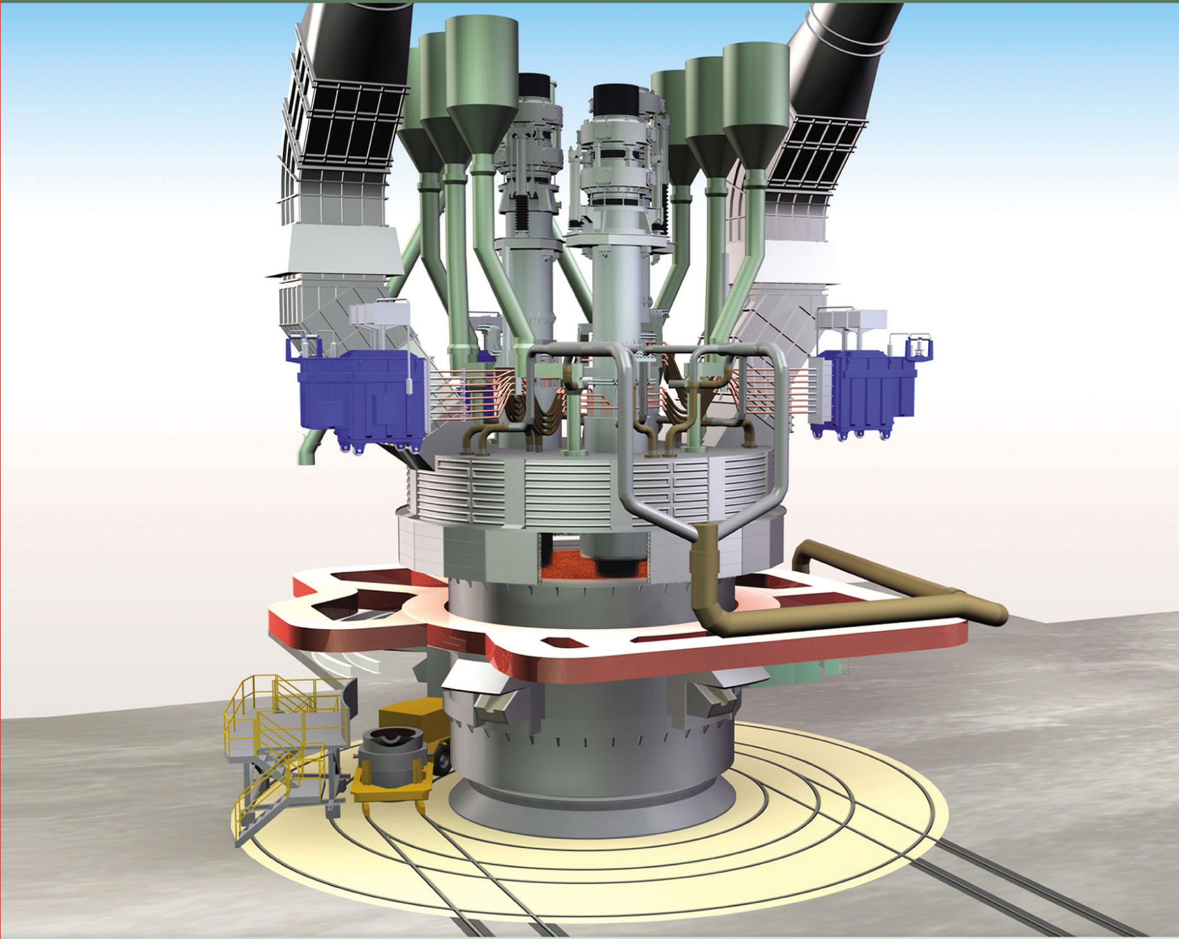
Concise Chemical Thermodynamics

Third Edition



A.P.H. PETERS

CRC Press
Taylor & Francis Group

Concise Chemical Thermodynamics

Third Edition

Concise Chemical Thermodynamics

Third Edition

A.P.H. PETERS

CRC Press
Taylor & Francis Group
Boca Raton London New York

CRC Press is an imprint of the
Taylor & Francis Group, an **informa** business

First published 2010 by CRC Press

Published 2019 by CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

© 2010 by Taylor and Francis Group, LLC
CRC Press is an imprint of the Taylor & Francis Group, an informa business

No claim to original U.S. Government works

ISBN-13: 978-1-4398-1332-4 (pbk)

This book contains information obtained from authentic and highly regarded sources. Reasonable efforts have been made to publish reliable data and information, but the author and publisher cannot assume responsibility for the validity of all materials or the consequences of their use. The authors and publishers have attempted to trace the copyright holders of all material reproduced in this publication and apologize to copyright holders if permission to publish in this form has not been obtained. If any copyright material has not been acknowledged please write and let us know so we may rectify in any future reprint.

Except as permitted under U.S. Copyright Law, no part of this book may be reprinted, reproduced, transmitted, or utilized in any form by any electronic, mechanical, or other means, now known or hereafter invented, including photocopying, microfilming, and recording, or in any information storage or retrieval system, without written permission from the publishers.

For permission to photocopy or use material electronically from this work, please access www.copyright.com (http://www.copyright.com/) or contact the Copyright Clearance Center, Inc. (CCC), 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400. CCC is a not-for-profit organization that provides licenses and registration for a variety of users. For organizations that have been granted a photocopy license by the CCC, a separate system of payment has been arranged.

Trademark Notice: Product or corporate names may be trademarks or registered trademarks, and are used only for identification and explanation without intent to infringe.

Library of Congress Cataloging-in-Publication Data

Peters, A. P. H.
Concise chemical thermodynamics -- 3rd ed. / A.P.H. Peters.
p. cm.
Rev. ed. of: Concise chemical thermodynamics / J.R.W. Warn and A.P.H. Peters. 2nd ed. 2002.
Includes bibliographical references and index.
ISBN 978-1-4398-1332-4 (alk. paper)
1. Thermodynamics. I. Warn, J. R. W. (John Richard William), 1935- Concise chemical thermodynamics. II. Title.

QD504.W38 2010
541'.369--dc22 2010014708

Visit the Taylor & Francis Web site at
http://www.taylorandfrancis.com

and the CRC Press Web site at
http://www.crcpress.com

Contents

Preface

This is the third edition of a book that was first published by Dr. J. R. W. Warn in 1969. The book was successful for many years and in 1994 I took up the task of writing a revised second edition, which was published in 1996. Although the subject has not changed basically since the two most important publications of Gibbs in 1876 and 1878, I believe that it is necessary for a thermodynamic textbook to be up to date.

Today's students are comfortable with computers. As a result, I have written a number of new problems with the use of programs such as Mathcad or Excel in mind. Students should graph data, explore expressions and fit experimental data, and plot functions that describe physical behavior.

Also, for professionals and students who are taking graduate courses in thermodynamics, very good and user-friendly software are now available for their thermodynamic calculations. FactSage and HSC Chemistry are two of them. They were also used in the preparation of the third edition of this book.

All popular features of the previous editions are retained while new ones have been added. The main body of the text remains largely unchanged. I have added new material to several chapters. In Chapter 1, there is an extensive outlook on the world's current energy consumption and the role of renewable energy in the future. In Chapter 6, an example of an exothermic reaction is added. In the so-called Mond process for extracting and purifying nickel, the "battle" between enthalpy and entropy is explained as a function of temperature. In Chapter 7, it is shown how a plot of the Gibbs energy for a reaction mixture versus the extent of reaction is calculated with the help of Mathcad. Students are asked to do this themselves in some additional problems. In Chapter 9, the Lambda sensor, which reduces vehicle emissions, is explained electrochemically with the Nernst law. In Chapters 10 and 11, the production of silicon in an arc (oven) furnace is described and calculated in detail with the aid of the professional FactSage software.

After working many years with this book, I have seen students making the same mistakes over and over again in some problems. Therefore, these problems have been reworked and more hints are given. Furthermore, new problems have been added to several chapters.

The list of suggested readings has also been updated. A solutions manual that contains solutions to all exercises in the text is available as a PDF file for instructors only. I also used the opportunity to correct old typographical mistakes, and if readers should detect some in this new edition, please do not hesitate to contact me at: a.peters@hszuyd.nl.

I would like to thank two of my students: Marc Linssen, for preparing a usable Word file from the e-book version of the second edition, and especially Jurrie Noordijk, who did a great job by retyping all tables, preparing numerous figures, and retyping all formulas with MathType.

I am very glad to know Prof. Dr. Klaus Hack, who is the managing director of GTT Technologies (Gesellschaft für Technische Thermochemie und –physik mbH) and professor at the Rheinisch-Westfälische Technische Hochschule in Aachen, Germany. He helped me with the preparation of Chapters 10 and 11 by providing data from the Scientific Group Thermodata Europe database, and with the computations by the FactSage program. I also am grateful for the discussions via e-mail about things I was not sure of.

I also wish to thank Annti Rone and Satu Mansikka from Ouotec Research Oy company in Finland. They provided me with the latest HSC Chemistry software program for free. I used this program for numerous calculations in the third edition and I can recommend it to all instructors who teach and students who follow courses in thermodynamics. For providing me with a photo of a silicon arc furnace for the cover of the third edition, I would like to thank Dr. Ing. Rolf Degel, general sales manager of SMS Siemag AG in Düsseldorf, Germany. And last, but not least, I would like to thank CRC Press, which has contributed to this new edition.

Ir Toon Peters
Heerlen, The Netherlands

Preface to the Second Edition

I switched to higher professional education in 1989, having worked as a secondary school teacher for four years. I started to work as a chemistry teacher in the higher laboratory education of the Hogeschool Den Haag, where I was requested to teach thermodynamics. Since a suitable course book was not available, I was at liberty to introduce a book of my own choice on thermodynamics. This choice was easily made after comparing a number of books: The first edition of *Concise Chemical Thermodynamics* explained thermodynamics in a simple way without slipping into complicated mathematical deductions. In addition, the book stood out due to the many practical examples that were used to illustrate the possible applications of thermodynamics in many disciplines. Owing to a pending merger of the higher laboratory education of the Hogeschool Den Haag with another Hogeschool, I switched to the higher laboratory education of the Hogeschool Heerlen, now Hogeschool Limburg, in 1990. Here, again, I was asked to teach thermodynamics and was allowed to choose my own course book. As my experience with Dr. Warn's book was extremely positive, I naturally introduced his book at my new school.

However, I had noticed that the book had not been updated since the first edition. After having used the book for five years, I had drawn up a list of suggestions and improvements which I sent to the publisher in 1994. It appeared that the publisher had intended to have the book revised for some time and was looking for a suitable candidate for the job. When I was asked to do this, I consented. I have tried to bring the book up to date and, where necessary, to introduce improvements. Without the help of a number of people, I would not have been able to complete this task successfully. I would like to thank Prof. Dr. Ir Erik Cordfunke and Ir Robert de Boer of the Netherlands Energy Research Foundation at Petten, who provided data for Chapters 1 and 9. I am very grateful to Dr. Klaus Hack of GTT Technologies at Herzogenrath, Germany, who not only provided data for Chapter 11 and Appendix III but also allowed me to use the computer program MicroTherm. Furthermore, I would like to thank my colleague, Mrs. Sis Achten, whom I often bothered with English-language problems. Finally, I would like to thank one of my students, Sjef Cremers, for typing and checking all the data used in Appendix III. Last, but not least, I would like to thank everyone at Chapman & Hall who have contributed to this new edition.

Ir Toon Peters
Heerlen, The Netherlands

Taylor & Francis
Taylor & Francis Group
http://taylorandfrancis.com

Preface to the First Edition

Thermodynamics, like classical music, is an acquired taste. The initiation must be sensitively carried out; otherwise, the mathematical rigor, like the formal structure of the music, acts to discourage a deeper relationship. It is sad but true that some students, both of thermodynamics and of Bach, never recover from the initial shock. In this, we are all losers. In this book, therefore, I have tried to present thermodynamics in a way which uses little mathematics, but which includes many practical and lively examples. I hope it will provide a basis for an introductory course at Honors Degree level, and will also suffice for Higher National Diploma and Certificate students.

In general, my aim has been to develop an understanding of Gibbs free energy fairly early on and then to apply this concept in several different fields. I have used many examples from chemical industry, in the firm belief that the basic *usefulness* of the subject must be demonstrated. I have therefore included a brief discussion of Ellingham diagrams in Chapter 10 and, for a similar reason, have omitted any mention of the Carnot cycle. I have used symbols consistent with the recommendations of the International Union of Pure and Applied Chemistry and have adopted units of the Système International d'Unités. Accordingly, all thermochemical data are given in joules, not calories. At the time of writing, general agreement has not been reached on the replacement of atmosphere and gram mole by bar and kilogram mole, and so the older units have been retained.

During the writing of this book, I have drawn on the experience and advice of many individuals and organizations. I am very grateful to Drs. John Golden and Ron Perrett for reading major parts of the manuscript, and for helpful comments and discussions. In the writing of Chapter 10, I was much indebted to the personnel of Magnesium Elektron Limited, British Hydrocarbon Chemicals Limited, and the British Iron and Steel Research Association (who provided data for Figure 10.1). Thanks are also due to the Dow Chemical Company (for permission to reproduce sections of the JANAF tables), National Bureau of Standards, Washington, D.C. (for Figure 3.1 and for data from which Table 2.1 was compiled), and Royal Institute of Chemistry (for permission to include questions from previous examination papers, which appear herein as Problems 7.5, 7.7, 8.5, 9.8, and 9.11). Miss Hazel Hawkes, who typed the manuscript against great odds, also has my gratitude. Notwithstanding all of this help, I would never have completed this task without the continuous and firm support of my wife and family; to them, I am indeed very grateful.

My publishers have worked long and well in the removal of errors and ambiguities from the manuscript. It is possible, however, there may be some which remain, which I have hidden too well for detection by even their practiced eyes. To me must fall the blame for these errors; I would, however, be glad to know those detected by readers.

J. R. W. Warn
Hertford

Author

I was born in 1955 in Maasbracht in the south of The Netherlands. From 1968 to 1973, I attended high school at the Bisschoppelijk College in Roermond. From 1973 to 1977, I studied chemistry at the HTS (College of Advanced Technology) in Eindhoven. After graduation from this college in 1977, I went to the University of Technology in Eindhoven to study chemical engineering. One of the principal subjects was thermodynamics. In my final year I did research on solid-state nuclear magnetic resonance.

I interrupted this study for one year to serve in the army, and in 1984 I graduated from this university. Besides chemistry I also had other interests. In 1973, I took up correspondence chess and in 1998 I was rewarded with the title of International Correspondence Chess Master.

During my student days, I came to be acquainted with the music of Frank Zappa, who is still one of my favorite musicians. In the 1980s and 1990s, I also participated in numerous marathon events worldwide. Boston marathon is my most favorite one.

After graduating from college in 1984, I worked for four years as a chemistry teacher at a secondary modern school. In 1989, I switched to higher vocational education. In the school year 1989–1990, I was lecturer in physical and analytical chemistry at the Hogeschool Den Haag in The Hague. Due to a reorganization, I left this school in 1990 and went to the Hogeschool Heerlen (now Zuyd University).

At Zuyd University, I am currently employed as a senior lecturer in physical and analytical chemistry and internship coordinator for the chemistry and chemical engineering department. From 2004 until 2009, I was also coordinator of the chemistry department and starting in 2010 I am coordinator internationalization for our faculty. At Hogeschool Den Haag and Zuyd University, I was asked to lecture on thermodynamics because this was not a popular subject among lecturers and students (probably because most textbooks are rather difficult to understand for undergraduate students) and because I liked thermodynamics.

At both schools, I was free to choose a new textbook. After comparing several books, I chose Dr. Warn's *Concise Chemical Thermodynamics*. With this book, I was very satisfied. After sending a lengthy list of suggested corrections to the publisher in 1994, I was asked to revise the book. In 1996, the second revised edition was published by Chapman & Hall and in 2010 the third edition was published by CRC Press.

A. P. H. Peters

Symbols and Abbreviations

The symbols and abbreviations given below are based on *Quantities, Units and Symbols in Physical Chemistry*, 2nd ed., published by the International Union of Pure and Applied Chemistry, Blackwell Scientific Publications (1993).

a	(relative) activity
(aq)	aqueous solution
atm	atmosphere, unit of pressure
bar	bar, unit of pressure
c	concentration
°C	degree Celsius
C_P	heat capacity at constant pressure
C_V	heat capacity at constant volume
e	elementary charge
E	electromotive force
F	Faraday constant
f	fugacity
G	Gibbs energy (F in some books by American authors)
(g)	gas phase
H	enthalpy (heat content)
i	electric current
k	Boltzmann constant
K	equilibrium constant
K	Kelvin
kg	kilogram, unit of mass
L	liter, unit of volume
(l)	liquid phase
log	decadic logarithm
ln	exponential logarithm
m	molality (of a solute)
M	molar, unit of concentration
N_A	Avogadro constant
N	amount of substance, chemical amount
P	pressure
p_B	partial pressure (the definition applies to entities B, which should always be indicated by a subscript or in parentheses)
Q	reaction quotient
q	heat added to system
R	gas constant (molar)

(s)	solid state
S	entropy
t	time
T	thermodynamic temperature
U	internal energy
V	volume
w	work done on system
χ	mole fraction, amount fraction
α	expansion coefficient
γ	activity coefficient
Δ	change of function of state, final less initial
μ	chemical potential
$\sum$	summation sign

OTHER SYMBOLS AND CONVENTIONS IN CHEMICAL THERMODYNAMICS

(i) Symbols used as subscripts to denote a chemical process or reaction

Ads	adsorption
At	atomization
c	combustion reaction
dil	dilution (of a solution)
dpl	displacement
f	formation reaction
fus	melting, fusion (solid → liquid)
imm	immersion
mix	mixing of fluids
r	reaction in general
sol	solution (of solute in solvent)
sub	sublimation (solid → gas)
trs	transition (between two phases)
vap	vaporization, evaporation (liquid → gas)

(ii) Recommended superscripts

‡	activated complex, transition state
E	excess quantity
id	ideal
∞	infinite solution
*	pure substance
0	standard

(iii) Examples of use of these symbols

The subscripts used to denote a chemical process, listed under (i) above, should be used as subscripts to the Δ symbol to denote the change in an extensive thermodynamic quantity associated with the process.

Examples

$\Delta_{vap}H = H(g) - H(l)$, for the enthalpy of vaporization
$\Delta_{vap}H_m$ for the molar enthalpy of vaporization
$\Delta_s^l H^0 = \Delta H^0(l) - \Delta H^0(s)$, the change in (molar) standard enthalpy when a substance changes from solid to liquid state.

The standard enthalpy of combustion of gaseous methane is $\Delta_c H^0$ (CH_4, g, 298.15 K) = −890.3 kJ mol^{-1}, implying the reaction:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

The standard (internal) energy of atomization of liquid water is $\Delta_{at}U^0(H_2O, l)$ = 625 kJ mol^{-1}, implying the reaction:

$$H_2O(l) \rightarrow 2H(g) + O(g)$$

1 Energy

1.1 THE REALM OF THERMODYNAMICS

Our world is characterized by a multitude of natural phenomena. It is a world of change, of movement and energy–of storms, earthquakes, cosmic rays, and solar flares. The range and complexity of these changes is so great that it would seem the height of foolishness to attempt to find a common thread or theme that runs through all of them. Nonetheless, over the centuries, by patient and careful observation aided by the occasional flash of insight, men have come to a partial understanding of the factors involved. At the heart of such a science is the concept of *energy*. Thermodynamics, as we now know it, derived its name originally from studies of the "motive power of heat" and had to do primarily with steam engines and their efficient use. The main reason why the idea of energy was so poorly understood is that energy, the capacity for doing work, appears in so many different forms. However, after heat and work were understood to be but different forms of the same thing and calculations of the efficiencies of steam engines were carried out, thermodynamics was applied more generally to all changes, both chemical and physical.

Thermodynamics is a science of the *macroscopic* world. That is, it requires no prior understanding of atomic and molecular structure, and all its measurements are made on materials *en masse*. This is not to say that an understanding of molecular phenomena cannot help us to grasp some difficult concepts. The branch of the subject known as statistical thermodynamics has assisted greatly in our understanding of entropy, for example, but the basic theories of thermodynamics are formulated quite independently of it. This point is even more evident if we consider a complete description of, for example, the steam in a kettle of boiling water. A description in molecular terms would involve the position and nature of each particle, and its velocity at any instant. As there would be well over 10^{21} molecules present, this would be a humanly impossible task. On the macroscopic scale, however, we are glad to find that the chemical composition of steam, its temperature and pressure, for example, are quite sufficient to specify the situation. If we accept that such variables as temperature, pressure, and composition are a sufficient description of such a system, and if we are prepared to follow energy in all its various disguises, then we shall find that thermodynamics is a reliable pathfinder and guide to new and unexplored phenomena. We shall find that by taking relatively simple measurements such as heats of reaction and specific heats, we can predict the outcome, and even calculate the equilibrium constants, of changes that may never have been attempted before.

Thermodynamics is a reliable guide in industrial chemistry, plasma physics, space technology, and nuclear engineering, to name but a few applications. We shall now discuss some aspects of the two main fields of application, which spring from the first and second laws of thermodynamics. The first law is the energy conservation law, which requires a clear understanding of energy's disguises. The second law deals with the concept of entropy, an increase of which may be regarded as one of nature's two fundamental forces. (The other driving force is the minimization of energy.)

1.1.1 ENERGY BOOKKEEPING

The rate of physical and mental development of the species *Homo sapiens* was previously limited by naturally occurring genetic processes. Revolutionary extensions to man's faculties have been made in the last two centuries. They are the extension of his mental capacity that came with the introduction of the electronic computer in the mid-twentieth century, and the extension of his physique that came with the development of machinery in the Industrial Revolution. We shall be concerned with this second aspect. There is a close link between the per capita consumption of energy and the state of physical advancement of a nation.

The current (2009) economic downturn is dampening near-term world energy demand growth. In the International Energy Outlook 2009 (IEO2009) projections from the U.S. Energy Information Administration (EIA), total world consumption of marketed energy is projected to grow by 44% between 2006 and 2030 as economic recovery spurs future demand growth (Figure 1.1 and Table 1.1) [1].

The largest projected increase in energy demand is for the non-OECD economies. The OECD (Organization for Economic Cooperation and Development) groups 30 member countries in a forum to discuss, develop, and refine economic and social policy.

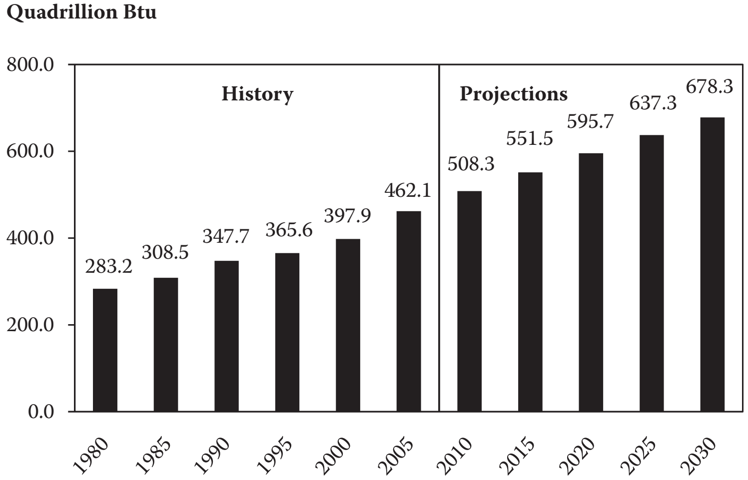


FIGURE 1.1 World marketed energy consumption 1980–2030. (Sources: History: Energy Information Administration (EIA), *International Energy Annual 2006* (June–December 2008), website www.eia.doe.gov/iea. Projections: EIA, World Energy Projections Plus, 2009.) A quadrillion BTU is equal to the amount of energy in 45 million tons of coal, or 1 trillion ft^3 of natural gas, or 170 million barrels of crude oil. In terms of electricity, 1 quad is equal to 293 GW h.

TABLE 1.1
World Marketed Energy Consumption by Country Grouping, 2005–2030 (Quadrillion Btu)

Region	2005	2010	2015	2020	2025	2030	Average Annual Percent Change, 2005–2030
OECD	**241.3**	**242.8**	**252.4**	**261.3**	**269.5**	**278.2**	**0.6**
North America	121.6	121.1	125.9	130.3	135.6	141.7	0.6
Europe	81.4	82.2	84.8	87.9	90.0	91.8	0.5
Asia	38.4	39.5	41.8	43.1	43.9	44.6	0.6
Non-OECD	**220.7**	**265.4**	**299.1**	**334.4**	**367.8**	**400.1**	**2.4**
Europe and Eurasia	50.6	54.0	57.6	60.3	62.0	63.3	0.9
Asia	109.4	139.2	163.2	190.3	215.4	239.6	3.2
Middle East	22.7	27.7	30.3	32.2	34.6	37.7	2.0
Africa	14.5	16.2	17.7	19.1	20.6	21.8	1.6
Central and South America	23.4	28.3	30.3	32.5	35.2	37.7	1.9
Total World	**462.2**	**508.3**	**551.5**	**595.7**	**637.3**	**678.3**	**1.5**

Sources: History: Energy Information Administration (EIA), *International Energy Annual 2006* (June–December 2008), website www.eia.doe.gov/iea. Projections: EIA, World Energy Projections Plus, 2009.

The OECD consists of like-minded countries, with the 30 member states all sharing a commitment to a market economy. The organization began in 1961 as a group of European and North American nations and has since expanded to include Japan, New Zealand, Australia, Mexico, Korea, and four former communist nations, the Czech Republic, Poland, Hungary, and the Slovak Republic.

Although high prices for oil and natural gas, which are expected to continue throughout the period, are likely to slow the growth of energy demand in the long term, world energy consumption is projected to continue increasing strongly as a result of robust economic growth and expanding populations in the world's developing countries. OECD member countries are, for the most part, more advanced energy consumers. Energy demand in the OECD economies is expected to grow slowly over the projection period, at an average annual rate of 0.6%, whereas energy consumption in the emerging economies of non-OECD countries is expected to expand by an average of 2.4% per year, as shown in Figure 1.2.

China and India are the fastest growing non-OECD economies, and they will be key world energy consumers in the future. Since 1990, energy consumption as a share of total world energy use has increased significantly in both countries. China and India together accounted for about 10% of the world's total energy consumption in 1990, but in 2006 their combined share was 19%. Strong economic growth in both countries continues over the projection period, with their combined energy use increasing nearly twofold and making up 28% of world energy consumption in