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# **Chemical Technology**

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*Andreas Jess and Peter Wasserscheid*

Second Edition

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*To our wives Christina and Talke and our children Antonia, Friederike, Jonathan, Karolin, Lukas,  
and Theresa.*



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## Preface of First Edition (and Guidelines How to Use This Textbook)

This textbook tries to marry the four disciplines of chemical technology, namely, chemistry (key reactions, catalysis), thermal and mechanical unit operations (distillation, absorption/adsorption, mixing of fluids, separation of solids from fluids, etc.), chemical reaction engineering (thermodynamics, kinetics, influence of heat and mass transfer, reactor modeling), and general chemical technology, that is, the pedigree of routes from raw materials via intermediates to final products and environmental aspects of chemical technology.

The development and understanding of chemical processes relies on knowledge of all four disciplines. This book is an approach to integrating these disciplines and to enlivening them by problems and solutions of industrial practice. The book intends to enable students of chemical engineering as well as of chemistry (especially those with a focus on technical chemistry) to understand industrial processes and to apply these fundamental disciplines for the design of reactors, including pre- and posttreatment of feedstocks and products.

We emphasize that the depth of specialist literature cannot and should not be reached; but students who want to study certain aspects in more detail will find further references.

The book is organized into three main parts:

- The first half provides a comprehensive examination of the fundamental disciplines of chemical technology: after a short introduction, the subsequent chapters survey chemical aspects (Chapter 2), thermal and mechanical unit operations (Chapter 3), and chemical reaction engineering (Chapter 4).
- Chapter 5 gives an overview of raw materials and energy sources (fossil fuels, renewable energy), in which economical, ecological, and social aspects of energy consumption are also covered. Thereafter, the routes from fossil fuels (natural gas, oil, and coal) to fuels, petrochemicals, bulk chemicals, and final products are described, and the main inorganic intermediates and final products are also given. Finally, some main environmental aspects of chemical technology (air and water pollution) and the costs of manufacturing fuels and chemicals are discussed.
- In the last part (Chapter 6), 20 industrial chemical processes and their design are analyzed, exemplifying the inherent applied nature of chemical technology. By this means the reader can recapitulate, deepen, and exercise the chemical and engineering principles and their interplay (hopefully learned in Chapters 1–5) and will extend them to industrial practice. The processes have been selected such that they all differ with respect to at least one important aspect like the type and design of the reactor, the chemistry involved, or the separation process used.

The book is supplemented by a brief survey of selected modern trends such as microreactors, and new solvents for catalysis like ionic liquids, which should convince the reader that chemical technology is not a “completed” discipline, but a developing field with huge future challenges such as solving the energy problems for generations to come.

Several chapters are based on bachelor and master courses the authors have taught students of chemistry and of chemical engineering at different universities for many years (Aachen, Bayreuth, Erlangen, Karlsruhe). We have tried to consider the challenges specific to instructing chemists and engineers in chemical technology; for example, the problems both groups have in integrating the different disciplines: according to our experience, chemists tend to be too anxious with regard to chemical engineering methods (and most notably with the mathematics involved). In contrast, engineers often feel uncomfortable if chemical aspects have to be examined and come to the fore.

We hope that students both of (technical) chemistry and chemical engineering will appreciate this book and that chemical engineers will acquire a sufficient feeling for chemistry and, likewise, chemists for the principles of chemical engineering.

To facilitate learning, the reader will find many instructive figures, examples, and rules of thumb for estimations of parameters and data of chemical media, many examples utilizing data from industrial processes, and in some cases partly the results of the authors' research. Complicated mathematical operations will only be used if mandatory. Numerous literature references are cited to guide the reader, where certain aspects are documented in more detail.

To simplify consultation of this textbook, several equations are accentuated by two types of exclamation marks:

- ▼ In our opinion, chemical engineers and technical chemists should know these important equations by heart.
- ▽ These equations are useful and often used (without the need to memorize them in detail).

To illustrate certain aspects in more detail and to facilitate the use of the derived equations, several insertions marked either as "topics" or "examples" have been added.

At the end of each main chapter, a summary with "take-home messages" is given.

This book cannot, and is not intended to, compete with specialized textbooks, but hopefully gives a comprehensive and integrated outline of the fascinating subject of chemical technology and all its facets. It intends to be of value to all students of chemical engineering and technical chemistry, as well as to researchers and people from industry needing a concise book that covers all main aspects of industrial chemistry.

A book such as this could not have appeared without the sustainable help of a number of people. Only a few of them can be mentioned by name.

Our understanding of chemical technology owes much to having been fortunate in working and discussing the subject with Professor Wilhelm Keim, Professor Kurt Hedden, and Professor Gerhard Emig, and we are grateful to all three of them.

We would like to thank our students who followed our courses and/or did their PhD thesis in our institutions. They provided us with plenty of feedback.

We express special gratitude to Dr. Christoph Kern, Dr. Wolfgang Korth, and Professor Bastian Etzold for fruitful discussions, ideas, and critiques; Michael Gebhardt and Dr. Stephan Aschauer for all the work and care invested in preparing numerous figures; Dr. Eva Öchsner and Dr. Sebastian Willmes for their assistance in preparing Sections 6.9, 6.11.2, 6.12, 6.15; Prof. Udo Kragl for his assistance in preparing

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Finally, we would like to express our appreciation to our wives and children, who witnessed the writing of this book in so many evening and weekend hours, continuously encouraged us, and patiently allowed us to spend a considerable amount of time during the last eight years on the preparation of this book.

If you like this book, please recommend it to others. If you have suggestions for improvements or discover faults (inevitable despite of all our efforts), please send us an e-mail<sup>1</sup>.

*Prosit!* (Latin: it may be useful)

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Bayreuth/Erlangen, October 2012

## Why a Second Edition?

Since the first publication of our book in 2013 and since the end of our data compilation around 2011, there have been important developments in this rapidly changing world: (i) Global energy and raw material flows and production rates of chemicals have significantly increased in the last years, mainly driven by China's growing economy and by the so-called shale gas revolution in North America. (ii) Changes in the environmental and energy policy have already led to an alteration of the energy mix and to a higher share of renewables, in particular in Germany and other European countries but meanwhile also in China. (iii) This rapid growth of renewable power generation in several countries has already helped to decarbonize electricity production, but with regard to the imminent climate change the role of renewables is still too small. In the future, renewables will be important not only in the context of the electrical grid and transportation by electric vehicles but also toward electrification and decarbonization of the chemical industry and the reduction of the carbon footprint of fuels and chemicals.

In addition to the updating of consumption and production data and the correction of inevitable mistakes in writing of the first edition, we have not

<sup>1</sup> The corresponding author for Chapters 1, 3, 4 and Sections 5.1 (without 5.1.8), 5.2, 5.4, 5.5, 6.1–6.5, 6.7–6.9, 6.11.1, 6.13, 6.17–6.19, and 6.21–6.23 is Andreas Jess; the responsible author for Chapter 2 and Sections 5.1.8, 5.3, 6.6, 6.10, 6.11.2, 6.12, 6.14–6.16, 6.20, and 6.24 is Peter Wasserscheid.

only extended and improved several chapters but also added completely new ones:

- Section 1.3 illustrates the global economic map and its development from the fifteenth century until today.
- A method to determine the optimum extent of heat recovery (pinch technology) is now included in Section 3.3.
- The method to calculate the maximum wall thickness of a tubular pipe or vessel for a given material and internal pressure is presented in Example 3.4.2.
- Energy consumption in human history (new Section 5.1.7) and chemical energy technologies and power-to-X technologies are outlined (new Section 5.1.8).
- Section 5.2 (inorganic products) was extended with regard to ceramics, glass, fluorine compounds, and metals including material reserves and the criticality of metals such as cobalt, lithium, and neodymium against the background of new energy technologies.
- Section 5.4.2 on water consumption was enlarged, and the global water cycle, data on resources and availability, and the concept of a water footprint are now also presented.
- Section 5.4.3 presents environmental aspects of plastic pollution and the handling of plastic waste in different parts of the world.

- In Chapter 6, four important processes were added, production of  $\text{TiO}_2$  (Section 6.21), manufacturing of silicon (Section 6.22), production and chemical recycling of polytetrafluoroethylene (Section 6.23), and fermentative synthesis of amino acids (Section 6.24).

We express special gratitude to Dr. Patrick Preuster for contributing to Section 5.1.8, Prof. Thorsten Gerdes for his substantial input to Sections 6.21–6.23, Prof. Kathrin Castiglione for her input to Section 6.24, and Andreas Reul for preparing new figures and proofreading.

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We hope that the readers will appreciate this updated and extended second edition of our book. May it be useful for as many as possible!

Bayreuth/Erlangen  
November 2019

*Andreas Jess*  
*Peter Wasserscheid*



## Notation

The International System of Units (abbreviated SI from the French *Système international d'unités*) developed in 1960 is the modern form of the metric system. This system is nowadays used in many countries both in everyday life and in science. Unfortunately, the popular use of SI units is still limited in important countries like the United States and the United Kingdom, although this may lead to mathematical mismatches with disastrous consequences (see Section “Critical Units” at the end of this chapter).

As listed in Table 1, the SI defines seven base units, namely, meter, kilogram, second, ampere, kelvin, mole, and candela. All other units can be derived from these base units. Frequently used SI derived units are newton (N), the unit of force ( $1 \text{ N} = 1 \text{ kg m s}^{-2}$ ); pascal (Pa), the unit of pressure ( $1 \text{ Pa} = 1 \text{ N m}^{-2} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$ ); joule (J), the unit of energy ( $1 \text{ J} = 1 \text{ N m} = 1 \text{ kg m}^2 \text{ s}^{-2}$ ); and watt (W), the unit of power ( $1 \text{ W} = 1 \text{ J s}^{-1} = 1 \text{ kg m}^2 \text{ s}^{-3}$ ).

Throughout this book, all equations (and the respective symbols listed in Table 2) are related to SI units. As a consequence and a general rule for this book, insert all variables in SI units into the equations, and you will always get the correct result of a certain quantity in SI units. Nevertheless, the results of calculations are sometimes given in “handier” units, for example, with a prefix such as kJ or MJ instead of 1000 J or 1 000 000 J, or the well-known unit bar ( $= 10^5 \text{ Pa}$ ) is used for the pressure instead of Pa.

Other **unit prefixes** frequently used are:

tera (T)	$10^{12}$
giga (G)	$10^9$
kilo (k)	$10^3$
milli (m)	$10^{-3}$
micro ( $\mu$ )	$10^{-6}$
nano (n)	$10^{-9}$

**Useful conversion factors** are:

Length	$1 \text{ m} = 39.37 \text{ in. (inches)} = 3.2808 \text{ ft (feet)}$
Mass	$1 \text{ kg} = 0.001 \text{ ton (in this book always metric ton, e.g. 2 tons} = 2000 \text{ kg)}$
Volume	$1 \text{ m}^3 = 6.29 \text{ bbl (barrel) of oil} = 264 \text{ US liq. gal (gallon)}$ $1 \text{ bbl of oil} = 159 \text{ l}$ $1 \text{ US liq. gal} = 3.79 \times 10^{-3} \text{ m}^3 = 3.79 \text{ l}$
Concentration	$1 \text{ mol m}^{-3} = 2.3 \text{ vol\% (ideal gas } i, 0^\circ \text{C, } p_{\text{total}} \text{ of 1 bar), since } y_i = p_i/p_{\text{total}} = c_i RT/p_{\text{total}} = 1 \text{ mol m}^{-3} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 273 \text{ K}/10^5 \text{ Pa} = 0.023)$ $1 \text{ bar (partial pressure, ideal gas, } 0^\circ \text{C, 1 bar)} = 44 \text{ mol m}^{-3} \text{ (since } c = p/(RT))$ $1 \text{ vol\%} = 0.01 \text{ m}^3 \text{ m}^{-3} = 10.000 \text{ ppmv (parts per million volume)}$ $1 \text{ ppmv} = 10^{-6} \text{ m}^3 \text{ m}^{-3}$ $1 \text{ ppmw (parts per million weight)} = 10^{-6} \text{ kg kg}^{-1} = 1 \text{ mg kg}^{-1}$
Energy	$1 \text{ J} = 1 \text{ N m} = 1 \text{ kg m}^2 \text{ s}^{-2} = 2.78 \times 10^{-7} \text{ kWh}$ $1 \text{ kWh} = 3.6 \times 10^6 \text{ J} = 3.6 \text{ MJ}$ $1 \text{ kg oe (oil equivalent)} = 41.87 \times 10^6 \text{ J} = 41.87 \text{ MJ}$ $1 \text{ toe (ton of oil equivalent)} = 41.87 \times 10^9 \text{ J} = 41.87 \text{ GJ}$ $1 \text{ cal} = 4.18 \text{ J}$ $1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$

**Table 1** The seven base units of the SI.

Name	Symbol	Quantity	Definition
Meter	m	Length	Length traveled by light in vacuum during the time interval of $1/299\,792\,458\text{ s} = 3.3356 \times 10^{-9}\text{ s}$
Kilogram	kg	Mass	Mass of the <i>prototype kilogram</i> , a Pt–Ir cylinder kept at the Bureau International des Poids et Mesures in Paris. The kilogram is the only base unit with a prefix and is still not defined by a fundamental physical property, but there are ongoing efforts to introduce a new definition based on such properties
Second	s	Time	Duration of 9 192 631 770 periods of the radiation of the transition between two hyperfine levels of the ground state of the caesium-133 atom at a temperature of 0 K
Ampere	A	Electrical current	Constant current, which if maintained in two straight parallel conductors of infinite length and negligible cross section, placed one meter apart in vacuum, would produce a force between the conductors of $2 \times 10^{-7}$ newton per meter length
Kelvin	K	Thermodynamic temperature	The thermodynamic (or absolute) temperature is the fraction 1/273.16 of the absolute triple point temperature of water
Mole	mol	Amount of substance	Quantity that contains the same number of entities (atoms, molecules, etc.) as there are atoms in 12 g of carbon-12. This number – Avogadro’s number $N_A$ – is about $6.022 \times 10^{23}$
Candela	Cd	Luminous intensity	Luminous intensity in a given direction of a source that emits monochromatic radiation with a wavelength of 555 nm and a radiant intensity in that direction of $1/683\text{ W sr}^{-1}$

**Table 2** Symbols and abbreviations used in this book.

Symbol	Meaning	Unit
<i>Latin letters</i>		
$a$	Activity	—
$a$	Thermal diffusivity	$\text{m}^2\text{ s}^{-1}$
$a_{\text{cat}}$	(Remaining) activity of catalyst	—
$A$	Van der Waals constant	$\text{Pa m}^6\text{ mol}^{-2}$
$A$	Thermal diffusivity, conductivity of temperature	$\text{m}^2\text{ s}^{-1}$
$A$	Area	$\text{m}^2$
$A_{\text{ads}}$	Cross-sectional area of adsorption bed	$\text{m}^2$
$A_{\text{BET}}$	Internal surface area per mass of catalyst or solid measured by BET analysis	$\text{m}^2\text{ kg}^{-1}$
$A_e$	Electrode surface area	$\text{m}^2$
$A_h$	Area for heat transfer	$\text{m}^2$
$A_i$	Interfacial area	$\text{m}^2$
$A_{\text{int},V}$	Internal surface area per volume of solid (catalyst)	$\text{m}^2\text{ kg}^{-1}$
$A_{i,m}$	Specific interfacial area per mass of catalyst	$\text{m}^2\text{ kg}^{-1}$
$A_{i,V}$	Specific interfacial area per volume of reactor	$\text{m}^2\text{ m}^{-3}$
$A_{m,\text{ex}}$	External surface area per mass of catalyst or solid	$\text{m}^2\text{ kg}^{-1}$
$A_p$	External surface area of particle	$\text{m}^2$
$A_{\text{pore},\text{ex}}$	Cross-sectional area of pore	$\text{m}^2$
$A_{\text{pore}}$	Internal (mantle) area of pore	$\text{m}^2$

Table 2 (Continued)

Symbol	Meaning	Unit
$A_R$	Cross-sectional area of reactor	$m^2$
$A_t$	Cross-sectional area of tube	$m^2$
$A_V$	External surface area per volume of catalyst or solid	$m^2 m^{-3}$
$A_{V,s}$	Surface area per volume of solid	$m^2 m^{-3}$
$A_{wall}$	Area of wall for heating or cooling	$m^2$
$B$	Van der Waals constant	$m^3 mol^{-1}$
$C$	Production capacity	$kg s^{-1}$
$C_{BET}$	BET constant (in the equation for multilayer adsorption)	—
$C_{calorimeter}$	Heat capacity of calorimeter	$J K^{-1}$
$C_{Sutherland}$	Sutherland constant	K
$c$	Heat capacity of a fluid or solid with negligible small thermal expansivity and compressibility, that is, $c_p = c_v$	$J mol^{-1} K^{-1}$ or $J kg^{-1} K^{-1}$
$c$	Concentration	$mol m^{-3}$
$\bar{c}$	Mean concentration (in a porous particle)	$mol m^{-3}$
$c_s$	Concentration at the (external) surface	$mol m^{-3}$
$c_{cat}$	Concentration of catalyst	$kg m^{-3}$ or $mol m^{-3}$
$c_p$	Molar heat capacity of fluid at constant pressure	$J mol^{-1} K^{-1}$
$c_{p,m}$	Heat capacity related to mass	$J kg^{-1} K^{-1}$
$c_{p,m}$	Heat capacity of fluid related to mass at constant pressure	$J kg^{-1} K^{-1}$
$c_v$	Molar heat capacity of fluid at constant volume	$J mol^{-1} K^{-1}$
$c_s$	Concentration at the surface	$mol m^{-3}$
$c_s$	Heat capacity of solid	$J kg^{-1} K^{-1}$
$d, D$	Diameter, distance	m
$d_h$	Hydraulic diameter	m
$D$	Diffusion or dispersion coefficient (always diffusion coefficient if no specifying subscript or just a subscript denoting a component is used)	$m^2 s^{-1}$
$D_{ax}$	Axial dispersion coefficient	$m^2 s^{-1}$
$D_{eff}$	Effective diffusion coefficient (in a porous solid)	$m^2 s^{-1}$
$D_{Knu}$	Knudsen diffusion coefficient	$m^2 s^{-1}$
$D_{mol}$	Molecular diffusion coefficient	$m^2 s^{-1}$
$D_{pore}$	Diffusion coefficient in a pore	$m^2 s^{-1}$
$D_{rad}$	Radial dispersion coefficient	$m^2 s^{-1}$
$e_m$	Specific energy (work) related to mass	$J kg^{-1}$
$e_n$	Specific energy (work) related to molar amount	$J mol^{-1}$
$E$	Energy	J
$E$	Electromotive force, cell voltage, electrode potential	V
$E^0$	Standard value of electrode potential at 1.013 bar	V
$E_{th}^0$	Standard value of thermoneutral enthalpy voltage (at 1.013 bar)	V
$E$	$E$ function of residence time distribution	$s^{-1}$
$E$	Enhancement factor	$s^{-1}$

(Continued)

Table 2 (Continued)

Symbol	Meaning	Unit
$E_A$	Activation energy	$\text{J mol}^{-1}$
$E_{A,\text{app}}$	Apparent activation energy	$\text{J mol}^{-1}$
$E_{\text{kin}}$	Kinetic energy	$\text{J mol}^{-1}$
$E_\theta$	Dimensionless $E$ function of residence time distribution	—
$F$	Friction factor	—
$F$	Fugacity	—
$F$	Faraday constant (96 485)	$\text{A s mol}^{-1}$
$F$	$F$ -function of residence time distribution	—
$F_\theta$	Dimensionless $F$ function of residence time distribution	—
$G$	Acceleration of gravity	$\text{m s}^{-2}$
$G$	Gibbs function	$\text{J mol}^{-1}$
GHSV	Gas hourly space velocity	$\text{m}^{-3} \text{h m}^{-3}$
$g$	Gravitational acceleration (9.81)	$\text{m s}^{-2}$
HETP	Height equivalent of one theoretical plate	$\text{m}^{-1}$
HETS	Height equivalent of one theoretical stage	$\text{m}^{-1}$
$H$	Enthalpy	$\text{J mol}^{-1}$
$H_x$	Henry coefficient related to molar content	$\text{Pa mol}_{\text{liq}}^1 \text{mol}_{\text{gas}}^{-1}$
$H_c$	Henry coefficient related to concentration	$\text{Pa m}_{\text{liq}}^3 \text{mol}_{\text{gas}}^{-1}$
HHI	Herfindahl–Hirschman index	—
HTZ	Height of transfer zone	$\text{m}$
HR	Heating rate	$\text{K s}^{-1}$
$i$	Current density	$\text{A m}^{-2}$
$I$	Current	$\text{A}$
$I$	Investment costs	$\text{\$ or €}$
$k$	Boltzmann constant ( $1.38 \times 10^{-23}$ )	$\text{J K}^{-1}$
$k$	Reaction rate constant (depends on reaction order)	For first order: $\text{mol m}^{-3} \text{s}^{-1}$
$k_{\text{ads}}$	Rate constant of adsorption	$\text{s}^{-1} \text{Pa}^{-1}$
$k_A$	Reaction rate constant related to external surface area of solid or catalyst (depends on reaction order)	For first order: $\text{m}^3 \text{m}^{-2} \text{s}^{-1}$
$k_{\text{cool}}$	Reaction rate constant for $T = T_{\text{cool}}$	$\text{s}^{-1}$
$k_{\text{crit}}$	Reaction rate constant for $T = T_{\text{crit}}$	$\text{s}^{-1}$
$k_{\text{des}}$	Rate constant of desorption	$\text{s}^{-1}$
$k_{\text{LDF}}$	Overall mass transfer coefficient	$\text{s}^{-1}$
$k_{\text{M,mol}}$	Permeability of membrane related to molar flux	$\text{mol s kg}^{-1}$
$k_{\text{M,V}}$	Permeability of membrane related to volumetric flux	$\text{m}^3 \text{s kg}^{-1}$
$k_{\text{m}}$	Reaction rate constant related to mass of catalyst or solid (depends on reaction order)	For first order: $\text{m}^3 \text{kg}^{-1} \text{s}^{-1}$
$k_s$	Reaction rate constant related to overall (mostly internal) surface area of a catalyst	$\text{mol m}^{-2} \text{s}^{-1}$
$k_s$	Roughness equivalent to a grain of sand	$\text{m}$
$k_V$	Reaction rate constant related to volume	$\text{m}^3 \text{m}^{-3} \text{s}^{-1}$
$k_0$	Pre-exponential factor (unit depends on reaction order)	For first order: $\text{mol m}^{-3} \text{s}^{-1}$

Table 2 (Continued)

Symbol	Meaning	Unit
$K_1$	Equilibrium constant	$\text{mol s}^2 \text{kg}^{-1} \text{m}^{-2}$
$K_2$	Equilibrium constant	—
$K_3$	Equilibrium constant	—
$K_p$	Equilibrium constant with regard to partial pressures	—
$K_{\text{ads}}$	Equilibrium constant of adsorption	$\text{Pa}^{-1}$
$K_c$	Equilibrium constant with regard to molar concentrations	—
$K_{\text{ext}}$	Distribution ratio or partition coefficient of extraction related to molar content	$\text{mol mol}^{-1}/(\text{mol mol}^{-1})$
$K_{\text{ext,m}}$	Distribution ratio or partition coefficient of extraction related to mass content	$\text{kg kg}^{-1}/(\text{kg kg}^{-1})$
$K_f$	Equilibrium constant with regard to fugacities	—
$K_{\text{GL}}$	Overall gas–liquid mass transfer coefficient	$\text{m}^{-3} \text{m}^{-3} \text{s}^{-1}$
$K_M$	Michaelis–Menten constant	$\text{mol m}^{-3}$
$K_p$	Equilibrium constant with regard to partial pressures	—
$K_R$	Universal equilibrium constant (also denoted reaction quotient)	—
$K_W$	Ionic product of water ( $c_{\text{H}^+} c_{\text{OH}^-} = 10^{-14} \text{mol}^2 \text{l}^{-2}$ )	$\text{mol}^2 \text{m}^{-6}$ (mostly given in $\text{mol}^2 \text{l}^{-2}$ )
$K_x$	Equilibrium constant of a liquid phase reaction with regard to molar fractions	—
$K_y$	Equilibrium constant of a gas phase reaction with regard to molar fractions	—
$K_\phi$	Equilibrium term considering the fugacity coefficients	—
$K_\gamma$	Equilibrium term considering the activity coefficients	—
$L_p$	Length of perimeter	m
$L$	Length	m
LHSV	Liquid hourly space velocity	$\text{m}^3 \text{h m}^{-3}$
LUB	Length of unused bed	m
$m$	Mass	kg
$\dot{m}$	Mass flow	$\text{kg s}^{-1}$
$m_{\text{ads}}$	Mass of adsorbent	Kg
$M$	Molar mass	$\text{kg mol}^{-1}$
$n$	Number of moles	mol
$n_{\text{stirrer}}$	Stirrer speed	$\text{s}^{-1}$
$n_e$	Number of electrons	mol
$n_{\text{max}}$	Maximum number of layers	—
$\dot{n}$	Molar flux	$\text{mol s}^{-1}$
$N$	Rotational frequency	$\text{s}^{-1}$
$N$	Number of tanks of a cascade	—
$N$	Number of molecules	—
$N_{\text{act}}$	Number of active sites (relative to initial number)	—
$N_A$	Avogadro or Loschmidt number	$6.022 \times 10^{23} \text{mol}^{-1}$

(Continued)

Table 2 (Continued)

Symbol	Meaning	Unit
$\dot{p}$	Flux of momentum	$\text{kg m s}^{-2}$
$P$	Pressure, total pressure	Pa
$p^*$	Saturation vapor pressure	Pa
$p_0$	Standard pressure (1.013 25 bar = 1 atm)	Pa
$p_{\text{sat}}$	Saturation vapor pressure (of a pure liquid)	Pa
$p_{\text{vap}}$	Vapor pressure (of a pure liquid)	Pa
$P$	Power	W
$q$	Energy consumption	$\text{J kg}^{-1}$
$\dot{q}$	Heat flux per unit of area	$\text{J m}^{-2} \text{s}^{-1}$
$\dot{q}_{\text{HP}}$	Heat production per unit mass	$\text{J kg}^{-1} \text{s}^{-1}$
$\dot{q}_{\text{HR}}$	Heat removal per unit mass	$\text{J kg}^{-1} \text{s}^{-1}$
$Q$	Amount of heat	J
$\dot{Q}$	Heat flux	W, $\text{J s}^{-1}$
$Q_{\text{R}}$	Reaction quotient	—
$R$	Radius	m
$R$	(Equivalent) reaction rate	$\text{mol m}^{-3} \text{s}^{-1}$
$R_p$	Pressure ratio	—
$r_{\text{A}}$	Reaction rate per unit (internal) surface area	$\text{mol m}^{-2} \text{s}^{-1}$
$r_{\text{c}}$	Radius of the unreacted core	m
$r_{\text{m}}$	Reaction rate per mass of catalyst or solid	$\text{mol kg}^{-1} \text{s}^{-1}$
$r_{\text{v}}$	Reaction rate per volume of reactor or catalyst	$\text{mol m}^{-3} \text{s}^{-1}$
$R$	Ideal gas law constant (8.314)	$\text{J mol}^{-1} \text{K}^{-1}$
$R$	Dimensionless radial coordinate	—
$R$	Reflux ratio	—
$R$	Reaction rate	$\text{mol m}^{-3} \text{s}^{-1}$
$S$	Differential (instantaneous) selectivity	
$S$	Entropy	$\text{J mol}^{-1} \text{K}^{-1}$
$S$	(Integral) selectivity	—
SF	Security factor	—
$S_{\text{m}}$	Material strength	Pa
STY	Space–time yield	$\text{mol m}^{-3} \text{s}^{-1}$
SV	Space velocity	$\text{s}^{-1}$
$t$	(Reaction) time	s
$t_{\text{b}}$	Breakthrough time	s
$t_{\text{sat}}$	Saturation time	s
$t_{\text{st}}$	Stoichiometric time	s
$T$	Temperature	$^{\circ}\text{C}$ , K
$T_{\text{g}}$	Gas temperature (bulk phase)	$^{\circ}\text{C}$ , K
$T_{\text{h}}$	Cooling/heating temperature	$^{\circ}\text{C}$ , K
$T_{\text{s}}$	Surface temperature	$^{\circ}\text{C}$ , K
TOF	Turnover frequency	$\text{mol mol}^{-1} \text{s}^{-1}$
TON	Turnover number	$\text{mol mol}^{-1}$
$\bar{u}$	Mean velocity (of atoms and molecules)	$\text{m s}^{-1}$
$U$	Velocity	$\text{m s}^{-1}$
$u_{\text{s}}$	Superficial fluid velocity (related to empty reactor)	$\text{m s}^{-1}$
$U$	(Cell) voltage	V

Table 2 (Continued)

Symbol	Meaning	Unit
$U$	Internal energy	J or J mol <sup>-1</sup>
$U_h$	Overall heat transfer coefficient, thermal transmittance	W m <sup>-2</sup> K <sup>-1</sup>
$v_{\text{mol}}$	Molar volume	m <sup>3</sup> mol <sup>-1</sup>
$V$	Volume	m <sup>3</sup>
$\dot{V}$	Volumetric flow rate	m <sup>3</sup> s <sup>-1</sup>
$V_m$	Volume of particle (related to mass)	m <sup>3</sup> kg <sup>-1</sup>
$w$	Weight fraction	kg kg <sup>-1</sup>
$W$	Weight	kg
$W$	Work	J
WHSV	Weight hourly space velocity	kg h m <sup>-3</sup>
$x$	Coordinate	m
$x$	Liquid volume fraction, molar content	mol mol <sup>-1</sup>
$X$	Loading of a solid or liquid	kg kg <sup>-1</sup> or mol mol <sup>-1</sup>
$X$	Dimensionless length	—
$X$	Conversion	—
$y$	Gas volume fraction, molar content	mol mol <sup>-1</sup>
$Y$	Yield	—
$Y$	Loading of a gas	mol mol <sup>-1</sup>
$z$	Electron transfer number	—
$Z$	Real gas factor, compressibility factor	—
$z$	Coordinate	m
$z$	Dimensionless axial coordinate	—
<i>Greek letters</i>		
$\alpha$	Heat transfer coefficient	W m <sup>-2</sup> K <sup>-1</sup>
$\alpha_{\text{Bu}}$	Bunsen absorption coefficient	m <sup>3</sup> Pa <sup>-1</sup>
$\alpha$	Relative volatility	—
$\beta$	Mass transfer coefficient	m s <sup>-1</sup>
$\beta_{\text{LS}}$	Liquid–solid mass transfer coefficient	m s <sup>-1</sup>
$\gamma$	Activity coefficient	—
$\gamma$	Angle	—
$\delta$	Thickness of boundary layer, film thickness	m
$\delta_{0.99}$	Film thickness defined as distance from a surface where $\Delta T = 0.99 \Delta T_{\text{max}}$ (or $\Delta c = 0.99 \Delta c_{\text{max}}$ )	m
$\Delta G$	(Absolute) change of Gibbs enthalpy	J
$\Delta_{\text{F}}G$	Gibbs enthalpy of formation	J mol <sup>-1</sup>
$\Delta_{\text{R}}G$	Gibbs enthalpy of reaction	J mol <sup>-1</sup>
$\Delta_{\text{F}}H$	Enthalpy of formation	J mol <sup>-1</sup>
$\Delta_{\text{ads}}H$	Enthalpy of adsorption	J mol <sup>-1</sup>
$\Delta_{\text{R}}H$	Reaction enthalpy (for constant pressure) according to the stoichiometric equation	J mol <sup>-1</sup>
$\Delta p_t$	Pressure drop in an empty tube	Pa
$\Delta p_b$	Pressure drop in tube filled with particles (fixed bed)	Pa

(Continued)

Table 2 (Continued)

Symbol	Meaning	Unit
$\Delta S_{\text{sys}}$	Change of (absolute) entropy of system	$\text{JK}^{-1}$
$\Delta S_{\text{surr}}$	Change of (absolute) entropy of surrounding	$\text{JK}^{-1}$
$\Delta S_{\text{overall}}$	Overall change of (absolute) entropy	$\text{JK}^{-1}$
$\Delta_{\text{R}}S$	(Molar) reaction entropy	$\text{J mol}^{-1} \text{K}^{-1}$
$\Delta U$	Change of (absolute) internal energy	J
$\Delta_{\text{R}}U$	Change of molar internal energy by reaction	$\text{J mol}^{-1}$
$\Delta S$	Change of entropy	$\text{J mol}^{-1} \text{K}^{-1}$
$\Delta T_{\text{ad}}$	Adiabatic temperature increase	$^{\circ}\text{C}, \text{K}$
$\Delta T_{\text{arith,mean}}$	Arithmetic mean temperature difference	$^{\circ}\text{C}, \text{K}$
$\Delta T_{\text{ln,mean}}$	Logarithmic mean temperature difference	$^{\circ}\text{C}, \text{K}$
$\Delta T_{\text{max}}$	Maximum adiabatic temperature increase	$^{\circ}\text{C}, \text{K}$
$\Delta_{\text{ads}}H$	(Molar) enthalpy of adsorption	$\text{J mol}^{-1}$
$\Delta_{\text{vap}}H$	(Molar) enthalpy of vaporization	$\text{J mol}^{-1}$
$\Delta_{\text{vap}}S$	(Molar) entropy of vaporization	$\text{J mol}^{-1} \text{K}^{-1}$
$\Delta\phi$	Electrochemical potential	V
$\Delta\phi^0$	Electrochemical standard potential at 1.013 bar	V
$\epsilon$	Porosity (voidage of packed bed)	—
$\epsilon_{\text{V}}$	Fractional change of reaction volume	—
$\epsilon$	Fraction of liquid phase (gas–liquid system)	—
$\epsilon_{\text{p}}$	Porosity of particle	—
$\epsilon$	Surface emissivity	—
$\zeta$	Factor considering the particle shape	—
$\eta$	Dynamic viscosity	$\text{Pa s}^{-1}$
$\eta_{\text{anode}}$	Overpotential (voltage) of anode	V
$\eta_{\text{cathode}}$	Overpotential (voltage) of cathode	V
$\eta_{\text{current}}$	Current efficiency, yield of charge	—
$\eta_{\text{ex}}$	Effectiveness factor related to external diffusion resistance	—
$\eta_{\text{overall}}$	Overall particle effectiveness factor	—
$\eta_{\text{pore}}$	Pore effectiveness factor	—
$\eta_{\text{pore},0}$	Initial pore effectiveness factor	—
$\theta$	Dimensionless temperature	—
$\theta$	Surface coverage (relative to monolayer capacity)	—
$\kappa$	specific heat ratio or adiabatic exponent	—
$\lambda$	Wavelength	m
$\lambda$	Thermal conductivity	$\text{W m}^{-1} \text{K}^{-1}$
$\lambda$	Lambda value	—
$\lambda_{\text{p}}$	Thermal conductivity of particle	$\text{W m}^{-1} \text{K}^{-1}$
$\lambda_{\text{ax}}$	Axial dispersion coefficient of heat (effective axial heat conductivity in a packed bed)	$\text{W m}^{-1} \text{K}^{-1}$
$\lambda_{\text{p}}$	Effective thermal conductivity of particle	$\text{W m}^{-1} \text{K}^{-1}$
$\lambda_{\text{rad}}$	Radial dispersion coefficient of heat (effective radial heat conductivity in a packed bed)	$\text{W m}^{-1} \text{K}^{-1}$
$\lambda_{\text{s}}$	Thermal conductivity of (porous) solid	$\text{W m}^{-1} \text{K}^{-1}$
$\Lambda$	Mean free path	m
$\mu$	Chemical potential	$\text{Pa s}, \text{kg m}^{-1} \text{s}^{-1}$

Table 2 (Continued)

Symbol	Meaning	Unit
$\mu_{JT}$	Joule–Thomson coefficient	K Pa <sup>-1</sup>
$\nu$	Stoichiometric coefficient (reactants < 0, products > 0)	—
$\nu$	Frequency	Hz (s <sup>-1</sup> )
$\nu$	Kinematic viscosity	m <sup>2</sup> s <sup>-1</sup>
$\xi$	Dimensionless friction number	—
$\rho$	Density	kg m <sup>-3</sup>
$\rho_b$	Bulk density (of packed bed)	kg m <sup>-3</sup>
$\rho_c$	Density (concentration) of reactant in the core	kg m <sup>-3</sup>
$\rho_g$	Density of gas phase	kg m <sup>-3</sup>
$\rho_{mol}$	Molar fluid density	mol m <sup>-3</sup>
$\rho_p$	Density of particle	kg m <sup>-3</sup>
$\sigma$	Surface tension	N m <sup>-2</sup>
$\sigma$	Collision cross section	m <sup>2</sup>
$\sigma$	Stefan–Boltzmann constant ( $5.67 \times 10^{-8}$ )	W m <sup>-2</sup> K <sup>-4</sup>
$\tau$	(Mean) residence time (related to empty reactor)	s
$\tau_D$	Characteristic time of diffusion	s
$\tau_m$	Modified residence time (mean residence time related to mass of catalyst or solid reactant)	kg s m <sup>-3</sup>
$\tau_M$	Tortuosity of a membrane	—
$\tau_p$	Tortuosity of particle	—
$\tau_R$	Characteristic reaction time	s
$\phi$	Fugacity coefficient	—
$\phi_{12}$	Specific dissipation of energy	m <sup>2</sup> s <sup>-2</sup>
$\Phi$	Ratio of two Thiele moduli	—
$\omega$	Acentric factor	—
$\chi$	Association parameter	—
$\chi$	Heat capacity ratio ( $c_p/c_v$ )	—
<i>Subscripts</i>		
$\infty$	Infinity	
0	Related to initial condition	
A	Related to activity	
ad	Adiabatic	
ads	Adsorption, adsorbent	
app	Apparent	
approx	Approximated	
ax	Axial	
b, bed	Related to fixed or packed bed	
b	Bulk phase	
b	Bottom of separation column	
B	Breakthrough	
boil	Boiling	
BET	Method of Brunauer, Emmett, and Teller	
bulk	Bulk phase of fluid	

(Continued)

Table 2 (Continued)

Symbol	Meaning	Unit
C	Core	
cap	Capillary	
cat	Catalyst	
con	Convective	
charac	Characteristic	
comp	Compression, compressor	
cool	Cooling	
cp	Condensation point	
crit	Critical (pressure or temperature)	
cyl	Cylinder	
c	Cylindrical vessel	
CSTR	Continuously stirred tank reactor	
d	Distillate	
deact	Deactivation	
dis	Discharge	
eff	Effective	
eq	Equivalent	
equi	Equilibrium	
ex	External	
ext	Extraction	
f	Fluid	
fin	Final	
g	Gas phase	
gen	Generalized	
GL	Gas–liquid	
h	Heat, hydraulic	
HP	Heat production	
HR	Heat removal	
HW	Hougen–Watson (type of kinetic equation)	
i	Initial	
i	Interphase	
i	Component $i$	
in	Inlet of reactor	
int	Internal	
kin	Kinetic	
Knu	<i>Knudsen</i> (diffusion)	
L	Liquid, liquid phase	
lam	Laminar (flow)	
liq	Liquid	
LDF	Linear driving force	
LH	Langmuir–Hinshelwood (kinetic equation)	
LS	Liquid–solid	
M	Related to mass, membrane	
max	Maximum	
melt	Melting	
min	Minimum	

Table 2 (Continued)

Symbol	Meaning	Unit
mol	Molecular	
mon	Monolayer	
$n$	Related to reaction order $n \neq 1$	
ori	Orifice	
out	Outlet of reactor	
P	Particle	
P	Perimeter	
pore	Pore of solid or catalyst	
proj	Projection screen	
PFR	Plug flow reactor	
R	Reaction	
R	Reactor	
rad	Radial	
red	Reduced dimensionless variable (related to critical $p$ or $T$ )	
ref	Reference	
s	Solid	
s	Surface	
sat	Saturation	
st	Stoichiometric	
surr	Surrounding	
sys	System	
t	Tube	
t	Total	
turb	Turbulent (flow)	
V	Related to volume	
vap	Vaporization	
W	Wall	
$x$	Related to the coordinate $x$	
<i>Superscripts</i>		
0	Standard conditions (1.013 bar, 273 K)	
*	Saturation (vapor pressure), equilibrium	

**Dimensionless numbers**

Symbol	Definition (in words) and comments	Mathematical definition
$Bi_h$	The Biot number for heat transfer (with $L$ as ratio of volume to external surface) to the ratio of external heat transfer by convection to internal transfer by conduction, which is also the ratio of the heat transfer resistances inside of and at the surface of a body	$\frac{aL}{\lambda}$
$Bi_m$	The Biot number for mass transfer (with $L$ as ratio of volume to external surface) is a measure for the ratio of external mass transfer to the mass transfer by pore diffusion	$\frac{\beta L}{D_{\text{eff}}}$
$Bo$	The Bodenstein number represents the ratio of convective flux to diffusive (dispersed) flux in a reaction vessel. The reciprocal of $Bo$ is also called vessel dispersion number	$\frac{uL}{D_{\text{ax}}}$ (for a packed bed use $u = u_s/\epsilon$ )

(Continued)

Table 2 (Continued)

Dimensionless numbers		
Symbol	Definition (in words) and comments	Mathematical definition
$Da$	The Damkoehler number is the ratio of the reaction rate to the rate of convective mass transport and also equals the ratio of the mean reaction time $t$ (or mean residence time $\tau$ ) to the characteristic reaction time ( $= 1/k$ )	Depends on reaction order and reactor, for example, for a batch reactor and first order, $Da = kt$ , and for an $n$ th-order reaction (initial concentration $c_{A,0}$ ), $Da = kc_{A,0}^{n-1}t$ . For continuous reactors such as a CSTR or PFR, $Da = k\tau$ and $kc_{A,0}^{n-1}\tau$
$Fo$	The Fourier number can be regarded as the dimensionless time for transient heat transfer. Conceptually, it is the ratio of the rate of diffusive (conductive) heat transport to the rate of thermal energy storage	$\frac{at}{L^2_{\text{charac}}} = \frac{\lambda}{c_p \rho} \frac{t}{L^2_{\text{charac}}}$
$Gr$	The Grashof number considers the contribution of fluid motion by natural convection to the overall convective heat transfer	$\frac{gd_p^3 \Pr}{\nu^2} \frac{\rho_s - \rho_b}{\rho_s}$
$Ha$	The Hatta number is the ratio of reaction rate to rate of mass transfer for gas-liquid reactions	$\frac{\sqrt{k_{A,V} D_{A,1}}}{\beta_{A,1}}$
$Hi$	Hinterland ratio	$Hi = \frac{V_1}{V_{\delta,1}} = \frac{\beta_{A,1}}{A_{i,V} D_{A,1}}$
$N_{ad}$	Dimensionless number accounting for adiabatic temperature rise	$\frac{\Delta T_{ad} E_A}{RT_{\text{cool}}^2}$
$Ne$	Newton number of a stirrer (often termed power number)	$\frac{P}{\rho \omega^3 d_{\text{stirrer}}^5}$
$N_C$	Dimensionless number of cooling capacity	$\frac{U_h \frac{A_h}{V_R} \Delta T_{ad}}{k_{\text{cool}} (-\Delta_R H) c_{A,0}}$
$Nu$	Dimensionless number of heat transfer representing the ratio of total heat flux to flux by pure conduction <i>without</i> fluid motion	$\frac{ad_{\text{charac}}}{\lambda}$
$Pe_{h,ax}$	The Peclet number for axial dispersion of heat (e.g. in a fixed bed reactor) is a measure of the ratio of heat transfer by fluid motion (flow) to the (effective) conductive longitudinal heat transfer. A high number indicates a low rate of radial dispersion of heat	$\frac{u_s c_p \rho_{\text{mol}} d_p}{\lambda_{ax}}$
$Pe_{h,rad}$	The Peclet number for radial dispersion of heat (e.g. in a fixed bed reactor) is a measure of the ratio of heat transfer by fluid motion (flow) to the (effective) conductive radial heat transfer. A high number indicates a low rate of dispersion	$\frac{u_s c_p \rho_{\text{mol}} d_p}{\lambda_{rad}}$
$Pe_{m,ax}$	This Peclet number for axial dispersion of mass represents (like $Bo$ ) the ratio of convective flux (mass transfer by fluid motion) to dispersed axial flux (movement by longitudinal dispersion) in a reaction vessel; $Pe_{m,ax} = Bo d/L$ . A high number indicates low rate of radial dispersion. The reciprocal of $Pe_{m,ax}$ is called intensity of axial dispersion	$\frac{u_s d_0}{\epsilon D_{ax}}$ (tube diameter $d_t$ and not particle diameter $d_p$ for an empty reactor)
$Pe_{m,rad}$	This Peclet number for radial dispersion of mass (e.g. in a fixed bed reactor) is a measure of the ratio of mass transfer by fluid motion to radial mass transfer by dispersion. A high number indicates a low rate of dispersion	$\frac{u_s d_p}{\epsilon D_{rad}}$
$Pr$	The Prandtl number represents the ratio of molecular momentum transfer (viscous forces) to molecular heat transfer (heat conduction). For gases, $Pr$ is about 0.7	$\frac{\rho c_p \nu}{\lambda}$

Table 2 (Continued)

Dimensionless numbers		
Symbol	Definition (in words) and comments	Mathematical definition
$Re$	The Reynolds number (related to the tube diameter) is the ratio of the total momentum transfer (inertial forces) to the molecular momentum transfer (viscous forces)	$\frac{ud_t}{\nu}$ (for a packed bed $u$ : superficial velocity)
$Re_p$	Reynolds number (related to particle diameter)	$\frac{ud_p}{\nu}$ (for a packed bed $u$ : superficial velocity)
$Re_{p,bed}$	Reynolds number (related to particle diameter of particles in a fixed bed)	$\frac{u d_p}{\nu}$ ( $u$ : superficial velocity, $\varepsilon$ : porosity of bed)
$Re_{stirrer}$	Reynolds number of stirrer	$\frac{n_{stirrer} d_{stirrer}^2}{\nu}$
$Sc$	The Schmidt number is the ratio of the molecular momentum transfer (viscous forces) to molecular mass transfer by diffusion	$\frac{\nu}{D}$
$Sh$	The Sherwood number is the ratio of total mass transfer to molecular mass transfer by diffusion	$\frac{\beta L_{charac}}{D}$ ( $L_{charac}$ : characteristic length, e.g. $d_p$ )
$\beta_{ex}$	The (external) Prater number accounts for the ratio of heat production to the dissipation by convective heat transfer and is used to determine (together with $\gamma_{ex}$ ) the intraparticle temperature difference (with $T_s$ as surface temperature) in the case of a catalytic (or gas–solid) reaction and a (strong) mass transfer limitation by external mass transfer	$\frac{D_{A,g}(-\Delta_R H)c_{A,g}}{\lambda_g T_g}$ (reactant A)
$\beta_{int}$	The (internal) Prater number accounts for the ratio of heat production to the dissipation by conduction within a particle and is used to determine (together with $\gamma_{int}$ ) the intraparticle temperature difference (with $T_s$ as surface temperature) in the case of a catalytic (or gas–solid) reaction and a (strong) internal mass transfer limitation by pore diffusion	$\frac{D_{A,eff}(-\Delta_R H)c_{A,s}}{\lambda_p T_s}$ (reactant A)
$\gamma_{ex}$	The Arrhenius number is the ratio of the activation energy to the thermal energy and characterizes the temperature sensitivity of the rate of a reaction. $\gamma_{ex}$ is needed to determine (together with $\beta_{ex}$ ) the temperature difference between a (catalyst) particle and the surrounding fluid (gas) phase with temperature $T_g$	$\frac{E_A}{RT_g}$
$\gamma_{int}$	The Arrhenius number $\gamma_{ex}$ is a parameter to determine (together with $\beta_{int}$ ) the intraparticle temperature difference (with $T_s$ as surface temperature) in the case of a catalytic (or gas–solid) reaction and a (strong) mass limitation by pore diffusion	$\frac{E_A}{RT_s}$
$\phi$	The Thiele modulus (first-order reaction) describes the relationship between the reaction rate in porous catalyst pellets with no mass transfer limitations and the rate of internal (pore) diffusion	$\frac{V_p}{A_{p,ex}} \sqrt{\frac{k_m \rho_p}{D_{i,eff}}}$
$\phi_{gen}$	Thiele modulus (generalized for arbitrary reaction kinetics)	$\phi_{gen} = \frac{V_p}{A_{p,ex}} \frac{r_m \rho_p}{\sqrt{2D_{A,eff} \rho_p \int_{c_{A,eq}}^{c_A} r_m dc_A}}$
$\phi_n$	Thiele modulus ( $n$ th-order reaction)	$\frac{V_p}{A_{p,ex}} \sqrt{\left(\frac{n+1}{2}\right) \frac{k_m \rho_p c_{i,s}^{n-1}}{D_{i,eff}}}$
$\psi$	The Weisz modulus (first-order reaction) describes the relation between the effective (measured) reaction rate in porous catalyst pellets and the rate of internal (pore) diffusion; $\psi = \eta_{pore} \phi^2$	$\left(\frac{V_p}{A_{p,ex}}\right) \left(\frac{n+1}{2}\right) \frac{k_{m,eff} \rho_p c_{i,s}^{n-1}}{D_{i,eff}}$
$\psi_n$	Weisz modulus ( $n$ th-order reaction)	$\left(\frac{V_p}{A_{p,ex}}\right) \left(\frac{n+1}{2}\right) \frac{k_{m,eff} \rho_p c_{i,s}^{n-1}}{D_{i,eff}}$

(Continued)

Table 2 (Continued)

Abbreviations	
a.u.	Arbitrary units
AAS	Atomic absorption spectroscopy
ABS	Acrylonitrile butadiene styrene
AES	Auger electron spectroscopy
AFM	Atomic force microscopy
ALI	Adult literacy index
BASF	Badische Anilin und Soda Fabrik (German for “Baden Aniline and Soda Factory”)
BET	(Internal) surface area according to Brunauer, Emmett, and Teller (Section 3.3.5)
BIPHEPHOS	2,2'-Bis[(1,1'-biphenyl-2,2'-diyl)phosphite]-3,3'-di-tert-butyl-5,5'-dimethoxy-1,1'-biphenyl (molecular formula: $C_{46}H_{44}O_8P_2$ )
BMA	Blausäure aus Methan und Ammoniak (German for “hydrogen cyanide from methane and ammonia”)
CED	Cumulative energy demand
CFC	Chlorofluorocarbon compound
CGER	Combined gross enrollment index
CMC	Critical micelle concentration
CNG	Compressed natural gas
CSTR	Continuously stirred tank reactor
CT	Computed tomography
CVD	Chemical vapor deposition
DFT	Density functional theory
DLS	Dynamic light scattering
DMF	Dimethylformamide
DMFC	Direct-methanol fuel cell
DMSO	Dimethyl sulfoxide
DTA	Differential thermal analysis
EDX	Energy dispersive X-ray spectrometer
EI	Education index
EO	Ethylene oxide
EOL	End-of-life (strategy)
ESR	Electron spin resonance spectroscopy
ETFE	Ethylene tetrafluoroethylene
ETM	Electron tunneling spectroscopy
EXAFS	Extended X-ray absorption fine structure
FA	Fatty acid
FBR	Fluidized bed reactor
FCC	Fluid catalytic cracking
FTS	Fischer–Tropsch synthesis
GDP	Gross domestic product
GER	Gross enrollment index
GHG	Greenhouse gas
GHSV	Gas hourly space velocity
GNP	Gross national product
HC	Hydrocarbon
HCFC	Hydrochlorofluorocarbon
HDI	Human development index

Table 2 (Continued)

Abbreviations	
HDPE	High-density polyethylene
HDS	Hydrodesulfurization
HFP	Hexafluoropropene
HP	High pressure
HRC	Hydrogen- rich compound
HTZ	Height of transfer zone
ICE	Internal combustion engine
IR	Infrared spectroscopy
ISS	Ion scattering spectroscopy
LDF	Linear driving force
LDPE	Low-density polyethylene
LEI	Life expectancy index
LHSV	Liquid hourly space velocity
LHV	Lower heating value
LNG	Liquefied natural gas
LOHC	Liquid organic hydrogen carrier
LP	Low pressure
LPG	Liquefied petroleum gases (mainly butane and propane)
LPO	Liquid phase oxidation or Low pressure oxidation
LUB	Length of unused bed
MAH	Monocyclic aromatic hydrocarbon like benzene, toluene, and xylene
MAO	Methylaluminoxane
MG	Metallurgical grade
MG	Metallurgical grade
MOCVR	Metal-organic chemical vapor deposition
MTBE	Methyl tert-butyl ether
Mtoe	Million tons of oil equivalent
MTZ	Mass transfer zone
NGL	Natural gas liquids
NMP	<i>N</i> -Methylpyrrolidone
NMR	Nuclear magnetic resonance
NTP	Normal temperature and pressure (20 °C, 1.013 bar)
OECD	Organisation for Economic Co-operation and Development
ON	Octane number or Oxidation number
OPEC	Organization of the Petroleum Exporting Countries
Ox	Oxidant, oxidizing agent
PAA	Phthalic acid anhydride
PAH	Polycyclic aromatic hydrocarbon like naphthalene and anthracene
pc	Per capita
PC	Polycarbonate
PE	Primary energy (or polyethylene)
PEM	Proton exchange membrane or polymer electrolyte membrane
PET	Polyethylene terephthalate
PFG	Pulsed field gradient (NMR)
PFR	Plug- flow reactor

(Continued)

Table 2 (Continued)

Abbreviations	
PFTR	Plug-flow tubular reactor (also abbreviated simply as PFR)
PMMA	Poly(methyl methacrylate)
PNP	Pincer ligand <i>N,N'</i> -bis(diphenylphosphine)
PO	Propylene oxide
PP	Polypropylene
PPP	Purchasing power parity
PS	Polystyrene
PTA	Terephthalic acid
PTFE	Polytetrafluoroethylene
PUR	Polyurethane
PV	Photovoltaic
PVC	Polyvinyl chloride
QSDFT	Quenched solid density functional theory
rds	Rate depending step
Red	Reductant, reducing agent
RT	Room temperature (about 20 °C)
RTD	Residence time distribution
SAN	Styrene acrylonitrile resin
SATP	Standard ambient temperature and pressure (25 °C, 1.013 bar)
SBR	Styrene-butadiene rubber
SEM	Scanning electron microscopy
SIMS	Secondary ion mass spectroscopy
STM	Scanning tunneling microscopy
STP	Standard temperature and pressure (0 °C, 1.013 bar)
STY	Space–time yield
SV	Space velocity
SWB	Subjective well-being index
TEM	Transmission electron microscopy
TFE	Tetrafluoroethylene
TGA	Thermal gravimetric analysis
THF	Tetrahydrofuran
toe	Tons of oil equivalent
TOF	Turn over frequency
TON	Turn over number
TPD	Temperature- programmed desorption
TPO	Temperature- programmed oxidation
TPR	Temperature- programmed reduction
UPS	Ultraviolet photoelectron spectroscopy
VAM	Vinyl acetate (monomer)
WHSV	Weight hourly space velocity
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence
<i>Miscellaneous</i>	
$\bar{x}$	Mean value of quantity <i>x</i>

Pressure	1 Pa = 1 N m <sup>-2</sup> = 1 kg m <sup>-1</sup> s <sup>-2</sup> = 10 <sup>-5</sup> bar 1 bar = 10 <sup>5</sup> Pa = 0.1 MPa = 0.9869 atm (standard atmosphere) 1 atm = 1.013 25 bar
Power	1 W = 1 J s <sup>-1</sup> = 1 kg m <sup>2</sup> s <sup>-3</sup> = 1.341 × 10 <sup>-3</sup> hp (horse power) 1 hp = 746 W = 0.746 kW

### Presentation of Measured Values

In general, the result of a measurement is represented exactly by the measured (mean) value  $x$ , the measurement error  $\Delta x$ , and the unit  $[x]$ :

$$x = (x \pm \Delta x)[x]$$

For example the measured value of a length is correctly represented by

$$L = (5.81 \pm 0.005)m$$

Nevertheless, in most cases, the measured value is only given with the respective unit. For the above given example, a value of  $L = 5.81$  m would indicate that the true value is between 5.805 and 5.815 m. Thus a rough indication and crude way to represent the error is provided by the number of significant figures (also called significant digits). Rounding to significant digits is a more general technique than rounding to  $n$  decimal places, since it handles numbers of different scales in a uniform way. For example, if rounding to three significant figures,

### Comments on the Symbols Used in This Book

Throughout this book, we have tried to use available standards for all our symbols. Hence, most symbols agree with common practice. Unfortunately, there is yet no standard set of symbols in chemical engineering. Most notably, there are still differences between European and American practice. For the reader's convenience, Table 3 summarizes some important deviations of our (European) symbols from American practice.

**Table 3** Meaning and definition of symbols in this book and definitions/symbols used in American practice.

Meaning (name in this book)	Symbol and definition used in this book	Other symbols and definitions (most notably in American practice)
Thermal diffusivity	$a = \lambda/(\rho c_p)$	$\alpha$
Pre-exponential factor	$k_0$	$A, k_\infty$
Molar flow rate	$\dot{n}$	$F$
Volumetric flow rate	$\dot{V}$	$V$
Liquid volume content	$x$	$f$
Gas volume content	$y$	$f$
Heat transfer coefficient	$\alpha$	$h$
Mass transfer coefficient	$\beta$	$k$
Thermal conductivity	$\lambda$	$k$
Peclet number for axial dispersion of heat	$Pe_{h,ax} = \frac{u_s c_p \rho_{mol} d_p}{\lambda_{ax}}$	No name
Peclet number for radial dispersion of heat	$Pe_{h,rad} = \frac{u_s c_p \rho_{mol} d_p}{\lambda_{rad}}$	No name
No name	$Re \times Pr$	Peclet number $Pe = Re \times Pr = ud/a$ ( $a$ = thermal diffusivity)
Peclet number for axial dispersion of mass	$Pe_{m,ax} = \frac{u_s d_p}{\varepsilon D_{ax}}$ with $D_{ax}$ = axial dispersion coefficient	No name
Peclet number for radial dispersion of mass	$Pe_{m,rad} = \frac{u_s d_p}{\varepsilon D_{rad}}$ with $D_{rad}$ = radial dispersion coefficient	No name
Bodenstein number	$Bo (= uL/D_{ax})$ with $D_{ax}$ = axial dispersion coefficient	Reciprocal of vessel dispersion number
No name	$Re \times Sc$	Bodenstein number $Bo = uL/D$ with $D$ = molecular diffusion coefficient

- 19.341 becomes 19.3.
- 0.034 567 8 becomes 0.0346.
- 34 560 becomes 34 600.

One issue with rounding to significant digits is that the value of  $n$  is not clear if the last digit(s) is (are) zero. For example in the final example above,  $n$  could be anything from 3 to 5, that is, the value may lie in between 34 500 and 34 700.

The number of significant digits is particularly important with regard to *spurious accuracy*, as revealed by the following example. In September 2018, the Kenyan long-distance runner Eliud Kipchoge broke the marathon world record in 2:01:39 hours (7299 seconds). If we use a calculator, usually equipped with ten decimal places, and divide the distance (42 195 m) by the time, we get an average speed of  $5.780\,928\,894\text{ m s}^{-1}$ , which is equivalent to  $5\,780\,928\,894\text{ nm s}^{-1}$ . Quite evidently, the speed of the runner is not known with an accuracy of  $\text{nm s}^{-1}$ , and so it is more sensible to report it only to four significant digits ( $5.781\text{ m s}^{-1}$ ) as the time is also only measured to four significant digits (seconds), i.e. with an accuracy with regard to the speed of  $\text{mm s}^{-1}$ .

Experimental results are frequently evaluated by a pocket calculator or a computer, for example, the electrical resistance of a wire may be derived by dividing the adjusted voltage by the measured current. As a general rough rule as to how to present experimental results, we may state that the last but one digit should be really accurate and be secured by the experimental method used. In other words, you are not accountable for the last but for the last but one digit.

A general rule of how to handle additions, subtractions, multiplications, and divisions of experimental values is that the number of significant digits of the result of such operations is never greater than the smallest value of all significant figures. For example, the product of 1.142 and 2.345 678 should be given as 2.679 (and not as 2.678 764 276 4), or the sum of 1.142 and 2.345 678 should be given as 3.488 (and not as 3.487 678).

### Mean Value and Confidence Limits

Usually, we carry out experiments where we measure the value of a certain quantity  $n$  times. Now we want to know the *mean value*  $\mu$  and the *confidence interval*. The confidence limits for  $\mu$  are given by

$$\mu = \bar{x} \pm t \frac{s}{\sqrt{n}} \quad \text{with } s = \sqrt{\frac{\sum x^2}{n-1} - \frac{(\sum x)^2}{n(n-1)}}$$

and  $\bar{x} = \frac{\sum x}{n}$

**Table 4** The “ $t$ ” table.

Number of measurements $n$	$t$ values for confidence coefficient		
	90%	95%	99%
2	6.314	12.71	63.66
3	2.920	4.303	9.925
4	2.353	3.182	5.841
5	2.132	2.776	4.604
6	2.015	2.571	4.032
7	1.943	2.447	3.707
8	1.895	2.365	3.499
9	1.860	2.306	3.355
10	1.833	2.262	3.250
100	1.660	1.980	2.626
$\infty$	1.645	1.960	2.576

**Table 5** Example of how to determine the mean value and confidence interval.

Number of measurements	Measured reaction rates $x$ (e.g. in $\text{mol m}^{-3} \text{s}^{-1}$ )	$x^2$
1	2.05	4.20
2	2.33	5.43
3	1.98	3.92
4	2.05	4.20
5	2.29	5.24
6	2.10	4.41
7	1.97	3.88
8	1.96	3.84
9	2.21	4.88
10	1.94	3.76
$n = 10$	$\bar{x} = 2.088$ ( $\sum x$ ) <sup>2</sup> = 436.0	$\sum x^2 = 43.78$

The factor  $t$  depends on the *significance level* and on the number of measurements (Table 4). For the significance level, values of 5% or 1% are typically chosen, which is equivalent to a *confidence coefficient* of 95% and 99%, respectively. In most cases, the confidence coefficient is set to 95%.

*Example:* The reaction rate (at constant reaction conditions, i.e. constant concentration, temperature, etc.) is measured 10 times ( $n = 10$ ; Table 5). The confidence coefficient is set to 95%, and the  $t$  value is then 2.262 (see Table 4 above). Thus we get

$$\mu = \bar{x} \pm 2.262 \frac{s}{\sqrt{10}}$$

Here we obtain for the standard deviation

$$s = \sqrt{\frac{43.78}{9} - \frac{436}{90}} = 0.141$$

and thus we, finally, have

$$\mu = 2.088 \pm 2.262 \frac{0.141}{\sqrt{10}} = 2.088 \pm 0.101$$

In other words, at 95% confidence, we have a true mean value of the reaction rate lying between the 2.189 and 1.987.

### Problem of Outlier

It sometimes occurs in a series of  $n + 1$  measurements that one value ( $x_{n+1}$ ) lies far from the other values. A criterion as to whether this so-called outlier can be omitted is

$$|x_{n+1} - \bar{x}_n| > ks$$

The value of  $k$  depends on the number of measurements  $n$ . For  $n > 10$ ,  $k = 4$ , and for lower values of  $n$ ,  $k$  increases (e.g. for  $n = 4$ ,  $k$  is about 7).

For the given example (with  $k = 4$  and  $s = 0.141$ ), we get

$$|x_{n+1} - \bar{x}_n| > 0.564$$

and thus if the value of the rate of the outlier would be more than 2.65 ( $= 2.088 + 0.564$ ) or less than 1.54 ( $= 2.088 - 0.564$ ), it can be omitted.

### Critical Units

Conversions from one unit to another are very important. Two examples may illustrate this (found and adopted in/from S. S. Zumdahl (2009) Chemical principles. Brooks/Cole, Belmont, USA):

- If you ask the National Aeronautics and Space Administration (NASA), such conversions are very important. In 1999 NASA lost the US\$ 125 million *Mars Climate Orbiter* just as it was approaching the red planet. The problem? Unit conversion. NASA's scientists and engineers in Pasadena worked in metric units and assumed that the thrust data for the rockets on the orbiter they received from Lockheed Martin Aeronautics in Denver, which built the spacecraft, were in metric units. In reality, the units were imperial (pounds, miles, etc.), and the lack of conversion meant that the orbiter approached Mars from an altitude of 60 km instead of 150 km. As a result the friction from the atmosphere caused the craft to burn up. The root cause of the failure was that the flight system written to take thrust instructions used the metric unit newton (N), while the software on the ground, which generated those instructions, used the imperial measure pound-force (lbf). As a result, the thruster firings were underestimated by a factor of 4.45 (1 lbf = 4.45 N).

- The *Gimli Glider* is the nickname of an Air Canada aircraft that was involved in an aviation incident in 1983. At an altitude of 12 500 m, it ran out of fuel halfway through its flight from Montreal to Edmonton via Ottawa. The crew was able to glide the aircraft safely at a former Canadian Air Force base in Gimli, Manitoba. The subsequent investigation revealed that someone pumped 22 300 lb of kerosene into the aircraft instead of 22 300 kg.

The moral of both stories: remember to watch your units!

### Piping and Instrumentation Symbols Used in Flow Schemes (Table 6)

#### Symbols Used in Measuring and Control Technology

Measurement and control devices in flow schemes of chemical plants are denoted by a combination of up to four letters.

#### First letter (measured variable):

D: density  
E: electricity  
F: flow  
L: level  
M: moisture  
Q: quality (e.g. concentration)  
S: speed, rotational frequency  
T: temperature  
W: weight

#### Supplement letter:

D: difference  
F: fraction  
Q: quantity (e.g. total flow rate)

#### Consecutive letters (measured data processing):

I: indication  
R: recording  
C: control  
S: switch  
A: alarm  
+ (or H): upper limit (high)  
− (or L): lower limit

#### Examples:

PI: pressure indicator  
PICA +: pressure indicator and controller with alarm if an upper limit is exceeded  
TIR: temperature indication and registration

**Table 6** Flow scheme symbols.

		Valve		
				Heat exchanger
		Pump		
		Compressor		
		Multistage compressor		
		Filter		
		Cyclone		
		Turbine		
		Generator		
		Oven		
		Combustor furnace chamber		
		Condenser		
		Separator (gas/liquid)		
		Column with traps (distillation, absorption)		
		Distillation column		
		Absorption/extraction column		
		Fixed bed reactor adsorption column		

## 1

## Introduction

### 1.1 What Is Chemical Technology?

The field of *chemical technology* stands between:

- **classical chemistry**, which is the science concerned with the composition, behavior, and properties of matter and with the changes it undergoes during chemical reactions, and
- **chemical engineering**, which is the branch of engineering that deals with the application of chemistry, physics, life sciences, and mathematics to processes of converting raw materials or chemicals into more useful or valuable forms or to environmental processes and involves the design of large-scale processes and also of laboratory-scale plants. Modern chemical engineering is also concerned with the design and synthesis of new materials and is one of the major disciplines related to energy technology such as the development of efficient batteries and fuel cells, energy storage systems, and the use of solar energy and other renewables.

In the chemical industry, natural scientists (primarily chemists, but also biologists and physicists), engineers, and businessmen form a team, and the following questions may, for example, be important:

- What is the amount and purity of the product that the client would like to have?
- What apparatus are suitable to produce a certain chemical?
- How can the heat be provided for an endothermic reaction, and how can we efficiently cool a reactor in case of an exothermic reaction to get an optimal performance of the reactor as well as a safe operation without the danger of a thermal runaway?
- Is the process safe and economic?

- How can a current process be improved?
- What type of equipment is needed to separate a reaction mixture?
- Which catalyst is the best, and for how long is the catalyst still active and selective?
- Is the process environmentally benign?

Chemical technology should give answers to all these questions and relies mainly on knowledge of the following four key disciplines and on their application and integration:

- (1) (Physical) **chemistry** with a focus on key reactions, kinetics, and catalysis;
- (2) **Thermal and mechanical unit operations** to design processes like distillation, absorption, adsorption, extraction, pumping and compressing of liquids and gases, filtration, and so on;
- (3) **Chemical reaction engineering**, that is, knowledge of how to measure kinetic data for industrially relevant conditions, of the influence of heat and mass transfer on chemical reactions, and of all aspects of reactor design and modeling;
- (4) **General chemical technology**, that is, the pedigree of routes from raw materials such as crude oil, natural gas, coal, and biomass via intermediates to final products, but also environmental aspects and production costs.

This book covers all these disciplines: chemical aspects (Chapter 2), unit operations (Chapter 3), reaction engineering (Chapter 4), and general chemical technology (Chapter 5). In addition, 24 industrial processes are inspected (Table 1.1.1), covering the production of fuels and of various organic and inorganic chemicals, as well as environmental protection processes.

**Table 1.1.1** Industrial chemical processes inspected in detail in Chapter 6.

Chemical product or process	Subchapters in Chapter 6
<i>Syngas and products based on syngas</i>	
Syngas and Hydrogen	6.2
Ammonia Synthesis	6.1
Fuels and Chemicals by Fischer–Tropsch Synthesis	6.11.1
Methanol Synthesis	6.11.2
<i>Inorganic base chemicals</i>	
Sulfuric Acid	6.3
Nitric Acid	6.4
Chlorine and Sodium Hydroxide	6.19.2
Electrolysis of Water	6.19.3
<i>Refinery processes</i>	
Liquid Fuels by Cracking of Heavy Oils	6.7
Clean Liquid Fuels by Hydrotreating	6.8
High-Octane Gasoline by Catalytic Reforming	6.9
Refinery Alkylation	6.10
<i>Organic base chemicals</i>	
Basic Chemicals by Steam Cracking	6.6
Ethylene and Propylene Oxide	6.12
Catalytic Oxidation of <i>o</i> -Xylene to Phthalic Acid Anhydride	6.13
Hydroformylation (Oxosynthesis)	6.14
Acetic Acid	6.15
Ethylene Oligomerization Processes for Linear 1-Alkene Production	6.16
<i>Organic speciality chemicals and consumer goods</i>	
Production of Fine Chemicals (Example Menthol)	6.17
Polyethene Production	6.20
Polytetrafluoroethylene (PTFE)	6.23
Production of Amino Acids by Fermentation	6.24
<i>Metals and metal-based materials</i>	
Coke and Steel	6.5
Electrometallurgy (Purification of Metals by Electrowinning)	6.19.4
Titanium Dioxide	6.21
Silicon	6.22
<i>Environmental protection processes</i>	
Automotive Emission Control	6.18.1
Selective Catalytic Reduction (SCR) of NO <sub>x</sub> from Flue Gas from Power Plants	6.18.2

## 1.2 The Chemical Industry

The chemical industry, which can be briefly divided in industrial inorganic and organic chemistry, is a central part of the world economy and converts raw materials like coal, oil, natural gas, biomass, air, water, salts, minerals, and metals into many thousand products.

Important inorganic chemicals are base chemicals such as ammonia, nitric and sulfuric acid, sodium hydroxide, but also products of air separation (N<sub>2</sub>, O<sub>2</sub>, Ar) and other technical gases such as H<sub>2</sub>, CO, CO<sub>2</sub>, and Cl<sub>2</sub>. Important final inorganic products are ceramics including cement, concrete, and glass, as well as base and precious metals.

Industrial organic chemicals range from base chemicals such as ethylene, propylene, and aromatics to final products like polymers, detergents, and fine chemicals. They are mainly produced from oil derivatives, such as from naphtha and liquefied petroleum gases (LPGs), but – predominantly in North America – also from natural gas liquids (NGLs) (above all ethane and propane). These two feedstocks represent the vast majority of petrochemical sources around the world; the estimated annual production rate of organic chemicals derived from oil and natural gas is 450 million tons (see footnote a of Table 1.2.8).

Since the beginning of the nineteenth century, coal-based organic chemicals are used by the chemical industry, particularly aromatic hydrocarbons such as benzene and naphthalene, generated as by-products of blast furnace coke production in coking plants. Their annual global production is about 20 million tons (Section 5.1.5.2), which is today quantitatively of minor importance for the industrial chemistry. Dedicated coal-to-petrochemical processes are exceptional and conducted mainly in two countries: about 6 million tons of fuels (gasoline, diesel oil, jet fuel) and 1 million tons of petrochemicals like ethylene and propylene (Du Plessis 2010) are annually produced in South Africa from coal-derived syngas by Fischer–Tropsch synthesis (Section 6.11), and China produces methanol from coal via syngas, 30 million tons in 2016, 10 million tons of which are converted to olefins (Litvinenko and Meyer 2018). Overall, 50 million tons of coal-based petrochemicals are globally produced, a small amount compared with 450 million tons based on oil and gas.

Compared with the oil, gas, and coal industries, which are equally reliant on chemical technology, the chemical industry is small. In 2016, 4 of the 10 (7 of the 30) largest companies by revenue were primarily oil and gas companies, and the biggest chemical

company (BASF) was ranked only 126 (Table 1.2.1). Thus, the chemical industry, most notably with regard to organic chemicals, has a “free ride” in terms of energy and fuel consumption, which is still driven by the huge demand for fossil fuels for transportation, heating, and electricity. The following numbers elucidate this: in 2016, 4.4 billion tons of oil and not much less of natural gas and coal (3.2 and 3.7 billion tons of oil equivalent (toe)) were globally consumed, but the production of organic chemicals was “only” 0.5 billion tons (see footnote a of Table 1.2.8), i.e. 4% of oil, gas, and coal production (Lippert 2018).

The oil and gas business is still dominated by a small number of huge companies, each with annual revenues of typically more than US\$ 100 billion such as Sinopec, China National Petroleum, Shell, Exxon Mobil, and BP (Table 1.2.1). However, the number of chemical companies (even excluding pharmaceuticals) is much larger; in 2016, 113 companies had sales of more than US\$ 2 billion each (www.icis.com). The 10 largest chemical companies by sales and a geographic breakdown of world chemicals and pharmaceuticals sales are listed in Tables 1.2.2–1.2.4. Table 1.2.5 lists the top 10 pharmaceutical companies.

In recent years the role of the chemical industry in the European Union (EU) and also in North America has decreased in terms of share of global production of chemicals (Table 1.2.3); for example, the EU-28 share in 2006 was 28% compared with 15% in 2016. The respective numbers for North America are 24% (2006) and 16% (2016). To the contrary, the share of Asia (including China, but without Japan) has strongly increased between 2006 and 2016 from 24% to 52%. China’s share alone has grown from 13% (2006) to 40% (2016).

The sales of the chemical industry in the EU and North America in terms of absolute numbers have almost not changed during the last 10 years and are in both regions at US\$ 500 billion (Table 1.2.3), while the sales in Asia (including China but excluding Japan) jumped up from US\$ 530 billion in 2006 to US\$ 1930 billion in 2016. This is equivalent to an annual growth rate of 19% in China compared with the global average of 6% (see Table 1.2.3).

A geographic breakdown of the world consumption of chemicals and pharmaceuticals in 2016 as well as of export and import data is listed in Tables 1.2.6 and 1.2.7. Thirty five percentage of the chemicals and 50% of pharmaceuticals are consumed in highly industrialized (currently rich) countries (North America, Europe, Japan, and Australia), although these countries only have a share of 17% of the global

population. Forty percentage of all chemicals and 30% of pharmaceuticals are consumed in China with 19% of population. Hence, the remaining population of 64% living in Asia outside of China and Japan, in Latin America, and in Africa consume only 25% of the world’s chemicals and only 20% of the pharmaceuticals.

Net importers of chemicals and pharmaceuticals are Latin America, China, North America, Africa, and the rest of Asia. The only net exporter is Europe (see Table 1.2.7). Note that the consumption values have to be consistent with the export, import, and sales data by the correlation “consumption = sales – export + import”: for 2016, the data for chemicals (excluding pharmaceuticals) in the EU-28 are €467 billion consumption (Table 1.2.6), €507 billion sales (Table 1.2.3), €426 billion export, and €386 billion import (Table 1.2.7), which fulfills the correlation ( $467 = 507 - 426 + 386$ ).

Global production data of important base chemicals in about 2015 are listed in Table 1.2.8. *Note that throughout this book, the term ton refers to a metric ton equaling 1000 kg.* The structure of the chemical industry is characterized by a small number of inorganic base chemicals such as sulfuric acid, ammonia, and chlorine and also a small number of organic base chemicals such as ethylene, propylene, methanol, benzene, and *p*-xylene. These base chemicals are converted into intermediates like ethylene oxide, styrene, and vinyl chloride and finally into a huge number of consumer goods such as polymers.

Global mass flows in the chemical and petrochemical sector in 2013 are listed in Table 1.2.9 for chemicals based on fossil fuels. Important secondary reactants such as water (steam), O<sub>2</sub>, and CO<sub>2</sub> are included, but inorganic chemicals and reactants like acids are here not considered, although H<sub>2</sub>SO<sub>4</sub> (231 million tons in 2012) is also mainly produced from fossil fuels, e.g. from sulfur obtained as by-product of desulfurization of oil and natural gas.

In total, 0.68 billion tons of fossil feedstocks and 0.96 billion tons of secondary reactants are annually converted into 0.82 billion tons of chemicals such as nitrogenous fertilizers, polymers, solvents, explosives, and other chemical products. The same amounts (0.82 billion tons) of unwanted but unavoidable secondary products such as CO<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub>, HCl, and CaCl<sub>2</sub> are formed. The amount of CO<sub>2</sub> produced as secondary product is huge, 0.3 billion tons, but negligibly small compared with the global CO<sub>2</sub> emissions of 32 billion tons.

**Table 1.2.1** The 30 largest companies by revenues in 2016.

Rank	Company	Primary industry <sup>a)</sup>	Revenue in billion US\$	Employees in 1000	Country
1.	Walmart	General merchandisers	486	2300	USA
2.	State Grid	Utilities	316	926	China
3.	Sinopec Group	Petroleum refining	268	713	China
4.	China National Petroleum	Petroleum refining	263	1512	China
5.	Toyota	Motor vehicles and parts	255	364	Japan
6.	Volkswagen Group	Automotive	240	627	Germany
7.	Royal Dutch Shell	Petroleum refining	240	89	UK/NL
8.	Berkshire Hathaway	Conglomerate	224	368	USA
9.	Apple	Computers, electronics, entertainment	216	116	USA
10.	Exxon Mobil	Petroleum refining	205	73	USA
11.	McKesson	Healthcare	199	65	USA
12.	BP	Petroleum refining	187	75	UK
13.	UnitedHealth	Healthcare	185	230	USA
14.	CVS Health	Healthcare	177	204	USA
15.	Samsung Electronics	Electronics	174	325	South Korea
16.	Glencore	Mining, crude oil production	174	93	SW/NL
17.	Daimler	Automotive	169	282	Germany
18.	General Motors	Automotive	166	225	USA
19.	AT&T	Telecommunications	164	269	USA
20.	Exor	Diversified financials	155	303	Italy
21.	Ford Motor Company	Automotive	152	201	USA
22.	Bank of China	Financial services	148	462	China
23.	AmerisourceBergen	Pharmaceuticals	147	19	USA
24.	China Construction Engineering	Construction	145	264	China
25.	AXA	Financial services	144	98	France
26.	Amazon	Internet	136	341	USA
27.	Foxconn	Electronics	135	725	Taiwan
28.	China Construction Bank	Financial services	135	362	China
29.	Honda	Automotive	129	212	Japan
30.	Total	Oil and gas	128	102	France
126.	BASF	Chemical industry	64	115	Germany

a) Shares of revenues of the 30 largest companies grouped by segments: 25% oil and gas; 19% automotive; 14% electronics, Internet, and telecommunication; 12% healthcare; pharmaceuticals; 10% financial services; and 20% others.

Source: Data from UK, United Kingdom; NL, Netherlands; SW, Switzerland; [http://en.wikipedia.org/wiki/List\\_of\\_companies\\_by\\_revenue](http://en.wikipedia.org/wiki/List_of_companies_by_revenue) (last accessed 22.03.2018).

Today, bulk chemicals are increasingly produced in Asia and in the Middle East and not anymore predominantly in Europe, Japan, and North America. With regard to value, the most important chemicals are fine chemicals and pharmaceuticals (see Table 1.2.10 for the example of Germany in 2016). These two chemical product segments had a share of 47%, whereas the role

of organic and inorganic base chemicals is in Germany comparatively small (16% and 9%, respectively). Polymers and rubber account for 20%, and soaps, detergents, and cosmetics for 8%.

Global sales of the chemical and pharmaceutical industry (US\$ 5.1 trillion in 2016; Table 1.2.11) are about the same as those of the oil and gas

**Table 1.2.2** The 10 largest chemical companies by sales in 2010 and 2016 (excluding pharmaceuticals) ranked by sales in 2016.

Company	Country	Sales in 2010 in billion US\$ (rank)	Sales in 2016 in billion US\$ (rank)
BASF	Germany	73 (1)	61 (1)
Sinopec	China	31 (4)	48 (2)
Dow Chemical	United States	45 (2)	48 (3)
SABIC	Saudi Arabia	27 (7)	35 (4)
INEOS	United Kingdom	26 (10)	33 (5)
Mitsubishi Chemical	Japan	27 (8)	30 (6)
LyondellBasell	Netherlands	31 (5)	29 (7)
ExxonMobil Chemical	United States	41 (3)	26 (8)
DuPont	United States	26 (9)	25 (9)
Air Liquide	France	17 (15)	19 (10)

Source: Data from International Chemical Information Service, www.icis.com (last accessed 22.03.2018).

**Table 1.2.3** Geographic breakdown of global sales of chemicals in 2006 and 2016 ranked by sales in 2016 (chemicals excluding pharmaceuticals).

Country/region	Sales (billion €)		Share of world sales (%)		Average growth rate (period 2006–2016) (%/a)
	2006	2016	2006	2016	
China	238	1331	13.2 <sup>a)</sup>	39.6	18.8
NAFTA <sup>b)</sup>	435	528	24.1 <sup>a)</sup>	15.7	2.0
EU-28 <sup>c)</sup>	505	507	28.0	15.1	0
Rest of Asia (excluding China and Japan)	290	596	16.1	17.8	8.0
Japan	134	140	7.4	4.2	0.5
Latin America	91	127	5.1	3.8	3.5
Rest of Europe	69	90	3.8	2.7	2.8
Rest of the world	40	41	2.2	1.1	0
Total	1803	3360	100	100	6.4

a) The strong shift of the shares of different regions during the last two decades are underlined by the numbers in 2001: China 6% (40% in 2016), NAFTA 30% (16%), and Germany 7.5% (4.3%).

b) The United States, Canada, and Mexico.

c) EU-28: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Italy, Ireland, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Poland, Portugal, Romania, Slovak Republic, Slovenia, Spain, Sweden, and the United Kingdom.

Source: Data from www.cefic.org (last accessed 22.03.2018).

industry (US\$ 5.3 trillion) and the electrical and electronics industry (US\$ 4.5 trillion). The sales of mechanical engineering, of the automotive industry, of e-commerce, and of metals and mining are in a range of US\$ 1.4–3.1 trillion. Thus, the sales share of industries directly related to chemical engineering (chemical, pharmaceutical, and oil and gas industry)

within these major industrial activities is quite large: 43% compared with 18% of electrical and electronics industry, 13% mechanical engineering, 11% automotive industry, 9% e-commerce, and 6% metals and mining. Note that the metallurgical industry also relies on chemistry and chemical engineering, but this is here not considered.

**Table 1.2.4** Geographic breakdown of pharmaceuticals sales in 2016.

Country/region	Sales (billion €)	Share (%)
North America (United States and Canada)	277	21.4
EU-28	277	21.4
Rest of Europe	82	6.3
Japan	56	4.3
Australia/Oceania	8	0.6
North America, Europe, Japan, and Australia/Oceania	700	54.0
China	379	29.3
Rest of Asia (without China and Japan)	175	13.5
Latin America (including Mexico)	33	2.5
Africa	8	0.6
Asia (excluding China and Japan), Latin America, and Africa	216	16.7
Total	1295	100

Source: Data from [www.vci.de](http://www.vci.de) (last accessed 23.03.2018).

**Table 1.2.5** The 10 largest pharmaceutical companies by 2016 sales.

Company	Country	Sales in 2016 (billion US\$)
Novartis	Switzerland	46
Pfizer	United States	45
Hoffmann-La Roche	Switzerland	40
Sanofi	France	38
MSD	United States	37
Johnson & Johnson	United States	31
GlaxoSmithKline	United Kingdom	30
AstraZeneca	United Kingdom	26
Gilead Sciences	United States	24
AbbVie	United States	20

Source: Data from <http://de.wikipedia.org/wiki/Pharmaunternehmen> (last accessed 22.03.2018).

### 1.3 The Changing Global Economic Map

The production of chemicals with regard to the geographic breakdown has changed tremendously in the last decades. In 2016, Asia (excluding Japan) has a share of 57% of the global sales of chemicals compared with Europe, North America, and Japan combined

**Table 1.2.6** Geographic breakdown of consumption of chemicals and pharmaceuticals in 2016.

Region/country	Consumption of chemicals		Consumption of pharmaceuticals	
	Billion €	Share (%)	Billion €	Share (%)
North America (United States and Canada)	479	13.9	336	17.2
EU-28	467	13.6	217	17.1
Rest of Europe	109	3.2	53	4.2
Japan	121	3.5	76	6.0
Australia/Oceania	23	0.7	14	1.1
<i>North America, Europe, Japan, Australia/Oceania</i>	1199	34.9	696	55.0
China	1372	40.0	382	30.2
Asia without China and Japan	611	17.3	120	9.5
Latin America (including Mexico)	206	5.8	50	4.0
Africa	44	1.2	18	1.4
<i>Asia (excluding China and Japan), Latin America, Africa</i>	861	24.3	188	14.9
World	3432	100	1265	100

Italic emphasis indicates a group of regions.

Source: Data from [www.vci.de](http://www.vci.de) (last accessed 23.03.2018).

with 38% (Table 1.2.3). Ten years before (2006), these numbers were quite different with a 29% share of Asia (excluding Japan) and a 63% share of North America, Europe, and Japan.

A similar trend is valid for the distribution of the global gross domestic product (GDP), which is the commonly used measure for the economic performance of a country or a region: in 2017, North America, Japan, and the EU-28 have a combined share of 54% (compared with 68% in 2006), whereas China alone had a share of 15% in 2017 compared with only 5% in 2006. So we are living in a rapidly changing world, and it is therefore worthwhile to have a closer look on the changing economic map and the historical development of economic power in countries and regions of the world.

Table 1.3.1 shows the 15 largest countries with regard to GDP in current US dollars and in purchasing power parity (PPP). In 2017, these countries accounted for 75% of global GDP in current dollars. The United States is still the strongest economy in terms of current dollars, followed by China, Japan, Germany, the United Kingdom, India, and France. Western Europe has about the same economic power

**Table 1.2.7** Geographic breakdown of world export, import, and net imports (= [import – export]/import) of chemicals and pharmaceuticals (ranked by net imports in 2016).

Region/country	Chemicals (billion €)			Pharmaceuticals (billion €)			Chemicals and pharmaceuticals (billion €)		
	Export	Import	Net imports	Export	Import	Net imports	Export	Import	Net imports
Latin America	31	82	+51	6	23	+17	37	105	+68
China	87	128	+41	18	21	+3	105	149	+44
United States, Canada	130	109	–21	55	114	+59	185	223	+38
Africa	17	34	+17	1	12	+10	18	46	+28
Asia (excluding China and Japan)	225	240	+15	37	41	+4	262	281	+19
Australia, Oceania	4	12	+8	3	9	+6	7	21	+14
Japan	52	33	–19	5	24	+20	57	57	+0.3
Rest of Europe	41	60	+21	74	45	–29	115	105	–10
EU-28	426	386	–40	315	255	–60	741	641	–100

Source: Data from [www.vci.de](http://www.vci.de) (last accessed 23.03.2018).

in current dollars as the United States and even outplays (as also China does) the United States in terms of purchasing power (Table 1.3.1). The Western world (the United States, Canada, Western Europe, Australia) accounts for 50% of the global GDP (current dollars).

In 2014, China's economy surpassed the United States in terms of domestic purchasing power and will probably also do so in current dollar terms in the next decade. Nevertheless, China's GDP per capita (pc) (PPP) is still by a factor of 3.5 lower, which is due to the large population of China, 1368 million compared with the United States with 326 million in 2017.

The GDP of different regions is listed in Table 1.3.2. The Global North and East Asia (Table 1.3.2, no. 1–3) have a share of 82%, whereas all remainders, namely, Latin America, Africa (including The Middle East), and South Asia, only account for 18%.

Table 1.3.3 underlines that the economies of China and India – although the latter to a smaller extent – have strongly grown in the last decades.

This trend is also reflected by the regional distribution of the GDP during the last six decades (Table 1.3.4, Figure 1.3.1). Until 2000, the United States and the EU combined had always a share of around 60%, but since then this share is shrinking to today's value of 45%. This trend is valid for all OECD countries, but for China and India the trend is opposite: between 1960 and 2000, the combined share of their global GDP was only 5%, but then rises to today's value of 18%. Japan is a special case: at first, the share of the global GDP rose strongly from 3% in 1960 to a maximum of 15% in 2000, but thereafter dropped down to today's value of 6%.

The development of the GDP pc of selected countries and regions between 1960 and 2017 is shown in Figure 1.3.2 inflation adjusted in constant 2010 US dollars. Globally, the pc GDP has tripled from US\$ 3700 (at constant 2010 values) pc in 1960 to US\$ 10 600 pc in 2017. The increase in China and India is even more remarkable if we consider that the population of these two countries also strongly rose in that period (Figure 1.3.3). This trend is underpinned by the GDP growth rates: since 1980, China's growth rate is higher than 8%/a and for India not much less (Table 1.3.5). To the contrary, the rates in the United States, the EU, and in Japan are much lower and vary from almost 0 to not more than 4%/a.

The GDP per person adjusted for inflation and also for differences in purchasing power of selected countries (in contrast to Figure 1.3.2) are listed in Table 1.3.6 for the period of 1800–2000.

All these figures indicate that the prominence of the Western world, namely, of Europe and North America, will further shrink to a certain extent; vice versa, the role of Asian countries such as China and India will probably still rise in the decades to come.

It is beyond the scope of this book to speculate too much about the future global economic map, but the following brief historical review of the development of economic and political power and of the associated distribution of wealth and poverty over the last five centuries (or even more) might serve as inspiration for further thoughts of the readers.

Since ancient times, civilizations and empires have gone through cycles. Over time, their political and economic power has risen, has been stable for a period and then has fallen. In this context, Table 1.3.7

**Table 1.2.8** World production of important organic and inorganic base chemicals around 2016.

Base chemicals	Production (Mt)	Year
<i>Inorganic base chemicals</i>		
Calcium oxide	350	2016
Sulfuric acid (100%)	231	2012
Ammonia	146	2016
Chlorine	65	2016
Nitric acid (HNO <sub>3</sub> )	55	2014
Phosphoric acid (H <sub>3</sub> PO <sub>4</sub> )	43	2016
<i>Organic base chemicals<sup>a)</sup></i>		
Urea [CO(NH <sub>2</sub> ) <sub>2</sub> ]	164 (194; www.icis.com, February 2019)	2013 (2018)
Ethylene <sup>b),c)</sup>	134 (153)	2014 (2017)
Propylene <sup>b),c)</sup>	94 (102)	2015 (2017)
Ethanol (<1% synthetic ethanol)	80	2015
Methanol	86 (42 only in China based on coal)	2016
Isobutene and <i>n</i> -butenes	49	2010
Benzene <sup>d)</sup>	46	2015
Formaldehyde	41	2016
<i>p</i> -Xylene	38	2015
Ethylene oxide	21	2012
Methyl tertiary-butyl ether (MTBE)	15	2013
Toluene <sup>e)</sup>	12	2013
Acetic acid	12	2014
Butadiene	11	2014
Phenol	9	2012
Acetone	7	2016

- a) About 500 Mt of organic base chemicals (excluding urea and biomass-based ethanol) are produced per year: according to Lippert (2018), 450 Mt of oil derivatives and NGLs are converted by steam cracking into 360 Mt of base chemicals like olefins and aromatics (assuming a cracker yield of 80%; Section 6.6). Eighty million tons organic chemicals (methanol, Fischer–Tropsch chemicals, etc.; Table 5.1.28) are produced from syngas based on natural gas (approximately 50 Mt) or coal gasification (30 Mt), 40 Mt olefins and aromatics may be estimated as refinery products (e.g. FCC process; Section 6.7.2), and 20 Mt of aromatics are by-products of coal coking (Section 5.1.5.2). So 90% of the organic base chemicals are produced from oil and gas and 10% from coal.
- b) Two-thirds of ethylene and propylene are used for polyethylene (PE) and polypropylene (PP). According to Table 5.4.19, 64% are ethylene and 66% are propylene. This is in agreement with numbers given by Lippert (2018) for 2017: 59% of ethylene for PE and 68 of propylene for PP.
- c) The production of petrochemicals still increases. In 2017, the production of ethylene reached 153 million tons (41% from naphtha, 38% from ethane, 9% propane, 5% butane, 3% gas oil, and 4% from other feedstocks such as coal). This corresponds to a growth rate of 5%/a in 2014–2017; the production of propylene in 2017 was 102 million tons, which corresponds to a growth rate of 6% (Lippert 2018).
- d) 5 Mt are generated as by-product of coking plants (Section 5.1.5.2), 10% of total demand. Fifty percentage are produced in refineries by reforming of gasoline (and subsequent separation), 15% by hydrodealkylation or disproportionation of toluene, and 25% are by-products of steam cracking of oil products like naphtha (25%) (Levi and Cullen 2018). This underlines that oil and gas are far more important sources of petrochemicals than coal; an exception is naphthalene (1 Mt/a), derived mainly (90%) from coal tar.
- e) Only counting the net output. Production of raw toluene (in Mt) in 2013 was 23.1, 7.7 by steam cracking of naphtha and 15.4 by gasoline reforming in refineries, but 11.6 are converted by hydrodealkylation or disproportionation into benzene and xylenes.

Source: Data from [www.essentialchemicalindustry.org](http://www.essentialchemicalindustry.org) (last accessed 22.03.2018) value for toluene from Levi and Cullen (2018), value for methanol from Zhen and Wang (2015).

**Table 1.2.9** Global mass flows in the chemical and petrochemical sector in 2013: from fossil fuel feedstocks to chemical products.

Fossil fuel feedstocks and secondary reactants	Mass flow (million tons/a)	Share (%)
Coal (only for syngas production) <sup>a)</sup>	55	3.4
Natural gas and natural gas liquids (NGLs) <sup>b)</sup>	199	12.2
Refinery sourced olefins and aromatics <sup>c)</sup>	163	10.0
Liquid oil products <sup>d)</sup>	260	15.9
Total fossil feedstocks	676	41.3
Secondary reactants <sup>e)</sup>	960	58.7
Total feedstocks/reactants	1636	100
<i>Chemical products and secondary products</i>		
Nitrogenous fertilizers	275	16.8
Thermoplastics	222	13.6
Fibers and elastomers	107	6.5
Solvents, additives and explosives	107	6.5
Other chemical products	109	6.7
Total primary products	820	50.1
Secondary products <sup>f)</sup>	816	49.9
Total products	1636	100

- a) Only coal as feedstock for syngas production and subsequent conversion to ammonia and methanol not considering by-products (e.g. benzene and naphthalene) of coking plants.
- b) 50% as feedstock for syngas (natural gas) and 50% as light feedstock (NGLs) for steam cracking.
- c) By-products of refineries such as fluid catalytic cracking (olefins) or reforming of gasoline (aromatics).
- d) Mainly liquid crude oil products such as naphtha used as feedstock for steam cracking to produce olefins (230 million tons), but also feedstocks for production of carbon black (about 19 million tons of oil products) and for syngas production (11 million tons liquid oil products).
- e) Secondary reactants (million tons/a) are H<sub>2</sub>O (274), O<sub>2</sub> (221), CO<sub>2</sub> (152), N<sub>2</sub> (142), H<sub>3</sub>PO<sub>4</sub> (61), and others (110). For example, 90 million tons O<sub>2</sub> are needed for syngas from heavy oil or coal.
- f) Secondary products (million tons/a) are CO<sub>2</sub> (287), H<sub>2</sub>O (140), CH<sub>4</sub> (43), HCl (25), CaCl<sub>2</sub> (8), and other products (313). Note that CO<sub>2</sub> emissions related to the consumption of electricity, heat, etc., of the chemical industry are here not counted as “secondary product.”

Source: Data from Levi and Cullen (2018).

depicts the shares of global GDP and population of Western Europe, the United States, China, and India during the last five centuries. Data on the GDP pc (inflation adjusted) from even 1 CE to 2008 are given in Tables 1.3.8 and 1.3.9.

**Table 1.2.10** Important products (by value) of the German chemical industry (including pharmaceuticals) in 2016 (www.vci.de, last accessed 23.03.2018).

Products	Share of total production value (%)
Organic base chemicals	16
Inorganic base chemicals	9
Polymers and rubber	20
Fine and specialty chemicals	26
Pharmaceuticals	21
Soaps, detergents, and cosmetics	8

From 1500 until the end of the eighteenth century, China and India combined had a share both of global GDP and population of around 50% (Table 1.3.7); Western Europe and the United States combined had a share of the population of 14%, whereas the share in GDP already continuously increased from 15% (1500) to 23% (1800). So in 1500, the economic power per capita in the Western world and in India/China was very close, but by the end of the eighteenth century, the GDP pc in the Western world was already 80% higher compared with China and India, where the value remained static (Tables 1.3.7–1.3.9).

In the whole period from 1 CE to 1700, the GDP pc in all regions of the world only varied in a narrow range of 0.7 (Africa) to 1.6 (Europe) relative to the global average (Table 1.3.9). Thereafter the interregional spread strongly increased. Currently (values from 2008), the differences are much broader, ranging from 0.23 (Africa) to 4.1 (United States), hence a spread of 18 : 1. This strongly rising disparity with regard to economic power started in the second half of the eighteenth century by the onset of the Industrial Revolution in United Kingdom and subsequently in continental Europe and in the United States. This is also underlined by the strong change of determinants of growth (stock of machinery, years of education, and GDP per work hour) as listed in Table 1.3.10 for the examples of the United Kingdom and the United States for 1820–1998.

The Western empires, founded in the sixteenth and seventeenth centuries, further expanded in the next two centuries (Topic 1.3.1), partly due to the superiority of European technologies. This gave the West, among other things, a military advantage over the rest of the world. The technological progress combined with the morally condemnable imperialism had an enormous influence on the distribution of economic and political power in the nineteenth and twentieth

**Table 1.2.11** Global sales of chemical and pharmaceutical industry (2016), oil and gas business (2015), electrical and electronics industry (2015), mechanical engineering (2016), automotive industry (2016), e-commerce (2017), and metals and mining (2016).

Industrial sector	Sales in trillion (10 <sup>12</sup> ) (US\$)	Share (%)
Chemical industry (excluding pharmaceuticals)	3.7 <sup>a)</sup>	15
Pharmaceutical industry	1.4 <sup>a)</sup>	6
Oil and gas industry	5.3 <sup>b)</sup>	22
Subtotal (industries related to chemistry and chemical engineering)	10.4	43
Electrical and electronics industry <sup>c)</sup>	4.5 <sup>a)</sup>	18
Mechanical engineering	3.1	13
Automotive manufacturers and suppliers	2.8 <sup>a)d)</sup>	11
E-commerce	2.3	9
Metals and mining	1.4 <sup>e)</sup>	6
Total	24.5	100

- a) Values in € were converted in US\$ by using the average exchange rate in 2016 of 0.9 €/€.
- b) Estimation based on revenues of the 48 leading oil and gas companies (including State-owned enterprises) in 2015 (top 20 with a share of 80%: Saudi Aramco, Sinopec, China National Petroleum, PetroChina, Exxon Mobil, Royal Dutch Shell, Kuwait Petroleum, BP, Total, Lukoil, Eni, Valero Energy, Petrobras, Chevron, PDVSA, Pemex, National Iranian Oil Company, Gazprom, Petronas, China National Offshore Oil).
- c) Shares within electrical and electronics industry by sector: 24% electronic components and systems, 12% automation, 11% communications technology, 10% information technology, 6% power engineering, 6% household appliances, 6% consumer electronics, 3% lighting, 2% medical engineering, and 20% others.
- d) Estimation based on the revenues of major car manufacturers and suppliers: the revenues of the 17 leading car manufacturers (Toyota, VW, Daimler, GM, Ford, Honda, Fiat Chrysler, SAIC, Nissan, BMW, Hyundai, Peugeot-Citroen, Renault, Kia, Mazda, Suzuki, Mitsubishi) were US\$ 1.87 trillion (2016). The revenues of the 100 leading suppliers (top 10: Bosch, Continental, Denso, Magna, ZF Friedrichshafen, Hyundai, Aisin, Bridgestone-Firestone, Michelin, Faurecia) were US\$ 0.93 trillion in 2016 (top 10: US\$ 0.34 billion = 37% of top 100). Hence, the sum is US\$ 2.8 trillion. In 2017, 74 million passenger cars, 19 million light commercial vehicles, 4 million heavy trucks, and 0.4 million buses and coaches were globally produced.
- e) Estimation based on revenues of the 46 leading metal and mining companies (top 10 with share of 43%: Glencore (Al, Ni, Cu, etc.), JX Holdings (various materials), ArcelorMittal (steel), Wesfarmers (various), Thyssenkrupp (steel), Citic (steel), POSCO (steel), Itochu (steel, nonferrous metals), Rio Tinto (iron ore, coal, TiO<sub>2</sub>, Au, diamonds), and BHP Billiton (steel, Ag, Pb, Cu)). The top 15 steel companies had a revenue based on steel of US\$ 0.27 trillion.

Source: Data for chemicals and pharmaceuticals from [www.vci.de](http://www.vci.de); oil/gas from [https://en.wikipedia.org/wiki/List\\_of\\_largest\\_oil\\_and\\_gas\\_companies\\_by\\_revenue](https://en.wikipedia.org/wiki/List_of_largest_oil_and_gas_companies_by_revenue), electrical and electronic industry from [www.zvei.org](http://www.zvei.org), other industrial sectors from [www.statista.com](http://www.statista.com) (all last accessed 22.3.2018).

centuries (Table 1.3.7): in 1900, Western Europe and the United States had reached a share of 48% of GDP compared with China and India with 20%, although the shares of the global population were 21% (Europe, United States) and 40% (India, China). Hence, the Western world doubled its GDP share in the nineteenth century, and the share of India and China more than halved.

After WWII, the GDP share of Western Europe and the United States was still high, 52% in 1950, and low for China and India (9%), but since 1990 (Tables 1.3.3–1.3.9, Figure 1.3.1), the GDP and GDP shares of China and India are increasing, and those of Western countries are shrinking. The future will show whether and to what extent this trend will continue.

The remarkable achievements of mankind (despite the morally condemnable imperialism) over the last 200 years can be illustrated by the number and share of the global population living in extreme poverty: 94% in 1820, 90% in 1870, 76% in 1930, 60% in 1970, 37% in 1990, but “only” 10% in 2015. Since 1970, even the absolute number of extreme poor is shrinking (Figure 1.3.4): in 1820, there were 1.1 billion people in the world, of which the vast majority lived in extreme poverty. Over the next 150 years, the decline of the share of extreme poor people was not fast enough to offset the rapid rise of the world population, so both the number of non-poor *and* poor rose although the share of extreme poor continuously dropped. Since then, even the number of poor fell from the maximum

**Table 1.3.1** The 15 largest countries and selected regions by gross domestic product (GDP) in 2017 ranked by GDP in current US dollars.

Country	GDP in 2017 (current US\$)			GDP in 2017 (US\$) based on purchasing power parity <sup>a)</sup>		
	Trillion \$	Share (%)	1000 \$ pc	Trillion \$	Share (%)	1000 \$ pc
United States	19.4	24.0	59.5	19.4	16.1	59.5
China	12.2	15.2	8.8	23.3	19.3	16.8
Japan	4.9	6.0	38.4	5.6	4.6	43.9
Germany	3.7	4.6	44.5	4.2	3.5	50.7
United Kingdom	2.6	3.3	39.7	2.9	2.4	43.9
India	2.6	3.2	1.9	9.5	7.9	7.1
France	2.6	3.2	38.5	2.9	2.4	42.8
Brazil	2.0	2.5	9.8	3.2	2.6	15.5
Italy	1.9	2.4	31.9	2.4	2.0	39.8
Canada	1.7	2.0	45.0	1.7	1.4	46.4
Russian Federation	1.6	2.0	10.7	3.7	3.1	25.5
South Korea	1.5	1.9	29.7	2.0	1.7	38.3
Australia	1.3	1.6	53.8	1.2	1.0	47.0
Spain	1.3	1.6	28.2	1.8	1.5	38.1
Mexico	1.2	1.4	8.9	2.3	1.9	18.1
World	80.7	100	10.7	120.8	100	16.2
Listed countries in total	60.5	75	—	86.1	71	—
Western Europe <sup>b)</sup>	18.4	22.8 <sup>b)</sup>	34.7	21.2	17.5	40.2
Western world <sup>c)</sup>	40.7	50.4	—	43.5	36	—
OECD members	49.6	61.4	—	54.1	44.8	—

a) Purchasing power parity (PPP) is here – as usual – related to the purchasing power in the United States.

b) European Union (EU-28) including Norway, Switzerland, and Iceland. In 2000 (number needed in Table 1.3.4), the share was 27%. EU-28 only (2017): 17.3 trillion in current dollars and 20.3 trillion based on PPP.

c) The United States, Canada, Western Europe, and Australia.

Source: Data from [www.data.worldbank.org](http://www.data.worldbank.org) (last accessed 7.09.2018).

**Table 1.3.2** Gross domestic product (GDP) of different continents/regions in 2017 ranked by GDP in current US dollars.

	Continent/region	GDP in 2017 (current US\$)	
		Trillion (10 <sup>12</sup> ) \$	Share (%)
1.	East Asia and Pacific	24.00	29.7
2.	Europe and Central Asia	21.44	26.6
3.	North America (United States, Canada)	21.05	26.1
4.	Latin America and Caribbean	5.95	7.4
5.	South Asia <sup>a)</sup>	3.29	4.1
6.	Middle East and North Africa	3.27	4.0
7.	Sub-Saharan Africa	1.65	2.0
	World	80.7	100

a) India, Pakistan, Bangladesh, Afghanistan, Bhutan, Nepal, and Sri Lanka.

Source: Data from [www.data.worldbank.org](http://www.data.worldbank.org) (last accessed 7.09.2018).

**Table 1.3.3** Development of the gross domestic product (GDP) of the United States, the European Union, Japan, South Korea, China, and India between 1960 and 2017 in trillion US\$ (inflation adjusted, constant 2010 US dollars).

Year	GDP in trillion (10 <sup>12</sup> ) US\$ (constant 2010 \$)						
	1960	1970	1980	1990	2000	2010	2017
United States	3.1	4.8	6.5	9.1	12.7	15.0	17.3 <sup>a)</sup>
European Union (EU-28)	4.1	6.8	9.3	11.8	14.8	17.0	18.8
United States and EU combined	7.2	11.6	15.8	20.9	27.5	32.0	36.1
Japan	0.8	2.0	3.0	4.7	5.4	5.7	6.2 <sup>a)</sup>
South Korea	0.02	0.06	0.14	0.36	0.71	1.1	1.3 <sup>a)</sup>
China	0.13	0.19	0.34	0.83	2.2	6.10	10.2 <sup>a)</sup>
India	0.14	0.20	0.27	0.47	0.80	1.7	2.6 <sup>a)</sup>
China and India combined	0.26	0.39	0.61	1.30	3.0	7.8	12.8
Rest of world	3.0	5.2	8.5	11.0	14.1	20.6	25.1

a) The values for 2017 given in Table 1.3.2 differ from those of Table 1.3.1, as the numbers in the former case are chained to the value of the US dollars of the year 2010.

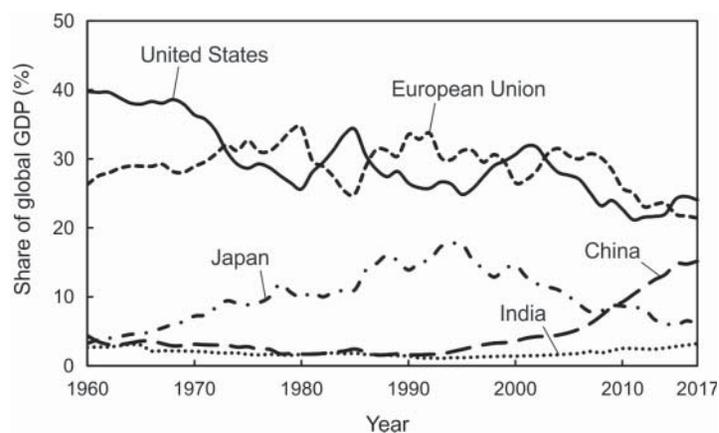
Source: Data from: [www.data.worldbank.org](http://www.data.worldbank.org) (last accessed 7.09.2018).

**Table 1.3.4** Share of global GDP of the United States, European Union, Japan, South Korea, China, and India between 1960 and 2017 (GDP in current US dollars).

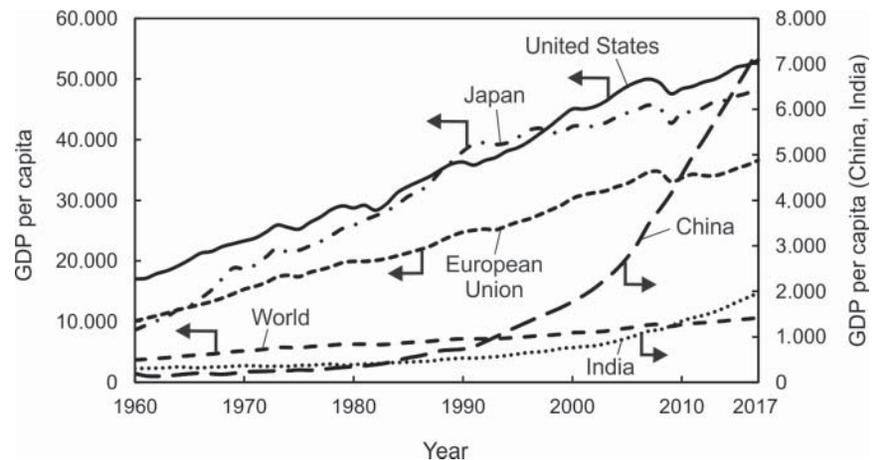
Year	Shares of global GDP (current US\$) (%)						
	1960	1970	1980	1990	2000	2010	2017
United States	39.8	36.4	25.6	26.5	30.6	22.7	24.0
European Union (EU-28)	26.3	28.9	34.5	33.5	26.5	25.8	21.4
<i>United States and EU combined</i>	<i>66.1</i>	<i>65.3</i>	<i>60.1</i>	<i>60.0</i>	<i>57.1</i>	<i>48.5</i>	<i>45.4</i>
Japan	3.2	7.2	9.9	13.9	14.6	8.6	6.0
South Korea	0.3	0.3	0.6	1.2	1.7	1.7	1.9
China	4.4	3.1	1.7	1.6	3.6	9.2	15.2
India	2.7	2.1	1.6	1.4	1.4	2.5	3.2
<i>China and India combined</i>	<i>7.0</i>	<i>5.2</i>	<i>3.4</i>	<i>3.0</i>	<i>5.0</i>	<i>11.8</i>	<i>18.4</i>
Rest of world	23.6	22.3	26.6	23.1	23.3	31.2	30.1
OECD members	78.4	80.9	78.5	82.9	81.6	67.6	61.4

Italic emphasis indicates the sum of US and EU.

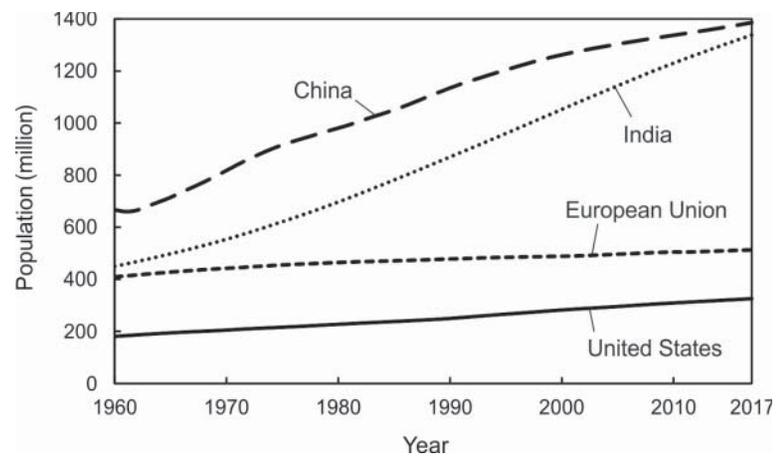
Source: Data from [www.data.worldbank.org](http://www.data.worldbank.org) (last accessed 8.09.2018).

**Figure 1.3.1** Share of global GDP of the United States, the European Union, Japan, China, and India between 1960 and 2017 (GDP in current US dollars). Source: Data from [www.data.worldbank.org](http://www.data.worldbank.org) (last accessed 8.09.2018).

**Figure 1.3.2** GDP per capita in selected countries and regions (1960–2017) (constant 2010 US dollars; www.data.worldbank.org, last accessed 9.10.2018). Values for 2017 slightly differ from Table 1.3.1. Here, the GDP value is inflation adjusted in constant 2010 dollars; numbers in Table 1.3.1 refer to 2017 value.



**Figure 1.3.3** Development of the population of the United States, the European Union, China, and India between 1960 and 2017. Source: Data from: www.data.worldbank.org (last accessed 12.09.2018).



**Table 1.3.5** Average annual growth rate of the GDP of selected countries and regions between 1970 and 2017 ranked by decreasing value in 2010–2017.

Year	Average annual growth rates of GDP (%/a)				
	1970–1979	1980–1989	1990–1999	2000–2009	2010–2017
China	7.4	9.7	10.0	10.4	7.9
India	2.9	5.7	5.8	6.9	7.3
United States	3.5	3.1	3.2	1.8	2.2
EU-28	3.6	2.3	2.2	1.6	1.5
Japan	4.3	4.3	1.5	0.5	1.5
World	4.2	3.0	2.7	2.8	3.9

Source: Data from www.data.worldbank.org (last accessed 29.12.2018).

of 2.2 billion in 1970 to 0.7 billion in 2015, which is still too much.

The huge improvement of the global material living conditions – at least on average – in the last two

**Table 1.3.6** GDP per person adjusted for inflation and differences in purchasing power (fixed 2011 prices) in selected countries between 1800 and 2000.

Year	GDP pc in US\$ 1000 (PPP, inflation adjusted)				
	1800	1850	1900	1950	2000
United States	2.1	3.1	7.0	15.0	49.4
Germany	1.6	2.2	4.6	6.9	40.4
Japan	1.1	1.1	1.8	2.5	35.8
China	1.0	1.0	0.9	0.5	9.5
India	1.0	1.1	1.2	0.9	4.4

Source: Data from www.gapminder.org (last accessed 25.10.2018).

centuries can be also well illustrated by the following numbers:

- o Between 1820 and today, the global average GDP pc (inflation adjusted) increased by a factor of more than 10 (Tables 1.3.8 and 1.3.9) compared with the relatively small increase of only 40% within almost the two former millennia between 1 and 1820 CE.

**Table 1.3.7** Western Europe, the United States, China, and India: shares of global GDP and of population in the last five centuries (estimations of GDP until 1950 from Ferguson (2012); for 2000/2017 see Tables 1.3.1 and 1.3.4; estimation of population shares until 1900 from [www.visualizingeconomics.com](http://www.visualizingeconomics.com), accessed 25.10.2018).

Year	1500	1600	1700	1800	1900	1950	2000	2017
<i>Shares of global GDP (% , estimations until 1950)</i>								
Western Europe	15	17	19	21	32	25	27	23
United States	—	—	—	2	16	27	31	24
China	25	29	23	31	12	5	4	15
India	24	23	25	17	8	4	1	3
Western Europe and United States	15	17	19	23	48	52	57	47
China and India combined	49	52	48	48	20	9	5	18
Rest of world	36	31	33	29	32	39	36	35
<i>Shares of global population<sup>a)</sup> (% , estimations until 1900)</i>								
Western Europe and United States <sup>b)</sup>	13	13	14	14	17	—	—	11
China and India combined	48	52	51	55	41	—	—	36
Rest of world	39	35	35	31	42	—	—	54 <sup>c)</sup>
<i>Ratio of share of GDP to share of population (rounded values)</i>								
Western Europe and United States	1.2	1.3	1.4	1.6	2.8	—	—	4.3
China and India combined	1.0	1.0	0.9	0.9	0.5	—	—	0.5
<i>Interregional spread: ratio of GDP pc in Western Europe and the United States and GDP pc in China and India</i>								
	1.2 : 1	1.3 : 1	1.6 : 1	1.8 : 1	6 : 1	—	—	9 : 1
<i>Global GDP in total (purchasing power parity, inflation adjusted) relative to 1500</i>								
	1	1.3	1.5	2.8	11	21	205 (2008)	

a) Global population (in billion): 0.46 (1500), 0.55 (1600), 0.60 (1700), 0.99 (1800), 1.65 (1900), 2.6 (1950), and 7.5 (2017).

b) US population (excluding Native Americans until 1900) in million: 0.05 (1650), 0.25 (1700), 5.3 (1800), 76 (1900), and 326 in 2017 ([https://en.wikipedia.org/wiki/demographic\\_history\\_of\\_the\\_United\\_States](https://en.wikipedia.org/wiki/demographic_history_of_the_United_States), accessed 8.11.2018). The numbers of Native Americans living in the area of the United States given by Ubelaker (1988) based on tribe-to-tribe estimates are 1.6 million in 1600, 1.2 in 1700 (83% of total US population), 0.9 in 1800 (15%), 0.5 in 1900 (0.6%), and 1.1 in 1970 (0.5%). In the census 2000, 2.9 million people reported American Indian or Alaska Native alone, and 2.3 million reported Native in combination with other races (5.2 million in total, 1.6% of US population). It is difficult to determine how many natives lived in the area of the United States before Columbus. Most estimates range from 1 to 12 million (Lord 1997); the numbers given by Maddison (2005) and Ubelaker (1988) are 2.3 (including Canada) and 1.7 million, respectively; comparison with the number of only 0.5 million Natives in 1900 underlines that the Indian population of North (and also Latin) America suffered a catastrophic collapse between 1492 until 1900.

c) Rising share of rest of world in 1900–2017 is mainly the result of Africa's fast-growing population: share of 7% in 1900 (120 million), 9% in 1950 (230 million), and 17% in 2017 (1.3 billion).

Source: Data from [https://en.wikipedia.org/wiki/List\\_of\\_regions\\_by\\_past\\_GDP\\_\(PPP\)](https://en.wikipedia.org/wiki/List_of_regions_by_past_GDP_(PPP)), accessed 7.11.2018. In 1500, global GDP was US\$ 250 billion (in 1990 international dollars) compared with 2008 with 51 000 billion.

- In 1820, the GDP pc (in 1990 US dollars) was only about US\$ 1200 in both Europe and the United States (Table 1.3.8); this is the value reached in India, a country considered as poor, in 1990. In 1900, the GDP pc (still in 1990 dollars) has increased in Europe and the United States to 2900 and 4100, respectively; this is comparable with the actual value in India (3000) in 2008.
- These historical developments and improvements of the GDP pc can also be illustrated very well taking Germany as a currently rich country as example, as depicted in Table 1.3.11 for the period 1700–1995. In addition to Germany's GDP pc, countries are named where the respective

historical value of Germany was reached in 2017. In 1850, the GDP pc in Germany was not higher than today in Kenya, in 1913 comparable with Guatemala today, and even in 1960 not higher than today in Costa Rica.

Closely linked to this remarkable improvement in global mean material living conditions in the last two centuries are improvements with regard to health (life expectancy) and education (literacy rate):

- The global average life expectancy was only 29 years in 1820, increased to 48 years until 1950, and rose further to today's value of 72 years (2016), ranging today from around 50 years in still poor

**Table 1.3.8** GDP per capita (inflation adjusted in 1990 international dollars) from year 1 CE until 2008 CE in selected countries and regions according to Angus Maddison from the University of Groningen, Netherlands (<http://www.ggdc.net/maddison/oriindex.htm>, accessed 7.11.2018; see also Maddison (2005)).

Year	GDP pc in US\$ 1000 (inflation adjusted in 1990 US\$)									
	1	1000	1500	1600	1700	1820	1900	1950	1990	2008
Western Europe	0.58	0.43	0.77	0.89	0.99	1.19	2.89	4.57	15.91	21.67
United States	0.40				0.53	1.26	4.09	9.56	23.20	31.18
Australia	0.40					0.52	4.01	7.41	15.91	25.30
Former USSR	0.40		0.50	0.55	0.61	0.69	1.24	2.84	6.89	7.90
Japan	0.40	0.43	0.50	0.52	0.57	0.67	1.18	1.92	18.79	22.82
China	0.45	0.47	0.60				0.55	0.45	1.87	6.73
India	0.45		0.55			0.53	0.60	0.62	1.31	2.98
Asia (total)	0.46	0.47	0.57			0.58	0.64	0.72	2.78	5.61
Latin America	0.40		0.42	0.44	0.53	0.69	1.11	2.51	5.07	6.97
Africa (total)	0.40	0.42					0.60	0.89	1.42	1.78
World	0.47	0.45	0.57	0.60	0.62	0.67	1.26	2.11	5.15	7.61
World relative to year 1 CE	1	0.96	1.21	1.28	1.32	1.43	2.68	4.49	10.96	16.19

**Table 1.3.9** GDP per capita relative to global average between 1 CE and 2008.

Year	GDP pc relative to global average (in inspected year)									
	1	1000	1500	1600	1700	1820	1900	1950	1990	2008
Western Europe	1.23	0.96	1.35	1.48	1.60	1.78	2.29	2.17	3.09	2.85
United States	0.85	0.89	0.70	0.67	0.85	1.88	3.25	4.53	4.50	4.10
Australia	0.85	0.89	0.70	0.67	0.65	0.78	3.18	3.51	3.09	3.32
Former USSR	0.85	0.89	0.88	0.92	0.98	1.03	0.98	1.35	1.34	1.04
Japan	0.85	0.96	0.88	0.87	0.92	1.00	0.94	0.91	3.65	3.00
China	0.96	1.04	1.05	1.00	0.97	0.90	0.44	0.21	0.36	0.88
India	0.96	1.00	0.96	0.92	0.89	0.79	0.48	0.29	0.25	0.39
Asia (total)	0.98	1.04	1.00	0.95	0.92	0.87	0.51	0.34	0.54	0.74
Latin America	0.86	0.88	0.74	0.73	0.86	1.04	0.88	1.19	0.98	0.92
Africa (total)	0.85	0.93	0.74	0.70	0.68	0.63	0.48	0.42	0.28	0.23
Interregional spread	1.4 : 1	1.2 : 1	1.9 : 1	2.2 : 1	2.5 : 1	3 : 1	7 : 1	22 : 1	16 : 1	18 : 1

Source: See Table 1.3.8.

African countries such as Sierra Leone (52 years) and Nigeria (53 years) to 84 years in Japan ([www.ourworldindata.org](http://www.ourworldindata.org); [www.worldbank.org](http://www.worldbank.org), last accessed 9.10.2018). The historical development and improvement of life expectancy in a currently rich country is depicted in Table 1.3.12 for the example of Germany for the period of 1875 until 1990. In addition, countries are named where the respective historical value of Germany was reached in 2016. Until about 1900, the life expectancy in Germany was lower than in any country today, in 1925 not higher than today in Burundi, in 1950 comparable with Kenya today, and even in 1980 not higher than today in Paraguay.

- The global literacy rate strongly increased during the last two centuries: 12% in 1800, 21% in 1900, 36% in 1950, 56% in 1970, and 85% in 2014. Today, all countries outside Africa with the exception of Afghanistan (32% in 2011) have rates above 50% ([www.ourworldindata.org/literacy](http://www.ourworldindata.org/literacy), last accessed 9.10.2018). African countries with a rate below 50% only mentioned for completeness are Niger (15% in 2012), Chad (22% 2016), Sierra Leone (32% 2011), Benin (33% 2012), Mali (33% 2015), Burkina Faso (35% 2014), Gambia (42% 2013), Senegal (43% 2013), Cote d'Ivoire (44% 2014), and Guinea-Bissau (46% 2014).

**Table 1.3.10** Determinants of growth in the United Kingdom and the United States in the period 1820–1998.

Year	United Kingdom	United States	United Kingdom	United States
	Machinery and equipment pc (1990 US\$)		Years of education per person employed	
1820	92	87	2	1.8
1870	334	489	4.4	3.9
1913	878	2 749	8.8	7.9
1950	2 122	6 110	10.6	11.3
1973	6 203	10 762	11.7	14.6
1998	11 953	25 153	15.1	19.5
Change 1998/1820 (%)	+13 000	+29 900	+760	+1 080
	Hours worked per head of population		GDP per work hour (1990 US\$)	
1820	1 153	968	1.5	1.3
1870	1 251	1 084	2.6	2.3
1913	1 181	1 036	4.3	5.1
1950	904	756	7.9	12.7
1973	750	704	16.0	23.7
1998	657	791	27.5	34.6
Change 1998/1820 (%)	−43	−18	+1 830	+2 660

Source: Data from <http://www.ggd.net/maddison/oriindex.htm> (last accessed 7.11.2018); see also Maddison (2005).

### Topic 1.3.1 The European Colonial Period

The European colonial period or imperialism began at the end of the fifteenth century with the *age of discoveries* led by the Portuguese and Spanish exploration of the Americas and the coasts of Africa, India, and East Asia. In the seventeenth century, England, France, and the Dutch Republic also established overseas empires. In 1500, the future imperial powers of Europe accounted for only 10% of the global land surface and at most 16% of its population (Ferguson 2012). By 1800, so just at the beginning of Industrial Revolution, Europeans already controlled 35% of the globe (<https://en.wikipedia.org/wiki/colonialism>; last accessed 11.09.2018). During the Industrial Revolution, the Western world obtained the technological and thus also the military superiority over the rest of the world by inventions such as the steam engine (1769), steam locomotive (1829), automobile with internal combustion engine (1885), and airplane (1903), just to name a few (see Section 5.1.7.2). At the onset of WWI (1914), 11 Western empires – Austria, Belgium, France, Germany, Italy, Netherlands, Portugal, Spain, Russia, the United Kingdom, and the United States – controlled 60% of the global territory and 80% of the population (Ferguson 2012).

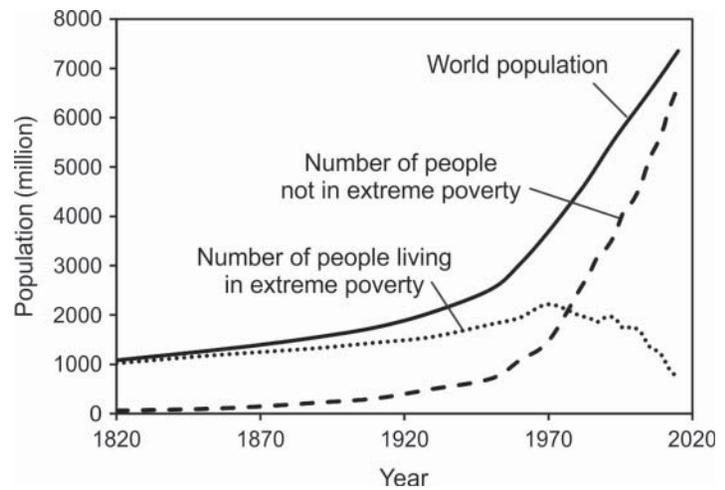
To elucidate the extent of the morally condemnable European imperialism, only 10 countries, representing 5% of the global land area, have never been colonized by Europeans, namely, Afghanistan, Bhutan, Iran, Japan, Mongolia, Nepal, North and South Korea (temporarily ruled by Japan and China), Thailand, and Turkey,

although some of these countries were temporarily at least in the European sphere of influence. Even if we count Ethiopia, only occupied by Italy for a short period (1936–1941), and China, where only coastal areas were temporarily controlled by Europeans, the total never colonized land area is only 12%.

It should be mentioned that besides a superior technology and its ruthless use, other factors also had a strong influence on the development of the economic and political power of the Western world since 1500 and of a civilization in general. According to Ferguson (2012) these (debatable) additional five factors are as follows:

- Competition by decentralization of political and economic life created the launch pad for capitalism.
- The production and purchase of consumer goods played a central economic role; without this consumer society, the Industrial Revolution would have been unsustainable.
- Property rights, protecting private owners and peacefully resolving disputes between them, formed the basis for the most stable form of representative government.
- Medicine improved health and life expectancy in Western societies and later in their colonies.
- The work ethic, a moral framework such as Protestant Christianity in the United States, Northern Europe, and parts of Western Europe, provided the glue for a dynamic, successful, and otherwise unstable society.

**Figure 1.3.4** World population living in extreme poverty over the last 200 years (1820–2015). Extreme poverty is defined as living with less than 1.9 US\$/day in 2011 purchasing power parity. Source: Data (and further details): [www.ourworldindata.org/extreme-poverty](http://www.ourworldindata.org/extreme-poverty) (last accessed 08.10.2018).



**Table 1.3.11** Historical development of GDP per capita (pc) in Germany 1700 until 1995 and country where the respective value of Germany was reached in 2017 (values in purchasing power parity, PPP, in 2011 international dollars).

Year	GDP pc in Germany (rounded values in 2011 US\$ PPP)	Country where Germany's GDP pc (in the indicated year) was reached in 2017
1700	1 900	Zimbabwe
1850	2 900	Kenya
1870	3 700	Zambia
1913	7 400	Guatemala
1929	8 200	Jamaica
1937	9 500	Namibia
1960	15 600	Costa Rica
1973	24 200	Greece
1995	34 600	Spain

Source: Data from <https://data.worldbank.org> (last accessed 9.11.2018).

More interesting aspects and details of human progress in the past are outlined, for example, by Hans Rosling (2018) and Steven Pinker (2018).

*BUT* on the other side of the coin of the growing average global prosperity, hopefully – as in the past decades – combined with a further drop in the number of extreme poor people, are environmental problems such as climate change, pollution of air, soil, and water, destruction of nature, and declining reserves and resources of raw materials such as of some metals and of easily exploitable (cheap) fossil fuels (see Sections 5.1, 5.2, and 5.4).

In addition, the human population is likely to keep growing until 2100, reaching an estimated 10 billion by 2050 and 11 billion by 2100. This is by all means a huge challenge with regard to a sufficient supply of humanity with food, clean water, and much less CO<sub>2</sub> generating energy sources (wind, solar, etc.) for electricity, heat, and transport.

**Table 1.3.12** Historical development of life expectancy in Germany 1875 until 1990 and country where the respective value of Germany was reached in 2016 (historical values of Germany: <https://ourworldindata.org/life-expectancy>; values of 2016: <https://data.worldbank.org>, accessed 9.11.2018).

Year	Life expectancy in Germany (years)	Country where Germany's life expectancy (in the indicated year) was reached in 2016
1875	38	None (Sierra Leone had the lowest value of 52 years in 2016)
1895	42	
1925	57	Burundi, Guinea-Bissau
1950	67	Kenya, Senegal, Guyana
1960	70	Nepal, Iraq
1980	73	Guatemala, Paraguay
1990	75	Thailand, Malaysia, Peru, Venezuela

To face these serious challenges with success, we should look with optimism into the future and not in the belief of an approaching apocalypse. “Enlightened environmentalism” is needed and not “misanthropic environmentalism,” as Steven Pinker (2018) pointedly put it: “Problems are solvable. That does not mean that they will solve themselves, but it does mean that we can solve them if we sustain the benevolent forces of modernity that have allowed us to solve problems so far, including societal prosperity, wisely regulated markets, international governance, and investments in science and technology.”

In any event, clever chemical technologies will be an important part of the solution to these challenges, and the development of sustainable chemical technologies is more important than ever to enable a positive development of mankind on our planet.



## 2

## Chemical Aspects of Industrial Chemistry

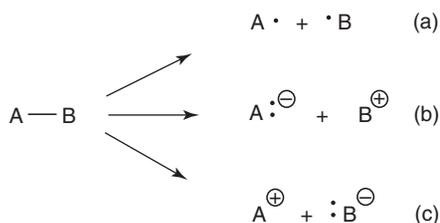
## 2.1 Stability and Reactivity of Chemical Bonds

Chemical reactions proceed by the linking and/or cleaving of chemical bonds. If we take the molecule A–B, for example, the covalent bond between A and B can be broken homolytically or heterolytically. In the first case each atom A and B receives one unpaired electron to form radicals; in the second case both electrons of the chemical bond go with either A or B, forming charged species (Scheme 2.1.1).

Radicals and charged species play a very important role as reactive intermediates in various organic transformations. Even if they may be present only in small quantities and for a short time (and thus are difficult to measure analytically), they are very relevant in the mechanism of the ongoing reaction.

Note that the reverse reactions to those shown in Scheme 2.1.1 play a very important role for the formation of new covalent bonds. In addition, radicals or charged species can attack neutral compounds to form different radicals and charged species involving new chemical bonds. Scheme 2.1.2 gives examples of some practical relevance in chemical technology. In transformation (a), a methyl radical attacks a chlorine molecule to form chloromethane and a chlorine radical. This reaction is one of the key steps in technical methane chlorination. In transformation (b), an isopropyl carbocation attacks water to form isopropanol with the release of a proton, the key mechanism in the technical production of isopropanol and all higher secondary and tertiary alcohols. In transformation (c), an anionic methanolate ion acts as starter for an anionic polymerization reaction – one possible starting step in technical anionic polymerization.

Note that the reactivity of radicals, carbocations, or carbanions (the negative charged counterpart of carbocations) is not always the same but depends strongly on the surrounding neighboring groups with their specific electronic and steric effects. As the influence of electronic and steric factors on the



**Scheme 2.1.1** Different modes of breaking the covalent bond in molecule A–B, forming either radicals (a) or charged species (b, c).

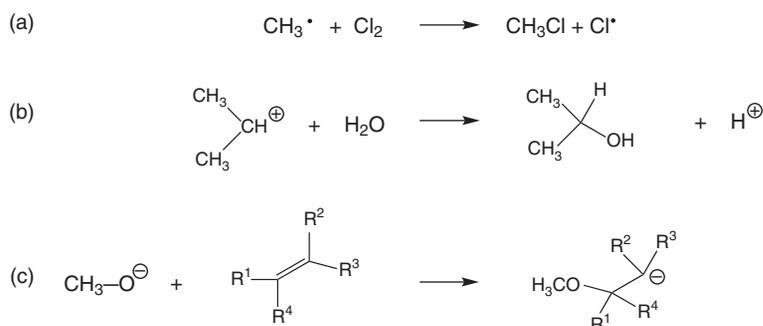
reactivity of molecules is also of key importance for many transformations in chemical technologies, we will devote the following subsections to introducing these phenomena. For a more detailed treatment of the reactivity of organic molecules – that is certainly indispensable for all research efforts into new chemical transformations – excellent textbooks in organic chemistry can be recommended (Sykes 1988; March 1992; Sykes 1996; Walter and Francke 1998; Fanghänel 2004).

## 2.1.1 Factors that Influence the Electronic Nature of Bonds and Atoms

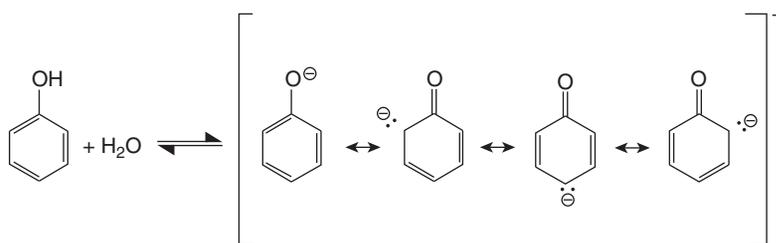
All effects that influence the electron density in a specific part of a molecule strongly affect the chemical reactivity of that part. While – for example – electron-rich parts show hardly any reactivity against  $\text{HO}^-$ , electron-poor parts will easily react with this strong electron donor.

The most important effects that influence the electron density of specific parts of a molecule are the inductive and conjugative effects.

Inductive effects on electron density originate from the fact that the electron pair in a covalent  $\sigma$ -bond that links two different atoms (e.g. carbon and oxygen in a C–O bond) is never shared evenly. The more electronegative atom (in our example oxygen) will always receive more electron density, which leaves the carbon with some lack of electron density. Thus,



**Scheme 2.1.2** Reactivity of radicals, carbocations, and carbanions exemplified for reactions of relevance in chemical technology: reaction of (a) the methyl radical with chlorine (key step in methane chlorination); (b) the isopropyl cation with water (key step in isopropanol synthesis from propene); (c) methanolate with an alkene to form a carbanion (key step in the start-up of an anionic polymerization reaction).



**Scheme 2.1.3** Stabilization of the phenolate ion by conjugative (or mesomeric) effects – note the two different notations of the arrows, indicating a reversible chemical reaction (left-hand side) and different mesomeric structures of the phenolate ion (three arrows in brackets).

a carbon atom attached to an oxygen atom (or any other strongly electronegative atom) always shows increased reactivity against strong electron-donor reagents relative to a carbon attached to another carbon. If the C—O bond is incorporated in a larger molecule, the carbon attached to the oxygen will also influence its immediate neighborhood by its ability to compensate for part of its electron deficiency by taking electron density from the surrounding atoms. Most groups attached to a carbon atom exert an inductive effect that pulls electrons away from the carbon (so-called  $-I$ -effect) because most atoms are more electronegative than carbon. Important exceptions are alkyl groups and metal atoms such as lithium (i.e. in organolithium reagents) or magnesium (i.e. in Grignard reagents of the type  $\text{RMgX}$ ). A carbon linked to these groups receives more electron density than usual (so-called  $+I$ -effect) and becomes an electron-rich reagent that searches for electron-deficient partners for reaction. Note that all inductive effects on electron density are based on the permanent polarization of bonds and, therefore, these effects are also expressed in the physicochemical properties of the molecules, for example, their dipole moment.

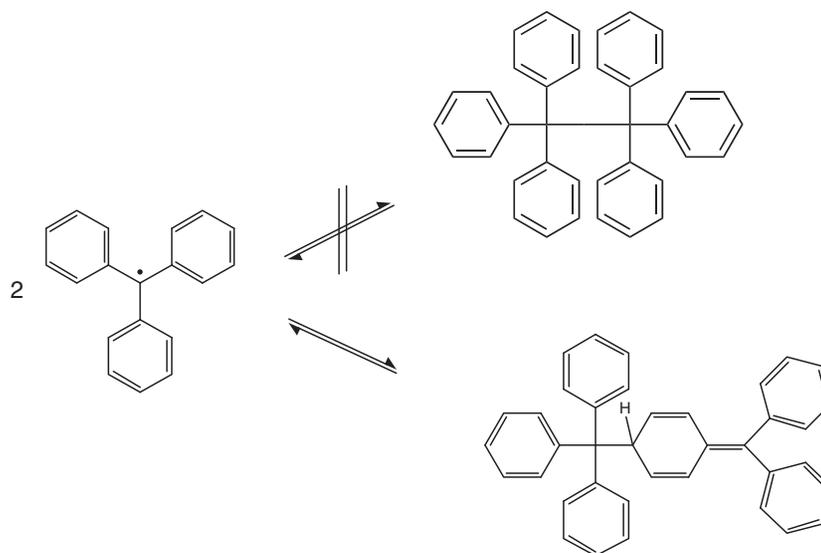
Conjugative effects on electron density are based on the high degree of polarizability of  $\pi$ -electrons in unsaturated and, especially, in conjugated systems (systems with alternating single and double bonds, such as butadiene). In contrast to inductive effects, conjugative or mesomeric effects influence the electron density distribution in a molecule over large

distances in expanded conjugated systems. Moreover, the conjugative effects result in atoms of alternating and fluctuating polarization and electron density in these systems. It is of great practical relevance that the possibility of stabilizing a positive or negative charge in a  $\pi$ -electron system by conjugative or mesomeric effects leads directly to a large increase in stability of such species. For example, the much stronger acid character of phenol compared with methanol can be understood as a direct consequence of the mesomeric stabilization of the phenolate ion after proton transfer (Scheme 2.1.3). Of course a similar kind of stabilization is not possible with any saturated aliphatic alcohol. Conjugative electronic effects are also permanent, and they influence strongly the physicochemical properties of molecules with unsaturated bonds and conjugated  $\pi$ -electron systems.

### 2.1.2 Steric Effects

Sometimes two molecules do not react even though they are expected to on the basis of the electronic nature of their reactive centers. In most cases, steric effects account for this reduced reactivity. To understand the nature of steric effects, we simply have to consider that two molecules have to approach each other very closely to enable the formation of a new covalent bond. If the reactive centers of both molecules are surrounded by bulky, inflexible, or geometrically restricted groups, the repulsive interaction of these surrounding groups can prevent

**Scheme 2.1.4** Reactivity of two trityl radicals. Due to steric reasons the expected combination of two radicals is suppressed, and instead a less sterically demanding dimerization takes place.



the two reactive centers from approaching in the required way. As a consequence, the two molecules do not react, or if they do the formed bond is very instable and can be cleaved easily by heating or by reaction with a less sterically demanding other reagent. Scheme 2.1.4 shows the unusual reactivity of two trityl radicals, which originates from the fact that the simple recombination of two trityl radicals is sterically too demanding to take place.

### 2.1.3 Classification of Reagents

Strong electron-donating reagents, such as  $\text{HO}^-$ , search for electron-deficient counterparts to lower their energy by forming a stable covalent bond. Therefore, these species are called nucleophiles or nucleophilic reagents. In an analogous manner there also exist reagents that themselves are very poor in electron density and, therefore, search for electron-rich counterparts for reactions. The latter are called electrophiles or electrophilic reagents. Table 2.1.1 gives an overview of technically important nucleophiles and electrophiles. Note that the electronic character of these species can be very much understood using the arguments discussed in Section 2.1.1. Note further that to establish an order of strength among different nucleophiles, one can take their basicity as a rough first approximation. An important difference, however, is that the terms “electrophilicity” and “nucleophilicity” are derived from kinetic experiments (therefore aspects like steric arguments can play a very important role), while the terms “acidity” and “basicity” are derived from a thermodynamic evaluation of the acid–base equilibria.

**Table 2.1.1** Technically important nucleophiles and electrophiles.

Technically important nucleophiles	Technically important electrophiles
$\text{H}^-$ , $\text{HO}^-$ , $\text{RO}^-$ , $\text{RS}^-$ , $\text{CN}^-$ , $\text{RCO}_2^-$ , $\text{R}'\text{-O-R}''$	$\text{H}^+$ , $\text{H}_3\text{O}^+$ , $\text{NO}_2^+$ , $\text{NO}^+$ , $\text{R}_3\text{C}^+$ , $\text{SO}_3$ , $\text{CO}_2$
$\text{R}'\text{-S-R}''$ , $\text{R}'_3\text{-N}$ , $\text{RMgX}$ , $\text{RLi}$	$\text{BF}_3$ , $\text{AlCl}_3$ , $\text{Br}_2$ , $\text{O}_3$

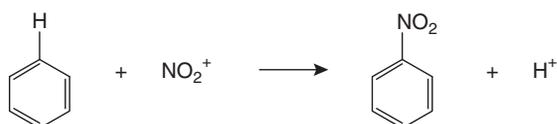
Atoms in bold refer to the atoms that transfer or accept electrons to the substrate according to their nucleophilic or electrophilic nature (R represents an alkyl or aryl group, X represents a halide).

## 2.2 General Classification of Reactions

Organic reactions can be grouped into four basic types of transformations that all play very important roles in chemical technology. These four types will be briefly presented here, and each type will be exemplified using one technically relevant example:

- Substitution reactions
- Addition reactions
- Elimination reactions
- Rearrangement or isomerization reactions

Substitution reactions are characterized by the fact that a substrate reacts with a second molecule by incorporating the second molecule in its structure and by releasing a part of the substrate. Substitution reactions can take place as electrophilic (see Section 2.2.5 for details), nucleophilic (Section 2.2.3), or radical substitution reactions (Section 2.2.2) depending on the nature of the attacking reagent. Scheme 2.2.1

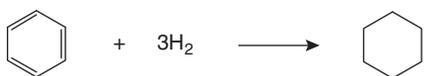


**Scheme 2.2.1** Electrophilic substitution of a hydrogen atom at benzene to form nitrobenzene.

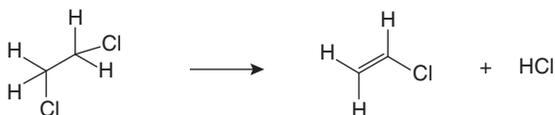
shows the electrophilic substitution of a hydrogen atom at benzene by the nitronium electrophile  $\text{NO}_2^+$ . This technically relevant reaction liberates a proton and forms nitrobenzene. It represents an important step in the synthesis of nitrobenzene, the key intermediate for the production of aniline.

Addition reactions proceed typically at unsaturated bonds such as  $\text{C}=\text{C}$ ,  $\text{C}=\text{O}$ ,  $\text{C}=\text{N}$ ,  $\text{C}\equiv\text{N}$ , or carbon-carbon triple bonds. A molecule is added to the substrate, and the product forms without release of any another molecule. With all substrates becoming part of the product, the atom economy of addition reactions is very favorable. Because today's chemical technology is largely based on unsaturated base chemicals obtained in the steam cracker process (e.g. ethylene, propylene, butenes, benzene; see Section 6.6), addition reactions are of the highest relevance in the whole petrochemistry. Scheme 2.2.2 shows as one important example, namely, the addition of hydrogen to benzene to form cyclohexane, a key intermediate in the production of, for example, adipinic acid or caprolactam (nylon).

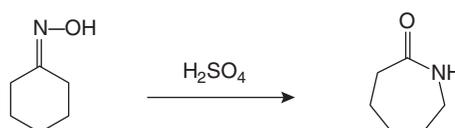
Elimination reactions can be regarded as the reverse of addition reactions. One substrate is converted into at least two molecules, with dehydrogenation, dehydration, dehalogenation, and dehydrohalogenation reactions being of highest technical relevance. Scheme 2.2.3 shows, as an example of a technically relevant elimination reaction, the dehydrochlorination of dichloroethane, a key step in the production of vinyl chloride.



**Scheme 2.2.2** Addition of hydrogen to benzene to form cyclohexane.



**Scheme 2.2.3** Elimination of HCl from dichloroethane to form vinyl chloride.



**Scheme 2.2.4** Rearrangement of cyclohexanone oxime to form  $\epsilon$ -caprolactam.

Rearrangement or isomerization reactions proceed typically at carbocations or other electron-deficient positions of a molecule. In rearrangement reactions the substrate stabilizes itself by rearranging its structure without changing the number and type of its atoms. Thus, rearrangement reactions proceed without addition/release of molecules other than substrate and product. Rearrangement reactions of technical importance are the isomerization of linear alkanes to branched alkanes (important to increase the quality of fuels), and the rearrangement of cyclohexanone oxime to  $\epsilon$ -caprolactam (Scheme 2.2.4).

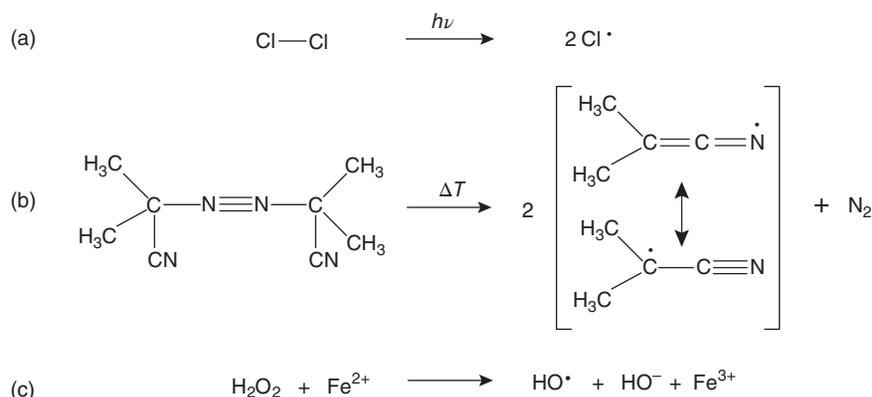
The following subsections highlight important mechanistic aspects of organic reactions. They focus on the question of how a certain organic transformation proceeds and how it can be influenced beneficially, for example, by the use and choice of a catalyst, the choice of solvent, or reaction parameters. Of course, a certain understanding of the type of reaction mechanism is also very helpful in choosing the right kinetic model for kinetic investigations in the context of process development studies.

### 2.2.1 Acid-Base-Catalyzed Reactions

Acid-catalyzed reactions are characterized by the fact that either a proton (in the case of Brønsted acid catalysis) or a strongly electron-deficient catalyst (in the case of Lewis acids) interacts with the substrate, typically by the intermediate formation of a carbenium ion. The latter is highly activated and undergoes transformations, for example, in the form of substitution, addition, or rearrangement. After reaction the acid catalyst is liberated from the product. Technically important examples of all three types of transformation are (i) Lewis acid (typically  $\text{AlCl}_3$ )-catalyzed electrophilic substitution to form ethylbenzene from benzene (key step in styrene production), (ii) Brønsted acid-catalyzed addition of water to ethene to form ethanol, and (iii) isomerization of *n*-hexane to iso-hexane catalyzed by strong Brønsted acids to improve the quality of fuel for Otto engines.

In the case of base-catalyzed reactions, the substrate comes into contact with either  $\text{HO}^-$  or any other highly electron-rich catalyst (e.g. alcoholates, strongly

**Scheme 2.2.5** Different ways of forming radicals exemplified for reactions of technical importance. (a) Photochemical cleavage of chlorine to form a chlorine radical as applied in the sulfochlorination of alkanes. (b) Thermal cleavage of bis- $\alpha$ -azoiso-butyronitrile as applied in the radical polymerization of styrene. (c) Formation of OH radicals from hydrogen peroxide as applied in radical oxidation reactions.



basic amines, metal alkyls). Again, the substrate is activated, typically via the intermediate formation of carbanion species. A technically important example of base catalysis is the transesterification of natural oils to fatty acid methyl esters (FAME, better known as “biodiesel”), a process typically catalyzed by methanolate salts.

### 2.2.2 Reactions via Free Radicals

As mentioned in Section 2.1, the formation of radicals requires the homolytic cleavage of a covalent bond. Energetically such homolytic cleavage is particularly favorable in gas-phase reactions and for liquid-phase reactions in nonpolar solvents. In polar solvents, however, the energy contribution from the solvation of ionic species formed in heterolytic cleavage reverses the picture, and heterolytic cleavage becomes more favorable.

Radical reactions are of greatest importance in chemical technologies. The combustion of hydrocarbons – surely the most important organic reaction in volumetric terms – involves the formation of radicals in the same way as most oxidation reactions for the production of chemicals (e.g. oxidation of cyclohexane to cyclohexanol). Other very important radical reactions include thermal cracking of hydrocarbons (e.g. in the steam cracker process [Section 6.6] or in the delayed coker process), radical substitution reactions (e.g. alkane chlorination or alkane sulfoxidation), and radical polymerization reactions (for the production of, for example, polystyrene, poly(vinyl

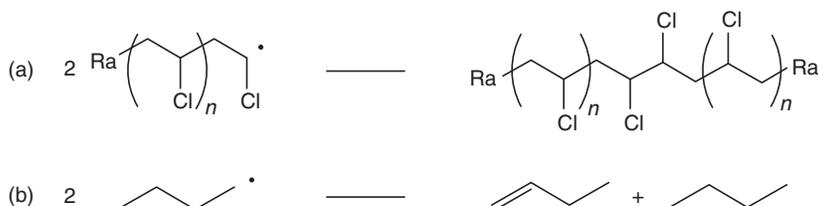
chloride), or polymethacrylate). The latter reactions involve formally the addition of a radical to the monomer alkene followed by chain propagation to form the polymer.

All radical reactions start with the initial formation of radicals in the reaction mixture. This decisive step can proceed either photochemically (for example, in the technical sulfoxidation and sulfochlorination processes) or thermally (as in all technical oxidation and cracking reactions as well as in most radical polymerizations). A third important type of radical formation proceeds via redox reaction with a one-electron transfer either using metal salts (e.g.  $\text{Fe}_2^+/\text{Fe}_3^+$  or  $\text{Cu}^+/\text{Cu}^{2+}$ ) or via electrolysis. Scheme 2.2.5 gives examples of technical relevance for all three radical formation mechanisms.

Radicals are very reactive due to their unpaired electron. Once formed, they typically react very quickly with organic molecules in addition, substitution, or rearrangement reactions. If radicals react with neutral molecules, new radicals form, and the reaction can quickly propagate as low energy barriers are characteristic for this kind of radical reactions. Note that, as a consequence of their high reactivity, radicals react in most cases in a less selective manner than carbocations or carbanions.

A radical reaction or radical chain propagation (such as in alkene polymerization) is terminated by either the reaction of two radicals or disproportionation of the radical into alkane and alkene (Scheme 2.2.6). The latter reaction plays the dominant role in petrochemical cracking processes.

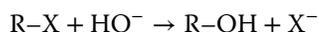
**Scheme 2.2.6** Chain termination in radical reactions by either (a) reaction of two radicals, exemplified for poly(vinyl chloride) synthesis, Ra = initial radical, or (b) disproportionation, exemplified for the reaction of two butyl radicals relevant in steam cracking.



Alternatively, a radical reaction can be stopped by adding to the reaction mixture substances that react very easily with radicals by forming very stable radicals themselves so that the propagation reaction is terminated. Examples of such radical scavenger molecules are phenols, quinones, and diphenylamines.

### 2.2.3 Nucleophilic Substitution Reactions

In a nucleophilic substitution, one substituent of a saturated carbon atom is exchanged with another substituent. A typical example is the reaction of a haloalkane  $R-X$  with the hydroxide ion  $HO^-$  to form the respective alcohol:



Kinetic studies of numerous nucleophilic substitution reactions have demonstrated that there exist two borderline cases. In the first case, also referred to as a  $S_N2$  reaction, the reaction rate is proportional to the concentration of both  $R-X$  and  $HO^-$  (Eq. (2.2.1)); in the second case, called a  $S_N1$  reaction, the reaction rate is only dependent on the concentration of  $R-X$  (Eq. (2.2.2)):

$$r \sim [R-X][HO^-] \quad (2.2.1)$$

$$r \sim [R-X] \quad (2.2.2)$$

A more detailed mechanistic analysis reveals that in the case of an  $S_N2$  reaction, both  $R-C$  and  $HO^-$  are involved in the rate-determining step (formation of the transition state), while in a  $S_N1$  reaction, heterolytic cleavage of the  $C-X$  bond is the rate-determining step, and, thus, only the concentration of  $R-X$  influences the kinetics. Scheme 2.2.7 displays the two different borderline cases and their rate-determining steps.

Several important factors influence whether a given nucleophilic substitution reaction proceeds more according to the  $S_N1$  or the  $S_N2$  mechanism:

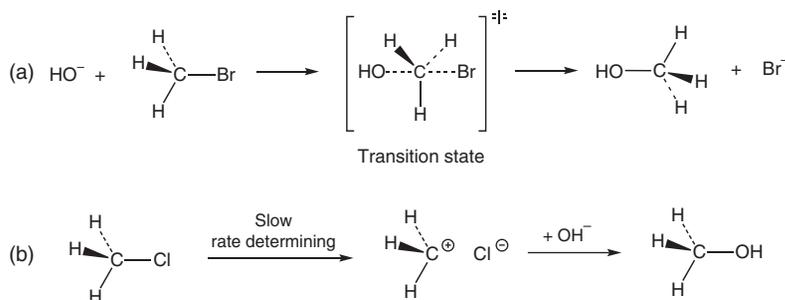
- *Choice of solvent:* The higher the dielectric permittivity  $\epsilon$  of the solvent, the better the solvation of the ion pair in the  $S_N1$  mechanism, leading to

increasing probability of an  $S_N1$  mechanism. Note that nucleophilic substitution according to the  $S_N1$  mechanism is typically not found in gas-phase reactions.

- *Groups surrounding the carbon atom at which the substitution reaction proceeds:* The higher the steric demand of the remaining substituents at the carbon atom, the more difficult it is to realize the transition state required by the  $S_N2$  route. Note that the  $S_N2$  mechanism requires an attack of the nucleophile from the opposite site of the leaving, weaker nucleophile. In addition, the groups surrounding the carbon atom also affect the probability of  $S_N1$  versus  $S_N2$  mechanism by means of their electronic influence. If the groups attached to the carbon atom exert an electron-donating inductive effect, such as in the case of a carbon atom attached to three methyl groups, then the carbenium ion formed in the  $S_N1$  reaction is greatly stabilized, and this mechanistic path becomes more probable.
- *Nature of the incoming group:* For obvious reasons the strength of the incoming nucleophile does not influence the rate of a  $S_N1$  reaction; the incoming nucleophile is not involved in the rate-determining step. For  $S_N2$  reactions the reaction rate increases with increasing nucleophilic character of the incoming group.
- *Nature of the leaving group:* The nature of the leaving group influences both the rate of  $S_N1$  and  $S_N2$  reactions. The relative tendency of a leaving group  $X$  to leave the molecule  $R-X$  is influenced by the strength and polarization of the  $R-X$  bond as well as by the stability and solvation of the leaving group  $X$ .

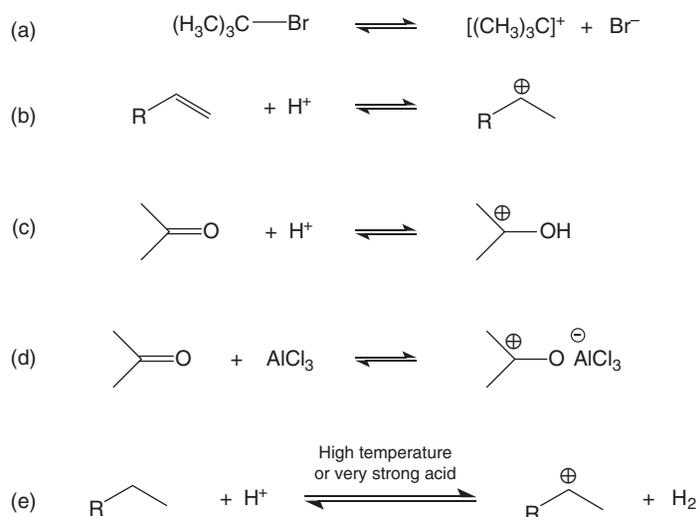
### 2.2.4 Reactions via Carbocations

Carbocations are formed by several reactions. One example has been discussed already in the context of the  $S_N1$  reaction (Scheme 2.2.8a). Other important options include the addition of protons to double bonds, for example, the addition of a Brønsted acid to



**Scheme 2.2.7** Mechanistic borderline cases in nucleophilic substitution reactions. (a)  $S_N2$  reaction with formation of the transition state being the rate-determining step. (b)  $S_N1$  reaction with heterolytic cleavage of the  $C-Cl$  bond being the rate-determining step.

**Scheme 2.2.8** Important routes for carbocation formation. (a) Heterolytic bond cleavage as observed in  $S_N1$  reactions. (b) Addition of acids to alkenes – key step in alcohol formation from alkenes. (c) Addition of protons to carbonyl bonds. (d) Addition of Lewis acids to carbonyl bonds. (e) Hydride abstraction.



an alkene or ketone (Scheme 2.2.8b,c, respectively). The addition of a Lewis acid to a carbonyl group can also lead to a type of carbocation, an effect that is exploited in all kinds of technical Friedel–Crafts acylation reactions (Scheme 2.2.8d). Finally, in high-temperature refinery processes, the formation of carbocations from alkanes is of highest relevance. Here acidic catalysts are usually applied that abstract a hydride from the alkane to form hydrogen and a carbocation at the alkane substrate (Scheme 2.2.8e).

The stability of carbocations increases for alkyl cations with the number of alkyl groups that surround the positive charge and thereby stabilize it by their inductive effects. Thus, a methyl carbocation  $\text{CH}_3^+$  is the most unstable and reactive one, while the *tert*-butyl cation  $[(\text{CH}_3)_3\text{C}]^+$  is the most stable and least reactive. This stability order is also the reason why carbocations frequently undergo isomerization and rearrangement reactions after formation, a reactivity that is very important for all isomerization reactions in refineries (here branched hydrocarbons are highly desired due to their higher octane number – see Sections 6.9 and 6.10).

Carbocations can – once formed – undergo in principle the following transformations:

- Combination with a nucleophile
- Abstraction of a proton
- Addition to an unsaturated bond
- Rearrangement

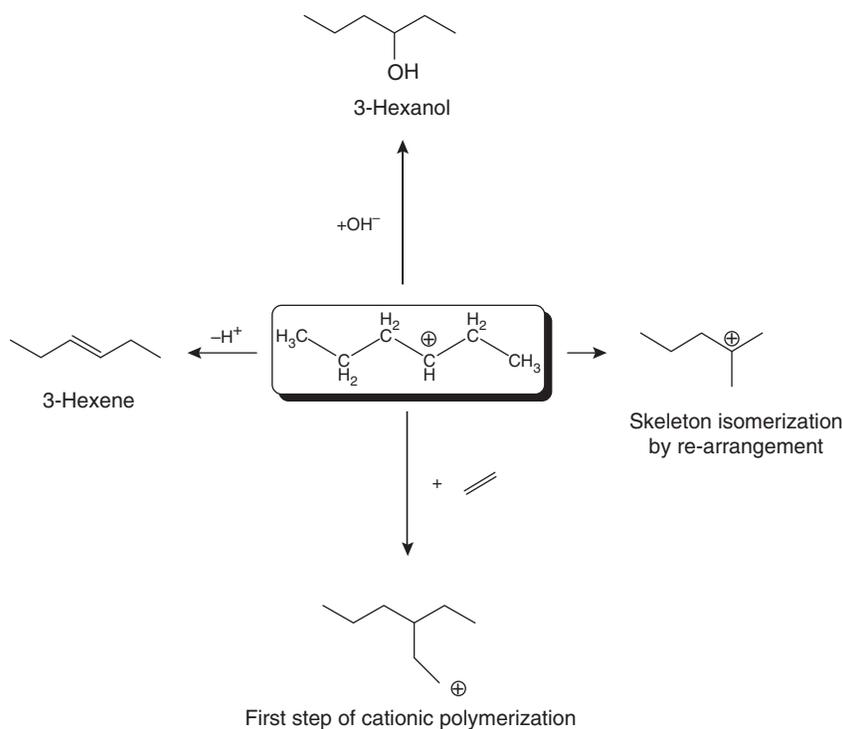
Scheme 2.2.9 demonstrates these different options for a  $\text{C}_6$  carbocation that carries its positive charge at carbon number 3 (C3). While the reaction with the nucleophile HO leads to 3-hexanol, abstraction of a proton will produce 3-hexene. Addition of ethylene or any alkene would result in an addition

reaction forming a new, very reactive carbocation. As a consequence, cationic polymerization would result from the addition of this alkene. Finally, the cation tends to rearrange itself to a more stable carbocation, for example, the 2-methylpentyl cation if no other reactant is around for reaction and the conditions are appropriate. The technical relevance of these different options is obvious for alcohol production from alkenes, for catalytic cracking (where significant amounts of alkenes are formed under specific, applied reaction conditions by proton abstraction from carbocations), for cationic polymerization processes, and for fuel reforming.

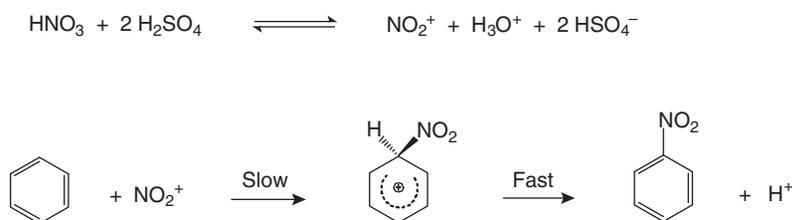
### 2.2.5 Electrophilic Substitution Reactions at Aromatic Compounds

Aromatic compounds are characterized by their  $\pi$ -electron systems, which create a high electron density above and below the planar six-membered ring of carbon atoms. Consequently, aromatic compounds are easily attacked by electrophiles, and the reconstitution of the energetically favored aromatic character leads to replacement of one substituent at the carbon ring with the attacking electrophile. In total, an electrophilic substitution reaction takes place. By the same argument, nucleophilic substitution reactions at aromatic rings are much more difficult but are possible if strong nucleophiles and activated aromatic substrates (e.g. nitrobenzol or pyridine) are used (see Sykes 1988; March 1992 for details). In the following paragraphs we focus solely on the technically very relevant electrophilic substitution reactions.

Scheme 2.2.10 displays the general mechanism of an electrophilic substitution reaction for the



**Scheme 2.2.9** Reactivity of carbocations exemplified for a hexyl ion carrying the cationic charge at carbon number 3 (C3).



**Scheme 2.2.10** Nitration of benzene using  $\text{HNO}_3/\text{H}_2\text{SO}_4$  – an example of an electrophilic substitution reaction of technical relevance.

important example of nitrobenzene synthesis from nitric acid/sulfuric acid and benzene. This reaction is a key step in the industrial synthesis of aniline, which is obtained subsequently by nitrobenzene hydrogenation.

While in the case of the nitration reaction, the attacking electrophile  $\text{NO}_2^+$  is generated from the  $\text{HNO}_3/\text{H}_2\text{SO}_4$  mixture; in other electrophilic substitution reactions, a Lewis acid catalyst plays a very important role in generating the reactive electrophile. Examples are the Lewis acid-catalyzed chlorination or bromination of aromatic compounds (typical catalysts:  $\text{FeCl}_3$  or  $\text{FeBr}_3$ ) and Friedel–Crafts alkylation with alkyl halide or alkenes (typical catalyst:  $\text{AlCl}_3$ ). In each case, interaction of the Lewis acid with the approaching nonaromatic substrate leads to a large increase in the electrophilicity of the attacking reagent. Another technically important example of a non-catalyzed electrophilic substitution reaction is the sulfonation of benzene and other aromatic compounds. The reaction proceeds quickly in mixtures of

$\text{SO}_3$  and sulfuric acid, in which  $\text{SO}_3$  acts as a strong electrophile.

A question of high practical relevance for all electrophilic substitution reactions is the influence of an already existing substituent Y on the aromatic ring on the reactivity and regioselectivity of a second substitution reaction with the electrophile X. Comparing substitution reactions with X for different aromatic starting materials (with Y = H for benzene as the reference), two distinctive patterns can be distinguished:

- The second substitution is comparably fast or even faster than in the case of benzene, and the second substituent is found preferably at the 2-(ortho) or 4-(para) position of the product (with respect to the substituent present in the aromatic substrate defining the 1-position).
- The second substitution is slower than in the case of benzene, and the second substituent is preferably found at the 3-(meta) position.

To explain these patterns, electronic influences are most relevant. In addition, steric factors play a certain role for substitution at the 2-(ortho) position. Substituents Y with a free electron pair on the atom that is to be attached to the aromatic ring (e.g. OCOR, NHCOR, OR, OH, NH<sub>2</sub>, NR<sub>2</sub>) provide this electron pair for conjugative stabilization of the cationic transition state formed after attack of the electrophile. This leads to an acceleration of the reaction (lowering of the energetic level of the transition state) and to preferable electrophilic substitution at ortho- and para-positions. For these positions, stabilization involving the free electron pair of Y is more favorable than for the meta-position.

In contrast, substituents Y with no free electron pair at the atom attached to the aromatic ring (e.g. R<sub>3</sub>N<sup>+</sup>, Cl<sub>3</sub>C, NO<sub>2</sub>, CHO, COOH) provide no electron pair for conjugative stabilization of the cationic transition state. Without this conjugative stabilization only the stronger electron-withdrawing effect of this group of higher electronegativity affects the reaction mechanism. These substituents exert an electron-withdrawing effect, and thus the electrophilic substitution is slowed down compared with the reaction with benzene. However, the ability to stabilize the positive charge of the transition state is greater for substitution at the meta-position than for the other two positions, leading to a preferred nucleophilic substitution at this position.

So far, our discussion has always referred to kinetic arguments. It has to be considered, however, that most reaction systems that undergo electrophilic substitution reaction can also promote intra- or even intermolecular exchange of substituents. In the case of intermolecular exchange, this results in an isomerization reaction of the different regioisomers with the relative thermodynamic stabilities of the different isomers as the driving force. As a consequence we can obtain in short-term experiments kinetic product mixtures (depending on the abovementioned arguments), and if we apply longer reaction times, these

kinetic mixtures transform into the thermodynamic mixture of regioisomers. Detailed knowledge of the substitution and isomerization kinetics as well as of the temperature-dependent equilibria allows us to adjust the obtained product mixture to a certain degree to meet market needs.

### 2.2.6 Electrophilic Addition Reactions

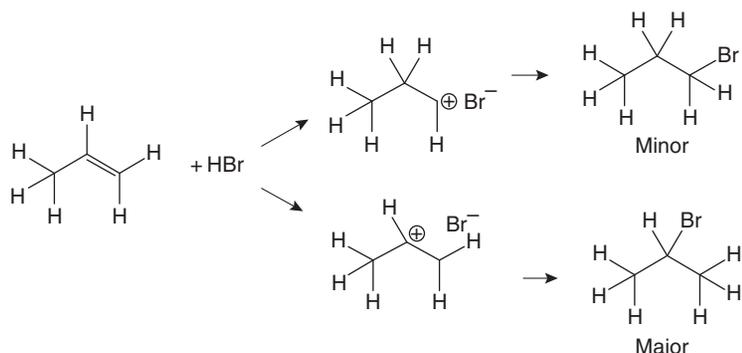
The technically most important electrophilic addition reactions proceed at alkenes and alkynes. The reactive  $\pi$ -electrons of these compounds are attacked by electrophiles, resulting in the formation of a positively charged reaction intermediate. Stabilization of this positive charge plays a very important role in the regioselectivity of electrophilic addition reactions. This is demonstrated in Scheme 2.2.11 for the addition of HBr to propene, a reaction that produces almost uniquely the product 2-bromopropane and almost no 1-bromopropane as a consequence of the inductive stabilization of the secondary propyl cation compared with the cation with the charge at C1. This selectivity, where the proton becomes attached to the carbon with fewer alkyl substituents, is known as Markovnikov's rule.

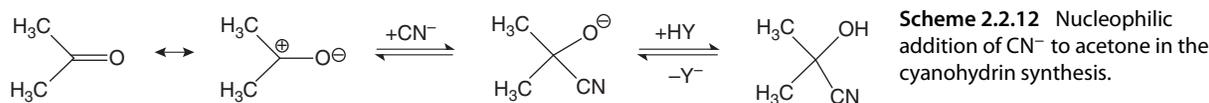
Besides the addition of halides and hydrogen-halide acids to alkenes or alkynes, other industrially relevant electrophilic addition reactions involve hydratization reactions (addition of water to alkenes and alkynes, forming alcohols), cationic polymerization (addition of carbocation to an alkene), hydrogenation (addition of hydrogen to alkenes to form alkanes), and Diels–Alder reactions (addition of an alkene to a conjugated diene to form complex, unsaturated hydrocarbon structures).

### 2.2.7 Nucleophilic Addition Reactions

Nucleophilic addition reactions are mainly of technical interest in the context of further reactions at C=O groups present in aldehydes or ketones. The

**Scheme 2.2.11** Electrophilic addition of HBr to propene. Due to the higher stability of the secondary carbenium ion, there is hardly any 1-bromopropane found in the product.





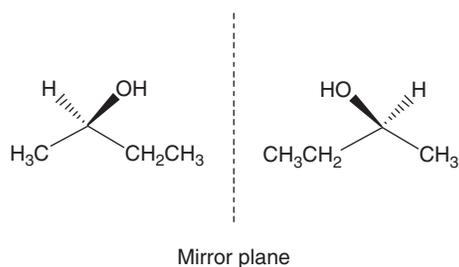
electronic nature of a carbonyl group is characterized by the greater electronegativity of the oxygen atom compared with the carbon atom. Thus, the carbon atom is the preferred place of nucleophilic attack, that is, of reaction with an electron-rich reagent. Scheme 2.2.12 gives as an example the technically important cyanohydrin reaction. Other important nucleophilic additions are the reaction of carbonyl compounds with alcohols and water, bisulfite, and metal hydrides.

### 2.2.8 Asymmetric Synthesis

A compound possessing a carbon atom that is surrounded by four different substituents exists in two stereoisomers that are like image and mirror image and are, therefore, not superimposable. Such a compound is said to be “chiral,” and both stereoisomers are called “enantiomers.” Figure 2.2.1 shows the two enantiomers of 2-butanol. The central carbon is also called “asymmetric,” and a synthesis that produces selectively one stereoisomer is therefore called an asymmetric synthesis.

The two enantiomers of a chiral compound have the same chemical and physicochemical properties in an achiral environment. Nevertheless, asymmetric synthesis is a very important field in preparative organic synthesis and fine chemicals production because nature is full of chiral receptors, catalysts, and reactants. Thus, the different enantiomers of chiral products typically exhibit very different performance and properties when applied as agrochemical, fragrance, or pharmaceutical in the chiral biological environment.

For compounds with more than one asymmetric carbon atom, there exist enantiomers and diastereomers. In detail, a compound with  $n$  asymmetric



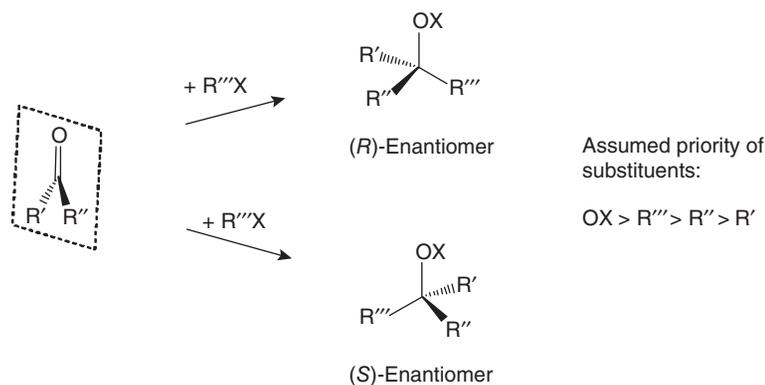
**Figure 2.2.1** The two enantiomers of 2-butanol.

carbon atoms can be formed in  $2^n$  different configurations. Some of these behave like image and mirror image – these are pairs of enantiomers. However, there are also pairs of stereoisomers that are not mirror images of each other. These are called diastereomers. Note that diastereomers differ in their physicochemical and chemical properties even in an achiral environment.

Synthesis of a chiral compound from an achiral compound requires a prochiral substrate that is selectively transformed into one of the possible stereoisomers. Important prochiral substrates are, for example, alkenes with two different substituents at one of the two C-atoms forming the double bond. Electrophilic addition of a substituent different from the three existing ones (the two different ones above and the double bond) creates a fourth different substituent and, thus, an asymmetric C-atom. Another class of important prochiral substrates is carbonyl compounds, which form asymmetric compounds in nucleophilic addition reactions. As exemplified in Scheme 2.2.13, prochiral compounds are characterized by a plane of symmetry that divides the molecule into two enantiotopic halves that behave like mirror images. The side from which the fourth substituent is introduced determines which enantiomer is formed. In cases where the prochiral molecule already contains a center of chirality, the plane of symmetry in the molecule creates two diastereotopic halves. By introducing the additional substituent diastereomers are formed.

The most important nomenclature for enantiomers is the so-called CIP system introduced by Cahn et al. (1966) and Prelog and Helmchen (1982). It is based on a priority rule for substituents at an asymmetric center – the higher the atomic number in the periodic table of elements, the greater the priority – beginning with the atoms bonded directly to the asymmetric center. If the atoms directly bonded to the asymmetric center are identical, atoms in the second sphere are considered. If those are identical, too, then the third bonding sphere is ranked. To determine the correct nomenclature for an enantiomer with an asymmetric C-atom according to the CIP system, we turn the molecule in such a way that the tetrahedron around the asymmetric C-atom points the substituent with the lowest priority (e.g. a hydrogen atom) away from the plane that is formed by the other three substituents. By looking at this plane, we identify the substituent with the highest

**Scheme 2.2.13** Nucleophilic addition to a prochiral carbonyl compound to form a new asymmetric C-atom with two enantiomers.



priority. For the order of the substituents in the plane, we can now distinguish two cases: (i) the order decreases clockwise (the enantiomer is then called a “*R*”-enantiomer” [from the Latin *rectus*, right]) and (ii) the order decreases anticlockwise (the enantiomer is called a “*S*”-enantiomer” [from the Latin *sinister*, left]). Scheme 2.2.13 shows an example of this nomenclature.

For sugars and amino acids, a historic nomenclature introduced by Emil Fischer in the 1880ies is still widely used. *D*- and *L*-sugars and *D*- and *L*-amino acids are assigned by using the so-called Fischer projection. The Fischer projection is obtained by drawing the structure of a sugar or amino acid with the main carbon chain in vertical direction and placing the most oxidized carbon atom at the top. If the OH-group (in case of sugars) at the bottom chiral center or the NH<sub>2</sub>-group (in case of amino acids) points to the right, the compound is referred to as *D*-sugar or *D*-amino acid, respectively. If the OH<sup>-</sup> at the bottom chiral center or the NH<sub>2</sub>-group points to the left, the compound is referred to as *L*-sugar or *L*-amino acid, respectively. The *D/L* nomenclature is historic and less universal than the CIP system. However, as this nomenclature is commonly used for amino acids, it is of relevance for Section 6.24.

In an achiral environment, both enantiotopic halves of the prochiral compound are even, which means the addition reaction in the case depicted in Scheme 2.2.13 would lead to a 1 : 1 mixture of the (*R*)- and (*S*)-enantiomers. Such a mixture is called a racemic mixture.

In chemical technology there are two ways to produce only one enantiomer in pure form: racemic resolution and stereoselective synthesis.

In racemic resolution processes a racemic mixture of the desired product is produced first. There are several techniques by which this mixture can be separated into its two enantiomers. A favorable option is to react the racemic mixture with another chiral

compound to form diastereomers. The latter have different physicochemical properties, and thus they can be separated, for example, by chromatographic or crystallization processes. After separation of the diastereomers, the chiral auxiliary compound is split off and separated to re-obtain the desired compound as pure enantiomer. In an alternative concept, called kinetic racemic resolution, the initial racemic mixture is reacted with a chiral reactant or in the presence of a chiral catalyst (e.g. an enzyme), and only one of the two enantiomers of the desired product is transformed into a new compound. The reacted and non-reacted enantiomers are usually easily separated. All processes of racemic resolution have the common disadvantage that both enantiomers, the desired and the undesired one, have to be synthesized initially. Consequently, half of the initial racemic mixture is the undesired enantiomer, which usually has no or very little commercial value. This problem is partially solved by applying racemization processes in which after separation the pure “wrong” enantiomer is reconverted into the racemic mixture. The latter is then applied in another round of racemic resolution again to increase the final yield of the desired enantiomer.

In a chiral environment the two enantiotopic halves of a prochiral compound behave differently. Thus, the addition of a reactant proceeds in a selective manner. The higher the degree of differentiation between the two halves, the higher the selectivity. The chiral information necessary to create stereochemically uneven halves at the prochiral center is called chiral induction. Typical ways to introduce chiral induction into a system to realize stereoselective syntheses are as follows:

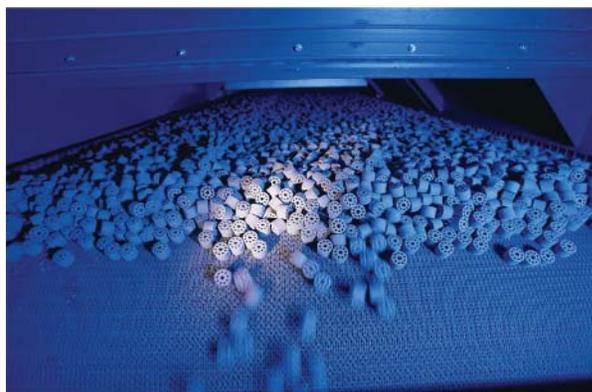
**Substrate induction:** Here the substrate already contains a chiral center so that this creates uneven diastereotopic halves. The reaction proceeds via diastereomeric intermediates with different energies. The product resulting from the diastereomeric intermediate with the lowest energy is kinetically favored.

*Auxiliary induction:* Here the prochiral substrate is reacted first with a chiral auxiliary to form, basically, the starting point for a substrate induction. After the reaction the auxiliary is split off, isolated, and can be reused often.

*Reagent induction:* In this case, the prochiral substrate is reacted in the presence of a chiral reagent to give a chiral product. The stereochemical information can be transferred either stoichiometrically or – very important in chemical technology – catalytically. In the latter case a chiral catalyst (e.g. a chiral transition metal complex, an organocatalyst, an enzyme, or a catalyst surface modified with chiral compounds) has to be applied.

## 2.3 Catalysis

Here we discuss catalysis and its relevance for chemical technology. Catalysis is applied industrially in the form of heterogeneous catalysis, homogeneous catalysis, and biocatalysis. All three forms follow the same general principles. However, the nature of the catalytically active center is different, varying from an active site that is part of a solid (heterogeneous catalysis), an active site that is part of a dissolved chemical compound (homogeneous catalysts), or an active site that is part of an enzyme or whole cell (biocatalysis).



Photograph of the drying step in the production of a heterogeneous catalyst. Source: Courtesy of Süd-Chemie, Germany.

### Catalysts:

- accelerate the reaction rate (kinetics) but do not influence the chemical equilibrium (thermodynamics) of a reaction;
- are not consumed during reaction and undergo catalytic cycles during operation;

- are characterized in their technical performance by their activity (expressed as turnover frequency, TOF), selectivity, and lifetime (expressed as overall turnover numbers, TONs); and
- can produce different reaction products from the same feedstock depending on their specific nature and composition.

### 2.3.1 Introduction and General Aspects

Catalysis is of greatest relevance for chemical technology. It is assumed that about 90% of all chemical processes work with the help of at least one catalyst. It is further assumed that 80% of the added value of the chemical industry and about 20% of the world economy depend directly or indirectly on catalysis. The catalyst market (the value of traded catalysts) was about €10<sup>9</sup> in 2007, but at the same time the value of the goods produced by these catalysts was at least 100 times higher (> €1 × 10<sup>12</sup> Weitkamp and Glaeser 2003). A recent article forecasts that the value of traded catalysts will reach US\$ 17.2 billion in 2014 with an actual rise of 6%/a (Letzsch 2011).

Industrial catalysts are found, to about the same extent (with respect to catalyst market value), in four different application areas: (i) environmental catalysts, with catalysts for exhaust gas cleaning in automotive applications and power plants being the most important examples; (ii) catalyst for refinery applications, for example, cracking catalysts, desulfurization catalysts, isomerization catalysts, and hydrogenation/dehydrogenation catalysts; (iii) catalysts for the production of polymers, such as Ziegler or metallocene catalysts for the production of polyethylene; and (iv) catalysts for transformations in the chemical and petrochemical industry, including catalysts for C–C coupling reactions, oxidations, hydrogenations, functionalizations, isomerizations, and many other reactions.

Our world would look very different without the catalysts that have been developed over the last 100 years. For example, supplying food for about 6 billion people on earth would be impossible without the catalytic transformation of nitrogen from air into ammonia, as only the latter allows the production of fertilizers for food production on today's scale. Without refinery catalysts we would certainly have much higher energy prices and would run out of oil much earlier. One can calculate that the annual consumption of crude oil would be more than 400 million/a higher, due solely to the lower efficiency of our refineries without the catalysts used today (for comparison, annual crude oil consumption was about 4 billion tons/a in 2005). Materials would be very different as

many plastics cannot be produced without catalysts that promote the polymerization process or that are needed for the production of monomers. Incidentally, we should not forget that nature is also full of biocatalysts that accelerate important processes like photosynthesis or the metabolism in our bodies and thus provide the fundamentals of life on earth.

Catalysis is of major socioeconomic importance. To solve future problems connected with limited resources and energy, as well as environmental protection, there is no way around catalysis. In fact, we can regard catalysis as *the* key technology for the sustainable production of chemicals since efficient catalysis saves raw materials and energy and avoids waste formation.

The term “catalysis” originates from the Greek word *καταλίσσιν*, which means “to dissolve, to loosen, to unfix.” Berzelius (1779–1848) introduced the term in 1836. Other pioneers of the concept of catalysis were Döbereiner (1780–1849), Mitscherlich (1794–1863), and Liebig (1803–1873). These first catalyst researchers observed in many cases that two substances that do not show a tendency for reaction do in fact react quickly in contact with a third substance that is not consumed in the reaction. Wilhelm Ostwald (see box) made a very significant contribution to the modern physicochemical understanding of catalysis:

**Wilhelm Ostwald** (1853–1932) was born in Riga and studied chemistry in Dorpat (now Tartu, Estonia). After his PhD thesis and habilitation, he worked as professor in Riga and Leipzig. Ostwald is regarded as the founder of physical chemistry in Germany. In 1909, he was awarded the Nobel Prize for his achievements in catalysis and his studies on chemical equilibria and kinetics. Notably, since Ostwald’s time many more Nobel Prizes have been awarded to catalyst researchers (Table 2.3.1), underlining the tremendous relevance of catalysis for the whole field of chemistry.

Ostwald realized that a catalyst only influences kinetics, leaving the thermodynamics unaffected. Thus, the equilibrium is reached faster, but the position of the equilibrium is not changed. Ostwald also found that the accelerating effect of the catalyst is linked to an active participation of the catalyst in the reaction mechanism, although the catalyst is not consumed during the reaction and thus does not appear in the stoichiometric equation.

Catalytic reactions are characterized by a reaction sequence in which one reactant (the catalyst)

is reformed in the final reaction step in the same stoichiometric amount as it was added. This behavior leads to a closed reaction cycle, the so-called catalytic cycle (as schematically shown in Figure 2.3.1). A catalyst is characterized (in contrast to a stoichiometric additive) by the fact that it undergoes more than one cycle.

Technically relevant catalysts undergo during their operational lifetime millions of cycles; therefore, a large number of product molecules can be formed with a small number of catalytic centers. The number of cycles that a catalyst can undergo prior to its deactivation is a very important performance criterion in catalysis. This dimensionless characteristic number for each catalyst is called the TON and describes the catalyst’s stability and lifetime. The TON, which originates from the field of enzymatic catalysis, is defined as the maximum amount of reactant (in moles) that a certain number of catalytically active centers (in moles) can convert into a certain product. For a  $A \rightarrow B$  reaction, we obtain

$$\text{TON} = \frac{n_{A,\text{converted,max}}}{n_{\text{cat}}} = \frac{n_{B,\text{produced,max}}}{n_{\text{cat}}} \quad (2.3.1a)$$

For a batch process, we obtain

$$\text{TON} = \frac{n_{A,0} - n_A(t_{\text{deactivation}})}{n_{\text{cat}}} \quad (2.3.1b)$$

where  $n_{A0}$  is the molar amount of reactant A at the start of the reaction,  $n_A(t_{\text{deactivation}})$  is the actual remaining molar amount of A, and  $n_{\text{cat}}$  is the molar amount of dissolved catalyst (in the case of homogeneous catalysis) or catalytic centers on the surface (in the case of heterogeneous catalysis). To obtain a reasonable quantity for the TON, the experiment has to be carried out to complete catalyst deactivation ( $t_{\text{reaction}} = t_{\text{deactivation}}$ ).

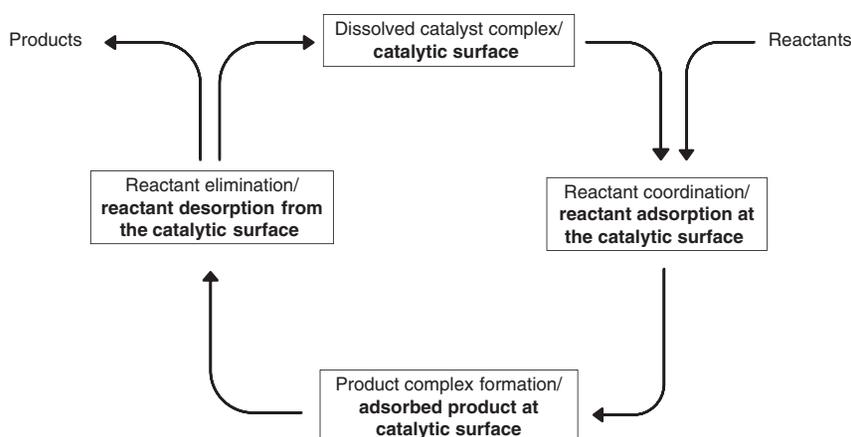
While TON indicates the overall catalyst lifetime, it is not an indicator of the catalyst activity per unit time. To compare the number of catalytic cycles per unit time, the TOF has been introduced (Eq. (2.3.2)) for a batch process and reactant (A). TOF values of industrial catalysts are typically of the order of  $1 \text{ s}^{-1}$  or higher:

$$\text{TOF} = \frac{1}{n_{\text{cat}}} \left( -\frac{dn_A}{dt} \right) \quad (2.3.2)$$

For enzymatic and homogeneous catalysis, in which well-defined catalyst molecules are generally present in solution, the TON and TOF can be directly determined. For heterogeneous catalysis, this is generally difficult because the activity depends on the size of

**Table 2.3.1** Nobel prizes in chemistry awarded for achievements in catalysis research.

Year	Name	Achievement
1907	Eduard Buchner (Germany)	“For his biochemical researches and his discovery of cell-free fermentation”
1909	Wilhelm Ostwald (Latvia)	“In recognition of his work on catalysis and for his investigations into the fundamental principles governing chemical equilibria and rates of reaction”
1912	Paul Sabatier (France)	“For his method of hydrogenating organic compounds in the presence of finely disintegrated metals whereby the progress of organic chemistry has been greatly advanced”
1918	Fritz Haber (Germany)	“For the synthesis of ammonia from its elements”
1929	Arthur Harden (UK) and Hans v. Euler-Chelpin (Germany)	“For their investigations on the fermentation of sugar and fermentative enzymes”
1931	Carl Bosch (Germany) and Friedrich Bergius (Germany)	“In recognition of their contributions to the invention and development of chemical high pressure methods”
1932	Irving Langmuir (USA)	“For his discoveries and investigations in surface chemistry”
1956	Sir Cyril N. Hinshelwood (UK)	“For researches into the mechanism of chemical reactions”
1963	Karl Ziegler (Germany) and Giulio Natta (Italy)	“For their discoveries in the field of the chemistry and technology of high polymers”
1972	Stanford Moore (USA) and William H. Stein (USA)	“For their contribution to the understanding of the connection between chemical structure and catalytic activity of the active center of the ribonuclease molecule”
1975	John Warcup Cornforth (UK)	“For his work on the stereochemistry of enzyme-catalyzed reactions”
1997	Paul D. Boyer (USA) and John E. Walker (UK)	“For their elucidation of the enzymatic mechanism underlying the synthesis of adenosine triphosphate (ATP)”
2001	William S. Knowles (USA), Ryoji Noyori (Japan), and K. Barry Sharpless (USA)	“For their work on chirally catalyzed hydrogenation and oxidation reactions”
2005	Yves Chauvin (France), Robert H. Grubbs (USA), and Richard R. Schrock (USA)	“For the development of the metathesis method in organic synthesis”
2007	Gerhard Ertl (Germany)	“For his studies of chemical processes on solid surfaces”
2010	Richard F. Heck (USA), Ei-ichi Negishi (Japan), and Akira Suzuki (Japan)	“For Pd-catalyzed cross couplings in organic synthesis”

**Figure 2.3.1** Representation of a catalytic cycle. Expressions in bold reflect heterogeneous catalysis, and expressions in normal print reflect homogeneous catalysis and enzyme catalysis.

the catalyst surface, which does not have a uniform structure. The number of active sites per unit mass and so on can be determined indirectly by chemisorptions measurements, but such measurements require great care, and the results are often not applicable to process conditions (Hagen 1999). Although the TON and TOF are attractive values due to their molecular simplicity, they should be used advisedly for solid catalysts in special cases. Alternatively, the catalyst activity can be given by the reaction rate of a catalytic reaction  $r$  referenced to some characteristic catalyst property, such as the mass of the applied heterogeneous catalyst (for details see Section 4.5.1, Topic 4.5.3):

$$r = \frac{1}{m_{\text{cat}}} \left( -\frac{dn_A}{dt} \right) \quad (2.3.3)$$

In catalytic reactions with very expensive catalyst metals, for example, ruthenium, iridium, or platinum, it is of special interest to know how much mass of product,  $m_{\text{product}}$ , can be produced with a given mass of the precious catalyst metal,  $m_{\text{cat, metal}}$ , per reaction time  $t$ . This important aspect leads to the definition of catalyst productivity according to Eq. ((2.3.4)):

$$\text{Productivity} = \frac{m_{\text{product}}}{m_{\text{cat, metal}} t} \quad (2.3.4)$$

The productivity is sometimes also related to the total mass of the catalyst, that is, to support plus active metal, but we recommend the definition according to Eq. ((2.3.4)) as the price of a catalyst is dominated by the metal that is used. The price of metals varies strongly over time. Thus, for a comparison, the actual prices should be used. In September 2010, the prices for some precious metals were €41 g<sub>Pt</sub><sup>-1</sup>, €14 g<sub>Pd</sub><sup>-1</sup>, €20 g<sub>Ir</sub><sup>-1</sup>, €59 g<sub>Rh</sub><sup>-1</sup>, and €5 g<sub>Ru</sub><sup>-1</sup>.

Finally, it is also important to know how much volume of a catalyst bed or a catalytic reactor is needed to produce a certain amount of product,  $m_{\text{product}}$  (kg) or  $n_{\text{product}}$  (mol). This knowledge is important as the size of the reactor determines largely the investment costs for the whole production plant. In Eq. ((2.3.5)) the space–time yield (STY) is introduced that reflects exactly this kind of information. Typical STY of commercial catalytic reactors are in the range 0.5–10 tons<sub>product</sub> m<sup>-3</sup> h<sup>-1</sup>:

$$\text{STY} = \frac{m_{\text{product}}}{V_{\text{cat, reactor}} t} \quad (2.3.5)$$

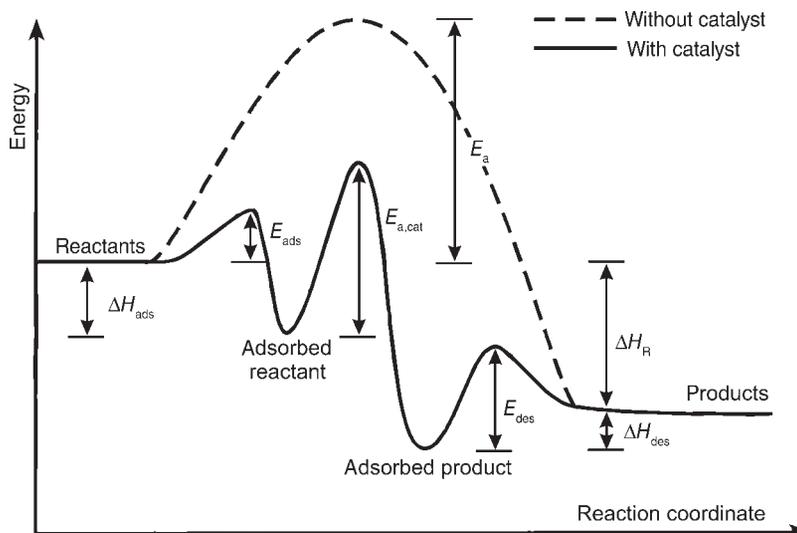
The STY may also be expressed in terms of mol of product per volume of reactor and time (see Eqs. (4.1.21) and (4.1.22)).

As mentioned above, one important characteristic property of a catalyst is its ability to enhance the rate of a chemical reaction. How can this be explained? As shown schematically in Figure 2.3.2, the interaction of reactants with the catalyst during a reaction opens up an alternative reaction pathway.

The latter is characterized by the fact that the energies of the transition states are generally lowered by interaction with the catalyst. Importantly, this leads to a lower maximum energy barrier that has to be overcome by the system on its way to product formation. As this maximum energy barrier is directly linked to the reaction rate, a lower maximum energy barrier results directly in a higher rate  $r$  and rate constant  $k$ .

Another very important feature of a catalytic reaction is that its energy profile should not have any deep troughs. Such a low-energy intermediate would reflect a stable “resting state” from which a huge energy barrier would prevent the successful closing of

**Figure 2.3.2** Schematic energy profiles of a catalyzed (terms refer here to a heterogeneously catalyzed reaction) and a non-catalyzed reaction (see also Topic 4.3.2 for a further explanation of the term *reaction coordinate*).



the catalytic cycle. Note that the value of the energy barrier schematically drawn in Figure 2.3.2 is not the same as the activation energy introduced in Section 4.3.1 with the Arrhenius law. The Arrhenius law is within the technically used temperature regime a very good approximation, but it is not a physically exact equation. For most Arrhenius activation energies derived from kinetic experiments, all temperature influences on the system are “summarized” within the parameter of the activation energy.

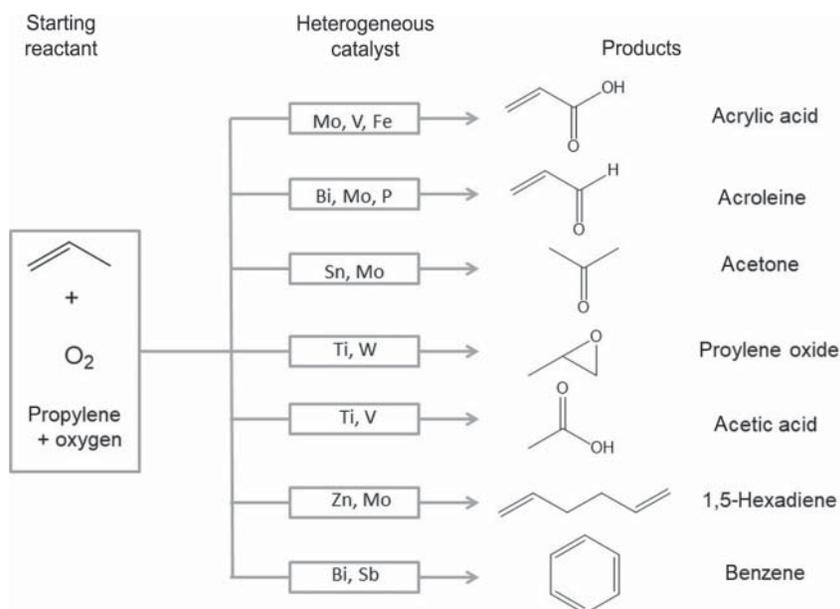
Technical reactions can profit in different ways from the higher reaction rate enabled by a catalyst. Obviously, a higher reaction rate leads to higher STY, and thus the same amount of product can be produced in a smaller reactor. This leads directly to lower investment necessary for the reactor inventory. For exothermic reversible reactions, for example, methanol synthesis, ammonia synthesis,  $\text{SO}_2$  oxidation, or the water–gas shift reaction, a catalyst of higher activity allows us to obtain the same reaction rate at a lower temperature, which leads to higher equilibrium conversion (see also Section 4.2.1 and Example 4.2.4). In addition, endothermic reversible reactions can also profit from a highly active catalyst that provides the same reaction rate at lower temperature. Even if the equilibrium conversion is lower at lower temperature here, the benefit in this case results from the fact that the catalyst helps to operate below a technically critical temperature, for example, the decomposition temperature of the product or a temperature that would require special reactor equipment. A typical example of the latter is steam reforming of methane to produce syngas.

Even more important than the rate-accelerating effect of a catalyst is its ability to favor one specific reaction pathway in the cases with more than one thermodynamically possible pathway. From an industrial perspective selectivity is generally more important than activity. This becomes understandable in view of the economic damage caused by converting a valuable feedstock into a worthless product. Figure 2.3.3 shows for the specific example of the heterogeneous catalyzed oxidation of propylene the influence of different catalysts on the main product formed.

In terms of the energy profile diagram in Figure 2.3.2, the catalyst’s influence on the selectivity means that more than one energy profile for the catalyzed reaction is found, with each profile leading to different products. For different catalysts the relative energies of the transition states on the way to the different products differ. A selective catalyst accelerates one specific pathway and slows all other possible pathways down. The resulting relative rate constants of the different pathways determine the selectivity, as exemplified by Eq. ((2.3.6)) for the least complicated case of a parallel reaction in which feedstock A is converted into product B or product C, with both reactions being of the same reaction order, with  $k_1$  as rate constant for conversion into B and  $k_2$  as rate constant for conversion into C (see Section 4.3.2 for details):

$$S_B = \frac{k_1}{k_1 + k_2}, \quad S_C = \frac{k_2}{k_1 + k_2} \quad (2.3.6)$$

Owing to the enormous relevance of rate acceleration and selectivity enhancement for the industrial



**Figure 2.3.3** Main products formed in the oxidation of propylene depending on the active metal of the applied heterogeneous catalyst.

**Table 2.3.2** Important discoveries in catalysis that led to major technical applications.

Year	Discovery
1913	Synthesis of ammonia from N <sub>2</sub> and H <sub>2</sub> (Haber–Bosch process)
1915	Oxidation of ammonia (Ostwald process)
1923	Methanol synthesis from CO/H <sub>2</sub>
1935	<i>Acetobacter suboxydans</i> for selective oxidation for vitamin C production
1936	Catalytic cracking of heavy oil fractions
1938	Liquid fuels from CO/H <sub>2</sub> (Fischer–Tropsch synthesis)
1939	Hydroformylation
1962	Synthesis gas from methane
1969	Immobilized acylase for optically pure amino acids
1975	Catalytic cleaning of automotive exhaust gases
1977	Higher olefins from ethylene (Shell higher olefin process)
1984	Enantioselective catalysis for menthol and others
1985	Enzymes are active in organic solvents
1993	Genetic engineering for improvement of enzymes
1996	Enantioselective hydrogenation for (S)-metolachlor production

production of chemicals, tremendous research efforts have been devoted over the last 100 years to developing improved catalysts and optimized catalytic processes. Table 2.3.2 shows an overview of important discoveries in catalysis research that have led to major technical applications. Given the great advances in spectroscopic and analytic techniques, in modeling, and in materials synthesis in the last 10 years, many more success stories and innovations can be expected from the “art of catalysis” in the years to come.

### 2.3.2 Homogeneous, Heterogeneous, and Biocatalysis

Many different compounds can act as a catalyst. For different reasons – that will be treated in more detail below – the use of solid materials as catalysts (so-called heterogeneous catalysis) plays the most important role in chemical technology. Solid contacts catalyze about 80% of all catalytic processes. Compounds that are dissolved in the reaction phase (so-called homogeneous catalysts) catalyze about 15% of all catalytic processes. Biocatalysts contribute the remaining 5%. They are applied as a soluble enzyme or as whole cell. Both types may be immobilized on a

support, forming a heterogeneous catalyst with slightly different properties than the heterogeneous catalyst described below.

When it comes to industrial catalysis, easy processing is the characteristic strength of heterogeneous catalysis compared with homogeneous catalysis. This advantage concerns mainly the isolation of a catalyst-free product combined with an easy recovery and recycling of the precious catalyst (note that catalytically active metals are usually rare and expensive). In the case of heterogeneous catalysis, the separation and isolation step is usually straightforward. Catalyst and products are already present in two different phases; separation by simple filtration is the method of choice.

Heterogeneous catalysis is a surface phenomenon. Therefore, a highly active heterogeneous catalyst requires a large specific surface area. As compact particles have specific surface areas below 1 m<sup>2</sup> g<sup>-1</sup>, most heterogeneous catalysts are porous in nature. Note that, in theory, the specific surface of compact materials could reach higher values for very small particles (about 100 m<sup>2</sup> g<sup>-1</sup> for  $d_p > 100$  nm; see Figure 4.5.1). However, it is very difficult and mostly impossible to handle such small particles in a catalytic reactor due to the resulting high pressure drop. Therefore, compact, nonporous catalyst are only found in applications where specific selectivity problems linked to the formation of consecutive reaction products make it unfavorable to realize longer residence times of the desired intermediate product in a porous solid or where the external mass transfer dominates the effective reaction rate, and thus the reactant concentration is nearly zero at the external surface (and also in the pores, if a porous catalyst would be used). A particular important example of the latter kind is ammonia oxidation to NO (Section 6.4).

Typical porous catalysts are characterized by specific surfaces of 100–1000 m<sup>2</sup> g<sup>-1</sup>. An important class of porous materials for heterogeneous catalysis is zeolites. These crystalline, hydrated aluminosilicates consist of a very regular three-dimensional, polyanionic network of SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra linked through oxygen atoms. The void spaces in zeolite networks have dimensions on the scale of the reactant and product molecules, which allow selective diffusion of molecules into the catalyst pores (“form selectivity”). Zeolites play a very important role in refinery and petrochemical processes, for example, catalytic cracking, isomerization, or alkylation. While in catalysis with pure zeolites the porous material acts itself as catalyst, other important classes of catalysts use porous materials such as alumina or silica to load it with the catalytically active transition metal. By a

fine dispersion of the active metal crystallites (ideally in their most active size) on the supporting porous solid, a very effective usage of the expensive metal component can be realized.

In contrast to heterogeneous catalysis, classical homogeneous catalysis takes place in the bulk of a solvent. However, due to the lack of a phase boundary, it is much more complicated in this case to isolate the fully dissolved transition metal complex from the desired reaction product. Often, distillation fails due to the thermal instability of the dissolved catalyst or the fact that unselective reactions occur in the bottom of the distillation column. Catalyst recovery and recycling strategies for homogeneous catalytic processes can therefore sometimes be rather complicated and involve steps like chemical treatment of the catalyst, salt precipitation, cosolvent addition, and solvent distillation steps. However, these difficult aspects of catalyst separation/recycling and thermal lability should not hide the fact that homogeneous catalysis offers several important advantages compared with heterogeneous catalyzed reactions. The applied catalyst complex is usually molecularly defined and can be rationally optimized by ligand modification. In principle, every metal atom is active in the reaction and displays the same reactivity. This allows mild reaction conditions ( $T$  usually  $<200\text{ }^{\circ}\text{C}$ ), leading often to high selectivities. Table 2.3.3 displays in a generalized manner the specific advantages and disadvantages of homogeneous and heterogeneous catalysts.

**Table 2.3.3** Homogeneous versus heterogeneous catalysis.

	Homogeneous catalysis	Heterogeneous catalysis
Selectivity	High, molecularly defined active centers	Variable, often undefined active sites
Reaction conditions	Mild, $T < 200\text{ }^{\circ}\text{C}$	Often harsh
Sensitivity toward poisons	Low	High
Variability of steric and electronic properties	Possible by ligand effects	Difficult
Understanding	Plausible under random conditions	Often very difficult ( <i>pressure and material gap</i> )
Catalyst/product separation	Difficult, often expensive	Straightforward
Robustness, thermal stability, service life	Often low	Often high

These points become understandable given that it is still somewhat impossible to synthesize a catalytic solid of technical relevance in which each active center is exactly in the same steric environment and has exactly the same electronic properties. In technical catalysis, the support is not an ideal surface but the product of a more or less defined precipitation, particle growth, or particle agglomeration process during its synthesis. Thus, the support is not uniform and contains many different sites at which the catalytic metal ends after the metal loading process (e.g. by impregnation, infiltration; see Section 2.3.3 for details of the catalyst preparation process). Of course these different sites at the faces, edges, or corners of the support will provide a different “ligand effect” to the supported metal. The situation is even more complex as very often defects, kinks, or other irregularities of the solid surface exert a very strong influence on the electronic properties of a catalytic metal deposited nearby. In the light of all these aspects, it is not surprising that in many heterogeneous catalysts only a minor part of the metal loading is responsible for the largest part of the catalytic activity observed.

In contrast, homogeneous catalysts are in most cases transition metal complexes, purified by washing, crystallization, or chromatography steps and used as pure compounds. These complexes are applied in a homogeneous and uniform solvent environment during catalysis. Consequently, every metal atom experiences, in principle, exactly the same electronic and steric effects, leading to an extremely well-defined reactivity. This is why homogeneous catalysis is usually applied in cases where high selectivity is needed (e.g. due to high feedstock value) and the selectivity pattern is complex (e.g. complex regio- or stereoselective reactions). Table 2.3.4 displays important examples of homogeneous catalyzed processes. Figure 2.3.4 displays the different chemical natures of typical homogeneous and heterogeneous catalysts for the examples of a chiral Ni complex for homogeneous catalyzed, asymmetric C–C linkage reactions and a schematic representation of a heterogenous, precious metal on a support catalyst.

An elegant way to combine the advantages of homogeneous catalysis with an efficient strategy for catalyst recycling is liquid–liquid biphasic catalysis: only one phase contains the dissolved catalyst, allowing easy product separation by phase separation (Figure 2.3.5). After decantation, the catalyst phase can be recycled without further treatment.

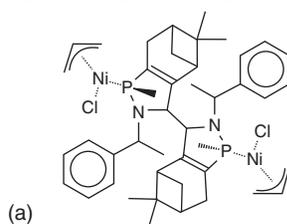
However, the right combination of catalyst, catalyst solvent, and product is crucial for the success of biphasic catalysis (Drießen-Hoelscher et al. 1998). The catalyst solvent has to provide excellent solubility

**Table 2.3.4** Important examples of homogeneous catalysis in the chemical industry.

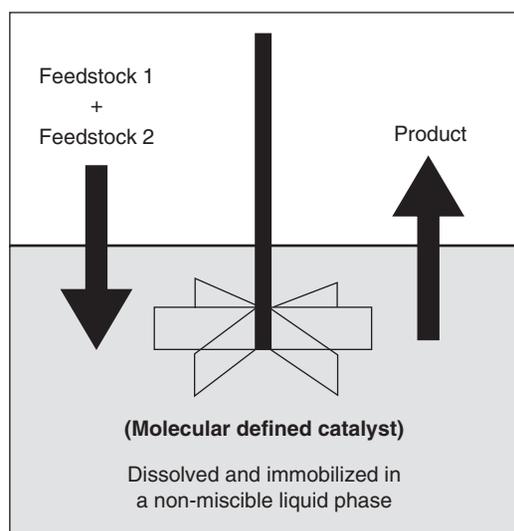
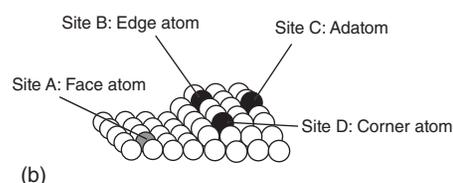
Process	Catalyst	Capacity (kt a <sup>-1</sup> )
Hydroformylation	HRh(CO) <sub>n</sub> (PR <sub>3</sub> ) <sub>m</sub>	3690
	HCo(CO) <sub>n</sub> (PR <sub>3</sub> ) <sub>m</sub>	2445
Hydrocyanation	Ni[P(OR <sub>3</sub> ) <sub>4</sub> ]	~1000
Ethene oligomerization (SHOP)	Ni(P <sup>o</sup> O)-chelate complex	870
Acetic acid (Eastman Kodak)	HRhI <sub>2</sub> (CO) <sub>2</sub> /HI/CH <sub>3</sub> I	1200
Acetic acid anhydride	HRhI <sub>2</sub> (CO) <sub>2</sub> /HI/CH <sub>3</sub> I	227
Metolachlor (Novartis)	[Ir(ferrocenyl-diphosphine)]I/H <sub>2</sub> SO <sub>4</sub>	10
Citronellal (Takasago)	[Rh(binap)(cod)]BF <sub>4</sub>	1.5
Indenoxide (Merck)	Chiral Mn(salen) complex	0.6
Glycidol (ARCO, SIPSY)	Ti(O <sup>i</sup> Pr) <sub>4</sub> /diethyl tartrate	Several tons

**Figure 2.3.4** Typical transition metal complex for homogeneous catalysis (a). Schematic view of the surface of a real precious metal on a catalyst support (b).

Ligand design in homogeneous catalysis:



Heterogeneous catalysis:

**Figure 2.3.5** Schematic view of a liquid–liquid biphasic catalytic reaction; note that the diagram shows the stirrer when it is switched off for phase separation.

for the catalyst complex for full catalyst immobilization but must not compete with the substrate for the free coordination sites at the catalytic center. Furthermore, a reaction system providing a miscibility gap throughout the whole conversion range is required. Finally, another prerequisite of liquid–liquid biphasic

catalysis is the provision of a catalyst solvent with enough solubility for the feedstock to allow sufficient reactant concentration in the reaction phase and thus sufficient reaction rate. A technical example of liquid–liquid biphasic catalysis is given in Section 6.15. The same section discusses modern aspects of solvent development and advanced solvents for the application in liquid–liquid multiphase catalytic processes.

Biocatalytic processes have been used for centuries, especially in the preparation of food and beverages. In the last century, biocatalysis were introduced into industrial production processes as well (Table 2.3.5). When speaking about biotechnological processes, one has to distinguish between fermentation processes where products are synthesized by microorganisms (bacteria, yeasts) or higher cells (animal cells, plant cells) from components in the fermentation broth such as carbohydrates, amino acids, and trace elements. Product examples are amino acids, vitamins, pharmaceuticals, or recombinant pharma proteins such as erythropoietin or factor VIII. On the other hand, the term biocatalysis or biotransformation is used for processes where a starting material is converted into the desired product in one step only. This can be done using either (partly) purified enzymes or whole cells. Product examples range from bulk

**Table 2.3.5** Important examples of biocatalysis in the chemical industry.

Process/product	Catalyst	Capacity (kt a <sup>-1</sup> )
Kinetic resolution of amino acids	Amino acylase	>1
Hydrocyanation	Hydroxynitrile lyase	0.01
Kinetic resolution of amines	Lipase	>1
6-Aminopenicillanic acid	Penicillin amidase	10
Acrylamide	Nitrile hydratase	>30
High fructose corn syrup	Glucose–fructose isomerase	>1000

chemicals such as acrylamide, fine chemicals, and chiral synthons such as chiral alcohols to food ingredients such as high fructose corn syrup. In addition, enzymes play an important role in daily life: “stone washed” jeans are obtained by bio-bleaching, citrus fruits are peeled with the help of pectinases, and enzymes are ingredients in washing powders.

Owing to evolutionary processes, biocatalysts function at low temperatures (10–70 °C) and ambient pressure and in an aqueous environment at a neutral pH. This may require different handling than for a heterogeneous or homogeneous catalyst as described above. However, enzymes in native form can be applied in liquid–liquid biphasic catalysis, normally with water or buffer as the phase containing the biocatalyst. Zaks and Klivanov demonstrated in the 1980s that enzymes also work in almost water-free organic solvents. A minimum amount of water – best described by the physicochemical water activity – has to be present to maintain the enzyme’s structure and activity. However, enzymes do not dissolve in organic solvents and are used either adsorbed or coupled to an insoluble support, mostly organic polymers. When an immobilized enzyme is used, mass transport limitations may occur and must be treated accordingly. The so-called Michaelis–Menten kinetics is a form of saturation kinetics found for most enzymes but is also observed for other homogeneously soluble catalysts.

### 2.3.3 Production and Characterization of Heterogeneous Catalysts

In principle, solids found in nature can display activity as heterogeneous catalysts (e.g. iron ores are applied in high temperature Fischer–Tropsch catalysis). However, after 100 years of intense research in catalysis, it has been found that in most cases synthetic materials

are more suitable as the reproducibility of their synthesis is higher and their specific properties can be adjusted by the synthetic procedure.

The most important method to produce catalyst supports or solid catalysts is *precipitation*. The precipitation process is realized by controlled addition of a precipitation reagent (very often a change of pH by addition of acid or base). Depending on the desired composition of the catalyst material, coprecipitation of more than one component is frequently applied. An alternative process is the precipitation of metal salts onto preformed support particles.

Precipitation is a complex sequence of supersaturation, seeding, and coagulation. All three steps determine particle size and size distribution of the obtained particles. The process is strongly dependent on the exact precipitation conditions and is still difficult to model. Table 2.3.6 displays examples of technically important catalysts or catalyst supports produced by precipitation.

A few industrial important heterogeneous catalysts are prepared by *melt processes*. Examples are the Fe catalyst for the Haber–Bosch process and the Pt/Rh net for the ammonia oxidation in the Ostwald process (see also Section 6.4). Melting is also the initial process step for the preparation of Raney-nickel and Raney-copper catalysts. For these catalysts an alloy of Ni/Cu and Al is prepared by melting. This alloy is later treated with NaOH to dissolve the Al from the solid to create pores and reactive surface sites. Raney-Ni

**Table 2.3.6** Important examples of catalysts or catalyst supports produced by precipitation.

Material	Application examples in catalysis
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Support for CoO–MoO <sub>3</sub> in the catalytic dehydrosulfurization of refinery cuts; catalyst in the Claus process; catalyst for the dehydration of alcohols
SiO <sub>2</sub>	Support for V <sub>2</sub> O <sub>5</sub> in the oxidation of SO <sub>2</sub> ; support for Pt, Pd, and Ni for catalytic hydrogenation reactions
Fe <sub>2</sub> O <sub>3</sub>	Catalyst for Fischer–Tropsch synthesis; catalyst component for the ethylbenzene dehydrogenation catalyst
TiO <sub>2</sub>	Catalysts component for the reduction of nitrogen oxides with NH <sub>3</sub>
Cu–ZnO/Al <sub>2</sub> O <sub>3</sub>	Catalyst for low pressure MeOH synthesis
(VO) <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	Catalyst for the selective oxidation of <i>n</i> -butane to maleic acid anhydride
Bi <sub>2</sub> O <sub>3</sub> –MoO <sub>3</sub>	Catalyst for the selective oxidation of propene to acrolein

and Raney-copper are very important hydrogenation catalysts.

For the synthesis of zeolites and related compounds, *hydrothermal synthesis* and *sol-gel* processes are of importance. In the hydrothermal synthesis a hydrogel is prepared from the Si and Al sources in an aqueous medium. The latter often contains ammonium salts and detergents as structural modifiers. This gel is later transferred to an autoclave and crystallized at temperatures of up to 200 °C.



Photograph of a homogeneously catalyzed, liquid-liquid biphasic reaction.

In a *sol-gel process*, metal-organic starting materials like triisopropylaluminum, tetrabutoxytitan, and tripropoxyzirconium are applied as starting materials of a controlled hydrolysis and condensation process. In contrast to precipitation, *sol-gel* processes are more complex and more expensive. However, *sol-gel* processes allow the preparation of oxide catalysts in higher purity and with better control of the pore system.

Many catalysts use a precious metal as active component. Owing to the high price of these metals, it is of great importance to prepare a support/catalyst system in such a manner that all metal atoms are fully available at the surface for the reaction (=100% dispersion, 10% of atoms are surface atoms and available for catalysis = 10% dispersion). The most important process by which to achieve a suitable metal loading on a support of choice is *impregnation*. During

*impregnation*, the support is typically contacted with an aqueous solution of a suitable precious metal salt or precursor. After adsorption of the metal component, the solid is isolated, thermally treated, and (often) reduced. Important technical catalysts prepared by *impregnation* are the CoO-MoO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst for the desulfurization of fuels (Section 6.8) and the Pt-Re/γ-Al<sub>2</sub>O<sub>3</sub> catalyst for the isomerization/dehydrogenation of fuels in the platforming process (Section 6.9).

If the catalyst support is an ion-exchange material (e.g. in the case of zeolites), *ion exchange* is another suitable process to load a catalytic active compound on a support. For zeolites, the Na<sup>+</sup> form of the material is often prepared by hydrothermal synthesis. This material is contacted with an electrolyte containing the salt of the intended active compound. By solid isolation, thermal treatment, and often reduction, the active supported catalyst is obtained.

All the processes mentioned above are characterized by the fact that a support is treated with a suitable solution of the precious metal. An alternative preparation method in which a solid reacts with a metal precursor from the gas phase is *metal-organic chemical vapor deposition* (MOCVD). In this process, a volatile metal-organic precursor strikes the hot surface of the support. This contact leads to the immediate thermal decomposition of the surface with formation of a metal species on the support that can be further treated thermally, often under reducing gas atmospheres.

For scientific studies and quality control, detailed characterization of the produced catalytic material is necessary. A key method to test a catalytic material is of course to study its performance in a reaction by a detailed analysis of its reactivity, selectivity, and lifetime. Note in this context that the observable kinetics of a heterogeneous catalyst or a catalyst in any multiphase reaction system is usually a complex interplay of diffusion and reaction processes (for details see Chapter 4).

Apart from catalyst characterization by kinetic investigations, modern catalyst research has a plethora of spectroscopic methods at hand to determine the size, shape, specific surface, porosity, chemical composition, surface composition, and chemical functionality of a heterogeneous catalyst. An overview of the most important methods is given in Table 2.3.7 (Weitkamp and Glaeser 2003). A detailed description of these methods is found in Ertl et al. (2008).

In the context of this textbook, only a few important methods will be described briefly to give an impression of their different measuring principles, the type of information provided, and potential interplay.

**Table 2.3.7** Important spectroscopic and analytic techniques used to characterize heterogeneous catalysts.

Probed property	Technique or method
Chemical composition	AAS, AES, XRF
Phases, phase transitions	XRD, SEM, TGA, DTA, TPR/TPO
Size and form of catalytic particles	SEM, TEM, DLS
Nature, size, and form of metal clusters within the catalyst particles	SEM, TEM, chemisorption (H <sub>2</sub> , O <sub>2</sub> , CO), magnetism, XRD
Internal surface and porosity	Physisorption (N <sub>2</sub> , Ar, He, CO <sub>2</sub> , noble gases) evaluated, e.g. via the BET or QSDFT method, Hg porosimetry, thermoporometry, micro-CT
Functionality/active centers	
Local structure (averaged over particle)	IR, Raman, UV/Vis, NMR, ESR, EXAFS, Müössbauer
Surface structure and composition	XPS, UPS, ISS, SIMS, ETM, AFM
Reactivity	TPD, adsorption of probe molecules (including spectroscopic characterization of adsorbats), catalytic test reactions

For definition of abbreviations, see Notation.

These short descriptions may also illustrate that the comprehensive characterization of a heterogeneous catalyst is a complex task and requires – along with the researcher's expertise – highly sophisticated and often expensive equipment.

*Atomic absorption spectroscopy* (AAS) is used to determine the chemical composition of the metal loading of a supported catalyst. In a sample preparation procedure, the catalyst is treated with very strong and often oxidizing acids to extract all metal atoms as ions in solution. This solution is injected into a spectrometer that gives a quantitative analysis of all metal components in the solution based on the spectral absorption (or emission in the case of Auger electron spectroscopy, AES) in a flame. Note that in this method all dissolvable metal atoms are analyzed, not only the catalytic active surface atoms.

*X-ray diffraction* (XRD) is the method of choice to analyze the crystalline structure of a catalyst or catalyst support. For example, it is the standard procedure used to determine and check the structure of crystalline zeolites after synthesis.

Owing to the importance of the catalyst pore structure for the performance of a catalyst, its determination is also highly important. Total surface

area, total pore volume, and pore size distribution are directly connected values. According to International Union of Pure and Applied Chemistry (IUPAC), pores are defined with respect to their pore diameters  $d_{\text{pore}}$  as micropores ( $d_{\text{pore}} < 2.0$  nm), mesopores ( $2.0 \text{ nm} \leq d_{\text{pore}} \leq 50$  nm), and macropores ( $> 50$  nm).

*Surface analysis via physisorption* is the appropriate technique to analyze the specific surface of a catalyst. The catalyst sample is contacted at different pressures (normally from vacuum to atmosphere) with a gas that physisorbs under appropriate temperature conditions (normally N<sub>2</sub> at 77 K) in a defined manner on its surface. Owing to this physisorption process, the pressure in the sample chamber changes. From this pressure drop, the physisorbed amount of gas per sample mass is determined. The adsorbed amount versus the applied pressure is called the sorption isotherm, and with different models, for example, the most common Brunauer, Emmett, and Teller (BET) model, the available surface can be calculated from the isotherm. Other models like the Barrett, Joyner, and Halenda (BJH) or modern density functional theory (DFT) methods also allow to evaluate the pore size distribution from the same data. Sample preparation, highly defined experimental conditions, and very precise pressure measurements are the key factors for accurate surface analysis. While sorption experiments probe pores in the size range from approximately 0.3 to 100 nm, *mercury porosimetry* is the method of choice to determine the total pore volume and the pore size distribution from 5 nm up to 500  $\mu\text{m}$ . The method pushes liquid mercury under high pressure into the porous material, and the Hg volume accommodated in the solid is monitored as a function of pressure. Following the Kelvin equation, a higher pressure is necessary to push the mercury into smaller pores. Therefore, from the amount of mercury infiltrated into the solid as a function of pressure, the pore size distribution can be obtained.

*X-ray photoelectron spectroscopy* (XPS) is an ultrahigh vacuum spectroscopic technique used to investigate the surface composition and surface structure of a catalyst. X-ray irradiation hits the sample and, by energy absorption of the surface elements, photoelectrons are emitted. The kinetic energy of the latter is determined in an analyzer. The energetic difference between the energy of the incoming X-ray irradiation and the kinetic energy of the photoelectrons determined in the analyzer gives a direct indication of the binding energy the electrons experienced in the element they originate from. In this way, XPS is a quantitative, element specific, oxidation state specific, and surface sensitive characterization method for solid catalysts.

### 2.3.4 Deactivation of Catalysts

During the operational lifetime of most catalysts, their activity decreases. Interestingly, the time period of economic operation can be very different even for commercial catalysts and ranges from a couple of seconds to many years. Table 2.3.8 gives an overview of some important heterogeneous catalyzed reactions, their reaction conditions, deactivation mechanism, possible regeneration options, and lifetime. It can be seen from the table that there is no direct correlation between thermal stress and lifetime.

In most cases, the deactivation of heterogeneous catalysts can be attributed to one of the four processes displayed in Figure 2.3.6.

*Poisoning* is a deactivation pathway in which at least one component of the reaction mixture adsorbs in a very strong – often irreversible – manner to the catalytic active center (Figure 2.3.6a). Kinetically speaking, the number and concentration of catalytic sites for this process reduces over time. In cases in which the catalytic material is characterized by different catalytic centers of different reactivity, the poisoning process can be selective for one sort of center. By selective poisoning experiments it is possible to learn more about the chemical nature of the different

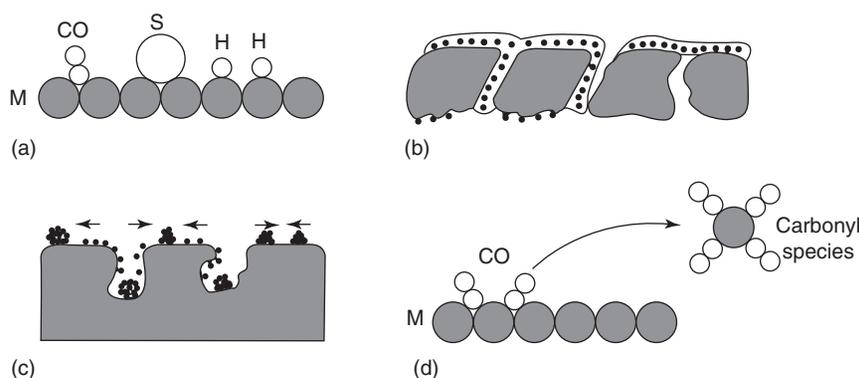
catalytic sites in a material. In technical catalysis, selective poisoning is sometimes used to eliminate unwanted side reactions caused by catalytic sites that are too active, for example, in the case of reforming of heavy fuels (Forzatti and Lietti 1999). Owing to the different reactivities of technical catalysts, the chemical nature of poisoning components can also be very different. Typical poisons for technical important heterogeneous catalysts are displayed in Table 2.3.9 (Weitkamp and Glaeser 2003; Kern and Jess 2006).

*Deposition of residues* or coking is a process in which process components form a solid, nonporous layer on the catalyst surface that prevents the reactants reaching the active sites or even entering the porous structure of the catalyst (Figure 2.3.6b). In terms of kinetic, coking is again a process in which the number of accessible catalyst centers reduces over time. It is frequently observed in high-temperature operations with hydrocarbon feedstocks, for example, in refinery or petrochemical processes. Depending on the temperature, coke is a hydrogen-rich carbon material (“soft coke” formed at low temperatures) or a polyaromatic, hydrogen-poor material (“hard coke” formed at high temperatures). In some refinery and petrochemical processes, coke deposits of up to 20% with respect to the catalyst mass have been reported.

**Table 2.3.8** Typical conditions and catalyst lifetimes for important heterogeneous catalysts.

Process	Catalyst	Reaction conditions	Catalyst lifetime (yr)
NH <sub>3</sub> synthesis	Fe-K <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	450–550 °C 200–500 bar	5–15
Steam reforming of natural gas	Ni-CaO/Al <sub>2</sub> O <sub>3</sub>	500–850 °C 30 bar	2–4
NH <sub>3</sub> combustion	Pt nets	800–900 °C 1–10 bar	0.1–0.5
Catalytic reforming	Pt/Al <sub>2</sub> O <sub>3</sub>	450–550 °C 5–50 bar	0.01–0.5 (coke formation; reversible deactivation) 2–15 (irreversible deactivation)
Catalytic cracking	Zeolites	500–600 °C 1–3 bar	10 <sup>-7</sup> = about 10 seconds (coke formation; reversible deactivation) 0.1 (irreversible deactivation)

**Figure 2.3.6** Schematic view of the four main processes leading to deactivation. (a) Poisoning. (b) Deposition of residues. (c) Sintering. (d) Loss via the gas phase.



**Table 2.3.9** Examples for typical catalyst poisons in industrial catalytic processes.

Reaction	Catalyst	Typical poison
$\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$	Fe	CO
$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$	Ni/ $\alpha$ - $\text{Al}_2\text{O}_3$	$\text{H}_2\text{S}$
$\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}$	Cu–ZnO/ $\text{Al}_2\text{O}_3$	$\text{H}_2\text{S}$ , $\text{AsH}_3$ , $\text{PH}_3$ , HCl
$\text{C}_2\text{H}_4 + 0.5\text{O}_2 \rightarrow \text{C}_2\text{H}_4\text{O}$	Ag/ $\text{Al}_2\text{O}_3$	$\text{C}_2\text{H}_2$
Automotive exhaust gas cleaning	Pt–Rh	Pb, P, $\text{SO}_2$

A convenient strategy to reduce coke formation is the addition of hydrogen or water vapor to the reactor. Hydrogen hydrogenates coke precursors to fluid hydrocarbons. This is the reason why in the reforming of heavy fuels (platforming), the reactor is operated at  $\text{H}_2$  pressures of up to 40 bar even though a low pressure would be favorable to shift the dehydrogenation equilibrium to the desired aromatic products (see also Section 4.2).

Once the catalyst is deactivated by coke, it is usually possible to perform an oxidative regeneration step to remove the carbon from the catalytic surface. Special care is necessary in this process, however, to keep the temperature in this strongly exothermic step ( $\Delta_{\text{R}}H = 393 \text{ kJ mol}^{-1}$ ) below the critical temperature at which the catalyst starts to suffer from the sinter processes (e.g.  $T_{\text{sinter}}$  is  $550^\circ\text{C}$  in the case of the Pt/ $\text{Al}_2\text{O}_3$  catalyst for heavy fuel reforming). Therefore, the engineering of an optimized catalyst regeneration process requires detailed knowledge of the kinetics of coke combustion and the development of quantitative models for the prediction of concentration and temperature profiles in the reactor (see Section 6.9.3 and Kern and Jess 2006 for details).

*Sintering* describes a thermally induced surface diffusion process in which the number of active catalytic centers reduces by an agglomeration process (Figure 2.3.6c). Sintering is mainly observed for supported metal or oxide catalysts. Two different mechanisms have been suggested for sintering (Forzatti and Lietti 1999): the migration of single metal atoms that are captured by particles, leading to particle growth, and the migration of small particles followed by agglomeration to bigger particles. As a rule of thumb, metal particles can start to undergo sintering at temperatures of  $0.3$ – $0.5 T_{\text{melt}}$ , depending on their particle size. Stabilizers in the catalyst formulation have been found to prevent or slow down sintering. Sintering is mostly irreversible, and the sintered catalyst has to be replaced by a fresh one.

*Loss via gas phase* occurs only if at least one of the catalyst species on the surface shows a relevant vapor

pressure under the reaction conditions (Figure 2.3.6d). Note that during a catalytic operation, for example, in the presence of impurities, volatile catalyst species may form that are not part of the catalytic cycle. Typical volatile complexes that can form under catalytic conditions in technical reactors are metal carbonyls. Another important example of catalyst loss via the gas phase is the catalytic oxidation of ammonia in the Ostwald process (Section 6.4). Here the catalyst, a nonporous Pt/Rh net, reacts at the very high reaction temperatures of  $900^\circ\text{C}$  with  $\text{O}_2$  to give  $\text{PtO}_2$  which is volatile enough under these harsh conditions to leave the reactor via the gas phase (Hagen 1999). By installation of Pd/Au wires behind the Pt/Rh net, up to 60% of the volatile precious metal vapor can be recondensed.

Catalyst deactivation also occurs in homogeneous catalysis. Here, similarly, catalyst poisoning means that one component from the reaction mixture coordinates in a very strong or even irreversible manner to the dissolved catalytic center. A major catalyst deactivation route in homogeneous catalysis is also thermal degradation of the active metal complex. To understand this phenomenon we have to take into account that hardly any organometallic transition metal complex is stable beyond  $200^\circ\text{C}$ , with many interesting complexes showing slow degradation even at much lower temperatures. Another very important deactivation route is the reaction of components and impurities with the ligand in a way that affects the ligand's ability to remain coordinated to the metal (e.g. the oxidation of phosphine complexes by traces of oxygen in the reaction system). Coking, sintering, and evaporation of catalyst components are irrelevant in most homogeneously catalyzed reactions, mainly due to the much lower-temperature level in these catalytic reactions.

The deactivation of a catalyst with activity  $a_{\text{cat}}$  (here dimensionless, that is, relative to the initial activity) occurs over time. To obtain manageable equations to describe in a quantitative manner catalyst deactivation, it is useful to define a rate of deactivation  $r_{\text{deact}}$  (dimensionless, i.e. the ratio of the actual reaction rate to the initial rate) that may be equivalent to the reduction of the number of active sites  $N_{\text{act}}$  (relative to the initial number) over time, Eq. ((2.3.7)). Note that  $t'$  is the time on stream of the catalyst, which may be different to the reaction time:

$$r_{\text{deact}} = \frac{da_{\text{cat}}}{dt'} = \frac{dN_{\text{act}}}{dt'} \quad (2.3.7)$$

In most cases  $r_{\text{deact}}$  will depend on the temperature  $T$ , the concentration of deactivating components  $c_{\text{deact}}$ , and/or on the activity  $a_{\text{cat}}$  itself (with  $k_{\text{deact}}$ ,  $k_{0,\text{deact}}$  and  $E_{A,\text{deact}}$  as rate constant, pre-exponential factor and activation energy, respectively, of the

deactivation). Consequently,  $r_{\text{deact}}$  may be expressed in quantitative terms as

$$\begin{aligned} r_{\text{deact}} &= k_{\text{deact}} f(a_{\text{cat}}, c_{\text{deact}}) \quad \text{with } k_{\text{deact}} \\ &= k_{0,\text{deact}} e^{-\frac{E_{A,\text{deact}}}{RT}} \end{aligned} \quad (2.3.8)$$

In the least complicated case, a power law rate expression can be applied:

$$r_{\text{deact}} = -\frac{da_{\text{cat}}}{dt'} = k_{\text{deact}} a_{\text{cat}}^n c_{\text{deact}}^m \quad (2.3.9)$$

For example, in a pure sintering process, no deactivating component is considered ( $m = 0$ ), and the deactivation is first order with regard to the (actual) remaining activity. Thus we obtain after integration for  $a_{\text{cat}}(t')$ :

$$a_{\text{cat}}(t') = e^{-k_{\text{deact}} t'} \quad (2.3.10)$$

To determine the reaction rate  $r$  of a reaction of interest, we can use  $a_{\text{cat}}(t')$  as a multiplicative term, with  $r_0$  being the initial rate of the fresh catalyst:

$$r = r_0 a_{\text{cat}}(t') \quad (2.3.11)$$

For an irreversible reaction of reactants A and B (with the initial relative activity  $a_{\text{cat}}(t' = 0) = 1$ ), and assuming power law first-order kinetics regarding both reactants A and B, we obtain for this example of a catalytic reaction under deactivation by a sintering process the following expression (with  $k$  as the initial rate constant of the reaction and  $k_{\text{deact}}$  as the rate constant of deactivation):

$$r = k c_A c_B e^{-k_{\text{deact}} t'} \quad (2.3.12)$$

Of course, depending on the assumption for the underlying catalyst deactivation mechanism, the parameters  $n$  and  $m$  of Eq. ((2.3.9)) may have different values, and, consequently, different equations can occur. Note that for catalyst poisoning by a reaction, the situation in the reactor can become rather complicated. For example, in a tube reactor, the catalyst deactivation process becomes then a function of the position in the tube.

### 2.3.5 Future Trends in Catalysis Research

Future trends in catalysis research can be related to the relevant application areas for industrial catalysts. New challenges arise from, for example, changing raw material availability and quality, new economic and even political boundary conditions, or new customer needs. These developments promote in many cases the search for new and better catalysts, which makes catalyst research highly important for sustainable economic growth. Important research topics within the actual catalyst development and optimization efforts are given below (Beller et al. 2010). The examples have been grouped according to

the four main application areas of industrial catalysts (see also Section 2.3.1):

#### Environmental catalysis:

- Better catalysts for cleaning water (e.g. nitrates from groundwater, catalytic degradation of pharmaceuticals from hospital wastewaters);
- Better catalysts for the degradation/decomposition of toxic and dangerous molecules (e.g. hydrodechlorination of chlorinated hydrocarbons, catalytic oxidation of toxic waste);
- Better catalysts for the decomposition of greenhouse gases (e.g.  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ ) and hydrocarbons from industrial flue gas streams;
- Reduction of the precious metal content in automotive exhaust gas catalysts;
- Reduction of the start-up temperature of exhaust gas oxidation catalysts;
- Long-term stable  $\text{NO}_x$  storage catalysts with a wide temperature window of operation.

#### Catalysts for refinery and energy applications:

- Catalytic refinery technologies (cracking, isomerization, dehydrosulfurization, hydrogenation, etc.) that can work efficiently with poor crude qualities (very heavy, high in sulfur, high contents of N, P, and metals);
- Development of catalysts for the direct conversion of alkanes (e.g. methane into aromatics or olefins; alkane oxidation, alkane dehydrogenation);
- Development of catalysts for the efficient transformation of components from coal (e.g. more efficient coke hydrogenation catalysts, S-resistant catalysts for coal gasification);
- Development of efficient catalysts for biorefinery concepts (e.g. depolymerization of cellulose, depolymerization of lignin, selective de-functionalization and re-functionalization of biogenic raw materials; note that biomass is rich in potential catalyst poisons, such as S, N, P);
- Better catalysts for the selective transformation of syngas ( $\text{CO}/\text{H}_2$ ) into fuels, olefins, and alcohols and development of catalysts for the transformation of  $\text{CO}_2$  into fuels or fuel equivalents (e.g. methane, methanol);
- Improvement of catalysts for the decentralized production of hydrogen from gas, oil, coal, and biomass (by reforming and water-gas shift catalysis) or water (by electrolysis or by photoelectrocatalysis).

#### Catalysts for the production of polymers and materials:

- Development of catalysts and catalytic processes for monomer production from gas, coal, or biomass;

- Better catalysts for the production of polymers, for example, higher tolerance against feedstock impurities and polar functional groups and better control of microstructure and morphology;
- Catalysts for the manufacture of biodegradable polymers.

#### Catalysts for chemical synthesis:

- New catalyst technologies for sustainable and selective functionalization of aromatic compounds, for example, introduction of hydroxyl, amino, carbonyl, and carboxyl groups;
- Catalytic technologies that combine the advantages of homogeneous and heterogeneous catalysis;
- Catalytic technologies that combine chemo- and biocatalytic steps;
- Catalytic technologies for chemical synthesis from renewable feedstocks.

Apart from these application related aspects, there are also several new methodologies in modern catalysis research that have already demonstrated their importance for the development of more efficient catalysts or processes. These include the following technologies:

- High-throughput experimentation;
- Multifunctional reactors (catalytic membrane reactor, reactive distillation);
- Catalytic microreactor technology;
- Advanced solvents and materials in catalytic systems (e.g. ionic liquids,  $\text{scCO}_2$ , metal-organic frameworks, nanostructures as catalyst supports, hierarchical materials as catalyst supports);
- *In situ* methods for catalyst monitoring or characterization;
- Multiscale modeling and simulation in catalysis.

#### Summary of Section 2.3 (Take-Home Messages)

- Catalysis is of **greatest relevance for chemical technology** because about 90% of all chemical processes work with the help of at least one catalyst.
- Catalytic reactions are characterized by a **reaction sequence** in which one reactant (the catalyst) is reformed in the final reaction step in the same stoichiometric amount as it was added (**catalytic cycle**). The number of cycles that a catalyst can undergo prior to its deactivation is a very important performance indicator in catalysis. This dimensionless characteristic number for each catalyst is called the **TON** and describes the catalyst's stability and lifetime.

- An important property of a catalyst is also its **ability to enhance the reaction rate** of a chemical reaction (activity). This can be characterized (mainly for enzymatic and homogeneous catalysis) by the number of cycles per time, the **TOF**. Alternatively, the catalyst activity can be given by the **reaction rate** referenced to some characteristic catalyst property, for example, the mass of a solid catalyst.
- More important than the rate-accelerating effect is the ability to **favor a specific reaction pathway** (selectivity) in the case of several thermodynamically possible pathways.
- Many different compounds can act as a catalyst. The use of solid catalysts (**heterogeneous catalysis**) plays the most important role in chemical technology. Solid contacts catalyze about 80% of all catalytic processes. Compounds that are dissolved in the reaction phase (**homogeneous catalysts**) catalyze about 15% of all catalytic processes. **Biocatalysts** contribute the remaining 5%.
- Heterogeneous catalysis is a **surface phenomenon**. Therefore, a highly active heterogeneous catalyst requires a large specific surface area. Typical porous catalysts have specific surface areas of  $100\text{--}1000\text{ m}^2\text{ g}^{-1}$ .
- Homogeneous catalysis and biocatalysis take place in the bulk of a solvent, which makes it complicated to separate the dissolved transition metal complex from the desired product. An elegant way to combine the advantages of homogeneous catalysis with an efficient way of catalyst recycling is **liquid-liquid biphasic catalysis**.
- During the operational lifetime of most catalysts, their activity decreases by **deactivation**. The time period of economic operation can be very different even for commercial catalysts and ranges from a couple of seconds to many years. Catalyst deactivation of heterogeneous catalysts can be attributed four processes:
  - **Poisoning**, in which a component of the reaction mixture adsorbs strongly;
  - **Coking**, whereby a solid carbon-rich layer is formed on the catalyst surface under high-temperature operations with hydrocarbon feedstocks;
  - **Sintering**, where the number of active centers is reduced by agglomeration;
  - **Loss via gas phase**, if one of the catalyst species shows a relevant vapor pressure under the reaction conditions. Typical volatile complexes that can form under catalytic conditions are metal carbonyls.

## 3

## Thermal and Mechanical Unit Operations



Distillation towers of ethylene plant in Secunda, South Africa. Source: Courtesy of SASOL.



Control valve of a urea plant. Source: Courtesy of Uhde, Germany.

In this chapter, the following thermal and mechanical unit operations will be examined.

### 3.1 Properties of Gases and Liquids

Ideal and real gas, heat capacity, Joule–Thomson effect, physical transformations of pure substances, and transport properties.

### 3.2 Heat and Mass Transfer in Chemical Engineering

Heat conduction, convection, boiling heat transfer, radiation, transient heat transfer, forced flow in pipes and packed beds, mass transfer by diffusion, and diffusion in porous solids.

### 3.3 Thermal Unit Operations

Heat exchangers, distillation, absorption, liquid–liquid extraction, adsorption, liquid–solid extraction, crystallization, and membranes.

### 3.4 Mechanical Unit Operations

Conveyance of fluids; pressure loss in tubes; fixed, fluidized, and entrained beds; compressors and pumps; mixing of fluids; and separation of solids from fluids.

Physical data of pure substances such as the phase behavior or the properties for transport of mass and heat are needed in many areas of chemical technology, ranging from thermal unit operations such as distillation up to catalytic processes that are frequently influenced by diffusion and heat transfer. In this chapter the following data on chemical media will be covered:



Typical technical gases. Source: Courtesy of Linde Engineering, Germany.

- Real gases deviate from ideal gas behavior at higher pressures and lower temperatures, which has to be accounted by real gas equations and the real gas factor  $z$ .
- The heat capacity is important, for example, to calculate the increase of temperature, if energy is released by a chemical reaction.
- During adiabatic expansion of a real gas, the temperature may decrease (*Joule–Thomson effect*), which is used for liquefaction of gases, for example, for air separation.
- Depending on pressure and temperature, phase transitions such as vaporization, liquefaction, and melting take place.
- If  $p$  and  $T$  exceed certain critical values, an isothermal change of  $p$  or an isobaric change of  $T$  no longer leads to a change of aggregation (supercritical stage).
- Gradients of temperature or concentration lead to heat and mass transfer by conduction and diffusion. Thus it is important to know the transport properties of gases and liquids such as the diffusivity and thermal conductivity.
- For velocity gradients in fluids, the flow of momentum is determined by the viscosity.



Plant for liquefaction of natural gas in Kollsnes, Norway. Source: Courtesy of Linde Engineering, Germany.

## 3.1 Properties of Gases and Liquids

### 3.1.1 Ideal and Real Gas

The kinetic theory of gases assumes that gas molecules or atoms occupy a negligible fraction of the total volume of the gas and that the forces of attraction between gas molecules are zero. Such a gas is called a perfect or ideal gas, and the equation of state is the “ideal gas law”:

$$pV = nRT \quad (3.1.1) \quad \blacktriangledown$$

which was developed based on the experiments of Robert Boyle, Edme Mariotte, and Joseph Gay-Lussac and later by calculations made by Amedeo Avogadro (see box). This equation relates the absolute pressure  $p$  ( $\text{N m}^{-2}$ ), the volume  $V$  ( $\text{m}^3$ ), the amount of substance  $n$  (mol), the temperature  $T$  (K not  $^{\circ}\text{C}$ ), and the ideal gas constant  $R$  ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ).

#### Originators of the Ideal Gas Law

**Robert Boyle** (1627–1691) was an Irish chemist, physicist, and inventor who discovered the inverse relationship of volume and pressure in gases (*Boyle’s law*,  $V \sim 1/p$ ) and was the first to publish it in 1662. He made investigations into the expansive force of freezing water, on crystals, on electricity, and on hydrostatics, studied the chemistry of combustion, and conducted experiments in physiology.

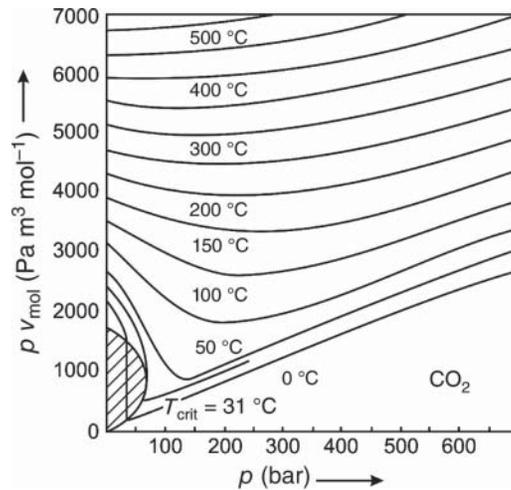
**Edme Mariotte** (1620–1684), a French physicist and priest, discovered *Boyle’s law* independently of Boyle

in 1676, so the law is also known as *Boyle–Mariotte’s* law. In 1660, *Mariotte* also discovered the eye’s blind spot. He worked on many subjects, such as the motion of fluids, the nature of color, the notes of the trumpet, the barometer, the fall of bodies, and the freezing of water.

**Joseph Louis Gay-Lussac** (1778–1850) was a French chemist and physicist. He is known mostly for two laws related to gases. In 1802, *Gay-Lussac* formulated the law that at constant pressure the volume of a gas increases by the same factor as its temperature ( $V \sim T$ ). This law was first published by *Gay-Lussac*, but he referenced an unpublished work of **Jacques Charles** (1746–1823, French scientist and balloonist) from around 1787. This reference has led to the law being also known as *Charles’s* law. The second law of *Gay-Lussac* states that the pressure of a gas at fixed volume is directly proportional to its temperature ( $p \sim T$ ). *Gay-Lussac* is also well known for his hot-air balloon ascent with *Jean-Baptiste Biot* (Section 3.2.1.5) to a height of 6 km in an early investigation of the Earth’s atmosphere (1804). In 1805, together with his friend and scientific collaborator *Alexander von Humboldt*, he also discovered that the composition of the atmosphere does not change with decreasing pressure and increasing altitude, respectively.

**Amedeo Carlo Avogadro** (1776–1856) was an Italian chemist, most noted for his contributions to the theory of molarity and molecular weight. In 1811, he declared the hypothesis of what we now call *Avogadro’s* law: equal volumes of gases, at the same temperature and pressure, contain the same number of molecules. Hence, the gas laws of *Boyle*, *Mariotte*, and *Gay-Lussac* in combination with *Avogadro’s* law can be generalized by the ideal gas law. The *Avogadro* constant  $N_A$ , that is, the number of molecules in one mol is  $6.022 \times 10^{23} \text{ mol}^{-1}$ , is named in his honor. The numerical value of  $N_A$  was first estimated in 1865 by **Johann Josef Loschmidt** (1821–1895), an Austrian scientist.

$N_A$  is related to the universal gas constant  $R$  by  $R = N_A k$  with  $k$  (and  $R$ , respectively) as the fundamental constant relating temperature to energy (Section 3.1.4). **Max Planck** (1858–1947) first introduced  $k$  and gave an accurate value for it in his derivation of the law of blackbody radiation in 1900. The constant  $k$ , although **Ludwig Boltzmann** himself never introduced it, was named the Boltzmann constant, as he was the first (1877) who stated that the entropy of a gas is proportional to the logarithm of the number of microstates a gas can occupy with  $k$  as the factor of proportionality.



**Figure 3.1.1**  $p v_{\text{mol}}$  versus  $p$  plot for  $\text{CO}_2$  (dashed area: liquid). Source: Values from Jakubith (1998).

Equation (3.1.1) may also be written in terms of the molar volume,  $v_{\text{mol}}$  ( $\text{m}^3 \text{ mol}^{-1}$ ), as

$$p v_{\text{mol}} = RT \quad (3.1.2)$$

No gas is truly ideal, but many gases follow the predictions of the ideal gas law at normal temperature and pressure (1.013 bar,  $0^\circ\text{C}$ ) within 5% deviation. At lower temperatures or higher pressures, the behavior of a real gas may significantly deviate from that of an ideal gas, as shown in Figure 3.1.1 for the example of  $\text{CO}_2$  by the plot of  $p v_{\text{mol}}$  versus  $p$ . The ideal gas equation predicts that this plot should give horizontal lines that only depend on temperature, but we see by the experimental data that this is not the case (see also Example 3.1.1).

In 1873, Johannes van der Waals (see box) proposed a modification of the ideal gas law:

$$\left( p + \frac{a}{v_{\text{mol,real}}^2} \right) (v_{\text{mol,real}} - b) = RT \quad (3.1.3) \quad \nabla$$

**Johannes Diderik van der Waals** (1837–1923) was a Dutch scientist famous for his work on the relationship between the pressure, volume, and temperature of gases. He was the first to realize the necessity of taking into account the volume of molecules and the intermolecular forces, now generally named after him as van der Waals forces. His career was quite unusual: after he had studied mathematics and physics, he became at first “only” director of a secondary school (1866). In 1873, he obtained a doctoral degree for his thesis “On the continuity of the gas and liquid state,” for which he got the Nobel Prize in Physics (1910). In 1876, he was appointed the first professor of physics at the University of Amsterdam.

**Table 3.1.1** Van der Waals constants of selected gases.

Gas	$a$ (Pa m <sup>6</sup> mol <sup>-2</sup> )	$10^{-5}b$ (m <sup>3</sup> mol <sup>-1</sup> )
He	0.003	2.38
H <sub>2</sub>	0.025	2.67
N <sub>2</sub>	0.141	3.92
CO	0.151	4.00
O <sub>2</sub>	0.138	3.19
CH <sub>4</sub>	0.229	4.30
CO <sub>2</sub>	0.365	4.28
NH <sub>3</sub>	0.422	3.71

Source: Data from Jakubith (1998).

The van der Waals equation can describe the real gas behavior in sufficient approximation over a wide range of temperatures and pressures. It takes into account the molecular size as well as the molecular interaction forces by the introduction of two additional terms: (i) As the attractive forces tend to hold the molecules together, the pressure is lower than the ideal value. To account for this, the pressure is augmented by an attractive force term  $a/v_{\text{mol}}^2$  the internal pressure (where  $a$  is a constant). (ii) Likewise real molecules have a volume, and the interaction of molecules is strongly repulsive in close proximity. This is represented by the constant  $b$ , which is subtracted from the real volume to account for the fact that gases are not as compressible at high pressures as an ideal gas. Table 3.1.1 gives values of both van der Waals constants.

### Example 3.1.1 Magnitude of Deviation from Ideal Gas Behavior (Example CO<sub>2</sub>)

The magnitude of deviation from ideal gas behavior can be illustrated by comparing the results using the *ideal gas law* and the van der Waals equation for 1 mol of CO<sub>2</sub> at 50 °C. For a volume of 0.026 867 m<sup>3</sup>, the pressure would be exactly 1 bar according to the ideal gas equation (Eq. (3.1.1)). With the data of Table 3.1.1, we obtain 0.996 bar according to the van der Waals equation (Eq. (3.1.3)). Thus, both equations give essentially the same result for ambient pressure. But if the CO<sub>2</sub> is then compressed isothermally so that it fills a vessel that is 100 times smaller (0.000 268 67 m<sup>3</sup>), a pressure of 100 bar is predicted by the ideal gas equation, whereas the van der Waals equation yields a pressure of only 67.8 bar to achieve the same result.

For comparison, if we neglect the forces of attraction ( $a = 0$ ), we get 119 bar, and if we neglect the covolume ( $b = 0$ ), we obtain 49 bar. Thus, as the pressure increases, the van der Waals equation initially gives pressures that are lower than predicted by

the ideal gas law because of the forces of attraction. However, at very high pressures, we finally end up with pressures that are higher than the ideal values. The influence of the volume of the CO<sub>2</sub> molecules (repulsive force) then dominates, for example, for 100 °C at  $p > 600$  bar (Figure 3.1.1).

The deviation of a real gas from an ideal gas can also be expressed by only one parameter, the real gas or compressibility factor  $z$ , based on a simple extension of the ideal gas law:

$$pv_{\text{mol,real}} = zRT \quad (3.1.4) \quad \blacktriangledown$$

Comparison with the ideal gas law (Eq. (3.1.2)) leads to

$$z = \frac{v_{\text{mol,real}}}{v_{\text{mol,ideal}}} \quad (3.1.5)$$

Figure 3.1.2 shows the influence of pressure on  $z$  for different gases (Figure 3.1.2a) and the influence of temperature and pressure for the example of nitrogen (Figure 3.1.2b). At moderate temperatures  $z$  initially decreases with increasing pressure for most gases as the influence of the attractive forces dominates. Exceptions are H<sub>2</sub> and He, where even at room temperature  $z$  increases with  $p$  as the parameter for the attractive force (value of constant  $a$  in Table 3.1.1) is very small. At high pressures, the influence of the covolume has an increasingly strong influence for all gases – as for H<sub>2</sub> already at ambient conditions – and the repulsive forces lead to values of  $z$  that are greater than unity.

The deviation from ideal gas behavior is very significant near the boiling temperature (Figure 3.1.1) and decreases with increasing temperature (Figure 3.1.2b).

Based on the van der Waals equation (Eq. (3.1.3)), the compressibility factor  $z$  is given by

$$z = \frac{v_{\text{mol,real}}}{v_{\text{mol,real}} - b} - \frac{a}{v_{\text{mol,real}}RT} \quad (3.1.6)$$

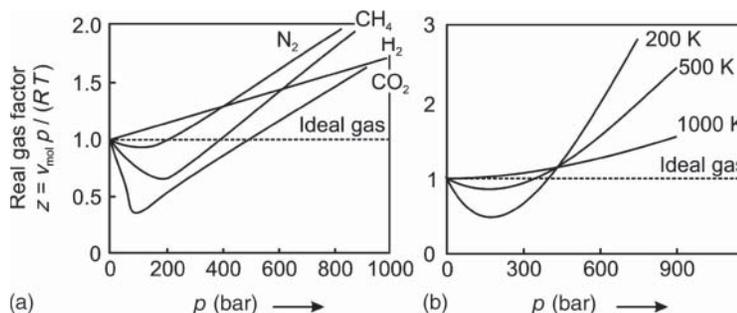
as deduced from Eq. (3.1.3) by multiplying with  $v_{\text{mol}}$ , subsequent rearrangement, and comparison with Eq. (3.1.4). As shown by Example 3.1.2 and Tables 3.1.1 and 3.1.2, the van der Waals constants can be calculated based on the critical temperature and critical pressure (explained below) as follows:

$$a = \frac{27}{64} \frac{R^2 T_{\text{crit}}^2}{p_{\text{crit}}} \quad (3.1.7)$$

$$b = \frac{1}{8} \frac{RT_{\text{crit}}}{p_{\text{crit}}} \quad (3.1.8)$$

The van der Waals equation does not account adequately for real gas behavior at high pressures and low temperatures (Figure 3.1.3). Thus, for accurate

**Figure 3.1.2** Real gas (or compressibility) factor versus pressure of selected gases at 300 K (a) and for N<sub>2</sub> at different temperatures (b). The data for CO<sub>2</sub> pertain to 313 K as it liquefies at 300 K ( $p = 67$  bar).



**Table 3.1.2** Values of critical temperature and critical pressure of selected substances.

Gas	$T_{\text{crit}}$ (K)	$p_{\text{crit}}$ (bar) ( $10^5$ Pa)	$a$ calculated by Eq. (3.1.7) ( $\text{Pa m}^6 \text{mol}^{-2}$ )	$10^{-5}b$ calculated by Eq. (3.1.8) ( $\text{m}^3 \text{mol}^{-1}$ )
He	5.2	2.3	0.003	2.35
H <sub>2</sub>	33.2	13	0.025	2.65
N <sub>2</sub>	126.2	33.9	0.137	3.87
CO	132.9	35.0	0.147	3.95
O <sub>2</sub>	154.6	50.5	0.138	3.18
CH <sub>4</sub>	190.9	46.0	0.231	4.31
CO <sub>2</sub>	304.2	73.8	0.366	4.28
NH <sub>3</sub>	405.6	112.8	0.425	3.74
H <sub>2</sub> O	647.3	216.9	0.563	3.10

calculations other real gas equations with, usually, more than two parameters (like  $a$  and  $b$  in Eq. (3.1.3)) should be used, for example, the *Redlich–Kwong* equation (1949), the *Soave–Redlich–Kwong* equation (1972), and the *Peng–Robinson* equation (1976) (details in Atkins and de Paula (2002) and Gmehling and Brehm (1996)).

The van der Waals equation does also not consider condensation. For example, Figure 3.1.4 shows isotherms of CO<sub>2</sub> according to the van der Waals equation. The oscillations, the van der Waals loops, are unrealistic – for example, an increase in pressure cannot lead to an increase in volume. Thus, we have

to replace the loops with horizontal lines representing condensation. The question is then how high above the  $v_{\text{mol}}$ -axis we must draw a horizontal line? *James Clerk Maxwell* (1831–1879) showed based on thermodynamic considerations that the loops have to be replaced by a horizontal line for which the areas above and below the line are equal. This horizontal line connects the liquid and vapor phases that coexist at equilibrium (so-called Maxwell construction), as shown in Figure 3.1.4 for a temperature of 273 K.

At a certain critical value of temperature and pressure, for example, 304 K and 74 bar for CO<sub>2</sub>, the two-phase region vanishes (Figure 3.1.4). Now an isothermal compression or an isobaric decrease in temperature no longer leads to a change of state of aggregation. The corresponding critical values,  $p_{\text{crit}}$ ,  $T_{\text{crit}}$ , and  $v_{\text{mol,crit}}$  can be calculated by the van der Waals equation in approximation (Example 3.1.2). Experimental values of  $p_{\text{crit}}$  and  $T_{\text{crit}}$  are given in Table 3.1.2.

The critical constants are characteristic properties, and dimensionless reduced variables obtained by dividing  $p$ ,  $T$ , and  $v_{\text{mol}}$  by the critical values are commonly used to produce to plots that are general and almost independent of the sort of gas. An example is shown in Figure 3.1.5, indicating that this method, called the “principle of corresponding states,” works well for spherical molecules. For non-spherical and polar molecules, deviations are stronger and the method fails.

**Figure 3.1.3** Real gas factor versus pressure of (a) N<sub>2</sub> (273 K) and (b) CO<sub>2</sub> (313 K): comparison of real values and calculations by the van der Waals equation (Eq. (3.1.6), with  $a$  and  $b$  as in Table 3.1.1).

