Inc., Hoboken, New Jersey.
Published simultaneously in Canada.

Library of Congress Cataloging-in-Publication Data:

Farrauto, Robert J., 1941–
Fundamentals of industrial catalytic processes / Robert J. Farrauto, Calvin H. Bartholomew. — 2nd ed.
p. cm.
Includes bibliographical references and index.
ISBN-13 978-0-471-45713-8
ISBN-10 0-471-45713-2
1. Catalysis. 2. Catalysts—Industrial applications. I. Bartholomew, Calvin H. II. Title.
QD505.F37 2005
660'.2995—dc22 2004026800

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

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To my family and especially my wife Karen, for patience, love, and support.

C.H.B.

To my Italian-American heritage and all my family members, past, present, and future, who have provided me with an understanding of what is important in life.

R.J.F.

PREFACE

The field of catalysis continues to evolve at an amazing pace. Since the launch of our first edition in early 1997, many new, exciting developments in catalyst science and technology have come to light. Priorities for research in industry and academia have shifted, and entire new areas of science and technology are being pursued. For example, there is new excitement regarding the potential of computational chemistry as a catalyst design tool and of combinatorial methods for developing new families of catalysts. Recent thrusts in fuel cell and hydrogen generation catalysis and nanophase materials are generating new technologies and business opportunities, for example, more thermally efficient microchannel reactor/heat exchangers for steam reforming. Fischer-Tropsch synthesis, first discovered some 80 years ago and practiced only to a limited extent in Germany and South Africa, is currently being implemented globally at enormous scales for production of high-quality diesel fuel from stranded natural gas. These and other developments support the notion of a viable, growing field of scientific discipline which supports a thriving field of business opportunities.

Many of these new developments are addressed in the Second Edition with updated or new information, including a new analysis of the catalyst market in Chapter 1, information on new materials and new analytical methods in Chapters 2 and 3, and the treatment of mechanisms of catalyst deactivation in Chapter 5. Descriptions of the most important catalytic processes in Chapters 6–12 have been updated with the incorporation of new mechanistic and kinetic data and the description of new catalyst, reactor, and process technologies. For example, descriptions of mechanisms, kinetics, and modes of catalyst deactivation for steam reforming, Fischer-Tropsch synthesis, hydrotreating and catalytic cracking have been substantially revised, updated, and expanded. Chapter 13, treating fuel cells, has been added to this Second Edition in response to the tremendous recent interest in this subject.

In this Second Edition we continue our initial concept, namely, that of a combined textbook and handbook that marries the fundamentals of catalysis with its practice. This marriage is based on a paradigm whose time has come—namely, that university education and industrial practice can no longer function independently of each other. Students of chemistry and chemical engineering who hope to work productively in industry must be trained not only in fundamentals of catalysts but also in the practical design of catalysts and catalytic processes. By the same token, professional scientists and engineers can no longer hope to be successful without a basic grasp of fundamentals and their applications in solving industrial problems, for example, designing catalysts, reactors, and process models which requires a detailed knowledge of reaction kinetics and mechanisms. Successful practice in this rapidly changing world also requires a broad understanding of catalyst technologies with a perspective of how the different areas of catalyst technology fit together and where the field is headed in the next 5–10 years.

This book has been designed to address the needs of both students and practicing professionals. It is intended as a resource for bridging the gap between the two different worlds of academic and industrial catalysis. It is written for both chemists and chemical engineers in an introductory, reader-friendly language. For the university setting, it is a stand-alone introductory textbook for advanced undergraduate and beginning to advanced graduate students in chemistry and chemical engineering departments. It teaches the fundamentals of catalytic science; catalyst properties, preparation, and characterization; and catalytic reactor design. It also contains a generous quantity of practical detail and data regarding many important catalytic processes which should be useful to students, faculty and practicing professionals. Included, for example, for each of these processes are useful details regarding process and catalyst chemistry, typical process conditions, process flow diagrams, typical catalyst deactivation problems, properties and suppliers of industrial catalysts, rate data and equations for catalyst and reactor design. Much of this detail is summarized in over 190 tables and 390 figures. Recommendations for further reading and a generous list of references have been provided at the end of each chapter. Each chapter also contains 20–30 exercises in the form of thought-provoking questions and practical design problems. The authors' perspectives (based on 60 years of combined experience) regarding anticipated future developments for important catalytic processes are also provided in each chapter. A glossary of terms and a table of nomenclature are provided to facilitate reader comprehension.

The book is organized into two parts containing altogether 13 chapters. The first part, Introduction and Fundamentals, contains five chapters dealing with: (1) fundamentals of catalysis; (2) catalyst materials, properties and preparation; (3) catalyst characterization; (4) reactors, reactor design, and activity testing; and (5) catalyst deactivation. The second part, Industrial Practice, includes eight chapters treating: (6) hydrogen production and synthesis processes; (7) hydrogenation and dehydrogenation processes; (8) oxidation processes; (9) petroleum refining and hydrocarbon processing; (10) environmental control of mobile sources; (11) environmental control of stationary sources; (12) homogeneous, enzymatic and polymerization catalysis; and (13) fuel cell catalysis. The authors recommend dividing the material into three, three-hour semester courses covering (1) fundamentals (Chapters 1–4 and part of 12), (2) catalyst deactivation (Chapter 5), and (3) industrial practice (Chapters 6–13). Variations of these three courses have been taught successfully to several hundred seniors and graduate students in chemical engineering at Brigham Young University over the past 24 years and over the past 15 years to over 500 professionals in industry (as short courses). Since the questions and problems at the end of each chapter range in difficulty from short and easy to difficult and long, teachers should exercise care in their selection. More difficult (but nevertheless realistic) problems are marked with an asterisk; these can be divided into less difficult shorter parts and/or worked in groups with some instructor assistance. An answer book will be made available to professors upon request.

ACKNOWLEDGMENTS

CHB: I wish to acknowledge many teachers and colleagues, who contributed to the ideas used in this book. I am especially grateful to Michel Boudart, John M. Thomas, Octave Levenspiel, J.M. Smith, Gabor A. Somorjai, Henrik Topsoe, James A. Dumesic, Wayne Goodman, and Charles Satterfield, who have paved and pointed the way. I am indebted to William C. Hecker, who helped to refine many of the concepts in Chapters 1-4 and James A. Dumesic and Jens Rostrup-Nielsen, for helpful comments and suggestions on Chapter 6.

RJF: I would like to acknowledge my 30 year professional collaboration with Dr. Ronald M. Heck whose partnership in environmental catalysis has been extremely productive. I would also like to thank Dr. David Stockwell for valuable insights into new cracking catalysts. I would like to express my sincere appreciation to Dr. Edward Wolynic and Dr. Terry Poles for their managerial support and encouragement throughout my career at Engelhard. A very special thanks to all the scientists and engineers at Engelhard who have advanced many of the catalytic topics included in this book. I would like to express my gratitude to the students at Stevens Institute of Technology, New Jersey Institute of Technology, Columbia University and Manhattan College whose desire to learn the applied aspects of catalysis led to the writing of this book.

Both authors are grateful to Kimberly Tregeagle, Allyson Schrock, Angie Leatherwood, Tyler Ward, Erica Hill, and Kirk Peterson, for their many hours of assistance in preparing drawings and in typing and editing the manuscript; to several students, but especially Aaron Nackos, Phillip Smith, Matt Svedin and Peter Ferrin, for helpful comments, suggestions, corrections, and content contributions (Aaron Nackos contributed substantially to the example in Chapter 7, Phillip Smith to the section on Enzymes in Chapter 12); and to the editors at Wiley, especially Bob Esposito and Jonathan Rose, for their exceptional patience.

NOMENCLATURE [a]

$\boldsymbol{a}$	activity, the rate at time t divided by the rate at $t = 0$
$\bar{\boldsymbol{a}}$	average activity
a_m	S_{ex}/W or the specific area/mass of catalyst in cm^2/g_{cat}
$\boldsymbol{a}_s$	steady-state activity
a_s, a_{gl}	specific surface area (m^2/m^3); subscript s for catalyst solid, gl for gas-liquid interface
A	pre-exponential or frequency factor; area or surface area (m^2)
A/F	air-fuel ratio
A_c	cross-sectional area
A_h	heat transfer area
AES	Auger electron spectroscopy
A/F	air-to-fuel ratio
AN	acrylonitrile
6-APA	6-aminopenicilanic acid
AR	metal alkyl, e.g. Al or Ti alkyls used in preparation of Ziegler-Natta catalyst
ASF	Anderson-Schulz-Flory model or kinetics
bhp	brake horsepower
bp	boiling point (K or °C)
B	breadth at half-height in the equation for XRD line broadening
c	constant in the BET equation
C_α	adsorbed, atomic carbon or surface carbide
C_β	polymeric, amorphous carbon film
C_C	crystalline, graphitic carbon in the form of a platelet or film
CFC	chlorofluorocarbon
C_γ	carbon dissolved in a metal, i.e. a metal carbide
C_i	concentration of species i; surface coordination site having i nearest neighbors
CN	coordination number (ligands per metal atom or ion)
C_P	heat capacity (J/mol/K))
CPSI	cells per square inch
CSTR	constant stirred tank reactor (well-mixed flow reactor)
C_V	vermicular carbon in the form of filaments, fibers, or whiskers
d	diameter of catalyst particles or reactor (m); crystallite diameter (nm); also order of deactivation
d_{pore}	pore diameter (m)
D	fractional dispersion or fraction of atoms exposed to the surface
D_{AB}	diffusivity of A in fluid B (m^2/s)
D_{eff}, D_e	effective diffusivity (m^2/s)
D_{eq}	limiting dispersion at infinite time
DBT	dibenzothiophene
DMSO	dimethyl sulfoxide
DOP	degree of polymerization or number of mers in a polymer chain
E	enzyme
E	potential energy; fraction of atoms (given kind) exposed to surface (same as dispersion D)
E_{act} or E_a	activation energy (J/mol)
E_{app}	apparent activation energy (J/mol)
EB	ethylbenzene
EO	ethylene oxide

ES	enzyme-substrate complex
f	the fraction of active element present in the metallic state; friction factor; the fraction of free radicals formed by initiation that undergo addition to a monomer
f_i	number fraction of species i
f_s	volume fraction of solids
$f(C)$	function of concentration of reactant and product species used in rate expression
FA	formaldehyde
F_{A_o}	inlet molar flowrate of A (mol/s)
FBR	fixed bed reactor
FCC	fluid catalytic cracking
FGD	flue-gas desulfurization
FT	Fischer-Tropsch
FTP	Federal Test Procedure
FTS	Fischer-Tropsch synthesis
g_{cat}	grams of catalyst
gal	gallon
G	superficial mass velocity (kg/m^2-s) based on cross-sectional area
ΔG	Gibbs free energy (J/mol)
GHSV	gas hourly space velocity on a volume basis (h^{-1})
GPLE	general power law expression
GSA	geometrical surface area (m^2)
h_o	heat transfer coefficient (J/(K-m^2-s)
H	Henry's Law constant
ΔH_a	enthalpy of adsorption (J/mol)
ΔH_{a1}	enthalpy of adsorption on the 1st layer (J/mol)
ΔH_c	enthalpy of condensation of gas (J/mol)
ΔH_o	enthalpy of adsorption at zero coverage (J/mol)
ΔH_r	enthalpy of reaction (J/mol)
HA	acid
HC	hydrocarbon
HCO	heavy cycle oil
HDM	hydrodemetallization
HDN	hydrodenitrogenation
HDO	hydrodeoxygenation
HDPE	high-density polyethylene
HDS	hydrodesulfurization
HFC	hydrofluorocarbon
HFCS	high-fructose corn syrup
HGR	host-guest recognition
HT	hydrogen uptake in the hydrogen-oxygen titration (micromoles/g_{cat}); hydrotreating
HY	hydrogen-Y zeolite
IR	infrared
IV	iodine value for determination of alkene saturation
k	reaction rate constant; also thermal conductivity
k_c	mass transfer coefficient with concentration driving force (m^3/m^2 s or m/s)
k_d	(i) deactivation rate constant (ii) desorption rate constant
k_g	gas film mass transfer coefficient (m^3/m^2-s or m/s)
k_{gl}	gas-liquid interfacial mass transfer coefficient (m/s)

k_{ls}	liquid-solid interfacial mass transfer coefficient (m/s)
k_s	sintering rate constant, surface reaction rate constant
K	equilibrium constant
K_γ	equilibrium constant expressing ratios of activity coefficients
K_m	Michaelis constant in the rate expression for enzyme reactions
K_P	equilibrium constant in terms of partial pressures
K_y	equilibrium constant in terms of mole fractions
ℓ, L	liter
L	length of a pore, pellet, or monolith channel (m); sum of surface concentrations of all surface species; Langmuir (1 Torr-s)
L-DOPA	2-amino-3-(3,4-dihydroxyphenyl)propionic acid
LCO	light cycle oil
LDPE	low-density polyethylene
LHSV	liquid hourly space velocity ($vol_{liq}\ vol_{cat}^{-1}\ h^{-1}$ or h^{-1})
LLDPE	linear, low-density polyethylene
LPG	light petroleum gas (C_1-C_4 hydrocarbons)
m	order of sintering, GPLE; mer molecular weight
m_i	number of moles of species i; m_i^o = initial number of moles
m.i.	manufacturing intermediate
M	metal atom
M_i	molecular weight of a polymer formed by i monomers; also species in a stoichiometric equation
M_n	number-averaged molecular weight of a polymer
M_w	weight-averaged molecular weight of a polymer
Mt	million tons (metric)
MA	maleic anhydride
MAO	methyl aluminoxane, a cocatalyst in polymerization
MASC	multifunctional, active, selective catalyst
MASI	most abundant surface intermediate
MAT	microactivity test
MCFC	molten-carbonate fuel cell
MEA	membrane electrode assembly
ML	monolayer
MON	motor octane number
MTBE	methyl-*t*-butyl ether
MW	molecular weight (g/mol); megawatts of power
MWD	molecular weight distribution
n	reaction or sintering order in simple power law rate expression; number of carbon atoms in the product
n_i	number of moles of species i; n_i^o = initial number of moles
N_{Av}	Avogadro's number (6.023×10^{23} molecules/mol)
N_i	number of atoms of catalytic species i; also turnover frequency for conversion or production of reactant or product species i (s^{-1})
NMHC	nonmethane hydrocarbon
NMR	nuclear magnetic resonance
NO_x	nitrogen oxides, especially NO and NO_2
N_S	number of surface atoms of a given catalytic species
NSCR	nonselective catalytic reduction (usually of NO with methane)
N_T	total number of atoms of a given catalytic species
ΔP	pressure drop (atm or bar)

P	pressure (atm or bar)
$P(t)$	probability that a site is accessible at time t
PBR	packed bed reactor
PC	particulate collector
PE	polyethylene
PEM	proton exchange membrane
PET	polyethylene terephthalate
P_i	partial pressure of a species i (atm or bar)
PLE	power law expression
PM2.5, PM10	particulate matter in ambient air having particle diameters of less than 2.5 or 10 μm
PNA	polynuclear aromatic
P_o	saturation vapor pressure of the adsorbing gas at a specified temperature (atm or bar)
P_T	total pressure (atm or bar)
PP	polypropylene
PS	polystyrene
psia	pounds per square inch absolute
PSD	pore size distribution
PVC	polyvinyl chloride
q	heat generation rate (J/s); also amount adsorbed (mol)
q_i	amount of adsorbed species i on the catalyst, usually in moles or micromoles
q_o	micropore capacity in the Dubinin equation (mol)
Q	heat transferred to the system from the surroundings (J)
r	reaction rate (mol/m^3-s or mol/g_{cat}-s); also radial distance (m)
$-r_A$	rate of disappearance of reactant A
r_C	rate of formation of coke
rds	rate determining step
ref	reference
r_H	hydraulic radius (m)
r_k	core radius in calculation of pore size distribution (m)
r_p	pore radius (m) or rate or reaction in a pellet (moles/g_{cat}-s)
R	gas constant, 82.1 cm^3 atm/K-mol or 8.314 J/mol-K
RFG	reformulated gasoline
ROC	reactive organic compounds
RON	research octane number
S	surface area (m^2); with ^ overstrike, specific surface area in (m^2/g)
S, s	surface site
$S(t)$	conditional probability that a site is not covered
ΔS	entropy (J/K-mol)
SCR	selective catalytic reduction (usually of NO_x with NH_3)
SEM	scanning electron microscopy
S_{ex}	surface area of the external surface (m^2); with ^ overstrike, specific surface area (m^2/g)
SG	stack gas
S_i	selectivity for a species i relative to some other species j
S_{in}	interior catalytic surface area of the pores (m^2); $\hat{s}_{in}$ (m^2/g)
SMDS	Shell middle distillate synthesis
SNG	substitute natural gas
SOF	soluble organic fraction of diesel emissions
SOFC	solid oxide fuel cell

SO_x	sulfur oxides, especially SO_2 and SO_3
SR	selectivity ratio (k_2/k_3) for hydrogenation of soybean oil
SSC	single-site catalyst for polymerization
STR	stirred-tank reactor (typically for hydrogenations)
SV	space velocity, the inverse of space time
t	time (s)
t	tons, metric tons
tons	metric tons
T	temperature (K)
TEM	transmission electron microscopy
TMC	transition metal complex
TOR	turnover rate (molecules/site-s)
TOF	turnover frequency, (molecules/site-s or s^{-1})
TOS	time-on-stream (s, h, or d (days))
TPD	temperature-programmed desorption
TPM	total particulate matter in gaseous emissions
TPO	temperature-programmed oxidation
TPP	tridendate phosphine ligand or triphenylphosphine group, $P(C_6H_5)_3$ or PPh_3
TWC	three-way converter
u	molar-averaged gas velocity or superficial velocity (m/s)
U_o	overall heat transfer coefficient (J/K-m^2-s)
UHMWPE	ultra-high molecular weight polyethylene
USY	ultrastabilized-Y zeolite
δv_f	change in multilayer volume due to thinning by desorption in calculation of PSD
v_k	core volume in calculation of pore size distribution (m^3/g_{cat})
v_o	volumetric flow rate (m^3/s) at the entrance to a reactor
v_p	pore volume in calculation of pore size distribution (m^3/g_{cat})
v_r	radial velocity (m/s)
v_z	axial velocity (m/s)
V	volume (m^3)
V_m	volume of gas required to provide a complete monolayer (m^3); with caret, specific volume (m^3/g_{cat})
$\hat{V}_{pore}$	pore volume in cm^3/g
VOC	volatile organic compound
VPO	vanadyl pyrophosphate, $(VO)_2P_2O_7$
w_i	weight fraction of the catalytic element present as either metal or oxide; weight fraction of a specified species
w_n	weight fraction of product containing *n* carbon atoms
w_o	mass flow rate (kg/s)
w_s	weight loading of solid (kg/kg)
W	weight (mass) of catalyst (kg)
WGS	water-gas-shift reaction
WHSV	weight hourly space velocity (kg kg_{cat}^{-1} h^{-1}) or h^{-1})
x	normalized vapor pressure of adsorbing gas, = P/P_o, P_o = vapor pressure at specified T
x_i	mole fraction of liquid species *i*
x_n	number-averaged number of mers in a polymer or degree of polymerization (DOP)
x_w	weight-averaged number of mers in a polymer
X	H_2 adsorption uptake (μmoles/g_{cat}); number of carbon atoms in a fatty ester or triglyceride
X_A	fractional conversion of species *A*

X_i	fractional conversion of species i
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
y_i	mole fraction of gaseous species i
Y	number of double bonds in a fatty ester or triglyceride
z	axial distance (along the catalyst bed) (m)
ZN	Ziegler-Natta

Greek Symbols

α	fraction of the total surface poisoned; surface area per molecule, 16.2×10^{-20} m^2 per molecule of N_2; chain growth propagation probability in Fischer-Tropsch Synthesis; parameter in Temkin isotherm and rate expression for ammonia synthesis
α_i	reaction order with respect to the species i
γ	surface tension of condensed adsorbate, usually liquid nitrogen (N/m)
γ_i	activity coefficient of the ith species
ε	porosity
ε_A	expansion coefficient or fractional increase in volume of species A through a reactor
ε_B, ε_P	void fraction of catalyst bed, catalyst pellet
η	effectiveness factor, i.e. fractional change in rate due to pore-diffusional resistance
η_d	effectiveness factor for deactivation
θ	contact angle of liquid in Kelvin equation; 2θ is the angle in X-ray diffraction; also residence time, the actual time spent by an element of fluid in the reactor
θ_i	fractional surface coverage of species i, $i = V$ refers to coverage of vacant sites
κ	constant in the equation for XRD line broadening, usually equal to 1
λ	X-ray wavelength (nm); also $(A/F)_{obs} / (A/F)_{stoichiometric}$
ν_i	stoichiometric coefficient in the stoichiometric reaction $\Sigma_i \nu_i M_i = 0$ involving species M_i; a subscript r refers to reactant species
ν_n	kinetic chain length in free-radical mechanism for polymerization (related to degree of polymerization)
ξ	extent of reaction (moles)
ρ	density
ρ_B	bulk or bed density
ρ_b, ρ_p, ρ_s	density: bulk, catalyst particle, and skeletal
σ	poisoning susceptibility, negative slope of activity concentration curve
τ	space time, time required to process one reactor volume at specified feed conditions
τ_w	weight time
ϕ_{pore}	Thiele modulus defined for a single pore by $\phi_{pore} = L(k\rho_p/D_{eff})^{1/2}$, L = pore length
ϕ_s	Thiele modulus for spherical pellets
Ω	global degree of coke coverage

Subscripts, superscripts, overstrikes, or parenthesis

a	adsorption, activation
act	activation
A	reactant species
b	bulk fluid or solid

d	desorption; also deactivation
ex	exterior
f	final state or exit of reactor; also thermodynamic quantity of formation
g	gas
i	species in reaction
init	initial
init	initial
int, in	interior
liq	liquid
m	mass transfer; also main, e.g. r_m refers to rate for main reaction
macro	macropores
mass tr. or mt	mass transfer
meso	mesopores
micro	micropores
o	initial
obs	observed value
p	particle or pore
prop	propagation
r	reaction
s	solid, surface
S	surface
T or tot	total quantity or value
term	termination
'	specific quantity per unit time, e.g. Q' is the heat transferred per unit time (J/s)
^	specific quantity, e.g. $\hat{S}$ specifies surface area in m^2/g
1	first, forward, or first-order, e.g. k_1 denotes first-order or forward rate constant

[a] Quantities are, with only a few exceptions, expressed in SI units; for example, mass is expressed in g, kg, or t (metric tons), pressures in atm or bar, and temperatures in °C or °K (the latter without the degree symbol according to convention).

CONTENTS